

2025 North America-Greece-Cyprus Conference (NAGC)

Syros, Greece

May 5-9, 2025



Supported by:



NAGC (North America, Greece & Cyprus) Meetings

The NAGC meetings are a biennial series of scientific gatherings that have been organized since 2005 by Professor George Christou (University of Florida, USA), Professor Spyros Perlepes (University of Patras, Greece), Professor Tasos Tasiopoulos (University of Cyprus, Nicosia), and a group of researchers from the National Center for Scientific Research "Demokritos" (Athens, Greece).

Over the years, NAGC meetings have alternated with the CTMNM (Current Trends in Molecular and Nanoscale Magnetism) meetings. For practical reasons, the 2017 and 2023 meetings—held in Paphos, Cyprus, and Spetses, Greece, respectively—were organized as joint events.

To celebrate the 20th anniversary of these congresses, the organizers have decided to unify them under the NAGC name. This new format allows for a broader range of scientific topics to be addressed, while preserving the tradition of alternating the venue between Cyprus and Greece.

The NAGC meetings continue to serve as a vital forum for faculty members and students from Universities/Research Centers in Greece, Cyprus and other countries, to connect with their North American peers, as well as with selected researchers across Europe and beyond. Following the outstanding success of previous workshops, this event will once again bring together a diverse group of researchers working across a wide spectrum of scientific disciplines.

The program spans various areas of chemistry, physics, and materials science, and welcomes contributions involving unpaired electrons in any context—whether molecular or non-molecular; organic, inorganic, biochemical, or biological; ground state or excited state; and across all phases of matter (solid, liquid, gas, or plasma). A key objective of the NAGC meetings is to bring together scientists from different backgrounds who might not typically attend the same conferences, fostering interdisciplinary dialogue and collaboration. Another central aim is to support early-career researchers by providing them with the opportunity to engage with leading scientists from around the world. The organizers have consistently encouraged the participation of students and postdoctoral researchers, striving to include as many as possible in the program.

To maximize the benefit for all attendees, senior speakers are expected to incorporate a tutorial aspect into their presentations, ensuring that students and young scientists can fully engage with and learn by attending all sessions.

Committees

International Organizing Committee

Pro. George Christou, Dept. of Chemistry, Univ. of Florida, USA Dr. Georgios Papavassiliou, INN, NCSR "Demokritos", Greece Prof. Spyros P. Perlepes, Dept. of Chemistry, Univ. of Patras, Greece Prof. Anastasios J. Tasiopoulos, Dept. of Chemistry, Univ. of Cyprus, Cyprus Dr. Vassilis Psycharis, INN, NCSR "Demokritos", Greece

Local Organizing Committee

Dr. Vassilis Psycharis, INN, NCSR "Demokritos", Greece Dr. Georgios Papavassiliou, INN, NCSR "Demokritos", Greece Dr. Catherine P. Raptopoulou, INN, NCSR "Demokritos", Greece Dr. Yiannis Sanakis, INN, NCSR "Demokritos", Greece Dr. George Mitrikas, INN, NCSR "Demokritos", Greece

LOCATION AND TIME

The Workshop will be held from May 5 to May 9, 2025 at the hotel Hermes, at the island of Syros, Cyclades, Greece. The lecture room is located in the hotel.

TRAVEL INFORMATION

Syros can be reached by plane, or by sea (Blue Star Ferries and Seajets).

If you are arriving in Athens **by plane** you can catch a flight to Syros from the Athens International Airport.

If you want to reach Syros **by sea**, you can catch the X96 bus leaving from the Athens International Airport every 30 minutes, 24 hours a day for the port of Piraeus. This takes about one hour to reach Piraeus. The terminal bus station in the port, is very close to **Gates E5** and **E1** where the **Blue Star Ferries** for Syros depart, and about 600m from **Gate E9** where the **Seajets** for Syros depart.

During the day you can also take the suburban railway leaving from the Athens International Airport direct to the port of Piraeus. This takes 1h 40 m total and the station is close to **Gates E5** and **E1** where the **Blue Star Ferries** for Syros depart, and 600m from **Gate E9** where the **Seajets** for Syros depart.

REGISTRATION

Registration desk

The registration desk will be open on Sunday, May 4, 2025 from 16:00 to 19:00 at the Hotel Hermes, Syros. On Monday, May 5 the desk will be open from 09:00 to 11:00 a.m. and for the rest of the days it will be open from 08:00 to 11:00 a.m. There is no registration fee for participants.

SCIENTIFIC PROGRAM

All presentations will be performed orally (30 and 15 minutes including discussion). Computer-screen projector (for Power-Point) will be available. The timetable given in the following pages may be subjected to small alterations.

SOCIAL PROGRAM

Reception

The reception (welcome party) will take place, on Sunday May 4th at Hotel Hermes at 19:00. All registered persons (participants and accompanying members) are cordially invited.

Official Dinner

The official dinner of the Workshop will take place on Tuesday May 6th, at 21:00. A supplement fee is required. Please conduct the registration desk for any diary preferences.

Free afternoon

On Wednesday 7, 2025 the lectures end at 13:00 and the rest of the day is free.

GENERAL REMARKS

Refreshments

During the coffee breaks, coffee and juices will be provided free to all participants.

WiFi

Free wifi in all areas of the Hotel Hermes will be available.

Climate

At the beginning of May, the weather in Greece is usually dry, however on the seaside the humidity levels are elevated. The average temperatures lie between $12-25^{\circ}C$ (53-77 °F). During the night, the weather is cooler but pleasant. All rooms and the lecture room are air-conditioned.

Acknowledgements

The Organizers wish to express their most cordial thanks to Mrs. V. Zatta for her assistance, as well as to our sponsors: NCSR "Demokritos", University of Florida and Blue Star Ferries.

TIMETABLE 2025 NAGC, Syros 5-9 May 2025

Time\Day	Monday, May 5	Tuesday, May 6	Wednesday, May 7	Thursday, May 8	Friday, May 9
8:00-8:20	Registration				
8:20-8:30	Welcome				
Chair	Spyros Perlepes	Kathryn E. Preuss	Mark Turnbull	Theocharis. C. Stamatatos	Ken Sakai
8:30-9:00	Liviu F. Chibotaru	Graham N. Newton	George Christou	Randy W. Larsen	Daniel Talham
9:00-9:30	Serena A. Cussen	Athanasios K. Boudalis	Melanie Pilkington	Anastasios J. Tasiopoulos	Grace Morgan
9:30-10:00	George E. Froudakis	Christina N. Banti	Michael Pissas	Mark M. Turnbull	Veronica Sofianos
10:00-10:30	Sotiris K. Hadjikakou	Dimitrios P. Gournis	Pantelis N. Trikalitis	Vassilis Tangoulis	Faidonas - Angelos P. Tsapalis
10:30-11:00	Coffee Break	Coffee Break	Coffee Break	Coffee Break	Coffee Break
Chair	Jeffrey Zaleski	Yiannis Sanakis	Anastasios J. Tasiopoulos	Eliseo Ruiz	Vassilis Psycharis
11:00-11:30	Andrew J. Pell	Mario Ruben	Eliseo Ruiz	Ronald K. Castellano	Catherine Raptopoulou
11:30-12:00	Kathryn E. Preuss	Theocharis. C. Stamatatos	Wassilios Papawassiliou	Hai-Ping Cheng	Panagiotis Kyritsis
12:00-12:30	Eufemio Moreno-Pineda	Mohamed Al Hosani	Nikolia Lalioti	Núria Aliaga-Alcalde	Closing Remarks
12:30-12:45	Konstantina. H. Baka	Doory Dan	Ioannis S. Athanasoulias	Laoura K. Komodiki	
12:45-13:00	Alexander Diodati	-	Ashlyn Hale	Andrew Cupo	
13:00-14:30	Lunch break	Lunch break		Lunch break	
Chair	George Christou	Piotr Kaszynski		Richard A. Layfield	
14:30-15:00	Richard A. Layfield	Jeremy M. Rawson		Ming-Hsi Chiang	
15:00-15:30	Gemma-Louis Davies	Susumu Takahashi		Peter Comba	
15:30-16:0	Stergios Piligkos	Jeffrey Zaleski	Froo	Piotr Kaszynski	
16:00-16:15	Eleni-Nefeli S. Bogdanopoulou	Charlotte Bailey	ITEE	Ioanna Th. Papageorgiou	
16:15-16:30	Maria Chrysina	Antonis Anastassiades	Afternoon	Nefeli Polycarpou	
16:30-17:00	Coffee Break	Coffee Break	, , , , , , , , , , , , , , , , , , ,	Coffee Break	
Chair	Graham Newton	Catherine Raptopoulou		Jeremy M. Rawson	
17:00-17:30	Sotirios Christodoulou	Ken Sakai]	Stephen Holmes	
17:30-18:00	Dimitris I. Alexandropoulos	Zoi G. Lada		George Papavassiliou	
18:00-18:30	Vassilis Psycharis	Karah E. Knope		George Mitrikas	

PROGRAM

	MONDAY 5 MAY, 2025		
8:00-8:20	Registration		
8:20-8:30	Welcome		
	Chair: Spyros Perlepes		
8:30-9:00	Author: Liviu F. Chibotaru		
	Title: Ab Initio Description of Luminecence in Lanthanide based SMMs		
9:00-9:30	Author: Serena A. Cussen		
	Title: Tuning high energy density cathodes for electrochemical energy storage		
9:30-10:00	Author: George E. Froudakis		
	Title: Gas adsorption meets Deep Learning		
10:00-10:30	Author: Sotiris K. Hadjikakou		
	Title: Antimicrobial Silver(I) Formulations and Biogenic Materials for Next-		
	Generation Medical approaches		
10:30-11:00	Coffee break		
	Chair: Jeffrey Zaleski		
11:00-11:30	Author: Andrew J. Pell		
	Title: Paramagnetic materials: challenges and opportunities for solid state NMR		
11:30-12:00	Author: Kathryn E. Preuss		
	Title: Coordination Complexes of New Asymmetric Thiatriazinyl Radical		
12:00-12:30	Author: Eufemio Moreno-Pineda		
	Title: µSQUID-EPR Investigations of Single Molecule Magnets		
12:30-12:45	Author: Konstantina. H. Baka		
	Title: Expanding the Lanthanide/Pnictogen Heterometallic Chemistry: New		
	{Sb ₂ Dy ₃ } and {Sb ₇ Dy ₄ } Single-Molecule Magnets		
12:45-13:00	Author: Alexander Diodati		
	Title: Covalently-linked Metalloporphyrin Dimers and their Magnetic and		
	Spectroscopic Properties		
12.0014.20			
13:00-14:30	Lunch break		
13:00-14:30	Chair: George Christou		
14:30-15:00	Chair: George Christou Author: Richard A. Layfield Tide. The Chamistre of Marked Directory Logidary		
14:30-15:00	Chair: George Christou Author: Richard A. Layfield Title: The Chemistry of Masked Divalent Lanthanides		
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	TUESDAY 6 MAY, 2025
	Chair: Kathryn E. Preuss
8:30-9:00	Author: Graham N. Newton
	Title: All Wrapped Up: How Molecular Encapsulation Impacts the Chemistry of
	Redox-active Molecules and Electrocatalysts
9:00-9:30	Author: Athanasios K. Boudalis
	Title: Addressing weakly coupled and g-asymmetric two-spin systems with
	nutation spectroscopy
9:30-10:00	-Author: Christina N. Banti
	Title: Exploring the Apoptotic Potential of Silver(I) Metallodrugs in 2D and 3D
	Cell Cultures; Insights into DNA and Enzyme Interactions
10:00-10:30	Author: Dimitrios P. Gournis
	Title: Design & development of new heterogeneous photocatalysts based on novel
	2D materials for environmental applications
10:30-11:00	Coffee break
	Chair: Yiannis Sanakis
11:00-11:30	Author: Mario Ruben
	Title: Molecular Nuclear Spin Qubits for Implementing Quantum Gates
	and Quantum Algorithms
11:30-12:00	Author: Theocharis. C. Stamatatos
	Title: Rekindling the interest in cluster-based SMMs: Large magnetic anisotropy
	and SMM properties in a $\{Mn_9\}$ double-decker metallacrown with $S = 5/2$
12:00-12:30	Author: Mohamed Al Hosani
10.00.10.15	<i>Title:</i> Greenitying the Blue – Challenges in Decarbonizing the Maritime Sector
12:30-12:45	Author: Doory Dan
	Title: Molecular Models for Single Cobalt lons Supported on Cerium Dioxide
	Nanoparticles: Heterometallic Ce/Co-oxo Clusters
10 15 10 00	
12:45-13:00	-
12:45-13:00 13:00-14:30	Lunch break
12:45-13:00 13:00-14:30	Lunch break Chair: Piotr Kaszynski
12:45-13:00 13:00-14:30 14:30-15:00	Lunch break Chair: Piotr Kaszynski Author: Jeremy M. Rawson Title: Conformational Polymorphism and Magnetic Ordering in an Organia
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12:45-13:00 13:00-14:30 14:30-15:00 15:30-16:00 16:00-16:15 16:15-16:30 16:30-17:00 17:00-17:30 17:30-18:00	Junch breakLunch breakChair: Piotr KaszynskiAuthor: Jeremy M. RawsonTitle: Conformational Polymorphism and Magnetic Ordering in an OrganicRadical: a, b, g and d-Polymorphs of Benzodioxepinyl-1,3,2-dithiazolylAuthor: Susumu TakahashiTitle: The effect of hydrostatic pressure on g-tensor and hyperfine couplingconstants of nitroxide radical characterized by ab initio calculationsAuthor: Jeffrey ZaleskiTitle: Diradicals as Medicines for DiseaseAuthor: Charlotte BaileyTitle: Use of 'Molecular Nanoparticles' of Cerium Dioxide as supports for d-blockTransition Metals: Unprecedented Models for CeO2-supported Industrial CatalystsAuthor: A. AnastassiadesTitle: A New Family of Heterometallic [Cu ₆ M ₄] (M = Gd, Tb, Dy and Y) ClustersDerived from the Combined use of Selected Pyridyl Poly-alcohol LigandsCoffee breakCoffee breakAuthor: Ken SakaiTitle: Photocatalytic CO2 Reduction in Aqueous MediaAuthor: Z.G. LadaTitle: Regulating Spin Crossover (SCO) Transition Temperatures towards SCObased Temperature Sensors in Food Packaging
12:45-13:00 13:00-14:30 14:30-15:00 15:30-16:00 16:00-16:30 16:00-16:15 16:15-16:30 16:30-17:00 17:00-17:30 17:30-18:00 18:00-18:30	Lunch breakLunch breakChair: Piotr KaszynskiAuthor: Jeremy M. RawsonTitle: Conformational Polymorphism and Magnetic Ordering in an OrganicRadical: a, b, g and d-Polymorphs of Benzodioxepinyl-1,3,2-dithiazolylAuthor: Susumu TakahashiTitle: The effect of hydrostatic pressure on g-tensor and hyperfine couplingconstants of nitroxide radical characterized by ab initio calculationsAuthor: Jeffrey ZaleskiTitle: Diradicals as Medicines for DiseaseAuthor: Charlotte BaileyTitle: Use of 'Molecular Nanoparticles' of Cerium Dioxide as supports for d-blockTransition Metals: Unprecedented Models for CeO ₂ -supported Industrial CatalystsAuthor: A. AnastassiadesTitle: A New Family of Heterometallic [Cu ₆ M ₄] (M = Gd, Tb, Dy and Y) ClustersDerived from the Combined use of Selected Pyridyl Poly-alcohol LigandsChair: Catherine RaptopoulouAuthor: Ken SakaiTitle: Photocatalytic CO ₂ Reduction in Aqueous MediaAuthor: Z.G. LadaTitle: Regulating Spin Crossover (SCO) Transition Temperatures towards SCObased Temperature Sensors in Food PackagingAuthor: Karah E. Knope

	WEDNESDAY 7 MAY, 2025	
	Chair: Mark Turnbull	
8:30-9:00	Author: George Christou	
	Title: Molecular Analogues of the LnMnO ₃ Lanthanide Manganites with the	
	Perovskite Structure	
9:00-9:30	Author: Melanie Pilkington	
	Title: The Design, Synthesis and Study of Multifunctional Single Molecule	
	Magnets	
9:30-10:00	Author: Michael Pissas	
	Title: Mixed orbital states and modulated crystal structures in La _{1-x} Ca _x MnO ₃ or	
	nanoscale heterogeneity	
10:00-10:30	Author: Pantelis N. Trikalitis	
	Title: Topotactic Metal Cation Exchange in Multicomponent Ultraporous MOFs	
10:30-11:00	Coffee break	
	Chair: Anastasios J. Tasiopoulos	
11:00-11:30	Author: Eliseo Ruiz	
	Title: Magnetism and Transport at Single-Molecule Level	
11:30-12:00	Author: Wassilios Papawassiliou	
	Title: What can we learn about spin-crossover complexes using solid-state NMR?	
12:00-12:30	Author: Nikolia Lalioti	
	Title: Luminescent Thermometer based on a Praseodymium (III) cyanide-based	
	metal-organic framework	
12:30-12:45	Author: Ioannis. S. Athanasoulias	
	Title: Carboxylate Effect on the Structural Identity of Ln ^{III} /2-hydroxy-4-	
	methoxybenzophenone Clusters	
12:45-13:00	Author: Ashlyn Hale	
	Title: Molecular Nanoparticles of Birnessite-type MnO ₂ via Reductive Aggregation	

	THURSDAY 8 MAY, 2025	
	Chair: Theocharis. C. Stamatatos	
8:30-9:00	Author: Randy W. Larsen Title: Host-Guest Interactions between Transition Metal Polyimines and Metal Organic Framework Pores: Pore Modulation of Guest Photophysics	
9:00-9:30	Author: Anastasios J. Tasiopoulos Title: Modulation of the Temperature and Gas Sensing Properties of New Metal– Organic Frameworks based on Hexanuclear Rare Earth Secondary Building Units through Single-Crystal-to-Single-Crystal Transformation Reactions	
9:30-10:00	Author: Mark M. Turnbull Title Polymorphs and an orthorhombic Jahn-Teller effect in [Cu(3-bromo-2- pyridone) ₆] (ClO ₄) ₂	
10:00-10:30	Author: Vassilis Tangoulis Title: Shape-dependent magnetic properties of Prussian Blue Analogue Sm[Fe(CN) ₆]	
10:30-11:00	Coffee break	
	Chair: Eliseo Ruiz	
11:00-11:30	Author: Ronald K. Castellano Title: Uniquely Programmable Supramolecular Polymers from Covalently- Fixed Monomers	
11:30-12:00	Author: Hai-Ping Cheng Title: Interaction between Magnetic Molecules and Surfaces	
12:00-12:30	Author: Núria Aliaga-Alcalde Title: Look at Curcuminoids: from Design to Use as Electronic Components and Sensors	
12:30-12:45	Author: Laoura K. Komodiki Title: Templated synthesis of a Zr ₆ -based sodalite MOF	
12:45-13:00	Author: Andrew Cupo Title: Floquet Engineering Molecular Spin Qubits	
13:30-15:30	Lunch break	
	Chair: Richard A. Layfield	
14:30-15:00	Author: Ming-Hsi Chiang Title: Enhanced Bio-electrochemical CO ₂ Fixation Efficiency by Embedment of Artificial Enzyme into Bacterial Membrane	
15:30-16:00	Author: Peter Comba Title: Modeling Spin for Applications of Metal Complexes	
16:00-16:30	Author: Piotr Kaszynski Title: Chiral Radicals and Diradicals: Synthesis, Properties and Opportunities	
16:00-16:15	Author: Ioanna Th. Papageorgiou Title: Adventures in the Coordination Chemistry of a Little Explored Salen – type Schiff Base with Lanthanoid and Actinoid Ions	
16:15-16:30	Author: Nefeli Polycarpou Title: Seeded-growth synthesis of InAs/ZnSexSx-1 colloidal quantum dots	
16:30-17:00	Coffee break	
	Chair: Jeremy M. Rawson	
17:00-17:30	Author: Stephen Holmes Title: Structure-Property Studies of Paramagnetic <i>N</i> -Heterocyclic Carbene and Amide Complexes	
17:30-18:00	Author: George Papavassiliou Title: NMR Detection of Electron Spin Fractionalization and the Manifestation of the Elusive Majorana Fermions in Kitaev Materials	
18:00-18:30	Author: George Mitrikas Title: Measuring electron spin coherence times of paramagnetic metal complexes with dynamical decoupling: opportunities and pitfalls	

	FRIDAY 9 MAY, 2025
	Chair: Ken Sakai
8:30-9:00	Author: Daniel Talham
	Title:-Interface and Matrix Effects on Spin Transition Solids
9:00-9:30	Author: Grace Morgan
	Title: Spin State Switching in Iron(III) Complexes – a Thermal and Optical Study
9:30-10:00	Author: Veronica Sofianos
	Title: Exploring amorphous bimetallic borides in direct seawater electrolysis for
	green hydrogen production
10:00-10:15	Author: Faidonas - Angelos P. Tsapalis
	Title: NOO'O" Schiff Bases as a Platform for the Synthesis of $\{Zn^{II}_{4}M^{III}_{2}\}$ and
	$\{Cd^{II}_2M^{III}_2\}$ (M ^{III} = Cr ^{III} , Fe ^{III}) Coordination Clusters
10:150-10:45	Coffee break
	Chair: Vassilis Psycharis
10:45-11:15	Author: Catherine Raptopoulou
	Title: Schiff base metallodrugs for anticancer and antimicrobial activity
11:15-11:45	Author: Panagiotis Kyritsis
	Title: Slow magnetization relaxation of some mononuclear 3d metal complexes
11:45-12:00	Closing Remarks

ABSTRACTS

Non-Innocent Ligands in Transition Metal and Lanthanide Coordination Chemistry

D. I. Alexandropoulos,^{a,*} K. R. Dunbar,^b B. S. Dolinar,^b K. R. Vignesh,^b

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Metal complexes containing redox-active, non-innocent ligands remain of significant interest across multiple research fields, including bioinorganic chemistry, catalysis, and molecular magnetism. Specifically, in molecular magnetism, employing radical-bridged complexes of 3d and 4f metals as potential high-spin systems and single-molecule magnets (SMMs) has proven highly effective. This effectiveness stems primarily from the strong direct magnetic exchange interactions arising from orbital overlap between metal centers and radical bridging ligands, significantly surpassing the indirect superexchange mediated through diamagnetic bridging groups.^[1]

In this work, we describe the synthesis and detailed magnetic characterization of a series of radical-bridged metal complexes. The fitting of magnetic measurements for all synthesized compounds consistently revealed strong magnetic exchange coupling constants.



Figure 1: $\chi_{M}T$ vs. T plot for the radical-bridged lanthanide complexes that will be discussed.

References

[1] S. Demir, I.-R. Jeon, J. R. Long, T. D. Harris, *Coord. Chem. Rev.* **2015**, *289-290*, 149-176.

Acknowledgments

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A look at Curcuminoids: from Design to Use as Electronic Components and Sensors

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Curcuminoids (CCMoids) are efficient molecular platforms with a direct correlation between structural tuning and target applications.[1-2] They have simple syntheses with reasonable yields. Well known for their biomedical applications, they are increasingly explored in other fields of nanoscience and nanotechnology. In this direction our group is working on the creation of new CCMoids with special interest in the study of their integration into different substrates/devices. The combination of molecular design and nanostructuring methods (sublimation, in solution or soft deposition techniques) has allowed us to (i) create monolayers of CCMoids covalently bonded to substrates and their use as BF3 sensors, (ii) the formation of different types of crystals, aggregates and films in FET-type devices for their electrical characterization[as well as (iii) their use as nanowires for single-electron transport experiments.[1-2] This is a learning by doing process in which the results allow redesigning new generations of CCMoid materials. This talk briefly summarizes our most relevant findings to provide an overview of possible and future applications of CCMoids.



Figure. Set-up of different studies of CCMoid systems (general structure in the center).

References

[1] T. Cardona-Lamarca, T. Y Baum, et al. Chem. Sci., **2024**, 15(39), 16347-16354.
[2] R. Gimeno-Muñoz, R. Díaz-Torres, et al. ACS Appl. Mat. Interfaces. **2025**. DOI:10.1021/acsami.4c19421.

Greenifying the Blue – Challenges in Decarbonizing the Maritime Sector

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The maritime industry is a major contributor to the global economy. As of 2019, the maritime industry contribution amounted to 24 Trillion USD¹. Around 90% of global trade by volume is transferred via the sea². The aforementioned facts highlight the importance of decarbonizing the maritime industry. Unlike other industries, the maritime industry faces unique challenges that has to be addressed separately. In this talk, we discuss these challenges, proposed solutions, and areas where further research is required.

References:

- [1] www.visualcapitalist.com
- [2] <u>www.oecd.org</u>

A New Family of Heterometallic [Cu₆M₄] (M = Gd, Tb, Dy and Y) Clusters Derived from the Combined use of Selected Pyridyl Polyalcohol Ligands

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^aDepartment of Chemistry, University of Cyprus, Nicosia 1678, Cyprus ^bDepartment of Chemistry, University of Copenhagen, DK-2100, Denmark Emails: anastassiades.antonis@ucy.ac.cy (presenting author) atasio@ucy.ac.cy (corresponding author)

Copper lanthanide complexes represent an interesting class of coordination compounds. The interest is driven by the potential for these molecules to exhibit unprecedented structural motifs and intriguing electronic and magnetic properties. ^[1] In particular, Cu/4f complexes usually exhibit ferromagnetic exchange interactions. As a result, complexes containing Cu²⁺ ions and highly anisotropic Ln³⁺ ions, such as Dy³⁺ and Tb³⁺ can exhibit single-molecule magnet (SMM) behaviour. Conversely, compounds combining Cu²⁺ ions with isotropic Gd³⁺ ions can display high spin ground state values and potential applications in magnetic cooling technologies.

The combined use of 2-(2-pyridyl)-1,3-propane-diol (pypdH₂) and 2-hydroxymethyl-2-(2-pyridyl)-1,3-propane-diol (pyptH₃) in Cu²⁺/4f chemistry has afforded a new family of isostructural [Cu₆M₄(pypt)₄(pypdH)₄(NO₃)₈] [M = Gd (1), Tb (2), Dy (3), and Y (4)] complexes. These compounds are based on an unprecedented three-layered symmetric [Cu₆M₄(μ -OR)₁₆]⁸⁺ structural core, formed from the connection of the metal ions by bridging alkoxide arms of the organic ligands. Direct current magnetic susceptibility studies for complexes 1 - 3 revealed the presence of dominant ferromagnetic exchange interactions, suggesting the existence of large spin ground state values.



Figure 1: (left) partially labelled representation of the structural core of {Cu₆M₄} clusters and (right) temperature dependence of $\chi_M T$ for the indicated complexes. Color scheme: Cu²⁺, cyan; Gd³⁺ yellow; O, red; C, black. Hydrogen atoms are omitted for clarity.

References

[1] Dey, A.; Bag, P.; Kalita, P.; Chandrasekhar, V. Heterometallic Cu^{II}–Ln^{III} complexes: Single molecule magnets and magnetic refrigerants. *Coordination Chemistry Reviews* **2021**, *43*2, 213707.

Acknowledgments

This work was supported by the Cyprus Research and Innovation Foundation Research Grant "EXCELLENCE/0421/399" which is co-funded by the Republic of Cyprus and the European Regional Development Fund.

Carboxylate Effect on the Structural Identity of Ln^{III}/2-hydroxy-4methoxybenzophenone Clusters

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Polynuclear metal complexes using trivalent lanthanide ions (Ln^{III}) continue to attract the intense interest of inorganic chemists and material scientists over the past few decades or so, due to their unique chemical and physical properties and their potential applications in the fields of molecular magnetism, optics, catalysis and bioinorganic chemistry. In recent years, particular emphasis has been placed on multifunctional molecular materials based on lanthanide coordination clusters, which combine two or more physical properties in the same chemical entity. For the synthesis of this type of materials the choice of organic ligands is of great importance since they should lead to discrete coordination compounds and promote (in combination with the metal ions) the desired physical properties [1]. The organic chelate ligand for this ongoing work was 2-hydroxy-4-methoxybenzophenone, which could potentially lead to discrete molecular clusters with unprecedented metal topologies and interesting magneto-optical properties [2]. Furthermore, the development of high-nuclearity lanthanidebased complexes can be promoted by carboxylate ligands due to their significant and proved bridging ability, as well as the variety of coordination modes that can adopt, leading to unique structural architectures. Moreover, carboxylate ligands possess oxygen donor atoms, thus satisfying the intense oxophilicity of Ln^{III} ions. In the present work, we report the synthesis of lanthanide-based coordination clusters derived from the combined use of the ligand 2hydroxy-4-methoxybenzophenone with various carboxylic acids, such as adamantane-1carboxylic acid, 3,3-dimethylbutyric acid and fluorene-9-carboxylic acid that afforded us three novel lanthanide coordination clusters (Figure 1).



Figure 1. The lanthanide coordination clusters derived from the combined use of the ligand 2-hydroxy-4-methoxybenzophenone with the carboxylic acids adamantane-1-carboxylic acid, 3,3-dimethylbutyric acid and fluorene-9-carboxylic acid.

[1] M. Murugesu et. al., *Chem. Sci.*, **2023**, *14*, 5827-5841.

Use of 'Molecular Nanoparticles' of Cerium Dioxide as supports for d-block Transition Metals: Unprecedented Models for CeO₂supported Industrial Catalysts

C. S. Bailey*, L. Dobrzycki, L. Wojtas, G. Christou

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Cerium dioxide (CeO₂ or ceria) nanoparticles (CNPs) are versatile materials which are employed or investigated for a wide range of applications, including new energy technologies, spintronics, industrial catalysis and, more recently, biomedical applications. In many of these applications, CeO₂ is used as a support material for deposition of catalytic, magnetic, or other units on its surface. The versatility and important properties of these materials are partially attributed to the facile and rapid interconversion between the Ce³⁺ and Ce⁴⁺ oxidation states. As such, the activity of CNPs depends on their size, shape, surface features, etc.

These factors, however, cannot be easily controlled using traditional nanoparticle syntheses, which typically use harsh conditions and suffer from poor size control. In addition, traditional nanoparticles cannot be structurally characterized to atomic resolution. These problems apply also to the synthesis and characterization of metals supported on CNPs.

To solve these problems, our group has developed synthetic routes to a family of ultra-small ceria nanoparticles with dimensions up to 2.4 nm [1-3]. Since they have the same structure as the bulk CeO₂ material, we call such compounds "molecular nanoparticles" (MNPs) of CeO₂. Their molecular nature means every MNP in a particular sample is exactly identical in size and shape, overcoming a major and longstanding problem with products from traditional nanoparticle syntheses that give a range of sizes and shapes. This also allows them to be crystallized, and thus structurally characterized to atomic resolution by single-crystal X-ray crystallography. This again is not possible with traditional nanoparticles.

More recently, our group has extended this approach to the use of CeO_2 MNPs as supports for transition metal catalysts. Given the very high importance of the group 10 metals (nickel, palladium, platinum), we are particularly interested in modeling group 10 metal ions supported on CNPs by depositing these metals on our MNPs. To date, we have been developing suitable methods using nickel [4] because of it lower cost, and have been applying methods and techniques utilized in the traditional nanoparticle literature, as well as developing new methods appropriate for molecular chemistry. In this presentation we shall describe our successful deposition of nickel on preformed CeO_2 MNPs, and the subsequent structural characterization of the products, providing unprecedented information on how nickel metal catalysts are bound to CeO_2 supports.

[1] Mitchell, K. J.; Abboud, K. A.; Christou, G. Nat Commun **2017**, 8 (1), 1445.

[2] Russell-Webster, B.; Abboud, K. A.; Christou, G. Chem. Commun. 2020, 56, 5382

[3] Russell-Webster, B.; Lopez-Nieto, J.; Abboud, K. A.; Christou, G. Angew. Chem. Internat. Ed. 2021, 60, 12591

[4] Kaiser, S. K., et al., Chem. Rev. 2020, 120, 21, 11703

Expanding the Lanthanide/Pnictogen Heterometallic Chemistry: New {Sb₂Dy₃} and {Sb₇Dy₄} Single-Molecule Magnets

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The synthesis of heterometallic complexes incorporating paramagnetic 3d- and 4fmetal ions has garnered significant research interest over the past few decades as a means of obtaining high-spin molecules and single-molecule magnets (SMMs) with unprecedented structural motifs. However, the inherently weak 3d-4f exchange coupling has been identified as a limiting factor, contributing to reduced energy barriers (U_{eff}) for magnetization reversal relative to their homometallic 4f-based counterparts. Recent studies suggest that the amalgamation of diamagnetic metal ions with anisotropic lanthanide ions (Ln^{III}) can enhance the $U_{\rm eff}$. To this direction, the vast majority of reported examples are limited to oligo- and polynuclear Zn^{II}/Ln^{III} and Co^{III}/Ln^{III} complexes, in which the diamagnetic metal ions can modulate the electron density distribution of the coordinated ligands through polarization effects, and, consequently, the strength of the crystal field, thus increasing the energy gap between the ground and first excited $m_{\rm J}$ states of the Ln^{III} ions [1]. Recent investigations have shifted towards the heterometallic Werner-type coordination chemistry of anisotropic Ln^{III} ions with diamagnetic post-transition metal ions, such as the pnictogen Bill [2]. This emerging subfield leverages the versatile coordination capabilities of Group 3-5 metal ions and their strong spin-orbit coupling (SOC). Despite its potential, the analogous chemistry of Ln^{III} ions with metalloids, such as Sb^{III}, remains largely unexplored, despite their unique covalent bonding tendencies and the manifestation of inert-pair effect, which is essentially the predilection of the two electrons in the outermost atomic s-orbital to remain non-bonding.

Herein, we report the self-assembly synthesis and magnetic characterization of two new heterometallic $\{Sb_2Dy_3\}$ and $\{Sb_7Dy_4\}$ clusters (**Figure 1**), which have resulted from the use of the *N*-salicylidene-o-aminophenol chelate and they both exhibit SMM properties.



Figure 1. The $\{Dy_3Sb_2\}$ (top left) and $\{Dy_4Sb_7\}$ (top right) clusters, and their magnetic dynamics (bottom).

[1] Vipanchi et. al., *ChemPhysChem*, **2024**, 25, e202400385.
[2] K. H. Baka et. al., *Inorg. Chem*, **2025**, 64, 1962-1974.

Exploring the Apoptotic Potential of Silver(I) Metallodrugs in 2D and 3D Cell Cultures; Insights into DNA and Enzyme Interactions

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The non steroidal anti-inflammatory drugs (NSAIDs) are known to accumulate in the mitochondria where the inflammation mechanism occurs. Notably, mefenamic acid (MefH), a member of the family of the fenamates modifies the permeability of the inner mitochondrial membrane, leading cells to death either by apoptosis. Moreover, MefH was found to promote cytostatic activity against various cancer types.

Recognizing that the metallodrugs can affect the breast cancer, the metallodrugs of formula [Ag(tpE)n(Mef)] (E= P, As, Sb; n= 2 or 3), inhibit effectively 2D monolayer cells, such as MCF-7 (hormone-dependent (HD)) and MDA MB-231 (hormone-independent (HI) cell lines. In the course of our studies on metallotherapeutics, it is suggested that the cell culture format (2D monolayer vs. 3D spheroid) plays a critical role in drug response and provides new insights into the mechanisms underlying silver(I) metallodrugs on breast cancer cells. The 3D spheroid model was studied, representing human breast cancer, was designed and applied as a clear proof of the remarkable therapeutic potential of silver(I) metallodrugs. Moreover, the ex vivo DNA binding affinity and enzymes inhibition (lipoxygenase and aldoketoreductase) was also studied in order to evaluate the binding mode of these metallodrugs.



3D spheroid morphology of MCF-7 cells treated with [Ag(tpE)n(Mef)]

References

[1] C.N. Banti, S.K. Hadjikakou et.al., New Apoptosis Inducers Containing Anti-inflammatory Drugs and Pnictogen Derivatives: A New Strategy in the Development of Mitochondrial Targeting Chemotherapeutics, J. Med. Chem. 2023, 66, 4131-4149

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Human Resources and Social Cohesion Programme

Slow Magnetization Relaxation in Families of Triangular {Co^{III}₂Ln^{III}} and Butterfly-like {Co^{III}₂Ln^{III}₂} Clusters

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The synthesis of heterometallic complexes featuring both paramagnetic 3d- and 4f-metal ions has gained considerable attention in recent years, especially for the development of high-spin molecules that exhibit single-molecule magnetic behavior. However, the weak 3d-4f exchange coupling has been identified as a limiting factor, resulting in lower energy barriers for magnetization reversal compared to homometallic 4f-based complexes. Recent research indicates that incorporating diamagnetic metal ions alongside anisotropic lanthanide ions (Ln^{III}) can enhance the anisotropy barrier. Most reported examples are focused on the preparation of oligo- and polynuclear Zn^{II}/Ln^{III} complexes, where the diamagnetic Zn^{II} ions influence the electron density distribution of the coordinated ligands through polarization effects, thereby strengthening the crystal field and increasing the energy gap between the ground and first excited m_J states of the Ln^{III} ions [1]. However, the heterometallic chemistry of the diamagnetic low-spin Co^{III} ions and lanthanides has been barely explored, despite that recent advances in the synthesis of 3d/4f SMMs have revealed the effective role of Co^{III} ions in the enhancement of the Ln^{III} magnetic dynamics [2].

To this perspective, in the present work we report the self-assembly synthesis and characterization of two new heterometallic Co^{III}/Ln^{III} families of complexes; the trinuclear $\{Co^{III}_2Ln^{III}\}$ triangles, where Ln^{III} are Tb^{III} , Dy^{III} and Er^{III} , and the tetranuclear $\{Co^{III}_2Ln^{III}_2\}$ butterfly-like clusters, where Ln^{III} are the Gd^{IIII}, Tb^{III} and Dy^{III} (**Figure 1**).



Figure 1. (left) The molecular structure of the {Co^{III}₂Ln^{III}} clusters and the frequency dependence of the out-of-phase (χ'') signals of {Co^{III}₂Dy^{III}}. (right) The molecular structure of the {Co^{III}₂Ln^{III}₂} clusters and the temperature dependence of the out-of-phase (χ'') signals of {Co^{III}₂Dy^{III}₂}.

[1] Vipanchi et. al., ChemPhysChem, 2024, 25, e202400385.

[2] D. I. Alexandropoulos, Th. C. Stamatatos et. al., Chem.Eur. J., 2023, 29, e202302337.

Addressing weakly coupled and *g*-asymmetric two-spin systems with nutation spectroscopy

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Two-spin systems represent the simplest possible example of electron spin-spin interaction (exchange and/or dipolar). In principle, therefore, their magnetic resonance properties should be a solved problem. This, however, is not the case when some simplifying assumptions do not hold: when the two *g*-tensors are asymmetric and when the interaction is moderate. Also when hyperfine interactions are operative.



This situation is of particular interest in the context of Quantum Information Processing, since the implementation of a two-qubit gate (such the CNOT) is a *sine qua non* for the derivation of a universal set of quantum gates, and such two-spin systems have been proposed for this role. Most importantly, however, it underlines the limits of modeling even of the most simple systems.

This talk will present the use of nutation spectroscopy, as well as other EPR techniques, to untangle these problems,1,2 as well as the challenges in interpreting such results.

1. Komeda, J. et al. Selective Transition Enhancement in a g -Engineered Diradical, Chem. – Eur. J. 2024, 30, e202400420 (DOI: 10.1002/chem.202400420).

2. Appleton, J. L. et al. *Nutation Spectroscopy of a Weakly Interacting Heterobimetallic Spin System, Chem. – Eur. J.* **2024**, e202403521 (DOI: 10.1002/chem.202403521).

Uniquely Programmable Supramolecular Polymers from Covalently-Fixed Monomers

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Synthetic supramolecular polymers (SPs) are now rivaling the form and function of biopolymers through advancements in chemical synthesis but also a sophisticated understanding of how monomer structure dictates assembly thermodynamics, kinetics, and expressions of chiral information. In recent years [1] we presented the idea that "covalent fixation" of two self-assembling SP monomers to produce a self-assembling cyclic dimer could lead to unique atomic level control of structure, dynamics, and stereochemistry on the supramolecular level. Our design features hydrogen bonding (H-bonding) between chiral cyclophanes through appropriate functional groups (e.g., amides); the result is a homochiral one-dimensional nanostructure featuring a double helical array of H-bonds, reminiscent of both peptides and DNA. The motif is robust, persisting in solution and the solid state (with little exception) despite changes in bridge structure, H-bonding unit structure/connectivity, and substituents. Structure-property relationships will be discussed showing how the assembly thermodynamics, and self-association energies, can be tuned over several orders of magnitude by small structural changes to the monomers. In hydrocarbon solvents these systems exist as processable supramolecular polymers. More sophisticated monomer designs will be presented that could provide new ways to probe. and even control, supramolecular polymer mechanism.[2]

^[1] Henderson, W. R.; Liu, G.; Abboud, K. A.; Castellano, R. K. "Tuning Supramolecular Polymer Assembly Through Stereoelectronic Interactions", *J. Am. Chem. Soc.* **2021**, *143*, 12688–12698.

^[2] Stearns, C. D.; Kumar, A.; Ghiviriga, I.; Dobrzycki, L.; Abboud, K. A.; Castellano, R. K. "Mixed Amide [2.2.]Paracyclophane Assemblies Emulating Supramolecular Copolymers", submitted.

Interaction between Magnetic Molecules and Surfaces

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In this talk, I first report our studies of the structural and magnetic properties of trilayer MnPc molecules adsorbed on NCO(001) and Pt(111) surfaces using DFT calculations. The lowest energy adsorption configuration was determined for the first-layer MnPc on both surfaces. The interlayer stacking between adjacent MnPc molecules was found to vary with the distance from the NCO(001) surface, but not for the Pt(111) surface. The spin Hamiltonian parameters, such as exchange coupling constants and the zero-field splitting, were calculated for the trilayer MnPc. It was found that surface adsorption has a strong influence on the spin Hamiltonian parameters, especially those involving the MnPc molecule in contact with the surface.

In the second part of this talk, I discuss our results of surface adsorption of two mononuclear lanthanide complexes, TbL1 and TmL1 (with L = $C_{33}H_{33}N_4O_3$), on a monolayer of MoSSe. Stable adsorption configurations are examined using a combination of methods, including the Lennard-Jones force field, the PM7 semi-empirical method, and density functional theory. The crystal field splitting of low-lying energy levels is calculated using the complete active space self-consistent field method before and after surface adsorption. The lowest-lying energy levels of both TbL1 and TmL1 correspond to a total angular momentum of J = 6. For an isolated TbL1, the ground state is dominated by $m_J = 0$, with the first and second excited states being quasi-degenerate. Upon surface adsorption, this quasi-degeneracy is lifted, resulting in a quasi-doublet formed by the ground state and the first excited state. For TmL1, the ground state and the first excited state are consistently dominated by $m_J = \pm 6$, regardless of the presence of the MoSSe substrate. The quasi-doublet of TmL1 becomes more separated from the higher energy levels after surface adsorption, which is desirable for quantum information applications.

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Enhanced Bio-electrochemical CO₂ Fixation Efficiency by Embedment of Artificial Enzyme into Bacterial Membrane

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An artificial membrane-bound enzyme was embedded into bacterial membrane to greatly enhance CO₂ fixation reactions. For autotrophs that are capable of utilizing CO₂ as carbon sources in the presence of hydrogen, the microorganismal activity is often limited by the low utilization of hydrogen due to liquid-phase diffusion barrier. Here, we designed a biocompatible artificial [FeFe] hydrogenase model that can be embedded in bacterial membrane and produces H₂ in situ for the microorganism to use. The system enhanced CO₂ fixation per kilowatt-hour (kWh) of electricity by 7.7 times, achieving nearly 100% utilization of hydrogen within our bioelectrochemical molecular catalytic hybrid system. The efficient utilization of hydrogen resulted from the direct transfer of hydrogen from membrane-bound molecular catalysts to the microorganisms. This artificial membrane-bound enzyme scavenged reactive oxygen species under various CO2 concentrations and flow rates, and enabled our system to integrate with commercial electrode materials. The maximum electricity conversion efficiency (η_{elec}) reached 16.3±1.1%, translating to a capture of 53.8±1.5 grams of CO₂ per kWh of electricity to produce bacterial biomass. In addition, over an average of a five-day period, a consistent nelec of 16.2% was achieved in a continuous culture setting.

Ab Initio Description of Luminecence in Lanthanide based SMMs

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Lanthanide complexes often exhibit concomitantly magnetization blocking and luminescence. Given the complexity of these properties, their description benefits much from *ab initio* insight. Although *ab initio* calculations have been widely used for the rationalization of magnetism of lanthanide based single molecule magnets (SMMs), they have not yet been applied for the description of luminescence in Ln complexes.

In this talk I will concentrate on the *ab initio* description of two aspects of luminescence in lanthanides. First, the relative contributions to the integral emission intensity from the six possible mechanisms of electrodipolar luminescence will be assessed on the example of ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ luminescent band of the erbium trensal complex [1]. It will be shown that the conventional Judd-Ofelt mechanism based on the electrostatic crystal field yields only a quarter of the integral intensity of this band. Accordingly, three quarters of it are contributed by covalent binding of erbium and ligand orbitals via three major mechanisms, the 4f-ligand and ligand–ligand electric-dipole transitions and covalent enhancement of the hybridization of 4f and even empty orbitals of erbium. Second, an *ab initio* approach for the calculation of vibronic luminescence bands will be presented [2]. On the example of the same Er(III) trensal complex, it will be show in particular that the assignment of vibrational satellites to the electronic emission lines can hardly be done without a detailed *ab initio* analysis.

[1] L. Ungur, B. Szabo, Z. A. ALOthman, A. A. S. Al-Kahtani, L. F. Chibotaru, *Inorg. Chem.*, **2022**,

61, 5972

[2] V. D. Dergachev, L.F. Chibotaru, S. A. Varganov, J. Phys. Chem. Lett., 2025, 16, 2309

Reversing the Synthesis of Colloidal Semiconductor Nanocrystals

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The synthesis of various semiconductor colloidal quantum dots (CQDs) has been vastly explored over the last 40 years, producing materials with excellent optoelectronic response, which renders them ideal for optoelectronic devices. Indeed, due to their unique properties, CQDs have been used in a wide range of optoelectronic applications such as photodetectors1, solar cells, light-emitting diodes (LEDs) and as optical gain media for the realization of lasing, demonstrating state-of-the-art performance. Therefore, the CQD technology has already been integrated into commercial applications, holding an over increasing market share.

Hence, the production of these semiconductor materials has been increased dramatically, while their life-cycle management and particularly their recycling, remains an underexplored pressing challenge. However, the widespread integration of semiconductor CQDs into the consumer market remains limited due to the inherent toxicity related to their size and composition, which raise critical environmental and health concerns. The most common recycling protocols of materials and devices include chemical and mechanical methods which mainly involve their pyrolysis for thermal energy recovery or their grinding and extrusion via temperature and high pressure.

In this work, we propose a facile a radical novel reaction scheme, environmentally friendly and low-cost chemical approach for recycling a large gamut CQDs spamming from metal chalcogenides to perovskite materials. We successfully employed a full recycle process back to precursor solutions and subsequently resynthesized new CQD materials in solution. The recycling process involves bond cleavage and detaching of atoms from the thermodynamically stable nanocrystals until their complete dissolution in the presence of chelate ligands, such as carboxylic acids forming stable precursor solution for further use.



Molecular Analogues of the LnMnO₃ Lanthanide Manganites with the Perovskite Structure

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The family of AMnO₃ manganite perovskites (A = a main group or lanthanide metal) is one of the most exciting within the field of materials chemistry because of the wide variety of important properties that they exhibit, and which are relevant to many present and future technologies. For example, the AMnO₃ perovskites, and their doped $M_xLn_{1-x}MnO_3$ (M = a M^{2+} ion) derivatives, exhibit magnetic properties spanning a wide range from antiferromagnets (A = La, Ca, etc) through to multiferroics (ferromagnetic and ferroelectric, A = Bi, Tb, etc). As part of our general program involving the synthesis of molecular metal/oxo clusters as a 'bottom-up' molecular route to ultra-small nanoparticles of important metal oxides such as CeO_2 – we prefer to call such clusters 'molecular nanoparticles' (MNP's) if the metal/oxo core is \geq 1 nm - we also initiated a search for molecular clusters structurally related to the heterometallic manganite perovskites. We were stimulated to do this by the possibility that such clusters might still exhibit properties of the bulk material, and that they might therefore behave as "single-molecule multiferriocs", exhibiting magnetic and ferroelectric properties, albeit at very low temperature, just as molecular clusters can function as "single-molecule magnets" And being molecular, they would be amenable to single-crystal X-ray diffraction studies to characterize their structure to atomic resolution, and single-crystal EPR, magnetoelectric coupling, and other solid-state studies, as well as in frozen-solutions. The breakthrough came several years ago with the synthesis of a {Ce₃Mn₈O₈} cluster whose core was structurally analogous to the repeating unit of the CeMnO₃ manganite perovskite (a cube of 8 Mn with a Ce at the center) [1]. The magnetic properties of this cluster were fascinating in their similarity to those of bulk manganites, Nevertheless, what has been a high priority in the last few years is extension of the project to the later Ln ions with larger magnetic moments and large magnetoanisotropy. Unfortunately, his proved very challenging. Nevertheless, our efforts were recently rewarded with the successful development of synthetic routes to products with the desired structure. We shall describe in this presentation some of our recent progress, including crystal structures and the results of preliminary magnetic studies.

[1] Thuijs, A. E.; Li, X.-G.; Wang, Y.-P.; Abboud, K. A.; Zhang, X.-G.; Cheng, H.-P.; Christou, G. *Nature Commun.* **2017**, *8*, 500.

Spectroscopic study of the high-spin S₂ state of the photosynthetic water splitting complex

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The Mn₄CaO_{5/6} complex of Photosystem II (PSII) is responsible for the catalytic splitting of water into molecular oxygen, protons, and electrons - an essential process for life on Earth. This reaction occurs through a five-step S-state cycle (S_0-S_4) , where the accumulation of oxidising equivalents on the Mn₄CaO_{5/6} eventually drives O–O bond formation. Multiple spin configurations of the S₂ state (Mn^{III}Mn^{IV}₃) occur, with the major component being the low spin S = 1/2 form. A high-spin form with S = 7/2 has been proposed to be an intermediate in the $S_2 \rightarrow S_3$ transition, potentially playing a role in water binding during this transition. Despite its functional significance, the structural and electronic properties of the S = 7/2 form remain unknown, making its characterization crucial for unraveling the mechanistic details of the $S_2 \rightarrow S_3$ and, in particular, the water binding step. In this study, the high-spin S_2 state (S = 7/2) from cyanobacteria was investigated using a combination of X-ray absorption spectroscopy (XAS) and electron paramagnetic resonance (EPR) spectroscopy, including electron-electron double resonance (ELDOR) detected NMR (EDNMR). XAS provide insights into the oxidation state and local geometry of the Mn ions, while high-field EPR and EDNMR probe the magnetic interactions and ligand environment of the Mn cluster. The results are discussed in the context of proposed structural models for the S = 7/2 S₂ state, contributing to a deeper understanding of the $S_2 \rightarrow S_3$ transition and the mechanism of water binding.

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Modeling Spin for Applications of Metal Complexes

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Unpaired electrons are of importance for the reactivity of transition metal complexes and are responsible for spectroscopic and molecular magnetic properties of transition metal and rare earth compounds. Thorough experimental studies combined with quantum-chemical modeling help to optimize systems for specific applications. Three examples are presented to demonstrate the relation between coordination geometry and electronic structure: (i) The activation of oxygen by high-valent nonheme iron complexes, where the efficient modulation of the energy gap between the spin ground and first excited states lead to the most reactive iron(IV)oxido catalyst known todate.^{1,2} (ii) A manganese(II) based MRI contrast agent with exceptional stability, manganese(II) selectivity and MRI efficiency.^{3,4} (iii) The validation of abinitio predicted magnetic anisotropies in dysprosium(III) compounds.⁵⁻⁷

- 2 P. Comba, G. Nunn, F. Scherz, P. H. Walton *Faraday Discussion*, **2022**, 234, 232.
- 3 P. Cieslik, P. Comba, D. Ndiaye, E. Toth, G. Velmurugan, H. Wadepohl *Angew. Chem. Int. Ed.*, **2022**,

e202115580.

4 D. Ndiaye, P. Cieslik, H. Wadepohl, A. Pallier, S. Meme, P. Comba, E. Toth *J. Am. Chem. Soc.*, **2022**,

144, 21555.

- 5 P. Comba, L. J. Daumann, R. Klingeler, C. Koo, M. J. Riley, A. E. Roberts, H. Wadepohl, J. Werner *Chem. Eur. J.*, **2018**, *24*, 5319.
- 6 P. Comba, M. Enders, M. Grosshauser, M. Hiller, D. Müller, H. Wadepohl *Dalton Trans.*, **2017**, *46*, 138.
- 7 P. Comba, M. Enders, M. Grosshauser, M. Hiller, R. Klingeler, C. Koo, D. Müller, G. Rajaraman, A. Swain, M. Tavhelide, H. Wadepohl *Chem. Eur. J.*, **2021**, *27*, 9372.

¹ P. Comba, D. Faltermeier, S. Krieg, B. Martin, G. Rajaraman Dalton Trans., 2020, 49, 2888.

Floquet Engineering Molecular Spin Qubits

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Magnetic molecules hold significant potential for guantum devices. Traditional chemical approaches undertaken by modifying the ligands surrounding the metal center, as well as the supporting surface, only enable discrete and time-fixed modifications to their energy level structure and spin coherence properties. Alternatively, by means of Floquet engineering in the form of a time-periodic magnetic field coupling to the emergent total spin, we demonstrate control of the low-lying energy levels that is continuous, ultrafast, and reversible. We focus on an S = 1 electronic spin Hamiltonian containing the zero-field and Zeeman terms. Remarkably, under the action of the linearly polarized Floquet controls, all three energy levels retain their stability against variations in an external static magnetic field for all driving amplitudes under consideration. This type of stability is closely linked to having a net-zero total Zeeman shift, which results from both static and effective dynamical contributions. Further physical insights are obtained from an effective Hamiltonian, derived analytically from second order van Vleck degenerate perturbation theory. Based on our theoretical predictions, experimentalists will be able to dynamically tune qubit energy gaps to values that are useful in their specific laboratory settings, while retaining the spin decoherence suppressing effect of maintaining a clock transition.



Tuning high energy density cathodes for electrochemical energy storage

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Layered Ni-rich oxides as cathode active materials offer the promise of high energy densities in Li-ion batteries, where quasi-spherical secondary assemblies are composed of smaller primary particles. Deleterious effects of secondary assembly cracking and the associated chain of degradation reactions that can occur with surrounding electrolyte significantly impinge upon capacity performance and retention. There is a strong morphology-structureproperty interplay at work here stemming from synthesis conditions, which have profound effects on the primary grain assembly, orientation and void formation within the secondary structure. In this talk, I will discuss our latest work on controlling the precipitation and growth of Ni-rich cathode particles, where alignment of primary particles can fine-tune Li⁺ transport modes. Single-particle nanoindentation studies reveal directionally-dependent mechanical strength, complemented by X-ray computed tomography (Figure 1) which elucidates grain boundary weakening and severe intergranular cracking exacerbated by void formation. These insights are validated by electrochemical cycling data. We show that cathode active material performance and lifetime can be optimised through design principles based on tailoring the orientation of primary particles within energy dense secondary assemblies. I will also discuss a new operando muon spectroscopy (µSR) method which can be applied to investigate how local A-length scale diffusion and internal field properties change in cathodes as a function of state-of-charge, which we have recently demonstrated for Ni-rich cathodes. Our design of a new Battery Analysis by Muon (BAM) cell allows monitoring of diffusional properties with highly correlated structural changes in the unit cell during operating conditions.



Figure 1. XRD-CT data of Ni-rich cathodes before and after cycling, demonstrating a change in crystallographic orientation in secondary particle assembles.

[1] I. McClelland, S. G. Booth, N. N. Anthonisamy, L. A. Middlemiss, G. E. Perez, E. J. Cussen, P. J. Baker and S. A. Cussen, *Chem. Mater.*, **2023**, *35*, 4149
[2] L. Wheatcroft, A. Bird, N. Gollapally, S. G. Booth, S. A. Cussen and B. J. Inkson, *Batteries and Supercaps*, **2024**, e202400077.

Molecular Models for Single Cobalt Ions Supported on Cerium Dioxide Nanoparticles: Heterometallic Ce/Co-oxo Clusters

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Cerium dioxide (CeO₂, ceria) nanoparticles (CNPs) have gained substantial interest in a wide range of fields including industrial catalysis and, more recently, biomedical applications. In addition, ceria-containing materials have often been used as redox support materials, solid oxide fuel cells, UV filters, and three-way catalysts (TWCs) for the control of auto-exhaust pollutants. This outstanding versatility is partially due to the significant natural abundance of cerium and its facile Ce³⁺/Ce⁴⁺redox capability.

Despite the widespread use of nanoceria, the current synthetic procedures suffer from poor size control (i.e., polydispersity) and often require extreme reaction conditions. Furthermore, the detailed structural analysis of nanoparticles to atomic resolution remains a massive challenge. Therefore, we have developed molecular 'bottom-up' routes to molecular cerium-oxo-carboxylate clusters that are ultra-small (1–3 nm) CNPs with outstandingly mild reaction conditions. These bring all the advantages of molecular chemistry to the area, including monodispersity (single-size), solubility, and crystallinity, the latter enabling structural characterization to atomic resolution by single-crystal X-ray crystallography. Given their strong resemblance to the bulk material, we classify these clusters as "molecular nanoparticles" (MNPs).¹⁻²

More recently, in the field of catalysis different elements, ranging from early to late transition metals with CNPs have been extensively synthesized and investigated for their use as catalysts. Therefore, we have extended this approach towards using CeO₂ MNPs as supports for early 3d transition metals such as Mn^{III} on their surface.³ However, there are no reports to date of molecular Ce/Co-oxo clusters that can be described as models of ceria-supported Co^{III} ions despite its significance in catalysis such as dehydrogenation of ethane and low temperature methanation at low partial pressure of CO₂.^{4,5} We have therefore taken on the synthetic challenge of attaining such compounds, and this presentation will describe the synthesis and structures of a family of novel Ce/Co-oxo clusters that represent molecular models of Co^{III} ions on CNP surfaces.

References

- 1. K. J. Mitchell, K. A. Abboud, G. Christou, *Nat. Commun.*, **2017**, 8, 1445.
- K. J. Mitchell, J. L. Goodsell, B. Russell-Webster, U. Twahir, A. Angerhofer, K. A. Abboud, G. Christou, *Inorg. Chem.*, 2021, 60, 1641-1653.
- S. Das Gupta, A. Thuijs, E. Fisher, K. A. Abboud, G. Christou, *Inorg. Chem.*, 2022, 61, 6392-6402.
- 4. Y. Hosono, H. Saito, T. Higo, K. Watanabe, K. Ito, H. Tsuneki, K. Hashimoto, Y. Sekine, *J. Phys. Chem. C.*, **2021**, 125, 11411-11418.
- 5. J. Struijs, V. Muravev, M. Verheijen, E. Hensen, N. Kosinov, *Angew. Chem. Int. Ed.*, **2022**, 62, e202214864 (1-9).

Developing MRI-based therapeutic and diagnostic tools: from cancer to chemical weapons

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Magnetic resonance imaging (MRI) is a highly effective non-invasive technique, and its diagnostic power is significantly enhanced with the introduction of contrast agents. While Gd-chelate-based molecular contrast agents (such as Dotarem®) are commonly used in clinical settings, they often fall short in terms of specificity for targeted disease diagnostics or biomarker detection. Additionally, they frequently exhibit suboptimal signal-to-noise ratios and limited blood circulation half-life, which can reduce their effectiveness in clinical applications. However, with precise engineering, contrast agents—particularly those utilizing nanomaterials—have the potential to address these limitations.

In this presentation, I will outline our strategies for the design and development of MRI contrast agents tailored for various applications. I will introduce nanostructured composites designed to report on drug release in a novel non-invasive manner, enabling the pharmacokinetic mapping of drug delivery for personalized medicine. I will also discuss recent breakthroughs in using molecular contrast agents to enhance the diagnosis of chemical weapon poisoning, describing how MRI can be harnessed as a tool to determine even weak binding interactions, offering insights which cannot be isolated using 'gold standard' fluorescence binding techniques.



Figure. (a) Schematic showing how pH-responsive composites containing MRI-active units and drugs can be used to monitor the release of a drug; (b) molecular Gd-chelate species capable of changing MRI signal as a result of displacing coordinated water molecules; (c) MRI relaxation titration showing how increased concentration of an analyte species results in changes in MRI signal due to the displacement described in (b); inset shows phantom MR image without (left) and with (right) competitive analyte showing signal change.

Covalently-linked Metalloporphyrin Dimers and their Magnetic and Spectroscopic Properties

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Research in our group in recent years has included the synthesis and study of covalently-linked oligomers of metal-oxo clusters that exhibit the appropriate magnetic and quantum properties to make them potential spin-based molecular components in new 21stcentury technologies. Such properties include exchange-biased quantum tunneling of magnetization (EB-QTM) and quantum superposition and entanglement states (QSE), all arising from weak exchange interactions between the linked clusters. Following our previous work using trinuclear Mn^{III}₃ and dinuclear Mn^{III}Mn^{IV} clusters with S = 6 and S = $\frac{1}{2}$ ground states, respectively, we have more recently shifted our focus to linking mononuclear metal complexes in order to obtain products that are more chemically rigid and robust, and that also allow variation of the metal ions incorporated. Therefore, we have targeted and now successfully synthesized a family of rigid, covalently linked, cofacial, bis-metalloporphyrin complexes designed to exhibit exchange interactions of the desired magnitude. This presentation shall describe the organic synthesis of the targeted bis-porphyrins, and the preparation and crystal structures of representative bis-metalloporphyrin derivatives, as well as their DFT computational results, SQUID magnetic properties, and electron paramagnetic resonance studies.
Gas adsorption meets Deep Learning

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In the era of big data, machine learning (ML), a subfield of artificial intelligence, offers powerful tools widely used in science and industry due to their significantly lower computational cost compared to conventional methods. However, the accuracy of ML predictions relies heavily on identifying the right parameters (features) that enable effective learning from past data. Additionally, the quality and size of the dataset used to train the algorithm are critical for reliable predictions.

In traditional ML, feature extraction involves manually identifying and engineering key characteristics from raw data to enhance model performance. In contrast, deep learning (DL) automates this process through layered neural networks that learn relevant features directly from data, making it especially effective for complex tasks like image and speech recognition. This end-to-end approach allows DL models to process high-dimensional data with minimal preprocessing.

Here, we propose a deep learning framework for predicting gas adsorption properties of materials, using the Potential Energy Surface (PES) as a descriptor [1]. This descriptor is universally applicable to various materials and properties, as PES uniquely combines the material's classical structural characteristics with its quantum electronic structure, encapsulating the material's information in both classical and quantum worlds - a fusion of chemistry and physics.

Furthermore, we developed a generalized deep learning framework that predicts gas adsorption properties from a point cloud representation of the material's structure, eliminating the need for hand-crafted features [2]. This approach requires only the unit cell structure, offering a complete yet simplified material representation.

Our algorithms were tested on CO2 uptake predictions in MOFs, where our deep learning models significantly outperformed the best ML-Random Forest model in the literature, which relied on geometric descriptors. This methodology was further validated across different materials (e.g., COFs), gases (e.g., CH4), and datasets, demonstrating broad applicability for diverse materials and properties.

References

- "Gas Adsorption Meets Deep Learning: Voxelizing the Potential Energy Surface of MOFs." Antonios P. Sarikas, Konstantinos Gkagkas, George E. Froudakis, Scientific Reports 14, 2242 (2024) <u>https://doi.org/10.1038/s41598-023-50309-8</u>
- "Gas Adsorption Meets Geometric Deep Learning: Points, Set and Match" Antonios P. Sarikas, Konstantinos Gkagkas, George E. Froudakis, Scientific Reports 14, 27360 (2024). <u>https://doi.org/10.1038/s41598-024-76319-8</u>

Design & development of new heterogeneous photocatalysts based on novel 2D materials for environmental applications

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2D materials are of great importance for a variety of applications involving catalytic processes and physicochemical properties such as adsorption and chemisorption, thanks to their extremely large active surface area per unit mass and their mechanical stability in contrast to large surface area nanoparticles. The last years, much of the research effort on 2D materials focuses on its use as building block for the development of novel hybrid structures with well-defined dimensions and behavior suitable for applications among else in gas storage, heterogeneous catalysis, gas/liquid separations, nanosensing and biology. Towards this aim, here we demonstrate the development of green and sustainable processes for the development of novel 2D heterogeneous catalysts. 2D Xanes of group-14 [germanane (GeH) and silicane (siloxane)], anionic layered double hydroxides (LDHs), cationic clay minerals and synthetic clay analogues (SCA) with high surface area, tunable pore size and functionalities were prepared using top-down synthetic approaches and applied as supports for the immobilization of active species such as photocatalytic molecules (e.g. anthraquinone and thioxanthone derivatives). All materials were characterized by a combination of analytical techniques. The heterogeneous catalysts were tested in photochemical upcycling of plastic wastes, such as polystyrene (PS), effective adsorbents for environmental remediation, gas (H₂ and CO₂) storage materials, as well as in other catalytic processes.

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Antimicrobial Silver(I) Formulations and Biogenic Materials for Next-Generation Medical approaches

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The rising prevalence of antimicrobial resistance (AMR) has emerged as a critical global health challenge, compromising the efficacy of conventional antibiotics and increasing mortality rates from bacterial infections. Silver-based biogenic materials and formulations present a promising alternative due to the broad-spectrum antimicrobial properties of silver(I) ions and nanoparticles. These materials effectively disrupt microbial cell membranes, interfere with DNA replication, and inhibit biofilm formation, making them ideal candidates for next-generation medical applications.

To address AMR, we integrate silver-based antimicrobial agents into biomaterials such as hydrogels, coatings, and medical implants, aiming to develop innovative and effective therapeutic strategies. The synthesized silver(I)-based biomaterials were extensively characterized using XRD, XRF, TG-DTA, DTG/DSC, and FT-IR-ATR to confirm their structural and physicochemical properties. Their antimicrobial efficacy was evaluated against key microbial keratitis pathogens, including the Gram-negative *Pseudomonas aeruginosa* and the Gram-positive *Staphylococcus epidermidis* and *Staphylococcus aureus*. Furthermore, the biocompatibility and safety of these materials were assessed through *in vitro* and *in vivo* toxicity studies, including evaluations using human corneal epithelial (HCEC) cells via the micronucleus assay, as well as toxicity screening with *Artemia salina* and *Allium cepa* models. The results highlight the potential of silver(I)-based biomaterials as advanced antimicrobial solutions for medical applications, paving the way for safer and more effective strategies to combat AMR.



References

[1] C.N. Banti, S.K. Hadjikakou et.al., Hydrogels containing water soluble conjugates of silver(I) ions with amino acids, metabolites or natural products for noninfectious contact lenses, Dalton Trans., 2021, 50, 13712-1372

Acknowledgements

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Human Resources and Social Cohesion Programme

Molecular Nanoparticles of Birnessite-type MnO₂ via Reductive Aggregation

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Recently, molecular nanoparticles (MNPs) have emerged as atomically precise materials displaying the same metal-oxo lattice as their bulk counterparts and having core dimensions larger than 1 nm. Molecular synthetic chemistry offers a powerful approach to the ultra-small size regime of nanoscience by offering monodispersity, true solubility, mild aerobic syntheses, and structural atomic resolution. Our research group first forayed into this area with the bottom-up synthesis of cerium dioxide MNPs which has now been extended to other important homometallic and heterometallic metal oxides. The nanoparticles of Mn^{III,IV} oxides have garnered immense interest for applications ranging from supercapacitors to catalysis to biomedical applications. The goal of this work was to synthesize MNPs of the birnessite-type MnO₂, a layered form of MnO₂ with the general formula of (A_x)(MnO_{2-x})•yH₂O for A²⁺ cations. The reductive aggregation procedure pioneered by our group was re-evaluated through this lens as it bears resemblance to a synthetic strategy used in the preparation of both Mn^{III/IV} oxides and nanoparticles. The prior work had produced Mn₁₂ and Mn₁₆ clusters, and it was predicted that a family of [Mn^{IV}_mMn^{III}_n]-oxo clusters, where $m = x \times y$ (x and y are integers) and n = 2(x+y), could be achieved.



Figure 1. The Mn-oxo cores of birnessite-type MnO₂ (left) to the Mn₁₂, Mn₁₆, and Mn₂₁ clusters (right); Blue: Mn^{IV}, green: Mn^{III}, red: O, Grey: C

In this presentation, we report a systematic synthetic investigation that yields the highly sought after Mn_{21} member of the reductive aggregation family. A comprehensive structural analysis identifying the $[Mn^{IV}{}_mMn^{III}{}_n]$ sheet-like clusters as molecular nanoparticles of birnessite-type MnO_2 is also reported for the first time. The magnetic properties have also been characterized, establishing these molecular nanoparticles as single-molecule magnets as well.

King, P. *et al. Angew. Chem. Int. Ed.* 2004, 43, 6338-6342.
 King, P. *et al. Inorg. Chem.* 2004, 43, 7315-7323.
 Thuijs, A. *et al. Inorg. Chem.* 2015, 54, 9127-9137.

Structure-Property Studies of Paramagnetic N-Heterocyclic Carbene and Amide Complexes

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Transition metal *N*-heterocyclic carbene complexes find extensive use in catalysis, medicinal, materials, and surface science applications. While numerous paramagnetic 3*d* complexes are known comparatively fewer 4*d* and 5*d* analogues have been described. Carbene ligands are generally considered to be competent σ donors in transition metal complexes owing to the radial extent and higher energies of the carbon-centered highest occupied molecular orbital. Late transition metal single-molecule magnets offer a variety of promising features relative to their 3*d* counterparts. First, heavier transition metal ions should generally have stronger metal-ligand bonds than 3*d* derivatives, owing to efficient orbital overlap with the carbene HOMO. Second, enhanced metal-ligand covalency, particularly with rigid ligands are present, should discourage vibronic interactions that reduce complex symmetry. Third, in comparison to 3*d* ions, considerably higher spin-orbit parameters are anticipated for the 4*d* and 5*d* series, roughly scaling with atomic number which may also engender higher magnetic anisotropy.

Another approach seeks to control spin-lattice relaxation via reduction of thermally populated excited state spin levels in the absence of ligand-centered nuclear spins. Examples include V^{IV} ($S = \frac{1}{2}$) complexes where long relaxation times are often seen offering the prospect of a tunable spin-qubit platform for molecule-based information storage. A survey of the chemical literature indicates that Nb^{III,IV} complexes are underexplored in comparison to their 3*d* congeners, being limited to cyanide, pyridyl, phosphine derivatives. In this presentation, recent efforts to develop new paramagnetic complexes containing sterically demanding *N*-heterocyclic carbene and amide (Figure 1) ancillary ligands, their structures, and magnetism will be described [1,2].



Figure 1. X-ray structures and magnetic data for (left) NbCl₄(IMes)₂ and (right) NbOCl₂(IMes)₂.

[1] Eissler, M.; Shen, F.; Rajamoni, J.; Holmes, S. M. *Eur. J. Inorg. Chem.* 2025, 28, e202400516.
[2] Shen, F.; Rajamoni, J.; Holmes, S. M. *Polyhedron* 2024, 257, 117017.

Chiral Radicals and Diradicals: Synthesis, Properties and Opportunities

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Chiral paramagnetic species with an electron spin delocalized in chiral π systems are rare and are of rapidly increasing interest for the study of the CISS effect and as components of spintronic devices. The main advantage of such open-shell compounds is their high chirality, favorable electrochemical properties and the presence of the unpaired spin. A potentially large class of such materials can be obtained by connecting the benzo[e][1,2,4]triazin-4-yl fragment to chiral building blocks, *e.g.* helicenes. For this purpose, we have developed several synthetic strategies, including azaphilic addition of aryllithiums, photocyclization and Pschorr-type cyclization, permitting the formation of stable radicals with extended π systems (*e.g.* 1–7). Thus, chiral atropisomers 1 were obtained by addition of aryllithiums to benzo[*e*][1,2,4]triazines. Similarly, the azaphilic addition was used to obtain the ring-fused Blatter radical 4 and diradicals 6 and 7 [1]. Ring-fused carbohelicenes 2 [2], oxahelicene 3 and azahelicene 5 were obtained by photocyclization of appropriate precursors.



Herein, general synthetic strategies, properties of the chiral species, and the effect of π curvature on spin delocalization in chiral radicals will be discussed.

- [1] Bartos, P.; Pomikło, D.; Sorenson, K.; Hietsoi, O.; Friedli, A. C.; Kaszyński, P. J. Am. Chem. Soc. 2025, 147, 125.
- [2] Singh, H. K.; Bodzioch, A.; Pietrzak, A. Kaszyński, P. Chem. Commun. 2025, 61, 496.

Rare Earth Element-oxo Cluster Chemistry

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Metal-oxo phases, including clusters and nanoparticles, are critical for understanding both fundamental and applied aspects of f-element chemistry. For the rare earth elements (REEs), in particular, lanthanide-oxo clusters have been of significant interest due to their promising materials properties, with applications in magnetism, catalysis, and luminescence. As a result, a significant catalog of lanthanide clusters has been reported. Yet the rationale synthesis of these phases has still not been fully realized, and there remains an ongoing need to elucidate the conditions and boundaries that define their phase space. Such advancements in our knowledge would not only help elucidate the chemical and physical properties of REE cluster-based materials, but may also be leveraged in the applications space. Towards this end, our group has been examining homo- and heterometal REE cluster formation and stabilization, with an eye towards understanding how differences in metal ion identity affect cluster composition and topology. Presented here will be an overview of our recent work on the synthesis, structural chemistry, and properties of homo- and heterometal REE cluster assemblies.



Figure 1. Luminescence of heterometal Eu: Tb hexamers can be leveraged to understand cluster composition.

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Templated synthesis of a Zr₆-based sodalite MOF

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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 rational design of 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 synthesis and characterization of a novel threedimensional zirconium-based MOF, named ZrFA-4. This compound represents only the third known Zr-MOF with the sodalite topology and is an uncommon example of a Zr - formate MOF. The synthesis of ZrFA-4 was achieved *via* a solvothermal reaction involving ZrCl₄, CoCl₂, a pyridine-carboxylate ligand, and an excess of formic acid in DMF. The presence of Co²⁺ ions and the HINAB ligand was found to play a crucial templating role, directing the formation of the sodalite framework (*fig. 1*). Notably, ZrFA-4 demonstrates high stability in common organic solvents and retains its integrity up to 250°C. These findings highlight the effectiveness of template-assisted strategies in MOF synthesis and provide valuable insights for designing new functional zirconium-based MOFs.



Figure 1. Representation of (a) a single truncated octahedral cavity, (b) the sodalite (**sod**) network of ZrFA-4, and (c) the template molecules that led to the formation of the structure.

References

- 1. H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**,1230444.
- X. Guo, S. Geng, M. Zhuo, Y. Chen, M. J. Zaworotko, P. Cheng and Z. Zhang, T, *Coord. Chem. Rev.*, 2019, **391**, 44–68.

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Slow magnetization relaxation of some mononuclear 3d metal complexes

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During the last 15 years, numerous mononuclear 3d-metal complexes have been shown to exhibit slow magnetization relaxation, most often associated with the existence of zero-field splitting (zfs).[1] Direct Current (DC) magnetometry and various spectroscopic techniques, such as high- frequency and -field EPR (HFEPR) and Far-IR Magnetic Spectroscopy (FIRMS), are methods of choice for the determination of the axial, *D*, and rhombic, *E*, components, of the latter.[2] Alternating Current (AC) magnetometry studies reveal the magnetization relaxation mechanisms involved.[1]

Specific examples of tetrahedral S = 2 Fe(II),[3] and S = 3/2 Co(II) [4] complexes, bearing {R₂P(E)NP(E)R₂}⁻, R = Ph, ⁱPr and E = O, S, Se; {PhC(O)NP(O)Ph₂}⁻ and thiosemicarbazones, as ligands, will be presented and discussed.

References

[1] J. M. Frost, K. L. M. Harriman, M. Murugesu, Chem. Sci., 2016, 7, 2470.

[2] J. Krzystek, J. Telser, Dalton Trans., 2016, 45, 16751.

[3] (a) S.A. Stoian, M. Moshari, E. Ferentinos, A. Grigoropoulos, J. Krzystek, J. Telser, P. Kyritsis, *Inorg. Chem.*, **2021**, *60*, 10990.

(b) M. Pissas, E. Ferentinos, P. Kyritsis, Y. Sanakis, ChemPlusChem, 2024, e202400109.

[4] (a) S. Sottini, G. Poneti, S. Ciattini, N. Levesanos, E. Ferentinos, J. Krzystek, L. Sorace, P. Kyritsis, *Inorg. Chem.*, **2016**, *55*, 9537.

(b) E. Ferentinos, M. Xu, A. Grigoropoulos, I. Bratsos, C.P. Raptopoulou, V. Psycharis, S.-D Jiang, P. Kyritsis, *Inorg. Chem. Front.*, **2019**, *6*, 1405.

(c) E. Ferentinos, D. Tzeli, S. Sottini, E.J.J. Groenen, M. Ozerov, G. Poneti, K. Kaniewska-Laskowska, J. Krzystek, P. Kyritsis, *Dalton Trans.*, **2023**, *52*, 2035.

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Regulating Spin Crossover (SCO) Transition Temperatures towards SCO based Temperature Sensors in Food Packaging

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Materials exhibiting the spin crossover (SCO) phenomenon are motivating for both scientific research and applications [1]. SCO materials are one of the most important examples of bistable molecular systems with potential applications as sensors, electronic memories and in opto-electronics. Thermal spin transition occurs nearly exclusively in 3d transition metal complexes with d⁴-d⁷ electronic configuration and octahedral geometry for the metal ion. The SCO transition which has been widely characterized following different techniques [2], may be abrupt, gradual, hysteretic or not, depending on a variety of parameters including among others the nature of the organic ligand and the intermolecular interactions. An ideal spin crossover system would exhibit a controllable spin crossover transition at a certain temperature, either with hysteresis or not depending on the desired application. The decisive and ambitious goal of this study is to regulate the Spin Crossover transition following a rapid and easy method, and develop SCO systems that would exhibit preferable SCO transition at different temperatures. In this study within the scope to address the important shortcoming of unpredicted SCO transitions, we followed a rapid method based on a controllable SCOpolymer interaction scheme into the description of preferable SCO transitions. This enables us to establish the thermal LS-to-HS SCO transition beyond the limited thermodynamic perspective and, most importantly, to gain access to the understanding and prediction of $T_{1/2}$ in SCO materials. Such an innovation is the accurate transmutation of the application of SCO materials as temperature sensors with a great scientific and technological importance. As a proof of concept approach the applicability of these sensors in food safety applications (refrigerated products) is considered along with the validated migration release studies following accredited protocols provided by the EU. Controlling SCO transition temperature offers precise manipulation over the properties and functionalities of materials, enabling a wide range of technological advancements across various fields.



Figure. Conceptualization towards the SCO-polymer materials exhibiting tunable transitions.

References

[1] G. Molnár, S. Rat, L. Salmon, W. Nicolazzi, A. Bousseksou, *Adv. Mater.*, **2018**, *30*, 17003862.
[2] Z. G. Lada, *Magnetochem.*, **2022**, 8(9), 108.

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Luminescent Thermometer based on a Praseodymium (III) cyanidebased metal-organic framework

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The trivalent praseodymium ion (Pr^{3+}) has emerged as a versatile rare-earth element with exceptional luminescent properties. Its intricate energy level structure, characterized by a ladder array of energy manifolds, enables the generation of light across a broad spectral range, spanning from the blue and green regions to reddish-orange and near-infrared wavelengths, through downshifting, downconversion, and upconversion processes. Moreover, both *intra-4f* and interconfigurational parity-allowed $5d \rightarrow 4f$ transitions are discerned, and this luminescence versatility, characterized by both fast and slow decay times, makes Pr^{3+} a promising candidate for applications in lighting, displays, healthcare, security, and sensing.

This work presents the synthesis and thorough characterization of a novel Pr^{3^+} -based coordination polymer, { $[Pr_2^{III}Pt_3^{II}(CN)_{12}(4,4'-bpyO_2)_4(H_2O)_6]\cdot 4H_2O_n$ (1), as a rare example of Pr^{3^+} luminescent thermometry. The reduction of Pt^{4+} to Pt^{2+} under aerobic conditions, facilitated by the redox activity of water molecules, represents a significant finding, providing deeper insights into the redox behavior within this coordination system. The coordination of Pr^{3^+} ions with cyanido-bridged Pt^{2^+} centers and 4,4'-bpyO₂ ligands was shown to enable effective energy transfer, resulting in strong luminescence emissions in both the visible and near-infrared (NIR) regions. These luminescent properties underscore the potential of this material for optoelectronic applications.

The application of this polymer as a luminescent thermometric revealed a distinct temperature dependence of the luminescence over a wide temperature range (12–386 K), demonstrating the suitability of this polymer for accurate luminescence-based temperature sensing using emission both in the visible and in the NIR spectral ranges. The relative thermal sensitivity values are slightly below 1 $\% \cdot K^{-1}$ and the minimum temperature uncertainty is about 0.2 K, showcasing the potential of the material as a promising candidate for applications in fields such as microelectronics, biomedical monitoring, and aerospace applications

Host-Guest Interactions between Transition Metal Polyimines and Metal Organic Framework Pores: Pore Modulation of Guest Photophysics

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Metal organic framework (MOF) materials are attractive candidates for the development of solar energy applications due to the modularity of design, high porosity, and relative ease of functionalization of these materials. The encapsulation of photoactive guests into porous MOFs is a particularly attractive strategy for the development of photosensitive MOFs since a wide array of light sensitive catalysts have been developed that can be encapsulated within the associated MOF cavities. Transition metal complexes, including metalloporphyrins and transition metal polyimines, are of specific interest in the development of light harvesting systems as these systems display electronic transitions across a wide span of energy (spanning the solar spectrum), are generally structurally robust, exhibit significant photostability and can be readily functionalized to impart specific photophysics/redox properties. A variety of transition metal complexes have now been encapsulated as guests with MOFs and these systems display pronounced perturbations in the guest photophysics. Here, the effects of encapsulation (confinement) on the photohysics of both Ru(II) polyimine and Zn(II) porphyrin complexes will be presented with an emphasis on the role of both noncovalent interactions between the guest and the framework as well as guest structural perturbations in both the ground and excited states (Fig. 1). Understanding the complex interplay between quest photophysics and the framework cavity properties is important for the development of new light harvesting applications in MOFs.



Figure 1: Illustration of the host-guest MOF (Left) and general categories of host-guest interactions that influence guest photophysics (right)

- "Photoactive Guest Encapsulation in Metal Organic Frameworks", C. R. McKeithan, J. Mayers, A. Alanzi, and R.W. Larsen, *Dyes and Photoactive Molecules in Microporous Systems- Structure and Bonding*, V. Martínez-Martínez, F. López Arbeloa, Eds, Springer Verlog, 2022.
- "Confinement-Guided Photophysics in MOFs, COFs, and Cages", G.A. Leith, C.B. Martin, J.M. Mayers, P. Kittikhunnatham, R.W. Larsen and N.B. Shustova, *Chem. Soc. Rev.* (2021), 50, 4382-4410

The Chemistry of Masked Divalent Lanthanides

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Lanthanide chemistry is dominated by the thermodynamically stable trivalent oxidation state, which is typically redox inactive. The attraction of the more exotic divalent oxidation state stems partly from its potential use as a one-electron reducing system for a variety of synthetic applications. However, whereas access to the divalent oxidation state is straightforward for the classical three divalent ions samarium(II), europium(II) and ytterbium(II), the same is not true for other lanthanides. Indeed, synthetic applications of non-classical divalent lanthanides have only been developed to a limited extent, which is likely a consequence of the instability of these species, including sensitivity to solvent and temperature.

An indirect solution to the challenge of developing divalent rare-earth reactivity involves storing the reducing electrons on a redox-active ligand bound to a trivalent lanthanide. Here, the aim is to deliver the additional electrons to the substrate, with the redox-active ligand subsequently oxidized and eliminated, and the trivalent lanthanide transferred to the reduced substrate.

We recently reported the trivalent rare-earth dinitrogen complexes $[(Cp^{ttt}_2)_2(\mu-1,2-N_2)]$ (**1**_M, M = various lanthanides; $Cp^{ttt} = 1,2,4-C_5{}^tBu_3H_2$), in which the reduced ligand $[N_2]^{2-}$ adopts the end-on coordination mode (Scheme 1).^[1] Having shown that **1**_M can act as 'masked' divalent lanthanides by transferring one electron per metal to bipyridyl, with the resulting radical anion coordinating to the metal and with N₂ eliminated, we have since expanded our reactivity studies to incorporate small-molecules such as CO and P₄, as well as polynucleating *N*-heterocyclic ligands. The results of these studies will be presented.^[2-5]



Scheme 1. Reactivity of 'masked' divalent lanthanide dinitrogen complexes.

- [1] A. Mondal, C. G. T. Price, J. Tang, R. A. Layfield, J. Am. Chem. Soc. 2023, 145, 20121.
- [2] A. Mondal, J. Tang, R. A. Layfield, Angew. Chem. Int. Ed. 2025, 64, e202420207.
- [3] S. De, A. Mondal, J. Pitcairn, L. Clark, J. Tang, A. Mansikkamäki, R. A. Layfield, *Angew. Chem. Int. Ed.* **2025**, *64*, accepted article (DOI: 10.1002/anie.202502455).
- [4] A. Mondal, C. G. T. Price, A. Steiner, J. Tang, R. A. Layfield, manuscript submitted.
- [5] A. Mondal, J. Tang, R. A. Layfield, manuscript in preparation.

Measuring electron spin coherence times of paramagnetic metal complexes with dynamical decoupling: opportunities and pitfalls

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With increasing interest in spin-based quantum computing and the quest for paramagnetic systems with long relaxation times, the measurement of reliable electron spin coherence times has become of paramount importance. Dynamical decoupling pulse EPR methods such as Carr-Purcell-Meiboom-Gill (CPMG) or XY4- and XY8-based sequences play a key role in this effort, as they help to disentangle different sources of decoherence and potentially reveal the intrinsic T_2 value, while they also provide a means to probe the noise spectrum of the paramagnetic system under study. Although these methods are mainly evaluated for their robustness and ability to mitigate pulse imperfections, to date little attention has been paid to the selectivity of the microwave (mw) pulses, despite the fact that they are consistently applied to paramagnetic systems having a wide range of line widths relative to the pulse excitation bandwidth [1].

As partial excitation of the spectrum of metal complexes is the norm in pulsed EPR spectroscopy, this factor can hinder the reliable determination of T_2 in two ways: first, unwanted stimulated echoes, which decay with T_1 , overlap with desired refocused echoes, resulting in overestimated values of T_2 . Second, under selective mw excitation, the amplitude of the different refocused echoes shows additional time decay even in the absence of relaxation processes.

Due to the complexity of the problem, one cannot predict the contribution of unwanted stimulated echoes to the reliable determination of T_2 in a straightforward way. Here, we investigate the characteristics of CPMG, XY4 and XY8-based sequences by performing numerical simulations for a two-level spin system. Using the Liouville space representation of the spin state, we introduce relaxation effects in the simulations. We show that our numerical calculations reproduce well all the features of the experimental echoes and allow for the accurate determination of T_2 times without the need to perform tedious phase-cycle protocols to eliminate unwanted signals.

References

[1] G. Mitrikas, J. Phys. Chem. Lett. 2023, 14, 9590–9595.

µSQUID-EPR Investigations of Single Molecule Magnets

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Lanthanide-based Single Molecule Magnets (SMMs) have been suggested for quantum technologies due to their interesting electronic characteristics. These lanthanide complexes have exhibited remarkable magnetic properties ranging from large magnetic anisotropy above nitrogen temperatures to long coherence, hence leading to their proposal as sensors, quantum computer scaffolds, qubits/qu*d*its, and advanced quantum error correction protocols, amongst others. As a result, these SMMs are expected to drive significant technological advancements, contributing to the second quantum revolution by applying quantum effects in practical scenarios. A notable achievement in this field is the successful implementation of the quantum Grover's algorithm using a single TbPc₂ unit, showcasing the potential of these systems for sophisticated quantum operations.



Figure 1. µSQUID-EPR investigations of an Et₄N[¹⁶⁰GdPc₂] complex at different transverse fields and angles revealing the Berry phase interference.

A comprehensive understanding of the physical parameters that define SMMs is crucial to achieving such implementations. We describe the investigation of a Gd-based SMM employing the μ SQUID-EPR technique at sub-Kelvin temperatures [1]. This technique allows the precise determination of high-order parameters by investigating the frequency, transverse field and angular dependence of the resonant absorption of the μ SQUID loops. Furthermore, the μ SQUID-EPR allow us to observe the Berry phase interference effect in a lanthanide-based SMM for the first time. The gained understanding could, in principle, allow for implementing field-resilient SMMs as qu*d*its.

[1] G. Taran, E. Moreno-Pineda, M. Schulze, E. Bonet, M. Ruben, W. Wernsdorfer, *Nature. Commun.*, **2023**, *14*, 3361.

Spin State Switching in Iron(III) Complexes – a Thermal and Optical Study

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Competing electronic and structural order parameters in molecular crystals with capacity for spin state switching often result in complex symmetry breaking patterns and structural frustration. Recently we have observed strong magneto-elastic and magneto-electric coupling in two types of Jahn-Teller systems where a new class of domain wall architecture could be induced by thermal manipulation of spin state.^{1,2} We have also observed a variety of symmetry-breaking events in iron(III) spin crossover complexes and here we compare the outcomes in single crystal and powder samples of the same complex and also compare different types of symmetry breaking that may be possible within the same complex family, Figure 1. Examples of both thermal and light-induced switching will be discussed.



Fig. 1. (a) Structure of Fe(III) SCO complex (1) showing two independent crystallographic sites; (b) Temperature dependent magnetic moment of (1) showing two-step crossover and photomagnetic response with evidence for two independent relaxation events.

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References

- (1) V. B. Jakobsen, E. Trzop, L. C. Gavin, E. Dobbelaar, S. Chikara, X. Ding, K. Esien, H. Müller-Bunz, S. Felton, V. S. Zapf, E. Collet, M. A. Carpenter, G. G. Morgan, *Angew. Chem. Int. Ed.*, 2020, *59*, 13305-13312. 10.1002/anie.202003041.
- (2) V. B. Jakobsen, E. Trzop, E. Dobbelaar, L. C. Gavin, S. Chikara, X. Ding, K. Esien, H. Müller-Bunz, S. Felton, E. Collet, M. A. Carpenter, V. S. Zapf, G. G. Morgan, *J. Am. Chem. Soc.*, 2022, *144*, 195-211. doi.org/10.1021/jacs.1c08214.

All Wrapped Up: How Molecular Encapsulation Impacts the Chemistry of Redox-active Molecules and Electrocatalysts

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Molecular metal oxides have received considerable attention in recent years as potential components in future energy storage devices thanks to their structural stability and rapid, reversible redox properties. Due to their discrete nature, their use as components in energy storage devices relies on their stable combination with conductive solid or liquid-phase supports. [1] In our recent research we have been developing a range of cluster-based redox materials and exploring their potential application in a range of technologies.

We recently showed that molecular metal oxide encapsulation within the cavities of single-walled carbon nanotubes leads to host-guest redox materials with exceptional long-term cycle stability (Figure 1). [2,3,4] Here, a range of new hybrid redox-active nanomaterials will be presented and their physical properties discussed.

Our recent studies have focussed on how these systems interact with different counterions and small molecules, leading to new understanding in energy storage and electrocatalysis of small molecules.[5]



Figure 1. Redox-active molecular metal oxides encapsulated within the cavities of singlewalled carbon nanotubes.

[1] Sadakane, M.; Steckhan, E., Chem. Rev. **1998**, 98 (1), 219.

[2] Jordan, J. W., Lowe, G. A., McSweeney, R. L., Stoppiello, C. T., Lodge, R. W., Skowron, S. T., Biskupek, J., Rance, G. A., Kaiser, U., Walsh, D. A., Newton, G. N., Khlobystov, A. N., *Adv. Mater.* **2019**, *31*, 1904182.

[3] Jordan, J. W.; Cameron, J. M.; Lowe, G. A.; Rance, G. A.; Fung, K. L. Y.; Johnson, L. R.; Walsh, D. A.; Khlobystov, A. N.; Newton, G. N. *Angew. Chem. Int. Ed.*, **2022**, *61*(8): e202115619.

[4] Jordan, J. W.; Fung, K. L. Y.; Skowron, S. T.; Allen, C. S.; Biskupek, J.; Newton, G. N.; Kaiser, U.; Khlobystov, A. N. *Chem. Sci.*, **2021**, *12*, 7377–7387.

[5] Jordan, J. W.; Mortiboy, B. Khlobystov, A. N.; Johnson, L. R.; Newton, G. N.; Walsh, D. A. *J. Am. Chem. Soc.* **2023**, 145, 16, 9052–9058.

Adventures in the Coordination Chemistry of a Little Explored Salen – type Schiff Base with Lanthanoid and Actinoid Ions

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Inorganic chemistry was dominated by transition metals in the second half of the 20th century. In the last 30 years or so, there has been a considerable shift of focus on the chemistry of f elements, mainly due to their important properties. Salen – type Schiff bases have played an important role in this area [1]. An almost unexplored ligand of this family is H₂L2, which contains bulky substituents on its imino carbons. In our presentation, we shall describe the reactions of Ln(III), Th(IV) and $\{UO_2\}^{2+}$ sources (Ln = lanthanoid) with H₂L2. The reactions have resulted in the isolation of complexes $\{[Ln_2(O_2CMe)_2(L2)_2(MeOH)]\}_n$ (Ln = Gd, Dy, Ho, Er, Yb), $[Th_4O(OMe)_4(NO_3)_2(L')_8]$ (L' is the monoanion of *o*-hydroxybenzophenone) and $[UO_2(L2)(S)]$ (S = MeOH, DMF). A new polymorph of H₂L2 was also isolated. Synthetic, structural and spectroscopic issues of the complexes, as well as the magnetic properties of the 1D Dy(III) compound will be briefly discussed.



[1] A.W. Kleij, Chem. Eur. J. 2008, 14, 10520 – 10529.

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NMR Detection of Electron Spin Fractionalization and the Manifestation of the Elusive Majorana Fermions in Kitaev Materials

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The exploration of topological systems has unveiled a diverse landscape of novel quantum phases and emergent quantum phenomena. Among these systems, Kitaev materials [1] have garnered significant attention due to their ability to harbor a quantum spin-liquid state [2] characterized by fractionalized excitations [3]. Recent observations, such as the breakdown of magnetic order [4] and the half-quantized thermal Hall effect in α -RuCl₃ [5], have sparked discussions in the scientific community regarding the nature of these phenomena. The central question that arises today is whether these intriguing behaviors signify spin fractionalization [3], as postulated by Kitaev in his seminal quantum spin liquid model [1], or if they can be explained by conventional antiferromagnetic interactions [6].

To shed light on this ongoing debate, we will present recent experimental ²³Na NMR data from the prospective Kitaev material Na₂Co₂TeO₆ (NCTO) [7], along with ¹H NMR data from another Kitaev candidate material, the Metal Organic Framework Cobalt Oxalate [Me₂NH₂)₃SO₄]₂[Co₂(ox)₃], exhibiting a Hyperoctagon Lattice [8]. Despite the structural differences of the two systems, experiments indicate that spin fractionalization arises as the predominant source of NMR relaxation at low temperatures. This discovery offers crucial insights into the behavior of Kitaev materials and lays the groundwork for a deeper understanding of the interplay between topology and exotic quantum states across diverse material platforms.

Furthermore, we will touch upon the emergence of Majorana Fermions in Kitaev QSL systems, as well as quantum spin entanglement and their implication for developing robust quantum computing technologies.

References

[1] Kitaev, A. (2006). Anyons in an exactly solved model and beyond. Annals of Physics 321(1), 2-111.[2] Balents, L. (2010). Spin liquids in frustrated magnets. Nature 464(7286), 199-208.

[3] Nasu, J., Udagawa, M., & Motome, Y. (2016). Thermal fractionalization of quantum spins in a Kitaev model: Temperature-linear specific heat and coherent transport of Majorana fermions. Physical Review Letters 116(11), 117202.

[4] Banerjee, A., et al. (2016). "Proximate Kitaev quantum spin liquid behaviour in a honeycomb magnet". Physical Review B 93, 214419.

[5] Kasahara, Y., et al. (2018). Majorana quantization and half-integer thermal quantum Hall effect in a Kitaev spin liquid. Nature 559(7713), 227-231.

[6] Hong, X., et al. (2024). Phonon thermal transport shaped by strong spin-phonon scattering in a Kitaev material Na2Co2TeO6. npj Quantum Materials 9:18;

[7] Papawassiliou, W., et al. (2024). The Role of Quantum Metastability and the Perspective of Quantum Glassiness in Kitaev Fractional Spin Dynamics: An NMR Study. arXiv:2407.14663 [cond-mat.str-el].

[8] Ishikawa H., et al. (2024). Jeff =1=2 Hyperoctagon Lattice in Cobalt Oxalate Metal-Organic Framework. Phys. Rev. Letters 132, 156702.

What can we learn about spin-crossover complexes using solidstate NMR?

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Understanding electron spin transitions is crucial for biochemical processes and molecular spin-control technologies involving transition metal molecules. These transitions are triggered by external stimuli such as temperature, light, pressure, or magnetic fields. The current arsenal of experimental techniques probing spin-crossover (SCO) molecules around their spin-transition includes macroscopic methods tracking collective molecular behaviour and microscopic methods monitoring changes at the metal centre or vibrational fingerprints during spin-transition. However, no established technique simultaneously tracks changes in the arrangement and the electronic structure of ligands during transitions. Solution state NMR can probe electronic changes, but vital information that can be extracted from anisotropic interactions coupled to a mostly limited temperature range and potential solvent effects can be potential pitfalls of the technique. Here, we employ variable-temperature broadband high-resolution solid-state NMR (ssNMR) methods [1], combined with state-ofthe-art quantum chemical calculations of the NMR/EPR parameters [2] in a series of mononuclear Mn(III) SCO complexes requiring experimental setups that range from lowtemperature Magic Angle Spinning (LTMAS) near cryogenic temperatures up to ultrafast MAS (100 kHz) around room temperature. Our findings demonstrate that ssNMR is an excellent tool for providing insights into the subtle changes of the electron spin density distribution in the ligands of SCO molecules as well as the macroscopic cooperative behaviour upon such transitions.



Figure 1. The calculated isotropic ¹H NMR spectra of a Mn(III) SCO complex for two spin states. The red dot denotes change of the ¹H NMR shift of the -NH group upon spin transition.

References

- [1] Pell, A.J., et al. Progress in Nuclear Magnetic Resonance Spectroscopy 2019, 111, 1–271
- [2] Vaara, J., et al. J. Chem. Theory Comput. **2015**, 11, 4840–4849.

Paramagnetic materials: challenges and opportunities for solidstate NMR

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Establishing links between the structure and properties of a material is the key to understanding how the material works, why it fails, and how to improve performance. This requires the careful measurement and evaluation of a variety of structural features, including particle size and morphology, long-range order, short-range local chemical environments, and structural dynamics. A full structural picture requires a combination of experimental techniques. For example, particle size and shape can be determined by electron microscopy, long-range crystalline order by X-ray diffraction, and local structure by solid-state NMR [1].

For paramagnetic systems, the local structure of a particular atom/ion is determined by its chemical bonding environment, which is dominated by the nearby open-shell metal ions. In solid-state NMR, the unpaired electrons can be used to probe differences in local structure via the hyperfine interaction to the observed nucleus, and to identify disorder in structure or composition [2]. However, this information is often difficult to obtain since these same unpaired electrons induce large chemical shifts and shift anisotropies of the signals in the spectrum, and accelerate the relaxation of these signals. The result is that the signals are difficult to excite, detect, and interpret using standard solid-state NMR methods [3].

We have developed several methods for solving these problems, including tailored pulses for broadband excitation, new two-dimensional schemes for separation of overlapping signals from complex disordered materials, and new theoretical formalisms and computational methods for calculating the chemical shifts, and assigning and interpreting the spectra. Here we highlight these methods on different systems, including inorganic battery materials and organometallic catalysts, demonstrating the far-reaching potential of paramagnetic solid-state NMR in different areas of chemistry and materials science. In each case we learn something about the local structure of the NMR-active nuclei, disorder in structure, and metal-ion composition, and the role of dynamics. This information is integrated with data from other structure determination methods to obtain a complete picture which is then used to understand the material properties.

[1] BF Chmelka, *J Magn Reson*, **2019**, *306*, 91–97
[2] J Koppe, AJ Pell, *ACS Phys Chem Au*, **2023**, *3*, 419–433
[2] A L Pell, G Pietaguda, CP Gray, Prog Nucl Magn Person Spectrose, **2019**

[3] AJ Pell, G Pintacuda, CP Grey, Prog Nucl Magn Reson Spectrosc, 2019, 111, 1–271

Coherent Dynamics of Lanthanide Coordination Complexes

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In recent years we have shown, that molecular Lanthanide-based coordination complexes hold potential for use as physical supports for the implementation of single- and entangledqubit quantum gates in Quantum Information Technology devices._{1,2} The coupled electronic qubit-nuclear qudit nature of this system allowed to propose a scheme for intrinsic implementation of efficient quantum error correction schemes.₂ Further, the multifrequency single crystal c.w.- and pulse EPR spectra of Gd(trensal), allowed to establish that vanishing angular orbital momentum results in decoherence suppression.₃ In addition, dipolar-interaction-coupled Yb(III) sites were exploited for the experimental demonstration of entangled-qubit gates.₄ Finally, very recently, we demonstrated the first ever implementation of a quantum simulation on molecular magnetic materials.₅

Recently we probed the fundamental factors that induce decoherence in ensembles of molecular magnetic materials.⁶ This was done by pulse Electron Paramagetic Resonance measurements at X-band (9.6 GHz) on single crystals of Gd@Y(trensal) at 0.5, 10-1, 10-2 and 10-3 % doping levels. At the lowest dilution level of 10-3 %, and under dynamic decoupling conditions, the ratio of T_m versus the time it takes to implement a quantum gate, T_G , reaches the order of 104, in the example of a single qubit π -rotation, which corresponds to a gate fidelity of 99.99 %.

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References:

[1] K. S. Pedersen *et al.*, *J. Am. Chem. Soc.*, **2016**, *138*, 5801-5804.;
[2] R. Hussain *et al.*, *J. Am. Chem. Soc.*, **2018**, *140*, 9814-9818.;
[3] C. D. Buch *et al.*, *J. Am. Chem. Soc.*, **2022**, *144*, 17597-17603.;
[4] B. Bode *et al.*, *J. Am. Chem. Soc.*, **2023**, *145*, 2877-2883.;
[5] S. Chicco *et al.*, *J. Am. Chem. Soc.*, **2024**, *146*, 1053-1061.;
[6] S. H. Hansen *et al.*, *Chem. Sci.*, **2024**, *15*, 20328-20337.

The Design, Synthesis and Study of Multifunctional Single Molecule Magnets

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Over the past three decades, research on molecular magnets has provided new fundamental science, including high spin (HS) molecules with potential applications ranging from ultra-high density storage to spintronics, quantum computing, and molecular refrigerants, yet many important challenges still remain. In this respect optospintronics is an emerging area that couples the magnetic properties of single molecule magnets (SMMs) with their luminescent characteristics to allow faster readout and manipulations of the encoded quantum information. In recent years, research in the Pilkington group has focused on the syntheses, and studies of multifunctional single molecule magnets assembled from crown ether,[1] cucubituril and Schiff-base macrocycles,[2] together with a pool of potentially chiral pyridyl alkoxide ligands.[3] Examples of mono- and polynuclear *3d* and/or *4f* complexes assembled from these families of ligands will be presented, together with an overview of their magnetostructural and optical properties.

- (1) E.L. Gavey, M. Al Hareri, J. Regier, L.D. Carlos, Rute A.S. Ferreira, F.S. Razavi, J.M. Rawson, M. Pilkington, *J. Mat. Chem. C*, **2015**, *3*, 7738-7747.
- (2) E.L. Gavey, Y. Beldjoudi, J.M. Rawson, T.C. Stamatatos, M. Pilkington, *Chem. Commun.*, **2014**, *50*, 3741-3743.
- (3) P. Abbasi, K. Quinn, D.I. Alexandropoulos, M. Damjanović, W. Wernsdorfer, A. Escuer, J. Mayans, M. Pilkington, T.C. Stamatatos, *J. Am. Chem.* Soc. **2017**, *139*, 15644-15647.

Mixed orbital states and modulated crystal structures in La_{1-x}Ca_xMnO₃ or nanoscale heterogeneity

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Several important phenomena have been observed in the model manganese perovskite $La_{1-x}Ca_{x}MnO_{3}$ ($0 \le x \le 1$), including ferromagnetic, antiferromagnetic, metallic/insulating behavior, charge and orbital ordering, and colossal magnetoresistance effects. The superlattice Bragg peaks observed in x-ray and neutron diffraction patterns of samples with x = 1/2, 2/3, and 3/4 support the presence of charge, orbital, and spin ordering in the system. The Goodenough model of charge, orbital, and spin ordering has been used to explain the ground states of these compositions. An important question that remains to be clarified is whether these compounds form a truly homogeneous system or if they consist of phase mixtures across various length scales when x is not a simple fraction. We will discuss experimental data (from neutron and x-ray measurements) for samples with calcium concentrations that are not simple fractions. The experimental results reveal that all such compounds undergo a structural transition at $T < T_{CO}(x) = 200-220$ K, accompanied by the appearance of superlattice Bragg peaks. These peaks can be indexed using a superstructure with a modulation propagation vector, τ . At 5 K, the modulation vector of the superstructure, $\tau = [\tau_a, 0, 0]$, is aligned along the a-axis, with τ_a varying linearly with x, $\tau \approx 1 - x$. We will also compare experimental results from the systems $TbMn_{1-x}Fe_xO_3$ (perovskite structure) and LiFe_{5-x}Mn_xO₈ (spinel structure). Our results may contribute to a deeper understanding of spin, charge, and orbital ordering phenomena, as well as colossal magnetoresistance, cuprate superconductivity, symmetry breaking, and emergent order in quantum systems.

Seeded-growth synthesis of InAs/ZnSexSx-1 colloidal quantum dots

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Indium arsenide (InAs) colloidal quantum dots (CQDs) constitute promising candidates due to their excellent optoelectronic properties in short-wave infrared (SWIR), resulting in the fabrication of highly efficient optoelectronic devices, including solar cells, lasers and photodetectors. Nowadays, most CQD optoelectronic devices in SWIR are based on toxic lead and mercury chalcogenides, with limited integration into the market. On the other hand, III-V semiconductor CQDs are promising candidates to complement this gap, such as InAs CQDs, which are classified as RoHS-compliant material ("Restriction of Hazardous Substances"). Nevertheless, InAs CQDs' applications have been limited by their low photoluminescence quantum yield (PLQY), approximately 1-2%, due to the intrinsic surface dangling bonds and surface trap states. To address this challenge, new synthetic approaches have recently been proposed, reaching PLQYs above 40% with the epitaxial growth of thin ZnSe shell¹. Therefore, here we synthesized and studied a series of InAs/ZnSe_xS_{1-x} core/shell CQDs with thin alloyed shells, aiming to further confine the carriers and reduce the Auger rates in the system. Hence, we introduce an optimized seeded-growth synthesis of InAs/ZnSe_xS_{1-x} CQDs reaching PLQYs up to 70%, while maintaining high crystallinity despite the large lattice mismatch.

 Zhu, D.; Bellato, F.; Bahmani Jalali, H.; Di Stasio, F.; Prato, M.; Ivanov, Y. P.; Divitini, G.; Infante, I.; De Trizio, L.; Manna, L. ZnCl2Mediated Synthesis of InAs Nanocrystals with Aminoarsine. *J. Am. Chem. Soc.* **2022**, *144* (23), 10515–10523

Coordination Complexes of New Asymmetric Thiatriazinyl Radical

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One of the core interests in our research group is the design of novel paramagnetic ligands based on thiazyl heterocycles. We have been interested in designing ligands using the 1,2,4,6-thiatriazinyl (TTA) heterocycle for some time, but we and others[1] have been unsuccessful until now. Using synthetic protocols to generate asymmetric TTA radicals[2] we have designed the 3-trifluoromethyl-5-pyridyl-1,2,4,6-thiatriazinyl ($pyCF_3TTA$) radical, capable of bidentate chelation of a metal ion. Moreover, this is the first evidence of coordination of a TTA heterocycle in a neutral radical oxidation state. TTA radicals are of particular interest as redox active ligands, readily reduced to a closed-shell anion. This work opens the door to redox non-innocence in a paramagnetic thiazyl ligand that has a propensity for electrostatic supramolecular contacts. We present preliminary work on the synthesis, structures, and magnetic properties of a series of first-row transition metal and pyCF3TTA lanthanide ion complexes of the radical, with 1,1,1,5,5,5hexafluoroacetylacetonato- (hfac) ligands providing processability and stability. (unpublished; Figure 1).



Figure 1. (left) Line drawing of the *hs*-Mn(II) complex of the pyCF₃TTA radical ligand; (right) excerpt of the crystal structure of the Mn(II)-radical complex, highlighting the pairwise interaction via electrostatic S^{δ+}...O^{δ-} contacts and showing only the O atoms of the hfac ligands for clarity

[1] K. L. M. Harriman, I. A. Kühne, A. A. Leitch, I. Korobkov, R. Clérac, M. Murugesu, J. L. Brusso *Inorg. Chem.* **2016**, *55*, 5375.
[2] R. T. Boeré, T. L. Roemmele, X. Yu, *Inorg. Chem.* **2011**, *50*, 5123.

Crystal structure study of a cocrystal formed by Lamotrigine and Citric Acid agents

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The wet grinding of Lamotrigine and citric acid in a 1:1 molar ratio using ethanol as a solvent resulted in the formation of a new crystalline phase, as evidenced by the recorded X-ray powder diffraction (XRPD) pattern of the final product. The presence of amine and aromatic nitrogen groups in Lamotrigine, along with the carboxylic acid and hydroxyl groups in citric acid, supports the potential formation of a cocrystal through favorable intermolecular interactions. A previous study [1] reported the formation of a new compound using the same reactants but did not provide details regarding the crystal structure of the resulting product. In the present work, we determine the crystal structure of the Lamotrigine–citric acid (1:1) cocrystal using a simulated annealing approach [2] applied to XRPD data collected with a laboratory diffractometer equipped with a CuKα radiation source. The initial structural model was further refined using the Rietveld method [3]. Structural characteristics of the cocrystal were analyzed using tools provided by the Cambridge Structural Database (CSD) [4a, b].



B. S. Satapathy, A. Patel, R. N. Sahoo, S. Mallick, *J. Serb. Chem. Soc. 2006, 86*, 51–61
 V. Favre-Nicolin and R. Cerny, (*FOX*), J. Appl. Cryst. 2002, 35, 734-743.
 T. Roisnel, J. Rodriguez-Carvajal, WinPLOTR: a Windows tool for powder diffraction patterns analysis Materials Science Forum, Proceedings of the Seventh European Powder Diffraction Conference (EPDIC 7), 2000, p.118-123, Ed. R. Delhez and E.J. Mittenmeijer
 a) Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. *Acta Cryst. Sect. B* 2016, *72*, 171–179. b) K. Kopczyńska, C. J. Kingsbury, E. Pidcock, A. A. Moldovan and I. D. Madura, Cryst. Growth Des. 2024, 24, 12, 5159–5170

Chiral Schiff Base Complexes with Anticancer and Antimicrobial Activity

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Chirality is an intrinsic property of the matter and is important in chemistry, biology, and physics, as it can affect the properties and reactivity of molecules. Chiral metal complexes that combine chirality with magnetic, optical, and electrical properties constitute a new and fast-growing class of multifunctional molecular materials [1]. Moreover, these compounds are equally important in modern medicine as therapeutics (metallodrugs), and can be selectively activated at the target site of a biomolecule by an external stimulus. Chirality plays a crucial role in the biological activity, selectivity or toxicity of chiral metallodrugs because it can affect their binding to biomolecules (like DNA, proteins, enzymes), their pharmacokinetics (absorption, distribution, metabolism) and pharmacodynamics as one enantiomer might be therapeutic while the other could be inactive of toxic. Thus, chirality can influence the target selectivity, cell uptake and metabolic pathways [2]. We will present our work on chiral complexes based on enantiopure salen-type Schiff base ligands. The antiproliferative activity of the chiral complexes was tested on human breast adenocarcinoma cells (MCF-7 and MDA-MB-231), and their toxicity was assessed in human fetal lung fibroblast cells (MRC-5). The in vitro mechanisms of action were elucidated via morphological and cell cycle studies, whereas the in vivo toxicity was evaluated by Brine Shrimp Artemia salina. The antimicrobial activity of the chiral complexes was tested, and it was shown that they can significantly reduce bacterial growth rates and biomass for E.coli bacterial cells.

[1] C.-M. Liu, R. Sun, B.-W. Wang, X. Hao, X.-L. Li, *Inorg. Chem.*, **2022**, *61*, 18510-18523.
[2] N. Senkuttuvan, B. Komarasamy, R. Krishnamoorthy, S. Sarkar, S. Dhanasekaran, P. Anaikutti, *RSC Advances*, **2024**, *24*, 33429-33448.

Conformational Polymorphism and Magnetic Ordering in an Organic Radical: α , β , γ and δ -Polymorphs of Benzodioxepinyl-1,3,2dithiazolyl

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Sublimation of the benzodioxepinyl radical **1** affords $\mathbf{1}\alpha$ (orthorhombic Pbca) in which the molecule adopts a 'chair' conformation. The temperature dependence of $\chi_m T$ reveals an initial increase in $\chi_m T$ upon cooling before reaching a maximum of 0.6 emu K mol⁻¹ at 8 K and then decreasing on further cooling. Divergence in the field-cooled and zero-field cooled susceptibility data below 4 K indicates the emergence of a spontaneous magnetic moment for $\mathbf{1}\alpha$. *M* vs *H* plots in the low temperature regime follow M = M_s + χ H consistent with canted antiferromagnetism and a canting angle of 0.08° was determined based on extrapolation of the spontaneous moment to H = 0, T = 0 [1]. Powder X-ray diffraction studies indicate $\mathbf{1}\alpha$ converts to a pancake-bonded dimer (*S* = 0) polymorph ($\mathbf{1}\beta$, triclinic P-1) on aging which adopts a twist-boat conformation. Conversely, heating $\mathbf{1}\alpha$ converts to another twist-boat polymorph $\mathbf{1}\gamma$ (monoclinic P2₁/n). Polymorph $\mathbf{1}\gamma$ retains its paramagnetism in the solid state but DFT and magnetic studies are consistent with an open shell antiferromagnetically coupled dimer (*J* = -97 cm⁻¹). Heating $\mathbf{1}\beta$ drives a transition to $\mathbf{1}\gamma$ *via* a metastable state, $\mathbf{1}\delta$ [2].



References:

- [1] D. Leckie, M. Harb, N. Mroz, J. D. Wrixon, J. Campo, A. Arauzo, H. Bakhshi, M. Pilkington and J. M. Rawson, *J. Amer. Chem. Soc.*, **2024**, *146*, 31371.
- [2] D. Leckie, D. J. Cutler, J. Campo, A. Arauzo, H. Bakhshi, M. Pilkington and J. M. Rawson, **2025**, manuscript in preparation.

Molecular Nuclear Spin Qubits for Implementing Quantum Gates and Quantum Algorithms

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Nuclear spin states in molecules will be proposed to act as quantum registers for Quantum Computing (QC). We report on the implementation of metal complexes into nanometre-sized spintronic/optotronic devices by a combination of bottom-up self-assembly and top-down lithography techniques. The controlled generation of magnetic molecular nanostructures will be shown and persistence of their magnetic properties under confinement Molecular Quantum Devices will be proven. The Hilbert space spanned by the nuclear spins will be engineered synthetically and addressed both electrically and optically, partially at the single molecule level [1-13]. Finally, Grover's quantum search algorithm will be implemented on the nuclear spin register of a TbPc₂ Qudit [10].



Figure Artistic representation of a Molecular Spin Transistor based on a TbPc₂ complex acting as a molecular Spin Qudit [8].

References

[1] S. Kyatskaya et. al. J. Am. Chem. Soc. 2009, 131, 15143-15151.

[2] M. Urdampilleta et al. Nature Mater. 2011, 10, 502-506.

[3] J. Schwöbel et. al. Nature Comms. 2012, 3, 953-956.

[4] R. Vincent et al. Nature 2012, 488, 357-360.

[5] M. Ganzhorn et al. *Nature Nano.* **2013**, 8, 165–169.

[6] M. Ruben et. al. *Nature Nano.* **2013**, 8, 377–389.

[7] S. Wagner et. al. *Nature Nano.* **2013**, 8, 575–579.

[8] S. Thiele, et al. Science 2014, 344, 1135-1138.

[9] M. Ganzhorn, et. al. Nature Comms 2016, 7, 11443.

[10] C. Godfrin et al. PRL 2017, 119, 187702 (perspective article by A. Morello Nature Nano 2018, 13, 9-10).

[11] H. Biard et. al. Nature Comms 2021, 12, 4443.

[12] S. Kuppusamy et. al. Nature Comms 2021, 12, 2152.

[13] D. Serrano et al. Nature 2022, 603, 241.

Recent Reviews:

"Molecular Spin Qudits for Quantum Algorithms."

E. Moreno-Pineda, C. Godfrin, F. Balestro, W. Wernsdorfer, and M. Ruben

Chem. Soc. Rev. 2018, 47, 501.

"Synthetic Engineering of the Hilbert Space of Molecular Qudits: Isotopoloque Chemistry."

W. Wernsdorfer and M. Ruben

Adv. Mat. 2019, 31, 1806687.

"Observation of Narrow Optical Homogeneous Linewidth and Long Nuclear Spin Lifetimes in a Prototypical [Eu(trensal)] Complex."

K. Kuppusamy, E. Vasilenko, W. Li, J. Hessenauer, C. Ioannou, O.Fuhr, D. Hunger, and M. Ruben *J Phys Chem C*, **2023**, 127, 10670.

Magnetism and Transport at Single-Molecule Level

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Magnetic molecules can exhibit intriguing behaviors, particularly at the single- molecule level. In this presentation, I will discuss the findings of a spin-crossover system where a single molecule shows hysteresis behavior.[1] This phenomenon was unexpected, as hysteresis is typically associated with intermolecular cooperative interactions. In this case, the blocking of one of the molecule's spin states hinders the spin transition, leading to hysteresis.

Additionally, I will present results about the measurement of transport properties through a single molecule using a scanning tunneling microscope (STM). Some magnetic systems show magnetoresistance effects in single-molecule junctions. We were the first to report such behavior at room temperature .[2] This effect occurs when using one magnetic electrode , and the inversion of the direction of the electrode's magnetization changes the conductance across the magnetic molecule at the junction. In the case of the Fe(II) complex of the Figure the magnetoresistance effect is almost perfect, because there is no transport for one of the magnetizations of the electrode (orange histogram).



Figure. STM measurements of single-molecule transport .

[1] Moneo-Corcuera et al. Chem, **2022**, 9, 1-17.

[2] Aragonès et al. Nano Letters, 2016, 16, 218-226.

Photocatalytic CO₂ Reduction in Aqueous Media

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To fabricate the technologies enabling practically useful renewable energy cycles, artificial photosynthesis based on photocatalytic carbon dioxide (CO₂) reduction into valueadded fuels has attracted increasing attention in recent years. As the initial approach to this issue, we demonstrated that a water-soluble heteroleptic copper(I) photosensitizer is highly effective in promoting photocatalytic CO₂ reduction into CO in the presence of a water-soluble cobalt porphyrin catalyst even in fully aqueous media. Our study demonstrated high selectivity in CO₂ reduction versus water reduction (Sel_{CO2}=90%) with a high turnover number (TON_{CO}=4000, 12 h). The high selectivity was rationalized by the mismatch in frontier MO association with a 1s(H⁺) orbital required to promote the H₂ evolution. Ionic interaction of the photosensitizer in aqueous media was also utilized to enhance the photocatalytic efficiency [1].

Our recent interest has concentrated on the selective formate formation due to its potential application in reversible hydrogen storage technology. However, selective catalysts for CO₂-to-HCOOH conversion is quite limited due to the predominant formation of $CO_2^{2^2}$ -coordinated intermediates. Although the formate formation was classically supposed to take place via the insertion of CO_2

into a metal-hydride bond (Type A), this concept is rather misleading since formate often forms via the nucleophilic attack of a metal-hydride (M-H) at the carbon center of CO₂ (Types B-D). Indeed, our recent studies strongly suggest that CO₂ reduction to formate undergoes via the M-H attack lack with the of any



O(formate)-coordinated products and directly ends up with the release of formate (Type D) [2]. The most remarkable finding in our report lies in the drastic change in the product selectivity induced by switching the reaction media from non-aqueous to aqueous/organic phase, leading to demonstrate outstanding efficiencies of $[Rh^{III}Cp^*(dihydroxy-bpy)CI]^+$ in CO₂-to-HCOOH conversion. This is the first example of report demonstrating such water-induced switching in selectivity for the CO₂-to-HCOOH conversion [2].

References

[1] F. Sueyoshi, X. Zhang, K. Yamauchi, K. Sakai, *Angew. Chem. Int. Ed.*, **2023**, *6*2, e202217807.

[2] D. Lee, K. Yamauchi, K. Sakai, J. Am. Chem. Soc., 2024, 146, 31597-31611.

Exploring amorphous bimetallic borides in direct seawater electrolysis for green hydrogen production

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Our planet is already drying up. According to the United Nations three-quarters of Earth's land became permanently drier in last three decades [1]. These drylands are projected to further increase due to climate change. So, where does the green hydrogen economy sit in all of this?

Green hydrogen is viewed as an appealing energy carrier because of its high energy-tomass ratio (120 MJ/kg), which can readily substitute fossil fuel usage, satisfying global energy demands. At present, the primary technology for generating green hydrogen is water electrolysis [2].

So, how can the green hydrogen economy flourish? When water scarcity is a reality and green hydrogen is competing for these precious resources, putting both energy supply and water availability at risk, especially during periods of drought. An emerging technology that has the capacity to produce cheap large-scale green hydrogen from water, without consuming the limited resources of freshwater, is direct seawater electrolysis.

In this presentation we will explore the advantages and disadvantages of direct sweater electrolysis for green hydrogen production, and how bimetallic borides can play a role in making this technology a reality.

References:

[1] U. NATIONS, The global threat of drying lands: Regional and global aridity trends and future projections, 2024.

[2] S. Dresp, F. Dionigi, M. Klingenhof, P. Strasser, Direct Electrolytic Splitting of Seawater: Opportunities and Challenges, ACS Energy Letters, 4 (2019) 933-942.

Rekindling the interest in cluster-based SMMs: Large magnetic anisotropy and SMM properties in a {Mn₉} double-decker metallacrown with S = 5/2

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The choice of the primary organic chelating/bridging ligand is of paramount importance for the synthesis of high-nuclearity 3d-metal clusters and single-molecule magnets (SMMs) with enhanced magnetic properties, such as large energy barrier for the magnetization reversal and hysteresis effects at high temperatures. The two key parameters to obtain an efficient cluster-based SMM are a large ground state spin, S, and a large and negative zerofield splitting parameter, D. Undoubtedly, the most challenging task for synthetic cluster chemists is to simultaneously control the magnitude of S and D. The anisotropy parameter D of a molecular compound is mostly affected by the single-ion anisotropies of the individual metal ions as well as the overall structural geometry of the resulting coordination compounds. Pecoraro and coworkers have reported several years ago a pentanuclear {Mn^{III}Mn^{III}₄} metallacrown-type cluster bearing the chelating/bridging ligand shi³⁻ (shiH₃ is salicylhydroxime), which exhibited a small S of 1/2 or 3/2, resulting from the antiferromagnetic interaction of the four Mn^{III} ions, but a large D value, arising from the quasiparallel alignment of the Mn^{III} Jahn-Teller axes. Hence, the square pyramidal {Mn^{III}Mn^{III}₄} metallacrown displayed hysteresis loops at very low-temperatures (~0.04 K) and a $U_{\rm eff}$ of 14.7 cm^{-1.[1]}

In the present work, we have managed to link together two { Mn^{III}_4 } planar units around a central, eight-coordinate Mn^{II} ion, which resulted in a fused double-square pyramidal { Mn^{III}_8 } cluster with an S = 5/2 and a large *D* value of ~-2.5 cm⁻¹. The described compound is an SMM, and it displays hysteresis loops at temperatures below 2 K, which are both temperature and field sweep-rate dependent (**Figure 1**).



Figure 1: Molecular structure (left) and hysteresis loops (right) of **1**. Color scheme: $Mn^{III} =$ blue; $Mn^{II} =$ yellow; O = red; N = green; C = grey. Hydrogen atoms are omitted for clarity.

References:

[1] T. Mallah, M. L. Kirk, V. L. Pecoraro, et. al. Inorg. Chem. 2011, 50, 11348.

The effect of hydrostatic pressure on g-tensor and hyperfine coupling constants of nitroxide radical characterized by ab initio calculations

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We present a computational study characterizing the effect of hydrostatic pressure on magnetic spin parameters, which enter the analysis of the electron paramagnetic resonance (EPR) spectra. Site-directed spin labeling (SDSL) in combination with EPR spectroscopy is a powerful tool for investigating the structures and dynamics of biological molecules. In studies using SDSL-based EPR spectroscopy, it is essential to know the spin parameters, such as the g-factor and the hyperfine constants, precisely. However, the experimental characterization of these spin parameters under extreme conditions is often challenging. We report quantum-chemistry calculations of g-tensors and hyperfine coupling tensors (Atensors) for the nitroxide radical spin label in the pressure range of 0-15 GPa [1]. The hydrostatic pressure causes structural changes, which, in turn, result in the linear changes of the g- and A-tensors. The observed linear dependence of the g- and A-tensors suggests that these quantities can serve as reporters of a local pressure in complex environments. The corresponding simulated EPR spectra at the 9 GHz and 230 GHz reveal that the changes of EPR spectrum are more pronounced in the former. Our results indicate that the computational approach can address the challenge of determining magnetic spin parameters under extreme conditions, such as under high hydrostatic pressure.

[1] A. Gurgenidze, A. Krylov and S. Takahashi, Submitted (2025). DOI: <u>10.26434/chemrxiv-</u> <u>2025-ft635</u>

Interface and Matrix Effects on Spin Transition Solids

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If switchable spin-transition magnetic networks are to be incorporated into complex architectures for applications ranging from spintronics to mechanical actuators, how behavior changes at surfaces or when coupled to other components must be understood. For example, when spin-transition materials are incorporated into thin-film or core-shell particle heterostructures, thermally- or optically-induced spin state changes couple across the interface to change the behavior of the second material. At the same time, the response of the spin-transition network also changes. Spin transitions alter metal-ligand bond distances leading to large volume changes, as high as 10-15%, resulting in significant coupling of the magnetic and elastic properties. This presentation will highlight recent results of spin-transition solids in core-shell particles, multicomponent thin films and 2D-3D heterostructures, showing how heterostructure behavior is influenced by the solid-solid interface and solid-state elastic properties of each component.



- 1. John M. Cain, Wanhong He, Mark W. Meisel and Daniel R. Talham *Eur. J. Inorg. Chem.* **2024**, 27, e202400446 <u>https://doi.org/10.1002/ejic.202400446</u>
- Yuwen Tao, Ruiquan Yang, Assel Aitkaliyeva, Charles J. Hages and Daniel R. Talham Chem. Mater. 2024, 36, 8714 – 8724. <u>https://doi.org/10.1021/acs.chemmater.4c01389</u>
Shape-dependent magnetic properties of Prussian Blue Analogue Sm[Fe(CN)₆]

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Reverse micelles and microemulsions have been widely used as soft colloidal templates for controlling the size and/or shape of the nanoscale materials. In particular, a variety of one-dimensional (1D) inorganic nanostructures such as BaCO₃ nanowires, BaCrO₄ nanorods and nanobelts have been successfully synthesized in reverse micelle systems. It is noted that nanosized molecular magnets with a cubic morphology have been previously synthesized in anionic reverse micelles. Recently, Prussian blue analogue Co₃[Co(CN)₆]₂ nanostructures with morphologies of polyhedra, cubes and rods have been synthesized in a cationic microemulsion; however, the shape-dependent magnetic properties of these nanostructures have not been explored.

In this work, SmFe(CN)₆·4H₂O particles with different shapes were synthesized by the reaction of K₃Fe(CN)₆ and SmCl₃ solubilized in reverse micelles using non-ionic surfactants. Interesting morphologies of nanoparticles were observed varying the ratio of ω_0 =[water]/[surfactant] from 10.0 to 2.0 including micro asterisks, daisy-like six petals shapes and spheroids while the average dimension was ranged from 6-8 µm to 150 nm respectively. The shape-dependent magnetic properties of these PBAs were studied revealing an increase in the coercivity due to an increase in the magnetic anisotropy from 700 to 3500 Oe.

Modulation of the Temperature and Gas Sensing Properties of New Metal–Organic Frameworks based on Hexanuclear Rare Earth Secondary Building Units through Single-Crystal-to-Single-Crystal Transformation Reactions

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Metal-Organic Frameworks (MOFs) have attracted a tremendous research interest because of their significant potential for practical applications in areas such as gas storage and separation, drug delivery, sensing, catalysis, etc.¹ MOFs with fine-tuned properties can be prepared through a process called post synthesis modification (PSM). PSM allows the introduction/exchange of functional groups of a MOF and is preferable to proceed in a single-crystal-to-single-crystal (SCSC) fashion because with this way direct structural information can be provided for the achieved structural modifications via single crystal x-ray crystallography.²

We shall discuss two families of trivalent rare earth (RE³⁺) MOFs based on a hexanuclear (RE³⁺)₆ SBU and their exchanged analogues. The first one involves 8-connected 2-D MOFs based on an angular dicarboxylic ligand 4,4'-(hydroxymethylene)dibenzoic acid (H₂BCPM), **UCY-17**(RE). A series of exchanged analogues **UCY-17**(Tb)/L produced from linker installation SCSC reactions of **UCY-17**(Tb) with selected dicarboxylic ligands shall also be discussed which resulted not only to the turn-on of the thermometric properties of these materials.³ The second family of compounds with the general formula {((CH₃)₂NH₂)₂[Y₆(µ₃-OH)₈(bpydc)₆]_n is based on the linear dicarboxylic ligand H₂bpydc= [2,2'-bipyridine]-5,5'-dicarboxylic acid. Its subsequent metalation with transition metal ions was achieved giving rise to a series of exchanged analogues with various metal ions. Gas sensing studies of the pristine and metalated compounds revealed a variety of different gas sensing capabilities. Thus, SCSC transformation reactions allowed not only the targeted modification of the structures of the two MOFs but also the modulation of their temperature and gas sensing properties.

References

- 1. Furukawa H. et al., Science, 341 (2013) 1230444.
- 2. Zhang J.P. et al., Chem. Soc. Rev., 43 (2014) 5789.
- 3. Komodiki L.K. et al., J. Mater. Chem. C, 12 (2024) 8684-8696.

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Topotactic Metal Cation Exchange in Multicomponent Ultraporous MOFs

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The chemistry of metal organic frameworks (MOFs) continues to expand rapidly providing materials with diverse structures and properties. The reticular chemistry approach, where well defined structural building blocks are combined together forming crystalline open framework solids, has greatly accelerated the discovery of new and important materials. However, its full potential toward the rational design of MOFs relies on the availability of highly connected building blocks because these are greatly reducing the number of possible structures. Towards this, building blocks with connectivity greater than twelve are highly desirable but extremely rare. We recently report the discovery of novel 18-connected, trigonal prismatic, ternary building blocks (tbb) and their assembly into unique MOFs, denoted as Fe-tbb-MOF-x (x: 1, 2, 3) with hierarchical micro- and mesoporosity.¹ The remarkable tbb is an 18-c super-trigonal prism, with three points of extension at each corner, consisting of triangular (3-c) and rectangular (4-c) carboxylate-based organic linkers and trigonal prismatic $[Fe_3(\mu_3-O)(-COO)_6]^+$ clusters. The **tbb's** are linked together by an 18-c cluster made of 4-c ligands and a crystallographically distinct Fe₃(μ_3 -O) trimer, forming overall a 3-D (3,4,4,6,6)-c five nodal net. The hierarchical, highly porous nature of Fe-tbb-MOF-x (x: 1, 2, 3) was confirmed by recording detailed sorption isotherms of Ar, CH₄ and CO₂ at 87, 112 and 195 K respectively, revealing an ultrahigh BET area (4263 - 4847 m² g⁻¹) and pore volume (1.95 - 2.29 cm³ g⁻¹). Because of the observed ultrahigh porosities, the H₂ and CH₄ storage properties of Fe-tbb-MOF-x were investigated, revealing well-balanced high gravimetric and volumetric deliverable capacities for cryo-adsorptive H₂ storage (11.6 wt%/41.4 g L-1, 77 K/100 bar - 160 K/5 bar), as well as CH₄ storage at near ambient temperatures (367 mg g-1/160 cm³(STP)cm⁻³, 5-100 bar at 298 K), placing these materials among the top performing MOFs.

To further expand this unique family of multicomponent MOFs we developed a facile topotactic singe-crystal-to-single-crystal transformation of Fe-**tbb**-MOF-x to Al-**tbb**-MOF-x and Cr-**tbb**-MOF-x (x: 1, 2, 3) under controlled reaction conditions.^[2] The complete metal cation exchange was confirmed by EDS analysis and the crystal structure was solved using synchrotron SCXRD measurements. The ultrahigh porosity of Al-**tbb**-MOF-x and Cr-**tbb**-MOF-x and Cr-**tbb**-MOF-x materials was confirmed by accurate Ar sorption measurements at 87 K and found increased compared to the Fe-analogues. Structural details and gas storage properties will be presented and discussed.

[1] Froudas, K. G.; Vassaki, M.; Papadopoulos, K.; Tsangarakis, C.; Chen, X.; Shepard, W.; Fairen-Jimenez, D.; Tampaxis, C.; Charalambopoulou, G.; Steriotis, T. A.; Trikalitis, P. N., *J. Am. Chem. Soc.* **2024** 10.1021/jacs.3c12679

[2] M.Vassaki, K. G. Froudas, C. Tsangarakis, X. Chen, W. Shepard, D. Fairen-Jimenez, C. Tampaxis, G. Charalambopoulou, T. A. Steriotis, P. N. Trikalitis. *Work to be submitted*.

NOO'O" Schiff Bases as a Platform for the Synthesis of $\{Zn^{II}_4M^{III}_2\}$ and $\{Cd^{II}_2M^{III}_2\}$ ($M^{III}=Cr^{III}$, Fe^{III}) Coordination Clusters

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The chemistry of heterometallic complexes continues to attract the interest of inorganic chemists, mainly because of the properties that different metal ions can bring to the compounds. Contrary to the thousands of d-f metal complexes [1], compounds containing 3d-3d' and 3d-4d metal ions are less studied. The choice of the bridging organic ligand is crucial for the synthesis of such species. We have been studying the use of the potentially tetradentate Schiff-base ligands saphHCOOH and 4ClsaphHCOOH in this chemistry. Using several reaction schemes, complexes of the general formulae $[Cd^{II}_{2}M^{III}_{2}(saphCOO)_{4}(NO_{3})_{2}(H_{2}O)_{2}],$ $[Cd^{II}_{2}Fe^{III}_{2}(4ClsaphCOO)_{4}(NO_{3})_{2}(H_{2}O)_{2}],$ [Zn^{II}₄M^{III}₂(saphCOO)₆(NO₃)₂(solvent)₂] $[Cd^{II}Cr^{III}_{2}(4ClsaphCOO)_{4}(solvent)_{4}],$ and $[Zn^{II}_{4}Fe^{III}_{2}(4ClsaphCOO)_{6}(NO_{3})_{2}(solvent)_{2}]$, where $M^{III} = Cr^{III}$, Fe^{III} and solvent= H₂O, EtOH, have been isolated, structurally characterized, and studied by a variety of spectroscopic and physical methods.



[1] Z.G. Lada et al., Inorg. Chim. Acta, 2022, 539, article 120954 (review).

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Polymorphs and an orthorhombic Jahn-Teller effect in [Cu(3-bromo-2-pyridone)₆](ClO₄)₂

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The use of substituted pyridine compounds as ligands for Cu(II) is ubiquitous due to the azaphilic nature of the copper ion. However, depending on the substituents, the pyridine may coordinate through an atom other than the ring nitrogen. Such is the case with [Cu(3-Br-2-pyone)₆](ClO₄)₂ [3-Br-2-pyone = 3-bromo-2-pyridone] [1] where the hydroxypyridine/ pyridone tautomeric equilibrium allows for either κ -N or κ -O coordination, κ -O in this case. We report here the temperature dependence of the crystal structure and color of the complex, three polymorphs of the compound (all κ -O), and the presence of an orthorhombic Jahn-Teller distortion. Intramolecular hydrogen bonding and intermolecular halogen bonding (Br...O) provide stabilization.



Figure 1. One polymorph of [Cu(3-Br-2-pyone)₆](ClO₄)₂

[1] F.E. Witkos, J.C. Monroe, C.P. Landee, M.M. Turnbull, J.L. Wikaira, J.L. *Trans. Metal Chem.* **2020**, *45*, 237-43.

¹ Posthumous

Diradicals As Medicines For Disease

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Our research interests lie in developing thermal and photochemical-Bergman cyclization reactivity in inorganic small molecules, porphyrins, and nanoparticle surfaces for carbonbased polymerization reactions, or as nature has taught us, biologically-relevant H-atom abstraction reactivity. While a considerable amount of our efforts are devoted to developing fundamental metal-catalyzed cyclization reactions, we have also applied these motifs to a subset of natural biopolymers such as plaques and fibrin clots.

Disease states resulting from metal-mediated biopolymer deposition can arise when the natural cleavage mechanisms become inoperative or function poorly, such as the formation of amyloid plaques which have been connected to the neurodegenerative disease Alzheimer's, as well as thrombotic disease (atherosclerosis) leading to heart attack or stroke. Current treatment options for amyloid plaque buildup involve inhibition or activation of specific enzymes involved in the disease pathway, while acute arterial thrombosis is combated via the use of anti-platelet agents or anti-coagulants that inhibit the thrombus. In the latter case, side effects associated with such anti-coagulants involve the risk of systemic bleeding which can supersede the benefit of the antithrombotic therapy.

Our approach to these problems involves developing small molecule enediyne ligands that extract metal directly from the plaque (Cu, Zn, of Ca), or incorporation of diradicalsgenerating ligands into optically-active Au and magnetically responsive Fe3O4 nanoarchitectures. Small molecules with N4-coordination have been developed for disaggregation of amyloid plaques by *in situ* activation and radical-formation upon chelation of Zn(II) and Cu(II), while larger-payload nanoparticles that can be activated photo-thermally or by magnetic induction hyperthermia are applied to dissolve fibrin clots. This presentation will describe several chemical and applied aspects of this work.

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