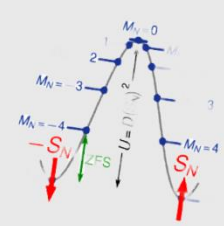
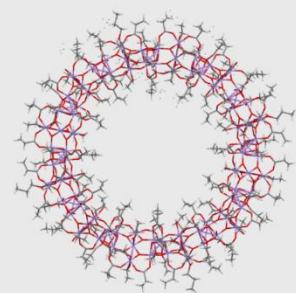
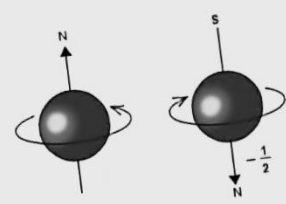
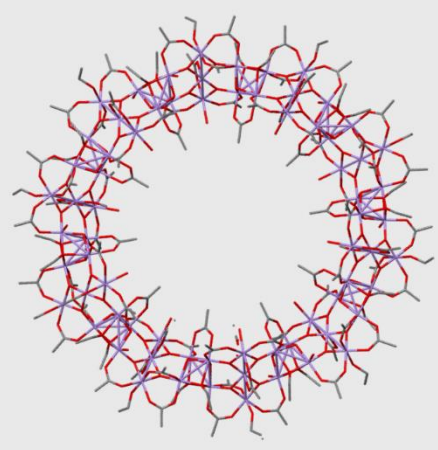




11th North America Greece Cyprus CONFERENCE ON PARAMAGNETIC MATERIALS

Protaras, Cyprus
April 22 - 26, 2024



Dedicated to the memory of Associate Professor Nikos Chronakis

Supported by:



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SCOPE

The NAGC Workshops are held every two years, alternating between Cyprus and Greece. They were established to provide a regular forum for the faculty and students at universities in Greece and Cyprus to meet and interact with their North American counterparts, as well as a select few people from other European countries and elsewhere. The Republic of Cyprus has been very actively trying to build up its higher education institutions, particularly since it joined the European Union on May 1, 2004. Its first and still main university was founded in 1989 and admitted its first students in 1992.

Following the outstanding success of the previous NAGC Workshops, the first of which was in 2005, we will again bring together a wide range of researchers working in diverse fields and applications. The program will span various areas of chemistry, physics, and materials science, and encompasses any kind of study on any kind of system involving unpaired electrons (although the latter need not be a focus of the talk): molecular or nonmolecular materials; organic, inorganic, biochemical or biological; ground state or excited state; solid, liquid, gas, or plasma.

Note that this is not a magnetism workshop (although some talks may be on magnetic materials) – instead, it is the objective of the workshop to bring together people from very different areas who would not normally attend the same meeting, to listen to and learn from each other.

DEDICATION

*NAGC 2024 is dedicated to the memory of Associate Professor
(Department of Chemistry, University of Cyprus) Nikos
Chronakis, who passed away recently.*

May he rest in peace.

His research interests were focused on Synthetic Organic Chemistry, especially in Fullerene Chemistry and Supramolecular Chemistry. His research work led to many publications in high impact peer-reviewed Chemistry journals, funded research projects, presentations in local and international scientific conferences and a patent.



GENERAL INFORMATION

The 11th NAGC 2024 is held on the beautiful island of Cyprus in the eastern Mediterranean, in the Ammochostos region of the north coast. The accommodations and lecture facilities are situated in the **Constantinos The Great Beach Hotel**. Information about the hotel may be found at the following website:

<https://www.tsokkos.com/hotel/Constantinos-The-Great-Beach-Hotel/>



Cyprus is an island of great beauty and archaeological interest, full of UNESCO World Heritage sites (of which ten are Byzantine churches). Whatever the season, Cyprus provides ample opportunity to experience something new, interesting, and exciting, including activities, events, customs, and places that are unique and special to the island. Other areas not to be missed are the capital Nicosia, Paphos on the west coast, and the central Mount Troodos (approximately 2000 metres or 6400 feet high) with its many picturesque villages. For general information about the Republic of Cyprus, see:

<https://www.visitcyprus.com/index.php/en/>

2024 NAGC CONFERENCE (PROTARAS, CYPRUS APRIL 22 – 26, 2024)

Monday, April 22	Tuesday, April 23	Wednesday, April 24	Thursday, April 25	Friday, April 26
8:45 – 9:00 Welcome A. Tasiopoulos, G. Christou				
Chair: George Christou	Chair: George Froudakis	Chair: Spyros Perlepes	Chair: Catherine Raptopoulou	Chair: Thanasis Boudalis
09:00 – 09:30 Spyros Perlepes 09:30 – 10:00 Jeff Zaleski 10:00 – 10:30 Juan Peralta 10:30 – 11:00 G.Papavasiliou	09:00 – 09:30 Mohamed Eddaoudi 09:30 – 10:00 Linda Doerrer 10:00 – 10:30 José Pedrosa 10:30 – 11:00 Sotiris Christodoulou	09:00 – 09:30 Grace Morgan 09:30 – 10:00 Anastasios Keramidas 10:00 – 10:30 G. Papaefstathiou 10:30 – 10:45 P. Rodosthenous 10:45 – 11:00 Christina Banti	09:00 – 09:30 Kathryn Preuss 09:30 – 10:00 Keith Searles 10:00 – 10:30 Laure Catala 10:30 – 11:00 Theodore Lazarides	09:00 – 09:30 Krzysztof Wozniak 09:30 – 10:00 Dimitrios Pantazis 10:00 – 10:30 Emmanouil Manos 10:30 – 11:00 Maria Chrygina
COFFEE BREAK	COFFEE BREAK	COFFEE BREAK	COFFEE BREAK	COFFEE BREAK
11:00 – 11:30	11:00 – 11:30	11:00 – 11:30	11:00 – 11:30	11:00 – 11:30
Chair: Dimitris Gournis	Chair: Pantelis Trikalitis	Chair: Juan Peralta	Chair: Stephen Hill	Chair: Vasileios Psycharis
11:30 – 12:00 George Christou 12:00 – 12:30 T. Stamatatos 12:30 – 13:00 Magdalena Wencka 13:00 – 13:15 Alex Diodati 13:15 – 13:30 Ioannis Ioannidis	11:30 – 12:00 Joaquin Silvestre 12:00 – 12:30 Sotiris Hadjikakou 12:30 – 13:00 John Beer 13:00 – 13:30 Stelios Choulis 13:30 – 13:45 Marios Stylianou 13:45 – 14:00 A.Themistokleous	11:30 – 12:00 Selvan Demir 12:00 – 12:30 Hai-Ping Cheng 12:30 – 13:00 Szczytko, Jacek 13:00 – 13:15 Alexios Plessas 13:15 – 13:30 F. G. Moscoco 13:30 – 14:00 Kim Christou	11:30 – 12:00 Sokrates Pantelides 12:00 – 12:30 Dawid Pinkowicz 12:30 – 13:00 C. Raptopoulou 13:00 – 13:30 Xiaoguang Zhang	11:30 – 12:00 Michael Inkpen 12:00 – 12:30 Thanasis Boudalis 12:30 – 13:00 Randy Larsen 13:00 – 13:15 A. Anastassiades 13:15 – 13:30 Maria Nikolaou 13:30 – 13:45 Laoura Komodiki
LUNCH BREAK	LUNCH BREAK	FREE TIME	LUNCH BREAK	Closing Remarks
13:30 – 15:30	14:00 – 16:00		13:30 – 15:30	
Chair: Kathryn Preuss	Chair: Sotiris Christodoulou		Chair: Jeff Zaleski	
15:30 – 16:00 Pantelis Trikalitis 16:00 – 16:30 Vasilis Psycharis 16:30 – 17:00 Alina Schimpf 17:00 – 17:15 Nikolaos Pliatsios 17:15 – 17:30 Charlotte Bailey	16:00 – 16:30 George Froudakis 16:30 – 17:00 Dimitris Gournis 17:00 – 17:30 Sofia Hayes 17:30 – 17:45 Angelos Amoirides 17:45 – 18:00 George Lefkaritis		15:30 – 16:00 Steve Hill 16:00 – 16:30 K. Boukheldaden 16:30 – 17:00 Ben Powell 17:00 – 17:15 P. Oikonomopoulos 17:15 – 17:30 Francesca Adami	
COFFEE BREAK	CONFERENCE DINNER Departure from hotel at 8:00 pm		COFFEE BREAK	
17:30 – 18:00			17:30 – 18:00	
Chair: Theocharis Stamatatos			Chair: Emmanouil Manos	
18:00 – 18:30 Jeffrey Rinehart 18:30 – 19:00 Panayiotis Kyritsis 19:00 – 19:15 Konstantina Baka 19:15 – 19:30 Sultan Aizuddin			18:00 – 18:30 Masayuki Yagi 18:30 – 19:00 Susumu Takahashi 19:00 – 19:15 Odysseas Keramidas 19:15 – 19:30 Pantelis Kotidis	

Social Activities Program

1. Sunday, April 21st

Welcome Reception, 19:00.

Constantinos The Great Beach Hotel

2. Tuesday, April 23rd

Official Conference Dinner (Restaurant Pinia in Pernera).

Departure from the hotel at 20:00.

Acknowledgements



University of Patras



Demokritos National Centre for Scientific Research



Drago Chair

Drago Chair



Cyprus Convention Bureau



Paralimni Municipality



ABSTRACTS

Investigation of Novel Fe(III) SCO Complexes and Hybrid Materials

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Spin crossover in Fe(III) is well studied, with several examples of structural phase transitions which accompany the thermal spin state switching having now been reported.^[1] These include examples with N₄O₂ donor sets embedded in chelate ligands where the flexibility of the ligand can affect the SCO profile.^[2] Since the research of Gütllich and coworkers in 1984, when they reported the first example of light-induced conversion of the low-spin Fe(II) to high-spin, interest towards studying related magneto-optical effects has developed also in Fe(III) complexes and in selected Fe(III) doped semiconductor surfaces for solar cell applications.^{[3],[4]} These studies involve the deposition of the complexes onto the semiconductor surface, which can be carried out in different ways including physical and chemical vapour deposition, sputtering, spin and dip coatings, and spray pyrolysis.^[5]

In this work, three new series of cationic Fe(III) complexes: [Fe(5-methoxysal)₂232]⁺, [Fe(4-methoxysal)₂232]⁺ and [Fe(5-methoxysal)₂223]⁺ have been synthesized and characterized to study the effect of symmetry, position of substituents and counterions on the SCO behaviour. In a second part different approaches to attachment of the complexes onto semiconductor and magnetoresistance surfaces will be presented. Spin coating was investigated to prepare smoothly covered glass slides, while both spin coating, drop casting and deep coating were used to attach the iron complexes onto them. A variety of spectroscopic techniques were used to yield information about the electronic structure of the new hybrid materials.

References

- [1] D. J. H. Harding, P. Harding, W. Phonsri, *Coord. Chem. Rev.*, **2016**, 313, 38-61.
- [2] M. Griffin, S. Shakespeare, H. J. Shepherd, C. J. Harding, J.-F. Létard, C. Desplanches, A. E. Goeta, J. A. K. Howard, A. K. Powell, V. Mereacre, Y. Garcia, A. D. Naik, H. Müller-Bunz, G. G. Morgan, *Angew. Chem. Int. Ed.*, **2011**, 50, 896-900.
- [3] S. Decurtins, P. Gütllich, C. P. Köhler, H. Spiering and A. Hauser, *Chem. Phys. Lett.*, **1984**, 105, 1-4.
- [4] G. Chastanet, C. Desplanches, C. Baldé, P. Rosa, M. Marchivie and P. Guionneau, *Chem²*, 2018, 2-2.
- [5] J. A. Oke and T.-C. Jen, *J. Mater. Res. Technol.*, 2022, 21, 2481-2514.

Mixed-Valence Manganese Carboxylate Clusters Derived from the Combined Use of Di-2-pyridyl Ketone with Selected Diols

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Manganese-containing coordination compounds have been the subject of investigation for many years since they often possess interesting physical properties and fascinating structural features.

A crucial parameter in the design of coordination complexes is the choice of the organic ligand because the latter dictates the structure, the topology and, therefore, the properties of the resulting compounds. One of the ligands that have been successfully employed in metal cluster chemistry is di-2-pyridyl ketone ((py)₂CO), which has a fruitful coordination chemistry [1]. Our group recently reported new high nuclearity [Mn₂₃] and [Mn₂₄] compounds as well as a series of Mn/4f complexes that were prepared from the combination of ((py)₂CO) with polyols [2]. Herein, we report an extension of these investigations that involve the synthesis of a series of homometallic Mn-based complexes from this ligand combination approach (Figure 1). The reported compounds possess rare nuclearities and unprecedented structural motifs as well as interesting magnetic properties.

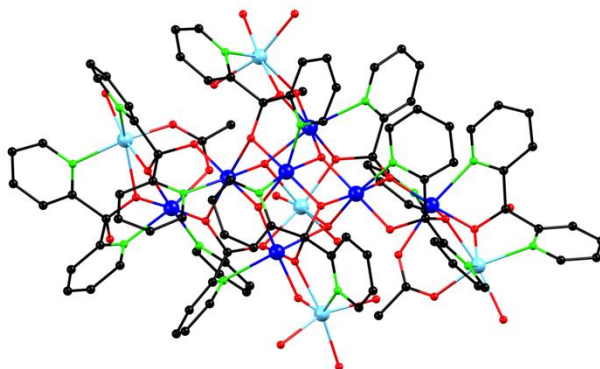


Figure 1: Molecular structure of [Mn₁₂O₂(OH)₃(OMe){(py)₂C(O)₂}₆{(py)₂C(OH)(O)₂(MeCO₂)₂(H₂O)₁₀}⁷⁺ cation, a representative compound discussed in this work. Color scheme: Mn^{II}, cyan; Mn^{III}, blue; O, red; N, green; C, black. Hydrogen atoms are omitted for clarity.

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[1] A. J. Tasiopoulos and S. P. Perlepes, *Dalton Transactions*, 2008, **41**, 5537-5555.

[2] K. Skordi, A. Anastasiades, A. D. Fournet, R. Kumar, M. Schulze, W. Wernsdorfer, G. Christou, V. Nastopoulos, S. P. Perlepes, C. Papatriantafyllopoulou and A. J. Tasiopoulos, *Chem. Comm.*, 2021, **57**, 12484-12487.

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.

Design and Modulation of Selectivity toward Vanadium(V) and Uranium(VI) Ions: Coordination Properties and Affinity of Hydroxylamino-Triazine Siderophores

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^a University of Cyprus, Department of Chemistry, 2109, Nicosia, Cyprus. ^b Department of Chemistry and Biochemistry, Faculty of Sciences University of Lisbon, 1749-016 Lisbon, Portugal. ^c School of Chemistry, The University of Glasgow, G12 8QQ, Glasgow, U.K. ^d Department of Chemistry, University of Ioannina, 45110, Ioannina, Greece.

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Siderophores, are a family of organic substitutes that contain hard atomic donors such as N and O, exhibiting high affinity and selectivity towards hard metal ions, including trans-U^{VI}O₂²⁺ and cis-V^{VO}O₂⁺. A scientific challenge is the design of chelators with improved properties that enhance both selectivity and thermodynamic stability in their interaction with metal ions. Based on the strong binding and high selectivity demonstrated by the substitute 2,6-di-[hydroxy(methyl)amino]-4-morpholino-1,3,5-triazine H₂bihyat for trans-U^{VI}O₂²⁺, a new family of organic substitutes with two complexation sites was designed.

The resulting binuclear complexes (Figure 1) from the incorporation of two hard metal centers with these substitutes are expected to be thermodynamically more stable than their mononuclear counterparts with H₂bihyat due to the increase in entropy associated with the formation of additional chelating rings. The reaction of the new substitutes with trans-U^{VI}O₂²⁺ and cis-V^{VO}O₂⁺ led to the isolation of six binuclear complexes.

The ability of the new organic molecules to bind hard metal ions compared to other hard donor-atom ligands such as dipicolinic acid, was examined by NMR. The selectivity of the new molecules towards binding trans-U^{VI}O₂²⁺ over cis-V^{VO}O₂⁺ increases at high pH, while overall, uranyl complexation is less favorable. The kinetics of the substitution of bound uranyl by vanadium species and vice versa were examined by NMR. Based on those studies, a mechanism that describes the Uranyl – Vanadate exchange on the ligand's binding sites is proposed.

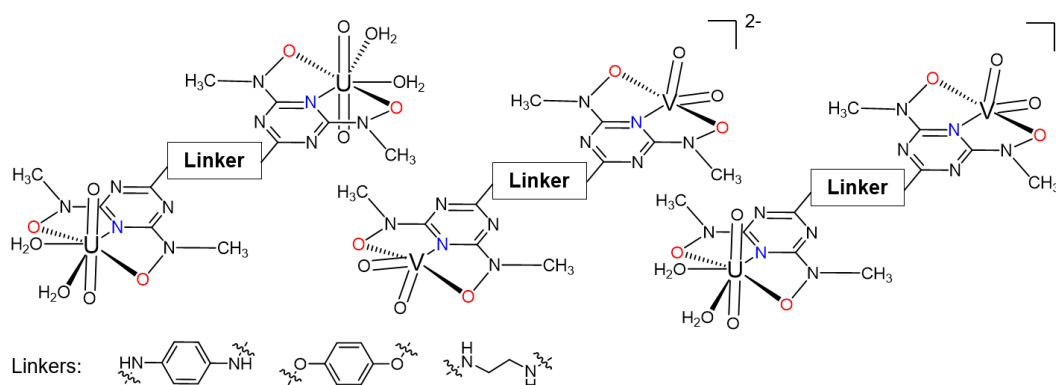


Figure 1: Homo- and heterometallic binuclear complexes.

References:

- [1] A. Amoiridis, et al. *Inorganic Chemistry* **2023** 62 (49), 19971-19985.
- [2] S. Hadjithoma, et al. *Inorganic Chemistry* **2018** 57 (13), 7631-7643.

{Cu₆M₄} (M = Gd, Tb, Dy, and Y) Clusters with a Multi-Layered Structural Core from the Use of Pyridyl Alcohol Ligands

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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.

Herein we report the syntheses, structures, and detailed magnetic studies of a new family of heterometallic {Cu₆M₄} (M = Gd, Tb, Dy, and Y) clusters afforded by the combined use of 2-(2-pyridyl)-1,3-propan-diol (pypdH₂) and 2-hydroxymethyl-2-(2-pyridyl)-1,3-propan-diol (pyptH₃) ligands. These compounds are based on an uncommon three-layered symmetric [Cu₆M₄(μ-OR)₁₆]⁸⁺ structural core that appears for the first time in metal cluster chemistry.

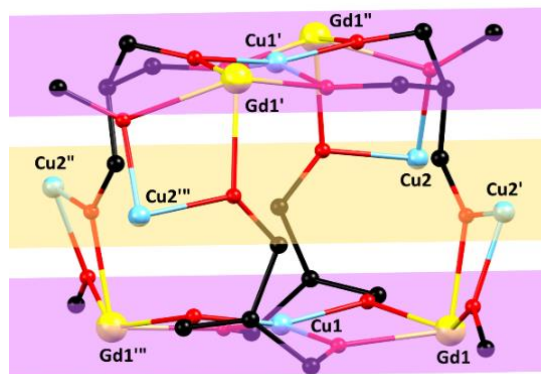
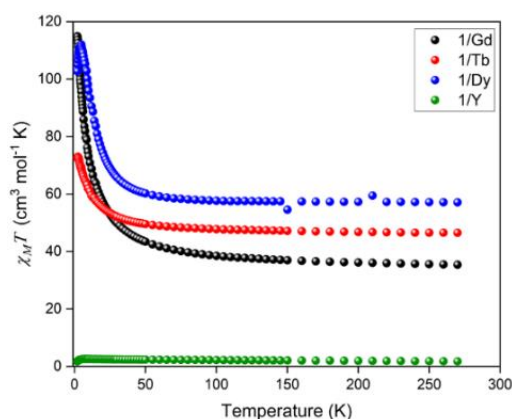


Figure 1: (left) partially labelled



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**, *432*, 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.

New synthetic entry to the family of molecular nanoparticles of cerium dioxide

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Cerium dioxide (CeO₂ or ceria) nanoparticles (CNPs) are versatile materials which are employed or investigated for a range of applications, including their use in energy applications, industrial catalysis and, more recently, biomedical applications. Owing to their radical scavenging activities, ultra-small CNPs are promising candidates as future therapeutic and theranostic agents. The versatility and important properties of these materials are partially attributed to the facile and rapid interconversion between the Ce³⁺ and Ce⁴⁺ oxidation states, and the presence of mobile oxygen-vacancy sites in the bulk lattice and on the surface. As such, the activity of CNPs depends on their size, shape, exposed surface facets, Ce³⁺ concentration, 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 analyzed to atomic resolution. As a result, many questions regarding the effect of the nanoparticle morphology and surface composition on the activity of the particle remain unanswered.

In an effort to improve our knowledge of this important material, our group has synthesized several cerium-oxo clusters with nanometer dimensions up to 2.4 nm which possess the same features as the bulk ceria lattice. We term these clusters 'molecular nanoparticles' owing to their molecular nature, size, and strong resemblance to the bulk material [1-3]. The molecular approach allows for the use of mild reaction conditions, as well as true monodispersity, solubility and crystallinity. The latter enables the clusters to be structurally analyzed by X-ray crystallography to evaluate completely their core structure and surface features to atomic resolution.

By making small changes to the established synthetic procedures, new members of the family can be isolated. In this presentation, we introduce synthetic methodologies to new cerium-oxo clusters that resemble a piece of the (111) surface of bulk ceria. The syntheses, crystal structures and properties will be discussed. We will also discuss the relevance of our new clusters to our established family of molecular nanoparticles.

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

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Molecular Heterometallic Dy^{III}-Sn^{II} Clusters: An Approach to Structurally Unique Compounds with Single- Molecule Magnetic and Toroic Properties

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The heterometallic chemistry of 3d/4f-metal ions has flourished over the past few decades, providing new structural motifs of nanosized molecular clusters, multifunctional compounds combining two or more physical properties within the same entity, and high-spin molecules with record spin values, as well as single-molecule magnets with enhanced magnetic dynamics. The analogous chemistry of 4f-metal ions with a post-transition metal ion, such as the tetrel Sn^{II}, has not been systematically explored, although Sn^{II} possesses high principal quantum number valence orbitals (5s), and strong spin-orbit coupling. These features create different effects on crystal field and magnetic exchange interactions with metal centers, when compared to the properties arising from the 3d-metal ions alone, and hence, Sn^{II} could -in principle- contribute to the enhancement of the molecular magnetic anisotropy [1].

Given the lack of any previously reported Dy^{III}-Sn^{II} heterometallic compounds bearing an organic chelate ligand to date, we decided to explore the Dy^{III}-Sn^{II} chemistry in order to obtain molecular compounds with interesting structural and physicochemical properties. Herein, we report the self-assembly synthesis and magnetic characterization of two new heterometallic clusters, namely {Sn₄Dy₈} and {Sn₂Dy₄}, bearing the ligand α -benzoin oxime [2], which exhibit single-molecule magnetic and toroic properties (**Figure**).

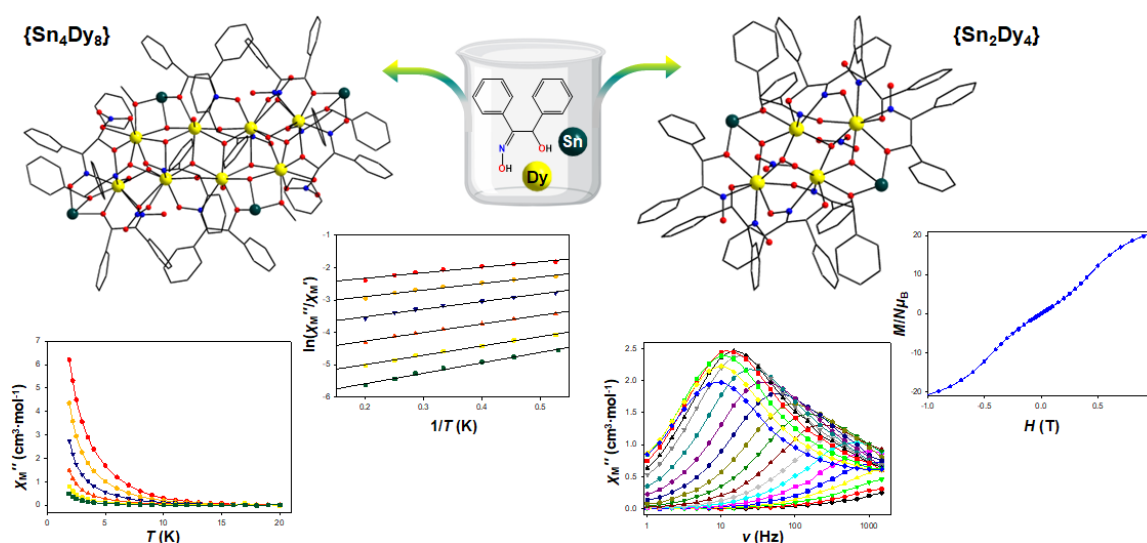


Figure. The {Sn₄Dy₈} (top left) and {Sn₂Dy₄} (top right) clusters and their magnetic properties (below).

[1] D. E. Freedman et. al., *Inorg. Chem.*, **2017**, 56, 8195-8202.

[2] G. Christou, Th. C. Stamatatos et. al., *Inorg. Chem.*, **2010**, 49, 3077-3079.

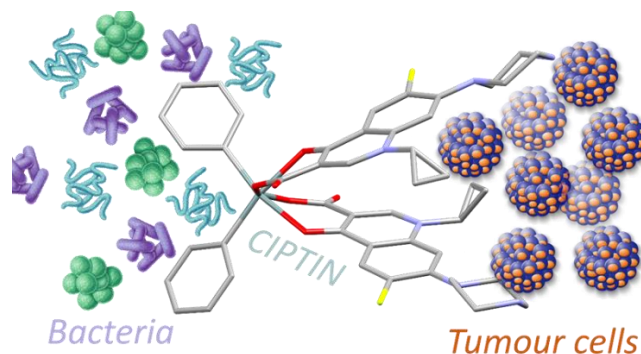
Controlled dual activity of organometallic antibiotic through micelle formulation

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Antimicrobial prophylaxis is essential for managing and averting infections in instances of immune suppression [1-2]. Therefore, prophylactic antimicrobial therapies could be considered as a targeted approach in cancer treatment [1-2]. Furthermore, individuals with cancer face a significantly elevated risk of infections caused by Gram-negative bacteria that are resistant to treatment [1]. Antibiotics are known as chemotherapeutic compounds [1-2]. Specifically, fluoroquinolones exhibit favorable pharmacokinetic profiles, as ciprofloxacin is capable of targeting both Gram-positive and Gram-negative pathogenic bacteria. Furthermore, studies have shown that ciprofloxacin exhibits antiproliferative and apoptosis-inducing effects on breast, prostate, and bladder cancer cells [1-2].

In the course of our research on the development of targeted chemotherapeutics with prophylactic antimicrobial properties, the known organometallic antibiotic $\text{Ph}_2\text{Sn}(\text{CIP})_2$ (**CIPTIN**) (a combination of diphenyltin and ciprofloxacin) [1] was encapsulated into micelles composed of Sodium Lauryl Sulphate (SLS) and Cetyltrimethylammonium bromide (CTAB). The micelles were characterized by spectroscopic techniques. The cytotoxic activity of **CIPTIN** and its micelles was assessed *in vitro* against MCF-7 (hormone depended (HD)) and MDA-MB-231 (hormone independent (HI)). Furthermore, the *in vitro* mechanism of action of the compounds was investigated through cell cycle arrest and permeabilization of the mitochondrial membrane assays. Additionally, the antibacterial activity of the micelles was evaluated.



Acknowledgements

The International PhD program, entitled “Biological Inorganic Chemistry (BIC), is acknowledged. This program is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Program «Human Resources Development, Education and Lifelong Learning 2014–2020» in the context of the subproject 6 “Biological Inorganic Chemistry (BIC)” (MIS 5162213).



Operational Programme
Human Resources Development,
Education and Lifelong Learning
Co-financed by Greece and the European Union



[1] M.P. Chrysouli, C.N. Banti, N. Kourkoumelis, E.E. Moushi, A.J. Tasio-poulos, A. Douvalis, C. Papachristodoulou, A.G. Hatzidimitriou, T. Bakas, S.K. Hadjikakou, Ciprofloxacin conjugated to diphenyltin(IV): a novel formulation with enhanced antimicrobial activity, Dalton Trans., 2020, 49, 11522

[2] A.-D.C. Magklaras, C.N. Banti, S.K. Hadjikakou, Antiproliferative Activity of Antibiotics through DNA Binding Mechanism: Evaluation and Molecular Docking Studies, Int. J. Mol. Sci. 2023, 24, 2563

Observation of spin-electric transitions in a molecular exchangequbit

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^b*Laboratoire National des Champs Magnétiques Intenses, Grenoble, France.*

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Electric fields represent an ideal means for controlling spins at the nanoscale and, more specifically, for manipulating protected degrees of freedom in multispin systems.^{1,2} In previous work, the required magnetoelectric coupling for such manipulations, was demonstrated within the ferric complex $[\text{Fe}_3\text{O}(\text{O}_2\text{CPh})_6(\text{py})_3]\text{ClO}_4 \times \text{py}$ (**Fe**₃) using Electron Paramagnetic Resonance under electric fields.^{3,4} Here, low-temperature magnetic far-IR spectroscopy on **Fe**₃ provide the first experimental evidence of spin-electric transitions in polynuclear complexes. The co-presence of electric- and magnetic-dipole transitions, allows us to estimate the spin-electric coupling. Based on spin Hamiltonian simulations of the spectra, we identify the observed transitions and introduce the concept of a generalized exchange qubit.

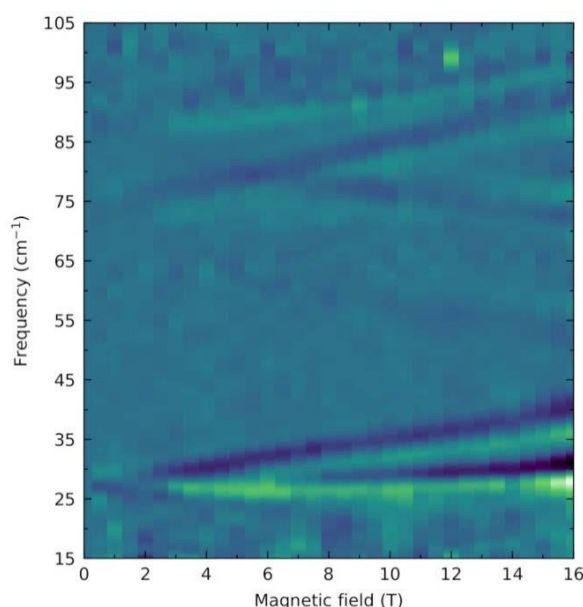


Figure. Variable-field magneto-FIR spectra of **Fe**₃.

[1]Trif, M. et al. Physical Review Letters 2008, 101, 217201.

[2]Trif, M. et al. Physical Review B 2010, 82, 045429.

[3]Boudalis, A. K. et al. Chem. Eur. J. 2018, 24, 14896–14900.

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Spatiotemporal Imaging and Modelling of Phase Transitions in Spin-Crossover Single Crystals.

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The imaging of the spatiotemporal dynamics of the spin transition phenomenon by optical microscopy (OM) at the scale of one single crystal has recently emerged as a highly efficient method allowing a deep understanding of the macroscopic behavior of spin crossover (SCO) materials along their transformation between the low-spin (LS) and high-spin (HS) states. In this communication, we will show some typical examples [1] of real time transformation of SCO single crystals exhibiting first-order transitions with well-defined front interfaces (see Fig. 1 for the case of $\{\text{Fe}(\text{2pytrz})_2[\text{Pd}(\text{CN})_4]\cdot 3\text{H}_2\text{O}\}$). The velocities, shapes and orientation of the HS/LS interfaces will be discussed in relation with the macroscopic shape of the crystals and the structural transformations of the unit cells along the LS to HS transitions.

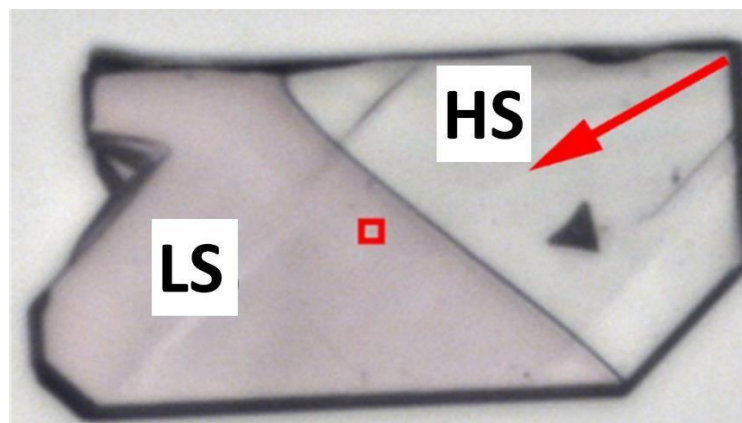


Figure. An example of a HS/LS interface along the thermal spin transition of a spin crossover single crystal.

Under light, the SCO solids display photo-induced phenomena through LIESST (Light-Induced Excited Spin-State Trapping) effect. When this process competes with thermal relaxation, Light-Induced Thermal Hysteresis (LITH) effect is obtained. Both of these phenomena and their spatiotemporal features have been characterized by OM, showing very different features. Finally, we will demonstrate that light irradiation can be used as a relevant and efficient stimulus leading to control the front interface as well as to select the nucleation point at which the spin transition can be triggered in a reversible way, although the latter effect is usually a stochastic process in thermal transitions. Overall, the spatiotemporal properties of the nucleation, growth and propagation of the spin domains will be discussed and their microscopic modelling [2] will be presented.

[1] H. Fourati et al., *Phys. Rev. B.* **2022**, 105, 174436.

[2] N. di Scala, N. E. I. Belmouri, M. A. Paez Espejo, and K. Boukheddaden, *Phys. Rev. B.* **2022**, 106, 144107

Ultra-small Prussian blue nanoparticles and self- assemblies for biomedical applications

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Sandrine Lacombe,^b Sophie Laurent,^c F. Gazeau,^d

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The introduction part of this communication will highlight the benefits of processing by a surfactant-free method several Prussian blue analogues and related coordination polymers as finely tuned nanoparticles for several types of applications [1]. Notably, in the biomedical field, Ultrasmall Prussian blue-like (USPB) have revealed a high T1-weighted contrast for MRI imaging and good photo-thermal therapy (PTT) efficiency [2]. Besides, we have shown that USPB including heavy metals may also serve as nanosensitizers for radiotherapy [3]. Some of these USPB have been shown to lead to novel worm-like self-assemblies through a green process with enhanced MRI contrast and efficient PTT. These USPB-assemblies can load doxorubicin with high encapsulation and loading capacities, with pH-triggered release [4], giving a first proof-of-concept for a new family of theranostics nanoplateforms.

[1] L. Catala et al, *Coord. Chem. Rev*, **2017**, 346, 32–61.

[2] L. Fétiveau et al, *Chemcomm* **2019**, 55, 14844-1484

[3] R. George et al, *Materials Advances*, **2023**, 4, 5314-5323

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Theoretical investigations of decoupled and coupled two spin-1/2 systems

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In this talk, I report two studies of two spin-1/2 systems. For the two decoupled system, we solve the problem of a single electron scattering from two magnetic impurities. We show that this treatment can map the scattering problem onto a quantum operation on the two impurities, and that for certain forms of the scattering potential this operation can be made unitary in order to realize two-qubit gates. We demonstrate that when the scattering potential is the *sd* exchange model, we can achieve a SWAP gate in a completely time-independent manner and without ever directly coupling the two impurities by appropriate location of a real-space barrier voltage term. We subsequently apply the same treatment to a SWAP^{1/2} gate. For the coupled two spin-1/2 system, we study the coherence in the presence of a bath of nuclear spins simulated using generalized cluster correlation expansion method. In our model, two electron spin qubits coupled with isotropic exchange or magnetic dipolar interactions interact with an environment of random nuclear spins. We study the time-evolution of the two-qubit reduced density matrix and resulting decay of the off-diagonal elements, corresponding to decoherence, which allows us to calculate gate fidelity in the regime of pure dephasing. We contrast decoherence when the system undergoes free evolution and evolution with dynamical decoupling pulses applied.

This work was supported as part of the Center for Molecular Magnetic Quantum Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award no. DE-SC0019330 and by DOE/BES DE-SC0022089.

$$\mathbf{U}_{SWAP}^{1/2} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1+i}{2} & \frac{1-i}{2} & 0 \\ 0 & \frac{1-i}{2} & \frac{1+i}{2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Figure. Operator for a universal gate

Electronic Materials for Emerging Photovoltaic Applications

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The advantages of organic and hybrid perovskite emerging photovoltaic technologies, such as their light weight, mechanical flexibility in addition to the small energy demand, and low-cost equipment requirements for roll-to-roll printing mass production, characterize them as interested candidate sources for future electrical power. The presentation aims in covering a range of scientific and engineering issues needed to bring emerging photovoltaics to commercial viability in terms of efficiency, lifetime and cost. A systematic understanding of the relationship between photovoltaic materials, interfaces and electrodes relevant to emerging photovoltaics product development targets will be presented [1,2].

[1] Silver Nanowires/Metal-Oxide based Transparent Electrode for High Performance Non-Fullerene Acceptor ITO-free Inverted Organic Photovoltaics, E. Georgiou, A. Ioakeimidis, I. Antoniou, I. T. Papadas, A. Hauser, M. Rossier, F. Linardi, and S. A. Choulis, ACS Applied Electronic Materials, 2023, 5, 1, 181–188.

[2] Optimized Doping of Diffusion Blocking Layers and Their Impact on the Performance of Perovskite Photovoltaics, F. Galatopoulos, S. Bitton, M. Tziampou, N. Tessler, S. A. Choulis ACS Applied Electronic Materials, 2023, 5 (10), 5580-5587.

Boosting the Photoluminescence Efficiency of InAs QDs via Shell Engineering

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CQD technology has delivered materials and devices with excellent optoelectronic properties and performances in the last two decades. Nevertheless, the research has centred on UV-Vis, while very few examples have been shown in the low-energy part of the electromagnetic spectrum. Most of the materials with bandgap below 1.77 eV are based on toxic Pb- and Hg- chalcogenides that fall under RoHS regulations. To date, the SWIR has been served by costly epitaxial III-V semiconductors, which are not monolithically integrated into silicon (CMOS) electronics and suffer from high growth cost and low-volume manufacturing. Hence the synthesis of low-cost III-V CQDs, would unleash the potential of SWIR in consumer electronics.

The synthesis of high-quality III-V CQDs is not trivial. The typical synthesis of InAs CQDs shows low PLQs due to the intrinsic surface dangling bonds III-V semiconductor. The synthesis of epitaxial shelling is crucial to passivate the surface trap state and boost the PLQY for optoelectronic applications. Here, we study two shelling approaches to enhance the system's optical and multiexciton response. Firstly, we report an optimised synthesis of InAs@ZnSe core@shell nanocrystals, allowing us to tune the ZnSe shell thickness up to seven mono-layers (ML) and boost the emission, reaching a quantum yield of $\approx 70\%$ at ≈ 900 nm¹. Finally, we introduce a seeded-growth approach to for the synthesis of InAs/ZnS_xSe_{x-1} reporting both high PLQYs and suppress Auger rates.²

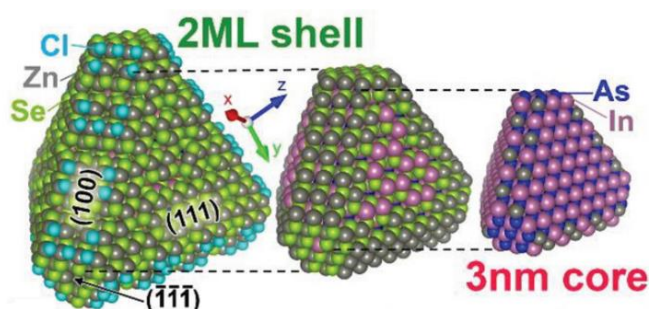


Figure. Atomistic structure of the whole core@shell NC (left), the core and the In-Zn-S/Se interlayer (middle) and the core (right).

[1] D. Zu *et. al. Advance Materials*, 2023, 2303621 DOI: 10.1002/adma.202303621

[2] N. Polycarpoy *et. al. under submission*

Supramolecular Oligomers of Magnetic Molecules: Control of Exchange Interactions and Quantum Properties

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Our group has long been interested in the beneficial impact of supramolecular chemistry on the properties of magnetic molecules (MM's), especially their quantum physics properties that make them potential spin-based molecular components in new 21st-century technologies. For example, exchange-biased quantum tunnelling of magnetization (EB-QTM) and quantum superposition and entanglement (QSE) states were discovered from single-crystal hysteresis loops and high-frequency EPR studies, respectively, on a $[\text{Mn}_4]_2$ hydrogen-bonded exchange-coupled dimer of a cubic single-molecule magnet (SMM) with ground state spin $S = 9/2$.^{1,2} More recently, we have returned to this area seeking methods that would provide greater control of the oligomeric extent of the products, and the magnitude and sign of the inter-MM exchange coupling (J) within them. We subsequently developed, using dioximate or dicarboxylate linkers, a family of covalently-linked $[\text{Mn}_3]_n$ ($n = 2, 4, 8$) oligomers of a triangular Mn_3 SMM with $S = 6$ that fulfilled these criteria. An overview of the development of this work over the years and its current status will be presented, comprising syntheses, structures, magnetic properties, and quantum behaviour of a selection of these oligomers, as well as questions being addressed by ongoing studies and those planned in the near future.

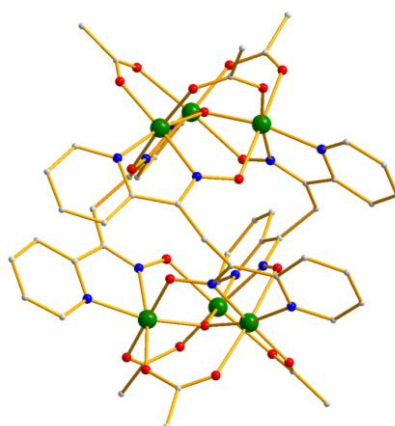


Figure. One of the $[\text{Mn}_3]_2$ dimers of an $S = 6$ SMM covalently linked by three dioximate groups.

1. Exchange-biased Quantum Tunneling in a Supramolecular Dimer of Single-Molecule Magnets. W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson, and G. Christou, *Nature*, **2002**, 416, 406.
2. Quantum Coherence in an Exchange-Coupled Dimer of Single-Molecule Magnets. S. Hill, R. S. Edwards, N. Aliaga-Alcalde, and G. Christou, *Science*, **2003**, 302, 1015-1018.

High-energy resolution fluorescence detected X-ray absorption spectroscopy studies of water splitting in Photosystem II

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Photosystem II of plant chloroplasts and cyanobacteria catalyzes water splitting using sunlight energy. The Mn₄Ca cluster stabilized by amino acid residues of Photosystem II undergoes the four-electron oxidation of water to dioxygen through five oxidation states: S₀→S₁→S₂→S₃→[S₄]→S₀. The oxygen is formed after the illumination of the S₃ state. The nature of the S₂→S₃ transition is debated and although spectroscopy concluded on Mn-based oxidation, some XFEL crystal structures proposed ligand-based oxidation. We utilize high energy resolution fluorescence detected (HERFD) X-ray absorption spectroscopy to describe the Mn pre-edge region for all S-states. The 1s-3d transitions observed in the pre-edge region give information about the local environment of the Mn ions. Unlike the edge of the XANES spectra that were used in the past for the determination of the oxidation states and treated empirically, the pre-edge spectra can be correlated with atomistic DFT models. All proposed models in the literature were tested. The data suggest that Mn-based oxidation occurs in all S-transitions.¹ The effect of methanol and ammonia that act as water analogues on the Mn₄Ca cluster and perturb the S-cycle was also tested to understand the water binding step during the S₂→S₃ transition.

[1] Chrysina et al. *J. Am. Chem. Soc.* **2023**, 145, 25579–25594

Acknowledgements

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Organometallic Single-Molecule Magnets Containing Radicals and Bismuth

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Single-molecule magnets (SMMs) are molecules that possess an energy barrier to spin inversion, giving rise to slow magnetic relaxation and magnetic hysteresis. To realize their intriguing potential applications, ranging from molecular spintronics, quantum computing, to high-density information storage, spin-reversal barriers (U_{eff}) and magnetic blocking temperatures (T_B) must be increased. Lanthanide ions are especially well-suited for the design of SMMs due to their large magnetic moments and magnetic anisotropy that originate from strong spin-orbit coupling of the 4f orbitals. One effective methodology to boost blocking temperatures of multinuclear compounds is to generate strong magnetic exchange between lanthanide centers using radical bridging ligands. In the event of large magnetic exchange coupling, undesirable relaxation pathways such as quantum tunneling of the magnetization can be suppressed.

Here, the first isolation of the bisbenzimidazole radical anion ($\text{Bbim}^{3-\cdot}$) and its use in radical-bridged SMMs will be discussed [1,2]. A second approach to strong coupling employs heavy p-block elements since their diffuse valence orbitals facilitate better penetration of the core electron density of the lanthanide ions relative to diamagnetic ligands comprising lighter p-block elements. Here, we will present the first lanthanide bismuth cluster SMMs containing a $[\text{Ln}_2\text{Bi}_6]$ heterometallobicubane core. We will also show that the $\text{Bi}_2^{3-\cdot}$ radical anion can be tamed with rare earth ions to give the first SMMs featuring bismuth radicals [3,4].

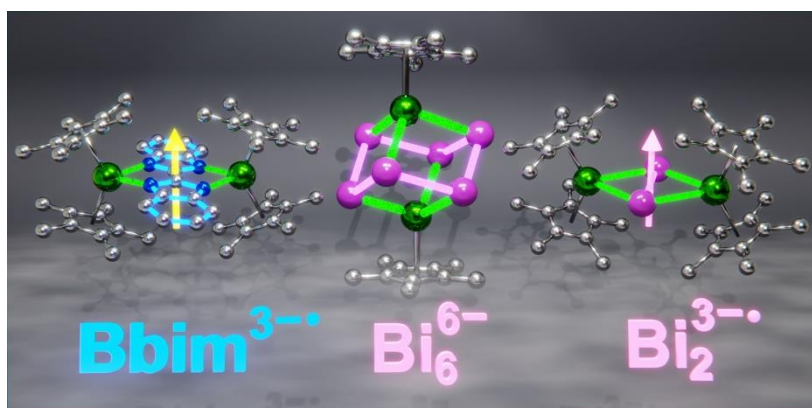


Figure. Structures of the isolated organometallic lanthanide complexes.

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Covalently-linked, Rigid Cofacial 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 novel the appropriate magnetic and quantum properties to make them potential spin-based molecular components in new 21st-century 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 single-ion complexes in order to obtain products that are more chemically robust and that also allow tunability of the metal ions incorporated. Therefore, we have now targeted and 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.

Heterobimetallic Complexes with 4f Elements for Potential QIS and Qubits

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The design and preparation of molecules that are potential qubits (or qudits) is of considerable current interest. Our group has created a family of heterobimetallic lantern (paddlewheel) complexes of the general form $[\text{PtMX}(\text{SOCR})_4]$ in which $M = d$ - or s -block metal center, $X =$ neutral or anionic ligand, and $R = \text{CH}_3$ or C_6H_5 . We have now extended this work to $M = \text{Ln}$ and will report new structural motifs and related magnetic properties. The rigid lantern framework is potentially useful for the vibrational isolation required d

Previously published work [1] described the combination of the d^f building blocks, $[\text{Pt}(\text{V}=\text{O})(\text{SOCH}_3)_4]$ and $[\text{Pt}(\text{V}=\text{O})(\text{SOC}_6\text{H}_5)_4]$ with $\text{Ln} = \text{Ce}, \text{Nd}$. Four heterotrimetallic complexes with linear $\{\text{LnOVPt}\}$ units were prepared: $[\text{Ln}(\text{ODtbp})_3\{\text{PtVO}(\text{SOCR})_4\}]$ ($\text{Ln} = \text{Ce}$, **3Ce** ($R = \text{CH}_3$), **4Ce** ($R = \text{Ph}$); Nd , **3Nd** ($R = \text{CH}_3$), **4Nd** ($R = \text{Ph}$); $\text{ODtbp} = 2,6$ -ditertbutylphenolate). Magnetic characterization confirms slow magnetic relaxation behavior and suggests antiferromagnetic coupling across $\{\text{Ln}-\text{O}=\text{V}\}$ in all four complexes, with variations tunable as a function of Ln and R .

Unpublished work includes the tetrametallic species shown in Figure 1 below, $[\text{PtNd}(\text{SOCCH}_3)_4(\text{m}_2\text{-ODipp})_2(\text{SOCCH}_3)_4\text{NdPt}]$ with $\text{ODipp} = 2,6$ -di-isopropylphenolate. This highly unusual compound has a short $\text{Pt}\dots\text{Nd}$ (3.201(2)) and $\text{Nd}\dots\text{Nd}$ (3.987(10)) distances (Å) as well as the relatively low coordination number of six at Nd . This presentation will include discussion of the synthetic path to this unusual compound, approaches to preparing related compounds with a similar tetrameric unit, and unexpected compounds that were isolated from these efforts.

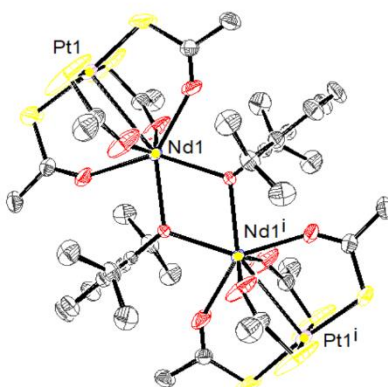


Figure 1. $[\text{PtNd}(\text{SOCCH}_3)_4(\text{m}_2\text{-ODipp})_2(\text{SOCCH}_3)_4\text{NdPt}]$.

[1] Beach, S. A., Guillet, J. L., Lagueux, S. P., Perfetti, M., Livesay, B. N., Shores, M. P., Bacon, J. W., Rheingold, A. L., Doerrer, L. H., *Chem. Commun.*, **2020**, 56, 11062

Metal-Organic Frameworks (MOFs) as Prospect Adsorbents and Membranes for Energy-intensive Separations and Carbon Capture.

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Demand for functional materials targeted for specific applications is ever increasing as societal needs and demands mount with advancing technology. Evidently, improvement of existing materials and quest for new approaches to the design of novel materials are both valuable paths worth pursuing in order to address the myriad technological challenges that face us, pertaining to energy and environmental sustainability.

Metal-organic frameworks (MOFs) are a unique class of solid-state materials amenable to design and manipulation for desired function and application, thanks to advancement in reticular chemistry and the various design strategies developed for its effective practice. Several design strategies have been utilized and developed to target viable MOF platforms, from the single-metal-ion molecular building block (MBB) approach to the hierarchical supermolecular building block and supermolecular building layer approaches (SBB and SBL, respectively) to the merged nets approach, and centering structure-directing agents (c-SDA) strategy. This inherent built-in information allows access to highly stable and made-to-order porous materials, with controlled pore-aperture size and/or inner pore system functionality, toward applications pertaining to energy and environmental sustainability. Specifically, MOF materials addressing the energy-intensive separations and carbon capture will be highlighted, as well as insights into MOF based membranes, namely pure MOF membranes and mixed matrix membranes (MMMs), construction and respective gas separation properties.

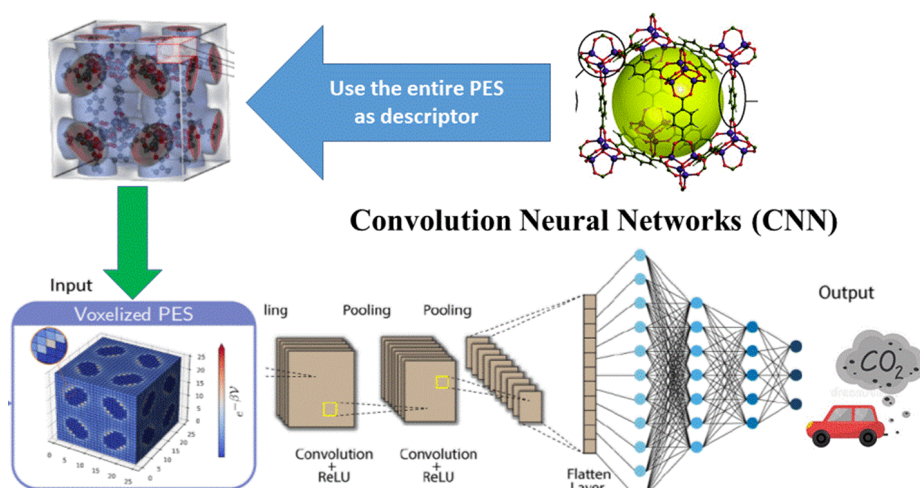
Gas Adsorption Meets Deep Learning: Voxelizing the Potential Energy Surface

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Intrinsic properties of metal-organic frameworks (MOFs), such as their ultra-porosity and high surface area, deem them promising solutions for problems involving gas adsorption. Nevertheless, due to their combinatorial nature, a huge number of structures is feasible which renders cumbersome the selection of the best candidates with traditional techniques. Recently, machine learning (ML) approaches have emerged as efficient tools to deal with this challenge, by allowing researchers to rapidly screen large databases of MOFs via predictive models. The performance of the latter is tightly tied to the mathematical representation of a material, thus necessitating the use of informative descriptors.

In this work, a generalized framework to predict gaseous adsorption properties is presented, using as one and only descriptor the capstone of chemical information: the potential energy surface (PES). In order to be machine understandable, the PES is voxelized and subsequently a 3D convolutional neural network (CNN) is exploited to process this 3D energy image. As a proof of concept, the proposed pipeline is applied on predicting CO₂ uptake in MOFs. The resulting model outperforms a conventional model built with geometric descriptors and requires two orders of magnitude less training data to reach a given level of performance. Moreover, the transferability of the approach to different host-guest systems is demonstrated, examining CH₄ uptake in COFs. The generic character of the proposed methodology, inherited from the PES, renders it applicable to fields other than reticular chemistry [1].



[1] Gas Adsorption Meets Deep Learning: Voxelizing the Potential Energy Surface of MOFs. Antonios P. Sarikas, George Konstantinos Gkagkas, George E. Froudakis, *Sci Rep* 14, 2242 (2024). <https://doi.org/10.1038/s41598-023-50309-8page>

2D Germanane: New synthetic strategies, derivatives and applications

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Abstract

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, tailored *nanostructured materials* based on 2D *germanane* (GeH)¹⁻⁵ with high surface area, tunable pore size and functionalities have been synthesized and studied by using top-down (bulk synthesis) and bottom-up (by combining the Langmuir-Schaefer and the self-assembly techniques) synthetic approaches. Hybrid materials were characterized by a combination of analytical techniques. Representative case studies addressing cutting edge processes of great importance such as the use of these hybrid nanostructures as catalysts, phase change materials, cytotoxic agents, effective adsorbents for environmental remediation, and gas (H_2 and CO_2) storage materials will be discussed.

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New apoptosis inducers containing anti-inflammatory drugs and pnictogens derivatives; A new strategy in the development of mitochondrial targeting chemotherapeutics

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A new era was recently opened in the discovery and development of new therapeutic agents, from the combination of two distinct classes of chemical or biological agents into a single entity. This provides the synergy effect, particularly when one component serves as a detector agent for the specific intracellular component, cell, tissue, etc., while the other interacts with the intended biological system.

The conjugation of mefenamic acid (MefH), a non-steroidal anti-inflammatory drug (NSAID) with a mitochondriotropic derivative of pnictogens tpE (tp= triphenyl- group, E= P, As and Sb), via silver(I) ions resulted in the formation of $\{[Ag_8(Mef)_8(\mu_2-S, O-DMSO)_2(\mu_2-O-DMSO)_2(O-DMSO)_8] 2(H_2O)\}$ (**1**), $[Ag(Mef)(tpP)_2]$ (**2**), $[Ag(Mef)(tpAs)_3]$ (**3**), $\{2 [Ag(Mef)(tpSb)_3](DMSO)\}$ (**4**) and their micelles with Sodium Lauryl Sulphate (SLS) termed as SLS@**1-4**. The characterization of **1-4** and SLS@**1-4** was performed through analysis of their spectral data and X-ray crystallography. They demonstrate the ability to hinder the growth of human breast adenocarcinoma cells, including MCF-7 (hormone-dependent) and MDA-MB-231 (hormone-independent). X-ray fluorescence analysis indicates the cellular uptake of silver. The absence of genotoxicity both *in vitro* and *in vivo* was verified through micronucleus (MN) assays, as well as assays involving *Artemia salina* and *Allium cepa*.

The mechanism of action was investigated through various methods, including examination of cell morphology, analysis of DNA fragmentation, Acridine Orange/Ethidium Bromide (AO/EB) staining, assessment of cell cycle arrest, evaluation of mitochondrial membrane permeabilization, inhibition of the aldo-keto reductases (AKRs), determination of DNA binding affinity, examination of LOX inhibitory activity, and interpretation via regression analysis.



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Disentangling the excited state dynamics of conjugated polyelectrolytes self-assembled with ss-DNA with a direct molecular probe

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Control over the conformation of conjugated polymers using nucleic acids (NAs) as templates can be very advantageous in inducing unique and readily controllable properties. Complexation of NAs with conjugated polyelectrolytes such as cationic polythiophenes (CPT) is facilitated by the presence of charged side groups on the backbone.[1] Previous studies on the biosensing ability of a certain CPT has revealed a tremendous impact of the ssDNA sequence on the optical response of the polymer, which reflected polymer backbone conformational changes.[2] In this talk I will present our efforts to understand in detail the sequence-dependent templating effect of single-stranded DNAs (ssDNAs) on the conformation of this polyelectrolyte and consequently on its photophysical properties and excited state dynamics combining vibrational spectroscopy as a direct structural probe and ultrafast spectroscopic methods as probes of the excited state dynamics.

Resonance Raman spectroscopy can provide ground state information on the conformation of conjugated polymers under various environmental conditions, however, the intensity of the Raman bands in a resonant experiment contains rich information that has been underexplored in organic electronics. Utilizing the selectivity provided by resonance Raman for a particular chromophore we were able to understand the interactions between a CPT and different ssDNAs that lead to particular templated conformations of the polymer. Resonance Raman intensity analysis then provided insights on the excited state vibrational-mode-dependent reorganization, through simultaneous modelling of the band intensities and the absorption spectrum, as a function of the extent of interactions between the polymer and the ssDNA. Finally, we combined this information with ultrafast transient absorption experiments in the near- and mid-IR to understand the effect of structural templating on the excited state processes.[3,4] We found that while certain ssDNA sequences can induce order in the conjugated polymer backbone through extensive interactions between the two partners in the complex, the templating scaffold does not seem to be a mere spectator but instead participates and affects the excited state behavior. This is something that needs to be considered in the design of functional templated conjugated polymers for their suitability for particular optoelectronic applications.

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Mn^{III} Spin Transition Materials: Insights from High-Field EPR

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In this talk, I will survey the results of extensive high-field EPR (HFEP) investigations carried out on a series of structurally similar Mn^{III} spin crossover (SCO) complexes with hexadentate Schiff base R-sal₂323 and nsal₂323 ligands [1-3]. These ligand systems impose a rare compressed octahedral Mn^{III} coordination geometry, with short axial Mn-O ligation *via* two *trans*-phenolate groups and four longer/weaker equatorial Mn-N bonds *via* pairs of *cis*-amine and *cis*-imine donors. The compression is particularly pronounced for the high-temperature, high-spin ($S = 2$) structure, destabilizing the d_{z^2} orbital relative to $d_{x^2-y^2}$, resulting in an orbitally non-degenerate $d_{xy}^1 d_{yz}^1 d_{xz}^1 d_{x^2-y^2}^1$ occupancy. HFEP measurements confirm a moderate easy-plane anisotropy, with an axial zero-field splitting (ZFS) parameter, $D \approx +5 \text{ cm}^{-1}$, as expected for an octahedrally compressed high-spin d^4 electronic configuration. Meanwhile, the low-spin ($S = 1$) structure is accessible *via* double occupancy of the d_{xy} bonding orbital, which is accompanied by a significant reduction in the equatorial Mn-N bond lengths. This contraction destabilizes the $d_{x^2-y^2}$ orbital to the extent that it offsets the electron repulsion penalty associated with the double d_{xy} occupancy. A near degeneracy associated with the $d_{xy}^2 d_{xz}^1 d_{yz}^1$ configuration gives rise to a significant magnetic anisotropy in all cases, again of easy-plane type, with an axial ZFS parameter, $D > +20 \text{ cm}^{-1}$. Backed up by *ab-initio* ligand-field theory, these HFEP results provide a clear picture of the ligand-imposed structural features that support the SCO behavior observed in this class of Mn^{III} compounds.

This work was supported by the US National Science Foundation (DMR-2004732) through a US–Ireland–Northern Ireland R&D Partnership, with counterpart funding from the Science Foundation Ireland (SFI 19/US/3631). Work performed at the National High Magnetic Field Laboratory is supported by the US National Science Foundation (DMR-2128556).

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Probing Charge Transfer/Transport Through Os(aryl)₄ Complexes

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We are developing new synthetic routes to access functionalized M(aryl)₄ compounds^[1] and studying the influence of substituents on their structures and electronic properties. For example, we have recently shown that these complexes can be formed in up to ~73% yield using a new (Oct₄N)₂[OsBr₆] precursor rather than OsO₄.^[2] We have also found that aryl Grignard reagents used to form Os(aryl)₄ can be prepared using relatively mild Grignard transfer approaches instead of magnesium activation. This has provided access to previously intractable complexes such as those functionalized with -Br or -I, amenable to onward Suzuki, Negishi, or lithiation reactions. Overall, these tetrahedral Os(IV), d⁴ species are air-stable, can be purified by chromatography, and display interesting redox-active and optical properties. We aim to increase the utility of this relatively underexplored class of organometallic complexes in established and emerging areas of molecular materials science.

Here we highlight the potential utility of Os(aryl)₄ as conducting 3D nodes for ordered polymers (OPs), replacing tetraphenylsilane/methane analogues that suffer from broken conjugation through the central sp³-hybridized Si or C atom. Single-molecule break-junction studies (**Figure 1a**) studies reveal Os(aryl)₄ wires are >1 order of magnitude conducting than their Si or C congeners. Spectroelectrochemical studies further reveal intervalence charge transfer bands can be observed in **OsFc₄** (**Figure 1b**) but not in analogous compounds with Si or C central atoms. Together, these studies lay the foundation to construct new classes of permanently porous, conducting bulk materials, helping to drive important conceptual advances relevant to future energy storage/conversion and chemical sensing technologies.

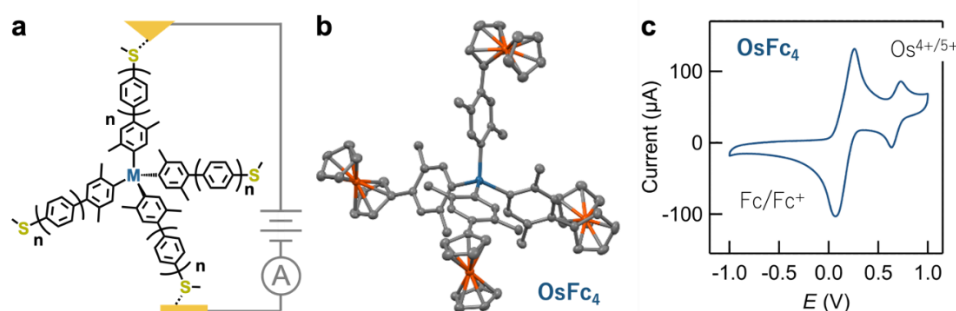


Figure 1. We probe electronic coupling across the central atom of M(aryl)₄ using single-molecule conductance measurements and spectroelectrochemistry (M = Os, Si, C). (a) M(aryl)₄ junctions (n = 0-2). (b) X-ray crystal structure of OsFc₄. (c) Voltammogram of OsFc₄ showing distinct redox features.

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Microplastics as Secondary Pollutants: Covert Carriers of Radionuclides in Aquatic Environments

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Plastic materials are widely used in our daily lives, serving various purposes. However, the excessive usage and improper disposal of plastic waste have resulted in its accumulation in different environmental systems, both on land and in water. Additionally, when exposed to environmental conditions, plastic surfaces degrade, leading to the formation of smaller particles called microplastics (MPs). Due to their large surface area, MPs have the ability to absorb different pollutants, including heavy metals like radionuclides, effectively acting as carriers of contaminants in both land and water ecosystems. This study specifically investigates how various types of MPs, such as polyamide 6 (PN6), polyethylene (PE), and polylactic acid (PLA), interact with different radionuclides in various oxidation states, ranging from +2 to +6 (e.g., Ra(II), Am(III), Eu(III), Th(IV), Np(V), U(VI)). The study also examines different factors influencing the adsorption capacity of MPs, such as particle type and size, pH of the solution, and composition of the solution (e.g., de-ionized water, groundwater, seawater). The findings reveal significant adsorption of radionuclides by the examined MPs, with distribution coefficient (K_d) values reaching up to 2670 (L/kg) for the adsorption of U-232 by PN6. Moreover, the study highlights that the release of radionuclides is particularly high under low pH conditions ($\text{pH} < 4$) and in the presence of complexing agents like EDTA. Overall, the study indicates that MPs can serve as carriers of radionuclides in various ecosystems, contributing to their persistence in the environment and facilitating their entry into the biosphere.

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Reductive Activation of O₂ to O₂²⁻ from a Vanadium(IV)-amidate Species

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The two electron reductive activation of O₂ to O₂²⁻ is of particular interest to scientific community mainly due to the use of peroxides as green oxidants and in powerful fuel-cells. Among the metal-ions which activate O₂, vanadium is of particular interest because of its numerous oxidative catalytic properties. Reaction of either V^{IV}OSO₄·3.5H₂O or V^{IV}OCl₂ with *N*-(8-quinolyl)pyridine-2-carboxamide (Hpbq) in CH₃OH solution under atmospheric O₂, at room temperature, resulted in the quick formation of [V^{VO}(k²-O₂)(pbq)(H₂O)](1). Compound 1 constitutes a rare example of formation of a (peroxo)oxidovanadium(V) complex from molecular O₂ and an oxidovanadium(IV) complex. The reaction of formation of compound 1 vs. time was monitored by ⁵¹V and ¹H NMR, UV-vis, cw-X-EPR, Resonance Raman spectroscopies and cyclic voltammetry revealing the formation of a stable radical intermediate [V^{VO}(k²-O₂)(pbq)(H₂O)]*⁺. Dynamic experiments in combination with computational calculations were used to elucidate the mechanism of the reaction. The galvanic cell {Zn|V^{III},V^{II}||*cis*-[V^{VO}O₂(bpq)], [V^{VO}O(O₂)(bpq)(H₂O)], [V^{IV}O(bpq)(H₂O)₂]⁺|O₂|C(s)} was manufactured, demonstrating that this technology can be used in Zn|H₂O₂ fuel cells generating H₂O₂ *in situ* from atmospheric O₂.

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On 1,1-dithiolates

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From early research stages, the “innocent” nature of the 1,1-dithiolates as coordinating agents was observed.^[1] This ignited curiosity in the chemical community, as the isomeric 1,2-dithiolate ligands which were synthesized a few years earlier were proven to be “non-innocent”,^[2] (Figure 1). The little structural changes between the two isomer ligands have a dramatic effect on the electronic properties of the coordinated complexes. For instance, the 1,1-dithiolates were able to stabilize high formal oxidation states of various metallic centers, whereas the 1,2-dithiolates could not. Even though 1,1-dithiolates find plenty of uses in many fields of chemistry, only a few derivatives have been explored thoroughly.

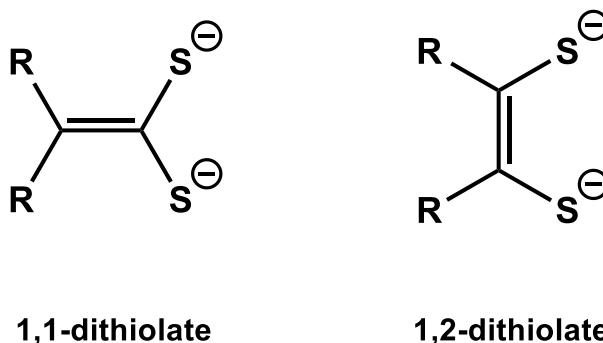


Figure 1. Chemical structure of 1,1-dithiolate and 1,2-dithiolate ligands

In this project new 1,1-dithiolate ligands have been synthesized, bearing electron-donating and electron-withdrawing groups on their backbone, and their properties as coordinating ligands were studied with their nickel and copper complexes. Routine spectroscopic experiments of these complexes confirmed a square planar geometry with the two 1,1-dithiolate ligands located on the xy plane.

The comparison of their electronic and bonding parameters in their metal complexes was conducted through CV, UV-vis, and EPR spectroscopy. The spectroscopic data were correlated with the Hammett parameters for each complex, and ultimately it was proven that the electronic properties of a bis homoleptic 1,1-dithiolate complex can be manipulated by changing the chemical groups of the backbone, on the 1,1-dithiolate ligand.

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Linker Installation Transformations in a 2-D Rare Earth MOF: Increase of the Dimensionality and Turn on of the Temperature Sensing Capability

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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, etc¹. MOFs with fine-tuned properties can be made through a process called post synthesis modification. PSM allows the introduction/exchange of functional groups of a MOF² and is preferable to proceed in a single-crystal-to-single-crystal (SCSC) fashion providing direct structural information for the achieved structural modifications via single crystal x-ray crystallography. Interestingly, one property that could be modulated through SCSC transformations of MOFs, is their temperature sensing capability which is based on the photoluminescence response of lanthanide ions (and organic ligands). Significant attention in this field is focused on Eu–Tb MOF luminescent thermometers, which take advantage of the unique luminescence properties of the constituent metal ions for accurate and responsive temperature measurements.

We herein report the synthesis and characterization of a new family of 8-connected 2-D MOFs; **UCY-17(RE)**, based on a hexanuclear (RE³⁺)₆ SBU and the angular dicarboxylic acid ligand 4,4'-(hydroxymethylene)dibenzoic acid (H₂BCPM) and their exchanged analogues; **UCY-17(Tb)/L** produced from linker installation SCSC reactions of **UCY-17(Tb)** with selected dicarboxylic ligands. Detailed photophysical studies revealed that the installation of a second linker in the **UCY-17(Eu_{0.05}Tb_{0.95})** bimetallic analogues has a significant effect on the sensitization efficiency of the Tb³⁺ and Eu³⁺ ions. In fact, the SCSC installation of these dicarboxylic ligands results not only in the turn-on of the thermometric properties of this family of materials but also to a variety of different thermometric performances.

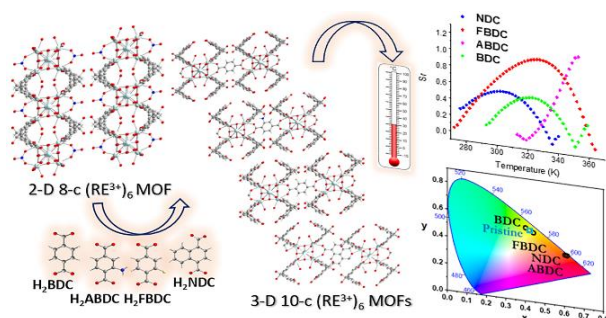


Figure 1: Representation of the SCSC linker installation reactions to a new 2-D 8-connected rare earth (RE) MOF based on a hexanuclear (RE³⁺)₆ SBU and the turn-on of the temperature sensing capability.

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Modified UiO-66-NH₂ type MOFs, suitable for heavy metal ion sorption in aqueous environment.

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Metal Organic Frameworks are coordination polymers containing metal ions, acting as nodes and organic ligands acting as edges. These crystalline materials usually present high porosity, making them suitable for multiple applications such as storage, separation, sensing. Another application concerns water purification from heavy metal ions, through sorption. For this, MOFs should be stable in aqueous environment and contain suitable functional groups. Free carboxylic groups have proved to increase the adsorption capacity towards UO₂²⁺ cations. [1,2] Consequently we reasoned that these groups will behave in a similar way towards heavy metal ion cations (Pb²⁺, Hg²⁺ etc.).

One popular MOF for its water stability is UiO-66-NH₂. It consists of Zr⁴⁺ ions, forming hexanuclear Zr⁴⁺ SBUs which coordinate with or 2-amino-terephthalic acid, forming a 3D network with **fcu** topology. To make UiO-66-NH₂ suitable for heavy metal ion sorption, we aimed to the modification of the amino group into a carboxylic acid. We came up with two strategies. In the first we modified the ligand prior to the MOF synthesis and in the second one the modification takes place after the polymer synthesis (PSM). The final products were characterized via PXRD, NMR and TGA analysis to confirm the construction of the desired network and to quantify the percentage of the modification and evaluate the defects caused by the modulator.

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Magnetostructural correlations in, and electrocatalytic reactivity of, some mononuclear 3d-metal complexes

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A large number of mononuclear 3d-metal complexes have been shown to exhibit slow relaxation of magnetization, most often associated with the presence of zero-field splitting (zfs).[1] Magnetometry and various spectroscopic techniques, such as high-frequency and -field EPR (HF-EPR) and Far-IR Magnetic Spectroscopy (FIRMS), are methods of choice for the determination of the latter.[2] The coordination chemistry of the $\{R_2P(E)NP(E)R_2\}^-$ ligands (E = O, S, Se; R = alkyl or aryl group) towards transition metal elements has been shown to be rather versatile.[3] Specific examples of tetrahedral $S = 1$ Ni(II),[4] $S = 2$ Fe(II),[5] as well as $S = 3/2$ [6] complexes, bearing these ligands and magnetostructurally investigated, will be presented. Two of the above complexes, namely $[M\{\text{Pr}_2\text{PSeNPSePr}_2\}_2]$, M = Ni,[7] Co,[8] have been shown to be electrocatalysts for the Oxygen Evolving and the Hydrogen Evolving Reactions (OER / HER, respectively). The structural, magnetic and electrocatalytic properties of two novel $S = 3/2$ tetrahedral Co(II) complexes of the general type CoS_2Cl_2 , containing **S** = thiosemicarbazone ligands, will also be discussed.

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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 photophysics of both Ru(II) polyimine and Zn(II) porphyrin complexes will be presented with an emphasis on the role of both non-covalent 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 guest photophysics and the framework cavity properties is important for the development of new light harvesting applications in MOFs.

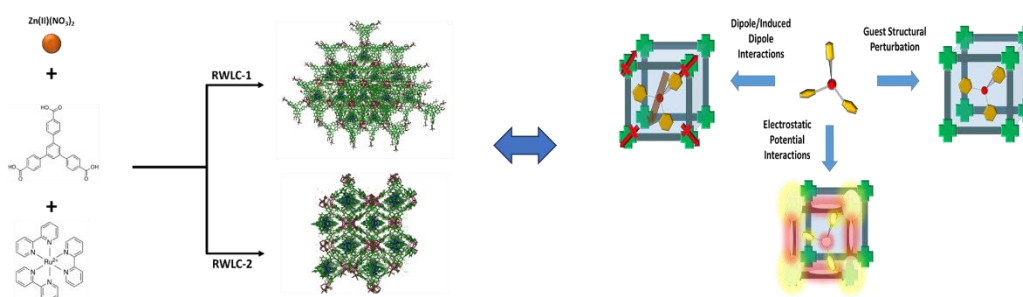


Figure 1: Illustration of the host-guest MOF (Left) and general categories of host-guest interactions that influence guest photophysics (right)

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Luminescent Metal-Organic Frameworks as Sensors for Environmental Pollutants

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The diverse chemistry of metal-organic frameworks (MOFs) offers unlimited opportunities for functionalization, including the possibility to construct new luminescent materials through the introduction of fluorophores, either in the bridging ligand and/or the metal ions. Combined with their inherent porosity, luminescent MOFs show great promise as sensory materials as the encapsulation of guest species (analytes) within their pores may be translated into a signal leading to recognition and quantification.^[1] In this contribution, we present a series of chemically robust MOFs, which can act as versatile platforms to accommodate a variety of different chromophores including strongly fluorescent bridging ligands bearing π -electron rich or chelating side groups, and metal ions including Zr^{4+} or Al^{3+} , which are known to promote hydrolytic stability. Through decoration of the bridging ligand with appropriate functional groups and the choice of metal ions, we achieve sensitive and selective sensing of environmental pollutants including nitroaromatics and heavy metal ions in aqueous media.

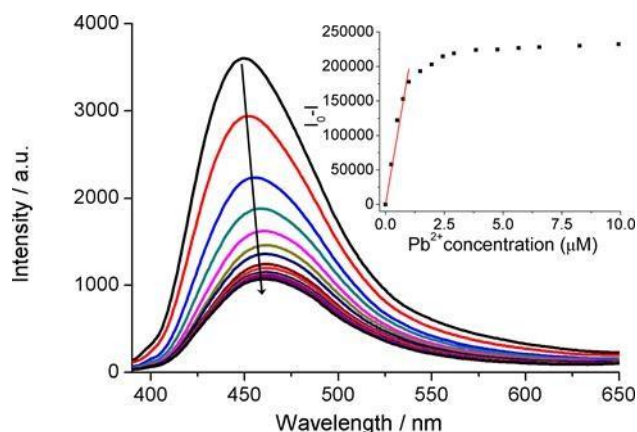


Figure. Fluorescence titration of an aqueous suspension of a Zr^{4+} MOF with Pb^{2+} ions.

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Regioselective Synthesis of a Bisadduct of C₆₀ Equipped with a Directional Cyclo-bismalonate Ester Tether

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To date, the synthesis of only a few fullerene-containing molecular and supramolecular architectures has been reported. Recently, attention in this field has focused on the preparation of such giant structures because of their unusual physicochemical properties and potential applications as superconductors [1] and ferromagnetic materials [2]. The shape of these architectures is determined by the stoichiometry of the building blocks used, their rigidity as well as any directionality they may impose.

The design and synthesis of a bisadduct of C₆₀, intended for use in the construction of covalent organic polyhedra (COPs), metal-organic polyhedra (MOPs) and H-bonded polyhedra, is presented.

Specifically, a bisadduct of C₆₀ was prepared, equipped with a cyclo-bismalonate ester tether carrying terminal catechol functional groups and saturated alkyl spacers. The X-ray crystal structure of the bisadduct containing ketal groups for the protection of the 1,2-diols, showed that it has a *cis*-2 addition pattern and that the catechol moieties are located parallel to each other. Ketal removal was then performed, which generated the corresponding deprotected bisadduct analogue with the free 1,2-diols also parallel. The 1,2-diols in this adduct will serve as the connection points of this ditopic fullerene derivative subunit with another ditopic subunit, a linear linker, for the synthesis of a COP, a MOP and a H-bonded polygon, depending on the nature of linker selected.

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MOFs for water remediation

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Water pollution resulting from various industrial and anthropogenic activities represents a global concern. Heavy metals such as lead (Pb) and oxoanions such as Cr(VI), and As(V) species are among the most common pollutants found in water sources, posing severe threats to humans and other beings. One of the most efficient methods for removing such pollutants from water is sorption, which offers several advantages over biological or chemical precipitation methods, including low cost, no secondary pollution, and high efficiency. Various materials have been tested, among which Metal Organic Frameworks (MOFs) present several attractive features as sorbents for toxic ions. These features include high porosity, a variety of functional groups (offering great selectivity for specific toxic species), and replaceable terminal ligands.[1]

In this contribution, we present several MOFs that have been studied for their capability to remove Pb²⁺ and oxoanionic species from water. The sorption efficiency of these MOFs has been investigated through detailed studies, including sorption kinetics, isotherm and variable-pH investigations, evaluation of the sorption performance in the presence of competitive species, and tests with real samples. The mechanism of the sorption processes was determined by applying several characterization techniques. MOF-alginate composites were also prepared and studied for the removal of toxic ions under continuous flow conditions. These studies also involve tests with industrial wastewater samples from chrome-plating processes. The results from the above investigations indicate the high potential of MOFs and their composites for application in environmental remediation.

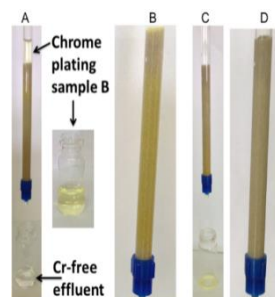


Figure. Purification of chrome-plating wastewater with a MOF-alginate composite.

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Spin State Switching in non-Centrosymmetric Crystals

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Chirality is important in magnetism[1] particularly in the development of new non-linear optical (NLO) materials[2] and in spintronic devices with spin polarized electrons.[3] Although the majority of spin crossover (SCO) materials are centrosymmetric, there is growing interest in those which crystallize in non-centrosymmetric enantiomorphic space groups.[4] In some cases this occurs by spontaneous chiral resolution,[5] but in the main, enantiopure SCO samples have been targeted by the use of chiral ligands[6] or chiral anions.[7] Use of an achiral chelating ligand confers chirality at the metal center by twisting around the ion in a clockwise (Δ) or anti-clockwise (λ) fashion and this chelate type is well known in SCO systems including the R-sal₂323 ligand series which promotes thermal spin state switching in Mn^{III}, Figure 1.5 We discuss here the factors which may be used for enantioenrichment of SCO crystals, the properties which emerge in spin state ordered systems and potential applications of non-centrosymmetric spin switchable crystals.

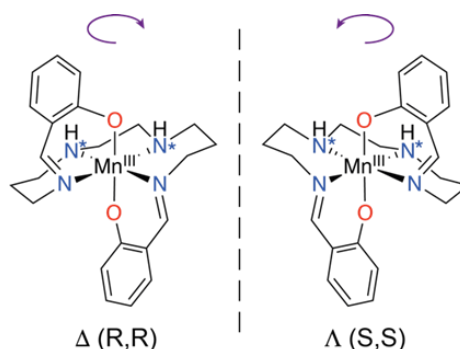


Figure. General structure of [Mn^{III}(sal₂323)]⁺ complexes showing the Δ and λ enantiomers. The amine nitrogens of the backbone (*) are chiral centers where the configuration is R,R (Δ) or S,S (λ).

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Exploiting nanosized Porphyrinic Metal–Organic Frameworks for the construction of transparent membranes as multi-responsive optical gas sensor

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The well-known and excellent colorimetric sensing capacity of porphyrins, along with the exceptional structural properties of metal-organic frameworks (MOFs), make porphyrin-based MOFs, such as PCN-222, ideal candidates for the generation/construction of a chemical sensor based on absorbance. However, there are two key requirements for this end which remain challenging: (i) the synthesis of nanoscale PCN-222 in order to minimize/avoid scattering in the absorbance measurement, and (ii) the deposition/integration of the PCN-222 into thin transparent membranes/films in an homogeneous manner without compromising the performance of the PCN-222 (i.e., accessible porosity to interact with analytes and distinctive optical response as a function of the analyte). Fortunately, using an optimized microwave-based synthetic method, we were able to prepare high-quality PCN-222 nanoparticles with a rod-shape and lateral size of ca. 100 nm, and almost negligible scattering in the absorbance spectrum when dispersed in water solution, thanks not only to the small size of the particles but also to their high colloidal stability. Moreover, using poly(dimethylsiloxane) (PDMS) for the formation of flexible and transparent membranes, we have proposed a simple method for the integration of the PCN into the membrane resulting in a multi-responsive optical gas sensor with excellent sensitivity, capable of discriminating between different VOCs through pattern recognition identification.

Controlled one pot synthesis of polyoxofluorovanadate molecular hybrids exhibiting peroxidase like activity

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Three unique mixed-valence polyoxofluorovanadate clusters have been synthesized through a facile preparation process. The structure of these clusters is controlled by the addition of organic ligands. Single-crystal X-ray diffraction revealed that the clusters have the formula $(XyH_2)_4[V^{V}_{10}V^{IV}_4O_{14}(\mu-O)_{10}(\mu_3-O)_{10}(\mu_3-F)_2F_4]$ (**1**), ($Xy = m$ -xylylenediamine), $(pyH)_4(H)_2[V^{V}_{10}V^{IV}_2O_{12}(\mu-O)_8(\mu_3-O)_{10}(\mu_3-F)_2(pic)_2]$ (**2**) and $(pyH)_4(H)_3(Na^+)[V^{V}_7V^{IV}_2O_9(\mu-O)_8(\mu_3-O)_4(\mu_5-F)(pic)_4]_2$ (**3**), ($py =$ pyridine, $pic^- =$ picolinate), with **2** and **3** representing the first examples of polyoxofluorovanadate clusters coordinated to a chelating ligand. The electron paramagnetic resonance (EPR) spectroscopy of **1** revealed that the spins of the V^{IV} centers are coupled to each other, in contrast to the isolated spins of the isostructural $[V^{V}_{12}V^{IV}_2O_{16}(\mu-O)_{10}(\mu_3-O)_{10}(\mu_3-F)_2(L)_2]^{6-}$, where $L: im =$ imidazole (**4**); py (**5**). The trigonal bipyramidal coordinated V^V atoms of **1**, **4** and **5** mimic the structure of the active site of the vanadium dependent peroxidases and **4** and **5** exhibit peroxidase like activity.

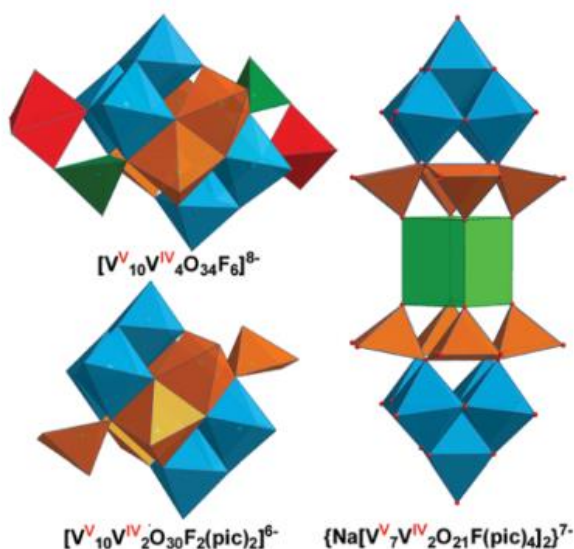


Figure 1. Polyhedral representation of the anions of 1–3.

Amide based MOFs for the water purification from heavy metals ions, Synthesis and Post Modification

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Metal-Organic Frameworks are porous crystalline materials, which result from the binding of metal ions or metal clusters by organic molecules, which are called bridging ligands, to form one- (1D), two- (2D), and three-dimensional (3D) coordination networks containing potential voids. Over the last years, our research group has been using bis-amide ligands as organic bridges for the synthesis of new MOFs and utilizing them as heavy metal ion sensors [1]. In addition, we follow a different approach that includes known water stable MOFs from literature. Having the experience with the amide reactions, we focus on the post modification of Al-CAU-10(NH₂) [2] which is based on the 5-amino-isophthalic acid. Al-CAU-10(NH₂), an aluminum rod-based MOF, offers amino groups in the pore of the network, that can be used for the decoration of the pore, by reacting the amino group with different types of dichloride derivatives. On the other hand, this can also be achieved by synthesizing new ligands from 5-amino-isophthalic acid and corresponding monochloride derivatives, ending to Al-CAU-10 analogues with increased sorption capacities for heavy metal ions in water treatment experiments.

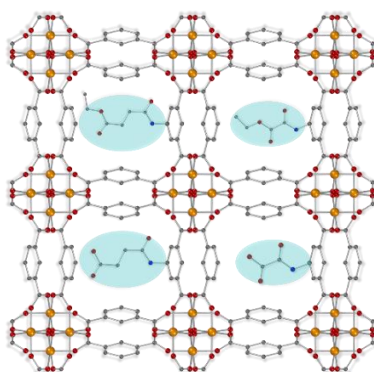


Figure. Schematic representation of the decorated pores in each the CAU-10 analogue.

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Correlating Structure with Spectroscopy in Ascorbate Peroxidase Compound II

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Ascorbate peroxidase (APX) is an essential heme peroxidase that plays a significant role in protecting cells from oxidative stress by detoxifying hydrogen peroxide using ascorbate (vitamin C) as the reducing agent. Structural and spectroscopic investigations of Compound II in ascorbate peroxidase have reached conflicting conclusions regarding the protonation state of the crucial Fe(IV) intermediate. Neutron diffraction and crystallographic data [1] support an iron(IV)-hydroxo formulation due to the long Fe–O bond length. By contrast, Mössbauer, X-ray absorption (XAS), and nuclear resonance vibrational spectroscopy (NRVS) studies appear consistent with an iron(IV)-oxo species [2]. Here we examine APX with spectroscopy-oriented QM/MM calculations and extensive exploration of the conformational space for both possible formulations of Compound II. We establish that irrespective of variations in the orientation of vicinal amino acid residues and potential reorganization of proximal water molecules and hydrogen bonding, the Fe–O distances for the oxo and hydroxo forms consistently fall within distinct, narrow, and non-overlapping ranges. The accuracy of geometric parameters is validated by coupled-cluster calculations with the domain-based local pair natural orbital approach, DLPNO-CCSD(T). QM/MM calculations of spectroscopic properties are conducted for many structural variants, encompassing Mössbauer, optical, X-ray absorption and X-ray emission spectroscopies, and NRVS. All spectroscopic observations can be assigned uniquely to a Fe(IV)=O form. A terminal hydroxy group cannot be reconciled with spectroscopic data. Interestingly, under no condition can the Fe(IV)=O distance be sufficiently elongated to approach the crystallographically reported Fe–O distance, which is most consistent with a Fe(III)-hydroxo species. These findings strongly support the Fe(IV)=O formulation of APX-II and highlight unresolved discrepancies in the nature of samples used across different experimental studies.

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[3]

The quantum physical reality of ionic bonding in molecules and solids and ionic transport

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Soon after Lawrence Bragg in 1913 used X-ray scattering to unveil the atomic structure of crystalline NaCl, Max Born developed a successful phenomenological electrostatic model that remains a component of virtually all books that cover the structure of crystalline materials. NaCl is viewed as a prototype “ionic solid” comprising Na⁺ and Cl⁻ point-particle sublattices that are held together by electrostatic Coulomb interactions (Madelung energies) that are balanced by short-range repulsive potentials. Parameters need to be fitted to data, but, overall, calculated and measured heats of formation and other properties provide supporting evidence. Quantum mechanics enters only in the way the nominal integral charges are identified: for example, the single Na valence electron is transferred to a partner Cl atom to arrive at $\pm 1e$ charges. The integral charge values, known as oxidation states, remain resilient today, but proved inadequate to cover a wider range of properties, molecules, and materials, leading to the concept of partially ionic and partially covalent bonds with fractional charges that can be quantified in multiple ways. Linus Pauling was first to define an electronegativity scale. His classic 1939 treatise “*The nature of the chemical bond*” and other writings laid the foundation of modern chemistry for several decades before quantum calculations for molecules and solids became practical and reliable.

This talk will review discoveries made via parameter-free, quantum calculations based on density-functional theory over the last ~20 years exploring the true quantum physical reality of atomic bonding in ionic molecules and solids and of ionic transport, and combining these discoveries with other known quantum results. The most surprising discovery is that in virtually all environments, in the absence of intentional charging, atoms in all molecules and solids are neutral. The quantification of this statement is robust and is done simply by comparing the spherically averaged radial charge distribution around any atom in a molecule or solid to its corresponding version in a case where the atom is guaranteed to be neutral, e.g. compare Mn and O charge distributions in MnO, MnO₂, Mn₂O₃, Mn metal, and O₂ molecule [1,2]. You might ask, what about ionic conductors? The answer is yes, those ions are for all practical purposes neutral atoms, but, in these and other circumstances, quantum mechanics and statistical mechanics dictate that such *atoms in motion* carry an effective integral charge, e.g., $-2e$ for oxygen “ions”, and Na and Cl ions in NaCl carry $\pm 1e$ charges!

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Synthetic routes for functionalization of water stable MOFs for water remediation

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Over the last year and a half, we have been targeting water stable MOFs for water remediation applications. Given the wide interest in such MOFs, we aimed toward the modification of such water stable MOFs by attaching functional groups on the bridging ligands. To this end, we utilized functional groups attached to alkyl chlorides as a means of functionalizing the amino groups of the bridging organic ligands. The modified ligands can be made by either solution or solid-state chemistry (mechanochemically) prior to the synthesis of the MOFs. Over the course of our experiments, we discovered that the degree of the MOFs' functionalization is not always guaranteed and highly depends on the reaction conditions as well as on the nature of the modified ligand and the nature of the targeted MOF. For this reason, we adjusted our synthetic plans to include solid-state synthesis for the functionalized MOFs as well as post synthetic modification of the MOFs. The latter can also be done by either solution or solid-state chemistry. In this presentation we will give an overview of the above synthetic efforts emphasizing on the synthetic routes which led to the best modification route for each MOF.

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Exploring Electron Spin Interactions in the Kitaev Candidate System $\text{Na}_2\text{Co}_2\text{TeO}_6$ and the Emergence of Spin Fractionalization

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The exploration of topological systems unveiled a diverse landscape of systems with novel quantum phases and emergent quantum phenomena. Among these systems, Kitaev materials [1], a specific class of topological materials, 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 $\alpha\text{-RuCl}_3$ [5], have ignited discussions in the scientific community regarding the nature of these phenomena. The central question that arises 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 elucidated by conventional antiferromagnetic interactions [6].

To illuminate certain aspects of this ongoing debate, we will present recent experimental data from the prospective Kitaev material $\text{Na}_2\text{Co}_2\text{TeO}_6$, along with findings from a wide range of topological materials, including topological insulators (e.g., $\text{Bi}_2\text{Se}_3/\text{Bi}_2\text{Te}_3$) [7] and Weyl semimetals (WTe_2) [8]. Notably, through conducting ^{23}Na NMR experiments on $\text{Na}_2\text{Co}_2\text{TeO}_6$ under different magnetic fields, specifically at 4.7 Tesla and 9.4 Tesla, compelling evidence has emerged, indicating that at high magnetic fields, as the system transitions to a quantum disordered spin state, spin fractionalization arises as a predominant source of NMR relaxation at low temperatures. This discovery not only offers crucial insights into the behavior of Kitaev materials but also lays the groundwork for a deeper understanding of the interplay between topology and exotic quantum states across diverse material platforms.

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Immobilizing Luminescent Metal-Organic Frameworks in Polymeric Films: An Effective Approach for Optical Gas Sensor Fabrication

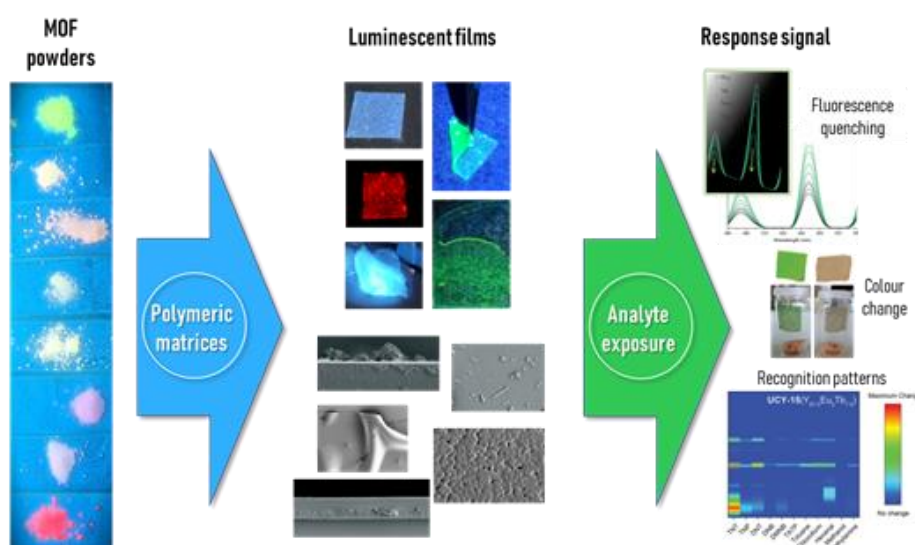
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In this contribution, we exploit the excellent sensing capabilities of luminescent metal organic frameworks (LMOFs) through their immobilization in optically inert polymeric matrices for the fabrication of sensing devices for gaseous analytes. Several polymeric materials have been employed, including polymethylmethacrylate (PMMA) polydimethylsiloxane (PDMS) and polyvinylidene fluoride (PVDF). Among the employed LMOFs, those which are lanthanide-based (Ln-MOFs) constitute excellent candidates for sensing applications due to the well-understood luminescence properties of lanthanide ions, their high luminescence quantum yield and the presence of characteristic narrow emission bands. For instance, Tb(BTC)@PDMS/PMMA films [1] have been successfully applied to the detection of NO₂ gas and vapours of nitroaromatic explosives. Also, trimetallic 2-D rare earth (RE=Y, Eu, Tb) MOFs exhibiting a combined emission spectrum were successfully used to create image-based recognition patterns for different volatile organic compounds (VOCs) [2]. Other MOFs like PCN-224 and more recently, a post-synthetically modified ZIF-8, have been used to detect amine vapours and hydrogen sulphide respectively [3]. The sensing properties have been analysed through kinetic studies, calibration curves and selectivity against potential interferences. It will be shown that, in contrast to sensing in solution, the used approach enables the development of miniature devices based on LED-CCD/CMOS technology and is able to detect target compounds in the gas phase, which also eliminates many potential interferences and expands its applicability to other scenarios.



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[3] F. G. Moscoso, et al. Mater. Today Chem. 2023, 28, 101366.

Magnetic Exchange Couplings in High-Nuclearity Transition Metal Complexes from Density Functional Theory Methods

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The magnetic characterization of molecular complexes containing dozens or even hundreds of magnetic centers is key to understanding many biological processes, future technology developments, and the discovery of novel quantum materials. In most cases, magnetic exchange couplings are the most elusive among the basic parameters involved in spin model Hamiltonians used for this purpose. The reason is that experimental methods cannot provide a detailed breakdown of the individual exchange couplings between all magnetic centers due to the multiple couplings present. In some cases, one may rely on magneto-structural correlations, provided that a consistent training set exists. For other cases, density functional theory (DFT) methods are the only option, considering the size of the molecular complexes at hand. Traditional methods to extract exchange couplings from DFT rely upon mapping the broken spin symmetry DFT solutions to broken spin symmetry Ising-like spin model energies. In this talk I will discuss approaches that can be used for this purpose, with focus on some recent benchmark cases. The long-term purpose is to develop computational protocols and methodology that do not incorporate empirical parameters, aiming to provide an “in-silico” characterization tool that complements existing experimental spectroscopies. I will introduce some of our new developments based on local rotations of the magnetization in different flavors¹ and show some examples such as Fe₂₂, Fe₂₄ clusters, and the Fe₃₆ ferric wheel.^{2,3}

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Chemistry and Football (Soccer): A Parallelism

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“Some people think football (soccer) is a matter of life and death. I don’t like that attitude. I can assure them it is much more serious than that”. This historical phrase was said by Bill Shankly ca. 50 years ago; Shankly was the great manager who transformed Liverpool F. C. from a moderate team to a winning machine and glorious team [1]. We have grown up with this statement. In our presentation we shall try to illustrate the relationship between Chemistry (mainly Inorganic) and Football. Just as elements combine in Chemistry to produce different compounds, so the disparate elements in football sometimes combine to produce something out of the ordinary. We have arranged the key elements of football, the players, managers and few officials, in 18 vertical groups and two long series at the bottom (just like in the Periodic Table of Elements) according to the characteristics and influence they brought (and still bring) to the game. For example, Group 1 players (Figure) correspond to precious metals. Our presentation is based on ideas developed in ref. [2], but we have modified the Table, simply because our knowledge of Chemistry and Football is better than that of Nick Holt!



Figure 1. Some players who can be considered as precious metals.

[1] G. Sephton, “*The Voice of Anfield*”, Atlantic Books Ltd., London, UK, **2021**.

[2] N. Holt, “*The Periodic Table of Football*”, Ebury Press, London, UK, **2016**.

Six valence states of the tripak system

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Metal complexes are known for their electron exchange capabilities and multiple valence states. Organic molecules, on the other hand, show generally restricted redox activity, often with only two or three available states. Access to multiple reversible redox events within a compact organic structure remains a challenge. During the talk a new platform for molecular multivalency will be presented – the first example of the oligo(dioxothiadiazole) family – benzo[1,2-*c*:3,4-*c'*:5,6-*c''*]tris([1,2,5]thiadiazole) 2,2,5,5,8,8-hexaoxide (**tripak**). [1,2] **Tripak** comprises only 21 atoms, yet it is able to reversibly exchange up to six electrons (Figure 1). Five states were isolated and characterized structurally by scXRD. Multivalency provides compartmentalization of multiple functionalities. The neutral tripak⁰ forms remarkably strong anion- π interactions with various anions. Tripak¹⁻ and tripak³⁻ are radicals and can be used in spintronics as qubits or as organic-based molecular magnets. The native tripak²⁻ state is a very strong blue dye and displays fluorescence. Finally, tripak⁴⁻ shows a diradicaloid character which provoked investigation of the aromaticity types present in this molecular system.

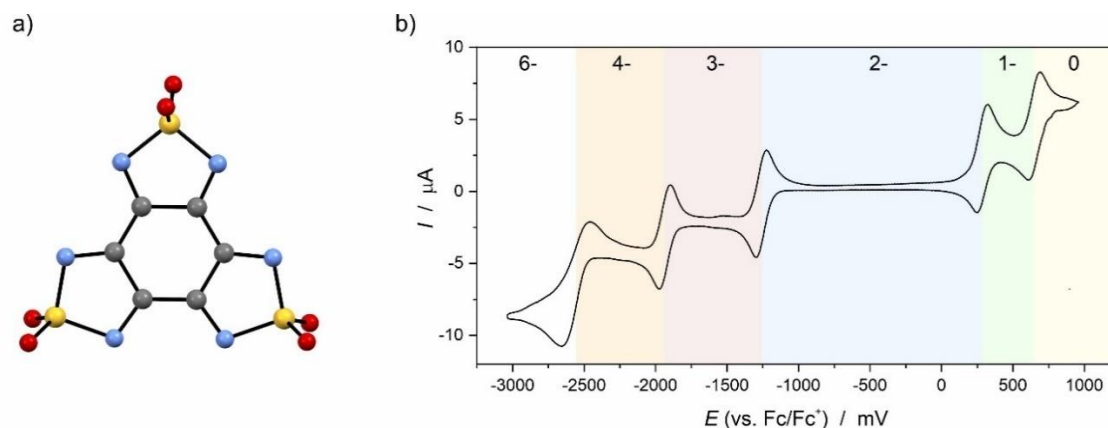


Figure. The structure of the **tripak** system (a) and an example of its cyclic voltammetry in THF (b) demonstrating an extremely rich redox chemistry despite a very simple molecular framework.

[1] P. Pakulski, M. Magott, S. Chorazy, M. Sarewicz, M. Srebro-Hooper, D. Tabor, Ł. Łapok, D. Szczepanik, S. Demir, D. Pinkowicz, *Chem*, **2024**, *10*, 971-997

DOI: 10.1016/j.chempr.2023.12.024

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Synthesis and characterisation of MOF-COOHs for water remediation: Pre- and post-synthetic modification approach of amide ligands

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Since the dawn of industrialization, water, one of the most valuable materials on earth, suffers from constant contamination of organic and inorganic compounds. In this study, we focus on heavy metal ion pollution of water supplies, and the ways this can be remediated through the use of porous and water stable materials.

Metal-Organic Frameworks, abbreviated as MOFs, are a class of hybrid materials consisting of metal ions and organic bridging ligands, giving rise to one, two and even three-dimensional networks. Due to their exceptional stability towards water and other solvents, temperature, and pH, they have been studied as sorbents for heavy metal ions in water purification applications. MOF-COOHs [1] is a term introduced lately to describe MOFs bearing free carboxylic groups decorating the interior of their pore, rendering them more promising for sorption and sensing capabilities.

In this project we focus on a well know MOF from the literature, namely Al-MIL-53(NH₂) [2], based on 2-amino-terephthalic acid. Our attempts focus on either the post-synthetic acylation of the free -NH₂ group of the ligand with a variety of dichlorides of dicarboxylic acids, or the pre-synthetic acylation of the ligand with the corresponding monochloride or monoesterified derivatives of the same dicarboxylic acids. Finally, the product undergoes treatment with H₂O to produce the desired carboxylic groups decorating the pores of the MOF.

Acknowledgements: Single crystal and powder diffraction data were collected in the National and Kapodistrian University of Athens X-ray Diffraction Core Facility.

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Luminescent metal-organic frameworks as an effective alternative for wastewater treatment

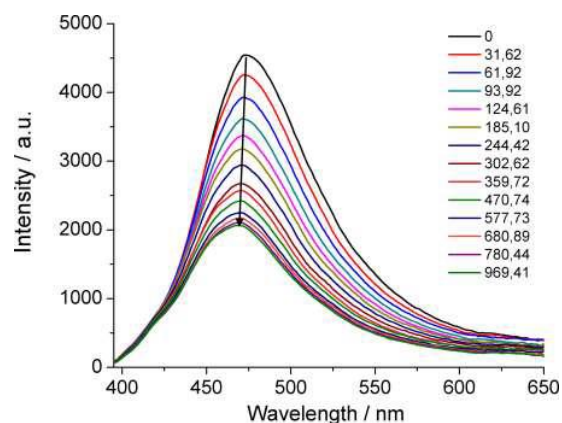
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The utilization of metal–organic frameworks in environmental remediation, particularly for the removal of pollutants through adsorption in wastewater, is widespread because of their ease of synthesis, increased adsorption and regeneration ability and due to the enhancement of their adsorptive properties through ligand functionalization.^[1,2] In this contribution we present the synthesis and characterization of three luminescent MOF materials, bearing two different organic ligands, aiming to examine their effect on the materials' properties. The effect of different metal nodes is also investigated, along with their efficiency in detecting and/or removing heavy metal ions from wastewater. The crystallinity of the materials was determined through PXRD measurements, which revealed the structural resemblance to UiO-66 and MIL-53 respectively. The presented MOFs also exhibit stability in aqueous media. Fluorescent titration experiments in water samples with increasing concentrations Cu²⁺ ions and in samples with potentially competitive metal ions, show strong evidence of detection, with LOD and LOQ values being several orders of magnitude below the proposed limits of World Health Organizations. In general, the results demonstrate a connection between the metal-ligand combination and the detection ability of the resulting material.



Scheme 1. Fluorescence titration of an aqueous suspension of Zr-MOF (0.1 mg mL⁻¹) upon gradual addition of a 10⁻⁴ M aqueous solution of CuCl₂·2H₂O ($\lambda_{exc} = 365$ nm).



Με τη χρηματοδότηση της Ευρωπαϊκής Ένωσης
NextGenerationEU



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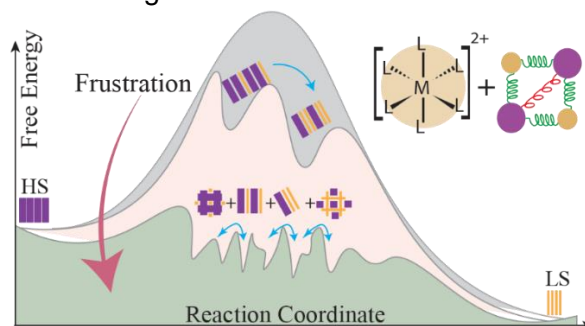
Theory of the relaxation of spin crossover materials after LIESST: the interplay of single-molecule and collective effects

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Spin-crossover (SCO) materials display many fascinating behaviors including collective phase transitions and spin-state switching controlled by external stimuli, e.g., light and electrical currents. As single-molecule switches, they have been fêted for numerous practical applications, but these remain largely unrealized—partly because of the difficulty of switching these materials at high temperatures.

We introduce a semiempirical microscopic model of SCO materials combining crystal field theory with elastic intermolecular interactions [1]. We show that, for realistic parameters, this model reproduces the key experimental results including thermally induced phase transitions, light-induced spin-state trapping (LIESST), and reverse-LIESST. Notably, we reproduce and explain the experimentally observed relationship between the characteristic temperature of the thermal transition, $T_{1/2}$, and the highest temperature for which the trapped state is stable, T_{LIESST} , and explain why increasing the stiffness of the coordination sphere increases T_{LIESST} . Increased crystal rigidity increases T_{LIESST} stabilizes the HS state at low temperatures yet leaves the LS state stable at high temperatures. We show that such highly cooperative systems offer a realistic route to robust room-temperature switching, demonstrate this *in silico*, and discuss material design rationale to realize this.



Secondly, we argue [2] that SCO materials are relatively simple, highly tunable systems that offer a unique playground to study the universal aspects of complex dynamics. Understanding the factors that give rise to complex kinetic processes is of fundamental interest to many research areas, such as protein folding, photochemistry, and quantum materials. A diverse range of relaxation dynamics of trapped spin-states are observed in SCO materials. Our model reproduces and explains this full range of relaxation behaviors. We show that frustrated intermolecular interactions lead to multiple energetically competitive ordered phases even in systems that contain only one crystallographically distinct SCO site. This rugged free energy landscape leads to dynamic disorder and thence complex dynamics. We show that the same frustrated interactions are responsible for multistep thermal transitions.

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Magnetic Ordering in Crystalline Metal-Radical Complexes

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The McConnell I mechanism postulates the ferromagnetic (FM) coupling between molecular p-radicals based on overlapping regions of positive (a) and negative (b) spin density [1]. However, there are relatively few literature examples in which the observed magnetic properties of species cannot be explained by simple molecular orbital overlap models. In our work designing paramagnetic ligands from thiazyl radicals, we have encountered an increasing number of instances in which understanding the relationship between the structure and the measured magnetic properties requires the McConnell I mechanism. We have observed FM coupling in 1D between Ni(II)-radical complexes [2], FM ordering between – [Sm(III)-radical]_n⁻ chains [3], and recently FM ordering between Co(II)-radical complexes (unpublished; Figure 1).

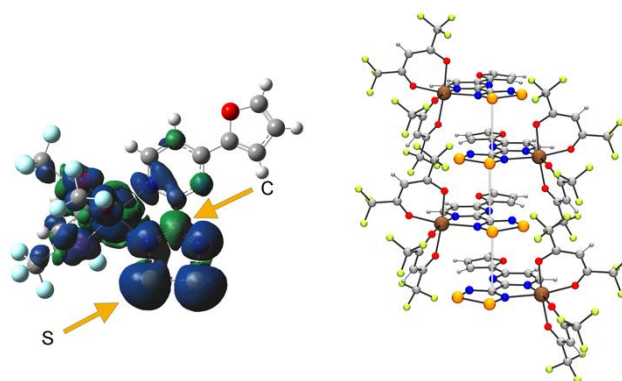


Figure 1. (left) Calculated total spin density surface of the Co(II)-radical complex; (right) excerpt of the crystal structure of a new Co(II)-radical complex that exhibits FM ordering, consistent with overlapping regions of a and b spin density, per the McConnell I mechanism

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Pentanuclear Thorium(IV) Coordination Cluster with a Kuratowski $K_{3,3}$ Graph Topology

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In Graph Theory, molecules are considered as graphs by representing atoms and bonds as vertices and edges, respectively. The topologically trivial (those which can be drawn on a plane so that no two edges intersect except at a vertex) and non-trivial graphs are classified also as planar and non-planar graphs in abstract Mathematical Graph Theory. According to the theorem of Casimir Kuratowski, all the non-planar graphs contain only one of the two planar graphs K_5 or $K_{3,3}$ as a subgraph. The $[MZn_4X_4(L_6)_6]$ (with X^- a halide atom and L : a bta type ligand) complexes [1] have been characterized as a $K_{3,3}$ family of Kuratowski non-planar coordination compounds and belong to a family of rare organic or inorganic compounds with this topology. The $Th(NO_3)_4 \cdot 5H_2O/di(2\text{-pyridyl})$ ketone $[(py)_2CO]$ reaction system gives the pentanuclear cluster $[Th_5(NO_3)_8\{(py)_2C(O)_2\}_6]$ [2] containing the doubly deprotonated form of the *gem*-diol derivative of the ligand. The cluster consists of a tetrahedral arrangement of four Th^{IV} ions centered on the fifth ion, which is the first characterized Th^{IV}_5 complex. The analysis of its structure reveals that this is a Kuratowski type coordination compound and thus expanding the family of inorganic compounds with this topology. The interesting for this topology is related to the fact that these units are isostructural to the MOF-5 and MFU-1 units of frameworks and they can easily integrate in regular 3D porous networks (MOFs). The lattice of the studied complex contains voids that host lattice solvent molecules in analogy with the MOFs which are built by using Kuratowski-type secondary building units [1].

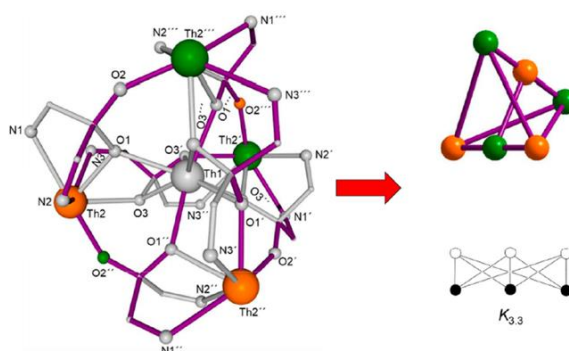


Figure. Schematic derivation of the $K_{3,3}$ Kuratowski graph for a coordination compound.

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Chiral Complexes with Enantiopure Salen-type Schiff Base Ligands

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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. Metal coordination complexes can exhibit two types of chirality: (a) chirality at metal which arises by the certain arrangement of ligands around the metal ion and disappears upon the separation of the metal and the ligands [1], and (b) chirality which imparts by the presence of chiral ligands around the metal ions [2]. From the synthetic point of view, the latter approach of using enantiopure ligands is the most efficient method for the enantioselective synthesis of chiral coordination complexes [3]. Chiral metal complexes that combine chirality with magnetic, optical, and electrical properties constitute a new and fast-growing class of multifunctional molecular materials [4]. Also, chiral metal complexes are important in modern medicine as therapeutics (metallo-drugs), and can be selectively activated at the target site of a biomolecule by an external stimulus. We will present our work on chiral complexes based on enantiopure salen-type Schiff base ligands. The affinity of complex $[Zn(L1)(MeOH)] \cdot H_2O$ (**1**) for CT DNA was studied via titration studies by various spectroscopic techniques, which showed intercalation of **1** between the base pairs of CT DNA. The anti-proliferative effects of **1** was assessed on the MCF-7 human breast adenocarcinoma cell line using the sulforhodamine B (SRB) assay upon 48 hours of incubation. The IC_{50} values for **1** is $42.6 \pm 1.7 \mu M$. In comparison, etoposide, a topoisomerase II inhibitor widely used in chemotherapy, shows an IC_{50} value of $49.2 \pm 7.8 \mu M$ against MCF-7 cells [5].

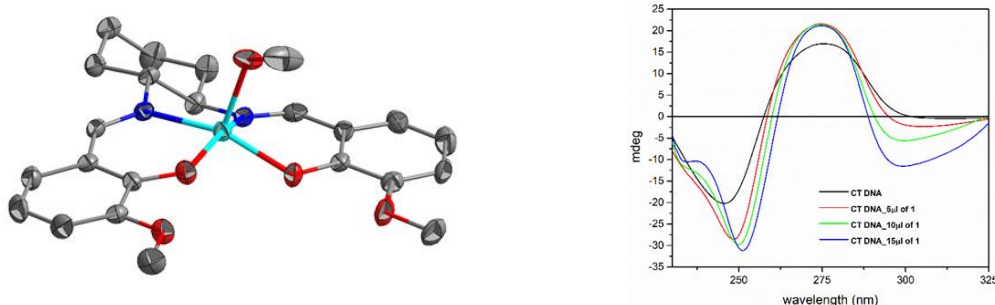


Figure. The molecular structure of $[Zn(L1)(MeOH)] \cdot H_2O$ (**1**) (left), and the CD titration study of **1** with CT-DNA (right).

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Synthetic Inorganic Chemistry as a Pathway to Spin-based Properties by Design

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Since their discovery, orbital-based models have been at the core of chemical intuition, driving the creation of novel materials with remarkable success. The versatility of the hydrogenic orbital, however, is purchased at the expense of correctly modeling the electronic spin. In many areas of modern chemistry, advances in measurement, computation, and synthetic capability have begun to suffer from the disconnect between observations and the ideas that form the basis of chemical intuition. As much of the driving force in materials and measurement is fundamentally shifting towards properties intrinsic to the quantum level, it is vital to develop predictive structure-property relationships that incorporate the intrinsic spin of the electron. The Rinehart Group constructs spin-centric models for material design through a targeted synthetic building-block approach. Utilizing the directed angular momentum of $[\text{Er}(\text{COT})]^+$ as a fundamental unit of oriented spin, we combine synthesis with theoretical and computational insights, crafting molecules where spin dynamics are intricately linked to their crystal field environment via spin-orbit interactions. This connection forms the foundation for 0-3D interactions driven by internal magnetic fields of precise, crystallographic origin. Through targeted design, the underlying symmetries of the spin manifest in new mixing and orthogonality with respect to the lattice and external interactions. This talk will develop the theory and evidence we use for hypothesis-driven synthesis of materials with specific spin structures of interest. From this model, we delve into the complex symmetries of oriented spin manifolds, leveraging internal and external electromagnetic fields to draw out an unprecedented level of intuition about multicenter, spin-orbit, spin-spin, and crystal-field coupled systems. This approach carves out a generalizable method to synthesize complex quantum state interactions with control over tunneling dynamics and symmetry, demonstrating the ability for synthetic inorganic chemistry to drive the development of new quantum materials.

Theoretical Studies on the Transport Properties of 2D InAs Colloidal QD Films

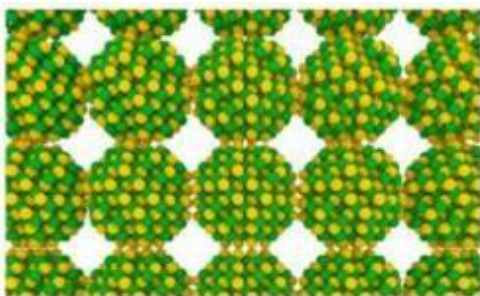
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Two-dimensional quantum dot (QD) arrays are considered promising candidates for a wide range of applications that heavily rely on their transport properties. Existing QD films, however, were used to be made of either toxic or heavy-metal-based materials, limiting their applications and the commercialization of devices. As a result, there is an increasing trend in looking for non-toxic alternatives, in

an effort to replace the toxic ones and enhance their commercial applications. This theoretical study provided a detailed analysis of the transport properties of environmentally-friendly colloidal QD films (In-based and Ga-based), identifying possible alternatives to their currently used toxic counterparts. Specifically, 2D colloidal QD films based on InAs QDs were modeled and compared with existing relevant experimental work, highlighting how changing the composition, stoichiometry, and the distance between the QDs in the array affects the resulting carrier mobility for different operating temperatures. Additionally, this work showed that by engineering the QD stoichiometry, it is possible to enhance the film's transport properties, paving the way for the synthesis of higher-performance devices. The mobility of the films was calculated for temperatures ranging between 50 and 350 K (corresponding to a realistic range for device operation).

The isolated QDs were generated following the state-of-the-art semi-empirical pseudopotential method, forming a periodic array when placed in a square lattice. Following a tight-binding model, the electronic structure of the system was calculated, i.e., the QD film miniband structure, from which the transport properties (e.g. carrier mobility) were extracted. The main scattering mechanism was considered due to the presence of impurity dots (smaller dots compared to the periodic dots), and thus a 1% density of impurities was assumed as a realistic value in accordance with experimental samples.

The results of this study provided a strong indication that 2D films based on InAs colloidal QDs can become a potential replacement for existing CdSe, and Pb-based films while having similar temperature decay trends with other experimental results on InAs QD films. [1].

[1] Band-like transport in “green” quantum dot films: The effect of composition and stoichiometry, P. Rodosthenous, E. S. Skibinsky-Gitlin, S. Rodríguez-Bolívar, M. Califano, F. M. Gómez-Campos, *J. Chem. Phys.* 156, 104704 (2022)

Polyoxometalate-Based Coordination Networks as Doped Metal Oxide Materials

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Complex metal oxides display a variety of electronic, photophysical and magnetic phenomena, making them vital components for a myriad current and emerging semiconductor technologies. The assembly of cluster or superatom building blocks into extended solids has revolutionized materials synthesis, leading to the creation of modular semiconducting materials, including molecule-based metal oxide materials. We have developed a method for the assembly of the Preyssler polyoxoanion ($[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$) bridged with transition metal or lanthanide cations as a route to doped metal oxide materials. We have demonstrated tunability of the architecture, connectivity, and void-volume via inclusion of additional cations. Polymer infiltration of the framework enables easy processing into gel and film form-factors. The frameworks can be reversibly photochemically reduced to contain electron densities on the order of 10^{21} cm^{-3} , revealing their potential for electron-manipulation and charge-storage applications. This talk will discuss the structure–composition–property relationships of polyoxometalate-based coordination networks, with an emphasis on tunable optical, electronic and magnetic properties.

Leveraging Homogeneous and Heterogeneous Chemistry in the Catalytic Conversion of Hydrocarbon Substrates

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Organometallic precursors have proven useful for synthesizing well-defined heterogeneous catalysts using surface organometallic chemistry (SOMC). This approach allows for the development of molecularly defined heterogeneous catalysts from which structure-activity relationships can be readily developed using principles of homogeneous chemistry. Single-site catalysts prepared by SOMC have shown a wide-range of activity in a variety of hydrocarbon transformations involving the activation and formation of C-H and C-C bonds. Described in this talk are our laboratory's recent developments in using organometallic precursors of group IV and V transition metals to prepare catalysts capable of several transformations including alkane dehydrogenation, olefin metathesis, and olefin hydrogenation. In addition, these reactions can be performed in conjunction for the metathesis of alkanes. Based on preparation methods, divergent performance, stability, and reactivity trends of the catalysts are observed. Structural characterization of the pre-catalysts and the active species, through a variety of spectroscopic techniques and isotopic labeling studies, will be described. The well-defined nature of these materials has allowed for the development of structure-activity relationships and offers new directions in the design of heterogeneous catalysts for hydrocarbon conversions.

Structural flexibility in zeolitic imidazolate frameworks (ZIFs) upon adsorption

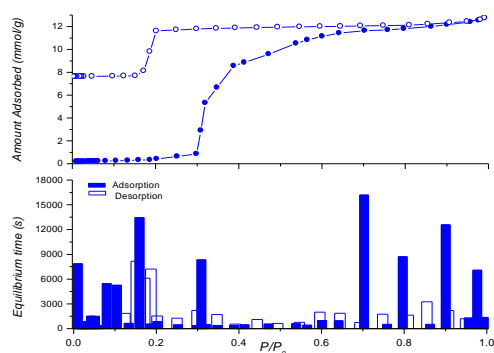
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Removal of chemical contaminants (POP, CEC, PFOAs, etc.) in wastewater and air streams requires the design of novel adsorbents able to selectively retain/concentrate these pollutants with a high adsorption capacity. Activated carbons, zeolites, silicas, and metal-organic frameworks (MOFs) are among the most frequently used adsorbents to this end. Application of MOF materials offers significant advantages, e.g., porous structure and surface chemistry can be tailored to match specific applications, rendering them as highly versatile tools for adsorption processes.

Zeolitic imidazolate frameworks (ZIFs), a sub-class of MOFs, are characterized by a high specific surface area, a hydrophobic porous structure, a high chemical and thermal stability and, more importantly, a unique structural flexibility [1]. These structural changes/transformations upon an external stimulus (e.g., gas adsorption, heat treatment, high-pressure), include gate-opening phenomena, phase-to-phase transitions, breathing effects, and so on [2,3]. Interestingly, the nature of these phenomena highly depends on the nature of the imidazolate linker, including the presence of functional groups, i.e., depends on the competition between strong non-bonding interactions, which favor the formation of highly dense structures, and bonding interactions, which favor the formation of a high symmetry, low-density crystal structures.



Furthermore, these intracrystalline interactions can be altered/modified, depending on the nature of the adsorbate molecules, thus opening the gate to unexplored adsorption phenomena in gas and liquid-phase processes.

Fig. 1. N₂ adsorption/desorption isotherm for ZIF-7 at 77K (upper panel). Time requested to reach equilibrium for each of the adsorption and desorption points (lower panel).

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Acknowledgements:

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Air-stable and high-performance Dy^{III} Single-Molecule Magnets with D_{6h} symmetry

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The search for new molecules exhibiting slow relaxation of magnetization under a plausible blocking temperature is currently one of the most appealing research topics in the interdisciplinary fields of inorganic and coordination chemistry, materials science, physics, and theoretical chemistry. Lanthanide(III) ions play a pivotal role in the quest for efficient single-molecule magnets with potential applications in memory storage, molecular spintronics, and quantum computation. This is mainly due to the large magnetic anisotropy that most 4f-metal ions possess, which arises from the strong spin-orbit coupling and the crystal-field effects from the coordinated ligands.^[1]

Seeking for new synthetic strategies towards the preparation of air-stable, single-molecule magnets (SMMs) with large energy barriers for the thermally-assisted relaxation of magnetization, the focus of our research is placed around mononuclear Dy^{III} complexes with designed ligands suitable to yield the targeted D_{6h} coordination geometry and subsequently reducing the efficiency of the through-barrier relaxation pathways.^[2] Herein, we report the synthesis, structural and magnetic characterization of two new families of mononuclear, air-stable Dy^{III} SMMs. These were derived by the employment of the macrocyclic effect, which has yielded N₆, N₃O₃, and N₄O₂ equatorial ligation around a single Dy^{III} ion resulting from rare (in hexagonal equatorial ligation) [1+1] metal-assisted condensation reactions (**Figure 1**). As a result, we have been able to chemically engineer new coordination compounds with D_{6h} geometries, bearing strongly bound axial ligands and exhibiting SMM behaviors with large U_{eff} values, among the highest yet reported for D_{6h} SMMs.

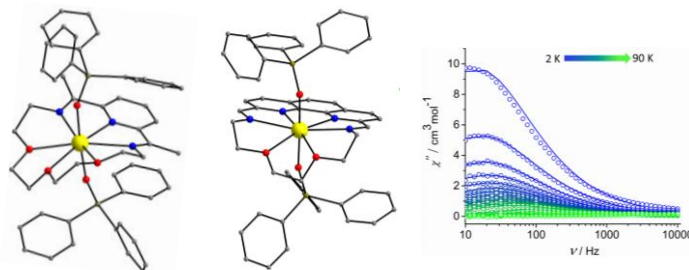


Figure 1: Molecular structures and ac magnetic dynamics of representative D_{6h} complexes discussed in this work. Color scheme: Dy=yellow; O=red; N=blue; C=grey. Hydrogen atoms are omitted for clarity.

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Synthesis and Optical Characterization of PbS/CdS Colloidal Quantum Dots emitting at telecommunication wavelength

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Colloidal quantum dots (CQDs) have been attracted considerable attention due to their excellent optoelectronic properties such as tunable band gap and high optical stability. In the visible regime, CQDs materials have already been successfully employed in optoelectronic devices. On the other hand, the burst of near infrared (NIR) technologies such as detectors, face recognition, food monitoring and telecommunication, prerequisites materials emitting at the low energy part of the electromagnetic wavelength. Nevertheless, despite the plethora of semiconductors in visible region, only a few examples exist with a tunable band gap in NIR with lead sulphide (PbS) semiconductor CQDs taking the lead due to the high spectral tunability (500-3000nm). Therefore, here we focus on the synthesis of PbS CQDs emitting at telecommunication wavelengths (1500-1620nm) for lasing applications. The high degeneracy of PbS (8-fold) is the main bottleneck for the realization of low-threshold lasing due to the Auger limited gain. Hence, we synthesised a series of core/shell PbS/CdS CQDs with suppressed Auger rates and tunable band-edge absorption across the telecom spectral window. The epitaxial growth of the CdS shell was achieved via cation exchange reaction producing CQDs of high optical stability, narrow size distribution and low trap state density reaching Auger lifetimes up to 320 ps.

Incorporation of Spin-Crossover Compounds on Semiconductor Surfaces for a Light Harvesting Device

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Light induced spin-crossover can be seen in Mn³⁺ and Fe³⁺ complexes. Incorporating this with semiconductors of similar energy gaps as the low spin and high spin forms may produce a new form of dye-sensitised solar cell DSSC [1]. Anchorage of complexes on semiconductors is required and we report here the results of our attachment studies through use of carboxylate tails by a bottom-up approach [2]. Photo-induced spin-crossover of the hybrids will be studied further to study the mechanism for incorporation with the conduction band of the semiconductor. Surface preparations were also conducted via various routes e.g., spin coating or dip coating methods.

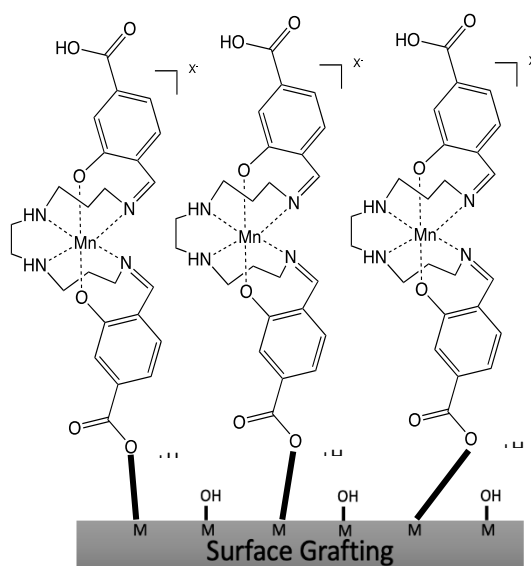


Figure 1. Spin-Crossover compound anchored on semiconductor surface via carboxylate tails

Complex precursors are anchored on surfaces through chemisorption means by hydrothermal synthesis via two methods: one-pot approach or pre-coated surface approach. Characterisation of the hybrids included DLS, zetapotential, XPS, SEM and AFM techniques in addition to characterisation of the free complexes by single crystal X-ray diffraction, SQUID magnetometry, solution and solid-state UV-vis spectroscopy.

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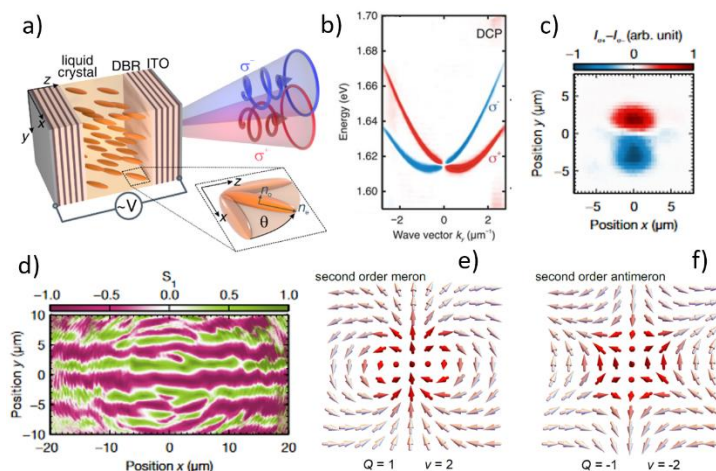
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Topological Photonics and Magnetic Analogues in Liquid Crystal Microcavities: Engineering Spin-Orbit Coupling of Light

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Topological photonics carries a key promise for the development of integrated optical circuits as photons, being uncharged, cannot be directly steered by an electric field. We have invented a method to control electrically spin-orbit coupling (SOC) of light using specially designed photonic structures - birefringent microcavities: liquid crystal layer enclosed between two parallel distributed Bragg reflectors (Fig. **a**). In solid-state systems with broken inversion symmetry, SOC gives rise to the Dresselhaus and Bychkov-Rashba SOC Hamiltonians, key to spintronics, topological insulators, and superconductors. Unlike SOC in solid-state matter, which is challenging to manipulate, birefringent optical cavities offer substantial tunability of photonic modes. This has led to observing an optical analogue of the spin Hall effect and creating artificial gauge fields for parameters extending far beyond those previously considered experimentally and theoretically [1]. We discovered Rashba-Dresselhaus spin-orbit coupling in a photonic system and showed control of an artificial Zeeman splitting [2] (Fig. **bc**). Moreover, we've shown how to structure light so its polarization mimics spins in a ferromagnet, forming half-skyrmions (merons) (Fig. **ef**, [3]). Recently we observed optical analogue of persistent spin helix, reciprocal Young's and Stern-Gerlach experiments [4] (Fig. **d**) and a new type of chiral Rashba-Dresselhaus lasing [5]. Our results illustrate an effective approach of engineering artificial gauge fields and synthetic Hamiltonians with photons for the simulation of nontrivial condensed matter and quantum phenomena – also in magnetism. Currently, we want to explore magnetic materials that can integrate with our optical devices, promising new directions in topological photonics [6].



FIGURE

a) scheme of liquid crystal microcavity; **b)** polarization-resolved reflectivity showing Rashba-Dresselhaus spin-orbit coupling of light [2]; **c)** optical analogue of Stern-Gerlach experiment [4]; **d)** optical persistent spin helix (experiment) [4,5]; **e)** polarization texture of second order meron and **f)** second order anti-meron [3] (model).

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Quantum Sensing using Spins in Diamond

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Quantum technology, including quantum computing, sensing, and communication, is one of the most revolutionary technologies of our time. Quantum sensing is based on the same foundations as those for quantum computing. It is less well known, but also important and expected to be available earlier than quantum computing. Quantum sensing allows for more accurate measurements and could offer higher accessibility than existing sensors (e.g., through device miniaturization). For example, quantum sensors can measure magnetic field, temperature, and rotation with extreme sensitivity. The potential applications of quantum sensing are also those for which no technology alternative exists. The promising quantum sensors include atomic clocks, superconducting flux qubits, and spins in solids and molecules.

In this talk, we will discuss quantum sensing using spins in diamond. A nitrogen-vacancy (NV) center is a fluorescent impurity center found in the diamond lattice. The NV center is one of the most promising tools for fundamental research in quantum information science and its applications because of its unique properties. The NV center is an excellent quantum sensor. NV quantum sensing has been applied to various systems from solid-state materials to biological macromolecules. NV-detected electron paramagnetic resonance (EPR) from a single electron spin has been demonstrated. Additionally, NV-detected nuclear magnetic resonance (NMR) with a nanometer scale has been demonstrated. Here, we will discuss NV-detected EPR and NMR techniques and the development of an NV-NMR/EPR spectrometer operated at 4 and 8 Tesla [1, 2]. In addition, we will discuss about the photo-physics of NV and other fluorescence defects in diamond.

This research was supported by NSF (ECCS-2204667 and CHE-2004252 with partial co-funding from the Quantum Information Science program in the Division of Physics).

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Synthesis and Interaction Studies of Novel Thiazole Orange Styryl Derivatives for G-Quadruplex Recognition

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This study focuses on the synthesis and interaction analysis of three thiazole orange styryl derivatives, of which two novel ones, 2-((*E*)-4-(benzofuran-3-yl)styryl)-1-methyl-4-((*Z*)-(3-methylbenzo[*d*]thiazol-2(3*H*)-ylidene)methyl)quinolin-1-ium iodide (TO-BF) and 1-methyl-4-((*Z*)-(3-methylbenzo[*d*]thiazol-2(3*H*)-ylidene)methyl)-2-((*E*)-4-(thiophen-3-yl)styryl)quinolin-1-ium iodide (TO-Thio), designed for recognition G-quadruplex (G4) structures. G4s are non-canonical nucleic acid structures with vital roles in gene regulation and potential therapeutic targeting. Through strategic synthetic routes, these three derivatives were developed, aiming to explore their binding affinity and selectivity towards G4 motifs. Spectroscopic techniques, including UV-Vis, fluorescence, circular dichroism and resonance Raman spectroscopy, were employed to investigate the interaction between the synthesized derivatives and various G4 DNA structures. Results indicate the derivatives' ability to recognize and bind to G4s, as evidenced by distinct spectral changes indicative of complex formation. Molecular modelling studies provided insights into the binding modes and structural preferences of the derivatives within the G4 motifs. These findings advance our understanding of G-quadruplex recognition and offer potential avenues for the development of novel G4-targeting agents with applications in biotechnology and therapeutics.

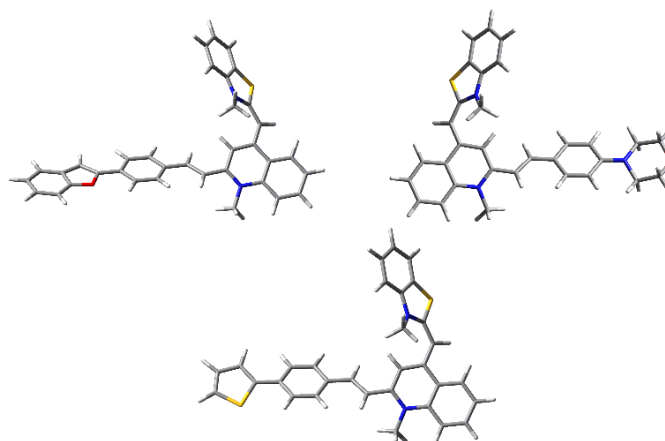


Figure 1. Molecular structures of the three derivatives after optimization of their quantum chemical geometry. In clockwise order: TO-BF, TO-Morpho and TO-Thio (Grey: C, Blue: N, Yellow: S, Red: O).

Ultraporous MOFs based on 18-connected Ternary, Trigonal Prismatic Superpolyhedra

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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 report here 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 [Fe₃(μ₃-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(μ₃-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. The present work opens new directions to apply reticular chemistry for the construction of novel MOFs with tunable porosities, based on contracted or expanded tbb analogues.

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Paramagnetism of high-entropy alloys and their relatives

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Considering magnetic applications, high-entropy alloys (HEAs, alloys that are formed by mixing equal or relatively large proportions of usually five or more elements and exhibit chemical disorder of elements within ordered crystal lattice) are produced thinking about their soft ferromagnetism toward AC applications [1]. In such a case we usually observe the phase transition between paramagnetic and ferromagnetic states at particular Curie temperature T_c . Studied by us magnetic state of single-crystalline Fe-Co-Cr-Mn-Al two-phase nanocomposite is determined by the interplay of its two constituents. Since in the temperature region between $T_{c1} = 425$ K and $T_{c2} = 370$ K, one of them is already in a magnetically ordered state, while the other is still paramagnetic, it is possible to unravel the magnetism of each constituent separately [2]. Upon cooling, the predominantly Fe–Cr–Mn chemically disordered *bcc* matrix orders first at 425 K in an asperomagnetic-type magnetic state. Below 370 K, the *B2* nanoplatelets that are predominantly an $\text{Al}_{30}(\text{Co}, \text{Mn})_{70}$ pseudo-binary intermetallic compound, start to order in a ferromagnetic (FM)-type manner. In the temperature range between the T_{c1} and T_{c2} the nanoplatelets are still in the paramagnetic state. The magnetism of the $\text{Al}_{1-x}\text{Co}_x$ *B2*-structure alloys is controlled by the amount of antistructure Co defects occupying the Al sites and the stoichiometric $\text{Al}_{50}\text{Co}_{50}$ is paramagnetic. In this case we find paramagnetic behaviour in magnetoresistance measurements. Studied by us Co-Cr-Fe-Mn-Ni HEA that is a fully random solid solution of the five magnetic elements, the source of paramagnetism are the Ni paramagnetic moments were predicted to be nonzero (although they are smaller than the moments of the other four elements) [3]. When the size difference of each individual element becomes too large, bulk metallic glass (BMG) forms instead of HEA. Studied by us Zr-Cu-Al-Pd BMGs are nonmagnetic, conducting alloys, where the Pauli spin susceptibility of the conduction electrons is the only source of paramagnetism [4]. Another example of paramagnetic metallic phase is coronary stent cobalt-chromium alloy. The susceptibility of the cobalt–chromium stent shows qualitatively a Curie-type paramagnetic behaviour ($\chi \propto 1/T$) with $\chi_c = 1.57 \times 10^{-7} \text{ m}^3/\text{kg}$ [5]. In this case the paramagnetic susceptibilities are a sum of the positive paramagnetic contribution due to localized paramagnetic ions and the small paramagnetic Pauli spin susceptibility of the conduction electrons. For the two last mentioned alloys the ferromagnetic behaviour was deliberately avoided following applications where electromagnetic field is involved that may cause strongly unwanted movement of metallic parts.

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Quantum Crystallographic Studies of Phase Transition in Minerals under Pressure

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Quantum Crystallography (QCr) uses various types of aspherical atomic electron densities (consequently aspheric atomic scattering factors) in the refinement of the structures of crystals and their electron densities against X-ray diffraction data. The main methods of QCr are: the refinement of multipole model of quantitative electron density distributions, the refinement of experimental wave functions and the refinement of the crystal structures using the Hirshfeld atom method (HAR). All these QCr methods provide better refinement results than the commonly used routine crystallography methods based on spherical atomic electron densities (IAM).

In this presentation, we will present the main ideas of quantum crystallographic methods along with their applications to the study of phase transitions in the structures of Calcite and Natrochalcite.

An important biomineral, Calcite (CaCO_3) is one of the primary carriers of carbon in geochemical reservoirs. Carbonate rocks serve as hosts to various natural resources, including ores, oil, and gas, and are transported deep into the deep mantle at subduction zones. We traced a reversible phase transformation of Calcite to Calcite-II, from $R\bar{3}c$ to $P2_1/c$ symmetry at pressure ranging from 0.85 GPa to 2.07 GPa. The reversible phase transition takes place at 1.5 GPa. It involves twinning of crystals into two domains. The decrease of pressure removed twinning in all crystals which regained the quality suitable for multipole modelling. Will present detailed changes of electron density at atoms under pressure.

Natrochalcite is rare mineral possesses H_3O_2^- units forming one of the shortest hydrogen bond (HB) reported so far in inorganic compounds. High pressure conditions can lead to the formation of an extremely short single-well HB in natrochalcite and to the phase transition connected with symmetry lowering above 2 GPa. It crystallizes in the monoclinic space group $C2/m$ and it has usually emerald green colour. Natrochalcite gained ground in recent years as an anode material for lithium – ion batteries used in powering consumer electronics and vehicles. In this contribution, we will present details of changes of H-bonding in this mineral as a function of pressure as well as analyse variation of electronic parameters.

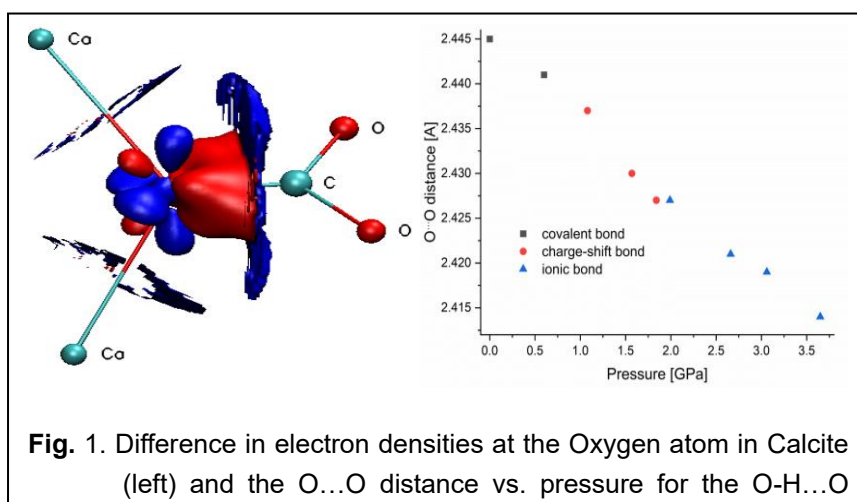


Fig. 1. Difference in electron densities at the Oxygen atom in Calcite (left) and the O...O distance vs. pressure for the O-H...O

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Highly Efficient Water Splitting by an Electrolyzer Fabricated via Mixed Metal Imidazole-Complexes

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Hydrogen (H₂) is a promising sustainable energy carrier alternative to fossil fuels for the future global energy demand due to its high mass energy density (120 MJ kg⁻¹) and zero emissions of greenhouse gases. However, over 90 % of H₂ is produced from fossil fuels by steam reforming with great emission of CO₂ causing global warming up to now. Water splitting driven by a renewable energy source is one of the most promising sustainable and eco-friendly approaches for H₂ production with zero CO₂ emission. Development of efficient and robust electrolyzer equipped with an anode and a cathode for oxygen and hydrogen evolving reactions (OER and HER), respectively is indispensable for H₂ production *via* water splitting. We newly developed a unique technique called “a mixed metal-imidazole casting (MiMIC) method” for preparation of single- or multi-metal oxide films adhering rigidly on various electrode substrates. This is a one-pot procedure to form the metal oxide films by casting precursor methanol solutions (or suspensions) of the corresponding metal ions and imidazole derivatives, followed by calcination. The MiMIC method is useful for mass production of a large variety of metal oxide-based films that are necessary for practical device fabrications due to advantages of its simplicity and scalability.

We report the mixed metal oxide film of FeNiWO_x adhering rigidly on a nickel foam (NF) electrode, showing the very low overpotentials of $\eta_{O_2}^{10} = 167$ mV (The superscripts represent the attained current densities of 10 mA cm⁻²) with a Tafel slope of 49 mV dec⁻¹ and at least 100 h stability in OER, which compare advantageously with only a few state-of-the-art OER anodes with excellent $\eta_{O_2}^{10} < 200$ mV. The electrochemical data indicate synergistic coupling among ternary metal centers of Ni, Fe and W to decrease the η value.[1] On the other hand, We also report a Pt/NiO_x composite film deposited on a NF electrode *via* a MiMIC method” to demonstrate extremely efficient and stable HER performance with overpotentials of $\eta_{H_2}^{10} = 4.2$ and $\eta_{H_2}^{100} = 26.6$ mV at geometrical current densities of 10 and 100 mA cm⁻², respectively in 1.0 M KOH solutions,[2] which are the lowest overpotentials among state-of-the-art cathodes for HER to the best of our knowledge. The mass activity (0.42 A cm⁻² mg_{Pt}⁻¹) of the Pt/NiO_x composite film at $\eta_{H_2} = 50$ mV is 60 times higher than that of the commercial 10 wt % Pt/C film on the NF electrode as a commonly used HER electrocatalyst. The extremely stable HER electrocatalysis was first demonstrated at the high current density of -100 mA cm⁻² for 60 h in 1.0 M KOH solutions. This study opens up a new avenue towards practical application of the electrolyzer equipped with the FeNiWO_x film and the Pt/NiO_x composite film as an efficient OER anode and HER cathode to large-scale and commercial systems for water splitting.

[1] Z. N. Zahran, E. A. Mohamed, Y. Tsubonouchi, M. Ishizaki, T. Togashi, M. Kurihara, K. Saito, T. Yui, M. Yagi, *ACS Appl. Energy Mater.*, **2021**, 4(2), 1410-1420.

[2] Z. N. Zahran, Y. Tsubonouchi, D. Chandra, T. Kanazawa, S. Nozawa, E. A. Mohamed, N. Hoshino, M. Yagi, *J. Mater. Chem. A*, *in press*.

Unpaired Spins as Promoters of Biological and Materials Chemistry

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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 carbon-based 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, or Ca), or incorporation of diradicals-generating 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 including the synthesis of novel nanocatalysts for CO₂ reduction.

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