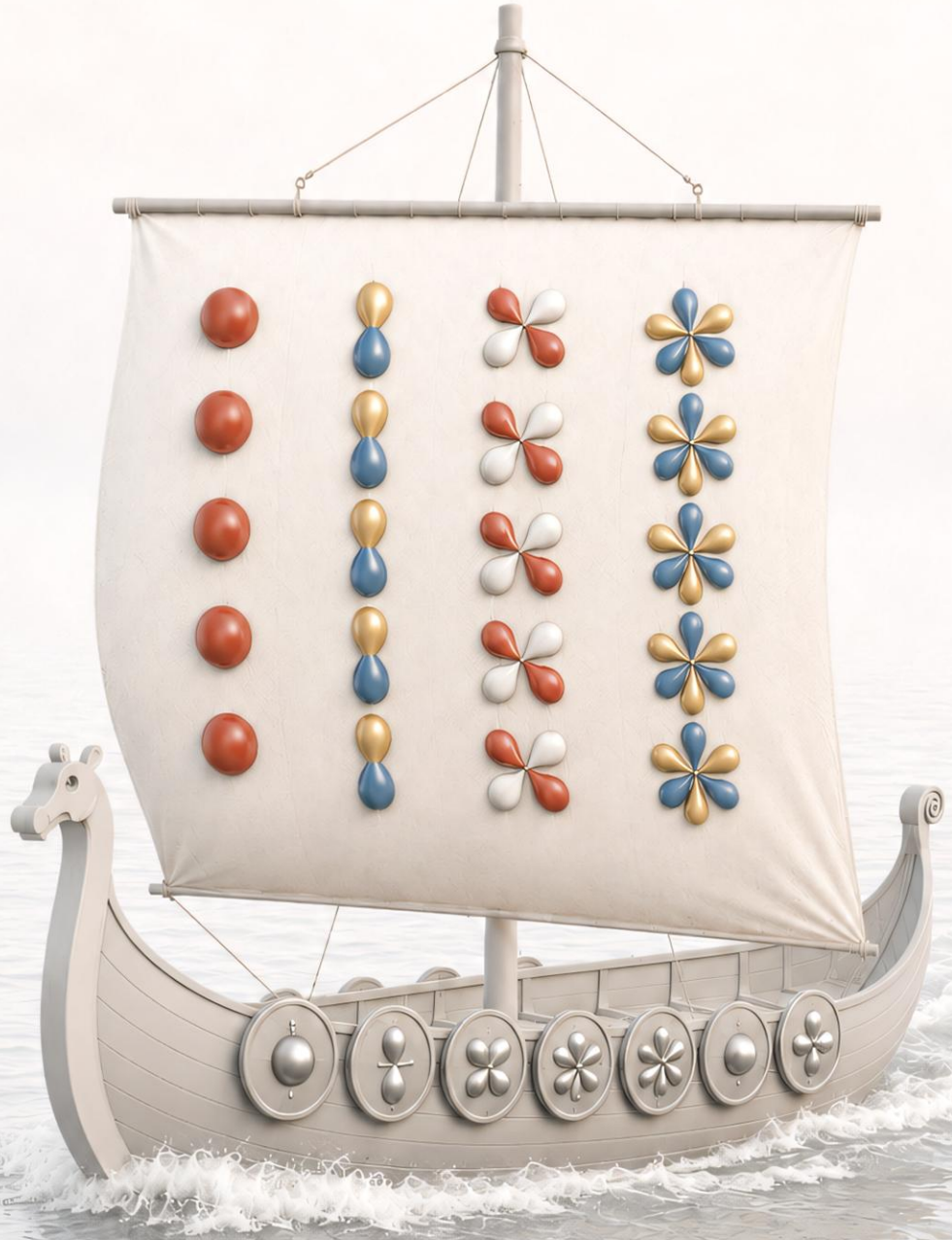
ABSTRACTS FOR POSTER CONTRIBUTIONS



46th
International Conference on
Coordination Chemistry

ODENSE, DENMARK
June 28th-July 3rd 2026

Poster flash presentations Monday late afternoon June 29th

	4: Hall K4	5: Room 200	6: Room 207	7: Room 107	8: Room 105	9: B+C+D
	Chair: Christina Wegeberg	*Chair: Michael Roy*	*Chair: Erik Hedegård*	*Chair: Mathias S. Neumann*	*Chair: Mads Sondrup Møller*	*Chair: Changzu Wu*
	ES	**ND/MG**	**CB**	**BM/SM/MM/CB**	**MM**	**ND**
16.35	**Gowri Satish ES-840-F**	**Tetsuya Kambe ND-850-F**	**Anju Balakrishnan Syamala CB-860-F**	**Joanna Masternak BM-870-F**	**Jack Hemingway MM-880-F**	**Jan Chrubasik ND-890-F**
16.40	**Catherine Getty ES-841-F**	**Dawid Babula MG-851-F**	**Ayano Umakoshi CB-861-F**	**Chi-Fai Leung BM-871-F**	**Jérémy Leroy MM-881-F**	**Antonia Edenholm ND-891-F**
16.45	**Chiara Lenzi ES-842-F**	**Emeric Schubert MG-852-F**	**Benedikt Kerscher CB-862-F**	**Reza Khaleghi Abasabadi SM-872-F**	**Timon Zankel MM-882-F**	**Christopher Chang ND-892-F**
16.50	**Rafael Sanchez ES-843-F**	**Huanxin Zhang MG-853-F**	**Cenna Toullec CB-863-F**	**Conner Dykstra MM-873-F**	**Renan Bertoloni MM-883-F**	**Elena Dürr ND-893-F**
16.55	**Oliver Townrow ES-844-F**	**Giorgia Scorzoni MG-854-F**	**Caterina Damiano CB-864-F**	**Shweta Singh CB-874-F**	**Dean O'Brien MM-884-F**	**Fabrizio Enrico Napoli ND-894-F**

Poster flash presentations Tuesday late afternoon June 30th

	4: Hall K4	5: Room 200	6: Room 207	7: Room 107	8: Room 105	9: Room B+C+D
	Chair: Christina Wegeberg	*Chair: Michael Roy*	*Chair: Erik Hedegård*	*Chair: Mathias S. Neumann*	*Chair: Mads Sondrup Møller*	*Chair: Changzu Wu*
	MG/ES	**CB**	**BM**	**ES**	**MM**	**ND**
16.35	**Shuilian Xu MG-845-F**	**Dean McGettigan CB-855-F**	**Zuzana Baranova BM-865-F**	**Katsuhiro Wakamatsu ES-875-F**	**Naoki Eguchi MM-885-F**	**Adedayo Dada ND-895-F**
16.40	**Amelia Swarbrook MG-846-F**	**Irene Ligielli CB-856-F**	**Benjamin Hofmann BM-866-F**	**Karolina Gutmańska ES-876-F**	**Harvey Bance MM-886-F**	**Noor Alnahdi ND-896-F**
16.45	**Paul C. Ruer ES-847-F**	**Lucas Mello CB-857-F**	**Galina Gencheva BM-867-F**	**Sodai Miyamoto ES-877-F**	**Raul Mendoza-Baez MM-887-F**	**Hugh Sanderson ND-897-F**
16.50	**Alexander Watson MG-848-F**	**Marina Uzelac CB-858-F**	**Luca Fiorini BM-868-F**	**Vitaliy Masliy ES-878-F**	**Sriram Sundaresan MM-888-F**	**Jonas Lorenz ND-898-F**
16.55	**Hirak Kumar Basak MG-849-F**	**Robert Richstein CB-859-F**	**Tommaso Lorenzon BM-869-F**	**Jonas Oliver Wenzel ES-879-F**	**Srividhyadevi Chandrasekaran MM-889-F**	**Martin Smith ND-899-F**

Poster flash presentations Thursday late afternoon July 2nd

	3: Hall K3	4: Hall K4	5: Room 200	6: Room 207	7: Room 107	8: Room 105	9: Room B+C+D
	Chair: Anders Reinholdt	*Chair: Christina Wegeberg*	*Chair: Michael Roy*	*Chair: Erik Hedegård*	*Chair: Mathias S. Neumann*	*Chair: Mads Sondrup Møller*	*Chair: Changzu Wu*
	ES/CB	**MG**	**ND**	**ND**	**SM**	**CB**	**FB/MG/ND**
16.35	**Cristiana Cesari ES-930-F**	**Huanhuan Dong MG-940-F**	**Saya Hirama ND-950-F**	**Leon Schoendorf ND-960-F**	**Leanna Karn SM-970-F**	**Ioannis Vagiakos CB-980-F**	**Till Sawallisch FB-990-F**
16.40	**Amélie Kochem CB-931-F**	**Imogen Squire MG-941-F**	**Shumpei Take ND-951-F**	**Lisa Gremmel ND-961-F**	**Kuba Lemanski SM-971-F**	**Roel Bienenmann CB-981-F**	**Rupesh Rupesh FB-991-F**
16.45	**Mattias Tan CB-932-F**	**James Ste-wart-Moreno MG-942-F**	**Tak Hin Wong ND-952-F**	**Michal Straka ND-962-F**	**Giorgio Cagossi SM-972-F**	**Jieun Jung CB-982-F**	**J. A. De Azeve-do França ND-992-F**
16.50	**Rupesh Kumar Tiwari CB-933-F**	**Preslav Smits MG-943-F**	**Victoria Martín Quiles ND-953-F**	**Mateusz Reczyński ND-963-F**	**Kinga Szczecinska SM-973-F**	**John Miecznikowski CB-983-F**	**Samuel Thompson MG-993-F**
16.55	**Sunita Sharma CB-934-F**	**Tomoya Ueda MG-944-F**	**Robert Wolf ND-954-F**	**Raul Diaz Torres ND-964-F**	**Joseph Bunyan SM-974-F**	**Ben Johnson CB-984-F**	**Lisa Kreimer MG-994-F**

Poster placements (all in Concert House foyers)	**Location**
Coordination chemistry in biology and medical applications (BM)	**1M (lower)**
Catalysis and bond activation (CB)	**1L (lower)**
Coordination compounds for energy and sustainability applications (ES)	**2L (ground)**
4f/5f-elements (FB)	**1R (lower)**
Main group elements (MG)	**1R (lower)**
Electronic and molecular structure – methods and modeling (MM)	**2R (ground)**
New Directions in Coordination Chemistry (ND)	**3M (balcony)**
Supramolecular chemistry and 3D materials (SM)	**2R (ground)**

Welcome to the 46th International Conference on Coordination Chemistry

The ICCC has long served as a premier conference for advancing our understanding of coordination chemistry, spanning fundamental principles of the electronic and geometric structure of metal complexes and their implications for bond and substrate activation, to applications across numerous fields, including catalysis, materials, medicine, biology, energy, and sustainability.

This year's conference continues that proud tradition, offering an inspiring scientific program organized around eight themes that highlight cutting-edge discoveries and emerging directions.

Beyond the formal sessions, we encourage you to take full advantage of the opportunity to exchange ideas, establish new collaborations, and reconnect with colleagues. We are especially pleased to welcome many early-career researchers and students, whose energy and perspectives are essential to the future of our discipline. In this spirit, the poster sessions lie at the heart of the 46th ICCC, featuring three dedicated sessions, with posters displayed throughout the conference. These sessions are intended to provide relaxed environments that foster informal interaction and meaningful scientific dialogue.

We also encourage you to explore the thousand-year-old city of Odense and enjoy its unique atmosphere. The social program offers opportunities to visit the surrounding countryside and local attractions.

We are delighted to welcome you to Odense and look forward to sharing your company as well as your science. Thank you for contributing to what will be a scientifically stimulating and memorable 46th ICCC with the perfect blend of Danish *hygge* and Swedish *lagom*.

Organizing Committee:

Christine McKenzie, University of Southern Denmark
Susanne Mossin, Technical University of Denmark
Jesper Bendix, Copenhagen University, Denmark
Ola Wendt, Lund University, Sweden

Program overview

Parallel sessions will follow the timings in this schedule. There can be small variations in the balance of speaker types.

Sunday 28th June	
14.00-17.00	REGISTRATION
17.00-17.20	Opening ceremony
17.20-18.00	Plenary
18.00-20.00	Welcome Reception

Friday 3rd July	
09:00-09.30	Keynote
09.30-09.50	Invited
09.50-10:05	Contributed
10:05-10.20	Contributed
10.20-10:40	Invited
10:40-11.00	COFFEE
11.00-11.15	Contributed
11.15-11.30	Contributed
11:30-11:50	Invited
12.00-12.40	Plenary
12.40-13.00	Closing ceremony
13:00-13:45	LUNCH

	Monday 29th June	Tuesday 30th June	Wednesday 1st July	Thursday 2nd July
08.00-08.30	Registration desk open			
08.30-09.10	Plenary	Plenary	Plenary	Plenary
09.25-09.45	Invited	Invited	Invited	Invited
09.45-10.00	Contributed	Contributed	Contributed	Contributed
10.00-10.15	Contributed	Contributed	Contributed	Contributed
10.15-10.35	Invited	Invited	Invited	Invited
10.35-11.00	COFFEE	COFFEE	COFFEE	COFFEE
11.00-11.30	Keynote	Keynote	Keynote	Keynote
11.30-11.45	Contributed	Contributed	Contributed	Contributed
11.45-12.00	Contributed	Contributed	Contributed	Contributed
12.00-12.20	Invited	Invited	Invited	Invited
12.20-13.40	LUNCH	LUNCH	LUNCH	LUNCH
13.40-14.00	Invited	Invited	**Social Program** Egeskov Castle (13:30-17:30) **or** Dinner at Holckenhavn castle (17:00-23:00)	Invited
14.00-14.15	Contributed	Contributed		Contributed
14.15-14.30	Contributed	Contributed		Contributed
14.30-14.45	Contributed	Contributed		Contributed
14.45-15.05	Invited	Invited		Invited
15.05-15.35	COFFEE	COFFEE		COFFEE
15.35-16.05	Keynote	Keynote		Keynote
16.05-16.20	Contributed	Contributed		Contributed
16.20-16.35	Contributed	Contributed		Contributed
16.40-17.05	5 Poster Pitches	5 Poster pitches		5 Poster pitches
17.00-19.00	Poster Session 1 refreshments/beer	Poster Session 2 refreshments/beer		Poster Session 3 refreshments/beer
19.00-23.30				Conference Banquet

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Mette Søndergaard
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Sally Brooker, University of Otago, New Zealand
Isabel Correia, University of Lisbon, Portugal
Mike Hannon, University of Birmingham, United Kingdom

Themes with associated symposia



Coordination Compounds for Energy and Sustainability Applications

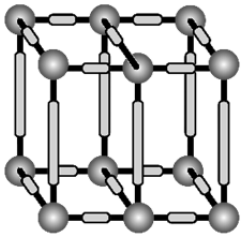
Coordination Chemistry for Sustainability
Inorganic and Hybrid Materials for Chemical Sensing Applications
Molecular Electrocatalysts for Energy Conversion
Photophysics and Photochemistry of Transition Metal Complexes
Sustainability and Catalysis for Green Molecular Transformations



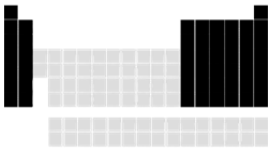
Catalysis and Bond Activation
Bioinspired Oxidation Catalysis with Iron Complexes
Bioinspired Small Molecule Activation: Electronic Structure Governs Reactivity
Confined Catalysis within Coordination Capsule
Early Transition Metal Chemistry: From Fundamental Systems to Applications
Merging Molecular Electrocatalysis and Coordination Chemistry for Organic Synthesis
New Directions in Organometallic Chemistry
Nordic Organometallics Meeting
O-O Bond Formation and Activation
Proton-coupled Electron Transfer Reactivity of Natural and Bioinspired Complexes
Sustainable CO_2 Valorization through Electrocatalysis and Photocatalysis



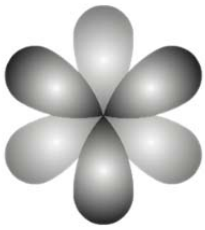
Coordination Chemistry in Biology and Medical Applications
Design of Anti-Cancer and Other Therapeutics
Radiopharmaceuticals in Nuclear Medicine
Metallo-supramolecular systems in biology
Light-, Redox-, and Structure-Controlled Metal Complexes in Biology and Medicine
MRI and PET Diagnostic and Theranostic Applications
Metal ions in neurodegenerative disease (MIND)
Light-driven Processes as Targets in Potential Therapeutics



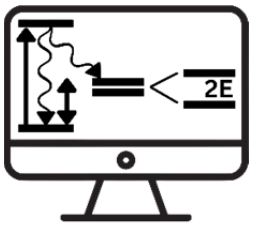
Supramolecular Chemistry and 3D Materials
Coordination Cages
Innovations in Reticular Synthesis and Framework Assembly
MOF Research and Applications
MOFs as Platforms for Catalysis and Reactivity Control
MOFs for Analysis and Analysis for MOF
MOFs for Sustainable Energy, Environment, and Resource Applications
Quantum Phenomena and Emergent Properties in MOFs



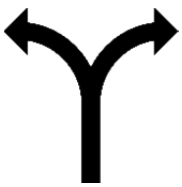
Main Group Elements
Main Group Catalysis and Materials Science
P-block Elements in Exotic Electronic States and Constrained Geometries
Phosphorus in Low Valency and Low Coordination



4f/5f-Elements
Lanthanide Luminescence for Advanced Applications
Contemporary Molecular Magnetism



Electronic and Molecular Structure – Methods and Modeling
Advanced EPR for Coordination Chemistry
Advanced X-ray, Diffraction, and Ultrafast Optical Methods
Modelling of Metal-Organic Frameworks
Quantum Bio-Inorganic Chemistry
Spin states and reactivity



New Directions in Coordination Chemistry
Fluorinated Ligands in Coordination Chemistry
From Interfacial to Spatially Confined Organometallic Chemistry
Metal Oxo Clusters and Oligonuclear Oxo Complexes - from Building Blocks to Function
Molecular Spin Qubits and Molecular Spintronics Based on Molecular Magnets
Organoradioelement Chemistry
Triggered Assembly of Functional Coordination Complexes

Symposium organizers

We extend a very special thank you to those who answered our call in mid-2025 with proposals for symposia and those who accepted being volunteered by us to do this job.

Alexander Schnegg, Max Planck Institute for Chemical Energy Conversion, Germany
Amy Cordones-Hahn, SLAC National Accelerator Laboratory, USA
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Wesley Browne, University of Groningen, Netherlands
Wonwoo Nam, Ewha Womans University, South Korea
Yisong Guo, Carnegie Mellon University, USA
Zoe Pikramenou, University of Birmingham, UK

Plenary Speakers



Professor Paul Donnelly, The University of Melbourne, Australia.
Sunday 28th June 17.20pm.
Professor Paul Donnelly is the Richard Robson Chair of Chemistry at the University of Melbourne and a leader in bioinorganic chemistry. His research focuses on the design of metal-based agents for imaging and therapy. He has co-authored over 200 publications and is an inventor on more than 18 patents, many commercially licensed. His work has led to clinical trials involving radiopharmaceuticals for cancer as well as therapeutics for neurodegenerative diseases. Donnelly's contributions have been recognized with numerous awards, including the David Syme Prize and multiple honors from the Royal Australian Chemical Institute.



Professor Erwin Reisner, University of Cambridge, United Kingdom.
Monday 29th June 8.30 am.
Professor Erwin Reisner is Professor of Energy and Sustainability at the University of Cambridge. Trained in Vienna, MIT, and Oxford, his research develops sustainable chemical systems inspired by biology, including solar-driven catalysis. He holds an ERC Advanced Grant and a Royal Academy of Engineering Chair in Emerging Technologies. Reisner has received major recognitions including the Royal Society's Hughes Medal and the RSC Tilden Prize. He serves on advisory boards for leading journals and is widely recognized for advancing artificial photosynthesis and renewable energy chemistry.



Professor Marinella Mazzanti, EPFL, Switzerland.
Tuesday 30th June 8.30 am.
Professor Marinella Mazzanti is Chair of Coordination Chemistry at EPFL. Her research explores the chemistry of f- and d-block elements, with emphasis on redox reactivity, supramolecular systems, and small molecule activation. After training in Pisa, Lausanne, and California, she held a long-standing position at CEA Grenoble before joining EPFL in 2014. She has published over 200 articles and currently serves as Associate Editor of *Chemical Communications*. Her recent work focuses on dinitrogen activation and unusual oxidation states in f-element chemistry, earning her major international awards.



Professor Amy C. Rosenzweig, Northwestern University, USA.
Wednesday 1st July 8.30 am.
Professor Amy C. Rosenzweig is the Weinberg Family Distinguished Professor of Life Sciences at Northwestern University. A pioneer in bioinorganic chemistry and structural biology, she studies metalloproteins and metal-mediated biological processes. Her work on methane monooxygenase has provided key insights into biological methane oxidation. She is a member of the U.S. National Academy of Sciences and a MacArthur Fellow. Her numerous awards include the Alfred Bader Award and the Joseph Chatt Award. Rosenzweig's research continues to shape understanding of metals in biology.



Professor Mizuki Tada, Nagoya University, Japan.
Thursday 2nd July 8.30 am.
Professor Mizuki Tada is Professor of Chemistry at Nagoya University. She received her PhD from the University of Tokyo and has held positions there, at the Institute for Molecular Science, and at RIKEN's SPring-8 facility. Her research focuses on the design of metal-complex catalysts, heterogeneous catalysis, and advanced operando imaging techniques such as XAFS-CT. She studies functional materials including catalysts, MOFs, and fuel cells, with an emphasis on understanding structure–activity relationships under working conditions.



Professor Frank Neese, Max Planck Institute for Kohlenforschung, Germany.
Friday 3rd July 12.00 pm.
Professor Frank Neese is Director at the Max Planck Institute for Kohlenforschung and a leading figure in theoretical chemistry. He is renowned for developing computational methods for transition metal chemistry and spectroscopy, including the widely used ORCA program. Neese has authored over 700 publications and is consistently ranked among the most highly cited chemists worldwide. His work spans electronic structure theory, spectroscopy, and reactivity of metal complexes and metalloenzymes. His honors include the Leibniz Prize, Schrödinger Medal, and ACS Award in Inorganic Chemistry.

Social Program Wednesday 1st July

Egeskov Castle



Egeskov Castle, 22 km south of Odense on the island of Funen, is one of Europe's best-preserved Renaissance water castles. It was built in 1554 during a period of political unrest following the Reformation. The castle stands on a lake, supported by thousands of oak piles driven into the ground, which inspired its name, meaning "oak forest." Designed as a fortress, it features thick walls, secret passages, and defensive towers. Over the centuries, the estate passed through several noble families, often through inheritance and marriage. In the 18th century, the surrounding gardens were redesigned into elegant, landscaped parkland. Today, the castle remains inhabited by the Ahlefeldt-Laurvig-Bille family. It has been open to the public for several decades. Visitors can explore historic interiors, museums, and extensive gardens. An afternoon tour including afternoon tea is arranged for delegates.

Holckenhavn Castle



Holckenhavn Castle, 23 km south-east of Odense is a striking example of late Renaissance architecture. It was built between 1588 and 1590 on the site of a former monastery. The castle was designed with symmetrical red-brick wings, decorative gables, and four corner towers, reflecting both elegance and strength. Surrounded by a moat and set within a landscaped estate, it combines defensive features with refined noble living. It has been in the hands of the Holck family for ten generations. The wine-paired dinner arranged for the delegates will be held in the Knight's Hall where the walls and ceiling are covered with frescos dating back to the early 17th century.

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Novo Nordisk Foundation

Support for Plenary lectures and symposia in Bond Activation and Catalysis

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Abstract number: **A-BCD-E**

A: Theme code:

BM: Coordination Chemistry in **B**iology and **M**edical Applications
CB: **C**atalysis and **B**ond Activation
ES: Coordination Compounds for **E**nergy and **S**ustainability Applications
FB: 4f/5f-Elements (=**F**-**B**lock)
MG: **M**ain **G**roup Elements
MM: Electronic and Molecular Structure – **M**ethods and **M**odeling
ND: **N**ew **D**irections in Coordination Chemistry
SM: **S**upramolecular Chemistry and 3D **M**aterials

B: Time slot:

	Monday	Tuesday	Wednesday	Thursday	Friday
Morning (9.25-12.20)	**0**	**2**	**4**	**5**	**7**
Afternoon (13.40-16.35)	**1**	**3**		**6**	
Flash (16.40-17.05)	**8***	**8***		**9**	

*Monday: Talk numbers 0-4, Tuesday: talk numbers 5-9.

C: Lecture hall:

Hall 2+4	Hall 1	Hall K2	Hall K3	Hall K4	Room 200	Room 207	Room 107	Room 105+106	Room B+C+D
0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

D: Talk number within session.

E: Presentation type:

K: Keynote
I: Invited talk
O: Oral (contributed talk)
F: Flash presentation and poster
P: Poster

For posters without flash presentation, numbers are above 1000: **A-1xxx-P**
Authors should be at their posters for discussions:

P: Monday (17-19) if the abstract number is **blue**.
The last two digits are 01, 04, 07, 10, .. etc
Tuesday (17-19) if the abstract number is **red**.
The last two digits are 02, 05, 08, 11, .. etc
Thursday (17-19) if the abstract number is **green**.
The last two digits are 03, 06, 09, 12, .. etc

F: In the poster session immediately after the corresponding flash presentation

Example 1:
Ola Wendt, ES-045-K
This Keynote lecture (**K**) is under the theme **ES** = ”Coordination Compounds for Energy and Sustainability Applications”.
It will take place Monday morning (**0**) in K4 (**4**) as talk number **5**.

Example 2:
Reza Khaleghi Abasabadi, SM-872-F
This flash presentation (**F**) is under the theme **SM** = ”Supramolecular Chemistry and 3D Materials”
It will take place in the flash presentation time slot Monday (16.40-17.05) (**8**) in Room 107 (**7**) as talk number **2**.
The corresponding poster has the same number. The author will be available for discussions in the poster session Monday right after the flash presentation

Example 3:
Ellis Smith, BM-1012-P
This poster (**P**) is under the theme **BM** = ”Coordination Chemistry in Biology and Medical Applications”.
The last two digits are **12** which means the author will be available for discussions at the poster session Thursday.

Poster with Flash Talk

ES-840-F *Satish, G.*, *University of York, York, UK*
GETTING THE GOLD IN: ONE-POT TRANSMETALLATION MEDIATED BY PALLADIUM(II) COMPLEXES

ES-841-F *Getty, C.*, *University of Wisconsin-Madison, Madison, United States*
ELECTRONICALLY-TUNABLE DIRUTHENIUM ELECTROCATALYSTS FOR THE AMMONIA OXIDATION REACTION

ES-842-F *Lenzi, C.*, *University of Bologna, Bologna, Italy*
HOMOGENEOUS BIOETHANOL HOMOLOGATION: A MULTI-SCALE STUDY FROM MICROWAVE SYSTEM TO AUTOCLAVE SCALE-UP

ES-843-F *Sanchez, R.*, *The University of Nottingham, Nottingham, United Kingdom*
SYNTHESIS AND CHARACTERISATION OF COBALT-BASED HETEROLEPTIC POLYPYRIDYL PINCER COMPLEXES

ES-844-F *Townrow, O.*, *Karlsruhe Institute of Technology, Karlsruhe, Germany*
STABLE SINGLE-ION SOURCES OF IRON(I)

MG-845-F *Xu, S.*, *Soochow University, Suzhou, P.R. China*
SYNTHESIS AND REACTIVITY OF ZINC RADICALS

MG-846-F *Swarbrook, A.*, *University of Oxford, Oxford, UK*
THE SYNTHESIS AND REACTIVITY OF BORAZINE TOWARDS MAIN GROUP COMPOUNDS

ES-847-F *Ruer, P.C.*, *TU Dortmund University, Dortmund, Germany*
INVESTIGATIONS INTO MOLECULAR COPPER(I) PHOSPHIDO COMPLEXES

MG-848-F *Watson, A.*, *University of York, York, UK*
METHYL, ETHYL, PROPYL: SIDE-CHAIN ELONGATION IN POLYAMINOBORANES THROUGH MECHANISM-LED CATALYST DESIGN

MG-849-F *Basak, H.*, *Indian Institute of Technology Dehli, New Dehli, India*
ENHANCING THE VALENCE BAND CHARGE LOCALIZATION VIA ZINC DOPING INTO $MnWO_4$ TO PROMOTE SELECTIVE AMMONIA ELECTROOXIDATION

ND-850-F *Kambe, T.*, *University of Tsukuba, Tsukuba, Japan*
ASSEMBLY OF BOROPHENE-ANALOGOUS LAYERED MATERIALS FOR EMERGENT ELECTRONIC AND IONIC FUNCTIONS

MG-851-F *Babula, D.*, *University of Bath, Bath, UK*
FROM METALS TO REDUCTANTS: MECHANOCHEMICAL ROUTES TO REACTIVE MAGNESIUM REAGENTS

MG-852-F *Schubert, E.*, *Technical University of Munich, Garching, Germany*
MODULAR MONO – AND BIMETALLIC Ni COMPLEXATION AT Ge^{II} INTERFACES

MG-853-F *Zhang, H.*, *University of Birmingham, Birmingham, United Kingdom*
A SODIUM ANION COMPLEX: GRAMME-SCALE SYNTHESIS, STRUCTURE, REACTIVITY

MG-854-F *Scorzoni, G.*, *University of Bologna, Bologna, Italy*
REACTIVITY OF HOMOLEPTIC PENTACOORDINATED Ga(I)-AMIDE COMPLEXES OF Fe IN THE PRESENCE OF AlCp*

CB-855-F *McGettigan, D.*, *University of York, York, UK*
DIRECT ONE SCAN OBSERVATION OF ^{103}Rh NMR SPECTRA IN ALKYL PHOSPHINE COMPLEXES VIA PARAHYDROGEN-INDUCED POLARIZATION

CB-856-F *Ligielli, I.*, *National and Kapodistrian University of Athens, Athens, Greece*
FUNCTIONALIZED CAACS BEARING 3d METALS (Cu, Fe, Co) SYNTHESIS, CHARACTERIZATION AND CATALYTIC STUDIES

CB-857-F *Mello, L.*, *Lund University, Lund, Sweden*
PALLADIUM COMPLEXES WITH β-BLOCKED $POC^{sp3}OP$ LIGANDS: THE (FAILED) QUEST FOR POCOP-Pd CARBENE COMPLEXES

CB-858-F *Uzelac, M.*, *University of Bath, Bath, UK*
SYNTHESIS AND STRUCTURAL CHARACTERISATION OF MANGANESE DIISOPROPYLAMIDE COMPLEXES

CB-859-F *Richstein, R.*, *University of Vienna, Vienna, Austria*
ROBUST ONE-STEP FORMATION OF NHC@AuNP THROUGH COUNTERION-DEPENDENT MILD BASE ACTIVATION

CB-860-F *Balakrishnan Syamala, A.*, *Okinawa Institute of Science and Technology (OIST), Okinawa, Japan*
ISOLATION OF A 17-ELECTRON $FeCp(CO)_2$ DERIVATIVE

CB-861-F *Umakoshi, A.*, *Hiroshima University, Japan*
CATALYSIS OF A BRØNSTED SUPERACIDIC OXO–HYDROXO ALUMINA CLUSTER IN WEAKLY POLAR APROTIC SOLVENTS

CB-862-F *Kerscher, B.*, *Technical University of Munich, Munich, Germany*
MASS SPECTROMETRIC ANALYSIS OF ELUSIVE BIMETALLIC COPPER-ALUMINUM CLUSTERS BY CHEMICAL LABELLING

CB-863-F *Toullec, C.*, *Université Claude Bernard Lyon 1, Villeurbanne, France*
NEW CATALYTIC PATHWAYS FOR CARBENE INSERTION INTO Si-H AND S-H BONDS CATALYZED BY PHTHALOCYANINE COMPLEXES

CB-864-F *Damiano, C.*, *University of Milan, Milan, Italy*
IMMOBILIZED METAL PORPHYRINS AS RECYCLABLE CATALYSTS FOR ON-WATER CARBENE TRANSFER REACTIONS

BM-865-F *Baranova, Z.*, *Xavier University of Louisiana, New Orleans, USA*
IMPORTANCE OF INTRAMOLECULAR HYDROGEN BONDING FOR THE MOLECULAR GEOMETRY OF OXOVANADIUM COMPLEXES WITH PYRAZOLES

BM-866-F *Hofmann, B.J.*, *University of Warwick, Coventry, UK*
COPPER(II) PICOLINAMIDE COMPOUNDS WITH HIGH SELECTIVITY TOWARDS OSTEOSARCOMA

BM-867-F *Gencheva, G.*, *Sofia University "St. Kliment Ohridski", Sofia, Bulgaria*
RATIONAL DESIGN STRATEGIES FOR METAL-BASED DRUGS BEYOND CLASSICAL STRUCTURE–ACTIVITY PARADIGMS

BM-868-F *Fiorini, L.*, *University of Padua, Padua, Italy*
PHOTOCHEMICAL ACCESS TO NOVEL *N*-HETEROCYCLIC CARBENE LIGAND PRECURSORS FOR THE DEVELOPMENT OF ANTICANCER METAL–NHC COMPLEXES

BM-869-F *Lorenzon, T.*, *University of Padua, Padua, Italy*
GOLDEN HYBRIDS: A SILVER-FREE APPROACH TO BIOACTIVE NHC-Au(I)-NSAID COMPLEXES

BM-870-F *Masternak, J.*, *Jan Kochanowski University, Kielce, Poland*
FROM PHYSICOCHEMICAL PROPERTIES TO BIOACTIVITY: SIMILARITIES AND DIFFERENCES IN CYCLOMETALLATED Rh(III) AND Ir(III) COMPLEXES

BM-871-F *Leung, C.-F.*, *The Education University of Hong Kong, Hong Kong, China*
TRANSFORMABLE CIS–TRANS ISOMERISM OF RUTHENIUM(II) COMPLEXES WITH PHOTOACTIVATED ANTICANCER ACTIVITY

SM-872-F *Khaleghi Abasabadi, R.*, *University of Turin, Turin, Italy*
DESIGN OF EXPERIMENTS: A VALUABLE TOOL FOR FINE-TUNING CATALYTIC PERFORMANCES OF Ce-UiO-67 FOR THE ALLYLIC PARTIAL OXIDATION OF CYCLOHEXENE

MM-873-F *Dykstra, C.*, *The Ohio State University, Ohio, USA*
TIME-RESOLVED OPEN-ACCESS SCIENCE AT THE NEXUS X-RAY SPECTROSCOPY BEAMLINE

CB-874-F *Singh, S.*, *Technische Universität Darmstadt, Darmstadt, Germany*
LIGAND SPHERE EFFECTS ON DINITROGEN ACTIVATION IN BIMETALLIC COMPLEXES

ES-875-F *Wakamatsu, K.*, *Kwansei Gakuin University, Hyogo, Japan*
ENTROPY-DRIVEN SOLVATION ENGINEERING OF POLYOXOMETALATE REDOX SPECIES TOWARD HIGH-PERFORMANCE THERMO-ELECTROCHEMICAL CELLS

ES-876-F *Gutmańska, K.*, *Gdańsk University of Technology, Gdańsk, Poland*
STRUCTURAL DETERMINANTS OF EMISSION EFFICIENCY IN THIAZOLE-SUPPORTED COPPER(I) AND SILVER(I) COMPLEXES

ES-877-F *Miyamoto, S.*, *The University of Osaka, Osaka, Japan*
SYNTHESIS, PHOTOLUMINESCENT PROPERTIES, AND SINGLET OXYGEN GENERATION CAPABILITIES OF TECHNETIUM AND RHENIUM COMPLEXES WITH *N*-HETEROCYCLIC CARBENE LIGANDS

ES-878-F *Masliy, V.*, *Université de Rennes, Rennes, France*
CATALYSTS WITH TAILORED LIGANDS TO IMPROVE THEIR RECYCLING

ES-879-F *Wenzel, J.O.*, *Catalysis Research Laboratory (CaRLa), Heidelberg, Germany*
Pd-CATALZYED SUZUKI–MIYAURA CROSS-COUPLING OF ARYL CHLORIDES AT LOW CATALYST LOADINGS IN WATER

MM-880-F *Hemingway, J.*, *Newcastle University, Newcastle upon Tyne, UK*
SYNTHESIS AND STRUCTURE OF A STERICALLY LESS-HINDERED $[B2H5]^-$ ANALOGUE WITH A STRONG B-B BOND

MM-881-F *Leroy, J.*, *Université Claude Bernard Lyon 1, Villeurbanne, France*
REACTIVITY OF GRIGNARD REAGENTS TOWARDS NITRILE IN CONTEXT OF POLYMERIZATION CATALYSIS

MM-882-F *Zankel, T.*, *Technical University of Darmstadt, Darmstadt, Germany*
DISTINCTION OF *fac / mer* ISOMERS VIA ^{57}Fe NMR SPECTROSCOPY

MM-883-F *Bertoloni, R.*, *Universidade de São Paulo, Ribeirão Preto, Brazil*
ACCURATE QUANTITATIVE EVALUATION OF Ni AND Co UV-VIS SPECTRA CALCULATED BY TD-DFT FUNCTIONALS

MM-884-F *O'Brien, D.J.*, *University of Queensland, Brisbane, Australia*
OBSERVING EXCITED STATE PROPERTIES OF RUTHENIUM POLYPYRIDIL COMPLEXES IN THE SOLID STATE

MM-885-F *Eguchi, N.*, *Technical University of Denmark, Lyngby, Denmark*
DIMENSIONAL ENGINEERING AND SPIN-STATE PROGRAMMING IN METAL–ORGANIC MAGNETS VIA HEISENBERG PLATFORMS, SPIN-CROSSOVER ALLOYING, AND HYDROGEN-REDUCTION

MM-886-F *Bance, H.*, *University of Leeds, Leeds, UK*
DEUTERATION OF IRON(II)/TRIAZOLE SPIN-CROSSOVER COORDINATION POLYMERS

MM-887-F *Mendoza-Baez, R.*, *Centro de Investigación y de Estudios Avanzados del IPN (Cinvestav), Mexico City, Mexico*
MODULATION OF SPIN CROSSOVER PROPERTIES IN A SERIES OF $[Fe^{II}(N_4S_2)]$ COMPLEXES BY LIGAND-DISSYMETRY

MM-888-F *Sundaresan, S.*, *Academy of Sciences of the Czech Republic, Praha, Czech Republic*
MULTIFUNCTIONAL Fe(II) MOLECULAR CHAMELEONS BASED ON 1,3,4-OXADIAZOLE LIGANDS

MM-889-F *Chandrasekaran, S.*, *Université de Bordeaux, Pessac, France*
TARGETING HIGH T(LIESST) IN SPIN-CROSSOVER COMPLEXES

ND-890-F *Chrubasik, J.*, *University of Cologne, Cologne, Germany*
PRECURSOR DESIGN EN ROUTE TOWARDS THE CHEMICAL VAPOR DEPOSITION OF f-ELEMENT NITRIDES

ND-891-F *Edenholm, A.*, *Technical University of Munich, Munich, Germany*
HOMOLEPTIC NICKEL(I) COMPOUNDS STABILIZED BY LOW VALENT MAIN GROUP METALLO LIGANDS

ND-892-F *Chang, Ch.*, *Colorado State University, Fort Collins, USA*
UNUSUAL BONDING INTERACTIONS AND PRONOUNCED CIS-INFLUENCE IN 6-COORDINATE OXOVANADIUM COMPLEXES

ND-893-F *Dürr, E.*, *Technical University of Munich, Munich, Germany*
CLUSTER GROWTH OF MOLECULAR COBALT-ALUMINUM COMPLEXES

ND-894-F *Napoli, F.E.*, *Technical University of Munich, Munich, Germany*
MODELLING FISCHER-TROPSCH RELATED PHASES AND REACTIVITY WITH MOLECULAR CLUSTERS

ND-895-F *Dada, A.*, *The University of Nottingham, Nottingham, United Kingdom*
PYRIDYL-PHOSPHONATE FUNCTIONALISED POLYOXOMETALATES AS MODULAR PLATFORMS FOR HYBRID CATALYTIC SYSTEMS

ND-896-F *Alnahdi, N.*, *The University of Nottingham, Nottingham, United Kingdom*
THE SYNTHESIS OF CARBOXYLATE-DERIVED ASYMMETRIC HYBRID POLYOXOMETALATES

ND-897-F *Sanderson, H.*, *Ecole Polytechnique, Palaiseau, France*
REDOX CHEMISTRY OF THE CYCLONONATETRAENYL LIGAND IN LATE LANTHANIDE COMPLEXES: A TALE OF ANTIAROMATICITY AND COMPROPORTIONATION

ND-898-F *Lorenz, J.*, *Leibnitz Institute of Surface Modification (IOM), Leipzig, Germany*
LINDQVIST POLYOXOVANADATES IN ELECTRONICS: FROM SYNTHESIS AND CHARACTERIZATION TOWARDS APPLICATION

ND-899-F *Smith, M.*, *Loughborough University, Loughborough, United Kingdom*
REVERSIBLE FORMATION OF MONO-/HETERODI-NUCLEAR DIPHOSPHANE COMPLEXES

ES-930-F *Cesari, C.*, *University of Bologna, Bologna, Italy*
METAL CARBONYL CLUSTERS: FROM MOLECULAR DESIGN TO TAILORED NANOSTRUCTURED MATERIALS

CB-931-F *Kochem, A.*, *Université Grenoble Alpes, Grenoble, France*
THE GOLDEN AGE OF IRON: HOMOGENEOUS IRON CATALYSTS FOR SUSTAINABLE BORROWING HYDROGEN TRANSFORMATIONS

CB-932-F *Tan, M.*, *Lund University, Lund, Sweden*
PHOSPOHAVINYL FORMATION THROUGH TRAPPING OF PHOSPHINIDENE

CB-933-F *Tiwari, R.K.*, *Trinity College Dublin, College Green, Ireland*
SURFACE-ENHANCED AND ELECTRIC FIELD-MODULATED REACTIVITY OF Fe(IV)=O COMPLEXES: UNVEILING THE SYNERGY OF LEWIS ACID ADDITIVES, Au(111), AND GRAPHENE SURFACES IN BIOMIMETIC C–H ACTIVATION

CB-934-F *Sharma, S.*, *J. Heyrovsky Institute of Physical Chemistry, Praha, Czech Republic*
DISSECTING REBOUND VERSUS SECOND HYDROGEN ATOM ABSTRACTION SELECTIVITY IN TETRACARBENE IRON(IV)-OXO SYSTEMS

MG-940-F *Dong, H.*, *University of St. Andrews, St. Andrews, UK*
Si–Si BONDING IN AN UNSUPPORTED N-HETEROCYCLIC SILYLENE DIMER STABILIZED BY AN IMINOPHOSPHORANE-BASED SCORPIONATE LIGAND

MG-941-F *Squire, I.*, *King’s College London, London, UK*
A NEUTRAL CYCLIC ALUMINIUM (I) TRIMER

MG-942-F *Stewart-Moreno, J.*, *University of Oxford, Oxford, UK*
SYNTHESIS AND REACTIVITY OF ALUMINYL–ZINC COMPLEXES

MG-943-F *Smits, P.*, *Université Grenoble Alpes, Grenoble, France*
REDOX PROPERTIES OF FREE N-HETEROCYCLIC CARBENES

MG-944-F *Ueda, T.*, *The University of Osaka, Osaka, Japan*
STRUCTURE, PROPERTIES AND REACTIVITY OF INDIUM(I) COMPLEXES BEARING A PHENALENYL-BASED LIGAND

ND-950-F *Hirama, S.*, *The University of Osaka, Osaka, Japan*
TETRAHEDRAL INVERSION IN PENTANUCLEAR METAL COMPLEXES

ND-951-F *Take, S.*, *Hiroshima University, Japan*
STEPWISE INTRODUCTION OF ORGANOPHOSPHONATO LIGANDS AND TRANSITION METAL CATIONS INTO HEXAVACANT LACUNARY POLYOXOMETALATE

ND-952-F *Wong, T.H.*, *Ecole Polytechnique Federale de Lausanne (EPFL), Lausanne, Switzerland*
Cp*M COMPLEXES WITH THE N-HETEROCYCLIC VINYLIDENE LIGAND IPrC

ND-953-F *Martín Quiles, V.*, *Universidad Autónoma de Madrid, Madrid, Spain*
MELTING, GLASS FORMATION, AND LUMINESCENCE IN Cu(I)I COORDINATION POLYMERS

ND-954-F *Wolf, R.*, *Technical University of Munich, Munich, Germany*
SYNTHESIS OF IRON-GALLIUM COMPOUNDS BY ACID/BASE INDUCED SOLVENT ACTIVATION AND CLUSTER GROWTH REACTIONS

ND-960-F *Schoendorf, L.*, *University of Innsbruck, Innsbruck, Austria*
STRONGLY DONATING BIPYRIDINES WITH PROTON-SWITCHABLE PROPERTIES

ND-961-F *Gremmel, L.*, *Technical University of Munich, Munich, Germany*
PALLADIUM CLUSTERS BEARING GALLIUM-LIGANDS FOR SEMIHYDROGENATION OF ALKYNES

ND-962-F *Straka, M.*, *Czech Academy of Sciences, Prague, Czech Republic*
BEYOND LINEAR COORDINATION IN Ag(I) CHEMISTRY: Ag(I)···H WEAK INTERACTIONS AND MULTICENTER BONDING IN CARBORANES

ND-963-F *Reczyński, M.*, *Jagiellonian University, Kraków, Poland*
CYANIDE-BRIDGED MOLECULAR PROTON CONDUCTORS WITH SWITCHABLE FUNCTIONALITIES

ND-964-F *Diaz-Torres, R.*, *Universitat de Barcelona, Barcelona, Spain*
HALOGEN BONDING CONTROL OF A THERMALLY INDUCED SC–SC TRANSFORMATION IN A SPIN CROSSOVER COMPLEX

SM-970-F *Karn, L.M.*, *Simon Fraser University, Burnaby, Canada*
TARGETTING $M^{II}\cdots Au^{III}$ METALLOPHILIC INTERACTIONS

SM-971-F *Lemanski, K.*, *The University of Nottingham, Nottingham, United Kingdom*
ALTERNATIVE SOLUTION-BASED APPROACHES TO VANADIUM(II) MOFs

SM-972-F *Cagossi, G.*, *Università di Parma, Parma, Italy*
MECHANOCHEMISTRY REDEFINES PILLARED MOFs: FROM TWISTING POLYMORPHISM TO HIGH-ENTROPY MIXING

SM-973-F *Szczecinska, K.*, *Jagiellonian University, Kraków, Poland*
RHODIUM(III) AND IRIDIUM(III) COMPLEXES FOR FINE TUNING OF PHOTOLUMINESCENT AND DIELECTRIC PROPERTIES IN SUPRAMOLECULAR PEROVSKITE-LIKE HYBRIDS

SM-974-F *Bunyan, J.*, *King's College London, London, uk*
AZACRYPTATES REVISITED: EXPLORING SMALL MOLECULE ACTIVATION POTENTIAL THROUGH REACTIVITY AND STRUCTURAL ANALYSIS

CB-980-F *Vagiakos, I.*, *University of Bern, Bern, Switzerland*
STRUCTURAL AND SYNTHETIC INSIGHTS ON ALKALI-METAL AMIDO NICKELATE COMPLEXES

CB-981-F *Bienenmann, R.*, *University of Bern, Bern, Switzerland*
A NICKEL-ALUMINIUM DIHYDRIDE COMPLEX ENABLES COOPERATIVE ALKENE ISOMERIZATION

CB-982-F *Jung, J.*, *Nagoya University, Nagoya, Japan*
INTRAMOLECULAR ELECTRON TRANSFER ENABLES EFFICIENT CO_2 PHOTOREDUCTION BY A (PNNP)Mn CATALYST

CB-983-F *Miecznikowski, J.*, *Fairfield University, Fairfield, USA*
PREPARATION, CHARACTERIZATION, AND REACTIVITY OF COBALT(II) AND NICKEL(II) COMPLEXES CONTAINING REDOX ACTIVE ONO PINCER LIGANDS

CB-984-F *Johnson, B.A.*, *Technical University of Munich, Straubing, Germany*
A GEOMETRIC INTERPRETATION OF KINETIC ZONE DIAGRAMS FOR MECHANISTIC UNDERSTANDING OF MOLECULAR ELECTROCATALYSTS

FB-990-F *Sawallisch, T.*, *Helmholtz-Zentrum Dresden - Rossendorf, Dresden, Germany*
OCTAHEDRAL COMPLEXES OF THE ACTINIDE TETRACHLORIDES

FB-991-F *Rupesh, .*, *University of Hamburg, Hamburg, Germany*
STERICS DICTATED REACTIVITY BETWEEN HYBRID O/P-DONOR LIGANDS AND URANIUM

ND-992-F *de Azevedo França, J.A.*, *University of Florence, Sesto Fiorentino, Italy*
μ_4-OXO-BRIDGED $(COPPER)_4$ ASSEMBLY DRIVEN BY VORICONAZOLE COORDINATION: SYNTHESIS, STRUCTURE AND EPR EVIDENCE OF MAGNETIC EXCHANGE

MG-993-F *Thompson, S.*, *University of St. Andrews, St. Andrews, UK*
SYNTHESIS OF A MAGNESIUM COMPLEX WITH A BRIDGING PLANAR METHYL ANION

MG-994-F *Kreimer, L.*, *Technical University of Munich, Munich, Germany*
THE COLOURFUL WORLD OF ARYL-PHOSPHIINIDENES: REACTIVITY AND OPTOELECTRONIC PROPERTIES

Poster Presentations

BM-1001-P ***Morrow, J.***, *The State University of New York, New York, US*
OCTAHEDRAL COORDINATION CAGES OF Co(II) AND Ni(II) AS METABOLITE RESPONSIVE PARASHIFT AGENTS

BM-1002-P ***Tei, L.***, *Università del Piemonte Orientale, Alessandria, Italy*
DEVELOPMENT OF SEMI-RIGID NONADENTATE CHELATORS FOR RADIOLABELLING WITH ^{177}Lu AND ^{133}La

BM-1003-P ***Ghazawneh, A.***, *Louisiana State University Shreveport, Shreveport, United States*
EXPLORING THE BINDING POTENTIALS OF HALO-SUBSTITUTED BENZOYL THIOUREAS AND THEIR COBALT(III) COMPLEXES

BM-1004-P ***Manicum, A.-L.E.***, *Tshwane University of Technology, Pretoria, South Africa*
ANTIMICROBIAL AND ANTICANCER ACTIVITY OF IMIDAZOLE-FUNCTIONALIZED 2-(PYRIDIN-2-YL)-QUINOXALINE RHENIUM(I) TRICARBONYL COMPLEXES

BM-1005-P ***Freire-García, A.***, *Universidade da Coruña, Coruña, Spain*
NOVEL ACYCLIC CHELATORS FOR LUTETIUM-177 RADIOPHARMACEUTICALS

BM-1006-P ***Hajdu, B.***, *University of Copenhagen, Copenhagen, Denmark*
EQUILIBRIUM PROPERTIES IN SOLUTION OF A SELF-HYBRIDIZING DNA-SILVER NANOCONSTRUCT

BM-1007-P ***Acosta, C.***, *University of Puerto Rico Río Piedras, San Juan, Puerto Rico*
DefNEtTrp's ROLE ON THE FUTURE OF ANTICANCER THERAPY

BM-1008-P ***Siakalli, Ch.***, *Imperial College London, London, UK*
COORDINATION CHEMISTRY OF HYDROXYQUINOLINE-BASED MACROCYCLIC LANTHANIDE COMPLEXES

BM-1009-P ***Esteban-Gómez, D.***, *Universidade da Coruña, Coruña, Spain*
IRON(III)-BASED MRI PROBES FOR TNBC DIAGNOSIS

BM-1010-P ***Pell, E.***, *University of Warwick, Coventry, UK*
THE APPLICATION OF REDOX ACTIVE VANADIUM COMPOUNDS IN CANCER TREATMENT

BM-1011-P ***Goyne, E.***, *University of Melbourne, Victoria, Australia*
FUNCTIONALISED AZA-MACROCYCLES WITH POTENTIAL APPLICATIONS IN NUCLEAR MEDICINE

BM-1012-P ***Smith, E.***, *University of Southern Denmark, Odense, Denmark*
PENTADENTATE N_3S_2 CHELATORS FOR THE MEDICAL DELIVERY OF THERANOSTIC ISOTOPES OF ANTIMONY

BM-1013-P ***Delahunt, E.***, *Dublin City University, Dublin, Ireland*
EVALUATION OF CLICK CHEMISTRY DERIVED COPPER COMPLEXES FOR DNA DAMAGE

BM-1014-P ***Tanguy, E.***, *Université Paris-Saclay, Gif-sur-Yvette, France*
STUDY OF A NOVEL DIAZA MACROCYLE FOR EUROPIUM CHELATION

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RHENIUM COMPLEXES AS ANTIMICROBIAL AGENTS: LATEST DEVELOPMENTS

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TUNING THE ANTICANCER PROPERTIES OF Ru(II) CYMENE COMPLEXES VIA PHOSPHINE LIGAND MODIFICATION

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SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF NEW RUTHENIUM (II) COMPLEXES WITH ISOQUINOLINE AND NITRITE LIGANDS

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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NOVEL AZOLE–PLATINUM(II) COMPLEXES WITH EVALUATION OF THEIR PHYSICOCHEMICAL AND ANTICANCER POTENTIAL

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RADIOACTIVE COPPER COMPLEXES WITH TWO DIFFERENT TARGETING MOLECULES FOR IMAGING AND TREATMENT OF CANCERS

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RARE EARTH METAL ORGANIC FRAMEWORKS AS THERANOSTIC MATERIALS

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FROM NATURAL PRODUCT TO COMPLEX POTENTIAL

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COMPLEXATION OF β-LACTAM ANTIBIOTICS WITH METAL IONS OF BIOLOGICAL RELEVANCE: A POTENTIOMETRIC AND SPECTROSCOPIC APPROACH

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SYNTHESIS OF HALF-SANDWICH Ir(III), Ru(II), AND Os(II) COMPLEXES WITH A DIPHOSPHINE DERIVED FROM HOMOPIPERAZINE

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AROYLHYDRAZONE-BASED MANGANESE COMPLEXES OF PHYSICOCHEMICAL AND PHARMACOLOGICAL INTEREST

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CYSTEINE-MEDIATED AGGREGATION PATHWAYS OF MUTANT Cu/Zn-SUPEROXIDE DISMUTASE ASSOCIATED WITH AMYOTROPHIC LATERAL SCLEROSIS

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SYNTHESIS, PHYSICOCHEMICAL CHARACTERIZATION AND ANALYSIS OF THE ANTIPROLIFERATIVE ACTIVITY OF CYCLOMETALATED RHODIUM(III) COMPLEX WITH 2,2'-BIIMIDAZOLE

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OXIDATIVE RNA MODIFICATIONS

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INCREASING THE BINDING AFFINITY OF TRIVALENT METAL IONS TO NAPHTHALENEDIOL-BASED LIGANDS

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NEW CHELATORS FOR THE MEDICAL DELIVERY OF THERANOSTIC ANTIMONY ISOTOPES

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ROS-HYPERTHERMIA SYNERGY: THIOCARBOHYDRAZONE-Cu(II) COMPLEX WITH SELECTIVE CYTOTOXICITY AGAINST COLORECTAL CANCER COUPLED TO RHENIUM-SILICA NANOPARTICLES TO ENHANCE IN VIVO ACTIVITY AND DELIVERY

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DESIGN OF FLUORESCENT IMINE SYSTEMS FOR METAL-ION DETECTION AND OPTOELECTRONIC APPLICATIONS

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HALF-SANDWICH Os(II), Ir(III) AND Ru(II) COMPOUNDS WITH PHOSPHINO-HOMOPIPERIDINE CONJUGATES – BIOMOLECULES' INTERACTIONS STUDIES AND ANTICANCER ACTIVITY *IN VITRO*

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COORDINATION BEHAVIOR OF A FLUORINATED SCHIFF BASE LIGAND TOWARD D-BLOCK METALS: FROM TITRATION TO CRYSTALLOGRAPHY

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EXPLORING BIOMOLECULAR INTERACTIONS OF WATER-SOLUBLE PHOSPHINO Ir(III), Ru(II) AND Os(II) COMPLEXES AS A POTENTIAL APPLICATION IN ANTICANCER THERAPY

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COMPREHENSIVE DESIGN, SYNTHESIS OF METHYL SUBSTITUTED BENZIMIDAZOLE-BASED MONONUCLEAR COPPER(II) COMPLEXES AND EVALUATION OF DNA CLEAVAGE AND ROS-INDUCED APOPTOSIS

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SILVER(I) COMPLEXES OF A WATER-SOLUBLE PHOSPHINE LIGAND: *TRIS*(2-CARBOXYETHYL)PHOSPHINE

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"IF YOU LIKE IT, YOU SHOULD PUT A RING ON IT" A PHOTOCATALYTICALLY ACTIVE ROTAXANE MIMICKING PS I

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DE NOVO DESIGNED BINDERS SUPPRESS AGGREGATION OF Cu/Zn-SUPEROXIDE DISMUTASE IMPLICATED IN AMYOTROPHIC LATERAL SCLEROSIS

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SMALL CHANGES, BIG CONSEQUENCES: A BIOACTIVITY SURVEY OF SALICYLATOCOPPER(II) COMPLEXES

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A NEW [20]-MEMBERED MACROCYCLE WITH A LARGE CAVITY

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EXPLORING THE COORDINATION CHEMISTRY OF CEFADROXIL WITH TRANSITION AND LANTHANIDE METAL IONS

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COPPER COORDINATION BY A BACTERIAL TRANSCRIPTIONAL REPRESSOR

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COORDINATION CHEMISTRY OF Cu(II) IONS WITH TYROSINE AND ADENINE NUCLEOTIDES

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INVESTIGATION OF THE COMPLEXATION OF GALLIUM IONS WITH BARBITURIC ACID DERIVATIVES

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THE BILOSOME Ru-Cu STRIKES BACK. THE TUMOR REBELLION

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SYNTHESIS OF DINUCLEAR NAPHTHALINDIOL-BASED COMPLEXES WITH MIXED CARBOXYLATE- AND NITROGEN-DONORS FOR THE STABILISATION OF TRIVALENT METAL IONS

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RHENIUM CARBONYL COMPLEXES WITH 2-MERCAPTOPYRIDINES

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CONTROL OF COPPER NUCLEARITY BY METAL SOURCE AND BASE

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DOES SIZE MATTER? CHIRAL MACROCYCLIC CHELATORS FOR ^{68}Ga RADIOLABELING

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SPIN-RESOLVED CHARGE DISPLACEMENT FUNCTION: PCET

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STRUCTURAL MODULATION OF CERIA WITH Cu AND In FOR THE SELECTIVE HYDROGENATION OF CO_2 TO CH_3OH

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STABILIZATION OF REACTIVE RARE EARTH ALKYL COMPLEXES THROUGH MECHANISTIC STUDIES

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EFFICIENT DESIGN OF MOLECULAR ELECTROCATALYSTS FOR CO_2 REDUCTION: INVESTIGATING THE IMPACT OF IMPULSE ELECTROCHEMISTRY ON SELECTIVITY

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DIRECTING THE O_2-DEPENDENT OXIDATION OF NONHEME IRON-THIOLATE COMPLEXES THROUGH LIGAND DESIGN

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OXYGEN REDUCTION TO H_2O_2 THROUGH PROTON AND H-ATOM RELAY BY PHENOL(ATE) APPENDED TO COPPER COMPLEXES: INSIGHTS INTO THE LYTIC POLYSACCHARIDE MONOXYGENASE (LPMO) ACTIVE SITES

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EXPERIMENTAL AND THEORETICAL STUDY ON A NEW PHOTOCATALYST

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MANGANESE(III) AMINOBIS(PHENOLATE)S

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SITE-SELECTIVE SUZUKI-MIYAURA COUPLINGS THROUGH NICKEL CATALYSIS

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REACTIVITY OF METAL NITRIDES TOWARDS SMALL MOLECULE SUBSTRATES

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USE OF CARBON NANOTUBE SUPPORTED Pd CATALYST IN THE SYNTHESIS OF N-METHYLGLUCAMINE FROM GLUCOSE

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NICKEL-CATALYZED ARYL-ALKYL SUZUKI-MIYAURA CROSS-COUPLING

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COBALT-BASED PROTON-COUPLED ELECTRON TRANSFER MEDIATOR ENABLES EFFICIENT N2 REDUCTION CATALYZED BY A TUNGSTEN COMPLEX

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A VERSATILE, READILY AVAILABLE AND BENCH STABLE IRON CATALYST ACTIVE IN CARBENE TRANSFER REACTIONS

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MECHANISTIC INSIGHTS INTO CAGE ESCAPE FOR BIOINSPIRED C-H BOND OXIDATION CATALYSIS

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ASYNCHRONOUS PCET AND MECHANISTIC SWITCHING IN NICKEL(III)-MEDIATED C–H ACTIVATION REACTION

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AMIDOBORANE DOPING FOR THE CONTROLLED SYNTHESIS OF POLYAMINOBORANES

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SYNTHESIS OF OER CATALYSTS FOR BIOHYBRID PHOTOSYSTEMS

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MANGANESE-CATALYZED BORROWING HYDROGEN AND ASYMMETRIC TRANSFER HYDROGENATION PROCESSES

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GENERATION AND REACTIVITY OF HIGH-VALENT DIIRON INTERMEDIATES

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NOBLE-METAL FREE COMPLEXES AS WATER OXIDATION CATALYSTS

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FLAVIN-BASED RUTHENIUM COMPLEXES FOR SECONDARY COORDINATION SPHERE MODULATION TOWARD AMMONIA OXIDATION

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SYNTHESIS, CHARACTERISATION AND REACTION OF VARIOUS INDENYL BASED Zr METALLACYCLES

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BIMETALLIC AND MONOMETALLIC COMPLEXES FEATURED BY A NOVEL DINUCLEATING BIS(β-DIKETIMINATO) LIGAND SYSTEM

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REEVALUATION OF SCHROK-OSBORN CATALYST EFFECTIVENESS FOR ^{1}H & ^{13}C PARAHYDROGEN INDUCED POLARISATION NMR

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1D AND 2D VIBRATIONAL SPECTRSOCPY OF DIRUTHENIUM AZIDES

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ONE-ELECTRON OXIDATION OF AN ORGANOMETALLIC OXIDOIRON(IV) COMPLEX GENERATES A HIGHLY REACTIVE INTERMEDIATE WITH AXIAL RADICAL LIGAND

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FABRICATION OF ULTRAHIGH-LOADING DUAL COPPER SITES IN NITROGEN-DOPED POROUS CARBONS BOOSTING ELECTROREDUCTION OF CO_2 TO C_2H_4 UNDER NEUTRAL CONDITIONS

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MANGANESE CATALYSED DIHYDROGEN RELEASE FROM FORMIC ACID

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DUAL ACTIVATION OF H_2 AND CO_2 BY A PINCER-TYPE Ni−Zn HETEROBIMETALLIC COMPLEX

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BIS(HYDROSILYL)ALKYNES: UTILIZING Si-H OXIDATIVE ADDITION FOR THE ASSEMBLY OF HETEROBIMETALLIC COMPLEXES

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LOW VALENT Rh(I) COMPLEXES WITH CARBAZOLE BASED PNP LIGANDS AND THEIR CAPACITY OF CH ACTIVATION

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MACROCYCLIC COMPLEXES OF IRON AS HIGHLY ACTIVE CATALYSTS FOR THE OXIDATION OF ORGANIC COMPOUNDS WITH H_2O_2

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RATIONAL OPTIMIZATION OF SELF-REPORTING ALCOHOL-OXIDIZING Rh^{III} COMPLEXES

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PHOTOACTIVE NEUTRAL Cu(I) COMPLEXES STABILISED BY AN ANIONIC N-HETEROCYCLIC CARBENE

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A DINITROGEN-BRIDGED DIIRON COMPLEX: SYNTHESIS OF DIMETALLOTETRYLENES VIA ACTIVATION OF SILANE, GERMANE, AND STANNANE

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GENERATION OF $Fe^{IV}Fe^{IV}$-INTERMEDIATES TO MODEL SMMO USING A DINUCLEATING LIGAND SYSTEM

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VISIBLE-LIGHT-INDUCED CYCLODIMERIZATION OF INTERNAL ALKYNES VIA TITANIUM PHOTOCATALYSIS

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DINUCLEAR ZIRCONOCENE-HYDRIDE COMPLEXES FOR ACTIVATION OF SMALL MOLECULES

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ADDITIVE-FREE ALKENE HYDROGENATION CATALYZED BY A DIPHOSHINE-SUPPORTED PENTAHYDRIDO-MOLYBDENUM COMPLEX

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DESYMMETRIZATION OF MALONIC MONOESTERS AND MALONIC ACIDS VIA ENANTIOSELECTIVE CATALYTIC $C(sp^3)$-H OXIDATION

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SYNTHESIS OF MORPHOLINE DERIVATIVES FROM AMINOALCOHOLS: PALLADIUM-CATALYZED C-N AND C-O BOND FORMATION

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UNDERSTANDING THE INFLUENCE OF EXCITED STATE DYNAMICS ON PHOTOCATALYTIC PERFORMANCE

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EXPLORING THE REACTIVITY OF HIGH VALENT IRON INTERMEDIATES IN WATER

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NITROGEN CENTERED AQUEOUS OXYGENATION OF AN IRIDIUM(V) NITRIDO COMPLEX

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SELECTIVE CATALYTIC CONVERSION OF NITRITE TO AMMONIUM BY AN OXYGEN-TOLERANT MOLECULAR COBALT COMPLEX

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STRUCTURE AND REACTIVITY OF NOVEL MANGANESE(II) ENOLATES FORMED VIA ALKALI-METAL AMIDOMANGANATES(II)

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SQUARE PLANAR CHIRAL Ni(II)-IMIDAZOLE-2-YLIDENE-PYRIDONATE CATALYSED CO_2 REDUCTION: PATHWAY TO SELECTIVE N-FORMYLATION OF AMINES TO N-FORMAMIDES AND N-METHYLAMINES

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COFACIAL MANGANESE PORPHYRIN FOR OXYGEN EVOLUTION AND OXYGEN REDUCTION

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LEWIS ACID PROMOTED IRON-CATALYZED SELECTIVE OXYGENATION OF ALKENES WITH H_2O_2: INSIGHTS INTO THE ROLE OF SUPPORTING LIGANDS

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TUNABLE SELECTIVITY IN IRIDIUM-CATALYZED HYDROSILYLATION OF CO_2-DERIVED ALKYL FORMATES: ACCESS TO SILYLACETALS, ALKOXYSILANES, AND BIS(ALKOXY)SILANES

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CYCLOMETALATED RUTHENIUM(II) CATALYSTS FOR ESTER HYDROGENATION

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ELECTRIFYING BIOINSPIRED OXIDATION CATALYSIS

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QUINOLINE-BASED IODINE(I) COMPLEXES AS EFFICIENT IODINATION REAGENTS

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Rh(I) DIPHOSPHINE CATALYSED DEHYDROPOLYMERISATION OF AMINE BORANES: SELECTIVITY CONTROL THROUGH SECONDARY COORDINATION SPHERE EFFECTS

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Ti(III/IV) AMINO BISPHENOLATE COMPLEXES: REACTIVITY TOWARDS OXALTE AND RELATED COMPOUNDS

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PREVENTION OF THE CAGE ESCAPE IN OXIDATION CATALYSTS

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SELECTIVE HYDROAMINATION OF STRAINED AND SILYL ALKENES

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PREPARATION OF Mn(I)-PC(sp2)P COMPLEXES VIA ONE STEP Ar-H AND Ar-OCH_3 BOND ACTIVATION

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COMPUTATIONAL MAPPING OF THE SIX-ELECTRON NAPHTHALENE OXIDATION PATHWAY BY HIGH-VALENT IRON(IV)-OXO INTERMEDIATES

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SUBSTRATE-CONTROLLED SELECTIVITY IN SET-ENABLED C–H ALKYLATION OF *N*-ARYL AZOLIUM SALTS WITH PRIMARY ORGANOCHLORIDES: MECHANISTIC INSIGHTS INTO LIGAND-DEPENDENT REACTIVITY

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MIMICKING NATURE'S NspF COPPER ENZYME: A MECHANISTIC STUDY OF Cu_2O_2-MEDIATED AMINE OXIDATION

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[PSiP] LIGAND DESIGN TOWARD MAIN-TRANSITION METAL PLATFORMS FOR CO_2 TRANSFORMATION

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SYNTHESIS AND CHARACTERIZATION OF MOLYBDENUM(II) COMPLEXES FOR CO_2-INSERTION

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FROM UPTAKE TO STORAGE: UNCOVERING HIDDEN PATHWAYS OF BACTERIAL COPPER HOMEOSTASIS

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SUPRAMOLECULAR CATALYSTS LEVERAGE AMMONIUM-CROWN ETHER INTERACTIONS FOR DIRECTED ALKENE ISOMERIZATION

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Ru(II) COMPLEXES OF REDOX-ACTIVE LIGANDS TOWARD SOLAR FUEL GENERATION

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LOW-VALENT IRON CATALYSIS FOR CROSS-ELECTROPHILE COUPLING

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PHOTOFUNCTIONAL METAL COMPLEXES OF A PI-RICH AMIDINE *N*-OXIDE LIGAND

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TUNING FUNCTIONS IN AMIDINE *N*-OXIDE (AMOX) LIGANDS AND THEIR COORDINATION COMPLEXES

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FERROCENE-BASED DONOR–ACCEPTOR ARCHITECTURES AS MEMRISTIVE COMPONENTS IN MOLECULAR JUNCTIONS

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SIMULTANEOUS ENHANCEMENT OF THERMOPOWER AND CONDUCTIVITY IN MOLECULAR JUNCTIONS

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FROM IRON(III) TO MANGANESE(II) CARBENES: COMPARING EXCITED-STATE DYNAMICS IN d^5 SYSTEMS

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SINGLE CATALYST FOR REVERSIBLE HYDROGEN STORAGE-RELEASE

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METALLATION APPROACHES FOR IMPROVING STABILITY OF DITHIAFULVENE-FUNCTIONALIZED PORPHYRINS IN DYE-SENSITIZED SOLAR CELLS

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PHOTOCATALYTIC CO_2 REDUCTION BY USING Fe PHOTOSENSITISER

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EXTENDED TETRATHIAFULVALENE PORPHYRINS FOR BULK HETEROJUNCTION ORGANIC SOLAR CELLS

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NICKEL(II) BIS(FORMAZANATE) COMPLEXES FEATURING NANOSECOND EXCITED STATE LIFETIMES

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SYNTHESIS AND PHOTOPHYSICAL CHARACTERISATION OF FIVE BIS(FORMAZANATE) IRON(II)COMPLEXES

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PLASMONIC NON-NOBLE METAL BASED BI-FUNCTIONAL PHOTO-ELECTROCATALYST FOR REDOX TRANSFORMATIONS

ES-1213-P ***Shah, B.K.***, *Indian Institute of Science Education and Research Pune, Pune, India*
RECYCLING PLASTICS WASTE THROUGH DEPOLYMERIZATION: LITHIUM-AMIDE CATALYSED MILD AND GRAM-SCALE APPROACH

ES-1214-P ***Kiene, C.I.***, *Georg-August-University Göttingen, Göttingen, Germany*
DINITROGEN DERIVED ELECTROCHEMICAL ACETONITRILE RELEASE FROM A RHENIUM PNP-PINCER COMPLEX

ES-1215-P ***Göbel, D.***, *Julius-Maximilians-Universität, Würzburg, Germany*
MERGING PYRROLE WITH BORON: π-EXTENSION, POLYMERIZATION, AND COORDINATION

ES-1216-P ***Mandal, D.***, *Nicolaus Copernicus University, Torun, Poland*
METAL OXIDE – SCHIFF BASE COMPOSITE AS NOVEL OPTICAL SENSORS FOR METAL ION DETECTION IN AQUATIC ENVIRONMENT

ES-1217-P ***Shevchnko, D.***, *Medical University of Gdańsk, Gdańsk, Poland*
THE SYNTHESIS AND ELECTRONIC PROPERTIES OF REMOTELY TUNED NHC SYSTEM

ES-1218-P ***Sarkar, D.***, *Indian Institute of Technology Jodhpur, Jodhpur, India*
BIFUNCTIONAL WATER SPLITTING ENABLED BY METAL-LIGAND COOPERATIVITY IN MOLECULAR COBALT(III) COMPLEX

ES-1219-P ***Jain, D.***, *Leibniz Institute for Catalysis, Rostock, Germany*
NON-NOBLE METAL PINCER COMPLEX MEDIATED SOLID-STATE TRANSFER HYDROGENATION OF AMIDES

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ZnO-BENZIMIDAZOLE COMPOSITE FOR SELECTIVE DETECTION OF Zn^{2+} AND Mg^{2+} IONS

ES-1221-P ***Hsiang, E.***, *University of Calgary, Calgary, Canada*
POLYMER-SUPPORTED TRIPODAL LIGANDS FOR THE SELECTIVE EXTRACTION OF RARE EARTH ELEMENTS

ES-1223-P ***Gaschk, E.***, *The University of Western Australia, Perth, Australia*
MULTISTATE SWITCHING OF SOME RUTHENIUM ALKYNYL AND VINYL SPIROPYRAN COMPLEXES

ES-1224-P ***Shepard, E.***, *Colorado State University, Fort Collins, USA*
MONOMER–DIMER BEHAVIOR OF DIOXOVANADIUM(V) SCHIFF BASE COMPLEXES

ES-1225-P ***Prajapati, F.***, *Université de Bordeaux, Pessac, France*
COOL-SPS-ENGINEERED SPIN-CROSSOVER CERAMICS FOR NEXT GENERATION BAROCALORIC COOLING

ES-1226-P ***Wota, G.***, *Jagiellonian University, Kraków, Poland*
1D AND TWO 2D COORDINATION NETWORKS BASED ON $[Ni(cyclam)]^{2+/3+}$ AND $[Ru(CN)_6]^{4-}$ AND THE NICKEL REDUCTION

ES-1227-P ***Vashisth, G.***, *University of Otago, Dunedin, New Zealand*
EFFECT OF LIGHT-HARVESTING UNITS ON BACKBONE FLEXIBILITY AND ELECTRONIC PROPERTIES OF HETEROLEPTIC Cu(I) COMPLEXES

ES-1228-P ***Eggenweiler, H.***, *University of Basel, Basel, Switzerland*
ROOM-TEMPERATURE LUMINESCENCE OF AIR-STABLE NICKEL(0) COMPLEXES

ES-1229-P ***Heo, H.***, *Jeonbuk National University, Jeonbuk, Republic of Korea*
ATOMISTIC SIMULATION OF ARGYRODITE SULFIDE SOLID ELECTROLYTES FOR FAST LITHIUM-ION TRANSPORT

ES-1230-P ***Friedländer , I.***, *University of Basel, Basel, Switzerland*
CONTROLLING PHOTOACTIVE EXCITED STATES IN Co(III) AND Ni(II) COMPLEXES THROUGH LIGAND ELECTRONICS

ES-1231-P ***Roy, I.***, *Indian Institute of Technology Hyderabad, Telangana, India*
HETEROLEPTIC MONONUCLEAR Co(II) COMPLEXES AS ELECTROCATALYSTS FOR HYDROGEN EVOLUTION REACTION IN NON-AQUEOUS MEDIA

ES-1232-P ***Sen, I.***, *TU Dortmund University, Dortmund, Germany*
LINEAR HETEROLEPTIC COPPER (I) COMPLEXES ENABLING EFFICIENT NIR-TADF AND ROOM TEMPERATURE SINGLE PHOTON EMISSION

ES-1233-P ***Kubota, J.***, *Osaka Institute of Technology, Osaka, Japan*
ELECTROCHEMICAL RELEASE OF AMMONIA FROM A STIMULI-RESPONSIVE RUTHENIUM COMPLEX

ES-1234-P ***Sander, J.***, *Johannes Gutenberg-University Mainz, Mainz, Germany*
THE CARBAZOLATO-CARBENE CHROMIUM(III) COMPLEX $[Cr(bimca)_2]^+$ - EXCITED STATE DYNAMICS AND PHOSPHORESCENCE INHIBITION

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NOT *BREAKING BAD*: REVERSIBLE MULTISTEP SC–SC TRANSFORMATIONS IN COPPER HYDRAZONE COMPLEXES

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HETEROMETALLIC ALKALI METAL-GROUP 13 ALKOXIDES AS CATALYSTS IN CHEMICAL RECYCLING OF POLYCAPROLACTONE

ES-1237-P ***Takahara, K.***, *University of Hyogo, Hyogo, Japan*
THERMOCHROMIC WHITE-LIGHT CIRCULARLY POLARIZED EMISSION IN SINGLE MOLECULAR SOLID-STATE SYSTEM

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ELECTROCATALYTIC CO_2-TO-C_3 CONVERSION USING A DINUCLEAR Cu(I) COMPLEX AND MECHANISTIC ANALYSIS

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EXCIPLEX FORMATION LEADING TO STIMULI RESPONSIVE PHOSPHORESCENCE IN COPPER(I) COMPLEXES

ES-1240-P ***Zhuo, L.-T.***, *Fu-Jen Catholic University, Taiwan*
A REPORT OF Ru-(CYCLOMETALATED LIGAND) PHSOPORESCENCE OF MIXED-LIGAND BIS(BIPYRIDINE)-(CYCLOMETALATED LIGAND)-Ru COMPLEX

ES-1241-P ***Leimkühler, M.***, *University of Stuttgart, Stuttgart, Germany*
(SPECTRO-)ELECTROCHEMISTRY OF IRIDIUM Cp* COMPLEXES WITH PYRIDYL-MIC LIGANDS

ES-1242-P ***Morello, M.***, *University of Perugia, Perugia, Italy*
CATALYTIC UPCYCLING OF POLYETHYLENE WASTE VIA DEHYDROGENATED INTERMEDIATES

ES-1243-P ***Meißner, M.***, *Georg-August-University Göttingen, Göttingen, Germany*
SYNTHESIS AND REACTIVITY OF A SQUARE-PLANAR GROUP 8 COMPLEXES

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STRUCTURE–PHOTOREACTIVITY RELATIONSHIPS IN CHROMIUM AND MOLYBDENUM PHOTOCORMS FOR LIGHT-TRIGGERED CARBON MONOXIDE RELEASE

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Mn(II) FORMAZANATES SHOWING LIGHT-INDUCED SPIN CROSSOVER BEHAVIOUR WITH NANO- TO MICROSECOND LIFETIMES

ES-1246-P ***Lin, M.***, *Fukushima University, Fukushima, Japan*
SYNTHESIS AND INTERCONVERSION OF HALF-SANDWICH Ru(II) COMPLEXES BEARING THE COENZYME-NAD ACTIVE SITE

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PHOTOINDUCED CHARGE SEPARATION IN IRON N-HETEROCYCLIC CARBENE SOLIDS

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STRUCTURE-PROPERTY-REACTIVITY STUDIES OF ORGANOFUNCTIONALIZED THIOMOLYBDATE CLUSTERS FOR PHOTOCATALYTIC HER

ES-1249-P ***Wójcik, P.***, *University of Siedlce, Siedlce, Poland*
BIS-CYCLOMETALATED RHODIUM(III) AND IRIDIUM(III) COMPLEXES WITH THE EVALUATION OF THEIR PHOTOPHYSICAL PROPERTIES

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REALIZING NEAR-IR LUMINESCENCE IN Pd(0) AND Pt(0) COMPLEXES

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DEHYDROGENATION OF FORMIC ACID CATALYZED BY A PN^3P-RUTHENIUM PINCER COMPLEX: CATALYTIC PERFORMANCE AND MECHANISTIC INSIGHTS

ES-1253-P ***Zhu, Q.-Y.***, *Soochow University, Suzhou, P.R. China*
AN ELECTRON DONOR-ACCEPTOR MOF OF TTF-NDI FOR HIGH PERFORMANCE HYBRID LITHIUM-ION CAPACITORS

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LUMINESCENT IRON(III) COMPLEX WITH NANOSECONDS EXCITED STATE LIFETIME AND PHOTOREDOX ACTIVITY

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WATER OXIDATION CATALYSIS WITH DINUCLEAR RUTHENIUM AND IRON COMPLEXES

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PHOTOCATALYTIC HYDROGENATION OF AROMATIC COMPOUNDS

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BNB- AND NBN-DOPED PHENALENYLS: CONTRASTING BUT COMPLEMENTARY CHROMOPHORES AS BUILDING BLOCKS FOR DYADS, OLIGOMERS, POLYMERS, AND RYLENE DYES

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TRANSFER HYDROGENATION OF FURFURAL TO LEVULINIC ESTER USING Ru-BASED HOMOGENEOUS CATALYSTS

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LIGAND-DIRECTED PATHWAY DIVERGENCE IN ELECTROCATALYTIC HYDROGEN EVOLUTION BY RATIONALLY DESIGNED COBALT(II) COMPLEXES

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EMPLOYING LONE PAIR-PI INTERACTIONS IN A REDOX-ACTIVE KONERAMINE COMPLEX FOR ACTIVATION OF SO_2

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EFFICIENT OXIDATIVE BREAKDOWN OF RECALCITRANT BIOMASS VIA LPMO-INSPIRED COPPER COMPLEXES

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HYDROGEN ISOTOPE SEPARATION AT EXCEPTIONALLY HIGH TEMPERATURE BY A COORDINATIVELY UNSATURATED COMPLEX

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AIR-STABLE Fe(II) HEXA-NHC COMPLEX AND ANALYSIS OF PHOTOEXCITED STATE BY ULTRAFAST SPECTROSCOPY

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DESIGN AND EXCITED-STATE CHARACTERIZATION OF Fe(II) ISOCYANIDE COMPLEXES WITH BIDENTATE AND TRIDENTATE LIGANDS

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PHOTOACTIVE RHENIUM(II) COMPLEXES AS POTENT PHOTOREDOX CATALYSTS

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LUMINESCENCE OF AN IRON(III) COMPLEX WITH MERIDIONAL TRIDENTATE N-HETEROCYCLIC CARBENE LIGAND

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STRUCTURE–PROPERTY RELATIONSHIPS IN OXIDOVANADIUM(V) HYDRAZONE COMPLEXES

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A BRIGHT NEW LINK – A NOVEL LIGHT-SWITCH-CAPABLE BRIDGING LIGAND IN PHOTOACTIVE METAL COMPLEXES

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PHOTOPHYSICAL STUDY OF [Ir(piq)2(acac)]: EXPLORING INTRINSIC PARAMETERS IN SPIN-ORBIT COUPLING MEDIATED INTENSITY STEALING

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PHOTOSWITCHING IN P-CENTERED BI- AND TETRARADICALOID–GROUP 4 METALLOCENE HYBRIDS

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COMPARISON STUDY OF DISUBSITUTED-1,10-PHENANTHROLINE BASED HETEROLEPTIC Cu(I) COMPLEXES WITH ETHYLENE SPACER

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FROM WASTE TO RESOURCES: RECOVERY OF RARE EARTH ELEMENTS FROM NdFeB MAGNETS

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RATIONAL DESIGN AND EVALUATION OF THE SENSING MECHANISM OF A EUROPIUM(III)-BASED LUMINESCENT TURN-ON CHEMOSENSOR FOR CITRATE

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ORTHOGONAL TURN-ON LUMINESCENT LANTHANIDE COMPLEXES FOR BIOLOGICAL APPLICATIONS

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USING A STERICALLY BULKY GUANIDINATE LIGAND FOR STABILIZATION OF DIVALENT LANTHANIDE METAL COMPLEXES

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REACTIVITY OF URANIUM COMPLEXES BASED ON A TRISANIONIC PINCER SCAFFOLD

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H_2 SPLITTING AND N_2 HYDROGENATION BY A LUTETIOCENE COMPLEX

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CO-DERIVED ETHYNEDIOLATO AS A PLATFORM FOR SMALL MOLECULE FUNCTIONALISATION

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PHOTO-ELECTROCHEMICAL GENERATION OF Ln(II) SPECIES

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SEPARATION OF RARE EARTH METALS USING MULTIDENTATE PHOSPHINE OXIDES

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RATIONAL DESIGN OF NON-CENTROSYMMETRIC LANTHANIDE COMPLEXES FOR ENHANCED SPIN–ELECTRIC COUPLING (SEC)

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ADVANCES AND EMERGING TRENDS IN MOLECULAR CHEMISTRY OF THE f-ELEMENTS

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EUROPIUM(II) BASED SYSTEMS FOR MAGNETIC REFRIGERATION

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AN INTRAMOLECULAR FRUSTRATED LEWIS PAIR BASED ON A BISMUTH(III) ACID SITE

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REDOX-DRIVEN ASSEMBLY OF A RADICAL-BRIDGED YTTERBIUM 2D COORDINATION NETWORK

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TAMING THE BENZENE RADICAL TRIANION IN AN INVERSE-SANDWICH YTTRIUM COMPLEX

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SYNTHESIS AND REACTIVITY OF THORIUM HYDRIDE COMPLEXES

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SYNTHESIS OF RARE EARTH-MAGNESIUM HETEROMETALLIC COMPLEXES AND THEIR APPLICATION IN CATALYZING CYCLOADDITION REACTION OF CO_2 AND EPOXIDES

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CYCLIC (ALKENYL)(AMINO)CARBENES ($CA_{en}ACS$) AND CARBENE-DERIVED IMINO-ANCHORED OLEFINS

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INDIUM HYDRIDE: A NEW SOURCE OF HYDRIDE FOR REDUCTION AND DOUBLE HYDROINDATION

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THE SYNTHESIS OF BIS(METHYLENE)-λ^5-PHOSPHANE ANION

MG-1404-P ***Pico-Pérez, A.R.***, *King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia*
SYNTHESIS, CHARACTERIZATION, AND STRUCTURAL ANALYSIS OF PN^3(P)-ANTIMONY(III) COMPLEXES AND THEIR REACTIVITY IN TRANSMETALATION WITH NICKEL AND COBALT

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EFFECT OF THE ANCILLARY LIGANDS ON THE PROPERTIES OF 8-HYDROXY QUINOLINE BISMUTH COMPLEX

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SYNTHESIS AND ONE-ELECTRON REDUCTION OF UNPRECEDENTED DONOR-ACCEPTOR-STABILIZED Si^{II}-E^{II}-Si^{II} TRIMETALLYLENES (E = Ge, Sn, Pb)

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HIGH CONTENT SODIUM METAL DISPERSION WITH SODIUM TERTIARY ALKOXIDE CLUSTERS ENABLES RAPID SULFONAMIDES CLEAVAGE AND SULFONYL DELETION

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CYCLIC (ALKENYL)(AMINO)CARBENE ($^{SMe}CA_{en}AC$): MODULATING THE HOMO–LUMO ENERGY GAP

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TETRYLENES AND BEYOND: COORDINATION CHEMISTRY OF PHOSPHANYL-SUPPORTED LOW-OXIDATION STATE GROUP 14 SYSTEMS

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CONTROLLED Al(II)-TRANSFER AT CADMIUM ALUMINYLS

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FOUR-MEMBERED CYCLIC ALKYL(AMINO) CARBENE STABILIZED-TETRAATOMIC SILICON(0) CLUSTER

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AN ISOLABLE TRIARYLPHOSPHINE RADICAL CATION ELECTRONICALLY STABILIZED BY THROUGH-SPACE RADICAL DELOCALIZATION

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REACTIVITY OF A POTASSIUM ALUMINYL ANION WITH CROSS-CONJUGATED HYDROCARBONS

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NUCLEOPHILIC GALLYL ANIONS: Ga–Au BIMETALLIC N–H AND O–H ACTIVATION

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SEQUENCE-DEFINED HETEROMETALLIC LANTHANIDE OLIGOMERS BY STEPWISE CLICKZIP ASSEMBLY

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INVERSE SANDWICH COMPLEXES FOR THE TRANSFER OF GROUP 13 ELEMENTS IN THE +1 OXIDATION STATE

MG-1417-P ***Zhang, J.-Y.***, *ShanghaiTech University, Shanghai, China*
IMINE OLEFINATION WITH ARYLMETHANE AND ITS C=C BOND CLEAVING REVERSE REACTION CATALYZED BY SODIUM ALKYLAMIDE LADDER STRUCTURES

MG-1418-P ***Barik, J.***, *Indian Institute of Technology Madras, Chennai, India*
ANILIDO-PYRAZOLE LIGAND SUPPORTED GERMYLENES: SYNTHESIS, STRUCTURE, AND CATALYTIC *N*-FORMYLATION OF AMINES USING CO_2

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TRAPPING GALLIUM MONOFLUORIDE BY COORDINATION TO NICKEL

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TOWARDS HOMOLEPTIC GROUP 13 TADF EMITTERS

MG-1421-P ***Vollmar, K.***, *University of Konstanz, Konstanz, Germany*
LUMINESCENT COORDINATION COMPOUNDS OF THE PNICTOGENS WITH DIPYRIDINE PYRROLIDE LIGANDS

MG-1422-P ***Gaurav, K.***, *Indian Institute of Science Education and Research Pune, Pune, India*
ACCESS TO LOW VALENT GROUP 14 SPECIES UTILIZING CYCLIC ALKYL AMINO OLEFINES (CAAOs)

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PHOSPHOLE-BASED INTRA- AND INTERMOLECULAR FRUSTRATED LEWIS PAIRS AS FLUORESCENT AND STIMULI-RESPONSIVE SYSTEMS

MG-1424-P ***Lim, L.F.***, *Technical University of Munich, Garching, Germany*
COOPERATIVE C-H ACTIVATION OF BENZYLIC ARENES BY A p-BLOCK 3d-METAL SCAFFOLD

MG-1425-P ***Doležal, L.***, *University of Pardubice, Pardubice, Czech Republic*
FIRST *P,C,P*-PINCER ORGANOBISMUTH COMPOUNDS

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HEAVY PNICTOGEN, TETREL, AND COINAGE METAL COMPLEXES WITH ISOMERIC BIS[CYCLIC (ALKYL)(AMINO)CARBENE] LIGANDS

MG-1427-P ***de Vere-Tucker, M.***, *King's College London, London, UK*
CYCLOTRIALUMANES AND BEYOND

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C=O METHYLENATION MEDIATED BY ORGANO-ALKALI METAL REAGENTS: METAL IDENTITY AND LIGAND EFFECTS

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COPPER(-I)? A XAS STUDY OF COPPER — MAIN GROUP COMPOUNDS

MG-1430-P ***Antoni, P.W.***, *Technische Universität Dortmund, Dortmund, Germany*
FROM DIAZOALKENES TO TRIPLET VINYLIDENES AND METALLOVINYLIDENES

MG-1431-P ***Shaw, P.***, *The University of Edinburgh, Edinburgh, UK*
REACTIVITY OF LOW-VALENT MAGNESIUM(I) COMPLEXES WITH EPOXIDES AND EPISULFIDES

MG-1432-P ***Schneider, P.***, *Julius-Maximilians-Universität, Würzburg, Germany*
CATALYTIC Si/B EXCHANGE CONDENSATION AS A MILD AND EFFICIENT ROUTE TO CONJUGATED ALKYNYL-SPACED BORANES

MG-1433-P ***Chlebík, R.***, *University of Pardubice, Pardubice, Czech Republic*
Probing Catalytic CO_2 activation with P,C,P- pincer germanium(II) and tin(II) hydrides

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CALCIUM HYDRIDE COMPLEXES FOR THE HYDRODEFLUORINATION OF F-CONTAINING MOLECULES

MG-1435-P ***Biswas, S.***, *Humboldt Universität zu Berlin, Berlin, Germany*
INTRAMOLECULAR Al/P FRUSTRATED LEWIS-PAIRS BASED ON AN INDOLINE BACKBONE – TWO REACTION SITES FOR SMALL MOLECULE ACTIVATION AND HYDRODEFLUORINATION

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BIS(PYRIDINO-O-CARBORANYL) PHOSPHENIUM: A PLATFORM FOR DUAL-SITE REACTIVITY IN SMALL-MOLECULE ACTIVATION

MG-1437-P ***Singh, V.***, *Indian Institute of Technology Dehli, New Dehli, India*
FROM TRIS(GERMYLENE) TO TRIPODAL COPPER CATALYST: SYNTHESIS, UNUSUAL OXO-CATION FORMATION, AND CuAAC ACTIVITY

MG-1438-P ***Schuetz, V.***, *Julius-Maximilians-Universität, Würzburg, Germany*
POLY(FERROCENYLENE IMINOBORANE), RELATED COPOLYMERS AND MACROCYCLES

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DO ANIONIC LEWIS ACIDS DISCRIMINATE CHARGE IN SUBSTRATE BINDING? INSIGHTS FROM A β-OCTABROMO-CALIX[4]PYRROLATO ALUMINATE

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A DFT STUDY ON DIFFERENT CONFORMATIONS OF IRON-OXO 14-TNC

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EXPLORING THE LIGAND CHEMICAL SPACE OF THE $[Cr(Tpm^R)_2]$ SPIN-CROSSOVER FAMILY

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SINGLET VS TRIPLET DIRADICALS: CONTROL OF SPIN COUPLING VIA CONFORMATIONAL CHANGE

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STRUCTURAL DIVERSITY AND PHOTOLUMINESCENT PROPERTIES OF ZINC AND CADMIUM SILANETHIOLATES WITH PYRIDINE DERIVATIVES

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MULTI-SCALE MODELLING FOR AN ACCURATE PREDICTION OF REDOX POTENTIALS IN IRON COORDINATION COMPOUNDS

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MAPPING THE INVERTED MARCUS REGION OF NOVEL COBALT BASED COMPLEXES

MM-1507-P ***Chesher, G.***, *University of Leeds, Leeds, UK*
PHOTOACTIVE IRON(II) *bis*-(2,6-DIPYRAZOL-1-YL PYRIDINE) SPIN-CROSSOVER COMPLEXES FUNCTIONALISED WITH PROXIMAL HETEROARYL AZO SUBSTITUENTS

MM-1508-P ***Bassi, G.***, *Technical University of Munich, Munich, Germany*
DENSITY MATRIX RENORMALIZATION GROUP TO TARGET CORE EXCITED STATES OF TRANSITION METAL COMPLEXES

MM-1509-P ***Chomiuk, J.***, *University of Oxford, Oxford, UK*
SPIN-POLARON INTERACTIONS IN PARAMAGNETIC PORPHYRINS

MM-1510-P ***Becker, J.-G.***, *Johannes Gutenberg University, Mainz, Germany*
DOES CHIRALITY MATTER? DISENTANGLING SYMMETRY AND PACKING EFFECTS IN Fe(II) COMPLEXES

MM-1511-P ***Raue, K.***, *ETH Zurich, Zurich, Switzerland*
RELATIONSHIP BETWEEN Fe-Co PEROVSKITE STRUCTURES AND THEIR NÉEL/CURIE TEMPERATURES

MM-1512-P ***Schmitz, M.***, *RPTU University Kaiserslautern-Landau, Kaiserslautern, Germany*
FAST SPIN-CROSSOVER PROCESSES IN IRON(II) COMPLEXES CONTAINING π-RADICAL LIGANDS

MM-1513-P ***Diederich, T.M.***, *Ruprecht-Karl-University Heidelberg, Heidelberg, Germany*
PROPERTIES OF IRON PHTHALOCYANINES BY pNMR

MM-1514-P ***Li, Y.***, *Soochow University, Suzhou, P.R. China*
SPIN CROSS-OVER (SCO) PROPERTIES OF A SERIES OF IRON(II) COMPLEXES

MM-1515-P ***Lee, Y.***, *Jeonbuk National University, Jeonbuk, Republic of Korea*
DFT INVESTIGATION OF SPIN-STATE-DEPENDENT NITRITE REDUCTION VIA AN $\{FeNO\}^6$ INTERMEDIATE IN A MONONUCLEAR IRON(II) COMPLEX

MM-1516-P ***Zhang, Y.***, *Tsinghua University, Beijing, China*
A CRYSTALLINE IRON COMPLEX STABILIZING A BENT, DOUBLY REDUCED PYRAZINE

MM-1517-P ***Wojdyla, Z.***, *Czech Academy of Sciences, Prague, Czech Republic*
EXPLORING THE SHIFT FROM PROTON-COUPLED TO HYDRIDE-COUPLED ELECTRON TRANSFER

ND-1601-P ***Lichtenberg, A.***, *University of Cologne, Cologne, Germany*
CHEMICAL VAPOR DEPOSITION OF ACTINIDE-BASED THIN FILMS FROM ACTINIDE COORDINATION COMPOUNDS

ND-1602-P ***Long, D.-L.***, *The University of Glasgow, Glasgow, UK*
DISCOVERY AND CHARACTERISATION OF NEW GIGANTIC POLYOXOMOLYBDATES

ND-1603-P ***Silvestre-Llora, A.***, *Universitat de Barcelona, Barcelona, Spain*
SWITCHING HOSTS, SWITCHING TIMES: RELAXATION DYNAMICS OF ENCAPSULATED FERROCENIUM

ND-1604-P ***Webster-Hirst, A.***, *University of Warwick, Coventry, UK*
THERMODYNAMIC LIGAND EXCHANGE STUDIES IN METAL-OXO CLUSTERS WITH NMe_4 SALTS

ND-1605-P ***Kitos, A.A.***, *Technical University of Denmark, Lyngby, Denmark*
TUNING MAGNETIC AND ELECTRONIC PROPERTIES IN A CHROMIUM-PYRAZINE COORDINATION FRAMEWORK VIA AXIAL HALIDE LIGAND SUBSTITUTION

ND-1607-P ***Chikara, A.***, *University of Warwick, Coventry, UK*
OPTIMISING TITANIUM OXO CLUSTER-BASED MATERIALS FOR PHOTOCATALYSIS

ND-1608-P ***Drahoš, B.***, *Palacký University, Olomouc, Czech Republic*
OPTIMIZATION OF THE SYNTHESIS OF MACROCYCLIC LIGANDS USING LINEAR PUMPS AND A FLOW REACTOR

ND-1609-P ***Tezcan, B.***, *Çukurova University, Adana, Turkey*
NOVEL FLUORINE-SUBSTITUTED BIAN LIGANDS AND THEIR SILVER(I) COMPLEXES: SYNTHESIS AND CHARACTERIZATION

ND-1610-P ***Rosenberg, C.***, *University of Warwick, Coventry, UK*
SITE-SELECTIVE PHOTOREDOX REACTIVITY OF TITANIUM-OXO CLUSTERS IN THE SINGLE CRYSTAL PHASE

ND-1611-P ***Wang, C.***, *University of Leeds, Leeds, UK*
INFLUENCE OF Ru(II) AND Zn(II) DOPING ON THE SPIN-CROSSOVER PROPERTIES OF AN Fe(II) 2,6-*bis*(PYRAZOLYL)PYRIDINE DERIVATIVE

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HETEROVALENT MANGANESE ALKYNYL CLUSTER

ND-1613-P ***Kelly, C.T.***, *University College Dublin, Dublin, Ireland*
BROKEN SYMMETRY AND ELASTIC FRUSTRATION IN ISOSTRUCTURAL MANGANESE(III) SPIN CROSSOVER CRYSTALS

ND-1614-P ***Venegas-Yazigi, D.***, *Universidad de Santiago, Santiago, Chile*
DODECAVANADATE COORDINATED TO LANTHANIDE IONS. A NEW FAMILY OF MIXED-VALENCE POLYOXOVANADATES

ND-1615-P ***Fragkis, D.***, *National and Kapodistrian University of Athens, Athens, Greece*
ACCESS TO MIXED VALENT POLYNUCLEAR Ni COMPLEXES FROM Ni(II) PIANO-STOOL TYPE COMPLEXES

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SYNTHESIS OF Co(III)-AMMINE HETEROPOLYOXOMOLYBDATES WITH SELECTED d-BLOCK ELEMENTS

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PRODUCTION EFFICIENCY FOR LOW-CARBON CONCRETE IN PRECAST MANUFACTURING

ND-1618-P ***Hamade, F.***, *Université Paris-Saclay, Orsay, France*
LUMINESCENT SPIN CROSSOVER COMPLEXES

ND-1619-P ***Saggiotti, G.***, *University of Padova, Padova, Italy*
THE CHEMISTRY OF ATOMICALLY PRECISE GOLD NANOCLUSTERS FOR ELECTROCHEMICAL AND BIOLOGICAL APPLICATIONS

ND-1620-P ***Im, H.***, *Korea Advanced Institute of Science and Technology, Daejeon, Republic of Korea*
REPURPOSING AN ORGANIC COFACTOR: METALLOFLAVINS THAT INVERT THE IRVING–WILLIAMS STABILITY TREND VIA OUTER-SPHERE HYDROGEN BONDING

ND-1621-P ***Sawka, J.***, *University of Wroclaw, Wrocław, Poland*
SLOW MAGNETIC RELAXATION IN MONOMERIC PENTACOORDINATE Mn(II) COMPLEXES NOT GOVERNED BY THE ORBACH PROCESS

ND-1622-P ***Beall, J.***, *University of Warwick, Coventry, UK*
TUNING THE ELECTRONIC STRUCTURE AND PHOTOCHEMICAL PROPERTIES OF IRON(III)-OXO CLUSTERS

ND-1623-P ***Dai, J.***, *Soochow University, Suzhou, P.R. China*
GELATION PROPERTIES OF CATECHOL DERIVATIVE MODIFIED TITANIUM-OXO CLUSTERS

ND-1625-P ***Sharrock, K.***, *University of Warwick, Coventry, UK*
ELUCIDATING THE CAPABILITY OF PHOTOACTIVATED Ti-oxo CLUSTERS TO PERFORM OF MULTIELECTRON PROCESSES THROUGH BDFE STUDIES AND STRUCTURAL MANIPULATION

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ULTRAFAST PHOTOINDUCED CHARGE-TRANSFER DYNAMICS AT ROOM TEMPERATURE IN A Co-W CYANIDE-BRIDGED SYSTEM

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NOVEL SPIN CROSSOVER IRON(II) COMPLEXES FOR BAROCALORIC EFFECT

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HYPERFINE INDUCED CLOCK-LIKE T_2 ENHANCEMENT IN A MAIN GROUP RADICAL

ND-1629-P ***Sulzbacher, M.***, *Johannes Gutenberg-University Mainz, Mainz, Germany*
SYNTHESIS AND CHARACTERISATION OF A HETEROMETAL FUNCTIONALIZED OCTADECAVANADATE

ND-1630-P ***Remmers, M.***, *Johannes Gutenberg-University Mainz, Mainz, Germany*
^{17}O-ENRICHED POLYOXOVANADATES REVEAL OXYGEN SITE DYNAMICS VIA ^{17}O NMR SPECTROSCOPY

ND-1631-P ***Parammal, M.J.***, *University of Basel, Basel, Switzerland*
MECHANISM-GUIDED PRECISION HYDROLYSIS OF EARLY TRANSITION METALS TO ACCESS (MIXED-METAL) OXO CLUSTERS

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BORANE-APPENDED Ru(II) COMPLEXES: A "PUSH-PULL" STRATEGY FOR COOPERATIVE CO_2 ACTIVATION

ND-1633-P ***Sato, N.***, *Tohoku University, Sendai, Japan*
NICKEL(II) PORPHYRIN/FULLERENE C_{70} POROUS MOLECULAR COCRYSTAL FEATURING A ROBUST ONE-DIMENSIONAL CHANNEL

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ELECTROCHEMICAL EVALUATION OF POLYOXOMETALATE COORDINATION CLUSTERS FOR BIOMASS OXIDATION CATALYSIS

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SYNTHESIS AND CHARACTERISATION OF LANTHANIDE DOPED NANOSCALE Ce-oxo CLUSTERS

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SIGNATURES OF METAL IONS AND POLYOXOMETALATES IN SOLUTION WITH PAIR DISTRIBUTION FUNCTION

ND-1638-P ***Shoji, R.***, *Tohoku University, Sendai, Japan*
DIPYRRIN-BASED PHOTOFUNCTIONAL COORDINATION ARCHITECTURES FOR LIGHT HARVESTING

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CONTRASTING MAGNESIUM AND MANGANESE IN N_2 AND BENZENE ACTIVATION

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UNLEASHING PHOSPORUS MONONITRIDE

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HYDROGEN BONDING PROPAGATED PHASE SEPARATION IN QUASI-EPITAXIAL SINGLE CRYSTALS: A Pd–Br MOLECULAR INSULATOR WITH ENANTIOMERIC AND RACEMIC LIGAND

ND-1642-P ***Koyama, Y.***, *Chuo University, Tokyo, Japan*
VALENCE TAUTOMERIC COMPLEXES RESPONSIVE TO MULTIPLE EXTERNAL STIMULI AND THE SOLUTION ENVIRONMENT

ND-1643-P ***Fan, Z.***, *Technische Universität Dortmund, Dortmund, Germany*
ZINC HALIDE FLUX-ASSISTED VITRIFICATION OF METAL-ORGANIC FRAMEWORKS ENABLES CHEMICAL DIVERSIFICATION AND TUNABLE GAS SORPTION

SM-1701-P ***Clutterbuck, K.***, *The University of Sydney, Darlington, Australia*
DUAL-RESPONSIVE CHIROPTICAL PROPERTIES IN A COFACIAL TTF-BASED METAL-ORGANIC FRAMEWORK

SM-1702-P ***Lee, A.***, *University of Calgary, Calgary, Canada*
SUPRAMOLECULAR CHEMISTRY IN THE 3D CHANNELS OF MOLECULAR COMPLEXES WITH TETRAPHOSPHINE LIGANDS

SM-1703-P ***Blyth, A.E.***, *University of Cambridge, Cambridge, UK*
INVESTIGATING TARGETED CATION ORDERING IN METAL ORGANIC FRAMEWORKS BUILT FROM INERT METALLOLIGANDS

SM-1704-P ***Tasiopoulos, A.***, *University of Cyprus, Nicosia, Cyprus*
TEMPLATED SYNTHESIS OF A Zr-FORMATE ZEOLITE - LIKE METAL ORGANIC FRAMEWORK

SM-1705-P ***Peuronen, A.***, *University of Turku, Turku, Finland*
O_2 CAUGHT IN AN IRON-PORPHYRIN MOF

SM-1706-P ***Raveendranathan, A.***, *Karlsruhe Institute of Technology, Karlsruhe, Germany*
METALLOGEL-MEDIATED CRYSTAL GROWTH OF A Cu(II)-Ho(III) HETEROMETALLIC METAL-ORGANIC FRAMEWORK WITH UNUSUAL NODE DISORDERS

SM-1707-P ***Ghosh, A.***, *Indian Institute of Technology Madras, Chennai, India*
TEMPLATE INDUCED ORIENTATIONAL SELECTIVITY OF LIGANDS IN A DOUBLE CAVITY COORDINATION CAGE

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COORDINATION CAGES AS SCAFFOLDS FOR MONODISPERSE MULTI-GLYCAN ARRAYS FOR LECTIN BINDING

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EXPLORING MOF-GELS FOR TRACE PFAS REMOVAL FROM WATER

SM-1710-P ***Jain, C.***, *The University of Osaka, Osaka, Japan*
A NOVEL PENTANUCLEAR IRON-BASED COVALENT ORGANIC FRAMEWORK ENABLING ANION-REGULATED ELECTROCHEMICAL CO_2 REDUCTION

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UNLOCKING A NEW GEOMETRY IN PORPHYRIN METALLACYCLES

SM-1712-P ***Rodríguez Boscà, Ch.***, *Universidad de Valencia, Valencia, Spain*
LIGHT CONTROLLED SOLUBILITY ON HETEROLEPTIC METAL-ORGANIC CAGES

SM-1713-P ***John, D.***, *Indian Institute of Technology Madras, Chennai, India*
LIGAND ISOMERISM IN ENDOHEDRALLY LOW-SYMMETRY DISCRETE COORDINATION CAGES AND THEIR DIFFERENTIAL SWITCHING MODES

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SEPARATION AND ISOLATION OF HETEROLEPTIC COORDINATION CAGES VIA PHASE TRANSFER

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IRON–PORPHYRIN METAL–ORGANIC FRAMEWORKS FOR HETEROGENEOUS OXIDATION CATALYSIS IN WATER REMEDIATION

SM-1716-P ***Ripoll, G.***, *Universidad de Valencia, Valencia, Spain*
BIMETALLIC Pd-Fe MOF FOR C-2 ARYLATION OF INDOLES

SM-1717-P ***Kurz, H.***, *University of Bayreuth, Bayreuth, Germany*
NOVEL DINUCLEAR BUILDING BLOCKS FOR HETEROLEPTIC CAGES

SM-1718-P ***Chen, H.***, *Max-Planck-Institut für Kohleforschung, Mülheim/Ruhr, Germany*
MODELING THz EPR/MAGNETIC IR SPECTROSCOPY INCLUDING SPIN-PHONON COUPLINGS USING AN EXTENDED SPIN HAMILTONIAN

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SYNTHESIS AND ELECTRONIC PROPERTIES OF Cr-BASED METALLOSUPRAMOLECULAR POLYMERS

SM-1720-P ***Wiśniewska, J.***, *Nicolaus Copernicus University in Toruń, Toruń, Poland*
NOVEL HYBRID MATERIALS BASED ON BIOACTIVE GLASS MODIFIED BY MIL-100 FRAMEWORK: PROPERTIES AND BIOMEDICAL APPLICATIONS

SM-1721-P ***Sundberg, J.***, *Technical University of Denmark, Ballerup, Denmark*
TRACE ADSORPTION OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) USING MULTIVARIATE METAL-ORGANIC FRAMEWORKS

SM-1723-P ***Sotirakopoulos, K.***, *Universitat de Barcelona, Barcelona, Spain*
DRIVING MAGNETIC BEHAVIOUR THROUGH SUPRAMOLECULAR ENCAPSULATION OF COORDINATION COMPLEXES

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EFFECT OF LIGAND METHYLATION ON DIASTEREOISOMERISM OF M_4L_6 TETRAHEDRA

SM-1726-P ***Trivedi, M.U.***, *Chalmers University of Technology, Göteborg, Sweden*
MODULAR TRIAZOLE-BASED MACROCYCLES FOR HALIDE AND METAL ION DETECTION

SM-1727-P ***Boursier, M.***, *University of Amsterdam, Amsterdam, The Netherlands*
Fe-PORPHYRINIC METAL–ORGANIC FRAMEWORKS WITH TUNABLE Fe···Fe DISTANCES FOR C–H ACTIVATION

SM-1728-P ***Gedikoglu, N.***, *Technical University of Denmark, Ballerup, Denmark*
AN AUTOMATED FLUIDIC WORKFLOW FOR REPRODUCIBLE AND SCALABLE FABRICATION OF METAL-ORGANIC-FRAMEWORK-BASED QCM SENSORS

SM-1729-P ***Serrano-Laguna, P.J.***, *University of Huelva, Huelva, Spain*
IN CRYSTALLO AMMONIA UPTAKE IN $CsBAr^{F}_{4}$

SM-1730-P ***Seglen, P.S.***, *University of Oslo, Oslo, Norway*
HETEROGENIZED BIOINSPIRED COPPER-COMPLEXES WITH ADJACENT STERIC GROUPS FOR C-H BOND ACTIVATION

SM-1731-P ***Velmurugan, P.***, *Indian Institute of Technology Madras, Chennai, India*
REDEFINING THE COORDINATION MODE OF 1,2,4-TRIAZOLYLIDENE: BRIDGING THE GAP BETWEEN MOLECULAR ORGANOMETALLIC CHEMISTRY AND EXTENDED POROUS ARCHITECTURES

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STRUCTURAL CHARACTERISATION OF INDIUM(III) THIOCYANATE

SM-1733-P ***Tanaka, S.***, *Konan University, Kobe, Japan*
SYSTEMATIC STUDY OF REVERSIBLE TRANSFORMATION BETWEEN MIL-53 AND MIL-68: EFFECTS OF DEFECT DENSITY AND PARTICLE SIZE

SM-1734-P ***Capomolla, S.***, *University of New South Wales, Sydney, Australia*
CATALYSIS BY A METASTABLE PHOTOSWITCHABLE CAGE

SM-1735-P ***Zimmermann, S.***, *University of Wuppertal, Wuppertal, Germany*
LARGE GOLD AND SILVER RINGS BASED ON BRIDGING NHC LIGANDS

SM-1736-P ***Mondal, S.***, *Chonnam National University, Gwangju, South Korea*
COORDINATION-DRIVEN ASSEMBLY OF β-DIKETONATE HYDRAZONE-BASED CAGES

SM-1737-P ***Baca, S.***, *Moldova State University, Chisinau, Moldova*
TUNING THE DIMENSIONALITY OF COORDINATION POLYMERS BASED ON COBALT(II) CARBOXYLATE DIMERS

SM-1738-P ***Gopalakrishnan, S.***, *Technical University of Denmark, Ballerup, Denmark*
METAL-ORGANIC FRAMEWORK FUNCTIONALIZED SENSOR ARRAYS FOR DISSOLVED GAS SENSING

SM-1739-P ***Amatsu, T.***, *Graduate School of Osaka Institute of Technology, Osaka, Japan*
METAL HYDROGEN-BONDED ORGANIC FRAMEWORKS ASSEMBLED VIA PHOTOINDUCED SELF-ASSEMBLY

SM-1740-P ***Dakua, T.***, *Indian Institute of Technology Madras, Chennai, India*
LINEARLY CONJOINED MULTICAVITY DISCRETE COORDINATION CAGES: MOLECULAR SOYBEANS

SM-1741-P ***Patra, U.***, *University of Southern Denmark, Odense, Denmark*
METAL–ORGANIC FRAMEWORKS FEATURING CLUSTERS OF ZERO-VALENT ATOMS

SM-1742-P ***Paredes-García, V.***, *CEDENNA, Santiago, Chile*
SCHIFF BASE COORDINATION COMPOUNDS WITH *3d* AND *4f* METAL CENTERS. STRUCTURAL DIVERSITY AND FUNCTIONALITY

SM-1743-P ***Qomfo, V.***, *Nelson Mandela University, Gqeberha, South Africa*
LIGAND-DIRECTED SUPRAMOLECULAR ASSEMBLY OF COPPER(II) PADDLEWHEEL COMPLEXES FEATURING PHENACYL-ESTER LIGANDS

SM-1744-P ***Takashima, Y.***, *Konan University, Kobe, Japan*
SYNTHESIS OF Bi_2Te_3 NANOPARTICLES WITH Bi-BASED MOF AS PRECURSOR

IMPORTANCE OF INTRAMOLECULAR HYDROGEN BONDING FOR THE MOLECULAR GEOMETRY OF OXOVANADIUM COMPLEXES WITH PYRAZOLES

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A series of mononuclear vanadyl(IV) complexes derived from vanadyl(IV) sulfate, ($[V(O)(R\text{-}pzH)_4(SO_4)]\cdot Z$, Z = H_2O, MeOH, or R-pzH), with 4- or 3-substituted pyrazoles were synthesized and characterized crystallographically, spectroscopically (IR, UV-vis), and magnetochemically. Molecular structure is controlled primarily by intramolecular hydrogen bonding between sulfato ligand and coordinated pyrazoles and fine-tuned by intermolecular hydrogen bonding between counter anions or solvent molecules and coordinate pyrazoles. Presented complexes represent precursors for the study of polynuclear pyrazolato complexes.

COPPER(II) PICOLINAMIDE COMPOUNDS WITH HIGH SELECTIVITY TOWARDS OSTEOSARCOMA

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Picolinamides are versatile ligands with flexible coordination modes to metal centres and low cytotoxicity in mammalian cell lines. They have been complexed to late transition metals such as Ir(III), Ru(II)/(III) or Rh(III) and shown to have promising anticancer activity,[1-3] or to Co(II), giving compounds which show no cytotoxicity towards mammalian cell lines but high antifungal activity, especially in *Aspergillus fumigatus*.[4]

Due to their tight endogenous control, detoxification, and alternative modes of action, research has focused on the development of metal based drugs incorporating essential trace elements like copper.[5] Here, we present a series of Cu(II) picolinamide complexes of the type ML_2 (where M = Cu and L = picolinamide), which have been successfully characterized by IR, EPR, cyclic voltammetry and single crystal X-ray diffraction (sc-XRD). The compounds biological activity has been tested against a range of mammalian cell lines and their uptake assessed by ICP-MS. The results highlight an important link between the compounds' cytotoxicity and relative stability (supported by DFT calculations) which can be tuned by ortho functionalisation of the picolinamide ligand.

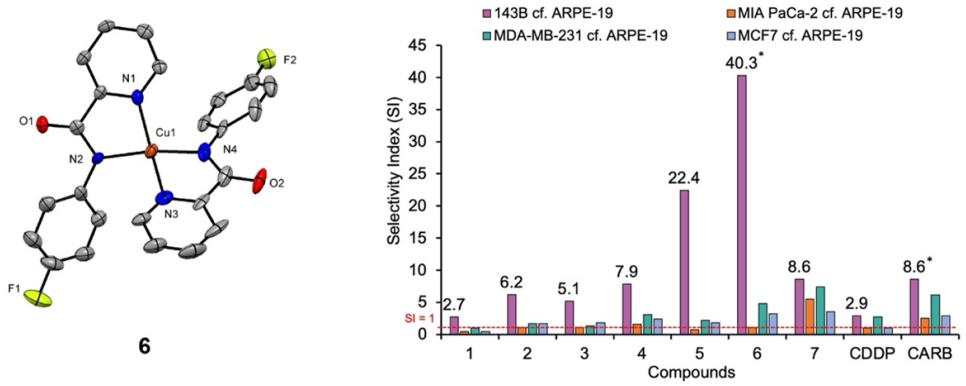


Figure: sc-XRD structure of the most active Cu picolinamide complex **6** (left) and the selectivity index for all tested compounds comparing various cancer cell lines with the human retinal epithelial cell line ARPE-19 (right).

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RATIONAL DESIGN STRATEGIES FOR METAL-BASED DRUGS BEYOND CLASSICAL STRUCTURE–ACTIVITY PARADIGMS

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In anticancer drug design, metal complexes offer significant advantages over purely organic compounds. Their variable coordination numbers and structural diversity, accessible redox states, and the ability to fine-tune thermodynamic stability and ligand-substitution kinetics provide considerable potential for applications in cancer therapy. In this context, the rational design of the coordination compounds presented here as potential drug candidates was guided by several essential requirements: adequate solubility of the prodrug form, kinetic stability and limited reactivity in the bloodstream, selective cellular accumulation, controlled activation within tumor cells, and the induction of cytotoxic effects. To achieve these objectives, several strategies were employed: (i) construction of specific coordination polyhedra; (ii) substitution of platinum with ruthenium, palladium, or gold; (iii) utilization of higher and intermediate oxidation states (Pt(IV) (Fig. 1a) [1], Pt(III), Ru(IV) (Fig. 1b), Ru(III), Pd(III) [2], and Au(II)); (iv) development of polynuclear architectures; and (v) incorporation of ligands enabling selective targeting or structural similarity to biologically active molecules. The solid-state structures and behavior in solution of the novel coordination compounds were investigated by single-crystal X-ray diffraction, magnetic measurements, and NMR, EPR, IR, and UV/Vis spectroscopy. Their cytotoxic activity was evaluated against a panel of human tumor cell lines of different types and origins. The new metal complexes exhibit favorable physicochemical properties under physiologically relevant conditions, inhibit cancer cell growth at micromolar concentrations, and display a mechanism of action different from that of cisplatin.

a) b)

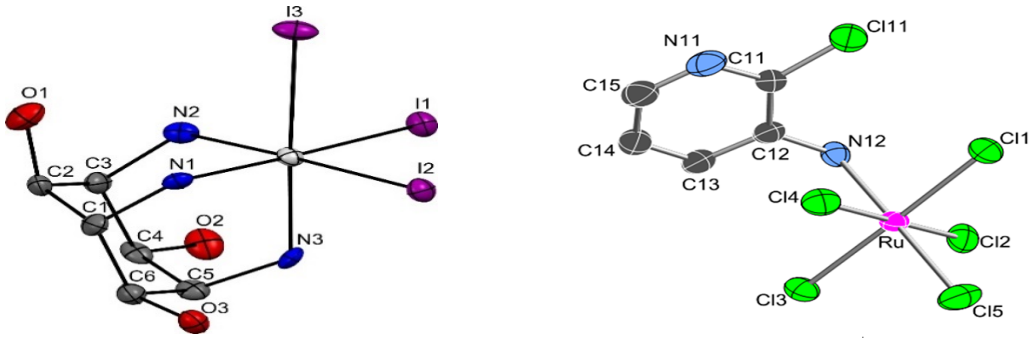


Fig. 1. The conformation and atom numbering of a) $[Pt(IV)I_3(taci)]^+$, (taci≡all-cis-2,4,6-triaminocyclohexane-1,3,5-triol) and b) $[Ru(IV)Cl_5(acp)]^-$, (acp≡3-amino-2-chloropyridin).

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PHOTOCHEMICAL ACCESS TO NOVEL *N*-HETEROCYCLIC CARBENE LIGAND PRECURSORS FOR THE DEVELOPMENT OF ANTICANCER METAL–NHC COMPLEXES

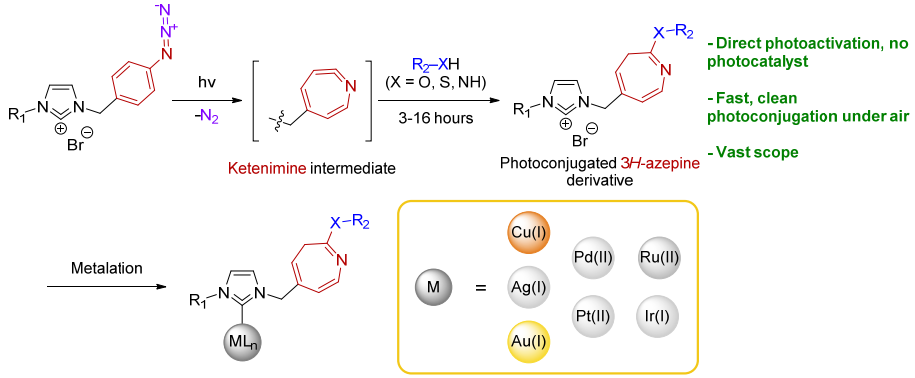
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N-heterocyclic carbene (NHC) metal complexes have emerged as a versatile class of compounds with promising applications in medicinal chemistry, particularly as potential anticancer agents [1]. In this context, expanding the structural diversity of NHC ligands is a key strategy to modulate the properties of the resulting metal complexes. Among the functional motifs that can be incorporated, photoactivatable groups (PGs) are particularly attractive: upon irradiation with light, PGs form high-energy intermediates, often unlocking otherwise inaccessible reaction pathways. For instance, under UV light, aryl azides generate reactive ketenimine intermediates that rapidly react with nucleophiles such as amines, alcohols and thiols, yielding azepine derivatives [2]. Recently, nitroarenes have been reported to display analogous behaviour under blue light [3].

Herein, we report the synthesis of a previously unexplored class of NHC proligands based on imidazolium salts bearing photoactivatable azidoarene and nitroarene pendants. Upon irradiation, these precursors react photochemically with a wide range of nucleophiles, affording imidazolium salts functionalized with diversely substituted azepine moieties. These species serve as versatile precursors for the preparation of unprecedented families of NHC metal complexes. Accordingly, the corresponding NHC complexes were synthesized by coupling the proligands with metal centres such as Au(I), Ag(I), Cu(I), Pd(II) and Pt(II), and will be investigated as potential anticancer metallodrugs.

Beyond enabling access to this new class of NHC metal complexes, the photoreactivity explored in this study lays the foundation for the future photoconjugation of NHC complexes with biomolecules, including cancer-relevant monoclonal antibodies, paving the way towards targeted antibody–metallodrug conjugates (AMCs) with improved selectivity and reduced systemic toxicity.



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GOLDEN HYBRIDS: A SILVER-FREE APPROACH TO BIOACTIVE NHC-Au(I)-NSAID COMPLEXES

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Gold complexes, particularly *N*-heterocyclic carbene (NHC)-gold derivatives, have been extensively investigated over the last decade for their cytotoxic anticancer properties, emerging as promising candidates for cancer therapy.[1] Several strategies have been explored to enhance their biological activity and selectivity. Among these, the conjugation of gold complexes with biologically active molecules, such as *nonsteroidal anti-inflammatory drugs* (NSAIDs), represents a particularly attractive approach. Gold complexes are widely reported to target thioredoxin reductase (TrxR), inducing oxidative stress and triggering multiple cell death pathways.[1,2] The incorporation of NSAIDs, which possess intrinsic biological activity, has been shown to further enhance the therapeutic potential of these systems. Notably, such hybrid compounds have demonstrated promising activity against cancer stem cells (CSCs)[3], highlighting their potential as effective anticancer agents.

However, the synthesis of Au(I)-NSAID complexes typically requires multistep procedures, the use of toxic solvents, and silver intermediates, leading to the generation of silver salt waste. By exploiting the reactivity of NHC-Au(I)-aryl complexes, an important class of compounds widely used in catalysis, it is possible to access NHC-Au(I)-NSAID derivatives through a straightforward one-step strategy employing non-toxic solvents and avoiding silver reagents. This approach provides a more sustainable and efficient route to this promising class of anticancer compounds.

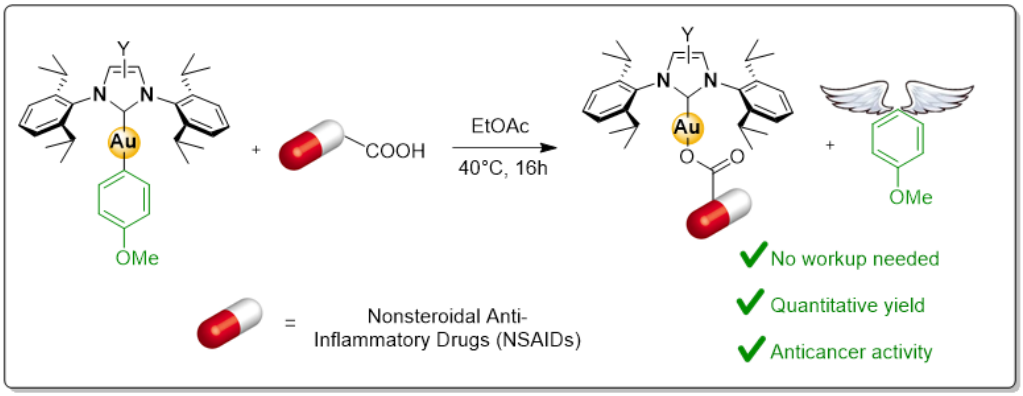


Figure 1. Facile synthesis of NHC-Au(I)-NSAIDs presented in this work.

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FROM PHYSICOCHEMICAL PROPERTIES TO BIOACTIVITY: SIMILARITIES AND DIFFERENCES IN CYCLOMETALLATED Rh(III) AND Ir(III) COMPLEXES

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Growing interest in non-platinum metallodrugs has expanded the scope of medicinal inorganic chemistry beyond the traditional focus on Pt(II) agents. This expansion is driven by the search for novel mechanisms of action, improved tolerability and enhanced efficacy against drug-resistant cancers. Among the transition metals of the second and third rows, octahedral d^6 complexes of Ru(III), Rh(III) and Ir(III) are attractive due to their rich coordination chemistry and tunable redox and photophysical behaviour. Comparative studies of Rh(III)/Ir(III) analogue pairs are particularly informative in this context, as they enable the separation of metal-centred effects from ligand-driven determinants - an essential but persistent challenge in rational metallodrug design.

Here, we present a comparative investigation of newly synthesized cyclometalated pyrazole-based Rh(III) complexes and their Ir(III) [1] analogues. We conducted a combined structural analysis and physicochemical characterisation, followed by biological evaluation in relevant cellular models. All analysed complexes were characterised in the solid state (SC-X-ray, FTIR and elemental analysis) and in solution (ESI-MS, ^{1}H, ^{13}C and ^{15}N NMR, UV-Vis and PL). Cytotoxicity studies were performed using four human cell lines: breast adenocarcinoma (MCF-7), chronic myelogenous leukaemia (K-562), acute lymphoblastic leukaemia (CCRF-CEM) and normal lung fibroblasts (MRC-5). Aligning matched metal–ligand pairs enables the systematic investigation of how the substitution of the metal centre from Rh(III) to Ir(III) modulates key physicochemical parameters and translates into distinct cellular response profiles.

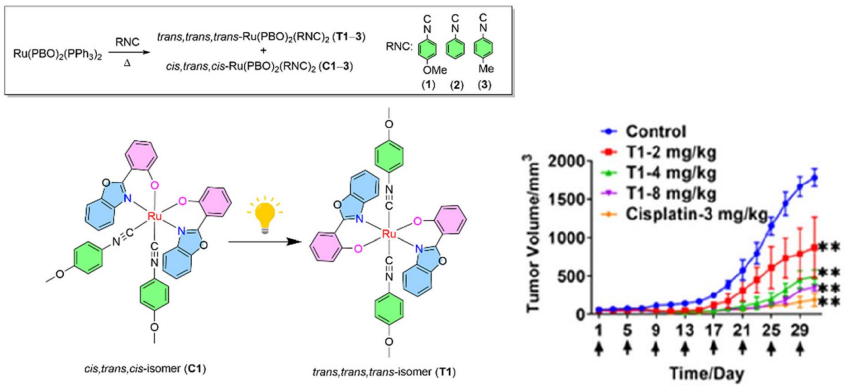
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TRANSFORMABLE CIS–TRANS ISOMERISM OF RUTHENIUM(II) COMPLEXES WITH PHOTOACTIVATED ANTICANCER ACTIVITY

Chen Pan[a], Pui-Yu Ho[a,b], Wan-Qiong Huang[a], Gui-Feng Huang[a], Li-Hua Zhang[b], Daniel Nnaemaka Tritton[d], Shek-Man Yiu[c], Wai-Lun Man[d], Chi-Chiu Ko[c], Chi-Fai Leung[b,*] and Wen-Xiu Ni[a,*]

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Photoactivated chemotherapy (PACT) provides a new alternative cancer treatment strategy compared to conventional therapy. In this study, a series of diisocyano ruthenium(II) complexes $Ru(PBO)_2(RNC)_2$ containing the 2-benzoxazol-2-ylphenolate (PBO) auxiliary ligand and their potential application as PACT agents are reported. The complexes exhibit two geometric isomers, i.e., trans, trans, trans (**T1–T3**) and cis, trans, cis (**C1–C3**) forms. Although **C1–C3** show minimal cytotoxicity (IC_{50} = 60.1 to >100 μM) toward various cancer cells in the dark, the corresponding **T1–T3** complexes exhibit much stronger cytotoxic effects (IC_{50} = 3.7–39.4 μM). **C1** can be readily photoconverted into **T1** upon visible-light irradiation (white light), as shown by UV/vis and ^{1}H NMR spectroscopy. The increased toxicity of the T-form is partially attributed to its reaction with glutathione, in contrast to the C-form analogue. The anticancer activities of **T1** were studied in vitro and in vivo. This is the first study that demonstrates the photoisomerization of the isocyano ruthenium(II) complex $Ru(PBO)_2(CNR)_2$ as an attractive approach for PACT. [1]



[1] Chen Pan, Pui-Yu Ho, Wan-Qiong Huang, Gui-Feng Huang, Li-Hua Zhang, Daniel Nnaemaka Tritton, Shek-Man Yiu, Wai-Lun Man, Chi-Chiu Ko, Chi-Fai Leung and Wen-Xiu Ni, *Inorg. Chem. Front.*, **2025**,*12*, 1969–1978.

OCTAHEDRAL COORDINATION CAGES OF Co(II) AND Ni(II) AS METABOLITE RESPONSIVE PARASHIFT AGENTS

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Department of Chemistry, University at Buffalo, the State University of New York, Amherst, NY 14260

Metal-organic cages are of interest as magnetic resonance imaging agents and as paramagnetic shift agents to capitalize on their unique properties including the ease of incorporating multiple functional groups for tissue targeting and cavities for encapsulation of drugs or multimodality imaging agents.[1, 2] We have prepared the ligand H_3L to produce self-assembled coordination cages with paramagnetic Co(II) or Ni(II) ions (Co_6L_4 and Ni_6L_4 below) and postulated that the highly symmetric, multinuclear architecture provided by the paramagnetic metal-organic cages would allow for multiple NMR-equivalent protons per molecule to significantly enhance the parashift probe.[3] The development of responsive probes is explored through host-guest chemistry with tetraalkylamines, some of which are metabolites, to produce responsive parashift agents. The solid-state structures and solution properties of octahedral M_6L_4-type metal-organic cages with acylhydrazone linkages containing paramagnetic Co(II), Ni(II) show that each metal-center is six-coordinate and has two methylpyridine groups serving to maintain the high-spin divalent center. NMR spectra were collected at 1.4 T, 9.4 T and 11.7 T and T_1 and T_2 times for reporter resonances were measured as well as the limit of detection (LOD) for the cages. ^{1}H NMR studies of host-guest interactions of the Co(II) and Ni(II) cages with various cationic guests were recorded. Cationic tetraalkylammonium or tetraethylphosphonium guests, including the metabolites acetylcholine and choline, were encapsulated within the Co(II) cage. These guests produced a shift in the cage proton resonances, which highlights the potential for mapping small molecules by magnetic resonance spectroscopy imaging.

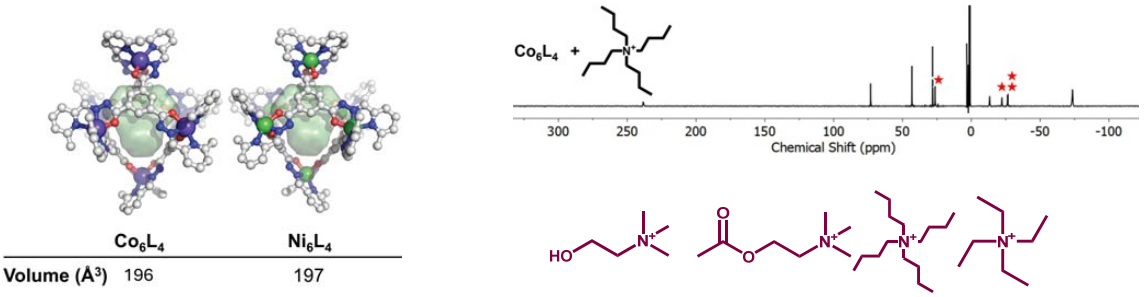


Figure 1. Crystal structures of cages with calculated cavity volume (left); ^{1}H NMR spectrum of Co(II) cage containing encapsulated guest and chemical structures of guests (right).

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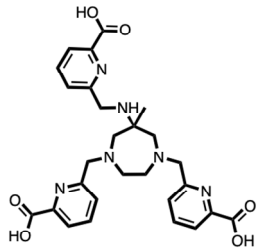
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DEVELOPMENT OF SEMI-RIGID NONADENTATE CHELATORS FOR RADIOLABELLING WITH ^{177}Lu AND ^{133}La

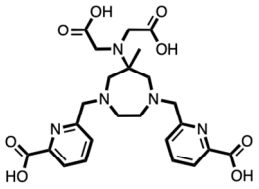
Lorenzo Tei[a], Sara Camorali[a], Jacopo Ferro[a], Elena Bertora[a], Marianna Tosato[b,c], Sara Franchi[d], Sven Stadlbauer[e], Constantin Mamat[e], Klaus Kopka[e,f] and Mattia Asti[g]

[a] DiSIT, University of Piemonte Orientale, Alessandria, Italy
[b] Department of Chemistry, Simon Fraser University, Burnaby, Canada
[c] Life Sciences, TRIUMF, Vancouver, British Columbia, Canada
[d] Department of Chemical Sciences, University of Padova, Padova, Italy
[e] Institute of Radiopharmaceutical Cancer Research, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany
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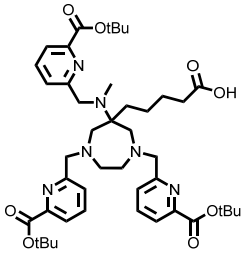
Lutetium-177 (^{177}Lu) is a radionuclide widely used in nuclear medicine, particularly for targeted beta therapy. This electron- and γ-emitter has favourable physical and chemical properties such as a sufficient physical half-life (6.65 days) that represents an optimal balance between effective radiation delivery and manageable decay time. Moreover, the moderate energy of β^- particles ($E_{\beta^-,\,mean}$ = 0.133 MeV) allows a penetration of 0.5-2 mm into the tissue. At the same time, lanthanum radiometals have strong potential in both positron emission tomography (^{132}La, $t_{1/2}$: 4.59 h, I_{β^+}: 42.1% and ^{133}La, $t_{1/2}$ = 3.9 h, I_{β^+}: 7.2 %) and targeted radionuclide therapy (^{135}La, half-life: 18.91 h, 100% EC).



AMPED-3PIC



AMPED-PICAc



MeAMP-3PIC-C_4COOH

In the search for new chelating agents suitable for Ln^{3+} ions of different ionic radii (Lu^{3+} and La^{3+} are at the two sides of the lanthanide series with ionic radii for the 9-coordinate complexes of 103.2 pm and 121.6 pm, respectively), we designed two nonadentate ligands based on the 6-amino-6-methyl-1,4-perhydrodiazepine (AMPED) scaffold functionalized with three picolinic acid (AMPED-3PIC) as well as two picolinic acid and two acetate pendant arms (AMPED-PICAc). Both chelating agents were efficiently radiolabelled with no-carrier-added [^{177}Lu]Lu^{3+} and cyclotron-produced [^{133}La]La^{3+}, with quantitative incorporation after 10-15 min at RT, pH 4.5 and a [L] = 10^{-5} M and pH 7 and [L] = 10^{-6} M, respectively. The stability of the resulting ^{177}Lu- and ^{133}La-complexes was assessed in PBS and human serum over 2 h for ^{133}La-complexes and 8 days for ^{177}Lu-complexes showing excellent stability under all tested conditions. Finally, AMPED–3PIC was identified as a highly promising chelator for both trivalent ^{177}Lu and ^{133}La and the bifunctional chelator MeAMP-3PIC-C_4COOH was synthesized to enable conjugation with peptide-based targeting vectors for imaging applications.

CATALYTIC CONVERSION OF ETHANOL TO BUTANOL: SYNTHESIS AND APPLICATION OF NAPHTHAQUINONE AND ANTHRAQUINONE COORDINATED IRIDIUM COMPOUNDS

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The catalytic upgrading of ethanol to higher-order alcohols such as butanol is a critical step toward the development of sustainable liquid fuels and energy-dense bio-based chemicals. In this study, we report the synthesis and characterization of a new class of iridium complexes coordinated with redox-active naphthaquinone and anthraquinone ligands. These complexes were synthesized via ligand substitution reactions starting from $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene), and structurally confirmed by NMR, IR, and single-crystal X-ray diffraction.

Catalytic evaluations reveal that these quinonoid-ligated iridium compounds exhibit enhanced activity in the Guerbet-type coupling of ethanol to butanol under mild conditions. The redox non-innocence of the quinone ligands appears to facilitate key dehydrogenation and C–C bond-forming steps through ligand-assisted electron transfer. Compared to classical phosphine- or nitrogen-based systems, these organometallic quinone complexes demonstrate improved selectivity, turnover number (TON), and thermal stability. This work highlights the potential of utilizing redox-active ligands in transition metal catalysis to promote complex multi-step transformations and lays the groundwork for designing advanced catalytic systems for renewable fuel production.

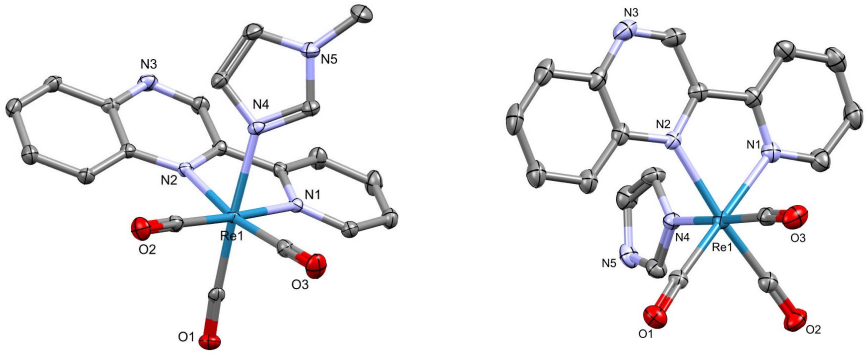
ANTIMICROBIAL AND ANTICANCER ACTIVITY OF IMIDAZOLE-FUNCTIONALIZED 2-(PYRIDIN-2-YL)-QUINOXALINE RHENIUM(I) TRICARBONYL COMPLEXES

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Quinoxaline and its derivatives have attracted considerable attention in medicinal chemistry due to their diverse biological activities, including anticancer and antimicrobial properties. Several studies have shown that quinoxaline-based compounds exhibit significant cytotoxic activity against cancer cell lines and inhibitory effects against both Gram-positive and Gram-negative microorganisms [1]. Furthermore, rhenium(I) tricarbonyl complexes have attracted significant interest as potential metallodrugs, exhibiting notable anticancer activity against several cancer cell lines and antimicrobial effects against pathogenic microorganisms [2,3].

This study reports on the synthesis of 2-(pyridin-2-yl)-quinoxaline bidentate ligand and its analogous coordinated rhenium(I) tricarbonyl complexes, with various imidazole-based monodentate ligands, to alter the cytotoxicity of the complexes for improved performance. Two new solid-state structures are reported (see Figure 1), and all the synthesised complexes were evaluated for their anticancer and antimicrobial activities. The study reports on the excellent cytotoxicity and selectivity of (**1**) against all the tested cancer cell lines, and its outstanding antimicrobial activity against various microbes.



1 **2**

Figure 1: Single crystal X-ray structures of (**1**) and (**2**).

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NOVEL ACYCLIC CHELATORS FOR LUTETIUM-177 RADIOPHARMACEUTICALS

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[b] Department of Radiation Science and Technology, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands
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Lutetium-177 is a key radionuclide in targeted radiotherapy and theranostics, exemplified by the clinical success of radiopharmaceuticals such as Lutathera [1]. The effectiveness of such theranostic agents strongly relies on the incorporation of chelating platforms able to provide rapid, high-yield radiolabeling under mild conditions while maintaining exceptional *in vivo* stability. Recent studies on novel acyclic polyaminopolycarboxylate chelator systems have focused on optimizing these coordination properties to surpass the limitations of traditional macrocyclic chelators [2, 3].

In this work, we developed and fully characterized a new family of structurally related acyclic chelators tailored for Lu(III) (*Fig. 1*). Radiolabeling studies were conducted under varying experimental conditions (pH, ligand concentration, reaction time, etc) to evaluate the radiochemical yields and labeling kinetics of the studied systems. Several ligands achieved high radiochemical yields of >99% at room temperature within short reaction times. This efficient complexation under mild conditions is key for their further conjugation with sensitive biomolecules as targeting vectors.

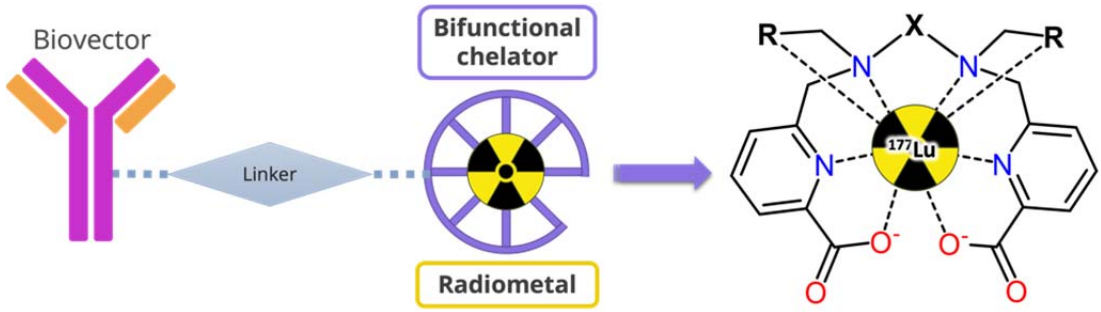


Fig. 1: General structure of the systems presented in this work.

In vitro stability of the corresponding ^{177}Lu complexes was assessed in human serum and in competition experiments using EDTA as a strong competing chelator. The most promising chelators demonstrated high kinetic inertness to dissociation and minimal transchelation, confirming their potential for stable radiometal retention *in vivo*. These findings suggest that this new set of acyclic ligands offers a versatile and stable platform for the development of next-generation ^{177}Lu theranostic agents.

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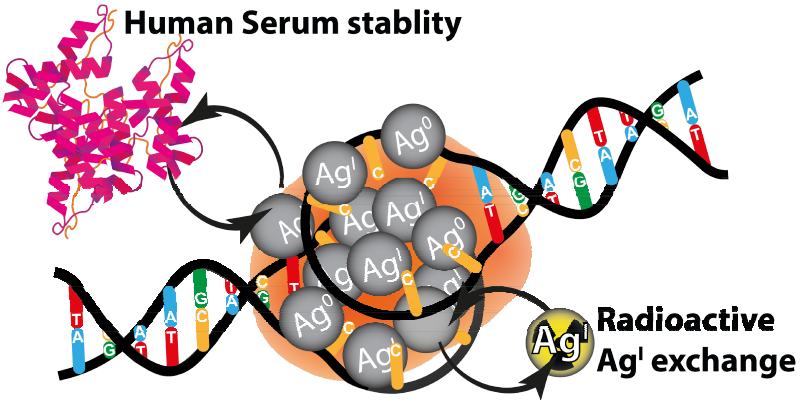
EQUILIBRIUM PROPERTIES IN SOLUTION OF A SELF-HYBRIDIZING DNA-SILVER NANOCONSTRUCT

Bálint Hajdu[a], Annamária Tóth[b], Simon Holm Jacobsen Eiby[c], Pratik Shah[d], Morten Jannik Bjerrum[a], Lars Hemmingsen[a], Peter Waaben Thulstrup[a]

[a]Department of Chemistry, University of Copenhagen, Copenhagen, Denmark
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DNA- or RNA-based nanotechnology is a prominent research area, as it allows the design of monodisperse and biocompatible nanoparticles, with numerous possible applications (e.g. catalysis, molecular machines nanofabrication, nanophotonics, nanoelectronics, bioimaging, drug delivery, and cancer treatment)[1,2]. However, nanoconstructs consisting only from oligonucleotides with classical Watson-Crick base pairs often lack sufficient stability, especially under physiological conditions (e.g. requiring > 5 mM Mg^{2+} -ion concentration). A solution to this may be the design of metal-containing nanoconstructs, where metal ions/metal nanoclusters can increase structural stabilization and protection against nucleases *in vivo*. Previously our research group investigated how C-loop hairpin structured oligonucleotides can form luminescent clusters with Ag/Ag^{+} [3].

DNA-metal nanoclusters are mostly studied from a materials science perspective, and negligible attention is paid to their possible solution equilibrium processes, although they can play a crucial role in the properties of a system [4]. Therefore, in our work, we have thoroughly studied the solution behaviour of the interfacially dimerized DNA-silver nanoconstruct. We studied the solution distribution of Ag^{+} and Ag/Ag^{+} cluster by Circular Dichroism (CD), UV-Visible spectroscopy and Fluorimetry and by the use of $^{111}Ag(I)$ radioactive silver isotope during native gel electrophoresis (PAGE). The stability of the nanoconstruct under physiological conditions (50% Human Serum) were also investigated.



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DefNEtTrp's ROLE ON THE FUTURE OF ANTICANCER THERAPY

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Cancer cells exploit elevated intracellular iron (Fe) to drive proliferation through Fe-dependent enzymes such as ribonucleotide reductase (RNR). RNR is essential for catalyzing the conversion of ribonucleotides to deoxyribonucleotides, a process crucial for DNA synthesis. This dependency highlights Fe chelation as a promising anticancer strategy. Our laboratory developed DefNEtTrp, a dual chelator conjugate combining deferasirox (hard Lewis base) and triapine (soft/intermediate Lewis base) to simultaneously target both redox states of the intracellular labile iron pool (LIP). DefNEtTrp exhibits broad-spectrum anticancer activity (average GI_{50} = 1.2 µM, NCI60 screen) [1], cancer-selective cytotoxicity, and induces both apoptosis and ferroptosis. This work investigates DefNEtTrp's Fe coordination chemistry and expands the platform through non-Fe metalation. MALDI-TOF MS, elemental analysis, EPR spectroscopy, and cyclic voltammetry confirmed that DefNEtTrp coordinates Fe(III) at the deferasirox moiety and Fe(II) at the triapine moiety, consistent with HSAB theory. Flow cytometry revealed G0/G1 arrest in Jurkat leukemia cells, indicating indirectly RNR inhibition by decreasing the LIP via Fe binding to prevent Fe binding of the R2 site (activation site) in the enzyme. Cytotoxicity studies confirmed Fe-dependent activity. To enhance potency, metalation with Ti(IV) and Cu(II) was explored. $Ti(DefNEtTrp)_2$ retained anticancer activity and cancer selectivity but presented solubility challenges. Cu(II) complexation of both deferasirox and DefNEtTrp significantly increased cytotoxic potency relative to the free chelators. These results support a transmetalation mechanism whereby metalated DefNEtTrp exchanges metals with the intracellular LIP to amplify cytotoxicity.

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COORDINATION CHEMISTRY OF HYDROXYQUINOLINE-BASED MACROCYCLIC LANTHANIDE COMPLEXES

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Heavier radionuclides such as [$^{149/161}Tb^{3+}$], [$^{177}Lu^{3+}$] and [$^{225}Ac^{3+}$] are increasingly important in nuclear medicine, particularly for theranostic applications enabling simultaneous diagnosis, monitoring, and treatment of disease.[1-4] The design and synthesis of novel radiopharmaceuticals relies on the stable complexation of the desired radionuclide within a bifunctional chelator, attached to suitable bioconjugate moieties for specific disease targeting and cell accumulation *in vivo*.[2] The coordination chemistry of state-of-the-art macrocyclic chelators, such as macropa, has been explored thoroughly and next-generation chelators developed to improve thermodynamic stability and radiochemical yield.[5,6]

This work explores the effect of replacing the picolinic acid pendant arms on macropa with 8-hydroxyquinoline moieties, yielding a series of novel aza-crown macrocycles (H_2KHQ, MHQ, PyMHQ). Their coordination with key lanthanide ions was investigated. H_2KHQ has demonstrated preferential binding to the larger lanthanide ions, supported by stability constants, forming two-fold symmetric complexes in solution and solid states. H_2KHQ was successfully radiolabelled with [^{161}Tb]$TbCl_3$ in 92% radiochemical yield under mild conditions.[7] Second generation chelators (MHQ, PyMHQ) aim to improve thermodynamic stability and enable dual-size selectivity. Coordination studies with La^{3+}, Tb^{3+}, and Lu^{3+} reveal a conformational toggle, enabling adaptation between coordination numbers 10 and 8 to accommodate both large and small lanthanide ions. By comparing the solution- and solid-state structures of the early *vs* late lanthanide complexes, we aim to delineate systematic trends in coordination number and thermodynamic stability arising from both the progressive ionic contraction of the series and the structural ligand changes. These results contribute to the broader understanding of lanthanide coordination chemistry and support future design efforts of theranostic radiopharmaceuticals.

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IRON(III)-BASED MRI PROBES FOR TNBC DIAGNOSIS

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Health and environmental concerns associated with the use of gadolinium-based contrast agents (GBCAs) in magnetic resonance imaging (MRI) have encouraged the development of alternative systems based on biologically compatible metals.[1] In this study, we report the synthesis and characterization of a new family of pH-sensitive iron(III) complexes that present a promising application as MRI contrast agents. The presence of a sulfonamide moiety in their backbone as a targeting vector could enable their interaction with triple-negative breast cancer (TNBC) cells, specifically the MDA-MB-157 cell line. Comprehensive structural and physicochemical characterization was performed both in solution and solid state using electronic absorption spectroscopy, cyclic voltammetry and single-crystal X-ray diffraction. Its suitability as a contrast agent was assessed through relaxation studies. To further explore its potential for *in vivo* application, cell viability was evaluated in both two-dimensional (2D) and three-dimensional (3D) cultures in the presence of the complex, and cellular localization was examined using staining techniques. Phantom studies conducted on a 3T MRI scanner demonstrated a correlation between signal intensity and compound concentration, as well as evidence of cellular interaction.

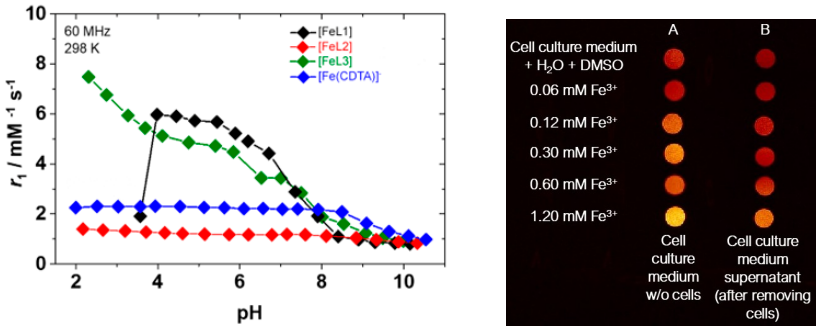


Figure 1. pH-dependency of r_1 for the Fe(III)-based MRI probes and T_1-weighted image of phantoms containing solutions of the most promising complex in cell culture medium: (A) without cells, and (B) with cells removed after 30 minutes of incubation.

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THE APPLICATION OF REDOX ACTIVE VANADIUM COMPOUNDS IN CANCER TREATMENT

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The anticancer potential of early transition metal-based drugs remains limited as the majority of research focuses on late transition metal compounds, e.g., Pt, Pd, Au, and Ru. Generally, the later/heavier transition metals have increased off-target interactions with healthy cells and a higher toxicity due to accumulation issues, and their ability to act as pseudo-elements of the body, thus interfering with metabolic processes.[1] In contrast, the earlier transition metals are low-cost, readily available, and have improved tolerability within the body, and they could be used to improve future drug design.

Vanadium is a trace element and has biological compatibility attributed to its chemical similarity to phosphates in the form of vanadate. The use of vanadium in cancer treatment has increased over the past decade, including V(IV) and (V) compounds, due to their desirable redox activity, ability to selectively trigger apoptosis and cell cycle arrest in cancer cells, and interaction with DNA.[2] Lord et al. and others have reported β-diketonate oxovanadium(IV) complexes with a range of activity against cancerous and normal cell lines.[3,4] The results also suggested modes of action by (i) apoptosis, (ii) generation of reactive oxygen species, (iii) oxidative DNA damage, and (iv) triggered DNA breaks (Figure 1a and b). One of the most promising molecules was the vanadium complex, which incorporates a symmetric β-diketonate ligand (Figure 1c), and this provided the rationale for new symmetric β-diketonate vanadium(IV) complexes. This work will present the synthesis, characterisation, stability, and cell line testing of a library of new V(IV) complexes, and a discussion of their potential as anticancer agents.

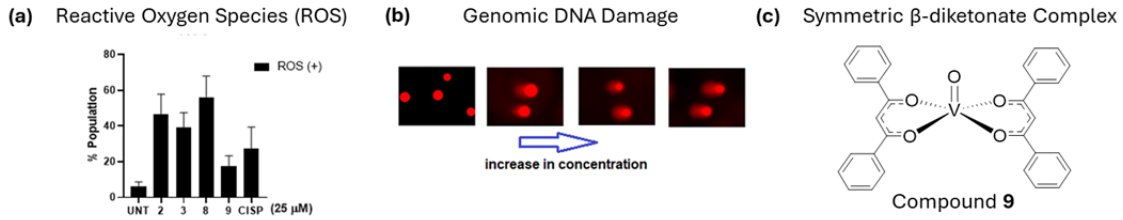


Figure 1: (a) increase in ROS; (b) dose-dependent genomic DNA damage (COMET assay); and (c) the symmetric β-diketonate compound (**9**).

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FUNCTIONALISED AZA-MACROCYCLES WITH POTENTIAL APPLICATIONS IN NUCLEAR MEDICINE

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There are several metal radionuclides that have potential to be used for molecularly targeted diagnostic imaging or radionuclide therapy. The use of metal radionuclides for imaging and therapy of cancer relies on their selective delivery to sites of disease.

One way to achieve this selectivity is through use of bifunctional chelators. These chelators need to form sufficiently physiologically stable complexes and contain a targeting group such as a peptide or antibody to bind selectively to the receptor of interest. Macrocycles have often been employed due to their increased thermodynamic and kinetic stability.

Alkylated tetraaza cyclen macrocycles, such as DOTA (Figure 1a), have been investigated extensively and found applications with $[^{68}Ga]Ga^{III}$ and $[^{177}Lu]Lu^{III}$. Different metal radionuclides may benefit from alternative chelators.[1]

DiAMMac (Figure 1b) is a C-substituted variant of cyclam formed through metal-directed template synthesis. [2-4] The pendent primary amine functional groups can act as a point for further functionalization to incorporate targeting molecules.

Different approaches to functionalise DiAMMac will be presented including ring-opening acylation reactions and reductive amination reactions. Structural characterisation of various metal complexes will also be presented.

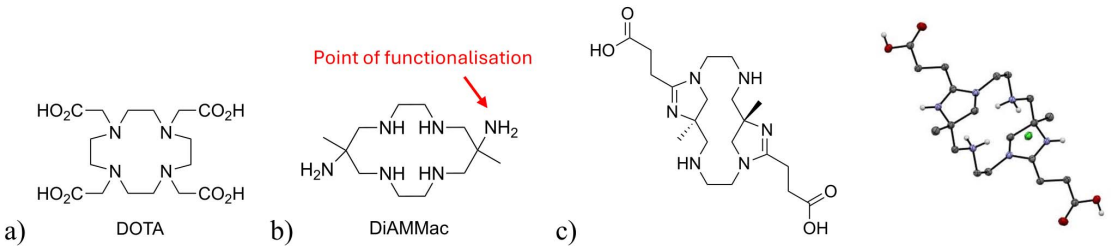


Figure 1 a) Molecular structure of DOTA b) Molecular structure of DiAMMac c) Molecular structure and ORTEP representation of the cation present in succ-diammac+$2H^+$.Cl.PF_6.H_2O with a thermal ellipsoid probability of 50%. Solvent molecules, hydrogens attached to carbons and counter ions omitted for clarity.

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PENTADENTATE N_3S_2 CHELATORS FOR THE MEDICAL DELIVERY OF THERANOSTIC ISOTOPES OF ANTIMONY

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The ^{117}Sb/^{119}Sb theranostic pair has untapped potential in SPECT imaging and Auger Electron therapy. However, a suitable chelator for Sb delivery has yet to be reported. This is a challenge because Sb complexes show an extremely high propensity towards hydrolysis, as well as facile transmetallation reactions with biologically abundant metal ions[1]. The purpose of this work is to produce chelators capable of forming physiologically-stable antimony complexes which are easy to functionalize with biological targeting vectors for the selective uptake into specific cancer cell types.

We have investigated a series of pentadentate diacetylpyridine bis(thiosemicarbazone) (dap-btsc) chelators **(Fig. 1a)** as candidates for Sb chelation[2], which shows rapid Sb(III) binding at ambient temperature. SC-XRD of the isolated ^{nat}Sb(dap-btsc) complexes **(Fig. 1b)** identifies pentadentate binding of the chelator, with two potentially protonated or deprotonated thiourea moieties. In solution-state stability studies using UV/vis spectrophotometry, it was determined that aryl-derived Sb(dap-btsc) complexes show the highest stability. Radiolabeling of a water-soluble derivative (R = $PhSO_3H$) demonstrates a high affinity of the chelator to [^{1XX}Sb]Sb^{III}, with the ability to radiolabel with 65% yield to 10^{-6} M chelator in 30 minutes at room temperature **(Fig. 1c)** – unprecedented for this underexplored semimetal. Radiocomplex stability studies are underway.

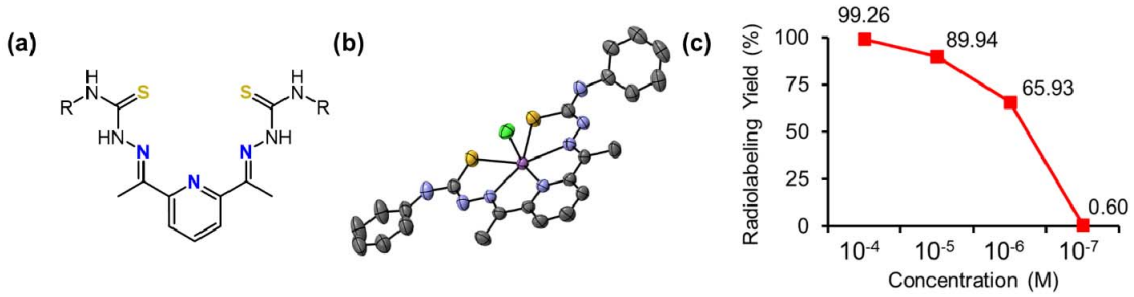


Figure 1: (a) General structure of dap-btsc chelators, (b) SCXRD of a Sb(dap-btsc) complex, and (c) radiolabeling study of dap-btsc (R = $PhSO_3H$) with ^{1XX}Sb (2 MBq, RT, 30 min, pH = 2).

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EVALUATION OF CLICK CHEMISTRY DERIVED COPPER COMPLEXES FOR DNA DAMAGE

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DNA damaging agents are clinically valuable therapeutics. Artificial Metallo-Nucleases (AMNs) are small molecules that cleave DNA and offer an alternative method of DNA damage to existing therapies. [1] The development of AMNs with sequence specificity is a promising strategy to curtail otherwise indiscriminate cellular oxidation. The synthesis of AMNs has become much more accessible in recent years by employing click chemistry during their preparation. After functionalising variable organic donors with alkynes, they can be clicked to a central triazide mesitylene core to synthesise a bio-active C_3 symmetric "Tri-Click" (TC) ligands which can chelate up to three copper ions. [2] AMNs face a significant challenge in the form of endogenous macromolecular chelating agents, such as metallothioneins, that serve to prevent uncontrolled redox activity by labile metal ions. Consequently, AMNs with high stability, reactivity, and sequence specificity lie at the forefront of AMN design. Here, we introduce Cu_3-TC-Pico (where Pico = picolinic acid) and Cu_3-TC-PA (where PA = picolylamine), the first tridentate TC ligands. Sequence specificity was evaluated using short DNA hairpin studies with Microscale Thermophoresis (MST) and Förster Resonance Energy Transfer (FRET) melting analysis. FRET melting analysis showed destabilisation at the TA/TA step reflecting selective perturbance of base-pairing. Gel electrophoresis experiments then showed DNA damage at low micromolar concentrations, primarily through superoxide and hydrogen peroxide-mediated mechanisms. Finally, Cu_3-TC-Pico displayed activity consistent with hypochlorous acid-mediated DNA damage, which is uncommon among preexisting AMNs. Overall, Cu_3-TC-Pico outperformed Cu_3-TC-PA showing that alkynyl donor derivatisation within this Tri-Click class has a significant impact on DNA recognition and AMN activity.

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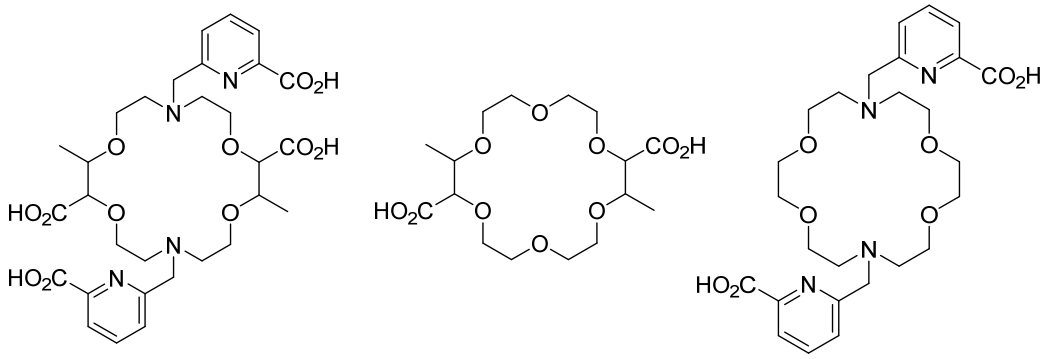
STUDY OF A NOVEL DIAZA MACROCYLE FOR EUROPIUM CHELATION

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Europium complexes have attracted significant interest for their luminescent properties and potential applications in bioimaging and sensing, particularly in PET imaging where the Eu(III)/Eu(II) redox couple can be exploited. Macrocyclic ligands such as macropa readily form complexes with both europium(II) and europium(III), making them promising candidates for such applications. However, such complexes lack the stability required for practical use, prone to decomplexation in competitive environment[1]. There is therefore a need for novel, more stable ligands capable of chelating both oxidation states of europium.

In this context, this work focuses on the synthesis and functionalization of a novel diaza macrocycle L1, bearing two picolinate arms on the nitrogen atoms and carboxylate groups on the carbon backbone, based on a macrocyclization reaction developed by Lacour's group [2]. The enhanced stability of L1 relative to macropa is expected to arise from the macrocyclic effect combined with its extended coordination sphere. Two related analogs, the 18-crown ether L2 [3] and the picolinate-armed diaza macrocycle L3, lacking the carboxylate groups, are also included for comparison. While L2 was efficiently synthesized, establishing a reliable synthetic route to L1 required particular attention to reagent and solvent purity. Hydrogenation was subsequently performed on both, L1 and L2, as a key step toward further functionalization. Once all target compounds are in hand, their complexation properties toward europium(II) and europium(III) will be compared.



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RHENIUM COMPLEXES AS ANTIMICROBIAL AGENTS: LATEST DEVELOPMENTS

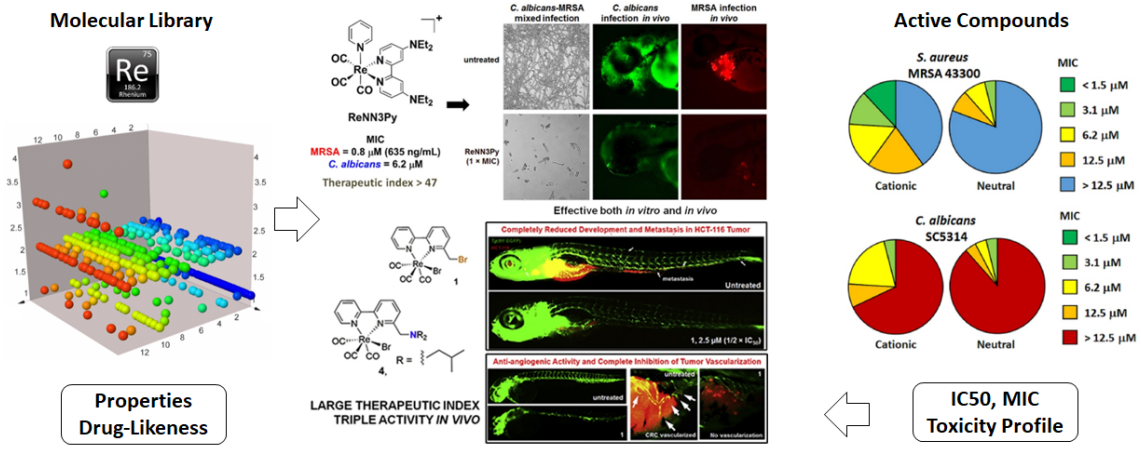
Gozde Demirci[a], Sara Nasiri Sovari[a], Kevin Schindler[a], Fatlinda Rahmani Mustafaj[a], Youri Cortat[a], Nikola Plackic[b], Aurelien Crochet[a], Aleksandar Pavic[b], Fabio Zobi[a]

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We report on recent advances in the development of rhenium-based antimicrobial agents. This contribution presents the design, synthesis, and biological evaluation of carbonyl, diarene and oxo rhenium complexes as antibacterial and antifungal compounds. Particular emphasis is placed on rational molecular design strategies aimed at optimizing stability and target engagement to enhance antimicrobial potency while maintaining low *in vivo* toxicity [1-2].

Comprehensive *in vitro* studies demonstrate potent activity against clinically relevant bacterial and fungal strains, including resistant pathogens, while mechanistic investigations provide insight into membrane interaction, intracellular targeting, and possible multi-target modes of action. Selected compounds were further evaluated *in vivo* to assess efficacy and tolerability. Our studies allowed already the identification of potent and non-toxic complexes active *in vivo* against *S. aureus* infections at MIC doses as low as 300 ng/mL [3-4], as well as against *C. albicans*-MRSA mixed co-infection, with no sign of cardio-, hepato-, hematotoxiciy or teratogenicity.

Collectively, the results presented will highlight the therapeutic potential of structurally diverse rhenium scaffolds and underscore the promise of metal-based compounds as next-generation antimicrobial agents.



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TUNING THE ANTICANCER PROPERTIES OF Ru(II) CYMENE COMPLEXES VIA PHOSPHINE LIGAND MODIFICATION

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Transition metal complexes have emerged as a key research area for anticancer drug development, with the strategic selection of ligands playing a pivotal role in the development of effective antitumour agents. The clinical success of platinum-based drugs, such as *Cisplatin*, has inspired extensive research into alternative metal-based complexes, focusing on compounds that exhibit reduced toxicity and enhanced efficacy against a wider spectrum of cancers.

Ruthenium complexes, in particular, have drawn substantial attention as potential anticancer agents due to their unique properties, such as their relatively inert nature under physiological conditions and ability to mimic iron in biological systems [1]. These properties allow for the design of ruthenium complexes with specific targeting capabilities and mechanisms of action, distinguishing them from traditional platinum-based chemotherapeutics. In this work, we present the synthesis, structural analysis, an *in vitro* cytotoxicity study as well as an *in silico* molecular docking investigation of a series of ruthenium complexes bearing indenyl phosphine ligands (Figure 1).

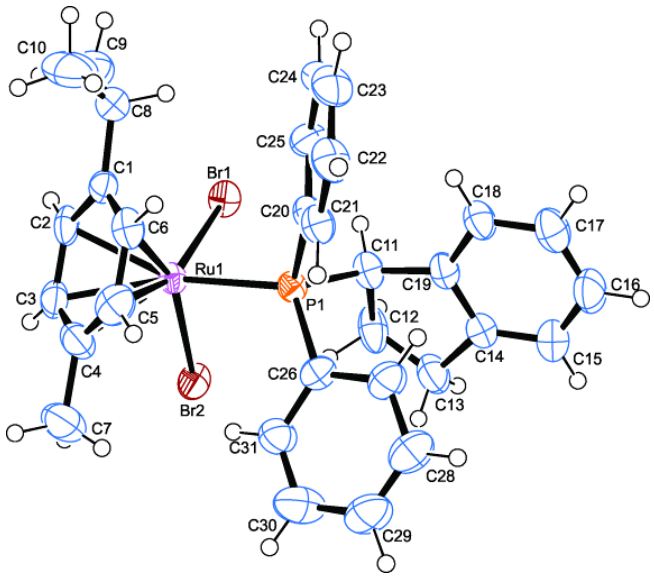


Figure 1. ORTEP diagram of ruthenium indenyl phosphine complex

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SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF NEW RUTHENIUM (II) COMPLEXES WITH ISOQUINOLINE AND NITRITE LIGANDS

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Ruthenium polypyridine complexes constitute a versatile class of coordination compounds that show great promise in various areas of research due to their unique photophysical and electrochemical properties [1]. Currently, one of the strategies researchers employ is combining bioactive ligands with the properties of these coordination compounds. For example, the use of nitrite (NO_2^-) and isoquinoline ligands in the coordination sphere can lead to applications related to NO release, pharmacological and cytotoxic effects [1,2]. This work presents the synthesis, characterization and chemical properties of new coordination complexes of formula $[Ru(bpy)_2NO_2(L)](PF_6)$ where bpy= 2,2'-bipyridine and L = 5-aminoisoquinoline (NH_2-iq)-**1**, 5,6,7,8-tetrahydroisoquinoline(thiq)-**2** and 5-phenylisoquinoline(Ph-iq)-**3** which are candidates for light-directed therapies. The syntheses were carried out according to literature [3], and the products were characterized by electronic spectroscopy, cyclic voltammetry, NMR and XRD (figure 1a). The complexes show strong absorption in the visible region of the spectra with $\lambda_{máx}$ close to 450 nm and ε=10000 $M^{-1}cm^{-1}$ assigned to MLCT. The $E_{1/2}$ values for the $Ru^{2+/3+}$ process of all complexes are in the range of 1.0 V, as shown for complex **2** (Figure 1b). The interconversion equilibrium between the coordinated NO^+/NO_2^- was determined by spectrophotometric titrations, and the pk values for complexes **2** and **3** were found to be 3.47 and 2.82 (Figure 1c), respectively. Future studies will aim to determine the quantum yields of ligand photosubstitution.

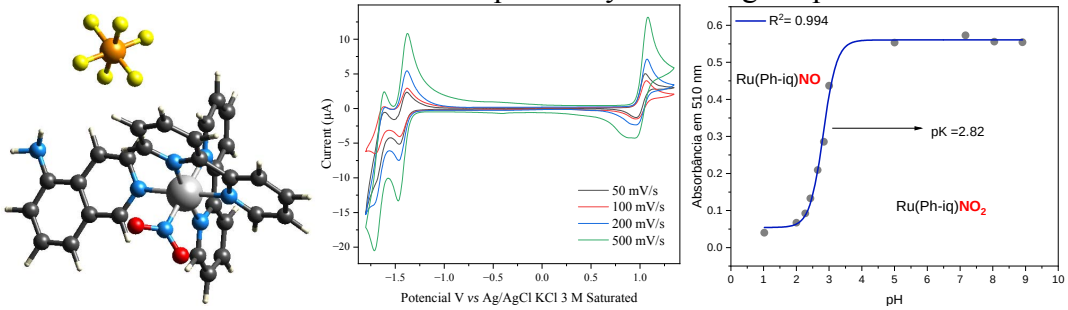


Figure 1. a) X-ray Crystal Struture of **1**. b) Cyclic voltammetry of complex **2** in acetonitrile (TBAPF6 0.1 M) at speed c) Sigmoidal fitting of spectrophotometric monitoring data collected for complex **3** ($\lambda_{máx}$ = 510 nm) in aqueous solutions at different pH values.

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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NOVEL AZOLE–PLATINUM(II) COMPLEXES WITH EVALUATION OF THEIR PHYSICOCHEMICAL AND ANTICANCER POTENTIAL

Iwona Łakomska, and Adriana Kaszuba

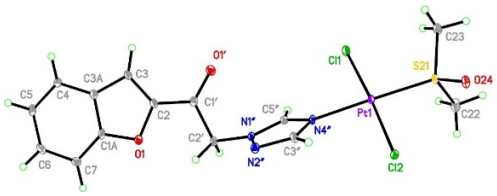
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Overcoming cisplatin resistance remains a major challenge in platinum-based chemotherapy, motivating the development of new platinum(II) complexes with improved physicochemical and anticancer properties.

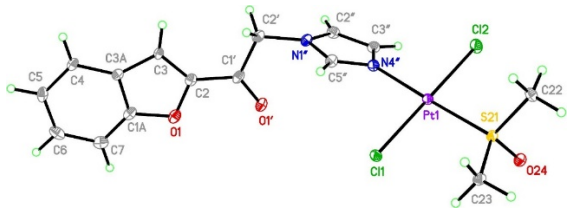
Herein, we investigate how the nature of azole ligands—triazole (**L1** - 1-(benzofuran-2-yl)-2-(1H-1,2,4-triazol-1-yl)ethenone) versus imidazole (**L2** - (benzofuran-2-yl)-2-(1H)-imidazol-1-yl)ethenone) influences the behavior of platinum(II) complexes.

Two novel platinum(II) complexes containing dimethyl sulfoxide (DMSO), *trans*-[$PtCl_2$(**L1**)(DMSO)] **(1)** and *trans*-[$PtCl_2$(**L2**)(DMSO)] **(2)**, were synthesized and fully characterized using spectroscopic methods (^{1}H, ^{13}C, ^{15}N, ^{195}Pt NMR; IR; X-Ray).

Spectroscopic and single-crystal X-ray diffraction data revealed square-planar geometries in both complexes, featuring *trans*-dichlorido coordination, an S-bound DMSO ligand, and a monodentate N-heterocycle (Figure 1). Complex **(1)** crystallizes in the monoclinic $P_{2_1/c}$ space group, whereas **(2)** adopts the triclinic $P_{\bar{1}}$ space group.



trans-[$PtCl_2$(**L1**)(DMSO)] **(1)**



trans-[$PtCl_2$(**L2**)(DMSO)] **(2)**

Figure 1. Structure of platinum(II) complexes with a numbering scheme and thermal ellipsoids at 30% probability.

The complexes exhibit moderate lipophilicity (logP ~ 0.92–0.95), supporting passive membrane permeation, in contrast to hydrophilic cisplatin, which relies on active transport. Reduced reactivity toward glutathione suggests decreased intracellular deactivation and prolonged cellular retention.

However, initial screening at 1 and 10 μM revealed no significant cytotoxicity against bladder (T24, HT1376, 5637) or lung (A549) cancer cells, whereas cisplatin markedly reduced cell viability. The lack of activity for the *trans*-configured DMSO-containing complexes suggests that enhanced kinetic stability limits ligand exchange processes required for biological activity.

Acknowledgements: The study was funded by the Excellence Initiative – Research University program awarded to the authors, who are members of the Centre of Excellence *"Towards Personalized Medicine"*.

RADIOACTIVE COPPER COMPLEXES WITH TWO DIFFERENT TARGETING MOLECULES FOR IMAGING AND TREATMENT OF CANCER

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The positron emitting radionuclide copper-64, can be used in tracers for positron emission tomography (PET) imaging. Molecules that are radiolabelled with copper-64 and bind selectively to receptors that are overexpressed in cancer can be used to diagnose disease. Upon diagnosis, the beta emitting radionuclide copper-67 can then be used in targeted radionuclide therapy for treatment of disease. As a 'true matched pair', the two copper radionuclides allow the same ligand to be used for diagnosis and therapy – namely theranostics – to create a personalised treatment approach.

In this work, two different targeting molecules have been bound to a central cage amine sarcophagine chelator, to form a 'heterobivalent' compound (Figure 1).[1] The aim of developing a heterobivalent compound is to create a single agent that is capable of targeting two different types of receptors with the potential to address lack of receptor homogeneity and address a change in phenotype midway through therapy. A heterobivalent compound called PSMA-Sar-BBN has been synthesised, radiolabelled with copper-64 and the tumour uptake and biodistribution evaluated in a dual-tumour mouse model.

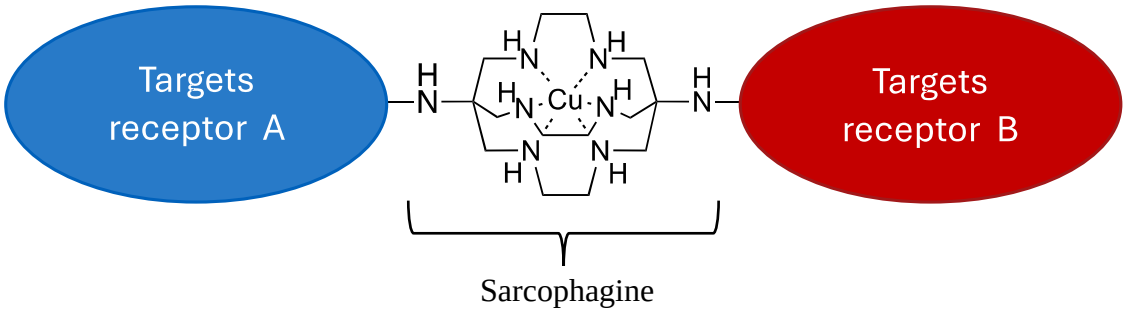


Figure 1. 'Heterobivalent' copper complex with targeting molecules that bind two different receptors attached to a central sarcophagine cage.

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RARE EARTH MOFs AS THERANOSTIC MATERIALS

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Although mostly studied for their gas capture and catalytic properties, metal organic frameworks exhibit remarkable qualities as a new generation drug delivery system (DDS). Firstly, they are intrinsically ultra-porous, capable of adsorbing drugs at a greater drug loading capacity compared to any other DDS class, demonstrating unparalleled tuneability, whilst exhibiting biodegradable coordination bonds. This body of work's contribution to new knowledge encompasses the synthesis and characterisation of 5 families of rare earth metal organic frameworks (RE-MOFs) **fcu**, **the-a**, **shp**, **gea** and **llk**, separated based on their underlying net. A robust, reliable, and scalable synthetic protocol was designed to produce high quality single crystalline RE-MOFs, leading to the determination of 40 RE-MOF single crystal structures. Moreover, using a reduced symmetry linker strategy, a novel hexanuclear RE-MOF series was discovered, presenting a 3-D Kagome structure, exhibiting the ultra-rare underlying **llk** topology. From these RE-MOFs, a selection of 10 different Er-MOFs were selected for anticancer drug loading assessment using 4 different FDA approved 1st in line anticancer drugs. For the first time, a study of drug loading using 4 different anticancer drugs was reported, with RE-MOFs were found to each anticancer drug in high drug loading capacity of up to 29% w/w, dependent on guest structure. Overall, RE-MOFs present an excellent platform for the adsorption of small molecule (<1000 Da) anticancer drugs and with their impressive, tunable characteristics, shows significant promise in the development for the next generation of anticancer drug delivery systems.

FROM NATURAL PRODUCT TO COMPLEX POTENTIAL

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We have been combating various microbes since the very beginning of our species. In the past century, we have achieved considerable success in this endeavor following the discovery of the first antibiotic and other antimicrobial agents. However, the overuse and misuse of antimicrobial agents have led to the development of antimicrobial resistance and superbugs, which now pose a public health threat also recognized by the World Health Organization [1]. This new challenge has shifted research towards innovative therapeutics and the search for new potential compounds. One promising candidate was discovered in 1959 during investigations of extracts from *Streptomyces caerules*. Researchers observed that the extract inhibited the growth of various filamentous fungi, yeasts, and even some bacteria. They isolated and characterized a novel asymmetric 2,2'-bipyridine, later named Caerulomycin A (CaeA) (Figure 1) [2]. Further research revealed that there is a whole family of these compounds, and they not only possess antifungal and antibacterial activity, but also exhibit significant anticancer, immunoregulatory, and other potential therapeutic properties [2-4].

We present an improved synthesis of Caerulomycin E (CaeE) with good yields on a gram scale in combination with the first synthesized complex with rhenium(I) and CaeE as a ligand.

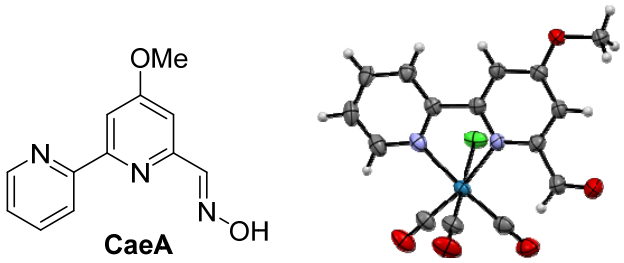


Figure 1: Structure of Caerulomycin A and rhenium(I) complex with CaeE

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COMPLEXATION OF β-LACTAM ANTIBIOTICS WITH METAL IONS OF BIOLOGICAL RELEVANCE: A POTENTIOMETRIC AND SPECTROSCOPIC APPROACH

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The coordination chemistry of β-lactam antibiotics with metal ions plays a crucial role in understanding how such interactions influence molecular stability and biological activity. In this study, three representative β-lactam antibiotics — ampicillin, cloxacillin, and ticarcillin — were examined as ligands capable of forming coordination complexes with Cu(II) and Eu(III) ions. These metal ions were selected due to their biological and diagnostic significance, as well as their distinct coordination behavior and spectroscopic properties.

The investigated systems were characterized using potentiometric and spectroscopic techniques, providing complementary insight into their solution equilibria and coordination modes. Potentiometric titrations were performed to determine protonation and stability constants of the formed complexes in aqueous solution. Spectroscopic methods, including UV–Vis, FTIR, and luminescence spectroscopy, were employed to identify the donor atoms and functional groups involved in metal binding, particularly the carboxylate, amide, and β-lactam carbonyl sites.

The obtained data indicate that both Cu(II) and Eu(III) ions form stable complexes with the studied antibiotics, with differences in coordination strength and geometry depending on the metal center and ligand structure. For Cu(II), the results suggest the formation of complexes involving mixed oxygen–nitrogen donor sets, while Eu(III) complexes exhibit luminescent behavior consistent with coordination through oxygen atoms.

These findings contribute to a deeper understanding of how β-lactam antibiotics interact with metal ions at the molecular level. The results highlight the potential of metal–antibiotic complexation to enhance drug stability and open new perspectives for the design of metal-based therapeutic and diagnostic systems.

SYNTHESIS OF HALF-SANDWICH Ir(III), Ru(II), AND Os(II) COMPLEXES WITH A DIPHOSPHINE DERIVED FROM HOMOPIPERAZINE

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The diphosphine ligand derived from homopiperazine used in this study was synthesized as part of my master's thesis and is currently employed to obtain half-sandwich complexes of Ru(II), Ir(III), and Os(II). Phosphines as ligands are widely used in medicine and pharmaceuticals. They enhance the properties of metal complexes, by increasing their solubility and improving biodistribution. [4] Furthermore, there is growing interest in introducing homopiperazine motifs into the structures of novel cytostatic agents.[5, 6] The selection of specific metal ions, such as ions of ruthenium (II), iridium (III), and osmium (II), is crucial for disrupting the redox balance in cancer cells and steering them toward ferroptotic death. [2]

We speculate that the complexes synthesized by using this ligand may hold therapeutic potential, particularly through ferroptosis of drug-resistant cancer cells. Some apoptosis-resistant cancer types appear to be particularly sensitive to ferroptosis. [1] Currently used cytostatics induce apoptotic cell death mainly by DNA damage and disruption of key metabolic functions. [2] Ferroptosis is non-apoptotic form of cell death, triggered by i.e. excessive generation of free radicals leading to redox imbalance through the overproduction of lipid peroxides. [3] Numerous metal-based drugs, especially phosphine complexes such as auranofin, have demonstrated the ability to induce ferroptosis. [2]

Acknowledgements: This project is founded by the National Science Centre (2023/51/B/ST4/00355) and the Pearls of Science II program (Registration No.: PN/02/0034/2023).

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AROYLHYDRAZONE-BASED MANGANESE COMPLEXES OF PHYSICOCHEMICAL AND PHARMACOLOGICAL INTEREST

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Aroylhydrazones are well-known for their tendency to readily undergo tautomeric transformations as a means to meet charge-neutrality requirements in metal-complex formation or stereochemical demands of certain metal ions. This coordination versatility enables them the stabilize a wide spectrum of metal ions. Aroylhydrazone complexes have been investigated as biological probes [1], DNA binding/cleaving agents [2], catalysts, sensing materials [3], corrosion inhibitors, etc. The inherent pharmacological behavior of aroylhydrazones has been amply demonstrated to be enhanced upon coordination to bioactive metal ions. The biological efficacy of these complexes is strongly influenced by the coordination interactions between the metal ions and the ligand donor atoms

Crystallographically characterized manganese aroylhydrazone complexes, particularly those exhibiting high electrovalency, are very rare. In this work, we have designed and produced a series of novel six-coordinate aroylhydrazone manganese complexes. Their chemical identities have been established by single-crystal X-ray analyses and corroborated by several analytical and spectroscopic techniques. The solid-state structures are dominated by fascinating intermolecular forces. The trivalent derivatives have been shown to readily undergo a base-assisted ligand-based redox process. The electrovalencies of the complexes have been determined by VT SQUID magnetic susceptibility measurements and their interconversions studied by cyclic voltammetry. As far as we are aware, manganese complexes of this type have never been investigated for antiproliferative activity in cancer cell lines such as HeLa and MCF7, which are of paramount interest in our research endeavor.

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CYSTEINE-MEDIATED AGGREGATION PATHWAYS OF MUTANT Cu/Zn-SUPEROXIDE DISMUTASE ASSOCIATED WITH AMYOTROPHIC LATERAL SCLEROSIS

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Mutant Cu/Zn-superoxide dismutase (SOD1) is a causative protein of familial amyotrophic lateral sclerosis (ALS) and is known to form inclusion bodies in spinal motor neurons. Our group has revealed several *in vitro* misfolding mechanisms of SOD1 that depend on the redox states of its Cys residues. SOD1 contains four Cys residues, two of which form a highly conserved intramolecular disulfide (S-S) bond. SOD1 with the S-S bond ($SOD1^{S\text{-}S}$) forms disulfide-crosslinked oligomers via disulfide shuffling [1], whereas the disulfide-reduced SOD1 ($SOD1^{SH}$) tends to form amyloid-like fibrillar aggregates [2]. Nonetheless, the SOD1 species that play key roles in disease pathogenesis remains unclear. We therefore evaluated the thiol-disulfide status of SOD1 in ALS model mice expressing G93A-mutant human SOD1. In the liver, a tissue not affected by the disease, SOD1 was fully oxidized and detected in the soluble fraction. In contrast, the spinal cord, the most affected tissue, contained substantial amounts of $SOD1^{SH}$ together with disulfide-crosslinked oligomers in the detergent-insoluble fraction. These results suggest that oligomerization of $SOD1^{S\text{-}S}$ and fibrillar aggregation of $SOD1^{SH}$ occur concurrently *in vivo*.

To examine which misfolding pathway is associated with disease progression, we focused on two mutant SOD1 variants: G41D, associated with a long disease duration (~15 years), and G41S, with a severe phenotype and short duration (~2 years). Regarding the disulfide-crosslinked oligomers *in vitro*, we could not detect obvious differences in the kinetics, amounts, and morphologies between G41D and G41S. In contrast, under disulfide-reducing conditions, G41S aggregated faster than G41D. However, the resulting aggregates of G41S exhibited lower turbidity, even though nearly all proteins of both variants were recovered in the insoluble fraction. These results suggest that G41S and G41D form amyloid-like fibrillar aggregates with distinct structural properties. In the reported fibril structure of wild-type SOD1 [3], which consists of two structural cores, Gly41 is located at their interface, implying that substitution at Gly41 may substantially alter the structural properties of fibrillar aggregates in the disulfide-reduced state. We are currently investigating whether such structurally distinct fibrillar aggregates are associated with differences in pathogenic features.

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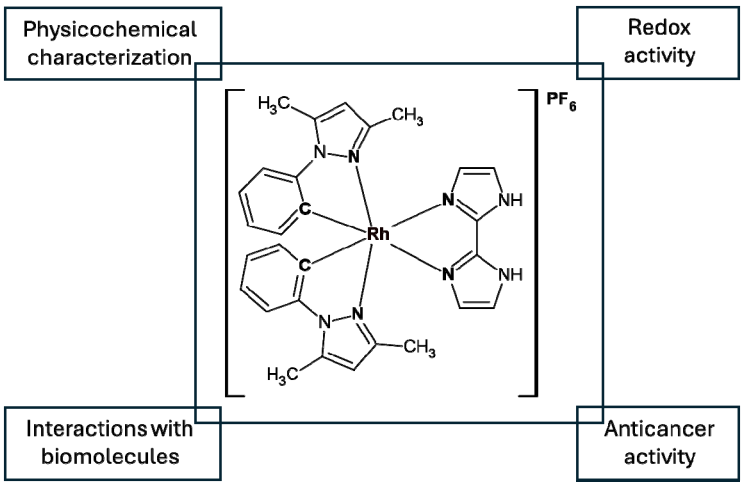
SYNTHESIS, PHYSICOCHEMICAL CHARACTERIZATION AND ANALYSIS OF THE ANTIPROLIFERATIVE ACTIVITY OF CYCLOMETALATED RHODIUM(III) COMPLEX WITH 2,2'-BIIMIDAZOLE

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Coordination compounds of d^6-electron metal ions, which were once considered inert, are now one of the most widely studied topics in modern chemistry. Cyclometalated complexes are used in light-emitting devices (OLEDs and LEECs) due to their attractive photophysical properties. However, research in this field is increasingly focusing on the antiproliferative potential of these chemical compounds. Heteroleptic Rh(III) and Ir(III) complexes with the {C2N4} chromophore often have a low half-maximal inhibitory concentration and inhibit important cellular enzymes [1, 2].

It is these intriguing properties that prompted the synthesis of a new cyclometalated Rh(III) complex with the biologically active auxiliary ligand 2,2'-biimidazole. The resulting compounds were characterised using spectroscopic methods (FT-IR, UV-Vis, NMR, ESI-MS and PL) and single-crystal X-ray diffraction. The biological activity of the synthesised complexes was determined *in vitro* using cancer and normal cell lines. Their mechanism of action was analysed, including the strength of interaction with biomolecules (human serum albumin and deoxyribonucleic acid), redox activity (interaction with glutathione and nicotinamide adenine dinucleotide), and cell cycle arrest.



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OXIDATIVE RNA MODIFICATIONS

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Oxidative modifications of RNA represent a critical challenge to RNA stability and function. RNA is inherently susceptible to oxidative damage because of its single-stranded structure and lack of protective proteins, yet RNA oxidation remains less well understood than oxidative damage to DNA and proteins. This project investigates the chemical and structural basis of RNA oxidation induced by metal-catalyzed oxidation (MCO), with a focus on copper mediated generation of reactive oxygen species (ROS), a group of highly reactive oxygen-derived species formed during metal-redox reactions, including superoxide, hydrogen peroxide, and hydroxyl radicals. Synthetic RNA sequences, including ssRNA and dsRNAs with diverse structural motifs, are subjected to controlled oxidation, enabling precise identification of early oxidative modifications using high-resolution ESI-MS, LC-MS, and capillary gel electrophoresis. The structural and dynamic consequences of RNA oxidation will further be probed via circular dichroism, NMR, and molecular dynamics simulations. In parallel, the protective effects of enzymatic and non-enzymatic antioxidant systems are evaluated.

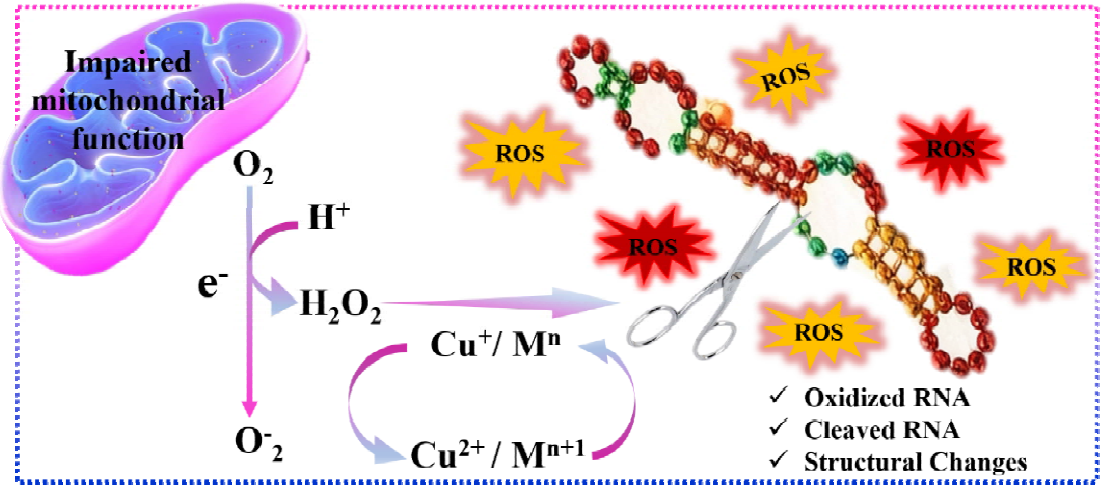


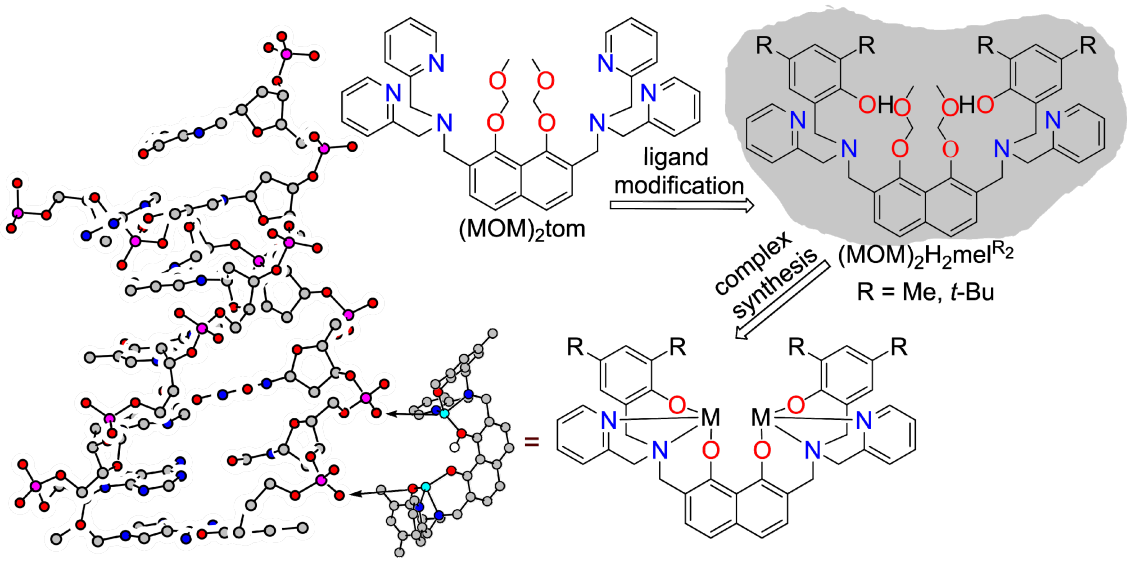
Figure 1. Schematic figure showing in vitro workflow for metal-ion mediated RNA oxidation

INCREASING THE BINDING AFFINITY OF TRIVALENT METAL IONS TO NAPHTHALENEDIOL-BASED LIGANDS

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In modern medicine metal complexes such as cisplatin occupy a major application in cancer therapy. According to current knowledge, its cytotoxic properties rely on the binding to two neighboring purine bases in the DNA strand, which leads to apoptosis of cancerous cells [1]. Addressing the phosphate diester backbone of the DNA with metal complexes would open up a new mechanism of action. A dinucleating naphthalenediol-based ligand system can be utilized in this respect wherefore the distances between metal ions correspond to the distance between two adjacent phosphate groups allowing for binding in accordance with the multivalence principle [2]. Dinuclear Cu^{II} and Ni^{II} complexes showed cytotoxic properties favored for cancerous instead of equally rapid proliferating human stem cells [3]. To increase the binding affinity to DNA, current efforts involve substitution of divalent by trivalent metal ions [4].



To better stabilize trivalent metal ions such as Fe^{III} and Ga^{III}, one pyridine of $(MOM)_2$tom was substituted with one phenolate, resulting in the new ligand $(MOM)_2H_2mel^{R_2}$. The ligand and complex syntheses will be presented.

The DNA fragment shown in the figure above was retrieved from the RCSB protein databank (PDB 1D65) and modified [5].

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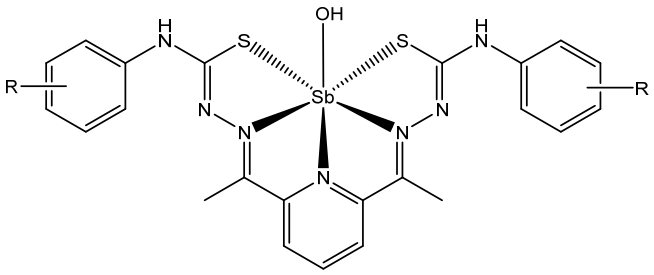
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NEW CHELATORS FOR THE MEDICAL DELIVERY OF THERANOSTIC ANTIMONY ISOTOPES

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Radionuclide therapy represents a promising approach in cancer treatment, leveraging the ability to deliver targeted radiation to cancerous cells while minimizing damage to surrounding healthy tissues[1]. In this study, the synthesis and preliminary evaluation of several chelators designed for potential use in targeted radionuclide therapy via binding of 119Sb and 117Sb are reported[1]. We report series of Sb(III) complexes formed with symmetric pentadentate ligands 2,6-diacetylpyridine bis(R-thiosemicarbazone)(R = 4-COOH, 4-Cl, 4-Methoxy, 4-SO_3, 3,5-dimethoxy)[2] As well as derivatives containing 2,6-diacetylisonicotinic acid – These chelators have been characterized and assessed for their binding affinities for Sb^{III}. X-ray diffraction studies confirmed the successful complexation of several chelators to Sb^{III}, which bound in a pentadentate fashion.



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ROS-HYPERTHERMIA SYNERGY: THIOCARBOHYDRAZONE-Cu(II) COMPLEX WITH SELECTIVE CYTOTOXICITY AGAINST COLORECTAL CANCER COUPLED TO RHENIUM-SILICA NANOPARTICLES TO ENHANCE IN VIVO ACTIVITY AND DELIVERY

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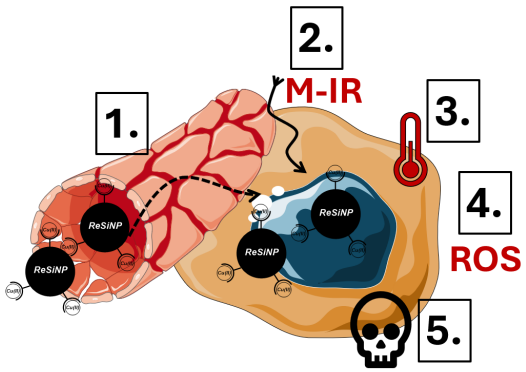
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The development of effective metal-based therapeutics requires chelators that combine biological activity, synthetic accessibility, and targeted delivery. Thiocarbohydrazones (TCHs) are promising ligands due to their mixed hard/soft donor system (S, N, O/P)[1], enabling coordination with diverse metal ions and broad-spectrum biological applications. However, improving therapeutic selectivity and efficacy remains a key challenge.

To address this, we designed a TCH ligand (**L**) featuring a carboxylate moiety, which enhances the aqueous solubility of its metal complexes and allows conjugation to targeting vectors. Coordination with Cu(II) yielded a stable, soluble and cheap complex (**LCu**) with potent *in vitro* activity. Pro-oxidant behavior was confirmed via ascorbate consumption[2] and pyrogallol auto-oxidation assays[3], while cytotoxicity assays demonstrated selective efficacy against colorectal cancer cells (CRC, HT29 cell line) at 10 µM after 24 hours, with a 5-fold selectivity index over healthy fibroblasts (HuDe). Preliminary DCFH-DA assays revealed elevated ROS levels in HT29 cells treated with **LCu**, supporting a ROS-mediated mechanism of selective cancer cell death.

To further enhance efficacy and delivery, we coupled **LCu** with rhenium/silica nanoparticles (**ReSiNP**), which generate localized *hyperthermia*[4] upon mid-infrared (MIR) irradiation. This process releases vibrational energy as heat, promoting revascularization in hypoxic tumor regions and increasing local dioxygen and ROS concentration[5], thereby amplifying **LCu**'s cytotoxic effect. Additionally, **ReSiNP** leverage the enhanced permeability and retention (EPR) effect for improved in vivo delivery, while their NIR activation—non-absorbed by biological tissues—enables precise targeting of colorectal cancer (CRC)-affected areas.

We optimized the synthesis of an **L-APTES** hybrid and successfully coated **ReSiNP**, with preliminary characterization showing promising results. *In vivo* studies are now underway to validate this dual-mechanism approach for targeted cancer therapy.



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DESIGN OF FLUORESCENT IMINE SYSTEMS FOR METAL-ION DETECTION AND OPTOELECTRONIC APPLICATIONS

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Imines containing an azomethine (–HC=N–) group are attractive compounds owing to their versatile coordination abilities and interesting photophysical properties. The presence of nitrogen and oxygen donor atoms enables thformation of stable metal complexes, making these materials promising for sensing and optoelectronic applications. Fluorescent imines exhibiting excited-state intramolecular proton transfer (ESIPT) are particularly interesting because of their unique luminescence behavior and sensitivity toward metal ions.[1] In macrocyclic Schiff bases, the rigid cyclic structure suppresses non-radiative relaxation, leading to enhanced luminescence efficiency. Moreover, chirality and the presence of electron-donating or electron-withdrawing substituents strongly influence their electronic and emission properties, which is especially important for OLED applications. Here we present the data of photoluminence sensor tests for imines towards several metal ions and the optical properties of isolated compounds and their ZnO beznizmidazole composites. (Figure 1)

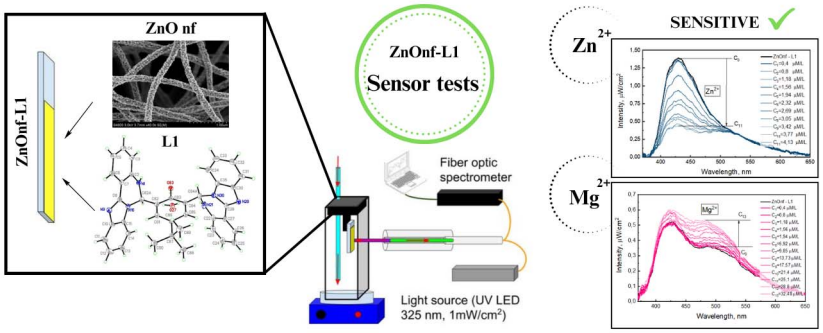


Figure 1. Outline of conducted study.

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HALF-SANDWICH Os(II), Ir(III) AND Ru(II) COMPOUNDS WITH PHOSPHINO-HOMOPIPERIDINE CONJUGATES – BIOMOLECULES' INTERACTIONS STUDIES AND ANTICANCER ACTIVITY *IN VITRO*

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Despite substantial scientific efforts and the availability of established therapeutic approaches such as radiotherapy and chemotherapy, the development of new anti-proliferative agents remains essential due to the increasing drug resistance observed in cancer cells. [1-2] Organometallic compounds are increasingly recognized as a promising new class of chemotherapeutic agents for future cancer treatments. They exhibit pronounced cytotoxicity toward tumor cells and hold significant potential for reducing adverse side effects in patients, while also offering strategies to overcome resistance mechanisms present in drug-resistant cancer types. [3-5] Homopiperidine-based compounds exhibit a broad spectrum of biological activities, including anticancer, antidepressant, and antibacterial properties. [6] A potential combination of homopiperidine-based motifs with *half-sandwich* organometallic compounds may contribute to highly favorable biological properties.

The main object of my project is to synthesize and characterize eight compounds: two phosphino-homopiperidine conjugates: $PPh_2CH_2N(CH_2)_6$ (**1**) and $P(C_6H_{11})_2CH_2N(CH_2)_6$ (**2**), Ir(III) complexes: $Ir(\eta^5\text{-}Cp^*)(Cl)_2PPh_2CH_2N(CH_2)_6$ (**Ir1**), $Ir(\eta^5\text{-}Cp^*)(Cl)_2P(C_6H_{11})_2CH_2N(CH_2)_6$ (**Ir2**); Ru(II) complexes: $Ru(\eta^6\text{-p-cymene})(Cl)_2PPh_2CH_2N(CH_2)_6$ (**Ru1**), $Ru(\eta^6\text{-p-cymene})(Cl)_2P(C_6H_{11})_2CH_2N(CH_2)_6$ (**Ru2**); and Os(II) complexes $Os(\eta^6\text{-p-cymene})(Cl)_2PPh_2CH_2N(CH_2)_6$ (**Os1**), $Os(\eta^6\text{-p-cymene})(Cl)_2P(C_6H_{11})_2CH_2N(CH_2)_6$ (**Os2**). All compounds were characterized in solutions by magnetic resonance spectroscopy (NMR) and mass spectrometry (MS). In addition, compounds **Ir1**, **Ru1**, **Os1** and **2** were characterized in the solid state by X-ray crystallography. All obtained compounds (**1, 2, Ir1, Ru1, Os1, Ir2, Ru2, Os2**) were subjected to: (i) stability tests in biological media; (ii) interactions with various biomolecules (*i.e.* NADH, GSH, cysteine); (iii) bioassay analysis to confirm the *in vitro* anticancer properties.

Acknowledgments: This project is co-funded by National Science Centre (2023/51/B/ST4/00355) and the Pearls of Science II program (PN/02/0034/2023).

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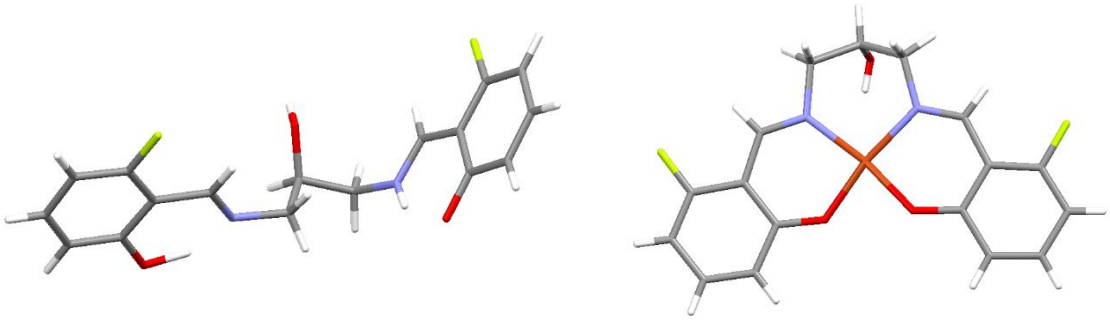
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COORDINATION BEHAVIOR OF A FLUORINATED SCHIFF BASE LIGAND TOWARD D-BLOCK METALS: FROM TITRATION TO CRYSTALLOGRAPHY

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Schiff base ligands play a key role in coordination chemistry, enabling the formation of systems with tunable structural and electronic properties. Of particular importance are modified ligands, which allow for the regulation of donor–acceptor interactions and stabilization of transition metal ions in diverse coordination environments. In this context, 1,3-bis(6-fluorosalicylidenamino)-2-propanol (H_3L, Figure 1) represents an interesting example in which the introduction of fluorine atoms at the 6-position of the aromatic rings significantly modifies its electronic character, increasing the acidity of the phenolic groups and influencing the donor properties of nitrogen and oxygen atom. The ligand was obtained by condensation reaction between 1,3-diamino-2-hydroxypropane and 6-fluorosalicylic aldehyde, while the complexes were obtained by the template method and the complexes of the formula [Cu(HL)], Figure 1 were obtained.



(a) (b)

Figure 1. Crystal structures of: (a) ligand H_3L and (b) complex [Cu(HL)].

The solution equilibria were investigated potentiometrically, revealing multi-step processes involving phenolic deprotonation and the formation of 1:1 and 1:2 metal–ligand complexes, indicating the coordination flexibility of the system. The ligand forms stable complexes in solution with Cu(II), Fe(III), and Mn(II) ions. Cu(II) complexes preferentially adopt square-planar salen-type geometries, while the metal center strongly influences the coordination structure and physicochemical properties. The results demonstrate that subtle electronic modifications within the ligand framework have a decisive impact on the stability and spatial arrangement of the complexes, making the studied system a relevant model for the design of functional coordination materials with potential catalytic and structural applications [1].

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EXPLORING BIOMOLECULAR INTERACTIONS OF WATER-SOLUBLE PHOSPHINO Ir(III), Ru(II) AND Os(II) COMPLEXES AS A POTENTIAL APPLICATION IN ANTICANCER THERAPY

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We present three novel organometallic complexes of ruthenium(II), iridium(III), and osmium(II) containing a dicyclohexyl-hydroxymethylphosphine ligand. The compounds were characterized using a range of techniques, including 1D and 2D NMR, ESI(+)-MS, elemental analysis, and UV–Vis spectroscopy (absorption and fluorescence).

The interactions of the synthesized complexes with biologically relevant molecules such as nicotinamide adenine dinucleotide (NADH), glutathione (GSH and GSSG), cysteine (Cys), and ascorbic acid (Asc) were investigated, revealing that selected complexes undergo reactions with these biomolecules. Furthermore, the redox activity of the complexes was confirmed by cyclic voltammetry.

Our results demonstrate that the nature of the central metal significantly affects the reactivity of the complexes toward biomolecules, which may be relevant to cellular redox homeostasis and biomolecular regulation. In the presentation, we will also discuss how these reactivity patterns correlate with the preliminary anticancer activity of the complexes, highlighting mechanistic insights into their potential modes of action.

This study underscores the therapeutic potential of these metal-based complexes and suggests that these newly developed compounds are promising candidates for further investigation as potential anticancer agents.[1][2][3][4]

Acknowledgement: The authors gratefully acknowledge financial support from the National Science Centre, Poland (Grant 2023/51/B/ST4/0035), the Polish National Agency For Academic Exchange in project Strategic Partnerships 2024 and from the program „Excellence initiative – Research University" for years 2025-2026, University of Wroclaw.

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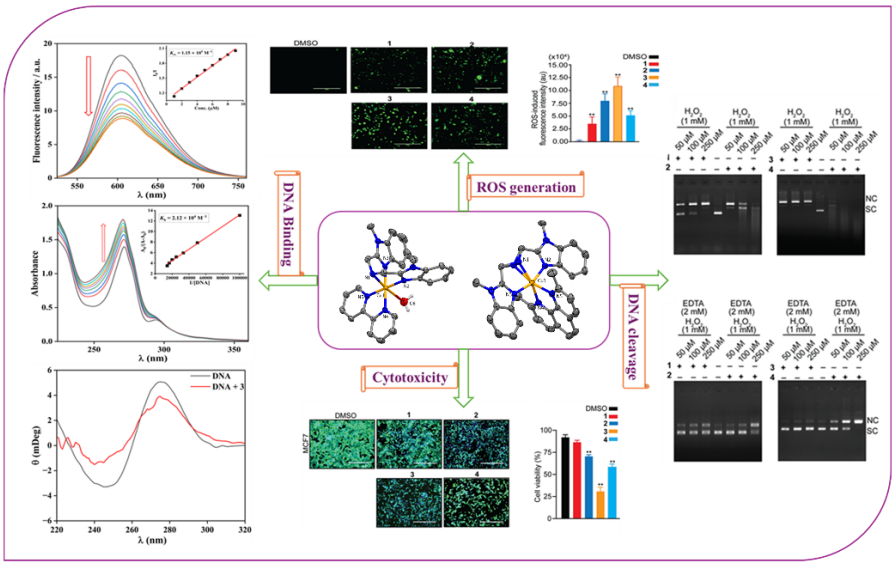
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COMPREHENSIVE DESIGN, SYNTHESIS OF METHYL SUBSTITUTED BENZIMIDAZOLE-BASED MONONUCLEAR COPPER(II) COMPLEXES AND EVALUATION OF DNA CLEAVAGE AND ROS-INDUCED APOPTOSIS

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Copper complexes have recently emerged as promising anticancer agents due to their superior activity and lower toxicity compared to clinically used platinum drugs.[1,2] Herein, four novel mononuclear Cu(II) mixed ligand complexes $[Cu(\mathbf{L})(NN')](ClO_4)_2$ **1**−**4**, where **L** is Bis-((1-methyl-1H-benzo[d]imidazol-2-yl)methyl)amine and NN′ is 2,2′-bipyridine (bpy) (**1**), 1,10-phenanthroline (phen) (**2**), 2,9-dimethyl-1,10-phenanthroline (2,9-dmp) (**3**), or dipyrido[3,2-d:2′,3′-f]-quinoxaline (dpq) (**4**), were synthesized and characterized by various analytical and spectroscopic techniques. The geometry around Cu(II) is distorted square pyramidal for complex **3**, while the other complexes exhibit distorted octahedral geometries. DNA-binding studies with salmon sperm DNA (ss-DNA) and ethidium bromide (EB) displacement assays revealed the binding affinity order **4** > **2** > **1** > **3**, indicating the strongest interaction of complex **4** with DNA. DNA cleavage was evaluated using an electrophoresis-based *in vitro* assay. Complexes **2**–**4** showed low micromolar IC_{50} values against MCF-7 and MDA-MB-231 cells. Although DNA cleavage followed the order **4** > **2** > **3** > **1**, complex **3** exhibited the highest cytotoxicity, ROS generation, and apoptosis (**3** > **2** > **4** > **1**), suggesting a ROS-mediated anticancer mechanism.



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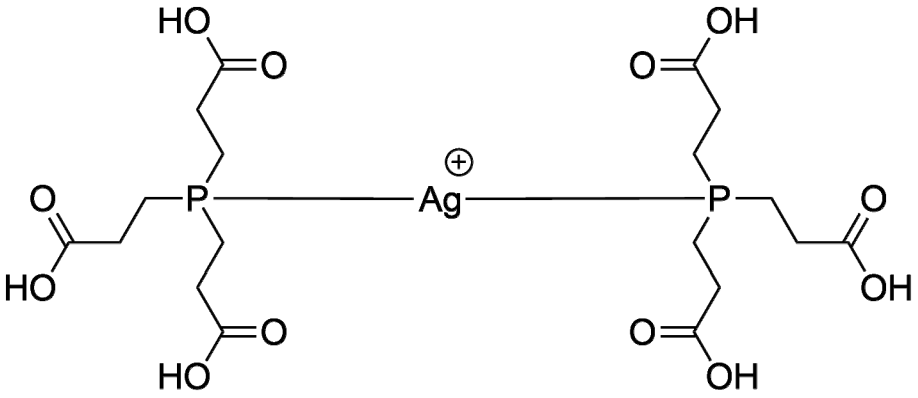
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SILVER(I) COMPLEXES OF A WATER-SOLUBLE PHOSPHINE LIGAND: *TRIS*(2-CARBOXYETHYL)PHOSPHINE.

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In this abstract we describe our ongoing research in forming biocompatible complexes of silver that ultimately may aid in development of new radioisotopes in diagnostics and therapy where ^{111}Ag and ^{103}Ag are potential candidates. We investigated the bis-complexes of *tris*(2-carboxyethyl)phosphine (TCEP) with Ag(I) using NMR, ESI-MS, and X-ray crystallographic methods. It is found that the observed bis-TCEP complex of Ag(I) (see figure below) exhibits stability over a very wide pH range and resists competition from e.g. chloride ions. Additionally, experiments are reported on Perturbed Angular Correlation of γ-rays spectroscopy (PAC) using ^{111}Ag to investigate the competition from human serum. The experimental data is supported by theoretical predictions of structures and parameters using density functional theoretical calculations. Ag(I)-TCEP interactions were previously described in relation to competitive silver binding to a mutant of the Cu(I) sensing protein CueR [1].



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"IF YOU LIKE IT, YOU SHOULD PUT A RING ON IT" A PHOTOCATALYTICALLY ACTIVE ROTAXANE MIMICKING PS I

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In synthetic settings, the prevention of catalyst deactivation from chemical changes to its molecular structure during active operation is the primary concern and remains elusive.[1] Inspired by membrane and protein integration of the natural photosynthetic apparatus of green plants ensuring structural integrity of key components, we report a photocatalytically active rotaxane mimicking photosystem I. In our Ru-Rh dyad system the two metal centers are connected by sensitive alkyne-units. By strategically burying the bridging ligand in a macrocycle cavity, i.e. in cucurbit[7]uril, the heterodinuclear rotaxane photocatalyst preserves both, structural integrity and activity of its components. Superior, long-term photocatalytic activity under enzyme-like H-bond-driven substrate preorganization at the catalytic center. These results underscore the pivotal function of rationally engineered interplay between supramolecular assemblies in catalysis and open new catalytic paradigms for advanced and sustainable supramolecular methodologies, with direct applications in artificial photosynthesis and light-driven water splitting.[2]

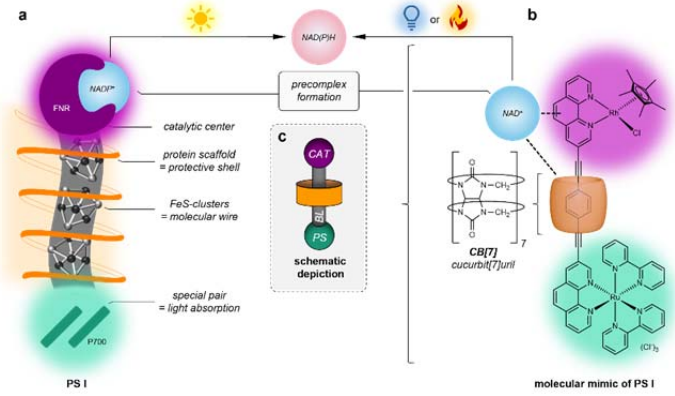


Figure 1. (a) Simplified representation of PS I, showing the special pair used for light absorption (cyan), followed by the molecular wire (Fe_4S_4 clusters & ferredoxin) connecting the special pair with the ferredoxin-$NADP^+$ reductase (FNR) serving as catalyst (CAT, purple). The molecular wire is shielded in a protective protein shell (orange helix). The FNR forms a precomplex with $NADP^+$ in its enzymatic pocket before conversion to NADPH takes place. (b) Chemical depiction of the herein presented PS I-mimicking rotaxane, showing the NAD^+ precomplex formation in its artificial binding pocket. Catalytic conversion of NAD^+ to NADH can be obtained either by photocatalysis or thermal catalysis. (c) Schematic depiction of the investigated rotaxane used in this study.

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DE NOVO DESIGNED BINDERS SUPPRESS AGGREGATION OF Cu/Zn-SUPEROXIDE DISMUTASE IMPLICATED IN AMYOTROPHIC LATERAL SCLEROSIS

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The accumulation of misfolded proteins is a pathological feature of various neurodegenerative diseases, making it a prime objective for therapeutic interventions. Despite its importance, discovering molecules that can effectively alter or prevent the protein aggregation continues to be a major challenge. Recent breakthroughs in computational protein design, specifically through machine-learning frameworks like RFdiffusion [1] and ProteinMPNN [2], have made it possible to engineer *de novo* proteins that bind to precise molecular targets.

Here, we utilized those computational approaches to create *de novo* binders for Cu/Zn-superoxide dismutase (SOD1). Pathogenic mutations in SOD1 lead to its abnormal aggregation, a process intimately linked to amyotrophic lateral sclerosis. While wild-type SOD1 normally operates as a highly stable homodimer, ALS-associated mutations destabilize the dimeric structure, promoting the formation of highly aggregation-prone monomers. Consequently, our objective was to computationally engineer proteins that selectively interact with those aberrant SOD1 monomers. By leveraging RFdiffusion alongside ProteinMPNN, we generated a pool of candidate binders and filtered them using computational confidence metrics, such as RMSD and i_pae. We then produced the top three designs recombinantly and assessed their interaction with SOD1 *in vitro via* biolayer interferometry. This experimental screening revealed one standout candidate, binder #313, which exhibited specific recognition of the monomeric state of SOD1. To further improve its binding properties, we utilized partial diffusion models [3] to refine the binder design, evaluating binding affinity using metrics such as computational free energy changes (ddG). This redesign process resulted in #313-604, a refined variant that maintained specificity for the SOD1 monomer but displayed improved binding strength. X-ray crystallography confirmed that the structural complex of #313-604 bound to the SOD1 monomer was in agreement with our initial computational model. Furthermore, *in vitro* assays demonstrated that the addition of #313-604 successfully prevented the monomeric SOD1 from assembling into oligomers and amyloid-like fibrils. Overall, our findings highlight the power of machine learning-driven *de novo* protein design as a viable, rational approach for developing inhibitors against the aggregation of disease-causing misfolded proteins.

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SMALL CHANGES, BIG CONSEQUENCES: A BIOACTIVITY SURVEY OF SALICYLATOCOPPER(II) COMPLEXES

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A comparative study of 13 phase-pure dinuclear copper(II) complexes $[Cu_2(N,N\text{-}L)_2(\mu\text{-}X\text{-}Sal)_2]$ is presented, combining either 1,10-phenanthroline (*phen*, **1**–**8**) or 2,2′-bipyridine (*bpy*, **9**–**13**) with variably substituted salicylates (H, Me, halogen, MeO, CF_3, diflunisal). DNA-binding studies (UV-Vis, viscometry, ethidium bromide displacement, thermal denaturation) revealed a mixed groove-binding/partial-intercalation mode with K_b values of $10^4 – 10^6$ M^{-1}, while BSA titrations indicated moderate static quenching [1]. Cyclic voltammetry confirmed a quasi-reversible Cu(II)/Cu(I) couple driving SOD-mimetic activity (IC_{50} = 1.04 – 9.84 μM)ROS generation in a Fenton-type system, and catecholase activity toward 3,5-DTBC. The most striking dichotomy emerged in antiproliferative assays against A549 and HepG2 cells: *phen* complexes reached IC_{50} = 0.88 – 2.69 μM, whereas *bpy* analogues remained an order of magnitude less active (12 – 23 μM). A parallel trend was observed in antibacterial screening, with complex **2** (3-Me-Sal) most effective against *S. aureus* [2].

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A NEW [20]-MEMBERED MACROCYCLE WITH A LARGE CAVITY

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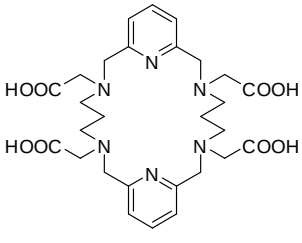
The α-therapy is one of promising methods in nuclear medicine as α-particles have a short range in tissue and high linear energy transfer. However, this type of treatment is almost exclusively limited for "large metal ions" such as $^{212}Bi^{3+}$, $^{212}Pb^{2+}$ or $^{225}Ac^{3+}$ which impose specific requirements for suitable ligands. More specifically, these ligands should possess large ligand cavities with multiple donor atoms (coordination number 8–10). The examples of such ligands are MACROPA [1] and PYTA [2]. In this work, we explored coordination behaviour of a ligand featuring even larger macrocyclic cavity in [20]-membered macrocycle bearing four acetic pendant arms (PPTA, Figure).

This new ligand can be prepared by template synthesis with La^{3+} ion followed by alkylation of four amino groups. Since the lanthanide(III) ions are considered analogues of actinide ions regarding their chemistry which is defined by their ionic radius, coordination behaviour has been described across a series of rare-earth metal complexes.

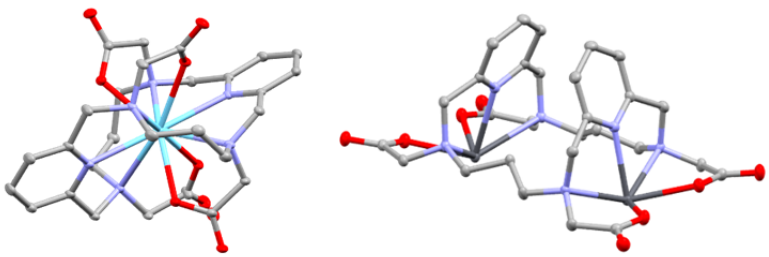
Unexpectedly, PPTA was found to form coordination compounds with a relatively low thermodynamic stability and limited kinetic inertness. Complexation of metal ions requires a relatively high pH (approx. above 7), unlike other known azamacrocyclic ligands containing pendant arms. Kinetic studies revealed that complexation occurs almost immediately within this pH range, yielding mixtures of several isomers. For larger lanthanide (III) ions, the major isomer in these mixtures was successfully isolated and structurally characterized. It contains two pendant arms coordinated above and two carboxylate groups below the N_6 plane of the macrocycle (Figure).

Within a specific pH range, a large size of cavity of the ligand enables the formation of dinuclear complexes of lanthanide(III) and Pb(II) ions in significant amounts. The solid-state structure of dinuclear complex with Pb(II) ion, the complex was successfully determined (Figure).

Overall, the investigated [20]-membered macrocycle derivative PPTA forms complexes with lanthanide (III) ions rapidly. However, due to its insufficient stability and inertness, this ligand is not suitable for application in nuclear medicine. Nevertheless, its ability to incorporate two large metal ions within a single macrocyclic cavity makes this ligand an interesting subject for structural studies.



PPTA



This work was supported by the Grant Agency of the Czech Republic (25-17964S)

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EXPLORING THE COORDINATION CHEMISTRY OF CEFADROXIL WITH TRANSITION AND LANTHANIDE METAL IONS

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Cefadroxil (Fig. 1) is an antibiotic from the cephalosporin group, i.e. β-lactam drugs widely used in the treatment of bacterial infections. It is characterized by a broad spectrum of activity and is used, among others, in the treatment of respiratory, urinary and skin infections. Its structure contains functional groups (including carboxylic, amino and hydroxyl) capable of binding metal ions, which creates the possibility of modifying its properties by creating new complexes. The study of these interactions allows for a better understanding of the mechanism of action of cefadroxil, and also opens up the prospect of developing more effective therapies in response to the growing problem of bacterial resistance to antibiotics.

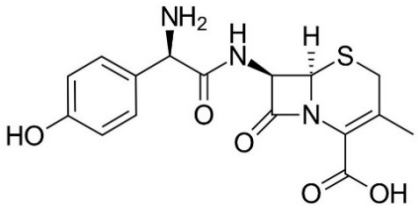


Figure 1. Structural formula of cefadroxil.

Complex compounds formed in metal-ion systems (Co(II), Cu(II), Eu(III), and Tb(III)) with cefadroxil were studied and characterized in terms of their thermodynamic stability, coordination mode, and composition. The objectives were determined using the potentiometric method and a range of spectroscopic methods: UV-Vis spectroscopy, EPR, IR, and extremely sensitive luminescence. The conducted studies showed that the type of metal ions of the d-, and f-electron elements had a significant effect on the complexation process with cefadroxil, leading to the formation of complex compounds with different thermodynamic stability, different spectroscopic and antibacterial properties.

The metal ions proposed for studies with cefadroxil exhibit diverse chemical properties that directly determine their ability to form coordination bonds with ligands and thus influence both the number and stability of the resulting complex species. It was shown that copper(II) ions form the greatest number and the most diverse types of complexes with cefadroxil, indicating that this metal interacts with the antibiotic in a particularly distinctive way.

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COPPER BINDING IN A BACTERIAL TRANSCRIPTIONAL REPRESSOR

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Transcriptional regulatory proteins control metal homeostasis by directing the production of metal chaperones and transporters. Most copper (Cu)-dependent transcriptional regulators maintain this homeostatic balance by activating the expression of Cu exporters and associated proteins under conditions of Cu excess [1]. The exception to this paradigm is the YcnK protein. YcnK represses transcription of the *ycn* operon under conditions of Cu excess [2,3]. This results in decreased production of the proteins YcnI and YcnJ that bind Cu(II) and work together to facilitate copper uptake [4,5]. However, very little is known about YcnK at a molecular level, nor have the details of its interactions with Cu been elucidated. In this study, we investigate how YcnK interacts with Cu ions through structural analysis, mutagenesis, spectroscopic studies, and binding affinity determinations. We find that the protein contains a highly conserved cysteine-rich binding pocket that houses a high affinity Cu binding site. These findings expand our understanding of protein-based metal coordination will inform future studies into how interactions with metal ions modulate the ability of the protein to repress gene transcription.

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COORDINATION CHEMISTRY OF Cu(II) IONS WITH TYROSINE AND ADENINE NUCLEOTIDES

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Understanding interactions between metal ions and biologically relevant ligands is important for explaining many physiological and biochemical processes [1]. In this study, copper(II) ions were investigated in model systems containing tyrosine (Tyr) and adenine nucleotides: AMP, ADP, and ATP. Tyrosine is involved in redox processes and can form biologically relevant complexes [2], while adenine nucleotides play essential roles in energy metabolism, signaling, and nucleic acid structure [3]. Therefore, Cu(II) interactions with these ligands may provide insight into metal–ligand behavior in biological systems [4].

Complex formation was studied in aqueous solution using potentiometric, UV–Vis, and EPR techniques, supported by DFT calculations (Figure 1). Based on the obtained results, coordination modes were proposed for the Cu(II)/Tyr and Cu(II)/Tyr/adenine nucleotide systems.

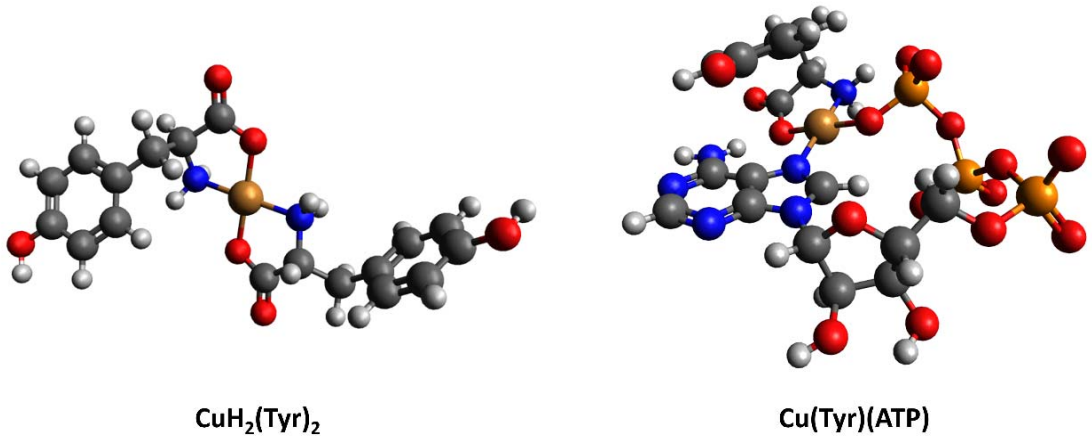


Figure 1. Structures of the complexes with the strongest interaction between Cu(II) and ligands molecules, obtained by molecular modelling and DFT studies.

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INVESTIGATION OF THE COMPLEXATION OF GALLIUM IONS WITH BARBITURIC ACID DERIVATIVES

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The search for new therapeutic agents remains a key objective in modern medicine, particularly in the context of improving efficacy while reducing adverse effects. Although barbiturates are widely known for their sedative, anticonvulsant, and anesthetic properties, their long-term use may lead to serious neurological side effects and accumulation in the body.

Barbituric acid and its derivatives, including azo and Schiff base compounds, have attracted interest due to their potential coordination with metal ions and associated biological activity. The presence of donor atoms, such as nitrogen and oxygen (Fig.1.), enables the formation of coordination bonds with metal ions. In solution, barbiturates typically undergo deprotonation and coordinate primarily through nitrogen atoms, although alternative coordination modes involving oxygen atoms may also occur depending on the metal ion. These features make barbituric acid derivatives promising candidates for further investigation in medicinal and coordination chemistry.

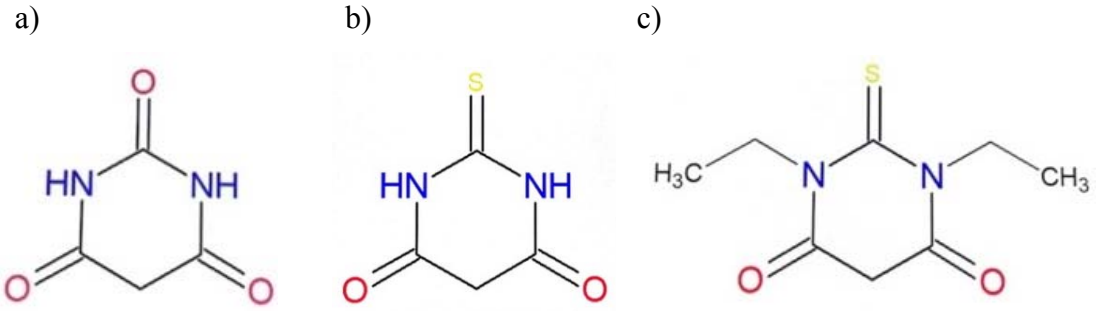


Fig. 1. Structural formulas of a) barbituric acid (BA), thiobarbituric acid (TBA), c) 1,3-diethylthiobarbituric acid (1,3 diEtTBA).

Gallium-based compounds represent a group of substances with promising anticancer activity. However, simple gallium salts exhibit significant limitations in vivo: gallium nitrate is associated with nephrotoxicity and optic neuropathy, while gallium chloride shows poor bioavailability. An alternative approach involves the use of gallium coordination compounds, particularly with ligands that possess therapeutic properties.

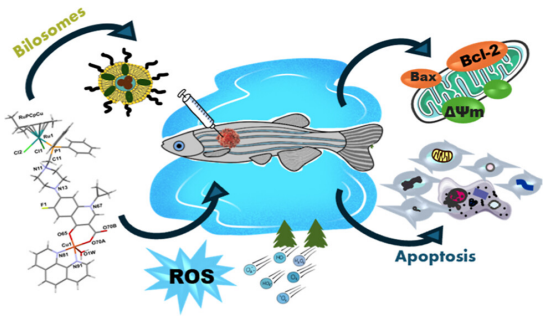
The literature describes gallium complexes with flavonoids as well as nanocrystalline structures based on tetraphenylporphyrin. However, the limited number of reports on the complexation of gallium ions with sulfur-containing ligands has motivated further investigation of thio-derivatives of barbituric acid and related compounds.

THE BILOSOME Ru-Cu STRIKES BACK. THE TUMOR REBELLION

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Novel heteronuclear Ru(II)-Cu(II) complexes have been investigated as rising stars among potential anticancer agents. The complexes RuPSfCu, RuPCpCu, RuPLmCu, and RuPNrCu were synthesized using phosphine ligands of the type $Ph_2P–CH_2–FQ$, where FQ represents fluoroquinolone antibiotics: sparfloxacin (HSfx), ciprofloxacin (HCfx), lomefloxacin (HLfx), and norfloxacin (HNfx). The obtained compounds were characterized by ESI-MS spectrometry, selected spectroscopic techniques, single-crystal X-ray diffraction, and density functional theory calculations, confirming their structures and coordination geometries.



The cytotoxicity was evaluated *in vitro* across multiple cancer cell lines (lung, breast, pancreatic, prostate) and noncancerous cells. In vivo toxicity was also assessed using a zebrafish (*Danio rerio*) larvae model. The results demonstrated that Ru(II)–Cu(II) complexes exhibit greater anticancer activity compared with cisplatin while almost being nontoxic toward control cells *in vitro*. Mechanistic studies revealed that their action involves nuclei accumulation, reactive oxygen species generation, lipid peroxidation, and mitochondrial membrane depolarization. The expression ratio of Bax to Bcl-2 mRNA correlates with apoptotic cell death. Additionally, encapsulation of the one Ru(II)–Cu(II) complex in bilosomes significantly improved its stability, selectivity, and therapeutic efficacy in three-dimensional (3D) cancer spheroid models. What's more experiments in 3D cancer spheroids and larval tumor xenograft models revealed statistically significant reductions in tumor volume and proliferation rates following treatment with the Ru(II)–Cu(II) systems. To the best of current knowledge, none of the complexes had previously been successfully encapsulated in bilosomal nanomaterials.

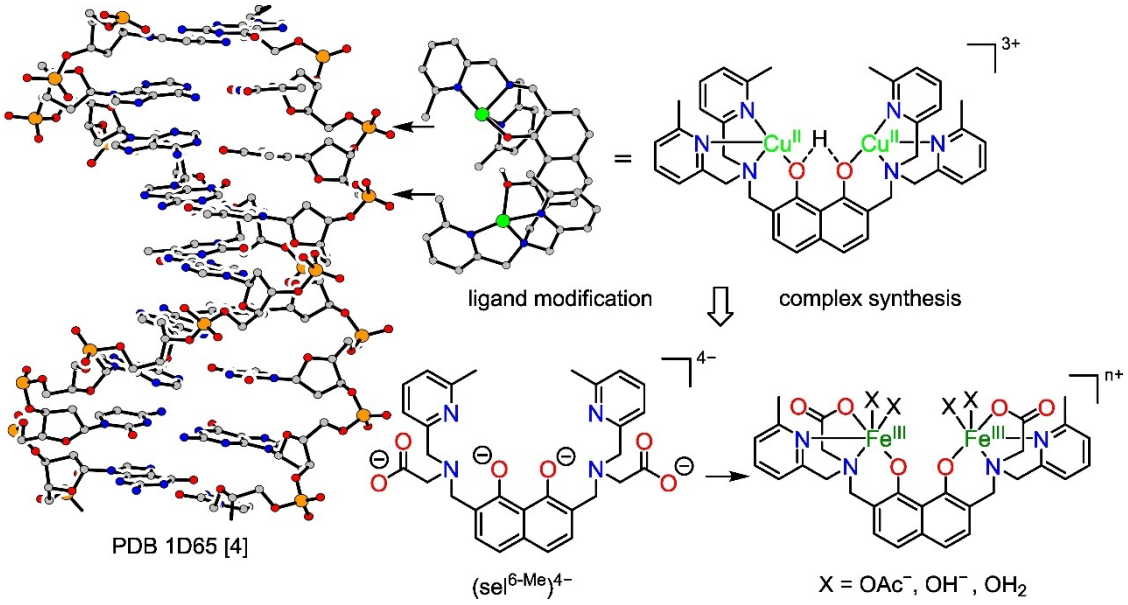
Acknowledgement: This research was funded by the National Science Centre, Poland (grant number 2023/51/B/ST4/00355 and 2023/49/N/ST4/00337). The support from the Department of Physical and Quantum Chemistry at Wroclaw University of Science and Technology is also gratefully acknowledged. Research project supported/partly supported by the program "Excellence initiative─research university" for years 2020-2026 for the University of Wrocław. The authors would like to thank the Zebrafish Facility Team at the Experimental Medicine Centre of the Medical University of Lublin for their assistance with zebrafish husbandry and breeding.

SYNTHESIS OF DINUCLEAR NAPHTHALINDIOL-BASED COMPLEXES WITH MIXED CARBOXYLATE- AND NITROGEN-DONORS FOR THE STABILISATION OF TRIVALENT METAL IONS

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In modern medicine, metal complexes such as cisplatin, the most prominent representative of classical cytostatic drugs, play a key role. The cytotoxic effect is achieved through binding of cisplatin to adjacent guanine bases in the DNA strand, which ultimately leads to apoptosis of cancer cells [1]. By targeting the phosphate diesters in the backbone of the DNA a new mechanism of action could be achieved. In this respect, we have developed a family of dinuclear naphthalenediol-based Cu^{II}- and Ni^{II}-complexes, which are designed to enable binding to two adjacent phosphate diesters in the DNA backbone according to the multivalence principle [2]. These metal complexes exhibit a preference for killing cancer cells rather than human stem cells with similar proliferation rates [3]. In order to strengthen the binding to DNA, trivalent metal ions would be preferred. To stabilize trivalent metal ions, a carboxylate-donor has been introduced instead of one terminal pyridine-donor in the original ligand, resulting in the new ligand $(sel^{6\text{-}Me})^{4-}$.



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RHENIUM CARBONYL COMPLEXES WITH 2-MERCAPTOPYRIDINES

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Rhenium(I) tricarbonyl complexes have been a prominent topic in recent years, mainly due to their physico-chemical properties and stability. They are particularly notable for their spectroscopic properties, which are useful in diagnostic applications. Additionally, rhenium(I) tricarbonyl complexes exhibit promising biological and catalytic activity and can serve as theranostic compounds [1].

In recent years, our research group has prepared various rhenium carbonyl complexes with different *N*,*N*- and *S*,*O*-donor ligands [2,3]. In most cases, the complexes displayed a predictable octahedral structure with a *fac*-tricarbonyl fragment, a bidentate ligand, and a monodentate ligand. While studying *S*,*O*-donor pyrithione ligands, we found that complexes exposed to light react to form 2-mercaptopyridine ligands and can lose carbonyl ligands. We prepared the previously known rhenium tricarbonyl complex with 2-mercaptopyridine using a new synthetic procedure [4]. We also successfully prepared a rhenium dicarbonyl complex with a 2-mercapto-3-fluoropyridine ligand and rhenium monocarbonyl complexes with a 2-mercaptopyridine ligand. While the dicarbonyl structure retains octahedral geometry, the monocarbonyl structure does not; it exhibits pentagonal bipyramidal geometry and rhenium in the +3 oxidation state.

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CONTROL OF COPPER NUCLEARITY BY METAL SOURCE AND BASE

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This work describes the design of a multidentate ligand platform and a systematic investigation of the factors controlling copper nuclearity in its coordination assemblies. In conventional coordination chemistry, particularly for macrocyclic ligands, nuclearity and structural outcomes are generally governed by the metal-to-ligand (M/L) ratio. In contrast, our results show that, in this system, nuclearity is largely independent of the M/L ratio and is instead governed by the combined effects of the metal source and the base.

Under basic conditions, the choice of copper precursor directs the formation of distinct nuclearities. $CuCl_2$ in the presence of NEt_3 or NaOH affords a heptanuclear complex, whereas $Cu(ClO_4)_2{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ preferentially yield hexanuclear and tetranuclear species, respectively. In the absence of an added base, both $CuCl_2$ and $Cu(NO_3)_2{\cdot}3H_2O$ produce the heptanuclear complex, indicating a distinct speciation pathway under neutral conditions. Further variation of the base provides an additional level of control: replacing NEt_3 with K_2CO_3 or Na_2CO_3 affords a trinuclear complex. Moreover, the use of $Cu(OAc)_2$, in which the acetate anion can act as an internal base, results in a structurally distinct tetranuclear assembly.

Preliminary catalytic studies indicate that these multicopper complexes exhibit activity relevant to phenoxazinone synthase models. Overall, this study establishes a strategy for tuning copper nuclearity through the selection of metal source and base, providing a controlled approach to the construction of multicopper architectures.

DOES SIZE MATTER? CHIRAL MACROCYCLIC CHELATORS FOR ^{68}Ga RADIOLABELING

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^{68}Ga radiolabeled macrocyclic complexes have been extensively studied and used for positron emission tomography (PET) imaging. Compared to the 12-membered DOTA macrocycle, NOTA's smaller macrocyclic ring makes it more suitable for ^{68}Ga-labelled PET imaging. However, studies of 10-membered DETA derivatives are still quite limited. Thus, we designed and synthesized four different sized chiral macrocyclic ligands **L1-L4** followed by radiolabeling, equilibrium and stability studies to reveal the influence of ring size and chiral substituents on Ga^{3+} chelation. The chiral NOTA **L1** gave nearly quantitative ^{68}Ga radiolabeling yields under all the investigated conditions. In comparison, the 10- and 12- membered chelators require increased temperature for a >90% conversion. **L1-L4** all exhibit high Ga^{3+} coordination stability, while the chiral DETA **L2** with an α-methyl group shows slightly better performance than its β-analogue **L3**. Serum stability tests and kinetic studies under acid and alkaline conditions highlighted the favorable kinetic inertness of these chiral ligands, making them suitable for potential ^{68}Ga-labelled PET imaging applications [1].

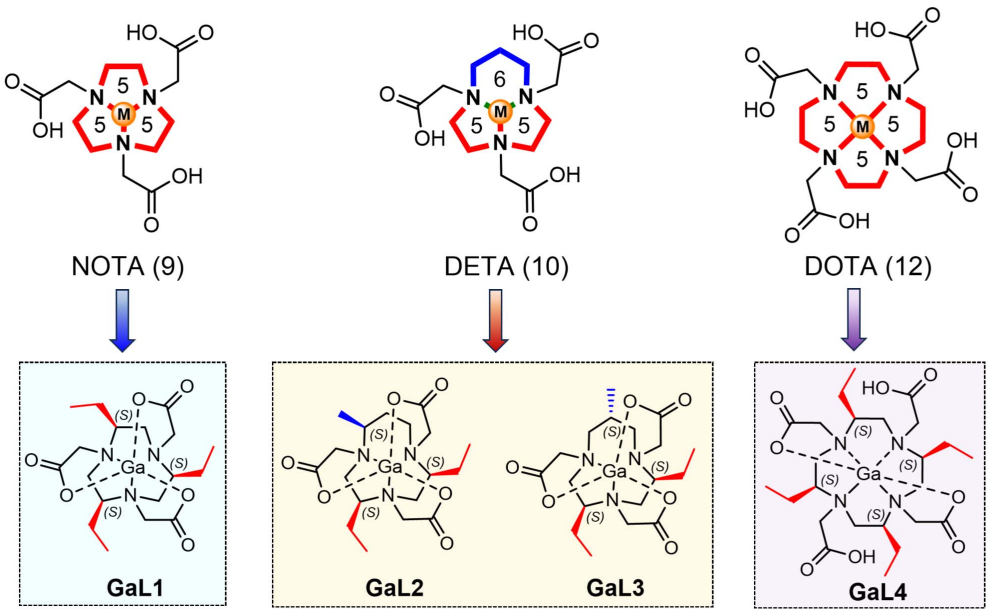


Figure 1. Structures of the Ga^{3+} complexes of ligands **L1-L4** reported in this work and their achiral parent ligands.

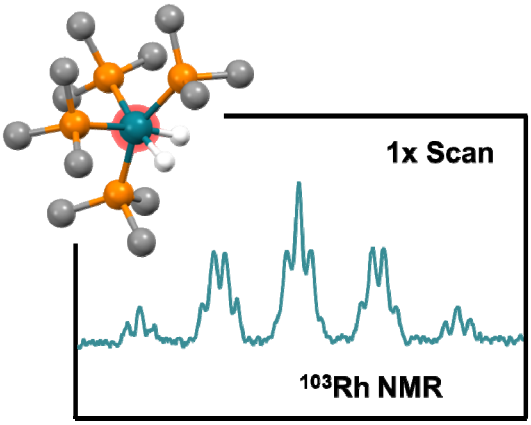
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DIRECT SINGLE-SCAN OBSERVATION OF ^{103}Rh NMR SPECTRA IN WILINSON TYPE CATALYSTS VIA PARAHYDROGEN-INDUCED POLARISATION

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Rhodium catalysts are industrially indispensable, particularly for hydroformylation reactions where their exceptional catalytic activity and efficiency make them far more desirable than cheaper alternatives such as cobalt [1]. These rhodium-based processes are responsible for the global production of over 10 million tons of 'oxo chemicals' annually [1]. Consequently, ^{103}Rh NMR represents a potentially powerful probe for studying the chemistry of these systems. However, the extremely low gyromagnetic ratio and long relaxation times of the nucleus often render direct detection impractical [2]. These limitations may be addressed by exploiting *para*-hydrogen, the lowest energy spin isomer of hydrogen, as a source of hyperpolarisation. Through the transfer of its unique magnetic spin order, *para*-hydrogen enables the detection of short-lived reaction intermediates and insensitive nuclei that are typically invisible to standard NMR techniques [3]. We report a significant sensitivity enhancement of ^{103}Rh signals in Wilkinson-type complexes by utilising a novel *para*-hydrogen-induced polarisation protocol. By exploiting a fast-exchanging catalytic mechanism, we have successfully sensitised the Rh(III) metal centre to a degree that enables the acquisition of high-quality 1D NMR spectra in a single scan. To demonstrate the utility of this method, we present the one-scan detection of two distinct Rh(III) dihydride complexes, as well as the corresponding ^{1}H, ^{13}C, and ^{31}P spectra. This approach bypasses the traditional limitations of ^{103}Rh NMR, offering a rapid and sensitive tool for the real-time characterisation of rhodium-based catalytic intermediates.



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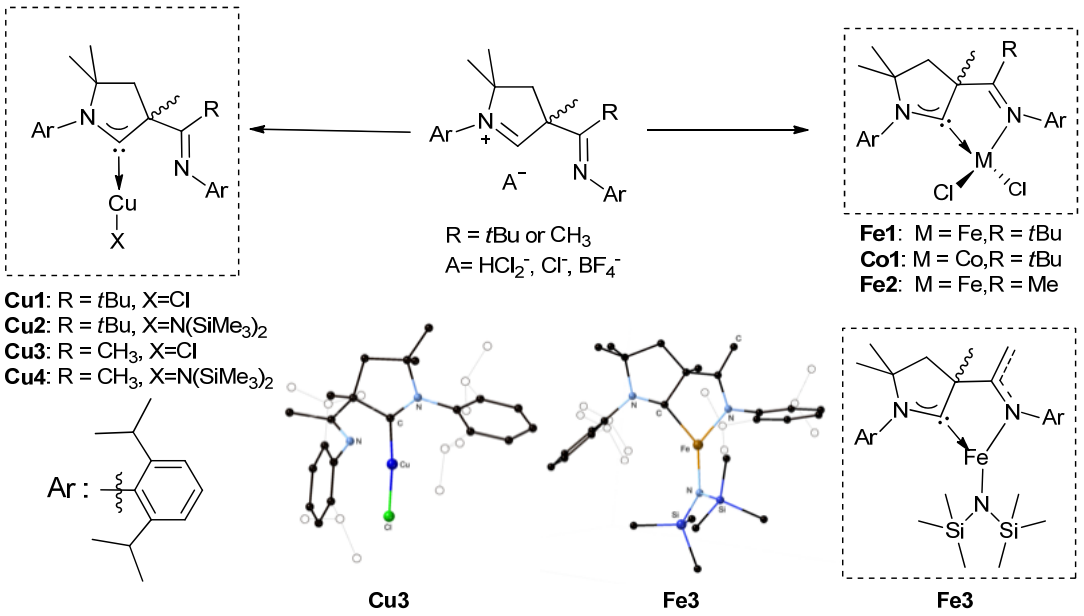
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FUNCTIONALIZED CAACS BEARING 3d METALS (Cu, Fe, Co) SYNTHESIS, CHARACTERIZATION AND CATALYTIC STUDIES

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[b]LCM, CNRS, Institut Polytechnique de Paris, Route de Saclay, France
[c]Institut de Chimie de Strasbourg, Université de Strasbourg, Strasbourg Cedex, France
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Cyclic Alkyl Amino Carbenes (CAACs) have gained popularity in organometallic chemistry, due to the combination of stronger σ-donor and better π-acceptor properties compared to classical NHCs.[1] Despite, their first appearance in 2016, functionalized CAACs (funCAACs), bearing a classical donor tethered to the carbene moiety, have received little attention.[2] In addition to the family of imine funCAAC complexes of Pd, there are scattered examples of funCAACs with heavier group 11 metals (Au, Ag) and even fewer with 3d metals (Cu and Cr).[2,3,4] This may be attributed in part to the capricious synthesis of the funCAAC complexes and the inherent instability of the corresponding free carbenes.[1,2] Herein, we will describe modified synthetic procedures to access funCAAC precursors and complexes with Fe, Co and Cu; catalytic studies of the latter in 'Click reactions', comparisons with analogous functionalized NHCs of imidazole and pyrimidine type, and mechanistic considerations will also be mentioned.



Scheme 1: Imine fun-CAAC complexes featured in this work

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PALLADIUM COMPLEXES WITH *β*-BLOCKED POC^{sp3}OP LIGANDS: THE (FAILED) QUEST FOR POCOP-Pd CARBENE COMPLEXES

Lucas Mello, Ruben Hansson, Tanguy Debaud, Linnea Nymberg, Francesca DiMari, Vasudevan Subramaniyan, Ola Wendt

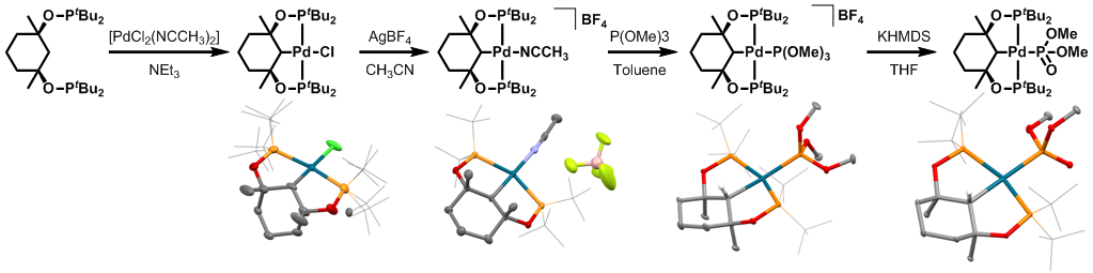
Centre for Analysis and Synthesis, Department of Chemistry, Lund University, Lund, Sweden

Carbon-metal double bonds are attractive platforms for small molecule activation.[1,2] Indeed, PCP pincer complexes in which the coordinated carbon atom is sp^3 hybridized are a suitable motifs for reversible M=C carbene formation, since the C-H bond on the central carbon can potentially be cleaved by strong bases[1] or by hydride abstractors,[3] leading to the formation of Schrock- or Fisher-like carbenes. Those carbene complexes may present fundamentally different reactivities and are therefore relevant for catalyst design and development. More specifically, there are reports of reversible hydrogen addition[2] over M=C and small molecule activation (*i.e.* H_2O, ROH, NH_3, H_2, RC≡CH).[1]

In the attempt to synthetize the first examples of Pd-POCOP carbene complexes, two *β*-blocked *bis*-phosphinite ligands were synthetized (**L^1**: 2,4-*bis*-[di-*tert*-butylphosphinito]-2,4-dimethylpentane and **L^2**: 1,3-*bis*-[di-*tert*-butylphosphinito]-1,3-dimethylcyclohexane). The metallation of those with $[PdCl_2(NCCH_3])_2]$ led to the first examples of Pd-POC^{sp3}OP organometallic complexes, [PdL^{n}Cl].

Deprotonation of the central carbon with KHMDS, KO*t*-Bu or KH was unsuccessful towards the chlorido complexes, so ligand substitution was investigated, leading to the isolation of $[PdL^n(NCCH_3)]BF_4$ and $[PdL^n(P(OMe)_3)]BF_4$. Substitution products with CO and CN^- ligands were observed *in situ* by NMR spectroscopy, but the formation was followed by decomposition over time, hindering isolation and/or characterization.

When $[PdL^2(P(OMe)_3)]BF_4$ was treated with KHMDS, ^{31}P NMR showed that all P signals were shifted upfield within 5 minutes, which would be expected in a species in which the doubly negatively charged carbon donor atom established a carbene with the metal center. Nonetheless, XRD crystallography showed unambiguously that the metal-carbene complex was not formed, and instead the phosphite complex underwent a Michaelis-Arbuzov-like demethylation reaction on the phosphite ligand to yield a phosphonite complex, [L^{2}Pd-P(O)(OMe)]. In fact, a S_N2 type reaction promoted the formation of MeHMDS and the coordinated anionic phosphonite ligand, as probed by a combination of XRD crystallography and NMR spectroscopy. Interestingly, alkyl phosphite complexes are known to be stable in the absence of strong nucleophiles,[4] yet in this case even the low-nucleophilic $[HMDS]^-$ base was able to promote the dealkylation reaction.



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SYNTHESIS AND STRUCTURAL CHARACTERISATION OF MANGANESE DIISOPROPYLAMIDE COMPLEXES

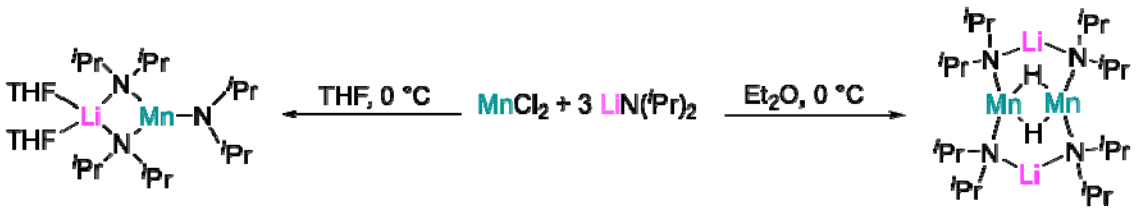
Finlay J. Sullivan,[a] Oliver Matys,[a] Gary S. Nichol[b] and Marina Uzelac[a]

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Amongst the catalogue of organomanganese(II) reagents, alkali-metal manganates have emerged as a new family of compounds which can deliver unique chemistry which cannot be replicated by conventional alkali-metal or manganese reagents on their own.[1] Formation of bimetallic architectures was shown to deliver enhanced reactivity[2] but also stability allowing isolation of species such as $[(TMEDA)_2Li_2Mn(^nBu)_4]$.[3]

Metal diisopropylamides, typified by lithium congener LiDA or turbo-Grignard reagent "(DA)MgCl·LiCl", have found widespread use in organic synthesis due to their combination of low nucleophilicity and high kinetic basicity.[4]

Bringing these two evolving areas together, this poster presents our study on synthetic approaches towards mono and bimetallic manganese diisopropylamide complexes. Salt metathesis of LiDA and $MnCl_2$ in different stoichiometric ratios and different solvent mixtures has been found to afford a variety of homoleptic and heteroleptic lithium amidomanganates (Scheme 1). The effects that chelating supporting ligands *N,N,N'N'*-tetramethylethylenediamine (TMEDA) and β-diketiminate impose on synthetic approach has also been assessed.



Scheme 1. Salt-metathesis of $MnCl_2$ and excess $Li(N^iPr_2)$ in THF and diethyl ether affording $[(THF)_2LiMn(N^iPr_2)_3]$ and $[Li_2Mn_2(H)_2(N^iPr_2)_4]$, respectively.

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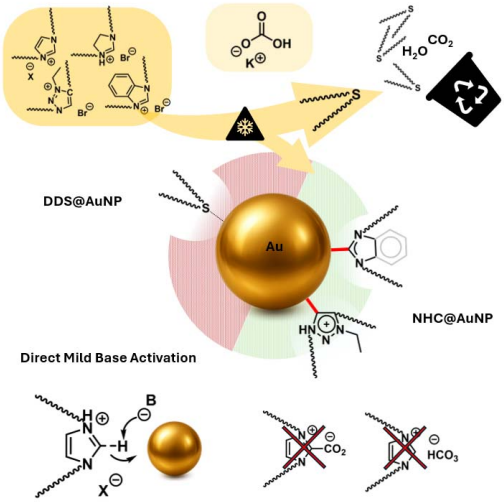
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ROBUST ONE-STEP FORMATION OF NHC@AuNP THROUGH COUNTERION-DEPENDENT MILD BASE ACTIVATION

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N-heterocyclic carbene (NHC) stabilized gold nanoparticles offer unmatched chemical and thermal stability, but traditional surface modifications rely on multistep procedures, harsh conditions, strong bases, or strictly inert conditions.[1] We report a one-pot method that achieves high coverage NHC functionalization directly on dodecyl sulfide stabilized gold nanoparticles using only imidazolium salts and a mild base. Mechanistic studies reveal that NHC formation occurs at the nanoparticle interface through a counterion-dependent pathway, bypassing the commonly observed Imidazolium-HCO_3^- or NHC-CO_2 intermediates.[2] Optimized conditions enable quantitative ligand exchange while suppressing particle ripening. The method tolerates air, moisture, and diverse NHC classes, including benzimidazolium, imidazolinium, and mesoionic precursors. This mild, general approach provides an accessible platform for robust NHC-gold nanomaterials, facilitating their application in catalysis and sensing without specialized equipment.



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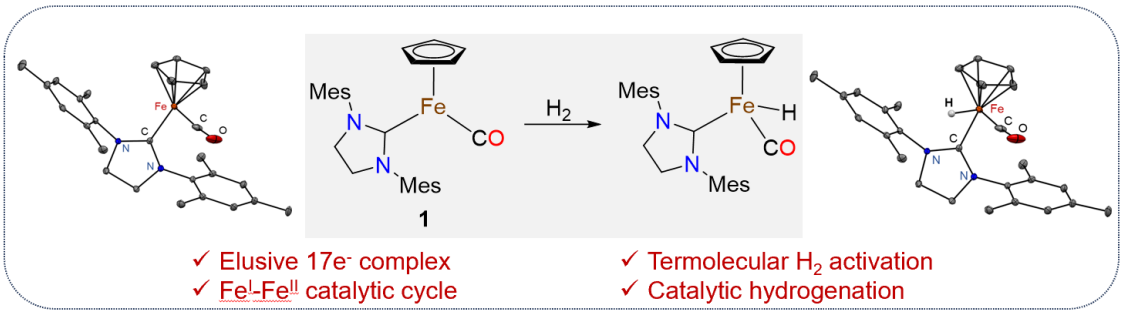
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ISOLATION OF A 17-ELECTRON $FeCp(CO)_2$ DERIVATIVE

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Okinawa Institute of Science and Technology (OIST), Okinawa, Japan

$[FeCp(CO)_2]_2$ (Fp_2) is among the earliest examples of modern organometallic complexes synthesized by Wilkinson et al.[1] Coordinated with strong-field ligands, Fp_2 serves as a useful starting point for studying diamagnetic organoiron complexes. Contrastingly, Fp_2 is also known to dissociate to a short-lived paramagnetic 17-electron monomer, $FeCp(CO)_2$ ($Fp^{\cdot}$), upon photoirradiation.[2] Extensive efforts have been made to isolate this elusive 17-electron species using bulky cyclopentadienyl ligands.[3,4] However, isolation of a 17-electron Fp derivative remain as an open challenge due to its propensity to dimerize.[5] Herein, we report the unprecedented synthesis and isolation of an derivative of $Fp^{\cdot}$, FeCp(CO)(NHC) (**1**). The substitution of a CO ligand in Fp_2 by a NHC ligand effectively inhibited the dimerization of the resulting radical species. The paramagnetic, S = ½, Fe^{I} complex **1** was characterized by methods including SC-XRD, EPR, FT-IR, NMR, and DFT calculation. The putative $Fp^{\bullet}$-mediated termolecular homolysis of chemical bonds was confirmed using the isolated radical **1**. Surprisingly, **1** homolytically cleaves H_2 via a termolecular mechanism and generates an isolable Fe^{II}–H complex. This elementary reactivity was successfully utilized for the catalytic formation of N–H and C–H bonds via a Fe^{I}–Fe^{II} catalytic cycle. This study demonstrates unique reactivities of a 17-electron iron complex which opens a new 1-electron catalytic cycle using odd-electron iron species.



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CATALYSIS OF A BRØNSTED SUPERACIDIC OXO–HYDROXO ALUMINA CLUSTER IN WEAKLY POLAR APROTIC SOLVENTS

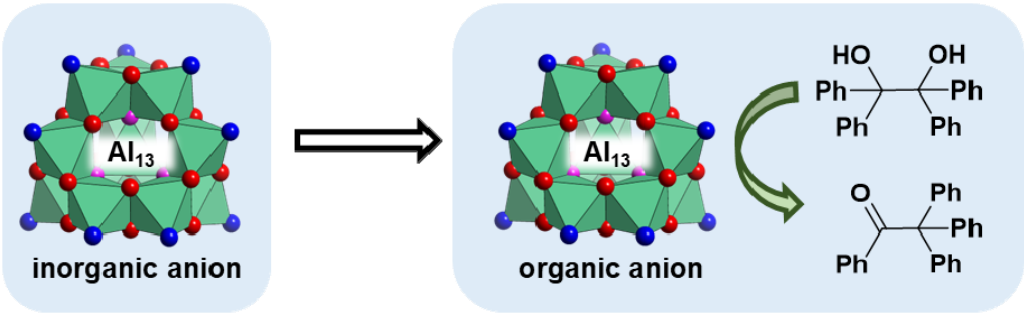
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Aluminum oxide (alumina) is the most abundant metal in the Earth's crust and has been employed for a wide range of industrial catalysts because of the thermodynamically stable structure and high specific surface area. [1] Aluminum complexes including bulk alumina can be utilized as Lewis acid catalysts, however, they are inactive as Brønsted acid catalysts. [2,3]

In contrast to bulk alumina, the Keggin-type molecular alumina cluster $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (**Al_{13}**) has a proton-rich structure and possesses Brønsted acid sites. Recently, Uchida et al. demonstrated that several types of ionic crystals composed of **Al_{13}** and anionic molecular metal oxide clusters acted as heterogeneous Brønsted acid catalysts for the pinacol rearrangement reaction. [4] They proposed that terminal aqua ligands served as the Brønsted acid sites based on the loss of catalytic activity upon dehydration of the compounds. Therefore, unlike conventional aluminum-based Lewis acid catalysts, **Al_{13}** has been revealed to function as a solid Brønsted acid. On the other hand, the acidity of **Al_{13}** itself in solution remains insufficiently understood, and no reports have described the use of **Al_{13}** as a homogeneous catalyst, presumably because the stable pH region of **Al_{13}** is narrow.

Therefore, we envisaged that development of an organic solvent-soluble **Al_{13}** with the bulky anion ($(B[C_6H_3(CF_3)_2]_4^-$) would achieve unique homogeneous catalyst in organic media. In this study, we discovered for the first time that organic solvent-soluble **Al_{13}** showed a superacid property in weakly polar aprotic solvents and excellent homogeneous Brønsted acid catalysis for the benzopinacol rearrangement reaction.



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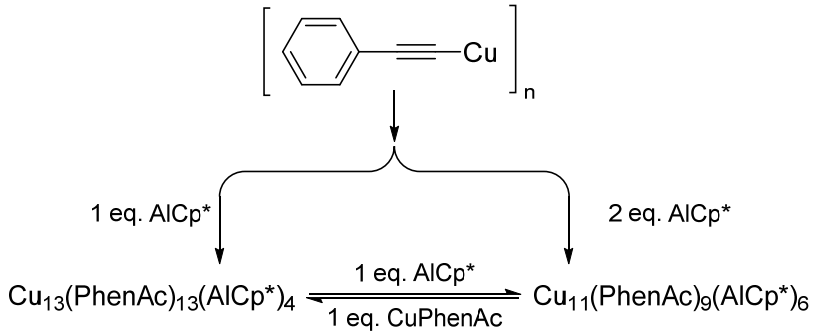
MASS SPECTROMETRIC ANALYSIS OF ELUSIVE BIMETALLIC COPPER-ALUMINUM CLUSTERS BY CHEMICAL LABELLING

Benedikt Kerscher, Christian Gemel, and Roland A. Fischer

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The selective synthesis and isolation of ligated metal clusters is often very challenging. This becomes even more pronounced for highly air- and moisture-sensitive mixed-metal clusters, where protic or highly polar solvents such as DMSO, acetonitrile, or alcohols, as well as silica-based chromatographic separation techniques, must be strictly avoided. However, we have recently demonstrated monitoring cluster growth and reactivity studies on entire "cluster libraries," by high-resolution mass spectrometry without separation of individual species.[1]

Herein, we follow this cluster library approach and report on the mass spectrometric characterization of all-alkynyl-ligated Cu/E cluster libraries (E = Al, Ga). A series of copper alkynyl compounds with varying steric demands were treated with various molar rations of the low valent metallo-ligands ECp* (Cp* = pentamethylcyclopentadienyl). Depending on the applied alkyne and the reaction stoichiometry, the cluster formation can be directed even toward few or single species. For example, the combination of phenylacetylide (CuPhenAc) with AlCp* in a 1:1 ratio yield $[Cu_{13}(C_8H_5)_{12}(AlCp^*)_4]$ as observed by ESI-MS analysis, whereas a 1:2 ratio results in the formation of $[Cu_{11}(C_8H_5)_9(AlCp^*)_6]$ (Scheme 1).



Scheme 1.

Chemical labeling was applied to AlCp*, in which one methyl group of the Cp* ligand was replaced by an ethyl group, resulting in a mass shift of 14 m/z. A similar strategy was employed for the copper alkynyl component, using 4-methylphenylacetylene instead of phenylacetylene, also resulting in a mass shift of 14 m/z. The results clearly demonstrate that each species can be selectively synthesized depending on the applied stoichiometry. Furthermore, the conversion of one species into the other could be monitored by the addition of stoichiometric amounts of the respective reactants.

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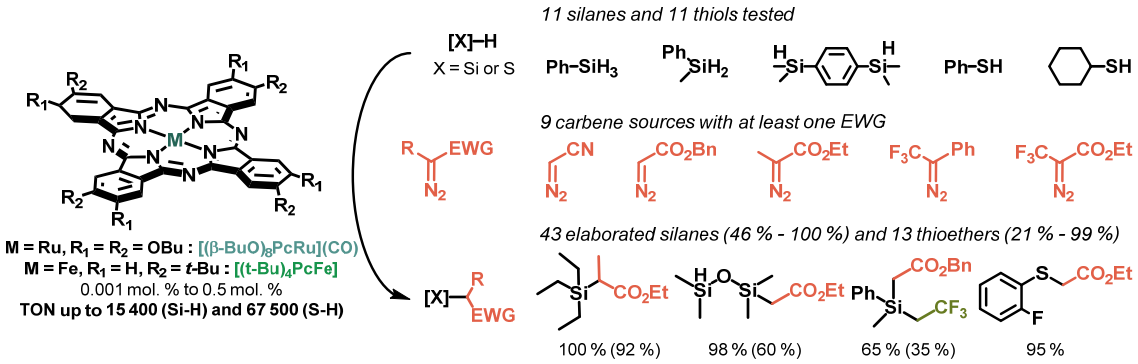
NEW CATALYTIC PATHWAYS FOR CARBENE INSERTION INTO Si-H AND S-H BONDS CATALYZED BY PHTHALOCYANINE COMPLEXES

Cenna Toullec,[a] Andrei P. Kroitor,[a,b] Wassim El Hazmi,[a] Alexander G. Martynov,[b] Yulia G. Gorbunova,[b] Alexander B. Sorokin*,[a]

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Carbene transfer reactions represent an important synthetic approach in organic chemistry providing a wide range of elaborated compounds using simple precursors. Metal porphyrin complexes and heme enzymes are efficient catalysts for these reactions [1, 2]. In contrast, readily accessible metal phthalocyanine complexes (MPc) are still underexplored in catalytic carbene transfer despite their high efficiency in a variety of reactions [3]. Although MPc are structurally similar to their porphyrin counterparts, their catalytic properties are not exactly the same and they are often superior to those of porphyrin complexes, *e.g.*, in nitrene transfer reactions.

In this context, FePc and RuPc were studied for the first time as catalysts for carbene insertions into Si-H and S-H bonds. The high efficiency of FePc and RuPc was shown to provide a wide range of structurally different elaborated compounds in high yields using small catalyst loadings (0.001 mol% - 0.5 mol%) featuring outstanding turnover numbers (TON), up to 15 400 for Si-H carbene insertions and 67 500 for S-H carbene insertions (Scheme 1).



Scheme 1. Carbene insertions into silane Si-H and thiol S-H bonds catalyzed by MPc.

A large scope of structurally different substrates and diazo compounds bearing acceptor and donor substituents have been transformed to functionalized silanes and sulfur compounds with high molecular complexity. The kinetic isotope effects study on the Si-H(D) and S-H(D) insertions provided a mechanistic insight into these reactions.

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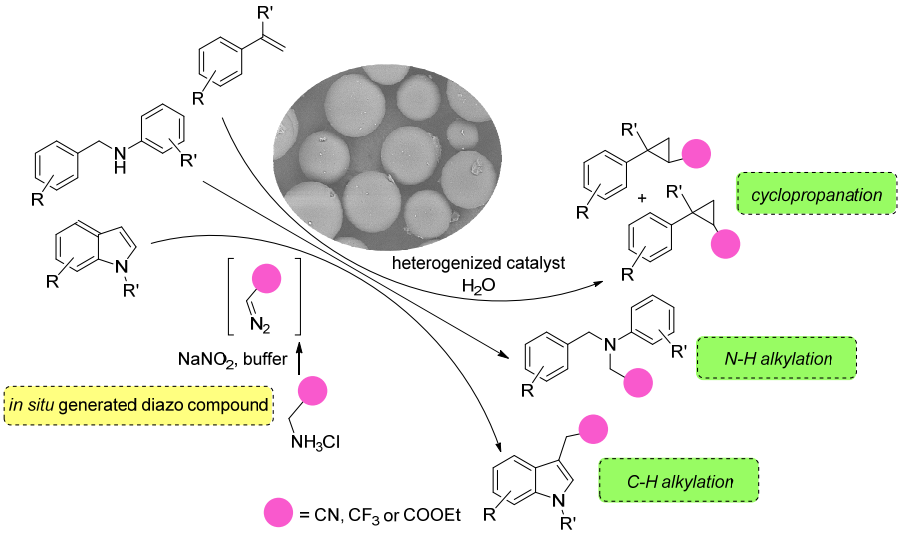
IMMOBILIZED METAL PORPHYRINS AS RECYCLABLE CATALYSTS FOR ON-WATER CARBENE TRANSFER REACTIONS

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Metal porphyrin complexes are widely recognized as efficient catalysts for carbene and nitrene transfer reactions in both organic media and biphasic systems.[1] Nevertheless, their application in homogeneous conditions often hampers product isolation, making purification laborious and economically demanding. To address these drawbacks, the immobilization of such catalysts onto solid supports has emerged as an effective strategy to enhance process sustainability while allowing straightforward recovery and reuse of the active species.[2]

Within this framework, naturally derived hemin and a properly functionalized iron porphyrin were covalently anchored to Merrifield® resin through amide linkages. The resulting heterogeneous iron-based materials were tested in carbene transfer reactions involving diazo compounds generated *in situ* and a range of organic substrates, including styrenes, amines, and indoles. Different diazo precursors were explored using a diazotization/carbene generation protocol[3] (Scheme 1) performed under "on-water" conditions, which contributed to improving the environmental profile of the methodology and enabled the formation of the target products in yields of up to 90%. Because the CF_3-substituted diazo precursor exhibited reduced reactivity, further investigations were carried out using ruthenium- and cobalt-based porphyrin analogues in place of the iron-supported catalysts, with the goal of enhancing both reaction efficiency and selectivity.



Scheme 1: "on water" carbene transfer reactions promoted by heterogenized metal porphyrins

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LIGAND SPHERE EFFECTS ON DINITROGEN ACTIVATION IN BIMETALLIC COMPLEXES

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Dinitrogen fixation is crucial chemical transformation to produce ammonia as a fertilizer and other N-containing compounds. Even though dinitrogen's abundance in the Earth's atmosphere is 80%, splitting dinitrogen under ambient conditions remains a challenge due to its kinetic inertness. The N≡N bond is strongand interactions with reactive atoms such as transition metals tend to be weak. In this work, we rationalize the factors influencing the reactivity of dinuclear end-on bridged (μ-η^1:η^1-N_2) complexes in different ligand environments. The first bridged dinitrogen complex for dinitrogen activation and metal-nitride complex formation was reported by Cummins. This complex features Mo(III) (d^3) supported by three NRAr ligands (R = Me_3C, Ar = 3,5-$C_6H_3Me_2$).[1] Another complex designed as an isovalent analog is reported by Mindiola. It contains V(II) (d^3) in a triply coordinated ligand scaffold, [(nacnac)V(Ntolyl$_2$)], but it does not cleave dinitrogen.[2] Sita's isostructural series of early transition metal complex with a η^5-cyclopentadienyl (Cp*) and η^2-amidinate ligand (Am) coordination sphere undergo successful dinitrogen activation to form a bridged diamond core.[3]Furthermore, we discuss the differences and similarities of these systems with the catalytically active Mo(I) pincer complex reported by Nishibayashi.[4] We systematically explore the potential energy surfaces and use electronic energy decomposition techniques to rationalize the equilibrium between the μ-η^1:η^1-N_2 form and the characteristic zig-zag transition state (Fig 1b). We identify multiple competing factors influencing the dinitrogen splitting chemistry and find that two different strategies for successful N_2 activation are realized in the synthetic complexes.

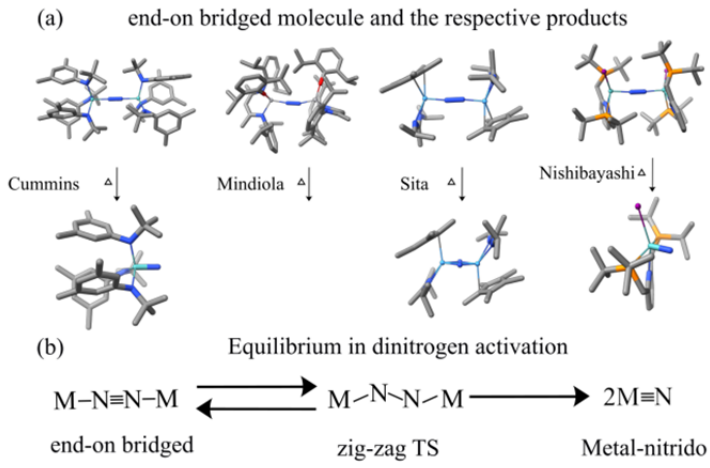


Fig1: (a) Products formed from the μ-η^1:η^1-N_2 complexes under thermal activation conditions. (b) Schematic reaction path from the μ-η^1:η^1-N_2 complex via the zig-zag transition state to the desired metal nitride product.

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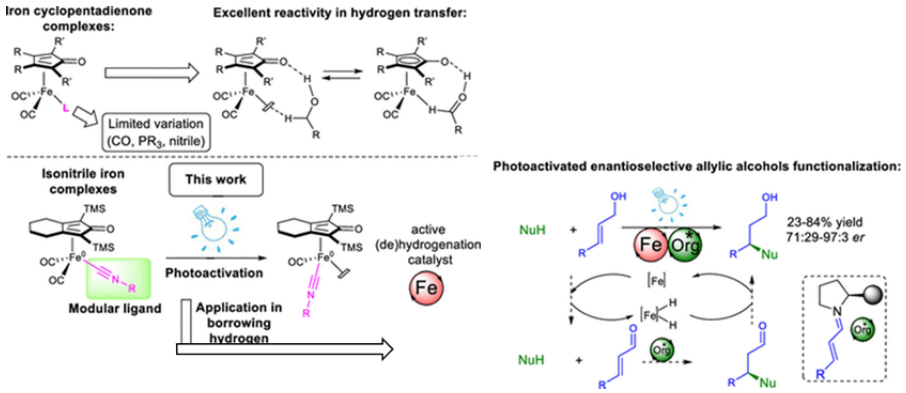
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THE GOLDEN AGE OF IRON: HOMOGENEOUS IRON CATALYSTS FOR SUSTAINABLE BORROWING HYDROGEN TRANSFORMATIONS

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Iron catalysis is currently undergoing a remarkable expansion, driven by the development of finely tuned cyclopentadienone platforms and their application to sustainable hydrogen-management strategies. Recent advances in our group have highlighted how precise electronic and structural modulation of iron cyclopentadienone complexes can dramatically enhance their reactivity, stability and photochemical response. In particular, we demonstrated that subtle ligand and CO/isonitrile exchange provides access to photo-activated catalysts with unprecedented control over activity profiles.[1,2] In parallel, we established new iron- and organocatalyzed borrowing hydrogen methodologies enabling the stereoselective construction of oxygen-containing heterocycles, including tetrahydropyrans, under mild and sustainable conditions.[3] Together, these studies reveal how the synergy between ligand design, mechanistic understanding and innovative hydrogen-shuttling manifolds can unlock highly efficient and environmentally benign catalytic transformations. This body of work positions iron complexes — small, earth-abundant, and mechanistically rich — as powerful tools for next-generation catalytic synthesis.



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PHOSPHAVINYL FORMATION THROUGH TRAPPING OF PHOSPHINIDENE

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The short-lived and elusive phosphinidene (M=P) is a highly reactive specie with large potential in phosphorus atom transfer (PAT) chemistry. In recent years, phosphinidene has been of interest due to its high reactivity for its possible way to be functionalized.[1],[2] The phosphinidene has been stabilized by both main-group chemistry[3] and as coordination with metalorganic complexes.[4] In this work, we demonstrate a multistep synthesis to generate an iridium-phosphinidene for PAT chemistry. By photolytic activation of [(PCP)Ir(PCO)], the short-lived iridium supported triplet phosphinidene intermediate [Ir=P:] was generated and trapped using different phosphorus ylides. This resulted in a formation of a room temperature stable phosphavinyl, complex [(PCP)Ir(P=CH_2)]. Notably the structure of the complex was elucidated by single-crystal X-ray diffraction, revealed that the [P=CH_2]$^-$ ligand sits in a plane perpendicular to the square planar pincer complex. Due to rotational restriction about the P=C double bond, the hydrogens on the [P=CH_2]$^-$ fragment are chemically inequivalent. This allowed the hydrogens to be identified by NOESY NMR, which showed which of the hydrogen is in closer proximity to the iridium ^{t}Bu group. Variable temperature NMR studies of the complex indicate an exchange of the hydrogen on [P=CH_2]$^-$ fragment and several scenarios of the exchange were considered in conjunction with DFT studies. Further reactivity of phosphavinyl showed an oxidation with an azide.

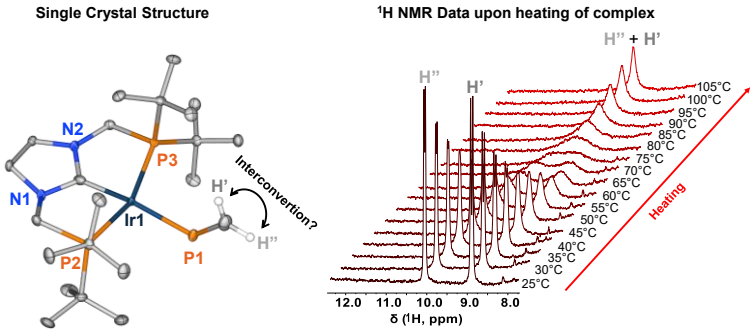


Figure 1, Crystallographic structure of iridium phosphavinyl and temperature variation ^{1}H NMR with the interconvertion of phosphavinyl hydrogens.

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SURFACE-ENHANCED AND ELECTRIC FIELD-MODULATED REACTIVITY OF Fe(IV)=O COMPLEXES: UNVEILING THE SYNERGY OF LEWIS ACID ADDITIVES, Au(111), AND GRAPHENE SURFACES IN BIOMIMETIC C–H ACTIVATION

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Achieving high reactivity and maintaining selectivity simultaneously is one of the holy grails of catalytic transformations; while metalloenzymes perform this task effortlessly, synthetic models that mimic their reactivity often struggle to achieve either of the goals set. High-valent Fe^{IV}=O species are highly reactive oxidants, but their elevated activity often limits catalytic turnover due to rapid catalyst degradation and over-oxidation of substrates. To overcome these shortcomings, here we have explored electrostatic and surface effects in tuning the reactivity of $[(F_8)Fe^{IV}(O)]$ (**1**) and $[(F_8)Fe^{IV}(O)](LutH)^+$ (**2**) using density functional theory (DFT) and periodic DFT calculations. To begin with, the effect of Lewis acid ($LutH^+$ 2,6-lutidinium triflate) is explored, which is found to induce a local electric field and diminishes the kinetic barrier by ~15 kJ mol^{-1}. As the addition of adducts and their direct role in the oxidation process are difficult to control, we explored the possibility of employing oriented external electric fields (OEEFs) to gain control over the reactivity and the oxidation process. Our results demonstrate that applying an OEEF along the  direction reduces the kinetic barrier further by ~29 kJ mol^{-1}, while along the  direction, proton transfer was preferred, offering an intriguing way to channelise selectivity. Surface interactions provide additional control: Au(111) lowers the barrier by ~58 kJ mol^{-1} under OEEFs, whereas graphene inhibits reactivity, requiring an OEEF along the +Z-direction to reduce the barrier by ~49 kJ mol^{-1}. By integrating chemical modifications and external control, this study offers a general framework for designing next-generation oxidation catalysts across diverse catalytic systems.

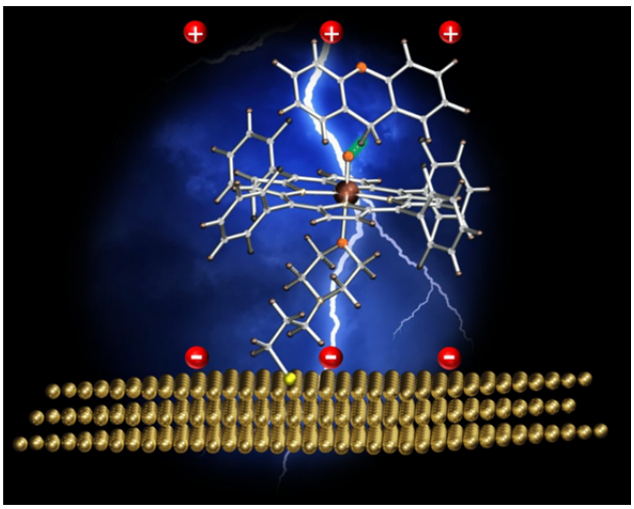


Figure 1. Schematic representation of applying OEEFs along reaction axis.

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DISSECTING REBOUND VERSUS SECOND HYDROGEN ATOM ABSTRACTION SELECTIVITY IN TETRACARBENE IRON(IV)-OXO SYSTEMS

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High-valent iron(IV)-oxo intermediates are key reactive species in both heme and nonheme oxidation chemistry, mediating C–H bond functionalization through hydrogen atom abstraction (HAA), followed by competing rebound and secondary hydrogen atom abstraction (2nd HAA) pathways. Although rebound hydroxylation is generally highly favored in enzymatic systems due to its thermodynamic preference, alternative post-HAA pathways, including 2nd HAA and desaturation processes, can become accessible depending on the electronic structure and ligand environment of the ferryl species. Understanding the factors governing such post-HAA selectivity remains crucial for controlling ferryl-mediated oxidative transformations and for the rational design of selective oxidation catalysts.

Previous studies established the remarkable C–H activation reactivity of tetracarbene-supported oxo-iron(IV) complexes bearing an axial −NCMe ligand [1]. In the present work, we computationally investigate a series of such organometallic iron(IV)-oxo complexes, together with computationally designed variants incorporating a broad range of strongly and weakly electron-withdrawing as well as electron-donating substituents at both axial and equatorial ligand positions, in an effort to tune the reaction selectivity toward the rebound pathway over competing secondary hydrogen atom abstraction (2nd HAA) processes.

Our studies demonstrate that systematic ligand perturbation effectively modulates the relative energetics of rebound and 2nd HAA pathways, indicating that selective tuning of ferryl reactivity toward rebound chemistry is achievable through rational ligand design. Ongoing investigations employing off-diagonal thermodynamic analysis aim to elucidate the key electronic factors governing ferryl reactivity and pathway selectivity. Collectively, these findings provide mechanistic insight into ligand-controlled modulation of rebound versus overoxidation pathways and establish guiding principles for the development of selectively rebound-active high-valent iron–oxo catalysts.

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STRUCTURAL AND SYNTHETIC INSIGHTS ON ALKALI-METAL AMIDO NICKELATE COMPLEXES

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Nickel amide complexes pose to be of great interest in modern organometallic chemistry due to their intermediacy in homogeneous catalysis eg. Buchwald-Hartwig amination [1]. Despite being proposed as catalytic intermediates, only a few examples of isolated Ni(II/I) complexes featuring a pendant amide functionality have been reported [2], while Ni(0)-amido complexes have remained elusive to date. Recent work from our group has shown that s-block metal nickelates can be accessed by co-complexation of Ni(0) precursors with the relevant organolithium or Grignard reagents [3]. Having this background, we wondered if a similar approach could be employed to access a new family of alkali-metal nickelates featuring amide ligands.

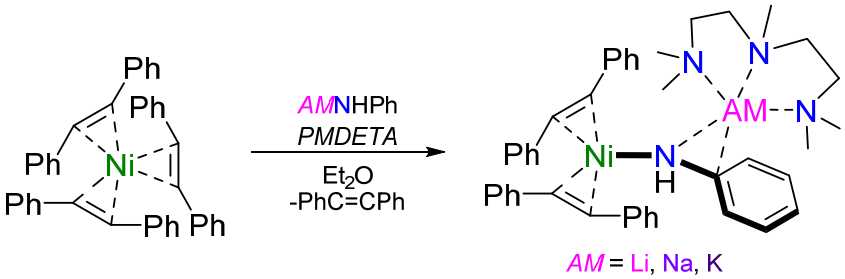


Figure 1: Schematic representation of the synthesis of the alkali-metal amido nickelate complexes.

In this work, we report our findings assessing the systematic reactivity of the bench-stable Ni(0) precursor Ni(stilbene)$_3$ [4] with a range of alkali metal amides to access a new family of alkali-metal amido nickelates (see Figure 1). Combining X-ray crystallographic analysis with NMR spectroscopic studies we provide insights into their constitution in solution and in the solid state. Experimental studies are combined with theoretical calculations to advance the understanding of the bonding present in these complexes. Their reactivity towards a range of organic electrophiles under both stoichiometric and catalytic regimes will also be discussed.

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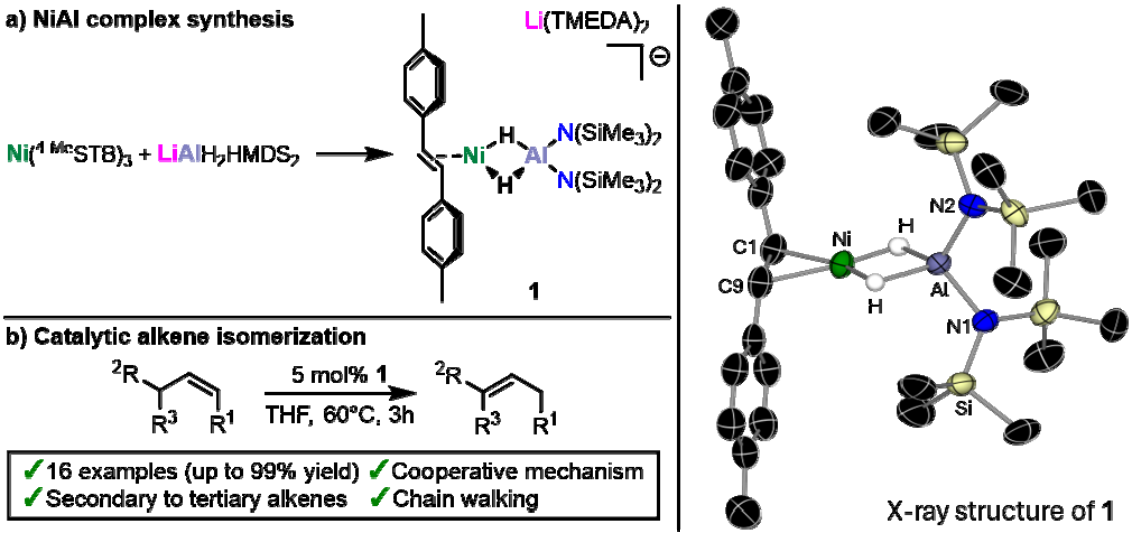
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A NICKEL-ALUMINIUM DIHYDRIDE COMPLEX ENABLES COOPERATIVE ALKENE ISOMERIZATION

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Cooperative catalysis, in which two metals collaborate to facilitate a chemical reaction, is emerging as a promising strategy for replacing expensive noble metal catalysts by those based on cheaper earth abundant metals. However, only relatively few examples of heterobimetallic cooperativity in catalysis are known and understood, hampering the rational use of this strategy. Here we synthesize the novel nickel-aluminate complex (**1**) using Ni(^{4Me}STB)$_3$ (^{4Me}STB = 4,4'-dimethylstilbene) as a Ni(0) precursor which reacts with one equivalent of lithium aluminate LiAlH$_2$(HMDS)$_2$ with the concomitant elimination of two olefin ligands (Figure 1a). Only a handful of NiAl hydride complexes have been reported, with even fewer showing cooperative reactivity or catalysis.[1][2] Switching on synergic effects, complex **1** is an active catalyst for the isomerization of alkenes (Figure 1b), a reaction typically caried out with noble metal hydrides.[3] Contrastingly, the individual precursors of **1**, LiAlH$_2$(HMDS)$_2$ and Ni(^{4Me}STB)$_3$ show no or poor activity in this reaction, indicating a cooperative mechanism for **1**. By studying the stoichiometric and catalytic reactivity of **1** with alkenes and other unsaturated molecules, we provide fundamental insights into this cooperative reaction to shed light on how nickel and aluminium can cooperate in catalytic reactions.



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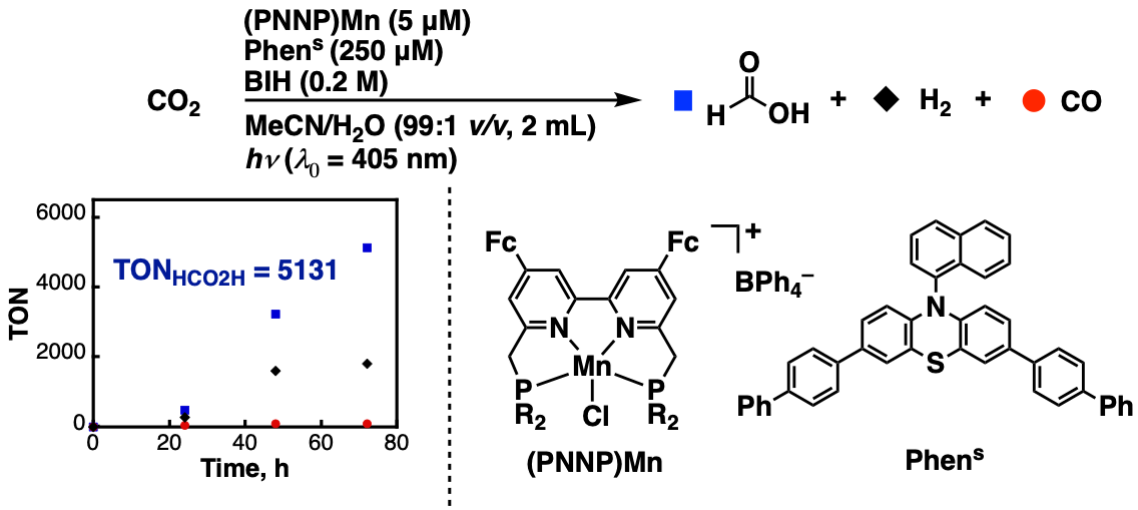
INTRAMOLECULAR ELECTRON TRANSFER ENABLES EFFICIENT CO_2 PHOTOREDUCTION BY A (PNNP)Mn CATALYST

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Photocatalytic carbon dioxide (CO_2) reduction is an attractive strategy for addressing global carbon emissions by converting CO_2 into value-added chemical fuels. Among the possible products, formic acid (HCO_2H), which could be produced from CO_2 reduction as a platform chemical such as a fuel in a direct formic acid fuel cell, can be provided as a valuable energy storage source. Previously, we reported that iridium complexes[1] bearing PNNP-type ligands exhibit excellent activity for CO_2 photoreduction. However, developing efficient, selective, and earth-abundant molecular catalysts for this transformation remains a challenge. To address these limitations, we report here new manganese (Mn) complexes coordinated with ferrocenyl-substituted PNNP ligands, which demonstrate high reactivity for the photocatalytic reduction of CO_2 to HCO_2H.

The photocatalytic performance of the Mn complexes was evaluated under visible-light irradiation (λ_0 = 405 nm) in the presence of an organic photosensitizer and a sacrificial electron donor, 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH), under a CO_2 atmosphere. Incorporation of the ferrocenyl moiety markedly enhances catalytic efficiency by facilitating intramolecular electron transfer and stabilizing key reaction intermediates. Compared to their non-ferrocenyl counterparts, these ferrocenyl-containing Mn systems exhibit higher turnover numbers (TON_{HCO2H} > 5131) for the formation of HCO_2H. To elucidate the underlying mechanism, we employed various analytical techniques, including transient absorption, electron paramagnetic resonance, and density functional theory calculations. In particular, we aim to clarify the effect of the ferrocenyl group on this reaction. Particular attention was given to clarifying the role of the ferrocenyl group in facilitating electron transfer and modulating the electronic structure of the catalytic center.



Scheme 1. CO_2 photoreduction using a (PNNP)Mn complex

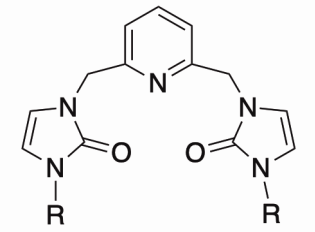
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PREPARATION, CHARACTERIZATION, AND REACTIVITY OF COBALT(II) AND NICKEL(II) COMPLEXES CONTAINING REDOX ACTIVE ONO PINCER LIGANDS

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[c] Department of Chemistry, University of Wisconsin-Madison, Madison, WI, United States of America
[d] Department of Chemistry, DePaul University, Chicago, IL, United States of America

We have developed and synthesized tridentate pincer ligand precursors, which possesses two oxygen- and one nitrogen-donor functionalities (ONO), based on a bis-imidazole precursor. The tridentate ONO ligand precursors are redox active. The ONO ligand precursors incorporate a carbonyl substituted imidazole functionality. We have prepared a flexible ligand system by employing the starting material 2,6-(dibromomethyl)pyridine to introduce a methylene linker into the pincer ligand precursors. We have metallated these ligand precursors to form cobalt(II), and nickel(II) complexes that contain these tridentate ligands. A detailed description of the preparation and characterization (NMR Spectroscopy) of the ligand precursor and of the metal complexes (X-ray crystallography, cyclic voltammetry, elemental analyses, UV-Visible spectroscopy magnetic susceptibility), will be presented. Electrocatalysis results with the metal complexes will also be presented.



R = mesityl, iPr, t-butyl, Et

A GEOMETRIC INTERPRETATION OF KINETIC ZONE DIAGRAMS FOR MECHANISTIC UNDERSTANDING OF MOLECULAR ELECTROCATALYSTS

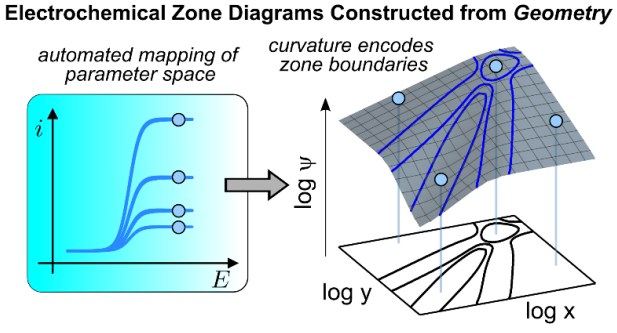
Ben A. Johnson

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A common feature among electrochemical systems for catalytic transformations such as heterogenous electrocatalysis, photoelectrochemical water splitting, or bioelectrocatalysis, is the inherent complexity of the underlying reaction and transport processes [1]. The interplay of the numerous parameters governing the overall performance makes it impossible to empirically probe all kinetic behaviors due to the large number of required experiments.

To generate a more comprehensive picture, kinetic zone diagrams have been used as maps to predict how to shift a given electrocatalytic system between kinetic states, enabling knowledge-driven design [2]. Despite their utility, the classical approach for constructing zone diagrams is constrained to simplified cases or systems with few controlling parameters.

Herein, we present a new approach to constructing zone diagrams by interpreting the current output as a multidimensional geometric surface [3]. We find that the curvature of such an abstract surface encodes zone boundaries and identifies distinct kinetic regimes. Thus, constructing a zone diagram for any electrocatalytic process, even ones with high complexity, is reduced to a simple geometric problem of computing curvature. Case studies of important electrocatalytic systems are presented, including mediated enzymatic catalysis in a redox film, CO_2 reduction by a molecular catalyst, and catalysis within porous electrodes mediated by molecular coordination complexes. Finally, it is shown how this approach can systematically map the multidimensional parameter space of any electrochemical system and automatically identify kinetic regimes.



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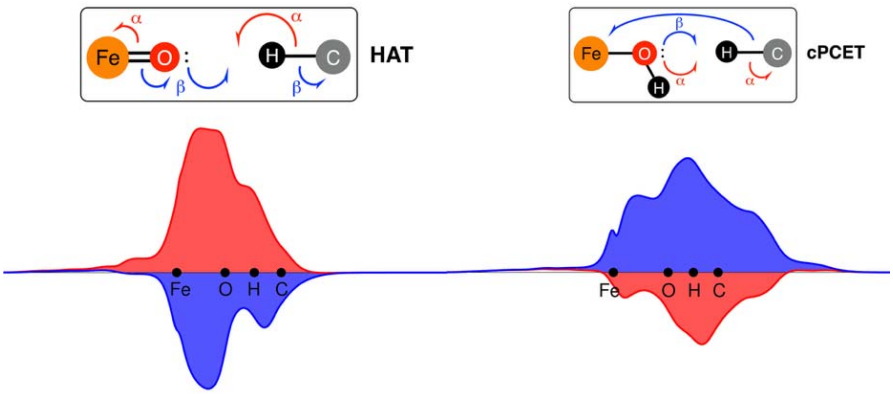
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SPIN-RESOLVED CHARGE DISPLACEMENT FUNCTION: PCET

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Proton-coupled electron transfer (PCET) is a ubiquitous process in chemistry and biology, covering areas as oxidation catalysis, enzymatic reactions and photosynthesis. The PCET concept is used ambiguously in any process involving the movement of a proton and an electron. However, in the literature the use of the term PCET is far from consistent, following different definitions that depend on whether the proton and the electron move together in space (same or different endpoint) and time (synchronous or sequentially). Indeed, a useful general guidance is to distinguish between (i) the stepwise mechanism where the electron transfer (ET) and the proton transfer (PT) take place in a sequential manner, and (ii) concerted PCET (cPCET) in which the proton and the electron are transferred simultaneously. A subclass of the latter are reactions where the proton and the electron are transferred in concert and travel together as hydrogen atom (radical), which are usually denoted hydrogen atom transfer (HAT) reactions. In 2020, we reported the spin-resolved version [1] of the charge displacement analysis [2], which was applied to two competing pathways in oxidation catalysis (hydrogen-atom transfer, proton-coupled electron transfer). The difference in electron flow between the two mechanisms was directly observable in this new analysis tool (see Figure).



Recently, we applied SR-CDF to the σ and π channels of HAT reactions [3]; based on the results obtained, and feedback from the community, we slightly adapted the SR-CDF protocol [4] to enhance the understanding of electron flow in these reactions. In the current contribution we revisit the original competition between HAT and cPCET and show how the modified protocol improves the differentiation between these mechanisms.

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STRUCTURAL MODULATION OF CERIA WITH Cu AND In FOR THE SELECTIVE HYDROGENATION OF CO_2 TO CH_3OH

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The adverse effect of large and continuous release of CO_2 into the atmosphere leads to the rapid development of efficient catalytic technologies to achieve the “net-zero carbon emission" goals, and CO_2 hydrogenation to “methanol” using heterogeneous catalysts is highly promising. Herein, we report the preparation of a surface-modified mixed-metal ceria catalyst with Cu and In ($Cu_{0.23}In_{0.05}CeO_z$) for efficient CH_3OH synthesis via selective CO_2 hydrogenation.

The $Cu_{0.23}In_{0.05}CeO_z$ catalyst was synthesized by a hydrothermal method using $Cu(NO_3)_2{\cdot}3H_2O$, $In(NO_3)_3{\cdot}3H_2O$, and $Ce(NO_3)_3{\cdot}6H_2O$ [1]. The as-prepared $Cu_{0.23}In_{0.05}CeO_z$ catalyst showed higher CH_3OH selectivity (65%) than $Cu_{0.23}CeO_z$ without In (43%), which produced CO as the major product at 533 K (**Figure 1a**). Despite high CH_3OH selectivity (>99%), CO_2 conversion was sufficiently low using $In_{0.05}CeO_z$. No significant improvement in CH_3OH selectivity was observed with the physical mixture of $Cu_{0.23}CeO_z$ and $In_{0.05}CeO_z$, indicating unique synergistic catalysis on the $Cu_{0.23}In_{0.05}CeO_z$ catalyst. At 493 K, high CH_3OH selectivity (93%) was achieved with $Cu_{0.23}In_{0.05}CeO_z$. The time profile showed that CO_2 conversion gradually increased, and afforded CH_3OH in an excellent yield (21%) at 328 h (**Figure 1b**). Moreover, $Cu_{0.23}In_{0.05}CeO_z$ exhibited high reusability, retaining the CH_3OH selectivity (**Figure 1c**).

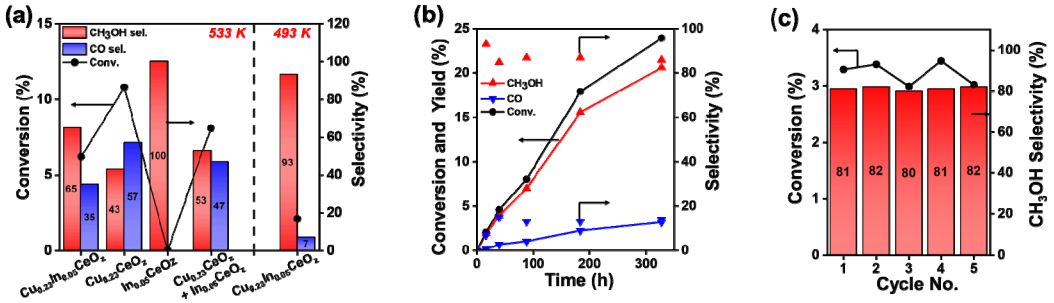


Figure 1: (a) Evaluation of catalytic activity at 533 K and 493 K for 16 h; (b) Time-profile with $Cu_{0.23}In_{0.05}CeO_z$ at 493 K; (c) Recyclability experiment with $Cu_{0.23}In_{0.05}CeO_z$ at 493 K for 40 h. Reaction conditions: CO_2: 1.0 MPa, H_2: 3.0 MPa, Ar: 0.1 MPa, catalyst, 58 mg.

The X-ray absorption fine structure (XAFS) analysis indicated that during the reaction, Cu (+2) was reduced to the metallic state (0) with the partial reduction of Ce (*c.a.* 53%), while In retained its valence state (+3). Highly dispersed In^{3+} and Cu^0 species on the CeO_z surface would activate CO_2 and H_2 synergistically. *In-situ* FT-IR spectra revealed that the incorporation of In with Cu ($Cu_{0.23}In_{0.05}CeO_z$) modified the CO_2 adsorption sites from the Cu surface to the O-vacant sites on CeO_z [2]. The reaction was proposed to proceed exclusively via a formate intermediate, inhibiting the reverse water-shift gas reaction and subsequent CO formation. The hydrogenation of formate afforded CH_3OH in high selectivity.

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STABILIZATION OF REACTIVE RARE EARTH ALKYL COMPLEXES THROUGH MECHANISTIC STUDIES

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Rare earth tris(alkyl) complexes such as $M(CH_2SiMe_3)_3(sol)_n$ are widely used as precursors for many compounds and as homogeneous catalysts for alkene polymerization and alkane functionalization. However, the thermal instability of those most conveniently made from the commercially available lithium salt of the neosilyl anion, $LiCH_2SiMe_3$, Li(r), restricts their utility. We present a new range of synthetically useful, more kinetically stable rare earth neosilyl solvates, derived from a full kinetic study of the various possible decomposition mechanisms of 7 known and 12 new solvated rare earth neosilyl complexes $M(CH_2SiMe_3)_3(sol)_n$ M = Sc(III), Y(III), Lu(III), Sm(III), and sol = THF; TMEDA; DMPE, diglyme ($CH_3(OCH_2CH_2)_2O$, G_2), triglyme ($CH_3(OCH_2CH_2)_3O$, G_3). Surprisingly, simply using higher-denticity donors to sterically disfavor neosilyl *gamma*-H elimination is not effective. While $Sc(r)_3(CH_3(OCH_2CH_2)_2O)$ has a half-life, $t_{1/2}$, of 258.1 h, six times longer than for $Sc(r)_3(C_4H_8O)_2$ ($t_{1/2}$ = 43 h), $Lu(r)_3(CH_3(OCH_2CH_2)_2O)$ and $Y(r)_3(CH_3(OCH_2CH_2)_2O)$ do not show the expected, analogous increased $t_{1/2}$. This is because new decomposition pathways appear for poorly fitting donors. Finally, kinetic studies demonstrate the impact of small, and increasing amounts of LiCl on the kinetics, and changing the mechanism of the reactivity of the alkyls $Y(r)_3(THF)_2$ and $Lu(r)_3(THF)_2$; molecules used in hydrocarbon chemistry and catalysis for fifty years. A new route to pure $Y(r)_3(THF)_2$, which avoids the traditional use of Li(r), is presented.

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EFFICIENT DESIGN OF MOLECULAR ELECTROCATALYSTS FOR CO_2 REDUCTION: INVESTIGATING THE IMPACT OF IMPULSE ELECTROCHEMISTRY ON SELECTIVITY

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Efforts to reintegrate excess anthropogenic CO_2 into the carbon cycle have become a central focus of sustainable research. In this context, circular strategies that convert waste CO_2 into value-added products using renewable energy are highly desirable.[1] Photoelectrochemical (PEC) CO_2 reduction (CO_2R), inspired by natural photosynthesis, represents a promising approach; however, challenges such as limited selectivity and catalytic efficiency persist, largely due to an incomplete understanding of interfacial processes in hybrid systems.[2]

Herein, we report the design and synthesis of iron porphyrin-based molecular catalysts incorporating second-sphere distal dicatechol functionalities. These catalysts exhibit significantly enhanced performance compared to the benchmark FeTPP system under homogeneous electrochemical conditions, demonstrating improved selectivity and catalytic activity for CO_2 reduction. Mechanistic insights were obtained through spectroelectrochemical studies, enabling the identification of key reaction intermediates involved in CO_2R.

Subsequently, the hydroxyl groups present in the second coordination sphere were utilized to anchor the molecular catalysts onto mesoporous TiO_2-coated FTO electrodes via chemical adsorption[3], thereby enabling heterogeneous electrochemical investigations. CO_2 reduction was examined in CO_2-saturated 0.1 M $KHCO_3$ electrolyte. Furthermore, pulsed electrochemical strategies were employed to modulate catalytic reactivity and product selectivity. Notably, preliminary results indicate a shift in product distribution beyond the conventional $2e^-/2H^+$ pathway, with evidence suggesting methanol formation under pulsed bias conditions.

Ongoing mechanistic studies aim to elucidate the role of interfacial effects in governing catalytic performance. Ultimately, this work seeks to advance the rational design of hybrid semiconductor–molecular systems for efficient and selective solar-driven CO_2 conversion, integrating both pulse voltammetry and optical modulation techniques.

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DIRECTING THE O_2-DEPENDENT OXIDATION OF NONHEME IRON-THIOLATE COMPLEXES THROUGH LIGAND DESIGN

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Nonheme iron enzymes that activate O_2 play a central role in the metabolism, regulation, and signaling mechanisms of sulfur-containing compounds related to the amino acid L-cysteine. The number of enzymes in this class has expanded in recent years with the discovery of *sulfoxide synthases*, such as EgtB and OvoA, that catalyze an oxidative S-C bond formation between thiol- and imidazole-based substrates[1]. Like the well-studied cysteine dioxygenase (CDO), the active sites of EgtB and OvoA feature a mononuclear Fe(II) center facially coordinated by three histidine (His) residues. Insights into the mechanism of CDO have been gained though the development of synthetic complexes that mimic its structure and function. In contrast, functional models of the sulfoxide synthases have not been reported, although our group has reported iron-thiolate complexes that mimic the substrate-bound active sites of EgtB and OvoA [2]. In order to build effective models of these challenging systems, it is necessary to account for additional features of the enzymatic active sites, especially noncovalent interactions between the primary and secondary coordination spheres. The inclusion of hydrogen-bonding (H-bonding) donors that stabilize $Fe/O_2(H)$ adducts and control substrate orientation is likely critical to the development of models that perform S-C bond formation reactions. To this end, we have designed and synthesized a novel and modular series of ligands with mixed pyridyl/imidazolyl donors that also feature outer-sphere N-H units capable of H-bonding interactions. The coordination chemistry of these ligands has been explored through the preparation and crystallographic characterization of Fe(II) and Co(II) complexes. Investigations into the reactivity of these complexes with O_2 (and related small molecules, like nitric oxide) are ongoing and will be presented.

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OXYGEN REDUCTION TO H_2O_2 THROUGH PROTON AND H-ATOM RELAY BY PHENOL(ATE) APPENDED TO COPPER COMPLEXES: INSIGHTS INTO THE LYTIC POLYSACCHARIDE MONOOXYGENASE (LPMO) ACTIVE SITES

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Lytic polysaccharide monooxygenases (LPMOs) are an important class of enzymes that catalyze the oxidative depolymerization of polysaccharides such as cellulose and chitin [1]. Structurally, the active site contains a mononuclear copper site coordinated to three nitrogen sites of two histidine, along with a weak interaction to the tyrosine residue [2]. LPMO has been proposed to activate dioxygen/H_2O_2 to generate the active copper(II)-oxyl species, capable of cleaving the glycosidic C-H bonds [3]. However, the precise identity of the primary oxidant (dioxygen versus H_2O_2) and the mechanistic pathway involved for the generation of active oxidant remain subjects of ongoing debate.

We herein employ a series of copper(I)/(II) complexes with a tethered phenolic arm mimicking the hemilabile tyrosine residue in the LPMO active site to investigate the biomimetic activation of O_2. Notably, the phenol appended copper(I) complex reacts with dioxygen to generate H_2O_2 and a purple colored copper(II)-phenolate complex. Interestingly, the copper(II)-phenolate complex participates in hydrogen-atom abstraction reactions in the presence of exogenous phenols, and thus regenerates the phenol-appended copper(I) complex. Driven by the detailed mechanism elucidation, this work also presents phenol oxidation coupled to the catalytic transformation of dioxygen to H_2O_2. Importantly, these findings highlight the possible role of the hemilabile tyrosine moiety in net H-atom relay during the catalytic process.

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EXPERIMENTAL AND THEORETICAL STUDY ON A NEW PHOTOCATALYST

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One of the principal challenges in the photoinduced water splitting reaction is constituted by the molecular oxygen production. This process involves a photosensitizer (usually metal complexes due to their long excited state lifetime), that absorbs light and, while it is in its excited state, interacts through a photoinduced electron transfer with the catalyst [1]. This bimolecular process is thereby limited by diffusion. To overcome this issue an appealing strategy consists in linking them together through a covalent bond. In this work we present a comparison between a new photocatalyst and a similar one reported in literature [2] showing very different behavior. The bridge plays a pivotal role in the electronic dynamics of this kind of assembled systems. A complete investigation has been carried out from both an experimental and a theoretical point of view.

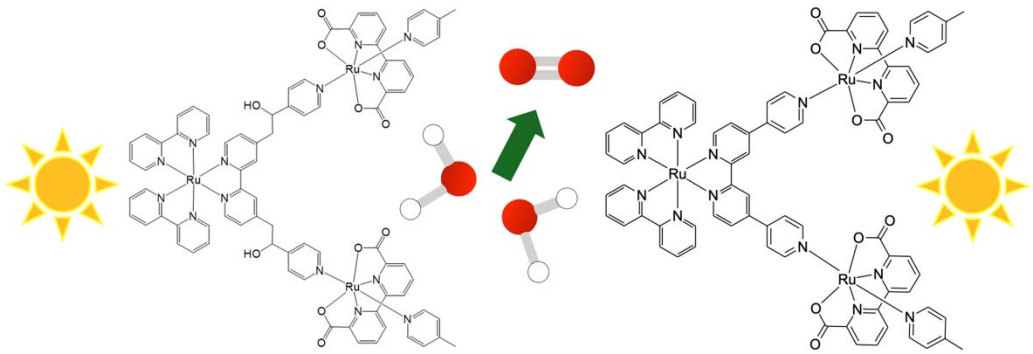


Figure 1. Assemble photocatalyst investigated

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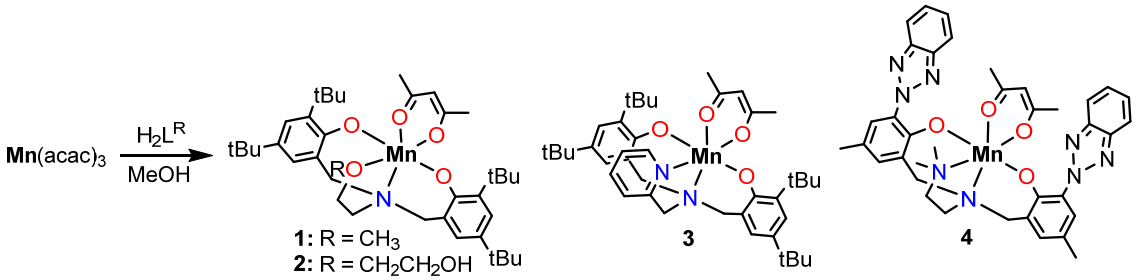
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MANGANESE(III) AMINOBIS(PHENOLATE)S

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The diverse reactivity of manganese enzymes has inspired the study of synthetic Mn(III) complexes as biomimetic catalysts. Aminobis(phenolate) ligands can stabilize Mn(III) in biologically relevant coordination environments and enable oxidation reactions reminiscent of enzymatic processes. The combination of phenolate oxygen and amine nitrogen donors closely mimics coordination environments found in manganese-containing enzymes, making these complexes valuable bioinorganic models. Their robust ligand frameworks, accessible redox chemistry, and tunable steric and electronic properties have also made them attractive platforms for studying oxidation catalysis and structure–property relationships.



Scheme 1. Syntheses of manganese(III) aminobis(phenolate)s.

This study reports the synthesis of four new manganese(III) aminobis(phenolate) complexes featuring acetylacetonate as a co-ligand. The air-stable complexes were prepared via a one-step reaction and isolated as single crystals suitable for X-ray diffraction analysis. Their catalytic activity was evaluated in the oxidation of organic substrates using H_2O_2 and tBuOOH as oxidants.

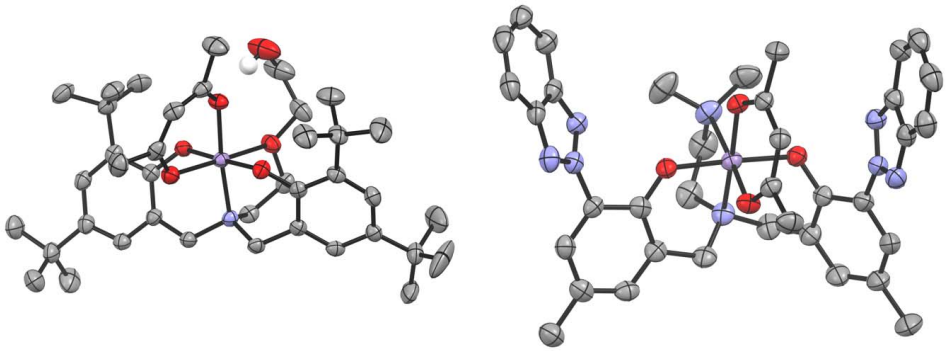


Figure 1. Molecular structures of **2** and **4**.

SITE-SELECTIVE SUZUKI-MIYAURA COUPLINGS THROUGH NICKEL CATALYSIS

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Suzuki-Miyaura cross-coupling has been the prime choice for C-C bond forming reactions for the past several decades [1-2]. Traditionally catalysed through palladium, the focus is shifting towards nickel due to associated benefits such as cost-effectiveness and electrophilic tolerance. Moreover, production of palladium constitutes a significantly higher global warming potential in comparison to nickel for every kg produced [3-4]. Dihalosubstituted heteroarenes have been identified as a crucial backbone for several Actie Pharmaceutical Ingredients [5-6]. However, regioselectivity in these substrates is heavily dictated by their inherent polarity, which represents a key limitation with the preferred site for cross-coupling being the C-X bond lying in the vicinity of the heteroatom (2-Ar in Figure 1) [7]. Previously, unconventional site-selectivity has been accomplished, using palladium catalysis [8-9]. This project aims to achieve cross-coupling at the C–X bond distal to the heteroatom (4-Ar in Figure 1) by employing nickel-based catalytic systems, while also investigating the underlying reaction mechanisms.

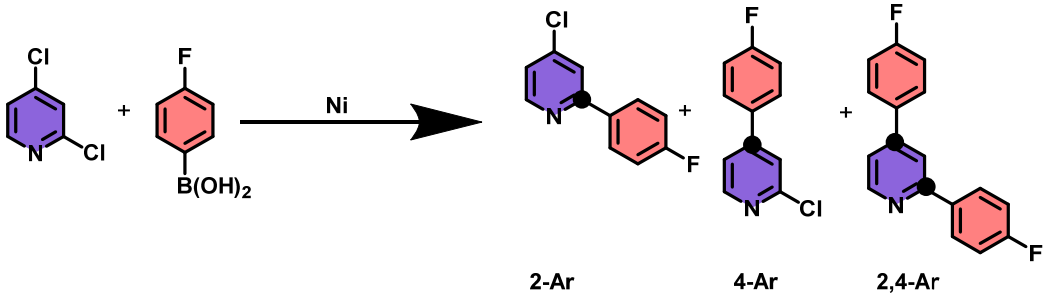


Figure 1 Ni-catalysed SMCC reaction of dihalopyridines with potential cross-coupled products.

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REACTIVITY OF METAL NITRIDES TOWARDS SMALL MOLECULE SUBSTRATES

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Transition metal complexes featuring a terminal nitride ligand have received interest for their properties in small molecule activation reactions and as reactive intermediates in homogeneous catalysis.[1] Metal nitrides also display reactivity in C-H bond activation and selective formation of C-N bonds; a crucial objective in synthetic chemistry due to the ubiquity of nitrogen containing motifs in pharmaceuticals, agrochemicals, and functional materials.[2] Nitride reactivity is dependent on the relative energy and character of metal versus nitride-based orbitals, and is further modulated by metal identity, oxidation state, and supporting ligand framework. In our group, redox-active salen ligands bearing *para* ring substituents (R=NO_2, CF_3, H, *t*Bu, OMe, *i*PrO, NMe_2, NEt_2) have demonstrated that remote ligand electronics dictate the locus of oxidation.[3] For electron-withdrawing substituents (R= NO_2, CF_3, H, *t*Bu, OMe, *i*PrO), one-electron oxidation at 233 K affords high valent Cr(VI) nitrides which are investigated in this work to establish electrophilic reactivity and accessible scope of intermolecular C-H bond amination as a function of substrate C-H bond strength and ligand electronics. Mechanistic studies to elucidate the pathways of C-N bond formation are performed using UV-Vis-NIR spectroscopy for monitoring kinetics and ESI-MS and HPLC to identify and quantify products. Furthermore, nitride activation by thermal, or photolysis conditions will be investigated to expand the accessible C-H bond strengths.

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USE OF CARBON NANOTUBE SUPPORTED Pd CATALYST IN THE SYNTHESIS OF N-METHYLGLUCAMINE FROM GLUCOSE

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This study investigates the selective catalytic hydrogenation of the Schiff base intermediate generated through the condensation of D-glucose and methylamine. By utilizing a palladium catalyst supported on functionalized multi-walled carbon nanotubes (Pd/CNT), high efficiency was achieved in the synthesis of *N*-methyl-glucamine (Meglumine), a critical pharmaceutical excipient and diagnostic intermediate. Compared to traditional heterogeneous systems, the Pd/CNT catalyst demonstrates superior stability and enhanced reusability. This report details the optimization of reaction parameters, catalytic performance, and comprehensive product characterization.

Palladium nanoparticles were immobilized onto functionalized multi-walled carbon nanotubes (MWCNTs) using a precision wet impregnation method to ensure uniform metal dispersion. Glucose and methylamine were reacted in a 1:1.2 molar ratio within a methanol/water solvent system. The mixture was stirred at ambient temperature for 45 minutes to facilitate the equilibrium formation of the Schiff base. The resulting mixture was charged into a high-pressure autoclave reactor in the presence of the Pd/CNT catalyst. The hydrogenation process was conducted at 50oC under a 10 bar H2 atmosphere for a duration of 4 hours. Quantitative analysis of product yield and chemical purity was performed using High-Performance Liquid Chromatography (HPLC) and Fourier-Transform Infrared (FTIR) spectroscopy. The Pd/CNT system exhibited remarkable chemo-selectivity, specifically targeting the C=N (imine) bond while suppressing the competitive direct reduction of the glucose carbonyl group to sorbitol. The implementation of the Pd/CNT architecture resulted in an N-methyl-glucamine selectivity exceeding 92%.Synergistic. The high effective surface area and unique electronic properties of the CNT support minimized intra-particle mass transfer limitations, significantly accelerating the reaction kinetics.

This research underscores the efficacy of Pd/CNT catalysts in the valorization of bio-derived feedstocks into high-value specialty chemicals. The ability to achieve high yields under relatively mild temperature and pressure conditions highlights the industrial scalability and atom-economical nature of this sustainable synthetic route.

Acknowledgment: The authors are greatly thankful to The Scientific and Technological Research Council of Turkey (TUBITAK-TEYDEB) with project number 5250005 for financial support.

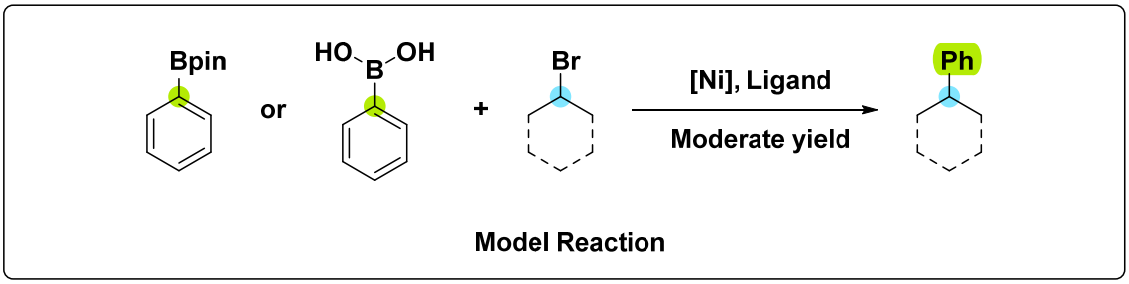
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NICKEL-CATALYZED ARYL-ALKYL SUZUKI-MIYAURA CROSS-COUPLING

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Although the discovery of new synthetic methodologies remains a central objective in organic chemistry, the optimization of established transformations is equally critical for enhancing efficiency and cost-effectiveness in pharmaceutical manufacturing. The Suzuki–Miyaura coupling (SMC) is among the most frequently employed carbon–carbon bond-forming reactions in the pharmaceutical industry, ranking second in overall usage [1]. Consequently, reducing the cost and improving the efficiency of SMC processes continue to be of significant industrial interest. Recent advances in nickel catalysis have demonstrated the potential for substantial economic benefits. Diao and co-workers reported a series of P,O-bidentate ligands enabling nickel-catalyzed sp^2–sp^2 SMC at catalyst loadings as low as 0.1 mol%, significantly enhancing catalytic efficiency [2] [3] [4]. More recently, Chirik, Beutner, Simmons, and collaborators developed phenoxyimine-type ligands for nickel-catalyzed sp^2–sp^3 SMC, achieving a 40% reduction in production costs for the synthesis of the Afimetoran core structure [5] [6]. These studies underscore the strategic importance of ligand design in advancing cost-effective cross-coupling methodologies. Herein, we describe our efforts to broaden the scope of these reactions targeting heteroatom-rich and electron-rich scaffolds, which are common in pharmaceutics. The presentation will highlight the novelty of catalytic system and the potential application in industry.



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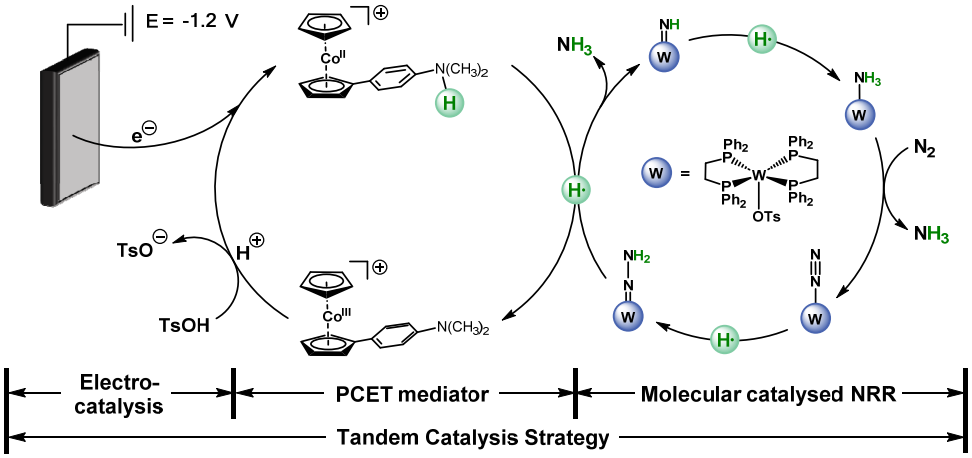
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COBALT-BASED PROTON-COUPLED ELECTRON TRANSFER MEDIATOR ENABLES EFFICIENT N2 REDUCTION CATALYZED BY A TUNGSTEN COMPLEX

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The traditional Haber-Bosch process for ammonia synthesis is plagued by intensive energy consumption and severe environmental pollution, while existing homogeneous electrocatalytic nitrogen reduction reactions (eNRR) suffer from high overpotentials and fierce competition from the hydrogen evolution reaction (HER), which drastically undermines Faraday efficiency. In 2020, Peters' team designed a proton-coupled electron transfer (PCET) mediator (cobaltocenium modified by a tethered Brønsted base) that enables NRR under mild conditions with 44.5% Faraday efficiency[1]. Based on this, this study uses density functional theory (DFT) calculations to explore the PCET mechanism in electrocatalytic NRR. Our results identify the most thermodynamically and kinetically feasible catalytic cycle, which proceeds via the intermediate sequence of $\mathbf{W}(N_2)^+ - \mathbf{W}(NNH_2)^+ - \mathbf{W}(NNH_3)^{2+} - \mathbf{W}(NNH_3)^+ - \mathbf{W}(N)^+ - \mathbf{W}(NH_3)^+ - \mathbf{W}(N_2)^+$. The protonation of the key intermediate $W(NNH_2)^+$ to form $W(NNH_2)^{2+}$ by the cobalt-based mediator $[(Cp)Co^{III}((C_5H_4)\text{-}p\text{-}C_6H_4\text{-}NH(CH_3)_2)]^{2+}$ is identified as the rate-determining step (RDS) of the entire reaction, with an energy barrier of 21.9 kcal/mol. The cobalt-based mediator $[(Cp)Co^{III}((C_5H_4)\text{-}p\text{-}C_6H_4\text{-}N(CH_3)_2)]^+$ is found to exert a dual regulatory effect: it reduces the energy barriers of NRR-related PCET steps and elevates the barriers of HER pathways, thereby effectively suppressing the competitive HER and improving the Faraday efficiency. Calculations on side reactions exclude the hydrazine formation pathway. This work elucidates the core reaction mechanism of tandem eNRR catalysed by tungsten complexes and Co-based PCET mediators, providing theoretical insights for the rational design of high-efficiency and high-selectivity eNRR electrocatalysts and advancing the development of sustainable ammonia synthesis technologies under mild conditions.



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MECHANISTIC INVESTIGATIONS IN IRON CATALYSED SUZUKI CROSS COUPLINGS

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In recent years, iron catalysed cross coupling reactions have developed into a valuable method for the formation of C-C bonds.[1] Remarkably, in contrast to the palladium catalysed reactions, the synthesis of biaryls remains difficult for the iron-catalysed couplings. Especially the Suzuki-type reactions under mild conditions is an ongoing challenge.[2] The only work worth mentioning here is of the Bedford group, applying an Fe(III) species as catalyst precursor and proposing Fe(I) as active species.[3]

We now report an ortho-directed Suzuki biaryl cross coupling: One focus here was on understanding of the mechanism and investigation of the oxidation state of the active iron species. In particular, kinetic investigations and stoichiometric experiments in combination with Mößbauer spectroscopy were able to provide a clearer picture of the reaction steps involved in the catalytic cycle. It was also possible to isolate and analyze intermediate stages.

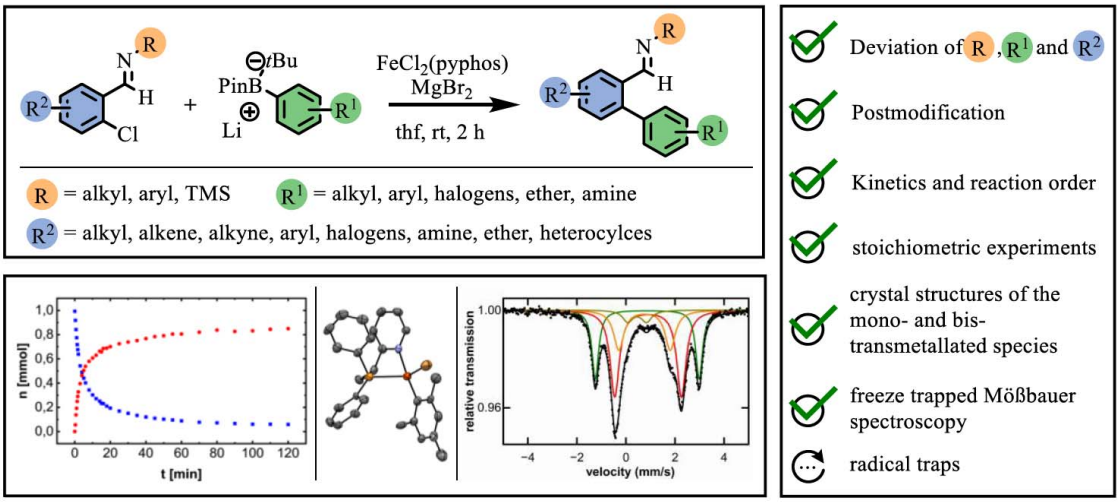


Figure 1: Reaction equation of iron-catalyzed Suzuki type cross-coupling (top left). Exemplary results of kinetic measurements, crystal structure of the monotransmetallated species and Mößbauer spectroscopy (botton left) and overview of synthetic and mechanistic studies conducted (right).

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A VERSATILE, READILY AVAILABLE AND BENCH STABLE IRON CATALYST ACTIVE IN CARBENE TRANSFER REACTIONS

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The development of C–H functionalization reactions catalyzed by non-precious metals is an important goal toward more sustainable chemical synthesis. In 1992, Hossain reported the first example of carbene transfer reactions using iron as a catalyst, $[CpFe(CO)_2(THF)]BF_4$[1]. Building on this work, iron has shown promising results in this field over the past decades[2].

Our group has previously described a synergy between an iron catalyst, $[Fe(^{F}pda)(THF)]_2$, and a lithium aluminate salt, $Li[Al(OC(CF_3)_3)_4]$. This catalytic system activates diazoesters under mild conditions, promoting both intra- and intermolecular functionalization of strong C(sp^3)–H bonds via carbene insertion[3,4].

During our research, we identified a simpler and more manageable catalyst, $[Fe(acac)_3]$, which, upon activation, exhibits superior performance, affording good yields in intramolecular C–H functionalization reactions via iron–carbene intermediates. It shows excellent selectivity, largely avoiding the formation of “hydride shift” side products, and is commercially available, inexpensive, and air- and moisture-stable. Furthermore, it demonstrates good functional group tolerance (e.g., ethers and silanes) and is also capable of accessing Buchner ring expansion products, generating cycloheptatriene derivatives.

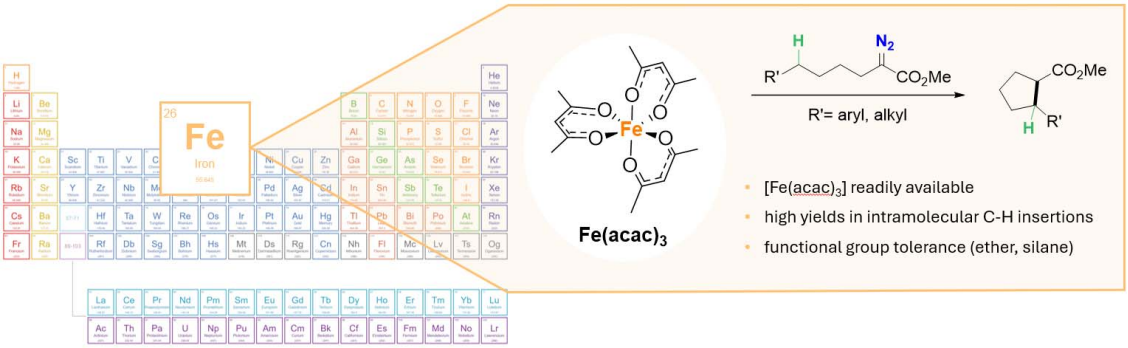


Figure 1. Schematic representation of $[Fe(acac)_3]$ reactivity in intramolecular C-H funtionalizations via iron-carbene intermediates.

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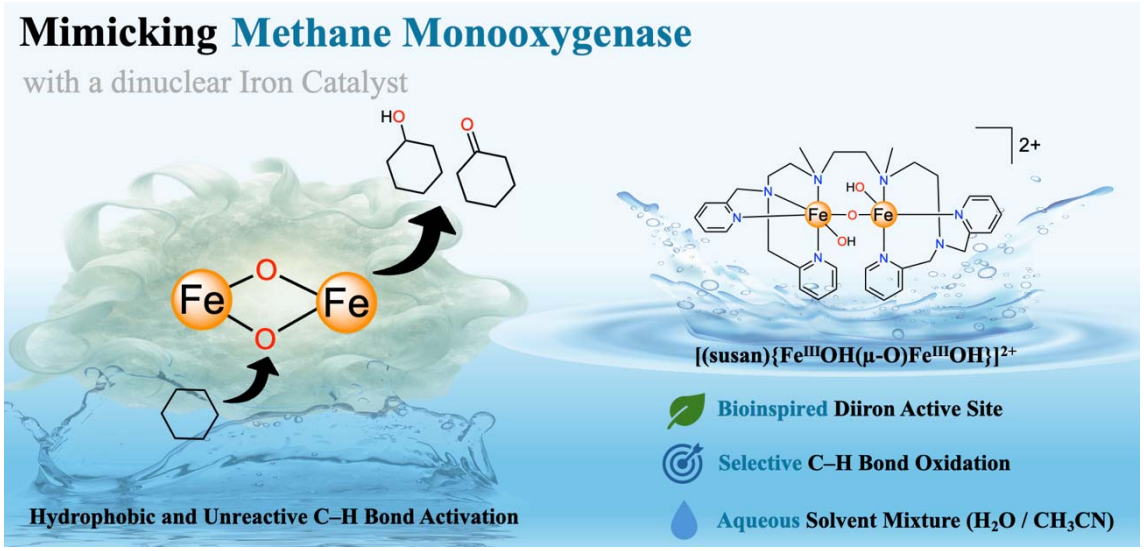
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MECHANISTIC INSIGHTS INTO CAGE ESCAPE FOR BIOINSPIRED C–H BOND OXIDATION CATALYSIS

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The C–H bond activation of cyclohexane (CyH) is an industrially important process, with ~10^6 tons of cyclohexanol (CyOH) and cyclohexanone (CyO) produced per year for nylon-6 and nylon-6,6 synthesis.[1] Current cobalt-based processes operate under harsh and environmentally non-friendly conditions, yielding only 4 % overall conversion at 80 % selectivity, making this the least efficient large-scale industrial process.[2] In contrast, methane monooxygenase (MMO) catalyzes the oxidation of methane under mild conditions and serves as a model for biomimetic systems.[3]



In this respect, we have developed a family of bis(tetradentate) dinucleating ligands, including the parent pyridine-based ligand susan.[4] We have evaluated dinuclear iron complexes for their catalytic performance in CyH oxidation. In acetonitrile, CyOH, CyO and cyclohexyl hydroperoxide (CyOOH) were found as the main products. The latter indicates a radical pathway, due to cage escape of the initially formed cyclohexyl radical (Cy·). This is supported by radical trapping experiments. The change to aqueous solutions decreases the cage escape. These findings provide mechanistic insights for the rational improvement of bioinspired C–H oxidation catalysts.

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ASYNCHRONOUS PCET AND MECHANISTIC SWITCHING IN NICKEL(III)-MEDIATED C–H ACTIVATION REACTION

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Proton-coupled electron transfer (PCET) plays a central role in the activation of X–H bonds in substrates (X = C, O). The sequence of proton and electron transfer dictates the nature of the PCET process, giving rise to pathways such as hydrogen atom transfer (HAT)/concerted PCET (CPET), electron transfer–proton transfer (ET–PT), and proton transfer–electron transfer (PT–ET). While such processes have been extensively investigated for high-valent manganese, iron, and cobalt complexes, studies involving high-valent nickel complexes remain limited.

Herein, we report the synthesis and detailed spectroscopic characterization of a formal nickel(III) complex (**1**) supported by a bis(amidate)–alkoxide–pyridine ligand framework in the primary coordination sphere (Figure 1). The PCET reactivity of **1** was examined using a series of alkanes spanning a wide range of C–H bond dissociation free energies (BDFEs). These reactions afford a Ni(II) complex featuring protonation at the alkoxide arm of the ligand. Detailed kinetic analyses support a CPET pathway, accompanied by a large kinetic isotope effect. Notably, a plot of log(k_2) versus BDFE reveals two distinct linear regions forming a V-shaped correlation, indicative of a mechanistic crossover. While similar trends have been reported for sulfoxidation and O–H bond activation, such behavior has not been observed previously for C–H bond activation reactions, underscoring the unique PCET reactivity of **1**. Furthermore, the study elucidates the extent of asynchronous PCET operative within the two regimes.

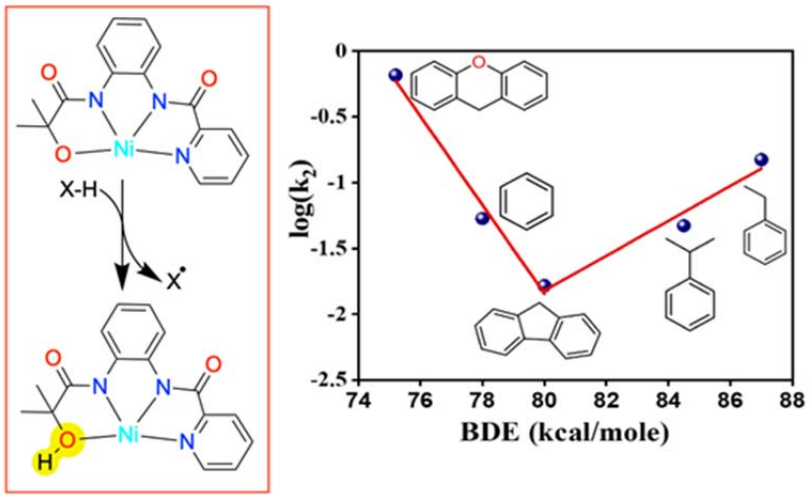


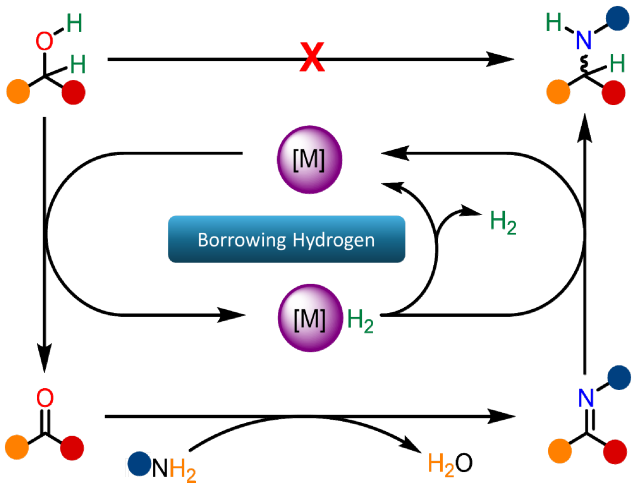
Figure 1. Reactivity studies of **1**.

DEVELOPMENT AND UTILIZATION OF CHIRAL BASE METAL CATALYSTS FOR ASYMMETRIC BORROWING HYDROGEN REACTIONS

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Nitrogen-containing compounds are of great interest in modern organic chemistry, as well as important building blocks in the agrochemical and pharmaceutical industry. Traditional syntheses often require harsh conditions and toxic reagents. Borrowing hydrogen (BH) methodology offers a more sustainable and atom-economical alternative for forming C–C and C–N bonds from readily available alcohols.[1] While early BH systems mainly relied on noble metals (e.g. Pt, Ir, Ru), [2] recent efforts have shifted toward earth-abundant metals such as Mn, Fe, Co, or Ni to improve sustainability and reduce costs.[**Fehler! Textmarke nicht definiert.**,3] However, asymmetric BH transformations remain underdeveloped, limiting access to enantioenriched amines. In this work, we focus on the design and development of novel chiral ligands for manganese-based catalyst to promote stereoselective BH reactions.[4] In parallel, asymmetric hydrogenation studies are conducted to provide and clarify the relationship between catalyst structure and performance. By integrating these studies, we aim not only to develop efficient chiral manganese-based systems, but also to gain a more comprehensive understanding of the factors that govern their activity and selectivity.



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AMIDOBORANE DOPING FOR THE CONTROLLED SYNTHESIS OF POLYAMINOBORANES

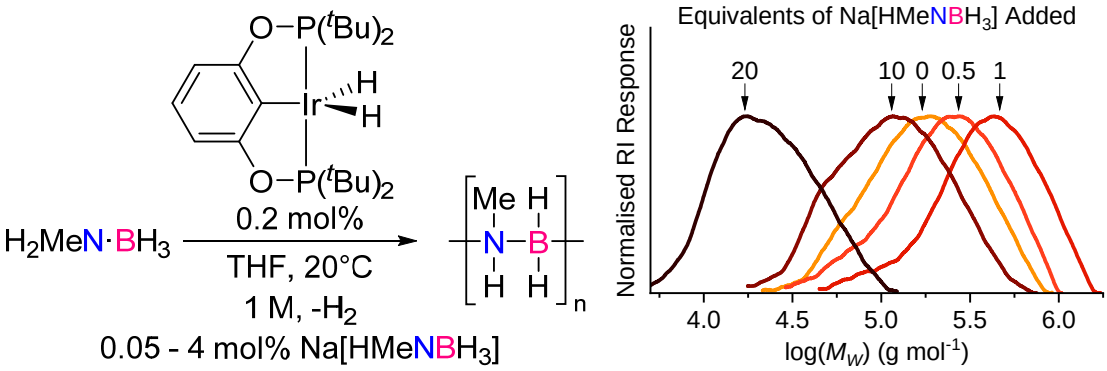
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Polyaminoboranes are main group polymers with a boron-nitrogen backbone, isoelectronic to polyolefins. These polymers can be formed selectively using transition metal catalysts via a cascade process: dehydrogenation of amine-boranes to form transient aminoboranes, followed by their head-to-tail polymerisation [1-3].

An emerging application of polyaminoboranes is as shapeable ceramic precursors for technologically important boron nitride materials. Controlling the polymer properties allows for greater control and optimisation of the formed ceramic. For example, the molecular weight of polyaminoboranes was shown to be important in controlling the viscosity of the polymer solutions used for making BN fibres via electrospinning [4].

In this work, we show that simple doping of amidoborane salts into the catalysis gives significant control over the resulting polymer, using the Ir(POCOP)H_2 catalyst. Compared to a control experiment (no additives, M_w = 211 000 g mol^{-1}), different Na[HMeNBH_3] loadings gave a wide range of molecular weights from M_w = 28 000 g mol^{-1} to M_w = 450 000 g mol^{-1}. An effect on the mechanism of the reaction was also observed, with changes in the induction period, and unique iridium speciation observed after catalysis. This molecular weight control over two orders of magnitude is also explanted in the synthesis of BN ceramic materials.



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SYNTHESIS OF OER CATALYSTS FOR BIOHYBRID PHOTOSYSTEMS

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Photoinduced water splitting, which involves the conversion of water into hydrogen and oxygen through the absorption of light energy, is a promising approach for renewable energy production. However, realizing efficient and robust systems is still a key challenge.

In photocatalytic cycles, the water photo-oxidation typically involves a bimolecular process between components, making diffusion rate a limiting factor. For this reason, organizing molecules in a covalent or supramolecular system could be a possible solution. [1-2] DNA, with its well-defined helical structure and programmable sequence, offers a unique scaffold to bind intercalating molecules with a precise spatial arrangement [3] (Figure 1).

Our aim is to design hybrid systems for water photo-oxidation, incorporating photosensitizers and catalysts into the DNA structure, which would act both as a scaffold for efficient light absorption and as a redox-active center, exploiting the oxidation potential of nucleobases, such as guanine, which may play a redox-active role.

We report the design and synthesis of novel OER catalysts—based on ruthenium complexes featuring dppz-derived planar ligands capable of DNA intercalation. The structural features of these complexes were elucidated by NMR spectroscopy, while their properties were investigated through electrochemical analysis and UV-Vis absorption. Electrochemical and kinetic experiments were specifically carried out to assess their ability to function as catalysts for water oxidation. Studies on photoinduced oxygen production were carried out to evaluate the photocatalytic performance. Pump–probe spectroscopy and laser flash photolysis were employed to investigate electron transfer processes between DNA and intercalated molecular components.

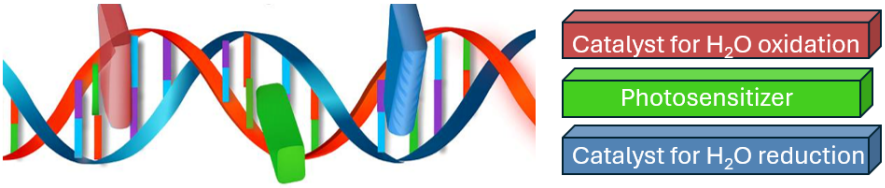


Figure 1. Schematization of the supramolecular assembly goal of the project

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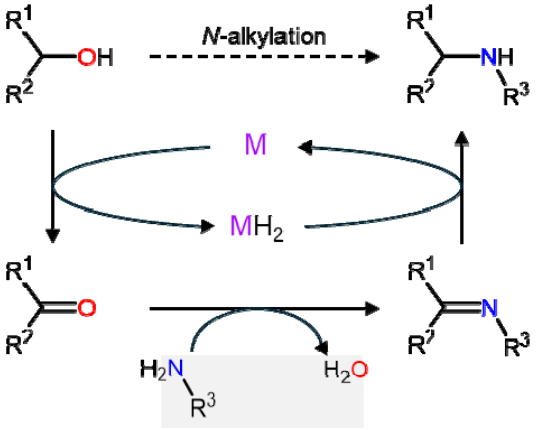
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MANGANESE-CATALYZED BORROWING HYDROGEN AND ASYMMETRIC TRANSFER HYDROGENATION PROCESSES

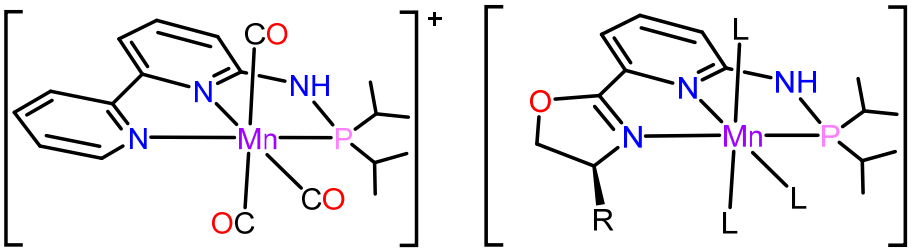
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The borrowing hydrogen process represents an efficient strategy to achieve the formation of new C–C or C–N bonds using cheap and readily available compounds, such as alcohols, as starting materials for the synthesis of valuable molecules, minimizing the formation of by-products and waste.[1,2]



Two of the three steps of the process are catalyzed by a metal complex, which is responsible for the oxidation and reduction of the substrate. Recently the development of catalysts based on abundant metals has become attractive due to their availability. Our group recently reported[3] the synthesis of a Mn(I) catalyst containing a bipyridine-based pincer [PNN] ligand (on the left), which proved to be highly active in the N-alkylation of amines with alcohols and in the synthesis of tetrahydroquinolines.[4]



This work focuses on the investigation of new base metal catalysts for borrowing hydrogen processes. These complexes (on the right) contain an oxazoline moiety to provide chirality and enable stereoselective control of the reaction. To further understand the action of these catalysts, reactions of asymmetric transfer hydrogenation, that mimic the last step of the borrowing hydrogen process, were performed.

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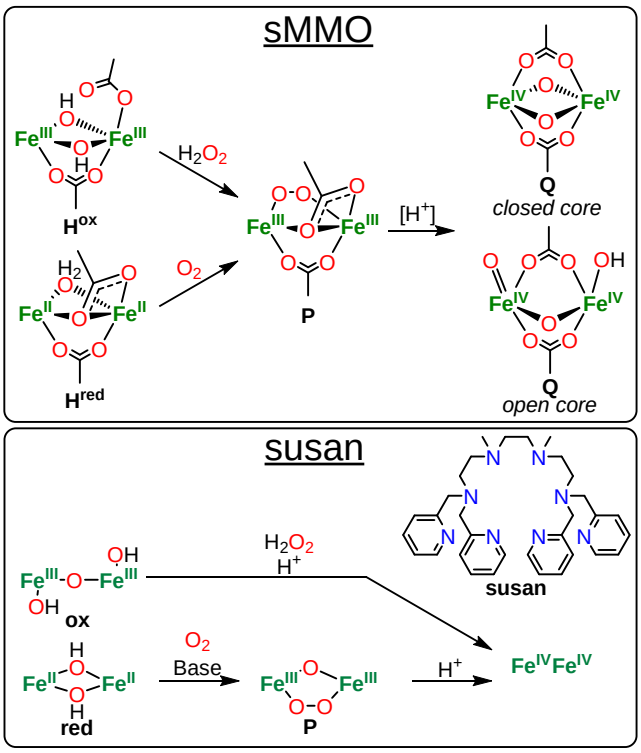
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GENERATION AND REACTIVITY OF HIGH-VALENT DIIRON INTERMEDIATES

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There are several instances in nature of the selective oxidation of C-H bonds being carried out by iron enzymes. The oxidation of methane to methanol is catalyzed by the dinuclear non-heme iron enzyme "soluble Methane Monooxygenase" (sMMO). After reaction of an $Fe^{II}Fe^{II}$ species with molecular oxygen to form a peroxo-bridged $Fe^{III}Fe^{III}$ species **P**, a proton-promoted step induces conversion to compound **Q**, which is the active oxidant of sMMO. The nature of **Q** is subject of ongoing investigations. It has been shown to contain high-spin Fe^{IV} and two proposed structures are the *closed core* and *open core* motifs.[1]

We have developed a family of dinucleating ligands to mimic the active sites of dinuclear enzymes and obtain insight into their reactive intermediates.[2,3]

The ligand susan forms a $Fe^{II}Fe^{II}$ complex that reacts with molecular oxygen to form a reactive, peroxo-bridged $Fe^{III}Fe^{III}$ complex.[4] Upon protonation, this peroxo-bridged species converts to a high-valent reactive species, shown via Mößbauer spectroscopy to contain high-spin Fe^{IV}. This same Fe^{IV} species can be generated by treating a $Fe^{III}Fe^{III}$ precursor with hydrogen peroxide in the presence of acid. The nature and reactivity of this Fe^{IV} intermediate will be presented.

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NOBLE-METAL FREE COMPLEXES AS WATER OXIDATION CATALYSTS

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With the growing demand for renewable energy sources, there has also been an increase in the need to convert light energy or electrical energy into energy-rich compounds such as hydrogen or hydrocarbons.[1] The field of artificial photosynthesis has set itself the task of achieving this. Typically, these reactions require protons and electrons, which can be obtained from the oxidation of water.[2]

Owing to the complicated kinetics involved, such as the formation of an oxygen-oxygen bond, water oxidation catalysis (WOC) is one of the more challenging processes. Initially, ruthenium complexes have been dominating WOC with more beneficial stability and catalytic activity. However, more abundant 3d metal complexes are developing into more promising and effective catalysts. [3]

Here, we report recent findings on new Fe(III) complexes based on Jäger-type ligands potentially active in WOC. The complexes are screened regarding their electrochemical properties, using cyclic voltammetry in presence of water and pyridine. UV/Vis spectroscopy provides information about the formation and stability of Fe-oxo species formed in a reaction with oxidants like H_2O_2, which we propose as a resting-state during catalysis.

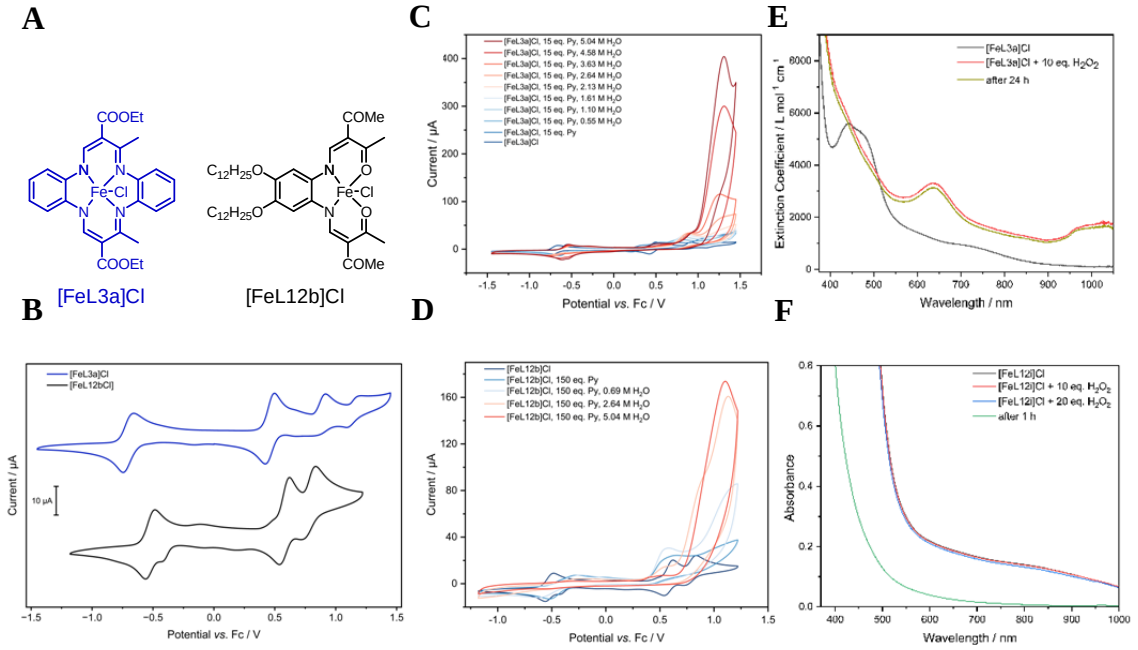


Figure 1. A: Structures of the investigated Fe(III) complexes; **B**: Cyclic voltammograms of the complexes in MeCN ($TBAPF_6$ 0.1 M, Analyte: 1 mM), WE: Glassy carbon, CE: platinum wire, RE: SCE; **C and D**: Cyclic voltammograms with subsequent addition of water and pyridine; **E and F**: UV/Vis experiment in MeCN with addition of H_2O_2.

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FLAVIN-BASED RUTHENIUM COMPLEXES FOR SECONDARY COORDINATION SPHERE MODULATION TOWARD AMMONIA OXIDATION

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Ammonia oxidation is a key reaction for utilizing ammonia as a carbon-free hydrogen carrier, yet its implementation with molecular catalysts remains challenging due to the high kinetic barrier associated with N–H bond activation and the sensitivity of reactivity to the local coordination environment. While most catalyst designs have focused on tuning the primary coordination sphere, emerging studies suggest that secondary coordination sphere interactions can play a critical role in modulating reactivity. Herein, we report a flavin-based tridentate ligand platform for exploring secondary coordination sphere effects in ruthenium complexes. The flavin scaffold offers a redox-active, tautomerizable, and proton-responsive framework capable of forming hydrogen-bonding interactions. A series of Ru–flavin complexes were synthesized by varying external ligands, including chloride, pyridine, DMAP, and ammonia, to investigate ligand-dependent coordination behavior. This work provides structural insight into hydrogen-bond-assisted secondary-sphere design strategies for the development of molecular ammonia oxidation catalysts.

SYNTHESIS, CHARACTERISATION AND REACTION OF VARIOUS INDENYL BASED Zr METALLACYCLES

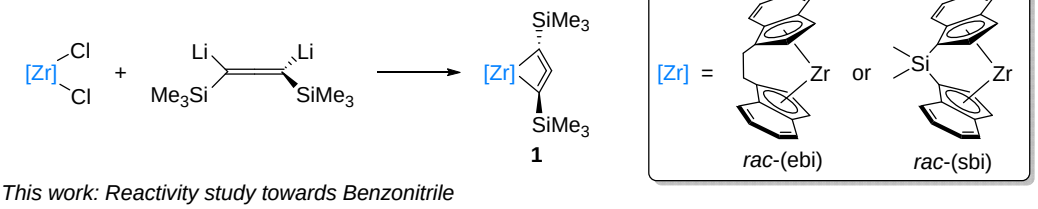
Helena M. Dziedzic, Xinzhe Shi, Fabian Reiß, and Torsten Beweries

Leibniz-Institute für Katalyse, Rostock, Germany

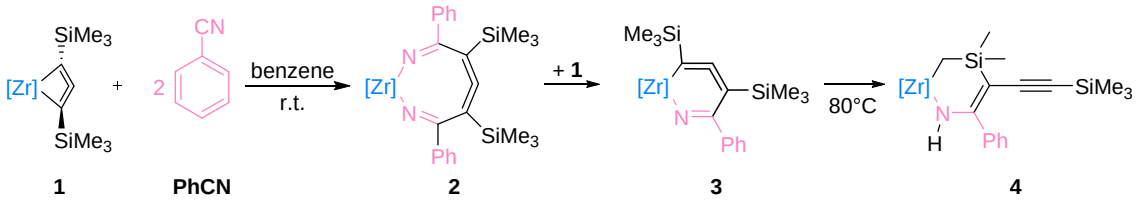
Over the past decade, we have discovered a convenient synthetic approach for the selective formation of unusual four-membered *deprotio*-1-metallacyclobuta-2,3-diene (MCB) complexes of titanocenes and zirconocenes (e.g. **1**).[1] Because of the unique bonding in group 4 metallacycles, they have been key in a variety of inorganic and organic applications.[2] A recent example would be the first cyclic polymerization of terminal alkynes by a non-metallocene-based titanacyclobuta-2,3-diene.[3]

This present work focuses on the formation of an 8-membered ring species (**2**) via nitrile insertion into the Zr-C unit of previously synthesized indenyl-based zirconacyclobuta-2,3-dienes (**1**).[4][5] The creation of these ring systems gives us further insight into their bonding as well accessing smaller 6-membered ring structures (**3**) upon addition of a further equivalent of starting material. Heating causes proton migration and C-H bond activation of the $SiMe_3$ substituent, producing 3-sila-6-aza -1-zirconacyclohexa-4-enes (**4**). Future work will investigate the effect of not purely Cp based ligands on titana- and zirconacyclobuta-2,3-dienes and their catalytic activity.

Synthesis of 1-Zirconacyclobuta-2,3-dienes



This work: Reactivity study towards Benzonitrile



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BIMETALLIC AND MONOMETALLIC COMPLEXES FEATURED BY A NOVEL DINUCLEATING BIS(β-DIKETIMINATO) LIGAND SYSTEM

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Bimetallic catalysis enables reaction pathways that are not accessible to similar monometallic complexes [1]. This applies in particular to activation processes that require coordinated interaction of two metal centers. The prearrangement of two metal sites at a defined distance can enhance cooperative interactions and can be advantageous for reactivity and selectivity in the catalytical active molecule [2]. To achieve this, careful ligand design is necessary in order to control nuclearity and intermetallic distances, thereby opening up further controllable elements to develop high specialized catalysts [3].

Since it is already known in the literature that various β-diketiminate complexes with bridging co-ligands form bimetallic complexes, we have designed a new ligand system in which two β-diketiminato binding pockets are connected at a defined distance via a xanthene backbone [4, 5]. The ligand system exhibits both dinucleating and mononucleating properties in complexation reactions. Bimetallic as well as monometallic first row transition metal complexes have already been synthesized and characterized (Figure 1). The reactivity of these complexes towards the activation of small molecules is currently being investigated.

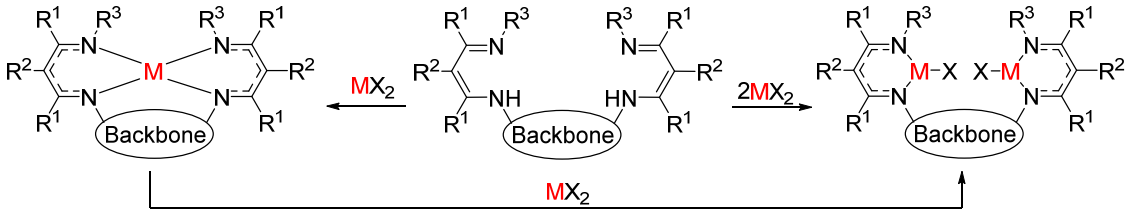


Figure 1. Monometallic and bimetallic complexes supported by a new Bis(β-diketiminate) ligand system.

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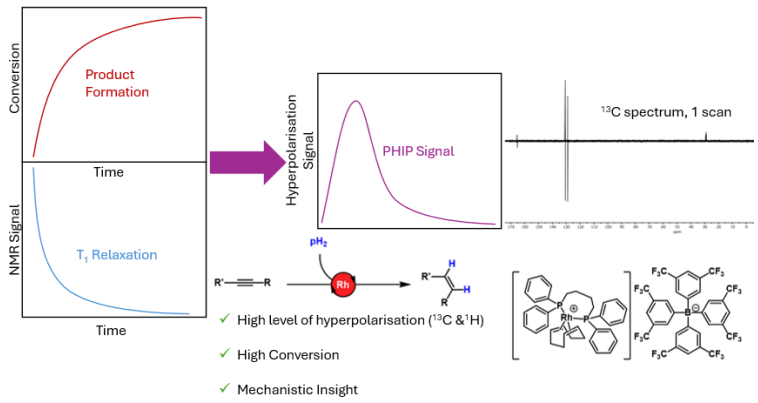
REEVALUATION OF SCHROCK-OSBORN CATALYST EFFECTIVENESS FOR ^{1}H & ^{13}C PARAHYDROGEN INDUCED POLARISATION NMR

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[a]Department of Chemistry, University of York, U.K.
[b]Centre for Hyperpolarisation in Magnetic Resonance, University of York, U.K.

Hyperpolarisation is a phenomenon the provides significant NMR signal enhancement by shifting the nuclear spin states of an analyte molecule away from thermal equilibrium. The enhancement is achieved by harnessing the singlet spin state of H_2 through the pairwise hydrogenation of an unsaturated alkyne. The H_2 isomer is restricted to the singlet state known as *para*-hydrogen (pH_2). While it constitutes 25% of H_2 under standard conditions, it can be enriched by cooling to cryogenic temperatures. The signal gains associated with *para*-hydrogen induced polarisation (PHIP) have been deployed across a range of applications, including investigating mechanism for homogeneous or heterogeneous catalysis, as well as in medical diagnostic imaging.[1] Notably, this signal enhancement enables the elucidation of short-lived and low-concentration intermediates by NMR spectroscopy, providing a means, to investigate catalyst speciation[2] and give mechanistic insight in dilute reaction mixtures.[3]

While many catalysts can create PHIP, they do so with varying degrees of efficiency. This efficiency is quantified by the field independent percentage polarization (ε), a parameter that relates the reaction flux and enables detailed kinetic and mechanistic probing.[4] However, the production and measurement of these polarised analytes are fundamentally limited by the spin-lattice relaxation (T_1) of the sensitised nuclei. This present investigation reports the use of PHIP to evaluate the performance of Schrock-Osborn type hydrogenation catalyst during alkyne hydrogenation, while simultaneously providing kinetic and mechanistic insight.



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1D AND 2D VIBRATIONAL SPECTRSOCPY OF DIRUTHENIUM AZIDES

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Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin, United States of America

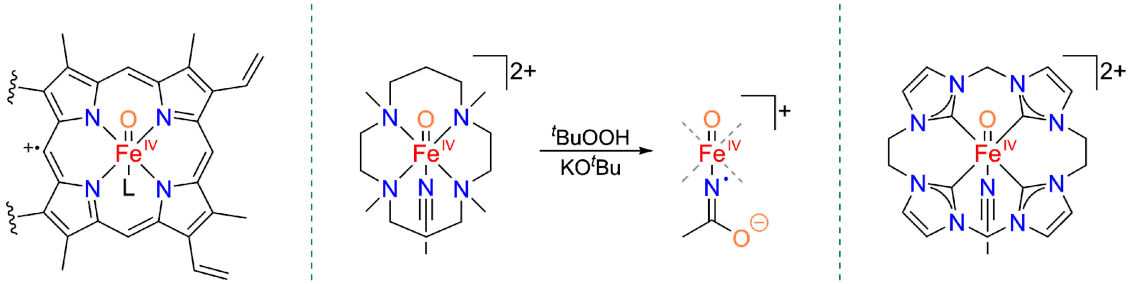
Due to their potential in nitrogen fixation, as well as a rich history of nitrogen insertion and transfer, metal nitride complexes remain an area of interest in inorganic chemistry. Within the family of metal nitride complexes, diruthenium paddlewheel nitrides have shown to be a promising class as their delocalized three center π^* orbitals make them highly electrophilic relative to two center systems with demonstrated reactivity towards aromatic C-H bonds and phosphines. So far, diruthenium azides have been the sole precursor used for nitride formation and reaction. Despite their promise, the connection between the azide ligand geometry driven by steric interactions and the thermal decomposition of the azide to the reactive nitride has heretofore been limited to a computational study of one diruthenium azide. 1D- Fourier-transform infrared spectroscopy (FT-IR) shows that the sterically hindered $Ru_2(dpf)_4N_3$, where dpf = diphenylformamidinate, has two distinct azide positions in solution state and can have two distinct positions in solid state, while the less sterically hindered $Ru_2(chp)_4N_3$, where chp = 2-chloro-6-hydroxypyridinate, only has one distinct azide position in solution and solid state. In addition to the linear spectra, Doubly Vibrationally-Enhanced Four-Wave Mixing spectroscopy (DOVE-FWM) was used to probe vibrational coupling between the azide asymmetric stretching mode and the diruthenium stretching modes. These vibrational modes have been implicated in transition states as requiring simultaneous motion based on density functional theory (DFT) calculations. Altogether, the 1D vibrational spectroscopy, 2D vibrational spectroscopy, and DFT calculations further our understanding of the differences of the azide geometry in diruthenium azide complexes and the role it plays in the thermal activation of diruthenium nitrides from diruthenium azide precursors.

ONE-ELECTRON OXIDATION OF AN ORGANOMETALLIC OXIDOIRON(IV) COMPLEX GENERATES A HIGHLY REACTIVE INTERMEDIATE WITH AXIAL RADICAL LIGAND

Jan C. Kruse and Franc Meyer

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Iron-containing heme enzymes and non-heme enzymes activate strong C—H bonds in nature, through the formation of highly reactive high-valent iron-oxido intermediates.[1] Understanding the mechanisms of these transformations has long been a central focus of bioinorganic chemistry, prompting the investigation of various synthetic oxidoiron(IV) model complexes.[2] In cytochrome P450 enzymes, the reactive oxidoiron(IV) intermediate **Cpd I** contains an additional oxidising equivalent delocalised on the non-innocent equatorial porphyrin ligand.[3] Que and co-workers reported that reaction of the oxidoiron(IV) model complex $[Fe^{IV}(O)(tmc)(MeCN)]^{2+}$ (**A**, tmc = tetramethylcyclam) with *tert*-butyl hydroperoxide produces an oxidoiron('V') species (**B**) which was spectroscopically characterised.[4] Computational studies indicated that this species possesses a predominant Fe(IV) character antiferromagnetically coupled to an axial acetylimidyl radical ligand,[5] resembling the electronic structure of iron('V') **Cpd I** with an equatorial radical ligand.



In our work, we investigated the organometallic oxidoiron(IV) complex (**1**),[6] which exhibits analogous reactivity towards *tert*-butyl hydroperoxide. Remarkably, the transient intermediate formed in this reaction demonstrates much higher hydrogen atom abstraction reactivity compared to **B**, making its spectroscopic characterisation challenging. Here, we present our findings on the reaction between **1** and *tert*-butyl hydroperoxide, along with characterisation of the resulting products and computational studies that provide insight into the differing reactivities of these oxidoiron('V') species.

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FABRICATION OF ULTRAHIGH-LOADING DUAL COPPER SITES IN NITROGEN-DOPED POROUS CARBONS BOOSTING ELECTROREDUCTION OF CO_2 TO C_2H_4 UNDER NEUTRAL CONDITIONS

Jin-Meng Heng, Pei-Qin Liao, and Xiao-Ming Chen

School of Chemistry, Sun Yat-Sen University, Guangzhou, China

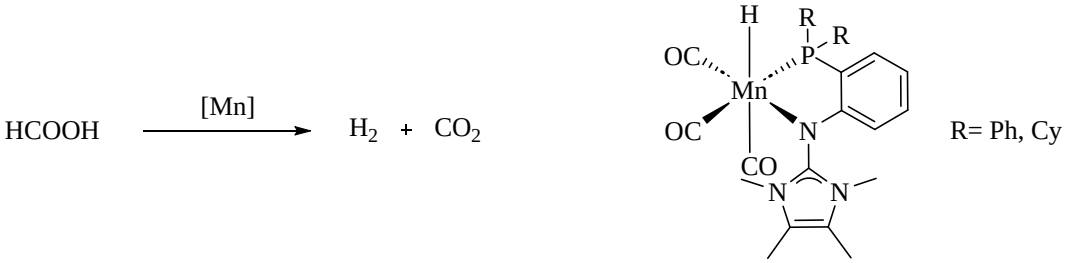
Synthesis of high-loading atomic-level dispersed catalysts for highly efficient electrochemical CO_2 reduction reaction (eCO_2RR) to ethylene (C_2H_4) in neutral electrolyte remain challenging tasks. To address common aggregation issues, a host-guest strategy is employed, by using a metal-azolate framework (MAF-4) with nanocages as the host and a dinuclear Cu(I) complex as the guest, to form precursors for pyrolysis into a series of nitrogen-doped porous carbons (NPCs) with varying loadings of dual copper sites, namely $NPC_{MAF\text{-}4}$-Cu_2-21 (21.2 wt%),$NPC_{MAF\text{-}4}$-Cu_2-11 (10.6 wt%), and $NPC_{MAF\text{-}4}$-Cu_2-7 (6.9 wt%). Interestingly, as the loading of dual copper sites increased from 6.9 to 21.2 wt%, the partial current density for eCO_2RR to yield C_2H_4 also gradually increased from 38.7 to 93.6 mA cm^{-2}. In a 0.1 m $KHCO_3$ electrolyte, at − 1.4 V versus reversible hydrogen electrode (vs. RHE), $NPC_{MAF\text{-}4}$-Cu_2-21 exhibits the excellent performance with a Faradaic efficiency of 52% and a current density of 180 mA cm^{-2}. Such performance can be attributed to the presence of ultrahigh-loading dual copper sites, which promotes C-C coupling and the formation of C_2 products. The findings demonstrate the confinement effect of MAF-4 with nanocages is conducive to the preparation of high-loading atomic-level catalysts.

MANGANESE CATALYSED DIHYDROGEN RELEASE FROM FORMIC ACID

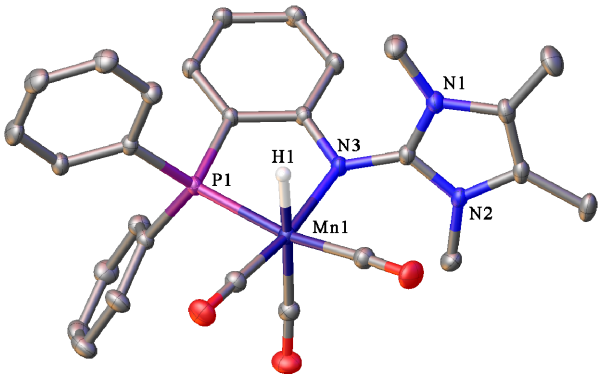
Julian Möller, Dirk Bockfeld, Matthias Tamm

Institut für Anorganische und Analytische Chemie,
Technische Universität Braunschweig, Braunschweig, Germany

Reversible chemical hydrogen storage relies on two key steps, binding and release of dihydrogen. In this work we present a potential manganese-based catalyst for dihydrogen release from formic acid.



The reaction of pentacarbonylmanganese bromide and phenylene bridged PN-Ligands [1,2] bearing imidazoline imine and phosphine moieties and subsequent ligand exchange via $NaBHEt_3$ yields the active catalyst.



In THF at 70°C in presence of bases such as NEt_3 hydrogen release from formic acid is observed with catalyst loadings as low as 0.1 mol%. In catalytic studies reaction parameters such as temperature, base and catalyst loading were varied. The results will be presented in this contribution together with a postulated catalytic cycle in accordance to previous work from Beller's group. [3]

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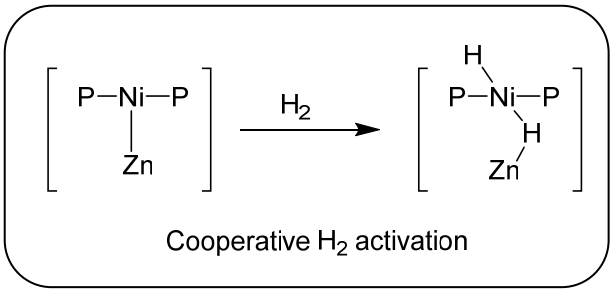
DUAL ACTIVATION OF H_2 AND CO_2 BY A PINCER-TYPE Ni–Zn HETEROBIMETALLIC COMPLEX

Krishnendu Dey, Matthias Borowski, Gregor Schnakenburg, and Connie C. Lu

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In transition metal chemistry metal ligand cooperativity is a very powerful strategy for small molecule activation. In nature, this strategy is employed by various enzymes in their active site for the activation of H_2. In synthetic systems, Lewis acidic elements can tune transition-metal reactivity via direct metal–metal interactions, offering opportunities for bifunctional catalysis.[1,2] Herein, we describe a structurally rare T-shaped Ni(0) complex supported by a pincer-type Zn metalloligand. The biphosphino-(biamido)amine framework stabilizes a low-coordinate Ni centre in proximity to an accessible Zn(II) site, establishing a cooperative bimetallic platform.

Reaction of this heterobimetallic complex with H_2 affords an isolable Ni-dihydride species through formal H–H oxidative addition, which was described earlier as the resting state during alkene hydrogenation. The Ni-dihydride complex further reacts with CO_2 to generate a reversible Ni-formate species, which releases CO_2 under vacuum. Notably, this transformation proceeds with complete atom economy, as direct H_2 and CO_2 activation yields the formate complex without base additives. These findings highlight the potential of Ni–Zn cooperativity for efficient and sustainable CO_2 hydrogenation, providing a new framework for catalyst development in carbon capture and utilization.



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BIS(HYDROSILYL)ALKYNES: UTILIZING Si-H OXIDATIVE ADDITION FOR THE ASSEMBLY OF HETEROBIMETALLIC COMPLEXES

Kristian Kunze, Wolfram W. Seidel

Institute of Chemistry, University of Rostock, Germany

α-Donor-substituted alkynes serve as versatile bridging ligands between two metal centers, adopting a μ-η²-C,C'-κ²-E,E'-bonding mode. While this system has already demonstrated remarkable flexibility in tungsten complexes with various donor atoms (C, N, O, P, S), we have now expanded its scope by introducing silicon as the heavier homologue of carbon.[1-6] Starting from the η²-acetylene tungsten complex, a hydrosilyl function is inserted through deprotonation of the alkyne ligand and subsequent addition of a chlorohydrosilane. This ligand design enables the straightforward construction of novel heterobimetallic complexes, linking tungsten with Group 9 and 10 metals.

A key result is the generation of a W-Ir system featuring a formal seven-coordinate iridium(V) center, accessed via twofold oxidative addition. While X-ray diffraction confirms the rigid bimetallic backbone, NMR studies reveal hydride fluxionality, suggesting a dynamic, reversible oxidative addition process. Furthermore, we demonstrate that certain W-Ir complexes tend to dimerize upon formal HCl elimination. Notably, the resulting monomers within this dimer are held together exclusively by an arrested state of oxidative addition (σ-SiH coordination), rather than by any conventional bridging ligands.

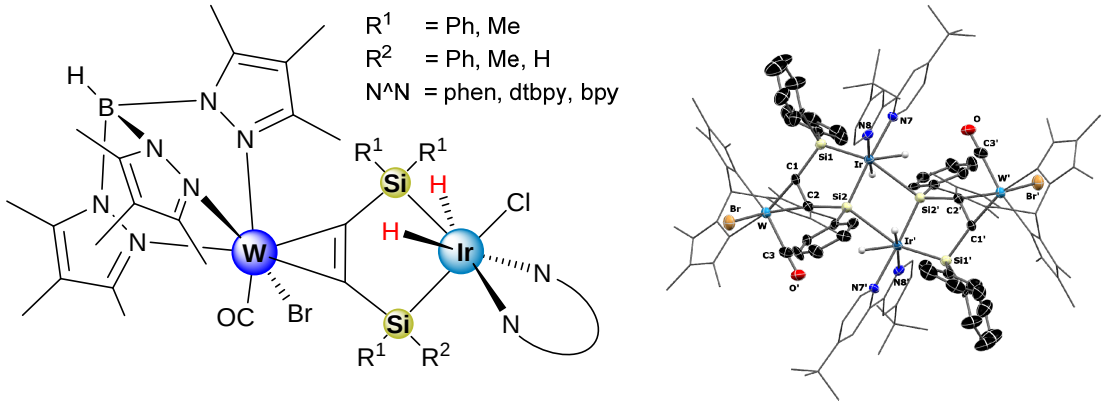


Figure 1: Heterobimetallic sevencoordinate W-Ir(V) complex (left) and dimer (right)

[1] W. W. Seidel, W. Dachtler, J. Semmler, M. Tänzler, A. Villinger, *Chem. Eur. J.* **2013**, *19*, 14702;

[2] J. Rüger, C. Timmermann, A. Villinger, A.Hinz, D. Hollmann, W. W. Seidel, *Chem. Eur. J.* **2016**, *22*, 11191.

[3] K. Helmdach, S. Dörk, A. Villinger, W. W. Seidel, *Dalton Trans*. **2017**, *46*, 11140.

[4] S. Ludwig, K. Helmdach, M. Hüttenschmidt, E. Oberem, J. Rabeah, A. Villinger, W. W. Seidel, *Chem. Eur. J.* **2020**, *26*, 16811.

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[6] P. Thiem, *Dissertation* **2023**

LOW VALENT Rh(I) COMPLEXES WITH CARBAZOLE BASED PNP LIGANDS AND THEIR CAPACITY OF CH ACTIVATION

Leon K. Paschai Darian, Joachim Ballmann, and Lutz H. Gade

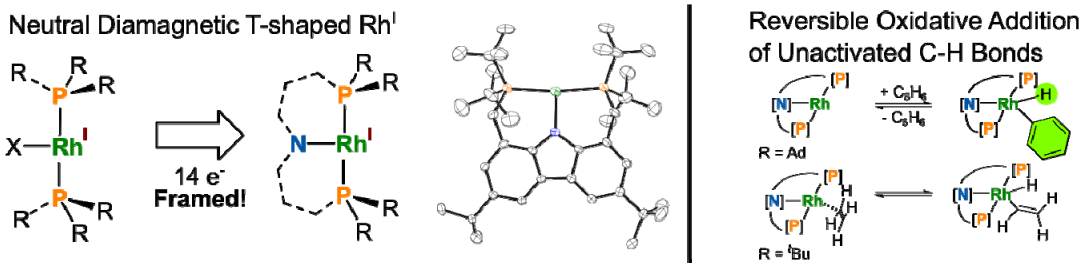
Institute of Inorganic Chemistry Universität Heidelberg, Heidelberg

Low coordinate rhodium(I) complexes are proposed as the active species in several catalytic reactions relevant to industrial applications. These include hydrogenations with Wilkinson's Rh catalysts but equally catalytic transformations involving aryl/alkynyl-H or aryl/silyl-X additions, carbonylations as well as alkane dehydrogenations. The investigation of low coordinate rhodium(I) species has led to the isolation of a handful of such complexes. However, the isolated complexes do not display C-H activations prominent in the catalytically active species.

Previous work on T-shaped complexes with the carbazole based PNP ligand, as well as work on T-shaped transition metal complexes with related ligand frameworks[1] led us to investigate the heavier group nine element rhodium.[2]

Two T-shaped 14-electron rhodium complexes, "framed" and thus stabilized by PNP pincer ligands, have been synthesized. The bis(*tert*-butyl)phosphine derived PNP^{tBu}-rhodium complex was isolated as the more stable cyclometalated Rh(III) hydrido complex and found to be in equilibrium with the T-shaped 14e$^-$Rh(I) complex. The cyclometallation is suppressed using an adamantyl substituted PNP^{Ad} ligand to give the analogous T-shaped Rh(I) species, stabilized through an agostic interaction with one of the adamantyl C-Hs. Depending on the solvent, the PNP^{tBu} complex reacted with ethylene either by π-coordination or C-H activation, giving a hydrido-vinyl Rh(III) species, both isomers being in equilibrium in solution. The PNP^{Ad} complex was found to reversibly C-H activate arenes to form the hydrido-aryl Rh(III) complexes.

Activation of other substrates, such as terminal alkynes as well as aldehydes, is also observed leading, to interesting follow up chemistry and transformation of the organic reagents.



[1] J. C. Ott, D. Bürgy, H. Guan, L. H. Gade, *Acc. Chem. Res.*, **2022**, 55, 857-868

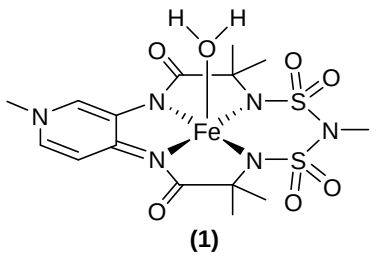
[2] L. K. Paschai Darian, J. Ballmann, L. H. Gade, *Angew. Chem. Int. Ed.*, **2024**, e202416814

MACROCYCLIC COMPLEXES OF IRON AS HIGHLY ACTIVE CATALYSTS FOR THE OXIDATION OF ORGANIC COMPOUNDS WITH H_2O_2

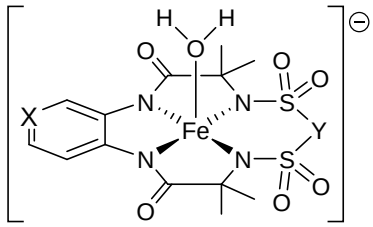
Yongjian Chen, Emma Bercich, Anna Bubley and L. James Wright

School of Chemical Sciences, University of Auckland, Auckland, New Zealand

We have synthesised the macrocyclic iron complex **1** depicted in Figure 1 and determined that it is an excellent catalyst for the oxidation of organic compounds with hydrogen peroxide in water at neutral pH and ambient temperature. The macrocyclic ligand of **1** contains two hybrid PYA/amidate donors and two sulfamidate donors [1, 2]. Analogues of **1** in which nitro-phenylene replaces the *N*-methylpyridine unit (**2**), or ethylidene replaces the *N*-methyl imido group (**3**) have also been prepared. We have studied the catalytic oxidation reactions of **1** – **3** and determined the key parameters associated with them. Our results show that **1** is superior to **2** and **3** in terms of the rate of catalyst activation, the rate of substrate oxidation by the activated catalyst and TON. Accordingly, catalytic oxidation of the surrogate pollutants Orange II and Safranine O is faster with **1** than **2** or **3**, and this is also the case for the actual micro-pollutant carbamazepine (CBZ). Even at very high dilution (nM) **1** still acts as a fast and efficient micropollutant oxidation catalyst using dilute hydrogen peroxide (μM). Under these conditions its catalytic oxidation reactions are 3-4 times faster than the current benchmark catalyst [3] and it is therefore a potential candidate for practical application in the final stages of wastewater treatment.



(1)



(2) X = C-NO_2, Y = N-CH_3

(3) X = $^+$N-CH_3, Y = $CHCH_3$

Figure 1. Oxidation catalysts

[1] Y. Chen, T. Söhnel, A. D. Ryabov, T. J. Collins, and L. J. Wright, *Inorg. Chem.* **2025**, *64*, *48*, 23436-23445. DOI: 10.1021/acs.inorgchem.5c03518

[2] T. Pfister, T. Sohnel, T. J. Collins and L. J. Wright, *Chem. Eur. J.* **2023**, *29*, e202301548. DOI: 10.1002/chem.202301548.

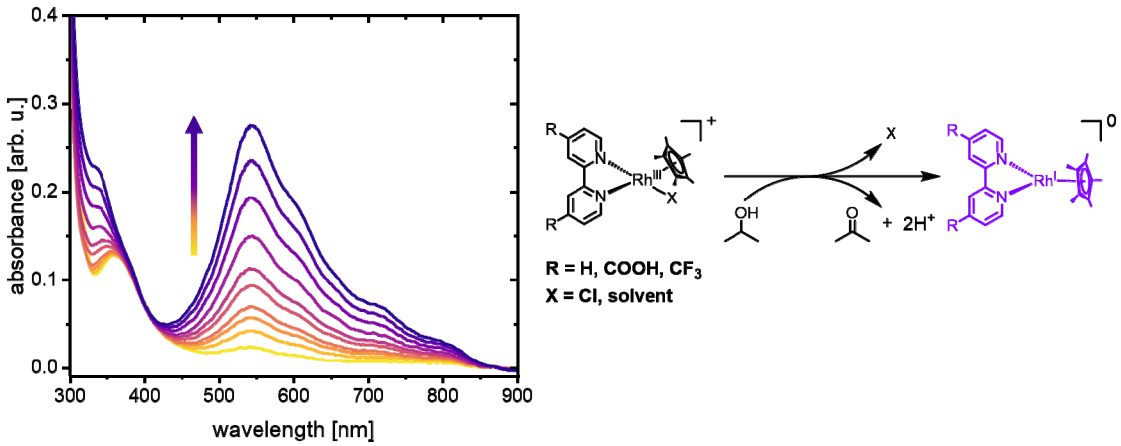
[3] G. R. Warner, Y. Somasundar, K. C. Jansen, E. Z. Kaaret, C. Weng, A. E. Burton, M. R. Mills, L. Q. Shen, A. D. Ryabov, G. Pros, T. Pintauer, S. Biswas, M. P. Hendrich, J. A. Taylor, F. S. Vom Saal, T. J. Collins. *ACS catalysis*, **2019**, *9*, 7023-7037.

RATIONAL OPTIMIZATION OF SELF-REPORTING ALCOHOL-OXIDIZING Rh^{III} COMPLEXES

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The efficient extraction of reducing equivalents from surrounding media is a fundamental requirement for the development of coupled redox systems. This research focuses on the rational optimization of α-diimine-coordinated Rh(Cp*) complexes capable of isopropanol oxidation in aqueous solutions. A central feature of these coordination compounds is their optical self-reporting property: the two-electron reduction from the Rh^{III} species to a stable Rh^{I} state is accompanied by a pronounced change in the absorption profile. This electronic transformation is characterized by the emergence of a distinct metal-to-ligand charge transfer (MLCT) transition in the UV/vis region. To elucidate the underlying structure-activity-correlations, time-resolved steady-state UV/vis spectroscopy and electrochemical analysis were employed to monitor the reaction kinetics *in situ*. A significant advancement was achieved by introducing strongly electron-withdrawing trifluoromethyl substituents (btfmb) into the ligand backbone, enabling isopropanol oxidation at neutral pH for the first time in Rh(Cp*) systems. Furthermore, the coordination environment was tuned by substituting the chloro ligand with a more labile acetonitrile (ACN) ligand. This modification enhances ligand lability and facilitates substrate coordination, thereby accelerating reaction kinetics. By combining these structural optimizations with mild thermal activation, the sub-stoichiometric conversion was successfully increased to approximately 80%. These findings establish key design principles for the implementation of Rh-based redox relays in advanced (photo)redox systems. A promising future direction is the integration of these optimized Rh units into intramolecular dinuclear architectures, which could represent an important step toward artificial photocatalysis in homogeneous solution.



[1] L. Hefty, G. Caniglia, M. Abdel-Hamied, A. K. Mengele, C. Kranz, S. Rau, 2025, DOI: 10.26434/chemrxiv-2025-78dls.

PHOTOACTIVE NEUTRAL Cu(I) COMPLEXES STABILISED BY AN ANIONIC N-HETEROCYCLIC CARBENE

L. J. Groth[a], L. E. Burmeister[b], P. R. Meinhold[a], J. P. Zurwellen[b], D. Bockfeld[a], R. Frank[a], M. Karnahl[b], S. Tschierlei[b] and M. Tamm[a,*]

[a]Institut für Anorganische und Analytische Chemie, TU Braunschweig, Germany
[b]Institut für Physikalische und Theoretische Chemie, TU Braunschweig, Germany

A prominent class of trigonal photoactive Cu(I) complexes employs N-heterocyclic carbenes (NHCs) as stabilizing (or ancillary) ligands in combination with neutral or anionic chelating donors. While cationic complexes with neutral ligands exhibit excellent photophysical properties in the solid state, their emission quantum yields (QYs) in solution typically drop below 0.1%.[1,2]

To suppress non-radiative decay pathways associated with ion pairing and mobile counter anions, we introduced an NHC decorated with a weakly coordinating anion (WCA) in the backbone, affording neutral zwitterionic congeners of the $[NHC\text{-}Cu\text{-}L]^+$ motif (Figure 1). These complexes show superior photophysical properties in solution with relatively high QYs and long excited-state lifetimes. Owing to their high excited-state energy, the complexes act as efficient photosensitizers and were successfully applied in the photocatalytic isomerization of norbornadiene to quadricyclane.[3]

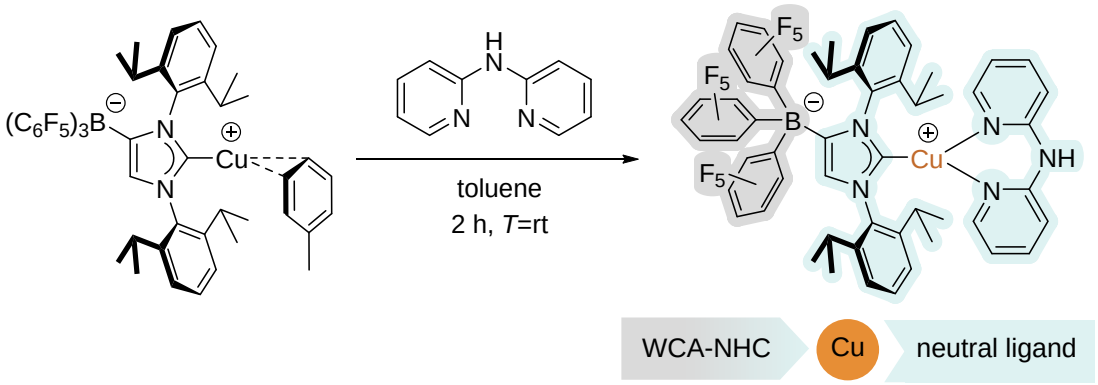


Figure 1. Synthetic strategy to access neutral complexes WCA-NHC-Cu-L.

[1] J. Beaudelot, S. Oger, S. Peruško, T.-A. Phan, T. Teunens, C. Moucheron, G. Evano, *Chem. Rev.*, **2022**, *122*, 16365.

[2] R. Marion, F. Sguerra, F. Di Meo, E. Sauvageot, J.-F. Lohier, R. Daniellou, J.-L. Renaud, M. Linares, M. Hamel, S. Gaillard, *Inorg. Chem.*, **2014**, *53*, 9181.

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A DINITROGEN-BRIDGED DIIRON COMPLEX: SYNTHESIS OF DIMETALLOTETRYLENES VIA ACTIVATION OF SILANE, GERMANE, AND STANNANE

Marco Flores, Joydeb Mondal, Gautam K. Mehta, John Kouvetakis, and Ryan J. Trovitch

School of Molecular Sciences, Arizona State University, Tempe, United States

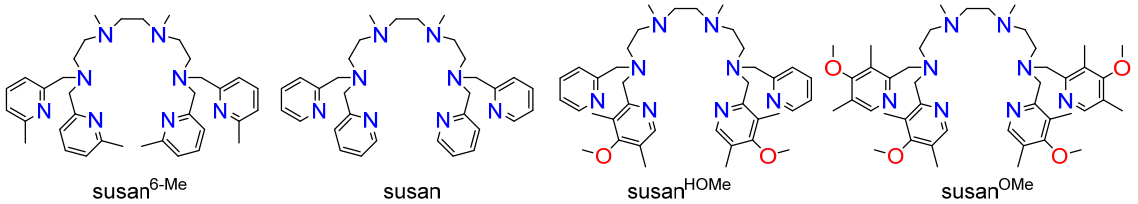
Upon adding Group 14 hydride gases to the recently prepared iron dinitrogen dimer, $[(Triphos)Fe]_2(\mu\text{-}N_2)$, a generalized methodology for the preparation of diirontetrylenes has been discovered. The all-bond activation of SiH_4 afforded the corresponding silicide, $(Triphos)(H)_2Fe{=}Si{=}Fe(H)_2(Triphos)$, which was found to feature a linear Fe_2Si core by single crystal X-ray diffraction. Activation of GeH_4 and SnH_4 by $[(Triphos)Fe]_2(\mu\text{-}N_2)$ yielded $(Triphos)(H)_2Fe{=}Ge{=}Fe(H)_2(Triphos)$ and $(Triphos)(H)_2Fe{=}Sn{=}Fe(H)_2(Triphos)$, respectively, which exhibit bent cores and extended iron-tetrel bond distances. Each dimetallotetrylene possesses *cis* iron hydride ligands that are coupled to magnetically equivalent Triphos phosphine donors in solution at ambient temperature. Computational studies revealed optimized geometries that more closely match the silicide and solution-phase structures, as well as iron-tetrel bond orders that decrease from 1.55 (Si), to 1.43 (Ge), to 1.27 (Sn) upon descending Group 14, an observation attributed to decreasing π-overlap.

GENERATION OF $Fe^{IV}Fe^{IV}$-INTERMEDIATES TO MODEL SMMO USING A DINUCLEATING LIGAND SYSTEM

Marwin Käthner and Thorsten Glaser

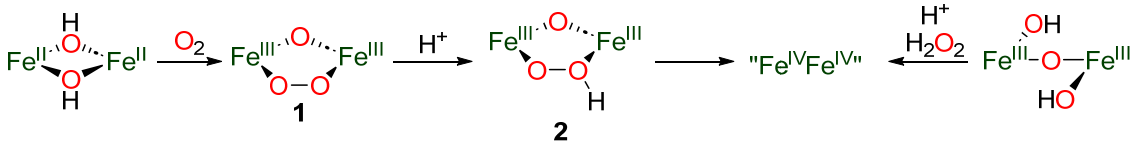
Fakultät für Chemie, Universität Bielefeld, Bielefeld, Germany

The ability of the enzyme methane monooxygenase (MMO) to activate otherwise inert C−H-bonds is of great interest for the development of new iron-based catalysts.[1] In this respect, we have developed a dinucleating ligand system with a common tetramine backbone, which allows for fine tuning of the ligands electronic properties by variation of the terminal donors.[2]



With the ligand susan$^{6\text{-Me}}$, the μ-1,2-peroxido bridged **1** can be crystallized and reversibly protonated to a μ-1,2-hydroperoxido complex **2**.[3] In contrast the analogous peroxo complex **1** of susan is reactive[4] and shows hydrogen atom transfer (HAT) reactivity.

Here we show that the more strongly donating ligands susan^{HOMe} and susan^{OMe} allow to generate several different $Fe^{IV}Fe^{IV}$ intermediates. We will present the spectroscopic characterization and reactivity investigations.



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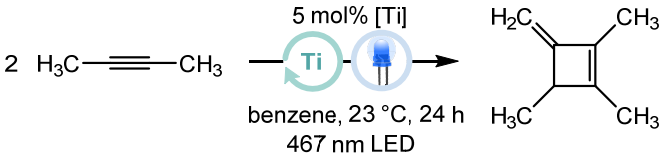
VISIBLE-LIGHT-INDUCED CYCLODIMERIZATION OF INTERNAL ALKYNES VIA TITANIUM PHOTOCATALYSIS

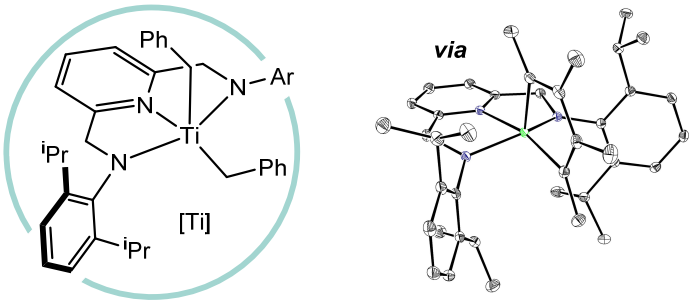
Maxi L. Heldner, Tobias Körner, Corinna Czernetzki, Patrick T. Geppert, Agniezka Nowak-Król, and Gabriele Hierlmeier

Institute of Inorganic Chemistry, Julius-Maximilians-University Würzburg, Germany

The oligomerization of alkynes is a well-known reaction in organometallic chemistry and provides useful building blocks from readily available chemicals. In the case of titanium, cyclotrimerization of terminal or internal alkynes to arenes is frequently reported.[1] Moreover, the dimerization of terminal alkynes to enynes is a well-precedented reaction.[2]

Using a pyridinediamido titanium dibenzyl complex,[3] we present the catalytic cyclodimerization of internal alkynes such as 2-butyne to afford methylenecyclobutenes. These molecules are complex building blocks containing an unsaturated four-membered ring, an exocyclic double bond and a new sp^3-hybridized carbon atom. Mechanistic investigations suggest light-accelerated formation of a titanacyclopentadiene, which is also the resting state during the reaction. Kinetic analyses give important insights into the rate-determining steps of the reaction. Additional mechanistic insights were obtained from stoichiometric reactions as well as TD-DFT calculations.[4] Additionally, the effect of heavier group 4 metals on alkyne oligomerization reactivity was investigated.





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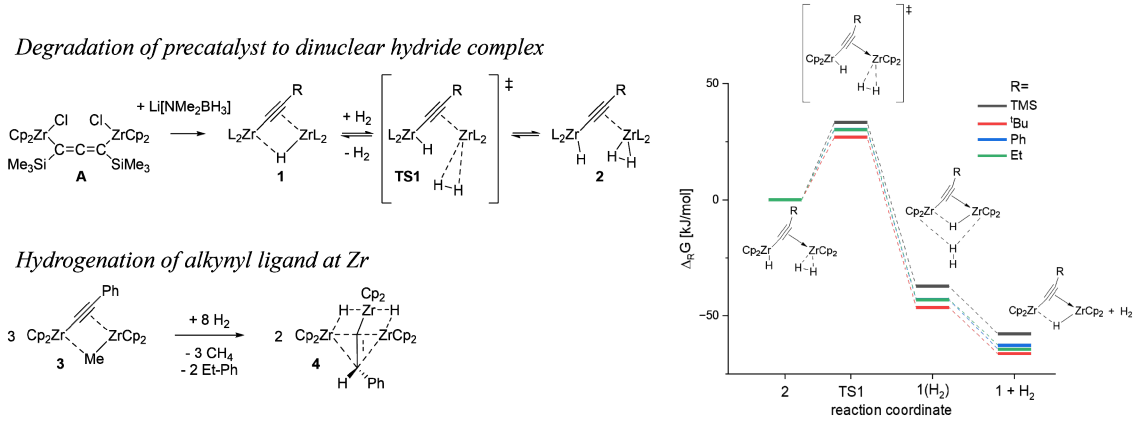
DINUCLEAR ZIRCONOCENE-HYDRIDE COMPLEXES FOR ACTIVATION OF SMALL MOLECULES

Maximilian Greiner, Fabian Reiß, and Torsten Beweries

Leibniz Institute for Catalysis (LIKAT), Rostock, Germany

In the past several zirconocene based catalysts were used to activate amine-boranes for dehydrocoupling reactions.[1] One of them is the dinuclear complex **A** leading to high conversions of $H_3B{\cdot}NMe_2H$ and $H_3B{\cdot}NMeH_2$ after addition of MeLi. In a previous study our group investigated mechanisms to explain this high activity.[2] It was found that **A** decomposes to active species **1** (with L = Cp and R = $SiMe_3$) after reaction with $Li[NMe_2BH_3]$ formed in the reaction mixture. A proposed catalytic cycle containing **1** was investigated by DFT, which revealed a relatively low activation barrier for H_2 release in the final step. Therefore, a reverse approach could be developed to use **1** for the activation of molecular H_2. In a later publication it was indeed shown that the related methyl species **3** can activate H_2 leading to full hydrogenation of the alkynyl and methyl ligands, resulting in formation of an unusual trinuclear zirconocene hydride species **4**.[3]

In the present theoretical study, the substitution pattern for L and R in **1** was systematically varied to investigate their influence on the barriers and thermodynamic properties relating to the activation of H_2. Interesting insights into the behavior of this system were obtained by DFT calculations. For instance, there is evidence for a change in reaction mechanism when bulkier ligands L come into play. Also, the influence of L and R on the formation of trinuclear species **4** was investigated *in silico*. These results set the basis for the development of new zirconocene-hydride platforms for activation of small molecules.



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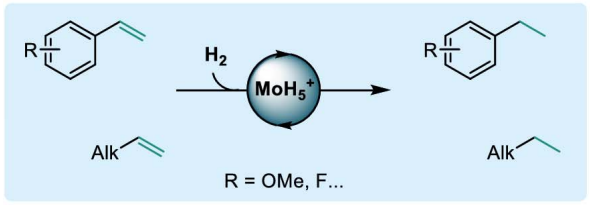
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ADDITIVE-FREE ALKENE HYDROGENATION CATALYZED BY A DIPHOSHINE-SUPPORTED PENTAHYDRIDO-MOLYBDENUM COMPLEX

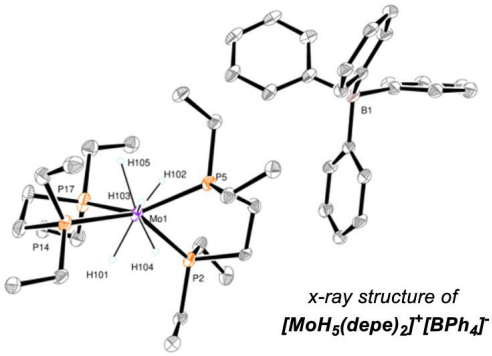
Arno Estival,[a] Michel Sigrist,[a] Nicolas Queyriaux,[a,*] Jorge J. Cabrera-Trujillo,[b,c] Nina Durvin,[a] Marie-Christine Boegli,[a] Laure Vendier,[a] Karinne Miqueu,[b,*] Antoine Simonneau[a,*]

[a]Laboratoire de Chimie de Coordination−CNRS, Université de Toulouse, France
[b]E2S-UPPA, CNRS, Université de Pau et des Pays de l'Adour, Pau, France
[c]Departamento de Química Orgánica, Universidad de La Laguna, Tenerife, Spain

Homogeneous hydrogenation is a powerful tool in organic synthesis, yet its widespread implementation is dominated by platinum group metal (PGM)-based catalysts. While these systems exhibit exceptional activity and selectivity, concerns regarding their scarcity, environmental impact, and toxicity increasingly cast doubt on their long-term sustainability.[1] This has driven the search for more sustainable alternatives, particularly hydrides derived from earth-abundant metals, a field that remains underdeveloped.



* First cationic molybdenum-catalyzed hydrogenation of alkenes
* Earth-abundant metal for sustainable catalysis
* Crucial and unusual mechanistic insights



x-ray structure of
$[MoH_5(depe)_2]^+[BPh_4]^-$

Fig. Molybdenum-catalyzed hydrogenation of aromatic and aliphatic alkenes.

In our group, we previously described the synthesis of a cationic molybdenum pentahydride complex, $[MoH_5(depe)_2]^+$ (depe = 1,2-bis(diethylphosphino)ethane), obtained by protonating its neutral tetrahydride precursor.[2] Herein, we report the first example of a cationic polyhydride molybdenum complex, showcasing broad alkene hydrogenation activity under relatively mild conditions. A mechanistic rationale is proposed, supported by kinetic studies, identification of key intermediates and DFT calculations, providing crucial insight into the distinct reactivity profile of this uncommon class of catalyst. These findings place molybdenum polyhydride complexes as promising, sustainable platforms for the development of next-generation hydrogenation catalysts.

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UNDERSTANDING VIBRATIONAL TEMPERATURE EFFECTS ON MÖSSBAUER QUADRUPOLE SPLITTING USING WIGNER SAMPLING

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^{57}Fe-Mössbauer spectroscopy is a widely utilized and powerful tool for investigating iron in various surroundings, such as bioinorganic chemistry, molecular complexes or amorphous materials. It is isotope-specific and can yield information on the spin state, oxidation state and symmetry of the coordination sphere. Quantum chemical calculations are often used to complement ^{57}Fe-Mössbauer spectroscopy for structural elucidation of the coordination spheres. A key challenge in linking theory and experiment is the temperature dependence of the experimentally obtained Mössbauer parameters, whereas the calculations formally represent the situation at 0 K.[1]

To tackle this challenge, we have developed a method based on a sampling approach to access the temperature dependent vibrational contribution to the Mössbauer parameters, especially the Mössbauer quadrupole splitting.[2] With Wigner sampling, we create an ensemble of structures mimicking the superposition of vibrationally accessible structures in the experiment. By ensemble-averaging the electric field gradient (EFG) tensor, which underpins the quadrupole splitting, a temperature dependent quadrupole splitting can be computed. A general workflow of the method is shown in **figure 1**.

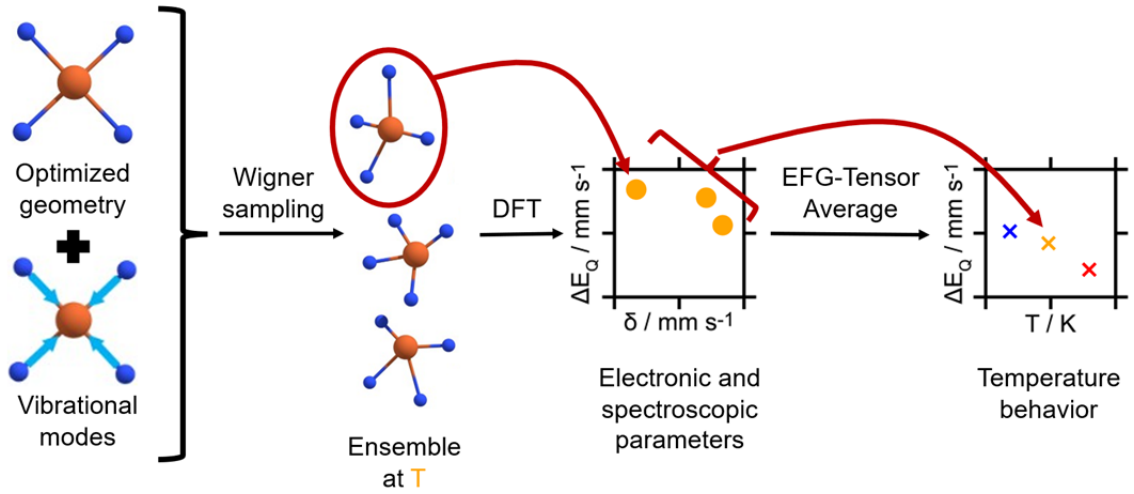


Figure 1: Workflow of our sampling-based method for predicting temperature dependent Mössbauer quadrupole splittings.

With our method, we were able to qualitatively predict the temperature behavior of the Mössbauer quadrupole splitting,[2] improving the predictive power even for low temperatures due to the incorporation of zero-point vibrations. We were able to identify vibration-induced changes in electronic structure and energetic orbital ordering as key reasons for the temperature behavior.

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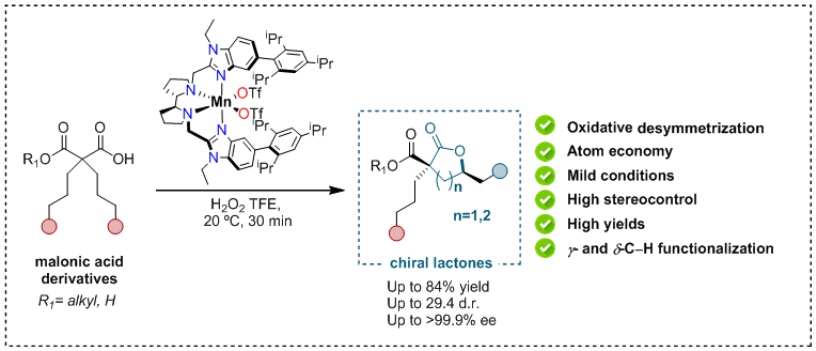
DESYMMETRIZATION OF MALONIC MONOESTERS AND MALONIC ACIDS VIA ENANTIOSELECTIVE CATALYTIC C(sp^3)─H OXIDATION

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All-carbon quaternary chiral centers are present in a *plethora* of pharmaceutical and biologically active molecules. Due to this, there is an increasing interest in the development of new and efficient catalytic methodologies for the enantioselective construction of these motifs.[1] Malonates and their derivatives rank among the best candidates as they are highly accessible starting materials with low cost. Over the last years, different approaches based on hydrolysis, reduction and addition reactions have been developed to construct chiral malonates from simple substrates.[2-4] Although the desymmetrization of malonates based on C─H bond functionalization has not been reported previously.

Leveraging asymmetric γ-lactonization can provide high stereo control in the oxidation of non-activated C─H bonds, [5] herein we proved that this reaction can be applied in the desymmetrization of homo-disubstituted malonates and diacids. The reaction provides outstanding levels of regio- and enantiodiscrimination when using sterically encumbered Mn catalysts and H_2O_2 as the oxidant. Our approach enables straightforward and general access to quaternary chiral centered scaffolds that can be valuable intermediates for the synthesis of pharmaceutical and bio-active products.



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SYNTHESIS OF MORPHOLINE DERIVATIVES FROM AMINOALCOHOLS: PALLADIUM-CATALYZED C-N AND C-O BOND FORMATION

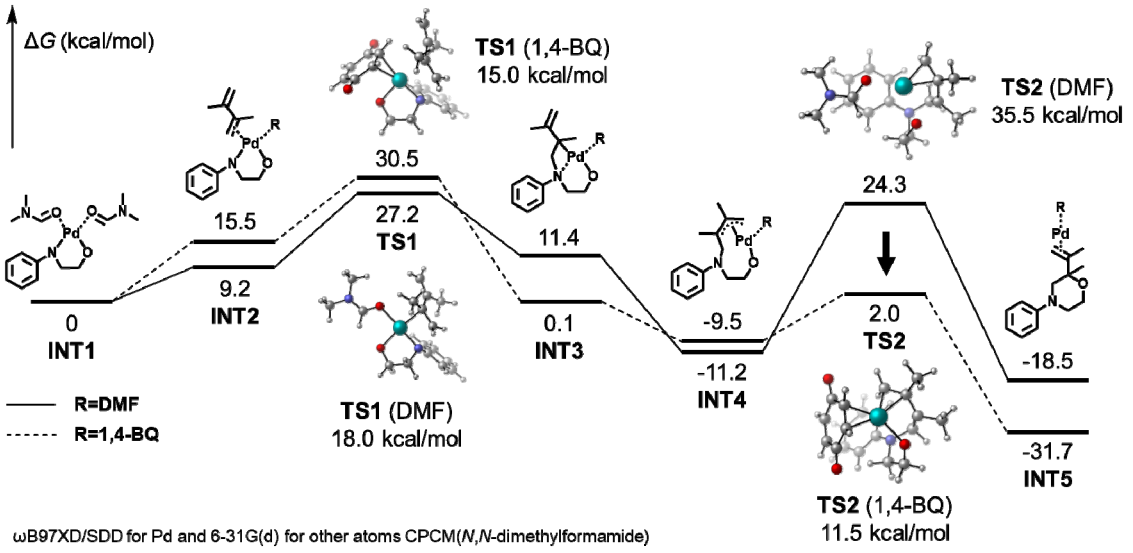
Nobuki Katayama and Yasushi Obora

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Morpholines are important heterocyclic motifs widely found in natural products and used as valuable synthetic intermediates. Metal-catalyzed approaches to morpholine derivatives have attracted considerable attention, particularly those involving intramolecular cyclization to form C–N, C–O, and C–C bonds. However, these methods often require prefunctionalized substrates and multiple steps to construct the morpholine ring, and they may generate by-products or require stoichiometric additives. Therefore, the development of simple and atom-economical methods remains highly desirable.

Metal-catalyzed intermolecular difunctionalization of 1,3-dienes represents a powerful strategy for constructing functionalized molecules [1]. As part of our ongoing studies on palladium-catalyzed difunctionalization of 1,3-dienes, we report here the aerobic synthesis of morpholine derivatives using amino alcohols [2]. This reaction enables the one-step formation of both C–N and C–O bonds on the 1,3-diene framework.

The proposed reaction mechanism is initiated by the formation of a five-membered Pd(II) complex (**INT1**), coordinated by DMF and an amino alcohol. Subsequent ligand exchange with a diene affords **INT2**, which undergoes *cis*-aminopalladation (**TS1**) to generate **INT3**. A π-allyl intermediate (**INT4**) is then formed, followed by reductive elimination (**TS2**) to yield **INT5**. DFT calculations indicate that coordination of 1,4-benzoquinone (1,4-BQ) lowers the energy barrier of **TS2** from 35.5 to 11.5 kcal/mol, suggesting that 1,4-BQ acts as a ligand to facilitate the reductive elimination step.



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UNDERSTANDING THE INFLUENCE OF EXCITED STATE DYNAMICS ON PHOTOCATALYTIC PERFORMANCE

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Despite its widespread use in synthetic chemistry, we know little more about photoredox catalysis than the sequence of electron transfers that occur, which undermines our ability to improve the efficiency of these reactions.

Heteroleptic iridium(III) complexes of the type $[Ir(C\hat{}N)_2(N\hat{}N)]^+$ (where C^N is a cyclometalated and N^N a diimine ancillary ligand, Figure 1a) are widely used as high performing photoredox catalysts. They are also known to have tuneable emission and redox properties, excellent thermal and photostability, and high phosphorescence quantum yields, making them a great candidate for mechanistic work [1].

In iridium(III) complexes, there are two accessible emissive states that are often both contributing to the emission spectra, the ^{3}MLCT state (localised on the N^N ligand) and the ^{3}LC state (localised on the C^N ligand). A recent combinatorial study of >1440 iridium(III) complexes investigated the interplay between these states, describing four excited state Types based on steady-state emission spectra (Figure 1b) [1]. Dominant ^{3}LC states are categorised as Type III and Type IV and are differentiated based on the ratio of the $Em_{0\text{-}0}/Em_{0\text{-}1}$ vibronic peaks. In this work we isolated nine of these complexes and one ^{3}MLCT complex and investigated their excited state dynamics using both spectroscopic and computational methods. We were then able to relate this to photocatalytic performance.

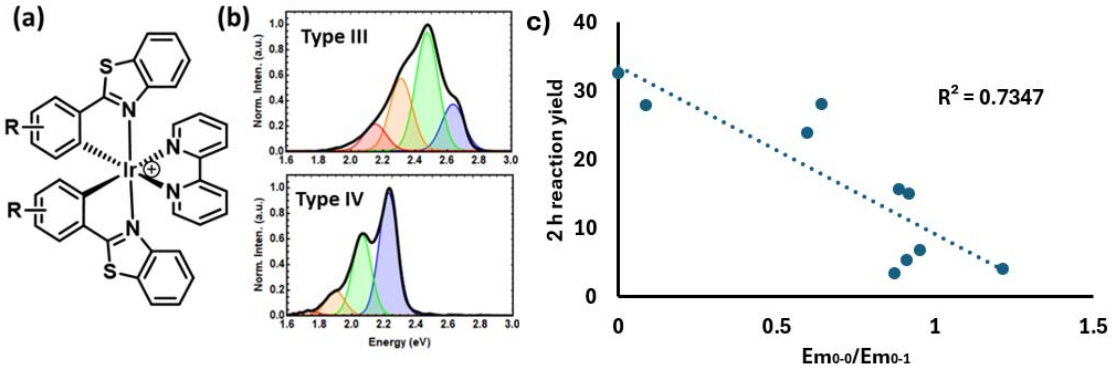


Figure 1. (a) A representative $[Ir(C\hat{}N)_2(N\hat{}N)]^+$ complex. (b) Emission spectra of Type III and IV ^{3}LC dominant excited states. (c) Plot of $Em_{0\text{-}0}/Em_{0\text{-}1}$ peak ratio and reaction yield.

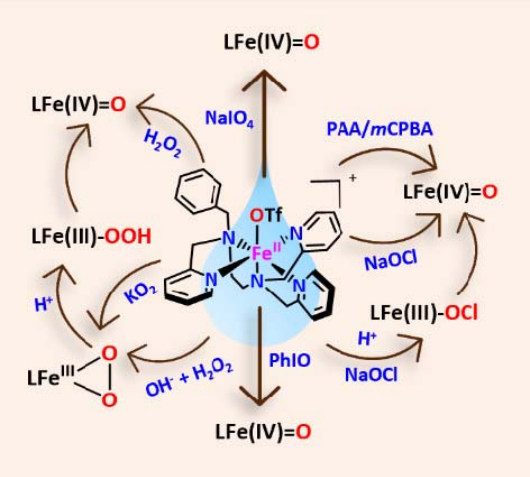
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EXPLORING THE REACTIVITY OF HIGH VALENT IRON INTERMEDIATES IN WATER

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The exceptional reactivity observed in non-heme iron enzymes can be attributed to their capability to access high-valent iron oxygen species in their active site. Numerous inorganic model complexes have been reported to date, providing insights into the intricate structural and spectroscopic features of many iron-containing enzymes and advancing our understanding of their enzymatic reaction pathways. While the reactivities of synthetic iron complexes have been evaluated using various oxidants, the investigation into the formation of reactive intermediates has primarily focused on acetonitrile. However, water, which serves as the medium in biological systems, has been less frequently employed in these studies. Motivated by this, we conducted a comprehensive study on the generation of key reactive species using various oxidants with a model complex, $[(BnTPEN)Fe(II)(OTf)]^{+}$ (**1**) (where BnTPEN = N-benzyl-N,N,N-tris(2-pyridylmethyl)-1,2-diaminoethane) in water, which yielded important findings. In water, a quantitative yield of Fe(IV)=O species was achieved with the oxidant $NaIO_4$. Additionally, we observed an equilibrium between side-on Fe(III)-OO and Fe(III)-OOH, with the latter eventually converting to Fe(IV)=O. The insights gained from this study are likely to be relevant in the chemistry of other Fe(II) complexes with polypyridyl pentadentate ligands [1].



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CONTROLLING C–H BOND ACTIVATION THROUGH EQUATORIAL LIGAND TUNING: IMPACT ON STABILITY AND THE TRIPLET–QUINTET SPIN-STATE ENERGY GAP

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Abstract: Understanding and controlling C–H bond activation by high-valent iron–oxo species remains a central challenge in oxidation catalysis and biomimetic chemistry. In this study, we systematically modulate the equatorial ligand environment of nonheme iron–oxo complexes to investigate its influence on thermodynamic stability, spin-state energetics, and reactivity toward inert C–H bonds. A series of structurally related complexes with varying donor strength and electronic properties in the equatorial plane were synthesized and computationally evaluated to establish clear structure and reactivity relationships. Spectroscopic and kinetic studies reveal that subtle changes in equatorial ligand field strength significantly alter the stability of the high valent iron–oxo and its C–H bond activation efficiency. Notably, tuning the ligand environment directly impacts the triplet–quintet energy gap, a key parameter governing two-state reactivity pathways. Complexes with reduced triplet–quintet energy separation exhibit enhanced hydrogen atom abstraction rates, consistent with facilitated spin-state crossing during the reaction coordinate. Conversely, stronger equatorial ligand fields increase thermodynamic stability but raise the spin-state barrier, leading to diminished reactivity. These findings demonstrate that equatorial ligand tuning provides a powerful strategy to engineer spin-state energetics and control the balance between stability and oxidative reactivity in nonheme iron–oxo systems. This work offers mechanistic insight into spin-state-dependent C–H bond activation and establishes design principles for developing more efficient and selective oxidation catalysts inspired by metalloenzymes.

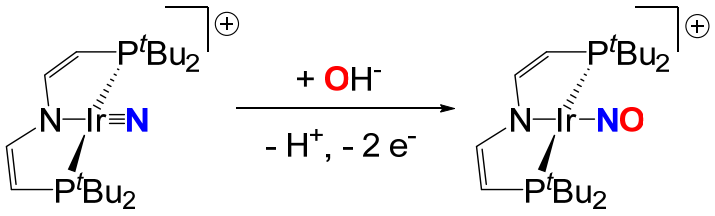
NITROGEN CENTERED AQUEOUS OXYGENATION OF AN IRIDIUM(V) NITRIDO COMPLEX

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Ammonia oxygenation is an industrially and biologically important process for the synthesis of high-valent nitrogenous compounds.[1] Early homogeneous models demonstrated the oxidation of coordinated ammonia in aqueous media to nitrosyl, and ultimately all the way to nitrate.[2] Terminal nitrido complexes were proposed as intermediates, but not isolated.[3] While the oxygenation of electrophilic nitrido ligands with O-atom transfer reagents is well known,[4] the use of water as oxygen source is rare and mechanistically not well examined.[5]

We here describe the N-centered oxygenation of an iridium(V) nitrido complex[6] upon oxidation in aqueous hydroxide solution (Scheme 1). The mechanism of N–O bond formation and associated proton-coupled electron transfer steps are discussed.



Scheme 1: Conversion of an iridium(V) nitride to the corresponding nitrosyl complex.

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SELECTIVE CATALYTIC CONVERSION OF NITRITE TO AMMONIUM BY AN OXYGEN-TOLERANT MOLECULAR COBALT COMPLEX

Rajaneesh Kumar Verma, Ankita Kumari, Amit Kumar Bera, Avijit Das, Durgesh Pandey, Dibyajyoti Ghosh*, and Sayantan Paria*

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Molecular Co complexes of a bis-pyridine-monooxime ligand (HBPML), $[Co^{III}(BPML)_2]^+$ (1) and $[Co^{II}(HBPML)Br_2]$ (2), have been synthesized and thoroughly characterized. Electrocatalytic nitrite (NO_2^-) reduction catalyzed by 1 was investigated in a 0.1 M sodium phosphate buffer solution (PBS) at pH 7, which revealed the selective conversion of NO_2^- to ammonium (NH_4^+) with 99% Faradaic efficiency and a turnover frequency of ~65 h^{-1}. Experimental investigations revealed that the initiation of the catalytic reaction begins through the coordination of NO_2^- to the Co^I site via the dissociation of one of the pyridine arms of the ligand, which makes the catalyst highly selective for the NO_2^- reduction reaction (NO_2^- RR). In fact, 1 was found inactive for the oxygen reduction reaction in PBS at pH 7, thus efficiently functioning NO_2^- RR under an oxygen atmosphere. Complex 2 is converted to 1 through a disproportionation reaction in the buffer solution and catalyzes the NO_2^- RR, implying that 2 is not capable of assisting the reduction of NO_2^- to NH_4^+. Further, theoretical investigations have been performed to understand the reaction mechanism. The detailed reaction mechanism of the NO_2^- RR has been demonstrated by combining experimental observations and in-silico studies. Overall, the study underscores the significance of ligand design aspects on the electrocatalytic reduction of NO_2^- to NH_4^+ by a molecular Co complex.

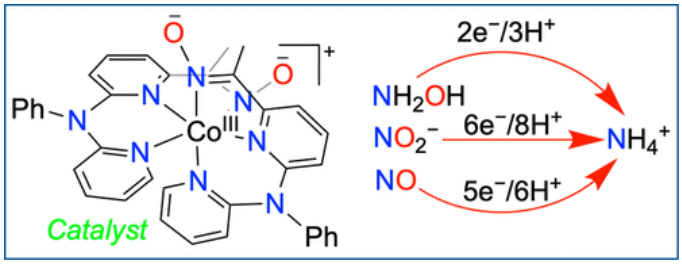


Figure. Electrocatalytic nitrite reduction to ammonium by molecular cobalt complex in phosphate buffer.

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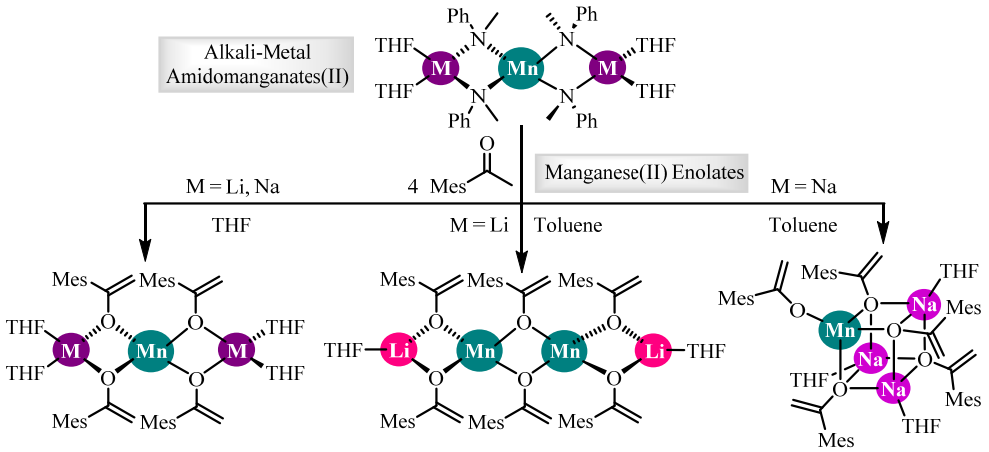
STRUCTURE AND REACTIVITY OF NOVEL MANGANESE(II) ENOLATES FORMED VIA ALKALI-METAL AMIDOMANGANATES(II)

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[b]School of Chemistry, University of Edinburgh, Edinburgh, UK

Bimetallic mixtures have become more established as alternative reagents to circumvent restraints of main group organometallics, with synergistic effects operating to enable enhanced reactivity not evident in the equivalent single metal systems [1]. In particular, alkali-metal manganates(II) are promising candidates capable of promoting direct Mn-H exchange of weakly activated molecules such as benzene [2], Mn-I exchange of aryliodides followed by oxidative C-C homocoupling [3] and catalytic hydroamination of styrenes [4]. Starting from commercially available reagents, we have recently demonstrated that lithium tetra(alkyl) manganate(II) $[(TMEDA)_2Li_2Mn(n\text{-}Bu)_4]$ [5, 6] can be used *in situ* for the general and efficient synthesis of a new series of lithium amidomanganates(II) by direct deprotonation of parent amine [6].

Building upon our previous work, this poster illustrates a direct alkali-metal exchange approach using heavier alkali-metal alkoxides to afford a family of alkali-metal *n*-methylanilide manganates(II), providing insight into structural differences invoked by the alkali-metal. Exploring their use as bases towards enolisable ketones, we present the preparation of the first structurally characterized Mn(II) enolates where the alkali-metal and solvent dictate the constitution and structure of the resulting complex (Scheme 1). Reactivity of Mn(II) enolates towards electrophiles has also been evaluated.



Scheme 1. Direct deprotonation of 2',4',6'-trimethylacetophenone with alkali-metal manganates(II) $[(THF)_4M_2Mn(N(Me)Ph)_4]$ (M = Li, Na) to afford Mn(II) enolates.

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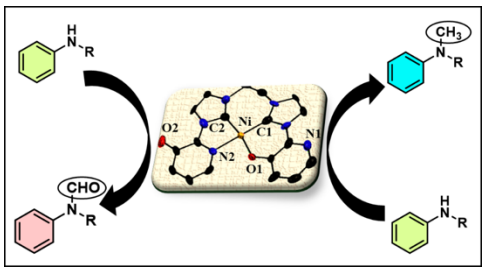
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SQUARE PLANAR CHIRAL Ni(II)-IMIDAZOLE-2-YLIDENE-PYRIDONATE CATALYSED CO_2 REDUCTION: PATHWAY TO SELECTIVE N-FORMYLATION OF AMINES TO N-FORMAMIDES AND N-METHYLAMINES

Rhitwika Chowdhury and Ganapathi Anantharaman*

Department of Chemistry, Indian Institute of Technology (IIT), Kanpur

The design and application of late transition N-heterocyclic carbene(NHC)-based catalytic systems, such as bidentate multifunctional NHC ligands incorporating an additional N- or O-donor site, have emerged as versatile platforms as they unite normal(or abnormal) carbene donors with hemilabile N/O coordination sites, which are able to stabilize various metals, which in turn enables various catalytic pathways.[1-3] Given this versatility, the conversion of CO_2 into valuable chemicals represents a sustainable approach to carbon utilization.[4] Among various strategies, reductive *N*-functionalization of amines provides direct access to *N*-formamides and *N*-methylamines, both of which are key intermediates in the chemical and pharmaceutical industries.[5] In this study, we present the synthesis of a tetradentate hydroxypyridine-functionalized NHC ligand and its corresponding distorted square-planar nickel(II) complex. The complex Ni(II) centre is coordinated through two carbene carbons, a pyridine nitrogen, and a pyridinoxy oxygen atom, forming a stable framework with high catalytic efficiency. This complex shows remarkable activity for amine functionalization using CO_2 as a renewable C1 source, selectively affording either *N*-formylated or *N*-methylated products by tuning reaction conditions such as temperature, pressure, and solvents. Importantly, this system replaces traditional toxic reagents like carbon monoxide and formaldehyde while demonstrating a broad substrate scope. These results highlight the potential of Ni(II)-NHC complex as a versatile catalyst for sustainable amine functionalization.



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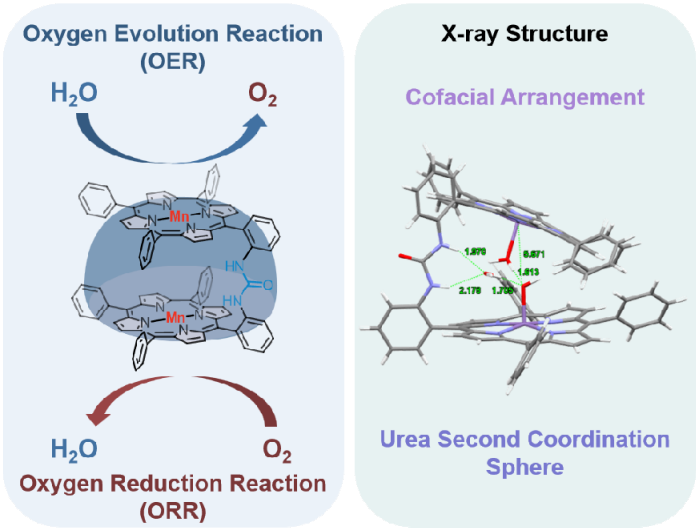
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COFACIAL MANGANESE PORPHYRIN FOR OXYGEN EVOLUTION AND OXYGEN REDUCTION

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Cofacial bimetallic architectures provide a valuable platform for probing cooperative effects in coordination chemistry, particularly in multi electron oxygen transformations. Herein, we report a structurally well-defined urea bridged cofacial manganese porphyrin that enforces a face to face geometry between two metal centers. This arrangement enables intramolecular metal-metal interactions, while the urea linker introduces hydrogen bonding functionality that facilitates proton coupled processes. The complex exhibits bifunctional reactivity toward oxygen evolution and oxygen reduction reactions, serving as a molecular model for studying multi electron oxygen chemistry. Combined spectroscopic investigations (UV–vis, IR, resonance Raman, and EPR) reveal key intermediates and support a cooperative bimetallic mechanism involving metal-metal interactions and proton-coupled electron transfer. This work highlights the role of second sphere interactions and spatial confinement in modulating reactivity in bimetallic coordination systems.



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LEWIS ACID PROMOTED IRON-CATALYZED SELECTIVE OXYGENATION OF ALKENES WITH H_2O_2: INSIGHTS INTO THE ROLE OF SUPPORTING LIGANDS

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The development of sustainable catalytic methods for the selective oxygenation of alkenes remains an important objective in oxidation chemistry.[1] In that pursuit, numerous iron-based complexes that promote the oxygenation of C=C bonds with peroxides have been developed.[2] The catalytic activity and product selectivity (epoxide vs. diol) of the iron complexes have been reported to depend on several factors, including the iron complex's spin state and geometry, as well as the use of additives.[3] Our recent study showed that a ligand-free iron salt combined with $Sc(OTf)_3$ in acetonitrile efficiently catalyzes alkene epoxidation with H_2O_2 under mild conditions.[4a] An iron(II)-scandium(III) triflate complex formed in the reaction mixture activates hydrogen peroxide, yielding a metal-based oxidant, thereby suggesting a mechanism distinct from Fenton chemistry.

To understand the influence of ligands in H_2O_2-dependent oxidation of alkenes, we have explored the activity iron(II) complexes of two N4 ligands, TPA (tris(2-pyridylmethyl)amine) and $6Me_3TPA$ (tris(6-methyl-2-pyridylmethyl)amine), in the presence of $Sc(OTf)_3$. Earlier reports indicate that the low-spin Fe(II)-TPA complex affords a mixture of epoxide and diol, whereas the high-spin Fe(II)-$6Me_3TPA$ complex selectively forms the cis-diol product; the two catalysts involve distinctly different active iron-oxygen oxidants.[3] In contrast, we found that in the presence of $Sc(OTf)_3$, both complexes exclusively yield epoxide. Additionally, Fe(II)–TPA promotes aromatic C-H hydroxylation.[4b] The role of the Lewis acid in directing the epoxidation of alkenes, irrespective of the nature of the supporting ligand, along with mechanistic insights into the reaction pathway, will be presented in this poster.

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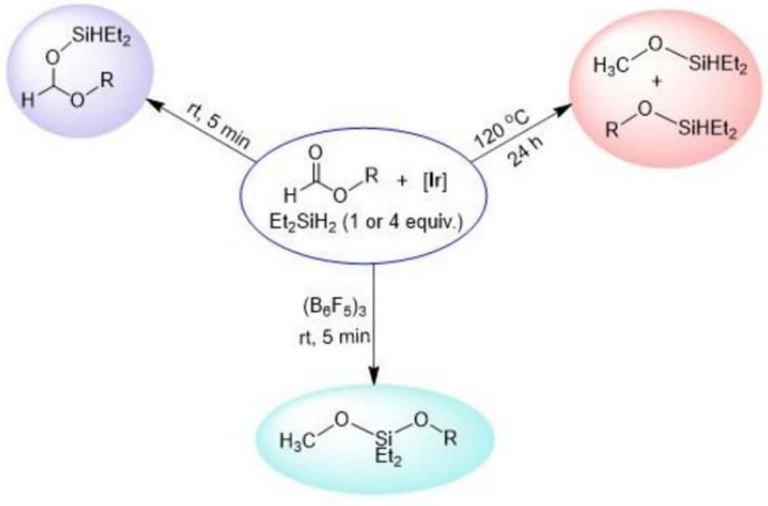
TUNABLE SELECTIVITY IN IRIDIUM-CATALYZED HYDROSILYLATION OF CO_2-DERIVED ALKYL FORMATES: ACCESS TO SILYLACETALS, ALKOXYSILANES, AND BIS(ALKOXY)SILANES

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The catalytic reduction of CO_2-derived feedstocks into value-added C1 building blocks remains a central challenge in sustainable chemistry.[1] Alkyl formates (HCO_2R), readily obtained from CO_2 hydrogenation in the presence of alcohols, are attractive substrates in this context, as their selective reduction can give access to several useful organosilicon products depending on the depth of C=O and C–O bond cleavage.[2] Their reduction, however, can give several different products, and controlling which form is usually difficult.[2]

Here we report that the hydrosilylation of alkyl formates with Et_2SiH_2 can be steered toward three distinct products simply by tuning the catalyst and reaction conditions. Using an iridium pincer complex at room temperature (5 min, 1 equiv. silane), the reaction stops cleanly at the silylacetal stage, with both oxygens bearing – $SiHEt_2$ groups on a common carbon. Raising the temperature to 120 °C with excess silane (4 equiv., 24 h) pushes the reaction to full deoxygenation, cleaving both C–O bonds to deliver the two corresponding alkoxysilanes ($H_3CO–SiHEt_2$ and $RO–SiHEt_2$). In contrast, switching to $B(C_6F_5)_3$ as a main-group catalyst at room temperature affords the unsymmetrical bis(alkoxy)silane $H_3CO–SiEt_2–OR$ in 5 minutes.



Scheme 1. Catalyst-controlled divergent hydrosilylation of alkyl formates with Et_2SiH_2.

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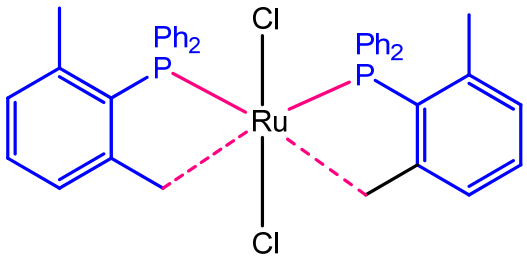
CYCLOMETALATED RUTHENIUM(II) CATALYSTS FOR ESTER HYDROGENATION

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Cyclometalated ruthenium chemistry has progressed remarkably since the pioneering 14-electron "**butterfly**" **Ru(II)**[1] framework first revealed the power of metal–ligand cooperation. Our work builds on this foundation through the synthesis and full characterization of new cyclometalated ruthenium complexes bearing acetate and pivalate ligands. Developing these systems required years of persistence, careful optimization, and deep experimental commitment, reflecting the real challenges of advancing organometallic chemistry. The resulting complexes provide a clear and reliable platform for studying reactivity and were applied to the selective hydrogenation of esters and triglycerides[3] under mild in-situ conditions. Their performance was evaluated alongside Baratta's[2] established system, with Ru–MACHO as an external benchmark. Under optimized conditions (S/C = 10 000, 27.5 bar H_2, 16 h), our complexes show competitive activity and demonstrate how subtle ligand variations shape ruthenium-mediated hydrogenation.





Ru-1

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ELECTRIFYING BIOINSPIRED OXIDATION CATALYSIS

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Developing selective C–H oxidation methods is a central challenge in organic chemistry, as they enable increased functional group diversity in synthetic routes. Traditional approaches, however, often suffer from poor selectivity, limited functional group tolerance, and low atom economy due to the use of toxic stoichiometric oxidants. Enzymes overcome these bottlenecks by catalyzing such reactions via high-valent metal–oxo species, which have inspired the design of synthetic analogues.

This work explores electrochemical strategies for the generation of high-valent metal–oxo intermediates and their application in the selective oxidation of unactivated C–H bonds. By combining bioinspired catalyst design with electrochemical and mechanistic studies, this approach aims to leverage proton-coupled electron transfer (PCET) reactivity to establish a scalable and sustainable platform for oxidative transformations powered by electricity as an alternative redox input, using H_2O as the source of protons and electrons.

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QUINOLINE-BASED IODINE(I) COMPLEXES AS EFFICIENT IODINATION REAGENTS

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The development of efficient halogenation reagents is of significant interest in organic synthesis. To date, iodine(I) complexes have been largely dominated by homoleptic N-heterocyclic cations such as $[I(pyridine)_2]BF_4$ (Barluenga's reagent).[1] This study reports the synthesis and characterization of a new series of homoleptic and heteroleptic iodine(I) carboxylate complexes based on quinoline and various 7-substituted derivatives as ligands (Fig. 1). Single-crystal X-ray diffraction (SCXRD) analysis reveals that the heteroleptic complexes exhibit pronounced steric strain, resulting in the longest I···N bond lengths observed in any iodine(I) complex to date.[2,3] These elongated bonds indicate a weakly bound nitrogen donor and suggest a direct link between coordination geometry and reactivity.

Comparative iodination studies using antipyrine as a substrate demonstrated that the heteroleptic complex, quinoline-stabilized iodine(I) 2,3,4,5,6-pentafluorobenzoate, serves as a superior reagent. It achieved comparable yields to Barluenga's reagent, yet completed the reaction in a fraction of the time. Furthermore, this heteroleptic O···I···N complex significantly outperformed its homoleptic $[N···I···N]^+$ analogue in both solution-phase and solvent-free mechanochemical protocols. These findings mark the first instance of a heteroleptic iodine(I) complex surpassing the reactivity of both its homoleptic analogue and Barluenga's reagent (often seen as the industry standard), highlighting the potential of this new class of iodination reagent.

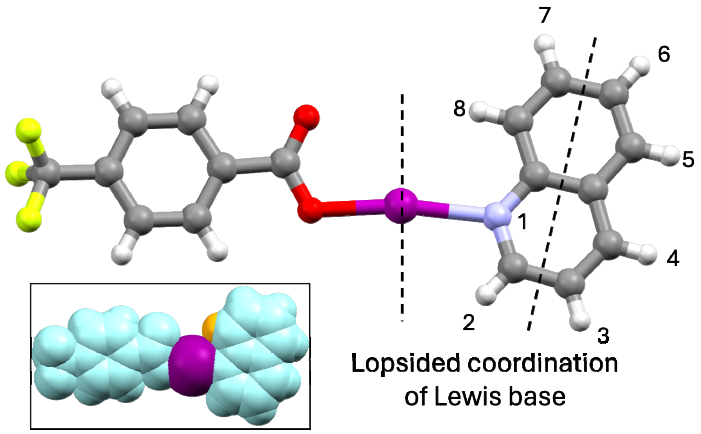


Fig. 1: The solid-state structure of $4\text{-}CF_3C_6H_4C(O)O···I···$(quinoline) as determined by SCXRD,[2] highlighting the lopsided coordination of the quinoline (with substituent numbering for the quinoline ligand included). Inset: block-colored spacefill representation of the same complex showing the steric strain between the iodine atom (purple) and quinoline hydrogen atom in the 8-position (orange).

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Rh(I) (DIPHOSPHINE) CATALYSED DEHYDROPOLYMERISATION OF AMINE BORANES: SELECTIVITY CONTROL THROUGH SECONDARY COORDINATION SPHERE EFFECTS

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The isovalence electronic analogy between B-N and carbon-based compounds and the expanding interest in polymeric materials based on main-group elements makes boron-nitrogen based polymers interesting targets. B-N polymers are promising materials for applications as preceramics or as nonlinear optical materials.[1] Catalytic dehydropolymerisation of amine boranes provides a promising atom efficient route to access these polymers that allows to adjust polymer properties.[2] In 2010, the Manners group demonstrated that primary amine-borane adducts can be dehydrocoupled by various transition metal complexes to afford linear poly(aminoboranes).[3] Recently, we also reported the use of late transition metal pincer complexes for dehydrocoupling and dehydropolymeristaion of amine boranes.[4] Cationic Rh(I) diphosphine complexes were first studied by the Weller group and showed good activity for the dehydropolymerisation of $H_3B{\cdot}NMeH_2$.[5]

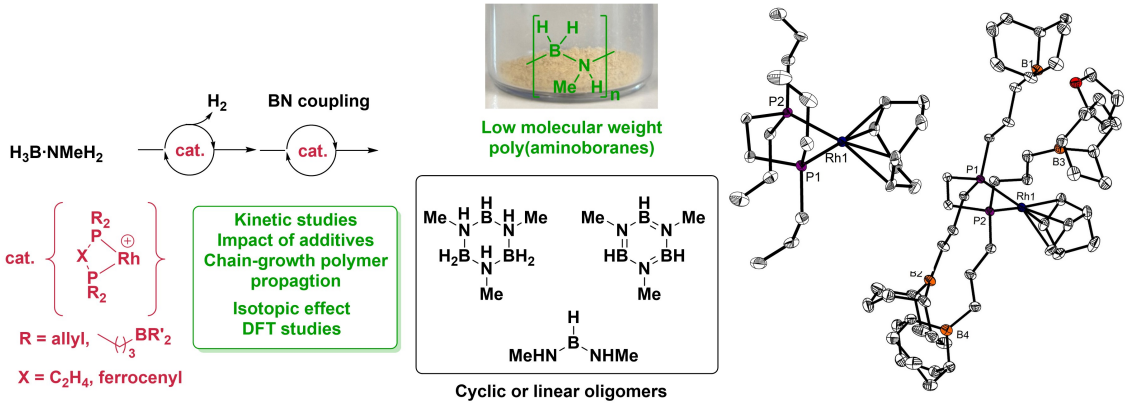


Figure 1: Dehydropolymerisation of methylamine borane, $H_3B{\cdot}NMeH_2$, using Rh(I) complexes.

Here, we report a new set of cationic Rh(I) diphosphine complexes bearing functional phosphine ligands with potential for binding the amine borane during dehydrocoupling or dehydropolymerisation (Figure 1). The structure of the diphosphine ligand affects the selectivity of the reaction, giving the desired poly(aminoboranes) or cyclic and linear oligomers, respectively.

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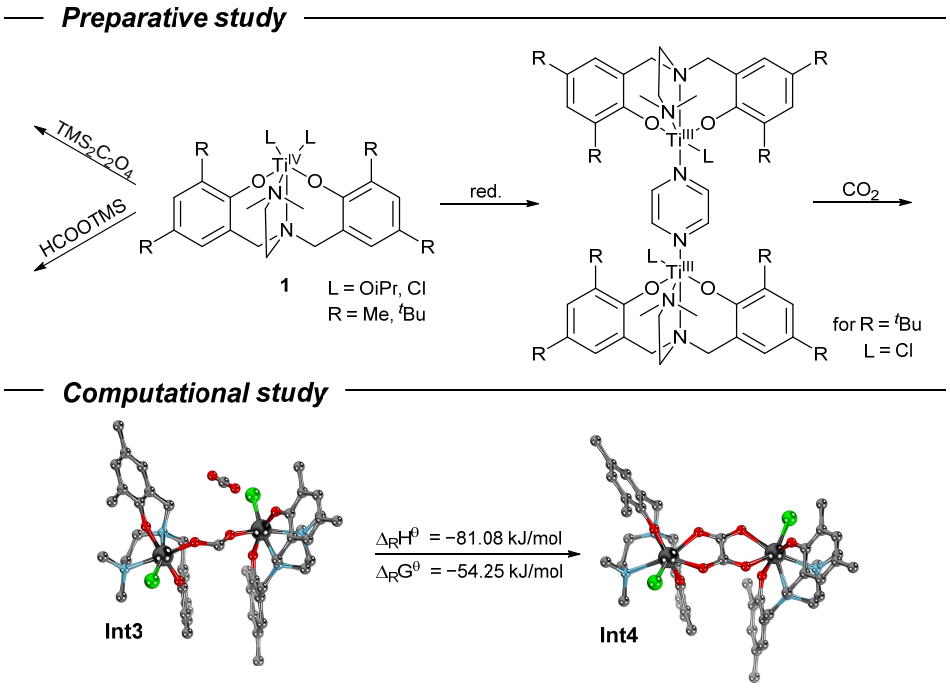
Ti(III/IV) AMINO BISPHENOLATE COMPLEXES: REACTIVITY TOWARDS OXALATE AND RELATED COMPOUNDS

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The global greenhouse effect is one of the main challenges of our society. The reductive coupling of CO_2 to C_{2+} compounds could offer an opportunity for using this greenhouse gas. The formation of oxalate from CO_2 represents the simplest form of direct reductive coupling. Early transition metal complexes carrying amine bis(phenolate) ligands are already known as catalysts for polymerisation of α-olefins and their ability to create very narrow molecular weight distributions.[1] Due to the presence of a relatively flexible pendant amine donor, amino bis(phenolate) complexes are an interesting type of compounds for binding and activating CO_2, whereas the Ti(III/IV) redox pair is known for small molecule activation involving one electron processes.[2]

To understand the coordination of possible reduction products and to find a pathway for the reductive coupling of CO_2 to oxalate we investigated the reaction of the corresponding Ti chloride and isopropoxide complexes with oxalate and related compounds simultaneously via synthetic and computational studies. Ti(III) and Ti(IV) amino bis(phenolate) complexes of the type **1** are easily achievable via a simple Mannich reaction, followed by reaction with an appropriate Ti precursor.[3]



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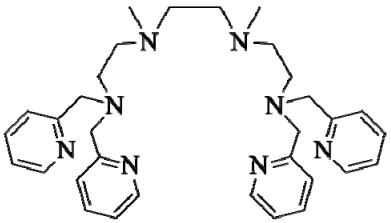
PREVENTION OF THE CAGE ESCAPE IN OXIDATION CATALYSTS

Sofie Gierke, Delia Hagemann, and Thorsten Glaser

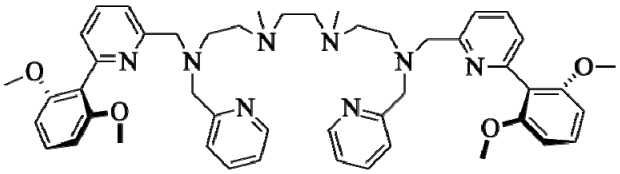
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The enzyme methane monooxygenase (MMO) oxidizes methane with O_2 to methanol under physiological conditions and is the raw model for the catalytic oxidation of not-activated C–H bonds.[1] The industrial cyclohexane oxidation uses harsh reaction conditions and provides only low yields.[2] Therefore, new catalysts based on the MMO are of interest.

We have developed a family of ligands based on MMO to generate oxidation catalysts.[3] Using the ligand susan, we have obtained an electrophilic μ-1,2-peroxo diferric complex.[4] Studies of the cyclohexane oxidation showed a radical pathway, whereby the resulting cyclohexyl radical leaves the binding pocket (cage escape) and undergoes other reactions with for example molecular O_2. To introduce a substrate binding pocket for preventing cage escape, we thought to add sterically demanding 2,6-dimethoxyphenyl-substituents (DMP) leading to the ligand susan^{HDMP}. Synthesis of ligand and complex and initial catalytic experiments will be presented.



susan



susan^{HDMP}

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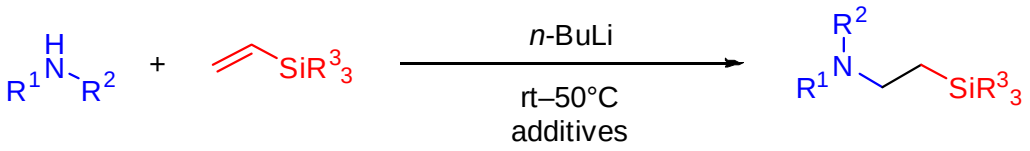
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SELECTIVE HYDROAMINATION OF STRAINED AND SILYL ALKENES

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Intermolecular hydroamination is an atom-economic strategy for C–N bond formation, yet achieving mild and selective intermolecular variants remains challenging [1,2]. We report an efficient base-catalyzed protocol employing low loadings of *n*-BuLi under mild conditions. Vinylsilanes react smoothly with secondary amines to give β-amino-substituted silanes with exclusive anti-Markovnikov selectivity. More than 20 structurally diverse products were synthesized in good to excellent yields, demonstrating broad substrate scope and operational simplicity. Beyond vinylsilanes, strained olefins such as norbornene exhibit promising reactivity [3]. Building on previously established studies within our group, *ortho*-terphenoxide yttrium complexes are being further investigated as alternative catalytic systems for the intermolecular hydroamination of vinylsilanes, and the present work aims to systematically extend and deepen these findings [4]. In parallel, the influence of additives on reactivity and regioselectivity is examined. Particular emphasis is placed on the selective synthesis of 1,4-azasilanes, pharmaceutically relevant motifs accessible under the developed mild conditions. Overall, this work establishes a practical and regioselective platform for intermolecular hydroamination, enabling streamlined access to functionalized organosilicon amines.



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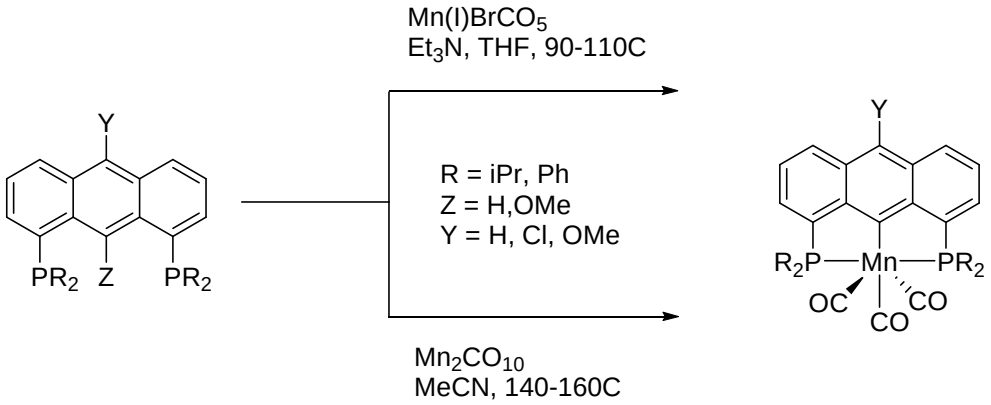
PREPARATION OF Mn(I)-PC(sp^2)P COMPLEXES VIA ONE STEP Ar-H AND Ar-OCH$_3$ BOND ACTIVATION

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Utilization of abundant, cheap and environmentally friendly 1st row transition metals (TMs) in organometallic catalysis has been a main goal of the last three decades as alternatives to the comparatively expensive and toxic late TM complexes. [1,2] Finding new pathways for synthesizing 1st row TM complexes increases our arsenal in the search for viable catalytic candidates. Furthermore, it strengthens our understanding of the chemical behavior of 1st row TMs.

In this work, we present our ongoing research into the one-step synthesis of anthracene-based Mn(I) complexes through two synthetic pathways: (a) activation of Ar-H bonds in the presence of a mild base; (b) the previously unreported activation of an Ar-OCH$_3$ bond with concurrent complexation with Mn(0). These complexes have been characterized by NMR, IR and X-ray crystallography. In addition, their redox properties were studied using CV and UV-Vis techniques.



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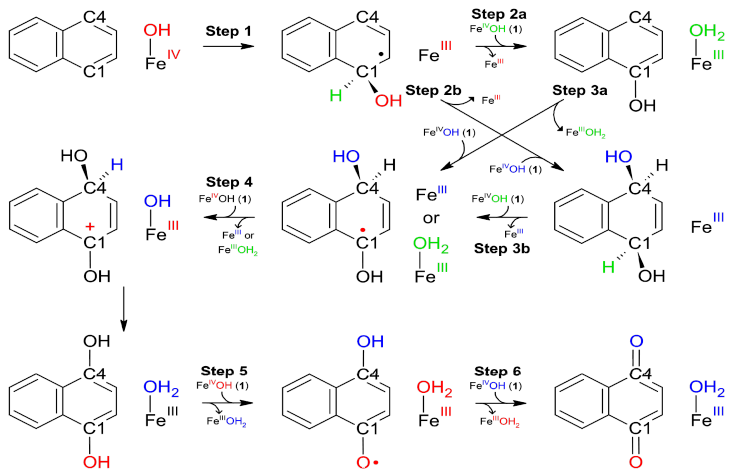
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COMPUTATIONAL MAPPING OF THE SIX-ELECTRON NAPHTHALENE OXIDATION PATHWAY BY HIGH-VALENT IRON(IV)-OXO INTERMEDIATES

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Understanding how high-valent iron-oxo intermediates oxidize inert aromatic substrates remains a central challenge in coordination chemistry and bioinspired oxidation catalysis. Here, density functional theory calculations were employed to define the reaction mechanism for the six-electron oxidation of naphthalene to 1,4-naphthoquinone by a heme-supported Fe(IV)–oxo system under experimentally relevant acidic conditions. The calculations show that a neutral Fe(IV)=O model does not catalyze the reaction, whereas the protonated Fe(IV)–OH porphyrin model provides an energetically accessible reaction pathway. The preferred mechanism proceeds through sequential hydroxyl-transfer and hydrogen-transfer steps across multiple spin states, ultimately accounting for the complete oxidation of naphthalene to 1,4-naphthoquinone. The computed energy landscape explains the experimentally observed kinetic isotope effect and electrophilic reactivity pattern, and identifies protonation of compound II as critical for productive aromatic oxidation. These results provide a computationally grounded mechanistic framework for arene oxidation by high-valent iron intermediates and offer design insight for future oxidation catalysts based on coordination-controlled proton and electron transfer. [1].



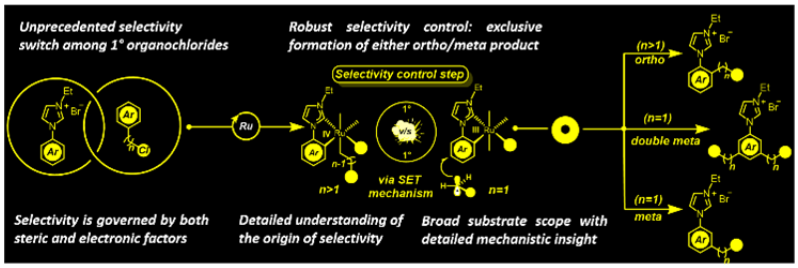
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SUBSTRATE-CONTROLLED SELECTIVITY IN SET-ENABLED C–H ALKYLATION OF *N*-ARYL AZOLIUM SALTS WITH PRIMARY ORGANOCHLORIDES: MECHANISTIC INSIGHTS INTO LIGAND-DEPENDENT REACTIVITY

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Substrate-dependent site selectivity provides a powerful approach for constructing structurally diverse molecules with broad synthetic utility. Present study unveils an unprecedented reactivity pattern of primary organochlorides, manifesting divergent selectivity between radical rebound and direct radical attack pathways, and thereby enabling Ru-catalyzed site-selective functionalization of *N*-aryl azolium salts without the need of any phosphine or carboxylate additives. Comprehensive mechanistic insight reveals that benzylation proceeds *via* a single-electron transfer (SET) mechanism under a Ru(II/III) redox regime, giving exclusive *meta*-selectivity, while the alkylation engages a SET-enabled Ru(II/III/IV)-manifold[1] with a radical rebound mechanism[2] to furnish the *ortho*-functionalized product. Electron paramagnetic resonance (EPR) spectroscopy identifies the distinct Ru(III) intermediates for each pathway while, the density functional theory (DFT) calculations clarify the origins of selectivity. Overall, the variations in organochloride chain length dictate the *ortho vs meta*-selectivity[3] through synergistic steric and electronic tuning of the ligand environment around the Ru-center, as endorsed by the radical Fukui index and percent buried volume analysis.



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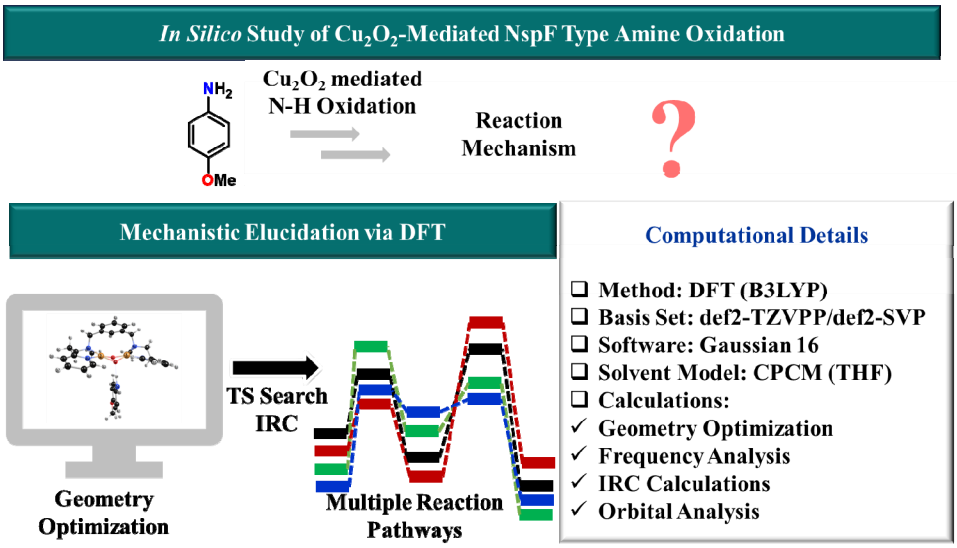
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MIMICKING NATURE'S NspF COPPER ENZYME: A MECHANISTIC STUDY OF Cu_2O_2-MEDIATED AMINE OXIDATION

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NspF is a coupled binuclear copper enzyme that catalyzes the oxidation of aminophenols to nitrosophenols[1]. Herein, we investigated the oxidation of aminophenol using a NspF-based biomimetic model containing a $[Cu_2O_2]^{2+}$ core by DFT calculations, experimentally studied by Karlin and coworkers[2]. To the best of our knowledge, no detailed mechanistic study for aminophenol oxidation mediated by a Cu_2O_2 core has been reported. Our calculations show that the reaction is initiated by O−O bond cleavage of the Cu_2O_2 unit through electron transfer from the nitrogen lone pair of aminophenol to the σ*(O-O) antibonding orbital. The next step involves proton transfer from aminophenol to the dicopper core, generating a μ-oxo-μ-hydroxo dicopper intermediate. This intermediate subsequently reacts with a second aminophenol molecule, which undergoes electron transfer followed by barrierless proton transfer to form a stable bis-μ-hydroxo dicopper core. Coupling of the two NH groups then leads to the formation of an NH-NH (hydrazine-type) intermediate. Finally, proton transfer from both NH groups to the two μ-hydroxo ligands produces an N=N intermediate along with two water molecules. The active catalyst is regenerated upon reaction with molecular dioxygen. These results provide a detailed and energetically feasible pathway for N-H oxidation of aminophenol mediated by a Cu_2O_2-based biomimetic model, offering computational insights into the reactivity of NspF and the development of related biomimetic oxidative systems.



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PSiP LIGAND DESIGN TOWARD MAIN GROUP–TRANSITION METAL PLATFORMS FOR CO_2 TRANSFORMATION

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PSiP pincer complexes of Group 10 metals are typically accessed through Si–H oxidative addition, forming square-planar d^8 silyl hydride species.[1,2] While effective, this pathway significantly limits the choice of metal precursors, particularly in the case of Ni(II), where the high reactivity required for Si–H activation can be problematic, particulary for mononuclear complex.

With this in mind, we designed a new family of rigid bis(diphosphine)silyl ligands [PSiP] (1–3) aimed at enabling an alternative route to metal coordination. By modifying the ligand backbone, our general strategy focuses on promoting Si–H deprotonation instead of oxidative addition, thereby providing access to Si–M–X motifs under milder and more flexible conditions. The ligands were obtained through a modular synthetic approach and fully characterized spectroscopically, including identification of the corresponding lithiated intermediates.

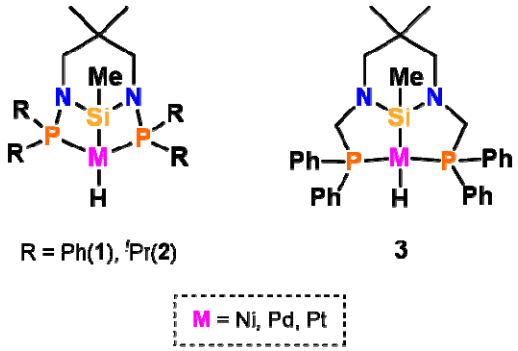


Fig 1. Ligands [PSiP] **1-3**.

Preliminary coordination studies were performed with Group 10 metals as a strategy towards new types of PSiP-supported transition metal complexes that can be difficult to access through oxidative addition pathways.

Beyond structural interest, these systems show promise as platforms for the reductive hydroboration of CO_2[3], offering a new approach to generating reactive metal–silyl environments relevant to catalytic small-molecule transformations[4-6].

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SYNTHESIS AND CHARACTERIZATION OF MOLYBDENUM(II) COMPLEXES FOR CO_2-INSERTION

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This work focuses on fundamental research on earth abundant and inexpensive homogeneous molybdenum complexes for catalytic applications. The study commenced with the synthesis of cationic Mo(II) allyl complexes of the type $[MoL(allyl)MeCNCO]^+$ bearing two different counter anions, $[BF_4]^-$ and $[BArF_{24}]^-$. The complexes were prepared via oxidative addition of allyl chlorides to the neutral $Mo(CO)_6$ precursor. Inspired by the growing success of redox non-innocent ligand L frameworks in catalysis, a series of terpyridine and bipyridine ligands was synthesized and coordinated to molybdenum.[1] The resulting complexes were thoroughly characterized, including electrochemical investigations by cyclic voltammetry. Single crystal X-ray diffraction confirmed the successful synthesis and structural integrity of selected complexes. Initial attempts toward chemical reduction were guided by electrochemical data, which indicated promising access to Mo(I) allyl species. These reduced complexes were subsequently investigated by EPR spectroscopy. The observation of electron rich reduced molybdenum complexes prompted preliminary studies on CO_2-insertion reactivity. These encouraging results motivate further investigations to establish structure activity relationships with respect to ligand framework, metal center, and counter anion, to optimize reaction conditions, and to elucidate mechanistic aspects relevant for future CO_2-activation chemistry.

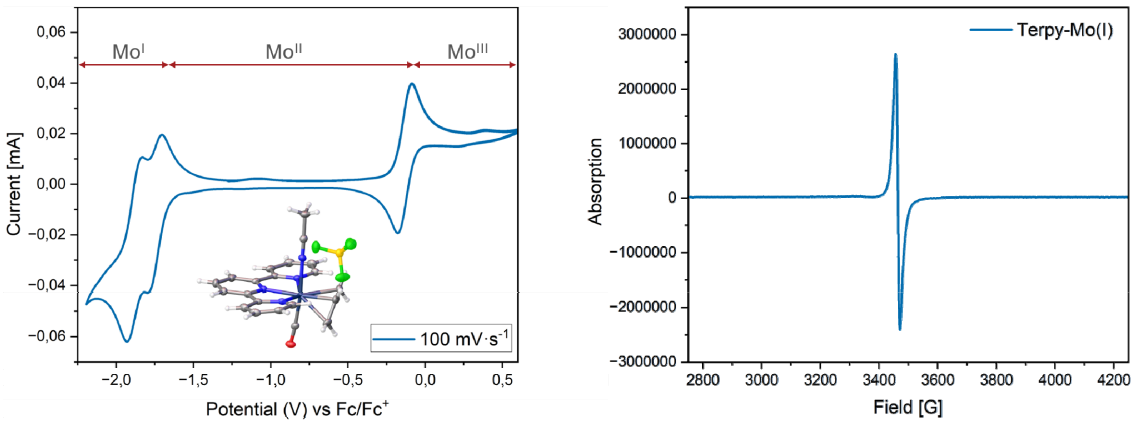


Figure 1: Left: Cyclic voltammetry of the Mo(II) allyl complex indicating accessible reduction processes. Right: EPR spectrum of the chemically reduced Mo-terpyridine complex, consistent with the formation of a paramagnetic Mo(I) species.

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FROM UPTAKE TO STORAGE: UNCOVERING HIDDEN PATHWAYS OF BACTERIAL COPPER HOMEOSTASIS

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Understanding copper homeostasis in bacteria is crucial for the development of novel antibacterial strategies, particularly those targeting metal acquisition pathways. Although copper efflux systems have been relatively well described, the processes responsible for its uptake, periplasmic trafficking, and intracellular storage remain largely unresolved [1,2].

Our recent studies indicate a functional cooperation between the periplasmic chaperone CopC and the inner membrane transporter CopD. CopD contains two metal-binding motifs (SPH and GHG) with distinct affinities for Cu(II) ions. The SPH site likely serves as the primary high-affinity Cu(II) binding site, whereas the GHG site may participate in the intermediate metal transfer steps. In contrast, the Met-rich loop in CopC with MX_2MXHX_2M motif, exhibits the lowest affinity for Cu(II), suggesting a role in transient copper coordination. Due to this relatively weak binding, CopC is unlikely to be transported as a protein-metal complex. Instead, it likely facilitates the transfer of Cu(II) ions to CopD, which mediates their translocation into the cytoplasm.

Cu(II)/Cu(I) homeostasis also relies on effective intracellular sequestration primarily mediated by metallothioneins (MTs). Recent metagenomic analyses have identified new MTs, including MT6, whose expression is strongly induced under elevated Cu(I) conditions, pointing to a potential role in copper storage and sequestration [3]. Our studied on MT6 have provided intriguing insights into its metal-binding properties, contributing to a better understanding of its function in intracellular copper management.

A detailed understanding of bacterial copper transport and trafficking could enable new antibacterial strategies, including inhibitors that target Cu(I)/Cu(II) binding sites and “Trojan horse” approaches, where antibiotics are linked to metal-binding domains to exploit these pathways for targeted uptake and improved efficacy.

Acknowledgments: The work was supported by the National Science Centre
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SUPRAMOLECULAR CATALYSTS LEVERAGE AMMONIUM-CROWN ETHER INTERACTIONS FOR DIRECTED ALKENE ISOMERIZATION

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Alkene transposition reactions hold promise as a method for preparing specific isomers with perfect atom economy, but accessing a single alkene isomer often proves challenging due to the small differences in energy between each of many accessible regio- and stereoisomers. To overcome this challenge, we have designed an iridium hydride catalyst featuring a pincer ligand with a pendent crown ether, which can leverage cation-macrocycle interactions with ammonium salt activators to tune the environment at the active site and affect selectivity of alkene isomerization. In this work, a new isomerization catalyst based on a large aza-24-crown-8 macrocycle is presented. This catalyst optimizes ammonium binding, resulting in rate acceleration for alkene isomerization in the presence of primary and secondary ammonium activators. We have investigated the extent to which a variety of ammonium salt cofactors impact regio- and stereoselectivity of alkene isomerizations. Alkenylammonium salts are introduced as “self-activating” substrates that provide an opportunity to probe the secondary coordination sphere interactions that drive catalysis.

Ru(II) COMPLEXES OF REDOX-ACTIVE LIGANDS TOWARDS SOLAR FUEL GENERATION

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As energy demands continue to rise, so too, does the demand for a more substantial sustainable energy economy. Among current methods of energy harvesting, photocatalysis shows promise by storing abundant solar energy in chemical bonds such as hydrogen. Ruthenium (II) polypyridyl complexes are useful in the development of photocatalysts due to their well-characterised photophysical and electrochemical properties and general stability to photocatalytic conditions.[1]

Many useful photochemcial reactions such as the reduction of H^+ into alternative fuels (e.g. H_2) or CO_2 into important feedstock chemicals (e.g. carbon monoxide and formic acid) require multiple electrons necessitating the storage of reduction potential. Including redox-active organic molecules capable of reversibly and controllably releasing electron equivalents as part of a photocatalyst is one approach to achieve this goal.[2]

This research has focused on the design of complexes with chelating ligands based on polypyridyls with attached *p*-quinone moieties (Figure 1). By incorporating redox active *p*-quinones into these complexes, we hope to observe the storage of redox potential as the equivalent hydroquinone in a form resistant to back electron transfer. Furthermore, analogous to the light-harvesting assemblies found in natural photosynthetic systems; we plan to bind these ligands between two ruthenium (II) light-harvesting units, aiming for faster photochemical charge-transfer, and to bypass rate-limiting steps like chemical reduction from sacrificial electron donors.

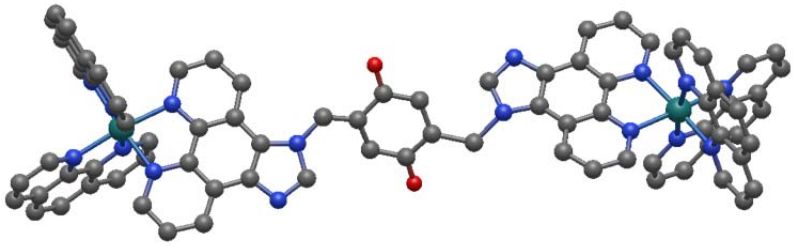


Figure 1: Representative structure of a *p*-quinone subunit included as part of an energy storage catalyst.

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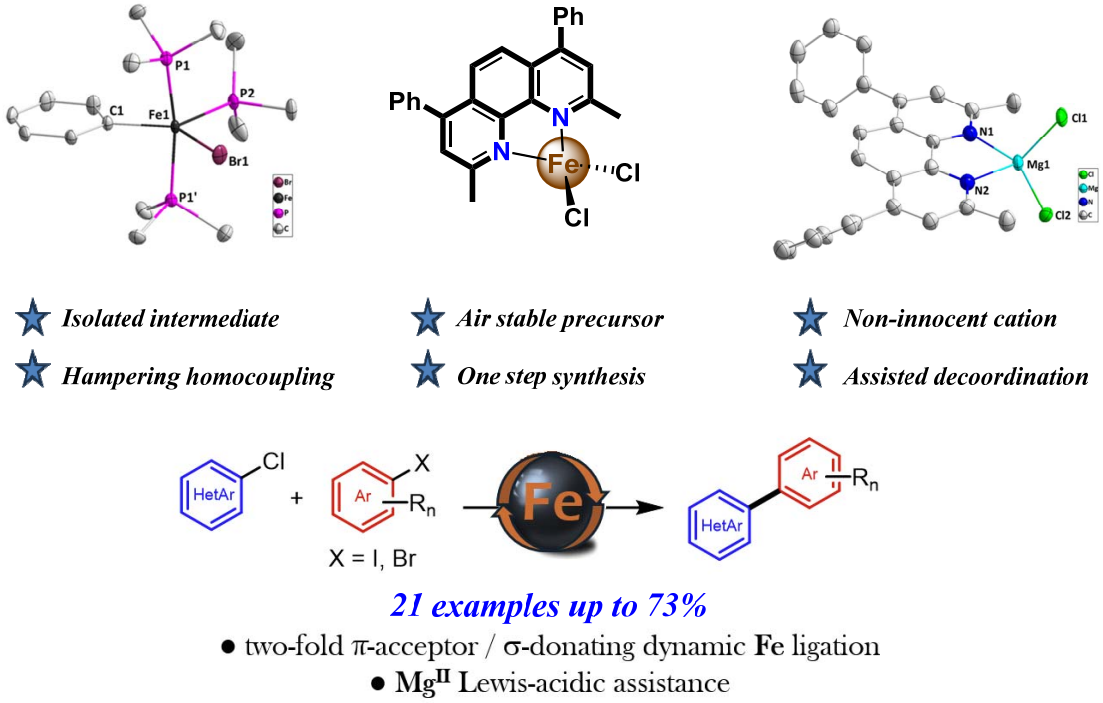
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LOW-VALENT IRON CATALYSIS FOR CROSS-ELECTROPHILE COUPLING

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Cross-electrophile coupling (XEC) is a promising methodology for C-C bond formation as it involves the use of commercially available starting materials without the need of converting them to hazardous organometallic species. Despite numerous works in this field dominated by nickel or noble metals [1], this approach has not been extensively studied with iron. In this work, reductive coupling of an aryl halide with a heteroaryl chloride or bromide is achieved using a new low-valent non-innocent iron system and magnesium as an electron source under mild conditions and straightforward procedure [2]. Our results have shown that the implementation of redox-active ligand and strongly donating phosphine is vital for hampering homocoupling products and increasing cross-selectivity. Mechanistic studies suggest a radical-based process and reveal the key influence of cation effects on the coordination sphere of the iron center. These findings highlight the potential of ligand-assisted low-valent iron catalysis for selective C-C bond formation in cross-electrophile coupling.



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GETTING THE GOLD IN: ONE-POT TRANSMETALLATION MEDIATED BY PALLADIUM(II) COMPLEXES

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Department of Chemistry, University of York, York, UK

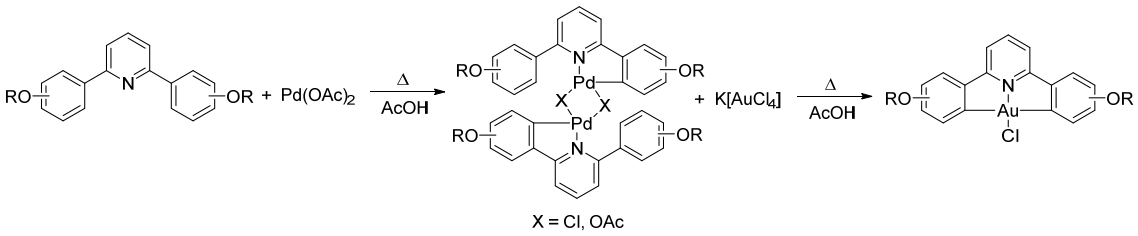
Doubly cyclometallated Au^{III} of 2,6-diphenylpyridines have attracted attention as triplet emitters in electroluminescent devices [1] and our own work has considered the advantages offered if these complexes also possess liquid crystal properties [2]. However, a major drawback is the fact that direct auration of these ligands is extremely challenging and normally proceeds through toxic Hg^{II} intermediates [3]

As part of studies to try to replace mercury in these syntheses, we recently reported that dinuclear di-μ-chloro palladium(II) complexes (Figure – X = Cl) can be formed using these ligands and then successfully be transmetallated using $[AuCl_4]^-$. [4]

Keen to explore this chemistry further, we prepared analogous dimers starting from palladium acetate (Figure – X = OAc), aiming to enhance the yields by profiting from the strongly basic nature of acetate in the subsequent C-H activation with gold.

The dimeric complexes can indeed be prepared and, unlike their chloro analogues, are found to be highly fluxional on the NMR timescale, with the interpretation of the dynamic behaviour being complicated by the presence of isomers. Furthermore, control over the synthetic conditions used can also yield a monomeric complex in which the palladium has an intramolecular bond to an oxygen from the alkoxy group of the ligand.

While these isolated complexes will indeed transmetallate using $[AuCl_4]^-$, it has also been possible to identify conditions for a one-pot reaction capable of 50 % conversion to the gold complex.



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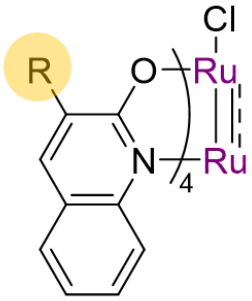
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ELECTRONICALLY-TUNABLY DIRUTHENIUM ELECTROCATALYSTS FOR THE AMMONIA OXIDATION REACTION

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In 2021, the Berry group published the electrochemical precatalyst $Ru_2^{II,III}(chp)_4OTf$ (chp^- = 6-chloro-2-hydroxypyridinate), which has the lowest reported overpotential, η, for the ammonia oxidation reaction (AOR) at an operating potential -225 mV [1]. This has applications in direct ammonia fuel cells (DAFCs), a developing form of low-carbon fuel [1-3]. Yet, further reducing AOR η is limited due to synthetic difficulties in modifying the hydroxypyridinate ligands of this catalyst [4].



$Ru_2(hq\text{-}R)_4Cl$

R = H, OCH_3, CH_3, CHO, Br

Here, we design, synthesize, and electronically and electrochemically characterize a series of second generation Ru_2 complexes with hydroxyquinoline derivatives as the equatorial ligands, $Ru_2^{II,III}(hq\text{-}R)_4L$ (hq^- = hydroxyquinoline, R = Br, CHO, H, CH_3, OCH_3, L = Cl, OTf). The family of hydroxyquinoline derivatives with various organic R-groups is more extensive than for the first-generation hydroxypyridinate ligands. [5-7]. Compared to the "control" complex, $Ru_2^{II,III}(hq\text{-}H)_4Cl$, the more electron-withdrawing aldehyde in $Ru_2^{II,III}(hq\text{-}CHO)_4Cl$ anodically shifts the redox potential by 740 mV, showing that small ligand modifications highly modulate the redox activity of the Ru_2 core. $Ru_2^{II,III}(hq\text{-}H)_4Cl$ has a redox potential that is already 70 mV more negative than the first-generation oxypyridinate counterpart $Ru_2^{II,III}(chp)_4Cl$, and we predict that the more electron-donating modifications will push this even more negative, thereby decreasing AOR η.

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HOMOGENEOUS BIOETHANOL HOMOLOGATION: A MULTI-SCALE STUDY FROM MICROWAVE SYSTEM TO AUTOCLAVE SCALE-UP

Chiara Lenzi,[a,b] Andrea Piazzi,[a,b] Elisa Roncarati,[a] Francesco Calcagno,[a,b] Ivan Rivalta,[a,b] Alessandro Messori,[a] Cristiana Cesari,[a,b] Rita Mazzoni [a]

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As global bioethanol production scales, its transformation into high-value chemicals beyond biofuels is essential for a sustainable biorefinery. This work explores the Guerbet reaction to convert ethanol into higher alcohols, such as butanol, through a sequential dehydrogenation, aldol condensation, and hydrogenation pathway (Figure 1). Utilizing homogeneous cyclopentadienonic- NHC Ru catalysts, we achieved high ethanol conversion and excellent butanol selectivity. A key advancement in our system is the incorporation of a co-catalyst, which proved instrumental in shifting selectivity toward longer-chain alcohols.[1] The catalytic performance was validated through upscaling studies, where optimized reactor configurations significantly improved the carbon balance, demonstrating the potential for practical implementation. By combining computational modeling with experimental validation, we successfully elucidated the synergistic role of the co-catalyst in the catalytic cycle.[2] Furthermore, the integration of microwave irradiation as a heating source allowed for a drastic reduction in reaction times from several hours to minutes, markedly enhancing process throughput and overall energy sustainability. This overall approach establishes a sustainable pathway for the synthesis of bio-derived alcohols, with its scalability successfully verified through 300 mL autoclave experiments.

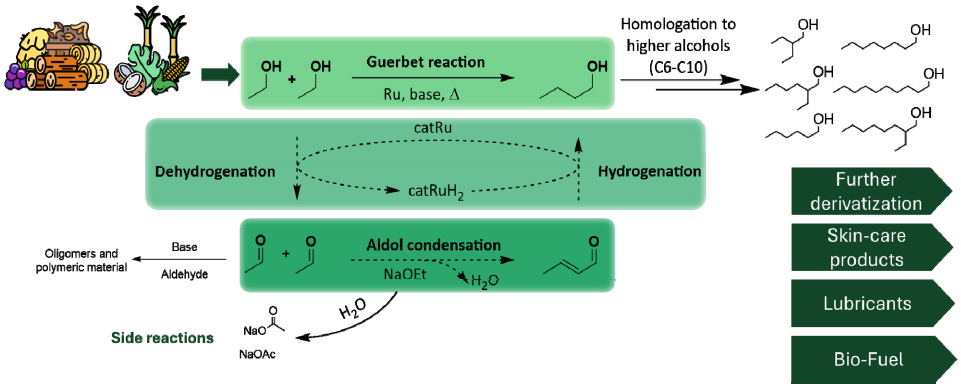


Figure 1

Ackowldegments: Authors wish to acknowledge PRIN 2022 "Biomass-derived alcohols and polyols valorization and use by dehydrogenation/hydrogenation reactions promoted by bifunctional, proton-responsive homogeneous catalysts (ALCOVAL)" CUP J53D23008500006 for financial support.

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SYNTHESIS AND CHARACTERISATION OF COBALT-BASED HETEROLEPTIC POLYPYRIDYL PINCER COMPLEXES

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Current electrocatalysts often rely on the platinum group metals and there is a need to move towards more sustainable alternatives. Studies have shown that pincer complexes of the first-row transition metals, such as cobalt, can act as catalysts for a variety of C–H activation processes [1]. From an electrochemical perspective, this type of pincer complexes are already reported to show accessible, tuneable redox couples and low-overpotential electrocatalytic activity [2]. More work is needed to understand the potential of the systems, by expanding the scope of ligand frameworks studied.

Here, we set out to prepare a range of sterically restricted heteroleptic polypyridyl complexes. Namely, a [3+1] configuration wherein a tridentate pincer complex is adjoined with a monodentate ligand moiety that can further support the structure and electronic property of the complex. This allows us to study the interplay between molecular structure, complex (ligand and metal ion-based) redox properties and electrocatalytic performance in the electrochemical HER. We show that these polypyridyl-based ligands, in a heteroleptic [3+1] arrangement, can be used to support a new range of mononuclear complexes and that the properties of the complexes can be tuned through modification of ligand substituents.

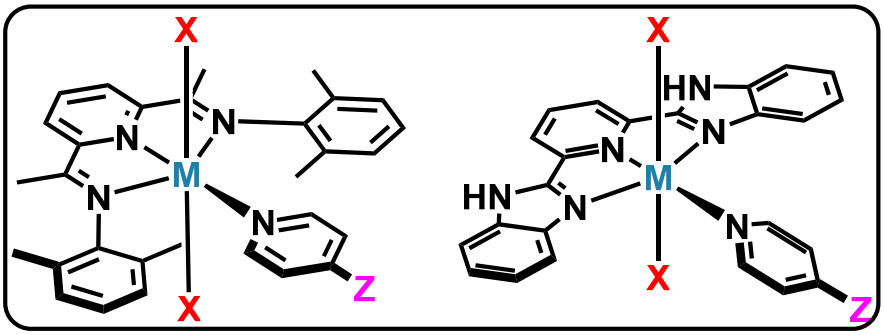


Figure 1. General structure of the [3+1] configuration of heteroleptic complexes reported in this work (M = Co; Z = CF_3, ^{t}Bu; X = Cl^-)

[1] A. Kasera, J. P. Biswas, A. Ali Alshehri, S. Ahmed Al-Thabaiti, M. Mokhtar and D. Maiti, *Coordination Chemistry Reviews*, 2023, **475**, 214915.

[2] L. Alig, M. Fritz and S. Schneider, *Chem. Rev.*, 2019, **119**, 2681–2751.

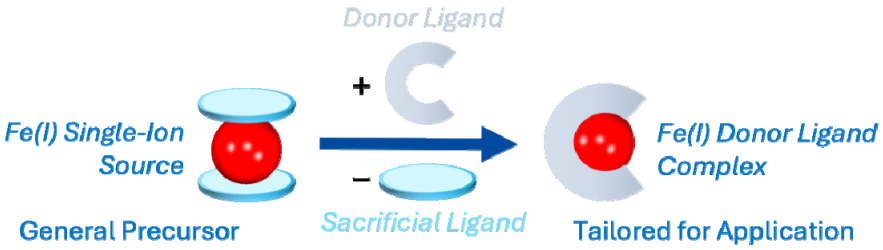
STABLE SINGLE-ION SOURCES OF IRON(I)

Oliver P. E. Townrow

Institute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, Germany

Soluble organometallic complexes which are capable of delivering the metal atom, or mono-cation through facile, redox-neutral ligand exchange have been well-studied for over half a century. Representative examples of these include: $[Rh(cod)_2][BF_4]$, $[Ni(cod)_2]$, and $[Pd_2(dba)_3]$. This chemical technology has become essential in the experimentalist's toolbox when synthesising well-defined low-oxidation state complexes and is indispensable in catalytic systems for providing the transition metal source.[1,2]

Although Fe(+I) has been long postulated as the lowest oxidation state in many catalytic reactions,[3,4] isolated examples of the monocation are still very rare, and there are currently no known examples of Fe(+I) complexes which can selectively transfer the cation to donor ligands. Therefore, to utilise such species in catalysis, one typically reacts a pre-ligated Fe(+II) or (+III) halide complex with a strong alkali or alkaline earth metal-based reductant.[5] When this is done in situ, it often leaves the catalyst ill-defined and reduces the functional group tolerance of the reaction mixture.



We have synthesised the first examples of Fe(I) single-ion sources which, on reaction with well-studied and commercially available ligands, have provided facile access to a library of 15 and 17 valence electron Fe(I) complexes. We have further demonstrated their use as drop in precatalysts for organic transformations.

[1] N. Hazari *et al.*, *Nat. Rev. Chem.*, 2017, 1, 1–16.

[2] P. Etayo *et al.*, *Chem. Soc. Rev.*, 2012, 42, 728–754.

[3] R. B. Bedford, *Acc. Chem. Res.*, 2015, 48, 1485–1493.

[4] B. J. S. Rowsell *et al.*, *Nat. Catal.*, 2024, 7, 1186–1198.

[5] R. B. Bedford *et al.*, *Angew. Chem. Int. Ed.*, 2013, 52, 1285–1288.

INVESTIGATIONS INTO MOLECULAR COPPER(I) PHOSPHIDO COMPLEXES

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Department of Chemistry and Chemical Biology, TU Dortmund University, Germany

Current research in efficient and sustainable OLED emitter materials focuses on the use of earth-abundant non-toxic metals. Among these, metals with a formally closed d subshell such as Cu(I) are particularly compelling,[1] because they lack metal centered states that typically promote non-radiative deactivation. In addition, the electrochemical properties of Cu(I) systems lead to a significant metal participation in the energetically lowest electronic transitions, since they are predominantly metal-to-ligand charge transfers (MLCT).[2] While most of the research around photoactive carbene copper(I) compounds focus on the use of amide ligands, the heavier congeners of the pnictogens remain drastically underrepresented. This is partly due to their tendency to form oligomeric structures depending on the steric properties, which hamper the predictable formation of monometallic structural motifs. In this work we investigated the coordination chemistry of both Ph_2P^- as well as Mes_2P^- ligands with copper(I) carbene complexes and were able to obtain stable oligomeric and linear monomeric structures, respectively. Due to phosphorus' higher polarizability, we observed a bathochromic shift of the emission compared to the nitrogen-based homologues,[3] as the monomeric complexes show bright emission in the orange spectral range. Time resolved investigations prove that generally desired thermally activated delayed fluorescence is the emissive path. When evaluating the excited state energies, lifetimes and the overall stability of the compounds in solution, we determined that the complexes would be suitable photocatalysts. Indeed, they proved to be efficient visible light photocatalysts for the hydrophosphination of terminal alkynes, a reaction that typically requires UV light or high temperatures.

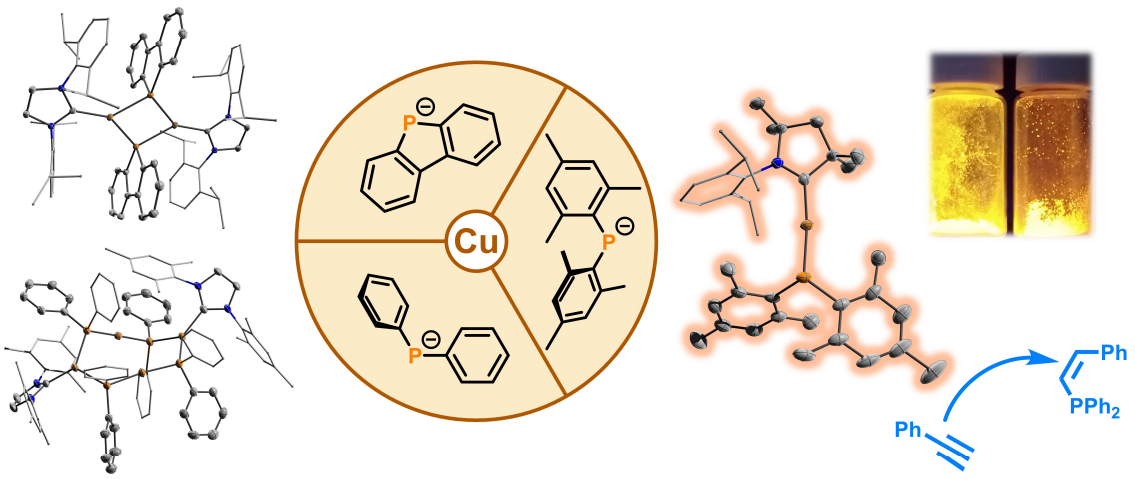


Figure 1. A great variety of carbene copper(I) phosphido complexes are accessible depending on the substituents at the phosphorus and at the *N*-heterocyclic carbene.

[1] J. Beaudelot, C. Moucheron, Gwilherm Evano et al. Chem. Rev. 2022, 122, 16365 – 16609.

[2] M. Gernert, J. Pflaum, A. Steffen et al. Chem. Eur. J. 2017, 23, 2206 – 2216.

[3] R. Hamze, G. Bertrand, M. E. Thompson et al., Science 2019, 363, 601 – 606.

ENTROPY-DRIVEN SOLVATION ENGINEERING OF POLYOXOMETALATE REDOX SPECIES TOWARD HIGH-PERFORMANCE THERMO-ELECTROCHEMICAL CELLS

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Graduate School of Science and Technology, Kwansei Gakuin University, Hyogo, Japan

The conversion of low-grade waste heat into electricity is crucial for sustainable energy technologies. Among thermoelectric systems, thermo-electrochemical cells (TECs) (Fig. 1(a)) generate voltage based on the temperature dependence of redox equilibria in solution and are attractive due to their low cost and environmental compatibility. The $[Fe(CN)_6]^{4-/3-}$ couple has been widely studied as a benchmark system [1]; however, further enhancement of the Seebeck coefficient (S_e) and conversion efficiency remains necessary. Here, we focus on polyoxometalates (POMs, Fig. 1(b)), which exhibit multi-electron redox activity and structural tunability. Although POM-based TECs have been reported [2], the relationship between solvent-induced solvation changes and thermoelectric performance remains unclear. We therefore investigated the S_e of aqueous POM systems containing organic additives, with particular attention to solvation entropy changes accompanying redox reactions.

The thermo-electrochemical performance of a Keggin-type molybdenum POM, $TBA_3[PMo_{12}O_{40}]$ [3], was examined (Fig. 1(c)). The aqueous POM system exhibited S_e = −1.39 mV/K, comparable to that of $[Fe(CN)_6]^{4-/3-}$ (−1.30 mV/K). Addition of solvents with moderate dielectric constants (ε = 30–50), including methanol (MeOH), tetramethylene sulfoxide (TMSO), methylsulfonylmethane (MSM), and dimethyl sulfoxide (DMSO), increased S_e to −1.57 to −1.79 mV/K, whereas low-dielectric tetrahydrofuran (THF, ε = 7.6) decreased S_e to −0.66 mV/K. These results indicate that dielectric-dependent modification of the solvation structure around POM clusters alters the entropy difference between oxidized and reduced states. Organic-additive-induced solvation engineering thus provides a molecular strategy for enhancing thermo-electrochemical performance. Detailed analyses of solvation structures and additive-concentration dependence will be presented.

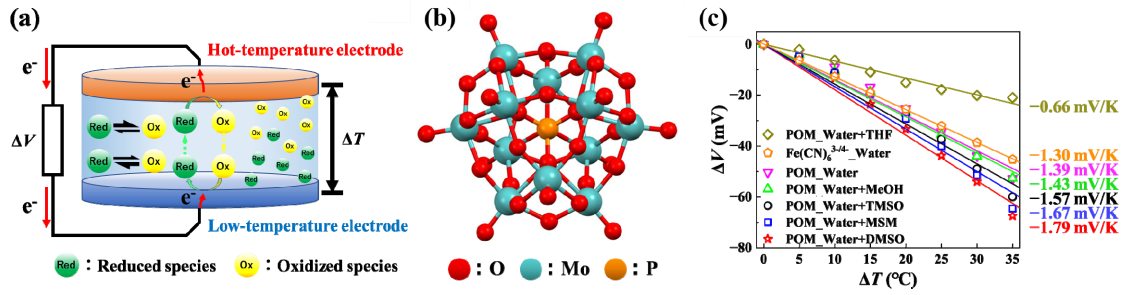


Fig. 1 (a) Schematic of a P-type TEC. (b) Structure of the Keggin-type molybdenum POM, $[PMo_{12}O_{40}]^{3-}$. (c) Temperature dependence of the thermoelectric voltage (ΔV).

[1] T. Kim, et al., *Nano Energy*, **2017**, 31, 160.

[2] E. S. Grape, et al., *ACS Appl. Energy Mater.*, **2024**, 7, 11423.

[3] K. Wakamatsu et al., *Batter. Supercaps*, **2022**, 6, e202200385.

STRUCTURAL DETERMINANTS OF EMISSION EFFICIENCY IN THIAZOLE-SUPPORTED COPPER(I) AND SILVER(I) COMPLEXES

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Luminescent complexes of d^{10} metals such as Cu(I) and Ag(I) are promising alternatives to rare-metal emitters, yet achieving high emission efficiency and structural stability remains challenging.

Herein, we present a systematic study of thiazole-based Cu(I) and Ag(I) complexes to identify key structural and electronic factors governing their photoluminescent properties. Controlled incorporation of ligands enables adaptable coordination environments that suppress non-radiative decay and promote metal-to-ligand charge transfer (MLCT) excited states. Emission efficiency is strongly influenced by coordination geometry distortion, ligand rigidity and planarity, electronic substituent effects within the thiazole framework [1], and—particularly for Ag(I)—metallophilic interactions.

Comparative photophysical analysis of Cu(I) and Ag(I) systems reveals distinct excited-state behaviors arising from differences in metal–ligand bonding and spin–orbit coupling. The results establish design principles for tuning emission color, quantum yield, and excited-state lifetime, highlighting strategies for constructing stable, highly emissive coordination architectures for optoelectronic and sensing applications.

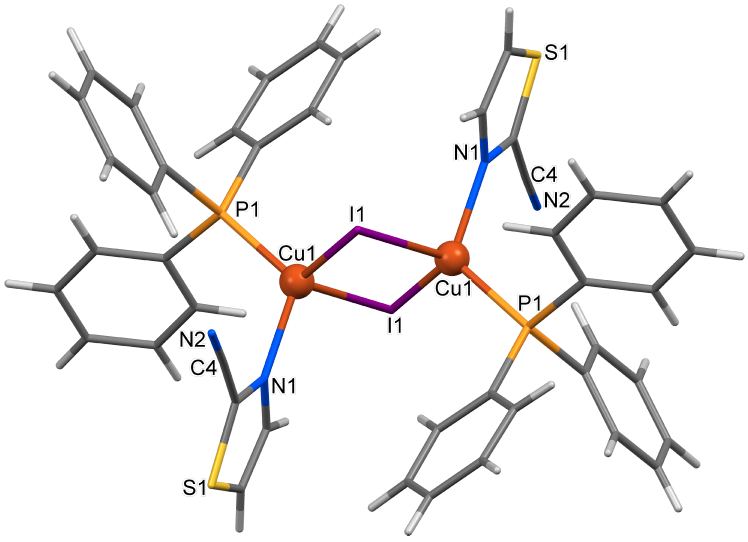


Figure 1. New Cu(I) complex with cyanothiazole and triphenylphosphine.

The authors acknowledge financial support from the Polish National Science Centre (NCN), OPUS programme (grant no. 2022/47/B/ST4/00728).

[1] K. Gutmańska, A. Podborska, T. Mazur, A. Sławek, R. Sivasamy, A. Maximenko, Ł. Orzeł, J. Oszajca, G. Stochel, A. V. Dev, C. Vijayakumar, K. Szaciłowski, A. Dołęga: From Donor-Acceptor Ligands to Smart Coordination Polymers: Cyanothiazole-Cu(I) Complexes for Multifunctional Electronic Devices. Chem.-Eur. J. 31 (2025) e202500215, doi: 10.1002/chem.202500215

SYNTHESIS, PHOTOLUMINESCENT PROPERTIES, AND SINGLET OXYGEN GENERATION CAPABILITIES OF TECHNETIUM AND RHENIUM COMPLEXES WITH *N*-HETEROCYCLIC CARBENE LIGANDS

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Technetium is an important diagnostic element in single photon emission computed tomography. A technetium complex that emits visible light and generates singlet oxygen is expected to be used for dual-modality imaging and photodynamic therapy. Photoluminescent studies of technetium complexes are still scarce, with a reported maximum emission quantum yield of 0.023 and no prior reports of singlet oxygen generation.

Herein, we report the photoluminescent properties of novel technetium complexes that exhibit high emission quantum yields and high singlet oxygen generation capabilities. We also provide a comparative evaluation of their rhenium analogs. The newly synthesized complexes were characterized by single-crystal X-ray diffraction analysis, IR, UV-Vis, and ^{1}H NMR spectroscopy. The technetium complexes are selectively yielded as the *cis* isomers, while the reactions with rhenium produced both *cis*/*trans* complexes. This is likely due to the difference in ligand substitution labilities of technetium and rhenium.

Fig. 1 shows the X-ray structures of the complexes. X-ray crystallography confirmed that the *cis* isomers of the technetium and rhenium complexes are structurally nearly identical. All of the complexes exhibited room-temperature photoluminescence in both the solid and solution phases. This is the first time that emission quantum yields and lifetimes of a technetium complex have been evaluated in the two phases. The technetium complexes in this study have significantly higher emission quantum yields, approximately 10 times higher than those of other reported technetium complexes. The emission lifetimes are four orders of magnitude longer than those of previously reported technetium complexes. The technetium complexes showed lower radiative (k_r) and non-radiative (k_{nr}) decay rate constants than the rhenium analogs, likely due to variations in the heavy atom effect and spin-orbit coupling. Density functional theory calculations were performed to provide theoretical support for the spectroscopic and photophysical properties. The singlet oxygen quantum yields for the technetium and rhenium complexes were ~0.7–0.8 in DMSO.

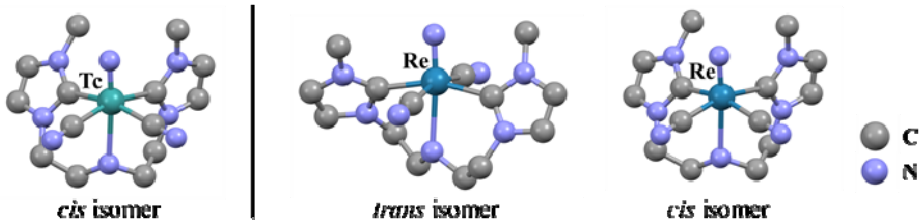


Fig. 1. The molecular structures of technetium and rhenium complexes.

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CATALYSTS WITH TAILORED LIGANDS TO IMPROVE THEIR RECYCLING

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[b] Leibniz-Institut für Katalyse, Rostock, Germany

Catalyst recycling has always been one of the cornerstones in homogeneous catalysis. The recovery of rare metals and tailored ligands, the latter which at times are more expensive than the rare metals themselves, is often essential at mass scale production to ensure sustainability and financial viability of many homogeneously catalyzed processes [1,2]. One of the newest techniques in this field is the organic solvent nanofiltration (OSN) [2]. This technique allows, without state change, the separation of molecules of different molecular weights, polarities and solubilities [2,3]. Although this eco-friendly and energy efficient technique is quite promising, it is still in its early developmental phase [2,3].

In this study, we describe the synthesis of a family of PEGylated-Xantphos ligands, especially tailored for improved OSN separation. We discuss and compare the catalyst recovery through OSN in the case of palladium-catalyzed hydroesterification and showcase an example of rhodium-catalyzed hydroformylation in biphasic media, both reactions were performed using bio-sourced substrates. The new catalysts return high conversions, and high regioselectivity, up to 85% in hydroesterification reactions. The catalysts show great rejections in OSN using a PDMS membrane, with the best ligand rejection up to 99.8%. For hydroformylation, a ligand with surfactant properties was successfully used and recycled 8 times maintaining full conversion with 98% regioselectivity.

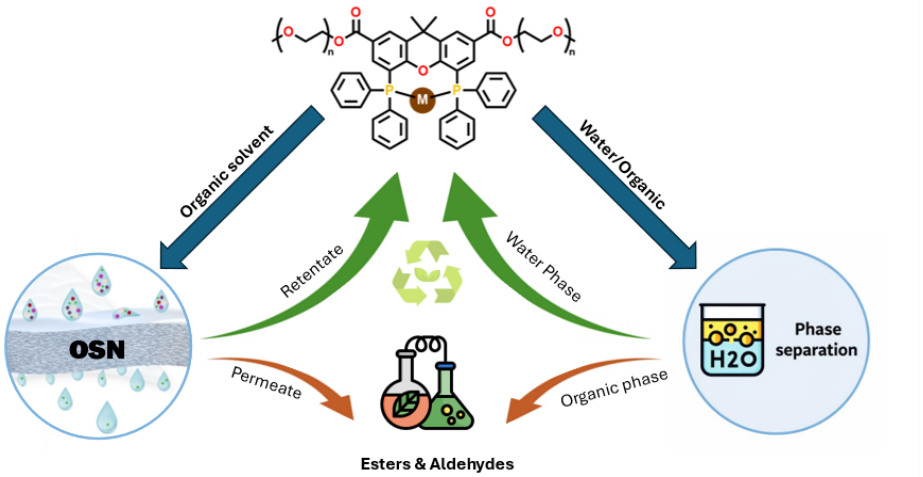


Figure 1. Graphical overview of catalyst recycling via a biphasic system and organic solvent nanofiltration (OSN)

[1] Fassbach, T. A.; Ji, J.-M.; Vorholt, A. J.; Leitner, W. **ACS Catal.** 2024, *14* (9), 7289–7298.

[2] Masliy, V.; Guillaume, S. M.; Fischmeister, C.; Carpentier, J.-F. **Coord. Chem. Rev.** 2025, *536*, 216640.

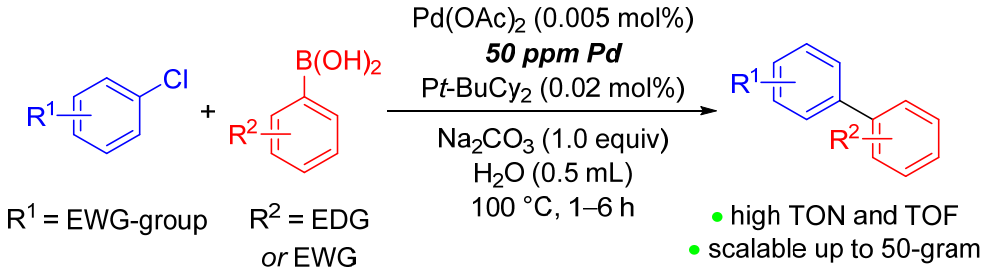
[3] Xiao, H.; Feng, Y.; Goundry, W. R. F.; Karlsson, S. **Org. Process Res. Dev.** 2024, *28* (4), 891–923.

Pd-CATALZYED SUZUKI–MIYAURA CROSS-COUPLING OF ARYL CHLORIDES AT LOW CATALYST LOADINGS IN WATER

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[a] Catalysis Research Laboratory (CaRLa), Heidelberg, Germany
[b] BASF SE, Ludwigshafen, Germany
[c] Heidelberg University, Heidelberg, Germany

The Suzuki-Miyaura cross-coupling reaction is the most employed transformation in industry for the synthesis of biaryl motifs.[1] One major goal towards industrial applicability of synthetic procedures is to use only minimal amounts of noble metal catalysts with high turnover numbers (TON) and sufficient recyclability. Herein, the Suzuki-Miyaura cross-coupling reaction of aryl chlorides in water is disclosed (Scheme 1).[2] Optimizations allowed to run the reaction in water with 50 ppm of Pd-catalyst loading. Kinetic studies revealed a very fast reaction rate, achieving high TON as well as turnover frequencies (TOF) for the formation of products. The reaction showed furthermore robust scalability (up to 50 gram), affording the biaryl product in good yield and with low Pd content.



Scheme 1: Suzuki-Miyaura cross-coupling of aryl chlorides in water.

[1] For the seminal work on Suzuki-Miyaura cross-coupling reaction, see: N. Miyaura, A. Suzuki, *Chem. Rev.*, **1995**, *9*, 2457–2483.

[2] P. Orecchia, D. S. Petkova, R. Goetz, F. Rominger, A. S. K. Hashmi, T. Schaub, *Green Chem.* **2021**, *23*, 8169−8180.

METAL CARBONYL CLUSTERS: FROM MOLECULAR DESIGN TO TAILORED NANOSTRUCTURED MATERIALS

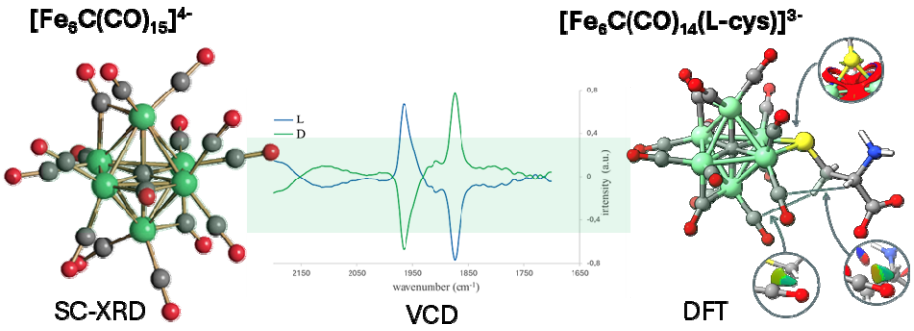
Cristiana Cesari,[a] Marco Bortoluzzi,[b] Francesca Forti,[b] Tiziana Funaioli,[c] Francesca Liuzzi,[a] Giorgia Scorzoni[a] and Stefano Zacchini[a]

[a]Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Via Bologna, Italy
[b]Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Mestre (VE), Italy
[c]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Pisa, Italy

Metal carbonyl clusters (MCCs) represent a unique class of molecular species featuring low-valent metal cores stabilized by CO ligands. Their atomically precise structures and tunable redox properties make MCCs highly attractive for the development of nanostructured materials with tailored functionalities.

Using alloy PtNi carbonyl clusters, we obtained well-defined and finely dispersed nanoparticles by impregnation procedure on different supports. These nanostructure materials were successfully employed in redox transformations, including the oxidation of 5-hydroxymethylfurfural (HMF) and reductive amination of furfural (FUR).[1]

In this work, we further report the synthesis of a series of homo- and heterometallic carbonyl clusters based on Ru and Fe. Comprehensive characterization through single crystal X-ray diffraction, multinuclear NMR, IR spectroscopy, and IR spectroelectrochemistry, supported by DFT calculations provide detailed insight into their electronic structure, stability and reactivity.[2] Moreover, the first vibrational circular dichroism (VCD) study performed on MCCs demonstrated that molecular chirality can be induced via coordination of an enantiopure ligand, opening new prospective for the design of more selective catalysts.[3]



[1] F. Liuzzi, F. Di Renzo, C. Cesari, A. Mammi, L. Monti, A. Allegri, S. Zacchini, G. Fornasari, N. Dimitratos, S. Albonetti, *Molecules*, **2025**, *30*, 2120.

[2] T. Funaioli, M. Bortoluzzi, G. Bresciani, C. Cesari, C. Femoni, M. C. Iapalucci, S. Zacchini, *Coordination Chemistry Reviews*, **2026**, *549*, 217365.

[3] F. Forti, A. Pellegrini, C. Cesari, C. Femoni, M. C. Iapalucci, M. Mancinelli, S. Zacchini, *Angew. Chem. Int. Ed.*, **2025**, e202513702.

PHOTOFUNCTIONAL METAL COMPLEXES OF A PI-RICH AMIDINE *N*-OXIDE LIGAND

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Photofunctional transition metal (TM) complexes have traditionally come from the second- and third-row of the d-block due to their favorable photophysical properties. These metal ions are, however, scarce, expensive, and pose more environmental concerns than their first-row TM alternatives. Despite these benefits, complexes with first-row TM ions often exhibit less desirable photophysical characteristics, such as shorter excited-state lifetimes and lower photostability. Overcoming these challenges through ligand design, coordination geometry optimization, and tuning of their electronic properties is crucial to unlock the potential of these metal ions for applications in solar energy conversion, photocatalysis, and light-emitting devices. Herein, we present a novel class of Co(III)-amidine *N*-oxide complexes exhibiting low-energy Ligand-to-Metal Charge-Transfer (LMCT) absorptions beyond 500 nm. Higher lying p-orbitals on the ligand scaffold lead to novel photophysical properties wherein the complexes exhibit higher energy emissions than the LMCT state, ie, they do not obey Kasha's rule. The nanosecond excited-state lifetimes of these Co(III) complexes pave new avenues for strong pi-donor ligands in the optoelectronic properties of complexes of abundant TM ions.

TUNING FUNCTIONS IN AMIDINE *N*-OXIDE (AMOX) LIGANDS AND THEIR COORDINATION COMPLEXES

Mathieu Lepage[a], Vivian Alexandra Montañez Valderrama[a], Elizabeth Lamothe[b], Arindam Saha[b], Cédric Gros, Jessica Castro[b], Garry S. Hanan[b], and Mihaela Cibian[a,b]

[a]Université du Québec à Trois-Rivières, Département de biochimie, chimie, physique et science forensique, and Institut de recherche sur l'hydrogène, Trois-Rivières, Québec, Canada
[b]Université de Montréal, Département de chimie, Montréal, Québec, Canada

In line with the study and the development of coordination compounds for specific applications, the central theme of our research is the Metal-Ligand interaction and how it can be modulated through ligand design and weak interactions to generate the properties targeted for these applications. The ligands under study are the *N,N'*-disubstituted amidine oxides (AMOXs) (also known as α-aminonitrones/ hydroxyamidines). Their synthesis and characterization as well as aspects of their coordination chemistry with zinc(II), aluminium(III), and boron(III) are discussed [1-5]. Representative solid-state structures are also highlighted. Specific interactions are responsible for aggregation induced emission (AIE) properties in the family of zinc(II) and boron(III) AMOX-based compounds [4-5]. Crystallization-induced enhanced emission, as well as reversible thermochromism, vapochromism, mechanochromism, and chronochromism were also observed for the latter (Figure 1) [5]. Such characteristics propose these compounds as interesting materials for optoelectronic and stimuli-responsive applications.

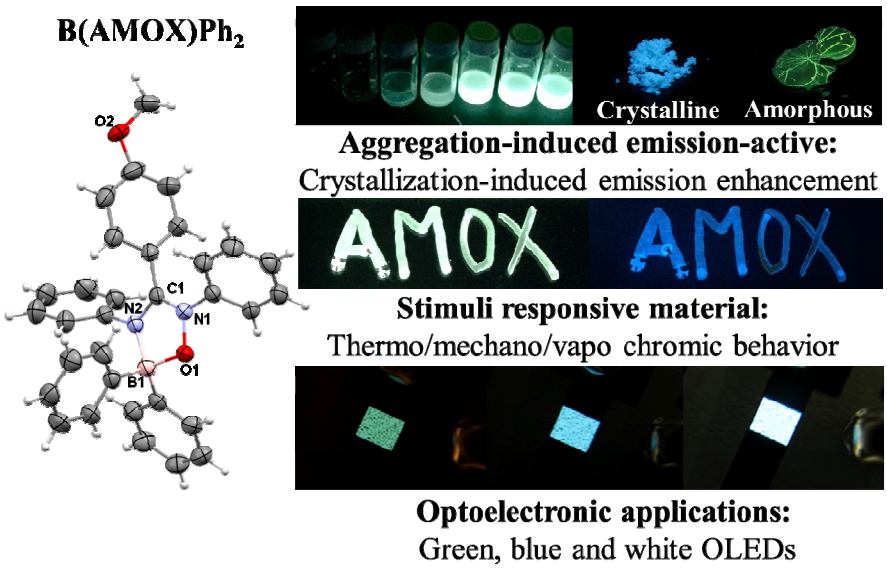


Figure 1. AMOX-based boron compounds and their properties.

[1] Cibian *et al.* (2015) *Eur. J. Inorg. Chem.* 2015 (1): 73;

[2] Cibian *et al.* (2015) *Chem. Eur. J.* 21: 9474;

[3] Cibian *et al.* (2016) *Eur. J. Inorg. Chem.* 2016 (1): 177;

[4] Cibian *et al.* (2018) *Eur. J. Inorg. Chem.* 39: 4322;

[5] Castro *et al.* – ready to be submitted.

FERROCENE-BASED DONOR–ACCEPTOR ARCHITECTURES AS MEMRISTIVE COMPONENTS IN MOLECULAR JUNCTIONS

William D. J. Tremlett[a], Cerys Cooper[b], Sam Harley[b], Samuel P. Jarvis[b], Colin J. Lambert[b], Benjamin. J. Robinson[b], Nicholas J. Long[a]

[a]Department of Chemistry, Imperial College London, London, W12 0BZ, UK
[b]Physics Department, Lancaster University, Lancaster, LA1 4YB, UK

The rapid expansion of artificial intelligence is driving unprecedented energy demands and significant waste heat generation, motivating the development of low-power computing paradigms such as neuromorphic architectures.[1] Memristors, resistive elements whose resistance or conductance is history-dependent, offer the ability to integrate memory and charge transport within a single device, making them central in enabling energy-efficient data processing.[2] Ferrocene (Fc) remains one of the most versatile organometallic building blocks in coordination and materials chemistry due to its synthetic accessibility, structural stability and reversible Fc/Fc^+ redox couple.[3] These properties make Fc an attractive redox-active donor unit for incorporation into donor–acceptor (D–A) molecular architectures. Such D–A systems have previously demonstrated unimolecular rectification,[4] and Fc integration offers a compelling route to controlled conductance switching and high on/off ratios. Here, we present the synthesis, characterization and surface self-assembly of a series of novel Fc-based D–A molecules on gold substrates. Atomic force microscopy (AFM) confirms the formation of well-ordered monolayers, while conductive AFM (c-AFM) measurements reveal hysteresis in current–voltage (I–V) sweeps, consistent with redox-mediated charge transport and emergent memristive behavior.

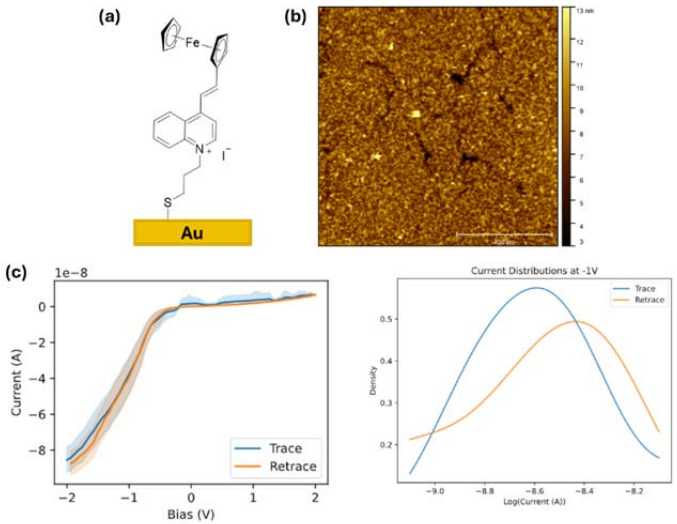


Figure 1. (a) Illustration of a novel Fc-based D–A molecule binding to gold, (b) AFM image of SAM formation, and (c) average trace-retrace (left) and current distributions (right) from c-AFM measurements.

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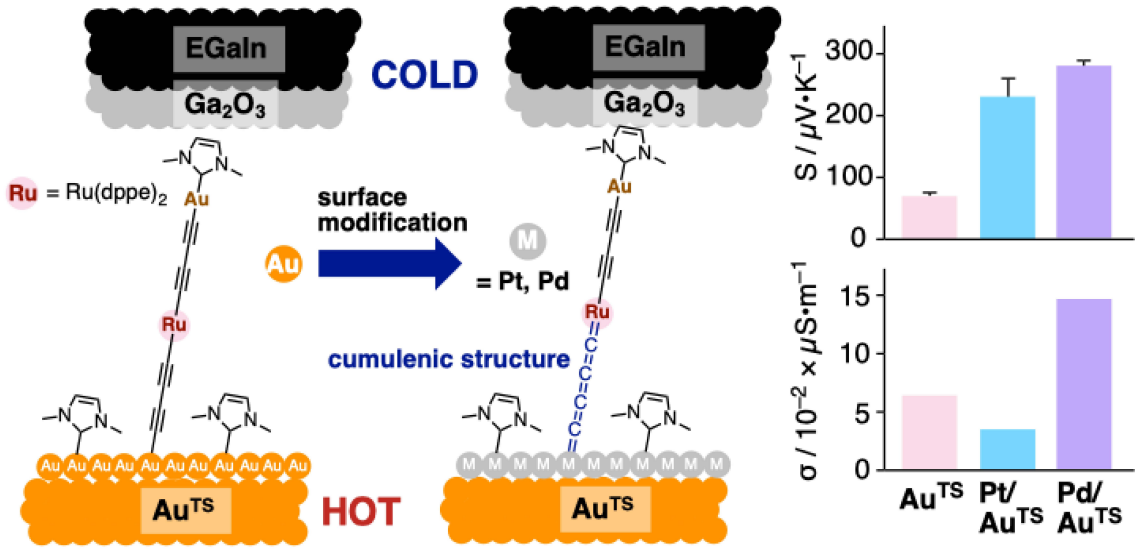
SIMULTANEOUS ENHANCEMENT OF THERMOPOWER AND CONDUCTIVITY IN MOLECULAR JUNCTIONS

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Molecular junction provides a powerful platform for probing charge transport through single molecules and self-assembled monolayers, yet simultaneous enhancement of thermopower and electrical conductivity remains a fundamental challenge.[1] In this work, we report that modulation of molecule–electrode coupling through acetylide anchoring chemistry enables simultaneous improvement of these two normally competing parameters in molecular junctions.[2]

Self-assembled monolayers of a π-extended Ru-diacetylide complex were fabricated on template-stripped Au electrodes, whose surfaces were further modified with monatomic Pt or Pd adlayers via underpotential deposition. Spectroscopic analyses confirmed that Pt and Pd electrodes induce stronger metal–acetylide coupling and promote cumulene-like π-delocalization along the molecular backbone. Thermoelectric measurements using large-area EGaIn-based junctions revealed that the Seebeck coefficient increases in the order Au < Pt < Pd, while the electrical conductivity is maximized for Pd-based junctions, leading to a power-factor enhancement of up to 111-fold compared to unmodified Au junctions. Transport analysis and NEGF-DFT calculations indicate that this enhancement originates from pronounced frontier-orbital splitting and reduced energy offset relative to the Fermi level under strong electrode coupling. These results establish acetylide–electrode interactions as an effective strategy for overcoming the conventional trade-off between thermopower and conductivity.



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FROM IRON(III) TO MANGANESE(II) CARBENES: COMPARING EXCITED-STATE DYNAMICS IN d^5 SYSTEMS

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Photosensitizers are essential for converting light into chemical energy in applications such as solar energy conversion and photoredox catalysis, yet the reliance on the noble metal systems limits sustainability. This has driven increasing interest in first-row transition metal-based photosensitizers which offer Earth abundance and structural tunability but often suffer from short-lived excited states. Over the past decade, iron-based photosensitizers with d^5 and d^6 electron configurations have undergone a remarkable transformation. Advances in ligand design, particularly the use of strong σ-donating N-heterocyclic carbene ligands, have enabled substantial improvements in excited-state lifetimes and photophysical properties, positioning iron as a viable alternative to precious metals.[1, 2]

Building on this progress, attention is shifting towards other Earth-abundant first-row metals with analogous electronic configurations. Recent studies highlight manganese(II) as a compelling alternative within d^5 configured systems, exhibiting excited-state lifetimes of up to 87 µs and demonstrating light-induced excited spin state trapping (LIESST) at unusually high temperatures.[3] In parallel, another report showed an air-stable manganese(II) carbene complex that exhibits room-temperature emission, underscoring the growing potential of manganese in photochemical application.[4] In this study, we present the synthesis and comparative excited-state dynamics of a pair of isostructural and isoelectronic manganese(II) and iron(III) carbene complexes. We aim to elucidate how metal identity influences the excited-state landscape and lifetimes, providing insight into the design of next-generation photosensitizers based on Earth-abundant metals.

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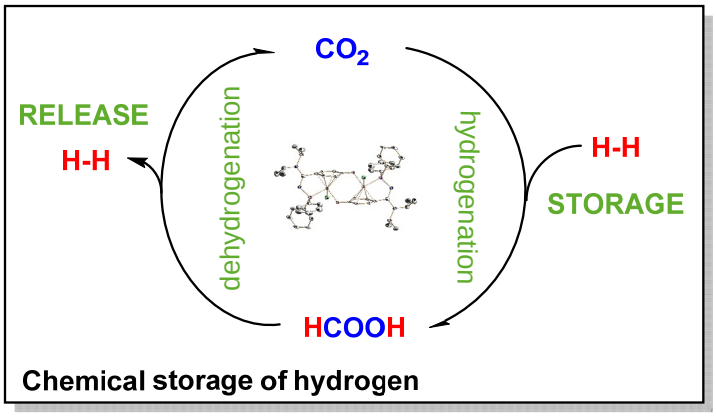
SINGLE CATALYST FOR REVERSIBLE HYDROGEN STORAGE-RELEASE

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Before our studies, η^5–phenoxy metal complexes were totally ignored from applications in homogeneous catalysis.[1] We set up a range of innovative chelate η^5–phenoxy metal complexes and lately we evidenced that our dimeric metal-ligand ruthenium catalysts featuring an acidic metal site and a basic ligand site where efficient for base-free conditions for the reduction of ketones under (transfer)hydrogenation.

We demonstrated the proof of concept of the reversible storage and release of hydrogen with formic acid as LOHC with the same single catalyst due to the cooperation between the acidic and basic sites



In our ongoing efforts on the implementation of LOHCs in homogeneous catalysis we are investigating the potential of our 2nd generation chelate metal-ligand cooperative catalysts in the base-free hydrogenation of CO_2 to methanol and the reverse methanol dehydrogenation transformation.

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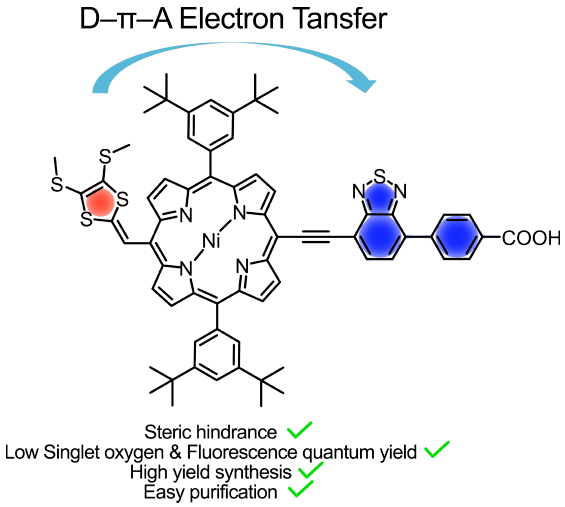
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METALLATION APPROACHES FOR IMPROVING STABILITY OF DITHIAFULVENE-FUNCTIONALIZED PORPHYRINS IN DYE-SENSITIZED SOLAR CELLS

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Singlet molecular oxygen ($O_2(^1\Delta_g)$) represents the main cause for stability issues when using dithiafulvene as a donor group in conjugated materials. This is because the vinyl bond can readily undergo cycloaddition, ultimately leading to cleavage of the fulvene.[1-3] This problem is exaggerated by systems causing their own degradation by self-sensitized photosensitization of $O_2(^1\Delta_g)$).[4] Porphyrins are known for their ability to achieve high extinction coefficients, moderate-high $O_2(^1\Delta_g)$) quantum yields, photostability and use in organic photovoltaics. By coordinating Ni(II) into the porphyrin scaffold we successfully quenched $O_2(^1\Delta_g)$) production, as internal conversion is facilitated, allowing dithiafulvene to be introduced as a donor group without impending stability issues by self-sensitization of $O_2(^1\Delta_g)$).[5] This approach allows combining dithiafulvene as a donor and porphyrin as a core in Dye-Sensitized Solar Cells and paves the way for symmetric technologies in Bulk-Heterojunction devices and materials chemistry.



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PHOTCATALYTIC CO_2 REDUCTION BY USING IRON PHOTOSENSITISER

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The conversion of carbon dioxide (CO_2) into reduced carbon products using light-driven catalytic systems is an attractive approach for sustainable fuel generation. In this study, a nickel-based pincer complex is investigated as a homogeneous catalyst for the photochemical reduction of CO_2 under visible-light irradiation. The catalytic system produces a mixture of reduced products, including carbon monoxide (CO), methane (CH_4), ethylene (C_2H_4), and ethane (C_2H_6), demonstrating the capability of the catalyst to promote both two-electron and multi-electron transformation pathways. The reaction system comprises the nickel pincer complex in the presence of a photosensitizer and a sacrificial electron donor. Upon light absorption, the excited photosensitizer transfers electrons to the nickel center, enabling CO_2 activation and subsequent reduction. CO is observed as an initial product, which is further transformed through sequential proton-coupled electron transfer steps to generate hydrocarbons. The formation of C_2 products suggests that carbon–carbon bond formation occurs during the catalytic cycle, likely involving coupling of reduced carbon intermediates at or near the metal center. Catalytic performance is influenced by experimental parameters such as irradiation conditions and reaction medium. The observed product distribution highlights the ability of nickel pincer architectures to facilitate deeper CO_2 reduction and multi-carbon product formation using an earth-abundant metal center. This work contributes to the understanding of light-driven CO_2 conversion mechanisms and supports the development of molecular catalysts for selective formation of higher-value hydrocarbon products.

EXTENDED TETRATHIAFULVALENE PORPHYRINS FOR BULK HETEROJUNCTION ORGANIC SOLAR CELLS

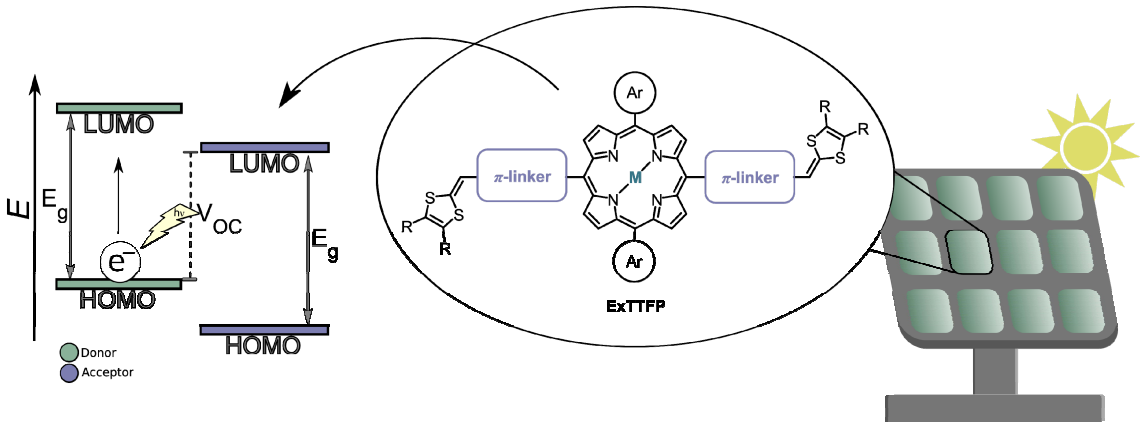
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As non-renewable sources of energy are being depleted, it is important to develop green and sustainable energy resources that can support the growing energy demand with minimum environmental effect. Organic photovoltaics (OPVs) have emerged as promising candidates due to their low cost, flexibility, and reliance on earth-abundant elements, offering an attractive alternative to conventional silicon-based devices.

This project focuses on the design and synthesis of novel donor molecules for bulk heterojunction (BHJ) organic solar cells, incorporating extended tetrathiafulvalene (ExTTF) units into porphyrin cores with varying metal centers. The combination of ExTTF (a strong p-type semiconductor) with porphyrins (robust chromophores) aims to enhance light absorption and charge transport.

In this work, we have successfully synthesized a series of ExTTF–porphyrin derivatives with different metal centers and integrated them into BHJ solar cell architectures. Device fabrication and preliminary testing reveal how metal variation influences stability, morphology, and photovoltaic performance. A key challenge with ExTTF-based materials is their poor stability under air and light, primarily due to photodegradation by singlet oxygen. Our findings indicate that tuning the porphyrin core metal significantly improves stability and overall OPV efficiency. This study provides valuable insights into molecular design strategies for efficient and durable organic solar cells.



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NICKEL(II) BIS(FORMAZANATE) COMPLEXES FEATURING NANOSECOND EXCITED STATE LIFETIMES

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The photophysical properties of octahedral first row transition metal complexes, such as iron(II) N-heterocyclic carbene complexes, have been widely investigated and their metal-to-ligand charge transfer (MLCT) excited state lifetimes have been significantly improved in recent years.[1] With its $3d^8$ electron configuration, MLCT excited states can also be promoted in square planar nickel(II) complexes. In contrast, there are only a few reports on photoactive planar nickel(II) complexes. Previous work has highlighted that obtaining long-lived ^{3}MLCT states in square planar nickel(II) complexes remains challenging due to solvent coordination, Ni-Ni interactions and geometrical distortions into dark metal-centred (MC) states.[2, 3, 4]

In this work, we present panchromatically absorbing square-planar nickel(II) bis(formazanate) complexes. Through interligand interactions, the formazanate ligands shield the nickel(II) metal, which prevents solvent coordination and hinders photoinduced distortion. This ligand arrangement therefore ensures high photostability for this class of compounds and allows access to low-energy MLCT states with enhanced excited state lifetimes.

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SYNTHESIS AND PHOTOPHYSICAL CHARACTERISATION OF FIVE BIS(FORMAZANATE) IRON(II)COMPLEXES

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Photochemistry is a rapidly growing research field, and finding new efficient photoactive complexes is therefore of great interest. Previously Ru(II) and Ir(III) chromophores have been dominating the field as the gold standards because of the attractive properties of their metal-to-ligand charge transfer (MLCT) excited states. However, their scarcity, cost, and environmental impact limit their large-scale applicability. Finding more sustainable and readily available alternatives is therefore important, and iron, being highly earth-abundant, is a strong candidate. Furthermore, iron(II) is isoelectronic with Ru(II) and Ir(III) making it the obvious alternative. However, many iron(II) complexes suffer from rapid deactivation pathways often due to low-lying metal-centered (MC) excited states arising from the weaker field splitting of first row complexes[1,2]. This leads to much shorter lifetimes than the Ru(II) and Ir(III) analogues. Several strategies have been used to alleviate this challenge. One strategy seeks to destabilize the MC states by using ligands with strong sigma-donation such as carbenes [3]. Another strategy is to increase mixing between metal-centered orbitals and ligand-centered orbitals[4], causing MLCT-like transitions that lead to a long-lived ^{5}MC state[5].

This project aims to understand how tuning the electronic (through electron-donating or -withdrawing groups) and steric effects of a ligand scaffold modifies the excited-state landscape of Fe(II) complexes. This is investigated through synthesis and subsequent transient absorption studies of five Fe(II)formazanate complexes. By correlating time-resolved spectroscopic features with systematic ligand modifications, we establish structure–property relationships that elucidate how electronic and steric parameters can change excited-state lifetimes, and relaxation mechanisms.

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PLASMONIC NON-NOBLE METAL BASED BIFUNCTIONAL PHOTO-ELECTROCATALYST FOR REDOX TRANSFORMATIONS

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Indian Institute of Technology Gandhinagar, Gujarat, India

The growing dependence on fossil resources underscores the need to valorize biomass-derived feedstocks such as 5-hydroxymethylfurfural (HMF) into value-added chemicals [1]. In this context, copper-based plasmonic materials have gained significant attention for solar-driven small-molecule activation due to their strong and tunable light absorption properties [2]. Herein, we report a noble-metal-free, light-responsive Cu-Ni photo-electrocatalyst that synergistically integrates the plasmonic excitation of Cu with the catalytic functionality of Ni [3]. The catalyst was prepared by pulse-electrodeposition and comprehensively characterized using XRD, SEM-EDS, TEM, XPS, and dark-field spectroscopy. Under 445 nm illumination, the system delivers a photocurrent density of 150 mA cm^{-2} at -0.7 V *vs.* RHE for the HMF reduction reaction (HMFRR), and 24 mA cm^{-2} at 1.8 V *vs*. RHE for the HMF oxidation reaction (HMFOR) under alkaline pH. Notably, light irradiation exhibits product selectivity toward 5-methylfurfuryl alcohol (MFA) and 2,5-bis(hydroxymethyl)furan (BHMF) during HMFRR, while promoting efficient formation of 2,5-furandicarboxylic acid (FDCA) in HMFOR. These findings demonstrate the dual functional capability of the Cu-Ni photo-electrocatalyst, highlighting its potential for sustainable and efficient conversion of biomass-derived molecules into high-value platform chemicals.

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RECYCLING PLASTICS WASTE THROUGH DEPOLYMERIZATION: LITHIUM-AMIDE CATALYSED MILD AND GRAM-SCALE APPROACH

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The widespread use of plastic materials leads to significant contamination of ecosystems, posing risks to both wildlife and human health.[1] There is an urgent need for efficient, economical, and environmentally friendly catalysts to depolymerize plastic waste into value-added compounds.[2,3] In this study, we utilized the easily accessible catalyst $[Li\{N(SiMe_3\}_2]_2.2(THF)$ and pinacolborane (HBpin) as a hydride donor to convert various types of plastic waste, biodegradable/non-biodegradable polyesters, and polycarbonates into respective borylated value-added alcohols under mild conditions without any pre-treatment up to 99% yield.[4] The borylated-1,4-benzene-*di*-methanol obtained from polyethylene terephthalate (PET) depolymerization is characterized by single crystal X-ray diffraction studies, NMR, and routine spectroscopic techniques. Additionally, the $[LiN(SiMe_3)_2]_2.2(THF)$ catalyst has been employed for the depolymerization of mixed/contaminated waste plastics, achieving selective and excellent yields of the borylated alcohols. This catalyst facilitated the gram-scale depolymerization of PET into eco-friendly alcohols, such as 1,4-benzene-*di*-methanol and ethylene glycol, *via* the depolymerization of polyethylene terephthalate (PET) waste bottles, which is stepwise characterized by NMR techniques. Furthermore, we propose a mechanistic cycle of Lithium bis(trimethylsilyl)amide (LiHMDS) with methyl benzoate (a monomeric ester) to analyze the single-site mechanism for the depolymerization of polyesters and polycarbonates.[5] To the best of our knowledge, this is the first example of alkali metal-catalyzed depolymerization of esters and carbonates containing waste polymers *via* a homogeneous method.

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DINITROGEN DERIVED ELECTROCHEMICAL ACETONITRILE RELEASE FROM A RHENIUM PNP-PINCER COMPLEX

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Reductive N_2 splitting into nitrido complexes is a promising strategy for nitrogen fixation beyond ammonia.[1,2] Electrochemically driven approaches are still in their infancy and recently gained more attention. In the last years, our group introduced rhenium pincer platforms that facilitate the electrochemically driven reductive splitting of dinitrogen.[3-6] In addition, synthetic strategies were developed to generate nitriles from N_2 through nitride alkylation and subsequent chemical redox steps.[7]

In this contribution, we present the transfer of this synthetic approach to the electrochemical redox regime. The formation of acetonitrile is demonstrated by electrolysis of an N_2 derived rhenium aldimido complex (Figure 1). The mechanism will be discussed based on electroanalytical examinations.

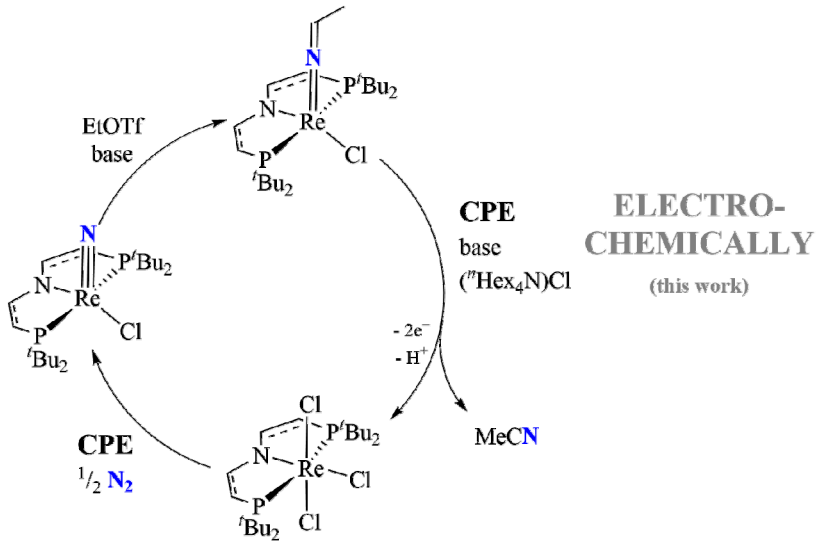


Figure 1: (Electro-)chemical conversion of Dinitrogen to Acetonitrile.

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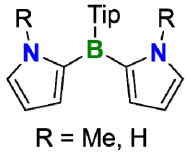
MERGING PYRROLE WITH BORON: π-EXTENSION, POLYMERIZATION, AND COORDINATION

Daniel Göbel, Andreas Helbig, and Holger Helten

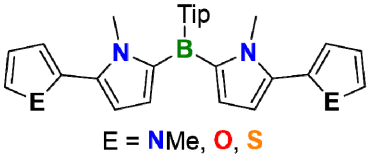
Institute of Inorganic Chemistry and Sustainable Chemistry & Catalysis with Boron (ICB), Julius-Maximilians-University Würzburg, Würzburg, Germany

Over the past few decades, π-conjugated materials that combine electron-rich organic building blocks with electron-deficient borane moieties have attracted considerable attention due to their applications in organic optoelectronics, sensors, and bioimaging [1]. Conjugated di(hetaryl)boranes, particularly those of thiophene, but also furan, have been extensively studied in recent years in this regard [2-4]. Pyrrole congeners thereof, on the other hand, have scarcely been investigated.

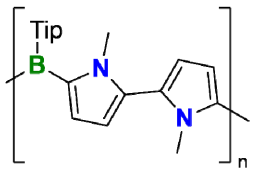
We developed a multigram scale synthesis of a dipyrryl(tri-*iso*-propylphenyl)boranes with methyl groups on the nitrogen atom as well as its unprecedented, unprotected *N*–H derivative. The new compounds show intense blue-light emission, with solvatochromic behavior, aggregation-induced emission enhancement (AIEE), and solid-state emission. TD-DFT calculations reveal that this is due to populated twisted intramolecular charge transfer (TICT) states of the excited state structure. The versatility of the dipyyrylboranes was demonstrated by their application as building blocks for π-extended tetrahetarene boranes, a polymer, and a zirconium(IV) complex [5].

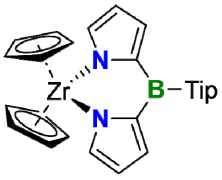


R = Me, H



E = NMe, O, S





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METAL OXIDE – SCHIFF BASE COMPOSITE AS NOVEL OPTICAL SENSORS FOR METAL ION DETECTION IN AQUATIC ENVIRONMENT

Debleena Mandal[a], Magdalena Barwiolek[a], Dominika Jankowska[a], Anna Kaczmarek-Kędziera[a], Tadeusz M. Muzioł[a], Iryna Tepliakova[b], Roman Viter[b]

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[b] Faculty of Science and Technology, Institute of Atomic Physics and Spectroscopy, University of Latvia, Riga, Latvia

The presence of metal ions in food, soil, and water at concentrations above or below the admissible limits poses a threat to the environment and human health [1]. Optical sensors based on absorbance and photoluminescence for metal ion detection are simple, low-cost, and can be integrated into a single system. Schiff bases (SBs) with their photoluminescence properties are potential candidates for detecting metal ions [2]. Two forms of the Schiff base compound, L1.EA and L1.MeOH were obtained by reacting 2,4-dihydroxybenzaldehyde with o-phenylenediamine. L1.EA exhibits luminescence at λ_{em}= 428 nm, λ_{ex}= 330 nm, whereas L1.MeOH emits at λ_{em}= 430 nm and λ_{ex}= 330 nm. Both compounds exhibit sensitivity to several metal ions, including Zn^{2+}, Cu^{2+}, Al^{3+}, Mg^{2+}, Co^{2+}, and Mn^{2+}. To improve the sensitivity of L1 to metal ions, a novel Schiff base-ZnO composite was obtained by combining L1 and zinc oxide tetrapods (ZnO tp). The composite of L1.MeOH and L1.EA with ZnO tp opened new possibilities as a luminescent sensor with sensitivity towards various metal ions like Zn^{2+}, Cu^{2+}, Al^{3+}, Mg^{2+}, Cr^{3+}, and Fe^{3+} ions.

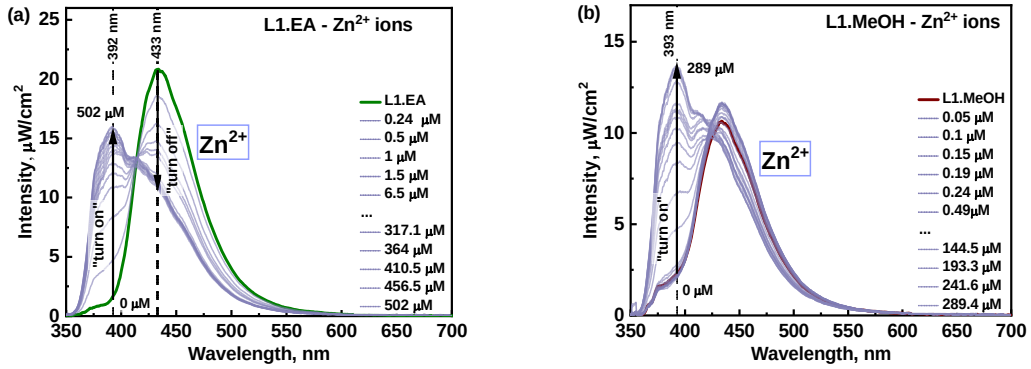


Figure 1. Photoluminescence spectra of (a) L1.EA with Zn^{2+} ions, (b) L1.MeOH with Zn^{2+} ions.

Acknowledgements: Research financed by Horizon Europe-the Framework Programme for Research and Innovation (2021-2027), HE-MCSA-RISE-2022, 101086364.

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THE SYNTHESIS AND ELECTRONIC PROPERTIES OF REMOTELY TUNED NHC SYSTEM

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[a]Department of Organic Chemistry, Faculty of Pharmacy, Medical University of Gdańsk, Gdańsk, Poland
[b]NanoBioMedical Centre, Adam Mickiewicz University, Poznan, Poland
[c]Department Chemical Technology of Drugs, Faculty of Pharmacy, Medical University of Gdańsk, Gdańsk, Poland
[d]Department of Chemistry and Centre for Sustainable Chemistry, Ghent University, Krijgslaan 281, 9000 Ghent, Belgium

Carbenes constitute a unique class of reactive intermediates characterized by a divalent carbon center possessing a six-electron valence shell, resulting in pronounced coordinative unsaturation. Among them, N-heterocyclic carbenes (NHCs) have emerged as versatile ligands in modern organometallic chemistry due to their strong σ-donor capabilities and tunable electronic properties. These features arise from the sp^2-hybridized lone pair on the carbene carbon, which readily engages in σ-donation to transition metal centers, complemented by π-back bonding interactions and additional π-donation from adjacent nitrogen atoms. To understand the inner workings of transition metal (TM) catalysis and predict the reactivity of TM complexes, the quantification of ligand stereo-electronic properties is key. Quantifying ligand electronic parameters in TM complexes has been mainly approached through the use of the Tolman Electronic Parameter (TEP) where the donating capability of a given ligand L is measured using the infrared frequency of the CO-bond in the corresponding $[Ni(CO)_3(L)]$ complex. Using this experimental technique the carbonyl stretching frequencies of a vast number of the most commonly used NHC ligands have been measured. To circumvent the use of the toxic $[Ni(CO)_4]$, alternative carbonyl bearing systems have been designed. Rh(NHC)(acac)(CO)] complexes have shown good correlation with data from the nickel system, thus allowing extraction of TEP data from these alternative systems [1].

We developed a novel class of NHC donors derived from the deprotonation of 2-alkyl-4-(phenylcarbamoyl)-[1,2,4]triazolo[4,3-a]quinolin-2-ium chlorides. These azolium salts were reacted with $Rh(acac)(CO)_2$ in the presence of potassium carbonate to form [Rh(NHC)(acac)(CO)] complexes. Infrared measurements of the CO stretching frequencies indicate that these ligands exhibit stronger donor properties than classical imidazolium-derived NHCs such as IPr, IMes, IPr*, SIPr, and SIMes. Additionally, the donor strength at the C1 carbene center within the fused [1,2,4]triazolo[4,3-*a*]quinoline framework can be finely tuned through modification of the 4-(arylcarbamoyl) substituent.

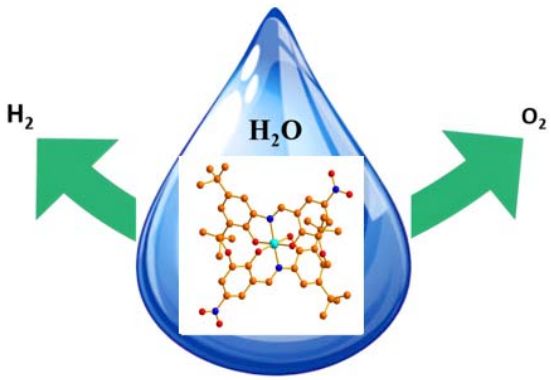
[1] F. Bru, R.S.C. Charman, L. Bourda, K. Van Hecke, L. Grimaud, D.J. Liptrot, C. S. J. Cazin; A simply accessible organometallic system to gauge electronic properties of N-heterocyclic carbenes *Dalton Trans*., **2024**, *53*, 16030.

BIFUNCTIONAL WATER SPLITTING ENABLED BY METAL–LIGAND COOPERATIVITY IN MOLECULAR COBALT(III) COMPLEX

Dipanjana Sarkar[a], Sarita Yadav[b], Madhulika Gupta[b] and Ramesh K. Metre[a]

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[b]Indian Institute of Technology Dhanbad, Dhanbad, India

The increasing global demand for sustainable and carbon-neutral energy sources necessitates the development of efficient technologies for renewable energy storage and conversion [1]. Water splitting, which involves the electrochemical generation of hydrogen and oxygen from water, represents a promising strategy for producing green hydrogen as a clean energy carrier with high gravimetric energy density and zero carbon emissions [2]. Thus, developing cost-effective, earth-abundant, and mechanistically well-defined catalysts capable of driving both half-reactions efficiently is therefore critical for enabling a sustainable hydrogen economy. A structurally well-defined mononuclear cobalt (III) complex incorporating a redox-active salicylaldiminate ligand derived from *o*-aminophenol has been synthesized and comprehensively characterized by spectroscopic methods, including single-crystal X-ray diffraction. The cobalt centre exhibits a distorted octahedral coordination environment, with weak intermolecular C–H···O interactions contributing to solid-state stabilization. Electrochemical studies reveal accessible ligand- and metal-centered redox processes in both homogeneous and surface-confined states. The complex operates as a bifunctional molecular electrocatalyst upon immobilization over glassy carbon electrode for reactions relevant to overall water splitting. Under alkaline conditions (1.0 M KOH), it promotes the oxygen evolution reaction with an overpotential of 410 mV at a current density of 10 mA cm^{-2} and displays favourable kinetics, as evidenced by a Tafel slope of 55 mV dec^{-1}. In contrast, under acidic conditions (0.5M H_2SO_4) the same catalyst facilitates the hydrogen evolution reaction, delivering 10 mA cm^{-2} at an overpotential of 350 mV through a predominantly metal-centered pathway. Post-catalytic spectroscopic analyses (UV–vis, FT-IR, and XPS) confirm the retention of molecular integrity under catalytic conditions. Density functional theory calculations further elucidate the mechanistic divergence, revealing a ligand-centered pathway for water oxidation and a metal centered pathway for proton reduction driven by metal–ligand cooperativity. Together, these findings highlight the potential of redox-active ligand frameworks in enabling bifunctional molecular electrocatalysts for overall water splitting.



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NON-NOBLE METAL PINCER COMPLEX MEDIATED SOLID-STATE TRANSFER HYDROGENATION OF AMIDES

Divya Jain, Hans-Joachim Drexler, Torsten Beweries *

Leibniz Institute for Catalysis (LIKAT Rostock), Albert-Einstein-Str. 29a, 18059 Rostock, Germany.

The reductive cleavage of amides is a significant challenge in synthetic chemistry due to their high resonance stability and strong hydrogen-bonding networks. While traditional methods often require noble metal catalysts or the addition of Lewis acids[1], transfer hydrogenation approaches for amides remain rare. An example has been reported in which C–N bond cleavage was achieved via transfer hydrogenation, requiring high reaction temperatures and a homogeneous Mn pincer complex.[2]

We now present the first and highly efficient protocol for the solid-state deoxygenative transfer hydrogenation of amides catalyzed by a stable Mn pincer complex (MnPNP). Our protocol mainly operates under Lewis acid additive-free conditions. By utilizing ball milling (mechanochemistry), we achieve high selectivity for the transformation of formamides into their corresponding higher amines. The reaction mechanism was proposed through deuterium labeling studies and control experiments, showing the reaction proceed via an imine-based pathway.[3] This solvent-free approach avoids the use of pressurised H_2 gas and high-boiling solvents, while the synergy between the Mn catalyst and mechanical force enables direct substrate activation. Overall, this protocol provides a practical and environmentally benign method for amide reduction and demonstrates the potential of solid-state transfer hydrogenation as a valuable tool for green and sustainable synthetic chemistry.

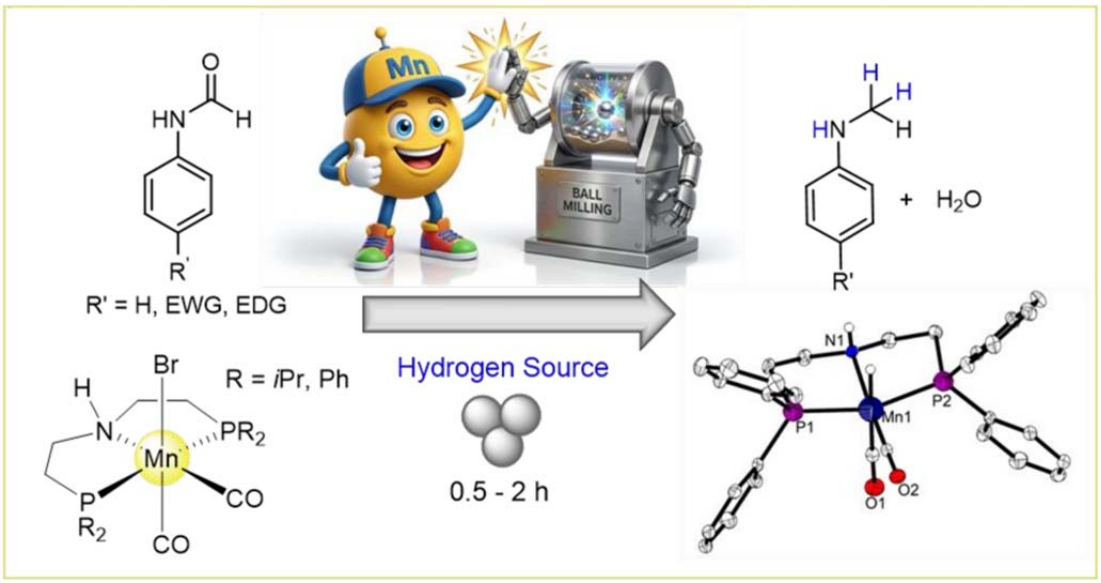


Figure 1: Mn catalyzed mechanochemical transfer hydrogenation of formamides.

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[1] J. R. Cabrero-Antonino, R. Adam, V. Papa, M. Beller, *Nature Commun.* **2020**, *11*, 3893. [2] X. Liu, T. Werner, *Chem. Sci.* **2021**, *12*, 10590–10597.

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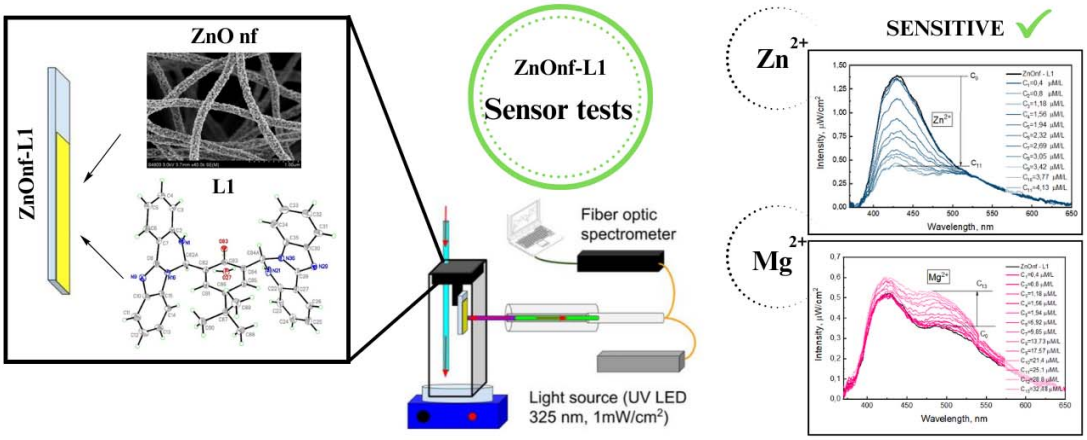
ZnO-BENZIMIDAZOLE COMPOSITE FOR SELECTIVE DETECTION OF Zn^{2+} AND Mg^{2+} IONS

Dominika Jankowska[a], Tadeusz M. Muzioł[a], Debleena Mandal[a], Anna Kaczmarek-Kędziera[a], Iryna Tepliakova[b], Roman Viter[b], and Magdalena Barwiołek[a]

[a]Faculty of Chemistry, Nicolaus Copernicus University in Torun, 87-100 Torun, Poland
[b]Faculty of Physics, Mathematics and Optometry, University of Latvia, 19 Raina Blvd., Riga, LV 1586, Latvia

Imines, such as benzimidazole derivatives and Schiff bases, are known for their luminescence, sensitivity, and biological properties. Hosting of the metal ions is an essential property of the imines, resulting in their optical properties, such as the shift of absorption and emission peaks and fluorescence quenching. Thus, imines have good potential for application in optical sensors.

A new ZnO-imine composite (**ZnOnf-L1**) was obtained for use as an optical chemical sensor. The novel composite **ZnOnf-L1** was designed and characterized by SEM, TEM, and optical methods. The composite **ZnOnf-L1** sensitively and efficiently detects Zn^{2+} ion at λ=427 nm ($\Delta\lambda_{ex}$=4 nm, C_{Zn2+}=0-4 μM) and Mg^{2+} ion at λ=427 nm ($\Delta\lambda_{ex}$=2 nm, C_{Mg2+}=0-32 μM). The sensitivity behaviour of **ZnOnf-L1** and the red shift of the emission band indicate that the composites are suited for use in environmental sensors. [1]



Funding: This research was funded by HE-MCSA-RISE-2022, Sens4Corn, 101086364

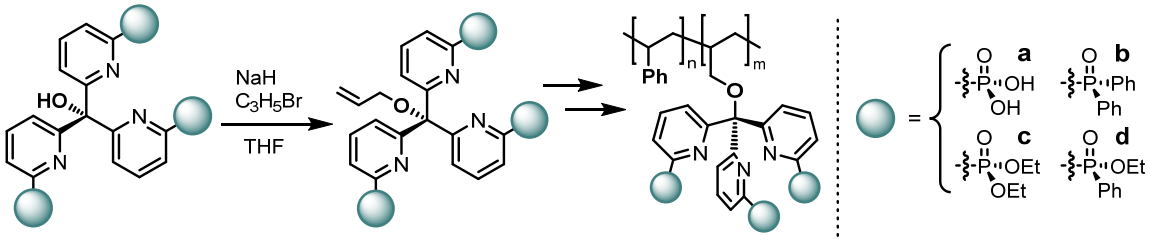
[1] D. Jankowska, T. M. Muzioł, D. Mandal, A. Kaczmarek-Kędziera, I. Tepliakova, R. Viter, M. Barwiołek, Spectrochim Acta A Mol Biomol Spectrosc. **343**, 126604, (2025).

POLYMER-SUPPORTED TRIPODAL LIGANDS FOR THE SELECTIVE EXTRACTION OF RARE EARTH ELEMENTS

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Department of Chemistry, University of Calgary, Alberta, Canada

Rare earth elements (REEs) include the fifteen lanthanide elements (atomic numbers' 57 - 71), as well as scandium and yttrium. These elements serve as vital enablers for emerging carbon-free and low-emission technologies such as electric vehicles (EVs) and wind turbines [1-3]. Due to their similar ionic radii, chemical properties, and geological occurrence, the separation of individual REEs is a notoriously challenging process. Currently, iterative liquid-liquid extraction is the most widely used method due to its high production efficiency [1,2]. This method involves multiple water-organic solvent partitions, using chemical extractants (ligands) dissolved in the organic layer to impart selectivity. While high purity REEs can be obtained using solvent extraction, this technique involves the consumption of large quantities of environmentally harmful solvents and is additionally energy intensive. As a greener alternative, solid sorbents have been gaining popularity as an alternative method for REE separation, where chelating sites on a solid support can selectively adsorb rare-earth ions in the aqueous phase with no need for an organic solvent [1-3]. This work showcases a novel tripodal ligand framework designed specifically for the extraction and separation of REEs. A series of phosphine oxide functional groups serve as the primary set of REE chelators, while a pendant alcohol group serves as a synthetic handle for incorporating the ligand into water-insoluble polymer frameworks (Scheme 1). The ligands' performance towards REE extraction and separation, their incorporation into polymeric structures, as well as the iterative process in refining our design will be addressed in this presentation.



Scheme 1.

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MULTISTATE SWITCHING OF SOME RUTHENIUM ALKYNYL AND VINYL SPIROPYRAN COMPLEXES

David Jago[a], Mark C. Walkey[a], Emma E. Gaschk[a], Peter R. Spackman[b], Matthew J. Piggott[a], Stephen A. Moggach[a], George Koutsantonis[a]

[a]Chemistry, School of Molecular Sciences, The University of Western Australia, Perth
[b]Curtin Institute for Computation, School of Molecular and Life Sciences, Curtin University, Perth

To study the switching properties of photochromes, we undertook the synthesis and characterisation of several organometallic complexes of the type [Ru(Cp*)(dppe)(C≡C-SP)] or [Ru(CO)(dppe)(PPh_3)Cl(CH=CH-SP)], where SP = spiropyran. The spectroscopic and electrochemical properties of the complexes were determined by careful cyclic voltametric and spectroelectrochemical experiments. Whereas the mononuclear alkynyl ruthenium complexes undergo one-electron oxidations localised over the metal alkynyl moiety, the oxidation of the mononuclear vinyl ruthenium complexes is centred on the indoline moiety of the spiropyran. Through these studies, we demonstrate access to several stable redox states, in addition to switching states attained via acidochromism and/or photoisomerization [1].

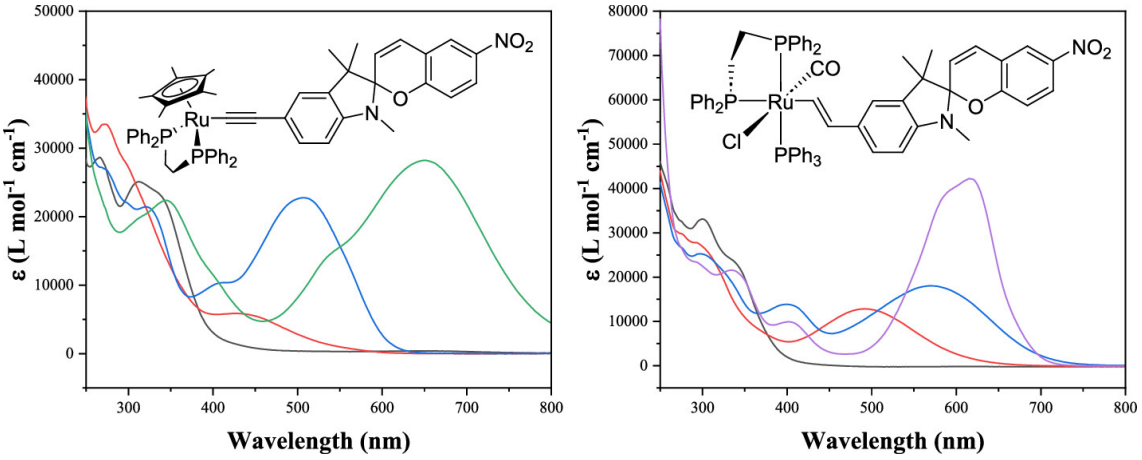


Figure 1. Representative UV-Vis spectra for the alkynyl-SP (left) and vinyl-SP (right) complexes.

[1] Jago, D.; Walkey, M. C.; Gaschk, E. E.; Spackman, P. R.; Piggott, M. J.; Moggach, S. A.; Koutsantonis, G. A. Multistate Switching of Some Ruthenium Alkynyl and Vinyl Spiropyran Complexes. *Inorg. Chem.* **2023**, *62* (31), 12283-12297. DOI: 10.1021/acs.inorgchem.3c01190.

MONOMER–DIMER BEHAVIOR OF DIOXOVANADIUM(V) SCHIFF BASE COMPLEXES

Eric Shepard[a], Chris Chang[a], Adam Miller[a], Andrew Bates[a], Avery Gibson[a], Debbie Crans[a,b], Craig McLauchlan[c], and Navamoney Arulsamy[d]

[a]Department of Chemistry, Colorado State University, Fort Collins, CO, USA
[b]Cell and Molecular Biology, Colorado State University, Fort Collins, CO, USA
[c]Department of Chemistry, Illinois State University, Normal, IL, USA
[d]Department of Chemistry, University of Wyoming, Laramie, WY, USA

Cis-dioxidovanadium(V) (cis-VO2+) moieties are one of the most fundamental groups in vanadium(V) chemistry and in this project we will examine formation of monomers and dimers of N-(salicylideneaminato)-N′-(2-hydroxyethyl)-1,2-ethanediamine (HSHED) dioxovanadium(V) Schiff base complexes in solution and in the solid state. The Crans group has recently worked on these compounds for brain cancer treatment, and found that they are superior to cis-platin. We specifically aim to study if the oxido-bridged dimers observed in crystal structures are retained in solution to investigate the fundamental coordination chemistry. Newly obtained structures include the dinuclear [VO2(5-Ad-3-OEtHSHED)]2, the monomeric [VO2(3-tBuHSHED)] and [VO2(3,5-ditBuHSHED)] crystal structures, which will be compared with related reported dinuclear [VO2(3-OEtHSHED)]2 and the unsubstituted dinuclear [VO2(HSHED)]2 complex. The [VO2(HSHED)] is known to crystallize as two visually distinct orange and yellow crystal forms, polymorphs, that were assigned as oxido-bridged dimers differing mainly in molecular positioning, hydrogen bonding, and V–O distances. The vanadium coordination environment of the new complexes will be characterized in the solid state by X-ray crystallography, in solution by NMR and UV-Vis spectroscopy, and by DFT calculations. This information will be compared to the known systems to explore generally when dimer formation is observed. Together, these combined approaches will allow us to determine the intrinsic coordination preferences, the effects of H-bonding, and steric hindrance on dimer formation in the solid-state and in solution.

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"COOL-SPS-ENGINEERED SPIN-CROSSOVER CERAMICS FOR NEXT-GENERATION BAROCALORIC COOLING"

F. Prajapati[a], Y. Sabater-Algarra[b], A. Inchausti[a], E. Duverger-Nédellec[a], N. Daro[a], M. Marchivie[a], G. Chastanet[a], O. Toulemonde[a], H. Shepherd[b], P. Rosa[a]

[a]ICMCB, Univ. Bordeaux, CNRS, INP, Pessac, France,33600
[b] University of Kent, Canterbury CB, Univ. CT2 7NZ, United Kingdom, CT2 7NH

Environmental change is one of the most critical challenges of the 21st century. Everyday refrigeration devices (air conditioners, refrigerators, heat pumps) consumed up to 20% of the world's electricity production in 2025 and represented 7.5% of global CO_2 emission.[1] More energy-efficient cooling systems need alternatives to vapor compression refrigeration. The mechanocaloric effect, that is adiabatic variations in temperature related to applied pressure (barocaloric) or stress (elastocaloric), is one of the most promising ones. In 2016, Spin CrossOver (SCO) materials were described as a promising candidates for barocaloric cooling devices.[2] Molecular SCO complexes, are well-known for their stimulus-induced (*T*, *p*, light, etc.) variation in electronic configuration. This variation cause structural, entropic, mechanical, magnetic, optical, and electronic changes as well.[3] Most interestingly, they may be sensitive to small pressure perturbations of a few kilobars or even less, due to volume changes of up to 11%.[4]

Such materials, which are typically only available as polycrystalline powders, must be shaped into macroscopic (poly)centimetric forms in order to be used technologically. We have demonstrated on variety of representative samples that Cool-SPS processing (SPS: Spark Plasma Sintering, $50 \leq T \leq 600$°C; $40 \leq P \leq 900$ MPa) can sinter powders into "molecular ceramics" [5], with relative densities that satisfactorily range from 85 to 95% of the corresponding crystal structures. Nevertheless, differences have been noticed regarding the morphology, phase identity (when dealing with polymorphs) and magnetic properties with the initial materials after the sintering process. A key tool for monitoring and managing sintering processes is the mapping of those complexes phase diagram, which is primarily accomplished through spectroscopic and diffraction studies on single crystals or polycrystalline powder to examine and comprehend the nature of the species seen when combining pressure and temperature changes.

Gratefully acknowledge funding from the European Innovation Council Pathfinder Challenge Clean and Efficient Cooling under the FROSTBIT project (Grant Agreement No. 101161137).

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1D AND TWO 2D COORDINATION NETWORKS BASED ON $[Ni(cyclam)]^{2+/3+}$ AND $[Ru(CN)_6]^{4-}$ AND THE NICKEL REDUCTION

Gaja Wota, and Beata Nowicka

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In green chemistry, ruthenium complexes are known for their catalytic behavior, and have been studied for electrooxidation of water [1]. The redox properties of nickel-cyclam complex (cyclam=1,4,8,11-tetraazacyclotetradecane) have been employed for oxidation of amines [2], hydrogen peroxide [3], or reduction of CO_2 to CO [4]. We used $[Ni(cyclam)]^{3+/2+}$ and $[Ru(CN)_6]^{4-}$ complexes as building blocks to construct a series of coordination polymers with potential redox activity. We obtained 1D chains $\{(NH_4)[Ni^{III}(cyclam)][Ru^{II}(CN)_6 \cdot 5H_2O\}_\infty$ (**1**), which negative charge is compensated by guest NH_4^+ cations, a positively charged 2D honeycomb-like network $\{[Ni^{III}(cyclam)]_3[Ru^{II}(CN)_6]_2(Cl) \cdot 16H_2O\}_\infty$ (**2**) with guest Cl^- anions, and a neutral 2D network $\{[Ni^{III}(cyclam)]_2[Ni^{II}(cyclam)][Ru^{II}(CN)_6]_2 \cdot 22.5H_2O\}_\infty$ (**3**) of the same topology based on mixed valence $Ni^{II/III}$ ions. All networks show stepwise loss of crystallization water accompanied by structural transformations. XAS analysis together with magnetic susceptibility measurements indicate that in the dehydrated phases of all compounds only Ni(II) is present. In similar networks based on hexacyanoferrate anions, reversible charge transfer between metal centers occurs [5]. However, in the hexacyanoruthenate - based networks **1**-**3** we did not observe oxidation of Ru(II). Since the oxidation potential of $[Ru(CN)_6]^{4-}$ ion is higher than that of H_2O, we assume that the Ni(III) ions are reduced by water in the process catalyzed by hexacyanoruthenate.

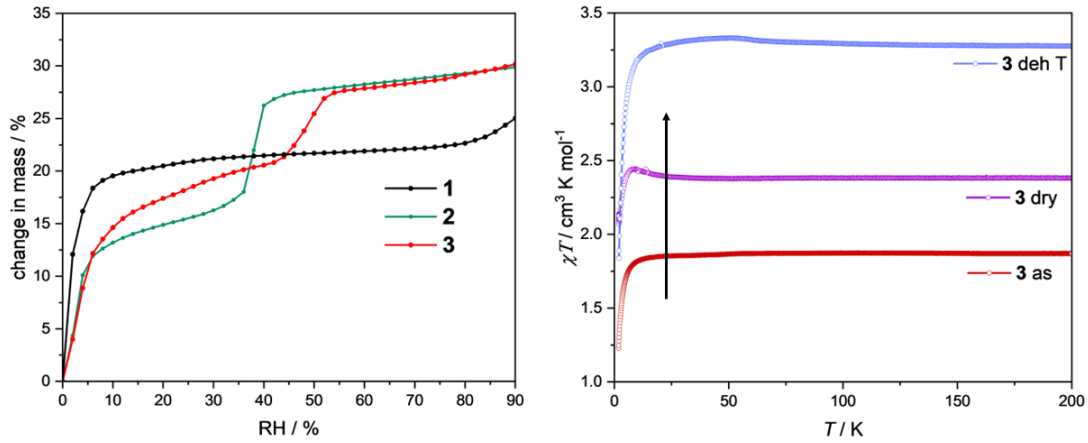


Figure 1. Water desorption isotherms of as-synthesized **1**, **2** and **3** (left); magnetic susceptibility of different phases of **3**: as synthesized (3 as), dried at RT (3 dry), dried at 75°C (3 deh T).

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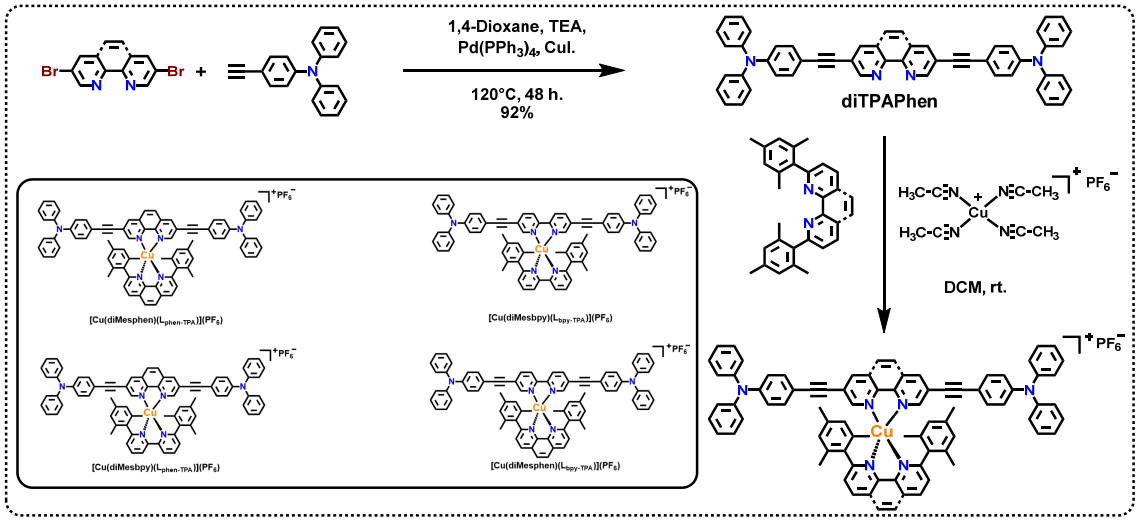
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EFFECT OF LIGHT-HARVESTING UNITS ON BACKBONE FLEXIBILITY AND ELECTRONIC PROPERTIES OF HETEROLEPTIC Cu(I) COMPLEXES

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Photosensitizers are the molecules responsible for light-harvesting and initiating the primary photo-induced electron transfer process in a photocatalytic system.[1] There is growing interest in the development of photosensitizers from earth abundant metal ion such as copper(I).[2] They absorbs light energy to drive chemical transformations, also critical components in sustainable energy technologies such as photocatalytic hydrogen production and carbon dioxide reduction. The phenanthroline based ligand (3,8-diTPAPhen) was reported by Whang and coworkers to study the sensitivity of Ir(III) photosensitizers.[3] To unlock full potential and study the light-harvesting effect of the ligand (3,8-diTPAPhen), we have developed an improved Sonogashira methodology that allows the generation of ligands featuring both phenanthroline and bipyridine cores.



Scheme 1. Synthesis of new Cu(I) heteroleptic complexes.

Those new diTPA ligands were used to synthesize four heteroleptic Cu(I) complexes (Scheme 1). The structures of three of the copper complexes were confirmed using X-ray crystallography. Low-frequency Raman spectroscopy showed that bipyridine complexes exhibit less lattice disorder than phenanthroline analogues. All complexes display strong ILCT absorption that masks the expected ~450 nm MLCT band. The diimine dihedral angle at the TPA site strongly influences the extinction coefficient.

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ROOM-TEMPERATURE LUMINESCENCE OF AIR-STABLE NICKEL(0) COMPLEXES

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In photochemistry and physics copper(I) complexes emerged as a suitable alternative for noble metals, like ruthenium or iridium.[1, 2] Their isoelectronic analogue, nickel(0), remained largely unexplored, although previous studies suggest that nickel(0) complexes could display favorable photophysical properties.[3, 4] Nevertheless, significant challenges persist, including the absence of photoluminescence in solution at room temperature and limited air stability.[5] To overcome these key limitations, strong-field ligands with sterically demanding substituents, resulting in rigid coordination environments, are required. Chelating isocyanide ligands fulfill these requirements, and our work aims to establish photoluminescent, bench-stable nickel(0) complexes and to study their properties in greater depth.

Herein, we report two new air-stable homoleptic nickel(0) isocyanide complexes, both exhibiting photoluminescence in solution at room temperature. The origin of the emission, attributed to a metal-to-ligand charge-transfer (MLCT) excited state, is investigated with time-resolved laser spectroscopy and DFT calculations. Our results illustrate part of the untapped innovation potential still existing in first-row transition metal photophysics and photochemistry.

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ATOMISTIC SIMULATION OF ARGYRODITE SULFIDE SOLID ELECTROLYTES FOR FAST LITHIUM-ION TRANSPORT

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Abstract: Sulfide-based argyrodite solid electrolytes are promising candidates for all-solid-state batteries due to their high ionic conductivity, yet practical implementation remains challenging. To overcome these limitations, we move beyond conventional experimental approaches by employing Ab Initio Molecular Dynamics (AIMD) simulations to gain fundamental atomic-level insights. In this study, we investigated the lithium-ion diffusion modes in Li_6PS_5Cl (LPSC), a representative sulfide-based solid electrolyte. Through our simulations, we observed the unrestricted migration of Li^+ ions within the crystalline framework. By quantifying ion mobility and identifying primary diffusion pathways, we successfully correlated crystal structure with transport kinetics. These findings provide a molecular perspective on ion-hopping mechanisms that are beyond the reach of current experimental observations. Ultimately, this work elucidates the fundamental diffusion mechanisms and offers critical design principles for the strategic development of next-generation solid electrolytes with enhanced performance.
[RS-2024-00443714]

CONTROLLING PHOTOACTIVE EXCITED STATES IN Co(III) AND Ni(II) COMPLEXES THROUGH LIGAND ELECTRONICS

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In photochemistry changing from well-established 4d and 5d metals to their more abundant 3d analogues comes with the challenge of an intrinsically lower ligand field splitting. This facilitates deactivation of metal-to-ligand charge-transfer (MLCT) states through lower lying metal-centered (MC) states yielding lower excited state energies, shorter excited state lifetimes and lower photoluminescence quantum yields. Therefore, understanding how to influence the ligand field splitting for 3d metals is needed to optimize their application potential. For this, a series of ligands with tuned electronics based on 2,6-di(quinoline-8-yl)pyridine (**dqp**) was synthesized and their influence on Co(III) and Ni(II) investigated.

The **dqp** ligand forms complexes with optimized bite-angles and a nearly ideal octahedral coordination geometry.[1-3] The substitution of the 4’-position of quinoline and the 4-position of pyridine with nitrogen yields the ligands 2,6-di(quinoxalin-5-yl)pyridine and 2,6-di(quinoxalin-5-yl)pyrazine with increasing π-acceptor and decreasing σ-donor abilities.[4]

The key finding is that the electronic structure of the chelate affects the ligand field in the case of the more positively charged Co(III) fundamentally differently than in Ni(II). The underlying reason for this finding appears to be that our bite angle-optimized ligands act as π-donors towards Co(III), whereas they act as π-acceptor ligands towards Ni(II). This effect had been suspected to occur previously in Fe(II) complexes, but in those cases was more difficult to probe due to overlapping MLCT absorptions.[5] The Ni(II) complexes investigated here provide clearer comparative insight in this regard.[6] These results contribute to an improved understanding of how ligand electronics can be tailored to achieve favorable photophysical properties in first-row metal complexes.

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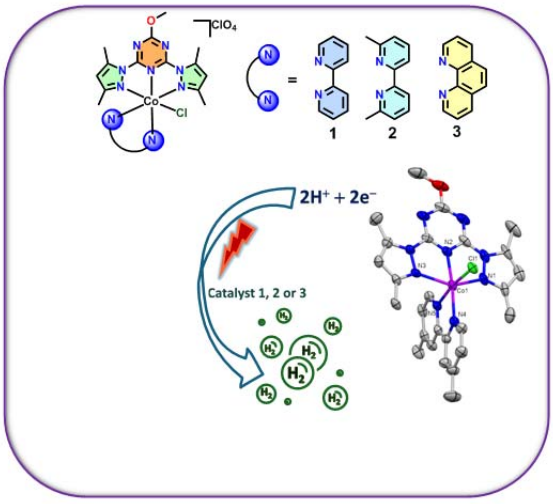
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HETEROLEPTIC MONONUCLEAR Co(II) COMPLEXES AS ELECTROCATALYSTS FOR HYDROGEN EVOLUTION REACTION IN NON-AQUEOUS MEDIA

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The development of efficient molecular electrocatalysts based on earth-abundant first-row transition metals is an important strategy for sustainable hydrogen (H_2) production *via* electrochemical proton reduction.[1,2] In this connection, three heteroleptic cobalt(II) complexes, [Co(**L**)bpyCl]ClO_4 (**1**), [Co(**L**)mebpyCl]ClO_4 (**2**), and [Co(**L**)phenCl]ClO_4 (**3**), have been synthesized using the triazine-based ligand **L** = 2-chloro-4,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,3,5-triazine in combination with bidentate co-ligands bpy (2,2′-bipyridine), mebpy (4,4′-dimethyl-2,2′-bipyridine), and phen (1,10-phenanthroline). Comprehensive spectroscopic and analytical characterization, including single-crystal X-ray diffraction, which confirms a distorted octahedral coordination environment around the Co(II) center in all three complexes. The electrocatalytic proton reduction activity of the complexes was investigated in anhydrous acetonitrile using acetic acid as the proton source. Cyclic voltammetry reveals a significant catalytic current enhancement upon addition of 10 mM AcOH, with an onset potential in the range of −1.2 to −1.4 V *vs* SCE, indicative of efficient electrocatalytic hydrogen evolution. The estimated overpotentials for the hydrogen evolution reaction (HER) lies between ~320 and 420 mV, depending on the electronic properties of the bidentate ligand core. Controlled potential electrolysis experiments confirm H_2 generation, with faradaic efficiencies of 90–100% for complexes **1** and **2** and 74% for complex **3**. Post-catalytic analyses rule out heterogeneous catalyst formation, establishing the molecular nature of the active species. Based on combined experimental and theoretical studies, a plausible mechanism for the electrocatalytic HER is proposed.



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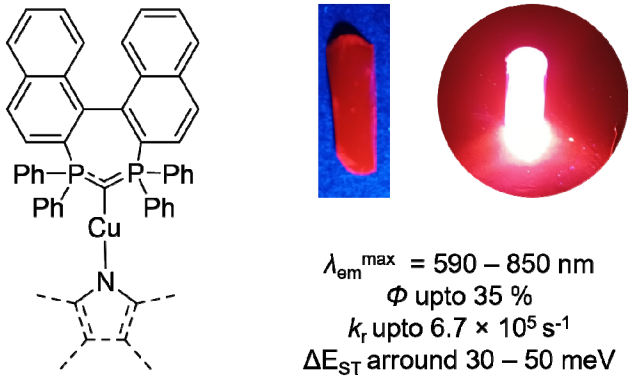
LINEAR HETEROLEPTIC COPPER (I) COMPLEXES ENABLING EFFICIENT NIR-TADF AND ROOM TEMPERATURE SINGLE PHOTON EMISSION

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The development of efficient near-infrared (NIR) emitters is crucial for emerging technologies including deep-tissue bioimaging, optical telecommunications, night-vision displays, and advanced sensing. Conventional fluorescent materials are fundamentally limited to a maximum internal quantum efficiency (IQE) of 25%, as only singlet excitons contribute to emission. Thermally activated delayed fluorescence (TADF) overcomes this limitation by enabling thermal up conversion of triplet excitons to emissive singlet states *via* endothermic intersystem crossing (RISC), allowing theoretical IQEs of up to 100% [1]. However, extending TADF emission into the NIR region remains challenging due to the energy gap law, which promotes non-radiative decay as emission energies decrease, particularly in purely organic systems with weak spin–orbit coupling [2].

Here, we report a series of heteroleptic linear Cu(I) complexes featuring a donor–metal–acceptor architecture incorporating carbodiphosphorane (CDP) with binaphthyl backbone act as an acceptor unit. These complexes exhibit intense emission spanning 590–850 nm and display tunable TADF behavior with enhanced rate constants up to $6.7 \times 10^5\ s^{-1}$. Electronic-structure analysis reveals very small singlet–triplet energy gaps of 30–60 meV, enabling efficient triplet harvesting and rapid reverse intersystem crossing. Notably, the most efficient complex shows clear photon antibunching in single-molecule photon-correlation measurements, confirming its capability as a room temperature single–photon emitter and highlighting its potential for quantum photonic and secure communication technologies.



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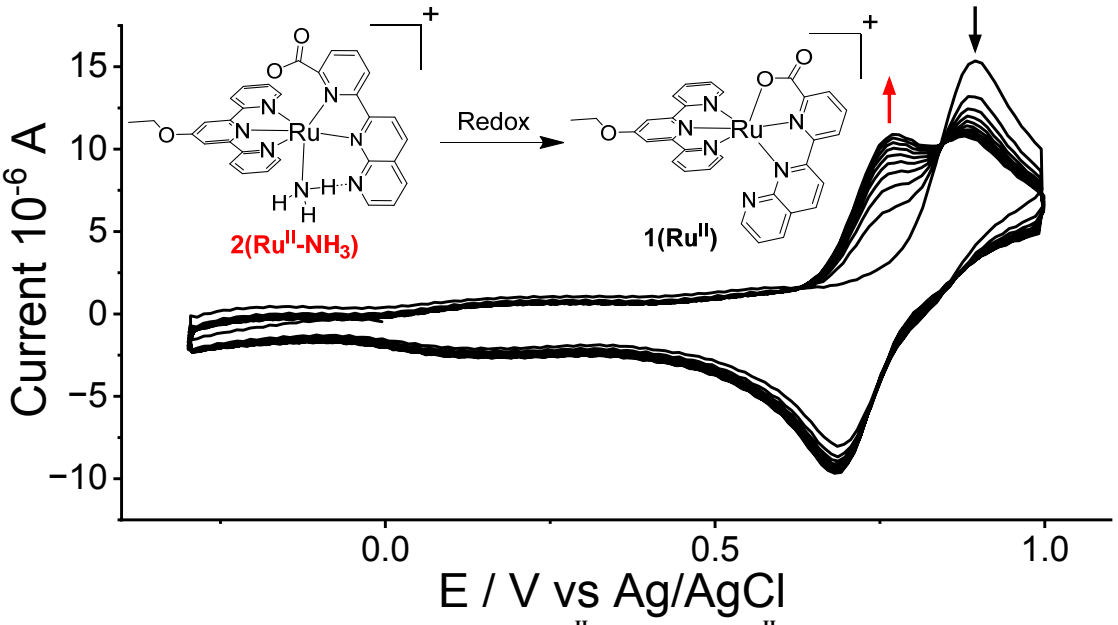
ELECTROCHEMICAL RELEASE OF AMMONIA FROM A STIMULI-RESPONSIVE RUTHENIUM COMPLEX

Jin Kubota, Kouta Shimotani, Takayo Moriuchi, Keiichi Fujimori, Masanari Hirahara

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Ammonia has attracted significant interest as a hydrogen energy carrier and a relevant molecule. Recently, several molecular systems that release ammonia in to external stimuli such as heat or light have been reported.[1] However, systems that respond to oxidative stimuli remain largely unexplored. We previously reported a molecule that releases water upon oxidation.[2] Herein, we synthesized **2(Ru^{II}-NH$_3$)** and investigated the electrochemical release of ammonia using cyclic voltammetry (CV).

Figure 1. Cyclic voltammograms of **2(Ru^{II}-NH$_3$)** at pH 3 from 1st to 20th scans. Red and black arrow



correspond to the oxidation of **2(Ru^{II}-NH$_3$)** and **1(Ru^{II})**, respectively.

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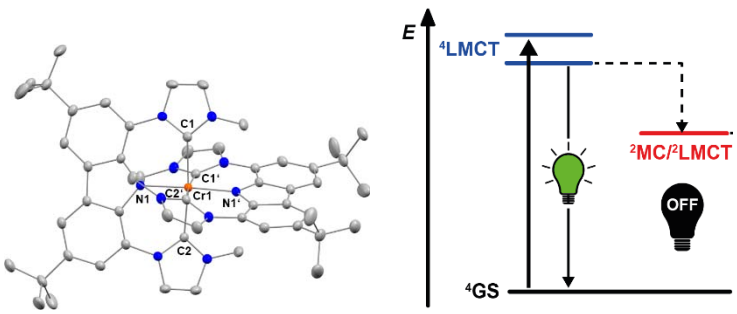
THE CARBAZOLATO-CARBENE CHROMIUM(III) COMPLEX $[Cr(bimca)_2]^+$ - EXCITED STATE DYNAMICS AND PHOSPHORESCENCE INHIBITION

Joan Sander,[a] Felix Gauder,[b] Sebastian J. Schicktanz,[b] Theo Maulbetsch,[b] Jens Kalmbach,[b] Dimitri Zorn,[a] Robert Naumann,[a] Christoph Förster,[a] Doris Kunz,[b,*] and Katja Heinze[a,*]

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Luminescent and photoactive transition metal complexes are essential in applications such as OLEDs, solar cells, sensing, and photocatalysis but often depend on scarce, costly metals like Ru and Ir. Thus, spin-flip (SF) emitters based on earth-abundant metals such as CrIII have gained attention for their distinct excited-state properties. In SF-complexes, the lowest excited state features the same electron configuration as the ground state, but with merely one flipped electron spin. This leads to only weakly distorted SF states and hence to sharp emission bands and long excited state lifetimes [1].

However, clear design principles for efficient SF emission are not yet well-established, and structural modifications can unexpectedly suppress luminescence. To better understand these effects, we combined spectroscopic methods with quantum chemical calculations to study the photophysical behavior of the carbazolato-carbene complex $[Cr(bimca)_2]^+$, where phosphorescence is suppressed completely and only weak ligand-centered fluorescence is observed [2].



Using a combination of static and time-resolved spectroscopy with quantum chemical calculations, we discuss possible reasons for this unexpected behavior [2].

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NOT *BREAKING BAD*: REVERSIBLE MULTISTEP SC–SC TRANSFORMATIONS IN COPPER HYDRAZONE COMPLEXES

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Single-crystal-to-single-crystal (SC-SC) transformations are rare solid-state processes in which structural changes occur while preserving single-crystal integrity. The reversibility of such transformations is particularly important, as it allows a direct correlation between structural changes and the resulting properties.[1] The study of SC-SC transformations therefore offers valuable insights into underlying mechanisms and can improve the design of functional materials, such as sensors and related applications.[2] Due to the diverse coordination of copper centers and the structural flexibility of hydrazone ligands, copper hydrazone complexes offer a fertile ground for studying SC-SC transformations.[3] In this study, we report a reversible multistep single-crystal-to-single-crystal transformation induced by exposure of the crystals to solvent vapors at room temperature. The process involves a solvent exchange, accompanied by a change in structural dimensionality, and variations in anion coordination modes, making this a unique example that offers valuable insights into the dynamic world of crystals.

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HETEROMETALLIC ALKALI METAL-GROUP 13 ALKOXIDES AS CATALYSTS IN CHEMICAL RECYCLING OF POLYCAPROLACTONE

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The most widely method of polymer recycling is a mechanical recycling involving repeated melting and reprocessing leading to a reduction in molecular weight and mechanical properties. This method is mainly applied to thermoplastics like polyethylene, polypropylene or polystyrene. Polycaprolactone (PCL) is a biodegradable petroleum-derived polyester widely used in packaging, films, carry bags, pouches, trays, reusable dishes, 3D printing, and other fields. It can also be applied in water treatment plants as it is biocompatible and environmentally friendly. PCL belongs to the group of compounds which cannot undergo mechanical recycling due to its tendency to hydrolytic degradation. Therefore, significant research efforts have focused on the chemical recycling of PCL through depolymerization of plastic waste into monomers or other chemical intermediates, which can be converted into other value-added products or repolymerized into polymers.[1, 2, 3]

In this work a series of heterometallic alkoxides: $[M'_6(sal\text{-}Me)_6]$ (M'^{+} = Li^+ (**1**), Na^+ (**2**), K^+ (**3**)), $[M'(sal\text{-}Me)]_n$ (M'^{+} = Rb^+ (**4**), Cs^+ (**5**)), $[Al(sal\text{-}Me)_3]$ (**6**), $[AlLi_3(sal\text{-}Me)_6]$ (**7**), and $[Ga_6Li(sal\text{-}Me)_6(OMe)_{12}]Cl$ (**8**) was synthesized and used as catalysts in chemical recycling of PCL to obtain alkyl esters of 6-hydroxyhexanoic acid which can be used for various commercial applications or as starting product to obtain new PCL material in a polycondensation reaction (*Figure 1*). Short-chain esters of 6-hydroxyhexanoic acid (6-HHA) are used as a fragrance ingredients, flavoring agents in food but also in skin care and hair care products for its mild and non-irritating properties. Esters of 6-HHA with longer chain are used as plasticizers for biodegradable polymers, lubricants, and surfactants due to their flexibility and hydrophobicity.

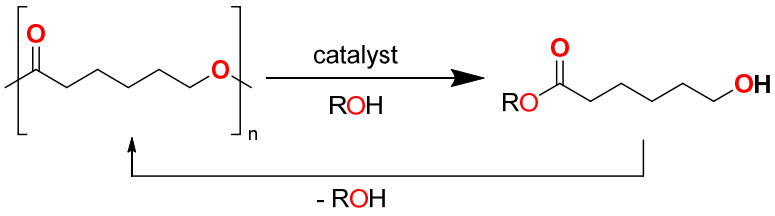


Figure 1. The scheme of chemical recycling of PCL.

Among the series of tested compounds, $[Rb(sal\text{-}Me)]_n$ and $[Cs(sal\text{-}Me)]_n$ exhibited the highest catalytic activity in the alcoholysis of PCL at 100°C with conversion yields up to 98%.

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THERMOCHROMIC WHITE-LIGHT CIRCULARLY POLARIZED EMISSION IN SINGLE MOLECULAR SOLID-STATE SYSTEM

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[c]Japan Synchrotron Radiation Research Institute (JASRI), Hyogo, Japan
[d]Research Institute for Interdisciplinary Science, Okayama University, Okayama, Japan
[e]Graduate School of Environmental, Life, Natural Science and Technology, Okayama University, Okayama, Japan

Circularly polarized luminescence (CPL) induces the direct encoding of chirality into emitted light and widens advanced photonic applications. However, the realization of stable, color-tunable, and especially white-color CPL (WCPL) emission from a single molecular system remains highly challenging. Herein, we present a new enantiomeric pair of homochiral tetracopper(I) clusters that exhibit solid-state thermochromic CPL and single-molecule WCPL, achieved via cryogenic CPL techniques (Figure 1). A well-balanced combination of intense yellow and blue dual emissions produces continuous color modulation across a wide temperature range, accompanied by high quantum yields. These emissions converge to WCPL with dissymmetry factors (g_{lum}) on the order of 10^{-3}, without the need for chemical mixing or external additives.

Notably, guest solvent-mediated crystal engineering opens facile tuning of both emission properties and CPL behaviors while retaining an identical molecular framework. Polymer-embedded films additionally show excellent water resistance along with stable thermochromic behavior and improved white-light emission. This study thus provides a new design strategy for atom-efficient chiroptical materials.

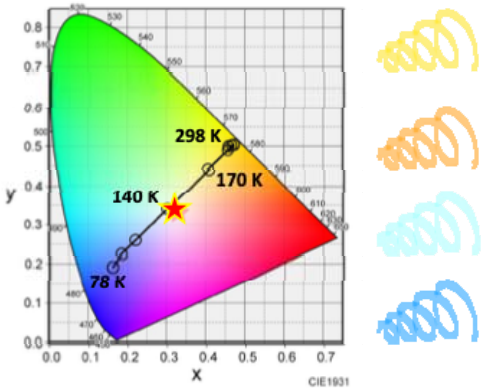


Figure 1. The schematic illustration of thermochromic CPL.

This work was supported by JSPS KAKENHI, Grant No. JP24K23108, as well as Iketani Science and Technology Foundation, Grant No. 0371189-A, Hyogo Science and Technology Association, Grant No. 7022, (all of these for K.T.). Synchrotron X-ray crystallography experiments were performed at the BL02B1 and BL41XU beamlines of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2024B1654, No. 2025A1698, and No. 2025B1025).

ELECTROCATALYTIC CO_2-TO-C_3 CONVERSION USING A DINUCLEAR Cu(I) COMPLEX AND MECHANISTIC ANALYSIS

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Toyota Central R&D Labs., Inc., Nagakute, Aichi, Japan

Electrochemical CO_2 reduction reaction (CO_2RR) for synthesizing high-value C_3 products is a promising approach toward a carbon-neutral society and has driven significant catalyst development. For highly selective C_3 formation, molecular catalysts are attractive because their catalytic performance can be tuned by the appropriate selection of the central metals and ligands. To date, however, examples of molecular catalysts that facilitate C_3 formation from CO_2 remain elusive. Here, we report CO_2RR catalyzed by a Br-bridged dinuclear Cu(I) complex (Figure 1a) [1]. The Faradaic efficiencies reach 50% for C_2 products (ethylene and ethanol) and 12% for the C_3 product (1-propanol) at –1.8 V vs. Ag/AgCl (Figure 1b). Using operando X-ray absorption fine structure (XAFS) analysis, we confirm that the molecular structure is maintained during the CO_2RR without the formation of metallic Cu. Operando surface-enhanced Raman spectroscopy (SERS), together with density functional theory (DFT) calculations, suggests that the C_3 product forms via C-C coupling between an adsorbed *CO species and a C_2 intermediate coordinated to two Cu centers through a single carbon atom, which is derived from a C_2 bidentate intermediate (Figure 1c). In this poster, we discuss the proton-coupled electron transfer (PCET) process from the C_2 bidentate intermediate toward the formation of ethylene and ethanol.

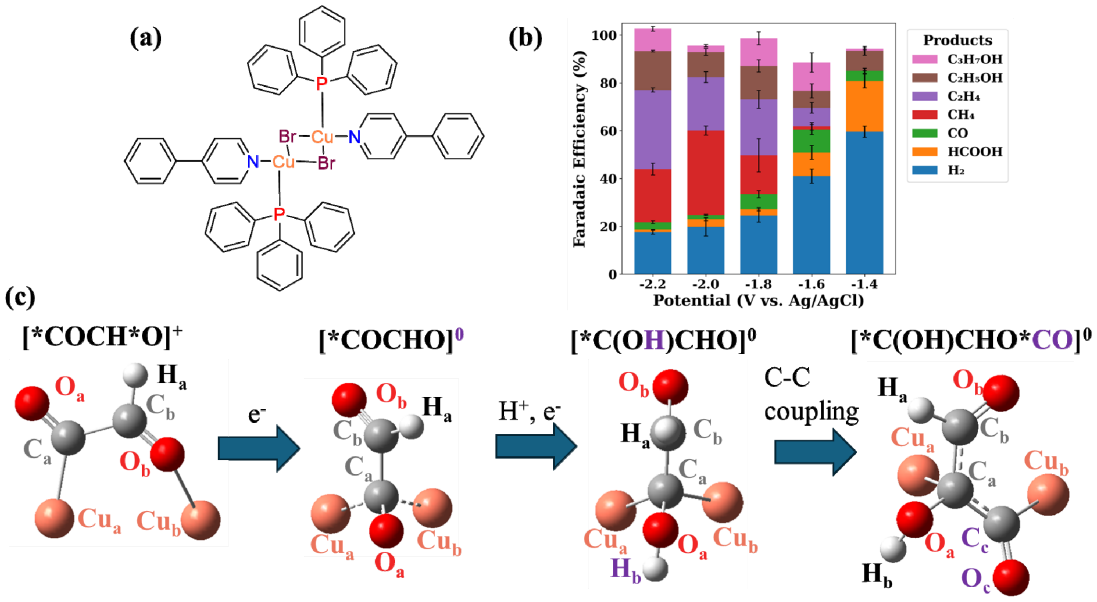


Figure 1. (a) Molecular structure of the Br-bridged dinuclear Cu(I) complex. (b) Faradaic efficiencies of the products obtained after 1 h of CO_2RR in a 0.5 M $KHCO_3$ electrolyte. (c) Structures of the adsorbates and Cu centers in the identified C_2 and C_3 intermediates [1].

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EXCIPLEX FORMATION LEADING TO STIMULI RESPONSIVE PHOSPHORESCENCE IN COPPER(I) COMPLEXES

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Stimuli responsive emissive molecules change their photophysical properties through the appliance of an external stimulus and show great potential for a variety of emerging technologies, ranging from life science to data encryption [1]. Until now, research in the field of stimuli responsive compounds has focused mostly on fluorescent molecules and polymers. Due to their high spin orbit coupling, organometallic complexes are able to access the excited triplet states, therefore enabling efficient phosphorescence. Since emission from triplet states is spin forbidden, they have substantially longer excited state lifetimes, giving the molecule more time to respond to an external stimulus. Due to its flexible coordination and ligand sphere, as well as its energetically advantageous frontier orbitals, copper complexes have established themselves as a cheap and abundant alternative to complexes based on expensive heavy metals like iridium or platinum [2]. In this project we try to elaborate the mechanism behind the anion controlled mechanochromic emission of cationic linear NHC copper(I) compounds, based on the previous work of HUPP *et al.*[3]. For this, we were able to synthesize a variety of dinuclear and mononuclear cationic homoleptic copper(I) carbene compounds, which were then thoroughly investigated regarding their photophysical properties and stimuli responsive behaviour.

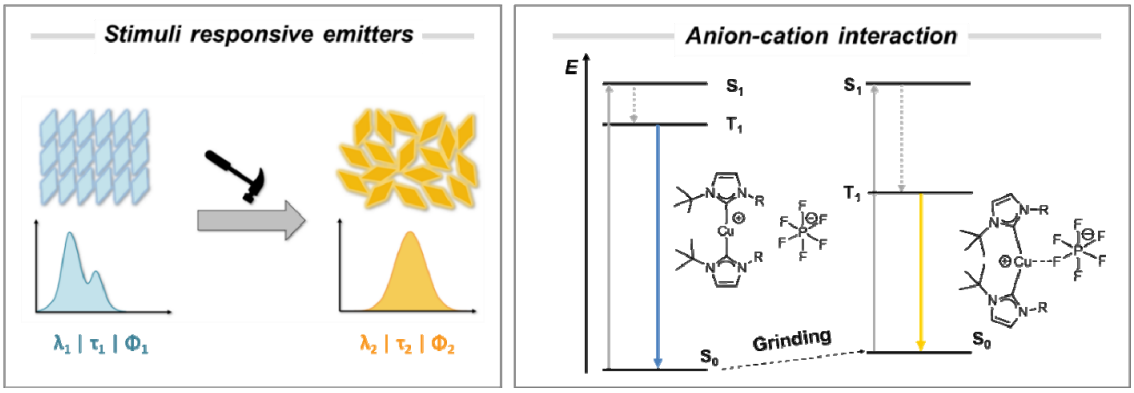


Figure 1: left: General principle of stimuli responsive luminescence; right: Proposed mechanism for the mechanochromic behaviour of linear NHC-Copper complexes, based on anion-cation interactions.[3]

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A REPORT OF Ru-(CYCLOMETALATED LIGAND) PHSOPORESCENCE OF MIXED-LIGAND BIS(BIPYRIDINE)-(CYCLOMETALATED LIGAND)-Ru COMPLEX

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This study reports the rare triplet charge-transfer emission from a phosphorescent Ru-(cyclometalated ligand) (Ru-CM) chromophore within two innocent bpy-ligands coordinated to the Ru center, where bpy denotes 2,2'-bipyridine.

Building upon our previous findings that photoinduced 77K phosphorescence of $[Ru(L)_2(CM)]^+$ complexes (L = diimine ligand) presents triplet metal-to-ligand charge-transfer (^{3}MLCT) characteristics of the Ru-bpy phosphorescent chromophore (L = bpy and CM = 2,3-diphenylpyrazine, dpz)[1] and of the Ru-CM phosphorescent chromophore (L = 2-pyrazol-1-pyridine, pzpy, and CM = dpz).[2] This phenomenon can be attributed to the coordinated pzpy moiety having relatively high π* energy level than the coordinated dpz moiety.[2]

However, by increasing the benzene ring count on the CM ligand to lower its π* level in $[Ru(bpy)_2(CM)]^+$ complexes, we observe a rare dual emission phenomenon associated with the low energy ^{3}MLCT excited states of Ru-bpy and Ru-CM phosphorescent moieties of $[Ru(bpy)_2(dpy)]^+$, and we further identify Ru-CM emission in $[Ru(bpy)_2(DBPZ)]^+$, where dpy and DBPZ denote 1,4-diazatriphenylene and dibenzo[a,c]phenazine, respectively.

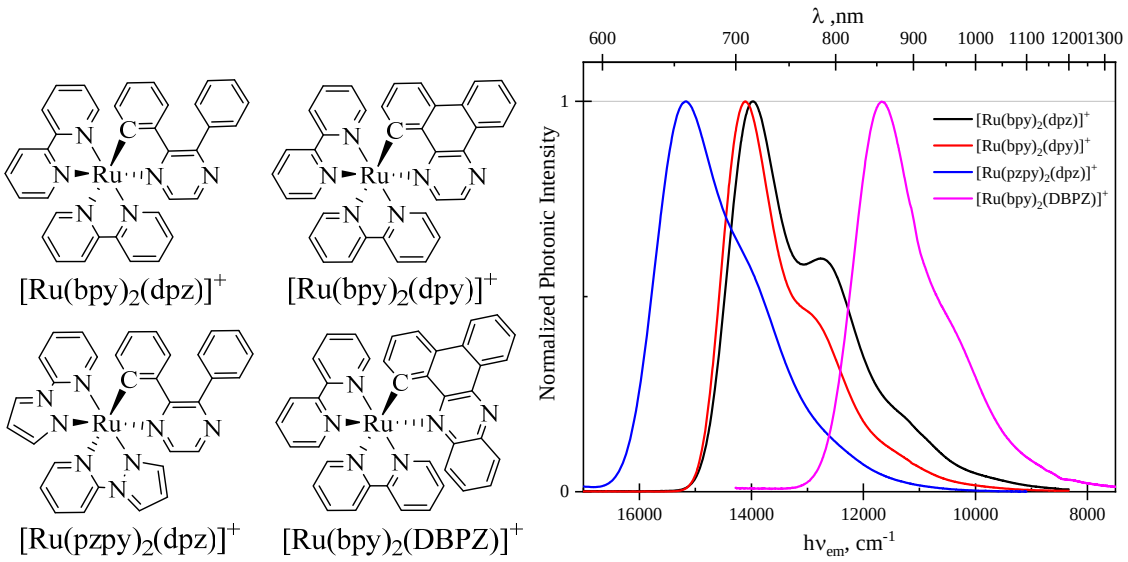


Figure. The structure (left) and 77K emission spectra in butyronitrile glasses (right) of $[Ru(bpy)_2(dpz)]^+$, $[Ru(bpy)_2(dpy)]^+$, $[Ru(pzpy)_2(dpz)]^+$and $[Ru(bpy)_2(DBPZ)]^+$.

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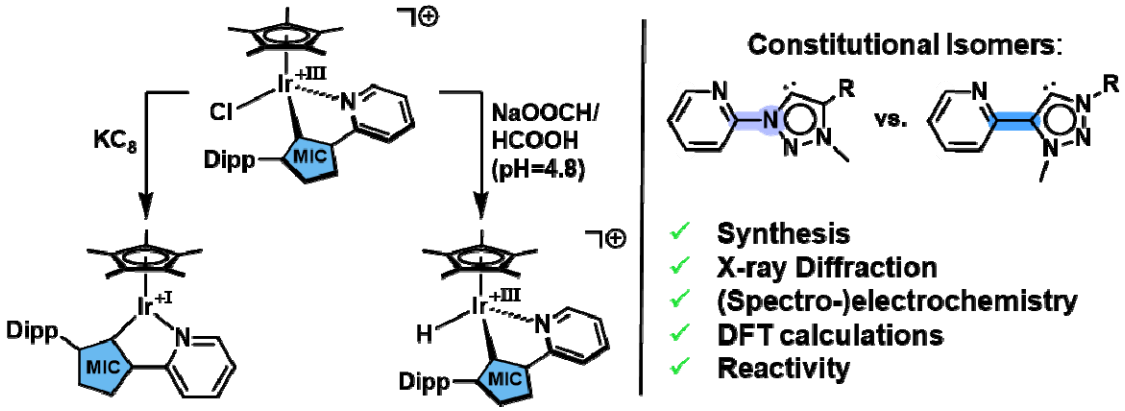
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(SPECTRO-)ELECTROCHEMISTRY OF IRIDIUM Cp* COMPLEXES WITH PYRIDYL-MIC LIGANDS

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Metal complexes featuring pyridyl-mesoionic carbene (py-MIC) ligands have gained recognition as highly efficient homogeneous and molecular electrocatalysts. When paired with iridium, these complexes act as highly active catalysts for hydrogenation, transfer hydrogenation, and hydrosilylation reactions.[1] In 2015, our group introduced a Cp*Co-py-MIC complex for electrochemical proton reduction using acetic acid.[2] More recently, key intermediates involved in reductive (electro)catalysis with Cp*Rh-py-MIC complexes have been explored.[3] Despite various reports of Cp*Ir-py-MIC complexes in a series of reductive catalysis, detailed experimental and theoretical insights into crucial catalytic intermediates – particularly reduced species and hydride species – remain scarce. Herein we present an in-depth investigation encompassing the isolation and crystallographic characterization of these intermediates, alongside (spectro)-electrochemical analyses and theoretical modeling. Notably, UV/Vis/NIR- and EPR-spectroelectrochemical (SEC) investigations of the iridium hydride species are reported, representing among the first such measurements for this class of compounds. Furthermore, the reactivity and properties of the hydride species are examined in detail, highlighting their ambiphilic behavior in facilitating the transfer of H^+, $H^\cdot$ and H^-.



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CATALYTIC UPCYCLING OF POLYETHYLENE WASTE VIA DEHYDROGENATED INTERMEDIATES

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The exponential growth in plastic production and consumption has generated a significant environmental crisis, driven by the persistence and accumulation of synthetic polymer waste. [1] Among commodity polyolefins, polyethylene (PE) is the most produced and discarded, yet its chemical inertness and thermodynamic stability make efficient depolymerization challenging.

Chemical upcycling offers a promising strategy to convert plastic waste into valuable products. [2] Dehydrogenation has been shown as a practical route to functional polyolefins and provides key intermediates for *end-of-life* upcycling. [3] Herein, we present an approach based on C–H activation to introduce reactive sites into polyethylene chains. Post-consumer polyethylene (PE) is first subjected to acceptorless, Ir-pincer catalyzed non-oxidative dehydrogenation, producing dehydrogenated PE (dePE) as a versatile platform. The subsequent diverse functionalization of the addressable unsaturated sites opens new pathways for polymer diversification and the synthesis of functional materials.

This approach highlights the potential value of dehydrogenated polymers as intermediates to enable circularity and polyolefin *end-of-life* management strategies.

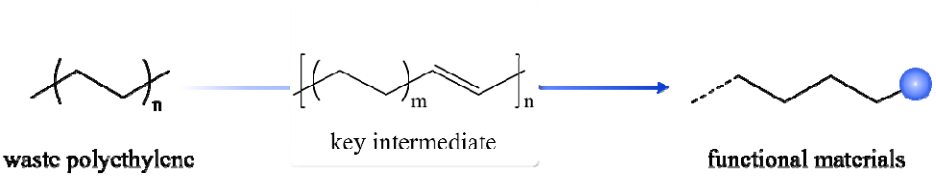


Figure 1. Chemical *upcycling* strategy for polyethylene waste plastic *via* catalytic dehydrogenation.

Acknowledgments: M.M. acknowledges the European Union Next-Generation EU (Piano Nazionale di Ripresa e Resilienza (PNRR)─Missione 4, Componente 1, CUP C96E23001080002) for a Ph.D. fellowship.

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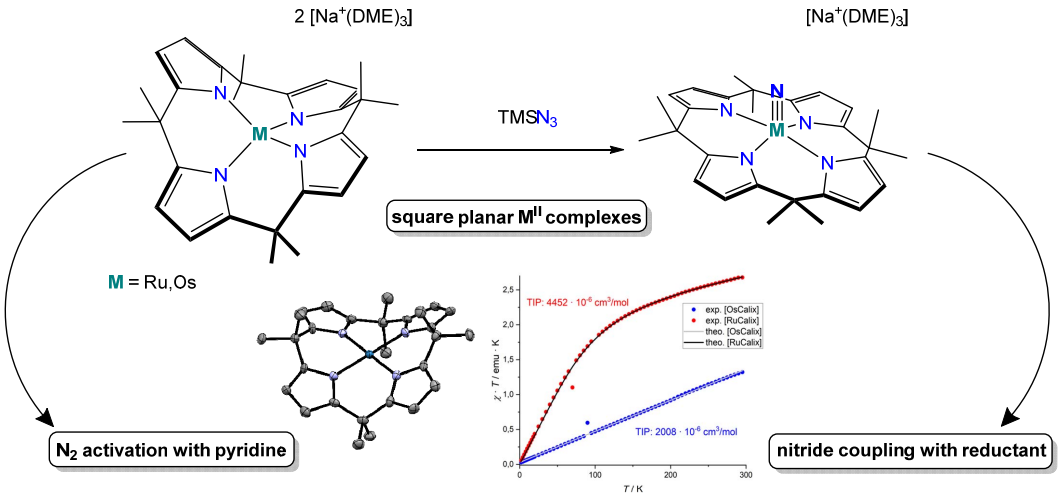
SYNTHESIS AND REACTIVITY OF A SQUARE-PLANAR GROUP 8 COMPLEXES

Maximilian Meißner, Simon Richter, Emelie Langner, Charlotte S. Meyran, Sandipan Maji, Sven Schneider*

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The coordination chemistry of the heavier, divalent group 8 metals (Ru^{II}, Os^{II}) is dominated by octahedral complexes. In contrast, four-coordinate Fe^{II} complexes are quite common and generally adopt tetrahedral (S = 2) or, in some cases, square-planar (S = 1) configurations.[1,2] In comparison, four-coordinate Ru^{II} and Os^{II} tends to form seesaw structures (S = 0). While a few examples for square-planar Ru^{II} have been reported,[3-5] only a single square-planar osmium(II) complex is known to date.[6]

Here, the synthesis as well as the spectroscopic, structural and magnetic characterization of a rare osmium(II) complex with square-planer coordination geometry are reported (Figure 1). The reactivity towards dinitrogen activation and nitride coupling for the ruthenium complexes are discussed.



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STRUCTURE–PHOTOREACTIVITY RELATIONSHIPS IN CHROMIUM AND MOLYBDENUM PHOTOCORMS FOR LIGHT-TRIGGERED CARBON MONOXIDE RELEASE

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Department of Chemistry, Imperial College London, London, UK

Photoactivatable carbon monoxide-releasing molecules (photoCORMs) based on chromium and molybdenum provide promising platforms for ight-triggered CO delivery. Here, a series of Cr and Mo photoCORMs with diverse ligand frameworks was synthesized to examine how metal identity and ligand environment influence photoreactivity.

Ten complexes were prepared and characterized by NMR, IR, UV–Vis spectroscopy, and single-crystal X-ray diffraction. Upon light irradiation, the complexes showed distinct photophysical responses, and qualitative assays confirmed photoinduced CO release.

DFT and TD-DFT calculations were used to probe electronic structures and excited-state features, providing insight into ligand field effects and observed spectral trends. Overall, this work establishes structure–photoreactivity relationships in Cr/Mo photoCORMs and highlights design principles for tuning visible-light CO release.

Mn(II) FORMAZANATES SHOWING LIGHT-INDUCED SPIN CROSSOVER BEHAVIOUR WITH NANO- TO MICROSECOND LIFETIMES

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[b]Faculty of Chemistry, Jagiellonian University, Kraków, Poland

Significant progress has been made towards the development of photoactive transition metal complexes and materials based on earth-abundant metals. Iron as the most abundant transition metal has received the most attention, particularly Fe(II) because it is isoelectronic with gold standard chromophores Ru(II) and Ir(III) [1]. However, Fe(III) complexes have become emergent alternatives, possessing ligand-to-metal charge transfer (LMCT) excited states with nanosecond lifetimes and strong oxidizing potentials [2, 3]. Mn(II) is isoelectronic with Fe(II). Despite being a highly abundant metal, Mn complexes remain underexplored as chromophores. Recent work on Mn(II) N-heterocyclic carbenes has, however, demonstrated that long excited state lifetimes and photochemically usable excited state energies are achievable [4, 5].

In this research, we expand upon this growing field by presenting a series of low-spin, panchromatically absorbing Mn(II) bisformazanate complexes. We show how selected substitutions on the tridentate formazanate ligands affect the electronic properties and excited state dynamics of the complexes. The excited state landscape of these complexes is investigated with femtosecond and nanosecond transient absorption spectroscopy, which demonstrates relaxation of a ^{2}LMCT state via a short-lived, strongly absorbing state that decays via branching pathways into a ^{6}MC state with nanosecond lifetime. We attempt to develop the light-induced spin crossover behaviour of these complexes towards useful LIESST (light-induced excited state spin trapping) applications by extending the ^{6}MC lifetime. Ligand design principles are used to manipulate the excited state landscape of the complexes via two different strategies, distortion and nesting, allowing us to extend the lifetime of the complexes into the microsecond regime.

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SYNTHESIS AND INTERCONVERSION OF HALF-SANDWICH Ru(II) COMPLEXES BEARING THE COENZYME-NAD ACTIVE SITE

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1. Introduction

To mimic the coenzyme-NAD system, various studies have focused on modeling its active site on metal complexes. In this study, we synthesized novel half-sandwich Ru(II) complexes incorporating nicotinamide, which is the active site of coenzyme-NAD. Base-induced chemical reductions as well as electrochemical redox reactions were also investigated to establish interconversion between NAD^+- and NADH-type complexes.

2. Experimental

1,10-Phenanthroline-based ligands linked to the NAD active site (pna^+ or its reduced form, pnaH) were synthesized according to previous reports [1]. Subsequently, target complexes (NAD^+-type and NADH-type in **Fig. 1**) were prepared using $[Ru(C_6H_6)Cl_2]_2$ as the precursor [2]. The obtained complexes were fully characterized, and their redox behaviors were evaluated by electrochemistry. Furthermore, interconversion between these complexes was investigated through electrochemical oxidation and chemical reduction via base addition, which represents an alternative approach to conventional methods.

3. Results and Discussion

As shown in **Fig. 1**, electrochemical oxidation of the NADH-type complex regenerated the corresponding NAD^+-type. Although both complexes exhibited a yellow color in solution, electrochemical reduction of the NAD^+-type complex led to color change of the solution to blue, suggesting the formation of a one-electron-reduced intermediate at the NAD^+ model site. Similar spectral changes were also observed upon addition of a base to DMF or DMSO solutions of the NAD^+-type complex, ultimately leading to formation of the reduced complex (NADH-type). These results demonstrate reversible interconversion between two states. The optimized reaction conditions and a proposed mechanism of the base-induced reduction will be presented.

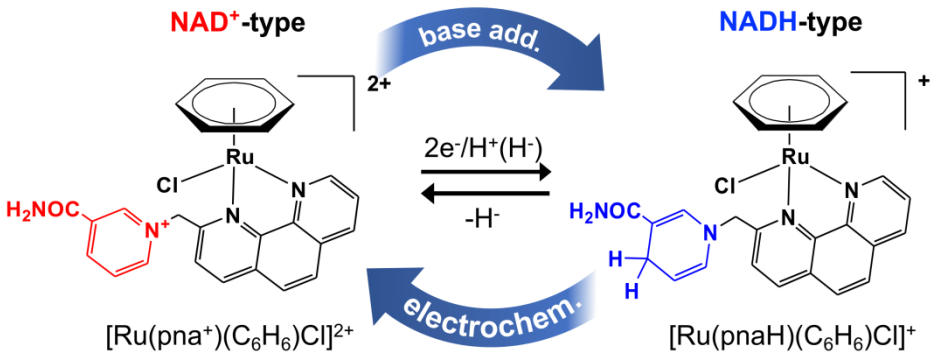


Fig. 1 Structures of NAD^+/NADH-Type Complexes and Their Interconversion

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PHOTOINDUCED CHARGE SEPARATION IN IRON N-HETEROCYCLIC CARBENE SOLIDS

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[b]Center for Analysis and Synthesis, Department of Chemistry, Lund University, Lund, Sweden

Iron N-heterocyclic carbenes (FeNHCs) have, in the recent decade, emerged as novel photoactive compounds and attracted tremendous attention for their potential in offering interesting excited-state reactivities [1]. The limited short excited-state lifetime (on sub-nanosecond scales) of most Fe(III)NHC compounds limits their potential applications. Symmetry-breaking charge separation has been widely investigated from both fundamental and application-oriented perspectives in organic molecular systems [2]. In recent years, bimolecular symmetry-breaking charge separation of an Fe(III) N-heterocyclic carbene chromophore ($[Fe(III)L_2]PF_6$ (L = [phenyl(tris(3-methylimidazol-2-ylidene))borate]−)) was demonstrated in both concentrated solution [3] and solid films [4]. The results show that the charge separation in $[Fe(III)L_2]PF_6$ solids happens on a subpicosecond scale, and the generated electron and hole carriers can be successfully collected by the contacting electrode. Herein, a follow-up study on photoinduced charge separation in Fe(III)NHC solids and the charge collection will be presented. Ultrafast transient absorption spectroscopy reveals that, followed by highly efficient charge separation, the generated charge carriers can be collected by the adjacent transport material and the electrode.

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STRUCTURE-PROPERTY-REACTIVITY STUDIES OF ORGANOFUNCTIONALIZED THIOMOLYBDATE CLUSTERS FOR PHOTOCATALYTIC HER

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Department of Chemistry, Johannes Gutenberg University Mainz, Mainz, Germany

Thiomolybdates are a promising class of molecular catalysts for photocatalytic or electrocatalytic hydrogen evolution reaction (HER). [1] The prototype cluster $[Mo_3S_{13}]^{2-}$ has been studied for HER catalysis under both homogeneous and heterogeneous conditions, providing a noble metal free alternative to commonly used platinum catalysts. [2,3] Although thiomolybdates have received increasing attention in recent years, their structural diversity remains limited. [4,5] This work focuses on establishing structural modifications of thiomolybdate clusters by functionalization with organic ligands, therefore accessing more structural diversity and investigating in the photocatalytic HER activity of these new compounds. Structural modifications allow to gain further insights into the mechanism of catalytic hydrogen evolution, by investigating ligand effects and follow degradation pathways using ligands with spectroscopic markers. Furthermore, organic functionalization can be utilized to design photocatalytic dyads and enable covalent matrix immobilization.

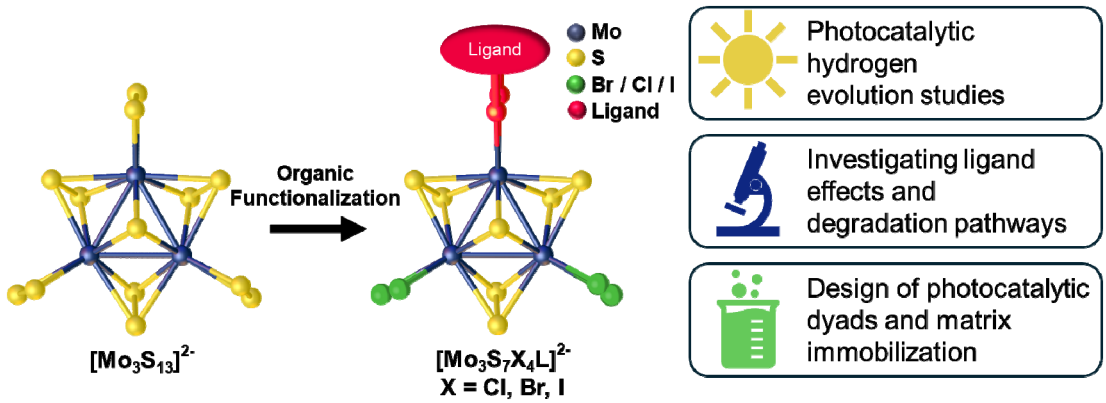


Figure 1. Simplified reaction scheme on the functionalization of $[Mo_3S_{13}]^{2-}$ with organic ligands and overview of main objectives.

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BIS-CYCLOMETALATED RHODIUM(III) AND IRIDIUM(III) COMPLEXES WITH THE EVALUATION OF THEIR PHOTOPHYSICAL PROPERTIES

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Bis-cyclometalated Rh(III) and Ir(III) complexes represent a versatile class of d^6 coordination compounds whose photophysical properties can be systematically modulated through ligand design [1, 2]. Owing to their closely related coordination geometries but distinct electronic characteristics of the metal centers, these systems provide an excellent platform for comparative studies of excited-state structure–property relationships.

A series of bis-cyclometalated cationic Rh(III) and Ir(III) complexes of the $[M(C\hat{}N)_2(N\hat{}N)]^+$ type with α-diimine ligands was investigated to evaluate the influence of metal identity, ligand electronics, and temperature on their photophysical properties. Spectroscopic investigations over a wide temperature range, structural studies and theoretical computations provided access to absorption features, emission behavior, excited-state lifetimes, and deactivation pathways. The Ir(III) complexes exhibit efficient room-temperature phosphorescence [3, 4], whereas the Rh(III) analogues are weakly emissive under ambient conditions but display significantly enhanced emission at 77 K [5, 6].

Low-temperature emission studies reveal long-lived triplet excited states, often displaying vibronic structure consistent with ligand-centered or mixed charge-transfer character. The observed differences in emission efficiencies and excited-state lifetimes are attributed to distinct non-radiative deactivation pathways and differences in the relative energetics of metal-centered and ligand-centered excited states. Overall, the comparative analysis highlights the key role of metal identity in governing emissive efficiency and excited-state dynamics in bis-cyclometalated complexes.

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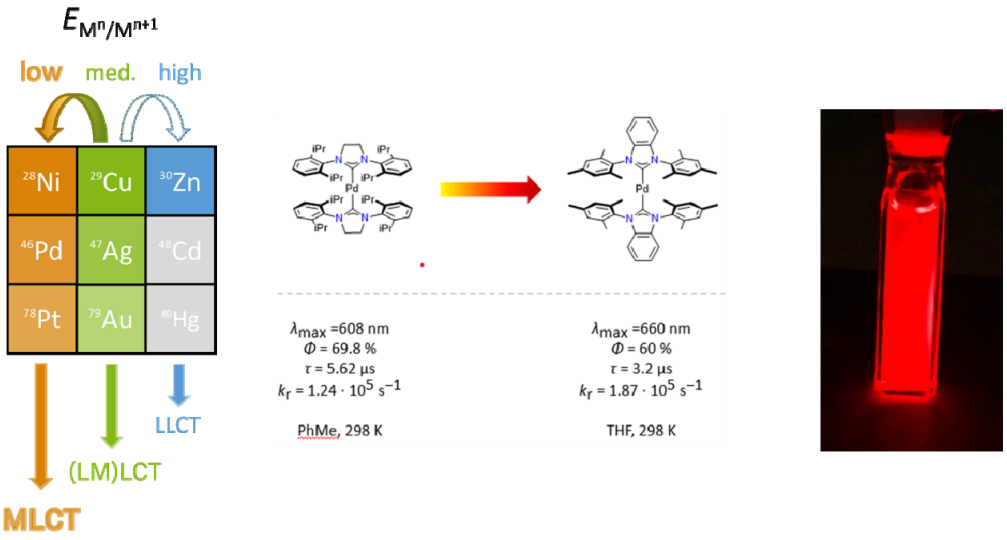
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REALIZING NEAR-IR LUMINESCENCE IN Pd(0) AND Pt(0) COMPLEXES

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Near-infrared (NIR) emission holds significant importance for everyday applications such as optical signal transmission. Additionally, it plays a crucial role in potential future uses like cryptography, *in vivo* bioimaging, and information storage. Transition metal complexes with photoactive properties offer distinct advantages over purely organic and lanthanide-based emitters, as they combine high radiative rate constants with elevated phosphorescence quantum yields. [1] Our focus lies on the investigation of metal complexes with a d^{10} electron configuration, preventing efficiency loss from non-radiative dd* transitions. Earlier studies on Cu(I) complexes revealed varied emission mechanisms based on different ligand combinations. [2] In this project, we aim to transition from coinage metal complexes to group 10 metals, specifically palladium and platinum. Limited research has been conducted on their zero-valent complexes concerning their photophysical properties. [3] Our goal is to establish Pd(0) and Pt(0) complexes with low-energy excited triplet states, enabling efficient phosphorescence in the NIR range. To achieve this, we utilized carbene ligand motifs and applied them to group 10 metals. Calculations suggest that this approach will benefit from distinct ^{3}MLCT states with minimal LLCT admixture. Ultimately, we aim to expand this knowledge to new coordination compounds, paving the way for a novel class of NIR emitters.



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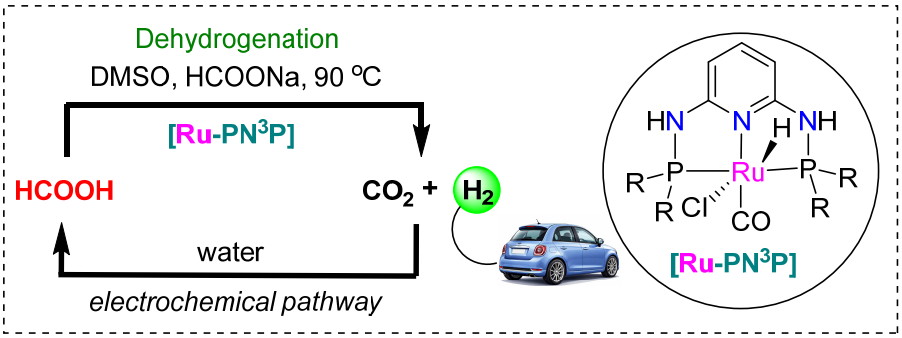
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DEHYDROGENATION OF FORMIC ACID CATALYZED BY A PN^{3}P-RUTHENIUM PINCER COMPLEX: CATALYTIC PERFORMANCE AND MECHANISTIC INSIGHTS

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Hydrogen is regarded as a promising low-carbon energy carrier and capable of decarbonizing the transportation sector, which remains heavily dependent on fossil fuels.[1] However, hydrogen storage and transport face major challenges due to the substantial energy penalties required for compression and liquefaction. In this context, Formic acid (FA) has emerged as a promising hydrogen carrier owing to its high volumetric hydrogen capacity of 53 g L^{-1} and its non-toxic, low-flammability liquid nature under ambient conditions enables safe transport and handling.[2] Moreover, the CO_2 byproduct can be sustainably recycled into formic acid using renewable electricity, enabling a closed carbon loop.[3] Although significant progress has been made in formic acid dehydrogenation over the past decade, developing stable and cost-effective catalysts remains essential for its practical implementation.[4] Here we report a Ruthenium complex [Ru-PN^{3}P] containing a pincer backbone, as a very efficient catalyst for formic acid dehydrogenation (Scheme 1). Under the optimized condition, the complex showed a TON of 70 million. To the best of our knowledge, this represents the highest TON reported for a Ru-based complex for FA dehydrogenation, with excellent selectivity. A detailed discussion of the catalytic performance, kinetic studies, and mechanistic insights will be presented.



Scheme1. Ru-PN^{3}P catalyzed dehydrogenation of FA.

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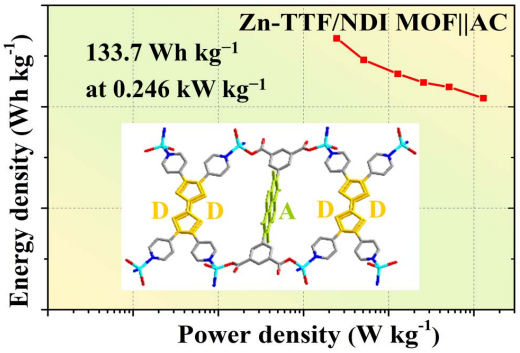
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AN ELECTRON DONOR-ACCEPTOR MOF OF TTF-NDI FOR HIGH PERFORMANCE HYBRID LITHIUM-ION CAPACITORS

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Integrating mixed electron donor (D) and electron acceptor (A) ligands into metal–organic frameworks (MOFs) is an effective yet relatively unexplored approach for improving the anode performance of hybrid lithium-ion capacitors (HLICs). In this study, using an electron donor 2,6-bis(4'-pyridyl) tetrathiafulvalene and an electron acceptor N, N'-bis(5-isophthalic acid) naphthalene diimide as ligands, a new Zn-TTF/NDI MOF (**1**) was constructed as a pseudocapacitive anode of HLICs. Crystallographic characterization revealed that MOF **1** adopts a two-dimensional (2D) coordination network. A three-dimensional (3D) supramolecular framework is formed through face-to-face TTF packing of adjacent 2D layers. As a result, the 2D MOF **1** with both electron-donating TTF and electron-accepting NDI units not only possesses abundant active sites and high charge conductivity for reversible Li^+ storage, but also, owing to its 3D-supramolecular architecture, provides open channels for ion transport. This leads to enhanced capacity utilization and high power density. The MOF **1**||activated carbon HLIC device delivered a maximum specific energy of 133.7 Wh kg^{-1} and a high specific power of 12.9 kW kg^{-1} with stable cycling performance. The remarkable performance originates from the synergistic effect of the mixed electron-donating TTF and electron-withdrawing NDI ligands, interligand charge transfer, and structural stability. This work offers an efficient strategy for developing high performance HLICs anodes through rational molecular engineering. [1]



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LUMINESCENT IRON(III) COMPLEX WITH NANOSECONDS EXCITED STATE LIFETIME AND PHOTOREDOX ACTIVITY

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Traditional photosensitizers and photoredox catalysts predominantly rely on precious metals [1], such as ruthenium and iridium, whose high cost and low abundance limit large-scale applications. The development of photoactive complexes based on Earth-abundant transition metals represents a critical challenge for sustainable solar energy utilization [2]. In recent years, photoactive first-row transition metal complexes—particularly those made of iron—have attracted considerable attention for photochemical energy conversion, due to the high abundance and low environmental impact of iron [3].

In this work, we present a new prototypical luminescent $3d^5$ Fe(III) complex bearing bidentate chelating ligands. The synergy of the σ-donating ability of the ligand and the pseudo-octahedral coordination geometry elevates the energy level of the metal-centered (MC) state and suppresses the non-radiative deactivation. The obtained Fe(III) complex shows ligand-to-metal charge transfer (LMCT) absorption in the visible range and deep red luminescence with lifetime values in the nanosecond regime (Figure 1). The Fe(III) complex is furthermore a strong photooxidant that allows efficient photoinduced electron transfer with various electron donors and facilitates photoredox catalytic reactions, including Aza-Henry reaction, decarboxylation reaction, and [4+2] cycloaddition.

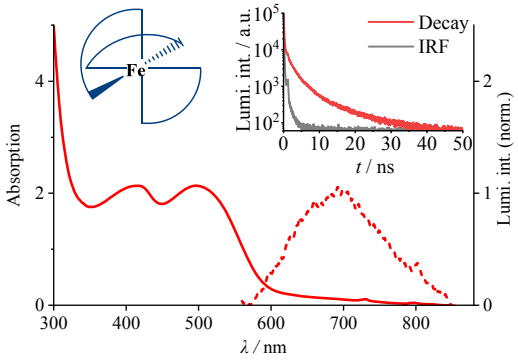


Figure 1. UV–Vis absorption (solid traces) and normalized luminescence spectra (dashed traces, excitation at 450 nm) of the Fe(III) complex in aerated acetonitrile at 293 K. Right inset: Time-resolved luminescence decay detected at 690 nm upon excitation at 450 nm, and the corresponding instrument response function (IRF). Left inset: simplified moleculart structure of the presented Fe(III) complex.

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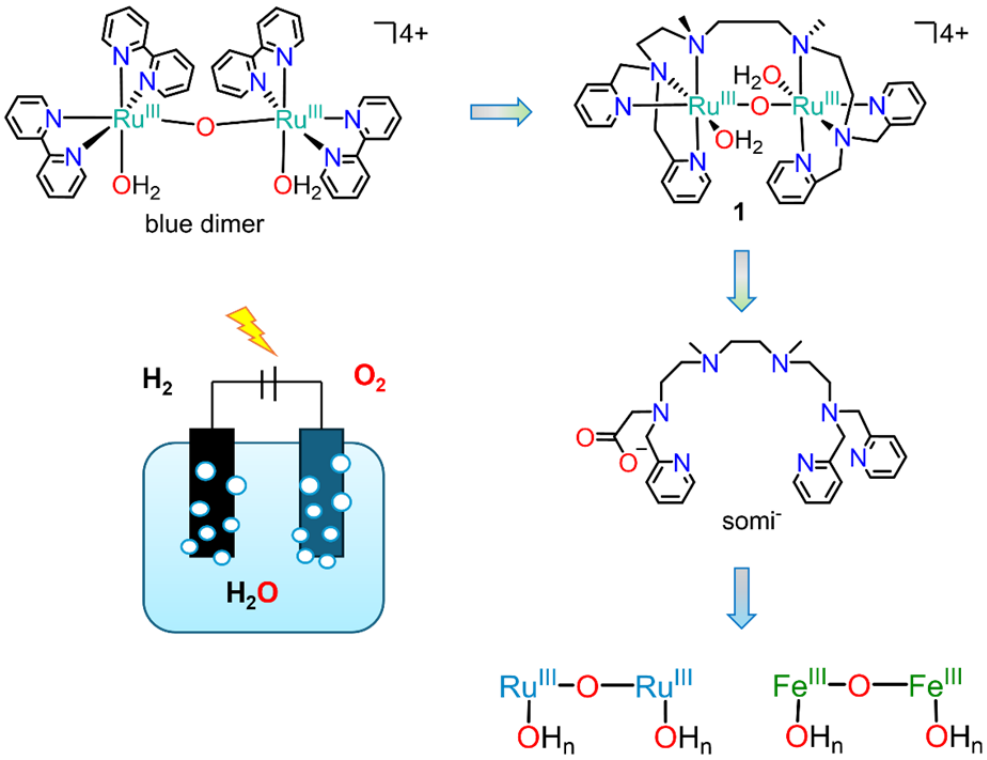
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WATER OXIDATION CATALYSIS WITH DINUCLEAR RUTHENIUM AND IRON COMPLEXES

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In natural photosynthesis the OEC is used to generate O_2 through the oxidation of water.[1] A well-known model complex for water oxidation catalysis is the 'blue dimer', which contains a $Ru^{III}(\mu\text{-}O)Ru^{III}$ core.[2,3] To prevent the dissociation into mononuclear units, we have developed dinucleating ligands based on a tetraamine backbone with varying terminal donors[4] for synthesising the $Ru^{III}(\mu\text{-}O)Ru^{III}$ complex **1**. The catalytic activity is still limited due to ligand exchange with negatively charged ligands, known as anation. To address this issue, we have developed the new ligand somi$^-$, which contains a carboxylate donor instead of pyridine, to reduce the positive charge of the complex. Here, we report the synthesis of this new ligand for use in the synthesis of dinuclear Ru^{III} and Fe^{III} complexes.



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PHOTOCATALYTIC HYDROGENATION OF AROMATIC COMPOUNDS

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Birch-reduction is the classic synthetic method for the reduction of aromatic substrates, but it requires strong alkali metal reductants and liquid ammonia as solvent. In fact, the low reduction potentials of aromatics can even be challenging for light-driven approaches via photoredox catalysis. Two-photon strategies[1] and excited state proton-coupled electron transfer (ES-PCET)[2] were therefore introduced as alternative approaches to obtain additional driving force. Chirik and co-workers established the photocatalytic hydrogenation of anthracenes via triplet energy transfer (EnT)[3]. However, the protocol requires blue light and higher H_2 pressures, and the iridium hydrido photocatalyst exhibits limited photochemical stability.

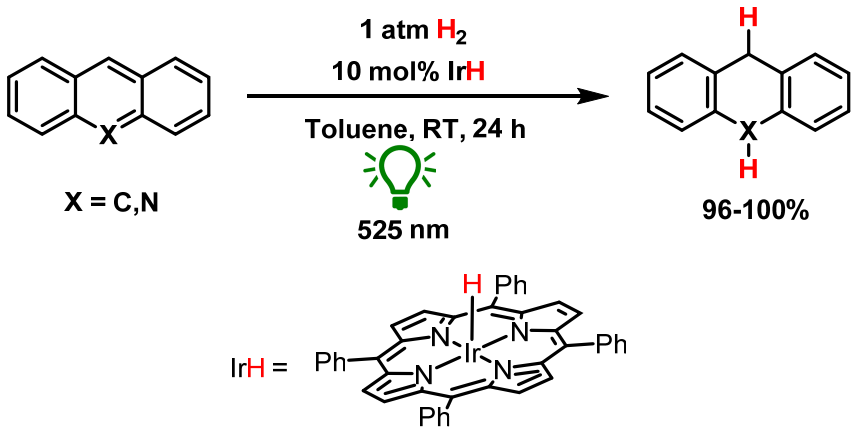


Figure 1. Photo-hydrogenation of arenes and heteroarenes.

We here report the light-driven hydrogenation of anthracenes and acridines, catalyzed by a novel iridium(III) porphyrin hydride (Figure 1)[4]. The photophysical properties of the hydrido photocatalyst, as well as mechanistic examinations of the photohydrogenation will be presented.

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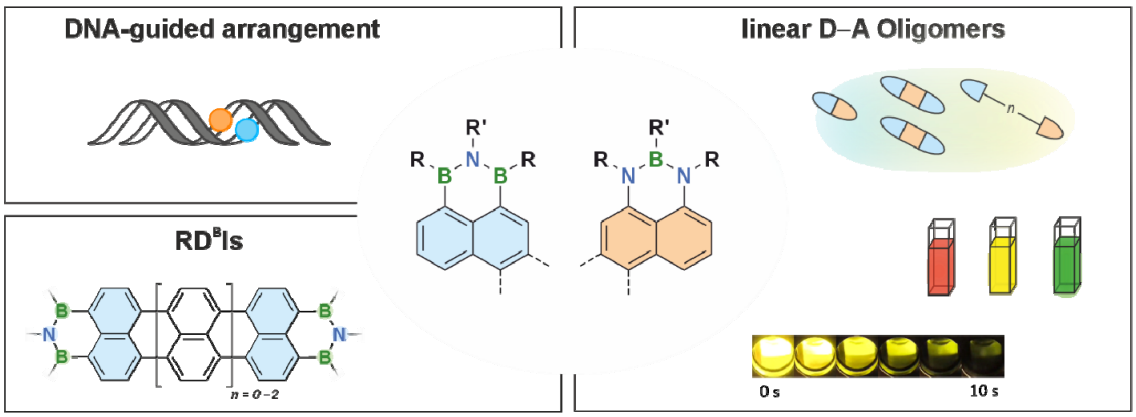
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BNB- AND NBN-DOPED PHENALENYLS: CONTRASTING BUT COMPLEMENTARY CHROMOPHORES AS BUILDING BLOCKS FOR DYADS, OLIGOMERS, POLYMERS, AND RYLENE DYES

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Replacing three adjacent carbon atoms in a phenalenyl framework with a BNB or NBN moiety, respectively, yields two neutral isosteric chromophores with contrasting electronic properties [1]. Using the DNA scaffold to arrange the complementary phenalenyls allowed us to systematically analyse intermolecular interactions and explore DNA-based applications [2]. By unlocking the effective functionalisation of the BNB-phenalenyls, we established the novel compound class of rylene diborinic imides (RD^{B}Is), which retain the favourable photophysics of classic rylene dicarboximides (RDIs) but demonstrate improved solubility and diminished aggregation [3]. Extending these strategies to NBN-phenalenyls, we then combined the two complementary chromophores to form linear D–A oligomers with controlled length and sequence [4]. These rigid systems exhibit highly environmentally sensitive intramolecular charge transfer, which imparts tunable photophysical properties to the materials. Collectively, these results identify site-specific coupling between heteroatom-doped phenalenyls as a rational strategy for engineering excited state architecture and provide access to conjugated materials with promising properties for use in optoelectronic applications.



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TRANSFER HYDROGENATION OF FURFURAL TO LEVULINIC ESTER USING Ru-BASED HOMOGENEOUS CATALYSTS

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The valorization of biomass into platform chemicals is an emerging strategy for sustainable chemical technology. The potential conversion of biomass-based materials has received much attention in the last decade, with important achievements in both heterogeneous and homogeneous catalysis.

Here we present a protocol for the conversion of furfural to small oxygenates under transfer hydrogenation conditions using isopropanol (IPA) as solvent and hydrogen donor. Commercially available PNP-pincer complexes of Ru were used as catalysts. Moderate to complete conversion of furfural with levulinic ester as the major product was observed under homogeneous catalytic conditions. The reaction cascade includes the combination of transfer hydrogenation and dehydration reactions leading to furan-derived small oxygenates. Brønsted acids were used to cover the dehydration function (Figure 1).

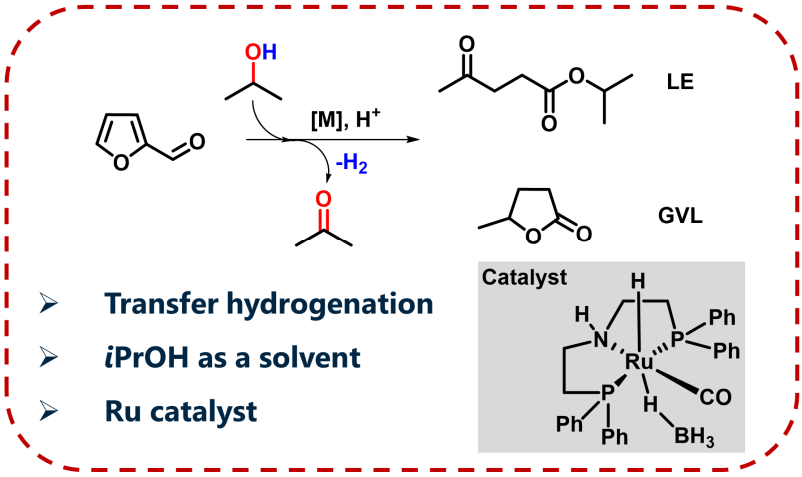


Figure 1. Conversion of furfural to value-added chemicals using Ru-based catalysts.

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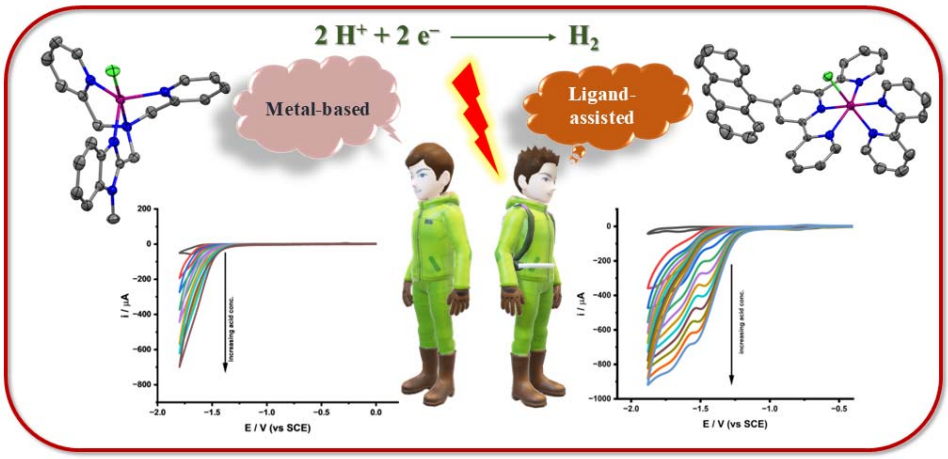
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LIGAND-DIRECTED PATHWAY DIVERGENCE IN ELECTROCATALYTIC HYDROGEN EVOLUTION BY RATIONALLY DESIGNED COBALT(II) COMPLEXES

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The rising demand for efficient, green energy has encouraged research into alternative sources to replace fossil fuels, with molecular hydrogen (H_2) emerging as a prime candidate due to its high energy density and clean combustion.[1,2] In the hunt of efficient molecular catalysts for hydrogen evolution reaction (HER), we report two cobalt(II) complexes featuring redox-inactive and redox-active ligands. Two cobalt (II) complexes, [Co(**L1**)Cl](ClO_4) (**1**) and [Co(**L2**)(bpy)Cl](ClO_4) (**1**) (where **L1** = 1-(1-methyl-1H-benzo[d]imidazol-2-yl)-N,N-bis(pyridin-2-ylmethyl)methanamine and **L2** = 4′-(anthracen-9-yl)-2,2′:6′,2″-terpyridine) containing redox inactive (**L1**) as well as redox active ligand (**L2**) systems were synthesized and thoroughly characterized by different spectroscopic and analytical tools. Their electrocatalytic hydrogen evolution studies were performed using acetic acid as external proton source and generated hydrogen was detected by gas chromatography. It was observed that ligand modification can merely shift the Co(II)/(I) redox potential significantly, but this will not assure the generation of cobalt-hydride at less negative potentials as the formed low valent cobalt species could be less nucleophilic to directly attack H^+ from acetic acid. Theoritical calculations have been also performed to support the experimental results and developing the mechanism at atomistic details. Post catalytic analysis also performed to check the integrity of metal complexes as molecular catalysis.



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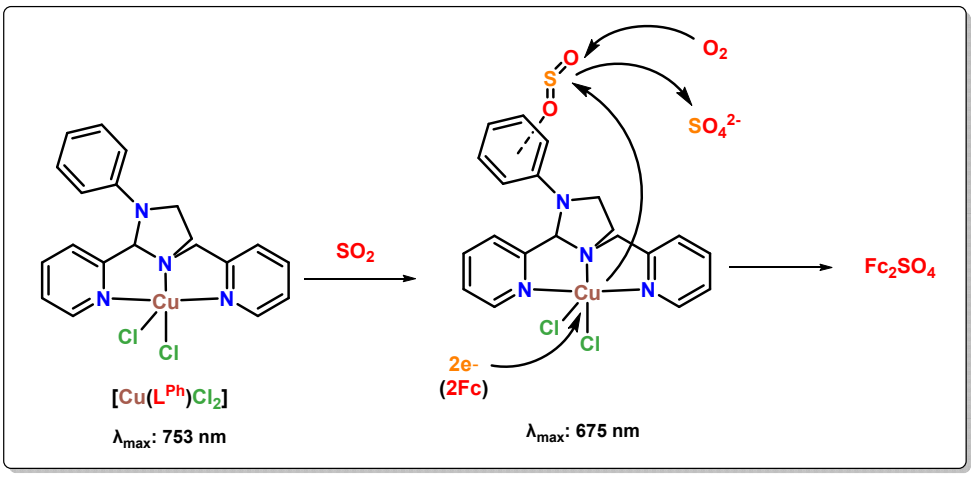
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EMPLOYING LONE PAIR-PI INTERACTIONS IN A REDOX-ACTIVE KONERAMINE COMPLEX FOR ACTIVATION OF SO_2

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Sulphur dioxide (SO_2) chemistry is of significant interest due to its detrimental effects on both the environment and human health. There is a pressing need to develop cost-effective methods to either capture SO_2 or convert it into useful commodities. Herein, we have reported an approach to activate SO_2 gas into sulfate dianions using a phenyl-appended koneramine complex. A recent report from our lab had shed light on a biologically relevant weak interaction between the lone pair of nucleophilic O atom of SO_2 and the aromatic ring of anthracene at 3.11 Å.[1] The Cu(II) koneramine complex $[Cu(L^{Ph})Cl_2]$[2, 3] was designed such that the incorporation of the phenyl moiety on the tertiary nitrogen of koneramine backbone facilitated weak interactions with sulfur dioxide,[1, 4] while the redox active copper metal intended electron transfer to SO_2 upon addition of ferrocene, leading to the generation of sulfate dianions in the presence of atmospheric oxygen at room temperature.[5] Ferrocene acted as a mild sacrificial electron donor, and gets converted into ferrocenium during the process. Stepwise reactions were also carried out with $[Zn(L^{Ph})Cl_2]$ to establish the necessity of a redox-active metal for electron transfer to occur. Furthermore, investigations with carbon disulphide (CS_2) revealed no reactivity of CS_2 under similar experimental conditions. Control experiments employing electronic absorption spectroscopy, cyclic voltammetry, and electron spray ionisation spectrometry were conducted to provide mechanistic insights into these processes.



[1] S. Singh, S. Dinesh, A. Yadav, S. Raje, R. J. Butcher, M. Sundararajan and R. Angamuthu, *Chem. Commun.*, 2024, **60**, 11104-11107.

[2] S. Raje, K. Mani, S. Dinesh, A. Yadav, M. Chahal, R. J. Butcher and R. Angamuthu, *Helv. Chim. Acta*, 2023, **106**, e202200188.

[3] S. Raje, A. Koner, S. Ghosh, R. J. Butcher, L. Mathivathanan, M. Sundararajan and R. Angamuthu, *Chem. Asian J.*, 2023, **18**, e202300706.

[4] S. Mehrotra and R. Angamuthu, *CrystEngComm*, 2016, **18**, 4438-4444.

[5] M. Chahal, S. Raje, G. Kotana and R. Angamuthu, *Green Chemistry*, 2019, **21**, 6372-6380.

EFFICIENT OXIDATIVE BREAKDOWN OF RECALCITRANT BIOMASS VIA LPMO-INSPIRED COPPER COMPLEXES

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Lignocellulosic biomass from non-edible plant residues is a promising resource for producing biofuels and chemicals without competing with food or water supplies. It is mainly composed of cellulose, hemicellulose, and lignin, forming a rigid and resistant structure. Cellulose and hemicellulose can be converted into sugars for bioethanol production, but efficient polymer breakdown is essential. The discovery of Lytic Polysaccharide Monooxygenases (LPMOs), copper-containing enzymes, enabled oxidative degradation of polysaccharides, improving biomass conversion.[1] However, challenges remain, including high enzyme production costs and the need to enhance saccharification yields. Addressing these limitations is crucial for advancing efficient and sustainable biomass valorization.

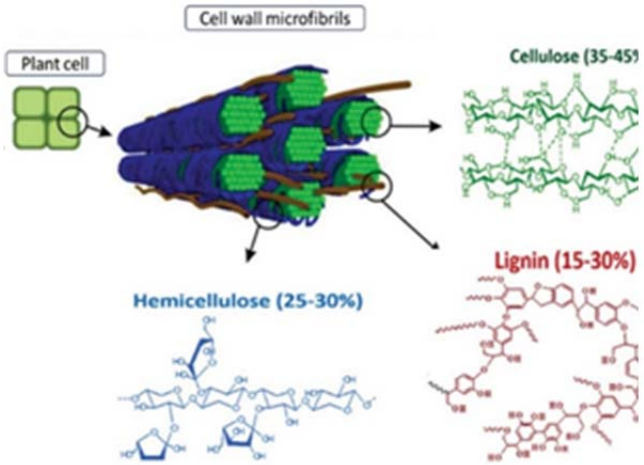


Figure 1. Representation of the structure and of the main components of lignocellulose.

Inspired by LPMOs, our group develops bioinspired mononuclear copper complexes mimicking the active site and activity of LPMO.[2,3] We have developed reproducible activity assays in aqueous solutions at near-neutral pH and mild conditions using substrates of increasing complexity: the model substrate para-nitrophenyl-β-D-glucopyranoside (p-NPG), cellobiose (glucose dimer). We recently obtained proof-of-concept evidence that bioinspired copper complexes can effectively promote the oxidative depolymerization of polysaccharides. However, different mechanistic pathways are likely involved across systems, depending on factors such as ligand topology, nuclearity, and the redox properties of the metal centers. This presentation will highlight our recent mechanistic investigations, along with efforts to improve catalyst stability.

Acknowledgements: This research is supported by the ANR project INSPIRE (ANR-23-CE43-0012).

[1] Alessia Munzone, Vincent G.H. Eijsink, Jean-Guy Berrin and Bastien Bissaro*, Nat. Rev. Chem. 2024, 8 (2), 106− 119.

[2] Rébecca Leblay, Iris Wehrung, Alda Lisa Concia, Subhankar Sutradhar, Bruno Faure, Marius Réglier, Olga Iranzo*, Maylis Orio*, A. Jalila Simaan*, Inorg. Chem. 2026, https://doi.org/10.1021/acs.inorgchem.6c01022. (*ASAP Article*)

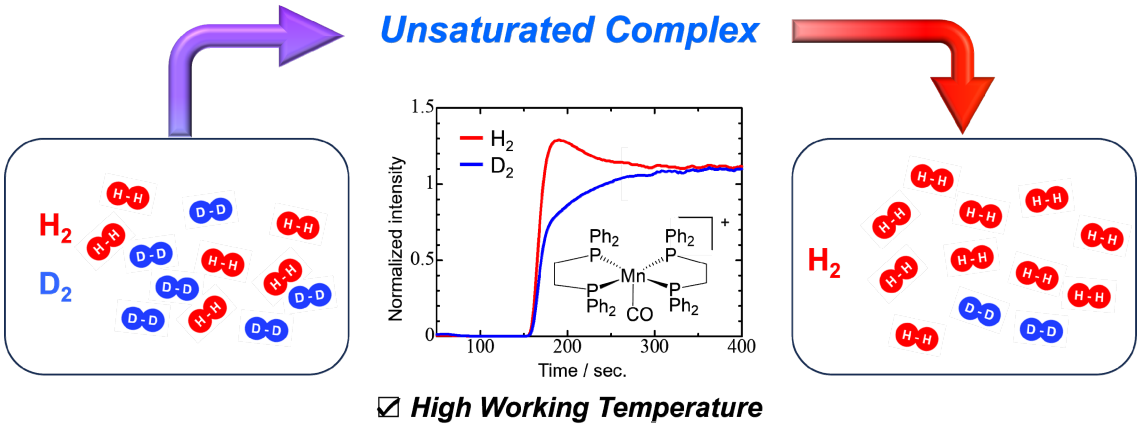
[3] Rébecca Leblay, Rafael Delgadillo-Ruíz, Christophe Decroos, Christelle Hureau, Marius Réglier, Ivan Castillo,* Bruno Faure, and A. Jalila Simaan*, ChemCatChem 2023, 15, e202300933.

HYDROGEN ISOTOPE SEPARATION AT EXCEPTIONALLY HIGH TEMPERATURE BY A COORDINATIVELY UNSATURATED COMPLEX

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Deuterium is an important chemical substance used in nuclear fusion power generation, medicine, semiconductor, and scientific research; however, the process of separating hydrogen from deuterium requires cryogenic temperature and enormous amounts of energy. In addition, the separation efficiency is quite low due to the similar physical properties of hydrogen isotopes. Herein, a highly efficient approach for hydrogen isotope separation even at ambient temperature was proposed using a coordinatively unsaturated organometallic complex.[1] Adsorption measurements of $[Mn(dppe)_2(CO)](BArF_{24})$ (Mn-dppe$^+$) (dppe = 1,2-bis(diphenylphosphino)ethane, $BArF_{24} = B[C_6H_3(3,5\text{-}CF_3)_2]_4$) with H_2 and D_2 revealed a significant difference in H_2/D_2 adsorption enthalpies at ambient temperature, much higher than in previous studies, indicating that D_2 molecules adsorb more strongly to unsaturated metal sites. Mixed gas (H_2:D_2 = 1:1) adsorption isotherms, calculated using ideal adsorbed solution theory (IAST), showed that D_2 uptake was much larger than H_2 uptake at each temperature. Column chromatographic separation using the difference in adsorption enthalpies indicated that deuterium could be concentrated, and DFT calculations suggest that this difference in adsorption force is due to the difference in vibrational potentials involved in metal–dihydrogen bonding. This study introduces a new separation approach that could enable hydrogen isotope separation in the ambient temperature range.



[1] T. Kitayama, T. Yamauchi, K. Uchida, S. Tanaka, R. Toyoda, H. Iguchi, R. Sakamoto, H. Xue, N. Kishimoto, T. Yoshida, T. Uruga, S. Noro, and S, Takaishi, *Dalton Trans.*, **2025**, *54*, 2621.

AIR-STABLE Fe(II) HEXA-NHC COMPLEX AND ANALYSIS OF PHOTOEXCITED STATE BY ULTRAFAST SPECTROSCOPY

Takuto Wakabayashi, Tomohiro Ogawa, Teruyuki Honda, Kaito Segawa, Toshiki Mochimaru, Tatsuya Yoshida, Kiyoshi Miyata, and Ken Onda

Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka, Japan

Photofunctional complexes with earth-abundant first-row transition metals such as Fe, Co are desired. However, the excited states of these complexes often form metal-centered (MC) and resulting in extremely short excited-state lifetimes. Complexes with N-heterocyclic carbene (NHC) ligands are being researched because their strong σ-donating properties provide a strong ligand field that can suppress this deactivation. [1] In Fe hexa-coordinated NHC complexes, the NHC typically stabilizes a trivalent state with a d^5 electronic configuration. In such cases, the transition between the excited state and the ground state is spin-allowed, leading to rapid deactivation. In contrast, divalent Fe state with a d^6 configuration, the transition becomes spin-forbidden, which is expected to extend the excited-state lifetime.

In this study, we used a triazole-based NHC ligand to provide a slightly weaker ligand field than conventional imidazole-based NHC, successfully synthesizing and isolating the Fe complex as an air-stable divalent species (Fig. 1).[2] The excited-state dynamics were analyzed using time-resolved spectroscopy and quantum chemical calculations. The product was identified via NMR, High-Resolution MS, elemental analysis and single-crystal X-ray structural analysis. The cyclic voltammetry revealed an Fe(III)/Fe(II) redox couple of 0.33 V (vs. $Fc^{+/0}$). This value is higher than that of similar Fe hexa-NHC complexes, confirming the stability of the divalent state. Femtosecond transient absorption spectroscopy (Fig. 2(a)) showed a two-component decay, with lifetimes of 1.4 ps for the first component and 26 ps for the second. Based on spectroelectrochemical measurements and DFT calculations, the first component was assigned to the ^{3}MLCT while the second was assigned to the ^{3}MC state (Fig. 2(b)). Although the obtained ^{3}MLCT state is very short-lived, this research paves the way for the utilization of ^{3}MLCT state in d^6 Fe hexa-NHC complexes.

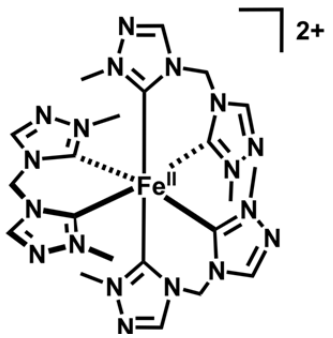


Fig. 1 The structure of Fe(II) hexa-NHC complex

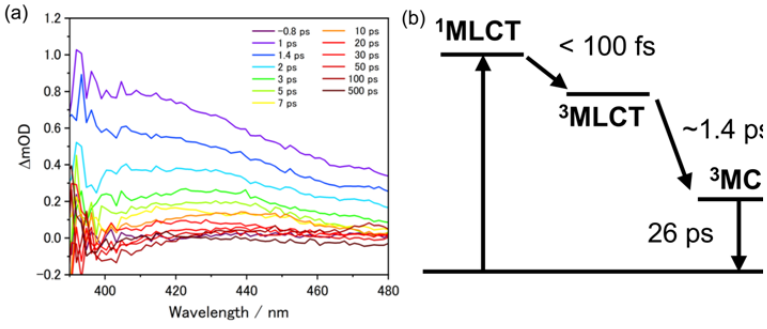


Fig. 2 (a) Transient absorption spectra of the complex (λ_{ex} = 320 nm). (b) Photoexcited Dynamics.

[1] P. Chábera *et al.*, *Nature* **2017**, *543*, 695-699. [2] T.Wakabayashi *et al.*, *Inorg. Chem.* **2026**, *65*, 767-775.

DESIGN AND EXCITED-STATE CHARACTERIZATION OF Fe(II) ISOCYANIDE COMPLEXES WITH BIDENTATE AND TRIDENTATE LIGANDS

Teruyuki Honda, Tatsuya Yoshida, Shintarao Yamamoto, Takuto Wakabayashi, Toshiki Mochimaru, Kaito Segawa, Kiyoshi Miyata, Tomohiro Ogawa, Ken Onda

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Fe(II) complexes have attracted attention as earth-abundant alternatives to Ru(II) and Ir(III) photosensitizers; however, their ^{3}metal to ligand charge transfer (MLCT) states are often rapidly deactivated through low-lying ^{3}metal centered (MC) states.[1] Isocyanide ligands are attractive candidates for controlling these excited-state energetics because their strong σ-donor character can increase the ligand-field splitting, while their π-acceptor character can stabilize MLCT states.[2] In this study, we designed new isocyanide ligands with extended π-conjugation and heteroatom incorporation to lower the ligand-centered π* orbitals and further stabilize MLCT excited states.

Based on this ligand design, we first synthesized a bidentate Fe(II) isocyanide complex (**Fe2CN**, Fig. 1) and investigated its photophysical properties using time-resolved spectroscopy.[2] **Fe2CN** exhibited an absorption band assignable to an MLCT transition around 400 nm and showed photoluminescence with a lifetime of 12 ns, which was assigned to emission from a ^{3}ligand-centered (^{3}LC) state.

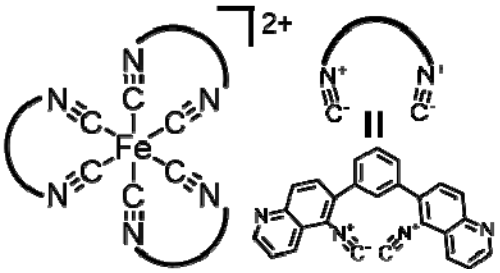


Fig. 1. Molecular structure of the bidentate Fe(II) isocyanide complex (**Fe2CN**).

In addition to **Fe2CN**, we have recently synthesized a tridentate Fe(II) isocyanide complex (**Fe3CN,** Fig. 2) to enhance the structural rigidity of the complex and investigate how the resulting coordination geometry affects the excited-state dynamics. The photophysical properties of **Fe3CN** were evaluated by the same spectroscopic approaches and compared with those of **Fe2CN**.

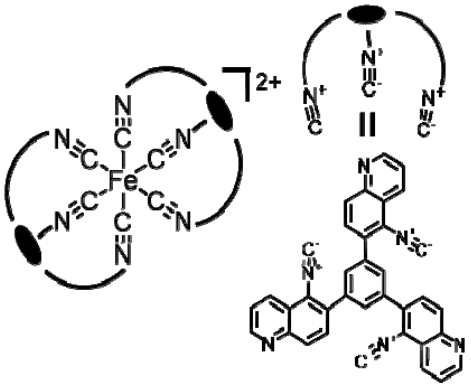


Fig. 2. Molecular structure of the tridentate Fe(II) isocyanide complex (**Fe3CN**).

In this presentation, we will discuss the excited-state dynamics, and quantum chemical calculations of **Fe2CN** and **Fe3CN**, with particular emphasis on how ligand structure influences the stabilization and deactivation pathways of the excited states in Fe(II) isocyanide complexes.

[1] C. Bressler, *et al*., *Science*, **2009** 323 489-492.

[2] C. Wegeberg, *et al*., *J. Am. Chem. Soc*. **2024**, *146*, 4605.

PHOTOACTIVE RHENIUM(II) COMPLEXES AS POTENT PHOTOREDOX CATALYSTS

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Department of Chemistry, University of Basel, Switzerland

Photoredox catalysis has emerged as a powerful strategy for enabling previously inaccessible bond-forming and bond-breaking events under mild conditions, leveraging single-electron transfer processes driven by visible-light-excited photocatalysts. The resulting open-shell intermediates grant access to diverse C–C, C–N, and C–O coupling reactions that are difficult to achieve through classical two-electron pathways.[1]

Typical photoredox catalysts rely on closed-shell (low-spin) d^6 or d^8-electron configurations, owing to their ground-state stability and long excited-state lifetimes. Recently, open-shell systems involving d^5-configurations have been reported with excited-state lifetimes in the nanosecond regime.[2] Rare examples of Re(II) complexes additionally feature high excited-state potentials, being able to oxidize aromatic hydrocarbons such as benzene.[3]

In this contribution, a new Re(I) isocyanide complex is reported (Fig. 1). By using a tridentate ligand, kinetic stability is achieved, while steric protection excludes solvent coordination. Oxidation leads to the corresponding Re(II) compound, which is analyzed in terms of excited-state potential and lifetime. Additionally, the excited-state dynamics are investigated by transient-absorption spectroscopy (TAS).

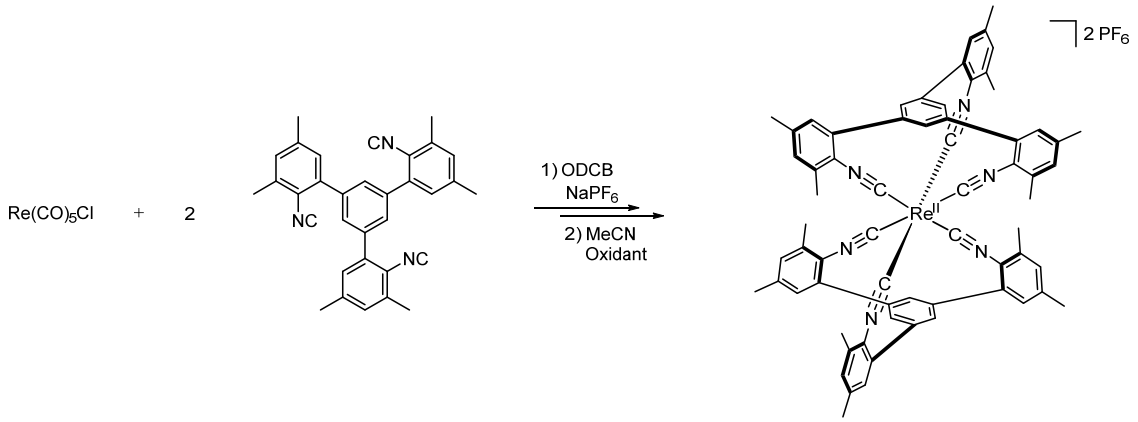


Figure 1: Synthesis and structure of a novel tridentate isocyanide complex of Re(II).

[1] M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* **2016**, *81*, 6898–6926.

[2] K. S. Kjaer, N. Kaul, O. Prakash, V. Sundström, P. Persson, R. Lomoth, K. Wärnmark et al., *Science* **2019**, *363*, 249-253; J. Wellauer, B. Pfund, I. Becker, F. Meyer, A. Prescimone, O. S. Wenger, *J. Am. Chem. Soc.* **2025**, *147*, 8760–8768

[3] T. M. Rodriguez, M. Deegbey, C.-H. Chen, E. Jakubikova, J. L. Dempsey, *Inorg. Chem.* **2023**, *62*, 6576–6585; C. Wegeberg, N. A. Calvet, M. Krafft, P. Chábera. A. Yartsev, P. Persson, *Chem. Sci.* **2025**, *16*, 21975-21990.

LUMINESCENCE OF AN IRON(III) COMPLEX WITH MERIDIONAL TRIDENTATE N-HETEROCYCLIC CARBENE LIGAND

Toshiki Mochimaru, Tomohiro Ogawa, Teruyuki Honda, Kaito Segawa, Takuto Wakabayashi, Yuto Harakawa, Tatsuya Yoshida, Kiyoshi Miyata, and Ken Onda

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Precious metal complexes based on Ru, Ir, and Pt have been used as photocatalysts and luminescent materials. Recently, the replacement of these metals with earth-abundant first-row transition metals such as Fe, Co, Ni has attracted increasing attention. However, photoexcited states of first-row transition-metal complexes generally exhibit rapid nonradiative deactivation through metal-centered (MC) states.[1] To destabilize these MC states, N-heterocyclic carbene (NHC) ligands have been widely used. While the NHC ligands have played an exclusive role in photoactive first-row transition-metal complexes,[2] ligand choice remains significantly limited.

Here, we report the synthesis of an Fe(III) complex bearing a methylene-bridged tridentate NHC ligand (Fig.1a) and investigate the relationship between its structure and excited-state dynamics. The complex was characterized by single-crystal X-ray crystallography. Continuous shape measure (CShM) analysis revealed that the Fe(III) complex adopts a better octahedral geometry than previous bidentate or *mer*-tridentate ligands. Time-resolved luminescence measurements (Fig.1b) showed prolonged ^{2}LMCT luminescence with a lifetime of 670 ps (Fig.1c) and a quantum yield of 0.6%. Compared with Fe(III) complexes containing bidentate NHC ligands or other *mer*-tridentate systems, this complex exhibits a more ideal octahedral structure and a significantly longer excited-state lifetime. The extended lifetime indicates that our new ligand is promising for the photoactive first-row transition metals.

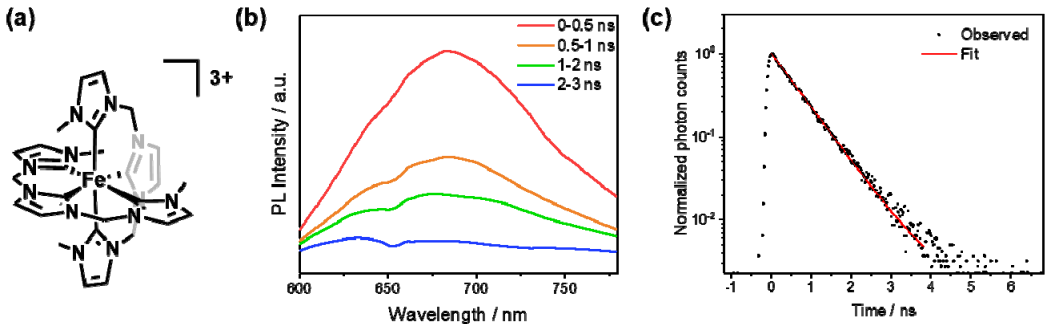


Fig.1 (a) Structure of $[Fe(tim)_2]^{3+}$ (H_3tim = 1,1'-((1*H*-imidazole-3-ium-1,3-diyl)bis(methylene))bis(3-methyl-1*H*-imidazol-3-ium)). (b) Time-resolved photoluminescence spectra. (c) Decay profile of photoluminescence.

[1] C. Wegeberg, O. S. Wenger, *JACS Au*, **2021**, *1*, 1860 [2] J. K. McCusker, *Science*, **2019**, *363*, 484.

STRUCTURE–PROPERTY RELATIONSHIPS IN OXIDOVANADIUM(V) HYDRAZONE COMPLEXES

Višnja Vrdoljak[a], Dino Kuzman[a], Josipa Sarjanović[a], Juraj Toplak[a], Danijela Musija[b], Jana Pisk[a], and Tomica Hrenar[a]

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[b]University of Zagreb School of Medicine, Department of Chemistry and Biochemistry, Šalata 3, 10000 Zagreb, Croatia

A series of 18 salicylaldehyde hydrazone ligands bearing diverse substituents, together with their oxidovanadium(V) complexes, was synthesised to investigate structure–property relationships. Comprehensive structural characterisation revealed tridentate hydrazone coordination, with the auxiliary pyridyl nitrogen playing a key role in coordination-driven self-assembly into oligonuclear species [1,2]. However, identical building blocks can self-assemble in different ways, yielding distinct structural outcomes that depend on ligand orientation, network topology, and subtle variations in reaction conditions. The complexes were evaluated as catalysts for the oxidation of benzyl alcohol using tert-butyl hydroperoxide, demonstrating pronounced structure–activity relationships. An integrated experimental and computational study provides novel insights into the structure-activity relationships of vanadium–hydrazone complexes, offering valuable design guidelines for the rational development of advanced oxidation catalysts with tailored functionalities.

[1] Topić, E.; Sarjanović, J.; Musija, D.; Mandarić, M.; Hrenar, T.; Pisk, J.; Vrdoljak, V. RSC Adv. 2025, 15, 3547–3561.

[2] Kuzman, D.; Sarjanović, J.; Mandarić, M.; Cindrić, M.; Agustin, D.; Pisk, J.; Vrdoljak, V. Inorg. Chem. Commun 2026, 183 (2), 115817.

A BRIGHT NEW LINK – A NOVEL LIGHT-SWITCH-CAPABLE BRIDGING LIGAND IN PHOTOACTIVE METAL COMPLEXES

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Institute of Inorganic Chemistry I, Ulm University, Albert Einstein Allee, 11, 89081 Ulm, Germany

A ruthenium(II) polypyridyl complex bearing an N,N′-di(p-tolyl)-1,10-phenanthroline-5,6-diamine ligand shows ground-state electronic decoupling between the RuII-coordinated diimine sphere and the diamine unit, so that electronic communication occurs mainly in the excited state and the characteristic ^{1}MLCT absorption remains largely independent of the protonation state of the para-phenylenediamine moiety. Deprotonation induces an ultrafast, non-emissive long-lived interligand charge-transfer state that can be reversed by coordination of Lewis-acidic metal ions such as Zn^{2+}, yielding a charge-neutral, light-switchable metalloligand that serves as a modular platform for structurally flexible multinuclear photocatalysts. [1].

Using the Buchwald–Hartwig strategy, new substitution patterns on the aryl rings attached to the amine can be introduced, thereby tuning the steric and electronic properties of the amine-based second coordination sphere. The ortho-methyl derivative shows strongly enhanced emission and is therefore particularly attractive, and its deactivation pathways, together with those of the other complexes, will be investigated in more detail. Moreover, the para-substituted diamine complex can form a dinuclear ruthenium species via the amine binding pocket as a second coordination site, and targeted exploitation of this bridging capability will be explored further.

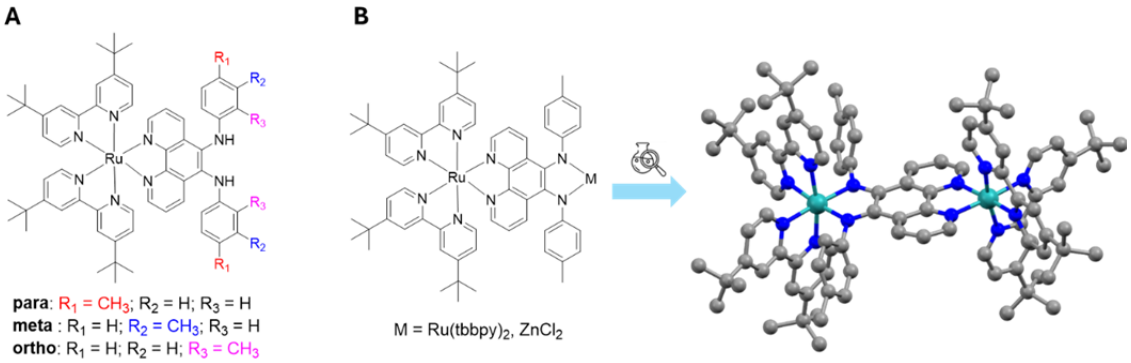


Figure 1 A: Chemical structures of different substitution patterns of the methyl group on the diamine complex. **B**: Possible dyads of diamine complexes with the XRD structure of the Ru-(para)diamine-Ru dyad.

[1] Isakov, D.; Witas, K.; Semwal, M.; Traber, P.; Rein, A. S. J.; Sorsche, D.; Hainthaler, A.; Rau, S. ChemRxiv 2025, Preprint, DOI: 10.26434/chemrxiv-2025-jd7c8.

PHOTOPHYSICAL STUDY OF [Ir(piq)$_2$(acac)]: EXPLORING INTRINSIC PARAMETERS IN SPIN-ORBIT COUPLING MEDIATED INTENSITY STEALING

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[b] Department of Chemistry, National Taiwan Normal University, Taiwan R.O.C.
[c] Department of Chemistry, Tamkang University, Taiwan R.O.C.

Previously, our laboratory investigated a series of Kasha-type emitting Ru-(bidentate cyclometalated-aromatic ligand), Ru-CM, chromophores exhibiting phosphorescence emission in the red-light to the NIR region, with phosphorescence quantum yields ($\phi_{em(p)}$) at 77K significantly higher than those of the reference Ru-bpy chromophore series, a result attributed to their intrinsically low 77K nonradiative rate constant (k_{NRD}) magnitude.[1]

Building upon these findings, this study aims to explore Ir(III)-CM chromophores series, which are also low-spin d^6 systems, and to compare their phosphorescence efficiencies ($\iota_{em(p)}$) with those of Ru(II)-CM chromophores series. As an initial entry point into this series, we investigated and compared the fundamental photophysical properties of [Ir(piq)$_2$(acac)] and [Ru(pzpy)$_2$piq]$^+$ complexes, including room-temperature absorption and emission spectra, complemented by ADF calculations to elucidate its excited-state characteristics, where acac, pzpy and piq denote acetylacetonate, 2-(1H-pyrazol-1-yl)pyridine, 1-phenylisoquinoline, respectively.

The experimental results indicate that [Ru(pzpy)$_2$piq]$^+$ exhibits a low-energy absorption band spanning 15000–35000 cm^{-1} (666–286 nm), with an emission maximum at 14700 cm^{-1} (680 nm). In contrast, [Ir(piq)$_2$(acac)] shows a low-energy absorption band in the range of 15000–23000 cm^{-1} (670–440 nm), along with an emission maximum at 16500 cm-1 (606 nm) and pronounced vibronic sidebands. Subsequent measurements of quantum yields will be conducted to determine the radiative ($k_{RAD(p)}$) and nonradiative (k_{NRD}) rate constants. This work provides a platform for systematically examining the intrinsic parameters in spin-orbit coupling mediated intensity stealing (SOCM-IS) modeling[2, 3] governing the characteristics of charge-transfer phosphorescence of Ru-CM and Ir-CM chromophores.

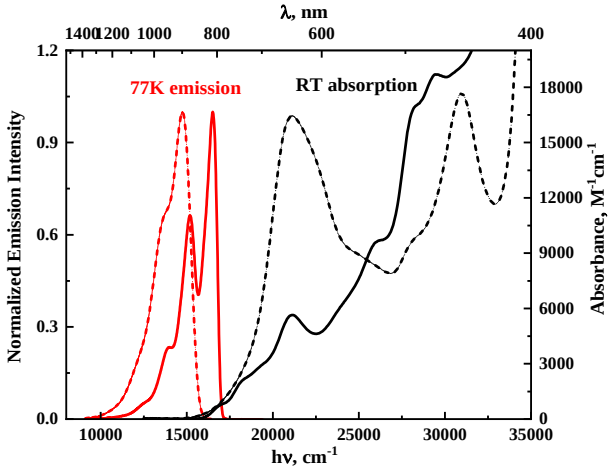


Figure 1. Comparison of the 298 K absorption spectra (black curve, in CH_3CN) and the 77 K emission spectra (red curve, in butyronitrile) of [Ru(pzpy)$_2$(piq)]$^+$ (dashed lines) and [Ir(piq)$_2$(acac)] (solid lines) in the left panel.

[1] Yin, C.-W.et al. 2024, 63 (46), 21981-21993. DOI: 10.1021/acs.inorgchem.4c03390.

[2] Thomas, R. A. et al. 2015, 119 (24), 7393-7406. DOI: 10.1021/jp510949x.

[3] Chen, J. Y.et al. 2026, 65 (9), 5096-5108. DOI: 10.1021/acs.inorgchem.5c05587.

PHOTOSWITCHING IN P-CENTERED BI- AND TETRARADICALOID–GROUP 4 METALLOCENE HYBRIDS

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Phosphorus-centered biradicaloids are attractive open-shell systems because of their unusual electronic structures and reversible bond-forming reactivity. In contrast, tetraradicaloids and especially tetraradicaloid-based molecular switches remain comparatively unexplored. Herein, we report the synthesis of group 4 metallocene hybrids incorporating one or two phosphorus-centered biradicaloid switching units, thereby enabling mono- and double-molecular switching behavior.

The target compounds were synthesized via insertion of metallocene-functionalized isonitriles into the biradicaloid $[\cdot P(\mu\text{-NTer})]_2$ (Ter = terphenyl), affording titanium and zirconium complexes containing one (9M) or two (10M) five-membered P-centered biradicaloid heterocycles. Upon irradiation with red light (638 nm), these systems undergo reversible transannular P–P bond formation to generate housane-type photoisomers (9Mh and 10Mh). In the tetraradicaloid systems, photoswitching occurs at two distinct biradicaloid subunits, resulting in a rare example of a double molecular switch based on open-shell phosphorus chemistry.

The switching processes and CO_2 activation behavior were investigated by multinuclear NMR and UV/Vis spectroscopy. In addition, quantum-chemical calculations were performed to examine the electronic structures, the isonitrile insertion mechanism, and the photoisomerization pathways, providing insight into the influence of the metallocene fragments on the open-shell framework.

These results demonstrate that group 4 metallocene fragments can be integrated into phosphorus-centered radicaloid architectures to generate photoresponsive transition-metal/main-group hybrid systems with tunable switching properties.

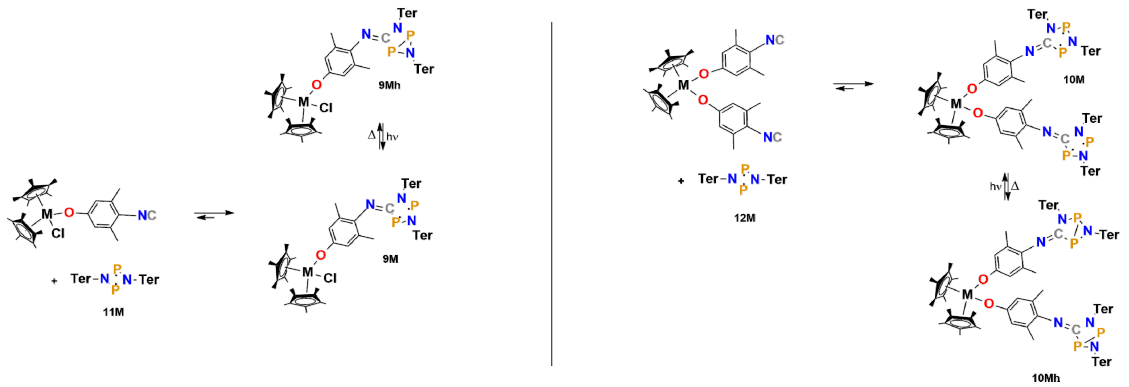


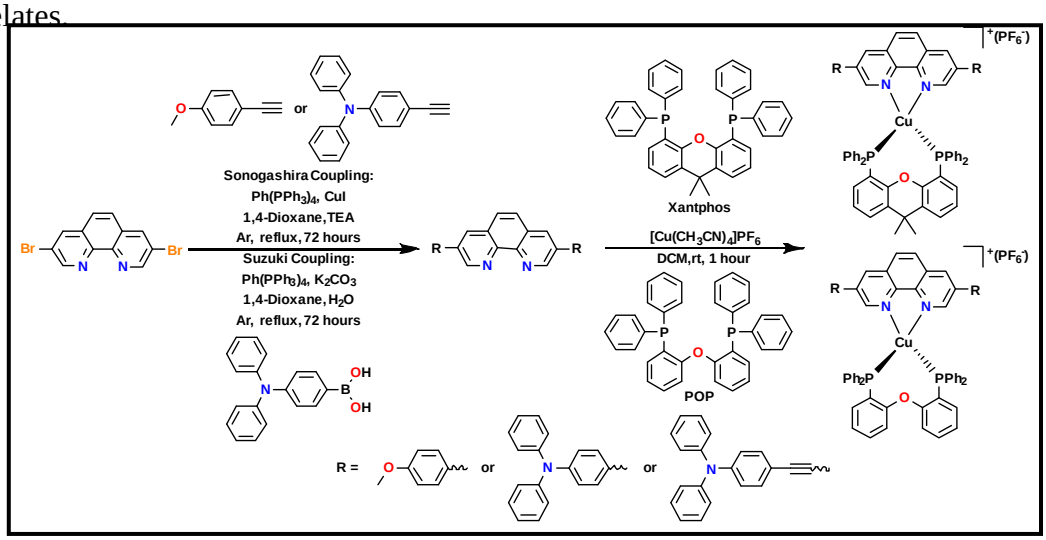
Figure 1. Synthesis of metallocene-bridged P-centered biradicaloid (9M) and tetraradicaloid (10M) for M = Ti, Zr and their photoisomerization to the housane species 9Mh and 10Mh (h = housane).

COMPARISON STUDY OF DISUBSITUTED-1,10-PHENANTHROLINE BASED HETEROLEPTIC Cu(I) COMPLEXES WITH ETHYLENE SPACER

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Photosensitizers are light-harvesting molecules that initiate the primary photoinduced electron-transfer process in photocatalytic systems. There is growing interest in the development of new photocatalysts based on earth-abundant metals as alternatives to rare-earth elements. 1,10-Phenanthroline-based (Phen) and triphenylamine (TPA) are widely used for light-harvesting compounds, to enhance photophysical properties of metal complexes [1]. Diphosphine chelates containing ether linkages, such as POP and xantphos, are also well known for their effectiveness in catalysis [2]. This work designed new photocatalysts featuring diTPAPhen ligands, copper(I) and diphosphine chelates.



Scheme 1. Synthesis of new Phen-based copper(I) complexes with POP/xantphos.

We have developed a high yield methodology to diTPAPhen ligands (Scheme 1). Six new heteroleptic copper(I) complexes were synthesized using three different diTPAPhen ligands and either POP or xantphos. The structures were confirmed by a combination of NMR, mass spectrometry and X-ray crystallography.

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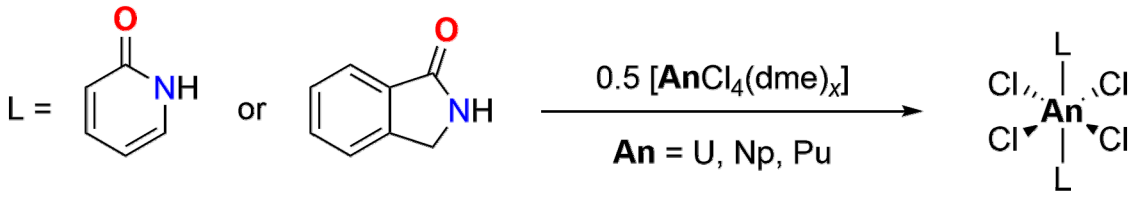
OCTAHEDRAL COMPLEXES OF THE ACTINIDE TETRACHLORIDES

Till Sawallisch[a], Dennis Grödler[a], Adrian Näder[a], Clara L. Silva[a,b], Peter Kaden[a], Michael Patzschke[a], Lucia Amidani[a,b], Kristina Kvashnina[a,b], Moritz Schmidt[a,c], and Robert Gericke[a]

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Coordination chemistry is a valuable tool to gain insights into the fundamental properties of metal ions such as magnetic and spectroscopic behavior and their electronic structure. While many of these aspects have already been well established for transition metals and lanthanides, the elements of the actinide series, especially the transuranium elements neptunium and plutonium, are still underexplored in this regard. This is partly due to the experimental difficulties associated with their radioactivity, but also some intrinsic properties of these heavy elements, starting from their large ionic radii favoring high coordination numbers with low symmetry to relativistic effects such as spin-orbit coupling, complicate the measurement and interpretation of the obtained data.

Here, we present a fundamental study on two series of octahedral complexes of the actinide tetrachlorides $[An^{IV}Cl_4(L)_2]$ (An = U, Np, Pu) with the relatively small amide-based ligands L = 2-pyridone and phthalimidine. The complexes are straightforwardly synthesized by layering solutions of metal chloride and ligand upon which pale crystals deposit. The compounds have been analyzed by a wide range of methods, including SC-XRD, NMR, IR, UV-vis, and X-ray absorption spectroscopy, as well as SQUID magnetometry, and quantum chemical calculations.



Despite their relatively small size, these ligands form stable complexes with the tetravalent actinides with the unusually low coordination number of six. With their symmetric, *pseudo*-octahedral coordination environment (D_{4h}), these complexes are suitable model systems to gain a deeper understanding for the electronic structure of these 5f-elements, including the derivation of ligand field parameters B^k_q and the corresponding splitting of the electronic states by combination of magnetometric data and quantum chemical calculations.

This research is funded by the German Federal Ministries of Research, Technology and Space via the FENABIUM-II project (02NUK077B) and for the Environment, Climate Action, Nature Conservation and Nuclear Safety via the Am-BALL project (1501667).

STERICS DICTATED REACTIVITY BETWEEN HYBRID O/P-DONOR LIGANDS AND URANIUM

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Uranium is one of the most intriguing elements among all lanthanoids and actinoids with regards to reactivity. It is known to exhibit multiple oxidation states and have a rich redox chemistry.[1] Low valent uranium species have been shown to activate small molecules like N_2, CO, CO_2 and H_2O.[2] Ligand design has been a major factor in tuning the reactivity at the uranium center.[3]

To further investigate the reactivity of low valent uranium species, we are developing a class of hemilabile ligands based on well-established aryloxide ligands. Utilizing the mismatch between the hard Lewis acid uranium and the soft Lewis base phosphorous, we designed aryloxide-phosphine hemilabile ligands and investigated their coordination chemistry with uranium.

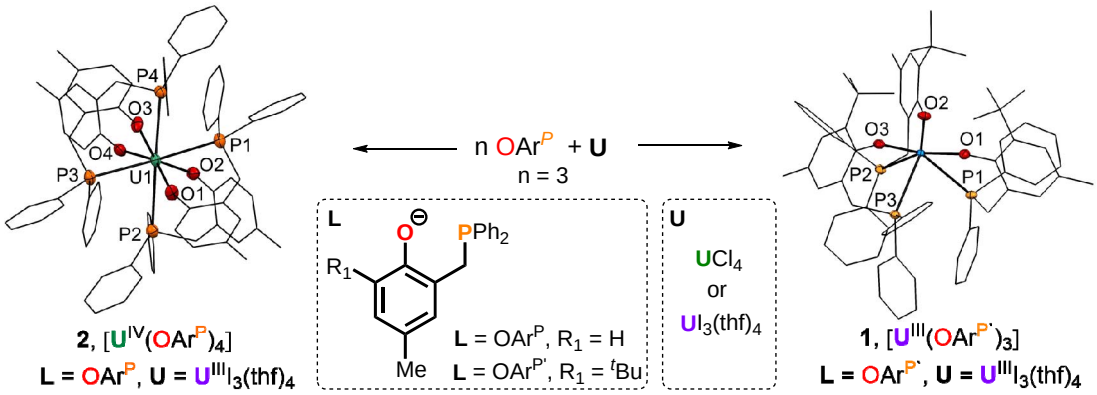


Figure 1. Synthesized hybrid ligands and the resulting uranium complexes.

We have found that ligand sterics play a vital role in the complex formation. U(III) in combination with the sterically demanding $OAr^{P`}$ ligand has been found to yield the expected U(III) homoleptic aryloxide complex **1**. However, when U(III) is combined with the sterically less demanding OAr^{P} ligand, it disproportionates and yields a homoleptic aryloxide U(IV) complex **2**. In this work, we investigate the underlying factors for the observed reactivity, as well as study the coordination chemistry of the OAr^{P} ligand with U(IV) precursors. Additionally, the reactivity of obtained U(III) complex **1** is investigated with the small molecules such as CO and N_2.

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FROM WASTE TO RESOURCES: RECOVERY OF RARE EARTH ELEMENTS FROM NdFeB MAGNETS

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Rare Earth Elements (REEs) are essential components in many advanced technologies, however their availability is influenced by geopolitical factors and market instability. [1] For this reason, the development of efficient recycling processes is essential to secure the supply and reduce the dependence on mining.

This work investigates the recovery of REEs from end-of-life NdFeB permanent magnets, a valuable secondary source of lanthanides, using a previously developed selective precipitation approach. A separation of neodymium and dysprosium was obtained through the use of commercially available 5-chloro-8-hydroxyquinoline as a ligand. [2] The process relies on the formation of metal complexes with contrasting nuclearity and solubility in ethanol. Nd forms a poorly soluble trimeric complex, whereas Dy forms a soluble tetrakis complex, allowing their separation by selective precipitation.

An extension of the methodology was applied, starting from a real NdFeB magnet sample and using a Box-Behnken Design to identify the experimental conditions leading to the most effective Nd/Dy separation. Overall, this ligand-controlled separation approach offers a promising pathway toward a more efficient and sustainable recycling of REEs from waste products.

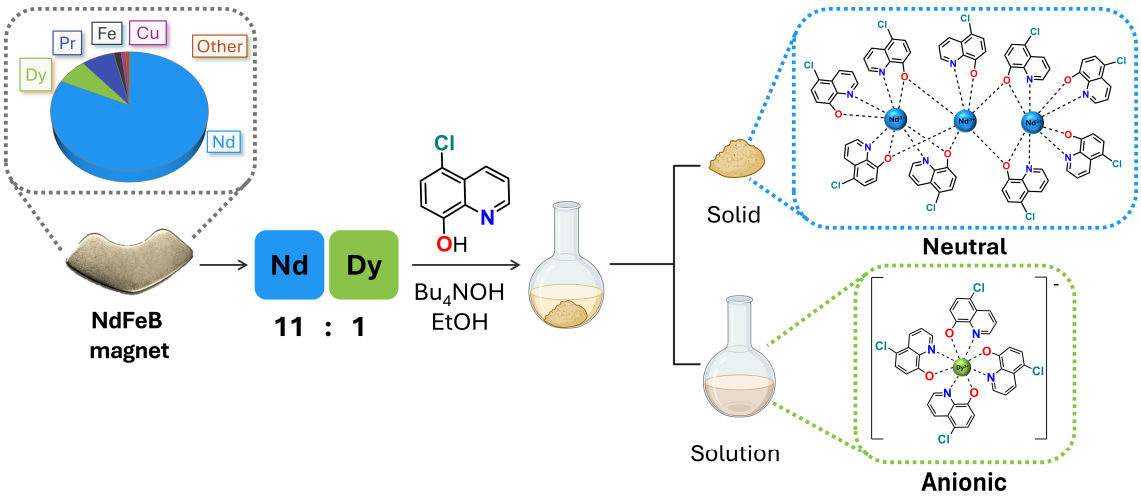


Figure. Scheme of the separation of Nd^{3+} and Dy^{3+} through selective precipitation in ethanol starting from a NdFeB magnet sample.

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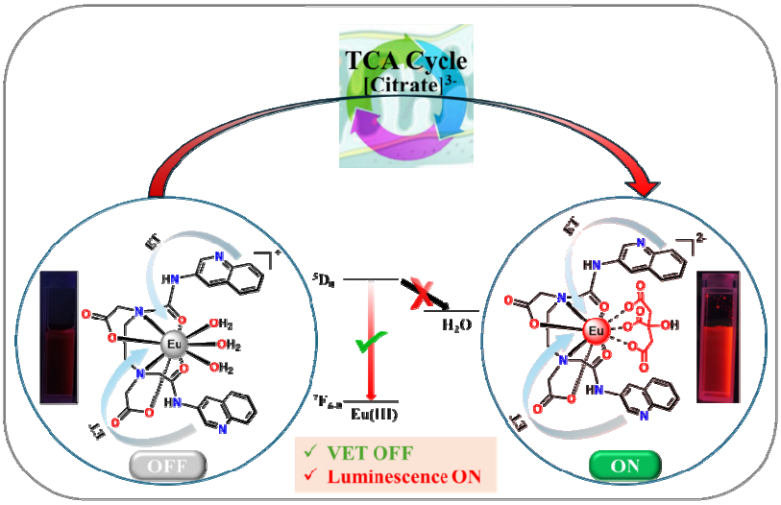
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RATIONAL DESIGN AND EVALUATION OF THE SENSING MECHANISM OF A EUROPIUM(III)-BASED LUMINESCENT TURN-ON CHEMOSENSOR FOR CITRATE

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Citrate plays a multifaceted and crucial role in biological systems. At the cellular level, it is a key intermediate in the Krebs cycle, the central metabolic pathway for energy production, or source of ATP in aerobic organisms. Abnormal citrate concentrations have been linked to various conditions, including cancer, kidney stones, and metabolic disorders, highlighting its diagnostic and prognostic value.[2,3] Therefore, the ability to accurately detect and monitor citrate is vital for advancing our understanding of these diseases, enabling early diagnosis, and guiding effective therapeutic strategies. In this context, hard luminescent lanthanide probes are emerging as particularly advantageous due to their unparalleled and unique optical properties.[4,5] Herein, we report a novel, sensitive, and highly selective Eu(III) probe holding a hexadentate EDTA-based bisamide ligand linked to two 3-aminoquinolines as antennae for the selective sensing of citrate^{3-} as an important regulatory metabolite at physiological pH using highly sensitive and selective time-resolved luminescence (TRL) from **Eu.1**. We established that the replacement of the inner-sphere water molecule by the citrate modulates the non-radiative vibrational energy transfer (VET) pathway, liable for the enhanced luminescence response. Furthermore, lifetime (τ), hydration number (q), ESI-MS, Jobs' plot, and density functional theory (DFT) calculations were performed to gain insights into the sensing mechanism. Thus, it acts as a selective and sensitive turn-ON sensor for the ppb level of citrate.



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ORTHOGONAL TURN-ON LUMINESCENT LANTHANIDE COMPLEXES FOR BIOLOGICAL APPLICATION

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Molecular imaging, particularly fluorescence imaging, is an essential tool in biological and biomedical research. Organic fluorophores dominate this field due to their high brightness and synthetic versatility. However, they present limitations such as broad emission bands that hinder multiplexing, small Stokes shifts leading to spectral overlap, limited photostability, and environment-dependent behavior (e.g., aggregation), often resulting in increased background from biological autofluorescence.[1]

Turn-on probes offer an attractive strategy to improve detection specificity by minimizing background signals. In this context, bioorthogonal pretargeting approaches, widely used in nuclear medicine, rely on the inverse electron-demand Diels–Alder (iEDDA) reaction between trans-cyclooctene (TCO) and tetrazine. When incorporated into a sensitizing antenna, tetrazine efficiently quenches luminescence through energy or electron transfer pathways, yielding non-emissive (OFF) probes. Upon reaction with TCO, tetrazine is converted into a dihydropyridazine, suppressing quenching and restoring emission (ON state).[2]

Lanthanide complexes, particularly Eu^{3+} and Tb^{3+}, provide a compelling alternative due to their unique photophysical properties. Their emission relies on the antenna effect, where an organic chromophore sensitizes the metal center. This results in long luminescence lifetimes suitable for time-gated detection (removing biological fluorescence background), large apparent Stokes shifts, narrow emission bands favorable for multiplex imaging and high photostability. These complexes have demonstrated utility in biological applications, including one- and two-photon microscopy, as well as in ratiometric sensing of pH, oxygen, and metal ions even if they require UV excitation.[3]

Here, we report the development of tetrazine-functionalized antenna ligands incorporated into Eu^{3+} and Tb^{3+} complexes, enabling bioorthogonal turn-on luminescence upon reaction with TCO-modified biomolecules. These probes target TCO- antibodies or peptides bound to specific receptors for applications in microscopy and image-guided surgery. In addition, this approach enables precise accurate estimation of the number of accessible TCO groups on antibodies, improving the reliability of pretargeting strategies in the nuclear imaging and therapy field. Initial synthetic and photophysical studies reveal unexpected behaviors, highlighting the potential of these systems for advanced bioimaging applications.

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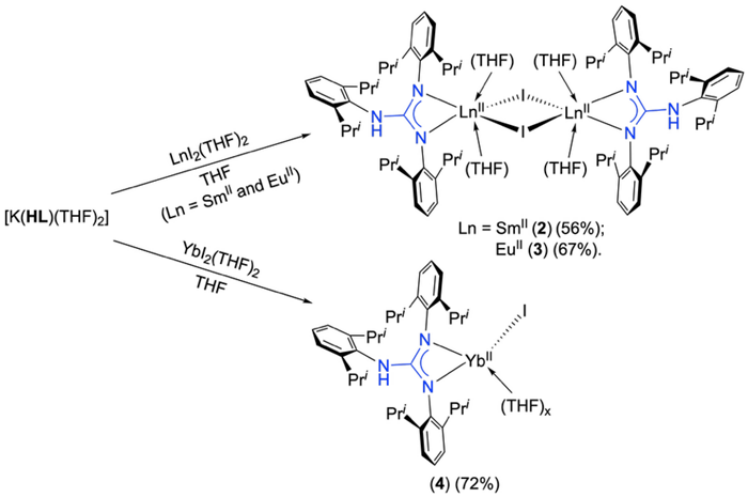
USING A STERICALLY BULKY GUANIDINATE LIGAND FOR STABILIZATION OF DIVALENT LANTHANIDE METAL COMPLEXES

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Guanidinate anions of the formula $[(R'_2N)C(NR)_2]^-$ (R, R' = alkyl, aryl or silyl substituents) exhibit rich coordination chemistry.[1] The tunable steric and electronic properties of guanidinate ligands can be achieved by introducing appropriate substituents at the nitrogen atoms.[2] Delocalization of anionic charge through the NCN backbone of guanidinate ligands enables stabilization of different metal complexes.[3]

In the present study, lanthanide(II) guanidinate complexes $[Sm^{II}(\mathbf{HL})(\mu\text{-}I)(THF)_2]_2$ (**2**), $[Eu^{II}(\mathbf{HL})(\mu\text{-}I)(THF)_2]_2$ (**3**) and $[Yb^{II}(\mathbf{HL})I(THF)_x]$ (**4**) (**4a**, x = 1; **4b**, x = 2), where $[\mathbf{HL}]^-$ = $[(2,6\text{–}Pr^i_2C_6H_3N)_2C(NHC_6H_3Pr^i_2\text{–}2,6)]^-$, were synthesized by salt metathesis reaction of the corresponding $LnI_2(THF)_2$ (Ln = Sm^{II}, Eu^{II}, Yb^{II}) with one equivalent of potassium guanidinate complex $K(\mathbf{HL})(THF)_2$ (**1**) in THF (Scheme 1). The reactivity of complexes **2** - **4** were studied in this work. Addition of 4-dimethylaminopyridine (DMAP) to complex **2** led to isolation of monomeric $[Sm^{II}(\mathbf{HL})I(DMAP)_2]$ (**5**). Reaction of complex **2** with dioxygen yielded dimeric samarium(III) μ-oxo complex $[\{Sm^{III}(\mathbf{HL})I(THF)\}_2(\mu\text{-}O)]$ (**6**). Treatment of $[Yb^{II}(\mathbf{HL})I(THF)_x]$ (**4**) with one equivalent of potassium anilide $K(NHC_6H_3Pr^i_2\text{–}2,6)$ gave $[Yb^{II}(\mathbf{HL})\{NHC_6H_3Pr^i_2\text{–}2,6\}(THF)_2]$ (**7**). Complex **4** reacted readily with azobenzene to yield $[Yb^{III}(\mathbf{HL})\{\mu\text{-}N(C_6H_5)\}(THF)]_2$ (**8**).



Scheme 1. Synthesis of Ln(II) guanidinate complexes **2** – **4**.

Acknowledgements. This work was supported by the Research Grants Council of Hong Kong in the form of a GRF Grant (Ref. No.: CUHK 14300020).

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REACTIVITY OF URANIUM COMPLEXES BASED ON A TRISANIONIC PINCER SCAFFOLD

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The development of well-defined uranium complexes is crucial for tackling modern-day challenges in fields such as nuclear waste remediation, catalysis, and small-molecule activation. To this avail, pincer ligands offer a versatile scaffold for accessing rigid uranium complexes with electronic and steric environments that can readily be tuned. Using such uranium-pincer pairings, our group has reported the functionalization of biphenylene with CO, leveraging the bulky pincer ligand to access the terminally bound arenide [1]. More recently, our group has reported the dinitrogen cleavage and hydrogenation by a U-hydride complex through unprecedented cooperativity between the uranium center and the bisanionic NON pincer ligand [2]. In this work we describe the synthesis and characterization of a U(IV) bisalkyl complex based on a trisanionic NNN pincer ligand [3-4]. We further detail our findings on the hydrogenolysis of this species, where the increased electron density on the U-center results in a U-hydride species with a markedly different reactivity to its bisanionic NON congener. Lastly, we report the reactivity of this U-hydride complex towards small molecules.

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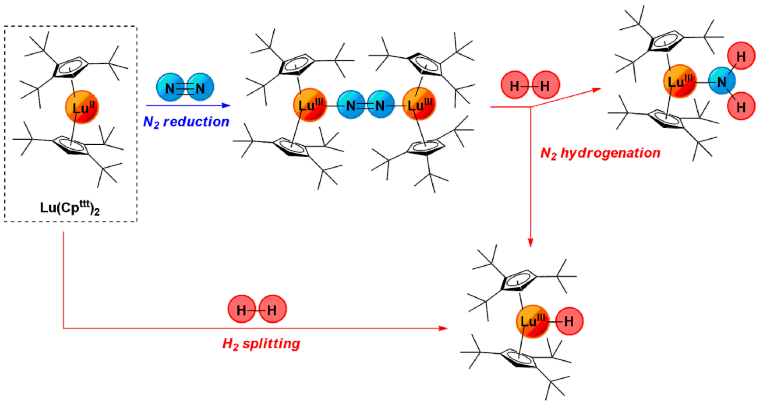
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H_2 SPLITTING AND N_2 HYDROGENATION BY A LUTETIOCENE COMPLEX

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[c]LPCNO, UMR 5215, Université de Toulouse-CNRS, INSA, UPS, Toulouse, France

The activation and functionalization of small molecules like H_2 and N_2 has long been the "holy grail" of synthetic chemistry, traditionally dominated by transition-metal catalysis and the energy-intensive Haber−Bosch industrial process to produce ammonia [1]. Lanthanides on the other hand, despite their unique electronic properties, have traditionally been limited for such transformations by virtue of the ionic nature of their bonds and large coordination numbers with ligands [2]. A particularly appealing and formidable approach in coordination chemistry to elicit transition-metal-like reactivity with lanthanides is the design of ligand environments capable of stabilizing low-valent lanthanide ions with low coordination numbers [3]. Herein, we present the synthesis and electronic structure of a neutral lutetiocene complex $Lu(Cp^{ttt})_2$ bearing a divalent lutetium ion (Lu^{II}), kinetically stabilized by a sterically demanding cyclopentadienyl ligand Cp^{ttt} scaffold [4]. This specific coordination environment allows the isolation of a kinetically stable yet electronically potent Lu^{II} species capable of direct H_2 splitting at ambient temperature; a first in lanthanide chemistry. Furthermore, we demonstrate that this Lu^{II} complex effectively binds N_2 to form an end-on coordinated diazenido N_2^{2-} species [5]. Remarkably, this complex undergoes hydrogenation under exceptionally mild conditions (1.2 bar of H_2, room temperature), leading to the formation of a unique Lu^{III}–NH_2 complex. These findings redefine the boundaries of rare-earth chemistry, proving that low-valent molecular lanthanide complexes can achieve direct N_2 cleavage and hydrogenation, offering a new molecular paradigm for small-molecule activation.



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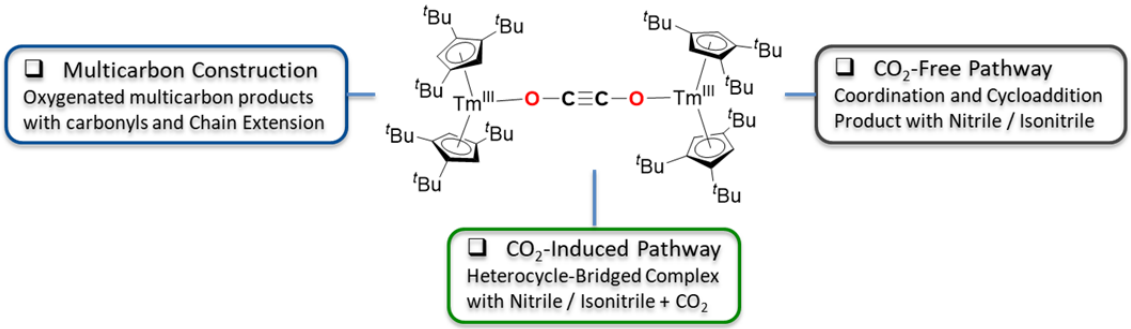
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CO-DERIVED ETHYNEDIOLATO AS A PLATFORM FOR SMALL MOLECULE FUNCTIONALISATION

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The transformation of carbon monoxide (CO) into multi-carbon oxygenated frameworks represents a key challenge and opportunity in small-molecule activation. Divalent lanthanide (Ln^{II}) complexes are attractive single-electron reductants for such transformations owing to their high oxophilicity and reactivity. The latter can be tuned by the nature of both the Ln^{II} metal centre and the ligand [1]. We have shown previously that, using a highly reductive and sterically hindered Tm^{II} complex, selective CO reductive dimerisation is possible, yielding an ethynediolato OCCO complex by controlling the stoichiometry of CO [2].



While ethynediolato complexes are known in f-block chemistry, only rare examples have focussed on their functionalisation reactivity [2][3]. In this study, we report two novel reactivity pathways of the ethynediolato intermediate generated from a Tm^{II} complex and CO:

(1) Divergent assembly of heterocyclic bridged complexes via nitrile and isonitrile functionalization under CO_2 and CO_2-free conditions.

(2) Direct functionalisation of the OCCO unit with C=O-based electrophiles, resulting in the formation of novel oxygenated multicarbon products.

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PHOTO-ELECTROCHEMICAL GENERATION OF Ln(II) SPECIES

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Lanthanides exhibit unique optical and magnetic properties, making them crucial in applications ranging from lasers and phosphors to MRI contrast agents.[1] While Ln ions in solution are most frequently found in their +3 oxidation state, in recent years, there has been a significant amount of research into the +2 and +4 oxidation states. The synthesis of Ln (II) complexes for all non-radioactive lanthanides has been accomplished,[2] which is a significant advancement, with applications in catalysis, magnetism, and biological imaging.[3-a,b,c]

Sm(II)-based stoichiometric reductants can mediate highly selective one-electron reductions, enabling diverse functional group transformations, as well as C–C and C–X bond formations. Despite decades of intensive effort to develop catalytic Sm(II)-mediated reductions, methodologies remained inferior to their stoichiometric counterparts in efficiency, selectivity, and substrate scope.[4] Our group has recently reported the first Ln (II) based photocatalysts with reactivity compared to, and in many cases better than, the stochiometric Sm(II) reagents.[5,6] In these systems, the active Ln(II) is generated via reduction of a stable Ln(III) precursor by a photoexcited chromophore. [5,6]

The sacrificial reductant regenerating the catalyst is an organic amine or ascorbic acid.[5,6] Despite the mildness of these reagents, replacing them with electrochemical reduction would significantly lower the costs of the process and its raw material requirements. To retain the broad scope and excellent selectivity of photocatalytic reactions, we aim to develop a protocol that couples photochemical Ln(II) generation would be coupled to electrochemical chromophore regeneration. We present results for a photo-electrochemical lanthanide-catalyzed reaction for a range of substrates and mechanistic investigations.

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SEPARATION OF RARE EARTH METALS USING MULTIDENTATE PHOSPHINE OXIDES

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The extraction, separation, and purification of rare earth elements (REEs) is a critical, ongoing area of global research.[1-3] Within this context, mono- and diorganophosphorus ligands have seen widespread applications as additives for solvent extraction or components in ion exchange resins.[4,5] Tri- and tetradentate organophosphorus ligands see more limited use due to lower synthetic accessibility relative to their mono- and bidentate counterparts.[4] We postulated that rigid, multidentate ligands featuring steric and electronic variability would be key to exploring selectivity trends in extracting REEs from aqueous solutions. Using common phosphine oxide and phosphonate moieties, two structural categories emerged: CH and N-O linked tripodal phosphine oxides, and aryl linked tetrapodal phosphine oxides. Phosphine oxide and phosphonate binding moieties were selected for exploration due to their ease of synthesis and chemical resilience.[6] Through a systematic approach using density functional theory, computational thermodynamic investigations of the ligands of interest were conducted to explore different coordination modes to REE nitrates and chlorides. Promising targets were selected and synthesized. Herein, we will present the synthetic methodology used to identify and test various multidentate chelating phosphine oxide ligands in the coordination and extraction of REE from aqueous media.

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RATIONAL DESIGN OF NON-CENTROSYMMETRIC LANTHANIDE COMPLEXES FOR ENHANCED SPIN–ELECTRIC COUPLING (SEC)

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Strong Spin–Electric Effect (SEE) in molecular systems remains challenging to observe requiring stringent control over structural and electronic parameters[1,2]. Key design criteria include strong spin orbit coupling, and non-centrosymmetric molecular structure, ideally within local high-symmetry environments that reduce the complexity of the crystal field Hamiltonian (e.g., C_3)[3]. Herein, we report the optimized synthesis of an isostructural series of non-centrosymmetric lanthanide complexes, [**Ln**Cl_3L_3] (**Ln** = Dy, Er, Y; L = 2,2,2-trichloro-N-(dipiperidinophosphoryl)acetoamide), figure 1, in which control of water competition and steric/solvation effects proved crucial for obtaining stable products. The crystal packing of [**Ln**Cl_3L_3] is predominantly governed by H···Cl (47.5%) and H···H (41.3%) interactions, ensuring structural stability. The complexes crystalize in the trigonal *R*3 space group exhibiting a threefold symmetry axis passing through the metal center. The lanthanide ions display coordination number six in an idealized trigonal antiprism geometry with a *fac* arrangement, generating an electric dipole moment. Magnetic measurements on the Dy-derivative show not superimposed reduced magnetization curves, due to the magnetic anisotropy of the Dy center. Torque magnetometry results confirm the presence of a strong easy-plane magnetic anisotropy, in agreement with *ab initio* calculations. Overall, these preliminary results suggest these complexes are promising candidates for future SEE investigations.

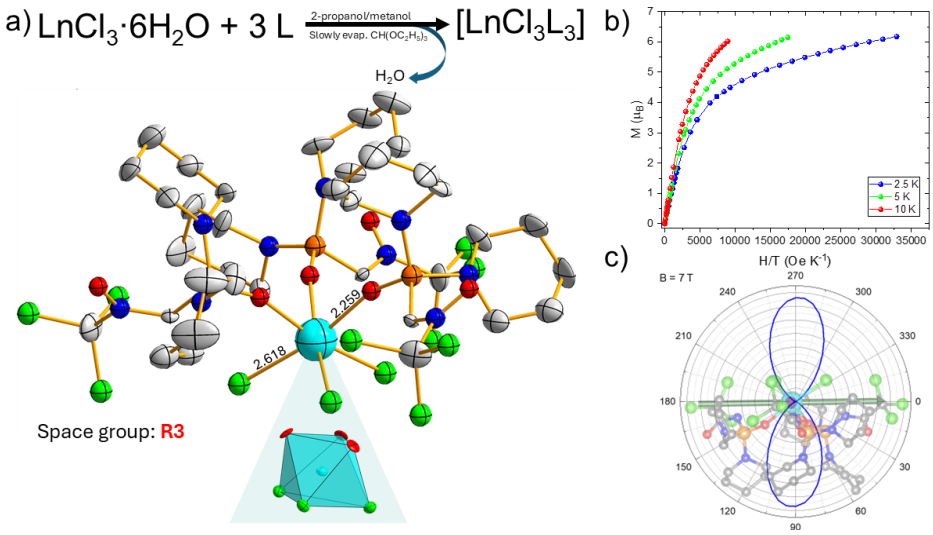


Figure 1. Molecular structure of [**Dy**Cl_3L_3], highlighting metal coordination geometry. (b) Reduced magnetization curves on a polycrystalline sample. (c) Magnetic free energy extracted from CTM data at 2K 7T.

Acknowledgements: Financial support by the European Union (ERC, ELECTRA, 101039890).

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ADVANCES AND EMERGING TRENDS IN MOLECULAR CHEMISTRY OF THE f-ELEMENTS

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The unique electronic characteristics of f-elements, especially the lanthanides, allow for the creation of advanced luminescent materials and molecular probes for advanced imaging and sensing. In our recent molecular f‑ element chemistry efforts, we have developed chiral macrocyclic lanthanide complexes delivering circularly polarized luminescence (CPL) and multimodal imaging capabilities, including magnetic resonance imaging (MRI). We have synthesized highly stable chiral macrocyclic europium complexes that display exceptionally high luminescence dissymmetry factors (g_{lum}) and unusual magnetic field-dependent CPL behavior, making them promising candidates for bioimaging probes and chiroptical sensors.[1] In addition, our gadolinium‑ based chiral DOTA derivatives show potential as MRI contrast agents, offering improved relaxivity and stability for enhanced diagnostic imaging.[2] Our work highlights the frontiers of molecular f‑ element chemistry and its potential for novel luminescent materials and bioimaging probes.

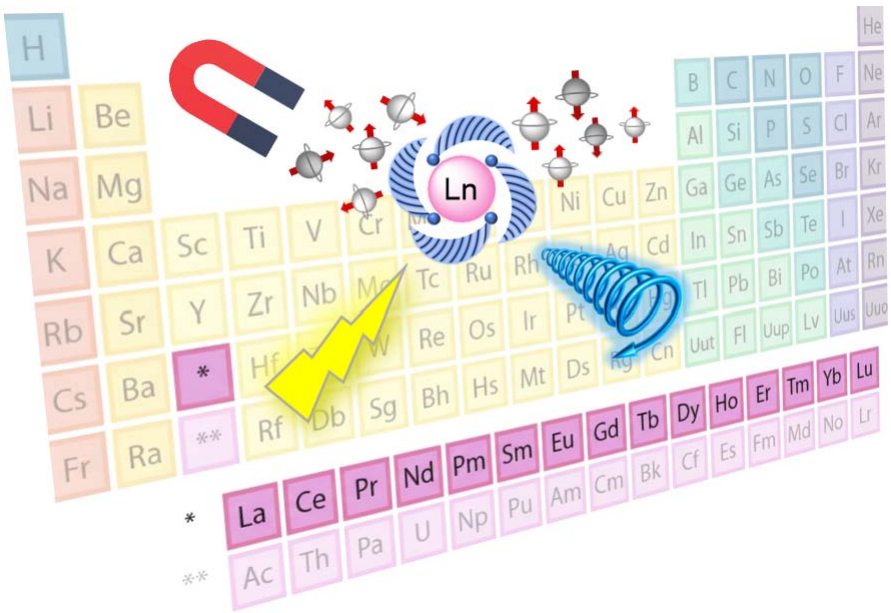


Fig. 1. The application of Lanthanide complexes in CPL and MRI.

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EUROPIUM(II) BASED SYSTEMS FOR MAGNETIC REFRIGERATION

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As gadolinium(III) is usually considered for new systems with large magneto caloric effect, based on the high number of unpaired electrons it is equally interesting to investigate the properties of Eu(II) systems for the same effect. Hence we have synthesized the new system $EuBeF_4$ as a possible candidate for magnetic refrigeration. The magnetic susceptibility has been measured, and from this an estimate of the magnetic caloric effect has been determined, see Figure 1, based on the following equation[1]:

$$\Delta S_m = \frac{\left(M(T_i, H_f) - M(T_f, H_f)\right) \cdot (H_f - H_i)}{\Delta T}$$

Based on the calculations the systems appear to be a good candidate for magnetic refrigeration at cryogenic temperatures, as $-\Delta S_m = 49 \frac{\mathrm{J}}{\mathrm{kgK}}$. For comparison the system EuF_2 has also been synthesized and measured, see Figure 2. The orthorhombic site symmetry of Eu(II) has been investigated by CW-EPR [2], measured on a powder, and compared with EuF_2.

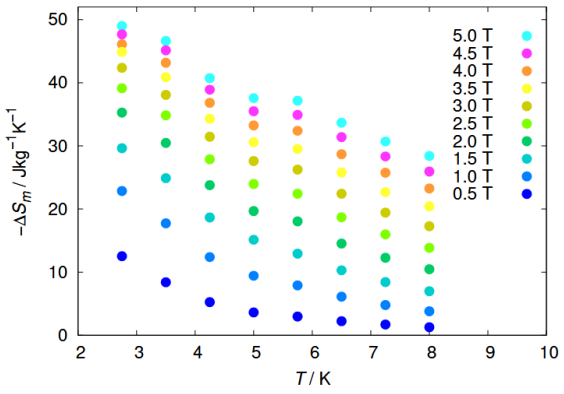


Figure 7.45: ΔS of $EuBeF_4$ based on the susceptibility measurements

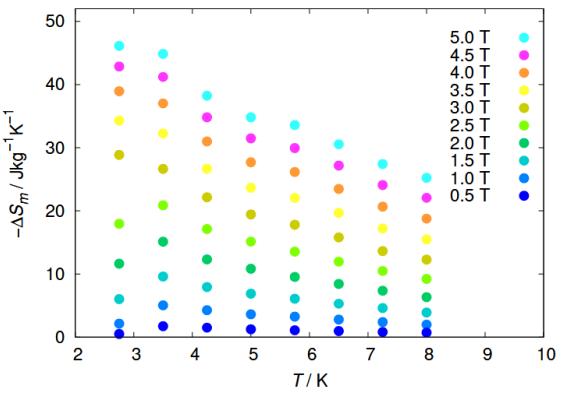


Figure 7.48: ΔS of EuF_2 based on the susceptibility measurements

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AN INTRAMOLECULAR FRUSTRATED LEWIS PAIR BASED ON A BISMUTH(III) ACID SITE

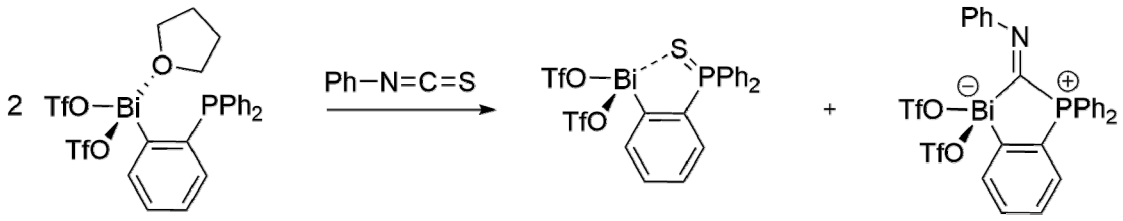
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Intramolecular frustrated Lewis pairs (FLPs) arise by attaching a Lewis acidic and a Lewis basic unit to a backbone that largely prevents adduct formation. Within the resulting tensioned framework, small molecules can be polarized and transformed via cleavage of σ- and/or π-bonds.[1] The extent and scope of substrate activation, is influenced by factors such as the distance between the reactive centers, and the strength and hardness of the Lewis acid and base, respectively. We are now reporting an FLP that makes use of a Lewis acidic bismuth(III) site. Lewis acidity is generated by triflate ligands, which due to their internal polarisation bind predominantly in an ionic way, causing the aciditiy to reach a level comparable to boron-based Lewis-acids such as $B(C_6F_5)_3$. Frustration between the acid and the base – a diphenylphosphine group – is achieved through using a 1,2-phenylene backbone, which limits adduct formation.

DFT calculations show that in contrast to simpler substituents like halides, that are bound in a more covalent way, triflate ligands lead to acceptor orbitals with predominant Bi(6p) character that undergo strong interaction with the phosphine donor function. For this the linker unit has to distort, however. Accordingly, $((Ph_2P)C_6H_4)Bi(OTf)_2(THF)$ is capable of binding/converting substrates in an FLP type manner. In an exemplary reaction, it abstracts an S atom from Ph-NCS to yield $((Ph_2PS)C_6H_4)Bi(OTf)_2$ and Ph-NC. Ph-NC in turn is bound as a 1,1 adduct complex.[2]

Current research aims at the development of representatives with increased distances between the Bi and P centres, and testing their corresponding reactivities.



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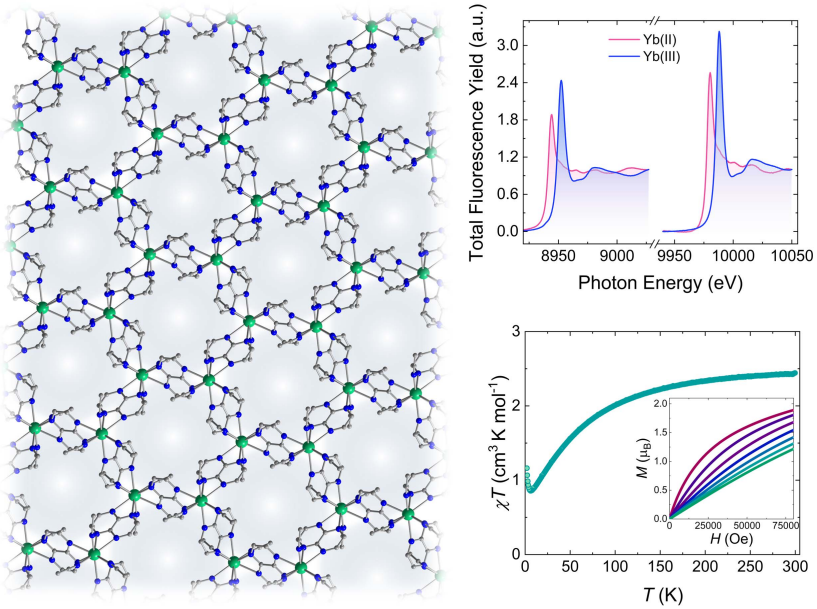
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REDOX-DRIVEN ASSEMBLY OF A RADICAL-BRIDGED YTTERBIUM 2D COORDINATION NETWORK

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[b]European Synchrotron Radiation Facility, Grenoble, France
[c]University of Montreal, Montreal, Canada

The integration of moderately to strongly reducing metal ions with π-conjugated ditopic linkers has emerged as an effective strategy for constructing electrically conductive and magnetically active two-dimensional (2D) coordination solids [1]. Among these, lanthanide-based systems are particularly compelling due to the high coordination numbers and rich electronic structures of the 4f ions, which support diverse structural motifs and 2D architectures. Moreover, the redox non-innocence accessible to certain lanthanide ions presents a unique opportunity for the incorporation of redox-active ligand scaffolds into these frameworks, thereby imparting distinctive properties such as tunable valence tautomerism, electrical conductivity and magnetic exchange interactions [2]. Here, we report the redox-driven assembly of a radical-bridged ytterbium coordination network generated from the reaction of formally divalent ytterbium (Yb^{II}) ions with the redox-active 1,4,5,8-tetraazanaphthalene (tan) ligand. Our synthetic efforts yielded the $[Yb(tan^{\bullet-})_{1.5}(MeCN)_3]I_{1.67}$ building unit, which undergoes polymerization into virtually hexagonal 2D sheets. Detailed magnetic studies reveal strong magnetic interactions between the Yb ions and the $tan^{\bullet-}$ radicals, while X-ray absorption spectroscopy and structural analysis collectively elucidate the charge distribution between the lanthanide center and the redox-active scaffold.



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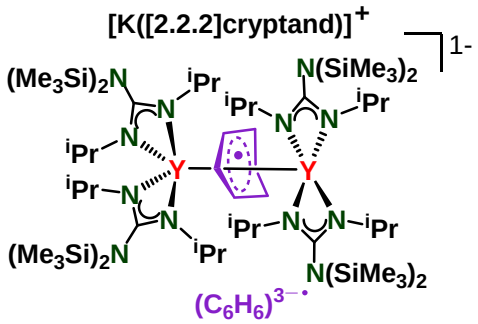
[2] a) Dunstan, M. A., *et al. Nat. Chem.* **2024**, *16*, 735; b) Viborg, A., *et al. Chem. Sci.* **2025**, *16*, 6879.

TAMING THE BENZENE RADICAL TRIANION IN AN INVERSE-SANDWICH YTTRIUM COMPLEX

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Highly reduced arene species are of fundamental interest due to their unique electronic structures and potential roles in small-molecule activation. However, the isolation and stabilization of highly charged arene radical anions, particularly the benzene radical trianion, remain extremely challenging.[1] This collaborative study reports the first isolation and unambiguous characterization of a benzene radical trianion stabilized within an inverse-sandwich yttrium complex, [K([2.2.2]-cryptand)][[{$(Me_3Si)_2NC(N^iPr)_2\}_2Y]_2(\mu$–$\eta^6$:$\eta^6$–$C_6H_6$•)] (**2**),[2] obtained via one-electron reduction of a neutral yttrium benzene dianion precursor [[{$(Me_3Si)_2NC(N^iPr)_2\}_2Y]_2(\mu$–$\eta^6$:$\eta^6$–$C_6H_6$)] (**1**)[3] with KC_8 in the presence of [2.2.2]-cryptand. Single-crystal X-ray diffraction, EPR, and UV–vis spectroscopy, supported by DFT calculations, reveal a [Y^{3+}–$(C_6H_6)^{3\bullet-}$–Y^{3+}] electronic structure with significant spin density localized on the benzene ring. This and other remarkable details will be discussed in my poster presentation.



2

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[2] W. Mao, S. Deshapriya, S. Yao, C. Lorent, M. Driess, S. Demir, *Angew. Chem. Int. Ed.* **2026**, *65*, e21849.

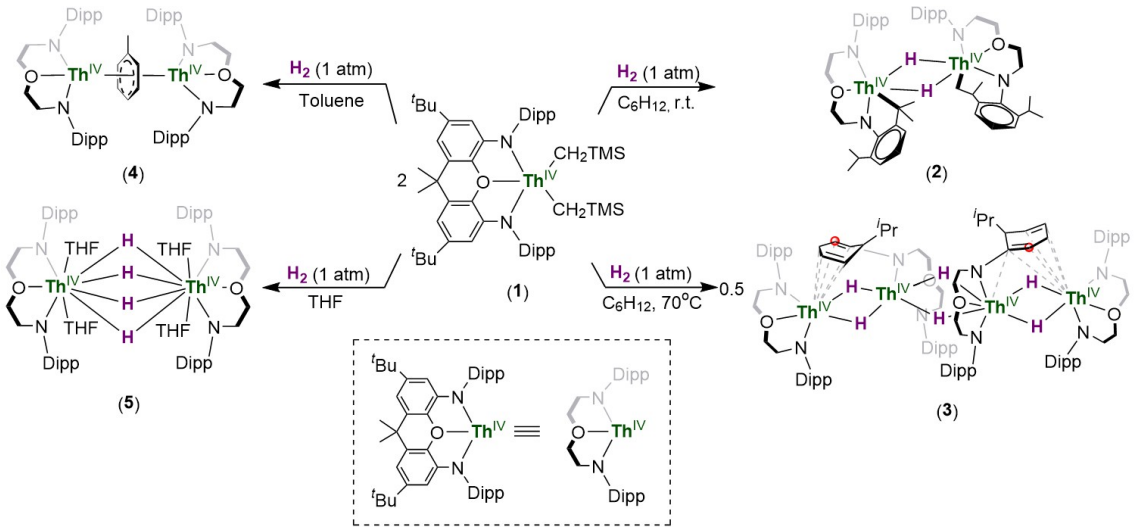
[3] F. Delano IV, S. Demir, *Angew. Chem. Int. Ed.* **2025**, *64*, e202417217.

SYNTHESIS AND REACTIVITY OF THORIUM HYDRIDE COMPLEXES

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Hydride complexes of *f*-block elements have attracted considerable interest due to their distinctive reactivity toward small molecules [1]. In particular, a diuranium(IV) hydride complex supported by the NON pincer ligand has recently demonstrated remarkable capability in N_2 cleavage and hydrogenation *via* metal-ligand cooperativity [2]. As part of our continuing efforts to advance the chemistry of actinide hydrides, we have sought to explore the synthesis and reactivity of pincer ligand-supported thorium analogues. Hydrogenolysis of the previously reported [3] thorium(IV) dialkyl complex **1**, supported by the bulky bis(anilido)xanthene (NON) ligand, under different solvent conditions yields a series of thorium hydride species that vary in nuclearity and binding modes (**Scheme 1**), exhibiting pronounced solvent dependence. These findings allow the isolation and characterization of rare examples of thorium hydride complexes and lay the groundwork for investigating their stoichiometric and catalytic transformations.



Scheme 1. Hydrogenolysis of the thorium dialkyl complex **1**.

[1] (a) Turnbull, R. D.; Bell, N. L. *Dalton Trans.* **2024**, *53*, 12814; (b) Shi, X.; Qin, G.; Deng, P.; Rosal, I. D.; Maron, L.; Cheng, J. *Chem. Sci.* **2025**, *16*, 16259.

[2] Pang, Y.; Batov, M. S.; Rajeshkumar, T.; Zivkovic, I.; Scopelliti, R.; Maron, L.; Mazzanti, M. *J. Am. Chem. Soc.* **2026**, *148*, 9231.

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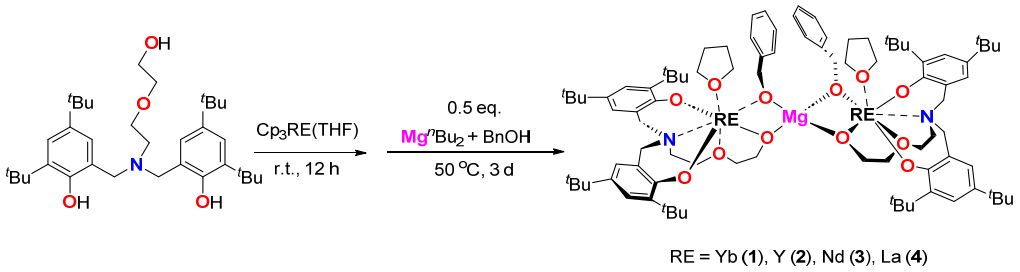
SYNTHESIS OF RARE EARTH-MAGNESIUM HETEROMETALLIC COMPLEXES AND THEIR APPLICATION IN CATALYZING CYCLOADDITION REACTION OF CO_2 AND EPOXIDES

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The catalytic cycloaddition of CO_2 with epoxides has been achieved using various catalytic platforms [1], In recent years, significant progress has been made with heterometallic catalysts, relying on their unique multi-metal center synergistic effects [2]. Our group has been devoted to developing RE-Zn complexes stabilized by the polydentate amine-bridged multi(phenolato) ligands [3]. Among these RE-Zn complexes, those stabilized by diglycolamine-bridged bis(phenolato) ligands demonstrated particularly high catalytic activity, catalyzing the cycloaddition reaction of disubstituted epoxides with CO_2 under atmospheric pressure [4].

Zinc and magnesium both belong to the category of bio-minerals, exhibiting similarities in ionic radius. Given the higher oxophilicity and variable coordination number of Mg(II), the synergistic interaction between RE(III) and Mg(II) may significantly enhance catalytic activity in cycloaddition reactions, warranting further investigation. In this study, four RE-Mg heterometallic complexes stabilized by the polydentate diglycolamine-bridged bis(phenolato) ligand were synthesized, and applied in catalyzing the cycloaddition of epoxide and CO_2 under ambient conditions.



Scheme 1 Synthesis of RE-Mg heterometallic complexes

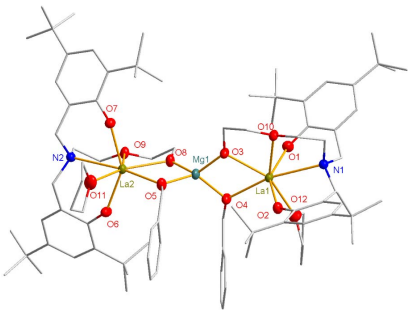


Fig. 1. Solid-state structure of complex **4**.

[1] J. Wu, Y. Du, X. Wang, F. Zhao, M. Zhu, J. Ma, *ACS Cat.*, **2025**, *15*, 1305.

[2] R. Singh, S. Sinhababu, N. Mankad, *ACS Catal.*, **2023**, *13*, 12519.

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SYNTHESIS AND REACTIVITY OF ZINC RADICALS

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Radical species play important roles in synthetic chemistry, materials science, and chemical biology due to their unique electronic structures and reactivity. However, zinc-centered radicals remain largely unexplored and exhibit a strong tendency to dimerize into Zn–Zn bonded species [1], which makes the study of zinc radicals particularly challenging. Building on our previous development of a catalytic synthesis of Zn–Zn bonded complexes and investigations of their reactivity [2], we recently demonstrated that the Zn–Zn bond can be cleaved via photoirradiation to generate zinc radicals. These transient species enable the selective reductive dimerization of alkenes and allenes [3]. Furthermore, by leveraging the cyclic (alkyl)(amino)carbene (cAAC) ligand, we successfully synthesized and structurally characterized a Zn–cAAC radical complex through a reductive strategy [4]. Experimental and theoretical analyses reveal that the spin density is predominantly localized on the carbenic carbon atom, with a non-negligible contribution at the zinc center, while reactivity studies further demonstrate zinc-centered radical behavior.

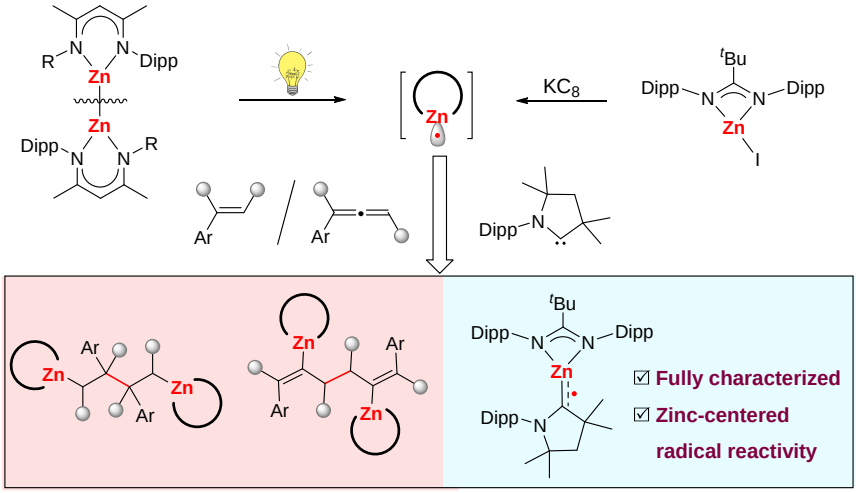


Fig. 1 Synthesis and reactivity of zinc radicals

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THE SYNTHESIS AND REACTIVITY OF BORAZINE TOWARDS MAIN GROUP COMPOUNDS

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Despite extensive research into the reactivity of benzene and its derivatives, its so-called 'inorganic sibling', borazine, has received comparatively little attention [1]. Although borazine is isostructural with benzene, the lack of uniformity of the π-system leads to decreased aromaticity [2]. This results in notably different reactivity, including its sensitivity to both air and moisture. Furthermore, this can make its manipulation challenging, with the synthesis of borazine and its derivatives remaining non-trivial. Whilst borazine holds potential as a versatile ligand, its reactivity with both d- and p-block metals remains largely unexplored. To date, the addition of the B–H bond to any element in the Periodic Table yet to be reported [3], despite the potential for such processes to be exploited in the synthesis of extended materials containing linked hexagonal BN 'building blocks'.

Here, we describe the B–H bond activation of borazine by means of main-group metal complexes, including an acyclic aluminyl compound [4] and a bis(boryl)stannylene [5] (Figure 1) [6]. NMR spectroscopy studies, in combination with single-crystal X-ray diffraction of the novel complexes allows for unambiguous structural determination, clearly demonstrating addition of the B–H bonds to the metal centres. We perceive that these examples of B–H bond activation may ultimately enable routes to BN-type materials through a dehydrogenative oligomer/polymer-ization.

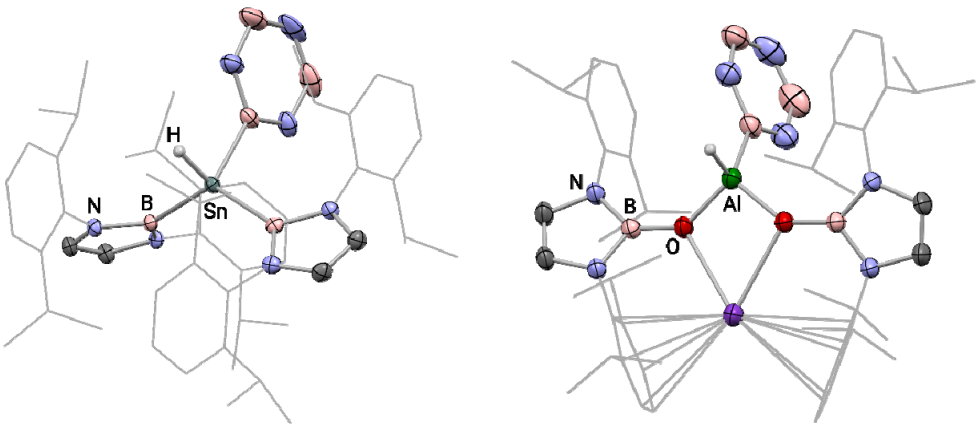


Figure 1. Solid-state structures of the B–H bond activation products $[B]_2Sn(Bz)H$ (left) and $AlK[BO]_2(Bz)H$ (right) ([B] = $B(NDippCH)_2$, [BO] = $OB(NDippCH)_2$ Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$, Bz = $B_3N_3H_5$).

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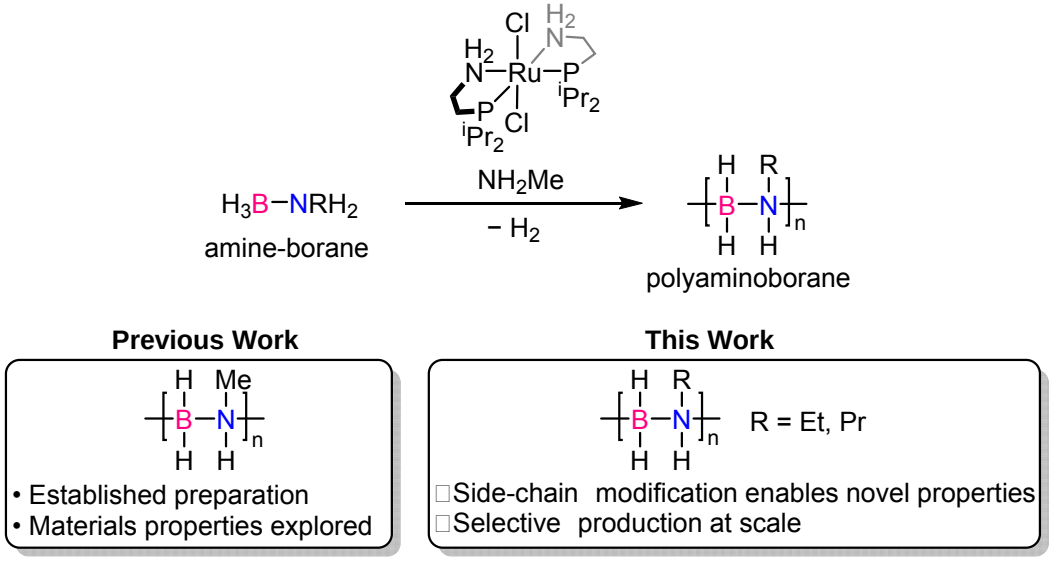
METHYL, ETHYL, PROPYL: SIDE-CHAIN ELONGATION IN POLYAMINOBORANES THROUGH MECHANISM-LED CATALYST DESIGN

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Polyaminoboranes are a class of polymers with a main chain composed of boron and nitrogen. Polyaminoboranes can be produced through the catalytic cascade dehydropolymerization of amine-boranes and have promising applications as preceramic polymers in the production of BN-based materials, such as boron nitride [1]. A mechanistic understanding of the dehydropolymerization of methylamine-borane has been demonstrated for a wide variety of catalysts [2,3]. The dehydropolymerization of substrates other than methylamine-borane (*i.e.*, ethyl or propylamine-borane) is challenging, and published examples are characterized by low selectivity for polymer formation and high catalysts loadings [4,5]. Varying the side chain of the polymer can result in changes to its materials properties, thus necessitating efficient catalytic routes for the dehydropolymerization of a range of amine-boranes.

This work will explore the use of a highly active ruthenium catalyst for the selective formation of poly(*N*-propylaminoborane). Reaction optimization and catalyst performance relative to other established amine-borane dehydropolymerization catalysts will be discussed. The scaled-up production of poly(*N*-propylaminoborane) will be demonstrated, along with a comparison to the better-known methyl derivative, where distinct changes to the thermal properties and viscosity were found.



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ENHANCING THE VALENCE BAND CHARGE LOCALIZATION VIA ZINC DOPING INTO $MnWO_4$ TO PROMOTE SELECTIVE AMMONIA ELECTROOXIDATION

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The electrochemical ammonia oxidation reaction (AOR) to selectively produce nitrate/nitrite under ambient conditions can be a potential alternative to the Ostwald process. However, the potential bottlenecks of the AOR are sluggish electrokinetics and the involvement of multiple steps, which lead to various parallel reactions and side products. Herein, 5–14% zinc (II) ions are doped into a Wolframite-type $MnWO_4$ nanostructure, $Zn_xMn_{1-x}WO_4$, which significantly localizes the valence-band state and makes the manganese centres more electropositive, leading to the production of an anodic material for the AOR. Among all the tested variants of $Zn_xMn_{1-x}WO_4$ and control materials like α-MnO_2, $MnWO_4$, and $ZnWO_4$, only 17 ± 3 nm $Zn_{0.1}Mn_{0.9}WO_4$ nanoflakes show a moderate onset potential (0.53 V *vs.* Hg/HgO) for the AOR in alkaline and near-neutral electrolytes. Electrokinetic study *via* Tafel analysis and hydrodynamic electrochemistry, and the corresponding Koutecký–Levich analysis indicates that the first $2e^-$ oxidation of adsorbed ammonia to hydroxylamine is the rate-limiting step, with a rate constant of $4.915 \pm 3 \times 10^{-3}$ cm s^{-1}. Product analyses following the chronoamperometric AOR study highlight that nitrate predominantly forms in a high yield rate of 160 (±25) µmol h^{-1} cm^{-2} and a faradaic efficiency of 70% ± 10% at 0.8–1.2 V (*vs.* Hg/HgO). An *in situ* spectrophotometric kinetics study infers the formed $[NO_2]^-$ as the intermediate, while accumulation of $[NO_3]^-$ follows pseudo-first-order kinetics with a rate constant of 4.20×10^{-5} s^{-1}. D_2O labelling, control studies, like electrochemical hydroxylamine and hydrazine oxidation under similar conditions, subsequent product identification and *in situ* infrared analysis of the electrolyte further emphasize hydroxylamine and nitrite as the AOR intermediates. $Zn_{0.1}Mn_{0.9}WO_4$/NF electrode is further used as an anode to fabricate an NH_3 electrolyzer to produce H_2 with a rate of 1.33 mL h^{-1} and 94% FE, and the performance of this NH_3 electrolyzer is nearly three times higher than the water splitting electrolyzer. Thus, doping of an atomically dilute quantity of zinc into the $MnWO_4$ lattice tunes the valence band to enhance AOR selectivity. The in-depth electrokinetic studies presented herein establish the AOR pathway and the nitrate selectivity, which will further help in interpreting the AOR mechanism on various earth-abundant metal catalysts.

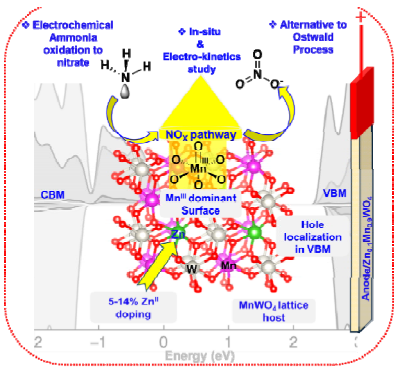


Figure. Enhancement of AOR activity by Zn doping in $MnWO_4$, a sustainable alternative route of Ostwald oxidation.

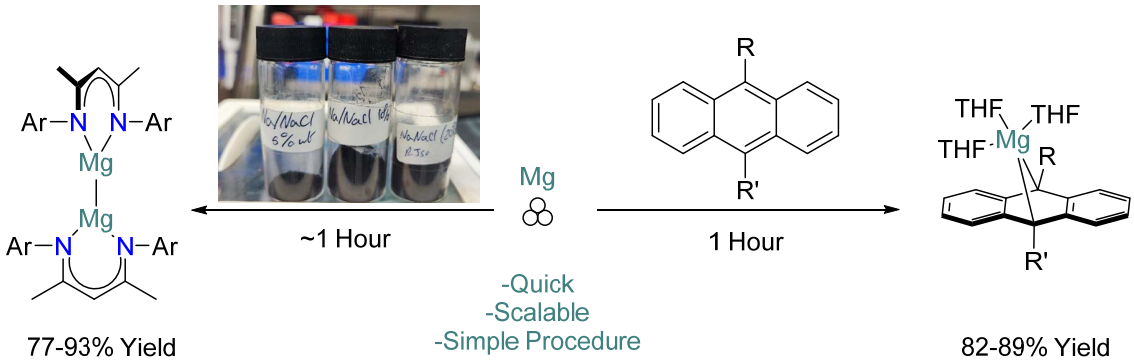
[1] Hirak Kumar Basak, Bhawna Kamboj, Jayanta Patra, Dibyajyoti Ghosh, and Biswarup Chakraborty* Enhancing the Valence Band Charge Localization via Zinc Doping into $MnWO_4$ to Promote Selective Ammonia Electrooxidation (*J. Mater. Chem. A*, **2026**, Advance Article, https://doi.org/10.1039/D5TA08125D)

FROM METALS TO REDUCTANTS: MECHANOCHEMICAL ROUTES TO REACTIVE MAGNESIUM REAGENTS

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Magnesium reducing reagents occupy an important place in synthetic chemistry, due to their combined strong reducing powers and versatile reactivity. As a result, they are particularly valuable tools in low-valent main-group chemistry, organometallic transformations, and a broad range of reductive transformations. Despite their utility, their synthesis remains challenging, often relying on poorly controlled metal activation processes, extended reaction times, harsh conditions, and hazardous alkali-metal reductants, all of which limit their wider applications. In recent years, mechanochemistry has emerged as an increasingly effective strategy for the synthesis of organometallic compounds, including organomagnesium complexes, frequently improving yields, reducing reaction times, and diminishing solvent usage [1].



Employing mechanochemical methods, we synthesised finely dispersed sodium metal supported on NaCl as a black, free-flowing, homogeneous, non-pyrophoric powder. This material proved to be a highly effective source of activated sodium for the mechanochemical synthesis of $[(^{Ar}BDI)Mg]_2$ complexes, reducing reaction time from days to minutes while simultaneously improving yields relative to conventional solution-phase routes [2]. In parallel, we developed a mechanochemical protocol for the synthesis of $[Mg(\eta^2\text{-}C_{14}H_{10})(THF)_3]$ and related derivatives in high yields on a one-hour time scale, thereby eliminating the need for magnesium activation, forcing conditions, and prolonged reaction times. Collectively, these results demonstrate that mechanochemistry can overcome these longstanding challenges associated with the preparation of these magnesium reductants, providing routes which are faster, simpler and more accessible than conventional solution-phase methods.

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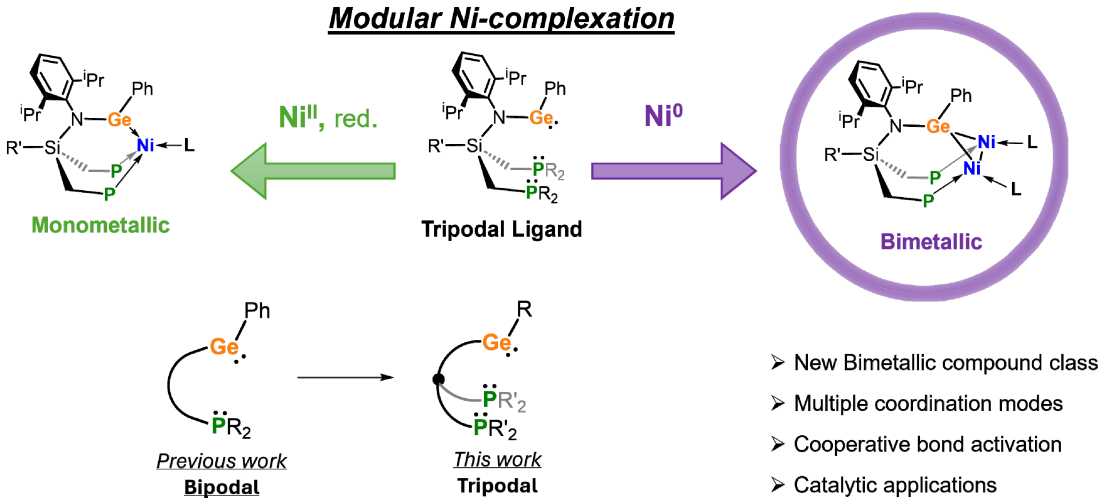
MODULAR MONO – AND BIMETALLIC Ni COMPLEXATION AT Ge^{II} INTERFACES

Emeric Schubert, and Terrance Hadlington

Department of Chemistry, Technical University of Munich, Garching b. Muenchen, Germany

Synergetic mechanisms have become increasingly relevant in homogeneous catalysis. Rationally designed novel catalytic systems thus often employ multiple reactive centres, *e.g.* using non-innocent ligands or multiple metal centres.[1] Building upon such concepts, our group studies interactions between low-valent, single-centre ambiphiles (SCAs) (*i.e.* Ga^{I}, Ge^{II}, Sn^{II}) and first-row TMs, exploring cooperative bond activation.[2] Ligand designs revolve around SCAs equipped with one phosphine arm so forming a bidentate chelate, introducing geometric constraints and tunability to the complexes, promoting cooperative mechanisms. Some examples include the reversible addition of dihydrogen across a Ge^{II}-Ni^{0} bond, the energetics of which can be directly tuned by variation of the germylene substituents, or the discovery of previously unknown mechanisms for the catalytic semi-hydrogenation of alkynes.[3,4]

In this work, we present a new germylene-centred, *tripodal* ligand family, equipped with a second coordinating phosphine arm. In a first instance, the ligand was successfully used in the formation of Ge^{II}-Ni^{0} complexes, accessed by the reduction of Ni^{II}-halide precursors. In contrast, the addition of a Ni^{0} precursor, *i.e.*, $Ni(cod)_2$, to this ligand class leads to the complexation of two Ni centres into the ligand sphere, forming an unprecedented [Ge-Ni-Ni] three-centre reactive core. Factors allowing for this new coordination mode, as well as examples of cooperative reactivity and applications in catalysis are discussed.



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A SODIUM ANION COMPLEX: GRAMME-SCALE SYNTHESIS, STRUCTURE, REACTIVITY

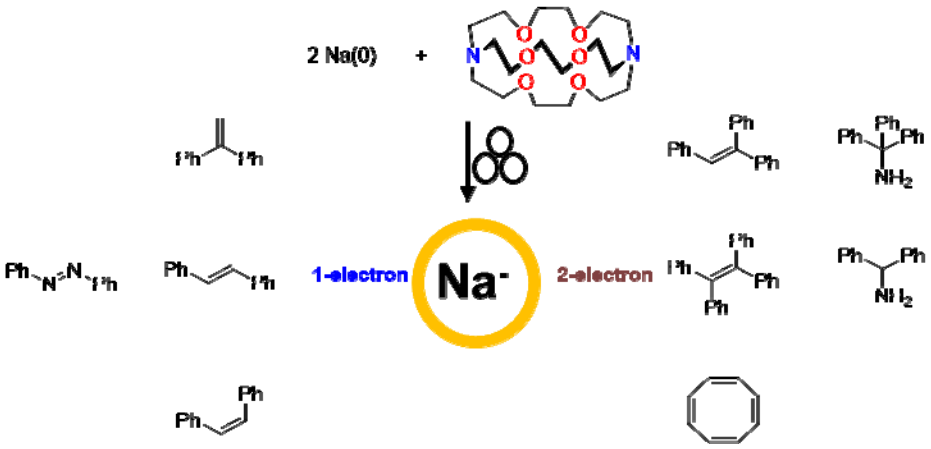
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School of Chemistry, University of Birmingham, Edgbaston, Birmingham, UK. B15 2TT

The chemistry of alkali metals is dominated by the +1-oxidation state. Another uncommon, yet still available, oxidation state of the alkali metals (except lithium) is −1. Complexes containing an alkali metal in the −1-oxidation state are known as alkalides, reported as early as the 1970s by James L. Dye [1]. However, their reactivity remains largely unexplored. This is due to their synthetic hurdles – alkalides are traditionally notoriously difficult to synthesise and handle, limiting their use in synthesis [2].

In 2024, we reported the first scalable synthesis of the archetypal sodide complex, [Na^+(2,2,2-cryptand)Na^-]. A solvent-free ball-milling protocol enabled the direct reaction of sodium metal with 2,2,2-cryptand under mild conditions, providing reproducible access to bulk quantities of an isolated and structurally authenticated Na^- complex [3]. This enabled the first systematic investigation of the reactivity of sodium anions. In addition, using a variety of *in-situ* and *ex-situ* techniques we investigated the mechanism of its formation in the solid-state [4].

The Na^- centre can act as one- or two-electron reductant in a substrate-dependent manner. In reactions with primary amines, selective two-electron C–N bond cleavage was achieved. In contrast, reactions of the sodide towards phenyl-substituted ethylenes demonstrate divergent outcomes depending on the substitution pattern, resulting in either 1-electron or 2-electron reduction. Reaction with a cyclic multiolefin, 1,3,5,7-cyclooctatetraene (COT), exhibits two-electron reduction to produce COT^{2-} species [5].



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REACTIVITY OF HOMOLEPTIC PENTACOORDINATED Ga(I)-AMIDE COMPLEXES OF Fe IN THE PRESENCE OF AlCp*

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[a]Department of Industrial Chemistry "Toso Montanari", University of Bologna, Bologna, Italy
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Molecular intermetallic clusters stabilised by low-valent Group 13 metallo-ligands such as ER* (E = Al, Ga, In; R* = bulky ligand), isolobal with CO, are well established [1]. Late transition-metal complexes coordinated by E(I) ligands have shown activity in bond-activation reactions, such as the C-H and Si-H activation of C_6H_6 and $HSiEt_3$ [2]. Recently, Muhr *et al.* identified polyhydride clusters $[Ni_3(GaTMP)_7(H)_x]$ (x = 2, 4, 6; TMP = 2,2,6,6-tetramethylpiperidyl) as key intermediates in the catalytic alkyne semi-hydrogenation. This follows a previous computational study that enhanced the link between intermetallic catalysts for semi-hydrogenation and related Hume-Rothery-inspired complexes and clusters [2, 3].

Here, we report the reactivity of the homoleptic iron complex, $[Fe(GaTMP)_5]$ (Figure 1), with the ER* ligand AlCp* (Cp* = C_5Me_5). Reaction monitoring by *in situ* ^{1}H NMR and LIFDI-MS revealed new ternary Fe-Ga-Al heterometallic species.

Preliminary catalytic studies were performed for the semi-hydrogenation of 3-hexyne to evaluate the potential of these site-isolated clusters as models for intermetallic catalyst surfaces.

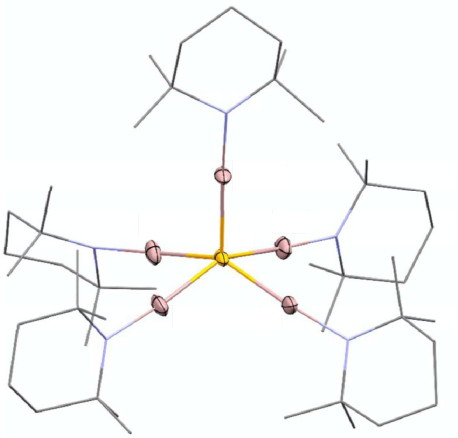


Figure 1. Molecular structure of $[Fe(GaTMP)_5]$ (yellow: Fe; pink: Ga; lilac: N; grey: C).

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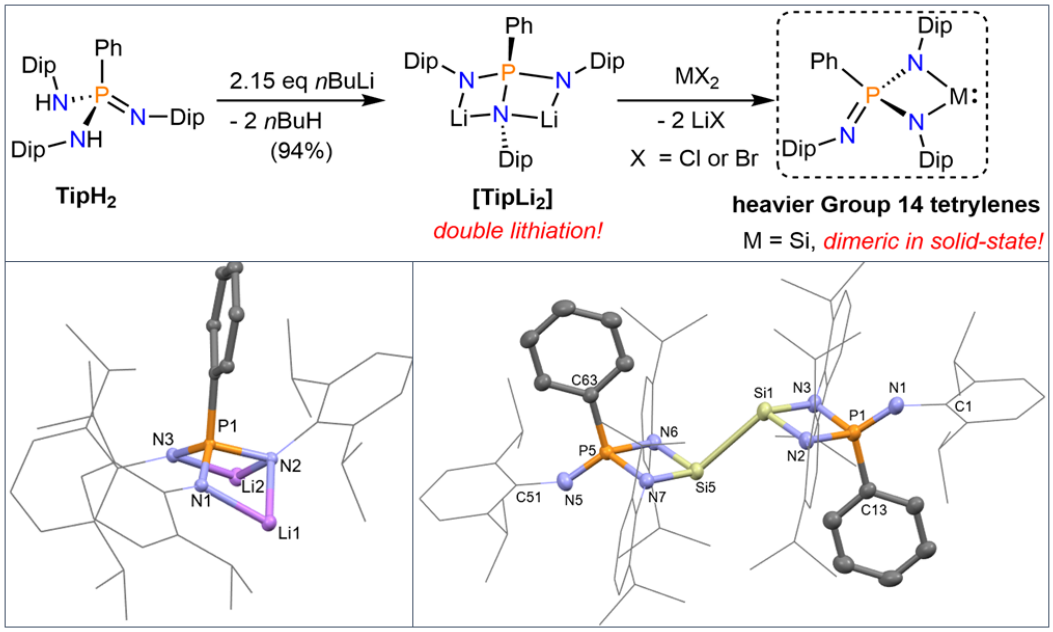
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Si–Si BONDING IN AN UNSUPPORTED N-HETEROCYCLIC SILYLENE DIMER STABILIZED BY AN IMINOPHOSPHORANE-BASED SCORPIONATE LIGAND

Huanhuan Dong[a], Rochelle Ferns[a], Luke W. Giles[b], Lea Fohlmeister[b], Connor Bourne[a], Samuel R. Lawrence[a], Aidan P. McKay[a], Alexandra M. Z. Slawin[a], David B. Cordes[a], Tanja van Mourik[a] and Andreas Stasch[a,*]

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It has been widely recognised that conventional N,N-chelating ligands disfavour element-element bonding in heavier group 13 and 14 alkene analogues.[1, 2, 3] Here we report a series of heavier group 14 element(II) compounds of a new sterically demanding iminophosphorane-based scorpionate ligand. The Si and Ge analogues exhibit head-to-head element–element bonded interactions in the solid state, whereas the Sn and Pb derivatives form one-dimensional head-to-tail coordination polymers. Notably, DFT calculations reveal a significant unsupported bonding interaction in the silicon complex, which represents the first structurally characterised example of a long-elusive N-heterocyclic silylene dimer.



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A NEUTRAL CYCLIC ALUMINIUM (I) TRIMER

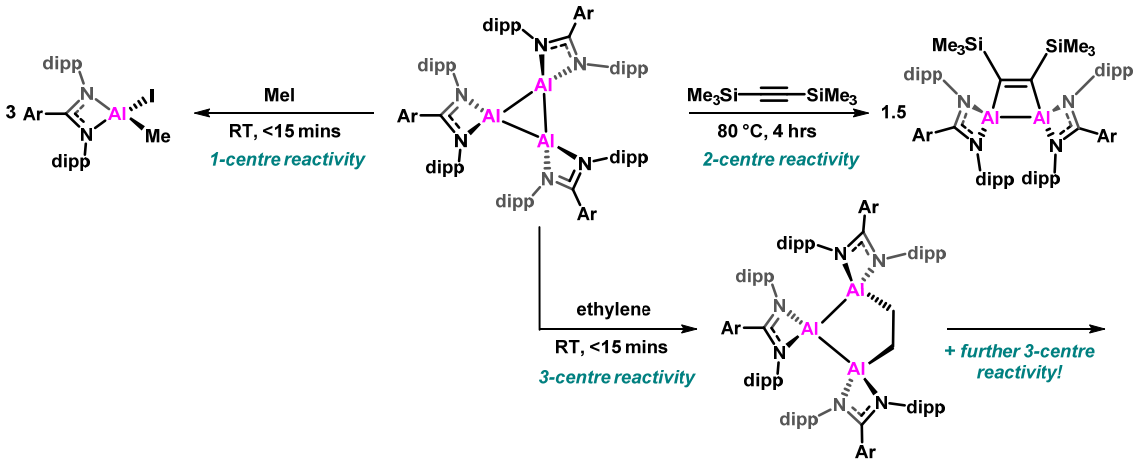
Imogen Squire[a], Matthew de Vere-Tucker[a], Michelangelo Tritto[a], Lygia Silva de Moraes[a], Tobias Krämer[b] and Clare Bakewell[a]

[a]Department of Chemistry, King's College London, London, United Kingdom
[b]School of Chemistry, Trinity College Dublin, Dublin, Ireland

In recent years, there has been renewed interest in the chemistry of aluminium, based on its reactivity in unusual oxidation states. Aluminium(I) can perform a range of oxidative addition reactions which were more traditionally associated with transition metals. More recently, redox catalysis cycling between Al(I)/Al(III) has been reported.[1]

A key Al(I) species is the monomeric complex reported by the Roesky group in 2000, supported by a bulky monomeric DippBDI ligand ($CH[C(CH_3)N\text{-}Dipp]_2$, Dipp = 2,6-diisopropylphenyl).[2] Using different ligands, tetrameric and dimeric Al(I) species have also been reported, and these different coordination modes lead to dramatically different reactivity.[3,4] In the case of at least one dialumene (Al=Al), there is an equilibrium between the dimeric and dissociated monomeric forms, and they exhibit both dimer-centred and monomer-centred reactivity.[5]

In this work, the first neutral trimeric Al(I) (cyclotrialumane) species has been isolated, and its bonding examined using experimental and computational methods.[6] Its reactivity towards a range of small molecules has been explored, leading to a range of monomeric, dimeric and even trimeric aluminium products. With ethylene, a multistep pathway forming four isolable products has been identified, and the reaction mechanism has been probed using DFT. Further investigations are ongoing into the diverse reactivity of this discrete aluminium cluster complex.



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SYNTHESIS AND REACTIVITY OF ALUMINYL–ZINC COMPLEXES

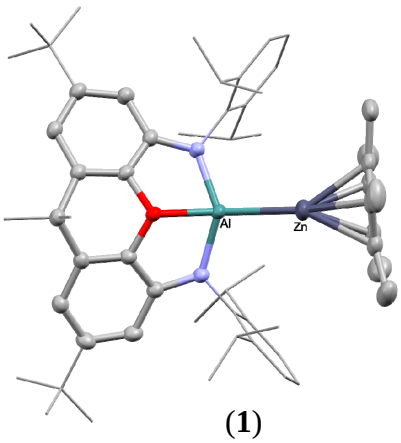
James Stewart-Moreno, Simon Aldridge, and Christiane Timmel

Department of Chemistry, University of Oxford, Oxford, United Kingdom

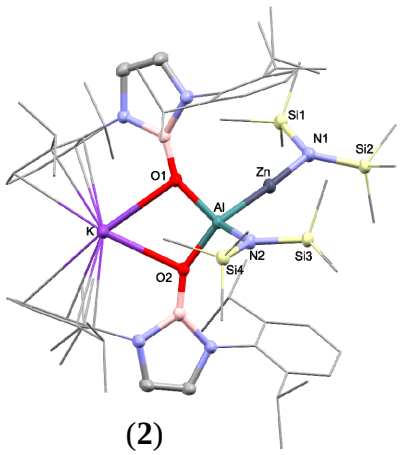
Bimetallic complexes are a subject of significant interest as they can react in synergistic fashion to allow patterns of reactivity that are otherwise inaccessible to either metal in isolation.[1,2] Aluminium is a promising candidate for such systems, as its vacant p-orbital and relative electropositivity compared to transition metals could lead to the formation of highly polar metal-metal bonds.

Since the initial report of an anionic Al(I) (or 'aluminyl') compound in 2018,[3] work in the field has utilised salt metathesis approaches for the formation of Al–Metal bonds; commonly using a transition metal halide and the potassium salt of an aluminyl reagent.[4-7] However, the highly reducing nature of the Al centre can, in some cases, lead to reduction at the *d*-block metal, rather than the desired Al–M bond. Taking inspiration from the formation of an Al–Be bond using beryllocene,[8] we have investigated leaving group alternatives to halides, such as pentamethylcyclopentadienyl (Cp*) and bis(trimethylsilyl)amide (HMDS). We envisaged that the enhanced π-donor capabilities of these X-type ligands would reduce the likelihood of competing reduction chemistry.

In this work zinc complexes were targeted as (diamagnetic) model systems for the development of Al–transition metal bimetallic complexes. Although the reaction with $ZnCp^*_2$ exhibited the expected salt metathesis, the use of $Zn\{N(SiMe_3)_2\}_2$ resulted in addition across the Zn–N bond instead, producing complex **2**, which can be viewed as an alane adduct of Zn(0). Herein, we present our work on the synthesis and reactivity of these novel Al–Zn bimetallic complexes.



(**1**)



(**2**)

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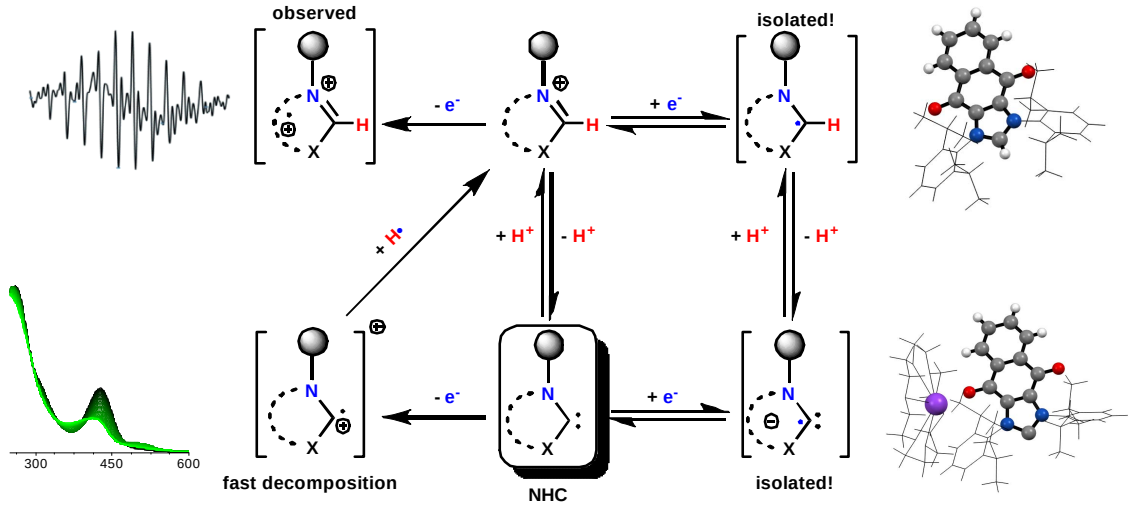
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REDOX PROPERTIES OF FREE N-HETEROCYCLIC CARBENES

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N-Heterocyclic carbenes (NHCs) have had incredible success in a variety of applications as ligands, thanks to their highly tuneable electronic and steric properties,[1] As free species, they can also act as organocatalysts, and have been shown to mimic metal-centred reactivity, particularly small molecule activation.[3,3] Unlike metal centres, however, the redox activity of free carbenes is limited, despite having been demonstrated as occasional redox non-innocent ligands in transition metal complexes.[4] As the high inherent instability of the carbene-derived reduced or oxidized species prevents their isolation, studies in this direction have been largely limited to transient methods or decomposition product analysis.[5] Within the scope of this work, attempts at the stabilization of singly oxidized carbene radical cations to allow for their observation with more direct methods will be discussed in the context of these species' proposed relevancy as an intermediate in some reductive NHC-catalysed radical processes. Furthermore, we detail our efforts into stabilizing the reduced state of several carbenes, culminating in the isolation and crystallization of the first stable singly reduced carbene radical anion, with a perspective on its electronic properties and reactivity.



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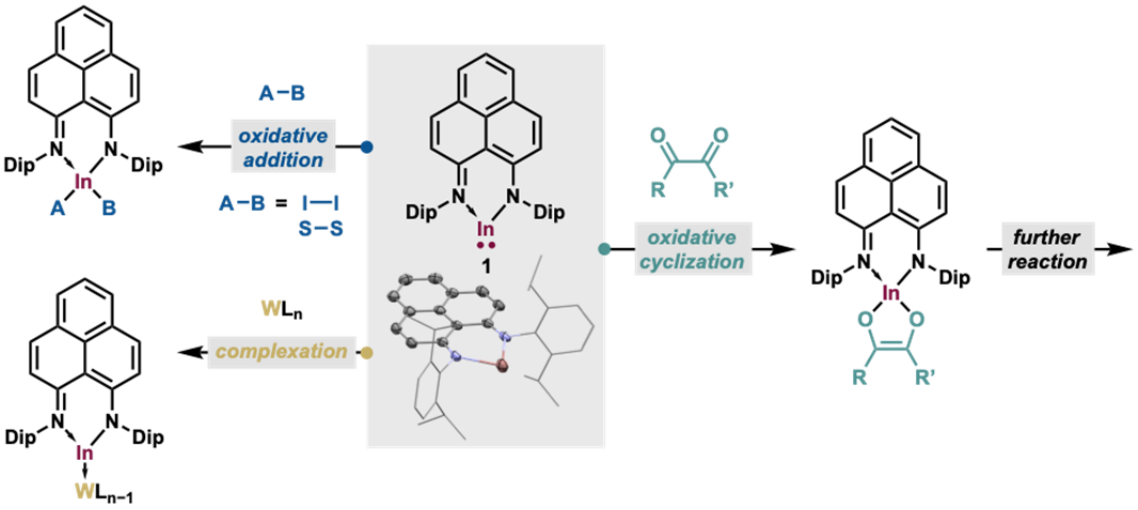
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STRUCTURE, PROPERTIES AND REACTIVITY OF INDIUM(I) COMPLEXES BEARING A PHENALENYL-BASED LIGAND

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Group 13 metallylenes (:ER, E = group 13 element) have attracted considerable attention in modern main-group chemistry because of their unique molecular structures, electronic properties, and distinctive reactivities[1]. Recently, we reported gallylenes [2] bearing a phenalenyl-based bidentate ligand [3]. Building on this platform, we extend this ligand system to an indylene, a heavier congener of gallylene [4]. Indylene **1** facilitates the oxidative addition of σ bonds as well as oxidative cyclization with *o*-quinones to give five membered indacycle. In addition, **1** coordinates to a tungsten complex to form an In–W bond. Further reactivities of the corresponding indium(III) complexes were also explored.



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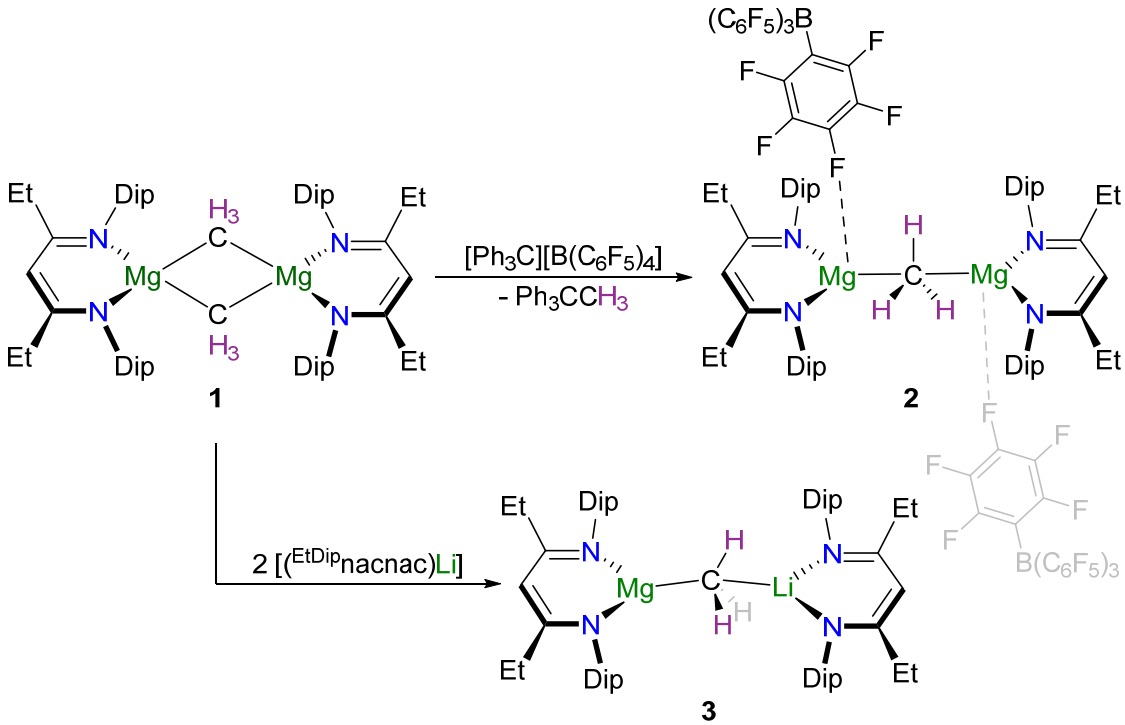
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SYNTHESIS OF A MAGNESIUM COMPLEX WITH A BRIDGING PLANAR METHYL ANION

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Bridging methyl ligands with a three-centre-two-electron M-C-M interaction represents a fundamental structural motif in polar organometallic compounds.[1,2] In these complexes, the M–C–M bond angle is typically less than 90°.[3] Complexes with bond angles approaching 180° are extremely rare, and no linear examples have been reported for homobimetallic s-block complexes.[4] This work presents the synthesis and characterisation of the first s-block complex (**2**) featuring a linear, symmetrical M–C–M bonding mode, prepared through the treatment of [{(^{EtDip}nacnac)Mg}$_2$(μ-CH_3)] (**1**, Dip = 2,6-diisopropylphenyl) with [Ph_3C][$B(C_6F_5)_4$]. In complex **2**, one fluorine atom of the anion coordinates in a κ^1-fashion to the magnesium atom, whilst an additional fluorine atom from a different C_6F_5 substituent of the same anion κ^1-coordinates to a magnesium atom of another independent cationic unit, resulting in a coordination polymer. The treatment of **1** with two equivalents of [(^{EtDip}nacnac)Li] yielded the heterobimetallic complex **3**, featuring a near-linear Mg-C-Li motif. Solution-state NMR spectroscopy, X-ray diffraction analysis, DFT studies, and additional reactivity investigations will be presented.



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THE COLOURFUL WORLD OF ARYL-PHOSPHIINIDENES: REACTIVITY AND OPTOELECTRONIC PROPERTIES

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Phosphorus(III) compounds are essential ligands in transition-metal complexes and are widely utilized throughout the diverse fields of organometallic chemistry. In contrast, phosphorus species in lower oxidation states, such as phosphinidenes and their dimers, diphosphenes, exhibit a more electron-rich coordination environment. Such P-compounds are unique ligands with diverse coordination chemistry. This is particularly evident in diphosphene metal carbonyl complexes, which display an array of binding modes,[1] and are even capable of undergoing photoinduced *cis-/trans*-isomerizations comparable to those observed in azobenzenes.[2]

In our work, we have developed a new family of carbene-stabilized bis-phosphinidene systems, which can also be described as inversely polarized phosphaalkenes. Chelating derivatives of these ligands undergo Ni-induced P-P homocoupling reactions, leading to the formation of an unprecedented class of bis-diphosphene macrocycles. Beyond the diverse coordination modes observed for nickel, heterotetrametallic Cu/Ni assemblies were also successfully constructed (Fig.1, left).[3]

In addition to their coordination behaviour, the low-valent phosphorus units exhibit pronounced electronic communication with conjugated organic π-systems.[4] This interplay allows for systematic modulation of optical properties through molecular design, providing access to P-containing chromophores with tunable absorption characteristics (Fig.1, right).[5] Our efforts to integrate these contemporary aspects of low-valent phosphorus chemistry - highlighting multifunctionality at the interface of coordination chemistry and photoresponsive materials - will be presented.

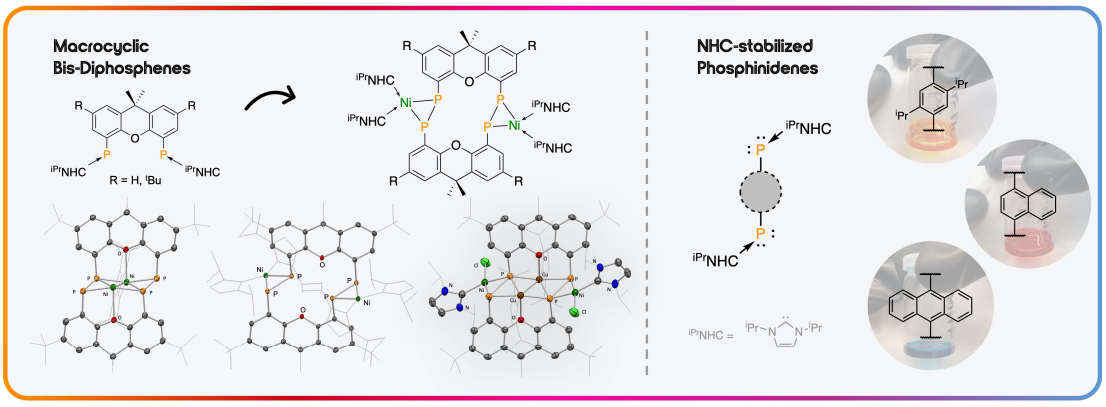


Fig 1. Exemplary representation of Macrocyclic Bis-Diphosphenes and colourful NHC-stabilized Phosphinidenes

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CYCLIC (ALKENYL)(AMINO)CARBENES ($CA_{en}ACS$) AND CARBENE-DERIVED IMINO-ANCHORED OLEFINS

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Compared to N-heterocyclic carbenes (NHCs), cyclic (alkyl)(amino)carbenes (CAACs) and related ligands exhibit stronger nucleophilicity (higher HOMO energy and enhanced σ-donation) as well as greater electrophilicity (lower LUMO energy and improved π-acceptance).[1] Consequently, CAACs have enabled the isolation of several otherwise unstable intermediates and have led to transition-metal catalysts with improved efficiencies compared to their NHC counterparts. To further tune the electronic properties of CAACs, we envisioned introducing an electronically conjugated alkenyl group in place of the quaternary carbon atom adjacent to the carbene center. Such a modification was expected to lower the LUMO energy while maintaining the characteristic high HOMO energy of CAACs. Based on this concept, we synthesized a cyclic (alkenyl)(amino)carbene ($CA_{en}AC$), which was isolated in a masked form and exhibits a significantly lowered LUMO energy while retaining a HOMO energy comparable to that of CAACs (Figure 1a).[2] Several $CA_{en}AC$ derivatives were subsequently prepared to further investigate the electronic structure and reactivity of this new carbene framework. In addition, this presentation will discuss the synthesis of bis-imino-anchored terminal olefins (Figire 1b) derived from NHC scaffolds and examine their structural features, electronic properties, and reactivity in comparison with traditional N-heterocyclic olefins (NHOs).[3]

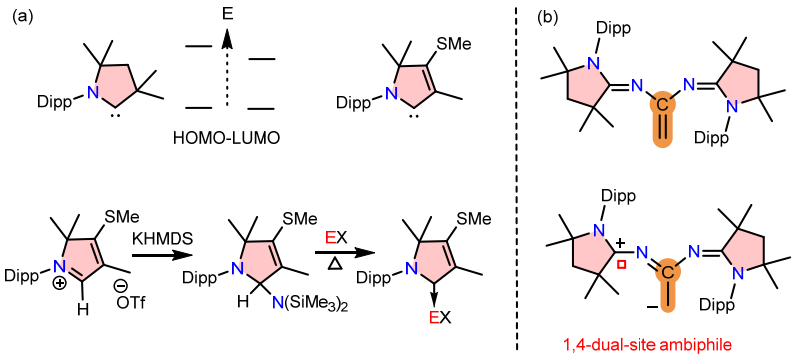


Figure 1: Representative examples of $CA_{en}AC$ and bis-imino-anchored terminal olefin.

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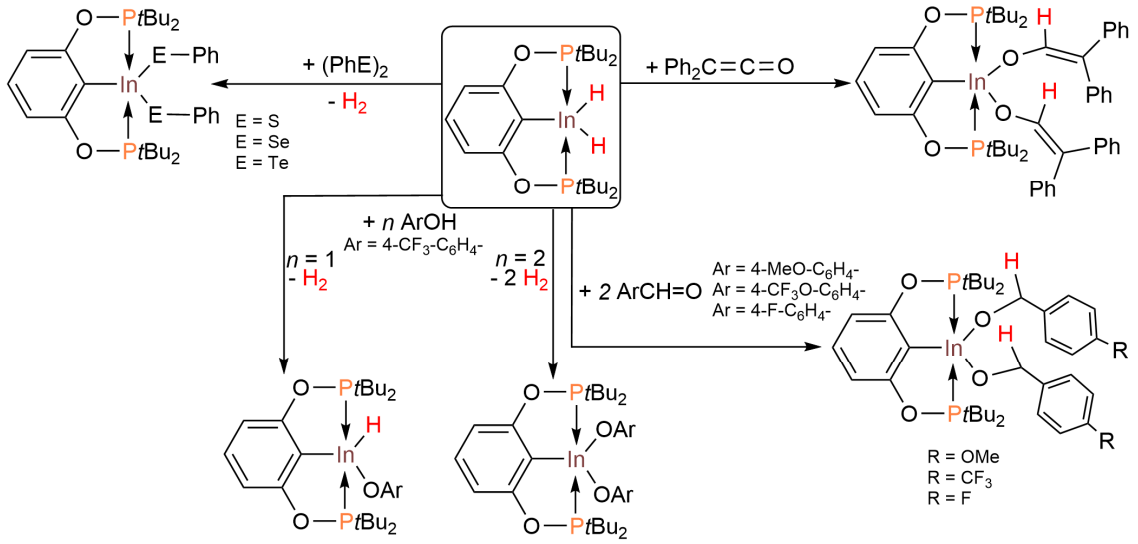
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INDIUM HYDRIDE: A NEW SOURCE OF HYDRIDE FOR REDUCTION AND DOUBLE HYDROINDATION

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Crystalline monomeric indane $ArInH_2$ (**1**) (Ar = 2,6-$(tBu_2PO)_2C_6H_3$), featuring two terminal In–H bonds, was prepared by reacting the P,C,P-pincer indium(III) chloride $ArInCl_2$ with 2 equiv. of $K[BEt_3H]$. The reactivity of **1** reveals its multifunctional character. As a reductant, it converts dichalcogenides $(PhE)_2$ into $ArIn(EPh)_2$ (E = S, Se, Te). As a hydride source, it reacts with 4-CF_3-C_6H_4OH to form either $ArIn(H)(4\text{-}CF_3\text{-}C_6H_4O)$ or $ArIn(4\text{-}CF_3\text{-}C_6H_4O)_2$, according to the applied stoichiometry, with concomitant evolution of H_2. Furthermore, **1** undergoes double hydroindation, reacting with aldehydes R-C_6H_4CHO (R = OMe, CF_3, F) to afford $ArIn(4\text{-}R\text{-}C_6H_4CH_2O)_2$ and with ketene $Ph_2C{=}C{=}O$ to yield $ArIn(Ph_2C{=}CH\text{-}O)_2$.



Scheme 1: Diverse reactivity of compound **1** as a reductant, hydride donor, and hydroindation agent, respectively.

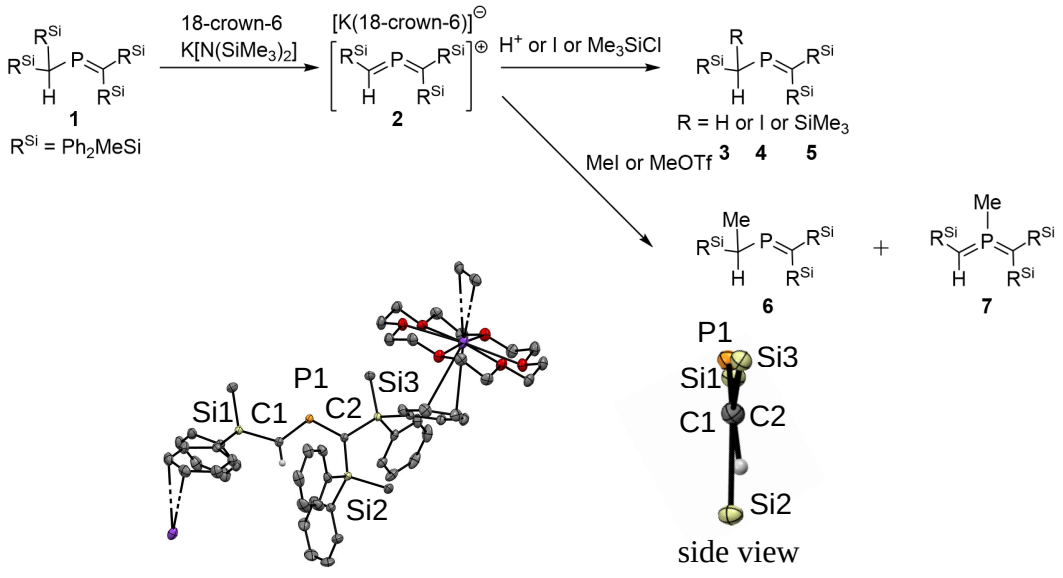
The authors would like to thank the Czech Science Foundation project. 26-20957S.

THE SYNTHESIS OF BIS(METHYLENE)-λ^5-PHOSPHANE ANION

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2-Heteraallenes, in which the central carbon atom of an allene is replaced with a heavier main group element, are known to exhibit unique structures and properties that differ from those of all-carbon allenes. The bis(methylene)-λ^5-phosphane anion, an anionic phosphorus-centered allene-type molecule featureing cumulative C=P π-bonds, which is isoelectronic with bis(methylene)-λ^4-sulfane,[1] has been synthesized and isolated as a stable compound.[2] Here, we report the synthesis, structure and reactivity of the first stable bis(methylene)-λ^5-phosphane anion **2**. Bis(methylene)-λ^5-phosphane anion **2** was synthesized via the desilylation of stable phosphaalkene **1** under ambient conditions. Unlike traditional all-carbon allene, bis(methylene)-λ^5-phosphane anion **2** exhibits bent-allene structure with coplanar terminal carbon planes. The p-bonding system of bis(methylene)-λ^5-phosphane anion **2** is characterized as a three-center four-electron (3c-4e) π-bond, as in the case of its isoelectronic analogue of bis(methylene)-λ^4-sulfane. It was found that the nucleophilic substitution reactions of **2** predominantly occurred at the terminal carbon atom bearing only one silyl group. Conversely, methylation reactions with methyl iodide (MeI) and methyl triflate (MeOTf) proceed at both the terminal carbon bearing one silyl group and the central phosphorus atom, giving the mixture of phosphaalkene **6** and bis(methylene)-λ^5-phosphane **7**.



Structure of bis(methylene)-λ^5-phosphane anion **2** (ORTEP drawing, 50% probability)

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SYNTHESIS, CHARACTERIZATION, AND STRUCTURAL ANALYSIS OF PN^3(P)-ANTIMONY(III) COMPLEXES AND THEIR REACTIVITY IN TRANSMETALATION WITH NICKEL AND COBALT

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We report the synthesis and characterization of a new class of antimony(III) complexes supported by PN^3(P)-pincer frameworks featuring phosphorus–nitrogen donor arms. These complexes exhibit versatile coordination behavior, adopting either bi- or tridentate binding modes depending on the structural features of the specific PN^3(P) platform. The complexes were thoroughly characterized in solution (^{1}H, ^{31}P, and ^{13}C NMR spectroscopy) and in the solid state by single-crystal X-ray diffraction analysis (SC-XRD). The antimony complexes can be readily transmetalated to form the corresponding well-defined pincer nickel and cobalt complexes, representing a new example of antimony-to-nickel/cobalt transmetalation. The behavior of the detached arm in the bipyridine complex is influenced by the strength of the P–Sb bond, which affects the rotation of the arm and determines the resulting conformer. This analysis is supported by Wiberg bond orders, the Intrinsic Bond Strength Index (IBSI), and QTAIM analysis.

EFFECTS OF ANCILLARY LIGANDS ON THE PROPERTIES OF 8-HYDROXYQUINOLINE BISMUTH COMPLEXES

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Bismuth, the heaviest stable pnictogen, has become an important element in coordination chemistry due to its strong Lewis acidity, notable relativistic effects, and environmentally benign nature. Its ability to form hypervalent and geometrically flexible coordination environments makes it an excellent platform for studying structure–property relationships in main-group complexes [1], [2].

Ancillary ligands profoundly tune metal complex properties by altering coordination geometry, orbital energies, and redox potentials, as seen across organometallic research. I have synthesized a series of bismuth complexes supported by 8-hydroxy quinoline based ligand having different ancillary ligands like, halide, pseudohalide, anions and aryl group. Complexes were well characterized by NMR spectroscopy, mass spectroscopy, SC-XRD, UV-vis and FT-IR. Density functional theory (DFT) calculations at the B3LYP-D3/SDD level were used to optimize the structures and to analyze frontier molecular orbitals, charge distribution, and metal–ligand bonding. The results show that stronger σ-donor ligands increase electron density at bismuth and stabilize higher-lying d-orbitals, which correlates with changes in absorption profiles and expected reactivity.

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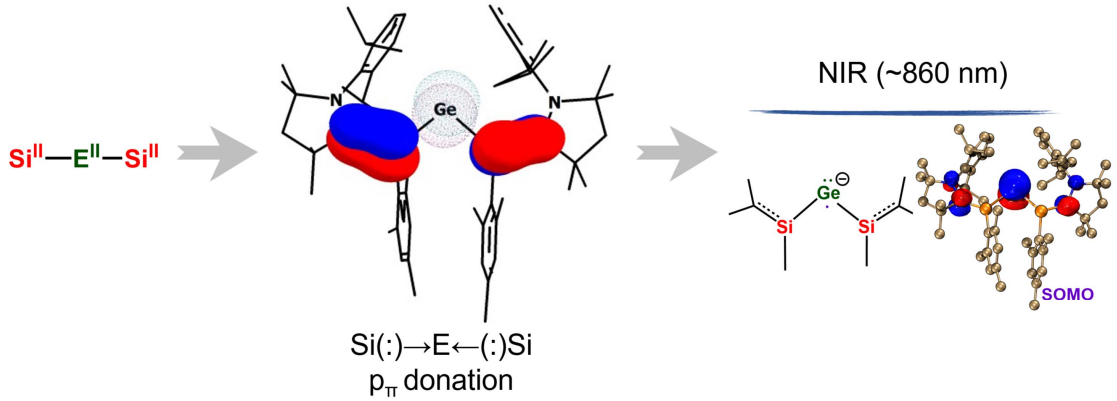
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SYNTHESIS AND ONE-ELECTRON REDUCTION OF UNPRECEDENTED DONOR-ACCEPTOR-STABILIZED Si^{II}-E^{II}-Si^{II} TRIMETALLYLENES (E = Ge, Sn, Pb)

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Catenated low-valent Group 14 compounds have attracted considerable interest due to their unique bonding and reactivity; however, well-defined trimetallylenes remain elusive. Building on our previous studies of bis(silylene)-supported Group 14 metallylones,[1] we herein report the synthesis and characterization of the first isolable Si^{II}–E^{II}–Si^{II} (E = Ge, Sn, Pb) trimetallylenes stabilized by p_π-type silylenyl donors, starting from a potassium silylenylide salt[2] and EX_2 precursors (X = halide, bis(trimetylsilyl)amide).[3] These compounds display remarkable donor–acceptor electronic structures, resulting in small HOMO–LUMO gaps and pronounced near-infrared absorption. Notably, one-electron reduction affords Ge^{I}- and Sn^{I}-centered radical anions, as supported by spectroscopic and computational analyses. This work establishes a new platform for accessing low-valent Group 14 species and expands the chemistry of catenated polynuclear metallylenes.



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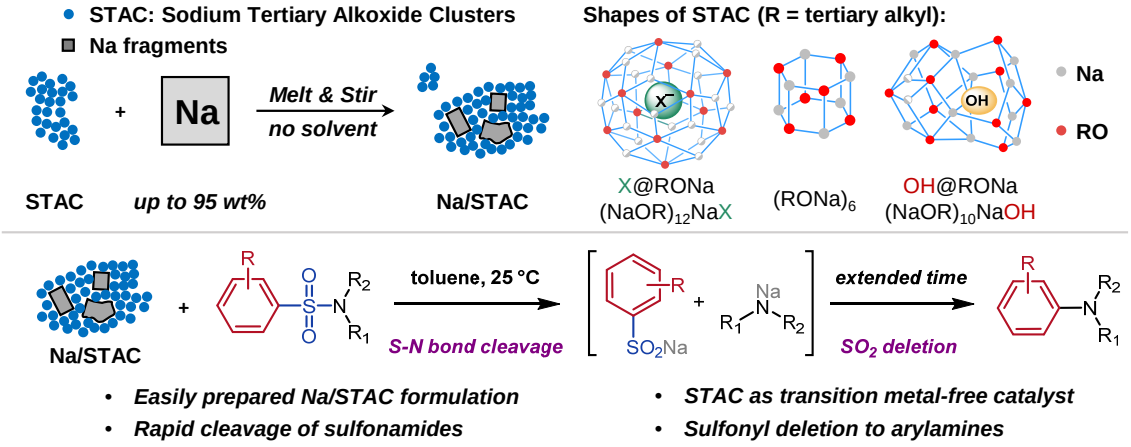
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HIGH CONTENT SODIUM METAL DISPERSION WITH SODIUM TERTIARY ALKOXIDE CLUSTERS ENABLES RAPID SULFONAMIDES CLEAVAGE AND SULFONYL DELETION

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[b] Lingang Laboratory, Shanghai, China
[c] Shanghai Key Laboratory of High-resolution Electron Microscopy, ShanghaiTech University, Shanghai, China
[d] State Key Laboratory of Advanced Medical Materials and Devices, ShanghaiTech University, Shanghai, China

Sodium tertiary alkoxide clusters are capable of dispersing sodium metal chunks into a solid mixture containing nanoscale sodium metal particles. In this new formulation of elemental sodium dispersion, sodium metal particles were physically separated by the sodium alkoxide clusters. The formulation containing up to 95 wt% metallic sodium could be made, much higher than other types of dispersed sodium. The dispersion enabled rapid cleavage of sulfonamide and sulfonate groups under mild conditions, in which the sodium alkoxide cluster acted as a catalyst.[1, 2] Continuation of the reaction afforded arylamines as formal sulfonyl deletion products. Mechanistic study indicated that the sulfonamide was cleaved into sodium amide and arylsulfinate, which reacted with each other and constructed the new C-N bond.



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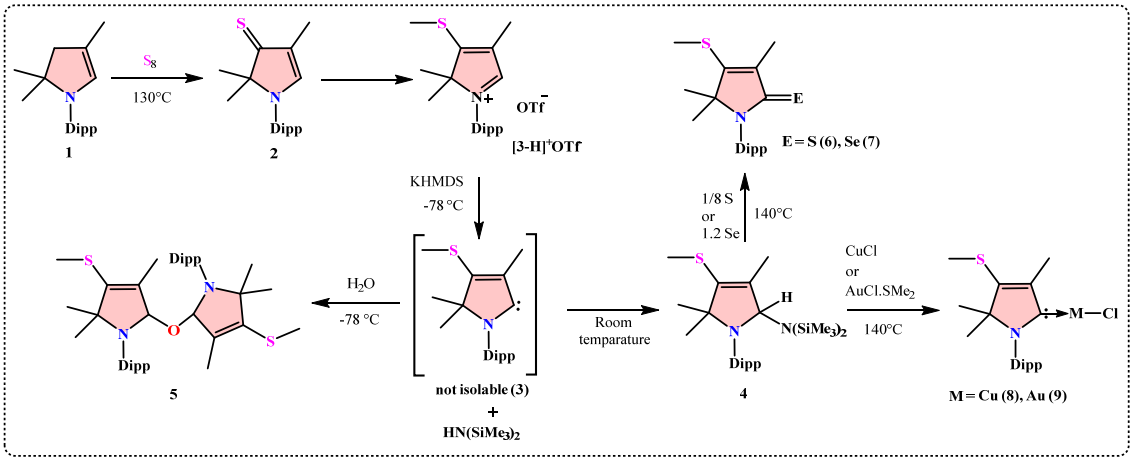
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CYCLIC (ALKENYL)(AMINO)CARBENE (^{SMe}CA$_{en}$AC): MODULATING THE HOMO–LUMO ENERGY GAP

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Cyclic (alkyl)(amino)carbenes (CAACs) are formed when one of the nitrogen atoms in a typical N-heterocyclic carbene is replaced with a quaternary carbon atom.[1] In general, CAACs possess a higher-energy HOMO and a lower-energy LUMO compared to saturated or unsaturated imidazole-based NHCs. Herein, we report the synthesis and reactivity of a new member of the CAAC family in which the quaternary carbon atom of CAACs is replaced with an sp²-hybridized carbon atom. This new carbene is described as a cyclic (alkenyl)(amino)carbene (^{SMe}CA$_{en}$AC). DFT analysis (B3LYP/def2-TZVPP) revealed a notable reduction in the singlet–triplet gap (37.05 kcal/mol) and a narrower HOMO–LUMO gap (3.92 eV) compared to CAACs.[2] The isolation of the free ^{SMe}CA$_{en}$AC carbene (**3**) was not possible due to its high reactivity. In this study, we therefore investigated the use of hexamethyldisilazane (HMDS) as a masking agent. The masked complex (**4**) regenerates the free carbene (**3**) upon heating. The ^{77}Se NMR analysis of the (^{SMe}CA$_{en}$AC)Se adduct shows a downfield chemical shift at +517 ppm compared to CAACs (+492 ppm),[3] indicating that ^{SMe}CA$_{en}$AC exhibits a higher π-accepting ability than CAACs. We further demonstrate the formation of carbene-anchored products, including metal complexes, under both low- and high-temperature conditions using the masked carbene derivative (^{SMe}CA$_{en}$AC)HMDS.



Scheme 1: Synthesis and reactivity of cyclic (alkenyl)(amino)carbene ^{SMe}CA$_{en}$AC (**3**).

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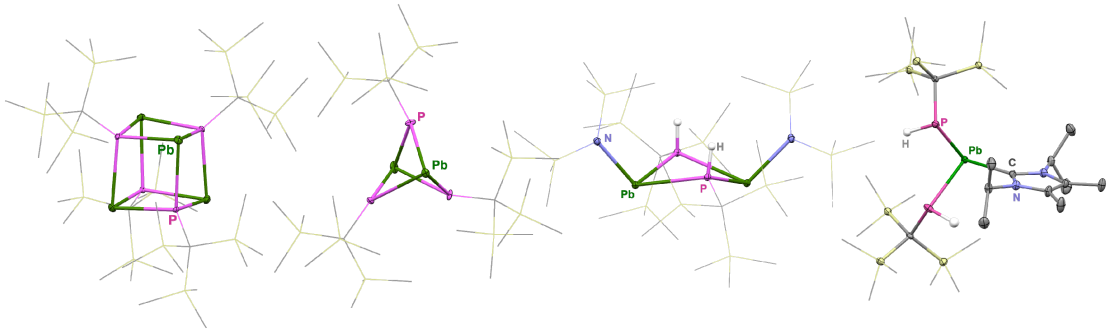
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TETRYLENES AND BEYOND: COORDINATION CHEMISTRY OF PHOSPHANYL-SUPPORTED LOW-OXIDATION STATE GROUP 14 SYSTEMS

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Phosphane donors are established, versatile ligands for transition metal chemistry, where tunable steric and electronic profiles enable diverse reactivity and coordination modes.[1,2] In contrast, phosphanyl-supported, low-valent p-block species – particularly heavier tetrylenes – remain comparatively underdeveloped[3-6] relative to their amide-based counterparts that surged after Arduengo's landmark synthesis of the first N-heterocyclic carbene (NHC).[7] Building on our recent identification of an amidophosphaplumbylene dimer $[(\mu2\text{-}R(H)P)Pb(N(SiMe_3)_2)]_2$ (R = $C(SiMe_3)_3$) and isolation of heteronuclear cluster motifs such as cubanes $[(RP)E]_4$ and [1.1.1]propellanes $[(RP)_3E_2]$ (E = Sn, Pb), we now expand the chemistry with a focus on controllable disruption of dimeric/oligomeric arrangements *via* NHC-coordination. We established a direct route to NHC‑ stabilized stannylenes and plumbylenes that bypasses dimer formation, yielding species with enhanced solution-state stability. This, in turn, enabled more detailed spectroscopic characterization and more controllable follow‑ up chemistry.



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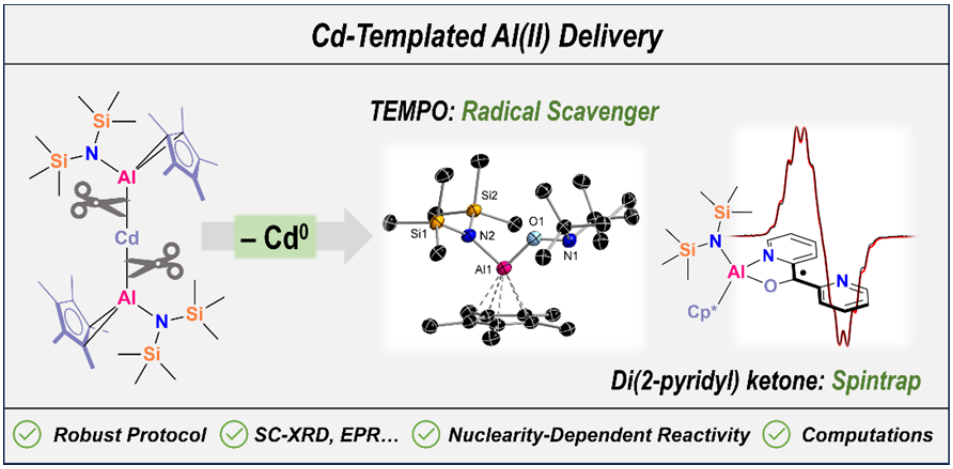
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CONTROLLED Al(II)-TRANSFER AT CADMIUM ALUMINYLS

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Low-valent aluminum chemistry continues to expand the boundaries of main-group reactivity, yet the selective generation and transfer of Al(II) fragments remain underexplored. Even rarer in the literature are Al(II)-transfer processes at multimetallic complexes, consisting only a few examples.[1] In our poster contribution, we expand the scope of Al(II)-transfer reactions with our reported heterometallic AlCd complexes $\mathbf{1}^{bi}$ (bimetallic) and $\mathbf{1}^{tri}$ (trimetallic), containing highly covalent Al-Cd bonds.[2] We demonstrate selective Al(II)-transfer to a variety of spin-trapping reagents and explore the role of nuclearity. While $\mathbf{1}^{tri}$ acts as an efficient $[Al]^{II}$-Cd^{0}-$[Al]^{II}$-synthon towards persistent nitroxides and diphenyl dichalcogenides under extrusion of Cd^{0}, $\mathbf{1}^{bi}$ can formally transfer Cd^{I} as well without extrusion in its metallic form. Notably, all reactions do not require any photochemical activation, proceed instantly and are highly selective. Spin-trapping of $\mathbf{1}^{tri}$ with ketones forms radical species which were unambiguously characterized by EPR-spectroscopy. Corroborating these experimental observations, DFT studies provide insight into the formation pathways, electronic structure, and stability of the resulting compounds. All results will be presented in detail throughout the poster presentation. An outlook is depicted below.



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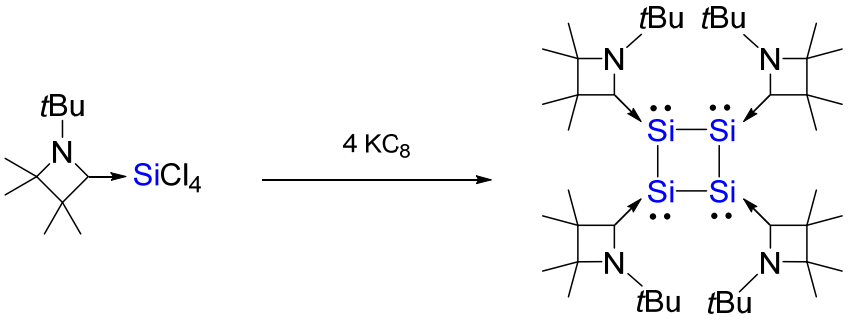
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FOUR-MEMBERED CYCLIC ALKYL(AMINO) CARBENE STABILIZED-TETRAATOMIC SILICON(0) CLUSTER

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Advances in the chemistry of Lewis base–stabilized silicon complexes in the formal zero oxidation state have been driven by their potential as silicon-based synthons.[1] By tuning the stereoelectronic properties of the supporting ligands, a range of carbene-stabilized mono- and diatomic silicon species has been successfully synthesized and isolated.[2] Although four-membered unsaturated Si_4 rings are well documented,[3] access to a tetraatomic silicon(0) cluster remains an attractive synthetic challenge. To this end, we propose that by using a cyclic alkyl(amino) carbene (CAAC) ligand with reduced steric bulk, while retaining strong electronic stabilization, would allow for access to such a species. Herein, we report the synthesis of a cyclic tetrasilicon(0) cluster coordinated by four-membered CAAC ligands (CAAC-4). The cluster displays versatile reactivity, undergoing fragmentation or isomerization, in response to nucleophilic or electrophilic stimuli.[4]



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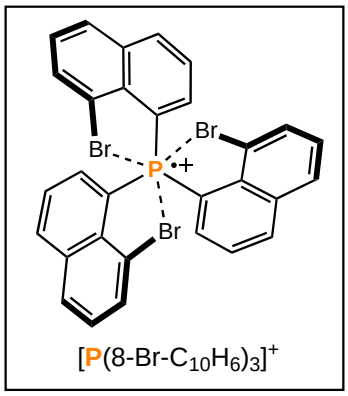
AN ISOLABLE TRIARYLPHOSPHINE RADICAL CATION ELECTRONICALLY STABILIZED BY THROUGH-SPACE RADICAL DELOCALIZATION

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[b]Department of Chemistry, Yonsei University, Seoul, Republic of Korea

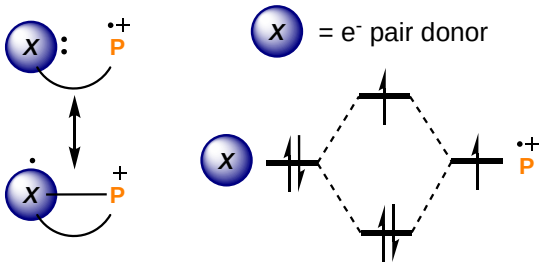
Synthesis and characterization of a thermally stable triarylphosphine radical cation, [P(8-Br-$C_{10}H_6)_3$][$BArF_{24}$] ([**1**][$BArF_{24}$], $BArF_{24}$ = tetrakis(3,5-bis(trifluoromethyl) phenyl)borate), enabled by stabilization through *peri*-bromo-substituted naphthalenes, are described. Unlike previously reported phosphine radical cations that rely on sterically bulky substituents for stabilization, our approach leverages electronic stabilization via "through-space" radical delocalization. Single-crystal X-ray diffraction of [**1**][$BArF_{24}$] reveals a tricapped tetrahedral geometry, resulting from the spatial proximity of the three bromine atoms to the phosphorus center, differentiated from the trigonal planar geometry observed in the previously reported triarylphosphine radical cations with sterically bulky substituents. EPR spectroscopy shows an isotropic signal with hyperfine couplings to both the phosphorus and the three bromine atoms, indicating spin delocalization over these four atoms and consequent formation of a four-center seven-electron (4c-7e) bond. DFT computational studies further support the through-space radical delocalization mechanism, revealing that the HOMO of **1** exhibits anti-bonding character between the phosphorus center and the three adjacent Br atoms, distinct from common triarylphosphines.

Electronically Stabilized Triarylphosphine Radical Cation



✓SC-XRD ✓EPR ✓DFT

“Through-Space” Radical Delocalization



A novel triarylphosphine radical cation
w/ unprecedented
(1) geometry (tricapped tetrahedron)
(2) electronic structure (anti-bonding HOMO)
(3) bonding structure (4c-7e) bond

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REACTIVITY OF A POTASSIUM ALUMINYL ANION WITH CROSS-CONJUGATED HYDROCARBONS

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Research School of Chemistry, Australian National University, Australia

Dendralenes, named after the Greek *δένδρον* (tree), are the archetypal family of cross-conjugated oligoenes. Their cross-conjugated architecture lends them privileged application in diene-transmissive cycloaddition sequences, whereby a [$_{\pi}4_{s}$ + $_{\pi}2_{s}$] cycloaddition furnishes a new diene for further cycloadditions. In larger dendralenes, the number of similarly accessible regioisomers and the irreversibility of cycloadditions often results in undesirable mixtures [1]. The possibility for a thermodynamically controlled addition to dendralenes may allow cycloadditions to become more selective toward a thermodynamic sink.

Aluminyl anions (anionic aluminium(I) compounds) have emerged as powerful nucleophiles, and participate in (4 + 1) cycloadditions with 1,3-dienes [2]. This work explores the cycloaddition behaviour of the parent dendralenes with dimeric and monomeric potassium aluminyl anions. Different site-selectivity was observed for different dendralenes, contrasting that of Diels-Alder reactions. Cycloaddition adducts rearrange to higher-substituted products *via* aluminium "chain walking" in the activated dendralene fragment, ultimately resting on the thermodynamic product.

This work represents one of the first investigations of the dendralene series from an organometallic perspective, and may provide access to new ways to selectively incorporate target-relevant complexity into the parent dendralenes (Figure 1).

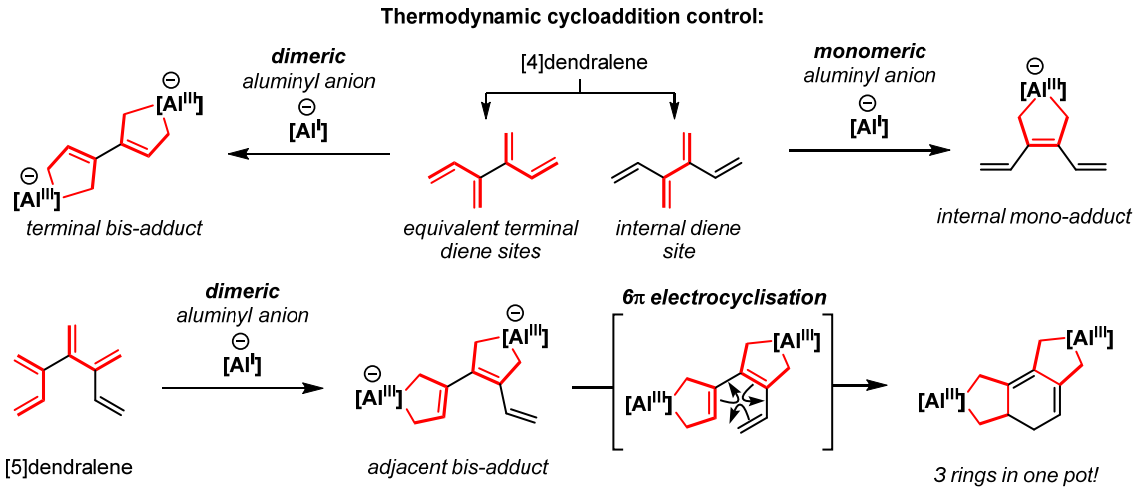


Figure 1. Reactivity of dimeric and monomeric potassium aluminyl anions with dendralenes.

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NUCLEOPHILIC GALLYL ANIONS: Ga–Au BIMETALLIC N–H AND O–H ACTIVATION

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The controlled activation of small molecules and strong σ-bonds remains a significant challenge in synthesis. While transition-metal complexes have traditionally dominated this area, low-valent main-group compounds, when paired with tailored ligand and counterion environments, can deliver comparable reactivity.[1-4] Harnessing activation of small molecules through aggregation and ion–paring of main-group nucleophiles, offers a new main-group metal route for cooperative bond activation.

The heavier congener gallium is an attractive target for main-group metal-mediated bond activation chemistry. Gallium(I) is softer and more polarizable than aluminum(I), and neutral gallylenes are already known to behave as powerful ambiphiles.[5-7] Here we report the synthesis of a family of charge-delocalized β-diketiminate gallyl anions, accessible across the Li–Cs series, whose aggregation and ion pairing can be tuned to furnish a cation-gated gallium(I) nucleophilic platform. These species exhibit clean nucleophilic reactivity toward Au compounds to give an unsupported Ga–Au bimetallic complex, analyzed by combining spectroscopic and computational studies. The resulting bimetallic system enhances the Lewis acidity at gallium(I) enabling N–H σ-bond activation of NH_3, $MeNH_2$ and analogous O–H activation of H_2O, MeOH under mild conditions.[8]

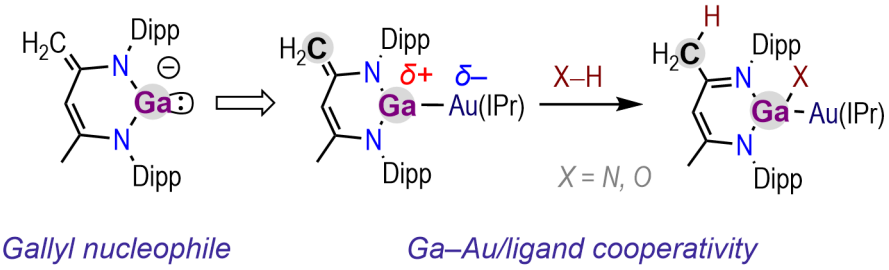


Figure 1. Nucleophilic gallyl carbene analogues for Ga–Au/ligand cooperativity.

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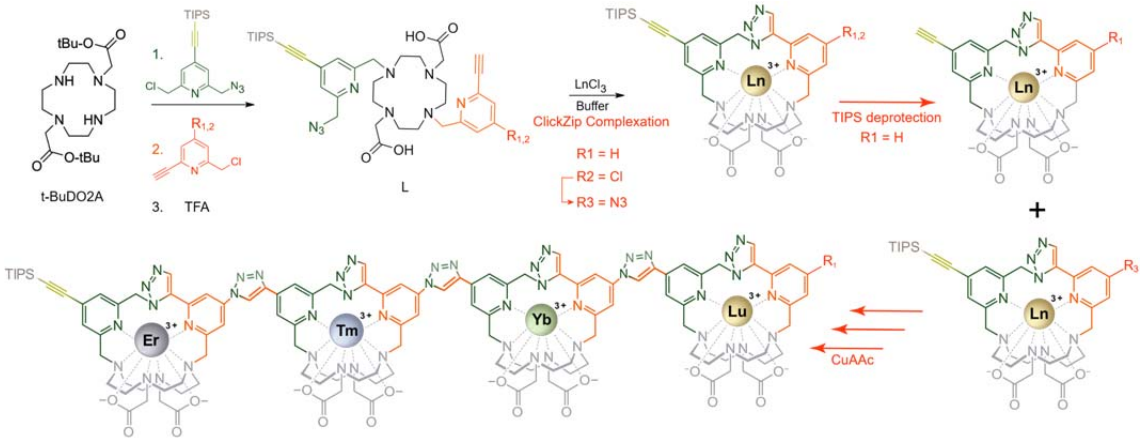
SEQUENCE-DEFINED HETEROMETALLIC LANTHANIDE OLIGOMERS BY STEPWISE CLICKZIP ASSEMBLY

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The controlled arrangement of multiple different metal ions within a single molecular framework represents a long-standing objective in coordination chemistry. Lanthanide ions are particularly attractive because of their unique optical, magnetic, and electronic properties. However, the selective incorporation of multiple distinct lanthanide ions into a single well-defined structure remains a fundamental challenge.

ClickZip is an ultra-inert lanthanide chelation platform formed through a coordination-templated cage-locking process, giving kinetically robust and nearly isostructural lanthanide complexes that can serve as modular building blocks [1]. This combination of high inertness and structural uniformity makes the platform suitable for the controlled construction of more complex heterometallic systems. Here, we report a stepwise bottom-up synthetic approach to sequence-defined heterometallic lanthanide oligomers based on orthogonally functionalized ClickZip monomers. Iterative TIPS deprotection and CuAAC coupling enabled controlled chain elongation with predefined metal order, giving discrete oligomers containing multiple different lanthanide ions, within a single molecular scaffold. A tetramer with Er-Tm-Yb-Lu sequence has been prepared on 30-mg scale and work on longer sequences is ongoing. This work opens a path towards a new class of multi-metallic compounds with potential applications in photonics, sensing, and molecular information storage [2].



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INVERSE SANDWICH COMPLEXES FOR THE TRANSFER OF GROUP 13 ELEMENTS IN THE +1 OXIDATION STATE

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Anionic compounds of group 13 elements in the +1 oxidation state, known as trielyl compounds, are isoelectronic to carbenes and therefore of interest in small molecule activation.[1,2,3] Synthesis of these complexes typically involves insertion of the group 13 element in the +3 oxidation state followed by reduction with an alkali metal compound.[1,2,3] This strategy poses several challenges, firstly requiring high dilution synthetic methods in order to prevent the formation of kinetically stabilised E(II) dimers, limiting the scale at which these complexes can be synthesised. Additionally, this method reduces the scope of trielyl complexes which can be synthesised, especially when considering redox flexible ligand scaffolds or complexes with multiple group 13 element centres which would have to be reduced. Some non-reductive methods of synthesising trielyl compounds do exist, however they are typically limited in scope, only reacting productively with a handful of ligands, therefore a more universal transfer agent would be desired. [4]

The compound $Ga_2Cp^*[Al[OC(CF_3)_3]_4]$ (Cp^* = pentamethylcyclopentadienyl) was synthesised from $GaCp^*$ and $Li[Al[OC(CF_3)_3]_4]$, the reactivity of this compound was then explored with a range of ligands, successfully synthesising previously reported gallyl complexes. Further reactivity with novel ligand systems, and the expansion of the chemistry to Al(I) is also being explored.

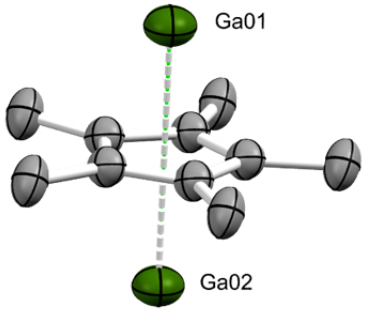


Figure 1: Molecular structure of $Ga_2Cp^*[Al[OC(CF_3)_3]_4]$ in the solid state as determined by X-ray crystallography. Thermal ellipsoids set at 50% probability, hydrogen atoms and $[Al[OC(CF_3)_3]_4]$ cation omitted for clarity

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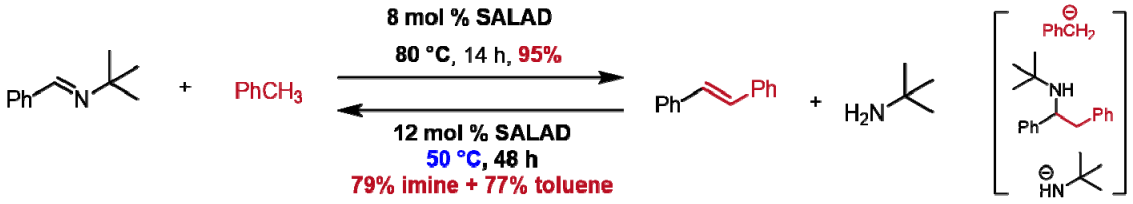
IMINE OLEFINATION WITH ARYLMETHANE AND ITS C=C BOND CLEAVING REVERSE REACTION CATALYZED BY SODIUM ALKYLAMIDE LADDER STRUCTURES

Jia-Yi Zhang[a], Zining Zhang[a], and Zhi Li[a,b,*]

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A polymeric sodium alkylamide ladder-shaped complex (SALAD) effectively catalyzed olefination of imine with arylmethane. The catalyst was derived from *tert*-butylamine and sodium oxide, and acts as an active catalytic base for deprotonative coupling between arylmethanes and benzyl imines, giving stilbenes as products. These E-style alkenes contain different groups are also convenient for further modification [1-3].

The same catalyst also enables the reversed reaction stilbenes cleavage with excess *t*-$BuNH_2$, to corresponding imines and arylmethanes. High regioselective products were obtained using certain substitution patterns of the stilbenes, allowing sequential transformation of widely available precursors such as arylboronates to arylimines and arylmethanes depending on demand.



Catalyst: Sodium alkylamide ladder structure (**SALAD**), $[t\text{-}BuNH_2 \cdot (t\text{-}BuNHNa)_3]_\infty$

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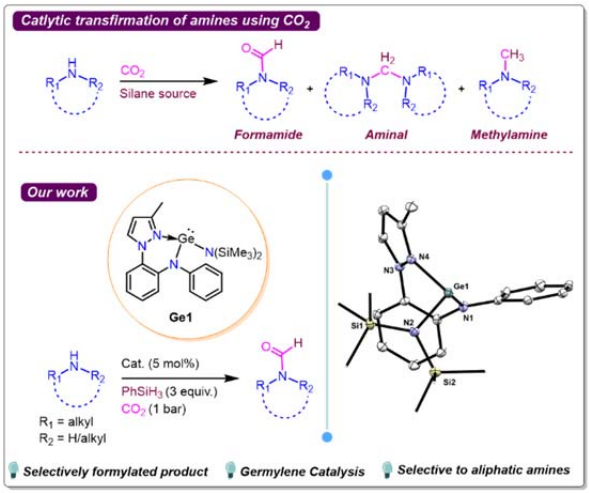
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ANILIDO-PYRAZOLE LIGAND SUPPORTED GERMYLENES: SYNTHESIS, STRUCTURE, AND CATALYTIC *N*-FORMYLATION OF AMINES USING CO_2

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The arrival of the new millennium paved the way for a surge in the development of main group chemistry, particularly their application in catalysis as a sustainable alternative to transition metal-mediated processes in various organic transformations.[1] In this aspect, monomeric low-valent group 14 element (commonly described as tetrylenes, E^{II}) complexes have been found to display electronic properties that mimic those of transition metals, positioning them as promising candidates for small-molecule activation and catalysis. Within group 14, germanium holds a transitional position, with an ideal orbital configuration and electronic structure that confer enhanced reactivity and stability compared to its congeners. In this aspect, germylene, the bivalent germanium species, has been an area of interest in the activation of small molecules and catalysis.[2] In this direction, germylene-catalyzed catalytic transformation of CO_2 to obtain several valuable products like amides, methylamines, heterocycles, and carboxylic acids has emerged as a field of growing significance owing to the dual advantages: CO_2 is a non-toxic, inexpensive, and renewable synthon[2], while germylene offers a more environmentally friendly alternative to traditional transition metal catalysts. In this direction we have developed anilido-pyrazolate ligand-supported Germylene complexes and studied their activity in *N*- formylation of amines using CO_2. The reaction mechanism was proposed based on various control experiments and DFT calculations, which suggested the important roles of the hemilabile pyrazole and amido ligands in the present protocol.[3]



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TRAPPING GALLIUM MONOFLUORIDE BY COORDINATION TO NICKEL

Johannes Stephan[a,b], Samia Kahlal[c], Jean-Yves Saillard[c], and Roland A. Fischer[a,b]

[a]Chair of Inorganic and Metalorganic Chemistry, TUM School of Natural Sciences, Technical University of Munich, Munich, Germany
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At room temperature, monovalent gallium halides are intrinsically unstable compounds, which can only be generated in the gas phase at temperatures around 1000 °C.[1,2] Although they are isoelectronic to CO, N_2, or CN^-, monovalent gallium halides are largely unexplored as ligands at transition metals. Herein, we report the isolation of a room-temperature stable gallium monofluoride, trapped in the coordination sphere of a dicationic nickel complex.[3] Starting from a nickel(II) nitrile complex with weakly coordinating anions (BAr^{F24}) and GaCp*, the GaF moiety forms as a product of $C(sp^3)$–F bond activation of the BAr^{F24} anion. This results from synergistic effects between nickel and gallium, which induce strong Lewis acidity at gallium[4] and lead to fluoride abstraction. This leads to $[(Cp^*Ga)_4Ni(GaF(NC^tBu)_2)](BAr^{F24})_2$ (**1**) as the target compound (Fig. 1).[3] The +I oxidation state of the GaF moiety in **1** is substantiated by NMR-spectroscopic methods as well as density functional theory calculations. Analysis of the bonding situation reveals strong σ-donating but negligible π-accepting properties for the GaF fragment at the nickel center. As an intermediate in the formation of **1**, the mixed nitrile/GaCp* complex $[Ni(GaCp^*)_4(NC^tBu)](BAr^{F24})_2$ (**2**) has been identified, which converts to **1** over 3 months. In addition, the gallium monofluoride moiety of **1** readily undergoes fluoride-transfer reactions. Examples include the formation of fluorinated products such as fluorosilanes and acid fluorides from organosilanes and acid chlorides, respectively.

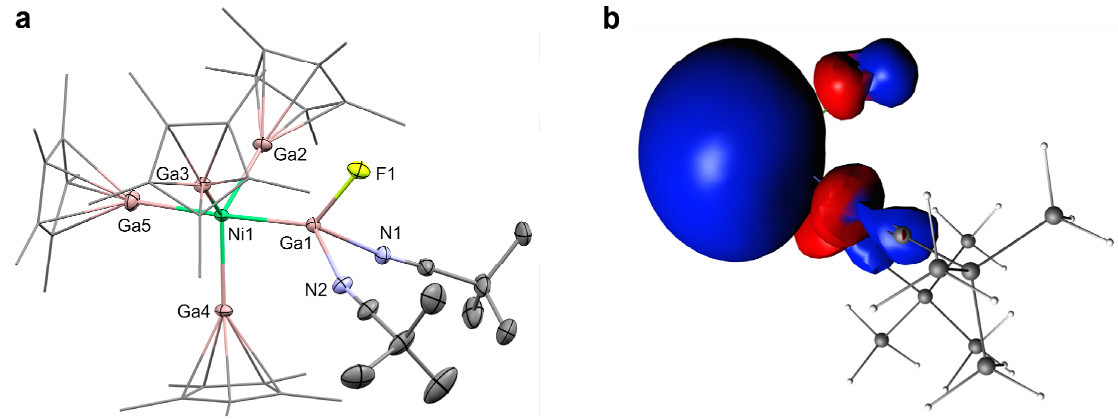


Fig. 1 | (**a**) Crystal structure of the diactionic part of **1** with GaF as a ligand at nickel and (**b**) calculated HOMO of the GaF moiety.

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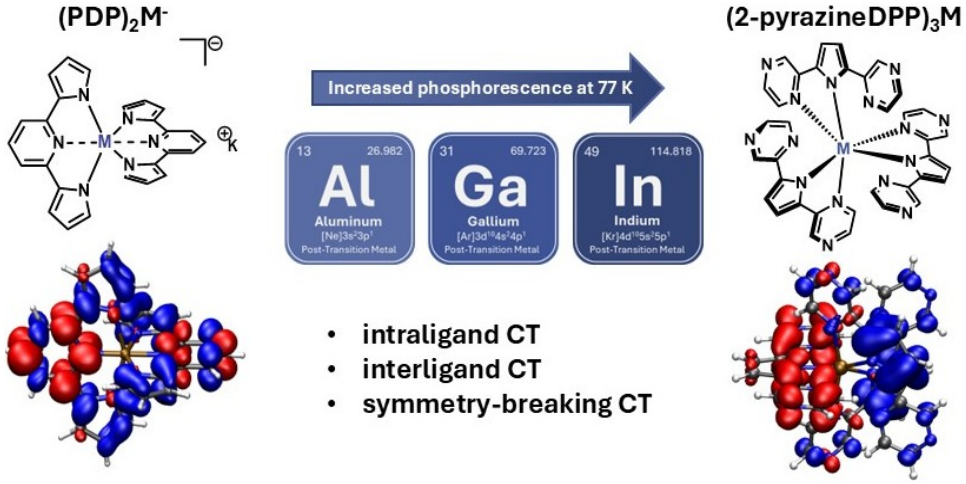
TOWARDS HOMOLEPTIC GROUP 13 TADF EMITTERS

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Molecular chromophores with long-lived excited states are at the heart important technological advancements, including photocatalysis,[1] photodynamic therapy,[2] chemo- and biosensing,[3] dye-sensitized solar cells,[4] and organic light-emitting diodes (OLEDs).[5] Most metal complexes used in these applications rely on heavy, rare and expensive precious 4d- and 5d-elements. Main group compounds with long-lived emissive states are much rarer but would provide more economic and better available alternatives to such precious metal-based chromophores. Recently, Milsmann and coworkers have reported on coordination compounds of the group 14 elements with bis(pyrrolide)pyridine (PDP^{2-}) ligands, which display long-lived excited phosphorescent states and thermally activated delayed fluorescence (TADF) emission, with an increasing propensity from silicon to tin.[6]

Herein we present homoleptic bis(pyrazine)pyrrolide complexes $(2\text{-pyrazineDPP})_3M$ and new anionic bis(pyrrolide)pyridine complexes $[(PDP)_2M]^-$ of the elements aluminum, gallium and indium. Combined experimental and computational studies demonstrate the HOMO-LUMO transition of these complexes has symmetry-breaking, inter- and intraligand charge-transfer character. Most of the complexes display dual emission at 77 K with increasing phosphorescence quantum yields from aluminum to indium. Room-temperature measurements for indium complexes demonstrated not only prompt fluorescence but also a second, longer-lived component with an excited-state lifetime in the microsecond range at the same wavelength as the prompt fluorescence, indicating TADF.



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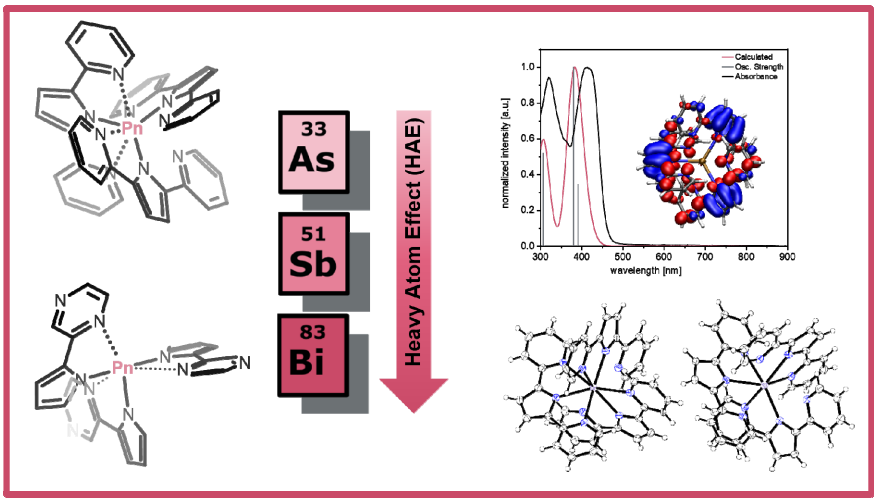
LUMINESCENT COORDINATION COMPOUNDS OF THE PNICTOGENS WITH DIPYRIDINE PYRROLIDE LIGANDS

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Their rigid structure, good and electron-donating properties and inherently emissive character render dipyridine pyrrolide (DPP^-) ligands a good choice for the design of luminescent complexes, several of which exhibit ligand-based phosphorescence at cryogenic temperatures.[1, 2] This present study combines the promising properties of the DPP^- scaffold with those of the pnictogen metalloids arsenic, antimony and bismuth. In spite of the high potential of both Sb and Bi for generating excited triplet states through their high spin-orbit coupling constants and heavy-atom effect (HAE), only a small selection of bismuth complexes exhibit room-temperature phosphorescence in fluid solution.[3, 4]

Herein, we present new complexes $(DPP)_3M$ of the elements arsenic, antimony and bismuth and study the impact of the HAE of the metal ion on their photophysical and emissive properties. Combined experimental and computational studies reveal symmetry breaking inter- and intraligand charge transfer excitations with participation of the pnictogen atom and intense phosphorescence emission at cryogenic temperatures. Crystallographic studies indicate that the stereoactive lone pair at the central ion 15 elements imposes considerable structural distortion from an octahedral coordination geometry, which is partially alleviated in analogous complexes with 2-pyrazine pyrrolide chelate ligands. Enhanced intraligand charge-transfer character endows such ligands and their coordination compounds with particularly favorable photophysical properties.



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ACCESS TO LOW VALENT GROUP 14 SPECIES UTILIZING CYCLIC ALKYL AMINO OLEFINES (CAAOs)

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N-heterocyclic olefins (NHOs) are zwitterionic compounds that have been utilized as nucleophilic ancillary ligands to stabilize low-valent main-group species,[1] having electron-donating capabilities comparable to those of the corresponding carbenes.[2] NHOs have emerged as suitable ligand tools for stabilizing elusive low-valent main-group species.[3] In addition, it has also been found to have broad applications in several areas of ongoing research, including polymerization, organocatalysis, organometallic chemistry, and coordination chemistry.[3] Surprisingly, despite the widespread utilization of cyclic alkyl amino carbenes (CAACs) in coordination, organometallic, and main-group chemistry, their olefin derivatives have remained entirely unexplored to date.

Herein, we have developed a new olefin derivative, derived from CAACs, which can be termed as cyclic alkyl amino olefins (CAAOs). This study will reveal the modified synthetic route of a new class of stable CAAOs and their derivatives. It exhibits exceptionally low basicity (pKa ~10), as determined experimentally. The DFT calculation reveals a higher HOMO energy for CAAO, indicating that it is a stronger σ-donor than its corresponding CAAC, as the HOMO is more destabilized. Isolated CAAO was further used for reactivity studies with small molecules, including NO_2, isocyanates, azides, isonitriles, etc. In addition, we demonstrate the utility of these CAAOs in the isolation of Si(II) species, where the steric environment surrounding the exocyclic olefinic center is found to be a decisive factor in kinetic stabilization. All isolated compounds are duly characterized by single-crystal X-ray diffraction studies, multinuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, and high-resolution mass spectrometry (HRMS) measurements.

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PHOSPHOLE-BASED INTRA- AND INTERMOLECULAR FRUSTRATED LEWIS PAIRS AS FLUORESCENT AND STIMULI-RESPONSIVE SYSTEMS

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The traditional use of frustrated Lewis pairs (FLPs) in small-molecule activation has recently been expanded to broader applications, including catalysis, materials chemistry, and responsive molecular systems[1-2]. Building on this concept, we report the development of phosphole-based Lewis pair systems designed to merge classical FLP reactivity with intrinsic optical addressability. Using 1,2,5-triphenylphosphole and 2,5-diphenylphosphole as a Lewis base throughout our studies, both inter- and intramolecular systems were synthesized to systematically evaluate the influence of preorganization and linker design on structure–property relationships (Figure 1)[3]. Intramolecular FLPs were designed by bridging the phosphole to a Lewis acidic center - $B(C_6F_5)_2$ *via* either a rigid phenyl spacer or a more flexible three-carbon alkyl chain, enabling controlled modulation of Lewis acid–base proximity and the degree of frustration. All systems exhibit strong fluorescence originating from the phosphole framework, allowing direct optical monitoring of their Lewis chemical behavior. Coordination of $AlCl_3$ results in efficient fluorescence quenching, establishing the phosphole phosphorus center as a sensitive optical reporter for external Lewis acid binding. Incorporation of the phosphole into an intramolecular FLP structure preserves this fluorescence responsiveness while introducing steric constraints that inhibit classical adduct formation, for the more strained phenyl linker. For the more rigid 3-carbon chain linker, an adduct is formed. Competitive binding experiments with DMAP induce changes in emission behavior towards a decrease in wavelengths, highlighting switchable donor–acceptor interactions and tunable electronic properties. Importantly, one of the intramolecular FLPs activates PH_3, demonstrating that genuine FLP reactivity can coexist with fluorescence-based Lewis acid sensing within a single molecular platform. Together, these results provide insight into phosphole-derived FLPs and establish them as promising platforms for stimuli-responsive systems, molecular sensing, and fundamental studies of FLP reactivity[3].

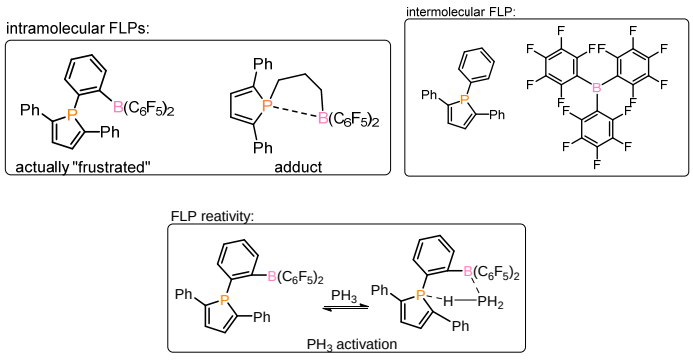


Figure 1. Exemplar of 2,5-diphenyl phosphole-based intra- and intermolecular FLPs used in this study and reactivity towards PH_3.

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COOPERATIVE C-H ACTIVATION OF BENZYLIC ARENES BY A p-BLOCK 3d-METAL SCAFFOLD

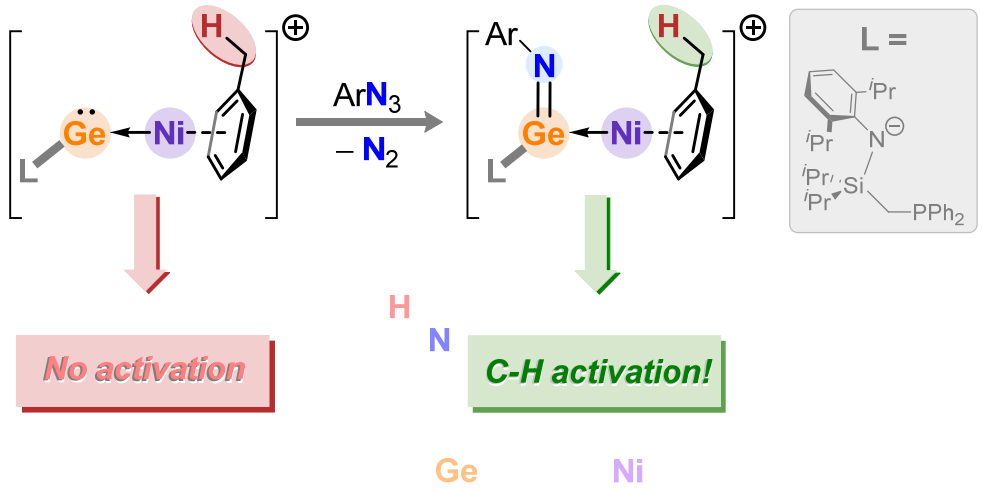
Philip Keil, Li Feng Lim, and Terrance Hadlington

Department of Chemistry, Technical University of Munich, Garching, Germany

The overwhelming majority of C−H activation reactions take place upon a single metal site, and accordingly proceed through one of several known mechanisms.[1] Leveraging the potential of two distinct element centres, however, opens a plethora of new pathways by which these reactions can occur – ones otherwise inaccessible to their monometallic counterparts.

This work describes the employment of a cooperative bi-elemental scaffold of germanium (a *p*-block element) and nickel (a 3*d* transition metal) in the preparation of a series of cationic arene complexes. Atypical of transition metal-germylene complexes,[2] the lone pair of electrons on the Ge^{II} centre remain amenable to manipulation – in this instance undergoing oxidation upon treatment with an aryl azide to deliver the corresponding germa-imine complexes.[3]

Contrary to the preceding Ge^{II}-Ni^{0} arene complexes, these germa-imine compounds undergo an intramolecular C−H activation with the coordinated arene molecule at accessible sp^3-hybridised positions. This accordingly produces the nickel-*benzyl* complex, with the germa-imine motif undergoing conversion to a secondary germa-*amine* in the process. These products exhibit a dynamic equilibrium in solution, alternating between the parent benzylic complex and its η^3-ligated allyl variant. Further chemistry and kinetic aspects will be discussed.



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FIRST *P,C,P*-PINCER ORGANOBISMUTH COMPOUNDS

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Over the past two decades, organobismuth compounds have attracted significant attention, with numerous species reported, particularly those stabilized by oxygen- and nitrogen-based ligands [1]. In contrast, compounds featuring intramolecular stabilization by phosphorus donors remain rare. A notable breakthrough was the development of univalent bismuthinidenes supported by *N,C,N*-pincer ligands [2], which have demonstrated remarkable potential as main-group redox catalysts, including applications in photocatalytic C–C coupling [3].

Building on these advances, we report the synthesis and characterization of novel *P,C,P*-pincer organobismuth chlorides bearing L^{PC} or L^{PO} ligands. Their reactivity, including phosphorus(III) oxidation, bismuth center ionization, and the potential formation of *P,C,P*-bismuthinidenes, will also be presented at the conference.

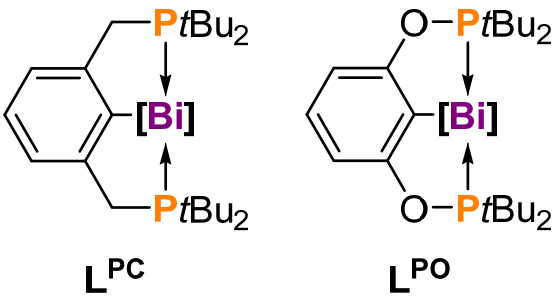


Figure 1. The studied *P,C,P*-pincer ligands used for stabilization of organobismuth species in this work.

Acknowledgements: The authors would like to thank Prof. Aleš Růžička and Dr. Zdeňka Růžičková for sc-XRD crystallography and the Czech Science Foundation (project No. 26-20957S) for the financial support.

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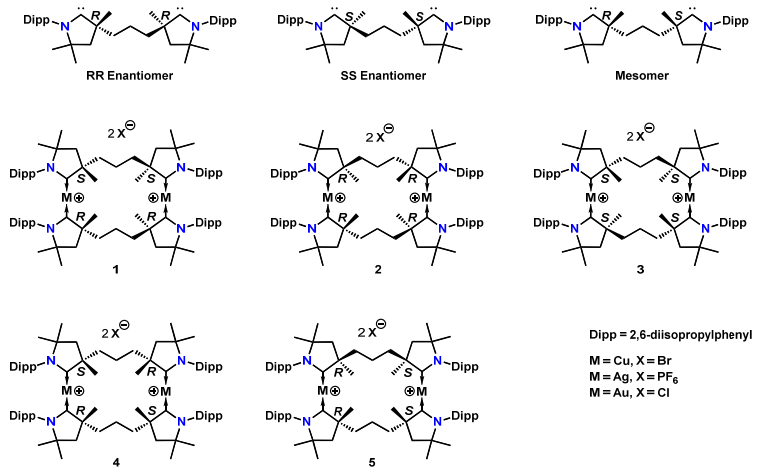
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HEAVY PNICTOGEN, TETREL, AND COINAGE METAL COMPLEXES WITH ISOMERIC BIS[CYCLIC (ALKYL)(AMINO)CARBENE] LIGANDS

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Since the discovery and isolation of the first cyclic (alkyl)(amino)carbene (CAAC) by Bertrand in 2005, the library of isolable of CAACs has expanded rapidly.[1] These carbenes have seen extensive application in both coordination chemistry and catalysis, given their exceptional σ-donating and π-accepting properties.[2–6] Our group recently reported the first isolable bis(CAAC) as a racemic mixture capable of chelating iron, cobalt, nickel, and zinc.[7] Herein, we present the isolation and characterization of the *meso* isomer, as well as the coordination of both the *meso*- (C_2-symmeric) and the *rac*- (C_s-symmetric) isomer with copper, silver and gold. Both ligand isomers form dicationic bridging dimers with the coinage metals, resulting in five possible configurational isomers of each of the ensuing complexes. For the racemic ligand, the three possible structures are a *meso* complex (**1**) and two enantiomeric complexes (**2**, **3**). The *meso* ligand can form either a *cis* (**4**) or *trans* (**5**) dimeric complex. All structural motifs have been isolated and characterized. Also discussed will be the low oxidation state chemistry of antimony, bismuth, germanium, and tin with these bis(CAAC) ligands.



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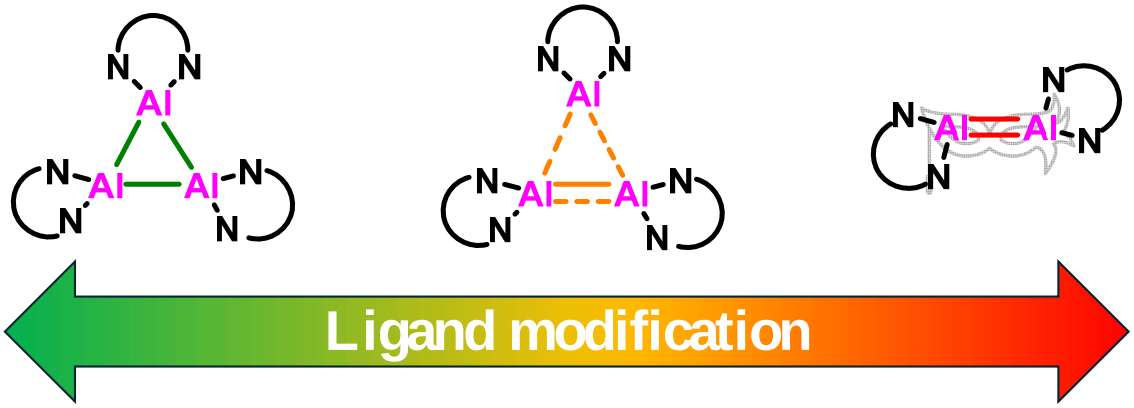
CYCLOTRIALUMANES AND BEYOND

Matthew de Vere-Tucker, and Clare Bakewell

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As the most abundant metal in the Earth's crust, aluminium represents an attractive alternative to problematic transition metals. Interest in the synthesis and reactivity of low-oxidation state aluminium compounds has exploded since the seminal first report of the synthesis of a stable aluminium(I) complex[1], the tetrameric $[AlCp^*]_4$ ($Cp^* = C_5Me_5^-$). This was followed by monomers[2] and dimers[3]. These species have been utilised for a rich range of reactivity, with applications in transition metal-like bond cleavage, small molecule activation, as stoichiometric reducing agents[4] and very recently, redox catalysis.[5]

This year, the Bakewell Group has presented for the first time a novel *tri*meric neutral aluminium(I) complex.[6] In this work we showed how the application of amidine ligands enabled a hitherto unknown trimeric nuclearity. This nuclearity was retained in solution and through reactivity with ethene trimer-based reactivity was observed, resulting in the isolation of unprecedented 5- and 7- membered heterocyclic mixed oxidation-state aluminium complexes.



In this poster, the effect of ligand modification on this system will be explored.[7] A significant expansion of the number of isolated trimeric species is detailed, with differences in structure and reactivity interrogated experimentally and using DFT. In one case, this ligand modification entirely changes the nuclearity and affords a novel "true" masked dialumene, and its reactivity with a range of substrates will be reported.

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C=O METHYLENATION MEDIATED BY ORGANO-ALKALI METAL REAGENTS: METAL IDENTITY AND LIGAND EFFECTS

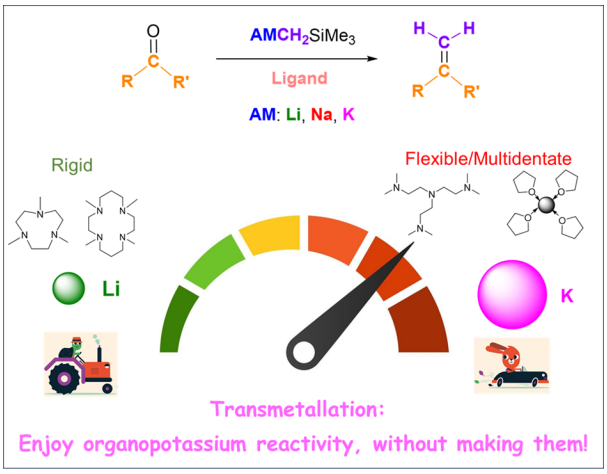
Nathan Davison,[a] Xiao Yang,[a] Matthew E. Lowe,[b] Paul G. Waddell,[b] Roly J. Armstrong,[b] Claire L. McMullin,[c,*] Matthew N. Hopkinson[b] and Erli Lu[a,*]

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[b]Chemistry – School of Natural and Environmental Sciences, Newcastle University, Newcastle Upon Tyne, United Kingdom
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Carbonyl methylenation is a cornerstone transformation in synthetic chemistry, traditionally dominated by Wittig- and Tebbe-type reagents. In addition, C=O methylenation mediated by α-silyl organo-alkali metal reagents, namely Peterson methylenation,[1] is a textbook reaction that has been widely employed in synthetic chemistry for over 50 years, however, key factors controlling the elimination step remain poorly understood.

In this work we systematically investigated metal identity and ligand effects in C=O methylenation reactions mediated by MCH_2SiMe_3 (M = Li; Na; K).[2, 3] These insights revealed that both the alkali metal cation identity (K > Na ≫ Li) and external Lewis base ligand play a critical role in determining the methylenation performance, with K^+ and neat tetrahydrofuran (THF) being optimal.

Leveraging these findings, a practical one-pot methylenation protocol was developed: nucleophilic addition using $LiCH_2SiMe_3$ followed by *in-situ* addition of KO^{t}Bu in THF enables transmetallation-driven elimination. This approach avoids the use of highly reactive organo-sodium/potassium reagents, delivering excellent yields across a range of ketones (including enolizable substrates) and aldehydes. The method employs commercially available reagents, offering a low-cost, easy-to-use alternative for the methylenation of ketones and aldehydes.[3]



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COPPER(-I)? A XAS STUDY OF COPPER — MAIN GROUP COMPOUNDS

Nicholas J. Evans, Lewis Parker, Ross Jackson, Matthew Stevens, Jon Kragskow, Kevin Lovelock and David Liptrot

Department of Chemistry, University of Bath, Bath, United Kingdom

Previous work proposed a new oxidation state of copper, copper(-I).[1] Synthesis of (6-Dipp)CuMg(DippNacNac) (6-Dipp = $C[N(Dipp)CH_2]_2CH_2$, DippNacNac = $HC[C(CH_3)N(Dipp)]_2$, Dipp = 2,6-$^{i}Pr_2C_6H_3$) was achieved through combination of $(DippNacNacMg)_2$ and two equivalents of (6-Dipp)CuOEt in toluene. This Cu-Mg compound showed through reactivity that it was the first consistent source of nucleophilic copper. This nucleophilicity at copper provided, for example, a pathway to the first unsupported Cu-Zn compound, (6-Dipp)CuZn(DippNacNac), through addition of (6-Dipp)CuMg(DippNacNac) to (DippNacNac)ZnI in a salt metathesis reaction. This reactivity, alongside computational calculations, supported the conclusion that (6-Dipp)CuMg(DippNacNac) contained Mg(II) and Cu(-I).[1]

In this work, we report spectroscopic data to assign the charge at copper within (6-Dipp)CuMg(DippNacNac). X-ray absorption spectroscopy (XAS) was used to determine charge, through derivation of the X-ray absorption near-edge structure (XANES). This technique required comparative compounds, with a series of 6-Dipp copper(I) compounds measured as reference species (**Figure 1**).

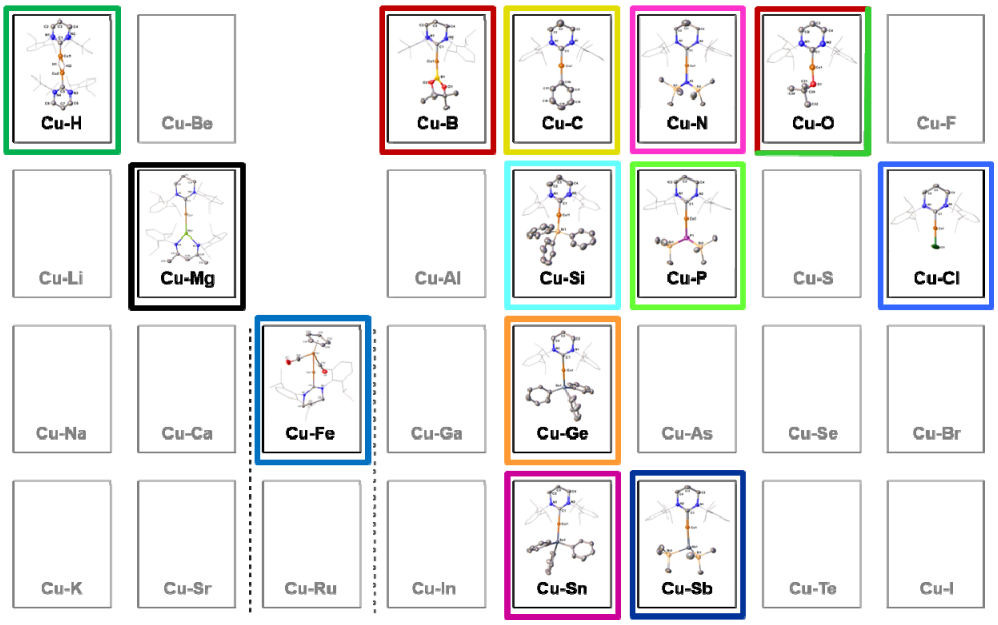


Figure 1. X-ray structure table of copper compounds XAS data was collected for.

The study provided data for accurate determination of charges at both Cu and Mg within (6-Dipp)CuMg(DippNacNac). This provided insight into the nature of the Cu-Mg bond, supported by more advanced computational methods, and the latest findings and conclusions for copper-magnesium chemistry will be described.

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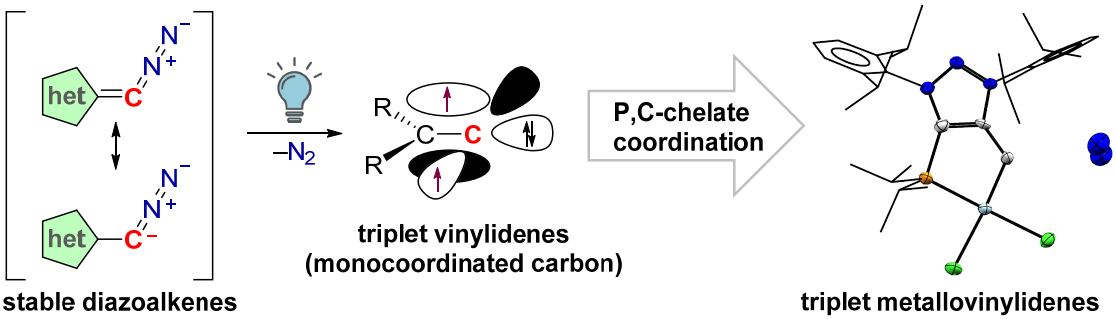
FROM DIAZOALKENES TO TRIPLET VINYLIDENES AND METALLOVINYLIDENES

Patrick W. Antoni, Yuri Kutin, Max Amann and Max M. Hansmann

Fakultät für Chemie und Chemische Biologie, Technische Universität Dortmund

Diazoalkenes, long considered elusive reactive intermediates, can be isolated through electronic stabilization *via* C=C bond polarization and represent a rapidly developing new class of compounds.[1] Beyond fundamental interest in bonding and reactivity, they serve as well-defined precursors for the photochemical generation of triplet vinylidenes, enabling access to carbon-centered diradicals featuring a monosubstituted carbon atom.[2] A series of heterocycle-derived diazoalkenes was developed as tunable platforms for vinylidene generation. Irradiation affords the corresponding triplet vinylidenes, which were investigated by EPR spectroscopy, providing systematic insight into their electronic structure and characteristic spectroscopic parameter.[3] While the singlet-triplet gap depends strongly on the heterocycle and substitution pattern, the zero-field splitting and ^{13}C hyperfine parameter remain in a narrow, characteristic range that unambiguously distinguishes triplet vinylidenes from the well-known triplet carbenes. Tuning of the steric environment suppresses C–H insertion pathways and significantly increases persistence.

Introduction of a rigid P,C-chelating diazoalkene ligand enables bidentate coordination to Pt and Pd, geometrically constraining the reactive carbon center.[4] Photoexcitation of the resulting complexes affords triplet metallovinylidenes with extraordinary zero-field splitting, reaching D = 124.5 cm^{-1} for platinum. Characterization by THz-EPR, SQUID magnetometry, and photochemically triggered *in crystallo* X-ray diffraction establishes metallovinylidenes as a new class of organometallic diradicals. The unusual coordination mode of this ligand platform opens broad prospects in photoresponsive organometallic chemistry and molecular magnetism.



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[3] Y. Kutin, J. Reitz, M. Drosou, P. W. Antoni, Y. He, V. R. Selve, S. Boschmann, A. Savitsky, D. A. Pantazis, M. Kasanmascheff, M. M. Hansmann, *JACS Au* **2025**, *5*, 2884–2897.

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REACTIVITY OF LOW-VALENT MAGNESIUM(I) COMPLEXES WITH EPOXIDES AND EPISULFIDES

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Since their inception, reactivity studies of magnesium(I) complexes have delivered exciting new chemistries.[1, 2] This includes the deoxygenation of N_2O and CO_2 to form oxo-bridged Mg-O-Mg complexes.[3] Here, we explore the potential of the magnesium(I) dimer $[^{Dipp}NacnacMg]_2$ (Nacnac = $HC(C(CH_3)N)_2$, Dipp = 2,6-(^{i}Pr)$_2$Ph, **1**) to deoxygenate epoxides and desulfonate episulfides. Reactivity studies show that **1** reacts with epoxides in a 1:2 ratio to deliver a bimetallic μ_2-hydroxide/allylic alkoxide complex (**2**, Figure 1, bottom left). This structural motif was consistent across external epoxides (propylene oxide (PO), isobutylene oxide, butylene oxide) and internal epoxides (cyclohexene oxide). In coordinating THF-d_8 solvent, one equivalent of PO instead fully consumes dimer **1** to generate the Mg-O-Mg bridged species **4·(**THF-d_8)$_2$ with concomitant propene elimination. Extending these reactivity studies to the analogous thiirane, propylene sulfide (PS, Figure 1, centre right), eliminated propene to generate the bimetallic mono- (**4**) and disulfide (**5**) bridged species. The formation of the Mg-S-Mg unit in **4** is analogous to the Mg-O-Mg motif generated with PO in **3**. Yet in contrast, the second equivalent of PS was not deprotonated, generating instead a disulfide-bridged complex **5.** Adding propylene oxide to the mono-sulfide adduct **4·(**$Et_2O)_2$ delivers a bimetallic O/S μ_2-hydroxide/bisulfide complex (**6**, Figure 1, right). These experiments demonstrate key reactivity differences and similarities between oxygen and sulfur.

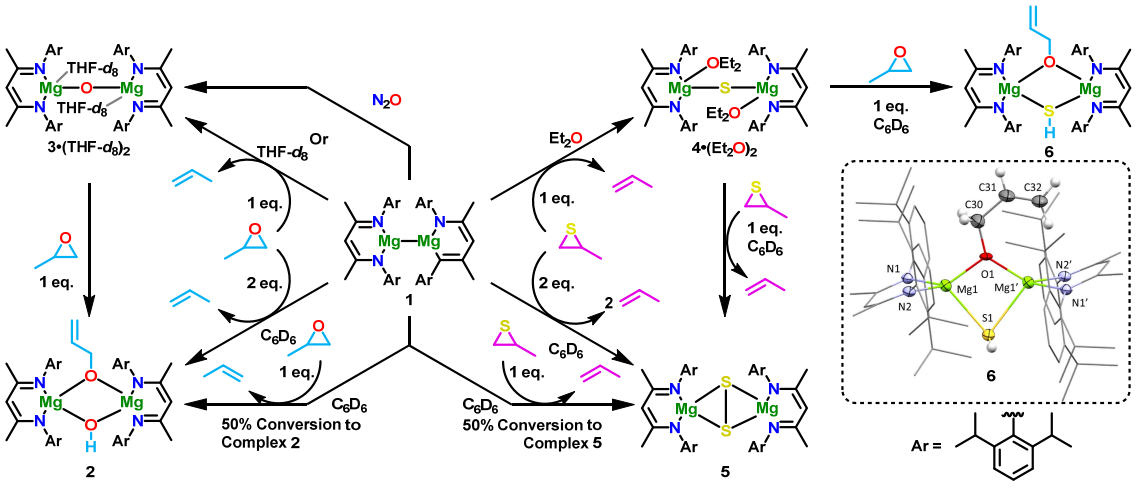


Figure 1 Reactivity of $[^{Dipp}NacnacMg]_2$ with one or two equivalents of propylene oxide or propylene sulfide in coordinating (THF-d_8) and non-coordinating (benzene-d_6) solvents.

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CATALYTIC Si/B EXCHANGE CONDENSATION AS A MILD AND EFFICIENT ROUTE TO CONJUGATED ALKYNYL-SPACED BORANES

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Institute of Inorganic Chemistry and Institute for Sustainable Chemistry & Catalysis with Boron (ICB), University of Würzburg, Würzburg, Germany

Conjugated organoboranes are the subject of intensive research efforts due to their versatile applications, for example in photovoltaics, light-emitting devices, sensors, and catalysis.[1] Their desired optoelectronic properties require effective overlap of the boron's vacant p_π-orbital with the adjacent π-system. Cyclolinear oligoboranes represent promising architectures in this regard;[2] however, steric constraints limit the selection of suitable aromatic building blocks, as bulkier groups can cause severe deviation from coplanarity in the molecules' backbone. A promising strategy for overcoming this problem is the introduction of an alkynyl spacer between the boron center and at least one of the substituents. Using catalytic Si/B exchange,[3] we synthesized a series of air- and moisture-stable alkynyl-spaced boranes and bisboranes in a modular approach. Their structures exhibit high planarity, which enables efficient π-conjugation across the molecular framework, as demonstrated by crystallographic, photophysical, electrochemical, and DFT studies.[4]

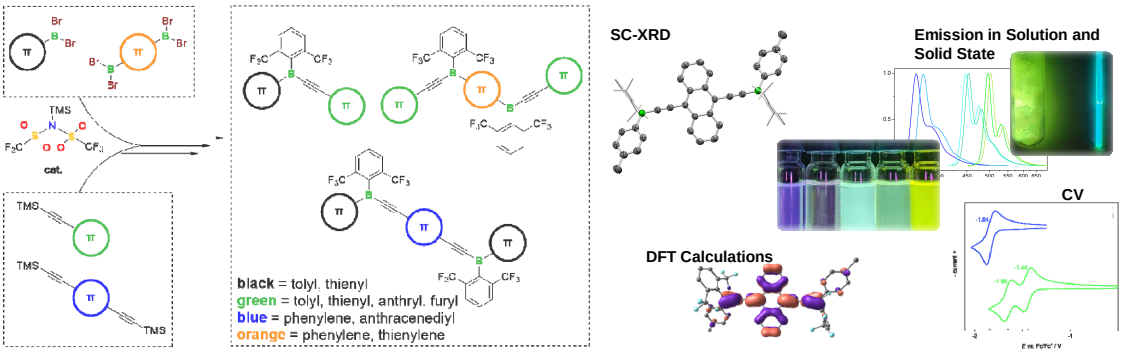


Figure 1: Schematic synthesis of alkynyl-spaced boranes via Si/B exchange condensation and examples that demonstrate their structural, photophysical, and electrochemical properties.

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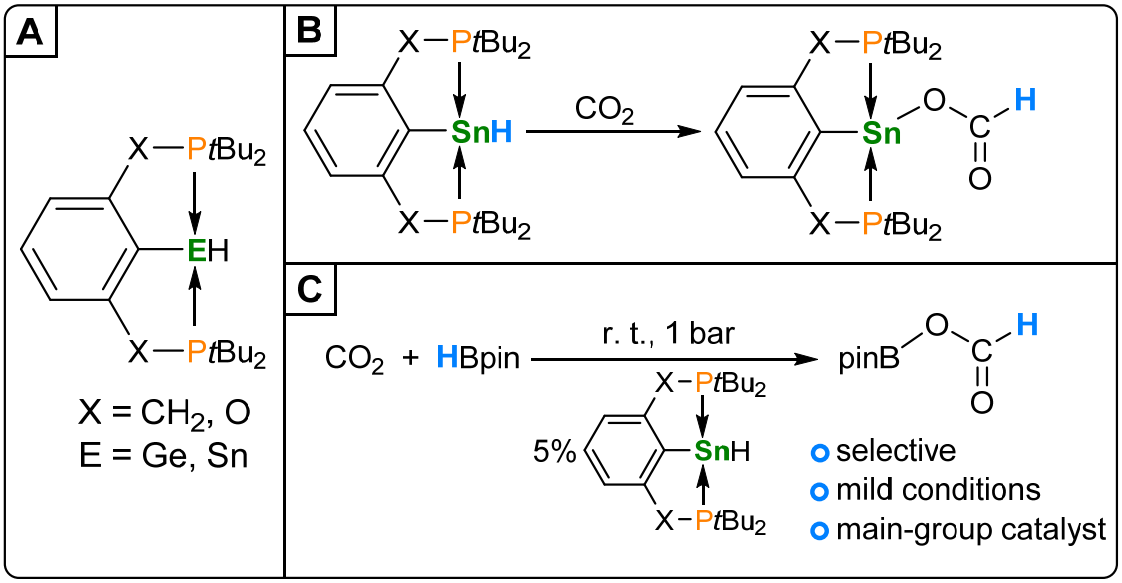
PROBING CATALYTIC CO_2 ACTIVATION WITH *P,C,P*- PINCER GERMANIUM(II) AND TIN(II) HYDRIDES

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[b]Department of Inorganic and Analytical Chemistry, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Hungary

Even though *P,C,P*- pincer compounds of transition metals are well known for over 50 years,[1] the research in chemistry of p-block elements began only recently.[2,3,4] Especially the stabilization of heavier low-valent p-block elements should be beneficial as they are softer Lewis acids than their lighter high-valent counterparts.

We explored the ability of these pincer ligands to stabilize germanium(II) and tin(II) hydrides (**Scheme 1A**), whereas the latter turned out to be capable of activating carbon dioxide under very mild conditions (**Scheme 1B**). We also studied ability of prepared formates to undergo reverse reactions with various hydrosilylation and hydroboration agents and use of this approach in catalytic manner (**Scheme 1C**).



Scheme 1A: Prepared hydrido-tetrylenes, **B:** Activation of carbon dioxide, **C:** Carbon dioxide hydroboration catalyzed by tin(II) hydrides

The authors would like to thank the Czech Science Foundation project. 26-20957S.

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CALCIUM HYDRIDE COMPLEXES FOR THE HYDRODEFLUORINATION OF F- CONTAINING MOLECULES

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Fluorine is ubiquitous across chemistry, being contained in molecules with applications ranging from pharmaceutical and agrochemicals to batteries and materials such as Teflon. Accessing these molecules and materials remains hazardous; fluorite must first be turned into hazardous and toxic HF, using sulphuric acid at high temperatures.[1] Recent work within our program has shown that anionic calcium fluoride complexes are able to act as sources of nucleophilic fluoride, which can be delivered to various electrophiles.[2] One route to synthesise these calcium fluoride complexes is via the corresponding calcium hydride analogues, which are able to abstract the fluorine from fluorine containing molecules.[3,4,5] In this way fluoride can be 'repurposed' from waste streams through the use of calcium complexation.

This work focuses on an investigation of both neutral and anionic calcium hydride complexes and their application in the hydrodefluorination of various fluorine containing substrates. Through the study of these reactions, and in particular their selectivity and kinetics, it is hoped that the underlying mechanism(s) of these processes can be elucidated.

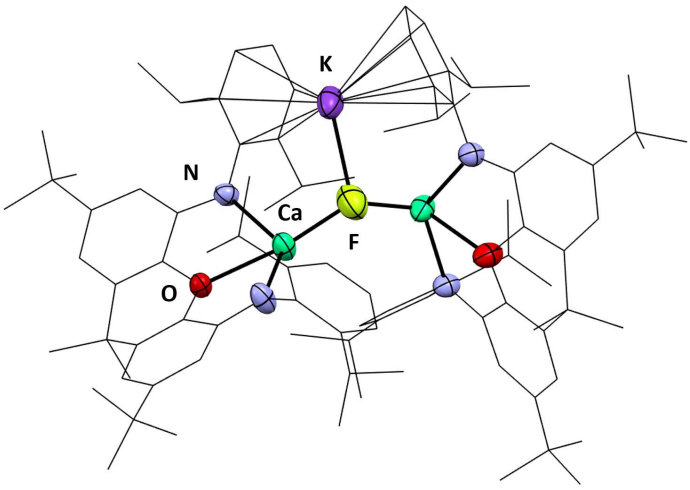


Figure 1: Selected example of anionic fluoride complex resulting from the reaction of an anionic calcium hydride with α,α,α-trifluorotoluene

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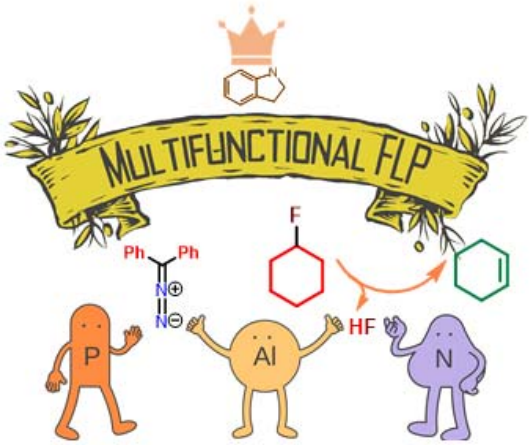
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INTRAMOLECULAR Al/P FRUSTRATED LEWIS-PAIRS BASED ON AN INDOLINE BACKBONE – TWO REACTION SITES FOR SMALL MOLECULE ACTIVATION AND HYDRODEFLUORINATION

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The synthesis of Al/P FLPs with an indoline spacer unit is reported. While the alane functions can be attached to the heteroatom via very straightforward synthetic procedures, we found that the ionic character of the Al–N bond renders the compounds highly prone to ligand exchange reactions. Reactivity studies revealed that the indoline backbone offers two reactive sites, namely the Al···P FLP reaction space and the aluminum amide function, giving rise to multifunctional FLP structures. Which site is triggered during an activation process depends on the nature of the investigated substrate. Furthermore, we have shown that simple alane compounds can be used for the dehydrofluorination of hydrofluorocarbons in the homogeneous phase. The ability of alane compounds to mediate HF elimination from the substrate depends on both the Lewis acidity of the aluminum center and the Brønsted basicity of its ligands.[1]



[1] *Intramolecular Al/P Frustrated Lewis-pairs based on an Indoline backbone -Two Reaction Sites for Small molecule Activation and Hydrodefluorination*, S. Biswas, S. Wolff, B. Cula, C. Limberg, *ChemRxiv* **2026**; DOI: https://doi.org/10.26434/chemrxiv.15001183/v1

BIS(PYRIDINO-O-CARBORANYL) PHOSPHENIUM: A PLATFORM FOR DUAL-SITE REACTIVITY IN SMALL-MOLECULE ACTIVATION

Shiv Kumar, and Roman Dobrovetsky

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Tel Aviv University Tel Aviv 69978, Israel

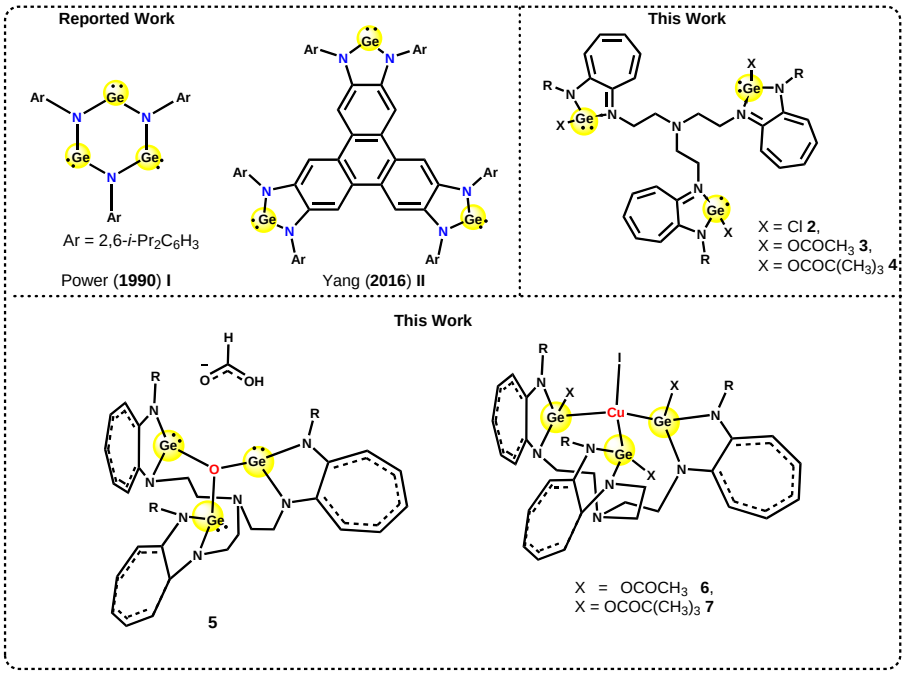
Phosphenium, [$\mathbf{L_2P^+}$][$B(C_6F_5)_4$], substituted by two bis(pyridino-ortho-carboranyl) groups, was prepared, fully characterized, and its preliminary reactivity with small molecules was studied. Surprisingly, cation [$\mathbf{L_2P^+}$][$B(C_6F_5)_4$] reacts differently with O−H and N−H bonds. With RO−H (R = H, Me, Ph), the reaction takes place at P center in [$\mathbf{L_2P^+}$][$B(C_6F_5)_4$], via hydrolysis or alcoholysis of the P−C bonds, leading to the carboranopyridinium salt ([$\mathbf{LH_2^+}$][$B(C_6F_5)_4$]) and the complementary $(RO)_2P(O)H$. In contrast, the reaction of [$\mathbf{L_2P^+}$][$B(C_6F_5)_4$] with R_2N−H (Ph(H)NH, ^{i}Pr(H)NH, Et_2NH) does not proceed at the P center, but takes place at the ortho-carboranyl (*o*Cb) moiety by deboronation, producing zwitterionic phosphenium ($\mathbf{L(L^{nido})P^+}$), with significant reduction in the reactivity of the P-center compared to $\mathbf{L_2P^+}$. Remarkably, [$\mathbf{L_2P^+}$][$B(C_6F_5)_4$] reacts with SO_2 in MeCN at both sites, the P and *o*Cb, stripping both oxygens from sulfur, leading to zwitterionic phosphonium sulfide ($\mathbf{L(L^{nido})P^+{=}S}$).

FROM TRIS(GERMYLENE) TO TRIPODAL COPPER CATALYST: SYNTHESIS, UNUSUAL OXO-CATION FORMATION, AND CuAAC ACTIVITY

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While monogermylenes and bis(germylenes) have been extensively studied as mono- and bidentate ligands, tris(germylenes) capable of simultaneously coordinating through three Ge(II) centers remain unexplored[1,2]. This study introduces a novel tripodal tris(germylene) **2**, stabilized by TREN-tris(aminotroponimine) **1**. Compound **2** was synthesized by treating the *in situ*-generated tri(lithium) salt of compound **1** with $GeCl_2$·(1,4-dioxane). Interestingly, in its reactivity with various carboxylate salts, compound **2** exhibited divergent behavior. The reaction of **2** with sodium acetate and sodium pivalate yielded tris(germylene carboxylates), **3** and **4**, respectively. However, **2**'s reaction with sodium formate resulted in the unprecedented cationic μ_3-oxo-bridged trigermanium derivative **5**. It can be considered a hitherto unknown digermylene oxide-stabilized germylene cation, revealing that TREN-based tris(germylenes) can function as tripodal ligands. This aspect is realized in the mononuclear Cu(I) complexes **6** and **7** isolated in the reactions of tris(germylenes) **3** and **4** with CuI, where all three germylenes were coordinated simultaneously with one copper atom, confirming that TREN-based tris(germylene) can indeed function as tripodal ligands. Furthermore, the utility of these copper complexes, **6** and **7**, as catalysts in the azide-alkyne cycloaddition (CuAAC) reactions is also demonstrated.



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POLY(FERROCENYLENE IMINOBORANE), RELATED COPOLYMERS AND MACROCYCLES

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The selective replacement of C=C units by B=N linkages has emerged as a powerful strategy for modifying organic compounds and creating novel materials with intriguing properties. In recent years, we have reported a variety of inorganic–organic hybrid polymers and oligomers featuring B=N bonds within their backbones.[1-5] These include a BN analogue of poly(*p*-phenylene vinylene) (PPV)[1] as well as inorganic analogues of polyacetylenes, namely poly(iminoborane)s.[2] In the present work, we introduce a new polymer consisting of B=N-linked ferrocene (fc) units (**1**)[3], along with related copolymers that incorporate additional *p*-phenylene (ph) building blocks (**2**).[4] Furthermore, we have developed an efficient synthetic route for incorporating 1,2,3,4,5-pentamethylferrocene into polymeric structures via a 1,3-bridging motif (**3**).[6] This approach enables access to a donor–acceptor backbone architecture arising from the NNBB sequence of the heteroatoms along the polymer chain. We provide detailed insights into the microstructure of these novel metallopolymers, as well as into the electronic communication mediated by the π-bonding of linear B=N units in general. In addition, we present 1,2,5-azadiborolane as a new building block for advanced macromolecular systems and describe an inorganic–organic hybrid polymer (**4**) that contains the longest inorganic BN chain segment reported to date.[5] X-ray crystallographic studies of the monomer and oligomeric species offer evidence for π-electron delocalization along the BN chain in these compounds.

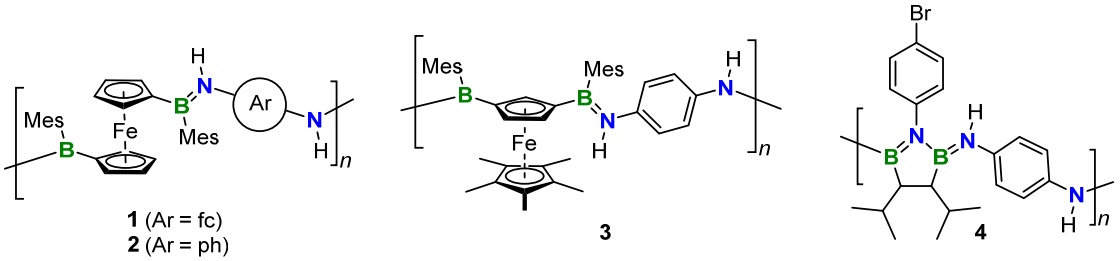


Figure 1. BN-doped polymers 1, 2, 3 and 4 (Mes = 2,4,6-trimethylphenyl).

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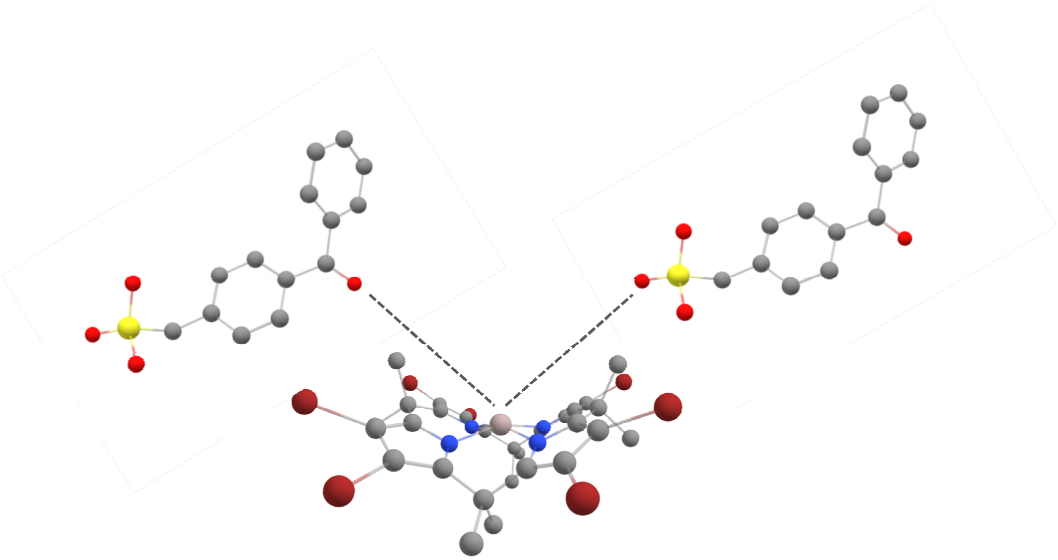
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DO ANIONIC LEWIS ACIDS DISCRIMINATE CHARGE IN SUBSTRATE BINDING? INSIGHTS FROM A β-OCTABROMO-CALIX[4]PYRROLATO ALUMINATE

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An extremely strong anionic aluminate Lewis acid is encapsulated within the cavity of β-octabromo-calix[4]pyrrole. On one side, it binds F^-, Cl^-, Br^-, and N_3^- anions, forming unprecedented dianionic adducts. On the other side, it binds weak donors such as benzophenone, exhibiting rare optical properties among main-group complexes arising from complex-to-substrate charge transfer. These unusual properties enable an investigation of charge-discriminating substrate binding, revealing a counterintuitive trend: anionic substrates, or substrates bearing an anionic moiety, bind preferentially and selectively, whereas the similarly strong neutral Lewis acid BCF shows no such selectivity. In addition, a dynamic coordination replacement of a carbonyl group by an SO_3^- group at the aluminate center can be monitored by the naked eye, as well as by ^1H NMR and UV–Vis spectroscopy. The observed kinetics suggest the presence of a Coulombic barrier, highlighting the potential of charge as a dedicated design element for sensing applications and catalytic transformations.



TIME-RESOLVED OPEN-ACCESS SCIENCE AT THE NEXUS X-RAY SPECTROSCOPY BEAMLINE

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The National eXtreme Ultrafast Science facilities in Columbus, OH hosts a range of exciting cutting-edge instrumentation for novel time-resolved research. This work reports on the development of an open-access time-resolved X-ray Absorption Beamline. The XAS beamline at NeXUS is driven by a 100 kHz, 700 W laser and produces ~1e13 X-ray photons/sec through High Harmonic Generation (HHG). The energy range spans from 36 eV to 72 eV which accesses the M-edges of 1st row transition metals, and the N- and O-edges of choice heavier elements (for example, Ir and I). The beamline has a flexible measurement geometry, operating in either transmission or reflection geometry, and gas cooling capability. The implementation of a few-cycle driver will push the temporal resolution to sub-10 fs and add spectral bandwidth. Further developments will add a circular polarizer for dichroic measurements and bring a liquid sheet endstation online.

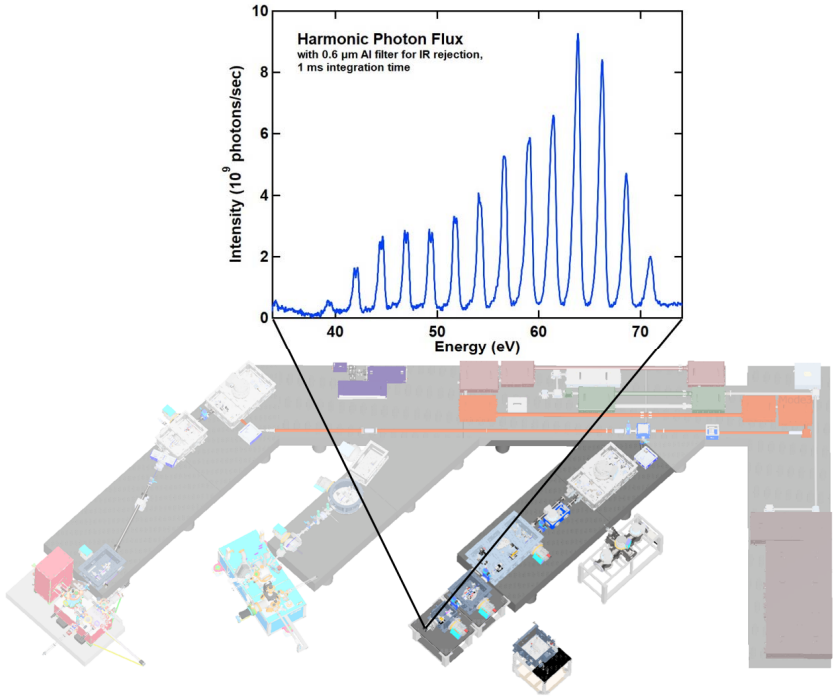


Figure 1. Extreme Ultraviolet X-ray Spectrum generated at the XAS/XRS beamline at the NeXUS facilities, demonstrating photon flux of ~1e13 photons/second. Depicted on the bottom is the layout of the NeXUS facilties.

SYNTHESIS AND STRUCTURE OF A STERICALLY LESS-HINDERED $[B_2H_5]^-$ ANALOGUE WITH A STRONG B-B BOND

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In recent years, main group chemistries have been the center of increased interest for their ability to react in similar ways chemically to transition metal complexes. One particular case is that of boron which is often cited for its relatively low toxicity and cost. Recent work within boron chemistry focuses on complexes containing boron-boron bonds [1].

Among reported B-B bonded complexes, μ-hydrido diborane anion (R_2B-$^{\mu}$H-BR_2) is of a particular interest with two potential reactive sites: the B-H and the B-B bond. The simplest form of such species, $[B_2H_5]^-$, has not been experimentally realized as a free anion, leading to the pursuit of substituted variants. Several efforts were made to synthesize and characterize stable molecules with such $[R_2B$-$^{\mu}$H-$BR_2]^-$ moiety. To date, all the successful reports employed bulky aryl groups as the R, to offer the essential steric stabilization [2, 3]. However, the C(sp^2) aryls may influence the electronic structure of the B-$^{\mu}$H-B moiety from the archetypical $[H_2B$-$^{\mu}$H-$BH_2]^-$. Additionally, the presence of sterically bulky aryl groups may result in the shielding of the reactive site from further reaction.

Herein, we report the reduction of a sterically less-hindered borane, 9-BBN. Using a sodide complex as the reductant, we successfully isolate complex (**1**) (shown in Figure 1(c)). The single-crystal XRD study reveals a B-B bond length of 1.623(3)/1.625(3) Å, with calculated WBI of 1.19. It should be noted that the reduction does not occur in the presence of Na metal, suggesting that the sodide is integral to the process. A preliminary reactivity study with PH_3 produces R_2BPH_2 and $[R_2B(H)_2]^-$.

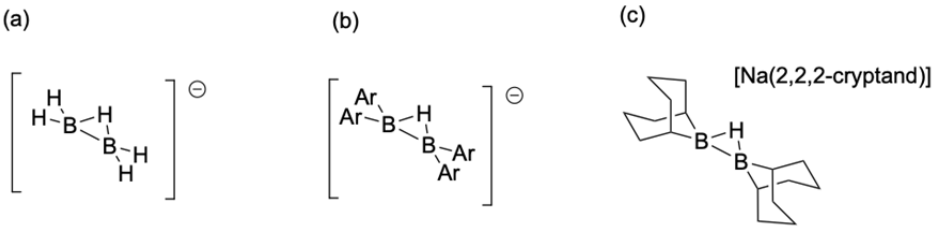


Figure 1: Shows the hypothetical structure of the $[H_2B$-$^{\mu}$H-$BH_2]^-$ (a), the state-of-the-art archetypical bulky aryl substituted anion $[R_2B$-$^{\mu}$H-$BR_2]^-$ (b) and complex **1** (c).

[1] M. Arrowsmith, H. Braunschweig and T. E. Stennett, Angew. Chem. Int. Ed., 2016, 56, 96-115

[2] X. Mao, J. Zhang, Z. Lu and Z. Xie, Chem. Sci., 2022, 13, 3009-3013

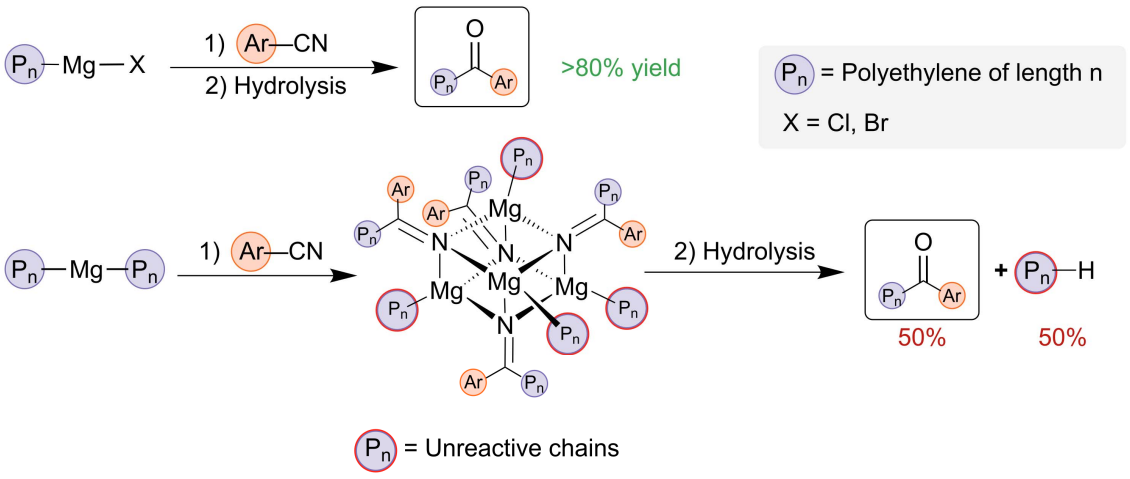
[3] A. Hübner, T. Kaese, M. Diefenbach, B. Endeward, M. Bolte, H. Lerner, M. C. Holthausen and M. Wagner, J. Am. Chem. Soc., 2015, 137, 10, 3705-3714

REACTIVITY OF GRIGNARD REAGENTS TOWARDS NITRILE IN CONTEXT OF POLYMERIZATION CATALYSIS

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The coordinative chain transfer (CCTP) polymerization of ethylene in toluene and diethyl ether uses neodymocene catalysts and organomagnesium complexes as chain transfer agents including dialkyl magnesium (MgR_2) or Grignard reagents (RMgX).[1] Reacting the Mg-C chain ends with nitriles affords ω-functionalized chains, enhancing polymers properties.[2] The nature of the organomagnesium compound plays a key role in the rate of functionalization. Grignard Reagents often aggregates and undergo Schlenk equilibrium which modify the reactivity along the reaction course.[3] This study relies on molecular modelling at the DFT level with extensive sampling to understand the influence of different chain transfer agents for functionalized polyethylene. The functionalization rate and extent can be limited by the formation of stable tetramers which trap unfunctionalized chains. The obstacles to efficient functionalization of polymers chain ends were identified thanks to extensive sampling of aggregation states. The outlined mechanism is not restricted to polymer chain end functionalization but also applies in the context of organic synthesis.



Scheme 1. Reactivity of P_nMgX and P_nMgP_n towards nitrile derivatives

[1] Ribeiro, R.; Ruivo, R.; Nsiri, H.; Norsic, S.; D'Agosto, F.; Perrin, L.; Boisson, C. *ACS Catal.*, **2016**, *6*, 851–860.

[2] Desgranges, A.; Jean-Baptiste-dit-Dominique, F.; Ngo, R.; D'Agosto, F.; Boisson, C. *Macromol. Rapid Commun.*, **2024**, *45*, 2400226.

[3] Peltzer, R. M.; Gauss, J.; Eisenstein, O.; Cascella, M. *J. Am. Chem. Soc.*, **2020**, *142*, 2984–2994.

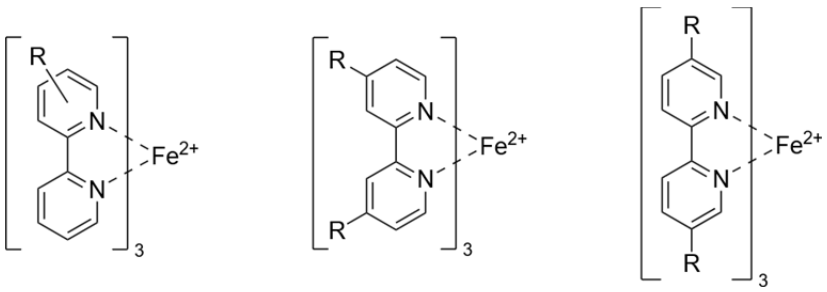
DISTINCTION OF *fac / mer* ISOMERS VIA ^{57}Fe NMR SPECTROSCOPY

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Technical University of Darmstadt, Darmstadt, Germany

Iron-57 is a spin ½ nucleus and the only NMR active iron isotope. Its low natural abundance (2.2 %) and extremely low gyromagnetic ratio (3.3 % relative to ^{1}H) make ^{57}Fe NMR spectroscopy challenging. The overall sensitivity is about three orders of magnitude smaller compared to ^{13}C at natural abundance. Despite these unfavourable magnetic properties, there is interest in ^{57}Fe NMR as it offers distinct advantages due to the high sensitivity of the nucleus to its chemical environment:[1] Like other transition metal nuclei, iron offers a very large chemical shift range covering several thousand ppm. With such a high signal dispersion, even minor structural changes result in separated ^{57}Fe signals, which allows for sensitive mapping of the electronic and magnetic surroundings of the iron atoms.[2] Secondly, while common NMR nuclei like hydrogen are often located in the periphery of transition metal complexes, the metal atom itself is associated with reactivity and therefore of special interest for direct probing. Given the inherent challenges in iron detection, ^{57}Fe NMR is still rather exotic. Currently, it is mostly applied for the investigation of Fe(0) and Fe(II) species, such as carbonyl complexes,[3] ferrocene derivatives[4] and iron in heme-like porphyrin structures.[5]

Herein we present the solution state ^{57}Fe NMR analysis of tris(bipyridine)iron(II) and a series of related homoleptic iron complexes with substituted bipyridine (bpy) ligands (structures shown below). The structures of these diamagnetic complexes are shown below. To date only one representative of this substance class has had its ^{57}Fe shift reported in the literature.[6] Utilising both direct and indirect detection techniques, we analyse the influence of the substitution pattern on the central iron atom and its chemical shift, and establish a frame of reference for ^{57}Fe chemical shifts in iron bpy complexes. Furthermore, we demonstrate that ^{57}Fe NMR spectroscopy allows the distinction of *facial* and *meridional* isomers, enabling the full signal assignment of these species in *fac/mer* mixtures.



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ACCURATE QUANTITATIVE EVALUATION OF Ni AND Co UV-VIS SPECTRA CALCULATED BY TD-DFT FUNCTIONALS

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This work presents a systematic benchmark of time-dependent density functional theory (TD-DFT) methodologies for predicting the ultraviolet-visible (UV-vis) absorption spectra of mononuclear nickel and cobalt coordination complexes. For this purpose, 20 nickel and 15 cobalt structurally diverse coordination complexes with experimental UV-vis spectra available were selected from the literature. All structures were optimized at the DFT/TPSSh(D4)/def2-TZVP/C-PCM(solvent) level of theory and TD-DFT calculations were made employing 17 functionals (BP86, OPBE, PBE, r^{2}SCAN revM06-L, TPSS, B3LYP/G, B97, M06, M06-2X, O3LYP, PBE0, TPSSh, CAM-B3LYP, ωB97X, ωPBE and PWPB95). The functionals were ranked according to a new strategy of quantitative evaluation that was introduced in our last work [1] that measure their effectiveness in reproducing both the excitation energies and the overall spectral shape observed experimentally, incorporating Gaussian broadening for bandwidth adjustment and applying energy shift corrections to the calculated transitions. For Ni compounds, the hybrid functional TPSSh yield the most accurate excitation energies while the also hybrid functional B97 demonstrated the best performance for reproducing the spectral shape, having a high average similarity to the experimental data while maintaining a smaller average shift. For Co compounds, the best performer for both excitation energies and spectral shape was the hybrid PBE0 functional by using the same criteria.

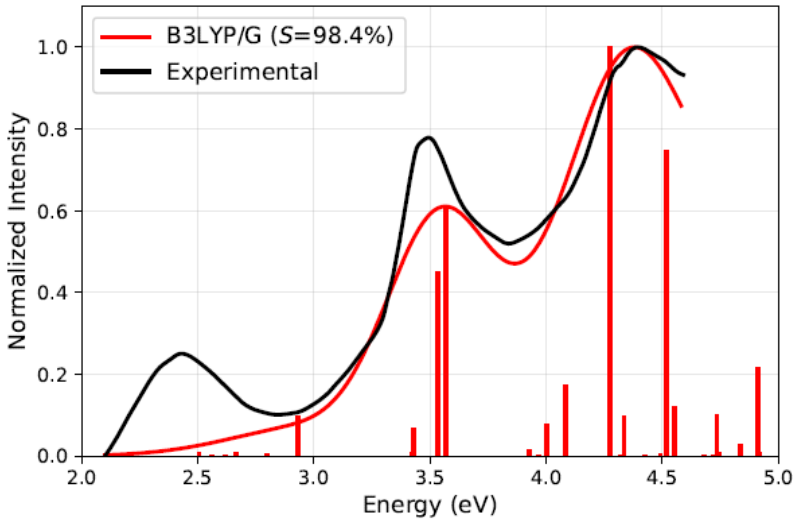


Figure 1: B3LYP/G/def2-TZVP calculated (red spikes) and optimized (red curve) TD-DFT spectrum of a Ni compound in comparison with experimental UV-vis data (black curve).

[1] Renan R. Bertoloni, Vania M. Ramos, Ana Paula de Lima Batista, and Antonio G. S. de Oliveira-Filho, "Benchmarking Structures and UV–Vis Spectra of Iron Complexes Against Experimental Data", J. Phys. Chem. A 2025, 129, 45, 10481–10495

OBSERVING EXCITED STATE PROPERTIES OF RUTHENIUM POLYPYRIDIL COMPLEXES IN THE SOLID STATE

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Photocatalysis continues to attract significant attention. Probing the electronic properties of these photocatalytic species typically involve measurements conducted in solution.

We introduce a development in single crystal X-ray diffraction to further expand the scope of this analysis into the solid state. Performing photocrystallographic measurements at subatomic resolutions allows features such as charge localisation and ligand preference to become experimentally observable that were once limited to computational methods.

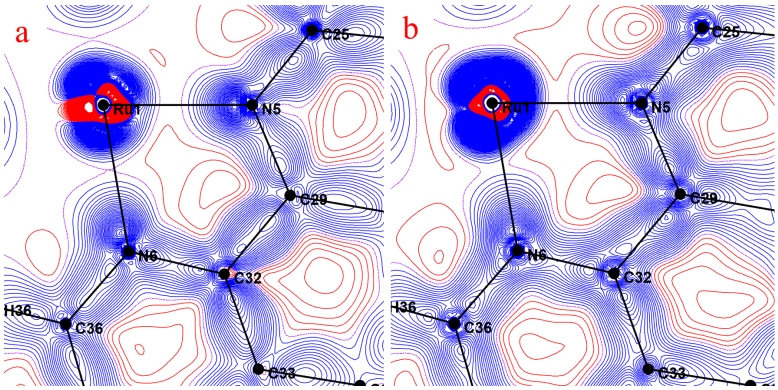


Figure 1. Static electron density map of ruthenium-nitrogen bonding of (2,2'-bipyridine)bis(1,10-phenanthroline)ruthenium(II) iodide when a) non-irradiated and b) irradiated.
Contour: 0.05 e/Å^2, blue: positive electron density.

DIMENSIONAL ENGINEERING AND SPIN-STATE PROGRAMMING IN METAL–ORGANIC MAGNETS VIA HEISENBERG PLATFORMS, SPIN-CROSSOVER ALLOYING, AND HYDROGEN-REDUCTION

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Molecule-based or low-dimensional framework magnetic materials are emerging as promising next-generation functional materials due to their rich quantum properties and structural tunability. Metal–Organic magnets, constructed through the self-assembly of metal nodes and organic linkers, provide exceptional lattice designability, precise control over exchange interactions, and the ability to reversibly modulate spin and electronic states through molecular design. Here we present a comprehensive strategy for dimensional engineering (1D–2D–3D) and spin/electronic-state programming in metal–organic magnets. An isostructural family of one-dimensional (1-D) chains, $[M(MeCN)_4(pyz)](BF_4)_2$ (**1-M**, M = Cu, Ni, Co, Cr, Mn; pyz = pyrazine), serves as a rare experimental platform that closely approximates ideal Heisenberg antiferromagnets. Systematic variation of the spin quantum number while preserving the isostructural chain framework provides an experimental platform grounded in well-established theoretical descriptions of 1-D antiferromagnets, as exemplified by the Bethe ansatz for S = 1/2 chains and Haldane's theory for integer-spin systems. Spin-crossover (SCO) Fe incorporation enables mixed-metal engineering in two structurally distinct pyz-based frameworks: the **1-Cr** chain and the redox-active Cr–pyz 2-D layer $[Cr(BH_3CN)_2(pyz)_2]$. Furthermore, hydrogen reduction of the trinuclear-cluster-based MOF MIL-101-(M) demonstrates a post-synthetic strategy for chemically modulating cluster electronic states, expanding the functional scope of porous metal–organic magnets. Collectively, these results establish a unified molecular design framework that integrates quantum model platforms, spin-crossover-driven alloying, and redox-controlled post-synthetic modulation, advancing metal–organic magnets toward switchable and tunable magnets.

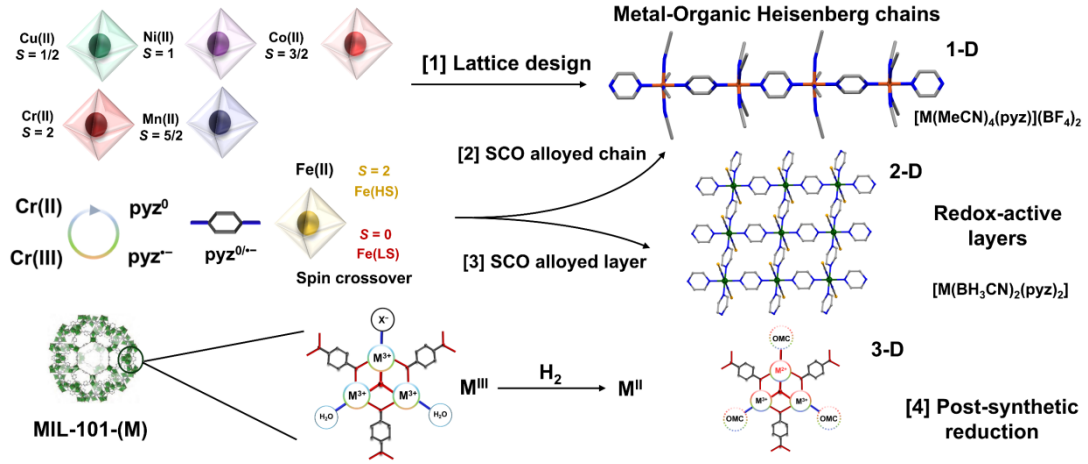


Figure 1. Schematic illustration of (i) Heisenberg-type 1-D chain platform (**1-M**), SCO-enabled mixed-metal (ii) 1-D and (iii) 2-D Cr–pyz frameworks. (iv) post-synthetic electronic-state modulation of 3-D MOFs MIL-101 via hydrogen reduction.

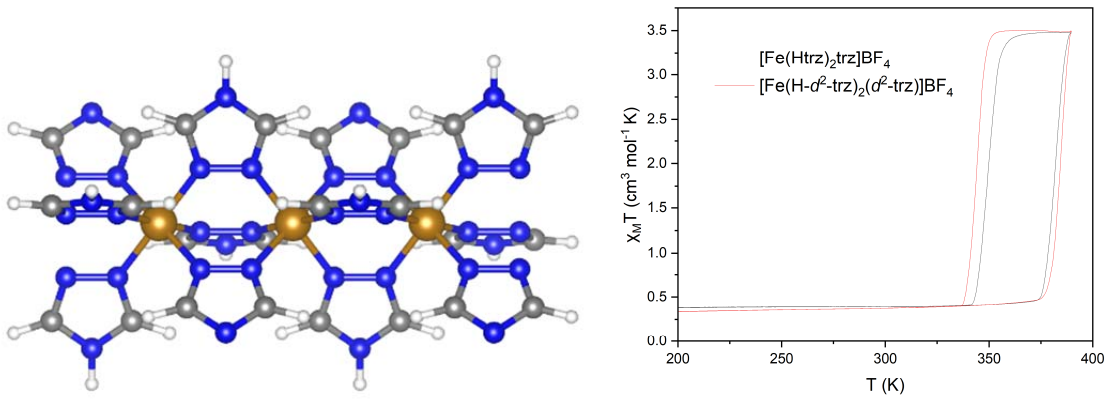
DEUTERATION OF IRON(II)/TRIAZOLE SPIN-CROSSOVER COORDINATION POLYMERS

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The coordination polymers $[Fe(Rtrz)_3][A]_x{\cdot}nH_2O$ (Rtrz = a 4-substituted-1,2,4-triazole, A = anion) have potential applications in nanoelectronics, mechanical actuators, memory devices, sensors and refrigeration, making them popular materials in spin-crossover (SCO) research. These 1-dimensional polymer structures with 1,2,4-triazole ligands show abrupt SCO transitions with thermal hysteresis, around and above room temperature [1]. Their Fe^{2+} cations have the ability to switch from diamagnetic to paramagnetic, creating an 'on' and 'off' function ideal for devices. While limited structural data are available, it is known the coordination polymer chains align co-parallel in the solid state, and are linked by strong intermolecular C−H···A hydrogen bonds [2].

Studies of the effect of deuteration on SCO materials have given contradictory results; different materials show a significant increase in $T_{1/2}$ [3], a smaller decrease in $T_{1/2}$ [4-7] and/or a narrowed hysteresis loop [8] upon deuteration. These inconsistent results have not yet been explained, and it is unclear why deuteration of an organic ligand should influence the spin state of a coordinated metal ion. To address those questions, we have prepared protio and per-deutero samples from the well-known $[Fe(Htrz)_2trz]BF_4{\cdot}nH_2O$ system [1,2]. THz spectra and solid state DFT calculations will be presented to quantify the effect of deuteration on their lattice entropy.



Left: fragment of a $[Fe(Htrz)_2trz]_n^{n+}$ coordination polymer chain [2]. Right: magnetic data from polymorph 1 of $[Fe(Htrz)_2trz]BF_4$ and $[Fe(H\text{-}d^2\text{-}trz)_2(d^2\text{-}trz)]BF_4$.

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MODULATION OF SPIN CROSSOVER PROPERTIES IN A SERIES OF $[Fe^{II}(N_4S_2)]$ COMPLEXES BY LIGAND-DISSYMETRY

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Spin crossover (SCO) complexes can reversibly switch between the high- and low-spin states upon application of an external stimulus, most commonly temperature. [1] This phenomenon occurs mainly in octahedral transition metal complexes within an N_6 coordination sphere. Concurrently with spin state switching, other physicochemical properties change as well, making these types of materials promising candidates for the development of sensors, molecular switches, and nanodevices [1,2]. Recent studies have shown that the N_4S_2 coordination sphere also produces SCO-active complexes, particularly those containing thioether groups that prevent oxidation to Fe^{3+}. SCO parameters, such as the transition temperature ($T_{½}$), can be tuned by the nature of the counterion, the ligand substituents, and/or the presence of solvent molecules [3]. However, the influence of the ligand symmetry remains largely unexplored. In this work, we studied a series of $[Fe^{II}(N_4S_2)][BF_4]_2$ complexes using symmetric (C_{2v}) and dissymmetric (C_s) ligands based on bis-(2-picolyl)thioether (Py_2S). The *dissymmetric* ligands contain different substituents on each pyridine ring. Magnetic measurements indicate that both complex types exhibit SCO in the solid state and in solution. A shifting of molecular symmetry is observed in complexes containing dissymmetric ligands, changing from C_{2h} point group to C_2 or C_i. In solution, complexes with dissymmetric ligands exhibit $T_{½}$ values intermediate to those of their symmetric counterparts, indicating that electronic effects predominate. Furthermore, the $T_{½}$ is predictable through a correlation between the ligand field (ΔO_h) and $T_{½}$, confirming that ligand dissymmetry allows for fine-tuning of SCO properties in solution. On the other hand, as expected, SCO properties in the solid phase are governed by packing effects, where ligand dissymmetry acts as a key factor in determining the supramolecular interactions within the crystal lattice.

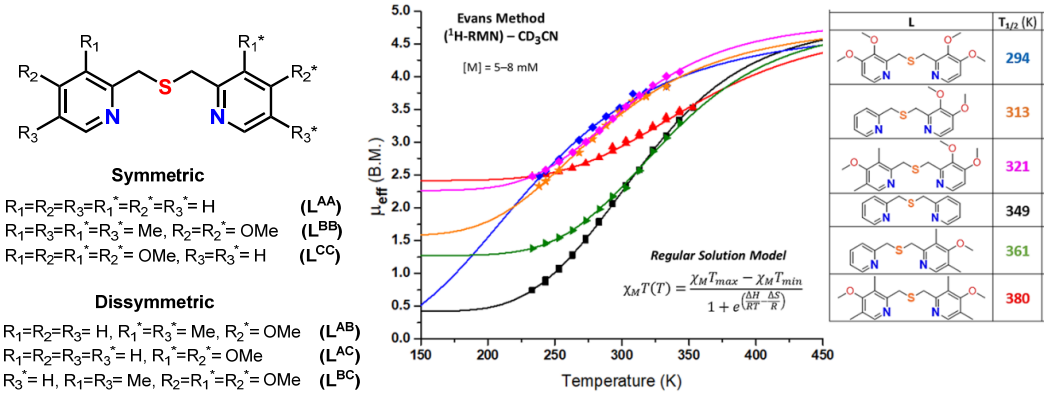


Figure 1. (2-picolyl)thioether-based ligands used in this work (left); magnetic profile in MeCN solution of $[Fe^{II}(N_4S_2)][BF_4]_2$ complexes (right).

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MULTIFUNCTIONAL Fe(II) MOLECULAR CHAMELEONS BASED ON 1,3,4-OXADIAZOLE LIGANDS

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Manipulating electronic arrangements in response to stimuli makes bistable spin switches an ideal candidate for potential application in various fields including sensors and displays. Divalent iron is most studied for spin transition because of its drastic change in the magnetic behaviour from S=0 to S=2.[1] In designing these molecular switches, materials chemist has bundled up other interesting properties including luminescence as this can be used to monitor the spin switch.[1] Complexes based on 1,3,4-oxadiazole showing spin transitions are seldom reported in literature. Here we report the first mono-nuclear Fe(II) spin crossover complex along with an interplay of luminescence and spin crossover properties.[2] In the presentation the effect of the co-ligand and the crucial role of the lattice solvent in tuning the geometry and spin crossover behaviour of these complexes will also be discussed.[3-5]

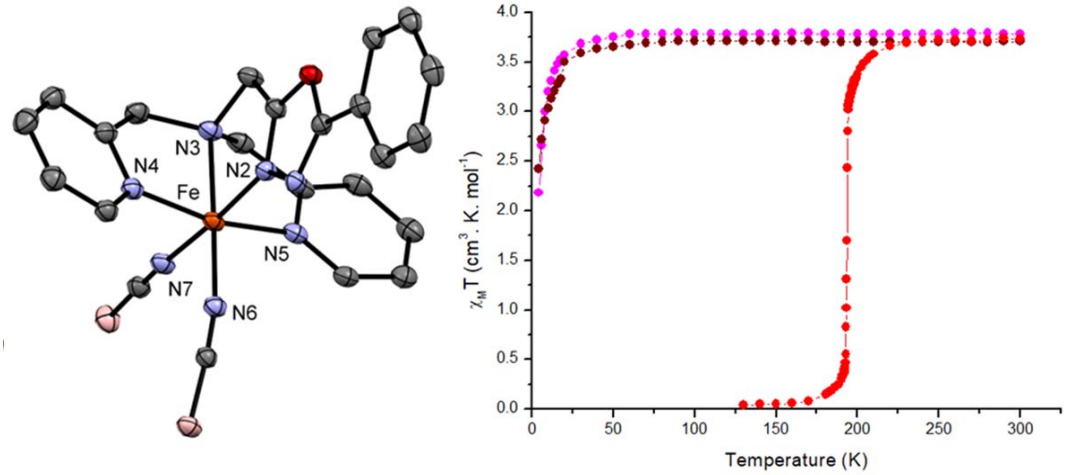


Figure. Left: Crystal strucutre of complex $[Fe^{II}(\mathbf{L}^{\mathbf{TertPy\text{-}ODA}})(NCBH_3)_2]$; Right: Temperature dependent $\chi_M T$ *vs* T.

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TARGETING HIGH T(LIESST) IN SPIN-CROSSOVER COMPLEXES

Srividhyadevi Chandrasekaran, Wenbin Guo, Guillaume Chastanet, François Riobe, Mathieu Marchivie, Nathalie Daro, Cédric Desplanches, Philippe Guionneau

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Spin-crossover (SCO) is a phenomenon observed in certain transition metal complexes, typically those of Fe(II), where the metal center can reversibly switch between low-spin and high-spin states in response to external stimuli, such as temperature, pressure, or light [1]. This transition is accompanied by changes in magnetic, optical, and structural properties, making SCO systems attractive for molecular switching and data storage applications [2]. The Light-Induced Excited Spin-State Trapping (LIESST) effect plays a pivotal role in the development of functional molecular devices based on spin-crossover (SCO) complexes [3]. A major challenge is the rational design of compounds that exhibit high T(LIESST) values, T(LIESST) being the temperature above which the lifetime of the photo-induced state becomes too short to consider applications. As reported by Marchivie et al., elevated T(LIESST) is associated with significant distortion of the Fe(II) coordination sphere during the spin-state transition [4].

In this work, we aim to enhance T(LIESST) by intentionally introducing structural distortions into the coordination environment. We focus on the well-known SCO family of complexes with the general formula $[Fe(PM\text{-}zA)_2(NCS)_2]$, where PM represents 2-pyridylmethylene and A is an aniline derivative. Selective substitution of one or two hydrogen atoms on the aniline ring with electron-donating methyl or electron-withdrawing fluorine groups at the ortho, meta, or para positions allows systematic evaluation of steric and electronic effects on the spin-transition properties. To rationalize the substituent effects, density functional theory (DFT) calculations were conducted in parallel with synthesis and experimental characterization.

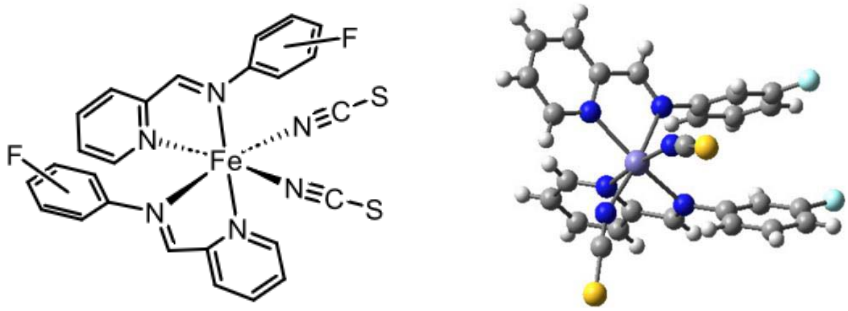


Figure: Target compounds $[Fe(PM\text{-}zFA)_2(NCS)_2]$ (z = o, m, p), Crystal structure of $[Fe(PM\text{-}mFA)_2(NCS)_2]$.

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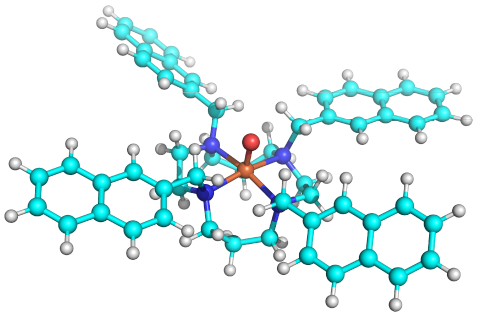
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A DFT STUDY ON DIFFERENT CONFORMATIONS OF IRON-OXO 14-TNC

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High-valence iron-oxo species as interesting intermediates found in biological reactions that are essential for life on Earth and, in recent years, understanding how the electronic structure of these species influence their reactivity has become a topic of great interest among researchers [1-2]. Transition metal centers, such as iron, play a very important role in biological and chemical reactions because these metals have the ability to bind oxygen and undergo redox transformation [1-4]. Inspired by these systems, numerous synthetic metal–oxo complexes have been developed and characterized [3, 5]. In this study, we seek to build upon previous study of the $[Fe(IV)(O)(14\text{-TNC})]^{2+}$ compound by replacing the N-methyl substituents in 14-TMC with naphthylmethyl pendant groups, affording 14-TNC. This structural modification introduces a significant bulk to the structure, and the consequences of this change on the geometry of the complex were investigated by DFT calculations. Our goal was to look into different spin multiplicities and structural conformations as they were systematically evaluated to determine the ground-state configuration of the complex. The triplet spin state was found to be the lowest in energy among all the multiplicities considered in this investigation. Along with that, the most stable geometric arrangement for $[Fe(IV)(O)(14\text{-TNC})]^{2+}$ is also reported and discussed.



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EXPLORING THE LIGAND CHEMICAL SPACE OF THE $[Cr(Tpm^{R})_2]$ SPIN-CROSSOVER FAMILY

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Spin-crossover (SCO) systems are transition metal complexes where the metal center can adopt two electronic states with different spin configurations close in energy. This allows the molecule to switch between states in response to an external stimulus such as temperature or pressure. As a result, these molecules are excellent candidates for molecular switches, with potential applications in memory storage devices.[1]

A key parameter in characterizing these systems is the transition temperature, $T_{1/2}$, defined as the temperature at which both spin states are in equilibrium.[2] For technological applications, $T_{1/2}$ must fall within the range of room temperature, making its accurate prediction crucial.

Although in principle these phenomena could be present for d^4 to d^7 metal ions, the SCO field is overwhelmingly dominated by Fe(II). In particular, Cr(II) based spin-crossover systems are quite scarce and just 6 systems have been synthesized. In 2025, Liu and co-workers reported that the $[Cr(Tpm)_2]X_2$ complexes (Tpm = trispyrazoyl methane, $X=BF^{4-}$ or ClO^{4-}) exhibits SCO behaviors with $T_{1/2}$ of 190K and 194K depending on the counterion, while the closely related system $[Cr(Tpm^{3,5\text{-}Me})_2]X_2$ is a high-spin molecule.[3] Expanding the set of d^4-Cr(II) based SCO systems is a challenging field. Thus, the computational study of these systems can shed light in how to explore the ligand chemical space to tune their $T_{1/2}$.

In this work electronic structure calculations on the $[Cr(Tpm^{R})_2]^{2+}$ molecule, figure 1, have been carried out to analyze the role of steric, inductive and resonant effects and their interplay over the splitting of the d-based molecular orbitals and the $T_{1/2}$.

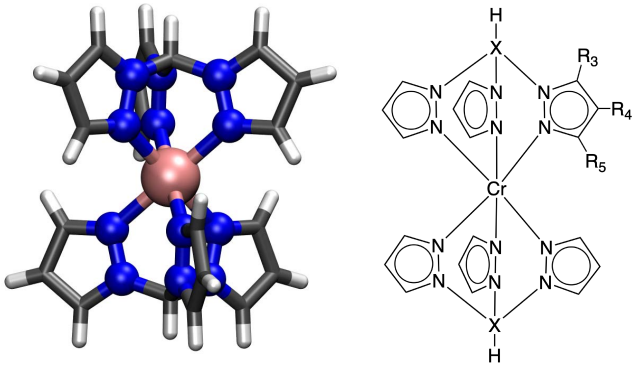


Figure 1: Left, molecular representation of $[Cr(Tpm^{H})_2]^{2+}$. Right, schematic depiction of the studied system with the pyrazole ring functionalized positions (R_3, R_4 and R_5) and the apical position of the ligand (X=C or B)

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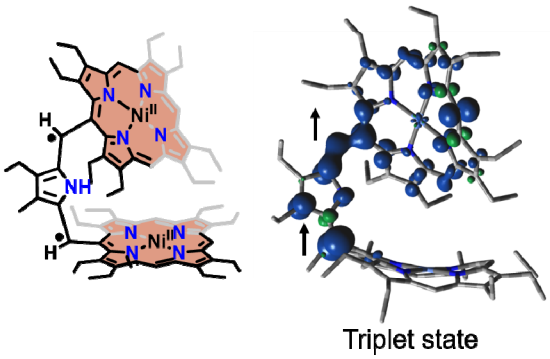
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SINGLET VS TRIPLET DIRADICALS: CONTROL OF SPIN COUPLING VIA CONFORMATIONAL CHANGE

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High-spin organic radicals are of significant interest because of their applications in spintronics, magnetic materials, and related technologies. While several nonporphyrinic systems stabilize diradical states through ligand design, porphyrins provide an attractive platform owing to their extended π-conjugation and redox versatility. Notably, examples have demonstrated triplet diradical stabilization in porphyrinoid systems. Herein, we report a diethyl pyrrole-bridged nickel porphyrin diradical, $Ni_2DEPO^{\bullet}$, generated under 390 nm photoirradiation. The complex exhibits a triplet ground state, confirmed by EPR spectroscopy and magnetic studies. This stabilization arises from the nearly orthogonal arrangement of the two porphyrin units, with the unpaired electrons localized on the bridging linker. Treatment with N-chlorosuccinimide (NCS) induces halogen substitution at the bridge, leading to a more open conformation that favors the singlet state. Similar singlet-state conversion is observed upon oxidation with $FeCl_3$ or $AgSbF_6$. These results establish a clear magneto-structural correlation, where the relative orientation of the two porphyrin units governs the spin state, providing a strategy for controllable singlet–triplet state in porphyrin diradicals. [1-6]



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STRUCTURAL DIVERSITY AND PHOTOLUMINESCENT PROPERTIES OF ZINC AND CADMIUM SILANETHIOLATES WITH PYRIDINE DERIVATIVES

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Gdańsk University of Technology, Gdańsk, Poland
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Adam Mickiewicz University in Poznań, Poznań, Poland

The development of new coordination systems exhibiting intense luminescence, high color purity and high quantum yields of emission is one of the main goals of modern coordination chemistry [1]. Thus, significant emphasis is put on understanding the structure-property relationship resulting from the combination of specific molecular precursors. Pyridine-based chromophores are widely used in visible light emitters with d- and f- block metals. In this study we investigate the structural-spectral relationships in Zn and Cd complexes containing aminopyridines and aminomethylpyridines as N-donor ligands and a bulky tri-*tert*-butoxysilanethiolate S-donor ligand, which facilitates the formation of diverse coordination architectures providing a structural stabilization to the resulting complexes [2]. A series of 14 new mono-, bi- and polynuclear complexes were synthesized and obtained as single crystals noticeably stable in atmospheric conditions. All compounds were thoroughly characterized by single crystal X-ray diffraction, FTIR, UV-vis spectroscopy and their luminescent properties were evaluated in both solution and the solid-state.

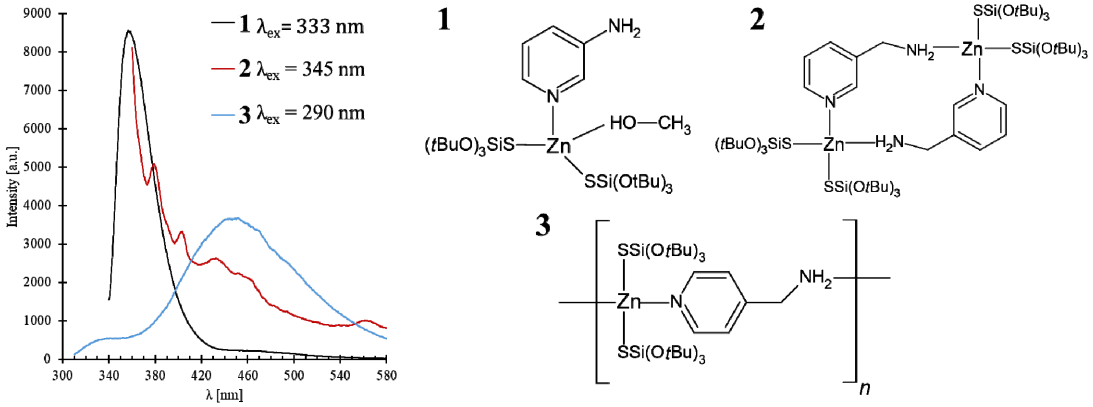


Figure 1. Solid-state emission spectra of compounds **1-3** (on the left) and their molecular structures (on the right).

Figure 1 presents emission spectra of selected representatives of Zn silanethiolates of different nuclearity. Compound $[Zn\{SSi(OtBu)_3\}_2(3\text{-ap})(CH_3OH)]$ (**1**) (3-ap - 3-aminopyridine) exhibit the most intense emission among all obtained complexes, whereas polynuclear complexes $[Zn\{SSi(OtBu)_3\}_2(\mu\text{-4-amp})\cdot CH_3OH]_n$ (**3**) (4-amp 4-aminomethylpyridine) displays broad emission profile, characterized by a significant bathochromic shift of emission bands.

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MULTI-SCALE MODELLING FOR AN ACCURATE PREDICTION OF REDOX POTENTIALS IN IRON COORDINATION COMPOUNDS

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Accurately predicting the absolute redox potentials of molecular systems remains a challenge in computational chemistry. Redox-active iron complexes possess a complex electronic structure, with multiple accessible oxidation states that require high-level quantum mechanical protocols. Besides, the electronic structure of iron complexes is strongly influenced by ligand-field effects, spin crossover effects and solvent interactions, increasing the complexity of an ideal model. Recent studies have demonstrated that a multistep explicit solvation approach, combining quantum mechanics/molecular mechanics (QM/MM) molecular dynamics with the linear response approximation, can provide highly accurate redox potential predictions for organic molecules.[1] The inclusion of corrections like solvent polarization and bulk solvation through explicit solvation significantly improves the agreement with experimental redox potentials compared to traditional implicit solvation models.[2] By extending this methodology to iron-based redox pairs, our study aims to explore its transferability and refine the computational framework to tackle the challenges posed by transition metal redox chemistry.

In this work, we develop a QM/MM molecular dynamics (QM/MM-MD) protocol to study redox reactions of mononuclear iron complexes in explicit solvation using a semi-empirical QM description through the python-based multiscale modelling program ASH.[3] A calibration set of iron complexes with reported experimental redox potentials was used to benchmark the accuracy of different levels of theory for the MD trajectories and the linear response snapshots. The final computed redox potentials offer insights into the influence of explicit solvation and spin-state effects and will be used to assess the accuracy and limitations of the method in the context of transition metal redox chemistry. We will discuss the performance of the method for anionic and cationic species, highlighting advantages and limitations of the approach.

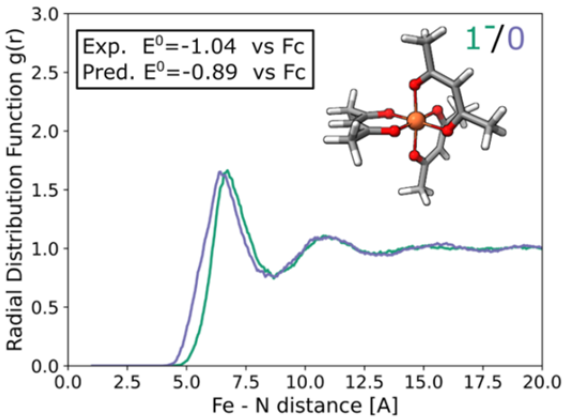


Figure 1. Radial Distribution Functions (RDFs) for the $Fe(acac)_3$ in its reduced (green) and oxidized (purple) states.

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MAPPING THE INVERTED MARCUS REGION OF NOVEL COBALT BASED COMPLEXES

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Recently, Co(III) complexes with suprisingly long-lived excited states and favourable photoredox properties were identified by the group of James McCusker and others. The long-lived nature of the underlying metal centered (MC) states is rationalized by their inverted Marcus region behaviour. [1-3].

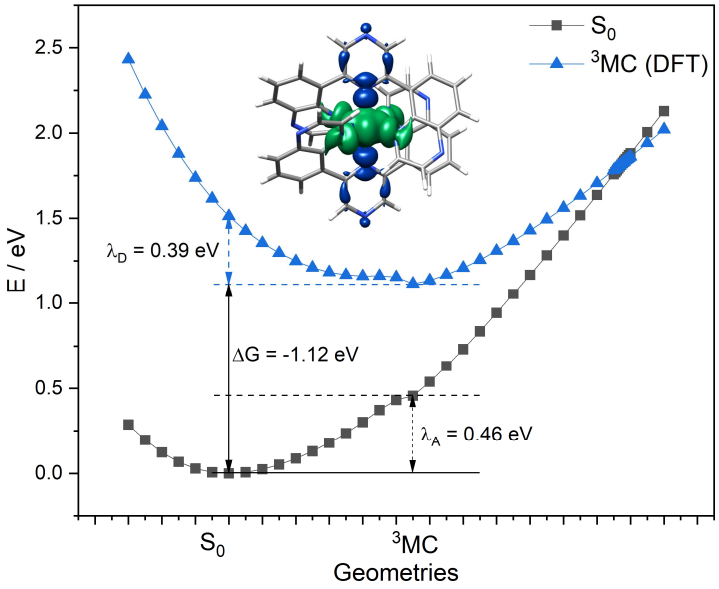


Figure 1: Quantum chemical mapping of the inverted Marcus region of $Co(dqxpz)_2^{3+}$. The inset represents the ^{3}MC spin density.

In the present study, we investigate a series of Co(III) complexes with different ligand spheres. Within this series $Co(bpy)_3^{3+}$ functions as parent species, while the impact of other bidentate and monodentate ligands are systematically investigated in a joint spectroscopic-theoretical approach, i.e. for $Co(dqxpz)_2^{3+}$, $Co(bpy)_3^{3+}$ and $Co(CN)_6^{3-}$. Interestingly, within the structurally diverse set of ligand fields the six $^{1/3}$MC states split into three energetically low-lying states which involve the $d_{x^2-y^2}$ acceptor orbital and three higher lying d_{z^2} acceptor states.

To address the non-radiative relaxation processes as well as the kinetics and lifetimes of the lowest ^{3}MC state, we apply semi-classical Marcus theory to these complexes. Furthermore, we map the Marcus inverted region at different levels of theory, such as XMS-RASPT2 as well as DFT/TDDFT.

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PHOTOACTIVE IRON(II) *bis*-(2,6-DIPYRAZOL-1-YL PYRIDINE) SPIN-CROSSOVER COMPLEXES FUNCTIONALISED WITH PROXIMAL HETEROARYL AZO SUBSTITUENTS

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Ligand Driven Light-Induced Spin Crossover (LD-LISC) is a photophysical phenomenon where certain 3d metal complexes, functionalised with photoactive molecular switch moieties in their ligand framework, can alter their spin-state equilibrium upon light irradiation due to photoisomerisation reactions (i.e. *cis/trans,* ring opening/closing) in the ligand framework, which cause alterations in the ligand field. [1-3] Due to their photochromic and photomagnetic properties, LD-LISC complexes are of interest within potential applications such as MRI contrast agents and data storage devices.[1-3] Heteroaryl azopyrazole groups (Ar−N=N−Pz – where Ar represents a non-pyrazolic aromatic group, Pz = pyrazole) are particularly good candidates for implementation within this area due to their near-quantitative, reversible, *E*↔*Z* photoswitching capabilities and high thermal stabilities of the metastable *Z*-isomers.[4]

Herein, we report the first iron(II) complexes synthesised with photoactive substituents at the 3-pyrazole position. The physicochemical effects which photoactive substituents located at such a proximity to the metal centre have upon the spin-crossover properties are yet unreported and remain of interest to our group. Solution-phase magnetic susceptibility data, calculated by Evans ^{1}H NMR, photoisomerisation data delineated by UV-visible spectroscopy, crystallographic and SQUID data will all be presented, as well as mechanistic insights via DFT calculations.

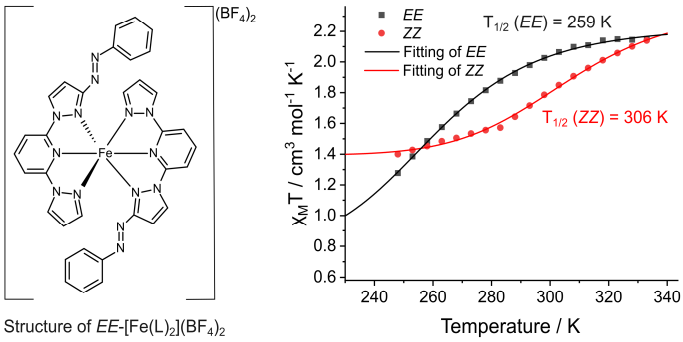


Figure – Structure of novel complex (left), MeCN solution phase magnetic data of *EE*-$[Fe(L)_2](BF_4)_2$ and *ZZ*-$[Fe(L)_2](BF_4)_2$ (right).

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DENSITY MATRIX RENORMALIZATION GROUP TO TARGET CORE EXCITED STATES OF TRANSITION METAL COMPLEXES

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Core-level spectroscopy offers a powerful tool to probe the electronic structure of molecules, but the accurate simulation of core-excited states remains challenging in systems with strong electron correlation. In this work, we combine core-valence separation (CVS) with the density matrix renormalization group (DMRG) to create an efficient and scalable framework for targeting core-excited states with large active spaces. The method avoids the need to resolve the full manifold of lower-lying valence states and is therefore well suited for difficult excited-state problems in multireference chemistry.

We test the approach on both a small benchmark system and transition-metal complexes, where it reproduces reference excitation energies and spectral features with high fidelity across multiple core edges. The results show that the method is robust for different types of core orbitals and remains effective even in cases where standard multireference treatments become impractical. Furthermore, the CVS framework is extended to a multi-core-valence separation scheme to describe hole-screening effects in doubly core-excited states. We also analyze the core-valence separation using quantum-information diagnostics, which provide a clearer picture of how the approximation acts on the wavefunction. Finally, a second-order perturbative correction is introduced to improve the accuracy of the excitation energies while preserving the computational advantages of the approach.

Together, these results establish core-valence separated DMRG as a practical tool for modeling X-ray spectra in strongly correlated molecular systems. The multi-core generalization could also be applied to systems with multiple metallic centers, where several localized core regions interact with a shared valence manifold. This opens a route toward more flexible and physically realistic simulations of complex core-level spectra in extended or multi-center transition metal systems.

SPIN-POLARON INTERACTIONS IN PARAMAGNETIC PORPHYRINS

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Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Oxford, United Kingdom

Porphyrins are well-studied aromatic macrocycles crucial in many biological processes like oxygen transport and photosynthesis [1]. Recently, due to strong coordination to transition metals and significant π-delocalisation, synthetic porphyrin nanostructures have become a popular and interesting platform for studying various molecular electronics and spintronics systems, such as spin valves [2], molecular qubits [3], molecular magnets [4], and quantum logic gates [5].

Earlier studies of those systems focused mostly on the behaviour of either the spin in the ligand's organic framework or the paramagnetic metal centres alone. We combine those two approaches, utilising metal-ligand interactions and the delocalized nature of ligand π orbitals to manipulate the spin behaviour of the copper(II) porphyrin nanostructures.

Adopting this strategy, we designed, synthesised, and characterised a series of copper(II) porphyrin complexes. Introducing the cationic polaron into the ligand's π system allowed us to extend control over the spin properties of those molecules. We discovered that, depending on the locus of the oxidation, the polaron can effectively quench the effects of exchange coupling in weakly coupled spin pairs or lead to the formation of the stable high-spin states (triplet, quartet) from simple copper(II) doublets.

This work provides a simple platform for on-the-spot generation of high-spin species and deepens our understanding of metal-ligand spin interactions. This insight is relevant for the design and implementation of molecular qubits, quantum logic gates and molecular spintronics.

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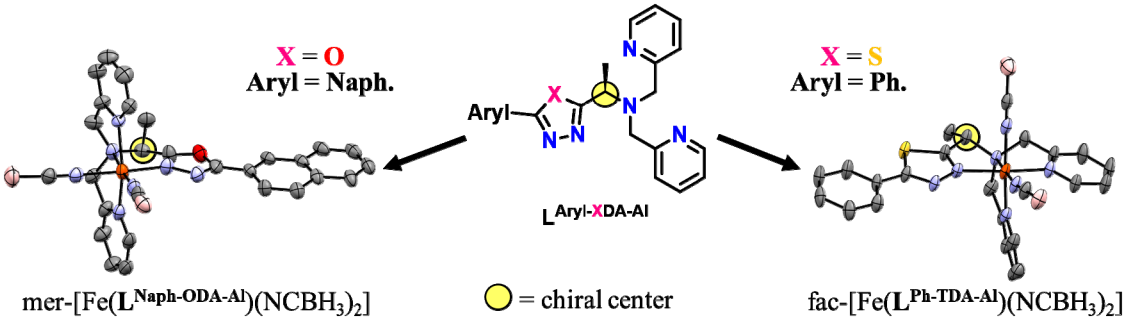
DOES CHIRALITY MATTER? DISENTANGLING SYMMETRY AND PACKING EFFECTS IN Fe(II) COMPLEXES

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Spin crossover (SCO) in Fe(II) (d^6) complexes, characterized by reversible switching between high-spin (S = 2) and low-spin (S = 0) states, is a well-established platform for molecular switching in coordination chemistry.[1,2]

The incorporation of chirality as a property within SCO systems extends the conceivable functions and plays a key role in the design of multifunctional materials. This ranges from ferroelectric devices to stereochemically controlled crystal architectures.[3,4] However differences in molecular packing between racemic and enantiopure systems typically lead to distinct SCO behaviors.[4] This presents a significant challenge in terms of disentangling the intrinsic influence of chirality.



Here, we address this challenge through rational ligand design. Two closely related ligand systems, differing only in the aryl substituent and the core heterocycle based on 1,3,4-oxadiazole vs. 1,3,4-thiadiazole, were developed, and their corresponding Fe(II) complexes were synthesized in both enantiopure (R, S) and racemic forms.

In case of fac-[Fe($L^{Ph\text{-}TDA\text{-}Al}$)$(NCBH_3)_2$], the racemate remains locked in the high-spin state, whereas the enantiopure complexes exhibit an abrupt spin transition ($T_{1/2}$ = 195 K), consistent with the expected paradigm. Detailed analysis of intermolecular interactions, supported by computational packing studies and nuclear inelastic scattering (NIS), provides a rationale for this behavior.

In contrast, mer-[Fe($L^{Naph\text{-}ODA\text{-}Al}$)$(NCBH_3)_2$] breaks this paradigm: all three complexes crystallize in the same space group and display identical gradual spin transitions ($T_{1/2}$ = 150K), as confirmed by PXRD, variable-temperature SCXRD, and SQUID magnetometry.[5] Continuous chirality measurements further reveal how subtle ligand modifications can decisively influence the spin-crossover characteristics.

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RELATIONSHIP BETWEEN Fe-Co PEROVSKITE STRUCTURES AND THEIR NÉEL/CURIE TEMPERATURES

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Fe-Co perovskites, such as $SrFe_xCo_{1-x}O_{3-d}$ (x = 0, 0.2, 0.4, 1 & d = 0-0.5) are catalysts for oxidative dehydrogenation of alkanes. Through oxygen vacancy (Vo) formation released lattice oxygen is used for the dehydrogenation as in a Mars-van Krevelen mechanism [1]. The formation of Vo changes the structure and the magnetic properties of the materials due to alteration of (super-)exchange interactions. The magnetic behaviour of these materials was probed with temperature series using continuous wave (CW) electron paramagnetic resonance (EPR) and a Curie-Weiss analysis (Fig. 1 left & middle). We derived structure proposals from EPR lineshapes recorded at >290 K during in-situ CW-EPR measurements. Additional valuable information about conductivity changes during reduction and oxidation was obtained from slow changes in reflected microwave power (Fig. 1 right).

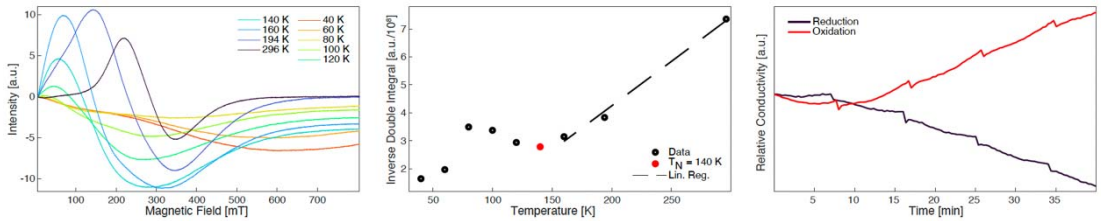


Fig. 1 Experimental results of $SrFe_{0.4}Co_{0.6}O_{3-d}$. CW-EPR temperature series (left), Curie-Weiss analysis (middle) of the data on the left, relative conductivity data measured during the in-situ CW-EPR (right).

The aim of this project was to theoretically understand the experimental findings by performing an in-depth analysis of the (super-)exchange interactions in these materials and relate the magnetic properties and conductivity to Vo and induced structural changes. We could rationalize the magnetic behaviour and the structures of three out of four of these perovskites using the Goodenough Kanamori rules [2], whereas these rules failed to explain the observed conductivity trend. To rationalize the conductivity we included the RKKY interaction, which deals with the exchange interactions of localized spins with itinerant electron spins [3]. We were able to analyse the $SrFeO_{3-d}$ material in more detail with the Anderson rules [4], because the crystallographic structures and data on magnetic properties of the oxygen-deficient structures were available [5]. With a few simple assumptions, we found a linear correlation between the amount of Vo in a unit cell and the relative number of antiferromagnetic interactions in this unit cell. We therefore hypothesize a correlation between the structures of perovskites and their magnetic properties, such as the Néel/Curie temperatures. To generalize this model, we will need to introduce weights for the various superexchange interactions in the unit cell, which take bond lengths and tilt from bond axis into account.

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FAST SPIN-CROSSOVER PROCESSES IN IRON(II) COMPLEXES CONTAINING π-RADICAL LIGANDS

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The most intensively studied spin-crossover (SCO) complexes contain iron(II) ions. In SCO processes of iron(II) complexes with closed-shell ligands, two distinct quadrupole doublets are typically observed in Mössbauer experiments for the participating low-spin and high-spin species below 250 K [1].

We are interested in SCO complexes in which the metal ion is coordinated to radical ligands [2,3]. As part of this study we prepared iron(II) complexes containing a neutral tetraazamacrocycle and anionic radical derivatives of an α-diimine as ligands. Characterization of the resulting octahedral iron(II) radical complexes by structural, magnetochemical and spectroscopic methods reveal that spin crossover equilibria occur between an $S = 1/2$ ground state and an $S = 3/2$ excited spin state. Using dynamic Mössbauer spectroscopy it can be shown that the spin interconversion rate at the iron(II) site is considerably enhanced by the presence of a coordinated π-radical.

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PROPERTIES OF IRON PHTHALOCYANINES BY pNMR

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Iron phthalocyanines are widely used as catalysts and as models for biologically relevant molecules. However, four-coordinate Fe(II) systems are barely soluble due to aggregation, which hinders solution studies and characterization. Most investigations have been carried out in coordinating solvents, which may alter the identity of the species under investigation. Magneto-electronic properties in particular are strongly influenced by such effects. Solubility in a non-coordinating environment can be achieved by either introducing bulky substituents [1] or by deformation of the Pc ligand [2]. We have synthesized several paramagnetic FePc derivatives and studied their magneto-electronic structure and their reactivity by pNMR spectroscopy. This approach enables the rapid identification of a wide range of iron phthalocyanine species, effectively transforming the NMR tube into our reaction flask.

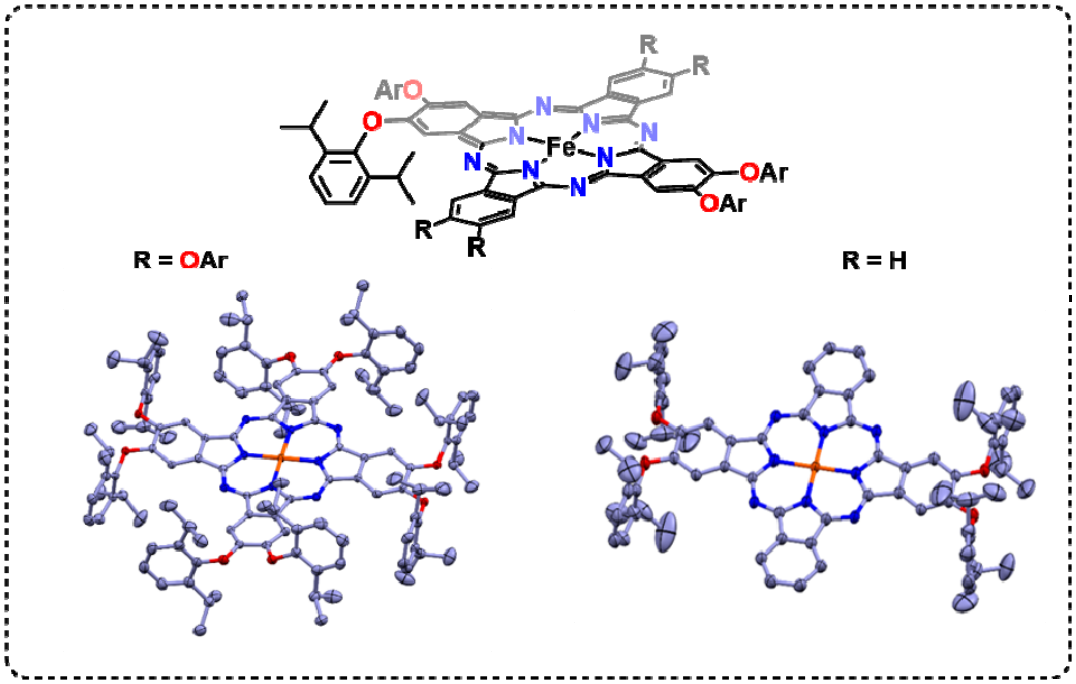


Figure 1. Solid state molecular structure of two iron(II)phthalocyanines in the absence of coordinating solvents.

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SPIN CROSS-OVER (SCO) PROPERTIES OF A SERIES OF IRON(II) COMPLEXES

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A series of mononuclear Fe(II) complexes, namely $[Fe(X\text{-}PIP)_3](ClO_4)_2 \cdot CH_2Cl_2$ (HPIP = 3-(pyridin-2-yl)imidazo[1,5-a]pyridine; X = Cl (**1**), Br (**2**), and I (**3**)) and $[Fe(X\text{-}PIP)_3](BF_4)_2 \cdot CH_2Cl_2$ (X = Cl (**4**), Br (**5**), and I (**6**)), were successfully synthesized and characterized to investigate the synergistic regulation of spin-crossover (SCO) properties by halogen substituents and counterions (Figure 1). Magnetic measurements verified that all complexes undergo gradual SCO, with transition completeness dominated by substituents: iodine-substituted complexes (**3**, **6**) achieved the most complete transitions due to flexible coordination environments and moderate ligand-field strength, while chlorine-substituted complexes (**1**, **4**) showed incomplete transitions caused by higher energy barriers from stronger ligand fields, and bromine-substituted complexes (**2**, **5**) presented intermediate behavior. Counterion effects were found to be coupled with substituent properties: in iodine-substituted systems, the ClO_4^- salt (**3**) showed more complete transitions than the BF_4^- analogue (**6**), whereas the opposite trend was observed in chlorine-substituted systems, demonstrating a complex synergistic mechanism modulating crystal packing, intermolecular interactions, and SCO cooperativity.

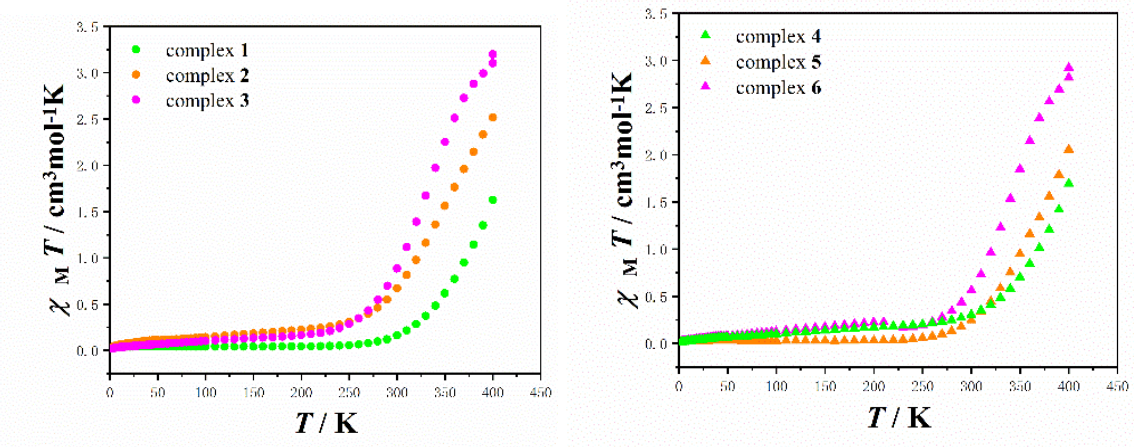


Figure 1. $\chi_M T$ - T plots for complexes **1**-**6**.

DFT INVESTIGATION OF SPIN-STATE-DEPENDENT NITRITE REDUCTION VIA AN {FeNO}^{6} INTERMEDIATE IN A MONONUCLEAR IRON(II) COMPLEX

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Jeonbuk National University, Republic of Korea

Nitrite reduction to nitric oxide is a fundamental transformation in biological nitrogen cycling and enzymatic signaling, yet the direct observation of key iron–nitrosyl intermediates remains challenging. In this work, our collaborators experimentally demonstrated that protonation of the mononuclear Fe(II)–nitrite complex $[Fe^{II}(TBDAP)(NO_2)(CH_3CN)]^+$ with HOTf generates an isolable low-spin {FeNO}^{6} intermediate.[1] This intermediate was characterized by UV–vis, ATR–IR, ESI–MS, EPR, and Fe K-edge X-ray absorption spectroscopies, and isotopic labeling confirmed that the nitrosyl ligand originates from nitrite. Kinetic and reactivity studies further showed that the formation of {FeNO}^{6} involves an associative reaction between Fe(II) and NO^+, and that subsequent one-electron reduction leads to $NO^{\bullet}$ release.

Based on these experimental findings, we performed density functional theory calculations to elucidate the mechanistic details of nitrite reduction at the Fe(II) center. The calculations indicate that initial protonation promotes dissociation of HNO_2 from the Fe(II) complex, followed by further protonation-induced heterolytic N–O bond cleavage to generate NO^+ and H_2O. Subsequent binding of NO^+ to Fe(II) forms the {FeNO}^{6} intermediate, but this process is strongly influenced by counterion stabilization, multiple accessible spin states, and spin-state crossing events. Theoretical analysis further rationalizes the divergent outcomes observed under stepwise proton/electron transfer and proton-coupled electron transfer conditions, leading either to $NO^{\bullet}$ release or to stabilization of a {FeNO}^{7} species. Overall, this combined experimental and computational study provides mechanistic insight into the role of an isolable {FeNO}^{6} intermediate in biomimetic nitrite reduction.

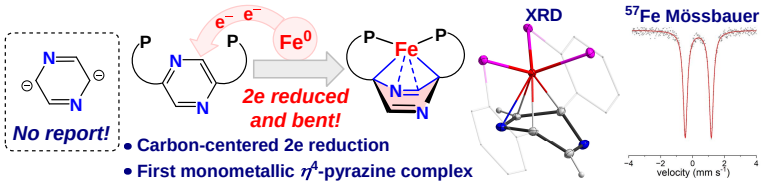
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A CRYSTALLINE IRON COMPLEX STABILIZING A BENT, DOUBLY REDUCED PYRAZINE

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Redox-active *N*-heteroarenes such as pyrazine and 1,3,5-triazine are attractive ligands for first-row transition-metal chemistry, yet controlling the site of reduction, binding mode, and ligand- versus metal-centered redox character remains challenging. We report a crystalline iron complex that stabilizes a bent, formally doubly reduced pyrazine in a monometallic π-complex. Reaction of a pyrazine-anchored diphosphine with $Fe(PMe_3)_4$ affords diazaferranorbornadiene **3**, the first Fe(η^4-pyrazine) complex, whose crystallographic bond metrics, diamagnetism, ^{57}Fe Mössbauer spectroscopic data, and DFT/ETS-NOCV analyses support a low-spin Fe(II) center coupled to a dearomatized pyrazine^{2-} fragment with two Fe–C_{ipso} σ bonds. The same design logic was applied to a triazine-anchored triphosphine. Its reaction with $Fe(PMe_3)_4$ leads to **4**, a high-spin Fe(0) complex featuring an unprecedented η^2-(C=N) triazine coordination mode with only minor ligand reduction. This divergent *N*-heteroarene reactivity reveals that donor topology can direct both hapticity and ligand-vs-metal redox participation at low-valent iron. The resulting π-bound *N*-heteroarene complexes are not only structurally distinctive but also catalytically competent in styrene dehydrogenative borylation, highlighting reduced *N*-heteroarenes as actionable motifs for base-metal catalysis.



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EXPLORING THE SHIFT FROM PROTON-COUPLED TO HYDRIDE-COUPLED ELECTRON TRANSFER

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This study explores an alternative mechanism to canonical proton-coupled electron transfer (PCET) - hydride-coupled electron transfer (HCET). HCET is a single barrier process, which involves hydride transfer coupled with electron transfer, as we observed in the set of reactions between a Cu^{III}–OH complex and various organic substrates [1].

First, the propensity of Cu^{III}–OH complex towards HCET was identified based on the connection between the thermodynamic cycles describing the reaction and reactivity [2,3] and our recent finding that the mechanism (whether HCET or PCET) is dictated by the cycle with more favorable off-diagonal thermodynamics [4].

The thermodynamic distinction between the mechanisms is evidenced by a match with electronic structure-based descriptors derived from atoms-in-molecule charges and volumes. In HCET, the hydrogen atom gains electron density and volume at transition state. which indicates hydride character, while in PCET, it loses electron density and volume signaling proton character. Moreover, intrinsic bond orbital analysis confirmed that HCET is a two-electron process (as opposed to one-electron PCET): it involves the complete transfer of the proton and the β-electron from substrate to the Cu ion while the α-electron undergoes a transient exchange, initially migrating to the Cu center before returning to substrate [1].

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ASSEMBLY OF BOROPHENE-ANALOGOUS LAYERED MATERIALS FOR EMERGENT ELECTRONIC AND IONIC FUNCTIONS

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Controlled synthesis of inorganic materials provides a versatile strategy for constructing low-dimensional architectures in which collective electronic and ionic functions emerge through structurally programmed assembly. In our previous studies, we explored interfacial coordination reactions yielding electrically conductive metal-complex nanosheets [1] and dendrimer-directed synthesis of atomically precise superatoms [2], demonstrating how coordination environments and spatial confinement trigger cooperative electronic states. Building on these design strategies, we have established boron-based two-dimensional assemblies as a unique functional material platform exhibiting emergent electronic and ionic properties.

Here, we focus on a borophene-derived layered crystal composed of oxidized boron monolayers stabilized by interlayer cations [3]. Unlike conventional two-dimensional borophene formed exclusively on metal substrates, this material forms a bulk crystalline phase via coordination-assisted structural stabilization, enabling macroscopic handling and solution processability. The partially ionic character of the boron–oxygen framework allows exfoliation into mono- to few-layer sheets in polar solvents, establishing a solution-based route to borophene-related nanosheets.

Importantly, this system exhibits emergent electronic and ionic properties arising from its unique bonding characteristics. Despite being in an oxidized state, the in-plane boron network retains metallic conductivity with near-zero activation energy [3a]. Thermal stimulation triggers structural reorganization into a liquid-crystalline phase over a wide temperature window, representing a rare example of dynamic mesophase behavior in boron-based materials [3b]. Furthermore, interlayer cation substitution serves as an external trigger to modulate ion mobility, significantly enhancing capacitance through facilitated ionic transport within the layered galleries [3c]. This ion-exchange-driven functional modulation highlights the intimate coupling between coordination environments and collective transport phenomena.

These findings demonstrate that cation-assisted assembly enables stabilization, exfoliation, and functional activation of borophene-derived architectures. By integrating structural design, ionic modulation, and external stimuli, we establish a new frontier in functional assembly, where boron-based layered materials exhibit coupled electronic conduction and dynamic ionic functionality. This approach provides a molecularly informed pathway for advancing boron-based low-dimensional materials toward quantum and electrochemical applications.

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PRECURSOR DESIGN EN ROUTE TOWARDS THE CHEMICAL VAPOR DEPOSITION OF f-ELEMENT NITRIDES

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Chemical vapor deposition (CVD) provides access to high-quality thin films, with controlled growth relying on precise precursor design and tuned thermophysical properties.

For f-element nitrides, suitable molecular precursors remain scarce, limiting access to thin films materials via CVD. These materials are of interest due to their unique combination of magnetic and electronic properties, as well as the relevance of uranium nitride (UN) in next-generation fuel applications.

Here, we report the synthesis and characterization of new volatile lanthanide and actinide amidinate, guanidinate, and triazenide complexes as molecular precursors for f-element nitride deposition. Notably, the synthesized triazenide-based complexes exhibit remarkable volatility, undergoing clean sublimation under high vacuum (10^{-5} mbar) at temperatures down to 75 °C.

HOMOLEPTIC NICKEL(I) COMPOUNDS STABILIZED BY LOW VALENT MAIN GROUP METALLO LIGANDS

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Bimetallic complexes, featuring direct bonds between transition metals (TM) in oxidation state zero and main-group elements (E) in formal oxidation state one, have attracted considerable attention as platforms for tuning transition-metal reactivity. [1,2] The chemistry of related TM/E complexes with TM in higher oxidation states still remains largely unexplored. This is partly due to undesired side reactions such as ligand transfer and metal-reduction pathways taking place during the synthesis. One possible entry to such systems is the reaction of GaCp* with cationic TM(II) complexes of the type $[TML_n][WCA]_m$. For example, the reaction of $[Ni(RCN)_6][BAr^F]_2$ (R = Me, ^{t}Bu) with GaCp* has been shown to yield complexes of the type $[(RCN)Ni(GaCp^*)_4][BAr^F]_2$ and induce unusual bond activation processes, including C–H and C–F bond activation.[3]

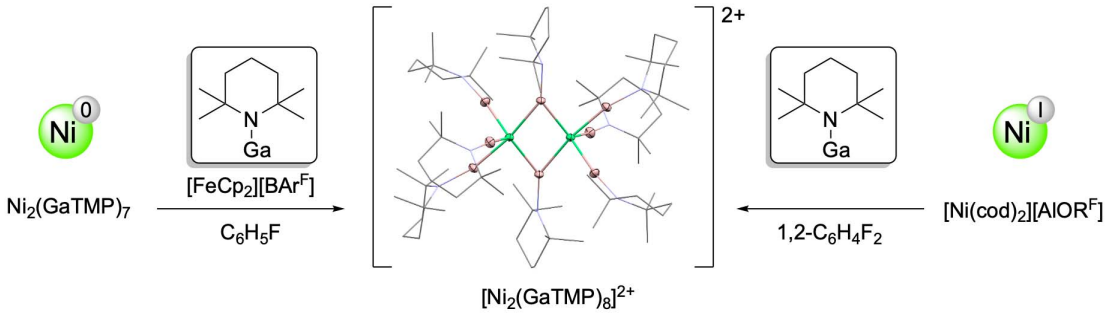


Figure 1: Synthesis of $[Ni_2(GaTMP)_8]^{2+}$ (TMP = 2,2,6,6-tetramethyl-piperidinyl) via oxidation of $Ni_2(GaTMP)_7$ with $[FeCp_2][BAr^F]$ (BAr^F = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) (left) and reaction of $[Ni(cod)_2][AlOR^F]$ ($AlOR^F$ = tetrakis(perfluoro-tert-butoxy)aluminate) with GaTMP (right).

In this contribution, we report the synthesis of $[Ni_2(GaTMP)_8][WCA]_2$, which features the homoleptic, dicationic complex $[Ni_2(GaTMP)_8]^{2+}$. The new compounds were accessed either by direct reaction of $[Ni(cod)_2][AlOR^F]$ with GaTMP or by oxidation of the neutral precursor $Ni_2(GaTMP)_7$ using $[FeCp_2][BAr^F]$. The choice of TMP as protecting group at the Ga center avoids transmetallation reactions which may occur in case of Cp* (i.e. formation of Cp*Ni-species). The dication $[Ni_2(GaTMP)_8]^{2+}$ is isoelectronic to the classic $[Co_2(CO)_8]$, and it is characterised using standard analytical methods, such as SC-XRD, NMR, IR and mass spectrometry. The proximity of Ni(I) centers and the more electrophilic gallium sites represent an unusual electronic situation, which may enable novel reactivity patterns, possibly relevant to elementary steps in catalysis.[3]

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UNUSUAL BONDING INTERACTIONS AND PRONOUNCED CIS-INFLUENCE IN 6-COORDINATE OXOVANADIUM COMPLEXES

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[b]Department of Chemistry, Illinois State University, Normal, Illinois USA
[c]Department of Chemistry, University of Wyoming, Laramie, Wyoming USA
[d]National Nanotechnology Center, NSTDA, Khlong Luang, Pathum Thani, Thailand

Six-coordinate oxidovanadium complexes of the form $VO^{IV/V}$(L1)(L2), where L1 is a tridentate Schiff base with one oxygen and two nitrogen donor atoms and L2 is a substituted catecholate ligand, have been described and are under investigation as potential anticancer agents. Previous structural and electronic investigation of these compounds has revealed distinctively noninteger oxidation states and highly asymmetric bonding of the catecholate ligand, although only a handful of crystal structures have been published. We present the synthesis and characterization of a series of such compounds bearing a salicylideneiminato-2-aminomethylpyridine ligand scaffold and either a substituted catecholate or β-diketonate as L2, including multiple new structures obtained from single-crystal X-ray diffraction. Using density functional theory and electronic absorption spectroscopy, we show that the presence of a noninnocent catechol ligand reorganizes the contributions of the salicylidene π-system to the populated molecular orbitals. Furthermore, key and unexpected similarities are observed in the bonding orbitals of the non-innocent catecholate and innocent β-diketonate ligands despite the differences in observed oxidation states, chelation ring size, and relative orbital energies. Finally, we demonstrate that the nature of L2 plays a deterministic role in the electronic effects of substitutions on the salicylidene ring of L1.

CLUSTER GROWTH OF MOLECULAR COBALT-ALUMINUM COMPLEXES

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The understanding of state-of-the-art *Fischer-Tropsch* Co/Al_2O_3 solid-state catalysts remain subject of considerable debate.[1] The development of molecular-scale model catalyst systems is one strategy to obtain information on active sites. All-hydrocarbon ligated heterobimetallic clusters, which consist of an electropositive group 12 or 13 metal and a low-valent transition metal, can be utilized for precise atomic-level studies related to catalysis.[2] These clusters can be obtained, processed and their chemistry can be monitored by wet-chemical methods including analytical techniques such as MS and NMR-spectroscopy.[2] However, the field of *Hume-Rothery*-inspired ligated Co/Al clusters is very limited, therefore new syntheses strategies need to be developed.

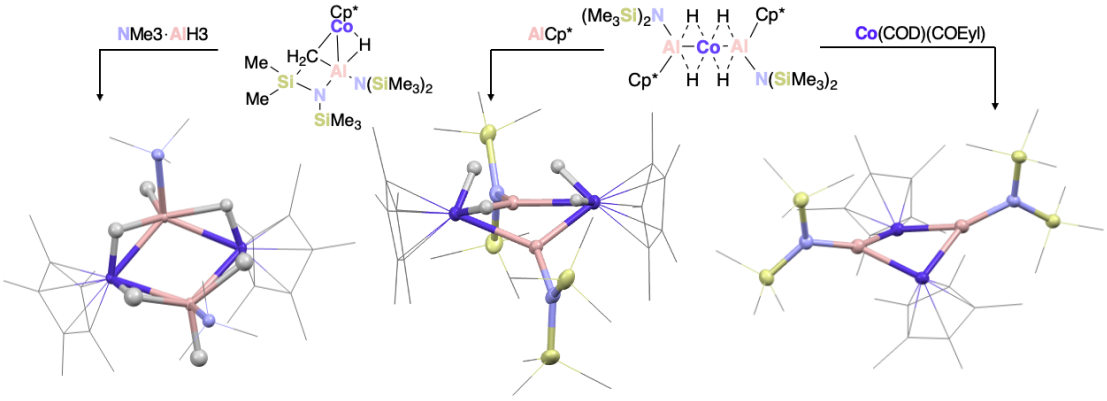


Figure 1: Synthesis overview of the three $Co_2Al_2Cp^*_2L_2H_x$. Left: x = 6, L = NMe_3, middle: x = 4, L = $N(SiMe_3)_2$ right: x = 2 or 4, L = $N(SiMe_3)_2$. Color code: purple = Co, rose = Al, light blue = N, yellow = Si, grey = C, white = H^-. All other hydrogen atoms are omitted for clarity.

We herein present three novel hydrides bearing Co/Al clusters, which show closely related structures resembling a transition from rectangular to a butterfly or tetrahedral Co_2Al_2 core. The synthesis was based on combining known Co/Al complexes [3] with various Co or Al precursors as cluster growth reagents, leading to a series of new compounds with the sum formula $Co_2Al_2Cp^*_2L_2H_x$ (L = $N(SiMe_3)_2$, NMe_3, Figure 1). This shows that Co/Al cluster growth can be realized by different reaction pathways. The novel Co/Al species represent different Co/Al bonding situations, numbers and types of hydrides, either bound terminally or bridging between Co and Al. Based on our preliminary results we are now aiming to realize further cluster growth and probing of reactivities towards *Fischer-Tropsch* related elementary reactions with synthesis gas and other small molecules.

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MODELLING FISCHER-TROPSCH RELATED PHASES AND REACTIVITY WITH MOLECULAR CLUSTERS

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Molecular, heterobimetallic clusters can be employed to mimic structural motifs and reactivity patterns of bimetallic catalytic phases.[1] One widely investigated catalytic system is $Co@Al_2O_3$ for *Fischer-Tropsch* synthesis. Insights into the catalytic mechanisms at the active centers on the heterogenous surface are limited. Nevertheless, these processes have been reported to involve the support metal (Al) by the formation of Cobalt-Aluminates as well as the re-oxidation of cobalt by the H_2O formed during the reaction.[2,3] Owing to their analytical accessibility, we investigate molecular, heterobimetallic cobalt-based clusters as molecular models for cobalt-based phases to elucidate structure-function relationships with respect to structural motifs and reactivity patterns of the parent intermetallic phases.

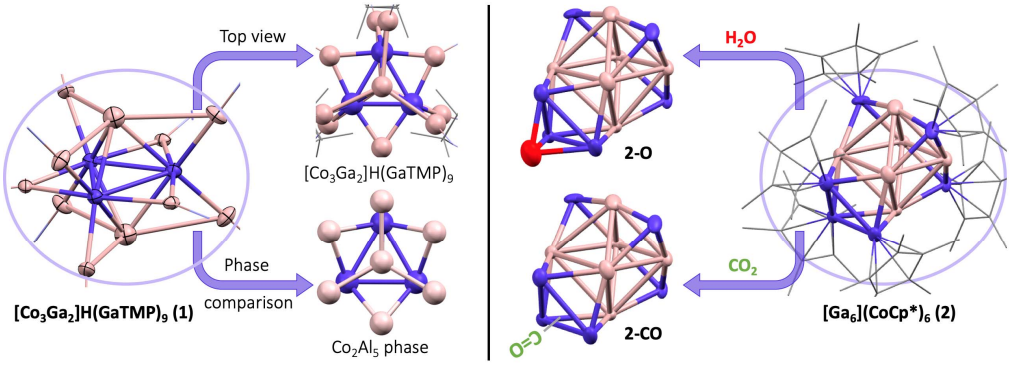


Figure 1. Left: Molecular structure of $[Co_3Ga_2]H(GaTMP)_9$ (1, TMP = Tetramethylpiperidinyl, ligands omitted) and comparison *(*top view) to Co_2Al_5 phase.[4] Right: Molecular structure of $[Ga_6](CoCp^*)_6$ (2, Cp* = Pentamethylcyclopentadienyl) and its reaction with CO_2 and H_2O. Color code: Co: violet, Ga/Al: rose.)

Herein we present two molecular Co/Ga clusters as molecular models: $[Co_3Ga_2]H(GaTMP)_9$ mimics the central structural motifs of the related intermetallic phase Co_2Al_5. This was achieved by a synthetic protocol that directly targets alloyed cluster cores without separation of the two metals into core and shell domains, as it is regularly observed.[5] The second cluster, $[Ga_6](CoCp^*)_6$, shows distinct and site-selective reactivity toward the *Fischer-Tropsch*-related small molecules CO, CO_2 and H_2O. In the case of CO_2 even a C-O bond cleavage is observed, leading to the corresponding CO-adduct. Thus, we were able to obtain molecular clusters that serve as molecular models from both structural and reactivity perspectives .

[1] L. Liu *et al.*, *Chem. Rev.* **2023**, *123*, 4855-4933.

[2] M. Wolf *et al.*, *Chem Catalysis* **2021**, *1*, 1014-1041.

[3] M. Wolf *et al.*, *Nature Catalysis* **2020**, *3*, 962-965.

[4] A. J. Bradley *et al.*, *Z. Kristallogr. – Cryst. Mater.* **1938**, *99*, 480-487.

[5] M. Muhr *et al.*, *Commun. Chem.* **2024**, *7*, 29.

PYRIDYL-PHOSPHONATE FUNCTIONALISED POLYOXOMETALATES AS MODULAR PLATFORMS FOR HYBRID CATALYTIC SYSTEMS

Adedayo O. Dada, Lee. R. Johnson, and Graham N. Newton

University of Nottingham, Nottingham, United Kingdom

Polyoxometalates (POMs) are redox-active metal-oxide clusters with tuneable electronic and structural properties, making them attractive building blocks for hybrid catalytic materials. However, the controlled and modular integration of molecular components with POM frameworks, while preserving their redox behaviour, remains challenging [1].

In this work, we report the synthesis of a new family of pyridyl-phosphonate functionalised Dawson-type POM hybrids derived from the lacunary precursor $K_{10}[P_2W_{17}O_{61}]$. Covalent grafting of pyridyl-containing organophosphonate ligands introduces well-defined coordination sites while preserving the redox-active POM framework. This strategy yields three novel materials: (i) a pyridyl-phosphonate functionalised POM featuring accessible nitrogen donor sites for coordination to transition-metal centres; (ii) a quaternised derivative bearing a C_{20} alkyl chain that resembles an amphiphilic hybrid capable of supramolecular self-assembly [2]; and (iii) a pyridyl-phenyl phosphonate analogue that extends the aromatic linker and modifies the coordination environment.

Multinuclear NMR, IR, and UV-visible spectroscopy, high-resolution mass spectrometry, and cyclic voltammetry confirms successful functionalisation and retention of the POM framework. These hybrids combine the redox versatility of the polyoxometalate core with ligand-directed coordination chemistry, providing modular platforms for constructing hybrid catalytic systems and self-assembled redox-active materials.

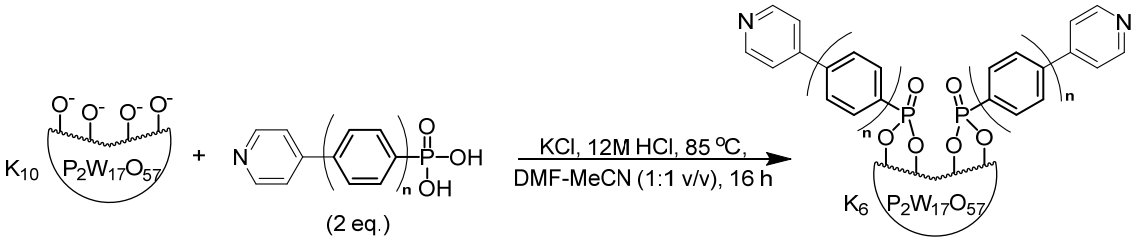


Figure 1: Synthetic pathway to obtain pyridyl-functionalised hybrid polyoxometalate

[1] A. O. Dada, K. D. Jones, D. A. Walsh and G. N. Newton, *Applied Polyoxometalate-based Electrocatalysis*, 2024, 27–58.

[2] S. Amin, J. M. Cameron, J. A. Watts, D. A. Walsh, V. Sans and G. N. Newton, *Molecular Systems Design & Engineering*, 2019, **4**, 995–999.

THE SYNTHESIS OF CARBOXYLATE-DERIVED ASYMMETRIC HYBRID POLYOXOMETALATES

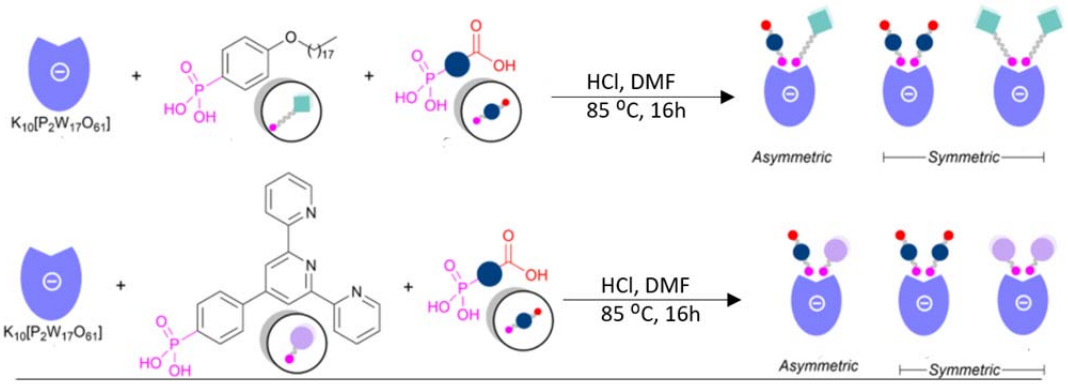
Noor Alnahdi, Kieran Jones, Graham Newton

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Hybrid polyoxometalates (POMs) combine the rich redox chemistry of metal-oxo clusters with the tunability of organic functional groups, enabling the design of multifunctional molecular materials. Among the different POM architectures, the Wells Dawson framework is particularly attractive due to its structural robustness and the availability of lacunary derivatives that allow controlled covalent functionalisation. While symmetric organic inorganic hybrids have been extensively explored, the preparation of asymmetric hybrid POMs bearing two distinct organic functionalities remains significantly more challenging but offers unique opportunities to introduce orthogonal properties within a single molecular scaffold.[1]

The talk discusses the synthesis and characterisation of carboxylate-derived asymmetric Wells Dawson hybrid polyoxometalates, whereby two distinct organic substituents are covalently attached to a $[P_2W_{17}O_{61}]$ framework.[2] The design incorporates two different ligands with complementary carboxylate groups, facilitating electrical communication, coordination, and supramolecular interactions within a single cluster. A series of four asymmetric hybrids was synthesised and characterised using structural methods, showing the effective asymmetric functionalisation of the Dawson core.

These hybrid systems demonstrate the potential of carboxylate-based functionalisation strategies to generate multifunctional asymmetric POM platforms, opening new opportunities for the development of redox-active molecular materials and coordination-driven assemblies.



[1] Hampson, E.; Cameron, J. M.; Amin, S.; Kyo, J.; Watts, J. A.; Oshio, H.; Newton, G. N. Asymmetric Hybrid Polyoxometalates: A Platform for Multifunctional Redox-Active Nanomaterials. *Angew Chem Int Ed* **2019**, *58* (50), 18281–18285. https://doi.org/10.1002/anie.201912046.

[2] Martin, C.; Kastner, K.; Cameron, J. M.; Hampson, E.; Alves Fernandes, J.; Gibson, E. K.; Walsh, D. A.; Sans, V.; Newton, G. N. Redox-Active Hybrid Polyoxometalate-Stabilised Gold Nanoparticles. *Angew Chem Int Ed Engl* **2020**, *59* (34), 14331–14335. https://doi.org/10.1002/anie.202005629.

REDOX CHEMISTRY OF THE CYCLONONATETRAENYL LIGAND IN LATE LANTHANIDE COMPLEXES: A TALE OF ANTIAROMATICITY AND COMPROPORTIONATION

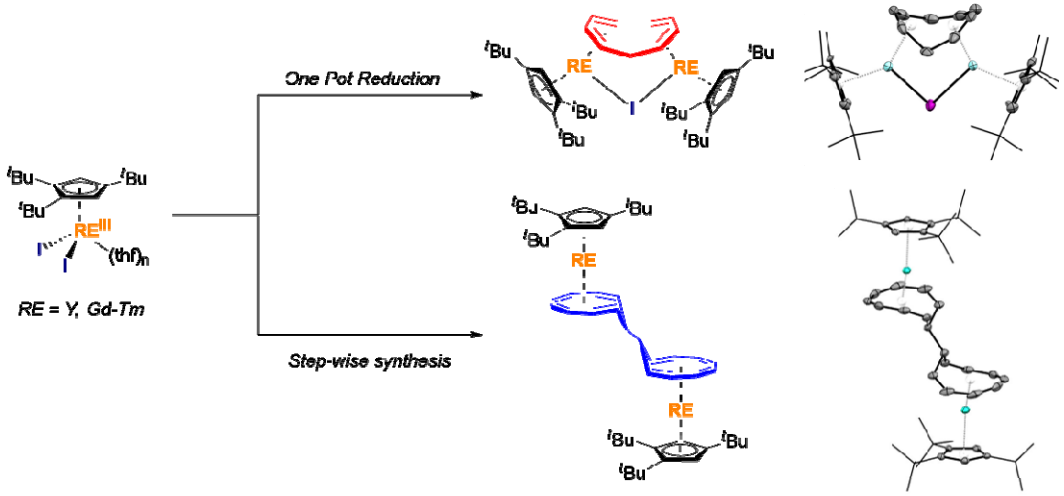
Hugh Sanderson, Mohamed Mounir, Thomas Simler, Gregory Danoun, Gregory Nocton

LCM, CNRS, École polytechnique, Institut polytechnique de Paris, Route de Saclay, 91120 Palaiseau, France

Since the discovery of ferrocene in 1951, cyclical aromatic π-ligands have become a staple of organometallic chemistry. With regards to the *f*-block the cyclopentadienyl (C_5H_5, **Cp**$^-$) and cyclooctatetraenyl ($C_8H_8^{2-}$, **COT**$^{2-}$) ligands, and their derivatives, have proven particularly effective scaffolds for developing complexes possessing intriguing electronic and magnetic properties and reactivity to small molecules [1].

The larger cyclononatetraenyl ligand ($C_9H_9^-$, **Cnt**$^-$) by comparison, is underexplored owing to its tendency to collapse to form indene or indenyl derivatives, existence of isomeric forms and can be easily displaced by donor solvents due to its relative charge diffusivity [2]. Despite these apparent drawbacks, recent years have witnessed a resurgence in Cnt chemistry with the syntheses of the homoleptic, [Ln(Cnt)$_3$] and heteroleptic, [Ln(COT)(Cnt)], trivalent complexes and the classical divalent sandwich complexes [Ln(Cnt)$_2$] [2].

Herein we explore attempts to access divalent heteroleptic complexes of the form [Ln(Cnt)(Cp)] via the reduction of the trivalent precursor. In doing so the highly redox sensitive nature of the Cnt ligand was observed with the formation of two distinct bimetallic species where the Cnt ligand displayed differing levels of reduction, despite the use of the same reductant. Two electron reduction led to the formation of a formally antiaromatic Cnt moiety, which displayed significant folding and bridged between two [Cp^{ttt}Ln] units. In contrast the one electron reduction led to coupling of two Cnt ligands to afford an extended sandwich type complex.



[1] N. Mahieu, J. Piątkowski, T. Simler, G. Nocton, *Chem. Sci.*, **2023**, 14, 443-457

[2] X. Sun, G. Nocton, P. W. Roesky, *Chem. Commun.*, **2025**, 61, 1761-1772

LINDQVIST POLYOXOVANADATES IN ELECTRONICS: FROM SYNTHESIS AND CHARACTERIZATION TOWARDS APPLICATION

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[b] Center for Advancing Electronics Dresden, TU Dresden, Faculty of Chemistry and Food Chemistry, Dresden, Germany
[c] Material Systems for Nanoelectronics, Chemnitz University of Technology, Chemnitz, Germany

Lindqvist-type polyoxovanadates (POVs) occupy a unique position within the broad class of polyoxometalates (POMs) by combining compact architectures with high stability, ligand post-functionalization, and redox flexibility. When integrated into device-like architectures, these POVs exhibit resistive switching behavior, displaying reversible transitions between distinct conductive states in response to electrical stimuli [1]. Multiresistive switching, as observed in scanning tunneling spectroscopy (STS) investigations, demonstrates the potential application of POVs as active elements in alternative memory and neuromorphic computing systems [2]. Here, we present results on surface-modified Au(111) substrates with solution-processed Lindqvist-type POVs (TBA-V_6OH), as well as a proof-of-concept resistive memory cell (Figure 1), which was achieved by stabilizing the POVs in a polymer film. We characterized the materials using various surface-sensitive microscopy and spectroscopy methods, as well as advanced electronic characterization methods, to analyze the materials from the molecular to the macro scale. These results lay the foundation for new applications of polyoxovanadates.

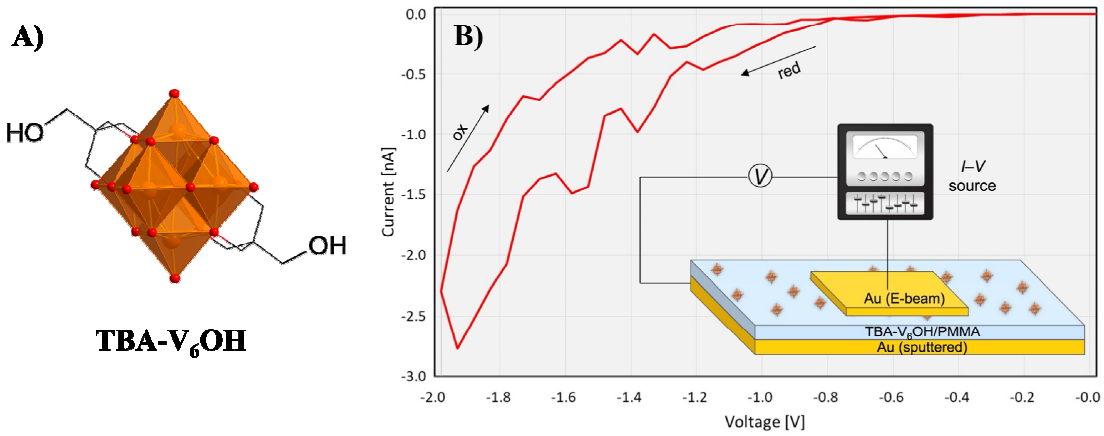


Figure 1: A) Structure of TBA-V_6OH and B) I–V characteristics of a model resistive memory cell Au//TBAV_6OH/PMMA//Au indicating the occurring vanadium reduction steps at different potentials.

[1] O. Linnenberg, M. Moors, A. Notario-Estévez, X. López, C. de Graaf, S. Peter, C. Baeumer, R. Waser, and K. Monakhov, *J. Am. Chem. Soc.* **2018**, *140*, 48, 16635 – 16640. DOI: 10.1021/jacs.8b08780.

[2] K. Monakhov, C. Meinecke, M. Moors, C. Schmitz-Antoniak, T. Blaudeck, J. Hann, C. Bickmann, D. Reuter, T. Otto, S. E. Schulz, H. Parala, and A. Devi, *Pure Appl. Chem.* **2024**, *96* (9), 1313 – 1331. DOI: doi:10.1515/pac-2024-0242.

REVERSIBLE FORMATION OF MONO-/HETERODI-NUCLEAR DIPHOSPHANE COMPLEXES

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m.b.smith@lboro.ac.uk

Unlike tertiary phosphines, the coordination chemistry of diphosphanes bearing a P–P single bond has been extremely poorly studied [1,2]. Herein a novel class of readily accessible diphosphanes, based on a rigid bicyclic $P_2C_4N_2$ framework, will be presented. Furthermore, it will be shown these air stable diphosphanes represent excellent scaffolds for supporting late transition metal fragments [3,4]. A unique feature of this work is the reversible nature by which the P–P bond can be cleaved and reformed within a bridging heterodinuclear complex (Figure 1). The unusual reactivity of such compounds towards C–C bond formation across adjacent P_2C_2N five-membered rings will also be illustrated.

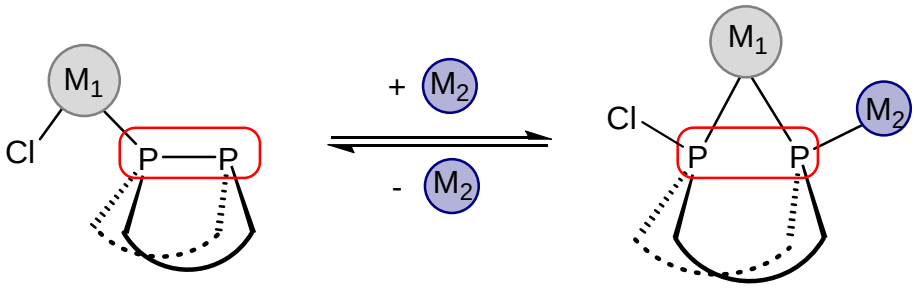


Figure 1.

[1] For examples, see: (a) Molitor, S.; Mahler, C.; Gessner, V. H. *New J. Chem.* **2016**, *40*, 6467-6474. (b) Velian, A.; Nava, M.; Temprado, M.; Zhou, Y.; Field, R. W.; Cummins, C. C. *J. Am. Chem. Soc.* **2014**, *136*, 13586-13589.

[2] Edgar, M.; Elsegood, M. R. J.; Liu, P.; Miles, C. R.; Smith, M. B.; Wu, S. *Eur. J. Inorg. Chem.* **2022**, e202200017.

[3] Coles, S. J.; Horton, P. N.; Kimber, P.; Klooster, W. T.; Liu, P.; Plasser, F.; Smith, M. B.; Tizzard, G. J. *Chem. Commun*. **2022**, *58*, 5598-5601.

[4] Coles, S. J.; Elsegood, M. R. J.; Horton, P. N.; Klooster, W. T.; Lastra-Calvo, N.; Liu, P.; Smith, M. B.; Tizzard, G. J. Manuscript in preparation.

TETRAHEDRAL INVERSION IN PENTANUCLEAR METAL COMPLEXES

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[b] Department of Chemistry, School of Science, Institute of Science Tokyo, Ookayama, Meguro-ku, Tokyo, Japan
[c] Department of Chemistry, Institute of Pure and Applied Sciences, University of Tsukuba, Tennodai, Tsukuba, Ibaraki, Japan
[d] Tsukuba Institute for Advanced Research (TIAR), University of Tsukuba, Tennodai, Tsukuba, Ibaraki, Japan

Molecular inversion is one of the most fundamental geometric transformations in chemistry, serving as the basis for various chemical phenomena by inducing the reversal of chirality and polarity. Pyramidal inversion, observed in three-coordinate molecules, has been extensively studied regarding changes in inversion behavior due to variation of the central atom or structural changes in substituents[1]. On the other hand, there are no experimental examples of such inversion occurring in tetra-coordinate molecules.

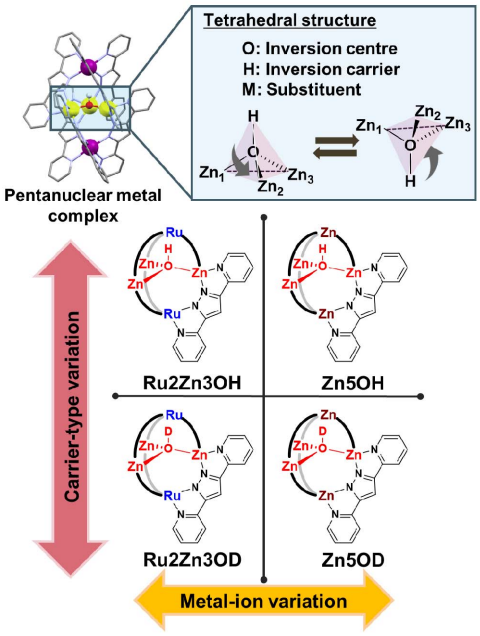


Figure 1. The structure of pentanuclear metal complexes.

Here, we demonstrate dynamic inversion within a tetrahedral core confined in a pentanuclear complex. We employed **Zn5OH** and **Ru2Zn3OH**[2] as rigid coordination cages to encapsulate a tetrahedral core composed of three zinc atoms and one proton coordinated to a central oxygen atom (Figure 1).

Variable-temperature NMR (VT-NMR) analysis revealed dynamic inversion behavior, with activation energies of 60.6 kJ/mol for **Zn5OH** and 73.3 kJ/mol for **Ru2Zn3OH**. These results indicate that the metal composition significantly influences the inversion barrier within the tetrahedral core. Furthermore, isotopic substitution was examined by replacing the proton with deuterium (**Zn5OD** and **Ru2Zn3OD**). The activation barriers increased by 1.2 kJ/mol and 3.3 kJ/mol, respectively. These findings demonstrate that both the identity of the metal ions and the hydrogen isotope play critical roles in governing tetra-coordinate inversion.

[1] M. D. Smith, *et al.*, *Nature* **2023**, *615*, 430–435.

[2] S. Masaoka, *et al.*, *Angew. Chem. Int. Ed.* **2024**, *63*, e202408514.

STEPWISE INTRODUCTION OF ORGANOPHOSPHONATO LIGANDS AND TRANSITION METAL CATIONS INTO HEXAVACANT LACUNARY POLYOXOMETALATE

Shumpei Take, Takuo Minato, Masahiro Sadakane

Graduate School of Advanced Engineering and Science, Hiroshima University, Japan

Polyoxometalates (POMs) are a family of anionic molecular metal oxide clusters, and various types of lacunary POMs can be synthesized by removing constituent $[M_xO_y]$ (X = W^{6+}, Mo^{6+}, etc.) units. Lacunary POMs attract much attention for precursors of catalysts and magnetic materials because various types of metal cations can be introduced in their vacant sites. Furthermore, various types of organic ligands can be also introduced onto metal cations allowing for the precise control of their coordination geometries, magnetic anisotropies, and redox potentials[1]. However, it is difficult to form coordinatively unsaturated metal species in the presence of organic ligands. When organic ligands are introduced into the vacant sites first, all of the vacant sites are basically capped by organic ligands, thus indicating that the formation of coordinatively unsaturated metal species in ligand-introduced POMs is challenging. Therefore, we focused on $[\alpha\text{-}P_2W_{12}O_{48}]^{14-}$ ($\{P_2W_{12}\}$) possessing a large vacant site. We recently synthesized organophosphonato ligands-introduced $\{P_2W_{12}\}$ as ammonium and tetrabutylammonium (TBA) salts (NH_4-$\{P_2W_{12}L_2\}$ and TBA-$\{P_2W_{12}L_2\}$), where $\{P_2W_{12}L_2\}$ still possesses vacant sites [2]. The TBA-$\{P_2W_{12}L_2\}$ was stable in organic solvents, and thus, the introduction of transition metal cations directly into the vacant sites of TBA-$\{P_2W_{12}L_2\}$ with maintaining ligands would be possible. In this study, we report the direct introduction of organophosphonato ligands and transition metal cations into the vacant sites of $\{P_2W_{12}\}$ in a stepwise manner (Figure 1).

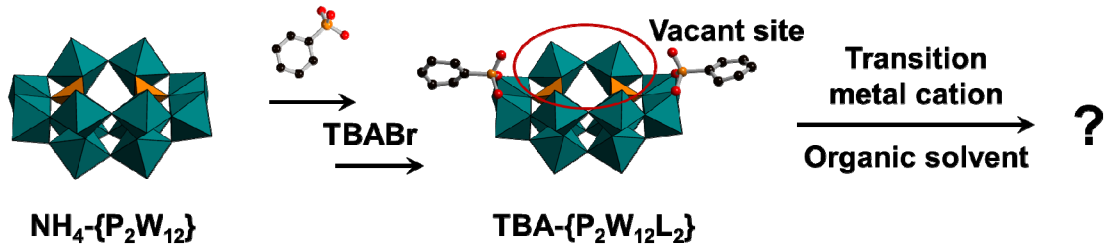


Figure 1. Stepwise introduction of organophosphonato ligands and transition metal cations into the vacant site of $\{P_2W_{12}\}$.

[1] A. Dolbecq, E. Dumas, C. R. Mayer, P. Mialane, *Chem. Rev.* **2010**, *110*, 6009.

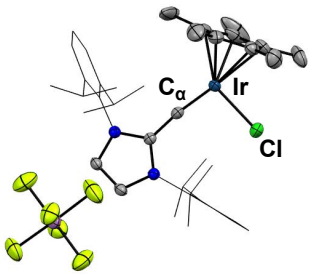
[2] S. Take, T. Minato, M. Sadakane, *Chem. Lett.* **2024**, *53*, upae118.

Cp*M COMPLEXES WITH THE N-HETEROCYCLIC VINYLIDENE LIGAND IPrC

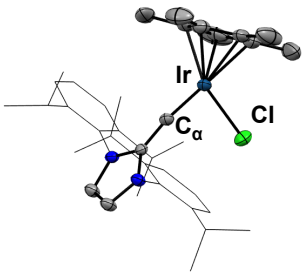
Tak Hin Wong, and Kay Severin

École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

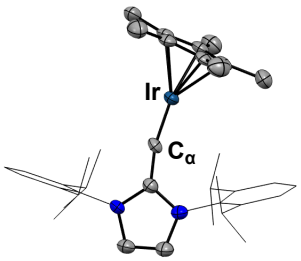
Room-temperature stable diazoolefins provide access to a unique class of carbon-donor ligands: *N*-heterocyclic vinylidenes. Herein, we describe Cp*M complexes with the N-heterocyclic vinylidene ligand IPrC (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene). Cationic complexes of type [Cp*IrCl(IPrC)]X (X = SbF_6, OTf) were obtained by reaction of $(Cp^*IrCl_2)_2$ with $IPrCN_2$, followed by chloride abstraction. Two-electron reduction instead of chloride abstraction gave a neutral Cp*Ir(IPrC) complex with a "pogo stick" geometry [1]. Single-electron reduction of the cationic complexes afforded Cp*IrCl(IPrC), in which the vinylidene ligand shows radical character. Combining $(Cp^*RuCl_2)_2$ with $IPrCN_2$ gave Cp^*RuCl_2(IPrC), in which the vinylidene ligand also shows radical character. Hydrogen abstraction from Et_3SiH yielded the carbene complex Cp^*RuCl_2(IPrCH). The diamagnetic complex Cp*RuCl(IPrC) was obtained by single-electron reduction of Cp^*RuCl_2(IPrC), whereas single-electron oxidation with [TEMPO]X provided ionic [Cp^*RuCl_2(IPrC)]X (X = BF_4, SbF_6) complexes [2]. The results underline the unique electronic properties of the vinylidene ligand IPrC in transition metal complexes.



Electrophilic C_α



Radical C_α



Nucleophilic C_α

[1] T. H. Wong, P. Varava, F. Faraei-Tirani, R. Scopelliti, K. Severin. *J. Am. Chem. Soc.* **2025**, *147*, 19911-19917.

[2] T. H. Wong, A. Sienkiewicz, S. Sivakumar, F. Faraei-Tirani, R. Scopelliti, K. Severin. *Manuscript in preparation.*

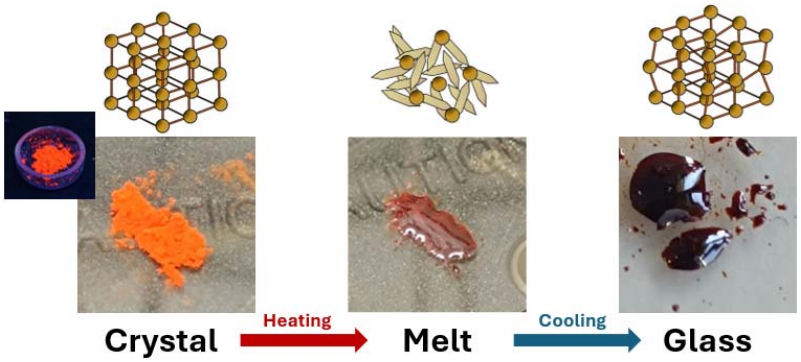
MELTING, GLASS FORMATION, AND LUMINESCENCE IN Cu(I)I COORDINATION POLYMERS

Victoria Martín-Quiles[a], Pilar Amo-Ochoa[a,b], and Javier Troyano[a,b]

[a]Dpto. de Química Inorgánica, Universidad Autónoma de Madrid, 28049 Madrid, Spain
[b] Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, 28049 Madrid, Spain

Inorganic–organic hybrid glasses derived from coordination networks have emerged in the last years as a promising new class of materials [1]. However, their study remains limited due to the difficulty in the characterization, as coordination polymers (CPs), typically undergo irreversible decomposition upon heating, instead of melting. Nevertheless, when meltable, they also enable easier processing, positioning them as highly versatile materials for new applications such as sensing, optoelectronic devices or X-Ray detection [2,3]. Even though CPs based on Cu(I) iodide are known for presenting luminescence [4], to date, no meltable CP based on CuI have been reported.

In this work, we report on the synthesis and a broad study of the thermal and luminescent behavior of four CuI based CPs incorporating thiobenzoamide (TBA) derivatives. All compounds exhibit one-dimensional structures and share the same crystalline motif, a double-rhomb. These structural similarities are reflected in their photoluminescence, as all CPs show an orange emission. Also, their difference in interchain interactions is reflected in their different thermal properties. This highlights the importance of these weak intermolecular interactions in the behavior of the CP. Remarkably, this new family have melting behavior, forming liquid phases from which glasses can be produced by rapid cooling. The study of the different changes between crystalline, liquid, and glass states, allowed to control the properties of the material. As such, this work introduces the first meltable CuI CP capable of forming glasses via rapid cooling.



[1] Umeyama, D., et al. Reversible Solid-to-Liquid Phase Transition of Coordination Polymer Crystals. Journal of the American Chemical Society, 2015. 137(2): p. 864-870.

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[3] Zhu, X., et al. Large-Area Metal–Organic Framework Glasses for Efficient X-Ray Detection. Advanced Materials, 2024. 36(51): p. 2412432.

[4] Murillo, M., et al. 2D Cu(I)-I Coordination Polymer with Smart Optoelectronic Properties and Photocatalytic Activity as a Versatile Multifunctional Material. Inorganic Chemistry, 2023. 62(28): p. 10928-10939.

SYNTHESIS OF IRON-GALLIUM COMPOUNDS BY ACID/BASE INDUCED SOLVENT ACTIVATION AND CLUSTER GROWTH REACTIONS

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[a]Department of Chemistry, Technical University of Munich, Garching, Germany
[b]Catalysis Research Centre, Technical University of Munich, Garching, Germany

Ligated *Hume-Rothery* inspired intermetallic metal clusters are useful study objects that can serve as mimics for the surface of complex heterogeneous bimetallic catalyst systems. In contrast to complex surfaces of solid-state materials, the exact molecular structure of heterobimetallic TM/E metal clusters (TM = transition metal, E = group 12/13 metal) can be accessed by a variety of analytical techniques (NMR, MS or SC-XRD) [1]. Such molecular clusters consist of a transition metal core, coordinated by organometallic subvalent group 12/13 compounds (e.g. $Zn_2Cp^*_2$, AlCp*, GaTMP). The organic ligand shell of these compounds does not only stabilize the clusters' cores but influences the reactivity of the cluster heavily [2]. Since cluster systems which are used as models of their solid state counter parts ideally show substrate interaction and mimic reactions sub steps, a highly tunable ligand sphere is crucial [3,4].

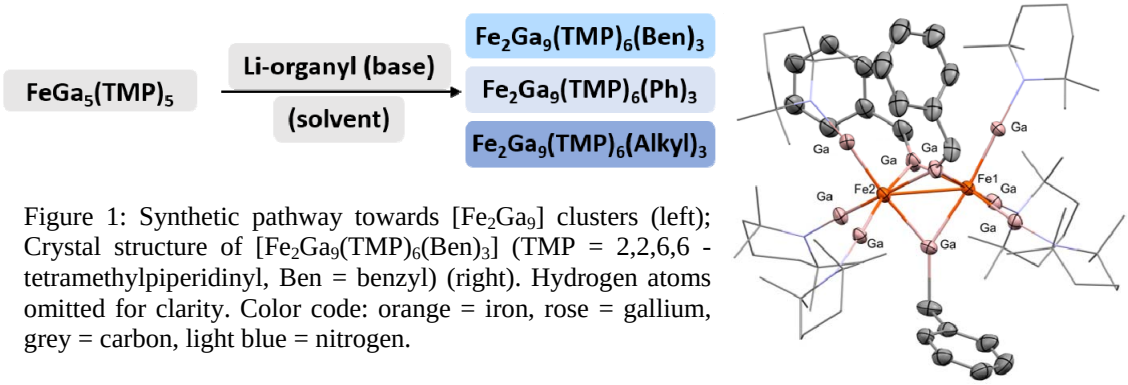


Figure 1: Synthetic pathway towards [Fe_2Ga_9] clusters (left); Crystal structure of [$Fe_2Ga_9(TMP)_6(Ben)_3$] (TMP = 2,2,6,6 - tetramethylpiperidinyl, Ben = benzyl) (right). Hydrogen atoms omitted for clarity. Color code: orange = iron, rose = gallium, grey = carbon, light blue = nitrogen.

This contribution will present the synthesis and reactivity of several intermetallic iron-gallium clusters created by acid/base reaction induced solvent activation and cluster growth reactions at the same time. The core structure of the formed [Fe_2Ga_9] clusters resembles a trigonal bipyramid with six terminal GaTMP ligands, and three bridging GaR ligands (R = aryls, benzyls and alkyls) between the two iron centers (Figure 1). Depending on reaction substrates (lithium amides, lithium- or aluminum organyls) and solvent (innocent or in the case of aromatic solvents as reaction partners), the ligand environment is tunable. This allows for selective transfer of comparatively less reactive R groups or deprotonated solvent molecules towards formation of their Ga(+I)R moieties in the coordination sphere of the intermediate Fe/Ga complexes and induces parallel cluster growth reactions. These compounds' bridging ligands undergo Ga-C bond cleavage by different forms of hydrogenation and are therefore also investigated as precursors for larger cluster systems. Furthermore, the synthesis strategy presented is expanded towards other related systems such as Ru/Ga or Co/Al.

[1] *Angew. Chem. Int. Ed.*, 2014, *53*, 7943.

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[4] *ACS Catal.*, 2019, *9*, 7073.

STRONGLY DONATING BIPYRIDINES WITH PROTON-SWITCHABLE PROPERTIES

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2,2′-Bipyridine ligands have been widely utilized in coordination chemistry owing to their ability to form stable complexes with a variety of Lewis acids, redox stability, and ease of functionalization.[1] Yet genuinely strong donor variants remain uncommon and typically rely on alkyl or amino substitution. Building on recent advances with N‑ heterocyclic imine (NHI) derivatives,[2] we present N‑ heterocyclic olefin (NHO)-functionalized bipyridines as a new class of strongly donating, proton-responsive ligands. These NHO-bipyridines exhibit pronounced tunability of donor strength governed by geometrical strain release and by NHO protonation, enabling proton-gated control over electronic properties (Figure 1a). The ligands are prepared via straightforward routes and can be used for the stabilization of main group cations and for proton-switchable photosensitizers (Figure 1b).

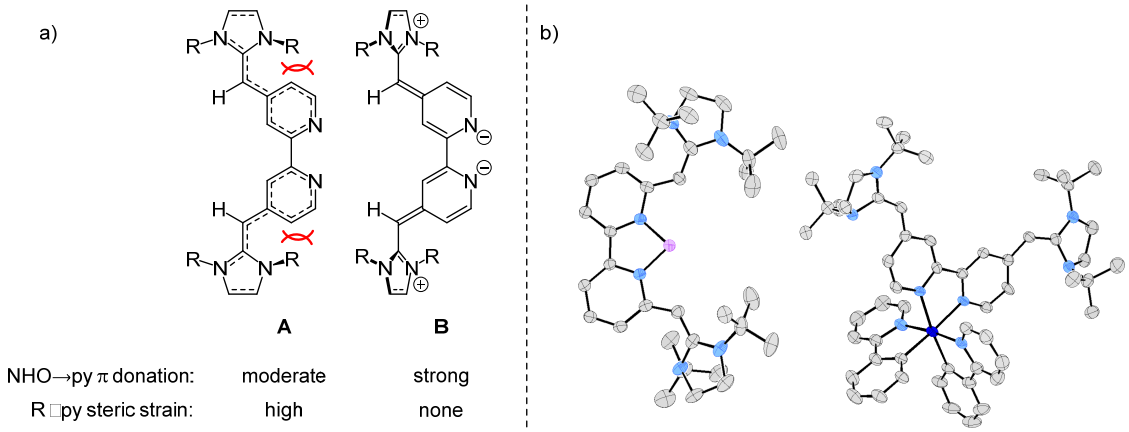


Figure 1. (a) Geometry-dependent donor properties of NHO-bipyridines. (b) Molecular structures of NHO-bipyridine complexes featuring a phosphorus(I) cation (left) and an iridium(III) photosensitizer (right).

[1] C. Kaes, A. Katz, M. W. Hosseini Chem. Rev., 2000, 100, 10, 3553–3590.

[2] S. Lempereuur, F. Glaser, J. H. Franzen, L. Schöndorf, M. Seidl, L. Troian-Gautier, F. Dielmann Chem. Eur. J. (2025), e03127.

PALLADIUM CLUSTERS BEARING GALLIUM-LIGANDS FOR SEMIHYDROGENATION OF ALKYNES

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[b]Catalysis Research Centre, Technical University of Munich, Garching, Germany

The incorporation of a second metal is an established strategy in heterogenous catalysis to enhance overall catalytic performance. In this context, Pd/Ga intermetallic phases have garnered considerable attention due to their ability to serve as highly selective, active, and long-term stable catalysts in the semihydrogenation of acetylene. Atom-precise transition metal/main-group element clusters have emerged as molecular model systems for the active sites of intermetallic solid-state materials, as they have shown the potential to mimic not only their structure but also their catalytic potential. Thus, intermetalloid Pd/Ga clusters, which feature structural cut-outs of the related solid state materials are of particular interest.

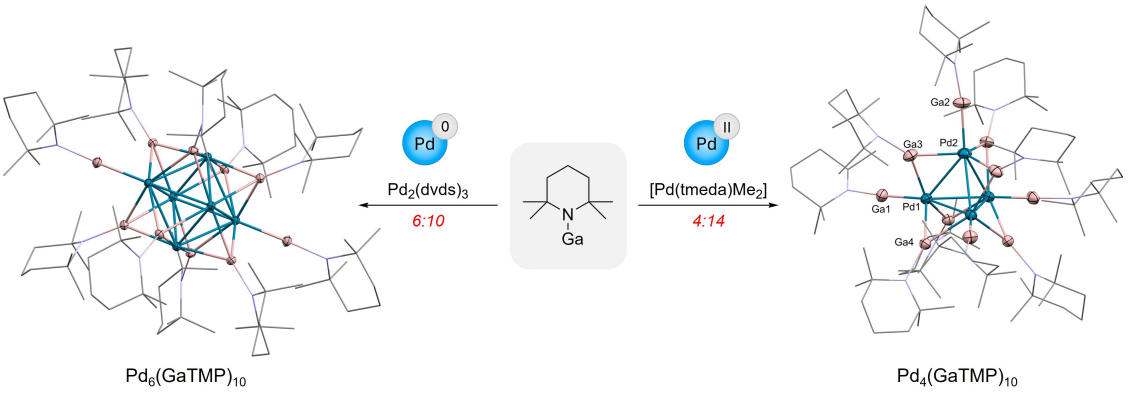


Figure 1: Synthesis of the intermetalloid Pd/Ga clusters $[Pd_4(GaTMP)_{10}]$(right) and $[Pd_6(GaTMP)_{10}]$ (left), starting from GaTMP with palladium complexes (TMP = 2,2,6,6 -tetramethylpiperidide).

Herein we describe two new compounds, which were obtained by the reaction of palladium complexes with the low valent group 13 metalloligand GaTMP (TMP = 2,2,6,6,-tetramethylpiperidinyl). The choice of the palladium precursor and the precise adjustment of the reaction stoichiometry and temperature allow control of the product formation, either $[Pd_4(GaTMP)_{10}]$ or the more palladium-rich $[Pd_6(GaTMP)_{10}]$. (Figure 1) were obtained. Accordingly, other related Pd/Ga-clusters are likely to be discovered. In both study cases, a palladium core is encapsulated by GaTMP ligands, imparting solubility and enabling characterization by conventional analytical methods, including SC-XRD, NMR, and mass spectrometry. The cluster $[Pd_4(GaTMP)_{10}]$ reveals catalytic activity in the selective semihydrogenation of 3-hexyne.

[1] J. A. Delgado, O. Benkirane, C. Claver, D. Curulla-Ferré, C. Godard, Dalton Transactions 2017, 46, 12381-12403.

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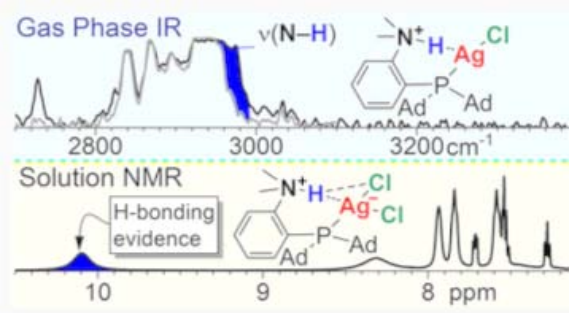
BEYOND LINEAR COORDINATION IN Ag(I) CHEMISTRY: Ag(I)···H WEAK INTERACTIONS AND MULTICENTER BONDING IN CARBORANES

Eric Andris,[a] Lubomír Rulíšek,[a] Martin Dračínský,[a] Jindřich Fanfrlík,[a] Miroslav Hnyk,[b] J. Holub,[b] and Michal Straka [a]

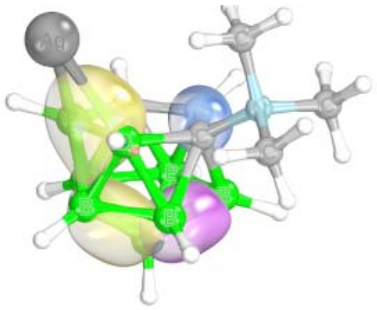
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Ag(I) is often treated as a soft d^{10} metal center with a preference for linear coordination. Here, I will discuss two less common bonding motifs involving Ag(I): Ag(I)···H hydrogen bonding[1] and multicenter bonding in silver carborane clusters.[2]

First, using gas-phase IR photodissociation spectroscopy, solution NMR, and quantum-chemical calculations, we found evidence for intramolecular Ag(I)···H–N^+ bond in the gas-phase. In solution, this interaction can compete with conventional Cl···H–N^+ hydrogen bonding.



Second, we studied reactions of Ag(I) salts with neutral carboranes and found unusual silver carborane species in which Ag(I) is stabilized by multicenter bonding to the open carborane cage, as illustrated in the figure showing intrinsic bond orders. NMR and HRMS experiments revealed several silver-carborane systems up to tri-carborane silver system. Calculations showed that ^{109}Ag chemical shifts are highly sensitive to the local bonding situation and the number of interacting carborane cages.[2]



This work was supported by Czech Science Foundation, Grant 25-15887S

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CYANIDE-BRIDGED MOLECULAR PROTON CONDUCTORS WITH SWITCHABLE FUNCTIONALITIES

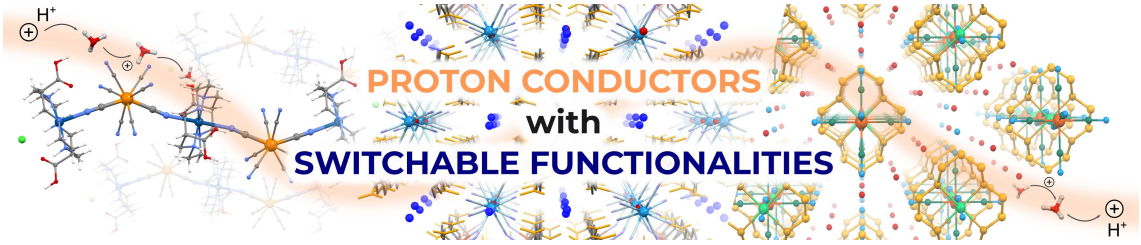
Mateusz Reczyński, Michał Magott, Michael Musioł, and Aleksandra Jankowska

Faculty of Chemistry, Jagiellonian University in Kraków, Kraków, Poland

Proton-conducting materials have attracted considerable attention due to their potential applications in energy-related technologies, particularly in proton-exchange membrane fuel cells, sensors, and electrochemical devices. The development of new proton conductors with tunable properties and additional functionalities remains an important challenge in materials chemistry. Here, we report our recent work on linking proton conductivity to switchable functional properties in cyanide-bridged coordination systems whose multifunctional character can be rationally designed.

The first group of studied materials is based on $[Cu(cyclam)(COOH)_x]^{2+}$ complexes (x = 2, 4) functionalized with acidic groups providing mobile protons and $[M^{IV}(CN)_8]^{4-}$ units (M^{IV} = Mo, W) bearing photomagnetic activity.[1,2] This combination enables the incorporation of H^+ conductivity and a photomagnetic effect within a single material. The coordination topology, and consequently the photomagnetic and electrical properties, are modulated by the number of acidic groups in the macrocyclic ligand. Although both functionalities occur at different temperatures, these results suggest a design strategy toward systems in which switchable properties overlap and produce cross-effects.

The switching of proton conductivity, accompanied by changes in magnetic and optical properties, was also observed in another CN-bridged compound, $NH_4[Ni(cyclam)][Fe(CN)_6]\cdot 5H_2O$ [3], whose switchable characteristics originate from thermally induced electron-transfer phase-transition (ETPT) between Ni^{II}-Fe^{III} and Ni^{III}-Fe^{II} valence states. The material exhibits bistability in both magnetic and electrical properties around room temperature. The ETPT affects proton relay pathways and charge distribution within the coordination skeleton, thereby influencing conductivity and activation energy of the process with an ON-OFF switching ratio of ~30 (295 K, 50% RH). Importantly, the thermally induced ETPT can be switched off by exchanging NH_4^+ with H_3O^+ via acid treatment and restored by exposure to gaseous NH_3, providing chemical control over the electrical and magnetic properties. These findings highlight the potential of CN-bridged coordination systems as platforms for designing stimuli-responsive proton conductors for protonic electronics, chemical sensors, and other switchable smart devices.



[1] M. Reczyński, M. Pazera, M. Magott, *Inorg. Chem.* **2025,** *64* (15), 7397.

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[3] M. Reczyński, D. Pinkowicz, K. Nakabayashi, C. Näther, J. Stanek, M. Kozieł, J. Kalinowska-Tłuścik, B. Sieklucka, S. Ohkoshi, B. Nowicka, *Angew. Chem. Int. Ed.* **2021,** *60* (5), 2330.

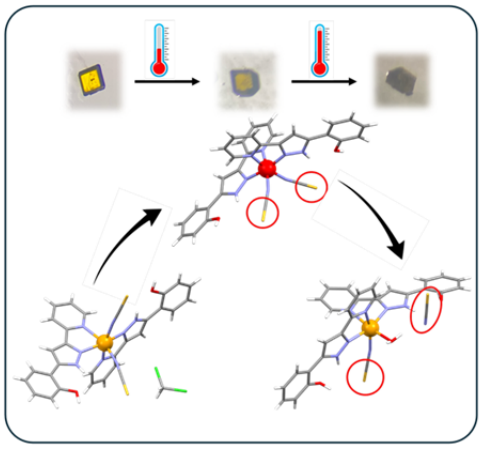
HALOGEN BONDING CONTROL OF A THERMALLY INDUCED SC–SC TRANSFORMATION IN A SPIN CROSSOVER COMPLEX

R. Diaz-Torres[a,b], O. Martínez[a], R. Couvreur[a], Y. Agudo[a], O. Roubeau[c], G. Aromí[a,b], D. Aguilà[a,b]

[a]Departament de Química Inorgànica i Orgànica, Universitat de Barcelona, Spain
[b]Institute of Nanoscience and Nanotechnology, University of Barcelona (IN2UB), Spain
[c]Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC and Universidad de Zaragoza, Spain

Structure and function are intimately linked in spin crossover (SCO) materials, where subtle structural variations can strongly influence switching behavior. SCO complexes reversibly interconvert between low-spin (LS) and high-spin (HS) states under external stimuli such as temperature, light, or pressure, making them promising candidates for molecular devices and sensors. Because these transitions arise from delicate structural and electronic factors, understanding how the coordination environment evolves during the transformation is essential. In this context, single-crystal-to-single-crystal (SC–SC) transformations provide a powerful approach to track structural changes in real time, offering direct crystallographic insight into coordination geometry, bond distances, and crystal packing that cannot be obtained from bulk measurements.

Here we report a thermally induced SC–SC transformation in $[Fe(L)_2(NCS)_2]\cdot DCM$ (1) (L = dipyridyl–pyrazolyl derivative), in which solvent loss, spin-state change, and coordination environment reorganization occur sequentially within the single crystal, yielding structurally and magnetically distinct phases. Remarkably, co-crystallization with the halogen-bond donor 1,4-diiodotetrafluorobenzene suppresses the transformation entirely — while simultaneously introducing additional supramolecular functionality into the material — highlighting a direct connection between crystal packing forces and coordination sphere stability.



[1] Inorg. Chem. Front., 2019, 6, 2194

[2] CrystEngComm, 2021, 23, 7899

μ_4-OXO-BRIDGED (COPPER)$_4$ ASSEMBLY DRIVEN BY VORICONAZOLE COORDINATION: SYNTHESIS, STRUCTURE AND EPR EVIDENCE OF MAGNETIC EXCHANGE

José Aleixo de Azevedo França, Jett Tao Janetzki, Lorenzo Sorace, José Severiano Carneiro Neto, Mauro Perfetti, Luigi Messori

Chemistry Department, University of Florence, Sesto Fiorentino, Italy

Coordination compounds featuring antifungal azoles have been increasingly explored due to their structural diversity and potential medicinal applications [1]. Here, the reaction of Cu(II) acetate with the antifungal drug voriconazole (HVRZ), initially aimed at forming the mononuclear species, unexpectedly yielded two crystalline products from the same conditions. Single-crystal X-ray diffraction showed that, besides the anticipated mononuclear complex, a structurally remarkable tetranuclear assembly forms, featuring a μ_4-oxo-centered $\{Cu_4(\mu_4\text{-}O)(\mu\text{-}OAc)_4\}$ core stabilized by voriconazole coordination.

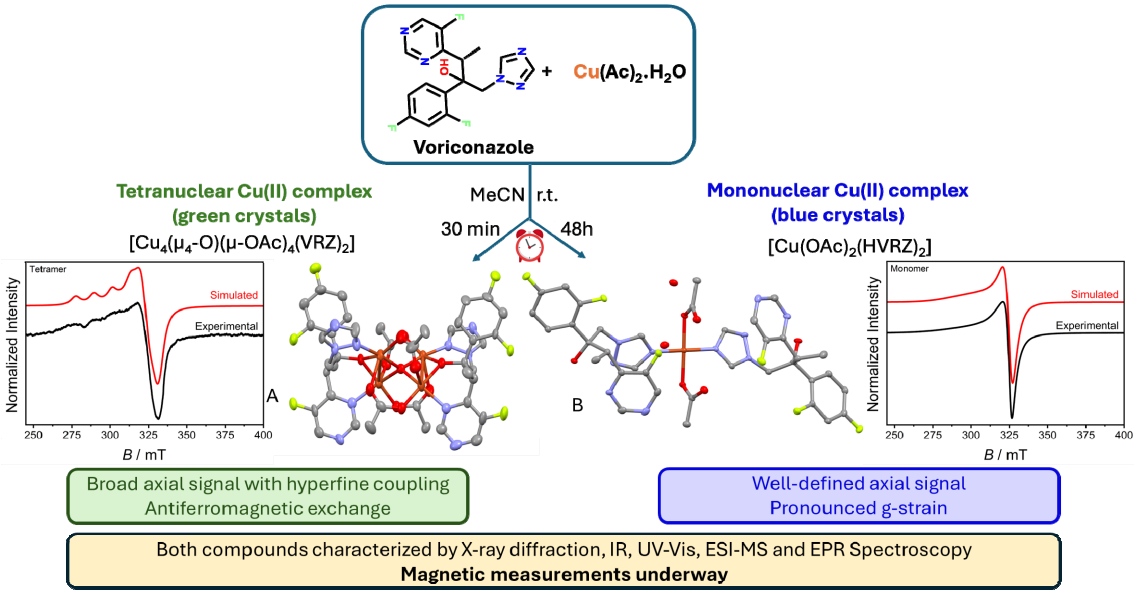


Figure 1. Reaction scheme and crystal structures of the tetranuclear (green) and the mononuclear (blue) Cu(II) complexes and X-band EPR spectra.

The EPR spectra recorded at room temperature show a well-defined axial signal for the mononuclear complex (gx = 2.06, gy = 2.07, gz = 2.26), with pronounced g-strain indicative of structural distortion. In contrast, the tetranuclear species exhibits a broader and weaker axial signal (gx = 2.03, gy = 2.087, gz = 2.27) with partially resolved hyperfine coupling (Az = 370 MHz), consistent with antiferromagnetic exchange interactions between Cu(II) centers mediated by acetate bridges and the central μ_4-oxo ligand. Magnetic measurements are underway to further support the magnetic behavior suggested by EPR. Overall, these results highlight how the electronic and magnetic properties evolve from the mononuclear to the tetranuclear species.

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CHEMICAL VAPOR DEPOSITION OF ACTINIDE-BASED THIN FILMS FROM ACTINIDE COORDINATION COMPOUNDS

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The deposition of actinide-containing thin films remains challenging due to the limited availability of suitable precursor systems for vapor phase processing. In this context, molecular actinide complexes provide promising precursor platforms for chemical vapor deposition (CVD), as their molecular structure can strongly influence volatility, transport behavior, and decomposition pathways during deposition.

This contribution focuses on the CVD processing of actinide-based thin films using thorium- and uranium-containing complexes as molecular precursors. The influence of deposition parameters and precursor characteristics on thin film growth and material formation is discussed with respect to phase formation, film morphology, and compositional control.

The presented results demonstrate how molecular precursor chemistry can enable the preparation of actinide-based thin films via CVD and underline the importance of precursor-driven approaches for the development of advanced actinide materials.

DISCOVERY AND CHARACTERISATION OF NEW GIGANTIC POLYOXOMOLYBDATES

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[a]School of Chemistry, The University of Glasgow, Glasgow, G12 8QQ, UK
[b]College of Chemistry and Chemical Engineering, Donghua University, Shanghai 201620, China

Polyoxometalates (POMs) represent an exceptional and continually expanding area of research in inorganic chemistry. Among them, gigantic polyoxomolybdates (POMos) occupy a particularly distinctive niche. Their structural complexity remained unresolved for more than two centuries, until the first giant Mo blue (MB) cluster, {Mo_{154}}, was structurally characterised in 1996. Despite nearly three decades since the breakthrough, the number of known analogous gigantic POMos remains surprisingly limited. Our recent work aims to broaden the structural diversity of these systems by exploring new assembly conditions and introducing modified functionalities. We have synthesised a series of highly unusual POMos under elevated temperature conditions and in the presence of organic ligands. One representative example is the cluster $[H_{24}Mo_{157}(H_2O)_{35}O_{456}(PO_3C_7H_6OH)_{18}]^{36-}$ {Mo_{157}}, whose structure is shown in Figure 1. The {Mo_{157}} cluster features a dodecameric MB wheel composed of two non-equivalent hemispherical shells, top {Mo_{82}} and bottom {Mo_{63}} connected by twelve {s-Mo_1} supporting units. The top {Mo_{82}} hemisphere consists of six {Mo_8} and six {Mo_3} building blocks arranged alternately to form an elliptical cavity that hosts a central ε-Keggin-based {Mo_{16}} guest. This {Mo_{16}} unit comprises a fully reduced ε-Keggin core {Mo^{V}_{12}} and four {Mo^{VI}} add-on units. Several potassium ions are located between the encapsulated {Mo_{16}} guest and the surrounding wheel framework; their ionic radius matches the cavity remarkably well, enabling them to reinforce the host structure while simultaneously anchoring the guest through electrostatic interactions. In contrast, the bottom {Mo_{63}} hemisphere, although also constructed from six {Mo_8} units, exhibits a distinct connectivity pattern in which three {Mo_3} and three {c-Mo_2} units alternate along the inner rim of the ring. This asymmetry between the two hemispheres contributes to the overall structural uniqueness of the {Mo_{157}} cluster and highlights the rich architectural possibilities accessible through controlled POMo assembly.

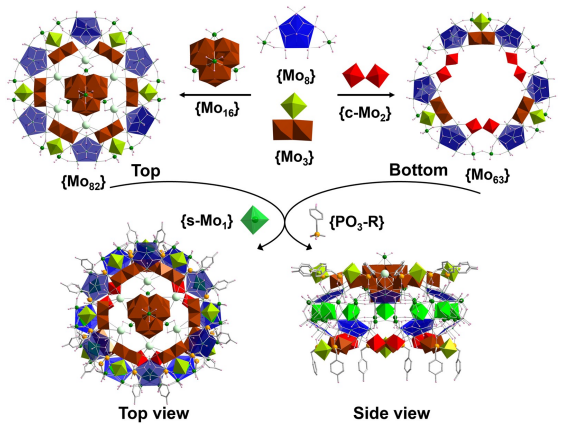


Figure 1. Schematic representation of the construction of {Mo_{157}}

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[2] Long, D.-L.; Cronin, L., *Adv. Inorg. Chem.* **2021**, *78*, 227-267.

[3] Long, D.-L.; Cronin, L. *Adv. Inorg. Chem.* **2025**, *86*, 29-58.

SWITCHING HOSTS, SWITCHING TIMES: RELAXATION DYNAMICS OF ENCAPSULATED FERROCENIUM

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Department of Inorganic and Organic Chemistry, Institute of Theoretical and Computational Chemistry, Barcelona, Spain

Molecular spin systems are promising candidates for emerging technologies based on quantum bits (qubits). Their ability to access multiple quantum states can significantly decrease the number of steps required in quantum computing algorithms [1]. A key requirement for these two-level systems is the preservation of quantum coherence, which demands sufficiently long coherence times. However, spin relaxation can take place through various pathways, including Orbach, Raman, direct, and local mode processes, as well as quantum tunneling of magnetization (QTM) [2]. The first four mechanisms are governed by spin–phonon interactions, whereas QTM arises from spin–spin interactions. While identifying and understanding these relaxation pathways is essential, controlling both the molecular structure and its surrounding environment is equally critical for enhancing coherence times. Several approaches have been proposed to achieve this improvement.

As the environment plays a crucial role in the dynamics of molecular systems, host–guest strategies are effective for modulating molecular behavior and reducing spin relaxation. In this work, different organic hosts (resorcin[4]arene, α-cyclodextrin, and cucurbit[7]uril) are explored due to their favorable binding properties for encapsulating ferrocenium hexafluorophosphate, a metallocene characterized by fast relaxation times arising from dipolar interactions between iron centers. The environment of these hosts is a key factor influencing system dynamics, and they are considered in order from smallest to largest cavity volume.

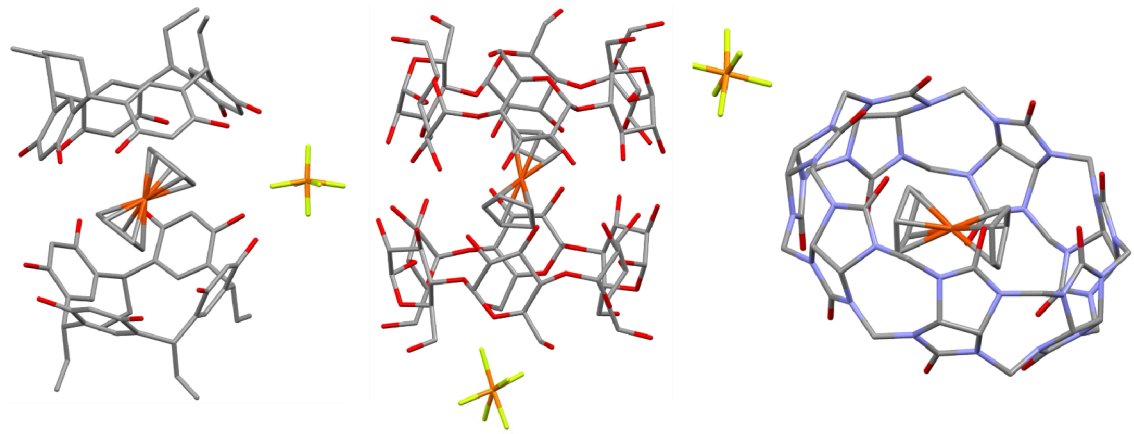


Figure 1. Stick representation of the crystal structures for encapsulated ferrocenium hexafluorophosphate at different organic hosts and ratios, from left to right: resorcin[4]arene, α-cyclodextrin, and cucurbit[7]uril.

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THERMODYNAMIC LIGAND EXCHANGE STUDIES IN METAL-OXO CLUSTERS WITH NMe_4 SALTS

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Department of Chemistry, University of Warwick, Coventry, United Kingdom

Metal-oxo clusters are widely studied precursors to metal-organic frameworks (MOFs), functioning as secondary building units (SBUs) in the extended structure. However, existing synthetic routes towards these MOFs require harsh solvothermal conditions that often result in degradation of the cluster precursor. Modulation is a common technique used in MOF synthesis, endeavouring to slow down the crystallisation process for growing single crystals, often utilising small carboxylic acids[1].

This work proposes an alternative type of modulator in the form of ammonium-carboxylate salts, which, in aprotic conditions, form rapidly exchanging equilibria with metal clusters that may enable a more controlled, room-temperature synthesis of MOFs that preserves the integrity of the cluster core, potentially leading to a diverse array of MOF structures not previously accessible.

A series of Zn- and Ti-oxo clusters and corresponding tetramethyl-ammonium salts of carboxylate and phosphinate ligands were synthesised and characterised. The ligand exchange equilibria were studied by a range of spectroscopic techniques, and kinetic and thermodynamic parameters were extracted. The findings from this work will enable a more controlled, room-temperature approach to synthesis of MOFs that preserve the integrity of the original cluster structure.

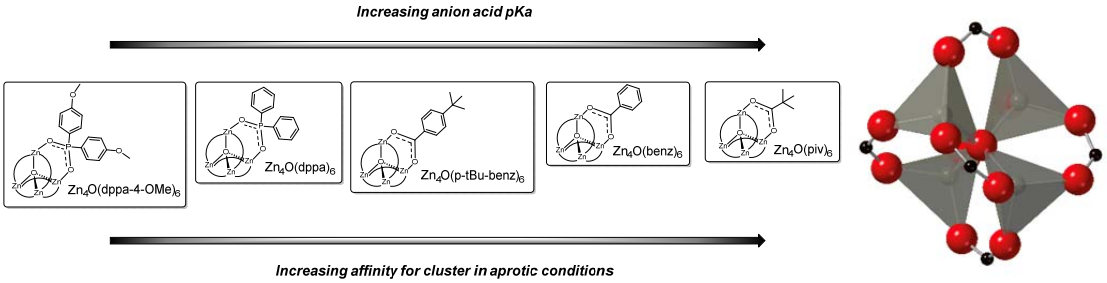


Figure 1: Scheme depicting the hypothesised relationship between pKa and affinity for Zn-oxo clusters in solution, investigated in this work, including crystal structure of Zn_4O core.

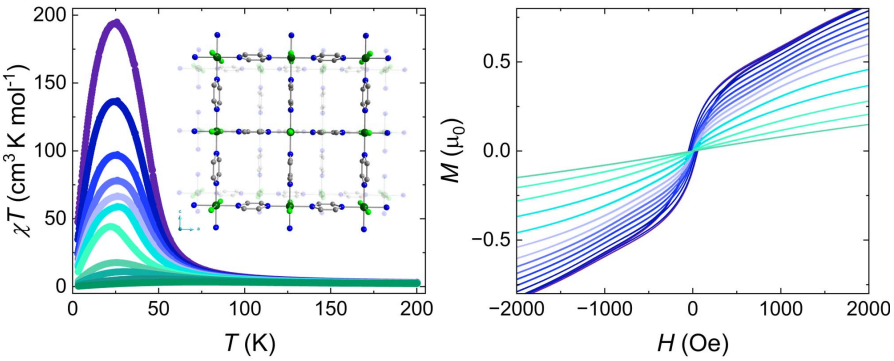
[1] R. S. Forgan, Chem. Sci. 2020, 5, 4546-4562.

TUNING MAGNETIC AND ELECTRONIC PROPERTIES IN A CHROMIUM-PYRAZINE COORDINATION FRAMEWORK VIA AXIAL HALIDE LIGAND SUBSTITUTION

Alexandros A. Kitos[a], Frédéric Aribot[a], Niki Mavragani[a], Anton Viborg[a], Nathan J. Yutronkie[b], Mariusz Kubus[a], Andrei Rogalev[b], and Kasper S. Pedersen[a]

[a]Technical University of Denmark, Kgs. Lyngby, Denmark
[b]European Synchrotron Radiation Facility, Grenoble, France

Two-dimensional (2D) magnetic materials have emerged as a fertile platform for exploring correlated electronic phenomena in reduced dimensions. In this context, redox-active coordination frameworks enable systematic tuning of electronic transport and magnetic exchange through chemical modification of the coordination environment [1]. In this work, we investigate a series of chromium–pyrazine coordination networks of the form $CrX_2(pyz)_2$ (X = halide; pyz = pyrazine), where systematic variation of the axial anion provides a means to tune metal–ligand interactions without altering the underlying square-lattice topology [2]. Herein, we report the synthesis and characterization of a fluoride-substituted analogue, $CrF_2(pyz)_2$, and compare its structural, electronic, and magnetic properties with those of the corresponding $CrX_2(pyz)_2$ ($X = Cl^-$, Br^- or I^-) frameworks. Structural and spectroscopic analyses reveal a predominantly Cr^{3+} electronic configuration alongside persistent ligand-centered reduction. Notably, fluoride substitution leads to enhanced electrical conductivity relative to the chloride analogue, while simultaneously modifying the magnetic ordering behavior. Comparative analysis across the halide series reveals that changes in anion identity can significantly influence both charge transport and magnetic interactions. These results demonstrate that anion substitution provides a useful strategy for tuning coupled electronic and magnetic properties in redox-active coordination networks.



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OPTIMISING TITANIUM OXO CLUSTER-BASED MATERIALS FOR PHOTOCATALYSIS

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Titanium-dioxide (TiO_2) is a pivotal semiconductor material widely utilized in applications such as self-cleaning windows and photocatalysis [1]. At the nanoscale, Titanium-oxo clusters bridge the gap between molecular and materials chemistry, presenting unique opportunities for photocatalytic applications due to their distinctive structural and electronic properties [2].

This study focuses on the electronic structure and photochemical properties of a series of Ti_6-oxo clusters and their impact on photocatalytic performance [3]. Through time-dependent density functional theory (TD-DFT) calculations, we demonstrate that the ligand-based energy levels can significantly influence the band structure of these clusters, akin to the HOMO/LUMO gap modulation in nanomaterials [4]. Our findings reveal that varying the ligand environment, including the use of long **π**-conjugated ligands, can optimise the photocatalytic efficiency by engineering the electronic properties. These insights enhance our understanding of photo-activity in titanium-oxo clusters and open new avenues for their application in sustainable energy conversion, environmental remediation, and chemical synthesis [5-6].

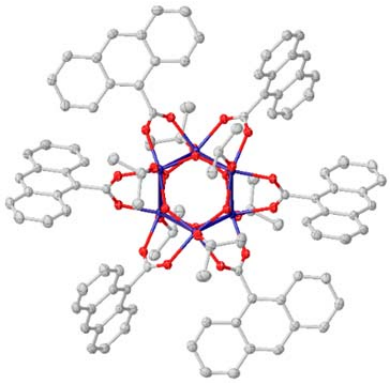


Figure 1. Molecular structure of $[Ti_6O_6(O^iPr)_6(9\text{-}AC)_6]$, H atoms omitted for clarity with Ti (blue), O (red) and C (grey).

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OPTIMIZATION OF THE SYNTHESIS OF MACROCYCLIC LIGANDS USING LINEAR PUMPS AND A FLOW REACTOR

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Template synthesis is one of the most widely used synthetic protocols for preparing macrocyclic ligands [1]. The synthesis of 15- and 17-membered pyridine-based macrocyclic ligands (15-pyN_3O_2, 17-pyN_3O_2, Fig. 1) [2, 3] is based on the formation of a Mn(II) Schiff base complex from pyridine-2,6-dicarbaldehyde and the corresponding diaminoether in the first macrocyclization step, followed by its reduction with $NaBH_4$ and demetallation. As part of its optimization, the method of adding reactants in the first step was varied from the simplest setup using a separating funnel for reactant addition to using one or even two linear pumps to the most sophisticated setup using a flow coil reactor. By changing the setup to improve the continuity of reactant addition and ensure uniform mixing without concentration fluctuations, we achieved a significant increase in reaction yields from ~70% to ~90% and reduced the amount of side products. The experimental setups discussed represent the future of the synthesis of analogous systems as well as other organic and coordination compounds.

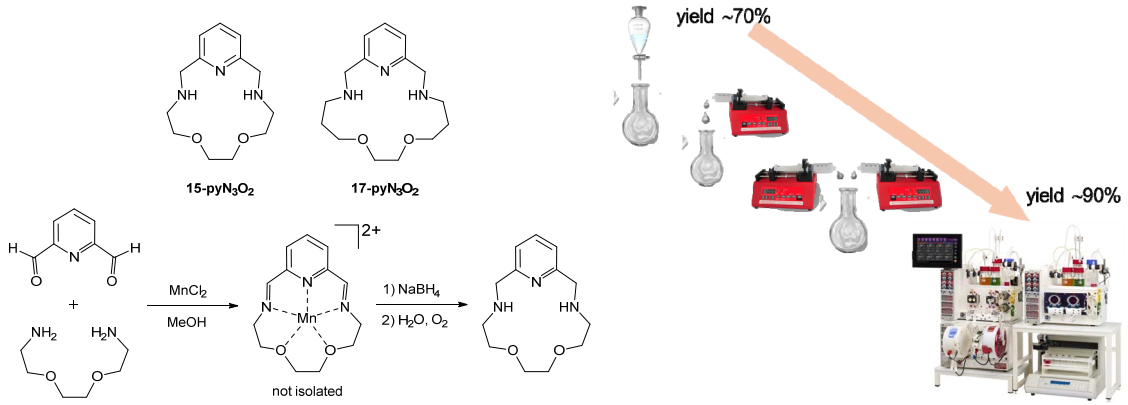


Fig. 1 Structural formulas of prepared ligands together with their synthetic scheme and illustration of employed setups for the first macrocyclization step.

This work was supported by the institutional sources of the Department of Inorganic Chemistry at the Faculty of Science, Palacký University in Olomouc.

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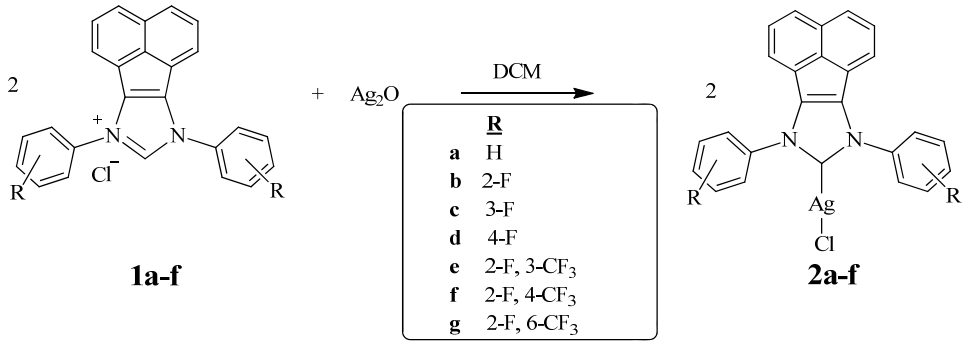
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NOVEL FLUORINE-SUBSTITUTED BIAN LIGANDS AND THEIR SILVER(I) COMPLEXES: SYNTHESIS AND CHARACTERIZATION

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In recent years, the synthesis of alternative molecules and the investigation of their applicability have become major areas of interest in anticancer research [1]. In particular, the widespread and effective potential use of silver(I) complexes in this field has attracted significant attention from researchers. In addition, the beneficial effects of fluorine-containing substituents on biological activity have been extensively documented in the literature [1]. In light of these considerations, novel BIAN-derived ligands bearing fluorine substituents, along with their corresponding Ag(I) complexes, have been synthesized in this study (Scheme 1).



Scheme 1. Synthesis of acenaphthyl-backboned NHC-Ag(I) complexes with fluorinated substituents

This study involved the synthesis of novel Ag(I) metal complexes obtained from N-heterocyclic carbenes (NHCs) including fluorinated substituents in the N-aryl region and an acenaphthyl framework. All synthesized compounds were characterized by various spectroscopic techniques, including ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, FT-IR spectroscopy, elemental analysis, and high-resolution mass spectrometry (HR-MS). The anticancer activities of these organometallic compounds will be evaluated.

Acknowledgment: The authors are greatly thankful to The Scientific and Technological Research Council of Turkey (TUBITAK) with project number 223Z317 for financial support.

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SITE-SELECTIVE PHOTOREDOX REACTIVITY OF TITANIUM-OXO CLUSTERS IN THE SINGLE CRYSTAL PHASE

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Titanium-oxo-alkoxide clusters (3–17 Ti atoms) serve as precise molecular models for TiO_2 surfaces in alcoholic media. Building on our group's first report of photoinitiated single-crystal-to-single-crystal (SC-SC) redox transformations [1], we now use in situ UV laser irradiation (305 nm) on synchrotron-mounted single crystals to directly capture photoproducts by X-ray diffraction. The results reveal exclusive oxidation of terminal alkoxides to aldehydes/ketones, while bridging alkoxides remain unreactive. This clear site-specificity uncovers a proton-coupled electron transfer (PCET) mechanism as the rate-determining step: reactivity is driven by short α-C–H···O distances (≤2.7 Å) that enable efficient hydrogen-atom transfer. In larger clusters (≥1 nm), low-coordinate surface oxo sites accept the proton, forming bridging hydroxides—mirroring theoretical predictions for ideal TiO_2 surfaces. Smaller Ti_3 clusters show no crystal-phase photoreactivity, indicating a critical nuclearity threshold for stable two-electron reduction. These SC-SC experiments provide direct atomic-level evidence for the PCET mechanism, explain terminal-site dominance in TiO_2 photocatalysis [2], and establish geometry- and size-dependent selectivity rules linking molecular clusters to heterogeneous systems.

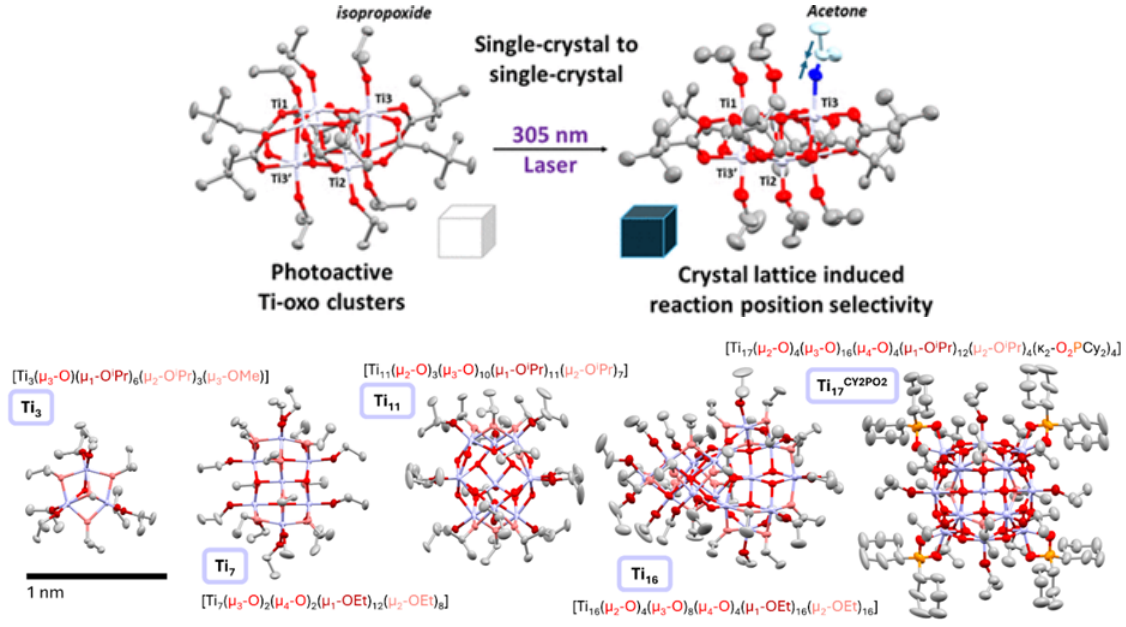


Figure 1 (top): Representative example of SC-SC photoreactivity in Ti-Oxo-Alkoxide clusters. (bottom): Range of different sizes and geometries of Ti-Oxo-Alkoxide clusters studied in this work.

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INFLUENCE OF Ru(II) AND Zn(II) DOPING ON THE SPIN-CROSSOVER PROPERTIES OF AN Fe(II) 2,6-*bis*(PYRAZOLYL)PYRIDINE DERIVATIVE

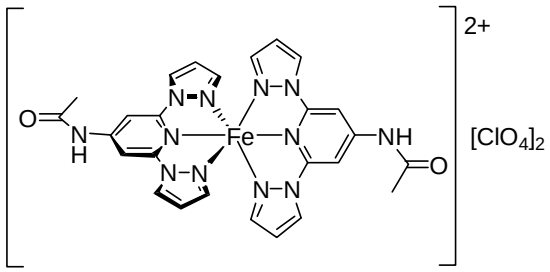
Changsheng Wang, Christopher M. Pask, Hari Babu Vasili, Malcolm A. Halcrow

School of Chemistry, University of Leeds, Leeds, UK

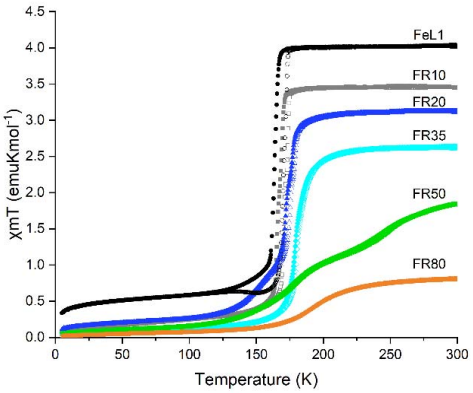
Spin crossover (SCO) is a reversible transition between the low-spin and high-spin states in complexes of transition metals, commonly Fe(II), which is induced by external stimuli such as temperature, pressure, or light [1]. Due to the associated changes in their magnetic, structural, and optical properties, SCO materials are of significant interest for applications in sensing, molecular switching, and memory devices [2]. Chemical doping has emerged as an effective strategy to tune SCO behaviour through modification of intermolecular interactions and lattice cooperativity.

The effects of inert metal doping on SCO behaviour are commonly rationalised using chemical pressure arguments [1,3]. However, recent studies on Ru(II)- and Zn(II)-doped $[Fe(bpp)_2][BF_4]_2$ systems (bpp = 2,6-*bis*{pyrazolyl}pyridine) have shown that while Zn substitution lowers $T_{1/2}$ as expected, Ru substitution increases $T_{1/2}$. That demonstrates that chemical pressure alone cannot fully account for the effects of doping on SCO behaviour. It was suggested the increased rigidity of the Ru(II) lattice influences the geometric flexibility of the surrounding Fe(II) switching centres and contributes towards stabilisation of the low-spin state [4].

The present study aims to investigate whether the effect of Ru(II) doping becomes more pronounced in SCO systems exhibiting larger structural changes between the high-spin and low-spin states. In this study, iron(II) *bis*[*N*-(2,6-di{pyrazol-1-yl}pyrid-4-yl)-acetamide] diperchlorate, $[Fe(L1)][ClO_4]_2 \cdot MeCN$ [5], was doped with Zn(II) and Ru(II) over a compositional range of 10–80%. Magnetic susceptibility measurements showed that Zn doping induces a comparatively smaller reduction in $T_{1/2}$, while Ru doping produces a greater increase in $T_{1/2}$ (Figure), relative to Zn/Ru doping in the $[Fe(bpp)_2]^{2+}$ system, which supports the proposed hypothesis. Structural data on the doped materials help to rationalise these results.



$[Fe(L1)][ClO_4]_2$



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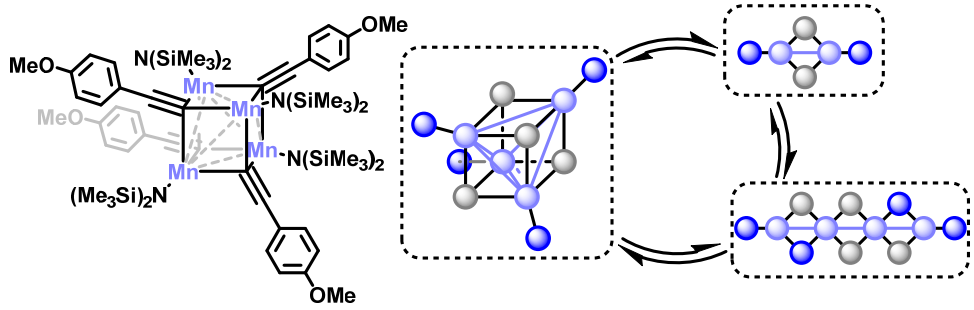
HETEROVALENT MANGANESE ALKYNYL CLUSTER

Chiara Looks, Yannik Appiarius, and A. Jacobi von Wangelin

Institute of Inorganic and Applied Chemistry, University of Hamburg, Hamburg, Germany

Low-valent metal clusters of 3d transition metals like manganese, iron and cobalt remain a challenging class of materials with diverse magnetic properties and intriguing metal-metal and metal-nonmetal bonding interactions [1]. Recently, our group reported the synthesis of two- and three-dimensional nanoclusters featuring μ_3-bridged alkynyl and hydride ligands [2, 3].

The clusters are accessible from reactive and highly soluble metal amide precursors, which readily undergo ligand-exchange reactions with terminal alkynes to form finite manganese tetramers. The geometries, ligand-bridging mode and magnetic behavior are influenced by the steric demand, ligand duality and electronic properties of the alkynyl substituent.



Scheme 1: Finite manganese alkynyl cluster with a postulated equilibrium between dimeric-tetrameric and linear-cubic structures.

Elucidation of the mechanism of the cluster formation is currently being pursued by quantum mechanical calculations and the isolation of intermediates by tuning the steric bulk. By varying the solvent and temperature we were able to influence the arrangement of the manganese tetramer, favoring either a linear or cubic structure. Ongoing studies explore the doping of the manganese tetramer with other 3d transition metals, as well as incorporating liker motifs to switch between 2D and 3D cluster architectures.

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BROKEN SYMMETRY AND ELASTIC FRUSTRATION IN ISOSTRUCTURAL MANGANESE(III) SPIN CROSSOVER CRYSTALS

Conor T. Kelly[a], Vibe B. Jakobsen[a], Ross Jordan[b], Solveig Felton[b], Helge Müller-Bunz[a] and Grace G. Morgan[a]

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Symmetry breaking spin state transitions in two of three isostructural salts of Mn^{III} spin crossover cations, $[Mn^{III}(3\text{-OMe-5-NO}_2\text{-sal}_2323)]^+$ are reported.[1] The ReO_4^- (**1**) salt undergoes two-step spin crossover which is coupled with a re-entrant symmetry breaking structural phase transition between a high temperature phase (S=2, $C2/c$), an intermediate ordered phase (S=1/S=2, $P2_1/c$), and a low temperature phase (S=1, $C2/c$). The AsF_6^- (**2**) complex undergoes an abrupt transition between a high temperature phase (S=2, $C2/c$) and a low temperature ordered phase (S=1/S=2,). The SbF_6^- (**3**) complex undergoes a gradual transition between a high temperature phase (S=2,) and a low temperature spin state ordered phase (S=1/S=2,). Correlation of the volume of the anion and the $T_{1/2}$ of the transitions in these complexes and three complexes with similar anions, BF_4^- (**4**), ClO_4^- (**5**), PF_6^- (**6**), reveals an increase in $T_{1/2}$ upon increasing the anion volume. We rationalise that this volume modulates the elastic interactions between the Mn^{III} sites, increasing elastic frustration with larger anions resulting in a two-stepped transition for **1** and the stabilisation of the mixed (HS:LS) state to low temperature for **2** and **3**.

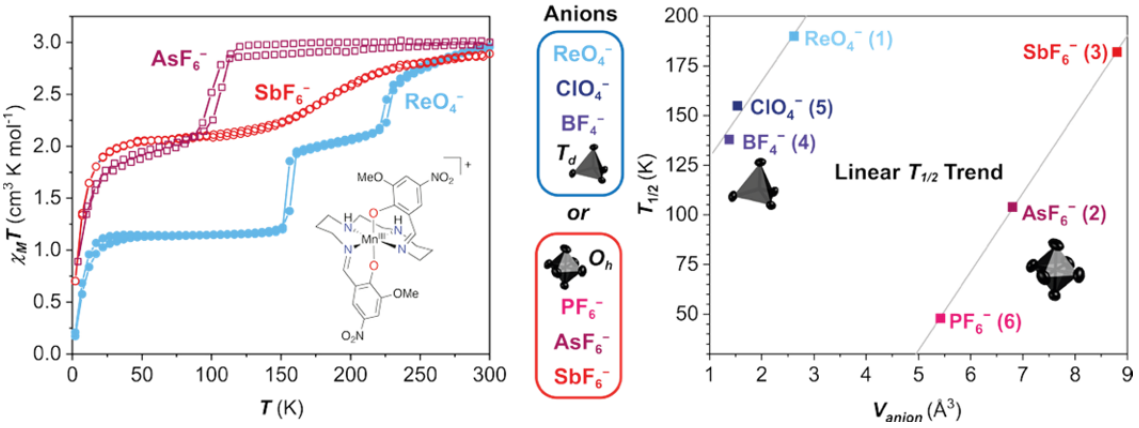


Figure *Left:* $\chi_M T$ versus T for **1** – **3**. *Right:* Correlation between anion volume and $T_{1/2}$.

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DODECAVANADATE COORDINATED TO LANTHANIDE IONS. A NEW FAMILY OF MIXED-VALENCE POLYOXOVANADATES

Diego Venegas-Yazigi[a,b], Patricio Hermosilla-Ibáñez[a], Verónica Paredes-García[b,c], Andrés Vega[b,c], Eric Le Fur[d], Marlen Gutierrez-Cutiño[b,e], Jose F. Marco[f], Walter Cañón-Mancisidor[b,g]

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[b] CEDENNA, Santiago, Chile
[c] Department of Chemical Sciences, Universidad Andres Bello, Santiago, Chile
[d] UMR6226, ENSCR, Rennes, France
[e] Faculty of Health and Odontology, Universidad Diego Portales, Santiago, Chile
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[g] Faculty of Engineering, Science and Technology, Universidad Bernardo O'Higgins, Santiago, Chile

Polyoxometalates (POMs) remain an intriguing family of oxido-metal clusters with a distinctive electronic structure. Their different geometries attract scientists, giving the possibility to build more complex materials using the POMs as building blocks. Among the polyoxometalates, the polyoxovanadates (POVs) are an interesting family. They can be diamagnetic or paramagnetic, ranging from fully oxidized to fully reduced. Due to the small difference in the redox potential V^V/V^{IV}, many POVs exhibit multiple oxidation states for the same structure. There is a polyoxovanadate that has an anion inside, i.e., the $[V^V_{12}O_{32}Cl]^{5-}$ anion. This anion can coordinate ions to form systems like$\{[Ln(L')_4]_2[V^V_{12}O_{32}Cl]\}^{n-}$.[1] As far as we know, all the lanthanide complexes show the $V_{12}O_{32}Cl$ core fully oxidized. There have also been informed complexes of the form $[M_2(L)_3V_{12}O_{32}Cl]^{2-}$, for M= Ca, Sr, where there is one center of vanadium(IV).[2]

In this work, we will discuss the structural, electronic, and magnetic properties of two compounds $\{TBA\}\{[Gd(DMF)_4]_2[V^{IV}_2V^V_{10}O_{32}Cl]\}$ and $\{TBA\}_4\{[Tb(DMF)_4]_2[V^{IV}_2V^V_{10}O_{32}Cl]\}_4$ $\{[Tb(DMF)_4]_2[V^{IV}_1V^V_{11}O_{32}Cl]\}$ where we postulate that two different oxidation states of the POV core co-crystallize. These systems are the first mixed-valence systems coordinating lanthanide ions within the $V_{12}O_{32}Cl$ core.

Acknowledgements: The authors acknowledge financial support from FONDECYT 1240549 and FONDECYT 1252136. The authors also acknowledge the CEDENNA ANID CIA250002 project and the FONDEQUIP EQM 130086 PPMS and EQM 140060 EPR projects. The IRP-CoopIC international project Chile-France is also acknowledged for support.

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ACCESS TO MIXED VALENT POLYNUCLEAR Ni COMPLEXES FROM Ni(II) PIANO-STOOL TYPE COMPLEXES

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Department of Chemistry, School of Natural Sciences,
National and Kapodistrian University of Athens, Zografou, Athens, Greece

The reaction between [Ni(η^4-COD)$_2$] and isoindol-2-ium fused Cyclic Aryl Amino Carbon Carbene triflate salt precursors [1] results in oxidative C–N bond cleavage furnishing new family of Ni(II) piano-stool type complexes. These complexes, which are structurally similar to ansa-metallocenes [2], allow the synthesis of a variety of Ni organometallic compounds in various formal oxidation states and nuclearities, such as a syn-bimetallic [$Ni^{(I)}_2$] and trimetallic [$Ni^{(I)}_2Ni^{(0)}$] complexes featuring *bona-fide* Ni-Ni bonds. Apart from such lower valent complexes, we have also been able to access dimeric formally [Ni(III)] complex, with a closed-shell doublet electronic configuration, from the reaction of afore-mentioned [Ni(II)] precursors with Tosyl-N_3 (Tosyl = *p*-CH_3-$C_6H_4SO_2$) leading to aromatic C–H bond activation and giving rise to a new pincer type ligand (**Figure 1**).

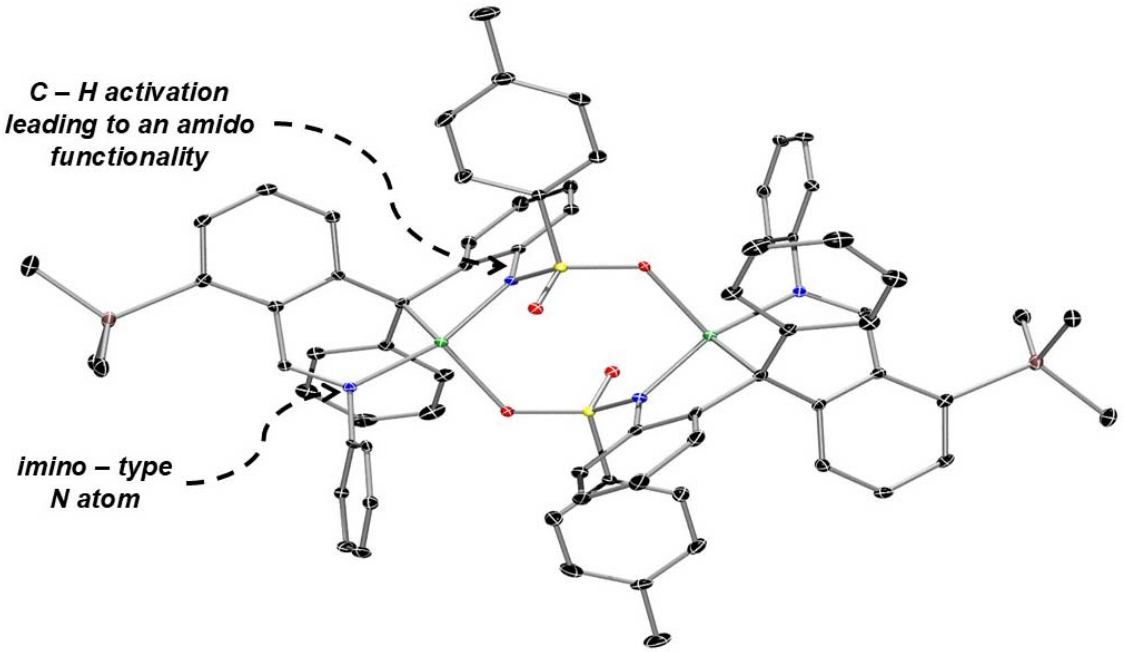


Figure 1: ORTEP representation of a dimeric formally Ni(III) complex, showing 50% molecular ADPs. H atoms, ^{i}Pr- fragments and two BAr^{F24} counterions are omitted for clarity. Colour code: Ni green, N blue, O red, S yellow, Si brown, C black.

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SYNTHESIS OF Co(III)-AMMINE HETEROPOLYOXOMOLYBDATES WITH SELECTED d-BLOCK ELEMENTS

Dino Kuzman[a], Vladimir Damjanović[b], Glorija Medak Spahić[c], Višnja Vrdoljak[a] and Marina Cindrić[a]

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[b]Department of Chemistry and Biochemistry, School of Medicine, University of Zagreb, Zagreb, Croatia
[c]Division of Materials Chemistry, Ruđer Bošković Institute, Zagreb, Croatia

Polyoxomolybdates (POMos) are a subclass of polyoxometalates formed through the condensation of $\{MoO_4\}$ building units. POMos represent a large and structurally diverse group of metal–oxygen clusters that are subdivided into isopolyoxomolybdates (isoPOMos), composed exclusively of molybdenum centers, and heteropolyoxomolybdates (heteroPOMos), which incorporate additional p-, d- or f-block heteroatom. This work investigates the influence of synthetic methods, reaction conditions, as well as crystallization conditions on the formation of POMos with different nuclearities in the solid state. Herein we employed both solution-based and mechanochemical synthetic strategies to prepare heteroPOMos containing chromium, cobalt, nickel or copper heteroatoms. We investigated reactions involving molybdate ion, malonic acid (serving as both a potential ligand and a structure-directing agent in the polyoxoanions self-assembly processes), cobalt(III) complex cations $[Co(C_2O_4)(en)_2]^+$ or $[Co(C_2O_4)(NH_3)_4]^+$, and a source of the selected d-block metal ion. By varying the reaction conditions and the cobalt(III) cations, several new $[X_xMo_mO_y]$ species were isolated. Selected products were evaluated for their photocatalytic activity in the degradation of the Safranin T. All products were characterized by single-crystal and powder X-ray diffraction and their thermal stability was tested.

PRODUCTION EFFICIENCY FOR LOW-CARBON CONCRETE IN PRECAST MANUFACTURING

Emilie L'Hôpital, Alexander Oliva Rivera, Ojas Arun Chaudhari, and Debadri Som

RISE Research Institutes of Sweden, Borås, Sweden

Achieving climate-neutral concrete by 2030 represents a major challenge for the prefabricated concrete industry, particularly due to the need for high early-age strength to maintain production efficiency. Reducing clinker content through supplementary cementitious materials (SCMs) is an effective pathway to lower CO_2 emissions. However, it results in delayed early strength development because of slower SCM reactivity. This poses a significant barrier for precast applications, where rapid demoulding is essential.

This project investigates strategies to enable accelerated early strength development in low-clinker concrete subjected to elevated curing temperatures, while ensuring long-term durability and compliance with SS-EN 137005:2025 [1]. Sulphate optimisation and the use of accelerator additives will be investigated to compensate for under-sulfation effects and modification of reaction kinetics that can occur in the blended binder system. Under-sulfation, intensified by filler effects and rapid C-S-H precipitation, can hinder clinker hydration and limit early strength. Optimised sulphate balance and targeted acceleration are therefore crucial to avoid early sulfate depletion, loss of strength, and durability risks such as delayed ettringite formation (DEF). This project investigates three binder systems: CEM II/A-LL, 60% CEM II/A-LL with 40% slag, and 80% CEM II/A-LL with 20% volcanic ash, combined with four accelerators with distinct chemistries: X140 (C-S-H seeds), MCUBE (diethanolamine-based), MHA (ammonium thiocyanate), and MSA (calcium nitrate), each at two dosages (1 % and 2 % by weight of binder). Isothermal calorimetry is being used to quantify improvements in cumulative heat release and sulphate balance, while early-age compressive strength testing assesses the ability to reach the target strength of 15 MPa after 16 hours. The sulphate adjustment is investigated with gypsum and hemihydrate addition. Three curing temperatures representative of precast production conditions (20, 40, and 60 °C) are being investigated to represent typical heat treatment regimes used in precast production.

Initial results show that CEM II/A-LL with 20% volcanic ash reach 34 MPA after 24h at 20 °C; therefore, no further investigations were carried out for this binder. However, CEM II/A-LL with 40% slag reaches 13 MPA at 20 °C and 18 MPA at 60 °C. Sulphate adjustment using gypsum together with the accelerator addition was investigated. Experiments at 60 °C are currently ongoing. Among the tested accelerators, X140 demonstrates the strongest early strength enhancement after 16h, which is consistent with its C-S-H seeding mechanism; MHA and Mcube also yield measurable improvements, while MSA exhibits comparatively limited acceleration, particularly at the dosages investigated. Ongoing investigations into sulphate adjustment with hemihydrate will further evaluate the impact of temperature-dependent solubility on reaction kinetics to optimise early strength development.

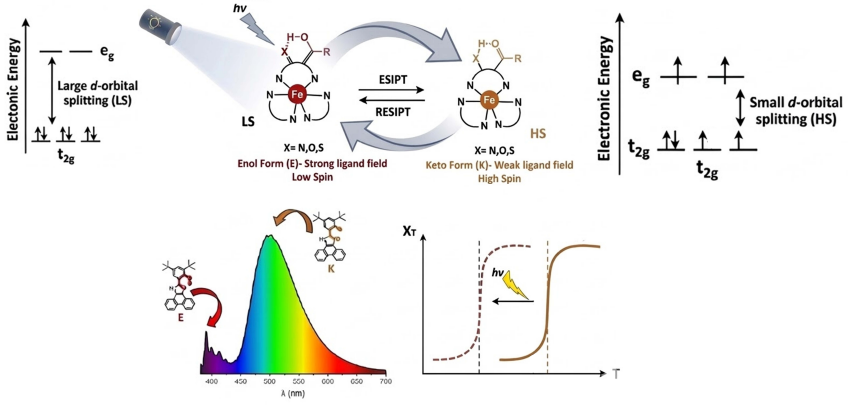
[1] SS 137005:2025, 'Precast Concrete Products - Commonrules – Application of EN 13369:2024 in Sweden'', Swedish institute for standards (SIS), 2025, Stockholm, Sweden (In Swedish)

LUMINESCENT SPIN CROSSOVER COMPLEXES

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The combination of the spin crossover (SCO) phenomenon with luminescence has attracted attention because of the potential applications that would follow (magneto-optical switches or sensors, new imaging techniques, *etc*.). The strategies that have been used up to now consist in either combining both properties in the same materials or preparing a SCO complex covalently linked to a fluorescent molecule, or even bearing fluorescent ligands. [1] However, it is not straightforward to preserve both properties because the two phenomena are extremely sensitive to subtle structural variations. In these molecular systems the structural and electronic changes occurring upon SCO transition cause modulation of the luminescence signal. In this work, we sought to develop molecules in which a luminescent ligand could impact the spin transition process through light irradiation. Using light as a trigger offers several advantages (high selectivity, rapid response times, minimal by-product formation) that are interesting for the design of multifunctional materials. Light-induced spin transition is already known through the LIESST (Light-Induced Excited Spin State Trapping) and LD-LISC (Light-Driven Ligand-Induced Spin Crossover) effects.[2][3] Our approach involves employing organic photoactive ligands based on the ESIPT (Excited State Intramolecular Proton Transfer) mechanism, a process known to be efficient both in solid and liquid state and at room temperature, a clear advantage compared to the known systems.[4] Irradiation of the ligand should trigger the intramolecular proton transfer, thus modifying the ligand field and modulating the spin transition process. [5][6] We have developed several Fe(II) SCO complexes that contain such photo-active ligands, and we are investigating the effect of the ESIPT process on the SCO behavior.



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THE CHEMISTRY OF ATOMICALLY PRECISE GOLD NANOCLUSTERS FOR ELECTROCHEMICAL AND BIOLOGICAL APPLICATIONS

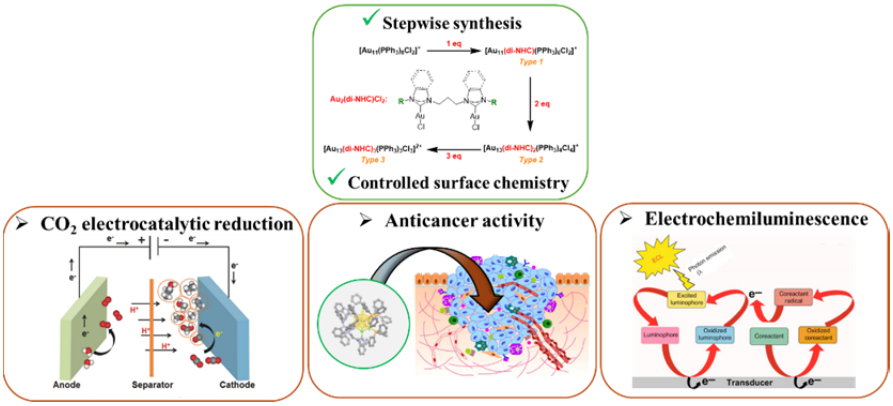
Giulia Saggiotti, Matteo Mauceri, Mattia Reato and Andrea Biffis

Department of Chemical Sciences, University of Padova, Padova, Italy

Despite their relatively recent emergence, molecular gold nanoclusters (AuNCs) stabilized by N-heterocyclic carbene (NHC) ligands have already demonstrated remarkable properties, including high stability, excellent reproducibility, and intense deep-red emission[1]. In recent years, our synthetic efforts have led to the development of two methodologies that enable precise control over cluster composition and geometry. In the first approach, three distinct classes of mixed PPh_3- and NHC-ligated AuNCs can be selectively isolated through stoichiometric control within a single reaction sequence[2]. In the second strategy, we exploit the reactivity of coordinated isonitriles [3] to generate a gold(I) bis-benzoxazolate staple grafted onto the nanocluster surface. To the best of our knowledge, this architecture is unprecedented in the context of NHC coordination chemistry on nanoclusters. The incorporation of this motif significantly influences the electronic structure owing to its enhanced π-accepting character and structural rigidity, leading to a narrower HOMO–LUMO gap and a red-shifted emission extending into the near-infrared (NIR) region.

These nanoscale molecular systems can be embedded in Nafion and investigated as heterogeneous catalysts for CO_2 electroreduction[4]. They have shown selectivity toward high-value products, such as formate and acetate, rather than CO. Furthermore, they display efficient electrochemiluminescence in solution, both in the absence (via annihilation) and in the presence of a co-reactant, with emission efficiencies surpassing that of $[Ru(bipy)_3]^{2+}$.

Finally, the precise atomic-level structural definition of these AuNCs has enabled the first systematic investigation of their cytotoxicity. The results reveal unprecedented selectivity and efficacy across different cancer cell lines. Preliminary studies of their biological mechanism of action suggest that, unexpectedly, it does not follow the commonly proposed pathway for gold-based compounds, namely the inhibition of thioredoxin reductase.



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REPURPOSING AN ORGANIC COFACTOR: METALLOFLAVINS THAT INVERT THE IRVING–WILLIAMS STABILITY TREND VIA OUTER-SPHERE HYDROGEN BONDING

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Inspired by the role of flavins in biological electron transfer, we previously developed a flavin-derived bidentate ligand, ^{all}**LH**, engineered to promote well-defined outer-sphere hydrogen-bonding interactions upon metal coordination. Variations in anion identity were shown to modulate the character of the outer-sphere hydrogen-bonding network, and base-induced tautomerization of ^{all}**LH** was found to reorganize noncovalent interactions, enabling selective substrate capture through switchable hydrogen-bond donor and acceptor sites.

Building on this foundation, we here report the synthesis of a complete isostructural series of octahedral 2:1 complexes, **(^{all}LH)$_2$MCl$_2$**, spanning the full Mn–Zn range. The N–H···Cl hydrogen-bonding network in the outer sphere stereoselectively directs all members into a single meridional isomer, providing a rare platform for direct thermodynamic comparison across the Irving–Williams series as a function of metal identity alone.

Strikingly, the stability trend observed within **(^{all}LH)$_2$MCl$_2$** series deviates fundamentally from classical Irving–Williams behavior: Cu(II), normally the thermodynamic maximum, emerges instead as the least stable member. Both experimental and computational analyses reveal that this reversal originates from the structural constraints imposed by the outer-sphere hydrogen-bonding network. These results demonstrate that noncovalent outer-sphere interactions are not merely structural accessories — they can influence the fundamental stability landscape of transition metal complexes, opening new avenues in the rational, bioinspired design of tailored coordination environments.

SLOW MAGNETIC RELAXATION IN MONOMERIC PENTACOORDINATE Mn(II) COMPLEXES NOT GOVERNED BY THE ORBACH PROCESS

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As the barrier to spin reversal in single-molecule magnets is proportional to the D-parameter value which rules the magnetic anisotropy, for rational tuning of the single-molecule magnetic behavior, knowledge of the D-parameter is beneficial. A lot of magnetostructural D-correlations have been carried out for Co(II) complexes. In contrast with the usual SMM/SIMs, for which a large anisotropy becomes a requirement, slow relaxation of the magnetization (SRM) for the cations with half-filled shell a priori, is not expected due to its negligible zero field splitting and the lack of double-well and the derived barrier for the SRM. This paradigm has been broken because a very small number of slow-relaxation magnetically isotropic compounds derived from the d^5 configuration have recently appeared in the literature. The d^5 high spin Mn^{II} complex ($^6A_{1g}$ term in high symmetry environments such O_h) with orbital contribution L = 0 becomes isotropic, and for an ideal topology, its D value is zero. However, the m_s degeneracy can be broken, reducing the symmetry by employing the adequate ligands in O_h coordination and/or changing the coordination number. Considering the above we present the study of structure and magnetic properties of two pentacoordinated Mn(II) complexes with 2,2'-[oxybis(methylene)]bis(1*H*-1,3-benzimidazole) (OMeBB) ligands and different linker ligands: thiocyanate and izocyanate about formulas Mn(OMeBB)(NCS) **[a]** and Mn(OMeBB)(NCO) **[b] (Figure 1)**. The reported complexes exhibit slow relaxation of the magnetization, and, from comparison with previously reported systems, it can be concluded that a low D value becomes crucial to promote SRM in this kind of isotropic systems and sign of D or rhombic/axial distortion is not determinant to promote SRM in the Mn^{II} case. Special attention should also be paid to the presence of a trivalent oxygen atom in the structure, which contributes to the unexpected role of the ligand's donor atom confirmed by X-ray diffraction and theoretical methods.

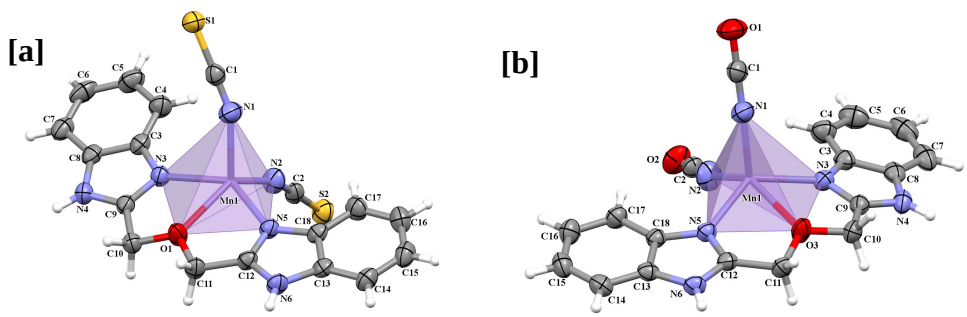


Figure 1. Molecular structures **[a]** and **[b]** along with the atom numbering. Thermal ellipsoids of non-hydrogen atoms are given at 50% probability level.

TUNING THE ELECTRONIC STRUCTURE AND PHOTOCHEMICAL PROPERTIES OF IRON(III)-OXO CLUSTERS

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To address the current global energy crisis, new technologies need to be developed to generate green fuels [1]. Hematite (α-Fe_2O_3) is a promising photocatalytic material due to its high natural abundance, low toxicity, and ideal band gap of ~2.2 eV, however, has short charge carrier distances of 2-6 nm [2]. Ultrasmall iron-oxide systems could be employed to overcome charge carrier recombination challenges. Quantum confinement effects can also be employed in these systems to tune the band gap of materials based on size, all with the view of rationally designing iron based solar absorbing materials for specific applications. Iron(III)-oxo clusters are atomically defined analogues of bulk oxide materials and can be used to study bulk oxide properties on a molecular scale [3,4]. This poster will explore the tuning of electronic structure and photochemical properties of iron(III)-oxo clusters, utilizing both quantum confinement effects and ligand structure. Analytical techniques including UV-Vis, Mössbauer and transient electronic absorption spectroscopies, and electrochemistry are employed to understand these changes.

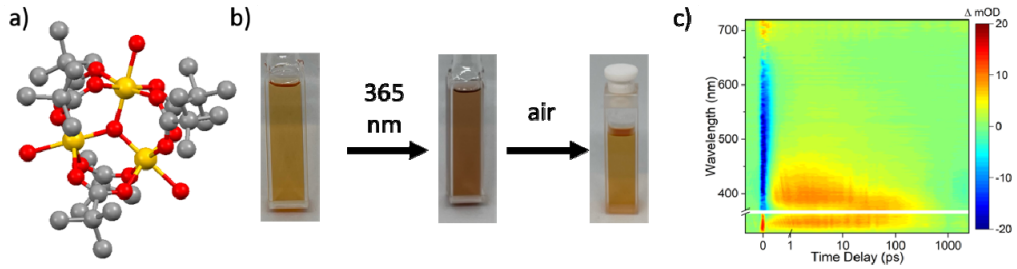


Figure 1: a) Crystal Structure of $[Fe_3O(H_2O)_3(O_2C^tBu)_6]^+[O_2C^tBu]^-$, b) Colour change showing photochemical reactivity of Fe_3 cluster upon 365 nm irradiation in $CHCl_3$:^{i}PrOH (3:1) and subsequent air exposure, c) False colour heat map of the transient absorption spectra for excitation of the Fe_3 cluster in $CHCl_3$:^{i}PrOH (3:1) with 365 nm irradiation

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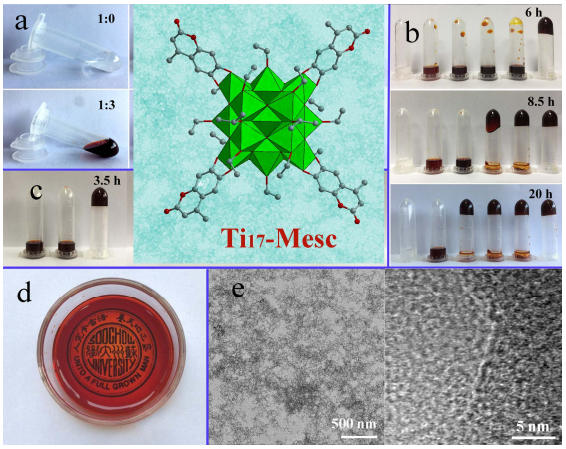
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GELATION PROPERTIES OF CATECHOL DERIVATIVE MODIFIED TITANIUM-OXO CLUSTERS

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Organic-inorganic hybrid metal–polyphenols as stable structural modules have gained extensive interest for their diverse applications [1]. However, titanium-oxo compounds (TiOCs) with large molecular polyphenols have been less explored and that were expected to be different from small polyphenols with isolated metal ions. Herein, 4-methyl-esculetin (Mesc), a catechol derivative, was selected to construct TiOC. The compound was structurally characterized as $[Ti1_7O_{24}(Mesc)_4(O^iPr)_{16}]$ (**1**). Photocurrent responses were evaluated using the compound sensitized TiO_2 electrodes. It was found that the current densities of **1** electrode is in relates to ligand to TiO core and ligand to ligand charge transfers (LMCT and LLCT). DFT calculation showed that the lowest ban gap of **1** originates from its LLCT. Compound **1** reacted with polyphenol tannin (TA) to form a fully transparent and robust gel (**1**-TA), and the gelation properties were investigated. Using the gel as nano-TiO_2 fixed agent, solar cell electrodes were prepared by a low temperature wet-method. The photocurrent responsive behavior of the **1**-TA/TiO_2 electrode was compared with that of **1** sensitized traditional high temperature treated TiO_2 electrode. Although the current density of the former is somewhat lower than that of the traditional electrode, the low temperature wet-preparation of **1**-TA/TiO_2 electrode is more energy efficient and sustainable. This work is a new challenge that extended the TiOC chemistry and application to polyphenol sole-gel systems.



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ELUCIDATING THE CAPABILITY OF PHOTOACTIVATED Ti-oxo CLUSTERS TO PERFORM OF MULTIELECTRON PROCESSES THROUGH BDFE STUDIES AND STRUCTURAL MANIPULATION

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Metal-oxo clusters are an area of great interest in chemistry due to the diverse structures and sizes that can be synthesised and their multitude of uses including as single source precursors for nanomaterials. In particular titanium-oxo clusters (TOCs) are known to be synthesisable with sizes from 4 to 52 titanium centres.[1] Added interest in TOCs comes from them sharing features with titanium dioxide which is well known for its applications in sunscreen, water treatment and importantly as a photocatalyst. These applications draw on titanium dioxide's ability to absorb light in the 3.0-3.2 eV region.[2] Many TOCs share this ability and exhibit added benefits of being discrete molecular units, in particular the benefit that they can be studied by molecular techniques such as NMR, SCXRD and EPR.

Certain TOCs, such as $Ti_6O_6piv_6(O^iPr)_6$, can also form stable photoactivated states when irradiated in the presence of coordinating solvents resulting in clusters containing both Ti(III) and Ti(IV) sites such as $Ti_6O_6piv_6(O^iPr)_4(HO^iPr)_4$, which has stored electrons and protons, and $Ti_6O_6piv_6(O^iPr)_4Py_2$ which has stored electrons.[3, 4] These electrons/protons may be accessible for redox processes, and the driving power they are able to exhibit can be determined by using a series quinones with known bond dissociation free energies (BDFEs).[5] Formation of the hydroquinone form of the quinones after exposure to the TOC $Ti_6O_6piv_6(O^iPr)_4(HO^iPr)_4$ demonstrates the potential for proton coupled electron transfer. Additionally, formation of the hydrocarbons in this way reveals a tendency for these TOCs to participate in alcohol exchange when in the presence of phenol-based alcohols, introducing a simple synthetic method for a large variety of clusters and potential implications for forming bridged clusters.[6]

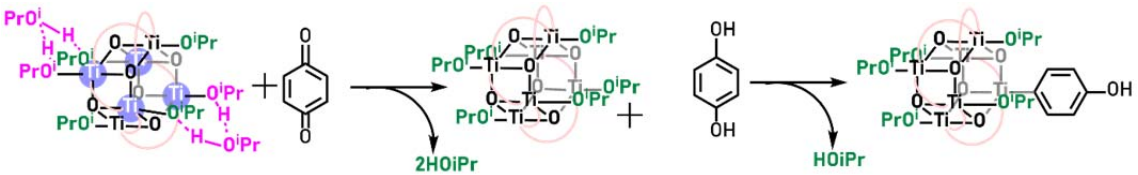


Figure 1: PCET process performed by TOC in the presence of an example quinone followed by alcohol exchange.

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ULTRAFAST PHOTOINDUCED CHARGE-TRANSFER DYNAMICS AT ROOM TEMPERATURE IN A Co-W CYANIDE-BRIDGED SYSTEM

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[b]DYNACOM IRL2015 University of Tokyo - CNRS - Universite de Rennes, Tokyo, Japan
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[d]Department of Chemistry, School of Science, The University of Tokyo, Tokyo, Japan

The design and control of physical properties in molecular materials represent a central challenge spanning fundamental science to technological applications. Among the various external stimuli, light is particularly attractive because it enables contactless, ultrafast, and selective manipulation of materials.[1] Phase transition materials have therefore attracted sustained interest owing to their capability to switch between distinct electronic, structural, or magnetic states.[2] For practical applications for such photonic devices, photoreversibility at room temperature—that is, the ability to both generate and erase multiple states under ambient conditions using light—is a crucial requirement. However, achieving such reversible optical control remains challenging, highlighting the need for material platforms that can combine robust bistability with efficient photoresponse near room temperature.

To address the subject, we focused on cyanide-bridged assemblies showing cooperative thermal and photoinduced phase transition via charge transfer (CT) and/or spin transition (ST) due to the metal selectivity. By employing cobalt and octacyanidetungstate as bimetals, we successfully synthesized a material showing both room temperature bistability and photo-reversible phase transition at low temperature between the low temperature (LT) Co^{III}-W^{IV} state and the high temperature (HT) Co^{II}-W^{V} state (Fig.1).[3] Herein, we present the ultrafast photoinduced dynamics of LT-to-HT and vice versa at room temperature using time-resolved optical spectroscopy and theoretical calculations.[4] Our finding provides new perspectives for the development of molecular photonic materials.

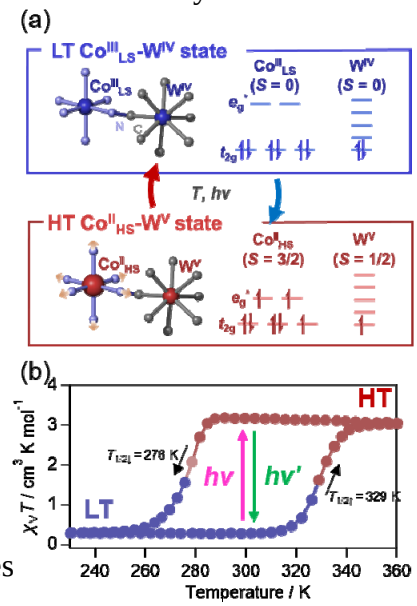


Fig.1 (a) electronic state in Co-W system. (b) $\chi_M T$-T plot.

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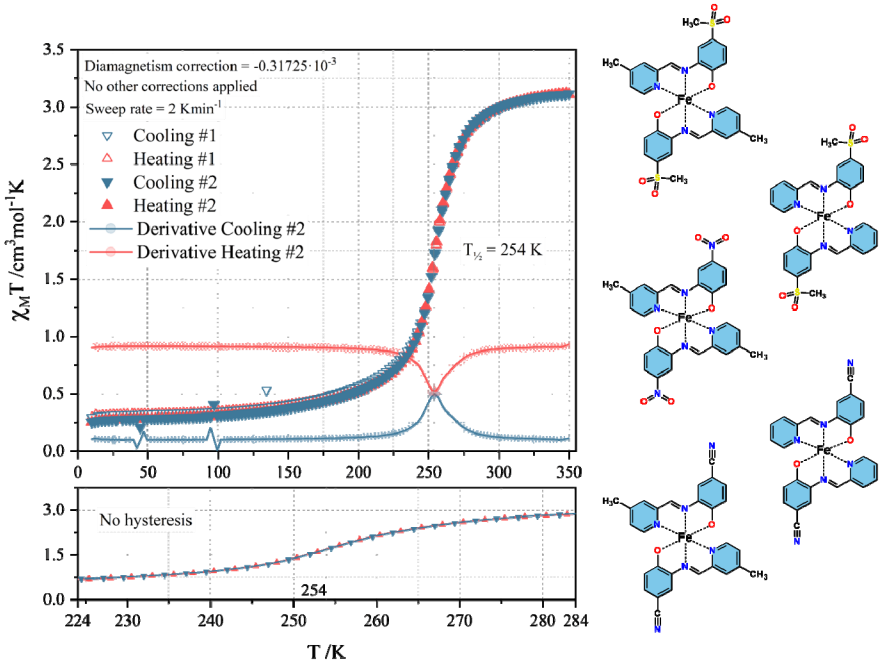
NOVEL SPIN CROSSOVER IRON(II) COMPLEXES FOR BAROCALORIC EFFECT

Massimiliano Ceci, Eric Rivière, Régis Guillot, Nathalie Bridonneau, and Talal Mallah

Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO), Université Paris-Saclay, Orsay, France

Spin Crossover (SCO) systems are molecular materials usually characterized by a thermal transition between two electronic states, monitored by the change of their magnetic, optical, and structural properties. Six-coordinate octahedral Fe(II) complexes with Schiff-base ligands are particularly appealing because the switch from the diamagnetic, low spin (LS, $S = 0$) state to a paramagnetic, high spin (HS, $S = 2$) is concomitant with a volume change that may reach 9%.[1] Such large change in volume can also be induced by pressure, making SCO molecular materials promising candidates for the development of efficient solid-state refrigeration technologies thanks to their large barocaloric effect (BCE) in comparison to current materials.[2]

The tridentate organic ligand (2-((pyridin-2-ylmethylene)amino)phenol) (*pap*) functionalized with NO_2 was previously prepared and the related [Fe(pap-NO_2)$_2$] SCO complex presented promising barocaloric behavior.[3] With the goal of improving the BCE performance of SCO complexes, we explored the class of *pap* ligands by preparing new derivatives with targeted groups as depicted below. The corresponding Fe(II) complexes show in some cases the ideal properties for barocaloric application.



Acknowledgments: This work has received support from EU (MSCA-DN MolCal, 101119865).

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HYPERFINE INDUCED CLOCK-LIKE T_2 ENHANCEMENT IN A MAIN GROUP RADICAL

Max Les[a], Edgar Zander[a], Benjamin Atkinson[a], Nicholas Cox[a], Nicholas Chilton[a,b] and Jamie Hicks[a]

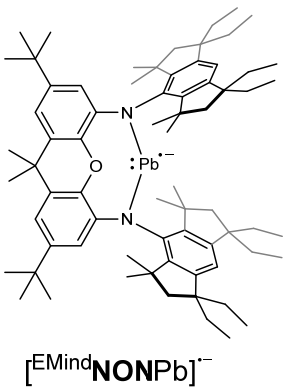
[a]Research School of Chemistry, Australian National University, Canberra, Australia
[b]Department of Chemistry, University of Manchester, Manchester, United Kingdom

Quantum information science is predicated upon the design of effective quantum bits (qubits), two-state quantum systems with controllable wavefunctions analogous to bits in classical computing.[1] One of the simplest possible two-state quantum systems is the spin-state of an electron in a molecule, the two-basis states being spin-up and spin-down. In the presence of an external magnetic field these spin-states become non-degenerate thanks to the Zeeman effect, and electrons can be manipulated from one state to the other using well understood electron paramagnetic resonance (EPR) techniques.

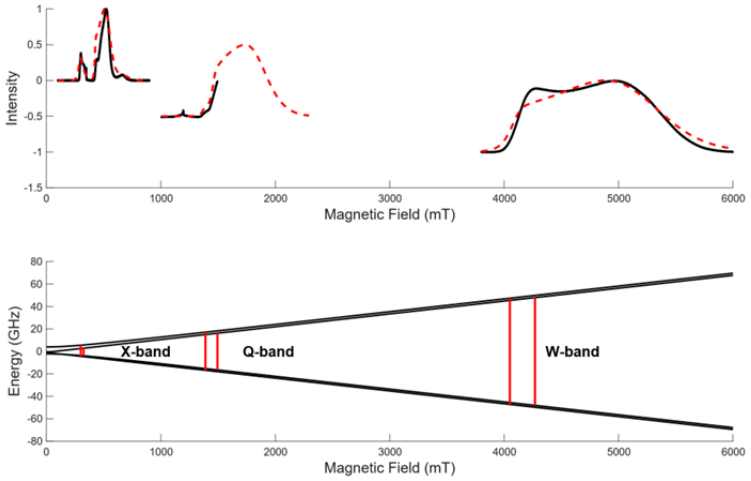
Large hyperfine coupling (coupling between nuclear and electronic spins) has emerged as an effect that can be exploited to increase control of the wavefunction in molecular spin qubits by creating clock-transitions (CTs) – regions where the EPR transition frequency is very well-defined.

Recently the Hicks Group synthesised the first anionic Pb(I) radical which was found to have an exceptionally large isotropic hyperfine interaction of 4929 MHz. However, it was extremely thermally sensitive and decomposed rapidly in solution, even at −80 °C.[2]

Herein, a new Pb(I) radical anion stabilised by an extremely bulky xanthene-based diamido ligand is reported, and was found to be stable in solution for weeks at −15 °C. This compound was investigated by continuous wave (CW) and pulsed electron paramagnetic resonance (EPR) techniques and was found to exhibit clock-like T_2 enhancement of up to 50% at low-field positions due to the second largest isotropic hyperfine coupling ever observed (Aiso = 5282 MHz).



[EMind**NON**Pb]$^{\bullet-}$



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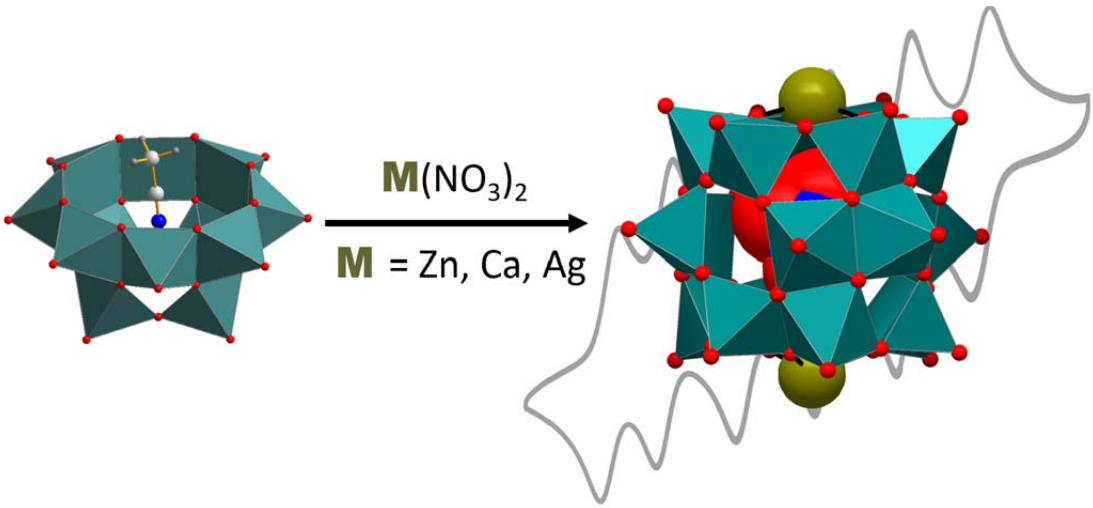
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SYNTHESIS AND CHARACTERISATION OF A HETEROMETAL FUNCTIONALIZED OCTADECAVANADATE

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Polyoxovanadates (POVs) are versatile materials formed via self-assembly, where solvent and templating effects play a decisive role.[1,2] Owing to the smaller size and lower charge of vanadium compared to molybdenum and tungsten, these systems exhibit enhanced structural flexibility together with rich and accessible redox behaviour.[1,3] As a result, POVs are promising candidates for applications in energy storage and redox catalysis.[1] Here, we report a novel synthetic approach to a heterometal functionalized octadecavanadate $\{V_{18}\}$ cluster. A general approach for the synthesis of high-nuclearity polyoxavanadates[4], leads to an octadecavanadate featuring two calcium ions. The improved method further enables the incorporation of alternative heterometals, such as zinc and silver. This enables a systematic modulation of the electronic structure and redox properties. Structural characterization was performed using ^{51}V and ^{17}O NMR spectroscopy, providing detailed insight into the cluster architecture.[2] The redox properties of the $\{V_{18}\}$ system were also investigated, demonstrating the potential of heterometal-functionalized POVs as tuneable redox-active materials.[3]



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^{17}O-ENRICHED POLYOXOVANADATES REVEAL OXYGEN SITE DYNAMICS VIA ^{17}O NMR SPECTROSCOPY

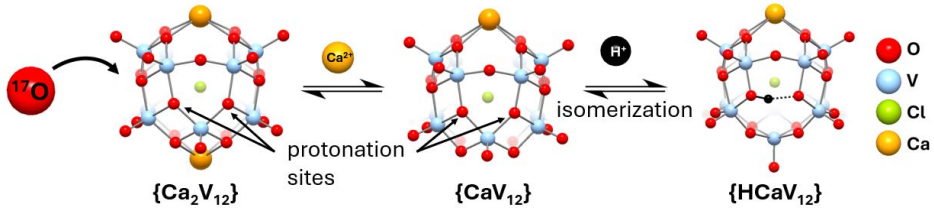
Moritz Remmers[a], Michelle Sulzbacher[a], Yuji Kikukawa[b] and Carsten Streb[a]

[a]Department of Chemistry, Johannes Gutenberg University Mainz, Germany
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Polyoxovanadates belong to the highly versatile class of polyoxometalates with applications ranging from energy storage and conversion, catalysis, and supramolecular assembly.[1-3] Their synthesis is typically governed by templated self-assembly. However, while the initial steps involving protonation and hydrolytic condensation reactions are well understood, the mechanisms leading to the formation of specific clusters remain poorly characterized. In particular, syntheses carried out under non-aqueous conditions are especially promising for the development of novel structures, since condensation is hindered by coordination solvent molecules, thereby enabling more complex self-assembly pathways.[4]

Further work by our group has focused on integrating heterometals into the cluster shell. Specifically, calcium or magnesium can be used for electrostatic stabilization to enhance the redox properties of polyoxovanadates and to serve as diamagnetic model systems ideally suited for mechanistic NMR studies.[5,6] These studies include a wide range of techniques, from one-dimensional NMR of the nuclei ^{51}V, ^{17}O, ^{35}Cl and ^{1}H to two-dimensional experiments such as ^{51}V-^{51}V TOCSY, COSY and HETCOR NMR as well as DOSY thus covering nearly all elements within the structure.

Among these, ^{17}O NMR has rarely been employed, primarily because of the low natural abundance of ^{17}O and the high cost of $H_2{}^{17}O$, often used for enrichment. In this work strategies for ^{17}O enrichment of polyoxovanadates are discussed and oxygen exchange rates are determined. The enriched samples provide valuable information on the most likely protonation sites as well as on the heterometal binding sites. The combination of single-crystal X-ray diffraction data and mechanistic NMR studies offers detailed insights into the proton-induced isomerization between two dodecavanadates and possible proton-coupled electron transfer (PCET) activity.



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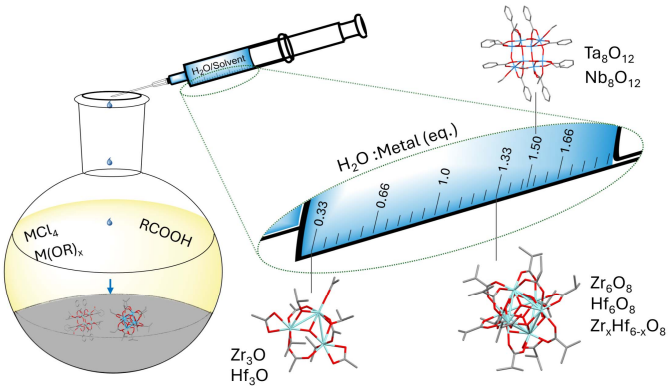
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MECHANISM-GUIDED PRECISION HYDROLYSIS OF EARLY TRANSITION METALS TO ACCESS (MIXED-METAL) OXO CLUSTERS

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Zirconium and hafnium oxo clusters are catalysts, and building blocks for MOFs, 3D-printing and polymer composites. However,their synthesis is often a matter of trial and error, and new structures are hard to design retrosynthetically. Here, we use our recent insight in the formation mechanism of $Zr_6O_4(OH)_4(OOCR)_{12}$ oxo clusters to redesign their synthesis with higher reaction rates, more economical precursors, more sustainable solvents, and higher atom economy, all at room temperature at gram scale. We add exactly 1.33 equivalents of water for the precision hydrolysis of the metals toward Zr6-carboxylate or Hf6-carboxylate oxoclusters (carboxylate = acetate, oleate, and 2-methylbutanoate). Furthermore, we use precision hydrolysis to synthesize the elusive bimetallic Zr/Hf oxo clusters and to expand rational oxo cluster synthesis to the group 5, accessing the new $Nb_8O_{12}(OEt)_8(OBz)_8$and $Ta_8O_{12}(OEt)_8(OBz)_8$ clusters (OBz = benzoate). Precision hydrolysis allows for a rational design and an economic production of oxo clusters on a multigram scale, with potential to become the workhorse for cluster synthesis.

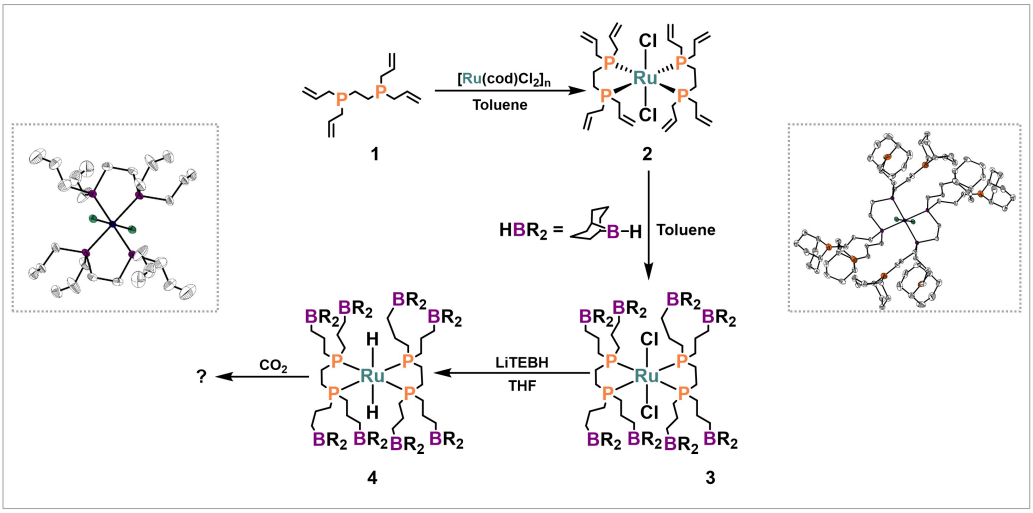


BORANE-APPENDED Ru(II) COMPLEXES: A "PUSH-PULL" STRATEGY FOR COOPERATIVE CO_2 ACTIVATION

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The rapid escalation of atmospheric carbon dioxide (CO_2) levels remains one of the most pressing environmental challenges of our time.[1] Converting CO_2 into value-added chemicals offers a dual benefit: reducing greenhouse gas concentrations and providing sustainable chemical feedstocks.[2] However, CO_2 is thermodynamically stable and kinetically inert, possessing a high C=O bond dissociation energy of 799 kJ/mol. Traditional catalytic methods often require harsh conditions to overcome this barrier. To address this, we look to the "push-pull" mechanism – a strategy that simultaneously activates the carbon center via electron-rich metal "push" and the oxygen atoms via Lewis acidic "pull".[3] This cooperative approach significantly lowers the activation energy, enabling transformations under milder conditions. Several studies have demonstrated the effectiveness of incorporating Lewis acids into the secondary coordination sphere of transition metal complexes.[4,5]



Building on the established literature, this work focuses on the practical execution of this design. Borane-appended Ru (II) complexes were successfully synthesized by integrating a Lewis acidic 9-BBN group into phosphine ligands. These complexes were fully characterized using NMR and MS techniques, along with single-crystal X-ray diffraction analysis. The reactivity of these complexes with CO_2 is currently being investigated, with initial results showing significant promise.

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NICKEL(II) PORPHYRIN/FULLERENE C_{70} POROUS MOLECULAR COCRYSTAL FEATURING A ROBUST ONE-DIMENSIONAL CHANNEL

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Molecular cocrystals are crystalline materials composed of multiple types of molecular components held together by noncovalent interactions. Among these, porphyrin-fullerene cocrystals represent a well-studied class of supramolecular assemblies.[1] The close packing arrangement between porphyrins and fullerenes is known to contribute to high crystallinity and structural stability. Porphyrin-fullerene cocrystal systems including C_{60}, which has a spherical shape, have provided insights on intermolecular interaction. In contrast, cocrystals incorporating C_{70}, which has an ellipsoidal shape, remain relatively unexplored, and the influence of fullerene shape on cocrystal structures and stability remains unclear. In this study, we investigate the differences between C_{60} and C_{70} using cocrystals of a nickel (II) porphyrin derivative (**NiTEPP**) with these fullerenes. Two distinct cocrystals were successfully obtained: the porous cocrystal **NiTEPP/C_{70}** featuring one-dimensional channels, and the nonporous crystal **NiTEPP/C_{70}-n**. (Figure 1) High-pressure single-crystal X-ray diffraction results show that these cocrystals maintained their single crystal structure under high pressure. Furthermore, intermolecular interaction energies depending on the fullerene species were evaluated using density functional theory calculations. The combined experimental and theoretical results demonstrate that the shape of the fullerene plays a crucial role in governing intermolecular interactions and structural stability, and these results provide valuable guidelines for the rational design of molecular cocrystals with controlled intermolecular interactions.

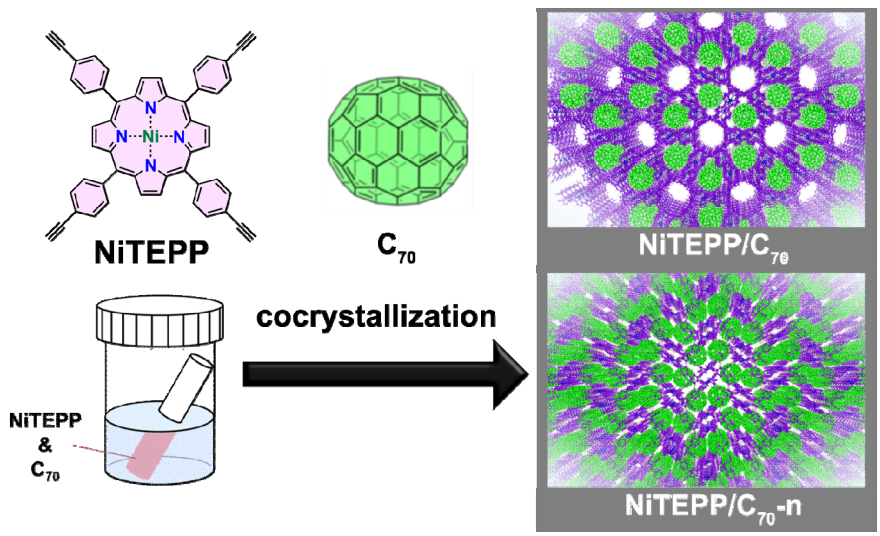


Figure1. Summary of this work.

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ELECTROCHEMICAL EVALUATION OF POLYOXOMETALATE COORDINATION CLUSTERS FOR BIOMASS OXIDATION CATALYSIS

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Polyoxometalates (POMs) are a versatile class of discrete, anionic metal–oxygen clusters composed of early transition metals in high oxidation states (typically W, Mo, or V). As multinuclear coordination compounds with well-defined structures, POMs occupy a unique position in coordination chemistry. Their tunable nuclearity, heteroatom incorporation, and substitution patterns enable precise control over electronic structure and redox properties. These features, combined with remarkable thermal and oxidative stability, make POMs highly attractive candidates for sustainable redox catalysis. Literature reports and prior studies demonstrate that POM-based systems are promising catalysts for the selective oxidation of biomass-derived substrates to value-added organic acids [1-4].

In this work, we investigated selected POMs as molecular oxidation catalysts for biomass conversion. The catalytic performance of these systems is, among other factors, governed by their redox behavior; however, a systematic electrochemical evaluation is missing. To address this gap, we performed detailed electrochemical investigations using cyclic voltammetry (CV) and square wave voltammetry (SWV) to determine reduction potentials, assess reversibility, and characterize electron-transfer properties in relevant solvent systems.

Since our primary interest lies in catalytic oxidation processes, particular attention was directed toward the first reduction event of the POM framework. This initial electron-transfer step is expected to govern substrate activation and overall catalytic efficiency. We hypothesize that the position of this reduction potential reflects the fundamental oxidizing power of the POM, such that a more positive potential corresponds to a greater thermodynamic driving force for electron uptake. In the context of the catalytic cycle, this enhanced ability to accept an electron translates into a stronger oxidant capable of promoting substrate oxidation. By analyzing peak potentials, current responses, and reversibility, we establish correlations between coordination environment, cluster composition, and redox activity.

The electrochemical data provide fundamental insight into how multinuclear metal–oxygen coordination frameworks mediate electron transfer and how structural variations influence catalytic performance. These findings contribute to a deeper understanding of POM-based oxidation catalysis and support the rational design of molecular, sustainable catalysts for biomass valorization.

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SYNTHESIS AND CHARACTERISATION OF LANTHANIDE DOPED NANOSCALE Ce-oxo CLUSTERS

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University of Warwick, UK

Ceria (CeO_{2-x}) is widely recognised for its reversible redox behaviour arising from the Ce^{3+}/Ce^{4+} redox couple, enabling efficient oxygen storage and release in catalytic processes.This property is central to its use in three-way automobile catalysts. At the nanoscale, cerium oxo clusters represent atomically defined analogues of bulk ceria, adopting a fluorite-like arrangement of Ce and O atoms within 1–2 nm dimensions. Stabilised by surface ligands such as carboxylates and pyridines, these molecular nanoparticles combine structural precision with high surface-to-volume ratios, leading to electronic structures and reactivity comparable to extended ceria materials.[1]

In this work, we synthesised and characterised mixed-valence and lanthanide-doped cerium oxo clusters to understand and modulate their redox properties. Characterisation confirms the presence of Pr^{+3} , Nd^{+3}, Ce^{+3} and Ce^{+4} centres.[2] These clusters serve as well-defined models to investigate how doping can influence the structure and electronic properties of Cerium-oxo clusters.

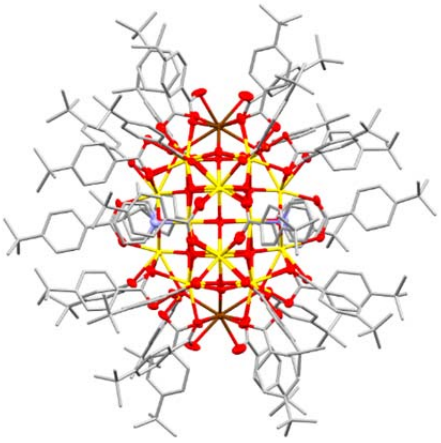


Fig 1. Single-crystal X-ray structure of Mixed valent Cerium-oxo cluster $Ce(III)_2Ce(IV)_{22}^{PhtBu}$.

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SIGNATURES OF METAL IONS AND POLYOXOMETALATES IN SOLUTION WITH PAIR DISTRIBUTION FUNCTION

Rebecca S. Silberg, Adam F. Sapnik, Nanna L. Bjerre, and Kirsten M. Ø. Jensen

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen

Understanding metal ion speciation in solution is central to characterizing and modeling many chemical reactions, including the formation and transformation of metal-oxo clusters and polyoxometalates. However, this phenomenon is complex even for the simplest salts, as it involves several processes, including ion-ion, ion-ligand and ion-solvent interactions. Pair Distribution Function (PDF) analysis of X-ray total scattering can provide structural information on ions, complexes, and clusters in solution, and can thus be highly valuable for speciation studies, as well as for in situ studies of cluster formation reactions in solution. Here, we provide a dataset with X-ray total scattering data and PDFs collected from a range of different ions in solution. Apart from distributing the data for wider use, we discuss the signatures of ions and metal-oxo clusters in solution and give examples of their analysis. We focus especially on metal chloride and nitrate salts and show how both cation and anion cluster structures can be identified from PDF, providing a structural foundation for understanding the early stages of metal-oxo cluster formation.

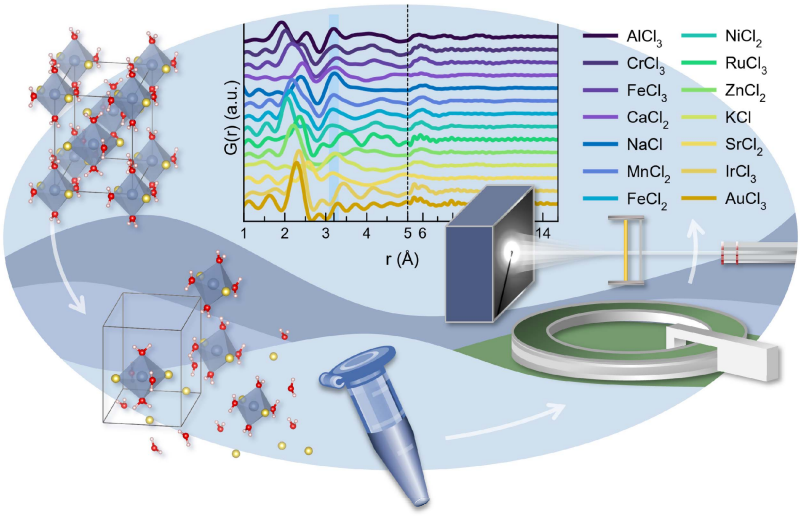


Figure 1. Experimental workflow for probing structural signatures of solvated metal ions and polyoxometalate building blocks in solution. Crystalline metal precursors are dissolved and measured using synchrotron X-ray total scattering, and the resulting Pair Distribution Functions (PDFs) reveal characteristic structural fingerprints of different metal chloride solutions and their local coordination environments.

DIPYRRIN-BASED PHOTOFUNCTIONAL COORDINATION ARCHITECTURES FOR LIGHT HARVESTING

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[a] Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, Darul Ridzuan, Malaysia

Efficient utilization of light energy is a crucial challenge in developing next-generation photofunctional materials. Inspired by natural light-harvesting systems, we have focused on zinc(II) dipyrrinato oligomers, which are known to exhibit high exciton transport capability [1], to construct advanced photofunctional coordination architectures. In this presentation, we report our recent progress in the development of one-dimensional coordination polymers and dye conjugates that exhibit efficient exciton migration and enhanced photosensitivity.

First, we synthesized a novel one-dimensional coordination polymer consisting of porphyrinatozinc(II) linked by bis(dipyrrinato)zinc(II) complexes (Fig. 1a) [2]. In this exfoliable molecular wire, we achieved the realization of photoluminescence and photoelectric conversion properties originating from the energy transfer between the two dye units.

Second, to explore long-range energy transfer in the solid state, we investigated coordination nanochains immobilized in polymer films (Fig. 1b) [3]. By suppressing non-radiative deactivation through low-concentration doping into low-polarity polymers, we confirmed that highly efficient exciton transport in the solid state is maintained even when the nanochains are elongated.

Furthermore, we applied this light-harvesting concept to a molecular photoswitch and developed a novel photoswitch in which a coordination nanochain is connected to azobenzene as a molecular antenna (Fig. 1c). By elongating the nanochain acting as an antenna, the molar absorption coefficient significantly increased, thereby achieving an enhancement in the photosensitivity of the azobenzene unit under visible-light (505 nm) irradiation.

In conclusion, precisely designed coordination architectures based on dipyrrin complexes and related chromophores provide a robust platform for controlling light energy. These systems hold great promise for applications in advanced optoelectronic devices and stimuli-responsive materials.

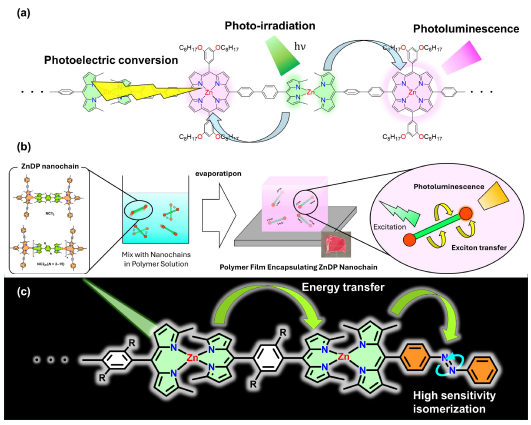


Figure 1. (a) Porphyrin-dipyrrin wire with optoelectronic properties. (b) Exciton migration in immobilized nanochains. (c) Antenna-connected molecular photoswitch.

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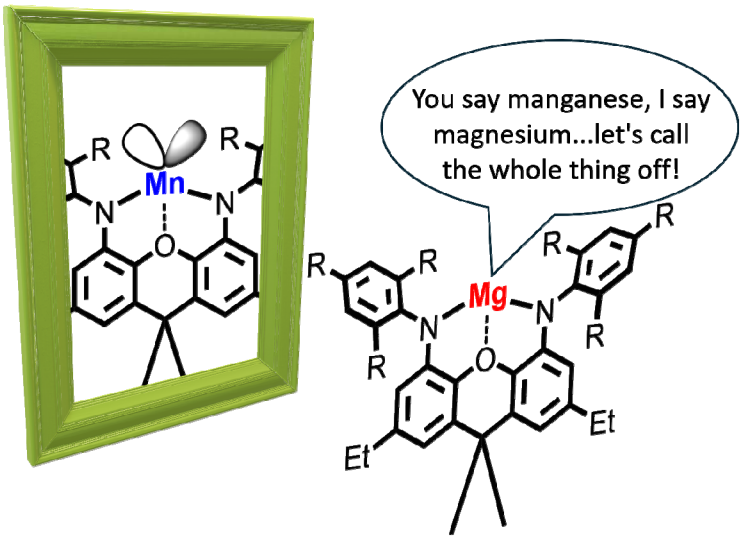
CONTRASTING MAGNESIUM AND MANGANESE IN N_2 AND BENZENE ACTIVATION

Siad Wolff, Christian Limberg*

Institut für Chemie, Humboldt Universität zu Berlin, Berlin, Germany

Despite the rich chemistry of transition metal complexes for N_2 fixation, only few examples involving manganese are known.[1] One key reason for this scarcity is the pronounced tendency of reduced manganese centres to form stable Mn–Mn bonds, which effectively suppress reactivity toward N_2. A similar behaviour is observed for magnesium(I) species, which are likewise prone to forming strong Mg–Mg bonds. Building on this parallel, strategies developed in the Jones group for magnesium-mediated N_2 activation were systematically transferred to manganese systems.[2-4] To this end, the manganese centres were embedded in extremely bulky and rigid xanthene-based diamido ligands, which sterically prevent Mn–Mn bond formation and thereby enable N_2 coordination. While instructive parallels to magnesium analogues can be drawn, the presence of accessible filled d orbitals in the Mn(I) intermediates results in a distinct reactivity toward benzene. In the absence of N_2, the manganese complexes undergo oxidative addition of aromatic C–H bonds, whereas the corresponding magnesium systems are limited to single-electron reduction processes, yielding Birch-type products.

Overall, this study not only reports the isolation of a novel Mn–N_2 complex, but also highlights key similarities and fundamental differences between the coordination chemistry of the s-block element magnesium and the open-shell transition metal manganese – a comparison that has thus far remained largely unexplored.



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[3] R. Mondal, M. J. Evans, D. T. Nguyen, T. Rajeshkumar, L. Maron C. Jones *Chem. Commun.* **2024**, 60, 1016–1019.

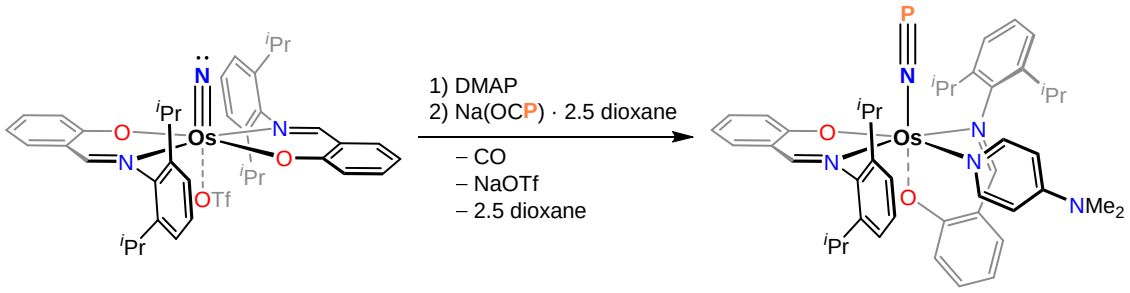
[4] S. Wolff, M. J. Evans, T. Rajeshkumar, D. T. Nguyen, K. B. Krause, A. Opis-Basilio, C. Herwig, L. Maron, C. Jones, C. Limberg *J. Am. Chem. Soc.* **2025** 147 (29), 25174-25179.

UNLEASHING PHOSPORUS MONONITRIDE

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[b] University of Texas at El Paso, USA
[c] ESRF-The European Synchrotron Radiation Facility, France
[d] Current affiliation: European Research Council Executive Agency
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The interstellar diatomic molecule, phosphorus mononitride (P≡N), is highly unstable under conditions typical on Earth, and its utility for constructing elusive P–N multiple-bonded archetypes is essentially uncharted. Herein, we show how Na(OCP) transfers a P atom to an electrophilic osmium nitride complex to form a terminally bound P≡N functionality. Quantum chemical calculations and X-ray absorption spectroscopy unveil a cumulenic [Os^{IV}=N=P] electronic structure comprising orthogonal Os=N and N=P bonding. The highly reduced P≡N ligand, formally $[PN]^{2-}$, undergoes two-fold oxidation with elemental sulfur to form a trigonal planar $[NPS2]^{2-}$ group. On reaction with Ph_3CCl, the P≡N ligand forms a bent [NPCl]– motif coordinated to OsIII (S = ½). [3+2] cycloaddition of this radical species with Me_3SiN_3 forms an aromatic heterocyclic interpnictide, $[PN_4]$–, that cannot be accessed from the parent P≡N system.



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HYDROGEN BONDING PROPAGATED PHASE SEPARATION IN QUASI-EPITAXIAL SINGLE CRYSTALS: A Pd–Br MOLECULAR INSULATOR WITH ENANTIOMERIC AND RACEMIC LIGAND

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In condensed matter systems, phase separation is closely associated with ferroic phenomena such as ferroelasticity, ferroelectricity, and ferromagnetism, as well as with electron correlation and crystallographic factors. These properties are central to nanoelectronic applications, including non-volatile memory devices. Nevertheless, quantitative insight into the lattice (atomic-scale) structure at phase boundaries remains insufficient in many materials. Establishing a clear correlation between electronic states and lattice structures is therefore essential for molecular-level device design.

In this study, we investigated the Pd^{II}–Pd^{IV}/Pd^{III}–Pd^{III} phase transition and phase separation behavior of $[Pd(cptn)_2Br]Br_2$ (cptn = 1*R*,2*R*-diaminocyclopentane), which propagates through an extended hydrogen-bonding network[1]. Although the Pd···Pd distance serves as a conventional indicator of the electronic configuration, the structural and electronic differences between the Mott–Hubbard (MH) and charge-density-wave (CDW) states were remarkably small, amounting to only 0.012 Å in Pd···Pd separation and 0.17 eV in optical gap. The N–H···Br···H–N hydrogen-bonding framework acts as a dynamic structural modulator, compensating for these subtle differences and enabling a visible ferroelastic phase transition and separation under a fluctuating N_2 gas atmosphere. Furthermore, the influence of phase separation on spin susceptibility and electrical conductivity was examined, revealing quasi-epitaxial crystal characteristics across the CDW–MH states. Furthermore, the phase transition and separation behavior of the racemic crystals will be presented, providing a direct comparison with the enantiomeric system to clarify the role of chirality in the hydrogen-bonding-mediated process.

These findings demonstrate that phase transitions and phase separation can be tuned through atomic- and molecular-level design strategies, such as the deliberate incorporation of hydrogen-bonding interactions.

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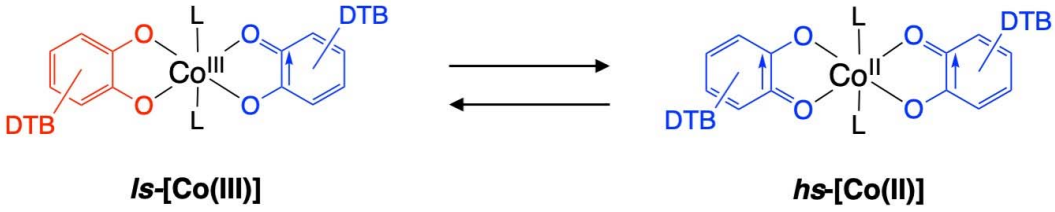
VALENCE TAUTOMERIC COMPLEXES RESPONSIVE TO MULTIPLE EXTERNAL STIMULI AND THE SOLUTION ENVIRONMENT

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Molecular-based systems that respond to external stimuli such as heat, light, and magnetic or electric fields have attracted considerable interest because of their potential applications in low-energy switches, memories, and information storage devices.[1] Among these systems, valence tautomerism (VT) is particularly fascinating, as it involves intramolecular charge transfer between two or more tautomeric states, often accompanied by pronounced changes in optical and／or magnetic properties (Scheme 1). Although VT can be triggered by heat, light, or pressure,[2] most studies to date have focused on temperature-dependent behavior. By contrast, examples of VT occurring under constant room-temperature conditions remain scarce.[3]

In this study, we report a series of newly synthesized complexes that exhibit valence tautomeric transitions in solution at room temperature in response to an external field. We present their synthesis and structural and spectroscopic characterization, highlighting their distinctive VT behavior observed under specific solution conditions. These findings provide insight into how subtle variations in the solution environment modulate tautomeric equilibria and electronic structures. The present systems offer a useful platform for investigating room-temperature switching behavior in molecular complexes and for guiding the design of stimuli-responsive functional materials.



Scheme 1. Valence tautomeric equilibrium

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ZINC HALIDE FLUX-ASSISTED VITRIFICATION OF METAL-ORGANIC FRAMEWORKS ENABLES CHEMICAL DIVERSIFICATION AND TUNABLE GAS SORPTION

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The vitrification of metal-organic frameworks (MOFs) enables melt processing into bulk, shaped and membrane-type porous materials, yet the limited chemical diversity of existing MOF glass formers restricts structural and functional tunability. In this work, we demonstrate a general flux-melting strategy in which the inorganic glass formers $ZnBr_2$ or ZnI_2 are co-melted with zeolitic imidazolate frameworks (ZIFs) spanning different imidazolate-type linkers and network topologies, including both established ZIF glass formers and frameworks that do not melt or vitrify on their own (**Figure 1**).[1] The zinc halides act as compatible co-network formers and reactive fluxes, promoting extensive ligand exchange between halides and imidazolate linkers in the melt. This process generates mixed halide-imidazolate coordination glass networks whose structure, connectivity and porosity can be tuned systematically through composition. These results establish zinc-halide flux melting as a general route to expand the compositional space of MOF glasses and introduce mixed coordination networks as a new design paradigm for functional porous glasses.

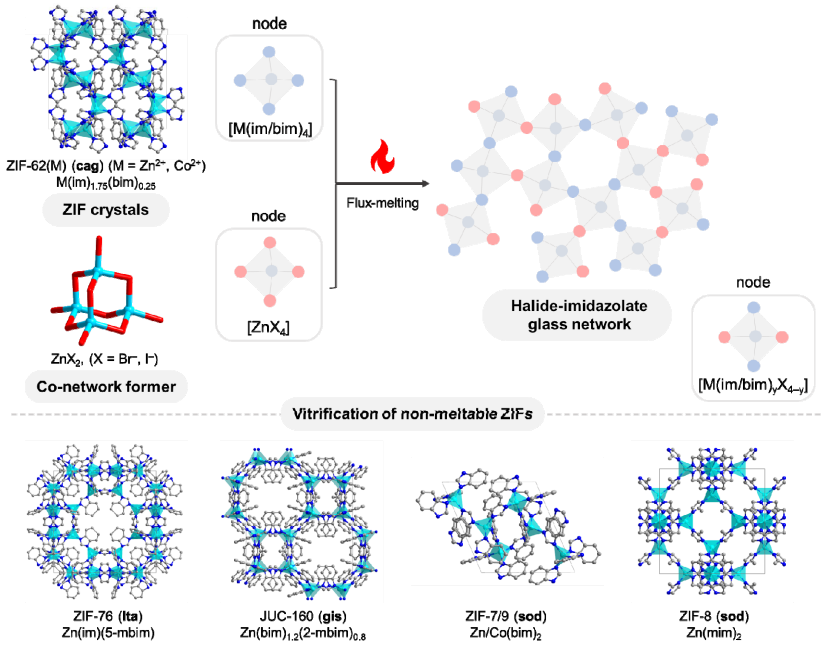


Figure 1. Top: Schematic illustration of this work, flux-melting of crystalline ZIFs with the assistance of zinc halides induces facile ligand exchange between halides and azolates to produce the mixed halide-imidazolate glass network (**ZIF-62(M)** (M = Zn^{2+}, Co^{2+}) is shown as a representative). Bottom: Scope of other crystalline ZIFs that form glasses with zinc halide fluxes in this work.

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DESIGN OF EXPERIMENTS: A VALUABLE TOOL FOR FINE-TUNING CATALYTIC PERFORMANCES OF Ce-UiO-67 FOR THE ALLYLIC PARTIAL OXIDATION OF CYCLOHEXENE

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Cyclohexene partial oxidation is a crucial reaction to produce 2-cyclohexenol and 2-cyclohexenone, used as intermediates in the chemical industry. Its uncatalyzed oxidation involved a radical mechanism, without optimization of product yield [1].

In our study a Ce-based metal-organic framework (MOF) has been investigated as a catalyst to perform cyclohexene oxidation in heterogeneous phase under ambient conditions [2]. Ce-UiO-67 was synthesized and characterized using Powder X-ray Diffraction, Thermo-Gravimetric Analyses and N_2 adsorption-desorption isotherms at 77 K. The preliminary catalytic tests for cyclohexene oxidation were performed at room temperature under previously reported conditions [3], using 162 mmol of cyclohexene and 39 mmol of tert-butyl hydroperoxide (TBHP) per gram of catalyst in 20 ml of dichloromethane in a 25 ml round-bottom flask. The catalytic performance of Ce-UiO-67 was compared with a synthesized Zr-UiO-67 MOF (Figure 1). The results show that cerium plays a key role due to its redox activity [2]. To optimize the reaction conditions, a Design of Experiments (DOE) approach was used to systematically study the effects of the amount of cyclohexene, initiator (TBHP), and oxygen (O_2) concentration with a limited number of experiments. As a result, the optimized conditions improved catalytic performance, with an overall productivity increase of about 50% compared to non-optimized conditions reported in the literature. In particular, the production of 2-cyclohexenone was enhanced by the presence of O_2. These results demonstrate that Ce-UiO-67 is an effective catalyst for the allylic oxidation of cyclohexene, and that DOE is a powerful tool for the rational development and optimization of catalytic processes.

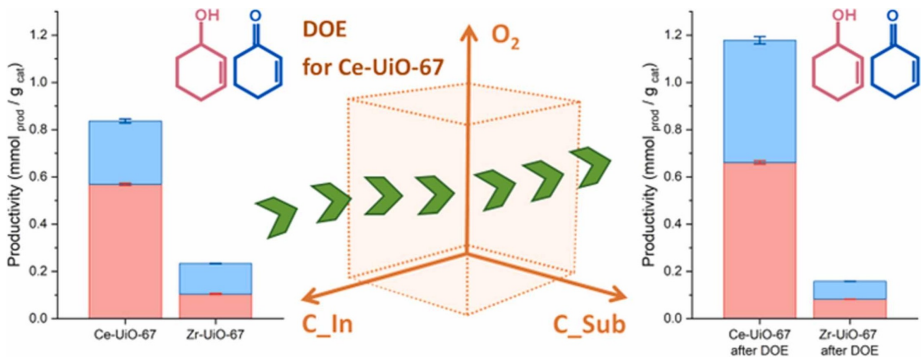


Figure 1. Comparison of the productivity of 2-cyclohexanol and 2-cyclohexenone at 24 h reaction time.

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TARGETTING $M^{II}\cdots Au^{III}$ METALLOPHILIC INTERACTIONS

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Metallophilic interactions are noncovalent, van der Waals-type attractions that typically occur between closed-shell d^{10} or d^8 metals, particularly Platinum(II) and Gold(I), with strengths comparable to hydrogen bonding (20-50 kJ mol^{-1}) [1]. Such interactions are powerful tools in supramolecular chemistry and crystal engineering, enabling increased structural dimensionality and the design of materials with emergent properties, such as luminescence [2,3]. In contrast, aurophilicity involving d^8 Au^{III} metal centres is exceedingly rare, with only a few reported examples [4], and the analogous heterobimetallic $d^8\cdots d^8$ $M^{II}\cdots Au^{III}$ (M = Ni, Pd, Pt) system has not been previously observed. Herein, we report the first example of a metallophilic interaction between Pt^{II} and Au^{III} featuring exceptionally short $Pt^{II}\cdots Au^{III}$ distances of 3.0024(4) and 3.0057(4). The analogous isostructural Pd^{II} and Ni^{II} analogues were also synthesized. Density functional theory calculations indicate the interaction is best described as donor-acceptor in nature.

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ALTERNATIVE SOLUTION-BASED APPROACHES TO VANADIUM(II) MOFs

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Metal-organic framework (MOF) materials have wide ranging applications across many sectors including energy storage, sensing and catalysis [1]. Quantum MOFs are of particular interest with high tunability of these materials allowing for control of various quantum properties including conductivity and magnetism [2]. Incorporating vanadium(II) centres into these materials can enhance these properties by activating non-innocent organic linkers [3]. Despite this, the number of vanadium(II) MOFS remains limited due to challenging air sensitive syntheses with current methods (often neat) requiring harsh conditions and resulting in low yields [4]. It is anticipated that solution-based approaches will lead to new materials using milder conditions and with improved crystallinity. However, a key challenge is identifying suitable metal precursors as commercially available vanadium(II) salts are virtually insoluble in common solvents [5].

In this work we describe the syntheses of soluble vanadium(II) precursors, we present their crystal structures and show preliminary findings in a reaction screening with a range of organic linkers. Synthesised materials were analysed by powder X-ray diffraction with diffraction patterns suggesting the emergence of novel MOF materials.

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MECHANOCHEMISTRY REDEFINES PILLARED MOFs: FROM TWISTING POLYMORPHISM TO HIGH-ENTROPY MIXING

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Mechanochemistry is emerging as far more than a green alternative to solution synthesis.[1,2] By promoting solid-state reactivity, mechanical activation can redirect selectivity, stabilizing unexpected phases and enabling structural and compositional complexity difficult to achieve in solution. In metal–organic frameworks, ball milling can reshape framework assembly, access new structural arrangements, and promote multimetal incorporation.

Coordination polymers and MOFs are particularly sensitive to these effects,[3] as subtle variations can drastically alter symmetry and topology. A clear example is PUM198, a Zn-based mixed-ligand pillared MOF previously obtained solvothermally.[4] Under ball milling, the material forms in just 5 minutes a new polymorph, PUM198-m. Although composition and connectivity are preserved, the two phases differ in symmetry, interlayer arrangement, pore geometry, and topology, representing the first case of interlayer-twisting polymorphism in a pillared MOF. As PUM198-m is obtained only as a flexible, guest-filled microcrystalline powder, its structure was solved through a combined 3DED, plane-wave DFT, and Rietveld refinement workflow. Mechanochemistry also enabled increased compositional complexity in PUM420(Zn), a similar double-interpenetrated pillared MOF reproduced in high yield by ball milling. Beyond Co- and Cu-analogues, a high-entropy[5] pentametallic variant containing equimolar Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, and Mn^{2+} was obtained with homogeneous metal distribution (~20% each). Preliminary proton conductivity measurements show a positive trend for the high-entropy analogue, highlighting the functional impact of entropy-driven multimetal mixing. Overall, mechanochemistry emerges as a powerful tool to redefine MOFs granting access to more complex frameworks while reducing environmental impacts.

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RHODIUM(III) AND IRIDIUM(III) COMPLEXES FOR FINE TUNING OF PHOTOLUMINESCENT AND DIELECTRIC PROPERTIES IN SUPRAMOLECULAR PEROVSKITE-LIKE HYBRIDS

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Recent years in the field of materials science have focused on the search for high-performing, intrinsically multifunctional materials operating on a molecular level.[1] This requires an interplay of various physical properties in a single phase, leading to an efficient and highly tunable material. This path, successfully realized in perovskite-type materials, can be further enhanced in diverse molecular hybrids by a proper choice of organic cations or metal complexes, leading to materials acting as switchable sensors and actuators, whose performance is further enhanced by solid-state luminescence.[2–4] Herein, we present a series of novel hybrid organic-inorganic salts with the general formula of $[Alk\text{-}dabco][M^{III}(CN)_2(ppy)_2]$ (Alk-dabco = N-alkylated cations of 1,4-diazabicyclo[2.2.2]octane; Alk/M = Me/Rh (**1**), Et/Rh (**2**), *n*Pr/Rh (**3**), *n*Bu/Rh (**4**), Me/Ir (**5**), Et/Ir (**6**), *n*Pr/Ir (7), *n*Bu/Ir (**8**); ppy – carbanion of 2-phenylpyridine). By linking stimuli-responsive photoluminescence of a metal-to-ligand charge-transfer character with dielectric relaxation of the organic cations, these materials exhibit mutual tunability of both properties, realized in a perovskite-like supramolecular framework.[5]

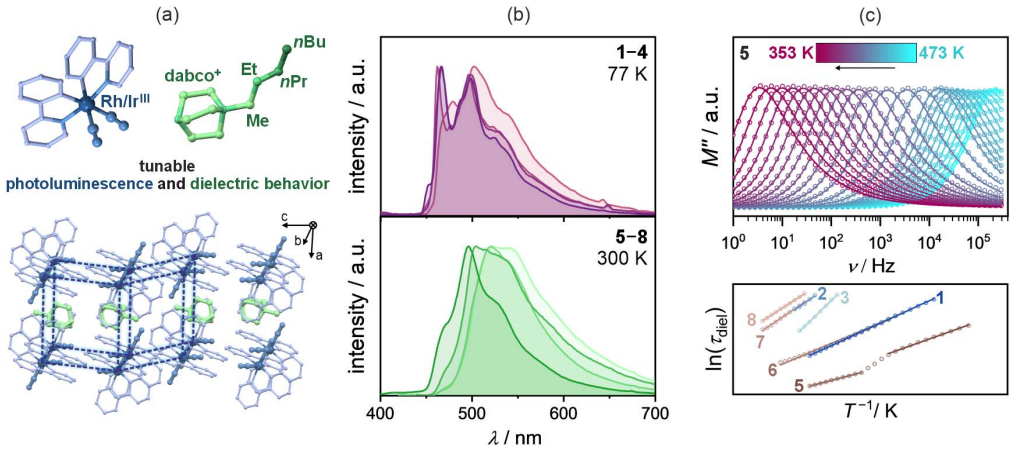


Fig. 1 Representative views on the metal complexes and organic cations in **1**–**8** (a); photo-luminescence of **1**–**4** at 77 K and **5**–**8** at 300 K (b); dielectric properties of **1**–**8** (c): *M"*(*ν*) plots for **5** (top) and the Arrhenius plots of dielectric relaxation times for **1**–**8** (bottom).

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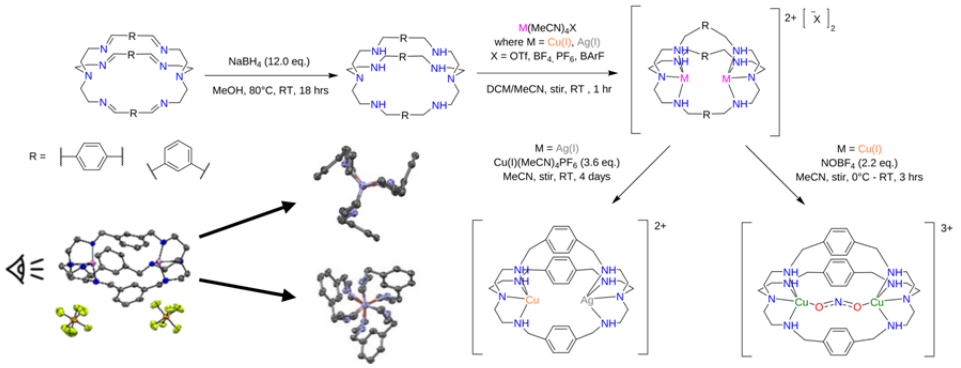
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AZACRYPTATES REVISITED: EXPLORING SMALL MOLECULE ACTIVATION POTENTIAL THROUGH REACTIVITY AND STRUCTURAL ANALYSIS

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The need for a deeper understanding into the chemistry of molecular cages only increases as many potentially lucrative new systems continue to emerge in the rapidly growing field of Supramolecular chemistry. Macrobicyclic azacryptands, first reported by J. M. Lehn in the 1980s, have attracted considerable attention due to their easy synthesis and versatility in forming bimetallic complexes of various transition metals.[1] The ability of these complexes to bind bridging anionic species between the coordinated metal ions, coined by Lehn as 'cascade chemistry' and remarkably developed by the Nelson group,[2] has led to a host of different applications including photocatalytic CO_2 reduction, anion recognition, small molecule activation and chemosensing.[3],[4] Despite the numerous publications on azacryptand chemistry, the majority of examples consist of the 'hexaimine' cages as opposed to the relatively underexplored 'octaamine' derivatives obtained upon chemical reduction. These more flexible azacryptand cages also benefit from greater stabilisation of highly charged TM cations, lower susceptibility to hydrolysis and greater chemical robustness, all of which warrant further research into their functionality as molecular hosts.[5]



With the intention of further exploring the true potential of 'octaamino' azacryptand complexes, our group's research has recently focussed on coordinating Cu(I) and Ag(I) ions into cages with different aromatic bridging spacers, and investigating the oxidation chemistry and reactivity of these complexes. This talk will discuss the synthesis and crystallographic insights into disilver(I) and dicopper(I) azacryptates, and how our understanding of these systems guides our choice of suitable substrates for small molecule activation. Particular attention will be given to the use of disilver(I) cryptates as precursors for the formation of heterobimetallic species and the current results on the NO activation chemistry exhibited by our dicopper(I) complexes.

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DUAL-RESPONSIVE CHIROPTICAL PROPERTIES IN A COFACIAL TTF-BASED METAL-ORGANIC FRAMEWORK

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[c]Sydney Analytical Core Research Facility, The University of Sydney, Darlington, NSW, Australia

Chiroptical materials that are responsive to multiple stimuli are critical to the development of next generation security, biological sensing, 3-D display and data storage materials.[1] Current limitations of these materials their low chiroptical responses and their lack of specific control over their response. Chiral Metal-Organic Frameworks (MOFs) may overcome these limitations due to their ability to generate supramolecular chirality which can increase chiroptical response.[2] Additionally, MOFs may exhibit properties additional or different to those of their component metal-ions and bridging ligands due to their ability to hold them in a particular orientation within a framework. MOFs containing TTF-based ligands demonstrate potential as dual-responsive materials due to their ability to undergo a light-induced [2+2] cycloaddition when cofacially arranged, and their susceptibility to oxidation.[3,4] We aim to develop multi-stimuli responsive chiral MOFs through the incorporation of TTF-based ligands and chiral co-ligands with an outlook for their use as sensors in logic gate materials.

We report the synthesis, structure and switching properties of a Cd-based MOF containing chiral camphorate and achiral 2,6-bis(4′-pyridyl)-tetrathiafulvalene (Py_2TTF) ligands. X-ray diffraction studies elucidated the cofacial arrangement of the Py_2TTF ligands, enabling the framework to undergo the [2+2] photocyclisation process, which is reversible with heating. Additionally, the reversible oxidation of the TTF moieties was investigated. Both switching techniques showed responsiveness to both the MOF's optical and chiroptical spectra. Results demonstrate the viability of this MOF for future applications as logic gates in optoelectronic devices.

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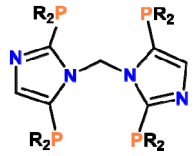
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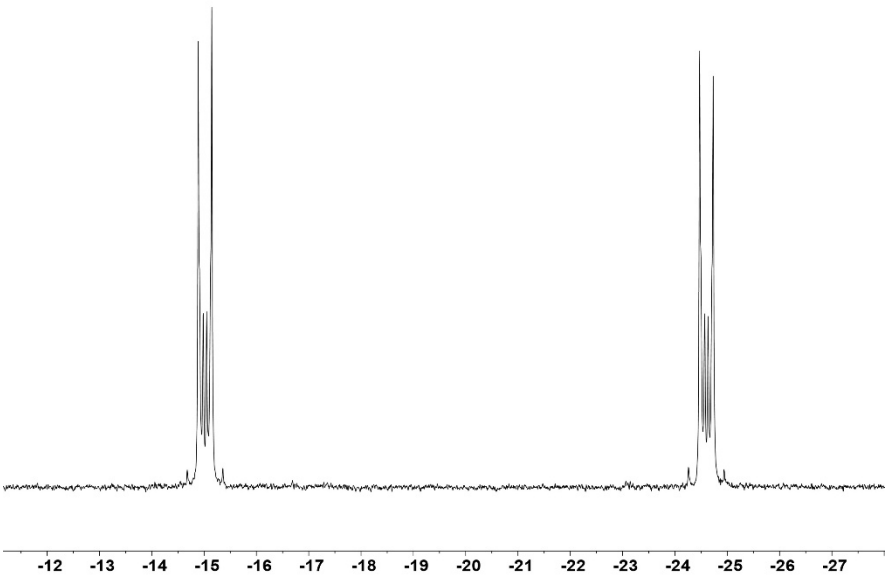
SUPRAMOLECULAR CHEMISTRY IN THE 3D CHANNELS OF MOLECULAR COMPLEXES WITH TETRAPHOSPHINE LIGANDS

Allison Lee, Chris Gendy, Alexander Harrison, Roland Roesler*

University of Calgary, Calgary, Canada

Chelating diphosphine ligands have played prominent roles in coordination chemistry and homogeneous catalysis [1,2]. Also notable are tripodal tri and tetraphosphines, possibly best known for their relevance in small molecule activation [3]. In turn, bis(chelating) tetraphosphines are much less investigated [4]. We have found that bis(imidazolyl)methane is a versatile scaffold for the generation of di, tri, and tetraphosphines, providing easy access to a family of ligands featuring unique geometries. Herein, we report a series of dinuclear coordination complexes of Fe, Co, Ni, Zn, and Pt featuring a tetraphosphine ligand with a bis(imidazolyl)ethane scaffold that allows for interesting conformational behavior not accessible through planar ligands [5]. This presentation will focus on the molecular wheels reliably formed via solid-state self assembly of some of these complexes. The central cavities of these wheels align to generate 3D structures with 1 nm diameter channels, which display a rich host-guest chemistry with small organic molecules.





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INVESTIGATING TARGETED CATION ORDERING IN METAL ORGANIC FRAMEWORKS BUILT FROM INERT METALLOLIGANDS

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The use of dopants in metal-organic frameworks (MOFs) to tune their conductive and magnetic properties is well-established [1]. Control over the distribution of the metal centres within a MOF is much more challenging. Previous research shows the development of the modular construction of two- and three-dimensional MOFs [2]. By 'preloading' a metalloligand with one metal and relevant ligand, it is possible, with the reaction with the second metal, to create ordered configurations under kinetic control. We have developed a synthetic approach targeting cation ordered, tuneable frameworks using inert metalloligands. To investigate the local ordering of these systems we have used both single crystal 3D-difference-electron-PDF [4] and power X-ray PDF [3] in combination with 3D electron diffraction for determination of the average structures, to probe the local correlations in pursuit of more detailed connections between local environments and the resulting measured macroscopic properties.

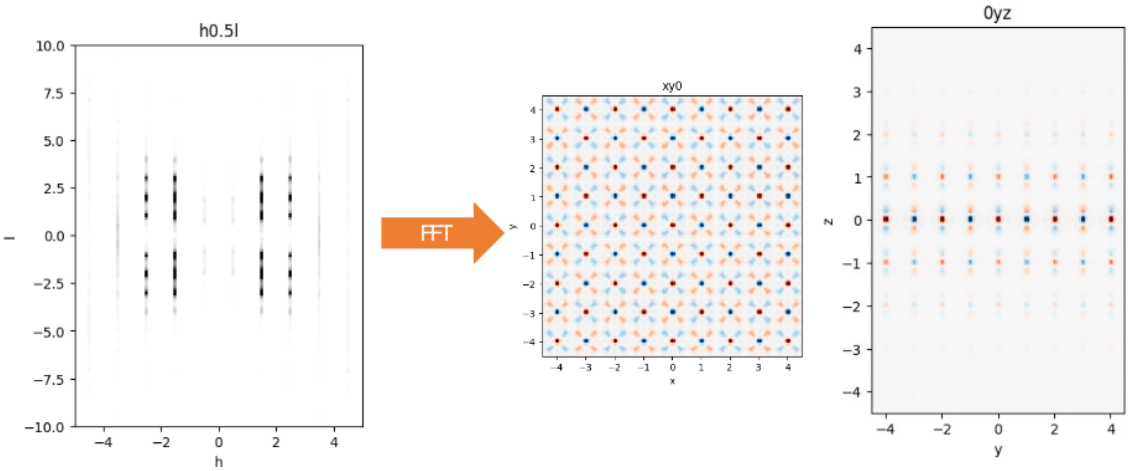


Figure 1: Showing the steps from diffuse reciprocal space electron diffraction data to a slice of the 3D-delta-PDF for use in exploring local structure of disordered materials

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TEMPLATED SYNTHESIS OF A Zr-FORMATE ZEOLITE - LIKE METAL ORGANIC FRAMEWORK

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Metal-Organic Frameworks (MOFs) have attracted significant research interest over the past decade due to their diverse chemical, structural, and topological properties. Their variability in network topologies, metal ions or secondary building units (SBUs), organic ligands and functional groups enables the design of a wide range of materials. Such materials are applied in diverse areas including gas storage/separation, catalysis, sensing and removal of pollutants from the environment.[1] A promising strategy for the synthesis of new MOFs is templated synthesis, where specific molecular species or metal-ligand interactions direct the self-assembly of the framework. This method facilitates the formation of unique network topologies while enhancing control over pore size, connectivity, and functionality.[2]

In this work we report the templated synthesis of a new 3-dimensional Zr-formate MOF named ZrFA-4 displaying a sodalite topology. The assembly of the hexanuclear Zr secondary building unit of ZrFA-4 to form the sodalite cage led to a giant $[Zr_6]_{24}$ capsule templated by organic and inorganic ions including $[CoCl_4]^{2-}$, Cl^-, $Me_2NH_2^+$ and 4-MepyH$^+$. These $[Zr_6]_{24}$ capsules are connected through anti-anti bridging formate groups giving rise to a 3-dimensional network. Its isolation highlights the structure directing capability of the template molecules which enabled the formation of the first 3-D Zr- formate MOF based on the simplest carboxylate ligand (formate) with a topology that could only be achieved previously by designed synthesis using organic ligands with appropriate geometrical characteristics. ZrFA-4 is stable in common organic solvents and displays a BET surface area of 262 m^2/g.

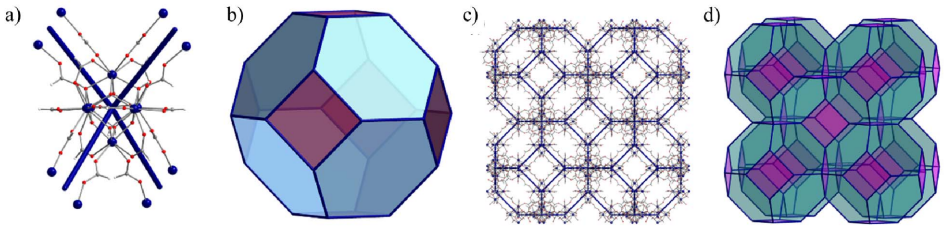


Figure 1. (a–d) Structural representations of selected fragments of the compound exhibiting sodalite topology.

Acknowledgement: This work was funded under the M-ERA.NET Call 2019 and the Republic of Cyprus through the Research and Innovation Foundation (contract no: P2P/M-ERA.NET/0319/0005; Acronym: SALMOS).

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O_2 CAUGHT IN AN IRON-PORPHYRIN MOF

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The heme-complex is an essential component of hemoglobin, the protein responsible for oxygen transport in the bloodstream. It consists of a four-coordinate porphyrin ligand and a mono-coordinate imidazole ligand (histidine) bound to an iron center. In this five-coordinate state, the complex binds molecular oxygen, formally involving oxidation of Fe^{2+} to Fe^{3+} and formation of an iron(III)–superoxide species, Fe^{3+}–$O_2^{\bullet-}$.

Due to its important biological role and its potential in the development of artificial oxygen carriers and functional materials such as catalysts, synthetic heme complexes have been extensively studied for several decades [1]. In this context, discrete molecular systems—where the iron-porphyrin core is functionalized to mimic the oxygen-binding site of hemoglobin—have been sought-after targets. However, the iron-porphyrin-based PCN-224 metal-organic framework (MOF) exhibits similar functionality, although in this system the iron–dioxygen adduct is less stable and dissociates well below room temperature, likely due to the absence of an axial imidazole ligand [2].

In this work, we report the synthesis of iron-dioxygen adduct confined into a new iron-porphyrin MOF, which is stable and can be characterized under ambient conditions. We present the single crystal X-ray structure, providing a detailed description of the Fe–O and O–O bonding in the adduct (Figure 1). Furthermore, Raman and Mössbauer spectroscopic results are discussed to support dioxygen binding in the bulk material, as well as to elucidate the oxidation and spin state of the iron center.

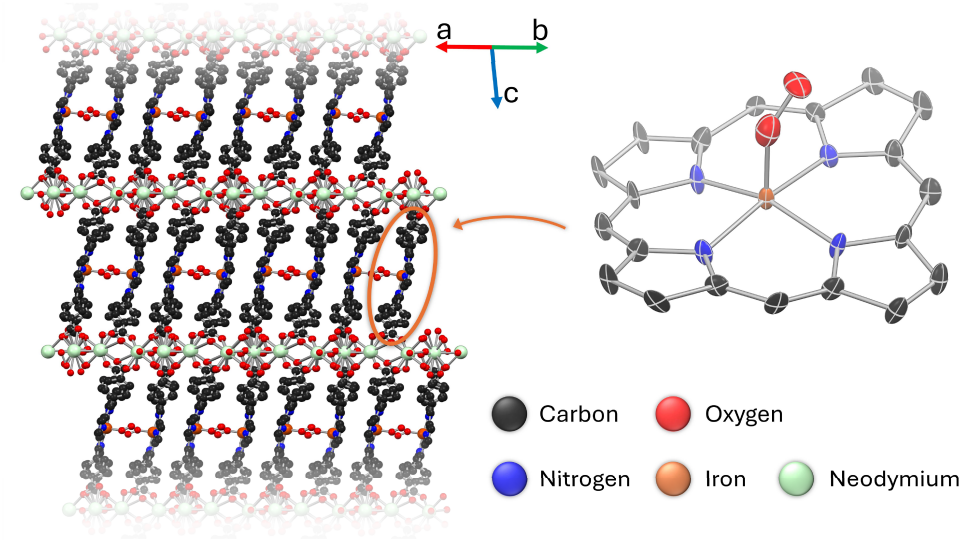


Figure 1. Illustration of the crystal packing (left) and dioxygen binding (right) in the iron-porphyrin MOF discussed in this presentation.

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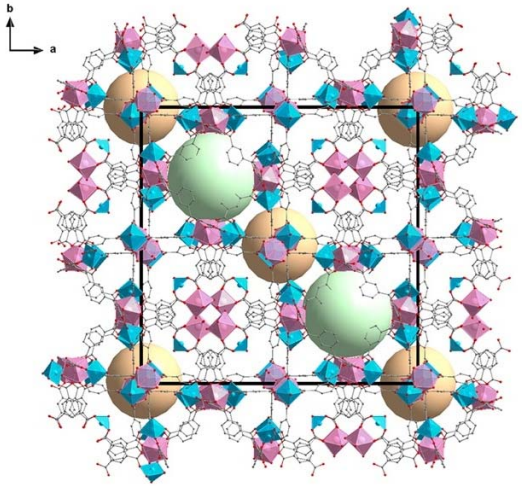
METALLOGEL-MEDIATED CRYSTAL GROWTH OF A Cu(II)-HO(III) HETEROMETALLIC METAL-ORGANIC FRAMEWORK WITH UNUSUAL NODE DISORDERS

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In this work, the structural details of a Cu(II)-Ho(III) Heterometallic Metal-Organic Framework (HMOF) that features unusual node disorders in the multimetallic Secondary Building Units (SBUs) are investigated. This HMOF, formulated as $[Ho_{3.75}Cu_{6.25}(nip)_{12}(H_2O)_{13.25}]^{(0.25)-}\cdot 9DMF$ (**1**), is comparable to multivariate MOFs,[1] which are isostructural frameworks that differ in the composition of a metal site in the crystal structure. The synthesis and crystal growth of the HMOF proceed through a metallogel route. The Cu-H_2nip metallogel, which is based on Cu(II) ions and H_2ni-nitroisophthalic acid), is used as the precursor here.

The single crystal X-Ray diffraction of **1** was challenging due to the intrinsic disorders in secondary building units, ligand and lattice solvents in the pores. The number of metal atoms with respect to the ligands in the formula unit of the compound is non-stoichiometric due to the node disorder. A quarter of a positive charge and the exact number of lattice solvent cannot be accounted for from the SCXRD data. Nevertheless, this example highlights the complex nature of crystal growth and the challenges in structural characterisation in the case of porous MOFs with disordered building units.



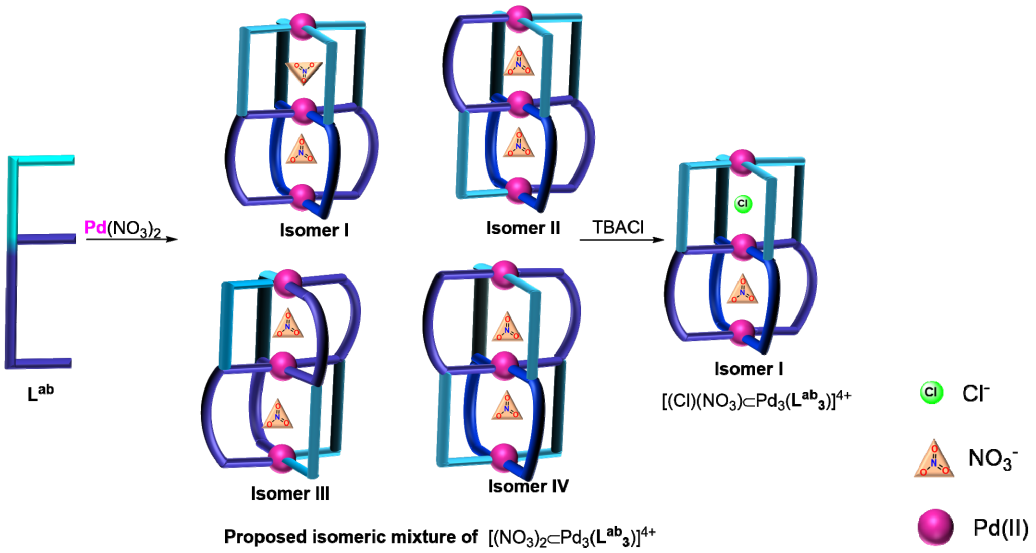
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TEMPLATE INDUCED ORIENTATIONAL SELECTIVITY OF LIGANDS IN A DOUBLE CAVITY COORDINATION CAGE

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Complexation of palladium(II) with designer symmetrical bis-monodentate ligands and tris-monodentate ligands is known to provide Pd_2L_4 type single-cavity coordination cages and Pd_3L_4 type double-cavity cages having two identical cavities. However, the construction of low-symmetry Pd_2L_4 type cages using unsymmetrical ligand is a relatively less explored area, more so for the Pd_3L_4 type cages. The present work is inspired by two different Pd_3L_4 type cages, prepared using $Pd(NO_3)_2$ and two different symmetrical tris-monodentate ligands ($\mathbf{L^{aa}}$ and $\mathbf{L^{bb}}$) that are slightly different from each other.[1,2] We have designed a new low-symmetry tris-monodentate ligand $\mathbf{L^{ab}}$ that possesses pyridines as donors where the central pyridine unit is disubstituted with 3-pyridyl appended arms of somewhat unequal length. An isomeric mixture of double-cavity Pd_3L_4 type cages was obtained by complexation of $Pd(NO_3)_2$ with the unsymmetrical tris-monodentate ligand as shown below. This is due to the fact that nitate being compatible with all isomers leads to lack of orientational selectivity. Orientational selectivity is achieved upon addition of chloride ion, one of the isomers got enriched in a dynamic manner where one cavity contains chloride and the other cavity contains a nitrate.



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COORDINATION CAGES AS SCAFFOLDS FOR MONODISPERSE MULTI-GLYCAN ARRAYS FOR LECTIN BINDING

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We have previously reported the use of self-assembled M_4L_6 and M_8L_{12} coordination cages (where M = Co(II) or Zn(II)) to prepare monodisperse and geometrically predictable glycoclusters with a valency of 12 and 24 glycans respectively and then conducted turbidimetry experiments to evaluate their ability to engage a range of lectins. The glycoclusters with 24 glycans showed increased binding to the appropriate lectins over the 12-glycan arrays, providing clear evidence of a *cluster glycoside effect*.[1]

In this work, we have extended our synthetic methodology to prepare mixed glycan arrays based on the M_8L_{12} cubic cage using two different routes: 1) using asymmetric ligands with a different glycan type appended to each end, to afford a single composition of 12 glycans of each type; and 2) using a 1:1 mixture of symmetrical ligands during the self-assembly process to afford a statistical mixture of assemblies. Surface plasmon resonance (SPR) and Microscale thermophoresis (MST) experiments were then conducted to quantify the binding of both the mixed glycan arrays and previously synthesised homo-glycan analogues, to lectins. Evaluation of the SPR kinetic data revealed two binding modes for the glycan arrays binding to lectins, when fitted to a heterogeneous ligand model.

Furthermore, we also present a new family of poly(2-oxazoline) functionalized coordination cages. These were fully characterized by ^{1}H NMR and GPC and their LCST behaviors were determined.

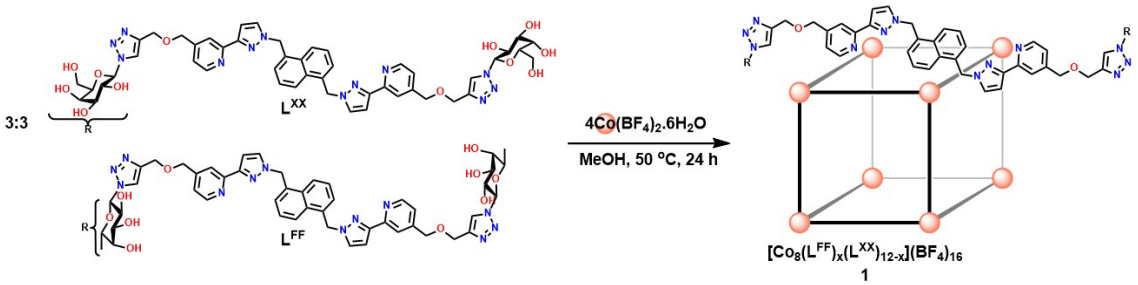


Figure 1 Synthetic route to $[Co_8(L^{FF})_x(L^{XX})_{12-x}](BF_4)_{16}$ using L^{XX} and L^{FF} in a 1:1 molar ratio where R = galactose or fucose. The cage sample contains a statistical mixture of 13 compositions $Co_8(L^{FF})_x(L^{XX})_{12-x}$ (where x = 0 - 12).

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EXPLORING MOF-GELS FOR TRACE PFAS REMOVAL FROM WATER

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Chalmers University of Technology, Göteborg, Sweden

Per- and Polyfluoroalkyl substances (PFAS) accumulation in water bodies, posing significant risks to human health and the environment. Due to their remarkable chemical stability, conventional water treatment techniques are often inadequate to remove PFAS down to allowable limits. Thus, there is a need for continued development of new materials for targeted PFAS trace removal from drinking water. Herein, we report the synthesis and investigation of various metal organic framework gels (MOF-gels) to capture PFAS from water at trace levels. A uniform and reproducible gelation process was designed by optimization of reaction parameters. A series of UiO-66 and MOF-808 MOF-gels incorporating different ligands were synthesized and characterized. These gels exhibited excellent water stability and retained swellability. PFAS sorption experiments with MOF-gels were conducted with various PFAS compounds using qNMR spectroscopy. MOF-gels exhibited good adsorption capacity (> 98%) towards various PFAS while MOF-808 type gels showed improved removal efficiencies for short-chain PFAS. Adsorption kinetics followed pseudo-second order model and defect rich architecture in MOF-gels enhanced opportunities to capture wide range of PFAS. Moreover, MOF-gels easily recovered by simple sedimentation or filtration then reused for several adsorption cycles without losing structural integrity and performance. Overall, this work presents potential use of MOF-gels as versatile adsorbents for removal of PFAS from water and provides insights into structural property relationship of PFAS and MOF-gels.

A NOVEL PENTANUCLEAR IRON-BASED COVALENT ORGANIC FRAMEWORK ENABLING ANION-REGULATED ELECTROCHEMICAL CO_2 REDUCTION

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[b]Division of Applied Chemistry, The University of Osaka, Suita, Japan
[c]Department of Chemistry, Tokyo Institute of Technology, Tokyo, Japan

Efficient conversion of carbon dioxide (CO_2) into value-added products is critical for advancing clean energy technologies[1]. The development of stable, selective, and high-performance electrocatalysts for CO_2 reduction reaction (CO_2RR) remains a critical yet challenging goal. Our group has demonstrated that the pentanuclear scaffolds are an effective platform for catalyzing small-molecule conversions and their heterogenization offers a promising approach to expand their applicability[2-3]. Here, we introduce Fe_5COF, a novel metal-covalent organic framework (M-COF) based electrocatalyst, synthesized by covalently linking pentanuclear iron-based complexes via polyimide linkages (Figure 1). This multinuclear catalyst shows high selectivity for CO formation in a non-aqueous medium. We investigated the effect of anions on the electrochemical CO_2RR kinetics and activity of Fe_5COF using tetrabutylammonium (TBA^+) salts with different anions (ClO_4^-, Cl^-, Br^-, and I^-) in acetonitrile. Our study revealed that Fe_5COF shows optimal performance in TBA^+I^-, achieving a faradaic efficiency of ~96.8% for CO formation. Electrochemical Impedance Spectroscopy (EIS) indicates enhanced electron transfer kinetics with TBA^+I^- evidenced by a relatively low R_S (8.475 Ω) and R_{CT} (0.89 Ω). These findings highlight two critical advancements: the integration of a redox active pentanuclear catalytic center into M-COF framework and the critical role of anions in modulating its catalytic performance for developing next-generation COF-based electrocatalysts with enhanced activity and selectivity towards electrochemical CO_2RR.

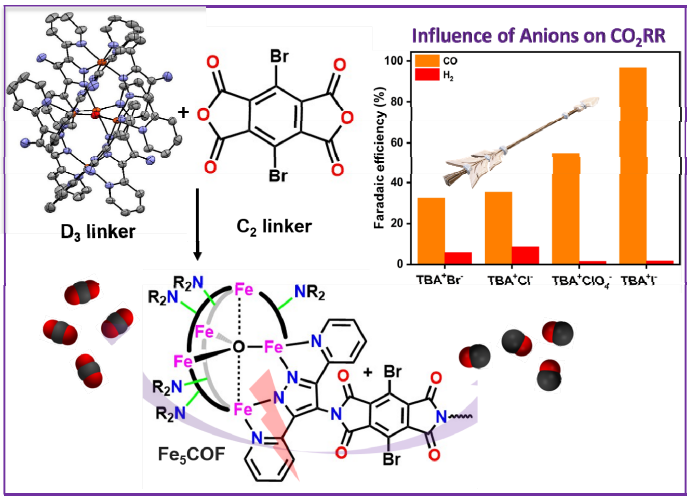


Figure 1: Schematic illustration of Fe_5COF synthesis and the effect of different anions on enhancing electrochemical CO_2 reduction performance.

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UNLOCKING A NEW GEOMETRY IN PORPHYRIN METALLACYCLES

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Discrete supramolecular multiporphyrin arrays have garnered considerable attention for their capacity to emulate the structural complexity of natural systems and for their potential applications in molecular recognition, catalysis, and energy conversion [1]. Among the various synthetic strategies available, metal-mediated self-assembly – particularly the directional-bonding approach – has emerged as a powerful and reliable method for their construction. In our previous studies, the neutral 90° metal fragment *trans,cis*-$Ru^{II}Cl_2(CO)_2$ was combined with 4′-*cis* and 3′-*cis*dipyridylporphyrins (4′-*cis*DPyP and 3′-*cis*DPyP) to afford robust bis-porphyrin metallacycles displaying distinct geometries – *planar* and *step-like* arrangements in Figure (a) and (b) [2]. These were successfully used as inert platforms to build more elaborate 3D assemblies [3]. More recently, we expanded this strategy by combination of 3′-*cis*DPyP with classical cationic 90° metal acceptors of the type *cis*-$[Pt^{II}(YY)]^{2+}$ (*e.g.*, YY = dppp). Notably, this approach enabled the formation of a new family of bis-porphyrin metallacycles in which the two chromophores adopt a "*pac-man*" configuration, Figure (c) [4]. Synthesis, comprehensive characterization of these new assemblies and investigations of their use as hosts in molecular recognition are presented. Self-sorting behavior of mixtures containing *cis*-Pt^{II} fragments and 4′-*cis*DPyP/3′-*cis*DPyP, in view of the assembling of heteroleptic metallacycles, will be briefly addressed.

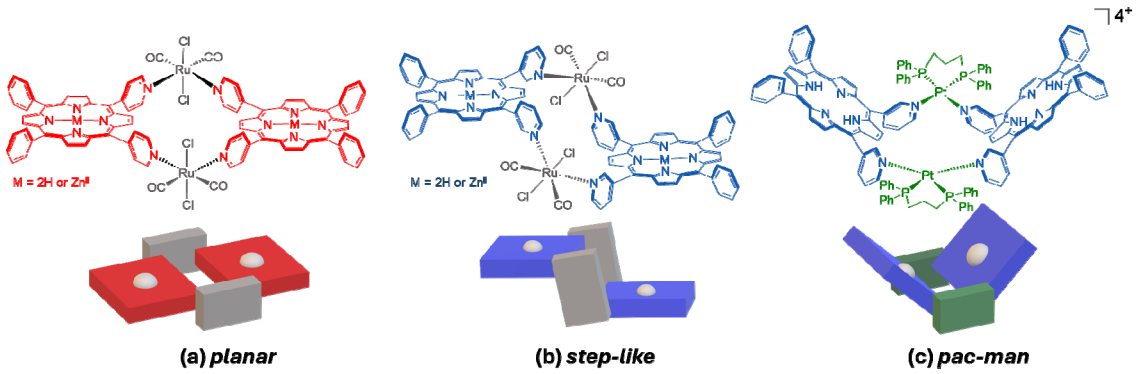


Figure: Schematic structures of three bis-porphyrin metallacycles presenting distinct geometries: (a) *planar*, (b) *step-like*, (c) *pac-man*.

This work was supported by the European Union - Next Generation UE P2022ZSPWF PRIN Project.

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LIGHT CONTROLLED SOLUBILITY ON HETEROLEPTIC METAL-ORGANIC CAGES

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Institute of Molecular Science, University of Valencia, Spain

In recent years, Metal-Organic Cages (MOCs) have emerged as potential architectures in supramolecular chemistry, offering unique processability compared to extended frameworks[1,2,3]. However, the reliance on homoleptic assembly often limits functional diversity. While traditional copper (II) analogues typically suffer from poor processability due to weak inter-cage interactions, this work describes the strategic synthesis of MUV-48, a novel family of heteroleptic Cu (II) based MOC with general formula $M_6L_6L'_6$. By breaking molecular symmetry, we demonstrate the ability to toggle between two distinct behaviors within a single structure: passive, permanent rigidity and active, stimuli-responsive solubility.

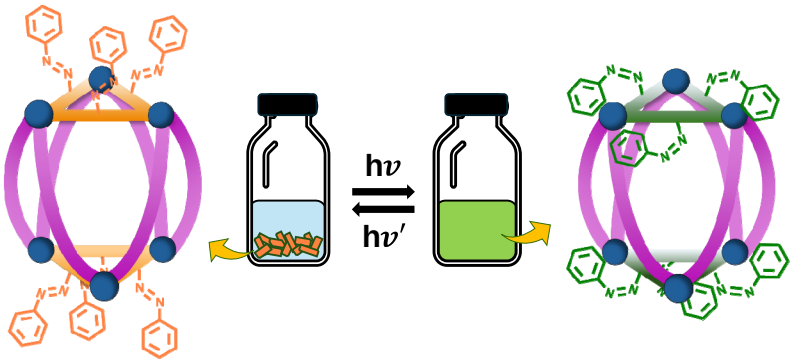


Figure 1. General Scheme on the solubility control of MUV-48

The integration of aliphatic chains grants complete dissolution in organic solvents through increased molecular mobility while the incorporation of photoactive azobenzene units enables optically-triggered solubilization. Upon UV irradiation, the trans-to-cis isomerization of the azobenzene ligands effectively disrupts the periodicity of the crystalline lattice and inter-cage stability, facilitating a facile, on-demand transition from an insoluble solid to a homogeneous solution without compromising the robust 0D cage integrity. Furthermore, a multivariate (MTV) approach was employed to investigate the limits of this triggered transformation. SCXRD, PXRD, MALDI-TOF mass spectrometry and ^{1}H-NMR confirmed a social self-sorting mechanism, resulting in a heteroleptic continuum where solubility thresholds can be precisely tuned by controlling the statistical ligand stoichiometry. These findings establish a robust methodology for the spatiotemporal control of cage processability, bridging the gap between solid-state storage and solution-phase applications in catalysis, sensing, and molecular encapsulation.

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LIGAND ISOMERISM IN ENDOHEDRALLY LOW-SYMMETRY DISCRETE COORDINATION CAGES AND THEIR DIFFERENTIAL SWITCHING MODES

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Complexation of Pd(II) with a symmetrical bis-monodentate ligand produces a cage or dynamic equilibrium of more than one cage of Pd_mL_{2m} formulation.[1] However, orientational isomers are expected when ligand is unsymmetrical.[1] Dynamic equilibrium of Pd_2L_4 and Pd_3L_6 type endohedrally low-symmetry cages containing orientational isomers (13 possibilities) were obtained from Pd(II) and pyridine-3-yl appended unsymmetrical ligand **L1** having amide-phenylene-ester spacer. Crafting geometric constraint (unequal-sized coordination-arms) in ligand should bring isomeric selectivity but with altered cage-shape/size.[1] To retain cage-shape/size, steric constraint was implanted by peripheral substitution on **L1**.[2] Quinolin-3-yl was placed instead of pyridine-3-yl at amide-end and ester-end of **L1** to obtain regioisomeric ligands **L2** and **L3**, respectively. Solvent dependent nuclearity control (Pd_2L_4 in CH_3CN; Pd_3L_6 in DMSO) and substituent driven isomeric control (all-*cis*(2,2) isomer) have been obtained by mixing Pd(II) with **L2** or **L3**. The obtained all-*cis*(2,2)-Pd_3L_6 of **L2** and **L3** are designated as isomer-1 and isomer-2 under ligand isomerism. The isomer-1 in DMSO could be switched to Pd_2L_4 form by adding CH_3CN, and reverted to Pd_3L_6 form by evaporation of CH_3CN. However, the isomer-2 in DMSO showed insignificant changes upon addition of CH_3CN. Thus, we demonstrated differential switching modes of a pair of isomeric cages that are endohedrally low-symmetry.

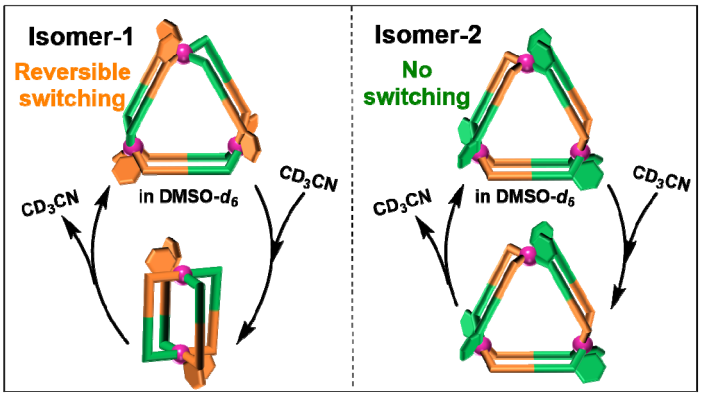


Figure 1: Cartoon representation showing the differential switching of isomer-1 and isomer-2

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SEPARATION AND ISOLATION OF HETEROLEPTIC COORDINATION CAGES VIA PHASE TRANSFER

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Heteroleptic coordination cages, assemblies of metal ions linked by two or more different organic ligands, are a promising class of low symmetry hosts. When combining ligands to assemble heteroleptic coordination cages, mixtures of homo- and heteroleptic cages are often formed. To avoid the generation of these mixtures, which have been thought to be inseparable, various strategies have been developed to ensure that only one cage is formed in the assembly, but these strategies limit the types of ligands that can be used. In this work, we present a novel method for isolating heteroleptic coordination cages from mixtures *via* phase transfer, a process where cages are driven between immiscible liquid phases using counterion exchange [1, 2]. As a proof of principle, we demonstrate the successful isolation of three heteroleptic coordination cages from a mixture.

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IRON–PORPHYRIN METAL–ORGANIC FRAMEWORKS FOR HETEROGENEOUS OXIDATION CATALYSIS IN WATER REMEDIATION

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Chlorination is widely used for drinking water disinfection but can result in the formation of harmful disinfection byproducts through reactions with organic pollutants. Iron-based oxidation systems have been shown to suppress disinfection byproduct formation under hypochlorite conditions, and kinetic studies have been enabled through membrane inlet mass spectrometry.[1,2] Iron–porphyrin complexes are effective biomimetic oxidation catalysts capable of intercepting reactive chlorine species and promoting pollutant degradation.[3] However, homogeneous catalysts suffer from limited recyclability and challenges in separation from treated water. Incorporation of metalloporphyrins into metal–organic frameworks (MOFs) offer a strategy to generate robust heterogeneous catalysts while retaining the desirable catalytic properties of the molecular active site.

In this work, iron–porphyrin MOFs incorporating meso-tetra(4-carboxyphenyl)porphyrin (FeTCPP) were synthesised and structurally characterised. Frameworks based on Fe_3O clusters and Zr_6 nodes were prepared to produce PCN600(Fe) [4] and PCN222(Fe) [5,6], respectively.

This work contributes to the development of metalloporphyrin-based coordination frameworks as emerging heterogeneous catalytic platforms. Ongoing studies aim to investigate the stability, accessibility, and reactivity of iron–porphyrin active sites within MOF architectures, and to understand how coordination environment and framework structure influence catalytic behaviour in oxidative water remediation.

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BIMETALLIC Pd-Fe MOF FOR C-2 ARYLATION OF INDOLES

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Palladium complexes incorporated as ligands in MOF architectures represent a powerful strategy to merge the high activity and selectivity of homogeneous catalysis with the robustness and recyclability of heterogeneous systems, while exploiting the intrinsic porosity, crystallinity, and host–guest interactions of MOFs.[1,2] Our group previously reported MUV-22, a bimetallic MOF constructed from Fe(III) clusters and Pd(II) metalloligands.[3] This SOC-topology material displays remarkable thermal and chemical stability, enabling its use as a recyclable heterogeneous catalyst while preserving a homogeneous-like catalytic environment through the metalloligand approach. Herein, we explore the C-2 arylation of indoles, a transformation of high synthetic value that provides access to key scaffolds such as 2-phenyl-1H-indole (OLED building block), 5-nitro-2-phenyl-1H-indole (antibacterial related activity), and DAPI dihydrochloride (DNA-selective fluorescent probe). We demonstrate that MUV-22 efficiently promotes the synthesis of a broad range of C-2 arylindoles, tolerating both electron-donor and electron-withdrawing substituents, as well as sterically demanding substrates, highlighting its potential as a robust and versatile catalytic platform.

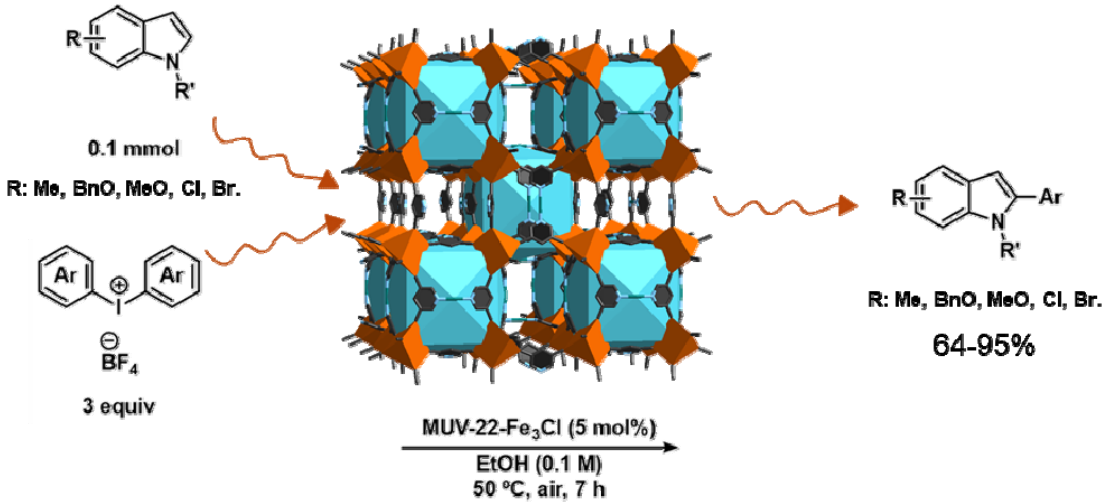


Fig. 1: MUV-22 as a Pd heterogeneous catalyst for C-2 indole arylation.

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NOVEL DINUCLEAR BUILDING BLOCKS FOR HETEROLEPTIC CAGES

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Heteroleptic coordination cages offer a modular route to multifunctional nanocapsules formed by controlled self-assembly. Their key advantage is the precise spatial arrangement of different functional units and guest molecules. This is highly relevant for light-driven applications such as sensing or photocatalysis, where electron and energy transfer dominate. Designing such cages remains challenging, as high metal-ion selectivity is required to avoid statistical mixtures or homoleptic self-sorting. Existing strategies towards heteroleptic cages include shape-complementarity,[1] steric control,[2] and charge-repulsion approaches.[3]

Here we present new types of heteroleptic cages based on dinuclear building units in combination with tri- or tetratopic monodentate ligands to yield prismatic or cubic cages (Figure 1a). One class of these cages is based on a bis-salphen Zn(II) building unit, which allows a facile synthesis and high tunability of the electronic properties. Upon self-assembly with tritopic phenyl- and triazine-based ligands, prismatic cages $\mathbf{(Zn_2L)_3L_2}$ could be synthesized quantitatively that show a high stability even at low concentrations (Figure 1b). While both cages display similar absorbance behaviour, a significant divergence in their photophysical behaviour was observed: the triazine-based cage is non-emissive, whereas the phenyl-based analogue exhibits a distinct orange emission.[4] In a second approach heteroleptic cages based on a Ir(III) organometallic building unit $\mathbf{(Ir_2L')_3L''_2}$ were developed (Figure 1c). Systematic variation of the bridging and tritopic units allows the self-assembly of a series of prismatic cages with varying pore sizes and shapes. These organometallic cages show guest binding with a high number of polycyclic aromatic hydrocarbons such as pyrene.

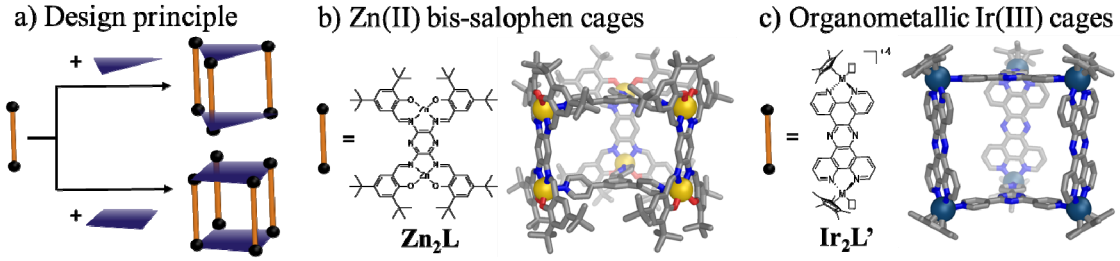


Figure 1: a) Design principle of heteroleptic cages based on dinuclear building units. MM2 models of a b) Zn(II) bis-salphen based cage and of an c) organometallic Ir(III) based cage are illustrated.

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MODELING THz EPR/MAGNETIC IR SPECTROSCOPY INCLUDING SPIN-PHONON COUPLINGS USING AN EXTENDED SPIN HAMILTONIAN

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Molecular electron spin qubits show great potential for quantum information storage and processing but require paramagnetic systems with slow relaxation, where coherence is limited by spin-phonon coupling.[1] Understanding this coupling remains challenging due to scarce observables and conflicting models, making direct experimental insights crucial. Vibrational spectroscopy (IR and Raman) under magnetic fields provides a promising approach.[2]

Intuitively, spin-flip transitions are field-dependent while vibrational transitions are not. In the presence of spin-phonon coupling, an interference pattern (the avoided crossing) may emerge when the energy of a spin-flip transition coincides with that of a vibrational transition. Although such direct spectroscopic evidence of spin-phonon coupling is challenging to obtain, magnetic IR (also referred to as THz-EPR) spectroscopy has demonstrated interference features between spin and vibrational transitions.[2] Nevertheless, simulations of these effects have, to date, typically relied on simplified energy-level diagrams and have omitted transition intensities or detailed light-matter interactions.

Here, we present the first comprehensive simulation protocol to extract spin-phonon coupling parameters from THz EPR/Magnetic IR spectra.[3] Using a tetrahedral high-spin Co(II) complex, we validate the method and benchmark it against quantum-chemical calculations. The dominant coupling is attributed to a twisting mode of the first coordination sphere. Excellent agreement among experiment, simulation, and computation demonstrate the power of THz EPR/Magnetic IR spectroscopy as a direct probe of spin-phonon coupling.

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SYNTHESIS AND ELECTRONIC PROPERTIES OF Cr-BASED METALLOSUPRAMOLECULAR POLYMERS

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Electrochromic (EC) materials are functional materials that exhibit reversible color changes accompanied by redox reactions upon the application of an external potential. They have been studied for applications such as smart windows and dimmable glass. They have also attracted attention as energy-efficient display materials due to their characteristic of consuming power only during color switching. However, organic EC materials suffer from limited durability, and conventionally used materials such as tungsten oxide and viologen-based systems have issues with insufficient response speed. In this study, we synthesized a new chromium (Cr) metallo-supramolecular polymer (**polyCr**) by using 6',6"-di(pyridine-2-yl)-2,2':4',4":2"'-quaterpyridine (Qpy), and reported electrochromic behavior.

The **polyCr** exhibited reversible and stepwise redox behavior over multiple potential regions, suggesting multi-step electron transfer processes at the Cr center in cyclic voltaglam. The **polyCr** showed stepwise color changes from yellow to gray, green, and blue depending on the applied potential. The coloration time of **polyCr** was 4.0 seconds, while the bleaching time was 2.4 seconds. These results indicate that **polyCr** is a material exhibiting multicolor electrochromic properties based on multi-step redox behavior. Its fast response and broad optical response across a wide wavelength range suggest promising applications.

NOVEL HYBRID MATERIALS BASED ON BIOACTIVE GLASS MODIFIED BY MIL-100 FRAMEWORK: PROPERTIES AND BIOMEDICAL APPLICATIONS

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Bioactive glass, due to its biocompatibility and bioactivity, is suitable for use as implants in the human body to repair and replace diseased or damaged bones. Metal-organic frameworks (MOFs) [1] can modify the properties of bioglass, increasing its effectiveness in bone reconstruction therapy. Its unique properties, e.g., high specific surface area, porosity, structural designability and drug encapsulation capacity have contributed to its wide range of applications. Novel research concern the synthesis and characterisation of core–shell hybrid materials consisting of bioactive glass nanoparticles (BG) and the MIL-100(Fe) framework ($Fe_3O(H_2O)_2OH(BTC)_2 \cdot nH_2O$, BTC: 1,3,5-benzenetricarboxylate). The formation of the MIL-100(Fe) shell on the BG core in MIL-100(Fe)@BG was directly confirmed by high-resolution transmission electron microscopy with EDS elemental mapping, infrared spectroscopy, X-ray powder diffraction, X-ray photoelectron spectroscopy, and synchrotron radiation-based X-ray absorption spectroscopy (XAS). These hybrid materials have been studied as potential regenerative materials for tissue engineering. Treating tissue defects using tissue-engineered products (tissue scaffolds) is a relatively new approach that holds great promise in regenerative medicine, which aims to restore the structure and function of damaged body parts. The MIL-100(Fe)@BG material demonstrated favourable cytocompatibility in a long-term (21-day) assay on mouse osteoblast precursor cells (MC3T3) and human dermal fibroblasts (HDF). At the same time, it did not induce ex vivo hemolysis at concentrations up to 1000 μg/mL. The induction of osteogenic differentiation in MC3T3 cells in the presence of MIL-100(Fe)@BG was confirmed by early osteogenic markers, including alkaline phosphatase (ALP) activity and alizarin red staining (ARS). Bioactivity studies revealed rapid formation of nanohydroxyapatite, beginning within the first hours of incubation. Importantly, under physiological conditions, the MIL-100(Fe) shell undergoes a controlled structural transformation, yielding highly dispersed nanoscale Fe_2O_3 particles. These nanoparticles induce the production of reactive oxygen species (ROS), which enhances the antibacterial activity of the MOF hybrid material, making the system active, without incorporating any additional antibacterial drug or silver nanoparticles, which seems to make this hybrid material highly innovative.

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TRACE ADSORPTION OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) USING MULTIVARIATE METAL-ORGANIC FRAMEWORKS

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Per- and polyfluoroalkyl substances (PFAS) are a class of emerging contaminants. Due to the strong C–F bond, PFAS are non-biodegradable and are therefore referred to as "*forever chemicals"*. Due to the high toxicity and bioaccumulation, EU drinking water regulations limit the sum of PFAS to 500 ng L^{-1}. Traditional sorbents for water purification, e.g., activated carbon, exhibit low to no selectivity and act as 'catch-all' materials. As a result, "*sorbent economy"* (pollutant-to-sorbent mass ratio) is prohibitively low, creating a need for more selective materials.

Metal-organic frameworks (MOFs) are a class of porous coordination polymers, constructed from inorganic clusters and molecular linkers. The predictive nature of their coordination chemistry provides a molecular toolbox for designing materials with specific physical and chemical properties. Although several MOFs exhibit high PFAS adsorption capacity, most studies focus on elevated PFAS concentrations (>1 mg L^{-1}) which translate poorly to real-world conditions. Recently, multivariate MOFs, frameworks constructed from two or more different linkers and/or metals, have yielded new materials with unexpected, and often improved, properties.

Herein, we describe the synthesis, characterization, and adsorption properties of a series of multivariate UiO-67 analogs with varying ratios of trifluoromethyl (*hydrophobic*) and amine (*hydrophilic*) linkers. We hypothesized that this combination would lock PFAS molecules into position via simultaneous head- and tail-group interactions, increasing the binding strength and as a result selectivity.[1] Our results show that at elevated levels (50 mg L-1), the multivariate material performs comparably to parent UiO-67. However, moving towards environmentally relevant concentrations (100 µg L^{-1}), the multivariate material achieves a 70% removal efficiency, compared to 10% for unfunctionalized UiO-67 (*seven-fold improvement*). Stability tests reveal negligible leaching of PFAS into water, while the material can be fully regenerated (e.g., using methanol). These findings highlight how the synergistic interplay of multiple chemical environments within a single framework can provide selectivity unattainable with homogeneous pore surfaces.

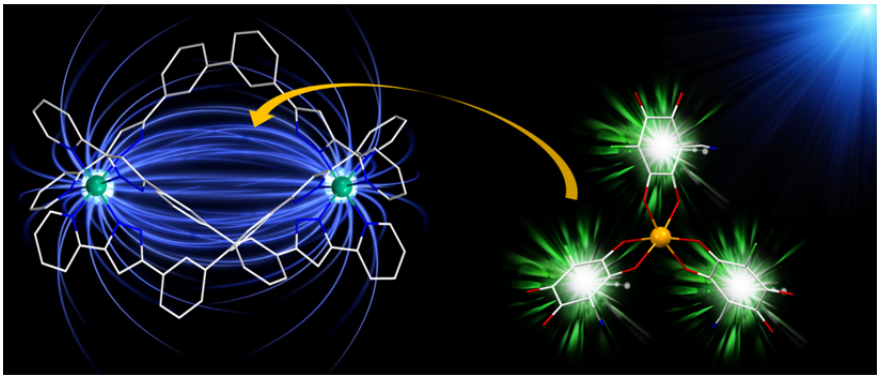
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DRIVING MAGNETIC BEHAVIOUR THROUGH SUPRAMOLECULAR ENCAPSULATION OF COORDINATION COMPLEXES

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Supramolecular chemistry has provided new avenues for the synthesis of molecular materials, exhibiting various crystal packing architectures, which allows for their properties' tunability. Our approach to this solution involves the synthesis of a novel series of host-guest supramolecular assemblies, which exhibit guest-modulated magnetic properties [1, 2]. The various guests that have been encapsulated in $[Fe^{II}_2L_3]$ helicates have been proven to affect the Spin-Transition Temperature for each of the Fe^{II} ions, while the encapsulation of the $[Cr^{III}(ox)_3]^{3-}$ complex promotes an unprecedented Single-Ion Magnet behavior for Cr^{III}. Meanwhile, the electronic density of the various guests that have been encapsulated in $[Co^{II}_2L_3]$ helicates affects the relaxation rates of their magnetization through Spin-Orbit Coupling. In this work, we report the synthesis of the complexes: $[Al(anilate)_3]@[Fe_2L_3](BF_4)$ (**1**), $[Al(anilate)_3]@[Zn_2L_3](BF_4)$ (**2**), $[Fe(ClCNAn)_3]@[Ni_2L_3](BF_4)$ (**3**), $[Cr(ClCNAn)_3]@[Ni_2L_3](BF_4)$ (**4**), $[Fe(ClCNAn)_3]@[Co_2L_3]Cl$ (**5**), $[Al(ClCNAn)_3]@[Co_2L_3]Cl$ (**6**), $[Fe(ClCNAn)_3]@[Zn_2L_3](BF_4)$ (**7**) and $[Al(ClCNAn)_3]@[Zn_2L_3](BF_4)$ (**8**) (Figure 1). Complexes (**1**) and (**2**) constitute the diamagnetic analogues of the published $[Fe(anilate)_3]@[Fe_2L_3](BF_4)$ structure, either regarding the encapsulated guest or the full helicate respectively. In the cases of (**3**) and (**4**), the employment of the asymmetric $ClCNAn^{2-}$ analogues can potentially lead to inequivalent magnetic interactions between the two Ni^{II} ions. Moreover, the encapsulation of the electron-rich $[M(ClCNAn)_3]^{3-}$ ($M = Fe^{III}$, Al^{III}) complex in (**5**) and (**6**) could lead to the enchancment of SOC and therefore improve the relaxation rates. Meanwhile, complexes (**7**) and (**8**) are structurally similar to (**1**) and (**2**) with the only notable difference between them being that their guests bear the $ClCNAn^{2-}$ instead of the $(anilate)^{2-}$ ligand. Finally, the luminescent properties of the $ClCNAn^{2-}$ ligand could lead to multifunctional materials which are sensitive to external stimuli.



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EFFECT OF LIGAND METHYLATION ON DIASTEREOISOMERISM OF M_4L_6 TETRAHEDRA

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Metal-organic cages (MOCs) are the thermodynamically favoured product of self-assembly of organic ligands and metal ions. MOCs have recently found applications in catalysis, sensing and separation. For the archetypically tetrahedral M_4L_6 MOC, incorporating bis-bidentate pyridyl imine based ligands, each metal ion is octahedrally coordinated and thus possesses either Δ or Λ chirality.[1] In solution, this gives rise to three potential MOC diastereoisomers with T (ΔΔΔΔ/ ΛΛΛΛ), C_3 (ΔΔΔΛ/ ΛΛΛΔ) and S_4 (ΔΔΛΛ) symmetry.[1] The distribution of these isomers may be effected by host guest binding or functionalization of the organic ligand.[2]

Self-assembly of 2,6-bis(4-aminophenyl)naphthalene (L_1), 2-pyridine carbaldehyde and iron(II) triflimide have previously been reported to yield a 13:49:38 ratio of T, C_3 and S_4 cages.[3] Two novel, structurally-related diamines (L_2 and L_3) have been synthesised and self-assembly was attempted with 2-pyridinecarbaldehyde and iron(II) bis(trifluoromethyl sulfonyl)imide (Figure 1). Reaction products were characterised via ^{1}H NMR, mass spectrometry, DOSY and where possible SC-XRD. Results indicate that complexation of L_2 yielded a single species with an M_4L_4 composition. In contrast, L_3 yields an M_4L_6 tetrahedron. Investigations into the influence of increasing steric bulk in the 3- position of the diamine ligand and the effect of the identity of the metal ion, on diastereoisomerism are ongoing.

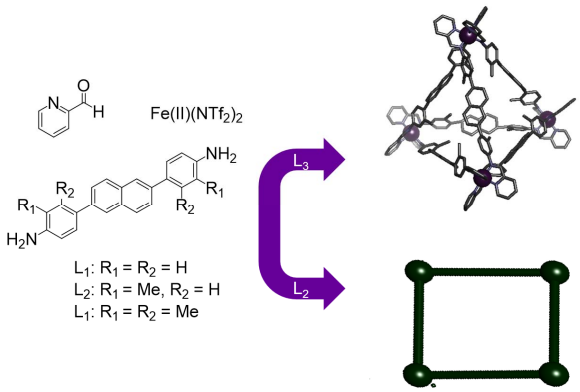


Figure 1: Self-assembly of iron(II) bis(trifluoromethyl sulfonyl)imide, 2- pyridine carboxaldehyde and L_2 and L_3.

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MODULAR TRIAZOLE-BASED MACROCYCLES FOR HALIDE AND METAL ION DETECTION

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A modular approach to triazole-based open-chain and macrocyclic synthetic receptors has been developed. The 1,4,5-trisubstitued-1,2,3-triazole monomers were prepared via ruthenium catalyzed azide-alkyne cycloaddition (RuAAC) and subsequently assembled into dimers and trimers via amide coupling, with selected structures also being subjected to macrocyclization. These receptors were characterized by 1D/2D NMR, MALDI and X-ray diffraction, and their ability to detect halide ion was evaluated. ^{1}H NMR investigation indicates that both dimers and trimers display affinity for chloride ion in preference to other halides. The fixed size of the dimer and trimer macrocycle cavity also provides a means for selective recognition of chlorine ion. The amide-based H-bond donors are believed to play a primary role in detection compared to the methylene protons adjacent to carbonyls. The results indicate that the described triazole-based structures could find use as synthetic receptors for various ionic species.

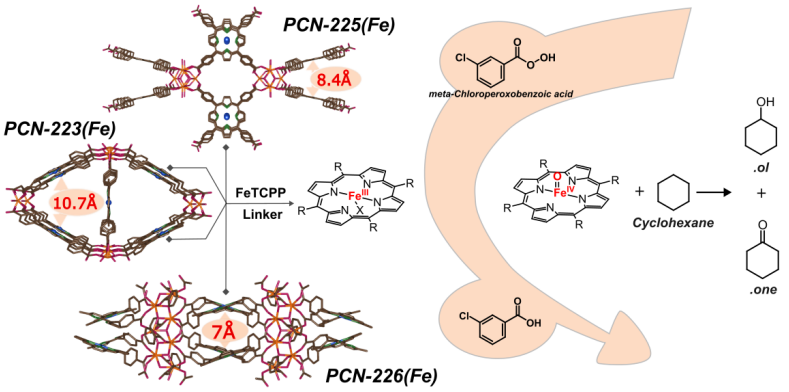
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Fe-PORPHYRINIC METAL–ORGANIC FRAMEWORKS WITH TUNABLE Fe···Fe DISTANCES FOR C–H ACTIVATION

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Selective C–H bond activation enables hydrocarbon valorization but remains challenging due to the inert nature of C–H bonds. Metalloenzymes can selectively oxidize strong C–H bonds to alcohols under mild conditions using O_2 as oxidant. These energetically demanding reactions are enabled by the coordination environment of the catalytic iron centers and precise Fe···Fe distances that facilitate O_2 activation and the formation of high-valent iron-oxo species [1]. Industrial C–H oxidation processes are commonly performed using iron-containing zeolites, yet these systems typically rely on strong oxidants and high temperatures to generate the reactive metal-oxo species [2]. More recently, it was shown that carefully controlled Fe···Fe distances in iron-containing zeolites can facilitate O_2 activation at low temperatures, drawing parallels with the active sites found in metalloenzymes [3]. Unlike zeolites, Metal-organic frameworks (MOF) enable precise control over the spatial arrangement and density of catalytic iron sites [4].



We probed the role of iron-site proximity in C–H activation using three iron-porphyrin-based MOFs, namely PCN-223(Fe), PCN-225(Fe), and PCN-226(Fe), which all contain Fe(III)meso-tetra(4-carboxyphenyl)-porphine chloride (FeTCPP) as organic linker and Zr-oxo clusters (see Figure). These MOFs exhibit distinct framework topologies and Fe···Fe distances, enabling investigation of structure-activity relationships. The MOFs were evaluated for cyclohexane oxidation as model reaction using m-chloroperoxybenzoic acid (mCPBA) and O_2 as oxidant. Ultraviolet-Visible (UV-Vis) and Electron Paramagnetic Resonance (EPR) spectroscopy indicated the formation of high-valent iron-oxo species, while Gas Chromatography (GC) confirmed the conversion of cyclohexane. Comparison with homogeneous FeTPP catalysis highlights the potential of Fe-porphyrinic MOFs as tuneable heterogenous platform for C–H activation.

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AN AUTOMATED FLUIDIC WORKFLOW FOR REPRODUCIBLE AND SCALABLE FABRICATION OF METAL-ORGANIC-FRAMEWORK-BASED QCM SENSORS

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Laboratory automation is increasingly being adopted in chemistry to accelerate workflows, reduce inefficiencies, and minimize human error. While commercial solutions exist for routine tasks, non-standard applications require custom integration of hardware and software components, some of which may need to be developed specifically for the application.

Here, we present an automated fluidic workflow for the growth of metal-organic framework (MOF) thin films on quartz crystal microbalance (QCM) sensors. We have previously demonstrated QCM sensors functionalized with MOF coatings as low-cost, fast, and selective sensors for gases such as CO_2 and CH_4 both in air and dissolved in water [1,2] and for water-soluble pollutants [3]. However, manual deposition of MOF thin films presents challenges in optimizing deposition conditions for each MOF, ensuring coating reproducibility, and scaling up production. An automated approach addresses these limitations by enabling systematic iteration over experimental parameters and consistent, reproducible sensor fabrication.

The automated system integrates syringe pumps, flow diverters, chemically resistant tubing, reagent reservoirs, and a flow cell in which MOF deposition takes place. As a first step, the workflow is being developed and validated at room temperature for a selection of known MOFs, with plans to expand to a heated system in order to broaden the range of accessible MOFs. This automated platform is designed to accelerate the optimization and reproducible fabrication of MOF-based QCM sensors, with the long-term goal of enabling scalable production of low-cost sensors of gas and dissolved analytes.

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IN CRYSTALLO AMMONIA UPTAKE IN $CsBAr^F_4$

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Solid-state organometallic chemistry based on discrete, well-defined molecular species provides a valuable bridge between homogeneous and heterogeneous reactivity, and single-crystal-to-single-crystal transformations offer a particularly powerful platform for probing solid/gas small-molecule uptake while retaining long-range order.[1] Most well-defined examples remain centered on transition-metal systems, whereas analogous s-block molecular solids are far less explored. Ammonia is an especially attractive target because of its relevance as a hydrogen-rich feedstock and energy vector, yet single-crystal-to-single-crystal ammonia uptake by molecular crystals remains rare.[2]

Here we report the direct and scalable synthesis of solvent-free anhydrous $CsBAr^F_4$ and show that it undergoes in crystallo uptake of NH_3 while preserving crystallinity (Figure 1).[3] Structural and solid/gas reactivity studies reveal that this alkali-metal molecular solid can capture and store NH_3 selectively, providing a rare example of ammonia trapping in a non-porous s-block crystal lattice. These results extend in crystallo gas reactivity beyond the transition-metal domain and identify $CsBAr^F_4$ as a new platform for molecular ammonia capture and storage in the solid state.

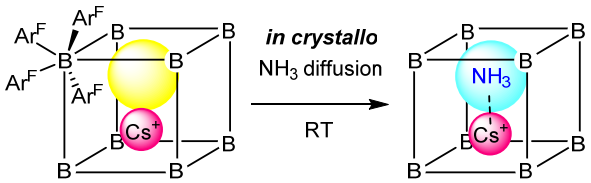


Figure 1. *In crystallo* NH_3 uptake by anhydrous $CsBAr^F_4$.

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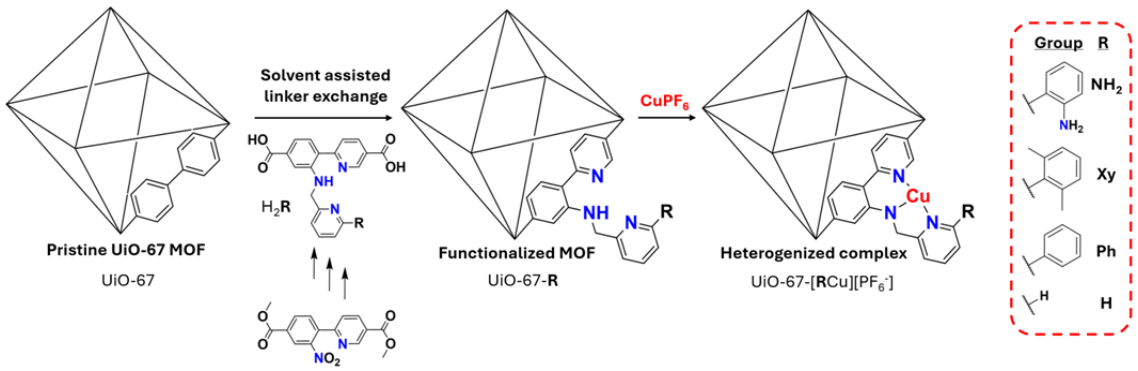
HETEROGENIZED BIOINSPIRED COPPER-COMPLEXES WITH ADJACENT STERIC GROUPS FOR C-H BOND ACTIVATION

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The selective oxidation of methane to methanol is crucial for the sustainable industrial production of oxygenated feedstocks and chemicals. However, it is a process prone to overoxidation and methane leakage.[1,2] To increase product recovery under milder conditions, inspiration for novel catalyst-design can be taken from C-H bond activating enzymes. One such enzyme is pMMO, which enables direct methane-to-methanol conversion in methanotrophic bacteria.[3] Previously, our research group has attempted to emulate the pMMO's Cu-coordination environment by incorporating multi-dentate Cu-chelating N-ligands into UiO-67 type metal-organic frameworks (MOFs), which have been tested for light alkane oxidation.[4] Furthermore, the pMMO architecture contains steric centres around several of its Cu-sites, postulated to increase light alkane affinity.[3] We are currently investigating the possibility of synthetically replicating this moiety through the installation of steric groups adjacent to the Cu-ligating sites.

In total, four such novel bioinspired ligands were synthesized and characterized using NMR, IR and MS. These ligands were subsequently incorporated into pristine UiO-67 MOF through solvent-assisted linker exchange, whereafter the structure, thermal stability and linker incorporation was characterized using pXRD, TGA and liquid-digestion NMR. Cu(I) was subsequentially anchored to the situated ligands under inert conditions using a solution of $Cu(MeCN)_4PF_6$. The Cu-content, crystallinity and porosity of the four metalated MOFs were evaluated using ICP-OES, pXRD and N_2 adsorption, respectively, and the oxidation state of the Cu-centres was studied using DR-UV-VIS.



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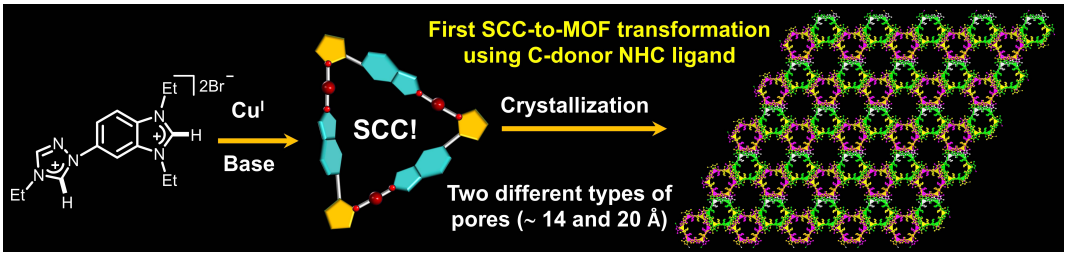
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REDEFINING THE COORDINATION MODE OF 1,2,4-TRIAZOLYLIDENE: BRIDGING THE GAP BETWEEN MOLECULAR ORGANOMETALLIC CHEMISTRY AND EXTENDED POROUS ARCHITECTURES

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N-Heterocyclic carbenes (NHCs) are well-established as strong σ-donor ligands with exceptional stability and tunability, finding widespread applications in catalysis and materials chemistry.[1-2] However, their use as primary structure-directing linkers in metal-organic frameworks (MOFs) remains highly underdeveloped, with most reported systems relying on post-synthetic incorporation rather than direct framework construction via metal-carbene (M-C_{NHC}) bonds. Here in, we report the first example of a discrete supramolecular coordination complex (SCC) to MOF transformation exclusively driven by C-donor NHC ligands. This transformation is enabled by a bis-(NHC) ligand incorporating a 1,2,4-triazolylidene core, which exhibits an unusual coordination behavior involving both the carbene carbon (C5) and the typically non-coordinating N2 site. In combination with the flexible coordination geometry of Cu(I), an initial discrete SCC formed in solution undergoes structural reorganization upon crystallization to yield extended MOFs. Notably, this represents a rare case where robust M-C_{NHC} bonds dictate the framework topology, in contrast to conventional N- or O-donor MOFs. Comprehensive experimental (XPS, FE-SEM, HR-TEM, TGA, PXRD) and theoretical (NCI, QTAIM, ELF) studies provide detailed insights into the structural features and origin of stability. This work establishes a new strategy for constructing NHC-based MOFs and highlights the untapped potential of 1,2,4-triazolylidene ligands in framework design.[3]



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STRUCTURAL CHARACTERISATION OF INDIUM(III) THIOCYANATE

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Thiocyanate (NCS^-) is a prototypical pseudohalide that exhibits versatile coordination behavior and occurs across diverse areas of chemistry.[1] Despite its apparent simplicity, indium (III) thiocyanate, has remained structurally ambiguous in the solid state. The original report (1966) established its synthesis and indexed the powder diffraction pattern to a cubic unit cell (a =12.00 $\pm$ 0.05 Å) but did not provide an atomistic structure model.[2] On this basis, extended NCS-bridged lattices were proposed, with indium coordination discussed in terms of mixed N/S environments (e.g., 3N3S versus higher N/S coordination and correspondingly large Z). Subsequent spectroscopic and reactivity studies concluded that solid $In(NCS)_3$ is a thiocyanate-bridged polymer without evidence for terminal NCS groups and showed that donor ligands form $In(NCS)_3L_3$ adducts, yet the parent binary itself remained without a definitive crystallographic solution due to air sensitivity and challenge of growing large size crystals.[3]

Here we resolve the structure of microcrystalline, air sensitive $In(NCS)_3$ using three-dimensional electron diffraction (3DED), enabling structure solution from sub-micron crystallites. It reveals an extended thiocyanate-bridged framework. Periodic DFT optimization validates the connectivity, refines the geometry, and interrogates plausible N/S binding motifs and lattice energetics, providing a robust structural basis for understanding $In(NCS)_3$ and its donor-adduct chemistry.[3]

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SYSTEMATIC STUDY OF REVERSIBLE TRANSFORMATION BETWEEN MIL-53 AND MIL-68: EFFECTS OF DEFECT DENSITY AND PARTICLE SIZE

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INTRODUCTION

Metal–organic frameworks (MOFs) are crystalline materials composed of metal ions and organic ligands, capable of forming a wide variety of structures through appropriate selection of metal nodes and ligand design. Owing to the flexibility of coordination bonds, certain MOFs can undergo structural transitions in response to external stimuli. Among these, structural transformations involving the breaking and reformation of coordination bonds are of particular interest, as they enable dynamic access to distinct framework structures. However, such transformations are relatively rare, and most reported examples are either irreversible or difficult to control.

In this study, we apply a strategy—the systematic control of particle size and defect density—to induce and regulate structural transformations in MOFs. We focus on the topological isomers MIL-53 and MIL-68, which share similar one-dimensional chain motifs but exhibit markedly different pore structures and properties. Achieving controlled transformation between these phases would enable reversible switching of functionalities that cannot be realized within a single framework.

RESULT AND DISCUSSION

To investigate the effects of defect density and particle size on the structural transformation from MIL-53 to MIL-68, a series of MIL-53-OH MX samples were synthesized using various modulators, including acetic acid (AA), formic acid (FA), trifluoroacetic acid (TFA), sodium acetate (SA), and hydrochloric acid (HCl), where M denotes the modulator type and X its molar equivalents relative to the ligand. The resulting samples exhibited a range of defect densities and particle sizes (**Figure**).

The MIL-53-OH MX samples were then heated at 250 °C in the presence of a free ligand (H_2BDC-OH) to induce transformation. Complete transformation was observed only for samples with small particle sizes (0.3–0.5 μm) and moderate defect density (~10%). At comparable particle sizes, higher defect densities suppressed the transformation, whereas at similar defect densities, smaller particle sizes promoted it. These results demonstrate that both defect density and particle size critically govern the transformation behavior [1].

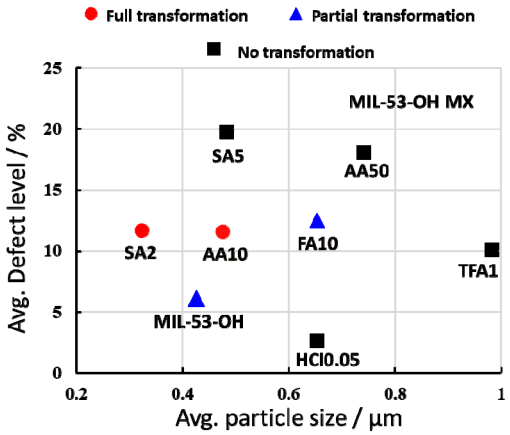


Figure. Plot of defect level versus particle size of MIL-53-OH and MIL-53-OH MX.

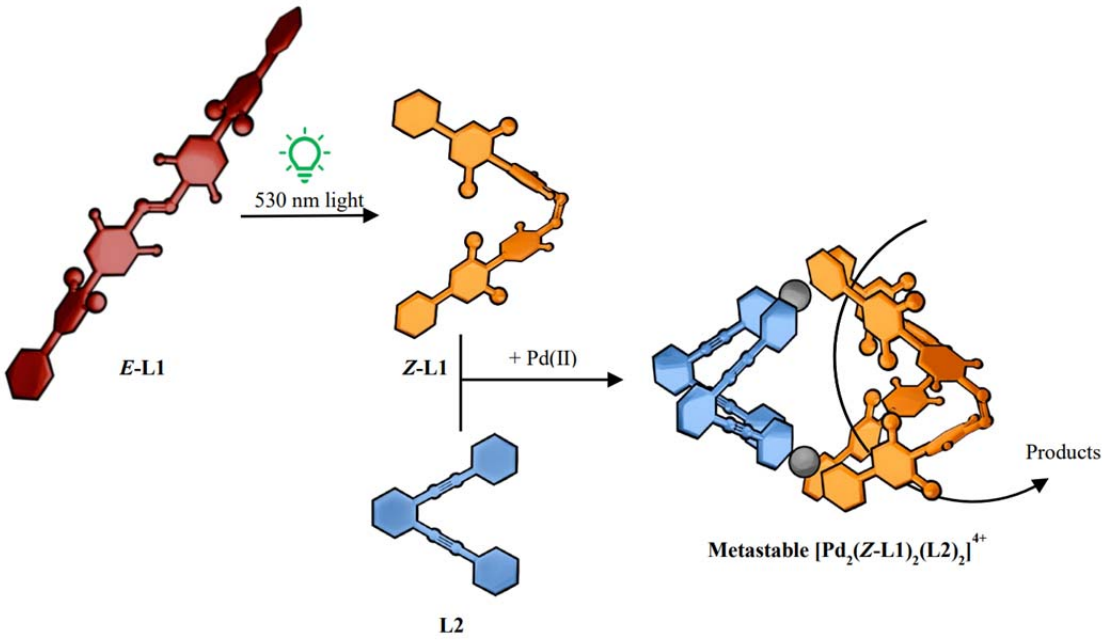
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CATALYSIS BY A METASTABLE PHOTOSWITCHABLE CAGE

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Ortho-fluoro azobenzene ligands are efficient building blocks in light-sensitive metallo-supramolecular self-assemblies. Based on previous work in our group [1-3] I will present the first example of a self-assembled heteroleptic cage containing a photoswitchable azobenzene-derived ligand in its metastable *Z*-isomeric form (***Z*-L1**) and a non-switchable shape-complementary ligand (**L2**). The lantern-shaped metastable [**Pd$_2$(*Z*-L1)$_2$(L2)$_2$**]$^{4+}$ cage is only accessible after light-irradiation with 530 nm light, offering an attractive out-of-equilibrium system. Once assembled, the heteroleptic metastable cage can encapsulate substrates for a variety of catalytic reactions including the Michael addition, as well as a chlorination reaction. The fact that the catalytically active cage is only formed after light irradiation allows us to control chemical reactions using a non-invasive method.



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LARGE GOLD AND SILVER RINGS BASED ON BRIDGING NHC LIGANDS

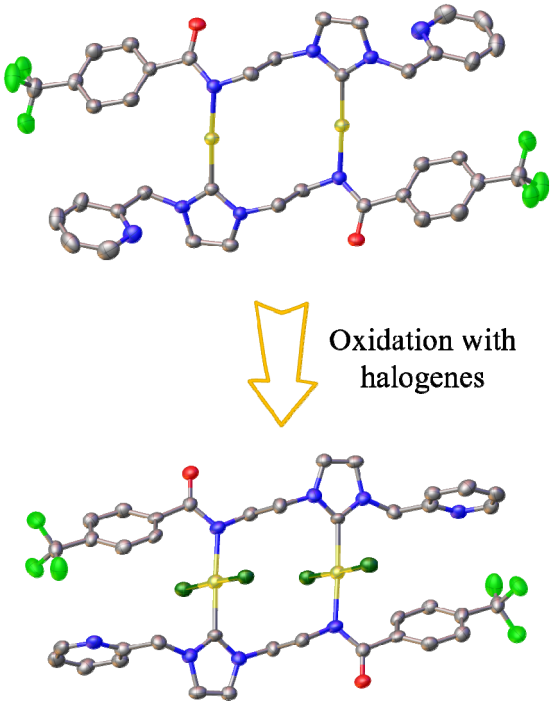
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In the past decades, *N*-heterocyclic carbene complexes have become an important class of compounds with a wide range of applications in homogeneous catalysis, medicine and materials chemistry [1].

We have previously developed ethylamido-functionalized imidazolium salts, which can adopt a variety of coordination modes metal carbene complexes. Apart from being simple NHC *C*-donor ligands, they can also act as bidentate anionic *C*,*N*-chelating ligands or as dianionic tridentate *C*,*N*,*C*-ligands [2]. The 2-picolyl-derivatives may even act as tetradentate *N*,*C*,*N*,*C*-chelates in complexes containing Pd(II).

We demonstrate here, that such imidazolium salts form 12-membered macrocycles with Au(I) and Ag(I), in which the ligands adopt a bidentate *C*,*N*-bridging coordination mode. The digold(I) metallamacrocycles are readily oxidized by halogens ($PhICl_2$, Br_2 and I_2), affording various types of gold(III) species. When equivalent amounts are used, the macrocycles remain intact, with only the gold-centres being oxidized, whilst with excess halogens metal oxidation is accompanied by cleavage of the Au-N-bond, resulting in opening of the rings [3].



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[2] B. Mell, J. Rust, C.W. Lehmann, R.J.F. Berger, D. Otte, M. Ertl, U. Monkowius and F. Mohr, Organometallics **2021**, *40*, 890.

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COORDINATION-DRIVEN ASSEMBLY OF β-DIKETONATE HYDRAZONE-BASED CAGES

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Metallacycles and metallacages constructed via coordination-driven self-assembly have attracted significant attention due to their well-defined architectures, functional versatility, and high synthetic efficiency [1]. Among multiple functional groups, the implementation of stimuli responsive units embeds such supramolecules with switchable properties [2]. In particular, the incorporation of molecular photoswitches into metallacycles and metallacages allows for the external modulation of structural features using light—a waste free and precise to administer stimulus—towards the design of light-responsive smart materials [3]. Herein, we develop a series of ligands based on bis-/tris- betadiketonate hydrazone moieties, well known for their light and pH responsive behaviour [4]. These new ligands are shown to assemble with Cu(II) cations, yielding a new class of supramolecular macrocycles and cages. The system is investigated by means of single-crystal X-ray diffraction and spectroscopic analysis.

[1] Chem. Sci., 2021, 12, 7269

[2] Chem. Soc. Rev., 2023, 52, 1129

[3] Nat. Chem. 2024, 16, 13

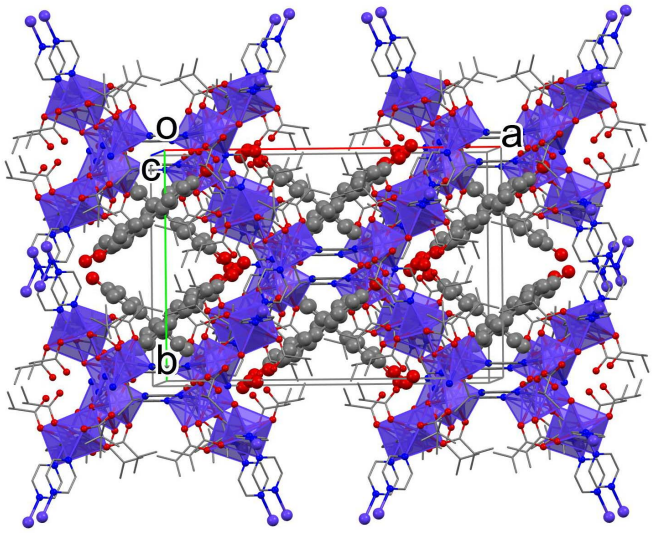
[4] J. Am. Chem. Soc. 2025, 147, 19444

TUNING THE DIMENSIONALITY OF COORDINATION POLYMERS BASED ON COBALT(II) CARBOXYLATE DIMERS

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Cluster-based coordination polymers (CCPs) attract considerable attention due to their diverse functional properties, such as magnetism, adsorption, catalysis, and luminescence. In continuation of our research [1] we have studied new CCPs assembled from dinuclear Co(II) isobutyrate clusters with N,N-, and O,O-auxiliary ligands. The studied CCPs include the 1D chains $\{[Co_4(\mu_2\text{-}H_2O)(ib)_8(hmta)_2(EtOH)(H_2O)_2]\ 0.5(bphen)\cdot EtOH\cdot H_2O\}_n$ (**1**), the 2D layers $\{[Co_2(\mu_2\text{-}H_2O)(ib)_4(Hib)(pyz)_{1.5}]\cdot(Hib)\ 0.5(bphen)\}_n$ (**2**), and a 3D framework $\{[Co_2(\mu_2\text{-}H_2O)(ib)_4(pyz)_2]\cdot(bphen)\cdot H_2O\}_n$ (**3**) (where Hib = isobutyric acid, pyz = pyrazine, bphen = 4,4′-dihydroxybiphenyl, and hmta = hexamethylenetetramine). Each of CCPs comprises a binuclear Co_2 carboxylate dimer which serves as a two-, three-, and four-connected node in **1**, **2** and **3,** respectively, with pyz or hmta serving as linkers. The tetrahedral nodes in **3** are linked into a diamond-like framework with the infinite channels filled with bphen and water molecules, (Fig. below). These crystalline polymers can be viewed as multicomponent cocrystals that contain a neutral MOF, neutral molecules, and solvent molecules. It was demonstrated that the dimensionality of the resulting architectures is effectively tuned by the geometry and bridging capability of the auxiliary ligands. Furthermore, the synthetic approach, including solvothermal and ultrasonic-assisted methods, played a crucial role in controlling the phase purity and morphological features of the obtained CCPs. Magnetic studies revealed that the dinuclear $[Co_2(\mu_2\text{-}H_2O)]$ units within these frameworks exhibit antiferromagnetic exchange interactions, which are further influenced by the inter-cluster connectivity. The theoretical calculations using the TB2J python package were performed to estimate the magnetic exchange couplings, providing results that are in good agreement with the experimental data.



Acknowledgements. The authors acknowledge the financial support provided by the Ministry of Education and Research of R. Moldova (subprogram 011202), as well as projects 25.80012.5007.87SE and 25.80013.5007.07GER, supported by the National Agency for Research and Development (NARD).

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METAL-ORGANIC FRAMEWORK FUNCTIONALIZED SENSOR ARRAYS FOR DISSOLVED GAS SENSING

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Aquatic ecosystems mediate more greenhouse gas (GHG) fluxes per unit area than the surrounding land, necessitating a need to understand their storage and transport roles. Methane and Carbon dioxide contributes to around 90% of anthropogenic global warming with aquatic ecosystems contributing at least half of these emissions. For instance, the net sink for atmospheric CO_2 as dissolved inorganic carbon (DIC) is estimated as 0.7 Pg C/a and groundwater-driven methane flux averages 3.9 ± 6.2 mmol/m²/day globally [1,2]. Highlighting this need, a chemical sensor was developed using quartz crystal microbalance (QCM) and porous metal-organic framework (MOFs/MOF) thin-films for selective adsorption that can detect changes for about 1-10 ng. The QCM is functionalized with a methane-selective, superhydrophobic Cu-MOF-2[Cu(hfipbb)(H_2O)], constructed through the Layer-by-Layer (LbL) technique, by alternating crystal surface exposure to different solutions to grow the final MOF film of 2.5 µm thickness. This sensing technology will be extended to an array of sensors that can detect dissolved CH_4 and DIC species in a mixture while differentiating response patterns using statistical data analysis tools. To hold these MOF-based sensors, a flow cell is developed, and this will be integrated into a fully functional prototype module, ready to be deployed on-site to monitor gas flux directly at the source.

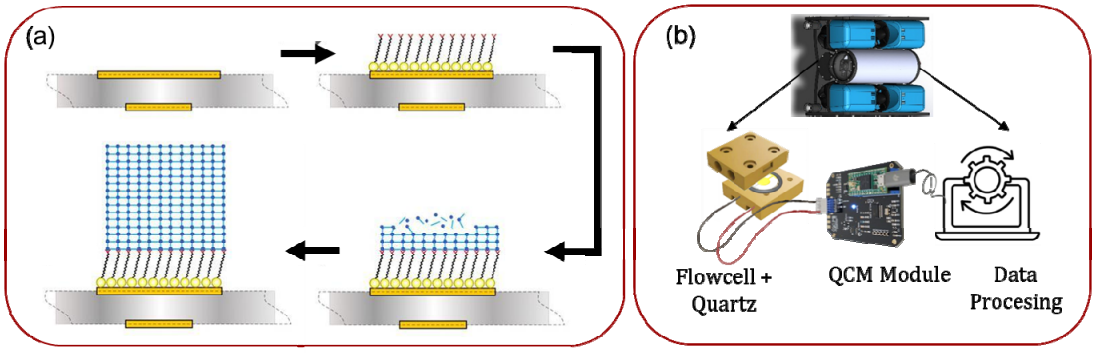


Fig 1. (a) MOF film growth by LbL technique, (b) Schematic of prototype

[1] Z. Liu, W. Dreybrodt, and H. Wang, “A new direction in effective accounting for the atmospheric CO2 budget: Considering the combined action of carbonate dissolution, the global water cycle and photosynthetic uptake of DIC by aquatic organisms,” Earth-Science Reviews, vol. 99, no. 3, pp. 162–172, May 2010, doi: 10.1016/j.earscirev.2010.03.001.

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METAL HYDROGEN-BONDED ORGANIC FRAMEWORKS ASSEMBLED VIA PHOTOINDUCED SELF-ASSEMBLY

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Metal hydrogen-bonded organic frameworks (M-HOFs), composed of metal ions and bridging ligands, are considered for practical applications in many fields, such as catalysis and photosensitization. Currently, the construction of such compounds typically involves ligand exchange reactions driven by heat. We have reported the construction of metal complexes via ligand exchange reactions driven by visible light (photoinduced self-assembly)[1][2].

In this study, ruthenium(II) complexes comprises branched bridging ligand were synthesized via photoinduced self-assembly and modified them onto an ITO substrate. Single-crystal X-ray diffraction analysis revealed the three-dimensional structure of the mononuclear complex, confirming the formation of a network structure via intermolecular hydrogen bonding. Single-crystal X-ray diffraction analysis and UV–vis spectroscopy of the ITO substrate suggest that an M-HOFs has formed on the ITO surface (Figure 1).

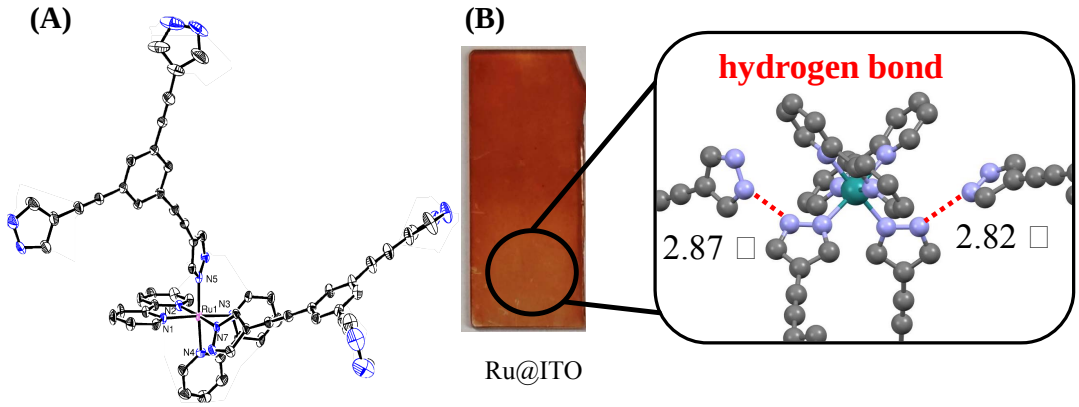


Figure 1. (A) Crystal structure of mononuclear complex obtained by photoinduced self-assembly.

(B) An ITO electrode covered with ruthenium complex by photoinduced self-assembly and proposed structure of the assembled ruthenium complexes.

[1] T. Honda, T. Hirake, M. Kondo, S. Masaoka, K. Fujimori, T. Moriuchi-Kawakami, M. Hirahara, *Chem. Eur. J.* **2024**, e202402993.

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LINEARLY CONJOINED MULTICAVITY DISCRETE COORDINATION CAGES : MOLECULAR SOYBEANS

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The Pd(II)-based Single-Cavity Discrete Coordination Cages (SCDCCs) of the type Pd_2L_4 are a special class of molecules having fascinating structural and functional features.[1] While the SCDCCs continue to be extensively studied, recent research has shown a new direction towards synthesis and exploration of Pd(II)-based Multi-Cavity Discrete Coordination Cages (MCDCCs).[1] The double-cavity Pd_3L_4 type MCDCC was prepared by combining Pd(II) with tris-monodentate ligand in 3:4 ratio.[1] In principle, it should be possible to prepare Pd_nL_4 type MCDCCs ($n \geq 3$) featured with (n-1) cavities where (n-1) units of Pd_2L_4 type cavities are linearly conjoined. We have recently reported a Pd_2L_4 type SCDCC capable of encapsulating one unit of pyrazine-*N*,*N*'-dioxide (PZDO) as guest.[2] This work presents a series of Pd_3L_4, Pd_4L_4, and Pd_5L_4 type MCDCCs featuring two, three and four cavities, respectively (Fig. 1).[3] The Pd_2L_4 type sub-frameworks crafted in the MCDCCs correspond to our reported PZDO-binding Pd_2L_4 type SCDCC. The double-, triple- and quadruple-cavity containing MCDCCs are found to accommodate up to two, three and four units of PZDO, respectively. The number of seeds in a Soybean pod usually ranges from 1 to 4; thus, the family of guest bound SCDCC and MCDCCs is considered here, from structural view point, as "Molecular Soybeans".

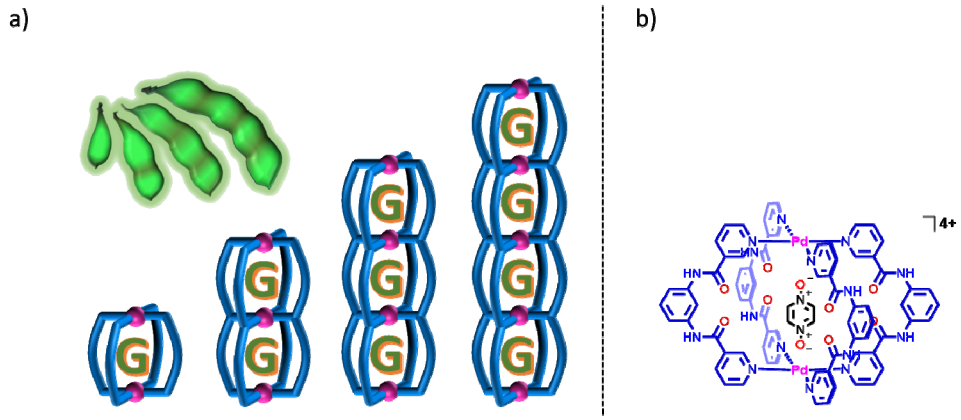


Fig 1: a) Cartoon representation of guest-bound Pd_2L_4 type SCDCC and Pd_nL_4 type MCDCCs, where n = 3,4,5 and b) Molecular structure of $[PZDO \subset Pd_2L_4]^{4+}$.

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[2] S. S. Mishra, S. Krishnaswamy and D. K Chand, *J. Am. Chem. Soc.*, 2024, 146, 4473–4488.

[3] T. Dakua, S. S. Mishra, A. Kumar, S. Krishnaswamy and D. K Chand, *Chem. Commun.*, 2025, 61, 8007-8010.

METAL–ORGANIC FRAMEWORKS FEATURING CLUSTERS OF ZERO-VALENT ATOMS

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Despite the considerable achievements and attention that metal–organic frameworks have received,[1] there are only very few examples constructed from inorganic structural building units with metals in low- or zero-valent oxidation states.[2] A stand-out example is McPherson and Pedersen's **Pd_3-MOF** (Figure 1),[3] the first example of a metal–organic framework featuring clusters of zero-valent metal atoms bound together at its nodes.

We are interested in exploring the chemistry of this new prototype of MOF: how the properties of the molecular building blocks can be used to control the framework assembly and predict the properties of the resulting materials; and what other organometallic clusters are amenable to similar synthetic strategies.

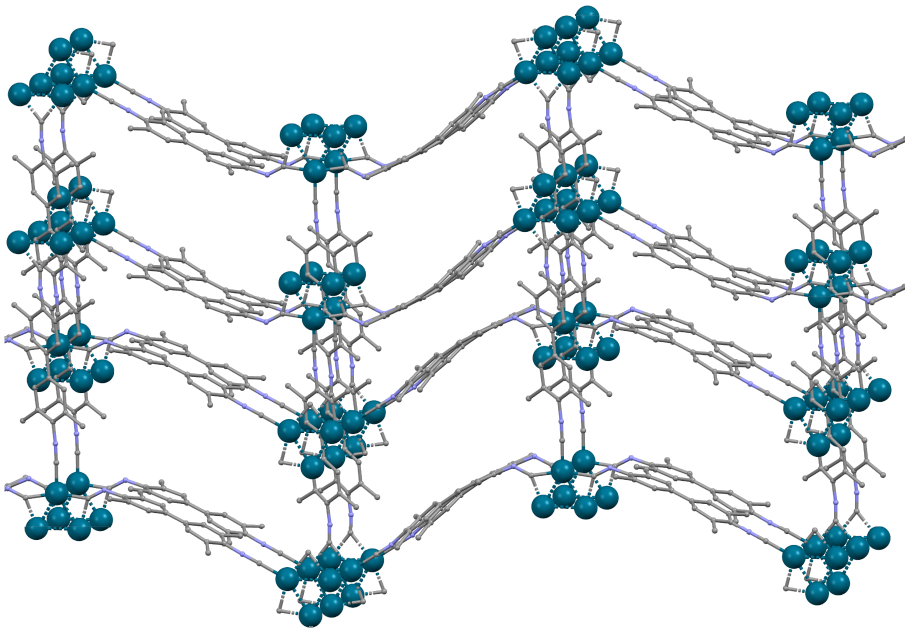


Figure 1: 3D structure of Zero Valent **Pd_3-MOF**

[1] Nobel Prize Outreach AB. *Nobel Prize in Chemistry 2025*. NobelPrize.org, October 8, **2025**.

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SCHIFF BASE COORDINATION COMPOUNDS WITH *3d* AND *4f* METAL CENTERS. STRUCTURAL DIVERSITY AND FUNCTIONALITY.IDINDIOL

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[b] Univ. Rennes, CNRS, INSA Rennes, ISCR (Institut des Sciences Chimiques de Rennes), Rennes F-35000, France
[c] CEDENNA, Santiago, Chile
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The rational design of multifunctional coordination polymers (CPs) remains one of the most active research areas in coordination chemistry due to the possibility of combining structural versatility with tunable physical properties [1]. In this context, Schiff base ligands constitute highly attractive building blocks because of their facile synthesis, modularity, and ability to provide multiple coordination sites capable of stabilizing transition-metal and lanthanide ions within extended architectures [2]. In the present work, a series of new coordination compounds based on Schiff base ligands and *3d/4f* metal ions were synthesized and structurally characterized, with special emphasis on the relationship between ligand design, dimensionality, and magnetic or optical behavior.

We used Schiff base ligands containing phenolic donor groups prepared through condensation reactions between aromatic amines and aldehydes under reflux conditions. Subsequent coordination reactions with *3d* and *4f* ions were carried out using conventional reflux, solvothermal, and liquid–liquid diffusion methodologies among other techniques (Figure 1). We show the versatility of Schiff base ligands as platform for constructing coordination compounds with diverse dimensionalities, architectures and functional behavior, contributing to the rational design of advanced molecular materials with potential applications in coordination chemistry and materials science.

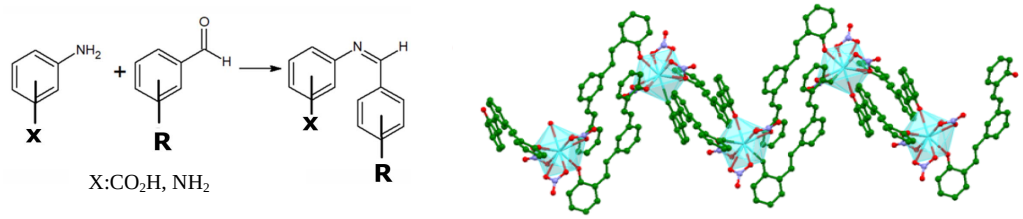


Figure 1. Scheme of Schiff base and coordination polymer.

Acknowledgements: The authors acknowledge financial support from FONDECYT 1252136 and FONDECYT 1240549. The authors also acknowledge the CEDENNA ANID CIA250002 project and the FONDEQUIP EQM 130086 PPMS and EQM 140060 EPR projects. The IRP-CoopIC international project Chile-France is also acknowledged for support.

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LIGAND-DIRECTED SUPRAMOLECULAR ASSEMBLY OF COPPER(II) PADDLEWHEEL COMPLEXES FEATURING PHENACYL-ESTER LIGANDS

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The design and characterization of supramolecular copper(II) paddlewheel complexes remain pivotal in advancing functional materials with potential applications in catalysis, sensing, and environmental remediation. In this study, we report the synthesis, single-crystal X-ray diffraction, spectroscopic, DFT analysis and Hirshfeld surface analyses of dinuclear copper complexes featuring phenacyl-ester ligands. The complexes exhibit square-pyramidal geometries with syn-syn bridging carboxylates, enabling extended supramolecular assemblies ranging from mononuclear units to tetranuclear networks.

Our investigation highlights how ligand substituents influence structural motifs, spectral properties, and thermal stability, providing insights into the rational design of adaptive materials. The use of bifunctional organic ligands facilitated the formation of one-dimensional supramolecular networks, underscoring the role of ligand architecture in directing assembly. Hirshfeld surface analysis revealed significant intermolecular interactions that stabilize the supramolecular frameworks, while FT-IR and thermal analysis confirmed the robustness of the complexes under varying conditions.

This work bridges fundamental inorganic coordination chemistry and applied materials science, contributing to the discourse on sustainable material innovation. The design principles demonstrated here—ligand-directed topological control in paddlewheel systems—are directly transferable to the construction of porous coordination polymers and metal-organic frameworks with relevance to gas capture, heterogeneous catalysis, and chemical sensing, aligning with the conference themes of Supramolecular Chemistry and 3D Materials, New Directions in Coordination Chemistry, and Coordination Compounds for Energy and Sustainability.

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SYNTHESIS OF Bi_2Te_3 NANOPARTICLES WITH Bi-BASED MOF AS PRECURSOR

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Department of Nanobiochemistry, Frontiers of Innovative Research in Science and Technology, Konan University, Kobe, Japan

Thermoelectric materials, which can directly convert thermal energy to electrical energy, have been studied for decades as potential solutions to energy and environmental issues. Bismuth telluride (Bi_2Te_3) is the most commonly used p-type thermoelectric material at room temperature. The efficiency of thermoelectric devices is determined by the dimensionless figure of merit ZT, defined as $ZT = S^2\sigma T / (\kappa_{ele} + \kappa_{lat})$, where S is the Seebeck coefficient, σ is electrical conductivity, T is absolute temperature, κ_{ele} is thermoelectric conductivity, and κ_{lat} is lattice thermal conductivity.

To enhance thermoelectric performance, several methods involving nanostructuring materials have been proposed. These include reducing crystallite size, introducing dislocations or lattice strains, and forming nanocomposites by combining host materials with nanoparticles, which help reduce lattice thermal conductivity. Bi_2Te_3 nanostructures are typically produced through melting and mechanical processes, resulting in highly pure bulk thermoelectric materials. Although these methods can yield high-performance materials, they require high-temperature annealing, which leads to materials with high electrical and thermal conductivities.

In this work, we aim to synthesize Bi_2Te_3 using a wet chemical process with metal-organic frameworks (MOFs) as precursors. MOFs are a class of porous materials made up of metal ions and organic linkers. Their main advantage lies in their tunable design, which allows control over not only their porosity but also their crystal size and defect density. This would make it possible to precisely control the formation of Bi_2Te_3 nanocrystals through ion-exchange reactions involving structurally controlled Bi-based MOFs and Te^{2-} [1].

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Arfa, C. ES-263-O
Argibay-Otero, S. BM-1009-P
Aribot, F. SM-472-O MM-885-F, ND-1605-P
Armenta, P. ***ES-148-O***
Armstrong, R. ND-437-O, MG-1428-P
Arnal, L. ES-043-O
Arnoff, A. CB-505-K
Arnold, P. ***CB-1103-P***, ***ND-666-K***
Arnold, P.L. CB-622-O
Arolla, B. CB-1157-P
Aromí, G. ND-355-I, ***ND-252-O*** FB-797-O, ND-754-O SM-1723-P, ND-964-F
Arora, S. ***CB-1168-P***
Arrigoni, F. ***MM-081-I***
Artero, V. ***ES-465-K***
Arulsamy, N. ND-892-F
Arun Chaudhari, O. ND-1617-P
Arvizo, I. ES-515-K
Arya, V.P. MM-183-O
Arylsamy, N. ES-1224-P
Asiki, H. CB-747-O
Assendjee, E. ND-494-I
Astashkin, A. BM-018-I
Asti, M. ND-566-O, BM-1002-P
Atanasov, M. MM-385-I
Atkinson, B. ND-1628-P
Atobekova, F. BM-1042-P
Atzori, M. FB-794-O, FB-592-O
Au, V.K--M. ***SM-671-I***
Audebrand, N. SM-1742-P
Audibert, D. ND-195-I
Aufricht, P. ***CB-426-O***
Aukauloo, A. CB-1104-P CB-1153-P, ***CB-401-I***
Austin, R. ***CB-606-K***
Avram, L. CB-304-O
Avsar, A. CB-1111-P
Awaga, K. ND-052-O
Awasthi, N. MM-1503-P
Azeem, S. BM-715-I

B

Baba, T. ***SM-774-O***
Babula, D. MG-547-O, ***MG-851-F***
Baca, S. ***SM-1737-P***
Bacchi, A. SM-972-F
Bacellar, C. MM-587-O, MM-686-K
Bacon, A.M. CB-626-K
Baek, Y. ***CB-101-I*** CB-1124-P, ND-1620-P
Bagh, B. ***CB-703-O***
Bähring, S. ES-1207-P, ES-1209-P
Baik, M.-H. ES-048-I
Bair, A.S. CB-1103-P
Bajaj, N. FB-796-O
Bajkowski, M. ***BM-1034-P***, BM-533-O
Baker, J. BM-722-I
Baker, M. FB-792-I

Baker, R. MM-873-F
Bakewell, C. MG-941-F, MG-1427-P
Bal, W. BM-132-O
Balakrishnan Syamala, A. ***CB-860-F***
Balas, J. ND-491-I
Balázs, G. ***MG-032-O***
Balducci, G. SM-1711-P
Balim, T. CB-1111-P
Ballico, M. CB-1157-P
Ballmann, J. CB-1134-P
Baltrun, M. CB-524-I
Banares, L. MM-683-O
Bance, H. ***MM-886-F***
Bandari, V. ND-898-F
Banerjee, A. MM-587-O
Banerjee, P. SM-572-O
Banik, S.K. ES-412-O
Bansal, S. ***CB-1156-P***
Banti, Ch. BM-011-I, ***BM-017-O***
Bányai, I. MM-083-O
Baran, P. ***MM-187-O***, BM-865-F
Baranova, Z. ***BM-865-F***
Barańska, J. BM-1033-P
Baranyai, Z. BM-727-O
Barath, E. ES-878-F, ES-1258-P
Baratta, W. CB-1157-P
Barbosa, H. ***BM-1017-P***
Bardehle, C. BM-731-K
Barik, J. ***MG-1418-P***
Barkas, E. FB-796-O
Barra, A.-L. ND-253-O
Barrera-Gómez, T.A. ***CB-1169-P***
Barrett, A. MG-031-I
Barrett, J. SM-271-I
Barrios, J. CB-1157-P
Barrios, L. SM-1723-P
Barrios, L.A. ND-252-O, FB-797-O
Barrios Moreno, L.A. ***ND-355-I***
Barszcz, B. BM-1026-P, BM-870-F, SM-1720-P
Bart, S. ***ND-565-K***
Barwiolek, M. ES-1216-P
Barwiołek, M. ES-1220-P, ***BM-1031-P***
Barzowska-Gogola, A. BM-1045-P
Baś, S. SM-973-F, FB-793-O
Basak, H. ***MG-849-F***
Bassi, G. ***MM-1508-P***
Bates, A. BM-135-I ***BM-333-O***, ES-1224-P
Batista, A.A. BM-134-O
Batov, M. ND-664-O
Battisti, U.M. ***ND-568-I***, FB-1303-P
Baumann, M. ES-517-O
Baumgartner, B. CB-122-O, ***SM-578-I*** SM-772-I, SM-1727-P
Bauri, S. CB-1167-P
Baya, M. ND-456-O
Bayardon, J. ES-143-O
Bazylińska, U. BM-1045-P, BM-533-O
Beale, E.V. MM-587-O
Beall, J. ***ND-1622-P***, ND-1610-P
Beardsley, M. ES-841-F
Beaumont, S. ES-042-O
Becer, R. SM-1708-P
Becker, J.-G. MM-888-F, ***MM-1510-P***
Becker, V. BM-714-O
Beetar, J. MM-873-F
Begum, N. ES-142-O
Bekaliyev, A. CB-221-I
Beleaev, E. SM-1737-P
Belle, C. CB-127-O
Bellini, G. ND-358-O
Bellouard, A. MM-483-O
Belpassi, L. CB-1101-P
Bendix, J. ND-496-O
Benkő, Z. MG-1433-P
Benny, A. ES-316-K
Benthin, G. MM-283-O
Bera, A.K. CB-1150-P
Bera, J.K. MG-1405-P
Bercich, E. CB-1135-P
Berggren, G. CB-427-O
Bergwerff, B. MM-482-O
Bernhardt, P. ***CB-503-O***
Bernhardt, P.V. CB-124-O
Bernkop-Schnürch, A. ***BM-117-O***
Berrin, J.-G. MM-181-I
Berro, M. ND-494-I
Berry, J. ES-841-F, ***MM-294-I*** CB-983-F, CB-1128-P
Berry, J.F. ES-148-O
Bertin, B. MM-483-O
Bertini, L. MM-081-I
Bertoloni, R. ***MM-883-F***
Bertolotti, N. CB-983-F
Berton, C. BM-634-O
Bertora, E. BM-1002-P
Bertrand, G. ***CB-425-K***
Besalú, P. CB-107-O
Besnard, C. FB-695-I
Betley, T. ***ES-515-K***
Bette, S. ND-556-O
Betz, R. SM-1743-P
Beves, J. ***SM-071-I***, SM-1734-P
Beweries, T. CB-522-O, CB-1141-P CB-1160-P, ES-1219-P ND-1632-P, CB-1125-P CB-1162-P, CB-626-K
Beyer, J. ND-055-K
Bezdek, M.J. ES-268-I
Bezuidenhout, C.X. SM-775-I
Bezuidenhout, Z. CB-328-O
Bhattacharya, B. SM-972-F
Bhavana, R. ***ES-1212-P***
Biagi, R. SM-576-O
Biasin, E. ***MM-784-O***, MM-788-I
Biednov, M. MM-686-K
Bienenmann, R. ***CB-981-F***
Bieńko, A. ND-1621-P
Bietti, M. CB-203-O CB-107-O, CB-1144-P
Biffis, A. ND-1619-P
Bigelli, C. ND-496-O, FB-795-I FB-1310-P, ND-498-I
Bisceglie, F. BM-1030-P
Biswas, S. ***MG-1435-P***
Bjerre, N.L. ND-1636-P
Bjerrum, M.J. BM-1027-P, BM-1006-P
Bjornsson, R. CB-026-O, CB-1153-P MM-1505-P, MM-284-I
Blanchard, S. ***ND-394-O***, ND-052-O
Blaszczak, E. ***BM-013-O***
Błaszczak, E. BM-1034-P, BM-1045-P BM-533-O, BM-1032-P
Blechschmidt, L. BM-1037-P
Bleher, K. ***CB-128-O***
Blignaut, J. ES-044-I
Bloch, W. SM-177-O
Blyth, A.E. ***SM-1703-P***
Blyth, B. BM-1019-P
Bo, C. ***ND-099-I***
Boča, R. ND-1621-P
Boccalon, E. ***ES-144-O***
Bockfeld, D. CB-1137-P, CB-1131-P
Bodensteiner, M. ND-661-K
Boegli, M.-Ch. CB-1142-P
Bogani, L. ND-658-O
Bogema, A. BM-236-O
Bognar, Z. SM-572-O
Boidachenko, K. ***ES-314-O***
Boisson, Ch. MM-881-F
Boisten, F. BM-731-K
Bokarev, S. ***MM-688-O***
Bokarev, S.I. MM-1508-P
Bokareva, O. ***MM-486-O***, ES-1270-P
Bollini, M. BM-114-O
Bominaar, E.L. CB-605-I
Bon, V. SM-278-I
Bonarek, P.J. ND-753-O
Bond, A. MG-031-I
Bonde , E. SM-1703-P
Bonetto, R. CB-227-O
Boniburini, M. ND-566-O
Bonnet, C. BM-330-K
Bonnet, C.S. BM-723-O

Bonnet, S. BM-63A-O
Booth, S. SM-278-I, ***SM-272-O***
Bootsma, J. CB-706-O
Borbas, E. ***ES-415-K***, FB-1308-P
Borden, O. BM-018-I, BM-1007-P
Bordiga, S. SM-872-F
Borgsson, R. CB-401-I
Boronski, J. MG-545-K
Boronski, J.T. ND-661-K
Borowski, M. ***FB-1313-P***, CB-1132-P
Borrell, M. MM-485-K
Borsari, M. ND-358-O, SM-576-O
Borter, J.-H. MM-684-O
Bortoluzzi, M. ES-930-F
Boskovic, C. ***ND-054-I***
Boström, H. MM-296-O
Botta, M. BM-1009-P
Boullart, L. ***ES-261-I***, SM-778-I
Bourissou, D. ***ES-616-K***
Bourne, C. MG-940-F
Boursier, M. ***SM-1727-P***
Bousseksou, A. ND-751-K, MM-292-O
Bowers, B.E. CB-067-O
Boyd, J. BM-236-O
Brabec, V. BM-713-O
Bracco, S. ***SM-775-I***
Bradley, J. FB-594-I
Braga, A.A.C. CB-322-O
Braidley, A.G. ES-840-F
Brandariz-Lendoiro, I. BM-1009-P
Brander, S. MM-181-I
Braun, A. CB-207-O
Braun, Th. ***ND-451-I***
Braunschweig, H. MG-641-I
Braunstein, P. CB-856-F
Brázda, P. MM-581-I, ***MM-584-I***
Bregier-Jarzębowska, R. BM-1043-P
Breijaert, T. ND-194-O
Bresciani, G. MM-762-I
Bresien, J. ES-1270-P
Bridonneau, N. ND-052-O ND-1618-P, ND-1627-P
Briganti, M. ND-358-O, ND-253-O ***FB-795-I***, ND-498-I
Brink, A. ES-041-I
Brites, C. FB-598-I
Britt, R.D. CB-622-O
Britton, A. SM-970-F
Britton, M. BM-724-O
Broere, D.L.J. ***ES-048-I***
Brohmer, E. ***MM-1506-P***
Brooker, S. ***CB-741-K***
Brookfield, A. ND-495-K, ND-661-K
Brooks, L. BM-134-O
Brotons-Rufes, A. ES-513-O
Brown, A. MM-283-O
Brown, C. ***SM-771-K***
Brown, S.E. ND-1607-P
Brown, S. ND-1610-P
Browne, W.R. ***CB-104-O***, MM-085-K
Bruce, D.W. ES-840-F
Bruzzese, P.C. ND-652-O
Bruzzese, P. ***MM-288-I***
Bubley, A. CB-1135-P
Bucher, Ch. CB-628-O
Buchmeiser, M. ***ND-551-I***
Buchwald, S. CB-327-O
Builds, J. ND-099-I
Bunyan, J. ***SM-974-F***
Burgos-Caminal, A. MM-683-O
Burke, J. CB-707-O
Burmeister, L.E. CB-1137-P
Burnett, A. MM-886-F
Burnett, S. MG-348-O
Burri, L. ***CB-023-O***
Buss, J. ***CB-206-O***
Byrne, K.M. MG-1414-P

C

Cabanillas-Gonzalez, J. ES-313-O
Cabrera-Trujillo, J. CB-1142-P
Cador, O. FB-794-O, FB-592-O
Cadot, E. ND-195-I
Cadranel, A. ***ES-218-I***
Cagossi, G. ***SM-972-F***
Cai, J. ***CB-167-O***
Caires, F. BM-1017-P
Calbo, J. ES-266-O
Calcagno, F. ES-842-F
Call, A. CB-203-O, CB-006-O ***CB-107-O***, CB-1144-P
Callea, L. MM-081-I
Calvo, R. MM-382-O
Cameron, S. CB-527-O
Cammarata, M. ND-051-I
Camorali, S. BM-1002-P
Camp, C. CB-526-O, ND-651-I
Campagna, S. CB-1107-P, CB-1120-P
Campi, M. SM-576-O
Cancelliere, A.M. CB-1107-P
Caniglia, G. CB-1136-P
Cano-Muñoz, M. BM-732-I
Cañón-Mancisidor, W. ND-1614-P
Canossa, S. SM-273-O
Cao, C. MM-1516-P
Cao, N. ***CB-302-O***
Cao, R. CB-1153-P, CB-401-I
Capellán, D. ***CB-1115-P***
Capocasa, G. CB-107-O
Capomolla, S. SM-071-I, ***SM-1734-P***
Capucciati, A. BM-336-K
Caravan, P. ***BM-232-K***
Carlos, L. FB-595-K
Carlos, L.D. FB-598-I
Carneiro Neto, A. FB-598-I
Carneiro Neto, J.S. ***FB-1310-P***, ND-992-F
Carpentier, J.-F. ES-878-F
Carrascal-Minino, A. BM-364-O
Carrella, L.M. MM-888-F, MM-1510-P
Carretta, S. ND-252-O
Carson, H. MM-686-K
Carter, K. ***MM-283-O***
Cartmell, O. SM-274-I
Casadevall, C. ***CB-221-I***
Casasus, I.M. MM-683-O
Casini, A. ***BM-13A-K***
Cassidy, C.M. BM-336-K
Castillo, R.G. MM-587-O
Castro, J. ES-1202-P
Castro-Ruiz, A. CB-323-O
Catala, L. BM-532-O
Cavalier, F. BM-726-O
Ceci, M. ***ND-1627-P***
Centrella, B. SM-872-F
Cesari, C. ES-842-F, ***ES-930-F***
Chabbra, S. MM-287-O
Chabera, P. ES-411-I
Chacón, K. BM-1042-P
Chafin, R. ND-492-O
Chakraborty, B. MG-849-F
Chalker, J. SM-177-O
Chamorau, L.-M. CB-1174-P
Champness, E. MM-1509-P
Chan, B. SM-774-O
Chan, M.C.W. ***SM-172-O***
Chan, W. ES-612-O
Chand, D. ***SM-074-I***
Chand, D.K. SM-1740-P SM-1713-P, SM-1707-P
Chandrasekaran, S. ***MM-889-F***
Chang, Ch. ***ND-892-F***, ES-1224-P
Chang, H.-C. ***ND-056-O***, ND-1642-P
Chanut, N. SM-778-I
Chaplin, A. ***ES-617-O***, MM-284-I
Charman, R. ES-617-O, MG-547-O
Chartier, B. ***FB-1303-P***
Charytanowicz, T. SM-973-F

Chastanet, G. MM-889-F MM-483-O, ES-1225-P
Chatterjee, P. ***BM-716-O***
Chavez, F. ***CB-744-O***
Chen, C.-H. ES-1269-P
Chen, H. ***SM-1718-P*** MM-288-I, ***CB-1113-P***
Chen, H.-Y. ES-1240-P
Chen, J. MM-085-K
Chen, L. MM-1516-P
Chen, S. MM-1514-P
Chen, S.-H. ***CB-403-O***
Chen, W. MM-286-O
Chen, X.-M. CB-1130-P
Chen, Y. CB-1135-P
Chen, Y.J. ES-1240-P, ES-1269-P
Cheng, M. ND-1602-P
Chengelis, D.A. FB-695-I
Chesher, G. ***MM-1507-P***
Cheung, O. ***SM-772-I***
Chiba, Y. ***ES-317-O***, ND-1638-P
Chiesa, M. ND-358-O
Chih, Y.R. ES-1240-P
Chikara, A. ***ND-1607-P***, ND-1610-P
Chilton, N. ND-1628-P
Chin, J.M. CB-859-F
Chlebík, R. ***MG-1433-P***
Cho, H.-L. CB-306-K
Cho, J. ***CB-301-I***
Cho, K.-B. ***CB-407-O***, MM-082-O CB-1166-P, CB-1168-P MM-1515-P, MM-1501-P
Chodkiewicz, M. MM-585-K
Chomiuk, J. ***MM-1509-P***
Chorazy, S. ***ND-753-O***, SM-973-F FB-793-O, ES-314-O
Chorozian, K. MM-181-I
Choua, S. CB-401-I
Choudhury, J. ***CB-745-I***
Choukairi Afailal, N. MM-485-K
Chowdhury, R. ***CB-1152-P***
Chrappa, M. ND-563-O, ***BM-1040-P***
Christodoulou, I. BM-532-O
Christodoulou, M.S. ES-043-O
Chrubasik, J. ND-1601-P, ***ND-890-F***
Chu, A. MM-388-O
Chu, J. ***CB-528-I***
Chudasama, V. BM-722-I
Chugh, V. ES-048-I
Chumakov, Y. SM-1737-P
Chung, C.H. ***FB-1304-P***
Cibian, M. ***ES-1202-P***, ***SM-173-O***
Cieśla, B. ***MM-1504-P***
Cindrić, M. ND-1616-P
Cini, A. ND-498-I
Ciofini, I. CB-1107-P
Cirelli, C. MM-587-O
Cirera, J. ***ND-053-O***, MM-1502-P
Ciurli, S. ***BM-014-I***
Cizerl, A. ***CB-423-O***
Claudio-Ares, Ó. BM-018-I
Clayton, H. ***BM-1016-P***
Clegg, J.K. MM-884-F
Clemente-León, M. ***ND-357-O***, SM-476-O
Clérac, R. ND-358-O ND-157-O, SM-477-O
Clever, G.H. ***SM-176-K***
Cliffe, M. SM-478-I SM-971-F, ***SM-475-K***
Cliffe, M.J. SM-1703-P
Clososki, G. BM-1017-P
Clutterbuck, K. ***ES-262-O***, ***SM-1701-P***
Cobo, S. ND-751-K
Coburger, P. ***MG-036-O***
Coche, M. BM-738-I
Coffetti, G. ES-043-O
Cohen, H. CB-304-O
Cole, J. ***ND-555-K***
Colebatch, A. CB-063-O
Collazo, V. BM-134-O
Collet, E.P.P. MM-683-O
Collet, E. ***ND-051-I***, ND-151-I ND-1626-P, MM-385-I
Collet, G. FB-695-I
Collingwood, J. ***BM-231-I***
Collison, D. ND-495-K, ND-661-K
Comba, P. ***CB-704-O***
Comotti, A. SM-775-I
Company, A. ***CB-705-I***
Condon, C. BM-714-O, BM-711-K
Conejero-Lara, F. BM-732-I
Conley, M. ***CB-625-I***
Connell, T.U. CB-1146-P
Consiglio, G. FB-694-O
Contel, M. BM-631-I
Cooke, K. SM-274-I
Cooper, C. ES-1203-P
Coote, M. SM-177-O
Coperet, Ch. ***ND-656-K***
Cordes, D. MG-348-O, MG-940-F
Cordes, D.B. MG-993-F
Cordones-Hahn, A. ***MM-786-O***
Cornia, A. ND-358-O, SM-576-O
Coronado, E. ND-357-O, ND-658-O ND-097-O, BM-715-I SM-476-O, ***ND-356-K***
Coronado-Puchau, M. BM-715-I
Corrales, M.E. MM-683-O
Cortat, Y. BM-1015-P
Cortez Sgroi Pupo, R. ***SM-573-O***, SM-1730-P
Costabile, C. ***ES-513-O***
Costa-DeDios, M. ***BM-362-O***
Costa de Santana, R. FB-598-I
Costa-Filho, A.J. BM-134-O
Costas, M. CB-203-O CB-006-O, CB-107-O CB-1115-P, CB-1158-P CB-1144-P, ***MM-485-K***
Couvreur, R. ND-964-F
Cowin, R. MM-686-K
Cox, N. ND-1628-P, ***MM-381-I***
Crans, D. BM-135-I BM-333-O, ND-892-F ES-1224-P, ***BM-339-I***
Crassous, J. FB-794-O
Cremer, S. CB-521-I
Crimmin, M.R. MG-347-O
Crochet, A. BM-1015-P
Cronin, L. CB-061-I, ND-1602-P
Cross, M. MG-848-F
Crowley, J. ***SM-175-I***
Crowley, J.D. ES-1227-P, ES-1271-P
Crumpton, A. MG-545-K
Cui, C. ***MG-248-I***
Cui, Y. ***CB-166-K***
Cula, B. FB-1313-P
Cullan, C. ND-492-O
Curcio, M. BM-635-I
Cuza, E. ND-151-I ES-267-O, MM-385-I
Czernetzki, C. CB-1140-P
Cziferszky, M. ***BM-632-O***

D

Da Costa Ferreira, A.M. ***BM-334-O***
Dad, P. ES-262-O
Dada, A. ***ND-895-F***
D'Agostino, S. SM-576-O
D'Agostino, S. ND-358-O
Dahl, J. ***CB-327-O***
Dai, C. ***CB-1112-P***
Dai, J. ***ND-1623-P***
Dakua, T. ***SM-1740-P***
D'Alessandro, D. ES-262-O, SM-1701-P
Dalla Pozza, M. ES-044-I
d'Amario, L. CB-427-O
D'Amato, A. ES-145-I
Damiano, C. ***CB-864-F***
Damjanović, V. ND-1616-P
Damsgaard, K. ***BM-1029-P***
Damsgaard, K.R. BM-1012-P

Dankert, F. ***ND-497-O***, MG-1410-P
Danopoulos, A. CB-856-F
Danoun, G. ND-494-I, ND-897-F, ND-663-O
Daolio, A. SM-972-F
Darkwa, J. ***ES-141-I***
Daro, N. MM-889-F, MM-483-O, ES-1225-P
Das, A. CB-1150-P
Das, B. FB-1308-P
Das, S. ND-556-O
Dautoras, D. MG-848-F, ***CB-1119-P***
Davison, N. MG-853-F, ND-437-O, MM-880-F, ***MG-1428-P***
Davy, M. ES-840-F
Dawson, J. MM-880-F
Day, C. CB-1170-P
Day, C.S. CB-1112-P
De, S. SM-378-O
Deakin, C. ND-495-K
de Azevedo França, J.A. ***ND-992-F***
Debaud, T. CB-857-F
DeBeer, S. CB-026-O, MM-767-O, MM-586-O, MM-682-O, ***CB-126-K***
de Bruin, B. ES-047-O, MM-482-O, ***CB-706-O***, MG-032-O
Dechambenoit, P. SM-477-O
Dechert, S. CB-308-O
Dederichs, T. ***MM-587-O***
Deegan, M. ***ND-492-O***
Deeth, R. ***CB-329-I***
De Gioia, L. MM-081-I
Degner, A. ***ES-1207-P***, ES-1209-P
De Kreijger, S. CB-226-O
de Kruijff, R.M. BM-1005-P
Delahunt, E. ***BM-1013-P***
Delaporte, S. ***ND-052-O***
Delfau, L. MG-943-F
Delferro, M. ES-1242-P
del Giorgio, E. FB-594-I
Della Croce, F. MM-762-I
del Rosal, I. FB-1306-P
Delsuc, N. BM-1030-P
De Marchi, L. ND-494-I, ND-663-O
Demeshko, S. CB-308-O, MM-1512-P
Demir, S. ***ND-258-I***, FB-1315-P
Demirbas, D. MM-287-O
Demirci, G. BM-1015-P
Demirci, I. ***MG-1415-P***
Demonti, L. FB-1306-P, FB-697-O
de Moraes, L.S. MG-941-F
de Nalda, R. MM-683-O
Deng, L. ***CB-502-O***
Deng, X. ND-661-K
Deplano, G. MM-682-O
de Prado, E. ES-267-O
de Prinse, Th. BM-1020-P
Deresz, K. ES-041-I
de Rond, T. BM-736-O
de Roo, C.M. CB-104-O, MM-085-K
De Roo, J. ND-393-O, ND-1631-P
Desage-El Murr, M. BM-330-K
Descher, H. BM-117-O
Deshapriya, S. FB-1315-P
Desplanches, C. ND-151-I, MM-889-F
de Toro, A. ND-456-O
Deuter, K. ND-433-O
de Vere-Tucker, M. MG-941-F, ***MG-1427-P***
Devic, Th. ***SM-372-O***, SM-378-O
Deville, C. ***BM-137-O***, SM-574-I, BM-726-O
de Visser, S. CB-708-I
de Visser, S.P. CB-1148-P
Dewick, S. MM-284-I
Dey, A. ***CB-701-K***
Dey, K. ***CB-1132-P***
Dey, S. CB-228-I
Dhara, S. ES-613-O, MG-1404-P
Diab, G. ND-556-O
Dias, R. ***ND-455-K***
Díaz-Torres, R. ND-754-O, ***ND-964-F***
Di Berto Mancini, M. ***CB-122-O***, CB-104-O, MM-085-K, SM-1727-P
Diederich, T.M. ***MM-1513-P***
Dielmann, F. ND-960-F, ***CB-421-I***
Dietz, M. MG-846-F, MG-642-O, MG-545-K
Dietzek-Ivanšić, B. BM-1037-P
DiMari, F. CB-857-F
DiNardi, R. SM-071-I
Dinesh, S. ***ES-1260-P***
Ding, H. ND-652-O
Dinse, K.-P. MM-388-O
Di Palma, G. SM-572-O
Di Paola, A. BM-869-F
Di pietro, M.L. CB-1120-P
Di Santo, T. BM-723-O
Dissanayake, A. BM-1001-P
Di Virgilio, A.L. BM-134-O
Djanashvili, K. BM-1005-P
Djebbar, F. ***CB-1174-P***
Djebrani-Oussedik, N. BM-330-K
Do, D.C.H. ***ND-667-O***
Dobado, J.A. BM-732-I
Dobrovetsky, R. MG-1436-P, ***MG-541-I***
Dolai, R. ND-152-O
Dołęga, A. ES-876-F
Doležal, L. ***MG-1425-P***
Domínguez-Martín, A. BM-732-I
Dominiak, P.M. MM-585-K
Donaggio, L. SM-1717-P
Dong, H. ***MG-940-F***
Donnelly, P. BM-1019-P, BM-1011-P, ***PL-1***
Donovan Hedegård, E. MM-181-I
Doonan , Ch. ***SM-571-I***
Doran, C. MM-788-I
Dostál, L. MG-1433-P, MG-1402-P, MG-1425-P
Dotou, M. ES-044-I
Double, K. ***BM-33A-K***
Douglas, R.J. ***MG-1434-P***
Dračínský, M. ND-962-F
Dragomir, M. MM-581-I
Draguicevic, A. MG-035-K
Drahoš, B. BM-332-O, ***ND-1608-P***
Draksharapu, A. CB-1147-P
Draper, H. MG-851-F
Draper, S. BM-714-O, ***BM-711-K***
Draper, S.M. CB-303-O
Drerup, K. MM-388-O
Drexler, H.-J. CB-1160-P, ES-1219-P, ND-1632-P
Driess, M. FB-1315-P, MG-1406-P
Drobná, E. BM-1039-P
Drosou, M. ***MM-087-O***
Duan, C. CB-167-O, CB-165-I, ***CB-065-K***
Duboc, C. CB-223-O, ***ES-462-K***
Ducey, A. BM-018-I
Duckett, S. CB-855-F, CB-1127-P
Duijnstee, D.R. CB-104-O, MM-085-K
Dunstan, M. SM-472-O, MM-885-F
Dunstan, M.A. ***FB-798-I***
Duppel, V. ND-556-O
Dupré, N. SM-372-O
Duquennoy, R. ND-253-O
Dürr, E. ***ND-893-F***
Dürrmann, A. ND-055-K
Durvin, N. CB-1142-P
Dutta, A. ***CB-224-I***
Dutta, I. ***ES-613-O***, ES-1252-P, MG-1404-P
Duverger-Nedellec, E. MM-483-O, ES-1225-P
Dworkowski, F. MM-587-O
Dykstra, C. ***MM-873-F***
Dziedzic, H. ***CB-1125-P***

E

E. Blyth, A. SM-1732-P
E. Brown, S. ND-1635-P
Eddaoudi, M. ***SM-673-K***
Edenholm, A. ***ND-891-F***
Edin, S. ***ND-1640-P***
Edwards, A. ES-042-O
Edwards, A.J. MG-647-O
Egerström, A. CB-207-O
Eggenweiler, H. ***ES-1228-P***
Egner, S. CB-1123-P
Eguchi, N. ***MM-885-F***
Ehtisham, M. ***CB-006-O***
Eickhoff, L. ***MG-647-O***
Eijsink, V.G.H. MM-767-O
Eisen, C. CB-859-F
Eisenberg, S. MM-283-O
Ekberg, L. CB-105-I
E. Lapi, S. BM-727-O
El Hazmi, W. CB-863-F
Elias, B. CB-226-O
Eliseeva, S. FB-691-I, ***FB-595-K***, FB-695-I
Elmaci, D. MM-184-O
El Mansour El Jastimi, H. ND-357-O
Elmendorf, L. CB-207-O
Elmers, H.-J. ND-351-I
Emmerling, F. SM-972-F
Enders, M. MM-1513-P
endix, J. FB-1312-P
Endo, K. ***SM-273-O***
English, L. MG-851-F
Enriquez Cabrera, A. MM-292-O
Enslin, L. ES-044-I
Erakovic, M. MM-1508-P
Erasmus, E. ES-044-I
Erben, M. MG-1402-P
Erickson, A. CB-1105-P
Erickson, S. CB-983-F
Eronen, A. CB-423-O
Errington, J. ***ND-192-O***
Ertem, M. CB-505-K
Eryılmaz, E. CB-226-O
Espinoza-Suárez, E.J. CB-221-I
Esteban-Gómez, D. BM-727-O, MM-182-O, BM-367-O, BM-362-O, BM-1005-P, ***BM-1009-P***
Estival, A. CB-1142-P
Ettayri, K. ***BM-1027-P***
Ettlinger, R. SM-772-I
Evangelisti, M. SM-472-O
Evans, J.D. SM-772-I
Evans, N. MG-547-O, MG-851-F, ***MG-1429-P***

F

Facchetti, G. ***ES-043-O***
Facchin, G. ***BM-134-O***
Fadel Pichet, G. BM-112-O
Fafián-Labora, J.A. BM-1009-P
Faglioni, F. ND-566-O
Falaise, C. ***ND-195-I***
Falcone, E. BM-330-K
Faller, P. ***BM-330-K***
Faltejsek, J. ND-563-O, ***BM-638-O***
Fan, S. MG-248-I
Fan, Z. ***ND-1643-P***
Fañanás-Mastral, M. SM-1716-P
Fandzloch, M. SM-1720-P
Fanfrlík, ND-962-F
Faraji, S. ES-317-O
Farías-Carreño, P. FB-598-I
Fasano, A. MM-081-I
Fateeva, A. ***SM-378-O***
Faulkner, S. FB-693-O, ***FB-696-K***
Faure, B. ES-1261-P
Fedorowicz, J. ES-1217-P
Fejes, I. ND-492-O
Fekete, L. ES-267-O
Feldman, D.M. CB-507-O
Felton, S. ND-1613-P
Femoen, V. MM-585-K
Femoni, C. MG-854-F
Fernandes, J. SM-778-I
Fernandez, I. MG-242-O
Fernandez, P. CB-505-K
Fernández, S. CB-505-K, ***CB-1158-P***
Fernández-Alarcón, A. ES-266-O
Fernández-Pisón, R. ES-517-O
Ferns, R. MG-348-O, MG-940-F, MG-993-F
Ferrara, F. SM-1726-P
Ferrari, E. ***ND-566-O***
Ferretti, F. ES-513-O
Ferro, J. BM-1002-P
Ferry, J.G. CB-605-I
Fest, M. MG-1432-P
Fiedler, A. ***CB-1105-P***
Fielden, J. BM-733-O
Finelli, V. SM-872-F
Finger, M. ES-1214-P
Fiorini, L. ***BM-868-F***
Firth, G. BM-722-I
Fischer, J.W.A. MM-285-K
Fischer, M. ***MG-644-O***
Fischer, R. MG-1419-P, ND-961-F, ND-954-F, ND-893-F, ND-891-F, CB-862-F
Fischer, R.A. ND-894-F, MG-854-F, ***ND-655-I***
Fischer, R.C. MG-1409-P
Fischmeister, C. ES-1206-P
Fish, H. ES-840-F
Fisher, O. ***BM-1042-P***
Fitchett, Ch. CB-1173-P
Fittipaldi, M. FB-795-I, ND-498-I
Flapper, J. CB-706-O
Fleege, J. ***SM-477-O***
Fleurat-Lessard, P. ES-143-O
Flichot, H. ***FB-592-O***
Flock, M. MG-1409-P
Flores, A.N. SM-1730-P
Flores, M. ***CB-1138-P***
Fodor, J. CB-303-O, ***BM-714-O***, BM-711-K
Fogar, G. SM-1711-P
Fohlmeister, L. MG-940-F
Folkjær, M. SM-574-I
Fonseca, J. ***CB-168-O***
Fontaine, Ph. CB-1103-P
Forsberg, Z. MM-767-O
Förster, Ch. ES-1234-P, ES-215-K
Fortage, J. MG-943-F
Forte, G. FB-694-O
Forti, F. ES-930-F
Fouad, M.A. ES-513-O
Foucault-Collet, A. FB-695-I
Fout, A. ***CB-306-K***
Fragkis, D. ***ND-1615-P***
Franchi, S. ND-566-O, BM-1002-P
Franco, F. CB-227-O
Frank, R. ES-413-O, CB-1137-P
Frank, S. SM-574-I
Franz, R. MG-548-I
Frei, S. MG-036-O
Freibert, A. MM-587-O
Freire-García, A. ***BM-1005-P***
Friedländer, l. MM-1506-P, ***ES-1230-P***
Friedrich, A. MG-1432-P
Fritsche, P. CB-521-I
Fritsky, I. ***CB-427-O***
Frymark,, J. BM-1041-P
Frymark, J. ***BM-1022-P***
Fuentealba, P. ***FB-598-I***
Fuentes, M.Á SM-1729-P
Fujii, H. ***CB-404-I***
Fujimori, K. ES-1233-P, SM-1739-P
Fujita, M. ***BM-535-K***
Fukatsu, A. SM-677-O
Fumanal, M. ND-158-O
Funaioli, T. ES-930-F
Furman, G. BM-112-O
Furukawa, Y. BM-1038-P, ***BM-131-I***, BM-1025-P
Fustier-Boutignon, M. CB-628-O

G

Gabbert, P. ES-048-I
Gade, L. CB-1134-P
Gajapathy, H. MM-873-F
Gakiya Teruya, M. ND-498-I
Galindo, M.A. ***BM-732-I***
Gallo, E. CB-864-F
Gallo, J. BM-728-I
Galvez-Guajardo, S. FB-598-I
Gamarra, S.R. SM-275-K
Gambino, D. BM-114-O
Gammons, R.J. ES-840-F
Ganapathi, A. CB-1152-P, ***SM-577-O***
Gandin, V. ***BM-115-I***
Gantsho, V. ES-044-I
Gao, D. ***ES-611-I***, ES-147-O
Gao, Q. MM-282-O
Gao, R. MM-1516-P
Garay-Ruiz, D. ND-099-I
Garcia, A. ***CB-501-I***
Garcia, C. CB-105-I
Garcia, G. CB-322-O
Garcia, Y. ND-151-I
Garcia-Bosch, I. ***CB-007-O***, CB-103-O
Garcia-Duran, A. ND-053-O, ***MM-1502-P***
Garcia-Keller, C. BM-339-I
Garcia-Lacuna, J. ES-517-O
García-Padilla, E. MG-032-O
Garcia-Roca, A. CB-107-O
García-Romero, Á. MG-648-O
Garçon, M. CB-1115-P
Garden, J. MG-1431-P
Garhwal, S. CB-327-O
Garrison, A. BM-236-O
Gaschk, E. ***ES-1223-P***
Gascoin, M. FB-592-O
Gaspar, A.B. ***ND-752-I***
Gasser, A.C. ES-268-I
Gasser, G. BM-713-O, ES-044-I
Gasulla, J. CB-006-O
Gau, M.R. CB-626-K
Gauder, F. ES-1234-P
Gaurav, K. ***MG-1422-P***
Gautier, N. SM-372-O
Gawelda, W. ***MM-683-O***
Gayathri, K.K. ES-1212-P
Gedikoglu, N. SM-372-O, ***SM-1728-P***
Gee, L. CB-707-O
Geilhufe, M. ***SM-474-I***
Geilhufe, R. SM-473-O
Gelman, D. ***ND-657-O***, CB-1165-P
Gelman-Tropp, S. ND-657-O, ***CB-1165-P***
Gemel, Ch. ND-961-F
ND-954-F, ND-893-F
ND-891-F, CB-862-F
ND-894-F, MG-854-F
Gencheva, G. ***BM-867-F***
Gendy, Ch. SM-1702-P
Genicio, N. BM-728-I
George, R. BM-532-O
George, T. MG-037-O
Georgiev, P. BM-338-O
Georgieva, M. BM-338-O
Geppert, P. CB-1140-P
Gericke, R. FB-990-F, ***ND-491-I***
Gerndt, L. CB-208-I
Gerszendorf, A. FB-593-O
Gesslbauer, S. CB-002-O, MG-343-O
Gessner, V. ***MG-544-I***
Getty, C. ***ES-841-F***
Getzner, L. ND-751-K
Ghatak, A. CB-1104-P
Ghazawneh, A. ***BM-1003-P***
Ghosh, A. CB-067-O
SM-1707-P, ES-316-K
Ghosh, D. CB-1150-P
Ghosh, R. CB-703-O
Ghosh, S.K. ***SM-371-I***
Gibney, A. BM-738-I, BM-1013-P
Gibson, A. ND-892-F, ES-1224-P
Gibson, D. BM-713-O
Gidron, O. FB-794-O
Gierke, S. ***CB-1163-P***
Gigli, L. SM-576-O
Gil, Y. FB-598-I
Gilch, F. MG-1426-P
Giles, L.W. MG-940-F
Gill, M. ***BM-734-O***
Gioppo Nunes, G. ***BM-112-O***
Giorgianni, F. ***CB-1120-P***
Giovanardi, D. SM-972-F
Glaser, T. ***CB-607-O***, CB-1116-P
CB-1163-P, BM-1028-P
BM-1046-P, ES-1255-P
CB-1122-P, CB-1139-P
Gleerup Christensen, F. SM-1721-P
Glover, P. FB-594-I
Göbel, D. ***ES-1215-P***
Godt, A. MM-381-I
Goetz, R. ES-879-F
Gogick, K.A. FB-695-I
Gogolák, R. MM-083-O
Goicoechea, J. ***MG-346-K***
Goicoechea, J.M. MG-648-O, MG-543-O
Gök, Y. ND-1609-P
Gómez-Coca, S. ND-1603-P
Gómez-Lado, N. BM-1009-P
Gonçalves, T.P. MG-1404-P
González, L. BM-1037-P
Goo, Z.L. SM-373-O, MM-583-O
Goodwin, C. FB-792-I, ***ND-495-K***
Gopalakrishnan, S. SM-1721-P, ***SM-1738-P***
Gopinath, J.S. MM-1517-P
CB-934-F, CB-102-O
Gorbunova, Y.G. CB-863-F
Gorczyński, A. FB-694-O
Gordon, D. ND-492-O
Gordon, K.C. ES-1227-P, ES-1271-P
Gorolomova, P. BM-867-F
Goud, B. ES-044-I
Gourlaouen, Ch. CB-856-F
Gouverneur, V. MG-1434-P
Goyne, E. ***BM-1011-P***
Grabbet, B. MM-482-O
Grainger, D. CB-1157-P
Gransbury, G.K. ND-498-I
Grau, S. CB-226-O
Gray, I. ***CB-1127-P***
Greb, L. ***MG-244-I***, MG-1439-P
Greco, C. MM-081-I
Greer, S. MM-283-O
Greiner, M. ***CB-1141-P***
Gremmel, L. ***ND-961-F***
Grice, K. CB-983-F
Griebel, J. ND-898-F
Griffin, L. ND-495-K, MG-545-K
Griffiths, A. BM-722-I
Grigas, D.B. CB-626-K
Grimm, B. ***MM-385-I***
Grisi, F. ***ES-145-I***
Grödler, D. FB-990-F
Grommet, A. SM-1714-P
Gröpl, K. ND-154-O
Gros, C. ES-1202-P
Groth, L.J. ***CB-1137-P***
Grøtli, M. SM-1726-P
Gu, H. MG-1407-P
Gudjonsson, H. CB-323-O
Guérard, F. ***ND-564-I***
Guerin, L. ND-1626-P
Guidolin, N. BM-727-O
Guihéry, N. ND-052-O
Guillot, R. ND-052-O, ND-1627-P
Guillou, N. SM-372-O, SM-378-O
Guionneau, P. MM-889-F, MM-483-O
Gumbo, M. SM-1726-P, SM-1709-P
Gumerova, N. BM-015-K, ***ND-398-O***
Gunther, M. ***CB-127-O***
Guo, W. MM-889-F
Guo, Y. ***CB-605-I***
Gupta, A. SM-576-O

Gupta, G. CB-227-O
Gupta, M. ES-1218-P
Gupta, P. SM-577-O
Gurung, K. MM-581-I
Gust, R. BM-117-O
Gutiérrez-Cutiño, M. ND-1614-P
Gutmańska, K. ***ES-876-F***
Güzel, B. ***CB-1111-P***
Gys, N. ES-261-I

H

Haak, H. MM-287-O
Hadjikakou, S. ***BM-011-I***, BM-017-O
Hadley, K. ***BM-724-O***
Hadlington, T. MG-994-F MG-852-F, MG-1424-P
Hage, R. CB-104-O, MM-085-K
Hagemann, D. CB-1163-P
Hagemann, D.L. ***CB-1116-P***
Hagenow, A. ND-351-I
Hahn, N. ***SM-473-O***
Hajdu, B. BM-1036-P, ***BM-1006-P***
Halcrow, M. ***MM-488-I***, MM-886-F MM-1507-P, ND-1611-P
Haldington, T.J. MG-242-O
Hallen, L. BM-714-O
Ham, G. MG-344-O, ***MG-1412-P***
Hamade, F. ***ND-1618-P***
Han, J. ***CB-162-O***
Hanan, G. ***ES-318-O***, ***ES-1201-P***
Hanan, G.S. SM-173-O, ES-1202-P
Handa, M. BM-1024-P
Hannibal, V. MG-244-I
Hannon, M. ***BM-531-I***
Hansen, A. ***ES-1210-P***
Hansen, A.B. ***ES-1211-P***
Hansmann, M. MM-387-O
Hansmann, M.M. MG-1430-P
Hanson, R. CB-857-F
Haouas, M. ND-195-I
Harada, R. ND-096-O
Haraguchi, N. ***ND-397-O***
Harakawa, Y. ES-1266-P
Hardie, M. ***SM-072-O***
Hareendran, A. CB-523-O
Harley, S. ES-1203-P
Harmer, J. MM-381-I
Harris, J. ***CB-1128-P***
Harris, M. ND-151-I
Harrison, A. SM-1702-P, MG-1426-P
Harriswangler, C. BM-727-O, BM-362-O
Hartinger, Ch. ***BM-111-I***
Hartinger, Ch.G. BM-736-O
Hartmann, J. ND-754-O
Haseloff, K. ES-413-O
Hashimoto, A. SM-1744-P
Hashmi, A.St. ES-879-F
Hashmi, A.St.K. ***CB-32A-I***
Hassan, M.A. MM-388-O
Hata, M. CB-201-I
Hatting Petersen, M. SM-1721-P
Haviv, E. ***CB-304-O***
Hayama, S. FB-792-I
Hayami, S. ***ND-155-I***
Hayward, M. ES-042-O
Hazari, N. CB-222-O, CB-505-K
He, Q. ES-1227-P, ES-1271-P
He, W. FB-792-I
He, Z. ES-047-O
Heaton, J. ***ND-553-O***, ES-042-O
Hebenbrock, M. BM-731-K
Hebert, D. CB-103-O
Hecel, A. ***BM-133-O***, CB-1171-P
Hefty, L. ***CB-1136-P***
Heilmann, A. MG-545-K
Heinze, K. ES-1234-P, ***ES-215-K***
Heisen, C. MG-1439-P
Helbig, A. ES-1215-P
Heldner, M. CB-521-I
Heldner, M.L. ***CB-1140-P***
Helten, H. MG-1438-P, ES-1215-P MG-1432-P, ES-1257-P
Helveg, S. SM-572-O
Hemingway, J. ***MM-880-F***
Hemmingsen, L. BM-1036-P, BM-1006-P
Hendon, T. CB-327-O
Heng, J.-M. ***CB-1130-P***
Henke, S. ND-1643-P
Henkelis, J. SM-072-O
Hennessy, J. BM-738-I
Henoumont, C. BM-234-O
Henrichsen, M. ***FB-1312-P***
Heo, H. ***ES-1229-P***
Hering-Junghans, Ch. ***MG-641-I***
Herle, D. ND-497-O, ***MG-1410-P***
Hermann, M. BM-117-O
Hermann, P. BM-138-O ***ND-563-O***, BM-638-O BM-368-O, BM-1040-P
Hermosilla-Ibáñez, P. ND-1614-P
Hernández, G. BM-114-O
Hernandez, M. ***CB-622-O***
Hernandez-Rollan, C. MM-181-I
Hernandez Sanchez, R. ***BM-534-I***
Hernandez Toledo, H. CB-105-I
Hernán-Gómez, A. CB-1115-P
Herres-Pawlis, S. ***ES-146-K***
Hervé, M. ND-051-I, ND-1626-P
Hetterscheid, D. ***ES-466-O***
Hevia, E. CB-981-F CB-980-F, ***CB-326-K***
Hibiya, R. CB-1102-P
Hicks, J. MG-647-O, MG-446-O ***MG-247-O***, MG-643-O MG-546-O, MG-1413-P ND-1628-P, MG-545-K
Hicks, Th. BM-364-O
Hidalgo, J.F. MM-683-O
Hierlmeier, G. ***CB-521-I***, CB-1140-P
Higuchi, M. SM-1719-P
Hill, S. ND-354-O, MM-385-I
Hiller, D. CB-308-O
Himeda, Y. ***ND-554-I***
Hindié, E. BM-726-O
Hirahara, M. ***BM-718-I*** ES-1233-P, SM-1739-P
Hirai, H. ND-092-O
Hirama, S. ***ND-950-F***
Hitomi, Y. ND-1642-P
Hizbullah, L. ***CB-747-O***
Hjelm, J. CB-603-O
Hnatejko, Z. MM-1504-P
Hnyk, M. ND-962-F
Ho, P.-Y. BM-871-F
Hochdörffer, T. ND-154-O
Hochmal, A. ***MG-1402-P***
Hofer, G. MM-585-K
Hoffman, A. ***FB-793-O***
Hoffmann, P.A. BM-1037-P
Hofmann, B. BM-118-O, BM-1010-P
Hofmann, B.J. ***BM-866-F***
Hofmann, E. ND-954-F
Högbom, M. MM-585-K
Hohloch, S. ***CB-524-I***
Holland, J. ***BM-536-K***, ***BM-1020-P***
Holland, J.P. BM-634-O
Holland, P.L. CB-507-O
Holldack, K. MM-387-O
Holmsen, M.S.M. SM-1730-P
Holthausen, M.C. CB-308-O
Holub, J. MG-443-O, ND-962-F
Holz, R. ***BM-236-O***
Honda, T. SM-1739-P, ES-1263-P ***ES-1264-P***, ES-1266-P
Hong, Y.H. ***CB-402-O***
Honolka, J. ES-267-O
Hood, Th. ES-617-O, MM-284-I

Hopkinson, M. ND-437-O, MG-1428-P
Hopping, G. MM-184-O
Horáček, M. ***CB-624-O***
Horsley Downie, Th. MG-547-O
Hosokawa, R. ES-875-F
Hosono, N. MM-768-I
SM-777-O, ***SM-773-O***
Hosseinzadeh, Z. FB-797-O
Hota, P.K. CB-1168-P
Hota, R.R. CB-703-O
Hrenar, T. ES-1267-P
Hrubý, J. ND-354-O
Hruska, E. MM-873-F
Hsiang, E. ***ES-1221-P***
Hsu, S. ***SM-178-O***
Hsu, S.C.N. CB-403-O, MM-487-O
Hu, C. ***FB-697-O***, ***MG-1406-P***
Hu, X. MG-1407-P
Hua, L. FB-1317-P
Huang, G.-F. BM-871-F
Huang, K.-W. ES-613-O, ES-1252-P
MG-1404-P, ***ES-464-I***
Huang, W.-Q. BM-871-F
Huang, Z. MM-181-I
Huber, Th. MM-381-I
Huf, E.M. BM-1021-P
Hultzsch, K.C. CB-1118-P
CB-1164-P, CB-1121-P
Humphrey, M. MM-783-O
Hunger, D. ND-661-K
Hunt, S. ES-1242-P
Hureau, C. ***BM-331-I***
Huse, N. MM-587-O
Hutchings, G.J. MM-586-O
Huzan, M. FB-792-I
Hwang, D. ES-048-I
Hwang, S.J. ***MG-241-I***

I

Iacomini, V. SM-576-O
Ibrahim, M. SM-1706-P
Iengo, E. SM-1711-P
Igau, A. ***ES-1206-P***
Iglesias-Martínez, E. BM-1009-P
Ignatev, V. MM-585-K
Im, H. ***ND-1620-P***
Imai, M. ND-654-O
Imai, Y. ES-1237-P
Imberti, C. ***BM-365-I***
Imperato, M. ND-358-O
Inchausti, A. ***MM-483-O***, ES-1225-P
Ineza, C. ES-142-O
Invernizzi, L. CB-864-F
Isayev, O. CB-103-O
Ishii, M. SM-678-O
Ishii, T. ***MM-297-O***
Isobe, H. ES-1237-P
Ito, H. ND-437-O
Itoh, S. ***CB-408-I***
Ivanova, I. BM-338-O
Iwano, T. ***ND-198-O***
Iwasaki, A. SM-774-O
Iwasaki, S. MG-447-O
Iwata, K. ES-875-F

J

Jackson, R. MG-547-O
MG-851-F, MG-1429-P
Jackson, T. ***CB-001-I***
Jacobi von Wangelin, A. CB-1114-P
Jacobsen Eiby, S.H. BM-1006-P
Jago, D. ES-1223-P
Jahn, M. ***ES-1248-P***
Jain, C. ***SM-1710-P***
Jain, D. ***ES-1219-P***
Jaiswal, N. ***MM-183-O***
Jakobsen, V.B. ND-1613-P
Jakoš, J. ***BM-1021-P***
Jakubaszek, M. ES-044-I
Jakubikova, E. ***ES-311-I***
Jalali, E. ES-044-I
Jambor, R. MG-1402-P
James, C.C. CB-068-I
Jamieson, S.M.F. BM-736-O
Jana, N.Ch. CB-703-O
Jancso, A. BM-1036-P
Janetzki, J. ***ND-253-O***
Jang, J. ES-1204-P
Jang, W.-D. MG-1412-P
Jankowska, A. ND-963-F
Jankowska , D. ***ES-1220-P***
BM-1031-P, ES-1216-P
Jankowski, R. ES-314-O
Jankowski, W. BM-1043-P
Jannuzzi, S.A.V. MM-767-O
Jansen, S. CB-1122-P
Janssens, T.V.W. MM-282-O
Jaritz, Y. ***ES-1268-P***
Jaromin, A. SM-1720-P
Jarvis, S. ES-1203-P
Jarzembska, K. ***ES-041-I***
Jastrząb, R. BM-1041-P
BM-1022-P, BM-1043-P
BM-1033-P, ***BM-1044-P***
Jay, R.M. MM-587-O
J. Cliffe, M. SM-1732-P
Jean-Baptiste-Dit-Dominique, F. MM-881-F
Jeanneau, E. CB-526-O, SM-378-O
Jędrzejowski, D. SM-772-I
Jeevanandham, G. CB-307-O
Jellinek, K. ***MG-1420-P***
Jenkins, A. MM-186-K, MM-873-F
Jenkins, D. ***SM-271-I***
Jensen, K. ***ND-091-I***, CB-327-O
Jensen, K.M.Ø. ND-1636-P
Jensen, M.L. BM-1036-P
Jensen, M. BM-137-O
BM-1036-P, BM-726-O
Jeschke, G. ***MM-285-K***, MM-1511-P
Jesuman, A. ND-752-I
Jiang, S.-D. ***ND-254-I***
Jiang, Z. CB-528-I
Jiao, L. ***CB-021-I***
Jimenez-Munoz, C. ***MM-1505-P***
Jin, K. ***CB-202-O***
Jin, Q. ND-652-O
Jin, W. MG-248-I
Jin, X. CB-1153-P
Jinschek, J.R. SM-572-O
J. Morris, A. SM-1732-P
John, A. MM-284-I
John, D. ***SM-1713-P***
John, Ł. ***ND-098-I***
Johnson, B.A. ***CB-984-F***
Johnson, L. ND-197-O, ND-895-F
Johnson, M. CB-1103-P
Johnson, P.J.M. MM-587-O
Johnston, M. SM-177-O
Jones, C. ND-432-O
Jones, K. ND-896-F
Jones, O. MG-031-I
Jones, R. ***CB-1151-P***
Jordan, R. ND-1613-P
Joseph Abou-Fayssal, C. ***CB-163-O***
Josephy, Th. CB-128-O
Joshi, G. ES-1212-P
Joven, D. MG-244-I
Joven-Sancho, D. ***ND-456-O***
Joyce, J. ***CB-026-O***
Jozefíková, F. BM-1039-P
Judd, M. MM-381-I
Jung, J. ***CB-982-F***
Junghans, Ch.H. ES-1258-P
Junkers, L.S. ND-099-I
Jupp, A. ***MG-448-I***
SM-974-F, MM-880-F

K

Kabanova, V. MM-587-O
Käch, D. ES-268-I
Kaczmarek, M. ***BM-1033-P***
Kaczmarek, M.T. BM-1041-P
Kaczmarek-Kędziera, A. ES-1220-P
BM-1031-P, ES-1216-P
Kadanuru Rajashekar, G.K. ***BM-234-O***
Kaden, P. FB-990-F, ND-491-I
Kagawa, F. ND-753-O
Kahlal, S. MG-1419-P
Kaimal, N. ***ND-1632-P***
Kaiser, A. SM-1721-P
Kaiser, Y.H. ES-1255-P
Kakizawa, A. CB-743-O
Kalandia, G. ND-396-K
Kalkuhl, T.L. ***MG-242-O***
Kallmeier, F. MG-1413-P
Kalmbach, J. ES-1234-P
Kaltsoyannis, N. CB-622-O, ND-661-K
Kambe, T. ***ND-850-F***, ND-950-F
ND-654-O, SM-1710-P
Kamecka, A. ES-1249-P
BM-1026-P, BM-870-F
Kamei, A. ES-1237-P
Kameo, H. ***ES-618-O***
Kamiński, R. ES-041-I
Kandy, A. ***CB-1106-P***
Kanegawa, S. ND-156-K
Kanga Banik, S. MM-684-O
Kann, N. SM-1726-P
Kapp, L.D. BM-1037-P
Kapustová, Z. MG-443-O
Kar, S. ***CB-1167-P***
Karadaş, F. ***ES-416-O***
Karadimov, T. BM-338-O
Karak, P. ES-613-O
ES-1252-P, MG-1404-P
Kardam, V. ***MM-082-O***
Kardas, K. ***BM-1023-P***
BM-533-O, BM-1032-P
Karlin, K.D. CB-1168-P
Karn, L.M. ***SM-970-F***
Karnahl, M. ***ES-413-O***, CB-1137-P
Karras, G. ND-1610-P
Kasagiri, T. ***ND-092-O***
Kaskel, S. ***SM-375-I***
Kästner, J. MM-086-O
Kaszuba, A. BM-1018-P
Katayama, N. ***CB-1145-P***
Käthner, M. ***CB-1139-P***
Kato, M. ES-312-O
Kauffeld, W. BM-1030-P
Kaupp, M. FB-1313-P
Kawaguchi, J. ***ND-654-O***
Kawano, M. SM-774-O
Kawasaki, M. MG-447-O
Kayne, M. CB-028-I
Kazimierczuk, K. BM-1026-P
MM-188-O, BM-870-F
Kehrig, A. FB-1309-P
Keil, P. MG-1424-P
Kelemen, Z. MG-548-I
Kellett, A. ***BM-738-I***, BM-1013-P
Kelly, C. MM-385-I
Kelly, C.T. ***ND-1613-P***
Kelm, H. ND-152-O, MM-1512-P
Kemell, M. CB-423-O
Kench, T. BM-63A-O
Kennedy, M. ***BM-532-O***
Kenrick, R. ***BM-364-O***
Kern, M. ***MM-388-O***
Kerridge, A. ND-495-K
Kerscher, B. ***CB-862-F***
Kertész, E. MG-1433-P
Kessler, V. ***ND-431-I***
Khakhulin, D. MM-686-K
Khaleghi Abasabadi, R. ***SM-872-F***
Khan, S. ES-1213-P
MG-245-K, MG-1422-P
Khan, Z. CB-1105-P
Khatua, S. ES-1212-P
Khemthong, P. ND-892-F
Kiene, C.I. ***ES-1214-P***
Kieslich, G. MM-296-O, ***MM-582-O***
Kikukawa, Y. ND-1630-P, ND-1629-P
Killian, L. ***MM-482-O***
Kim, D.Y. ES-1229-P
Kim, M. ES-317-O
Kim, S. ***MG-344-O***
CB-202-O, MG-1412-P
Kim, Y. ***MG-342-O***, MG-1412-P
Kim, Z.H. ES-1204-P
Kimchi, L. ***BM-363-O***
Kindler, T.-O. CB-1114-P
Kintzel, B. ND-055-K
Kipouros, I. CB-207-O
Kircher, B. BM-117-O
Kishi, R. MG-447-O
Kitagishi, H. CB-201-I
Kitase, K. ND-756-O
Kitayama, T. ***ES-1262-P***
Kitazawa, T. ***ND-756-O***
Kitchen, J.A. BM-736-O
Kitos, A.A. FB-1314-P, ***ND-1605-P***
Klassen, G. BM-112-O
Kleemiss, F. ND-496-O
Klein, J.E.M.N. CB-1101-P
Klement, W.J.N. CB-104-O
Klementova, M. ES-267-O
Kljun, J. CB-423-O
BM-1021-P, BM-1048-P
Klosin, J. CB-1103-P
Kloz, M. ES-315-I
K. Metre, R. ES-1218-P
Knapas, K. CB-423-O
Knope, K.E. ***ND-392-O***
Ko, C.-C. BM-871-F
Ko, V.C.-C. ***ES-514-I***
Kobashi, H. CB-201-I
Kobuta, K. ND-437-O
Kochem, A. ***CB-931-F***
Kochhar, A. CB-1117-P
Kodama, T. MG-447-O, MG-944-F
Kodera, M. ***CB-201-I***
Kögerler, P. SM-1737-P
Kojima, T. ***CB-205-K***
Kola, A. BM-133-O
Kolozsvári, N. BM-734-O
Komarnicka, U. BM-132-O, BM-1023-P
BM-1034-P, BM-1045-P
BM-113-O, BM-013-O
BM-533-O, BM-1032-P
Komodiki, L. SM-1704-P
Konar, S. ***ND-153-O***
Kondo, M. ND-950-F
ND-654-O, SM-1710-P
Konishi, R. ND-1642-P
Kopel, P. BM-533-O, ND-1621-P
Kopka, K. BM-1002-P
Körber, E. CB-626-K
Korbus, R.M. ***ES-1255-P***
Körner, T. CB-1140-P
Kornweitz, H. CB-307-O
Koshevoy, I. ***ES-217-O***
Kosone, T. ***ND-758-I***
Kossatz, S. BM-138-O
Köster, U. BM-1036-P
Kosugi, K. ND-950-F
Kotek, J. BM-138-O
BM-368-O, BM-1040-P
Kounalis, E. ***FB-1305-P***
Koutsantonis, G. ES-1223-P
Koutsianos, A. SM-778-I
Kouvetakis, J. CB-1138-P
Kovani, E. ND-394-O
Koyama, Y. ***ND-1642-P***
Koziel, S. BM-013-O
Kozieł, S. BM-1034-P
BM-1045-P, BM-533-O
Kraemer, T. ***MM-084-I***
Krafft, M. ***ES-1245-P***
ES-1211-P, ES-1205-P
Kragskow, J. MG-1429-P
Krajewski, S. CB-507-O
Kramer, P. CB-707-O
Kramer, S. ***CB-422-O***
Krämer, T. ES-617-O, MG-941-F
MG-1414-P, MM-284-I
Kramm, U.I. MM-287-O
Kranz, Ch. CB-1136-P
Krause, K. CB-1126-P

Kravtsov, V. SM-1737-P
Kreimer, L. ***MG-994-F***
Krewald, V. MM-1505-P, CB-1143-P ***CB-106-K***, CB-874-F
Krishnaswamy, S. SM-1740-P
Kristoffer Lindheim, T. SM-573-O
Kroeger, A. SM-177-O
Kroeker, S. SM-970-F
Kroitor, A. CB-863-F
Kroll, Th. FB-792-I
Kronenberger, S. ES-215-K
Krueger, J.-D. ND-1634-P
Krüger, H.-J. ***ND-152-O***, MM-1512-P
Kruse, J. ***CB-1129-P***
Kubas, A. MM-188-O
Kubíček, V. BM-138-O, ND-563-O BM-368-O, BM-1040-P
Kubicki, D. ND-437-O
Kubicki, M. FB-694-O
Kubota, J. ***ES-1233-P***
Kubus, M. SM-472-O, ND-1605-P
Kucharska, B. FB-593-O
Kühne, I. ND-151-I ***ES-267-O***, MM-385-I
Kulik, H. ***MM-761-K***
Kumah, R. CB-748-I
Kumar, A. CB-222-O SM-1740-P, CB-505-K
Kumar, H. ND-665-I
Kumar, K. ES-141-I
Kumar, R. MM-585-K
Kumar, S. ***MG-1436-P*** SM-077-O, SM-1731-P
Kumari, A. ***MG-1405-P***, CB-1150-P
Kumari, M. CB-228-I
Kumawat, M.K. ***BM-1035-P***
Kuncová, L. ND-563-O, ***BM-368-O***
Kundu, S. ***CB-022-O***, CB-1106-P MG-1408-P, ***MG-1401-P***
Künstner, S. MM-388-O
Kunz, D. ES-1234-P
Kunze, K. MM-684-O, ***CB-1133-P***
Kupfer, S. MM-1506-P MM-684-O, ***CB-108-O***
Kurashige, Y. ND-1633-P
Kurz, H. ***SM-1717-P***
Kurzydłowski, D. MM-581-I
Kushwaha, R. SM-1710-P SM-1703-P, ***SM-1732-P***
Kutin, Y. MG-1430-P
Kuzman, D. ES-1235-P ES-1267-P, ***ND-1616-P***
Kuzume, A. ND-654-O
Kvashnina, K. FB-990-F
Kwon, Y. CB-028-I
Kyzioł, A. BM-113-O, BM-533-O

L

La, N. BM-534-I
Lada, Z. ND-151-I
La Ganga, G. CB-1107-P, CB-1120-P
Lakhwani, G. ES-262-O, SM-1701-P
Łakomska, I. ***BM-1018-P***
Lalaoui, N. CB-223-O, ES-462-K
Lamač, M. CB-624-O
Lamb, R. CB-707-O
Lambert, C. ES-1203-P
Lambert, F. ND-052-O, ND-1618-P
Lamothe, E. ES-1202-P
Land, M. MG-037-O
Landrau-Correa, L. BM-018-I
Langen, S. ***BM-1046-P***
Langner, E. ES-1243-P
Lanza, A. CB-406-O
La Pierre, H. ***ND-561-K***
Lara, J. CB-622-O, CB-1103-P
Lara Belaunzaran, R. ND-492-O
Larsen, Ch. ***MM-788-I***
Larsen, Ch.B. BM-736-O
Larsen, F.T. ***SM-1715-P***
Łaski, P. ES-041-I
Lata, S. SM-1703-P
Latouche, C. ES-1249-P
Laurent, S. BM-234-O
Law, G.-L. BM-1050-P, FB-1311-P
Law, J. CB-327-O
Lawrence, S. MG-940-F
Lay, P. ***BM-135-I***, BM-333-O
Layfield, R. ND-667-O
Lazarevski, B. ***ES-412-O***
Lazarides, T. BM-63A-O, ***FB-691-I***
Lazarová, J. BM-368-O
Leal, W.G.D.S. BM-334-O
Leblay, R. ES-1261-P
Lebrette, H. MM-585-K
Lebruška, V. ***BM-138-O***
LeComte, A. ***CB-1110-P***, ***CB-627-O***
Lee, A. ***SM-1702-P***, MG-1426-P
Lee, E. ***MG-341-I***
Lee, H.K. FB-1304-P
Lee, J. ***SM-073-O***
Lee, M.H. ***MG-442-O***
Lee, Y.H. MG-442-O
Lee, Y. ***MM-1515-P***
Lefèvre, G. CB-1174-P
Lefroy, K. BM-723-O
Le Fur, E. ND-1614-P
Le Gendre, P. ES-143-O
Le Goff, A. CB-127-O
Le Guennic, B. FB-794-O, FB-592-O
Lehmann, M. FB-1313-P
Lehtonen, A. ***CB-1108-P***, SM-1705-P
Leihad, M. CB-747-O
Leimkühler, M. ***ES-1241-P***
Lemanski, K. ***SM-971-F***
Lempereur, S. ND-960-F
Lempinen, A. MG-243-O
Lemus, L. ES-313-O
Leng, K. CB-743-O
Lenzi, C. ***ES-842-F***
León Alcaide, L. ***SM-478-I***, SM-971-F
León-Alcaide, L. SM-275-K
Lepage, M. SM-173-O, ES-1202-P
Lerche, J. FB-692-O
Leroy, J. ***MM-881-F***
Les, M. MG-643-O, ***ND-1628-P***
Lesiów, M. ***BM-132-O***
Leskes, M. ***MM-281-I***
Leung, C.-F. ***BM-871-F***
Levina, A. BM-135-I, BM-333-O
Lewis, J. ***SM-076-O***
Lewis, R.J. MM-586-O
Lewis, W. SM-1701-P
Leznoff, D. FB-698-O
Leznoff, D.B. SM-970-F
L'Hôpital, E. ***ND-1617-P***
Li, B. ES-147-O
Li, C. ***MM-766-O***
Li, M. CB-165-I
Li, X. ***ND-493-O***, CB-165-I
Li, Y. ***MM-1514-P***
Li, Y.-X. CB-021-I
Li, Z. ES-147-O MG-1417-P, MG-1407-P
Liao, P-Q. CB-1130-P
Liao, P.-Y. ***ND-352-O***
Liao, R.-L. CB-1113-P
Liao, R.-Z. ***CB-305-I***
Liberka, M. ND-753-O
Lichtenberg, A. ***ND-093-O*** ***ND-1601-P***, ND-890-F
Lichtenberg, C. MG-1410-P
Licini, G. ***ES-511-K***
Liddle, S. ***ND-661-K***
Liebschner, D. MM-585-K
Liedtke, S. ES-411-I
Ligielli, I. ***CB-856-F***
Lim, L.F. ***MG-1424-P***
Lim, M.H. ***BM-130-K***
Lima, F. MM-686-K

Limberg, Ch. ***CB-708-I*** CB-1126-P, ND-1639-P MG-1435-P, FB-1313-P
Limberg, N. ***ND-457-O***
Lin, M. ***ES-1246-P***
Lin, R. ***CB-1153-P***, CB-401-I
Lin, Y.-F. ***BM-1049-P***
Lin, Y.-H. ***ES-1269-P***
Lin, Y.-T. ES-1240-P
Lindén, J. SM-1705-P
Lindner, J.-P.B. ES-879-F
Lindsay, C. ***MG-546-O***
Lips, K. MM-388-O
Liptak, J. CB-1128-P
Liptrot, D. ES-617-O, ***MG-547-O*** MG-851-F, MG-1429-P
Lištiak, M. ***BM-1039-P***
Litak, N. ES-515-K
Liu, C. ***MG-1407-P*** ND-396-K, FB-695-I
Liu, F. SM-378-O
Liu, L.L. ***MG-646-K***
Liu, Y. MM-288-I
Liu, Z. MM-181-I
Liuzzi, F. ES-930-F
Lizak, W. BM-133-O, ***CB-1171-P***
Llanos, L. ES-313-O
Llobet, A. CB-226-O
Lloret-Fillol, J. CB-227-O
Lock, N. ***SM-574-I***
Lo Leggio, L. MM-181-I
Lomoth, R. ES-1247-P
Long, D.-L. ***CB-061-I***, ***ND-1602-P***
Long, N. CB-002-O BM-364-O, BM-722-I ES-147-O, BM-1008-P ES-1203-P, ***BM-335-I***
Looks, C. ***ND-1612-P***
Lopez, R. CB-505-K
López, X. ***ND-391-I***
Lopez-Martin, A. MM-586-O
Lord, R. ***BM-118-O***, BM-1010-P
Lord, R.M. BM-866-F
Lorent, Ch. FB-1315-P, MG-1406-P
Lorenz, J. ***ND-898-F***
Lorenzon, T. ***BM-869-F***
Losada, I.B. ES-411-I
Lotsch, B. SM-273-O, ND-556-O
Lotsch, B.V. SM-377-O, MM-763-O
Lottes, B. MM-283-O
Louvain, N. SM-372-O
Lovelock, K. MG-547-O, MG-1429-P
Lowe, M. ***ND-437-O***, MG-1428-P
Lozada, I.B.M. ***MM-682-O***
Lozinšek, M. ***MM-581-I***
Lu, C. CB-1132-P
Lu, E. ***ND-436-O*** MG-853-F, ND-437-O MM-880-F, MG-1428-P
Luboradzki, R. MM-188-O
Lucas, A. CB-307-O
Luckay, R. ***ES-142-O***
Lüderitz, H. ***CB-1126-P***
Luis, F. ND-252-O, SM-476-O
Luis, J.M. CB-006-O, CB-107-O
Luneau, D. ***SM-471-I***
Luo, Q. ***MG-1439-P***
Luo, T.-Y. FB-695-I
Lusby, P. SM-1734-P
Lutfi, R.M. MG-442-O
Lutz, M. ES-048-I MM-482-O, CB-428-I
Lutz, S. ***ES-1257-P***
Lynam, J.M. ES-840-F

M

Ma, L. CB-165-I
Ma, M. BM-364-O ***BM-722-I***, BM-1008-P
Ma, X.-F. SM-376-K
Macchioni, A. ES-144-O
Macdonald, C. ***MG-037-O***
Macgregor, S. ND-553-O
Machado, I. BM-114-O
Machan, C. ***CB-504-I***
Machura, B. ND-1621-P
Maciejewska, N. BM-1026-P, BM-870-F
Maciel Wurzer, K. BM-112-O
MacKenzie, R. FB-792-I
Macpherson, J. MM-284-I
Macreadie, L. ***SM-278-I***, SM-272-O
Madabeni, A. ***CB-207-O***
Magott, M. ***ND-157-O***, ND-963-F
Mahapatra, S. ***CB-1155-P***
Mahato, S. SM-970-F
Mahawar, P. ND-665-I
Mahon, M. MG-547-O
Mailman, A. CB-1159-P
Maiti, D. CB-1167-P
Majchrzak, R. ***MG-446-O***
Maji, S. BM-1035-P ES-1231-P, ES-1259-P ES-1243-P, ***ES-1256-P***
Majumdar, M. ***MG-645-I***
Majumder, C. ***MG-1408-P***
Malacea, R. ***ES-143-O***
Malček Šimunková, M. BM-1039-P
Maldeni Kankanamalage, B.K.P. SM-676-K
Maldonado, M.J. FB-598-I
Male, L. MM-880-F
Malec, L. ND-157-O
Malhotra, J.S. ***SM-672-O***
Malikidogo, K.P. BM-723-O
Malischewski, M. ***ND-458-I***, ND-452-O
Mallah, T. ND-052-O ND-1618-P, ND-1627-P
Mallouk, Th. CB-505-K
Mamat, C. BM-1002-P
Mamedov, F. CB-427-O
Mamonov, K. BM-1014-P
Man, W.-L. BM-871-F
Managh, A. BM-866-F
Mandal, D. ES-1220-P BM-1031-P, ***ES-1216-P***
Manicum, A.-L.E. ***BM-1004-P***
Mann, M. SM-177-O
Manoury, E. CB-163-O
Manu, A. BM-631-I
Mao, W. ***FB-1315-P***
Maqueda-Márquez, H. ND-752-I
Marchetti, L.A. ***BM-723-O***
Marchiò, L. FB-1301-P
Marchivie, M. MM-889-F MM-483-O, ES-1225-P
Marcinkowski, D. FB-694-O
Marco, J.F. ND-1614-P
Mari, M. ND-566-O
Marinescu, S. ***CB-225-K***
Maris, T. FB-1314-P
Marker, S. ES-044-I
Markham, S. BM-135-I BM-333-O, ND-892-F
Maron, L. FB-1306-P, FB-1307-P ND-664-O, ND-052-O FB-697-O, CB-401-I
Marrero-Robles, C. BM-018-I
Marrero-Robles, C.I. BM-1007-P
Martín, A. ND-456-O
Martin, C. ***MG-246-O***
Martin, D. MG-943-F
Martínez, Ó. ND-964-F
Martínez-Martínez, A.J. MG-1414-P, SM-1729-P
Martín Quiles, V. ***ND-953-F***
Martín-Vaca, B. ES-616-K
Martynov, A.G. CB-863-F
Masaoka, S. ND-950-F ND-654-O, SM-1710-P
Masip-Sánchez, A. ND-391-I
Masliy, V. ***ES-878-F***
Mason, H. MM-385-I
Masternak, J. BM-1026-P MM-188-O, ***BM-870-F***
Masuyama, T. ND-1642-P
Mateo de la Fuente, H. MM-683-O
Mathonière, C. ND-157-O

Mathur, S. ND-093-O
ND-094-K, ***ES-1259-P***
ND-1601-P, ND-890-F
Matic, E. ***SM-1714-P***
Matinise, N. ES-142-O
Matoga, D. SM-772-I
Matsinha, L. ***SM-274-I***
Matson, E. ***ND-395-I***
Matsumoto, T. ***ES-615-I***
Matsuzaki, T. SM-1710-P
Matsuzaki, Y. BM-718-I
Matuszak, K. ***ES-1236-P***
Matys, O. CB-858-F
Mauceri, M. ND-1619-P
Maulbetsch, T. ES-1234-P
Maury, O. FB-592-O
Maurya, A.K. MM-183-O
Mauß, J.M. MM-586-O
Mavragani, N.
FB-1314-P, ND-1605-P
Mazuryk, O. CB-303-O
BM-714-O, BM-711-K
Mazzanti, M. ND-664-O
FB-697-O, FB-1316-P
FB-1305-P, ***PL-3***
Mazzeo, P.P. SM-972-F
Mazzoni, R. ES-842-F
McAdam, C.J.
ES-1227-P, ES-1271-P
McClain, T. CB-707-O
McConnell, A. ***SM-078-I***
McCubbin Stepanic, O.
MM-682-O
McCusker, J. ***ES-316-K***
McCusker, J.K. CB-067-O
McDonald, A.
CB-602-O, ***MM-481-I***
McDonald, A.R. CB-003-O
McGarrigle, E. BM-714-O
McGettigan, D. ***CB-855-F***
McGorman, B. BM-738-I
McGowan, P.C. BM-866-F
McInnes, E. ND-495-K
McKay, A.
MG-348-O, MG-940-F
McKay, A.P. MG-993-F
McKay, L. ***SM-1725-P***
McKenzie, Ch. SM-1715-P
CB-406-O, CB-603-O
McKenzie, Ch.J. BM-363-O
BM-1029-P, BM-1012-P
McLauchlan, C.
ND-892-F, ES-1224-P
McMahon, C. BM-722-I
McManus, C. MG-545-K
McMaster, J. ES-843-F
McMullin, C. MG-1428-P
McPeak, J.E. MM-388-O
McPherson, J.
SM-1715-P, SM-1741-P
Meade, Th. ***BM-235-K***
Medak Spahić, G. ND-1616-P
Mehta, G. CB-1138-P
Meier, D. ***MG-648-O***
Meijer, A. MM-686-K
Meikle, I. MM-686-K
Meinhold, P.R. CB-1137-P
Meißner, M. ***ES-1243-P***
Melegari, M. FB-1301-P
Mello, L. ***CB-857-F***
Melnikov, S. ES-048-I
Menargues-Sanz, N. SM-275-K
Mendoza-Baez, R. ***MM-887-F***
Menendez-Navarette, C.
BM-018-I
Mengele, A.K. BM-1037-P
CB-1136-P, ES-1268-P
Menjón, B. ND-456-O
Mercado, B. CB-983-F
Merimi, K. ND-391-I
Merlino, A. ***BM-016-O***
Mesárošová, M. BM-1039-P
Mesdom, P. ES-044-I
Messori, A. ES-842-F
Messori, L. ND-992-F
Metzger, Ch. ND-152-O
Meurer, F.
MG-032-O, ND-661-K
Meyer, F. MM-288-I, CB-308-O
CB-005-K, CB-1129-P
CB-934-F, MM-1512-P
Meyer, K.
MM-295-K, CB-626-K
Meyerstein, D. ***CB-307-O***
Meyran, Ch. ES-1243-P
Mézailles, N. CB-628-O
M. Guillaume, S. ES-878-F
Miao, Q. MM-286-O
Michaud-Soret, I. ***BM-116-K***
Miecznikowski, J. ***CB-983-F***
Miguel-Casañ, E. SM-1716-P
Miller, A.
CB-222-O, CB-1172-P
CB-505-K, ES-1224-P
Miller, P. ES-1244-P
Milne, Ch. MM-686-K
Min, K. ***FB-596-O***
Minato, T. ***ND-096-O***
CB-861-F, ND-951-F
Mindiola, D.J. ***CB-626-K***
Mínguez Espallargas, G.
SM-478-I
ES-266-O, SM-1712-P
SM-1716-P, ***SM-275-K***
Miquel Fosco, P. ***BM-733-O***
Miqueu, K.
CB-1142-P, ES-616-K
Miranda, M. ND-391-I
Mironova, O. ***ND-358-O***
Mirtcheva, G. BM-867-F
Misakabu, F. BM-1016-P
Misawa, A. BM-1025-P
Misawa, H. BM-1025-P
Mishra, A.
ES-1245-P, ES-1211-P
ES-1205-P, ***ES-1208-P***
Mishra, R. BM-718-I
Mishra, S.S. SM-1740-P
Miura, A. ND-096-O
Miyamoto, S. ***ES-877-F***
Miyasaka, H. ***ND-058-I***
Miyata, K. ES-1263-P
ES-1264-P, ES-1266-P
Mochimaru, T. ES-1263-P
ES-1264-P, ***ES-1266-P***
Mochizuki, S. ND-092-O
Moeller, H.E. BM-336-K
Moeller, J. ***CB-1131-P***
Mogale, R. ES-044-I
Moggach, S. ES-1223-P
Mohan, S. ***CB-1159-P***
Mohr, F.
BM-337-O, SM-1735-P
Moilanen, J.O. ***FB-796-O***
Moir, Ch. FB-792-I
Moise, G. MM-1509-P
Mollasalehi, S. ND-451-I
Møller, K.B. ***MM-782-I***
Møller, M. ***CB-406-O***
Mollo, M.C. BM-114-O
Molnar, G.
ND-751-K, MM-292-O
M. Omweric, J. BM-727-O
Monakhov, K. ND-898-F
Moncoľ, J. BM-1039-P
Mondal, B. ES-1212-P
Mondal, J. CB-1138-P
Mondal, S.
SM-1736-P, CB-933-F
Monot, J. ES-616-K
Montañez Valderrama, V.A.
ES-1202-P
Montilla-Suárez, J.M.
BM-134-O
Moon, H.W. ***MG-441-I***
Moonshiram, D. ***MM-681-I***
Moore, E.G.
CB-1146-P, MM-884-F
Moors, M. ND-898-F
Mordzińska-Rak, A. BM-533-O
Moreira, R. BM-114-O
Morello, M. ***ES-1242-P***
Moret, M.-E. ***CB-428-I***
Morgan, G. ***ND-151-I***
ES-267-O, MM-385-I
Morgan, G.G. ND-1613-P
Morgan, J. ***MG-1416-P***
Morgat, C. BM-726-O
Morikawa, T. ES-1238-P
Morisaki, Y. BM-1025-P
Moriuchi, T. ***ES-516-O***
ES-1233-P, SM-1739-P
Morrell, A. BM-722-I
Morrow, J.
BM-631-I, ***BM-1001-P***
Morrow, M. CB-504-I
Morshedi, M. MM-783-O
Mortreuil, N. MG-851-F
Moscoso, F. ES-313-O
Mosely, J. ES-042-O

Mossin, S. MM-885-F, MM-282-O
Motaln, K. MM-581-I
Motornov, V. ***ND-453-O***
Moudrakovski, I. ND-556-O
Mougel, V. ***ES-461-I***
Mounir, M. ND-494-I, ND-897-F
Mourik, T. MG-940-F
Moussawi, M.A. ND-396-K
Moya-Cabrera, M.M. CB-1169-P
Mucci, A. SM-576-O
Mucignato, Ch. ***SM-1711-P***
Muderspach, S. MM-181-I
Mudiyanselage, S. SM-177-O
Mueller, Ch. ***ND-438-I***
Mugnaioli, E. SM-972-F
Muhler, M. CB-523-O
Mujahed, S. ND-657-O
Mukai, N. ***MG-447-O***, MG-944-F
Mukherjee, C. ***BM-725-I***
Mukherjee, P. ***SM-075-K***
Muldoon, P.F. FB-695-I
Mullaliu, A. ND-393-O
Müller, J. ***BM-731-K***
Müller, L. CB-708-I, CB-523-O
Müller-Bunz, H. ND-151-I, ND-1613-P
Muñoz, K.S. BM-134-O
Munro, O. MM-488-I, MM-1507-P
Munz, D. ***MG-445-K***
Murakami, H. BM-333-O
Murakami, R. ES-1237-P
Muraki, N. BM-1038-P
Muratsugu, S. CB-1102-P, CB-062-O
Murayama, Y. ***ES-213-O***
Muresan, N. ES-042-O
Murugesu, M. FB-796-O
Musija, D. ES-1267-P
Musioł, M. ND-963-F
Müßler, M. ***BM-1037-P***
Mustafaj, F.R. BM-1015-P
Mustafar, S. ND-1638-P
Muttenthaler, M. MM-184-O
Muzioł, T. ES-1220-P, ES-1216-P
Muziol, T.M. BM-1031-P

N

Naaman, R. SM-576-O
Nadal-Moradell, J. CB-1115-P
Nadeem, R. ES-145-I
Näder, A. FB-990-F
Nagamine, A. CB-062-O
Nagendran, S. MG-1437-P
Nagy, T. MM-083-O
Naher, M. ***CB-124-O***
Nakabayashi, K. ND-1626-P
Nakajima, H. ES-1237-P
Nakajima, K. CB-062-O
Nakamura, K. ***ND-1626-P***
Nakane, D. ES-213-O
Nalaoh, P. SM-271-I
Nam, W. ***CB-601-I***, CB-202-O
Napoli, F. ND-893-F
Napoli, F.E. ***ND-894-F***
Narouz, M. CB-1103-P
Nastasi, F. CB-1120-P
Nataloni, A. ES-144-O
Natan, A. CB-707-O
Nathan, M. MM-788-I
Natrajan, L.S. ND-661-K
Natt, N. MM-293-O
Naumann, R. ES-1234-P, ES-215-K
Navalon, S. SM-378-O
Navarro, L. ND-053-O
Nazar, P. BM-1017-P
Ndiaye, D. BM-330-K
Ndima, L. SM-1743-P
Neale, S. MG-547-O
Neben, M. MM-387-O
Nebra, N. ND-456-O
Neese, F. SM-1718-P, MM-385-I, ***PL-6***
Neidig, M. ND-1622-P, CB-706-O
Nelson, C. BM-236-O
Nelson, J. ***FB-1309-P***
Nelyubina, Y. FB-797-O
Němec, V. MG-443-O
Nenova, E. BM-338-O
Neubauer, F. SM-273-O
Neumann, C. ***ND-558-I***
Neumann, C.N. ND-652-O
Neumann, R. CB-304-O
Neumann, T. ***CB-526-O***
Neuwirt, M. MG-036-O
Newton, G. ND-197-O, ND-896-F, ND-895-F, SM-971-F
Newton, G.N. ES-843-F
Ng, Z.J.G. ***MG-1411-P***
Nguyen, D. ***ND-432-O***
Nguyen, L.H.B. SM-372-O
Nguyen, T.-V. ES-143-O
Ni, L. MM-287-O
Ni, W.-X. BM-871-F
Nicaise, O. CB-983-F
Nichol, G. MG-1431-P, CB-1151-P
Nichol, G.S. CB-858-F
Nickel, Ch. ES-611-I
Nicolini, A. ND-358-O, ***SM-576-O***
Nidinji Kushalappa, N. SM-1738-P
Nielsen, C.B. CB-068-I
Nielsen, M. ***CB-027-O***
Nikolaou, S. BM-1017-P
Nikonov, G. ***MG-033-O***
Niorettini, A. BM-1034-P, BM-113-O
Nishad, R.C. SM-077-O
Nishiyama, S. SM-678-O
Njayappallil, V.A. SM-1706-P
Nkabyo, H. BM-1003-P
Nocton, G. ***ND-494-I***, ND-897-F, ND-663-O, FB-1306-P, FB-1307-P
Nogueira, J.J. MM-683-O
Nolan, S.P. ES-1217-P
Nomoto, A. ***MG-1403-P***
Nonaka, T. ES-1238-P
Nordlander, E. ES-141-I, CB-747-O, ***CB-105-I***
Nørholm, M. MM-181-I
Norton, E. ND-492-O
Nova, A. CB-322-O, CB-302-O, ***CB-321-I***
Nova, N. ES-1261-P
Nova-Fernández, J.-L. SM-1716-P
Novák, L. MM-083-O
Novikov, V. ND-355-I, ND-252-O, FB-797-O, ***MM-383-O***
Nowak-Król, A. CB-1140-P
Nowakowska, M. ***BM-737-O***
Nowicka, B. ES-1226-P
Nucera, A. BM-1009-P
Nuñez Bahena, E. CB-306-K
Nüsing, J.F. ND-754-O
Nutting, C. SM-1708-P
Nyman, M. ***ND-196-K***, BM-732-I
Nymberg, L. CB-857-F

O

Obora, Y. CB-1145-P
O'Brien, D.J. ***MM-884-F***
Odenwald, C. ES-1241-P
Oduro, A. BM-1042-P
Ogar, J. SM-971-F
Ogawa, T. MG-037-O, ES-412-O, ***MM-687-O***, ES-1263-P, ES-1264-P, ES-1266-P
Ohkoshi, S.-I. ND-753-O, ND-051-I, ES-314-O, ND-1626-P
Öhrström, L. SM-473-O, SM-675-I, SM-1709-P
Ohta, S. ***SM-678-O***
Ohtani, R. ***ND-757-O***

Ohto, T. ES-1204-P
Ojwach, S. ***CB-748-I***
Okada, K. SM-677-O
Okata, S. ES-875-F
Okazaki, M. SM-678-O
Okła, K. ***BM-1026-P***, BM-870-F
Okubo, H. ***SM-1719-P***
Oladipo, S. ES-142-O
Oldknow, S. SM-072-O
Ole Johnsen Laugerud, J. SM-573-O
Olguin, J. MM-887-F
Oline Kjus Joa, H. SM-573-O
Oliva Rivera, A. ND-1617-P
Oliveira, A.P.A. BM-334-O
Oliveira-Filho, A. MM-883-F
Oliver, A. ES-313-O
Olsbye, U. CB-302-O SM-573-O, ***SM-575-K***
Onda, K. ES-1263-P ES-1264-P, ES-1266-P
Oppermann, M. ***MM-785-I***
Oram, L. SM-974-F
Orecchia, P. ES-879-F
Orio, M. ***MM-088-I***
Orta-Rivera, A. BM-018-I
Ortí, E. ES-266-O
Osei, M. BM-534-I
Osuga, R. CB-062-O
Otero-García, L. BM-1009-P
Ott, S. ***ES-468-I***
Otte, M. ***ND-557-O***
Otting, G. MM-381-I
Oyama, D. ES-1246-P
Ozawa, Y. ES-1237-P
Ozerov, M. MM-385-I

P

Pacoste, L. ***MM-585-K***
Pagliero, M.C. ND-358-O
Paine, T.K. CB-1155-P
Pal, S. CB-1103-P
Pal, T. ***MM-763-O***
Palatinus, L. MM-581-I
Paliwoda, D. ND-751-K
Pallier, Á. BM-723-O BM-362-O, MM-083-O
Pallierd, Á. BM-330-K
Palmeira-Mello, M.V. BM-134-O
Paloc, S. ND-494-I, ***ND-663-O***
Palomino, L.P. BM-1012-P
Palone, A. CB-107-O
Pan, C. BM-871-F
Pan, Y. ES-268-I
Panagini, F. SM-872-F
Panagiotou, N. SM-1704-P
Pander, M. SM-772-I
Pandey, D. CB-1150-P
Pang, Y. ***ND-664-O***, FB-1316-P
Panizzi, A. ***FB-1301-P***
Pantazis, D. ***MM-764-O***
Panwar, P. ***CB-1148-P***
Papaefstathiou, G. SM-1704-P
Papajewski, M. ES-614-O
Papaldo, M. ***BM-1036-P***
Papangelis, E. ***FB-1306-P***, CB-856-F
Paparakis, A. MM-880-F
Parac-Vogt, T. ***ND-396-K***
Parac-Vogt, T.N. ND-393-O
Parammal, M.J. ND-393-O, ***ND-1631-P***
Parche, J. ***ND-452-O***
Paredes-García, V. ND-1614-P, ***SM-1742-P***
Paria, S. ***CB-608-O*** CB-1150-P, CB-1117-P
Park, B. ES-048-I
Parker, L. MG-547-O MG-851-F, MG-1429-P
Parra Cabrera, C. SM-778-I
Paschai Darian, L. ***CB-1134-P***
Pascual-Borràs, M. ***ND-193-O***
Pask, Ch. MM-1507-P, ND-1611-P
Patel, N. BM-722-I
Patel, P. CB-001-I
Paterson, B. BM-722-I
Patlolla, C.K. ***SM-1709-P***
Patra, A. FB-1302-P
Patra, U. ***SM-1741-P***
Patroniak, V. FB-694-O
Patterson, C. CB-206-O
Patzschke, M. FB-990-F
Pavic, A. BM-1015-P
Pavliuk, M. CB-427-O
Pavlova, E. ***BM-338-O***
Pawlig, A. ES-614-O
Peacock, A. BM-724-O
Pearce, J. ***CB-527-O***
Pearce, K. MG-851-F
Pecault, J. MG-943-F
Peck, L. MG-035-K
Pecoraro, V. FB-595-K
Pedersen, K. SM-472-O, ***ND-353-O*** MM-885-F, BM-726-O
Pedersen, K.S. BM-137-O ND-1640-P, FB-1314-P ND-1605-P, FB-798-I
Peeks, M. SM-177-O
Pelagatti, P. SM-972-F
Pell, E. ***BM-1010-P***
Pelosi, G. BM-1030-P
Penner-Hahn, J. CB-707-O, MM-685-I
Peredkov, S. MM-586-O
Perego, J. SM-775-I
Pérez-Bitrián, A. ND-457-O
Pérez-Romero, A. BM-732-I
Perfetti, M. ND-253-O ND-496-O, MM-283-O FB-795-I, FB-1310-P ND-992-F, ***ND-498-I***
Peris, M. CB-206-O
Perrin, M.-E, MM-881-F
Personeni, T. CB-628-O
Persson, P. ***ES-411-I***
Petkova, D.S. ES-879-F
Petoud, S. FB-691-I FB-595-K, ***FB-695-I***
Petrenko, Y. ND-357-O
Petroselli, M. BM-726-O
Petrovskii, S. ND-898-F
Petrus, E. ND-099-I
Petrus, R. ES-1236-P
Petrus Joseph Groenewegen, N. SM-573-O
Peuronen, A. CB-1108-P, ***SM-1705-P***
Pezzoli, G. BM-336-K
Pfund, B. ***CB-067-O***, ES-412-O
Pham, T. BM-722-I
Philippot, K. CB-163-O
Phillips, A. MM-296-O, ***ES-517-O***
Philouze, Ch. MG-943-F
Piacenza, P. BM-726-O
Piazzi, A. ES-842-F
Piccoli, A. BM-634-O
Pichugov, A.V. CB-526-O
Pickl, Th. BM-635-I
Pico-Pérez, A.R. ***MG-1404-P***
Piedrahita-Bello, M. MM-292-O
Pierre, V. ***BM-636-K***
Pietschnig, R. ***MG-548-I***
Piggott, M. ES-1223-P
Pike, S. ND-1622-P, ND-1625-P ND-1607-P, ND-1604-P ND-1610-P, ***ND-191-I***
Pikramenou, Z. ***FB-594-I***
Pilgrim, B. ***CB-161-I***
Piligkos, S. ND-256-O, FB-692-O
Pin Bonfanti, A.C. ***MM-1501-P***
Pinelli, S. BM-1030-P
Pinkas, J. CB-624-O
Pinkowicz, D. ES-1245-P ND-157-O, ***FB-791-K***
Pinter, B. ND-1640-P
Pisk, J. ES-1267-P
Piva, S. SM-775-I
Pižl, M. ES-315-I
Plackic, N. BM-1015-P
Pladzyk, A. MM-1504-P
Planas, O. ***MG-345-I***
Plaß, F. ***CB-1122-P***
Plass, W. ND-055-K

Platas-Iglesias, C. BM-727-O, BM-330-K, MM-182-O, BM-367-O, BM-362-O, ***BM-366-K***, BM-1005-P
Pleiss, J. SM-273-O
Ploetz, E. SM-772-I
Plutenko, M. CB-427-O
Poater, A. CB-006-O
Pointillart, F. ***FB-794-O***, FB-592-O
Poitoz, Ph. SM-372-O
Polasek, M. MG-1415-P
Poli, R. CB-163-O
Policar, C. BM-1030-P
Poller, M.J. ***ES-614-O***, ND-1634-P
Polonini, V. BM-1017-P
Ponikiewski, Ł. MM-1504-P
Poon, B. MM-585-K
Popenda, Ł. ES-1217-P
Popielarski, P. BM-1031-P
Poradowski, M.-N. MM-881-F
Porter, J. MG-647-O
Portes, M.C. BM-334-O
Portiolli Franco, M. ***CB-322-O***
Potempa, K. ES-041-I
Pöthig, A. ***BM-635-I***
Powell, A. ***ND-435-K***
Powell, A.K. SM-1706-P
Powell, B. MM-293-O
Powers, D. ***ND-552-O***
Powers, R. CB-222-O
Pragati, P. FB-697-O
Prajapati, F. MM-483-O, ***ES-1225-P***
Prakash, D. CB-605-I
Pražáková, M. ***BM-332-O***
Přeček, M. ES-315-I
Prescimone, A. ND-1631-P, ES-1230-P
Prętka, D. ***FB-694-O***
Price, Th.W. BM-728-I
Pritchard, C. ***SM-1708-P***
Pritchard, V. SM-072-O
Privault, G. ND-051-I, ND-1626-P
Prock, L. MG-032-O
Proft, F.D. ND-1607-P
Proserpio, D.M. SM-273-O
Pryce, M. CB-303-O
Psalti, A. FB-691-I
P. Tidey, J. SM-1732-P
Pucelik, B. BM-1045-P
Puchoňová, M. BM-1039-P
Puerta Lombardi, B. MG-1426-P
Pugh, D. SM-974-F
Puig, E. ES-1206-P
Pullen, S. ***CB-068-I***
Pulparayil Mathew, J. ND-1631-P
Punbyo, N. ***ND-1635-P***
Puntoriero, F. CB-1120-P
Purkait, K. ES-044-I
Puthiyadath, A. CB-001-I

Q

Qi, M. MM-381-I
Qi, Z. ***FB-792-I***
Qian, Y. ES-612-O
Qianzhu, H. MM-381-I
Qin, Y.-H. SM-376-K
Qomfo, V. ***SM-1743-P***
Quesada-Román, L. CB-221-I
Queyriaux, N. CB-1142-P
Quintanar, L. ***BM-136-I***

R

Raabe, J.-Chr. ES-614-O
Rabiller-Baudry, M. ES-878-F
Race, E. MM-686-K
Radan, K. MM-581-I
Radius, U. ***ND-454-I***
Ragaini, F. ES-513-O
Rahman, M.M. ES-1252-P
Rai, A. CB-605-I
Raibaut, L. BM-330-K
Raimbault, D. FB-795-I
Rajaraman, G. CB-933-F
Rajeshkumar, T. ND-664-O, ND-052-O
Rajnák, C. ND-1621-P
Rajora, A. SM-577-O
Ralle, P. ***ES-1251-P***
Ramachandran, A. CB-1167-P
Ramadan, D.R.M. ES-513-O
Ramchandran, R. BM-339-I
Ramirez Hernandez, J.J. SM-378-O
Ramogida, C.F. BM-362-O
Ranga, M. ***BM-727-O***
Rani, A. SM-577-O
Ranieri, A. ND-358-O
Rao, G. CB-622-O
Raptis, R. BM-865-F
Rapuš, U. ***BM-1048-P***
Rasheed, S. SM-071-I
Rasmussen, B. CB-707-O
Rath, S.P. MM-1503-P
Rau, S. BM-1037-P, CB-1136-P, ES-1268-P
Raue, K. MM-285-K, ***MM-1511-P***
Raveendranathan, A. ***SM-1706-P***
Ray, K. ***CB-702-I***
Raymond, J. BM-1001-P
Raza, A. ND-253-O
Réant, B. ND-495-K
Reato, M. ND-1619-P
Reczyński, M. ***ND-963-F***
Redrado, M. BM-713-O
Reger, J. ES-268-I
Réglier, M. ES-1261-P
Reichert, P. SM-1721-P
Reid, G. ***BM-361-I***
Reijerse, E. MM-287-O
Rein, A.St.J ES-1268-P
Reinholdt, A. CB-932-F
MG-038-I, ND-1640-P
Reisner, E. ***PL-2***
Reiß, F. ***CB-522-O***, CB-1141-P, CB-1125-P, CB-1162-P, CB-626-K
Reissner, M. MM-291-I
Reithofer, M. CB-859-F
Remili, Y. ND-751-K
Remmers, M. ***ND-1630-P***, ND-1629-P
Remoto, P.J.G. ES-1227-P, ES-1271-P
Renouard, T. ES-878-F
Rentschler, E. MM-765-I, ND-154-O, ***ND-351-I***, MM-888-F, MM-1510-P
Renz, F. BM-1039-P
Réocreux, R. ND-651-I
Repo, T. CB-423-O, MG-243-O
Repp, S. ***ND-556-O***
Reyes-Lillo, S. SM-472-O
Rezavand, A. ***MM-293-O***
R. Gamarra, S. ***ES-266-O***
Ribeiro, M. BM-1017-P
Ribson, R. CB-707-O
Richards, E. ***MM-284-I***
Richstein, R. ***CB-859-F***
Richter, S. ES-1243-P
Riddell, I. SM-1725-P
Riedel, S. ND-457-O
Riesinger, Ch. ***MG-347-O***
Rigamonti, A. SM-775-I
Rigonatto Brito, B. BM-112-O
Riisager, A. ES-614-O, CB-163-O
Rimoldi, I. ES-043-O
Riobe, F. MM-889-F
Ripoll, G. ***SM-1716-P***, SM-275-K
Rit, A. ***SM-077-O***, MG-1418-P, CB-1167-P, SM-1731-P
Rivalta, I. ES-842-F
Rivière, E. ND-052-O, ND-1618-P, ND-1627-P
Rizzolio, F. BM-634-O
Roager, F. SM-1715-P
Robb, M. ***MM-296-O***
Robert, M. CB-506-O
Roberts, B.M.W. BM-1037-P
Roberts, R. BM-364-O

Robertson, C. BM-1024-P
Robertson, K. MG-037-O
Robeyns, K. CB-226-O
Robinson, B. ES-1203-P
Roca Jungfer, M. ***ND-668-O***
Rodriguez, I. BM-018-I
Rodríguez, M. CB-1115-P
Rodríguez-Boscà, Ch. SM-275-K
Rodríguez Boscà, Ch. ***SM-1712-P***
Rodríguez-Camargo, A. ***SM-377-O***
Rodríguez-Rodríguez, A. BM-1009-P
Roemelt, M. ***CB-208-I***
Roesler, R. SM-1702-P, FB-1309-P, ES-1221-P, MG-1426-P
Rogalev, A. SM-472-O, ND-496-O, ND-157-O, ND-1640-P, FB-1314-P, ND-1605-P
Rogers, D. MM-886-F
Rohr, Å.K. MM-767-O
Röhs, F.L.B. CB-1122-P
Roller, C.A. ***MG-1409-P***
Romain, C. CB-002-O, ***MG-343-O***
Romanowska, M. FB-793-O
Rominger, F. ES-879-F
Rompel, A. ***BM-015-K***, ND-398-O
Roncarati, E. ES-842-F
Rønnekleiv, S.E. MM-767-O
Rønne-Nielsen, Th. MM-885-F
Rønne-Nielsen, T.K. ***MM-282-O***
Ronningen, T. MM-873-F
Rønnow, H. SM-472-O
Roodt, A. ***CB-328-O***, ES-041-I
Rosa, B. BM-134-O
Rosa, P. MM-483-O, ES-1225-P
Rosca, D.-A. ***ES-046-O***
Roseborough, A. ND-196-K
Rosenberg, C. ***ND-1610-P***
Rosenzweig, A. ***PL-4***
Rosi, N.L. FB-695-I
Rosso, F. SM-872-F
Röß-Ohlenroth, R. ***SM-276-O***
Roszek, K. SM-1720-P
Rouault, T. ***BM-237-K***
Roubeau, O. ND-355-I, ND-252-O, FB-797-O, ND-754-O, SM-1723-P, ND-964-F
Roudani, S. ***CB-1157-P***
Rousselin, Y. ES-143-O
Rouzières, M. ND-358-O, ND-157-O, SM-477-O
Rovaletti, A. MM-081-I
Roy, I. ***ES-1231-P***
Roy, M. ***FB-692-O***, ***MG-1426-P***
Roychowdhury, A. ***MM-1503-P***
Roztocki, K. ***SM-776-O***
Ruben, M. ***ND-255-K***
Rubio Zuazo, J. ND-354-O
Rudd, S. BM-1019-P
Ruer, P.C. ***ES-847-F***, ES-1251-P
Ruffo, F. ES-144-O
Ruiz, E. ND-1603-P
Rulíšek, L. CB-207-O, ND-962-F
Rumfeldt, J. CB-1159-P
Runowski, M. FB-694-O
Rupesh, . ***FB-991-F***
Russelisaac, S. ***CB-1166-P***
Russell, J. ES-1242-P
Russell, J.B. CB-626-K
Russo, S. ES-513-O
Růžička, A. MG-443-O, MG-1402-P
Růžičková, Z. MG-443-O, MG-1402-P
Ryder-Brown, R. SM-274-I
Rydh, A. MM-296-O
Rydz, M. BM-1045-P
Ryndyk, D. ND-898-F
Rzepiela, J. ND-753-O, SM-973-F, ES-314-O

S

Sá, J. CB-427-O
Sabater-Algarra, Y. ES-1225-P
Sabo, E. BM-236-O
Sachan, S.K. SM-577-O
Sączewski, J. ES-1217-P
Sadakane, M. ND-096-O, CB-861-F, ND-951-F
Sadek, M. ES-612-O
Sadowska, P. ***BM-1043-P***
Saedi, P. ***ND-1634-P***
Saggiotti, G. ***ND-1619-P***
Saha, A. ES-1202-P, SM-1707-P
Sahoo, P. BM-631-I
Said, T.A. CB-308-O
Sailer, R. ***FB-698-O***
Saillard, J.-Y. MG-1419-P
Saini, S. BM-727-O
Saito, S. CB-982-F
Sajtos, G.Z. MM-083-O
Sakamoto, N. ES-1238-P
Sakamoto, R. ES-317-O, ES-1262-P, ND-1633-P, ND-1638-P
Salazar Marcano, D. ND-396-K
Salcedo-Abraira, P. SM-372-O
Salles, F. SM-372-O
Sallier de la Tour, N. ND-654-O
Salmon, L. ***MM-292-O***
Salomon Johansen, K. MM-181-I
Salvadori, E. ND-358-O
Samanta, T. FB-593-O
Sambiago, C. BM-866-F
Sammon, L. ***CB-1173-P***
Sanadar, M. BM-330-K
Sanchez, M. ND-553-O
Sanchez, R. ***ES-843-F***
Sanchis-Gual, R. ***BM-715-I***
Sander, J. ***ES-1234-P***
Sanderson, H. ND-494-I, ***ND-897-F***
Sandoval-Pauker, Ch. CB-932-F, ND-1640-P
Sanna, A.L. FB-1301-P
Sansores-Paredes, M.L.G. CB-428-I
Santana, V.T. ***MM-382-O***
Santra, A. ***CB-1104-P***
Sañudo, E.C. ES-263-O, ***ND-354-O***
Sapkota, N. SM-1705-P
Sapnik, A. SM-472-O
Sapnik, A.F. ND-1636-P
Sapre, A. ES-267-O
Sarangi, R. ***MM-588-I***
Sardjan, A.S. MM-085-K
Sarjanović, J. ES-1267-P
Sarkar, A. CB-742-I
Sarkar, B. ES-1241-P, ***CB-228-I***
Sarkar, D. ***ES-1218-P***, ***CB-1117-P***, MG-545-K
Sarma, R. ***CB-103-O***
Sartini, D. FB-795-I, ND-498-I
Sartoris, R.P. MM-382-O
Sasaki, T. ES-1237-P
Sasamori, T. ***MG-034-I***, MG-1403-P
Sasitharan, K. ***SM-374-O***
Sastri, C.V. CB-1148-P, ***CB-604-O***
Satanova, Z. CB-1105-P
Sathyan, H. ***FB-1308-P***
Satish, G. ***ES-840-F***
Sato, K. ***ES-1238-P***
Sato, N. ***ND-1633-P***
Sato, O. ***ND-156-K***
Sato, S. ES-1238-P
Sato, T. ***CB-523-O***
Satukbugra Istek, M. SM-273-O
Saubamea, B. ES-044-I
Sauer, S.P.A. BM-1036-P
Savitsky, A. MM-381-I
Sawallisch, T. ***FB-990-F***
Sawka, J. ***ND-1621-P***

Sazanovich, I. MM-686-K
Scalese, G. ***BM-114-O***
Scattolin, Th. BM-634-O, BM-869-F, BM-868-F
Schafer, L.L. ***CB-525-K***
Schäfer, T. BM-731-K
Schatzschneider, U. ***ES-417-O***
Schaub, Th. ES-879-F
Schicktanz, S.J. ES-1234-P
Schill, L. CB-163-O
Schindler, K. BM-1015-P
Schlüschen, L. ES-047-O
Schmidt, E.M. SM-1703-P
Schmidt, M. FB-990-F
Schmidt-Räntsch, T. ***ES-1265-P***
Schmitz, M. ND-152-O, ***MM-1512-P***
Schnakenburg, G. CB-1132-P
Schnegg, A. SM-1718-P, MM-288-I, CB-308-O, MM-287-O, MM-387-O, ***ND-652-O***, CB-523-O
Schneider, J. MG-1438-P
Schneider, N. CB-128-O
Schneider, P. ***MG-1432-P***
Schneider, S. ***MM-298-I***, MM-387-O, ES-1214-P, ES-1243-P, ES-1256-P, CB-1149-P
Schoendorf, L. ***ND-960-F***
Scholer, E. CB-505-K
Scholes, G. ES-316-K
Schröder, Ch. ES-1248-P
Schubert, E. ***MG-852-F***
Schuetz, V. ***MG-1438-P***
Schulz, A. ES-1270-P
Schulz, Ch. CB-523-O
Schünemann, V. MM-765-I, ***ND-154-O***
Schüth, F. MM-586-O
Schutte-Smith, M. ***ES-044-I***
Schwarz, J. ES-1247-P
Schwarzer, D. ES-412-O, MM-684-O
Schwedtmann, K. MG-032-O
Scopelliti, R. ND-664-O, FB-697-O, FB-1316-P, FB-1305-P
Scorzoni, G. ES-930-F, ***MG-854-F***
Scott, A. ***MM-586-O***
Seed, J. ND-495-K
Seed, J.A. ND-661-K
Segado-Centelles, M. ND-099-I
Segantini, M. MM-388-O
Segawa, K. ES-1263-P, ES-1264-P, ES-1266-P
Seglen, P.S. ***SM-1730-P***
Seib, J. SM-1717-P
Seidel, W. CB-1133-P
Seidel, W.W. ***MM-684-O***
Seisenbaeva, G. ***ND-194-O***
Sekine, Y. ***ND-057-O***
Sekizawa, K. ES-1238-P
Sellmann, K. ND-1629-P
Semwal, M. BM-1037-P
Sen, A. CB-933-F
Sen, I. ***ES-1232-P***
Sénèque, O. BM-330-K, BM-723-O, FB-1303-P
Sen Gupta, S. ***CB-004-I***
Senkiw-Smith, L. FB-594-I
Sension, R. CB-707-O, ***MM-685-I***
Seon, S. CB-202-O
Serpa, C. BM-1017-P
Serpe, A. FB-1301-P
Serrano-Guarinos, J. ***FB-797-O***
Serrano-Laguna, P.J. ***SM-1729-P***
Serre, Ch. ***CB-064-I***
Serroni, S. CB-1120-P
Sessoli, R. ***MM-386-K***
Severin, K. ND-952-F
Shafaat, H. ***MM-186-K***
Shah, B.K. ***ES-1213-P***
Shah, P. BM-1006-P, ***BM-735-I***
Shah, S.J. MM-1503-P
Sharkawy, S. BM-713-O
Sharma, M. CB-1153-P
Sharma, P. ***CB-1147-P***, ***MM-783-O***
Sharma, S. ***CB-934-F***
Sharrock, K. ***ND-1625-P***
Shatruk, M. ND-498-I
Shaw, A.K. ***FB-1302-P***
Shaw, P. ***MG-1431-P***
Shearer, J. MM-186-K
Sheet, N. ***CB-1102-P***, ***CB-062-O***
Shekhar, P. SM-1710-P
Shenton, J. SM-1703-P
Shepard, E. ***ES-1224-P***
Shephard, A. FB-1306-P
Shepherd, H. ES-1225-P
Sherburn, M. MG-1413-P
Sheridan, P. CB-1105-P
Shevchnko, D. ***ES-1217-P***
Shi, X. ***FB-1316-P***, CB-1125-P
Shi, Y. CB-165-I
Shi, Z. MG-1407-P
Shillito, G. MM-1506-P
Shimotani, K. BM-718-I, ES-1233-P
Shin, J.S. BM-364-O
Shirai, S. ES-1238-P
Shoji, R. ES-317-O, ***ND-1638-P***
Shongwe, M. BM-1024-P
Shubham, S. ***CB-1160-P***
Shuku, Y. ND-052-O
Shushkov, P. ***ND-257-O***
Shustova, N. ***SM-676-K***
Shylin, S. CB-427-O
Siakalli, Ch. ***BM-1008-P***
Siakavaras, N. ***CB-1144-P***
Siczek, BM-1023-P, BM-1045-P
Siegbahn, P. ***BM-633-O***
Sieveres, R. ND-452-O
Sievers, R. ND-458-I
Siewert, I. ***MM-484-I***
Sigman, M. CB-203-O
Signorile, M. SM-872-F
Sigrist, M. ***CB-1142-P***
Silberg, R.S. ***ND-1636-P***
Silva, C. FB-990-F
Silvestre-Llora, A. ***ND-1603-P***
Simaan, A.J. ES-1261-P
Simaan, J. MM-088-I
Simler, Th. ND-494-I, ND-897-F, ND-663-O, FB-1306-P, FB-1307-P
Simmonds, H. SM-1725-P
Simonelli, F. ***CB-1121-P***
Simonneau, A. CB-1142-P
Sinclair, B. ND-1622-P, CB-1114-P
Singh, A. CB-506-O
Singh, G. CB-208-I
Singh, H. ***FB-1307-P***
Singh, N. SM-577-O
Singh, P. SM-1721-P, SM-1710-P
Singh, S. ***CB-874-F***
Singh, V. ***MG-1437-P***
Singha Hazari, A. CB-228-I
Sinisi, J. ND-556-O
Sioutka, Ch. CB-856-F
Sippach, L. MM-296-O
Sithole, S.A. BM-1004-P
Sitkowski, J. BM-870-F
Skavenborg, M.L. ***CB-603-O***
Skrobańska, M. BM-1044-P
Skrydstrup, T. ***CB-424-I***
Slawin, A. MG-348-O, MG-940-F
Slesarchuk, N. ***MG-243-O***
Słowik, G. SM-1720-P
S. Mandrekar, K. SM-1736-P
Smith, A. ES-1207-P, ***ES-1209-P***, ND-492-O
Smith, E. BM-363-O, BM-1029-P, ***BM-1012-P***
Smith, L. ***CB-707-O***
Smith, M. ***ND-899-F***
Smits, P. ***MG-943-F***
Snabilié, D.D. MG-032-O
Snelgrove, M. SM-072-O
So, C.-W. MG-1411-P
Sollinger, G.-M. ND-152-O
Solomon, E.I. CB-207-O
Som, D. ND-1617-P

Sommariva-Ucha, N. ***BM-367-O***
Sommerauer, S. ***CB-1164-P***
Song, S. CB-707-O
Soo, H.S. ***ES-612-O***
Sorace, L. ND-253-O, FB-795-I ND-992-F, ND-498-I
Sørensen, T.J. ***ES-264-I***, BM-1014-P
Soriano-López, J. ***ND-097-O***
Sorokin, A.B. CB-863-F
Sotirakopoulos, K. ***SM-1723-P***
Soto, E. ***MG-543-O***
Sour, A. BM-330-K
Sousa, C. ND-158-O
Sovari, S.N. BM-1015-P
Sozzani, P. SM-775-I
Spackman, P. ES-1223-P
Spannenberg, A. CB-1162-P
Sparks, H. MM-385-I
Speca, C. SM-476-O
Spiering, H. MM-1512-P
Spinks, J. ***BM-1019-P***
Spodine, E. FB-598-I
Squadrini, A. BM-1030-P
Squire, I. ***MG-941-F***
Šramel, P. MG-443-O
Srinivas, V. MM-585-K
Srirambalaji, R. SM-577-O
Srnec, M. MM-1517-P CB-934-F, CB-102-O
S. Sigman, M. CB-107-O
Stadlbauer, S. BM-1002-P
Staforelli, S. ES-313-O
Stańczak, A. CB-207-O
Stansfield, O. ***CB-1146-P***
Stark, V. BM-236-O
Stasch, A. ***MG-348-O*** MG-940-F, MG-993-F
Stasiuk, G. ***BM-728-I***
Steeples, E. BM-866-F
Stefanuik, R. MM-587-O
Steffen, A. ***ES-216-O*** ES-847-F, ES-1251-P ES-1239-P, ES-1232-P
Stegman, S. CB-983-F
Stein, B. MM-283-O
Stein, M. ***MM-184-O***
Steinhauer, S. ND-457-O
Stephan, J. ***MG-1419-P***, ND-961-F ND-891-F, ND-894-F
Stephant, N. SM-372-O
Stephen, D. ND-196-K
Stevens, M. MG-851-F MG-1429-P, SM-1732-P
Stewart, M. ***CB-063-O***
Stewart-Moreno, J. ***MG-942-F***
Stiegler, L. ***MG-1423-P***
Stier, M. ***MM-086-O***
Stievano, L. SM-372-O
Stjärnhage, J. ***BM-736-O***
Stöger, B. MM-291-I
Storchi, J. ND-566-O
Storm, D. ND-553-O
Storr, T. SM-970-F, CB-1110-P ***BM-139-I***, CB-627-O
Straka, M. BM-638-O, ***ND-962-F***
Strandfelt, A. ***ND-256-O***
Streb, C. ND-1630-P ES-1248-P, ND-1629-P
Streit, T.-N. ND-452-O
Stride, J.A. BM-1020-P
Stringer, T. BM-118-O
Struijs, J.J.C. MG-1434-P
Stuart, Z. ***CB-1172-P***
Suarez Antuna, I. ***CB-223-O***
Suarez-Antuna, I. ES-462-K
Suaud, N. ND-052-O
Subintoro, P. MM-283-O
Subramaniyan, S. ***ES-1258-P***
Subramaniyan, V. CB-857-F
Subramanyan, V. CB-932-F
Sue, K. BM-1038-P, BM-1025-P
Sugamata, K. MG-1403-P
Sugihara, M. SM-778-I
Sugimoto, K. SM-373-O, ***MM-583-O***
Suhr, S. ***CB-507-O***
Sullivan, F.J. CB-858-F
Sullivan, M.P. BM-736-O
Sullivan, S. CB-303-O
Sulzbacher, M. ND-1630-P, ***ND-1629-P***
Suman, S. ***CB-325-I***, CB-323-O
Sun, L. ***CB-405-K***, ES-462-K
Sundaresan, S. ***MM-888-F***, MM-1510-P
Sundberg, J. SM-672-O, ***SM-1721-P*** SM-1728-P, SM-1738-P
Suo, M. SM-477-O
Supper, M. ***SM-777-O***
Sutra, P. ES-1206-P
Sutradhar, S. ***ES-1261-P***
Suwinska, K. ES-1249-P
Suzenet, F. FB-595-K
Suzuki, D. ES-1237-P
Suzuki, H. ***MM-768-I***
Suzuki, K. ND-092-O
Suzuki, T. ES-1237-P
Svora, P. ES-267-O
Švorc, L. BM-1039-P
Swain, A. ND-355-I, FB-797-O
Swarbrook, A. ***MG-846-F***
Swart, M. CB-104-O ***CB-1101-P***, ***MM-085-K***
Szaciłowski, K. ES-876-F
Szaloki, G. CB-223-O
Szczecinska, K. ***SM-973-F***
Szilágyi, P.Á. SM-1730-P
Szmitka, M. BM-533-O, ***BM-1032-P***

T

Tacconi, L. FB-795-I FB-1310-P, ND-498-I
Tada, M. CB-1102-P CB-062-O, ***PL-5***
Taddei, M. ***MM-762-I***
Tagai, K. SM-174-O
Tailleur, E. MM-483-O
Takacs, Z. CB-932-F, ND-1640-P
Takahara, K. ***ES-1237-P***
Takahashi, M. SM-677-O, ***BM-1038-P***
Takaishi, S. ES-317-O, ND-1633-P ES-1262-P, ND-1638-P
Takase, T. ES-1246-P
Takashima, Y. ***SM-1744-P***, SM-1733-P
Takashita, T. MM-297-O
Take, S. ***ND-951-F***
Takebayashi, S. CB-860-F
Takeiri, F. SM-373-O, MM-583-O
Talavera, M. ND-451-I
Talebi Deylamani, S. ***SM-572-O***
Tamhankar, A. ***MM-767-O***
Tamhankar, M. ***CB-002-O***, MG-343-O
Tamm, M. CB-1137-P, CB-1131-P
Tan, G. ***CB-024-I***
Tan, M. ***CB-932-F***
Tanabe, T. CB-743-O
Tanahashi, E. CB-982-F
Tanaka, S. MM-583-O, ***SM-1733-P***
Tanaka, Y. ***SM-174-O***, ***ES-1204-P***
Tanguy, E. ***BM-1014-P***
Taniguchi, H. ND-1638-P
Taniguchi, K. BM-718-I
Tanuhadi, E. CB-1103-P
Tanyà, S. ND-754-O
Tao, Q. ***ES-1254-P***
Tao Janetzki, J. ND-992-F
Tasiopoulos, A. ***SM-1704-P***
Tassinari, F. SM-576-O
Tateishi, T. ND-1633-P, ES-1262-P
Tayebi, Z. ***ES-1270-P***
Taylor, Ch.A. ES-840-F
Tei, L. ***BM-726-O***, ***BM-1002-P***
Teixeira, I. ND-556-O

Tepliakova, I. ES-1220-P
BM-1031-P, ES-1216-P
Tessarolo, J. ***BM-717-O***, SM-1736-P
Teutloff, Ch. ***MM-384-O***
Tezcan, B. ***ND-1609-P***
Thanetchaiyakup, A. ES-612-O
Thanh, D.L. SM-372-O
Theibich, Y. MM-181-I
Theis, P. MM-287-O
Théron, B. ES-143-O
Thevenon, A. MM-482-O
Thibon-Pourret, A. CB-127-O
Thiele, Ch. MM-882-F
Thieuleux, C. CB-526-O, ***ND-651-I***
Thisgaard, H. BM-1012-P
Thomas, S. CB-859-F
Thompsett, D. ES-042-O
Thompson, S. MG-348-O, ***MG-993-F***
Thornton, R. MG-246-O
Thorogood, J.M. ***CB-003-O***
Thulstrup, P.W. BM-1027-P
BM-1036-P, BM-1006-P
Thummar, U. ES-878-F
Tian, X. BM-734-O
Tiddens, M.R. CB-428-I
Tidey, J. MM-284-I
Tidey, J.P. SM-1703-P
Tielens, F. ND-1607-P
Tilley, D. ***CB-508-I***
Tilly, M.-J. BM-330-K
Timmel, Ch. MG-942-F, MM-1509-P
Tinoco, A. ***BM-018-I***
Tinoco, A.D. BM-1007-P
Tircsó, G. ***MM-083-O***
Tiwari, A. ***CB-1109-P***
Tiwari, R.K. ***CB-933-F***
Tobisu, M. MG-447-O, MG-944-F
Toigo, J. ES-414-I
Toki, K. ND-1633-P
Toki, Y. ***SM-677-O***
Tokoro, H. ND-753-O, ND-051-I
Tokuda, S. SM-772-I
Tolboom, J. CB-706-O
Tomás-Mendivil, E. MG-943-F
Tomat, E. BM-018-I
Tomeček, J. ND-661-K
Tong, K.-M. ES-414-I
Tong, M.-L. ND-352-O
Toninelli, C. ND-253-O
Tonks, I. ***CB-621-I***
Tonon, G. ***BM-634-O***, BM-868-F
Toplak, J. ***ES-1235-P***, ES-1267-P
Torabi, K. ES-611-I
Tormos Feliu, E. ND-354-O
Torres, J. BM-134-O
Torres-Cavanillas, R. ***ND-658-O***
Torubaev, Y. CB-860-F
Torun, E. ND-1609-P
Tosato, M. ND-566-O, BM-1002-P
Tóth, A. BM-1006-P
Tóth, A.M. BM-1036-P
Tóth, E. BM-332-O, BM-362-O
MM-083-O, ***BM-721-K***
Toulemonde, O. ES-1225-P
Toullec, C. ***CB-863-F***
Townrow, O. ***ES-844-F***
Toyoda, R. ***BM-712-I***
ES-317-O, ND-1633-P
ES-1262-P, ND-1638-P
Trabitsch, K. MG-032-O
Train, C. FB-794-O
Tran, E. CB-103-O
Tran, T.A. ***CB-1170-P***, CB-1112-P
Trapali, A. MM-292-O
Travis, B. ***CB-222-O***, CB-505-K
Tremlett, W. ***ES-147-O***, ***ES-1203-P***
Trevino, R. MM-186-K
Tripathi, S. SM-577-O
Tripier, R. ***BM-637-O***
Tripodi, G. CB-223-O, ES-462-K
Tritto, M. MG-941-F
Tritton, D.N. BM-871-F
Trivedi, M.U. ***SM-1726-P***
Troian-Gautier, L. ***ES-214-I***
CB-226-O, ND-960-F
Troiano, R. ES-145-I
Tromp, M. MM-085-K
Trovitch, R. CB-1138-P
Troya, J. ND-357-O, ***SM-476-O***
Troyano Prieto, J. ND-953-F
Trucchio, J. CB-983-F
Trzop, E. ND-151-I, MM-385-I
Tsai, M.-K. ES-1240-P, ES-1269-P
Tsang, M.Y. ***FB-593-O***
Tschierlei, S. ES-413-O, CB-1137-P
Tsekova, D. BM-867-F
Tsoni, S.A. ***BM-63A-O***
Tsoureas, N. CB-856-F, ND-1615-P
Tsuji, Y. SM-677-O
Tsumura, M. ND-1633-P
Tsunoji, N. ND-096-O
Tsuruoka, T. SM-1744-P, SM-1733-P
Tsutsumi, S. ***SM-373-O***
Tuna, F. ND-661-K
Turcas, I. ND-495-K
Turel, I. BM-1048-P
Tyagi, N. BM-236-O
Tyurina, O. BM-728-I

U

Uchida, S. ND-397-O
ND-092-O, ***ND-755-I***
Ueda, T. ***MG-944-F***
Uekermann, B. SM-273-O
Uemura, T. MM-768-I, SM-777-O
Uemura, Y. MM-686-K
Ufnalska, I. BM-132-O
Ulatowska, M. BM-1044-P
Umakoshi, A. ***CB-861-F***
Umbert, C. SM-275-K
Ünal, L. ***ES-1239-P***
Ung, G. ***FB-591-I***
Unjaroen, D. CB-104-O, MM-085-K
Unniram Parambil, A.R. ND-393-O, ND-1631-P
Urakawa, A. ND-198-O
Uran, E. MM-581-I
Usov, P. SM-774-O
Uyanga, K.A. CB-162-O
Uzal-Varela, R. BM-1009-P
Uzelac, M. ***CB-858-F***, CB-1151-P

V

Vadra, N. FB-694-O
Vagiakos, I. ***CB-980-F***
Vaidhyanathan, R. SM-1710-P
Vaillant-Coindard, V. ES-143-O
Valencia, L. BM-727-O, BM-362-O
Valencia-Matarranz, L. BM-367-O
Valensin, D. BM-133-O
Valentová, J. BM-1039-P
Valovičová, D. ***CB-1118-P***
Valverde-Munoz, F.J. MM-385-I
van Alten, R.S. ES-1214-P
Van den Eynden, D. ND-393-O
van der Veen, R. ***MM-787-O***
van der Vlugt, J.I. ***ES-047-O***
van der Westhuizen, A. ES-141-I
Vandier, Ch. FB-595-K
van Driel, T. CB-707-O
van Gastel, M. SM-1718-P
Vanin, F. ES-147-O
van Leusen, J. SM-1737-P

Van Loenhout, R. SM-778-I
van Mourik, T. MG-348-O, MG-993-F
Vanoye, L. ND-651-I
van Rijn, M.C. CB-068-I
van Slageren, J. ND-661-K
Van Zuylekom, J. BM-1019-P
Váradi, B. MM-083-O
Varga, R. BM-1039-P
Varga, V. CB-624-O
Varna-Pannerec, M. BM-532-O
Vashisth, G. ***ES-1227-P***, ES-1271-P
Vashisth, K. MG-246-O
Vasili, H.B. ND-1611-P
Vasko, P. MG-1423-P, ND-667-O MG-545-K, MG-243-O
Vasudevan, V. CB-426-O
Vazquez Lopez, M. ***BM-538-I***
Vega, A. ND-1614-P
Vega-Aponte, J. BM-018-I
Vega-Aponte, J.A. BM-1007-P
Vela, S. ***ND-158-O***
Velasco-Garcia, L. CB-221-I
Velcheva, V. BM-867-F
Velian, A. ***MG-035-K***
Velmurugan, P. ***SM-1731-P***
Vendier, L. ND-751-K, CB-1142-P
Venegas-Yazigi, D. ***ND-1614-P***, SM-1742-P
Venkatachalam, R. SM-1713-P
Vennestrøm, P.N.R. MM-282-O
Verderi, L. ***BM-1030-P***
Vergara Aguilera, E. MM-683-O
Verma, R.K. ***CB-1150-P***
Verrieux, L. MM-881-F
Verron, R. ES-1206-P
Verstreken, M. ES-261-I, SM-778-I
Vettori, M. ***CB-227-O***
Veyre, L. ND-651-I
Viborg, A. ***SM-472-O*** FB-1314-P, ND-1605-P
Vicens, L. CB-107-O
Vidal, D. ND-053-O
Videa, H. ***MG-1414-P***, SM-1729-P
Vijayakumar-Syamala, V. ES-041-I
Vijayan, P. CB-748-I
Vilan, A. CB-304-O
Vilar, R. BM-63A-O
Vileno, B. BM-330-K
Villafuerte, K. SM-1742-P
Villechenous Rojo, A. ***CB-602-O***
Virtue, J. SM-177-O
Visentin, F. BM-634-O
Visser, H.G. ES-044-I
Viter, R. ES-1220-P, ES-1216-P
Vitter, R. BM-1031-P
Vlček, A. ***ES-315-I***
Vlcek, J. ES-267-O
Vodiani, M. BM-112-O
Vojtíčková, M. BM-368-O
Volkmer, D. SM-276-O
Volkova, I. ***CB-323-O***
Voller, J. BM-870-F
Vollmar, K. ***MG-1421-P***
von Delius, M. BM-1037-P
Vondracek, M. ES-267-O
Vondung, L. FB-991-F, ***ND-567-O***
von Hahmann, C. ND-451-I
von Meyenn, C. ***CB-1114-P***
von Rhein, N. ***CB-1143-P***
von Wangelin, A.J. ND-1612-P
Vrána, J. ***MG-443-O***
Vrdoljak, V. ES-1235-P ***ES-1267-P***, ND-1616-P
Vura-Weis, J. CB-707-O

W

Wach, A. MM-188-O
Wada, Y. SM-774-O
Waddell, P. MG-1428-P
Waglewska, E. BM-1045-P, BM-533-O
Wagner, D.S. ES-412-O
Wakabayashi, T. CB-982-F, ***ES-1263-P*** ES-1264-P, ES-1266-P
Wakabayashi, Y. MM-297-O
Wakamatsu, K. ***ES-875-F***
Waldmann, K.M. ***BM-1028-P***
Walensky, J. ***ND-665-I***
Walkenhorst, S. ***CB-1162-P***
Walkey, M. ES-1223-P
Waller, Z. BM-733-O
Wallstein, N. BM-336-K
Walsh, D. ND-197-O
Walter, B. CB-1157-P
Walter, F. ***CB-1123-P***
Walter, R.R.M. ES-1241-P
Walters, D. BM-135-I
Wang, B. ND-1607-P, ***MM-185-I***
Wang, Ch. CB-1119-P
Wang, C. ***ES-212-O*** ES-1254-P, ***ND-1611-P***
Wang, D. ***CB-028-I***
Wang, G. ND-052-O
Wang, H. CB-066-O
Wang, J. ND-753-O, FB-1307-P
Wang, Q. MM-1516-P, CB-162-O
Wang, W. ND-394-O, ***CB-121-I***
Wang, X. CB-528-I, ***CB-628-O***
Wang, Y. CB-103-O, FB-1317-P ES-316-K, SM-1726-P
Wannemacher, R. ES-313-O
Ward, A. ES-617-O
Ward, J. ***MG-542-O***
Ward, J.S. CB-1159-P
Ward, M. SM-1708-P
Wärnmark, K. ***CB-742-I***, ES-1247-P
Warren, M. ND-1610-P
Warren, T. ***CB-008-I***
Watanabe, N. SM-774-O
Watanabe, T. ND-758-I
Waters, M. CB-207-O
Watson, A. ***MG-848-F***, CB-1119-P
Wauteraerts, N. ES-261-I
Weber, B. ***ND-055-K***, CB-1123-P
Weber, S. ***CB-123-O***
Webster, R. ***MG-031-I***
Webster-Hirst, A. ***ND-1604-P***
Wech, F. CB-860-F
Wegeberg, Ch. ES-1210-P, ES-1245-P ES-1211-P, ES-1205-P
Wehrung, I. MM-088-I
Wei, J. CB-025-K
Weigand, J.J. MG-032-O
Weigend, F. CB-524-I
Weihe, H. FB-1312-P
Weinberger, P. ***MM-291-I***
Weinstein, J. ***MM-686-K***
Weißer, K. CB-708-I
Wellauer, J. ES-412-O
Weller, A. ND-553-O, ES-042-O MG-848-F, ***ND-653-O*** CB-1119-P, CB-1127-P
Wellnitz, T. MG-641-I
Wen, F. MM-282-O
Wendt, O. CB-857-F, CB-426-O
Wendt, O.F. ***ES-045-K***, CB-1156-P
Wenger, O. MM-1506-P ES-1265-P, ***ES-211-I***
Wenger, O.S. ES-412-O ES-1230-P, ES-1228-P
Wenzel, J.O. ***ES-879-F***
Wernet, P. MM-587-O, ***MM-781-K***
Wesner, A. ES-614-O
Wessel, L. ES-413-O
Weßing, J. ND-893-F
Wessling, R. CB-603-O
Wettstein, L. ***ES-268-I***
Wheeler, A. CB-983-F

White, A. MG-343-O, ES-1244-P
White, K.A. FB-695-I
White, M. ***ND-197-O***
Whitehead, Ch.B. ND-393-O
Whitehead, G. SM-1725-P
Whitehead, G.F.S. ND-661-K
Whitwood, A.C. ES-840-F
Wicht, K. CB-747-O
Wieduwilt, E. ***MM-181-I***
Wieser, P.A. ***CB-1149-P***
Wiggers, H. CB-523-O
Wilcken, R. ES-1232-P
Wilhelm, F. SM-472-O ND-157-O, ND-1640-P
Willans, Ch. CB-1109-P, ES-042-O
Willans, R. ***ES-042-O***
Williams, C.M. CB-124-O
Williams, G. MM-686-K
Willing, P. FB-1309-P
Wilson, H. ***ND-393-O***, ND-1631-P
Wilson, J.J. ES-044-I
Winter, R. ***ND-433-O***
Winter, R.F. MG-1421-P
Wiśniewska, J. ***SM-1720-P***
Witas, K. ES-1268-P
Witkowska, D. BM-133-O, CB-1171-P
Wittmann, A. ND-351-I
Witwicki, M. BM-113-O, ND-1621-P
Wójcik, P. ***ES-1249-P***
Wojdyla, Z. ***MM-1517-P***, ***CB-102-O***
Wojtala, D. BM-132-O BM-1034-P, BM-1045-P
BM-113-O, BM-533-O
Wolański, W. ES-1245-P, ND-157-O
Wolf, M. ***ES-414-I***
Wolf, R. ***ND-954-F*** MG-1426-P, MG-032-O
Wolff, M. ES-413-O
Wolff, S. ***ND-1639-P***, MG-1435-P
Wolny, J. ND-154-O
Wolny, J.A. ***MM-765-I***
Wolski, K. ND-753-O
Wong, A. CB-622-O
Wong, T.H. ***ND-952-F***
Woods, J. MM-283-O
Woodward, A.W. ND-661-K
Wooles, A.J. ND-661-K
Woolley, J. ND-1622-P
Wota, G. ***ES-1226-P***
Woźny, FB-694-O
Wright, J. CB-1128-P
Wright, L.J. ***CB-1135-P***
Wu, C. ***CB-164-O***
Wu, G. ***CB-204-I***
Wu, S.-Q. ND-156-K
Wurm, F. MG-1410-P
Wuttke, S. SM-772-I

X

Xi, Z. ***CB-025-K***
Xiao, Y. ES-612-O
Xiong, J. CB-605-I
Xu, H.-L. BM-534-I
Xu, H. MM-585-K
Xu, S. ***MG-845-F***
Xu, X. MG-845-F
Xuan, W. ND-1602-P

Y

Yadav, S. ES-1218-P
Yaltseva, P. MM-1506-P, ES-1230-P
Yam, V.W.-W. ***ES-265-K***
Yamada, H. ND-096-O
Yamada, T. ***CB-743-O***
Yamaguchi, K. ND-092-O
Yamamoto, R. CB-201-I
Yamamoto, S. ES-1264-P
Yamashita, M. ***ND-251-I***
Yamato, S. SM-174-O
Yang, F. SM-772-I
Yang, T.-A. BM-1049-P
Yang, T.-H. ***MM-487-O***
Yang, X. MM-292-O, MG-1428-P
Yao, S. FB-1315-P, MG-1406-P
Yao, Y. ***FB-1317-P***
Yap, G. ND-492-O
Yartsev, A. ES-411-I
Ye, J.-W. BM-1049-P
Ye, S. MM-288-I, ***MM-286-O***
Yerbulekova, A. MM-186-K
Yersin, H. ***ES-418-I***
Y. Fernández, C. BM-134-O
Yiu, S.-M. BM-871-F
Yoneda, A. SM-1710-P
Yonesato, K. ND-092-O
Yoo, C. ***CB-623-O***
Yoon, G. ***CB-1124-P***
Yoon, H.J. ES-1204-P
Yoshida, M. ***ES-312-O***
Yoshida, T. ***ND-1641-P*** SM-1719-P, ES-1263-P ES-1264-P, ES-1266-P
Yoshikawa, H. ES-875-F
Yoshimoto, S. ND-1641-P
Yoshimura, T. ES-877-F
Yoshinari, N. ES-312-O
Yoshizawa, M. SM-174-O
You, Y. ***ES-518-I***
Young, R. ***CB-746-O***
Yu, M. ***ES-1244-P***
Yu, Y. MG-1407-P
Yuan, D. FB-1317-P
Yusoh, N.A. BM-734-O
Yutronkie, N. SM-472-O ND-157-O, SM-477-O
Yutronkie, N.J. ND-1640-P FB-1314-P, ND-1605-P

Z

Zabiszak, M. ***BM-1041-P***, BM-1022-P BM-1033-P, BM-1044-P
Zacchini, S. ES-930-F
Zadrozny, J. MM-283-O
Zahradníková, E. BM-1039-P, ND-1608-P
Zajac, W. FB-593-O
Zakrzewski, J. FB-793-O
Zakrzewski, J.J. ND-753-O, SM-973-F
Zamader, A. ***CB-506-O***
Zampella, G. MM-081-I
Zander, E. ***MG-643-O*** MG-641-I, ND-1628-P
Zankel, T. ***MM-882-F***
Zanotti Gracias, A. CB-1157-P
Zardi, P. SM-576-O
Zareba, J.K. FB-593-O
Zaremba-Czogalla, M. SM-1720-P
Zecca, L. ***BM-336-K***
Zedler, L. BM-1037-P
Zelewski, S.J. FB-593-O
Zeng, X. ES-147-O
Zerdane, S. ND-051-I
Z. Ertem, M. CB-226-O
Zhai, H.-L. ND-1623-P
Zhang, C. CB-528-I
Zhang, F. ES-312-O
Zhang, H. ***MG-853-F***, ***CB-308-O***
Zhang, J.-Y. ***MG-1417-P***
Zhang, J.-D. ES-1253-P
Zhang, J. ***FB-1311-P***
Zhang, L. CB-528-I
Zhang, L.-H. BM-871-F
Zhang, M. ***SM-171-I***, ***ES-1247-P***
Zhang, M.-T. ***CB-125-I***
Zhang, S. MM-1516-P, ***MG-444-I***
Zhang, T. ***CB-165-I***
Zhang, Y. ***MM-1516-P***, MM-292-O CB-066-O, MM-085-K

Zhang, Z.
ES-1227-P, ***ES-1271-P***
MG-1417-P, MG-1407-P
Zhao, L. ***CB-066-O***
Zhao, S. CB-506-O
Zheng, L. ***SM-376-K***
Zhou, H. CB-743-O
Zhu, Q.-Y. ***ES-1253-P***
Zhu, Y. ***BM-1050-P***
Zhu, Z. ES-147-O
Zhuo, L.-T.
ES-1240-P, ES-1269-P
Ziegler, C.G.P. MG-032-O
Ziemann, L.
ES-847-F, ES-1239-P
Zienkiewicz-Machnik,
MM-188-O
Zimmermann, S. ***SM-1735-P***
Zimmeter, K. BM-330-K
Zivkovic, I.
ND-664-O, FB-697-O
Zobi, F.
BM-1015-P, CB-1171-P
Zois, K.P. BM-1037-P
Zorn, D. ES-1234-P
Zou, X. MM-585-K
Zucca, F.A. BM-336-K
Zuccaccia, C. ES-1242-P
Zucchi, G. ND-1618-P
Zulkarnain, R. MM-292-O
Zuluaga, A. ND-651-I
Zupanc, A. CB-423-O
Zurwellen, J. ES-413-O
Zurwellen, J.P. CB-1137-P
Zychowicz, M.
SM-973-F, FB-793-O