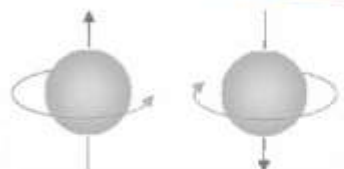


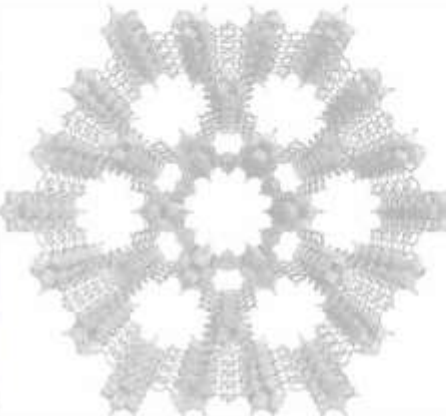
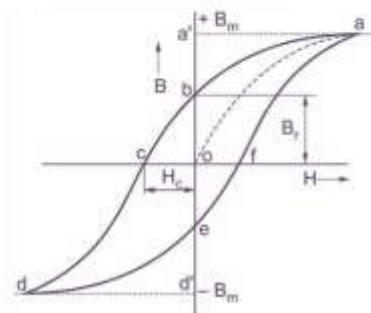
9TH
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**CONFERENCE ON
 PARAMAGNETIC
 MATERIALS**

Ayia Napa, Cyprus

May 9th - 13th, 2022



**PROGRAM &
 ABSTRACT BOOK**

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.

GENERAL INFORMATION

NAGC 2022 is held on the beautiful island of Cyprus in the eastern Mediterranean, in the Ammochostos region. The accommodations and lecture facilities are situated in the NissiBlu Beach Resort in Ayia Napa. Information about the hotel may be found at the following website:

<https://nissiblu.com/>

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/>

2022 NAGC CONFERENCE (AYIA NAPA, CYPRUS MAY 9 – 13, 2022)

9th NAGC – Cyprus 2022

Monday, May 9	Tuesday, May 10	Wednesday, May 11	Thursday, May 12	Friday, May 13
8:45 – 9:00 Welcome A. Tasiopoulos, G. Christou				
Chair: George Christou	Chair: Stephen Hill	Chair: Spyros Perlepes	Chair: Catherine Raptopoulou	Chair: Matthias Driess
09:00 – 09:30 Spyros Perlepes 09:30 – 10:00 Jesper Bendix 10:00 – 10:30 Juan Peralta 10:30 – 11:00 George Froudakis	09:00 – 09:30 Mike Zaworotko 09:30 – 10:00 Rudi Wehmschulte 10:00 – 10:30 George Kostakis 10:30 – 11:00 Sotiris Hadjidakou	09:30 – 10:00 George Christou 10:00 – 10:30 P. Paraskevopoulou 10:30 – 10:45 ChristiAnna Brantley 10:45 – 11:00 Xiang-Jing Kong	09:00 – 09:30 Richard Layfield 09:30 – 10:00 Yiannis Sanakis 10:00 – 10:30 B. Andraka-Christou 10:30 – 11:00 Theodore Lazarides	09:00 – 09:30 Selvan Demir 09:30 – 10:00 Hai-Ping Cheng 10:00 – 10:30 C. Raptopoulou 10:30 – 10:45 Naveen Kumar 10:45 – 11:00 Karam Assad
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: George Kostakis	Chair: Emmanouil Manos	Chair: Theodore Lazarides	Chair: Vasileios Psycharis
11:30 – 12:00 Piotr Kaszynski 12:00 – 12:30 Gideon Shapiro 12:30 – 12:45 Ashlyn Hale 12:45 – 13:00 Kyriaki Koupepidou	11:30 – 12:00 Stephen Hill 12:00 – 12:30 Kathryn Preuss 12:30 – 12:45 Chryssoula Drouza 12:45 – 13:00 Christina Banti	11:30 – 12:00 G. Papaefstathiou 12:00 – 12:30 Sotiris Christodoulou 12:30 – 13:00 Kim Christou	11:30 – 12:00 Lisa McElwee-White 12:00 – 12:30 Theodora Krasia 12:30 – 13:00 Nikos Panagiotou 13:00 – 13:15 Zoi Lada 13:15 – 13:30 Maria Koyioni	11:30 – 12:00 Matthias Driess 12:00 – 12:30 Grigoris Itskos 12:30 – 12:45 Andreas Kalogerou 12:45 – 13:00 Ethan Fisher 13:00 – 13:15 Angelos Amoiridis 13:15 – 13:30 Andreas Kourtellaris
LUNCH BREAK	LUNCH BREAK	FREE TIME	LUNCH BREAK	Closing Remarks
13:00 – 15:30	13:00 – 15:30		13:00 – 15:30	
Chair: Kathryn Preuss	Chair: Sotiris Christodoulou		Chair: Lisa McElwee-White	
15:30 – 16:00 Krzysztof Wozniak 16:00 – 16:30 T. Stamatatos 16:30 – 17:00 Vasileios Psycharis 17:00 – 17:15 Xia Li 17:15 – 17:30 Georgina Zissimou	15:30 – 16:00 George Papavasiliou 16:00 – 16:30 Anastasios Keramidas 16:30 – 17:00 Emmanouil Manos 17:00 – 17:15 Amin Koochaki 17:15 – 17:30 Dimitris Evagelou 17:30 – 17:45 George Lefkaritis 17:45 – 18:00 Konstantina Baka		15:30 – 16:00 Grace Morgan 16:00 – 16:30 Stelios Choulis 16:30 – 17:00 Yasser AlWahedi 17:00 – 17:15 Niki Mavragani 17:15 – 17:30 Raphael Stylianou 17:30 – 17:45 P. Oikonomopoulos	
COFFEE BREAK	CONFERENCE DINNER Departure from hotel at 8:00 pm			
17:30 – 18:00				
Chair: George Froudakis				
18:00 – 18:30 Dimitris Gournis 18:30 – 18:45 Alexios Plessas 18:45 – 19:00 Athanasia Psalti 19:00 – 19:15 Dimitris Fragkis 19:15 – 19:30 Rafail Machattos 19:30 – 19:45 Christian Bunker				

SOCIAL ACTIVITIES PROGRAM

1. Sunday, May 8th

Welcome Reception, 19:30.

NissiBlu Beach Resort

2. Tuesday, May 10th

Official Conference Dinner.

Departure from the hotel at 20:00.

ACKNOWLEDGEMENTS



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University of Florida,
Department of Chemistry



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Abstracts

Greenfying the Blue – Challenges in Decarbonizing the Maritime Sector

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Abstract

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

References:

[1] www.visualcapitalist.com

[2] www.oecd.org

VO₂⁺ and UO₂²⁺ complexes with siderophore multibinding hydroxylamino-triazine ligands: Structural and stability studies

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University of Cyprus, Department of Chemistry, 1678 Nicosia, Cyprus

Presenter Contact Details; e-mail: aamoir01@ucy.ac.cy

Over the past few years, an intense scientific effort is taking place to develop specific chelators for metal ions, including actinides, to combat environmental contamination caused by toxic heavy metals, which is considered a serious and widespread health hazard. Uranium is also an important target for separation and recycling since it is abundant in the radioactive waste produced by nuclear industries. Uranium's removal from the human body through chelation therapy is based on the same complexation processes that are also used for uranium recycling from nuclear waste. In the last few decades, multidentate complexing agents with oxygen donor atoms, based on phosphonic ligands, or siderophore-based units, and polysulfides have been identified as effective uranium chelators.

At present, amidoxime-based adsorbents are considered to be the most promising materials for the extraction of uranium from seawater. However, amidoximes lack selectivity for uranyl binding in the presence of high concentrations of transition metals, especially iron and vanadium, which strongly compete with uranium in the sequestration process.

A new family of compact nontoxic tridentate chelators, based on an *N,N*-disubstituted bis(hydroxyamino)-1,3,5-triazine motif (H₂Bihyat), were reported to form hydrolytically stable complexes with hard acids, such as Fe^{III} and Ti^{IV}, V^V and Mo^{VI} over a wide pH range of 3–11. H₂bihyat was found to exhibit the strongest and most selective binding of U^{VI}O₂²⁺ moiety in either U^{VI}O₂²⁺/Fe^{III} or U^{VI}O₂²⁺/V^{VO}₄³⁻ solutions at alkaline pHs to date, thus, suitable for UO₂²⁺ mining from the sea.

Herein, we synthesized the ligand H₄QTN that contains two H₂bihyat chelating moieties, targeting to enhance the stability of the complexes by increasing the overall entropy of the system. In addition, the UO₂²⁺ and VO₂⁺ dinuclear complexes were synthesized and characterized by X-ray crystallography and NMR spectroscopy. UV-Vis and NMR spectroscopies were used for the determination of the hydrolytic stability of the complexes. NMR spectroscopy was also used to determine the competitive complexation of UO₂²⁺ and VO₂⁺ between H₄QTN and other relatively strong chelators.

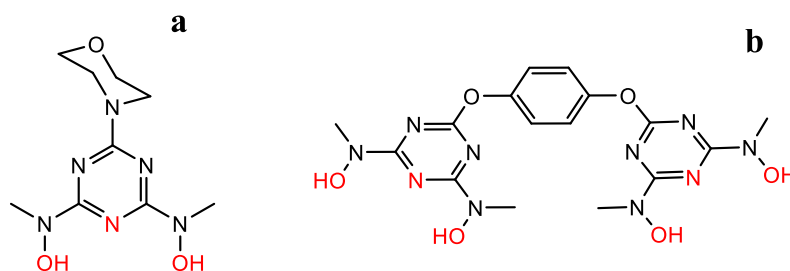


Figure 1: a; H₂Bihyat ligand. b; H₄QTN ligand

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Methadone and buprenorphine: lifesaving treatments for opioid use disorder

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The US is experiencing an unprecedented number of drug overdose deaths, with 80% involving an opioid¹. Opioid use disorder, a biopsychosocial health condition, increases the risk of overdose death. Fortunately, effective medications exist for treating opioid use disorder, namely methadone and buprenorphine, both of which have been FDA-approved for decades. A recent meta-analysis of randomized controlled clinical trials found that methadone and buprenorphine treatment each result in an approximately 50% decreased likelihood of overdose death². These medications work by activating mu opioid receptors in the brain, thereby preventing cravings, managing withdrawal symptoms, and blunting the effects of subsequent opioids – leading to decreased opioid misuse. Unfortunately, only approximately 50% of Americans with an opioid use disorder obtain methadone or buprenorphine³, a problem resulting from systemic, institutional, provider, and patient-level access barriers.

I will begin the talk with a summary of the US opioid overdose crisis, including its causes, and a description of opioid use disorder. Next, I will summarize the mechanisms by which methadone and buprenorphine treat opioid use disorder. I will then describe the range of methadone and buprenorphine access barriers Americans face. Finally, I will provide examples of potential solutions for increasing access to these medications, including examples from other nations with more widely available methadone and buprenorphine. This talk will highlight some of the key arguments from my book, *The Opioid Fix: America’s Addiction Crisis & The Solution They Don’t Want You to Have*, in a manner accessible to those without prior knowledge about opioid use disorder treatment.

References:

1. Ahmad FB RL, Sutton P. Provisional drug overdose death counts. . National Center for Health Statistics, Centers for Disease Control and Prevention. Accessed February 17, 2022. <https://www.cdc.gov/nchs/nvss/vsrr/drug-overdose-data.htm>
2. Santo T, Jr., Clark B, Hickman M, et al. Association of Opioid Agonist Treatment With All-Cause Mortality and Specific Causes of Death Among People With Opioid Dependence: A Systematic Review and Meta-analysis. *JAMA Psychiatry*. 2021;78(9):979-993. doi:10.1001/jamapsychiatry.2021.0976
3. Wu L-T, Zhu H, Swartz MS. Treatment utilization among persons with opioid use disorder in the United States. *Drug and Alcohol Dependence*. 2016;169:117-127. doi:10.1016/J.DRUGALCDEP.2016.10.015

First Synthesis of the Inherently Chiral *Equatorial_{face}* and *Trans-4'* Bisadducts of C₅₉N Azafullerene Utilizing the Tether-Directed Remote Functionalization Approach

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Heterofullerenes are a class of compounds in which carbon atoms of the fullerene cage have been replaced by heteroatoms. Aza[60]fullerene (C₅₉N)₂ is a heterofullerene in which one carbon atom of the fullerene cage has been replaced by a nitrogen atom. Aza[60]fullerene is the only stable heterofullerene that can be synthesized in macroscopic quantities and exists in a dimeric form.

In this work, the *equatorial_{face}*^[1] and *trans-4'*^[2] bisadducts were prepared, for the first time, by employing *cyclo*-[2]-octylmalonate and *cyclo*-[2]-dodecylmalonate as tethers in a Mannich-type reaction followed by an intramolecular Bingel cyclopropanation. The addition pattern of the newly formed bisadducts was revealed by X-ray crystallography.

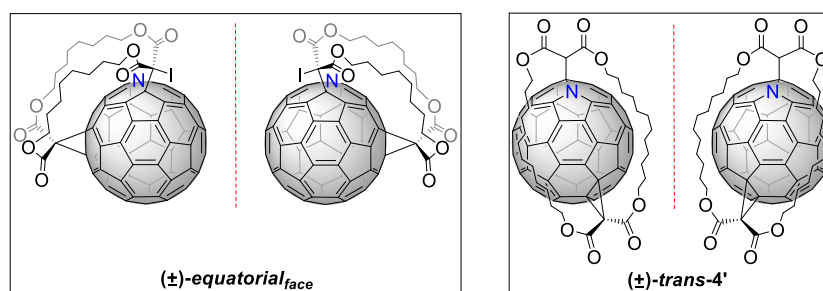


Figure 1: The inherently chiral *equatorial_{face}* and *trans-4'* bisadducts of azafullerene C₅₉N.

Examination of the optical properties of the *equatorial_{face}* bisadduct^[1] showed the evolution of new absorption bands, which can be used as signatures for the characterization of *equatorial_{face}* bisadducts of C₅₉N. Moreover, redox assays showed that the LUMO level of the *equatorial_{face}* bisadduct was increased compared to that of the parent (C₅₉N)₂.

The *trans-4'* bisadduct^[2] was subjected to enantiomeric resolution by chiral HPLC, unveiling two distinct enantiomers. The mirror-image relation of the two enantiomers was probed by circular dichroism spectroscopy and demonstrated the inherently chiral nature of the *trans-4'* bisadduct. The UV-Vis absorption spectra and the electrochemical data acquired for the *trans-4'* bisadduct suggests that the addition pattern has a reflection in the light-harvesting and redox properties of the bisadduct, as compared to the *equatorial_{face}* pattern.

[1] A. Stergiou, **K. Asad**, A. Kourtellaris, N. Chronakis*, N. Tagmatarchis*, *Chem. Eur. J.*, **2019**, 25, 5751-5756.

[2] **K. Asad**, A. Stergiou, A. Kourtellaris, N. Tagmatarchis*, N. Chronakis*, *Chem. Eur. J.*, **2021**, 27, 13879-13886.

Molecular Heterometallic Dy^{III}-Bi^{III} Clusters: An Approach to Structurally Unique Architectures with Enhanced Magnetic Anisotropy

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The heterometallic chemistry of 3d/4f-metal ions has flourished over the past 20 years or so, providing new structural motifs of nanosized molecular clusters, multifunctional compounds combining two or more physical properties within the same entity (magnetism and luminescence, catalysis and magnetism, etc.), 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 pnictogen Bi³⁺, has not been systematically explored, although Bi³⁺ has a large spin-orbit coupling and it could -in principle- contribute to the enhancement of the molecular magnetic anisotropy.^[1] From a synthetic perspective, it is definitely not straightforward to incorporate both a lanthanide(III) ion and bismuth(III) within the same molecular compound since both of these metal ions are oxophilic, they exhibit similar ionic radii and high tendency to undergo hydrolysis reactions, and they adopt large coordination numbers with a variety of coordination geometries. Given these challenges, and the lack of any previously reported Dy^{III}-Bi^{III} heterometallic clusters to date, we decided to take our chances and seek for synthetic routes to crystalline Dy^{III}-Bi^{III} molecular compounds with interesting structural and physicochemical properties. In this presentation, we report on the self-assembly synthesis and characterization of a new {Dy^{III}₃Bi^{III}₈} cluster bearing the Schiff base ligand *N*-salicylidene-*o*-aminophenol ^[2], and its deliberate expansion into the 1-D analogous chain via replacement of terminal halides with end-to-end azido groups (**Figure 1**).

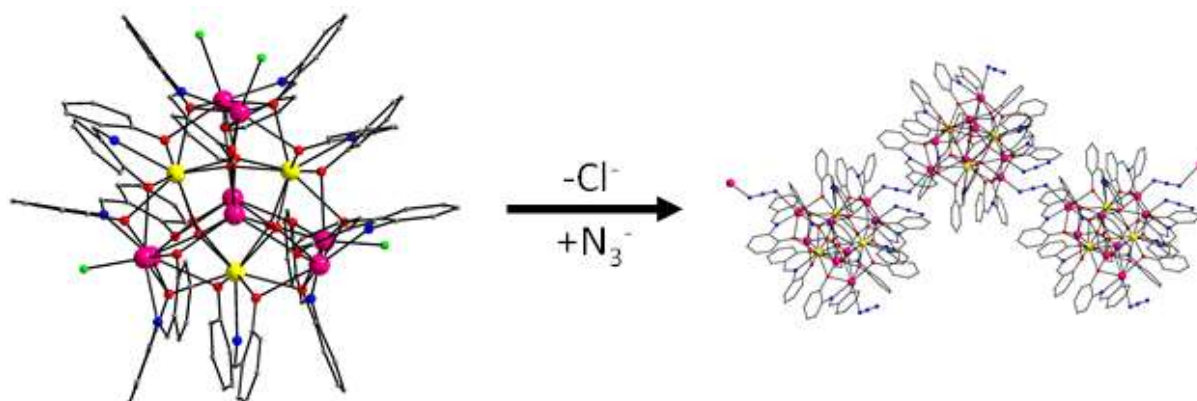


Figure 1. The {Dy^{III}₃Bi^{III}₈} cluster (left) and its analogous 1-D chain (right).

[1] S. C. Coste, B. Vlaisavljevich, D. E. Freedman, *Inorg. Chem.*, **2017**, *56*, 8195–8202.

[2] D. I. Alexandropoulos, T. N. Nguyen, L. Cunha-Silva, Th. F. Zafiropoulos, A. Escuer, G. Christou, Th. C. Stamatatos, *Inorg. Chem.*, **2013**, *52*, 1179–1181.

New strategies in the development of hydrogels for contact lenses that are able to reduce microbial infection risk.

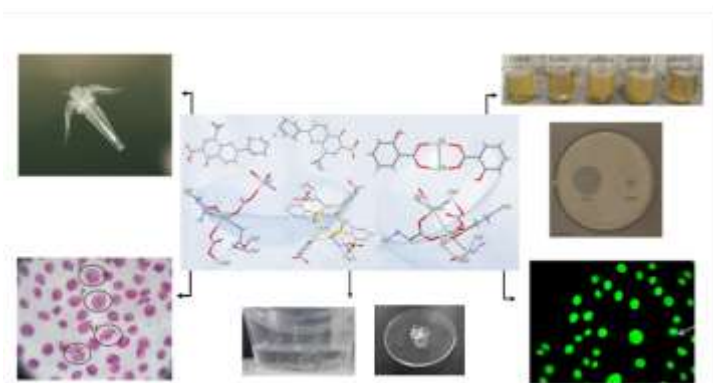
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The use of soft contact lenses is a popular method for correcting eye refractive errors [1]. Their poor handling and hygiene practices are the key reasons for their frequent contamination, which can lead to microbial keratitis (MK). The manufacturing of next generation soft contact lenses involves the use of novel active biomaterials which control microbial colonisation and thus the incidence of MK. Silver(I) ions, on the other hand, exhibit a broad spectrum of antimicrobial activity against both Gram-positive and Gram negative bacteria. Therefore, the development of contact lenses combined with silver based antimicrobial agents is a research, technological and financial issue. For this purpose, three strategies have been developed from our group. One involves the use of silver nanoparticles using extracts from natural products as combined reducing and capping agents. The second one involves the use of small molecules which act as antimicrobial agents as well, while the third one, small molecules which are ingredients of natural products.

In the course of our studies on the development of new antimicrobial agents and their non-infectious contact lens the novel biomaterials were synthesized by the dispersion in polymeric poly(2-hydroxyethyl methacrylate) (pHEMA) of AgNPs(natural products) or small bioactive silver(I) complexes. The biomaterials were characterized by XRD, XRF, TG-DTA, DTG/DSC and FT-IR-ATR analytical techniques. The prepared materials were evaluated for their antibacterial activity against the Gram-negative species *P. aeruginosa* and Gram positive ones *S. epidermidis* and *S. aureus* which are abundant in microbial keratitis. The *in vitro* and *in vivo* toxicity of the biomaterials was tested against human corneal epithelial (HCEC) cells, by the micronucleus assay, *Artemia salina* and *Allium cepa* models.



Acknowledgements: This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code:T1EDK-02990)».

[1] (a) C.N. Banti, M. Kapetana, C. Papachristodoulou, C. Raptopoulou, V. Psycharis, P. Zoumpoulakis, T. Mavromoustakos, S.K. Hadjikakou, Dalton Trans., 2021, 50, 13712-1372.;

Engineering geometry and symmetry in molecular magnetism

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The functional group is an immensely successful concept – possibly the defining one in preparative organic chemistry. However, it is largely lacking in inorganic chemistry. While assembly of discrete coordination complexes into more complicated structures of varying dimensionality is commonplace, the versatility of such approaches nowhere matches the synthetic control which is routine in organic synthesis.

In this presentation it will be argued that a significant broadening of the palette of orthogonal reactivities available to the preparative coordination chemist can be reached by consideration of metallophilic interactions and by systematic exploitation of ligand-metal preferences as conventionally expressed by the Pearson HSAB principle. Additionally it will be argued that rules for preferred geometries of ligands bridging metal centers can serve as strong predictors for the resulting structures.

Some successes in using functional-inorganic modules in targeted construction of more complex structures will be illustrated. These range from the use of robust fluoride complexes in assembly of mixed transition metal - lanthanide complexes[1] to the targeted synthesis of actinide chains directed by platinum-platinum metallophilic interactions.[2]

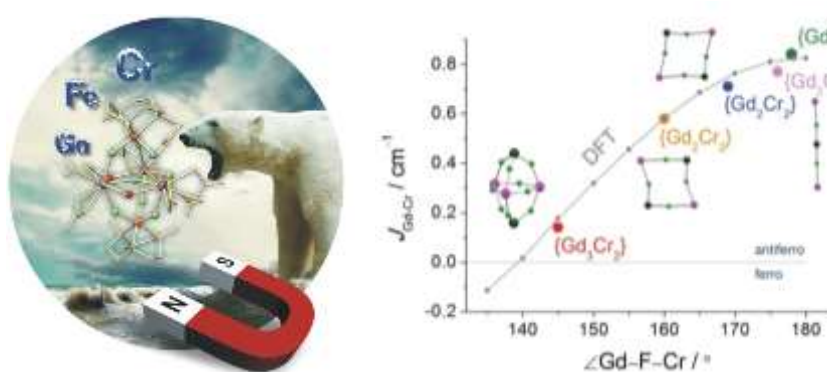


Figure: Geometric weakening magnetic coupling in hetero-metallic complexes. [1]

[1] Pedersen, K.S., Lorusso, G., Morales, J.J., Weyhermüller, T., Piligkos, S., Singh, S.K., Larsen, D., Schau-Magnussen, M., Rajaraman, G., Evangelisti, M. and Bendix, J. *Angew. Chem. Int. Ed.*, **2014**, 2394

[2] Sørensen, M.A.; Hansen, U.B.; Perfetti, M.; Pedersen, K.S...Bendix, J. *Nature Communications*, **2018**, 9, 1292

An Unusual Co₂ Complex: A Potential Molecular Route to Multi-Qubit Systems

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Molecular chemistry provides immense control over the synthesis of magnetic molecules, and this can be utilized as a powerful resource in the investigation of quantum properties that are vital to next-generation technologies. Their molecular nature allows for study by a variety of techniques in both the solid state and solution, including electron paramagnetic resonance (EPR) spectroscopy, magnetometry, and single-crystal X-ray crystallography. The assembly of quantum gates, which are comprised of multiple qubits, are crucial to the development of quantum information systems. Current approaches include trapped ions and defects in solids; however, the tuneability and scalability of these materials are limited greatly, hindering their development. Potential solutions to these limitations require a fundamental knowledge of quantum superposition and entangled states that are generated by the exchange-coupling (J_{ij}) between two or more magnetic molecules or ions and their sensitivity to external influences. For potential candidates, the spins of the magnetic ions must be inequivalent either by coordination geometry, spin state, or oxidation state, and should be weakly coupled. Recently, multiple approaches have been developed to synthesize families of multi-qubit systems which exhibit quantum superposition/entanglement states following these criteria. One approach is the synthesis of homo- and heterometallic dinuclear complexes with controllable permutations of metal ions and their spins. In this presentation, we will discuss the synthetic route and a detailed angle-dependent high-frequency EPR study of an unusual [Co₂(O₂PPh)₃(py)₄](ClO₄) complex comprising high-spin octahedral Co²⁺ and tetrahedral Co²⁺ ions that are weakly coupled together allowing independent excitation of the two spins within the dinuclear complex.

Tight-binding Scattering Solution for Electron Mediated Entanglement

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We theoretically investigate single electron scattering as a vehicle for manipulating the entanglement of molecular systems. We introduce a Green's function solution to calculate single electron transmission through a scattering region described by an arbitrary tight-binding Hamiltonian. We use this method to explore efficient generation of maximally entangled states in several model systems using entangled state switching. Finally, we show that even without entangled state switching, control of the entanglement is possible for a broad class of molecular systems. We demonstrate this ability in a first principles molecular dimer system.

Magnetic Molecule on Surfaces

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Molecule-substrate interactions play a pivotal role in quantum device fabrication. With first-principles calculations based on density functional theory, we investigated a few systems that consist of magnetic molecules on various substrates, including magnetic ones [1-2]. In this talk, we present our recent progress on Clar's goblet-graphene, Mn₁₂-MoS₂ and MPC-Pt and -NCO. We focus on modifications of magnetic properties of the molecules, such as changes in magnetic moments and couplings, and magnetic anisotropy resulting from structure relaxation, charge transfer, and orbital hybridization. We also apply a gate voltage to study effects of electric field and charge doping by gating. Flat band analysis is applied to understand interface processes.

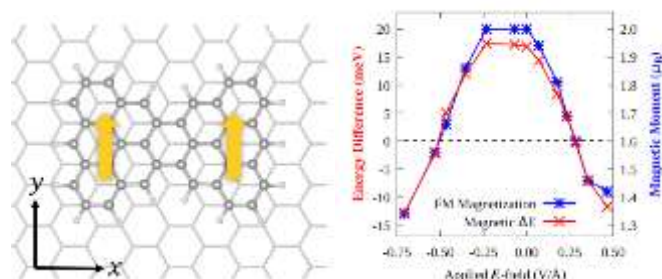


Figure. Left: Clar's goblet C₃₈H₃₈ on graphene; Right: Magnetic coupling vs. **E**-field

[1] Adam V. Bruce, Shuang-Long Liu, James N. Fry, Hai-Ping Cheng, (2022)
DOI: 10.1021/acs.jpcc.2c00177

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Solution Processed Electronic Materials for Next Generation Photovoltaics

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Light is one of the most valuable goods on earth: The sun is the single most clean and sustainable energy source which can solve all the energy needs of our world. The energy in the sunlight striking the earth for 40 min is equivalent to the global energy consumption for a year. Over the last decade solution processed organic and hybrid perovskite solar cells have been amongst the most prominent next generation photovoltaic (PV) technologies, reaching power conversion efficiencies (PCEs) of over 18 % and 24 % respectively [1,2].

However, both PV Technologies are facing product development issues, such as the need to achieve long-term stability and the development of carrier selective contacts for the reliable processing of high-performance devices. Their overriding attraction of both technologies is the potentially low production cost of the PV module, arising from the large-scale PV film production through printing techniques. The Presentation aims in covering a range of engineering and underpinning scientific issues needed to bring organic and hybrid perovskite PVs to commercial viability in terms of efficiency, lifetime and cost. A systematic understanding of the relationship between printed electronic materials [3], processing and solar cell performance relevant to next generation organic and hybrid perovskite PVs product development targets will be presented [4,5].

Acknowledgements

The author acknowledge the funding from the EU Horizon 2020 research and innovation program under grant agreement 862474 (project RoLA-FLEX).

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[3] S. Pozov, I. Theodorakos, K. Andritsos, E. Georgiou, A. Ioakeimidis, A. Kabla, I. Zergioti, S.A. Choulis, Highly Efficient Indium Tin Oxide-Free Inverted Organic Photovoltaics using Laser Induced Forward Transfer Silver Nanoparticle Embedded Metal Grids, submitted to *ACS Applied Electronic Materials*, 2022.

[4] Long Thermal Stability of Inverted Perovskite Photovoltaics Incorporating Fullerene-Based Diffusion Blocking Layer, F. Galatopoulos, I. T Papadas, G. S. Armatas, S. A Choulis, 5, 1800280, 2018.

[5] Apostolos Ioakeimidis, Alina Hauser, Michael Rossie, Flavio Linardi, and Stelios A. Choulis, High Performance Non-Fullerene Acceptor Inverted Organic Photovoltaics Incorporating Solution Processed Doped Metal Oxide Hole Selective Contact, submitted to *Applied Physics Letters*, 2022.

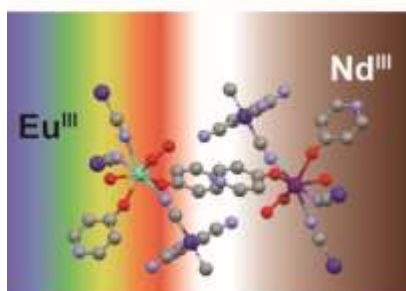
Dual emission in the near-infrared and visible from dual center cyanido bridged Eu^{III}/Nd^{III} (4-hydroxypyridine)-Co^{III} layered material

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Inorganic coordination polymers with a dual emission spanning from the visible (VIS) to near-infrared part (NIR) of the electromagnetic spectrum are of paramount importance for optical sensors, medical diagnostics and telecommunication technologies. We present the synthesis of heterometallic cyano-bridged layered $\{Eu_xNd_y(4-OHpy)_2(H_2O)_3\} [Co(CN)_6] \cdot 0.5H_2O$ networks where 4-OHpy = 4-Hydroxypyridine, with multi-colour emission profile across the VIS and NIR. We report the synthesis of a series of mixed lanthanide (Ln^{III}) CPs, along with their structural characterization and optical response. The crystals show an efficient energy transfer (ET) from the 4-OHpy ligand and the red phosphorescent $[Co(CN)_6]$ ions to the Eu^{III} and Nd^{III} resulting in enhanced photoluminescence (PL) efficiency. We study the ET with steady-state and time resolve photoluminescence PL reporting an energy transfer between the Ln^{III}. The excitation dependent emission of the mixed Ln^{III} CPs and our degree of freedom over the PL lifetime, yield new insights into the optoelectronic properties of these materials.



Molecular Nanoparticles: A Molecular Route to Ultra-small Nanoparticles of Important Metal Oxides

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Synthesis of truly monodisperse (single size) nanoparticles and their structural characterization to atomic resolution are extremely important challenges in nanoscience. For many nanoscale materials important to next-generation electronic, magnetic, catalytic, and biomedical systems/devices, the 'top-down' approach is reaching its limits as the fabrication of monodisperse nanoparticles becomes more and more difficult with decreasing size. The bottom-up molecular approach to ultra-small (<10 nm) nanoparticles promises a powerful alternative route if high nuclearity clusters that have the same structure as the bulk material can be synthesized. Such 'molecular nanoparticles' (MNPs) would bring the many powerful advantages of molecular chemistry to this area of nanoscience, particularly true monodispersity, solubility, and crystallinity, the latter allowing structural characterization to atomic resolution by single-crystal X-ray crystallography, including the monolayer shell of organic ligands, which is extremely difficult to characterize for traditional nanoparticles.

Nanoparticles of CeO₂, various Fe oxides, Mn oxides, and others are widely used in many areas from industrial catalysis to medical applications. For CeO₂, we developed routes to a family of MNPs with dimensions up to 2.4 nm using primarily carboxylate ligands [1,2], and since then breakthroughs have been achieved to MNPs of multiple other important metal oxides. In addition, we have recently been targeting MNPs containing 3d and/or 4f heterometals on their surface to model magnetic units or catalysts supported on traditional nanoparticles or other surfaces [3]. This presentation will describe a number of the above systems.

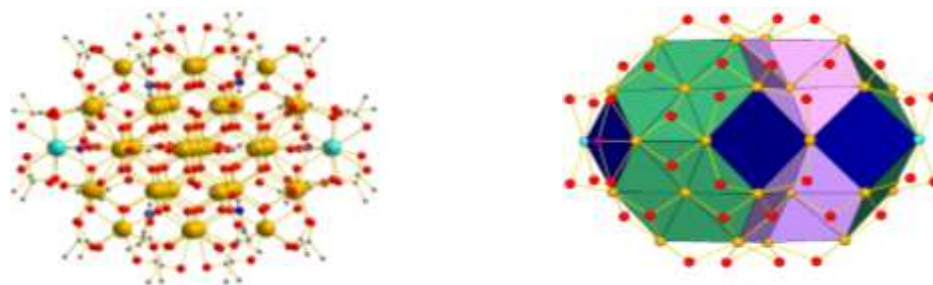


Figure. Structure of the Ce₄₀ MNP of CeO₂: **(left)** the complete structure with H atoms omitted for clarity; **(right)** the Ce/O core showing the surface facets. Atom sizes of C, N, and O are made small to emphasize Ce locations. Color code: Ce⁴⁺ gold, Ce³⁺ sky blue, O red, OH⁻ purple, N blue, C grey. Facets: (100) blue; (110) violet; (111) green.

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- [3] Mn^{III/II} and Ce^{III/IV} Units Supported on an Octahedral Molecular Nanoparticle of CeO₂. S. Das Gupta, A. E. Thuijs, E. G. Fisher, K. A. Abboud, and G. Christou. *Inorg. Chem.* **2022**, ASAP article DOI: 10.1021/acs.inorgchem.1c03719

Multifunctional Lanthanide Metallocenes: From High-Performance Single-Molecule Magnets to Small Molecule Activation

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Molecules that possess an energy barrier to spin inversion have intriguing potential applications in areas such as magnetic refrigeration, molecular spintronics and high-density information storage. For these applications, however, key performance characteristics such as large spin-relaxation barriers (U_{eff}) and high magnetic blocking temperatures (T_{B}) are required. Lanthanides have been proven to be particularly well-suited for the design of single-molecule magnets owing to their large magnetic moments and magnetic anisotropy that stem from strong spin-orbit coupling of the 4f orbitals. By using lanthanide ions such as Tb^{3+} , Dy^{3+} , and Er^{3+} which possess intrinsically large orbital angular momentum, significantly higher U_{eff} and T_{B} can be achieved. A general methodology to improve T_{B} in multinuclear single-molecule magnets is to generate strong magnetic exchange between lanthanide centers through the employment of radical bridging ligands with diffuse spin orbitals. Another successful approach to strong coupling targets the use of 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 synthesis of multiple lanthanide single-molecule magnets that contain radical ligands and bismuth clusters, respectively. The latter class of compounds were synthesized through a solution organometallic approach and represent the first single-molecule magnets containing bismuth donors which lead to new prospects in synthetic chemistry and physics, Figure 1 [1].

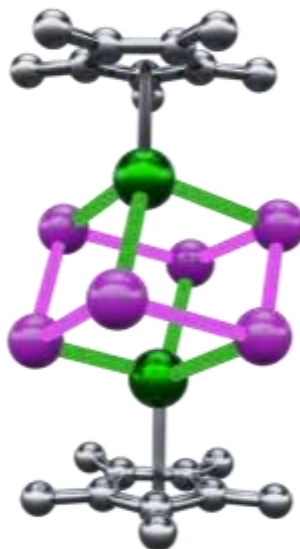


Figure 1. Structure of the $[\text{Cp}^*_2\text{Ln}_2\text{Bi}_6]^{2-}$ dianion in a crystal of $[\text{K}(\text{THF})_4]_2[\text{Cp}^*_2\text{Ln}_2\text{Bi}_6]$. Green, purple, and gray spheres represent Ln, Bi, and C atoms, respectively.

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Preparation of Chiral MOFs via Post-Synthetic Modification

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Homochiral molecules were well-known for the unreplacable application in biological activities. So obtaining the optically pure chiral molecules is crucial in pharmacy relevant industries. However, chiral isomers generally have similar physical properties, so enantiomers detection, separation and asymmetry catalysis would be full of challenge. What's more, the small chiral molecules generally exist as liquid which prohibit their absolute structure determination under single crystal X-ray diffraction (SC-XRD) instrument [1]. Chiral metal-organic frameworks (MOFs) were reported to have application in enantiomers separation and chiral crystalline sponge [2]. We introduce the method of post-synthetic modification (PSM) to obtain the chiral MOF with open pore channels. Chiral alcohol enantiomers were studied as the separation targets in chiral resolution experiment, and the performance was measured by high-performance liquid chromatography (HPLC) equipped with UV detector and chiral column. And the PSM result crystals also play the role as chiral crystalline sponge for the structural analysis of chiral small molecules under SC-XRD. The performance of chiral resolution experiment was reflected in the intermolecular hydrogen bond interactions between host and guests.

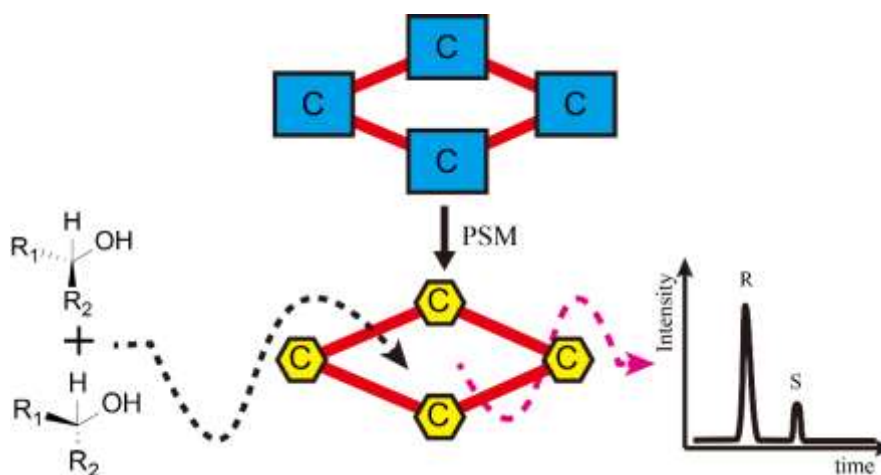


Figure 1. CMOM obtained through PSM reaction for chiral separation application.

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[2] Shi-Yuan Zhang, Lukasz Wojtas, Michael J. Zaworotko, *Journal of the American Chemical Society*, **2015**, 137, 12045-12049

An Octahedral {Mn₆} Cluster Surrounded by Fluorinated Alkoxide Ligands

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Work with perfluoropinacolate ligand, (pin^F)²⁻, has resulted in a highly symmetrical {Mn₆} complex as shown in Figure 1 below. This compound, [Mn₆(μ₃-OH)₄(μ₃-OK(THF))₄(pin^F)₆], has an equatorial square plane of four Mn(III) centers and two axial Mn(IV) centers and eight face-capping oxo or hydroxo groups. The remaining two sites of each six-coordinate Mn are occupied by the bidentate (pin^F)²⁻ ligand. In spite of the extensive work in Mn chemistry toward structural and functional models of the OEC (oxygen-evolving cluster) and SMMs (single-molecule magnets), to the best of our knowledge no other such pseudo-octahedral {Mn₆} clusters have been reported.

Chemical reactivity and physical characterization of this deep-brown cluster, and related species will be reported. The cluster is stable in the solid-state and solution in air for days before slowly hydrolyzing to form some [KMn(OH₂)(pin^F)₂]. An alternative synthesis results in terminal DME molecules instead of THF. This compound can be oxidized by one electron to form a red-brown compound and reacts with strong Brønsted bases. Magnetic susceptibility studies revealed an *S* = 11 ground state, as the 2 K magnetization saturates at 22 μ_B/molecule. The DC magnetic data also shows a sizable magnetic anisotropy, which was confirmed by high-field HF EPR measurements. EPR parameters are *g_x* = 1.993, *g_y* = 1.983, *g_z* = 1.992, *D* = -0.096 cm⁻¹, *E* = -0.022 cm⁻¹ and the fourth-order parameter *B*₄⁰ = -3.7 × 10⁻⁶ cm⁻¹. The AC susceptibility data exhibit field induced slow magnetic relaxation upon application of an external field *B*_{DC} = 0.2 T.

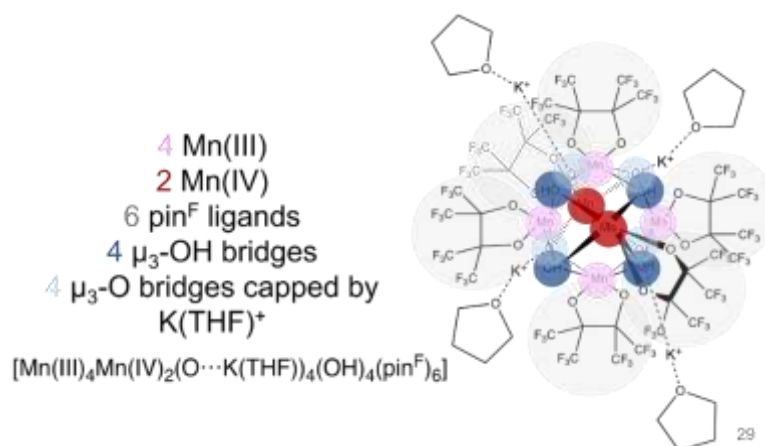


Figure 1. [Mn₆(μ₃-OH)₄(μ₃-OK(THF))₄(pin^F)₆] with colors indicating core components.

Organometallics Meet Emergence: Taking Advantage of the Molecular Precursor Approach for the Evolution of Electrocatalysts

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The low-temperature synthesis of inorganic materials and their interfaces at the atomic and molecular level provides numerous opportunities for the design and improvement of inorganic materials in heterogeneous catalysis for sustainable chemical energy conversion or other energy-saving areas. The transformation of molecules to materials is an emergence phenomenon, that is, the process creates novel complex properties of the resulting material entities which are absent in the starting material. Using suitable organometallic single-source precursors for functional inorganic nanomaterial synthesis allows for reliable control over uniform particle size distribution, stoichiometry which can help to reach desired chemical and physical properties.^[1] In my talk, I would like to outline selected achievements and challenges of the molecular precursor approach in light of recent developments of molecule-to-



nanomaterials synthesis for renewable energy applications, relevant for the oxygen evolution reaction (OER), hydrogen evolution reaction (HER) and overall water-splitting. Electrochemical water-splitting into hydrogen (H₂) and oxygen (O₂) is widely regarded as a promising approach to producing environmentally-friendly fuel for future energy supply. In the recent years, inexpensive, earth-abundant and environmentally benign transition-metal oxides, hydroxides and other functional self-supported materials in conjunction with semiconducting co-catalyst that can independently catalyze OER and HER have been established.^[2,3] Still the major challenge is to provide reliable catalyst systems for HER, OER and overall water-splitting which are highly efficient, robust and long-

term stable at least for several months without losing activity. The advantage of using the soft molecular precursor approach over CVD and classical solid-state methods will be discussed.

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Application of Metal-based radical initiators for the determination of the antioxidant/prooxidant activity of phenols/polyphenols of food

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Phenolics are activated by V^V and/or V^{IV} coordinated catalytic sites in the lipophilic matrix of oil mediated by dioxygen activation; in this oxidative environment free radicals are trapped by α -tocopherol to give α -tocopheryl radicals monitored by X-band cw-EPR vs time providing very useful quantification tool for the determination of the ability of the complexes to initiate radicals¹. The possibility to quantify α -Tocopherol in extra virgin olive oils by EPR spectroscopy has been investigated using vanadium (V) lipophilic metal complexes as radical initiators¹. The experimental results showed that there is a relationship between the intensity of the signal of the α -Tocopheryl radical in the EPR spectrum and the concentration of α -Tocopherol contained, upon addition in food samples The α -Tocopherol concentration values determined for the olive oils were validated by comparison with those determined by the ¹⁹F NMR method².

The metal-based radical initiators have also been applied for the investigation of the phenol/polyphenol content conducted through spin trapping on α -tocopheryl radicals, whereas, parameters associated to the nature of the phenolic compound and their prooxidant/antioxidant activity are determined through the kinetics of the radical initiation through O₂ activation reactions

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A robust Al³⁺ MOF as a highly selective As(V) sorbent and efficient luminescence probe for Cr(VI) and water.

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Herein, we report the synthesis and characterization of a new, non-porous Al³⁺ metal–organic framework MOF, [Al(OH)(PATP)]·solvent (**Al-MOF-1**, with PATP²⁻ = 2-((pyridin-2-ylmethyl)amino)terephthalate). **Al-MOF-1** exhibits superior chemical robustness from highly acidic (pH = 2) to basic (pH = 12) aqueous solutions or in the presence of As(V) and Cr(VI) oxoanions, in contrast to the related MIL-53(Al) MOF (Al(OH) (BDC), with BDC²⁻ = terephthalate). **Al-MOF-1** was found to be an effective sorbent toward As(V) with a sorption capacity of 71.9 ± 3.8 mg As/g, rapid sorption kinetics (equilibrium time ≤1 min), and high selectivity over various competing anions. Aiming at a practical wastewater treatment, we have also immobilized **Al-MOF-1** on a cotton substrate, coated with polydopamine. The fabric sorbent exhibited effective removal of As(V) species from aqueous media under either batch or continuous flow conditions. Furthermore, **Al-MOF-1** was proved to be a promising luminescence sensor for detecting trace amounts of Cr(VI) in real water samples.

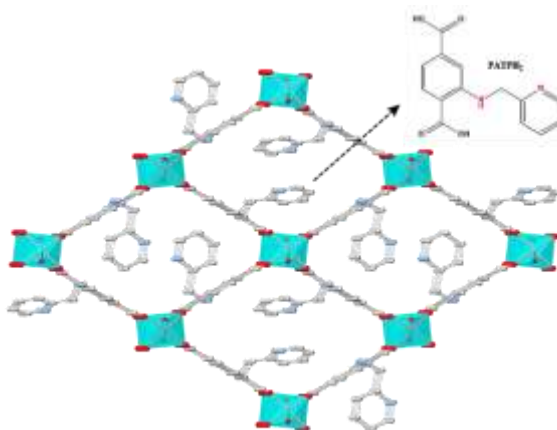


Figure. Representation of the structure of Al-MOF-1 (C, gray; O, red; N, blue; and Al, turquoise).

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Molecular Nanoparticles of Mixed-metal Oxides: Synthesis and Characterization of Ce/Ti-oxo Clusters

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CeO₂ (ceria) is a versatile metal oxide whose nanoparticles are finding a wide array of applications in our modern society, ranging from environmental remediation and renewable energy technologies, through biomedical applications. Nevertheless, there remains questions regarding their mechanism-of-action owing to the inherent drawbacks in traditional nanoparticle syntheses (e.g., polydispersity) and characterization techniques (e.g., limited resolution). Employing the complementary molecular bottom-up approach to ultra-small nanoparticles of CeO₂, we recently opened an avenue to explore some of these hotly-debated questions with atomic-level insight. A family of so-called "molecular nanoparticles of CeO₂" has been developed that represents a series of ultra-small (≤ 2.4 nm) nanoparticles of CeO₂ obtained as molecules, and these have allowed structural characterization to atomic resolution by single-crystal X-ray crystallography [1]. This success reflects our robust control of various factors involved in the synthesis of these molecular materials and the study of their structural/physical properties.

More recently, new thrusts have been initiated in the catalysis field to improve the catalytic activity of traditional CeO₂ nanoparticles by incorporation of a heterometal (M/CeO₂) [2]. While this method has enhanced the activities of these materials, doing so only increases their complexity, further limiting our ability to characterize these systems. To garner insight into these more complicated materials, a series Ce/Ti-oxo molecular clusters has been synthesized and characterized, and these products have been found to serve as molecular models for mixed-metal oxide surfaces and interfaces in the catalytically-active Ti/CeO₂ phases. The detailed syntheses, crystal structures, and catalytic potential of these clusters will be discussed.

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[2] S. Das Gupta., A. Thuijs, E. Fisher, K. Abboud, and G. Christou, *Inorg. Chem.*, **2022**, Article ASAP. DOI: 10.1021/acs.inorgchem.1c03719.

Magneto-Chiral Coordination Compounds Based on the 2-Pyridinemethanol Scaffold

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The introduction of chirality into molecule-based magnetic compounds opens up new opportunities for potential applications in the field of multiferroics, such as memory and logic devices owing to their potential capabilities for encoding information in both electric polarization and magnetization. In order for materials to exhibit ferroelectric properties, they need to have molecular structures that crystallize in non-centrosymmetric, polar point groups. With respect to studying the magneto-structural properties of homochiral molecule-based magnets, one of the major goals is to determine whether the inherent chirality suppresses the presence of an inversion center or mirror plane and then in turn, to investigate if this leads to different structural variations in the resulting coordination complexes when compared to their racemic counterparts. One of the most important factors for the construction of new coordination complexes with undiscovered topologies and nuclearities is the selection of the primary organic bridging and/or chelating ligands. Examples of such ligands employed in the field of 3d-metal cluster chemistry include 2-(hydroxymethyl)pyridine (hmpH), 2-(2-hydroxyethyl)pyridine (hepH), as well as 2,6-pyridinedimethanol (pdmH₂), and their derivatives. Despite the successful previous use of these ligands for the preparation of nanosized molecular clusters, high-spin molecules and single-molecule magnets, there has been limited progress in exploring the coordination chemistry of their chiral analogues. To address this, we have targeted the 3d-metal cluster chemistry of α -methyl-2-pyridinemethanol (mpmH),^[1] and its phenyl-derivative (ppmH), that can be prepared in both chiral and racemic forms (**Figure 1**). In this presentation, we will discuss our endeavors toward the synthesis and magneto-chiral study of several new 3d-metal clusters based on the ligands mpmH and ppmH.

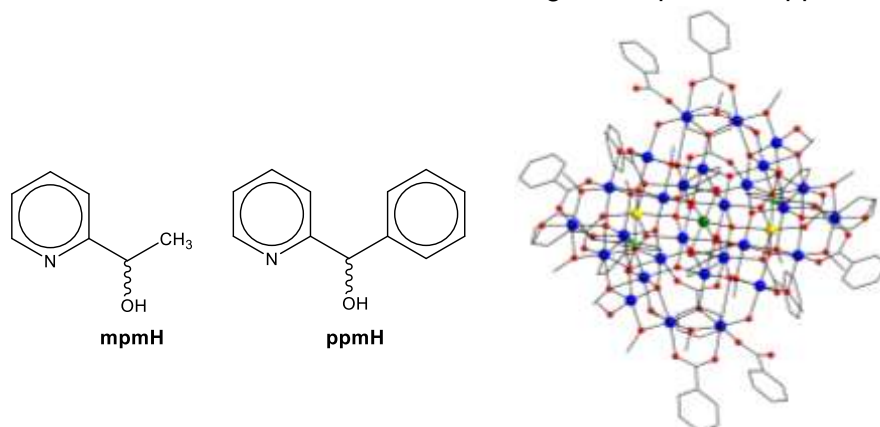


Figure 1. The ligands mpmH and ppmH (left) and the molecular structure of a {Mn₃₁} cluster derived from the use of mpmH (right).

[1] P. Abbasi, K. Quinn, D. I. Alexandropoulos, M. Damjanovic, W. Wernsdorfer, A. Escuer, J. Mayans, M. Pilkington, Th. C. Stamatatos, *J. Am. Chem. Soc.*, **139**, 15644-15647.

Designing Novel Nanoporous Materials for Applications in Energy and Environment.

From Multi-Scale Modeling to Materials Informatics.

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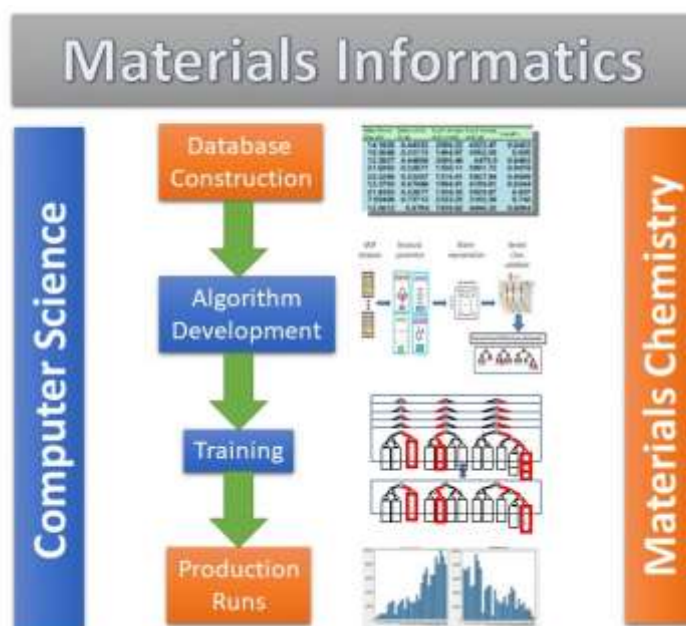
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Machine learning techniques (ML) are powerful tools already used in science and industry since their computational cost is by several orders of magnitude lower than that of the “conventional” approaches. However, their ability to provide accurate predictions strongly depends on the correct identification of those parameters (descriptors) that will allow the algorithm to effectively learn from past data. Other critical factors that affect the quality of the predictions are the size and the quality of the dataset used for the training of the algorithm as well as the correct estimation of the training size.

Aiming at both, the transferability of our model and the reduction of the training data set, we introduce different classes of descriptors, based on fundamental chemical and physical properties. On parallel, an automatic procedure of identifying the appropriate size of the training set for a given accuracy was developed. A novel training algorithm based on “Self-Consistency” (SC) replaced the standard procedure of linearly increasing of the training set.

Our SC-ML methodology was tested in 5.000 experimentally made MOFs for investigating the storage of various gases (H₂, CH₄, CO₂, H₂S, H₂O). For all gases examined, the SC-ML methodology leads to significantly more accurate predictions, while the number of MOFs needed for the training of the ML algorithm in order to achieve a specified accuracy can be reduced by an order of magnitude. In addition, the universality and transferability of our ML model was proved by predicting the gas adsorption properties of a different family of materials (COFs) after training of the ML algorithm in MOFs.



C₃H₄/C₃H₆ separation study in a flexible hybrid ultramicroporous material

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Propylene (C₃H₆) is a basic olefin and essential raw material for the production of a variety of chemicals including polypropylene, propylene oxide, acrylonitrile, cumene, butyraldehyde, and acrylic acid [1]. The industrial production of propylene mainly from cracking of naphtha or fractional distillation of hydrocarbons inevitably introduces trace amounts of propyne (C₃H₄) as impurities. The trace impurities must be removed to afford polymer-grade (≥99.95 %) propylene for downstream applications. C₃H₄ and C₃H₆ present similar physical and chemical properties with regard to their boiling points, kinetic diameter, and molecular weight. Therefore, it remains a huge challenge to develop an energy efficient and environment friendly separation approach to produce polymer-grade C₃H₆. Recently, crystal engineering approaches have been used to prepare a new-generation hybrid ultramicroporous material (HUMs) for gas separation [2]. However, C₃H₄/C₃H₆ separation is still understudied and there are only few reports available in the literature. In this context, we present a flexible HUM, which shows excellent C₃H₄/C₃H₆ separation performance.

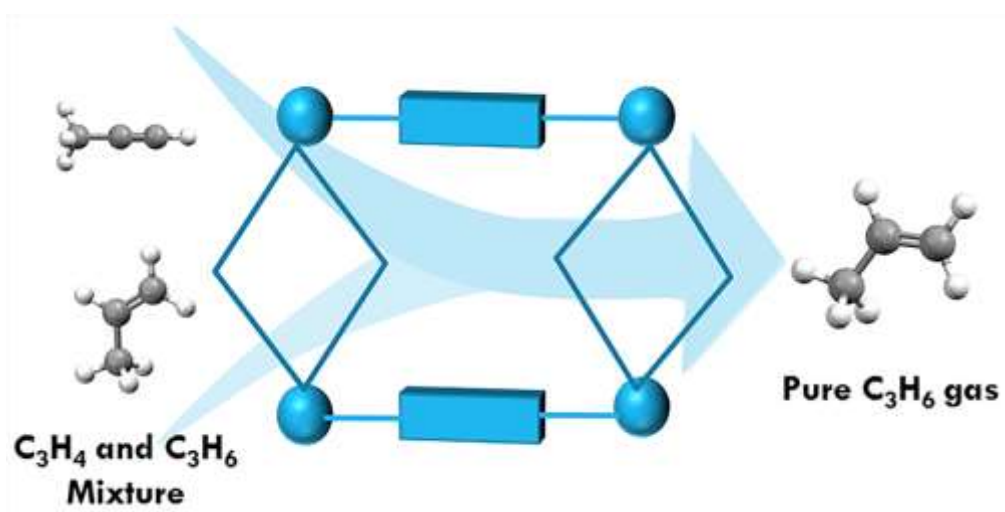


Figure. Illustration of a HUM exhibiting C₃H₄/C₃H₆ separation.

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2D functional hybrids using top-down and bottom-up synthetic approaches

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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, novel nanostructured materials based on 2D germanane (GeH)¹⁻⁴ and graphene-based matrices (graphene, graphene oxide and graphite nitrate)⁵⁻¹³ with high surface area, tunable pore size and aromatic 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, cytotoxic agents, effective adsorbents for environmental remediation, conductive inks and gas (H₂ and CO₂) storage materials will be discussed.

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Drug activation for the discovery and development of new targeted chemotherapeutic formulations

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Conjugation of a drug with a metal is the key for its biological activity enhancement. Moreover, 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 opportunity for synergistic effects, most notably when one of the components acts as a detector agent of the targeted intracellular component, cell, tissue etc and the other interacting with the desired biological system. In our laboratory we are examining closely the biological activity of new such conjugates of drugs, metabolite, anti-metabolites, and natural product ingredients with metals aiming in the development of new chemotherapeutic agents.

Clinical trials and epidemiological studies have shown that Non-Steroidal Anti-inflammatory Drugs (NSAID's) exhibit protective role against the incidence of mammary cancer. The conjugation of specific NSAID's with mitochondriotropic ligands, is used for the delivery of the drugs to mitochondria as "**Trojan horse**". The low toxicity against humans of silver(I) ions enables their use in the development of new metallotherapeutics.

The synthesis of a series of silver(I) metallotherapeutics of formulae $[Ag(D)(EAr_3)_n]$, (D= salicylic acid, aspirin, diclofenac, naproxen, nimesulide etc; E= P, Sb etc; Ar= Ph-, p-tolyl-, m-tolyl, o-tolyl) is reported. The compounds were characterized by spectroscopic (NMR, IR, Raman etc) and X-Ray diffraction techniques. These complexes were *in vitro* evaluated for their activity against human breast cells, MCF-7 (Hormone Depended) and MDA-MB-231 (Hormone Independent). Their toxicity was evaluated against normal human cells (normal human fetal lung fibroblast cells (MRC-5)).

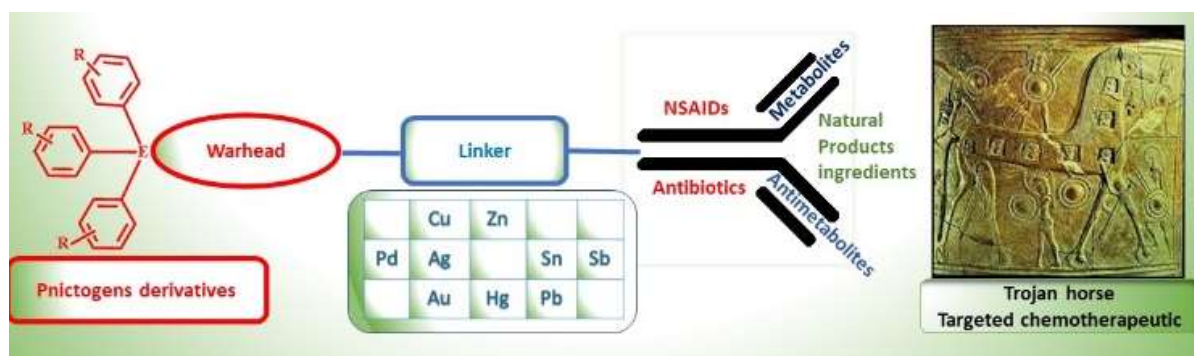


Figure. conjugation of pnicogens with NSAID in one entity

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Understanding the Magnetic Properties of Fe^{III}_x-oxo (x = 6, 7, 22) Clusters using a Two-pronged Experimental and Magnetostructural Correlation Approach

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Fe/oxo cluster chemistry is critical to such diverse fields as bioinorganic chemistry, materials science, and magnetism. As the magnetic properties of Fe^{III}/oxo clusters are important for various applications, it is crucial to quantitatively understand the nature of the pairwise Fe₂ magnetic exchange interactions, J_{ij} , to enable rationalization and/or prediction of ground state spins. Such a quantitative assessment of J_{ij} can also lead to identification of structural features that favor spin frustration and yield large ground state spins, S . Although multiple magnetostructural correlations (MSCs) for dinuclear Fe^{III}/oxo compounds have been developed over the years, we have found them less than useful for higher nuclearity Fe^{III}/oxo complexes. However, the various J_{ij} in high nuclearity Fe^{III}/oxo complexes are particularly difficult to determine from experimental or computational methods, owing to: (i) the many inequivalent J_{ij} typically present as nuclearity increases; (ii) the lack of a reliable MSC model for high nuclearity Fe^{III}/oxo clusters; (3) the increasing computational demands of theoretical methods as nuclearity increases; and (4) overparameterization and resulting false fits when fitting data with available fitting software.

To address these issues, our group has developed a semiempirical MSC for polynuclear Fe^{III}/oxo complexes based on the angular overlap model, finally providing a facile route to reliable J_{ij} from the Fe-O bond lengths and Fe-O-Fe angles within each Fe₂ pair in the clusters [1]. This has allowed, among other things, rationalization of experimental ground state S values, and reliable inputs for simulating and fitting the experimental data [1]. In recent work, we have employed the MSC for new clusters of Fe^{III}_x (x = 6, 7, 22) nuclearities to assist with data fitting, identification of spin frustration effects, and rationalization of the ground state S values. This work will be presented.

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Molecular Clock Qubits

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Electronic spins provide simple quantum states that can be manipulated using well developed magnetic resonance techniques. Meanwhile, coordination chemistry affords almost limitless tunability of such states in magnetic molecules, whilst also offering routes to large scale assembly via supramolecular approaches [1]. However, this flexibility comes at a cost in terms of coherence due to the inherent coupling to magnetic and vibrational noise associated with the environment [1,2]. This talk will focus on recent synthetic efforts aimed at protecting rare earth molecular spins from magnetic decoherence sources, with emphasis on so-called clock transitions – avoided level crossings associated with the Zeeman splitting of qubit states [1]. Spin clock transitions provide an optimal operating point at which the resonance frequency, f , becomes insensitive to the local magnetic field, B_0 . In this way, a molecular clock qubit is immune to magnetic noise [3]. There are several strategies for generating clock transitions. All that is needed is an interaction term in the spin Hamiltonian that does not commute with the Zeeman interaction. For molecules with integer spin (even number of unpaired electrons), the crystal field interaction can do the job [4]. Alternatively, clock transitions may be generated in rare earth ions possessing half-integer spin states (odd number of unpaired electrons) via the electron-nuclear hyperfine interaction, a strategy that is employed widely in trapped-ion quantum devices. Crucially, in the molecular case, the hyperfine interaction can be controlled using coordination chemistry to maximize unpaired electron spin density at the relevant nuclear site. A recent example involving a Lu^{III} ([Xe]4f¹⁴5d¹) organometallic compound has demonstrated that this is possible by varying the degree of s-orbital mixing into the spin-bearing d-orbital [5]. This approach has the added advantage of increasing the s-orbital character, which also reduces spin-orbit coupling that, in turn, suppresses spin-lattice relaxation – one of the other stubborn decoherence mechanisms in molecular spin qubits. The talk will provide an introduction to spin qubits, decoherence and the principles via which clock transitions protect molecular qubits against magnetic noise. This will be followed by a survey of the synthetic strategies that have been employed up to now for developing molecular rare earth clock qubits, together with the spectroscopic studies that demonstrate their enhanced coherence. To conclude, potential implementations of molecular clock qubits in future quantum technologies will be discussed.

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Physics and Optoelectronic Applications of Perovskite Nanocrystals

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Perovskite nanocrystals (PNCs) have emerged as outstanding light emitting materials exhibiting luminescence with near unity quantum yield and high optical gain that can be tuned across the visible spectrum via facile ion exchange reactions. The talk will review the main properties, prospects and challenges for PNC optoelectronics and present some recent work of the group on the spectroscopy and photonic applications of such nanomaterials.

In particular, the influence of surface ligands, encapsulation by polymers and solid-state processing on the photophysics and stability of PNC solids will be discussed. Furthermore, the high potential of PNCs as active gain media for optically pumped lasers and amplifiers will be demonstrated, providing examples of their outstanding optical amplification properties as thin films and in combination with solution-processed polymer resonators.

Chemistry and applications of 1,2,6-thiadiazines

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4*H*-1,2,6-Thiadiazines are important compounds as they find uses in the agrochemical and material sciences. While most syntheses of 1,2,6-thiadiazines rely on 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**)¹ as the thiadiazine starting material, we focused in developing the chemistry of 3,4,4,5-tetrachloro-4*H*-1,2,6-thiadiazine (**2**),¹ an overlooked but potentially versatile scaffold.

Tetrachlorothiadiazine **2** can be readily converted to 4-dicyanomethylene-1,2,6-thiadiazine **3**,² *N*-aryl-3,5-dichloro-4*H*-1,2,6-thiadiazin-4-imines **4**,³ 3,5-dichloro-4,4-dialkoxy-4*H*-1,2,6-thiadiazines **5** and 3,5-dichloro-4,4-bis(alkylthio)-4*H*-1,2,6-thiadiazines **6**.⁴ More recently, the degradation of tetrachlorothiadiazine **2** under reductive (dissolving Sn) or thermal conditions was investigated to reveal a plethora of interesting new fused heterocycles **9-12** identifying new chemistry of this system.

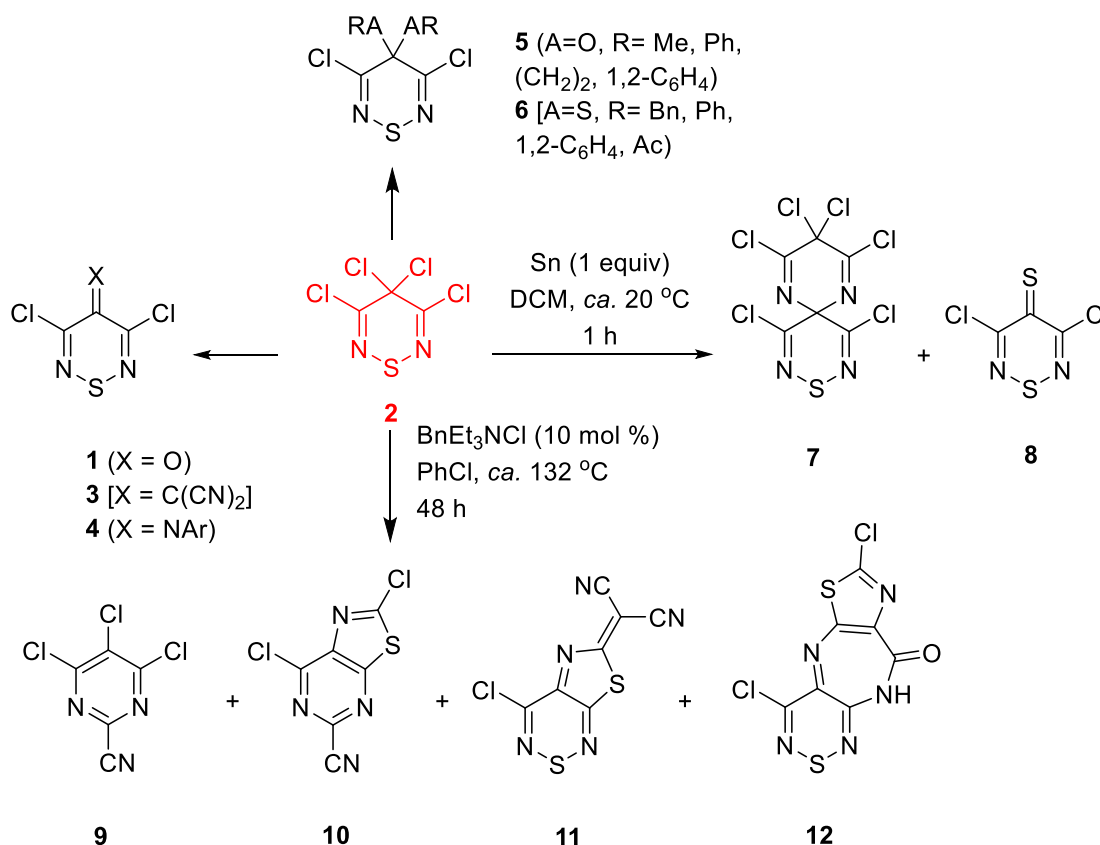


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Ring-fused π -delocalized stable radicals: Towards well-defined paramagnetic nanographenes

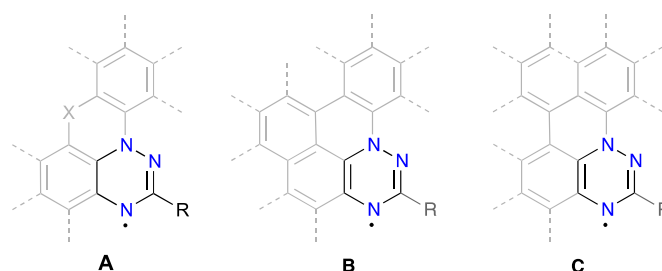
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The significance of large polycyclic aromatic systems (LPAS) and nanographenes is rapidly increasing mainly in the context of molecular electronics, spintronics, and photovoltaics. The bottom-up approach to nanographenes through LPAS avoids problems with lack of uniformity of graphene sheets and processing issues, and permits synthesis of well-defined materials of variable size of the π system with precisely tuned properties for specific applications. This approach drives the development of synthetic methods for functional LPAS and structure-property relationship studies in the context of modern technologies.

Paramagnetic LPAS with an electron spin extensively delocalized in the π system are rare and are of interest due to their magnetic properties, low band gap and favorable electrochemical behavior. We have envisioned three general classes of such paramagnetic LPAS (**A**, **B** and **C**), which could be obtained by formal docking of the 1,4-dihydro[1,2,4]triazin-4-yl unit with its *e* and *f* edges to closed-shell polycyclic aromatic and heteroaromatic systems. During the past several years we have developed synthetic strategies to all three systems and demonstrated several general cyclization methods [1] leading to the formation of stable polycyclic radicals. Analysis of several dozen available such derivatives permitted establishing extensive structure-property relationships. The largest system obtained thus far contains 29 π delocalized electrons.



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Reductive Activation of O₂ to O₂²⁻ from a Vanadium(IV) Species: Mechanism and Its Use in Fuel Cells

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Abstract

Reductive O₂ activation *via* oxidative addition of the molecular dioxygen to a transition metal center¹⁻² is a central reaction in biological, catalytic and green energy storage processes. Of particular interest is the two-electron O₂ reduction to produce H₂O₂, because H₂O₂ is a green renewable source of energy and clean oxidizing agent. In addition, it is of high economic and environmental value the use of O₂ instead of peroxides in the catalytic oxidations reactions. Recently, An et.al³ have demonstrated a cheap, high performance, designed to propel vehicles zinc-hydrogen peroxide fuel cell, which consists of a vanadium battery regenerated by zinc and hydrogen peroxide respectively. These processes in fuel cells and metal-air batteries convert chemical to electrical energy and it is desirable to replace H₂O₂ with O₂. To achieve such a goal, it is required a catalyst with high rates, selectivity, and energy efficiency. Herein, we report on the first systematic study of the exploration of the mechanism of O₂ reduction from a V^{IV}O²⁺ -amidate ligand complexes. The intermediate species towards the formation of peroxides has been monitored by ¹H NMR, EPR, RAMAN, UV-Vis spectroscopies and electrochemistry for the first time. A galvanic cell has been constructed demonstrating that these materials can be used in vanadium-Zn|H₂O₂ fuel cells and energy storage devices in which the H₂O₂ can be synthesized *in situ* from the atmospheric O₂.

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Trace removal of benzene vapor using double-walled metal-dipyrzolate frameworks

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In principle, porous physisorbents are attractive candidates for the removal of volatile organic compounds (VOCs) such as benzene by virtue of their low energy for capture/release of this pollutant. Unfortunately, many physisorbents exhibit weak sorbate-sorbent interactions resulting in poor selectivity and low uptake when VOCs are present at trace concentrations. Herein, we report that a family of double-walled metal-dipyrzolate frameworks, BUT-53 to BUT-58, exhibit high benzene uptakes at 298 K and low pressure. Breakthrough experiments revealed that BUT-55, a supramolecular isomer of the MOF Co(BDP), captures trace levels of benzene producing an air stream with benzene content below acceptable limits. Further, BUT-55 can be regenerated with mild heat. Insight into the performance of BUT-55 comes from the crystal structure of the benzene-loaded phase (C₆H₆@BUT-55) and DFT calculations, which reveal that C-H...X interactions drive tight binding of benzene. Our results demonstrate that BUT-55 is a recyclable physisorbent that exhibits high benzene affinity and adsorption capacity, making it a candidate for environmental remediation of benzene contaminated gas mixtures.

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Water Uptake Process from Air by Metal Organic Frameworks: Molecular Simulations Study

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Atmospheric water in the form of droplets and vapour is considered as a huge reservoir and accounts for about 13000 trillion liters [1], making it a potential source to address the global crisis. Exploiting crystalline porous materials, e.g. metal organic frameworks (MOFs), is one of the suitable methods to trap water, accumulate water, increase the humidity level, and thus provide a much higher dew point temperature. Understanding the atomic-level dependency of different water configurations and models with molecular simulations could be economically efficient and lead to general screening procedures to identify new candidates for faster water uptake kinetics. In this work, we used grand canonical Monte Carlo (GCMC) and molecular dynamics (MD) simulations to study the water adsorption isotherm of hydrophobic material **ROS-39** and its analogues obtained by adding a hydrophilic functional groups to its ligand to form **ROS-40** and **ROS-41**, respectively. The GCMC simulations predicted well the adsorption step of experimental isotherm when specific water model and configuration were used. MD simulations of a 2D slab are performed to explain the difference between higher uptake of water between GCMC simulations and experimental data (**Figure 1**).

Our systematic computational approach suggests the relevant configurational space of water needs to be extended for GCMC-simulations of water capture/release to predict experimental adsorption isotherms. We believe that future in-depth study of the onset of water sorption at the MOF external surfaces, employing different water configurations, will assist us in identifying other candidates for water uptake from air.

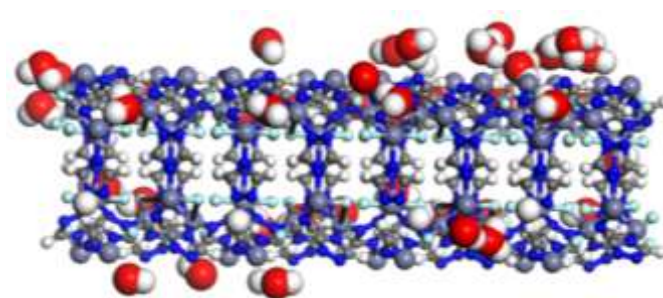


Figure 1. Snapshot of water film forming on the external surface of 2D **ROS-39** slab obtained with MD simulations. (Colour codes: N, blue; F, turquoise; Zn, lavender; O, red; H, white; C, grey).

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Sustainable Cu-based methods for valuable organic scaffolds

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Copper is an abundant, low cost and redox-plural (0/I/II/III) transition element, and frequently, its salts or complexes are used efficiently for molecular transformations of natural products, bioactive molecules, agrochemicals, and organic functional materials, thus representing an ideal candidate for developing sustainable metal-based catalytic protocols. Current, green and sustainable process development trends involve alternate energy inputs, i.e., microwaves, mechanochemistry, photochemistry, and produce functional chemicals with the utmost level of waste minimisation. This work details recent sustainable Copper-based methodologies that yield organic scaffolds of high pharmaceutical importance, such as but not limited to propargylamines, pyrroles, and dihydropyridines.

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Tuning the Adsorption Isotherm Shapes in Metal-Organic Frameworks

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In recent years, the rapid industrial growth paired with the environmental crisis the world is facing have created serious issues for scientists to address. The need for the reduction of CO₂ emissions to meet environmental goals by 2030 has led to the development of several carbon capture technologies, but also caused a shift to cleaner energy sources, such as natural gas. In this context, physisorbents behave in an advantageous way compared to chemisorbents, due to their significantly lower energy barrier upon capturing and regenerating guest molecules. Among physisorbents, flexible metal-organic materials (FMOMs) have emerged as a new energy-efficient class of materials able to overcome previous limitations of rigid sorbents. Switching materials are a subset of FMOMs, which can transform between closed to open phases when exposed to external stimuli, thus resulting in “gate-opening”. This behaviour corresponds to Type F-IV adsorption isotherms (Figure 1), which are highly desirable for storage applications, due to offering increased working capacities. Therefore, reliable control over the adsorption behaviour of FMOMs is necessary in order to achieve an optimum sorbent. Although fabricating a material with targeted capabilities is proven to be challenging, several strategies employed in the literature were successful in obtaining structure-property relationship information. This work introduces an innovative approach to tune the adsorption isotherm shapes of FMOMs, by generating additional symmetry in the components of a new FMOM platform.

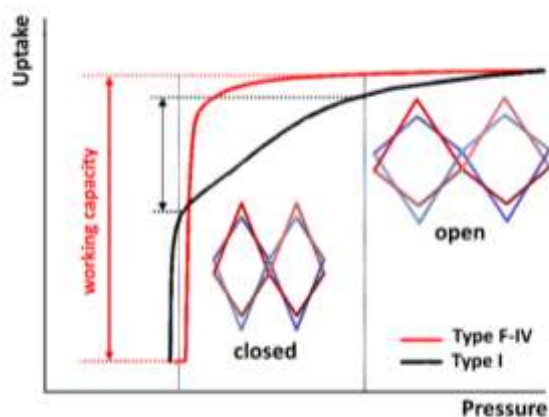


Figure 1. Type F-IV isotherms provide increased working capacities.

Isorecticular Design of Two Novel Metal Organic Frameworks and Their Single-Crystal-to-Single-Crystal Solvent Exchange Properties

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The synthesis and study of metal-organic frameworks (MOFs) have attracted significant attention because such compounds exhibit aesthetically pleasing structures and several important potential applications in diverse areas including gas storage and separation, magnetism, drug delivery, catalysis, etc. During MOF evolution, the most important milestones were the development of isorecticular synthesis¹ and postsynthetic modification² which allow tailoring of desired pore size/shape and properties.

We shall discuss the synthesis of two novel 3-dimensional microporous MOFs based on the Schiff base ligand 5-({4'-carboxy-(1,1'- biphenyl)-4-yl}methylene)amino)isophthalic acid (CBIPH₃) formulated as $\{[\text{Cd}_3(\text{CBIP})_2(\text{DMF})(\text{H}_2\text{O})_2]_n \cdot 8n\text{DMF} \cdot 4n\text{H}_2\text{O}\}_n$ **[1]** and $\{[\text{Nd}(\text{CBIP})(\text{DMF})(\text{H}_2\text{O})]_n \cdot 1.5n\text{DMF} \cdot 3n\text{H}_2\text{O}\}_n$ **[2]**.³ Interestingly, we were able to investigate a series of single – crystal – to – single – crystal (SCSC) transformation reactions in the case of compound **[2]**. These SCSC reactions involved the exchange of the coordinating and lattice solvent molecules of compound **[2]** and led to five new exchanged analogues formulated as $\{[\text{Nd}_2(\text{CBIP})_2(\text{DMF})_2(\text{H}_2\text{O})_2] \cdot 2(\text{benz})\}_n$ **[2@benz]**_n, $\{[\text{Nd}_2(\text{CBIP})_2(\text{DMF})_2(\text{H}_2\text{O})_2] \cdot 2(\text{tol})\}_n$ **[2@tol]**_n, $\{[\text{Nd}_2(\text{CBIP})_2(\text{DMF})_2(\text{H}_2\text{O})_2] \cdot 2(\text{m-xyl})\}_n$ **[2@m-xyl]**_n, $\{[\text{Nd}_2(\text{CBIP})_2(\text{DMF})_2(\text{H}_2\text{O})_2] \cdot 2(\text{o-xyl})\}_n$ **[2@o-xyl]**_n and $\{[\text{Nd}_2(\text{CBIP})_2(\text{NMP})_4] \cdot 2(\text{H}_2\text{O})\}_n$ **[2@NMP]**_n.

Overall, two new MOFs are discussed based on an elongated semi-rigid tricarboxylic ligand that has not appeared previously in MOF chemistry. Compound **[2]** was proven to be an excellent platform to study SCSC exchange reactions even with fairly bulky organic molecules due to the flexible coordination sphere of the Nd(III) ion and the presence of the CBIP³⁻ ligand which contains the semi-rigid imino group linkage that provides some flexibility to the framework.

Acknowledgement

This work was supported by the Cyprus Research and Innovation Foundation Research Grant "EXCELLENCE/1216/0076" which is co-funded by the Republic of Cyprus and the European Regional Development Fund

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Synthesis of canthin-4-ones and azepino-fused quinolones

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Canthinones are a subgroup of β -carboline alkaloids, represented by canthin-6-ones and canthin-4-ones. More than 40 natural analogues of canthin-6-ones¹ have been isolated to date, but only three natural canthin-4-ones: tuboflavine, norisotuboflavine, and isotuboflavine have been reported. While scarce, both natural and synthetic canthin-4-ones, have potential in medicinal chemistry as they exhibit antimicrobial activities, and phosphodiesterase-inhibitory activity.² Accessing diverse libraries of canthin-4-ones for structure activity relationship studies remains limited owing to the lack of good general syntheses. Early and recent routes to canthin-4-ones, are based on β -carboline precursors, proceeding via construction of the D-ring, thus diversification of the carboline backbone is limited. Herein, we describe a short synthesis of canthin-4-ones, and isocathin-4-ones, via construction of the B-ring which enables, facile diversification of the A ring. Furthermore, we describe the unexpected formation of azepino-fused quinolone as minor side products and reveal an alternative target orientated synthesis to access them in high-yield.

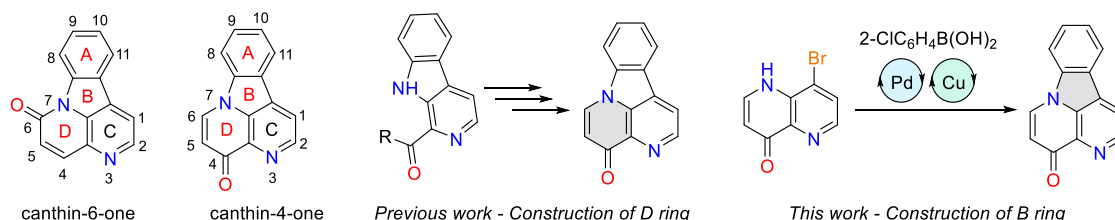


Figure 1. Synthesis of canthin-4-ones.

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Electrospun Fe₃O₄-Containing Superparamagnetic Fibrous Materials

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Polymer fibers with diameters in the nano- and micrometer size range attract high attention nowadays due to their unique properties including high surface to volume ratios, composition tailoring and facile introduction of multifunctionalities. One of the most versatile techniques employed for generating nano- and microfibers is electrospinning. Electrospinning that has already reached the industrial sector, can be used for the fabrication of polymer, ceramic and polymer-based nanocomposite fibers. The latter may be accomplished through the incorporation of inorganic nanoparticles within polymer fibers during electrospinning or *via* their anchoring onto the fibers' surfaces by following post-modification strategies. This fact renders the technique highly attractive and competitive in biomedical, optoelectronic, environmental, sensing, catalytic and energy-related applications.

In this presentation selected polymer-based electrospun nanocomposite fibrous systems will be discussed, including magnetite-containing electrospun microfibers and microrods with applicability in the biomedical field [1] and in water remediation processes [2, 3], white magnetic paper with zero remanence [4] and superparamagnetic nanocomposite fibrous mats employed in gas and pH sensing [5].

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Breaking the trade-off between selectivity and adsorption capacity for gas separation by a family of ultramicroporous physisorbents

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The trade-off between selectivity and adsorption capacity with porous materials is a major roadblock to reducing the energy footprint of gas separation technologies. To address this matter, we report herein a systematic crystal engineering study of C₂H₂ removal from CO₂ in a family of hybrid ultramicroporous materials (HUMs). The HUMs are comprised of the same organic linker ligand, three inorganic pillar ligands and two metal cations, thereby affording six isostructural **pcu** topology HUMs. Whereas all six HUMs exhibit strong binding sites for C₂H₂ and weaker affinity for CO₂, the tuning of pore size and chemistry enabled by crystal engineering resulted in benchmark C₂H₂/CO₂ separation performance. Fixed-bed dynamic column breakthrough experiments for an equimolar (*v/v* = 1:1) C₂H₂/CO₂ binary gas mixture revealed that one sorbent, SIFSIX-21-Ni, is the first C₂H₂ selective sorbent that combines exceptional separation selectivity (27.7) with high adsorption capacity (4 mmol·g⁻¹).

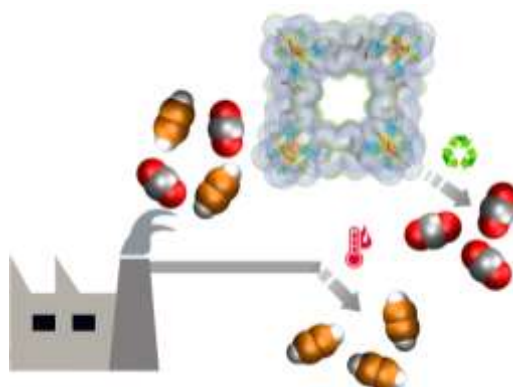


Figure. Schematic illustration to show C₂H₂/CO₂ separation by a hybrid ultramicroporous material.

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Metal Organic Frameworks (MOFs) based Surface Enhanced Raman Scattering (SERS) substrates towards emerging contaminants detection

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Metal–organic frameworks (MOFs) have emerged as an extensive class of crystalline materials with widespread application in storage of gases such as hydrogen and methane, and as high-capacity adsorbents to meet various separation needs. Recently MOFs have gained attention as promising materials for aqueous-phase sorption of emerging contaminants (ECs) mainly due to their high surface area, tunable porosity, hierarchical structure, and recyclability. The performance of MOFs and their selectivity toward targeted molecules can be regulated by judicious selection of metal ion and organic linker. A range of water-stable MOFs (e.g., MIL-53, MIL-100, MIL-101, UiO-66, and MIL-125) and their composites with other materials have been reported to adsorb ECs from water in their structures [1].

On the other hand, recent efforts are focused on the exploitation of MOFs potentiality as Surface Enhanced Raman scattering (SERS) substrates for the detection of molecules [2, 3], since they provide additional advantages on stability, target concentration, and selectivity to conventional SERS substrates. In the present work, we attempt, following a certain strategy (Fig. 1) to develop and investigate MOF based SERS substrates for the challenging detection of emerging environmental contaminants (i.e. Per- and polyfluoroalkyl substances, PFAS).

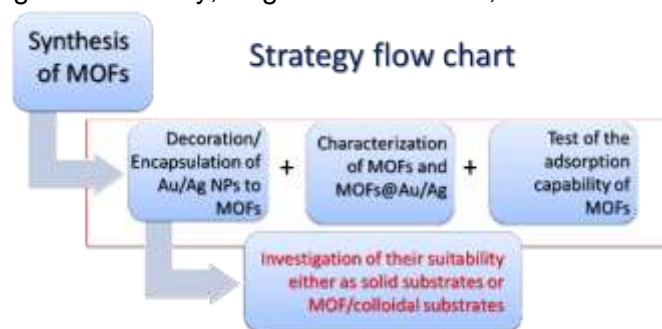


Figure 1. Strategy flow chart.

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Acknowledgments

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The Chemistry of Super-Reduced Uranium

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The oxidation state of an element is one of the most established, fundamental concepts in chemistry. The discovery of elements in new oxidation states is, nowadays, rare. The pursuit of stable compounds containing elements in previously unseen oxidation states is motivated by the fundamental insight obtained into bonding and electronic structure, and the possibility of using these species for further chemistry. A striking example of a main group element in an unprecedentedly low oxidation state is magnesium(0).^[1] Following the pioneering work of Lappert,^[2] the divalent oxidation state is now known for all the rare-earth elements.^[3] Several divalent uranium and later-actinide compounds were also subsequently isolated.^[4]

Recently, we reported the divalent uranium metallocene $[(\eta^5\text{-C}_5\text{Pr}_5)_2\text{U}]^{[5]}$ and have since studied its reactivity. Trivalent uranium is a well-known strong reducing agent, hence the *obvious* next step was to examine the reactivity of the divalent uranocene towards oxidizing agents, because that's what everyone expects us to do. Instead, we examined the reactivity of $[(\eta^5\text{-C}_5\text{Pr}_5)_2\text{U}]$ towards reducing agents, asking the question 'is it possible to isolate monovalent uranium?'. Progress towards answering this question will be presented. In the meantime, here is a picture of something much more beautiful than any of our molecules:



Figure 1. Synthesis of a monovalent uranium metallocene?

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Luminescent Metal-Organic Frameworks as Chemosensors

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The diverse chemistry of metal-organic frameworks (MOFs) offers practically unlimited opportunities for functionalization, including the possibility to construct new luminescent materials through the introduction of luminescent units, 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. Depending on the functional groups on the bridging ligand and the choice of metal ions, we achieve sensitive and selective sensing of analytes including nitroaromatics and heavy metal ions in aqueous media.

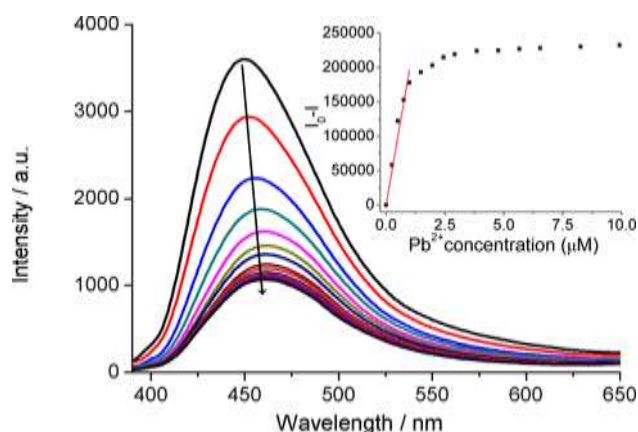


Figure. Fluorescence titration of an aqueous suspension of a Zr^{4+} MOF with Pb^{2+} ions.

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SYNTHESIS OF TYPE I [3:3] HEXAKIS ADDUCTS OF C₆₀ AS BUILDING BLOCKS FOR THE CONSTRUCTION OF A DYNAMIC COVALENT MOLECULAR CUBE

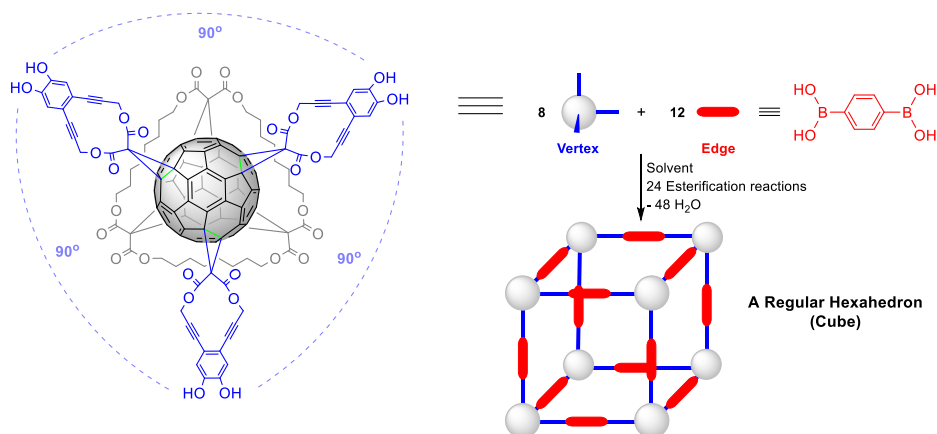
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The design and synthesis of type I [3:3] hexakis adducts of C₆₀ targeting the synthesis of a giant dynamic covalent molecular cubic structure, is presented. More specifically, these fullerene derivatives will function as the vertices of the cube while, phenyl diboronic acid spacers will represent its edges. Boronic esterification will be used to connect the catechol moieties with the boronic acid spacers in order to link the vertices of the cube with its edges by employing Dynamic Covalent Chemistry (DC_vC).

Up to date, only two molecular cubes have been synthesized using DC_vC. The first was prepared by Warmuth and co-workers^[1] and was constructed through the imine bond formation reaction between eight equivalents of chiral trialkoxy-triformylcyclobenzylene serving as the cube vertices and twelve equivalents of 1,4-phenylenediamine serving as its edges. The second one was prepared by Beuerle and co-workers^[2] and resulted from the dynamic boronic esterification reaction between eight equivalents of TBTQ used as the cube vertices and twelve equivalents of 1,4-phenylene diboronic acid used as its edges.

In the present work, hexakis adducts of C₆₀ were prepared consisting of monomalonate ester addends occupying three consecutive *equatorial* positions of the fullerene core. The remaining three *equatorial* positions are functionalized by a *cyclo*-[3]-octylmalonate ester macrocycle. The monomalonate ester addends contain triple bonds to ensure rigidity into their structure and bear catechol moieties as terminal functional groups which will serve as the connection points between the cube vertices and its edges. 1,4-Phenylene diboronic acid moieties were chosen to serve as the edges of the cube due to their linear geometry, rigidity and their capability of reacting with catechol moieties under DC_vC conditions.



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H₂O Sorption in a Switching 2D Coordination Network for Indoor Humidity Control

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Recently, water adsorbing materials have gained widespread interest because of their importance for many industrial applications which require water capture and release^[1]. As emerging water sorbents, flexible materials who can respond to chemical or physical stimuli through reversible structural transformation have displayed great performance on diverse applications of water adsorption. However, the deliberate design and synthesis of tunable porous solids with flexibility and high stability remain challenging. In this study, We report a 2D square lattice network **X-sql-1-Ni** which composed by two linear azo ligands and Ni ion that switches between non-porous (close) and highly porous (open) phases with effective and fast water sorption ability. The guest induced phase transition of **X-sql-1-Ni** was studied by single crystal XRD, in situ variable temperature PXRD and molecular modeling. The detailed structural analysis of rotation and twisting of ligands provides insight into the flexibility of **X-sql-1-Ni**. Through the introduction of ligands who bears a pendant group that act as building blocks for **X-sql-1-Ni**, the flexibility is achieved and S-shaped water sorption isotherms are featured. Meanwhile, **X-sql-1-Ni** possesses good thermal, chemical stability and recyclability which can maintain its good water uptake over 100 cycles without any working capacity reduction. Coincidentally, the hysteresis loop of water sorption isotherms located in 45%–65% RH which exactly is the recommended comfortable and healthy ranges of relative humidity for indoor ventilation. Its exceptional attributes of water-uptake working capacity/efficiency, recyclability and easy regeneration promise a great potential in confined indoor environment application.

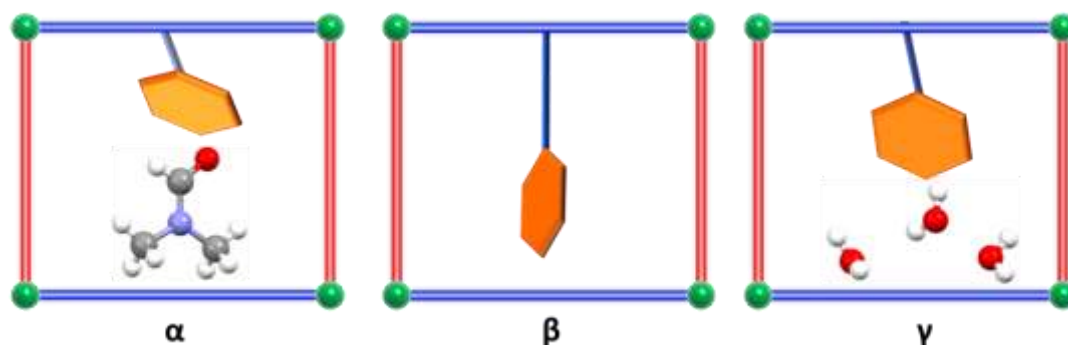


Figure. Scheme of a square lattice in three phases α (as synthesis phase), β (activated phase) and γ (water loaded phase) in **X-sql-1-Ni**.

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New 2-dimensional Cu²⁺ MOFs based on angular dicarboxylic ligands isolated from analogous synthetic routes

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Metal-organic frameworks (MOFs) have attracted a tremendous research interest due to their aesthetically pleasing crystal structures and numerous potential applications in various fields related to porous materials. As a result, several synthetic strategies have been employed targeting to the designed synthesis of functional MOFs. One of the most important strategies that are based mainly on the designed synthesis of MOFs with specific structural features that can lead to targeted properties, is the molecular building block (MBB) approach^[1] which involves the connection of well-known SBUs with the use of appropriate linkers giving rise to several new compounds with interesting structures and properties (**Figure 1a**).

In this presentation, we shall discuss three new microporous 2-D Cu²⁺ MOFs prepared from analogous synthetic procedures involving reactions of Cu(NO₃)₂·2.5H₂O with the angular dicarboxylic ligands shown in **Figure 1b**. Interestingly, these three compounds exhibit different structural features since [Cu₂(OBA)₂(DMA)₂]_n·2nDMA·11.5nH₂O (**1**)_n·2nDMA·11.5nH₂O and [Cu₂(HFPBBA)₂(DMA)_{1.42}(H₂O)_{0.58}]_n·5.5nDMA·11.5nH₂O (**2**)_n·5.5nDMA·11.5nH₂O are based on a Cu²⁺ - paddle – wheel SBU and exhibit 2-D structures with or without interpenetration, respectively, whereas compound [Cu(HSDBA)(μ-OH)]_n·nH₂O·0.7nDMA (**3**)_n·nH₂O·0.7nDMA is based on a 1-D Cu²⁺ chain SBU (**Figure 1b**). These compounds have been characterized with single-crystal X-ray crystallography, pXRD, variable temperature pXRD, TGA, IR and gas sorption studies^[2].



Figure 1: Representation of a) the dinuclear [Cu₂(COO)₄(DMA)₂] paddle-wheel SBU and b) the general synthetic scheme employed for the synthesis of compounds (**1**)_n - (**3**)_n discussed in this study.

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MOFs and MOF-based composites as superior sorbents for the removal of toxic oxoanions from aqueous media

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Metal Organic Frameworks (MOFs) are at the forefront of inorganic materials chemistry due to their intriguing structures, outstanding properties and strong potential for applications in various fields. MOFs, especially those based on Zr^{4+} metal ions, constitute probably the most promising sorbents for toxic and carcinogenic oxoanionic species (e.g. CrO_4^{2-} , $HAsO_4^{2-}$, $HSeO_3^-$ oxoanions), as they combine high porosity, exceptional stability in either acidic or basic aqueous media and capability for strong binding of the oxoanions to the metal centers.¹

In this presentation, we describe several Zr^{4+} MOFs that have been synthesized by our group as well as the detailed investigation of their oxoanion sorption properties. We also provide details of the structure of the anion-loaded materials obtained via powder X-ray diffraction methods. Finally, we show methods to fabricate the MOFs in forms that will allow their use in practical wastewater treatment.

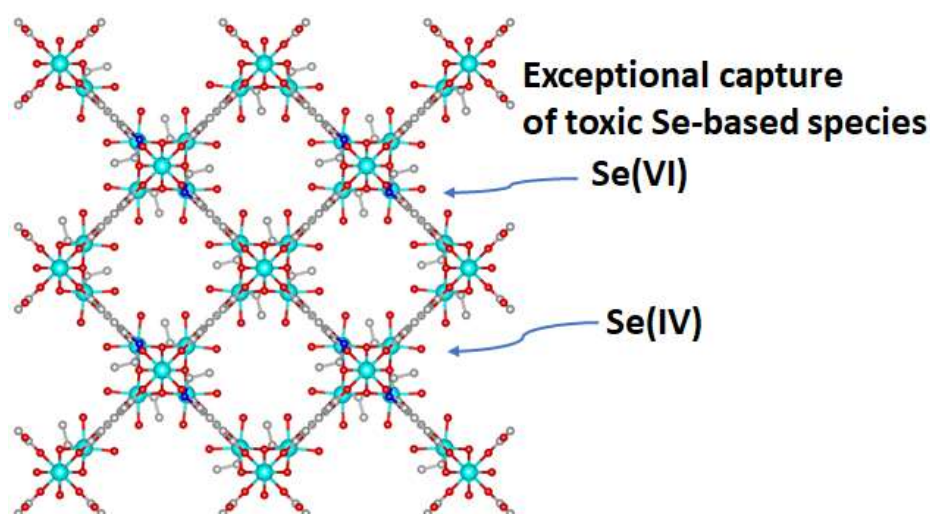


Figure. A Zr^{4+} MOF with exceptional capability for sorption of toxic Se(IV) and Se(VI) oxoanions.¹

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Incorporation of a tetrazine radical ligand in Ln₄ metallocene complexes with strong magnetic coupling and large coercive field

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Over the last years, the field of molecular magnetism has grown in fame with single-molecule magnets (SMMs) being one of the most active areas. The incorporation of paramagnetic ligands that can bridge lanthanide metallocenes has proven to be a fruitful avenue towards the isolation of strong magnetically coupled systems with enhanced SMM properties.^{1a} Although attempts towards this direction have been made, the synthesis of these systems has primarily been focused on dinuclear complexes, with the N₂³⁻ radical exhibiting remarkably high-blocking temperatures and large coercive fields.^{1b} Therefore, the need for an inorganic ligand that can lead to strongly coupled polynuclear radical-bridged Ln complexes still remains as it is not trivial to rationally incorporate N₂³⁻ or synthetically modify it. With this in mind we focused our attention on the relatively unexplored 1,2,4,5-tetrazine (tz). The diffuse spin orbitals of the tetrazinyl ring, ideally suited to penetrate the core-like electron density of the Ln ions, in addition to its four easily accessible nitrogen binding sites, promote greater chances for the isolation of a strongly coupled polynuclear system. Thus, by utilizing the high-performing {Cp*₂Ln}⁺ (where Cp* = pentamethylcyclopentadienyl; Ln = Dy or Gd) as building units while connecting them with tz⁻ radical ligands, the formation of two unprecedented tetranuclear complexes [(Cp*₂Ln)₄(tz⁻)₄]·3(C₆H₆), **Dy**₄ and **Gd**₄, was achieved. Through computational studies, simulation and fitting of the experimental direct current (dc) magnetic susceptibility of the **Gd**₄, supports the strong exchange coupling between the Gd^{III} ions and the tetrazinyl ring, with $J_{\text{Gd-tz1}} = -24 \text{ cm}^{-1}$ and $J_{\text{Gd-tz2}} = -15 \text{ cm}^{-1}$. Owing to this, the molecular species act as a true “giant-spin” system and promote the slow relaxation of the magnetization entirely through a thermally activated process for the **Dy**₄ analogue. Notably, hysteresis measurements reveal a sizeable coercive field of ~ 3 T, which makes this SMM one of the highest performing magnets in terms of magnetic hardness.



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Ru Three Ways: PACVD, FEBID and FIBID

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Precursor choice for any deposition method requires consideration of the reaction conditions and possible decomposition mechanisms for the particular method. This talk will present mechanism-based precursor design and deposition of Ru thin films and nanostructures by three different methods: Photo-Assisted Chemical Vapor Deposition (PACVD), Focused Electron Beam-Induced Deposition (FEBID) and Focused Ion Beam-Induced Deposition (FIBID).

Area Selective Deposition (ASD) on thermally sensitive patterned substrates is of interest for the manufacturing of electronic devices with organic components. We are developing techniques for deposition of Ru on organic substrates by PACVD, using terminal functional groups of self-assembled monolayers to define the growth and non-growth areas for ASD. In PACVD, the reaction with the surface is initiated by photolysis, but subsequent reactions on the substrate surface are thermal so an understanding of the precursor photochemistry and reactivity with surface functionality are necessary for precursor design. Examples of mechanistic studies and PACVD results for Ru deposition will be presented [1].

Techniques for fabrication of Ru-containing nanostructures have been of recent interest due to applications in building interconnect wires in semiconductor devices and, more importantly, the repair of photomasks for extreme ultraviolet lithography. Such nanostructures can be fabricated using FEBID and FIBID from organometallic Ru precursors. We are using mechanistic insights from electron- and ion-induced reactivity on surfaces and in the gas phase to design Ru precursors specifically for FEBID and FIBID [2]. Synthesis of candidate precursor complexes, evaluation of their reactivity with electrons and ions in the gas phase, and deposition of Ru-containing material under UHV surface science conditions and by conventional FEBID/FIBID will be discussed.

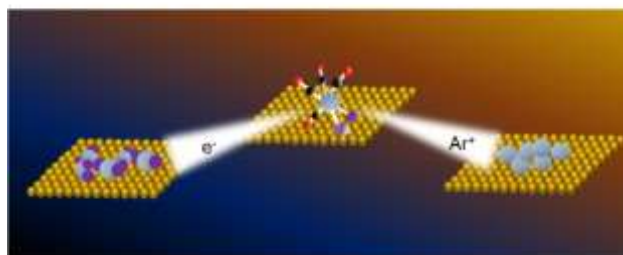


Figure. Representation of the results obtained from FEBID and FIBID using Ru(CO)₄I₂.

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Spin State Ordering and Domain Wall Formation in Ferroelastic Spin Crossover Complexes

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Competing electronic and structural order parameters in molecular crystals with capacity for spin state switching often result in complex symmetry breaking patterns and structural frustration. Recently we have observed strong magneto-elastic and magneto-electric coupling in two types of Jahn-Teller manganese systems where a new class of domain wall architecture could be induced by thermal manipulation of the spin state.[1],[2] We explore here domain wall architecture in different types of condensed matter systems such as ferromagnets and ferroelectrics, and examine where domain wall structure in spin-state ordered crystals sits in terms of magnitude and mobility Figure 1.

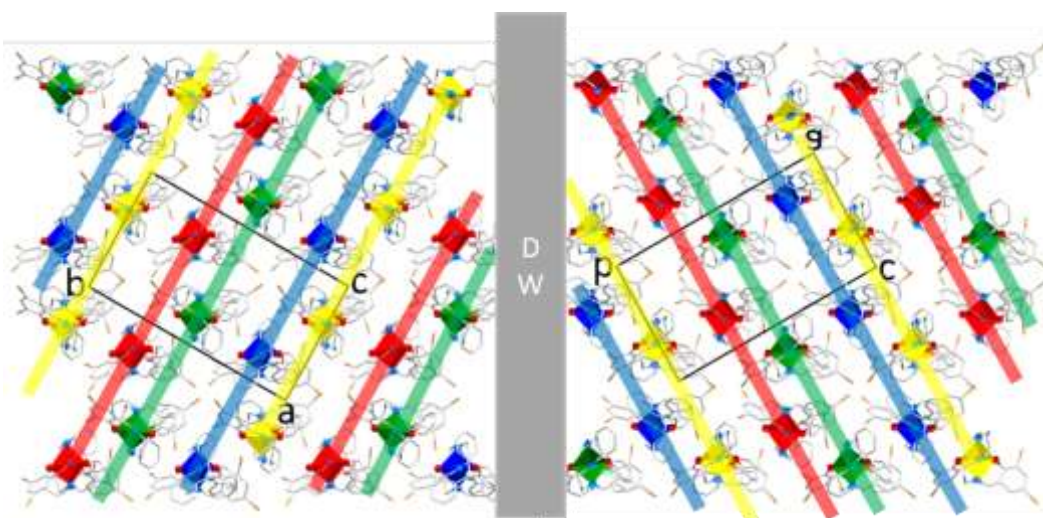


Figure. Domain wall formation in the spin-state ordered phase of a ferroelastic Mn³⁺ complex.

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Synthesis, characterization and potential applications of new oxalamide-based MOFs with 3d Transition Metal ions

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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 potentially empty voids [1]. Over the last years, our research group has been using oxalamide-based ligands as organic bridges. The exploitation of the tetra-carboxylic oxalamide ligand [N,N'-bis(2,4-dicarboxy-phenyl)-oxalamide (H₆L) with 3d transition metal ions afforded five new MOFs. Under solvothermal conditions in the presence of a base we obtained one 1D Ni-MOF, one 2D Fe-MOF, three isomorphous 3D MOFs based on Fe²⁺, Co²⁺ and Zn²⁺ as well as one 3D-Cu-MOF. The {[Ni(H₄L)(H₂O)₄]}_n·2H₂O was obtained in autoclave with the use of Et₄NOH while the same reaction system with Et₃N and Fe afforded the 2D {[Fe(H₄L)(H₂O)₂]}_n·2H₂O·0.5NMP. Similar reactions with excess of LiOH led to a new family of isomorphous MOFs with general formula {[M₂(H₂L)(H₂O)₅]}_n·2H₂O (M = Fe, Co, Zn). Finally the {[Cu₃L(H₂O)₂]}_n·2H₂O·4DMF was obtained with the use of LiOH after a month at room temperature. The two Fe-MOFs as well as the Co-MOF can be utilized as electrochemical electrode modifiers for glucose sensing because of their water stability and redox activity [2]. In addition, the MOFs which are based on paramagnetic metal ions such as Fe²⁺, Co²⁺ and Cu²⁺ may exhibit potential interesting magnetic properties [3].

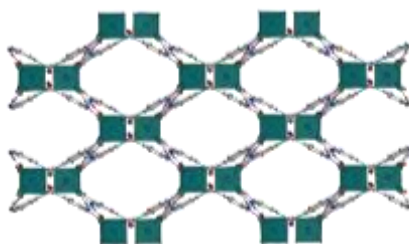


Figure: The structure of {[Cu₃L(H₂O)₂]}_n·2H₂O·4DMF.

Acknowledgment: This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH-CREATE-INNOVATE (project code:T2EDK-00028, MIS-5067540)

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Metal-Organic Frameworks based on hexanuclear secondary (M_6) ($M = Zr^{4+}$ and trivalent rare earth ions) building units and angular dicarboxylates with sorption and sensing capabilities

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We recently focused our attention on the synthesis of novel Zr^{4+} or trivalent rare earth (RE^{3+}) MOFs containing the hexanuclear SBU targeting to chemically stable MOFs that could be used for the removal and detection of various organic and inorganic species. Moreover, we utilized commercially available angular dicarboxylates possessing different functional groups to investigate the effect of such ligands in the structure and properties of the resulting MOFs. These efforts afforded 2D-8c-Zr-MOFs with the ligands $H_2HFPBBA$ (4,4'-(Hexafluoroisopropylidene)bis(benzoic acid)) ($[Zr_6(\mu_3-O)_4(\mu_3-OH)_4(HFPBBA)_4(OH)_4(H_2O)_4]_n$ - **UCY-13**) and H_2OBA (4,4'-Oxybis(benzoic acid)) ($[Zr_6(\mu_3-O)_4(\mu_3-OH)_4(OBA)_4(OH)_3(H_2O)_3(HCOO)]_n$ - **UCY-14**) that were stable in aqueous media, displayed appreciable internal surface areas and exhibited exceptional $U^{VI}O_2^{2+}$ sorption capability and selectivity.^[1] In fact, these findings triggered our interest on the synthesis, characterisation and applications of 2D MOFs. We thus, targeted the isolation of the analogous 2D MOFs of **UCY-13** and **UCY-14** based on RE^{3+} ions. However, the use of the angular dicarboxylic ligand H_2OBA (present in **UCY-14**) afforded a 12-c anionic **pcu**-MOF with the formula $\{((CH_3)_2NH_2)^+_2[RE_6(\mu_3-OH)_8(OBA)_6]_n\}(((CH_3)_2NH_2)^+_2(1)(RE); RE: Y, Tb, Dy, Ho)$ which proved to be a selective sensor for Cd^{2+} through an ion exchange mechanism.^[2]

The RE^{3+} analogue of **UCY-13** and **UCY-14** was isolated when the angular dicarboxylic acid ligand 4,4'-sulfonyldibenzoic acid (H_2SDBA) was used with the formula $RE_6(\mu_3-OH/F)_8(SDBA)_4(NO_3)_2(H_2O)_6]_n$ (**UCY-15(RE)**; RE: Y, Eu, Gd, Tb, Dy, Ho, Er). Compound **UCY-15(RE)** is an unusual example of a microporous 8-connected 2D network based on (RE^{3+}_6) -SBU. Thin films of **UCY-15(RE)** (RE: Y, Eu, Tb) embedded in polydimethylsiloxane (PDMS) were fabricated and evaluated for their sensing capability for vapours of selected VOCs and nitroaromatic compounds revealing different response to each analyte tested. A series of trimetallic analogues **UCY-15**($Y_{100-x-y}Eu_xTb_y$) ($x, y = 5, 7.5, 10$) were prepared aiming to superior sensing materials that combine the PL signals of **UCY-15(Y)**, **UCY-15(Eu)** and **UCY-15(Tb)**. The analogue **UCY-15**($Y_{87.5}Eu_{7.5}Tb_5$) achieved the emission of white light whereas **UCY-15**($Y_{87.5}Eu_5Tb_{7.5}$)@PDMS films was shown to selectively recognize the tested analytes.^[3]

Acknowledgements

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Metal-Organic Frameworks based on bis and tris-amide organic ligands

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Metal-Organic Frameworks (MOFs) have emerged as porous materials for a variety of applications. Over the last decade we have been synthesising families of organic bridging ligands that bear carboxylic acids and/or hydroxyl groups in their periphery and a bis or a tris amide backbone. In combination with various metal ions, including alkaline earth ions, transition metal ions and lanthanide ions, we have isolated a plethora of coordination polymers and MOFs. Some of the polymeric materials exhibit interesting magnetic properties or optical properties. Interestingly, some of the bis-amide ligands give rise to metal complexes that may serve as metallo-ligands for the construction of MOFs. The bis or tris-amide backbone of the ligands offers rigidity and hydrolytic stability to the resultant MOFs that enables them for applications in aqueous environments. To this end, several MOFs have been utilized as materials for the removal of heavy metal ions or their oxo-anions from waste waters while they have also served as electrode modifiers for the construction of electrodes for the electrochemical sensing of metal ions. Some of the MOFs are being utilized as electrode modifiers for the detection of glucose via electrochemical methods, aiming at the development of wearable devices that are capable of detecting glucose levels in human perspiration.

Acknowledgment: This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code: T2EDK-00028 / MIS 5067540).

Electron Energy States Resolved NMR crystallography: Detecting the invisible Dirac and Weyl Fermions in Topological Matter

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In the past decade there has been an explosion of interest regarding the role of topology in condensed matter physics. Undoubtedly, the most topical systems are topological insulators (TIs), hosting protected metallic electron states on their surface, and Dirac/Weyl semi-metals (DSM/WSMs) with the protected electron states residing in their bulk interior. The signature of nontrivial topology in all these materials is that the electron bands are crossing linearly ($E \sim k$) at specific points of the Brillouin zone, the so called Dirac or Weyl nodal points, granting a number of distinct quantum properties borrowed from High Energy Physics with unthinkable until today applications. Currently, the state-of-the-art method to detect topological electron energy bands is Angle Resolved Photoemission Spectroscopy (ARPES). However, despite the great effectiveness of ARPES, there is a particular shortage in monitoring and manipulating Dirac and Weyl fermions, which appear solely as low energy quasiparticle excitations.

Herein, we show that by applying DFT-assisted broadband solid-state Nuclear Magnetic Resonance (NMR) methods on specific TI and WSM systems, it is possible to resolve the hitherto invisible NMR signals assigned to the Dirac/Weyl electrons, thus enabling the detection of the - for long time searched - Dirac and Weyl Fermions.

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Polyurea-Crosslinked Biopolymer Aerogels: A New Class of Materials with Diverse Applications

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Biopolymer aerogels are attractive materials because they: (a) come from renewable (natural) resources; (b) are prepared in water; (c) bear a large number of functional groups available for coordination to metal ions, hydrogen bonding, functionalization etc.; (d) are biocompatible, biodegradable and non-toxic; and sometimes, (e) may be converted pyrolytically to carbon aerogels with ultra-high open porosities and surface areas. However, the main drawback of most biopolymer aerogels is that they are mechanically-weak materials. This was rectified recently with the synthesis of polyurea-crosslinked alginate (X-alginate) and chitosan (X-chitosan) aerogels [1-3]. For example, X-alginate aerogels can be as stiff as most organic aerogels at half or the one third of their density. X-alginate aerogels are hydrophobic, in contrast to native alginate aerogels that are extremely hydrophilic, and are stable in all aquatic environments with pH in the range of 3-9. In addition, certain X-alginate aerogels can be pyrolyzed to metal- and N-doped carbon aerogels in good yields. All the above render this new class of materials suitable for several applications, ranging from environmental remediation, to carbon electrodes and biomedicine (Figure 1).

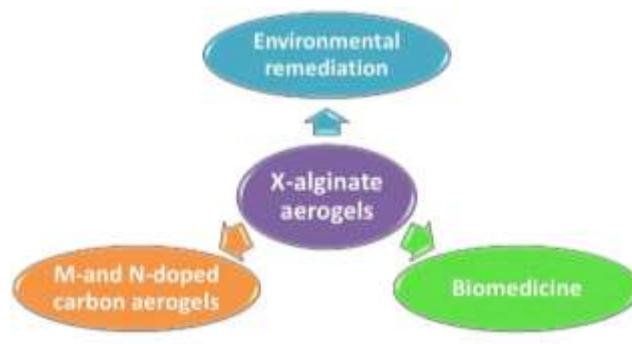


Figure 1. Polyurea-crosslinked alginate (X-alginate) aerogels and applications currently under study.

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Approaches to Calculate Magnetic Exchange Couplings in High Nuclearity Complexes

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The magnetic characterization of molecular complexes containing dozens or even hundreds of magnetic centers is at the heart of many biological processes, future technology developments, and materials science. Among the essential parameters that enter in the spin Hamiltonians used for this purpose, magnetic exchange couplings are the most elusive. The reason is that in most cases experimental methods are unable to provide a detailed characterization of the individual exchange couplings between all magnetic centers due to the multiple couplings present. In some cases, one can 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 typical molecular complexes of interest. Traditional methods to extract exchange couplings from DFT rely upon mapping the broken-symmetry DFT solutions to Ising-like spin model energies. These methods need a large number of energy evaluations and quickly become impractical for large, high nuclearity complexes. In this talk, I will review the existing methods to extract magnetic exchange couplings from DFT, with a particular focus on a method based on approximate perturbation theory that yields an Alder-Wiser style sum-over-states expression. This method is very attractive for this particular case since it can be very fast and can be automated to systematically screen a large number of diverse complexes. I will introduce some of our new developments based on local rotations of the magnetization in different flavors and show some examples such as Fe₂₂ and Fe₂₄ complexes.

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On the Way to 3d/4f-metal Coordination Complexes Using 2-pyridyloximate Ligands

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Molecular compounds (dimers, clusters, coordination polymers) possessing both 3d- and 4f-metal ions are relevant to a number of interdisciplinary research fields, including Molecular Magnetism, Optics, Catalysis and Materials Science. For the synthesis of mixed 3d/4f-metal complexes, one strategy and one route are often used. In both, the choice of the primary organic ligand is of great importance. Ligands that simultaneously have soft or intermediate basic sites (HSAB model) for preferential coordination of the 3d-metal ion (often intermediate or soft acid) and hard basic sites for selective binding of the oxophilic (hard acid) 4f-metal ion are preferable. In the last 10 years or so, we have been using deprotonated 2-pyridyl oximes for the construction of 3d/4f-metal compounds (Figure 1) [1].

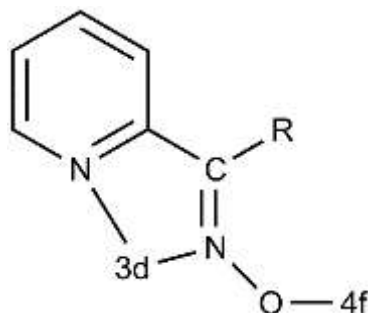


Figure 1. Our approach for the synthesis of 3d-metal complexes (R= H, Me, Ph, NH₂, 2-pyridyl).

Our talk will cover many aspects of the synthetic chemistry that has led to discrete 3d/4f-metal complexes which contain 2-pyridyloximates as primary ligands. Examples from “one-pot” routes, the “metal complexes as ligands” strategy and the “assisted self-assembly” approach will be described, with emphasis on design principles. Complexes containing the metal combinations {Ni^{II}Ln^{III}}, {Fe^{II}Dy^{III}}, {Zn^{II}Ln^{III}}, {Co^{III}Dy^{III}}, {Ni^{II}₂Ln^{III}}, {Co^{III}₂Ln^{III}}, {M^{II}Ln^{III}₂}, {Ni^{II}₂Ln^{III}₂}, {Co^{III}₂Ln^{III}₂}, {Fe^{II}₂Dy^{III}₂}, {Cr^{III}₂Ln^{III}₂}, {Co^{III}₄Dy^{III}₂}, {Ni^{II}₄Ln^{III}₄} and {Ni^{II}₈Ln^{III}₈} have been isolated mainly from our group, but also from other groups. Magnetic and optical properties of selected compounds will be briefly mentioned.

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MOF-74 Analogues and Cu(II) compounds as electrode modifiers for the electrochemical detection of glucose in human perspiration and / or glucose sorption.

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Monitoring glucose levels in human organism has met a great rise of interest due to the importance of this particular biomarker's effect in the human body. A slight variation of glucose levels in blood, outside the normal boundaries, can lead to a series of disfunctions, the most common being diabetes mellitus, leading to kidney failure, heart disease, and blindness [1]. Nowadays, commercially available glucose measuring devices are based on invasive techniques to acquire the analyte, and on enzymatic techniques for the determination of glucose levels. The enzymatic approach, although featuring good selectivity and high sensitivity, suffers from high production costs and variables (temperature, pH, humidity) that can affect the sensor's accuracy as a result of the enzyme's activity [2].

Since patients are more reluctant to undergo periodical invasive, and sometimes painful clinical tests to measure their glucose levels, the need for a non-invasive and painless measuring technique has grown to be of vital importance. An electrochemical approach to this problem promises such a technique by exploiting the presence of glucose in human perspiration (12.5 – 400 $\mu\text{mol} / \text{L}$), which can be determined either periodically or can be monitored in real time.

Moreover, the replacement of enzymatic techniques is of great importance, intended to cost reduction and stability improvement. To this point, the idea of using metal complexes and Metal-Organic Frameworks (MOFs), based on metals with red-ox capabilities, as electrode modifiers is of great interest. MOFs are porous coordination polymers based on metal ions or clusters, bridged by organic ligands. In most cases they are characterised by great thermal and water stability, catalytic capabilities, and remarkable porosity. In this work, MOF-74 [3] analogues based on bis-amide ligands and three Cu(II) complexes have been synthesised in order to study their ability to be utilized as electrode modifiers for the detection of glucose via electrochemical methods, aiming at the development of wearable devices that are capable of detecting glucose levels in human perspiration. Furthermore, the MOF-74 analogues are studied as glucose sorbents.

Acknowledgment: This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code: T2EDK-00028 / MIS 5067540).

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A Synthetic Chemist's Collaborations with Muon Physicists and Computational Chemists

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At first glance, it seems clear that the magnetic properties of a material are determined by the absence, presence, quantity, and interaction of unpaired electrons. However, the design of a molecule-based material with predictable magnetic properties relies on more than just the elements, oxidation states, and molecular architecture: it relies on the supramolecular structure and the multitude of weak interactions between molecules. Seemingly small changes to intermolecular contacts can result in dramatic differences in magnetic properties. Understanding and, ultimately, predicting the crystal packing of paramagnetic species is of value in the search for new materials for quantum computing, data storage, magnetic sensors, and other technological advances. Likewise, understanding the complexity of the local magnetic interactions and how these relate to the bulk structure can be highly informative.

My research group has been fortunate enough to establish collaborative projects with Prof. Erin Johnson (Dalhousie U.), a computational chemist specializing in crystal structure prediction, and Prof. Tom Lancaster (Durham U.), a physicist specializing in muon measurements. We have attempted to answer the following two questions: 1) Can periodic-boundary calculations be used to predict crystal packing and thus magnetic properties of molecule-based magnets? 2) Can muon measurements deliver unique information about the local "magnetic structure" in a molecule-based magnet? Herein, current results will be shared and discussed.

Luminescent lanthanide metal-organic frameworks: an approach on white light emission with a single emissive lanthanide

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The nature of f-f transitions in trivalent lanthanide ions (Ln³⁺) as well as the position of 4f orbitals provide specific luminescent characteristics to the Ln³⁺ ions such as sharp atomic-like emission spectra and long lifetimes reaching the order of milliseconds.^[1] Therefore, Ln³⁺ ions are suitable luminophores for a wide range of applications spanning the fields of telecommunications, sensors and lighting.^[2] In this contribution we present a series of mixed-lanthanide and mixed-ligand MOFs belonging to three structural types with emissions spanning the whole visible region thereby constituting favorable platforms for white-light emission. In particular, we investigate the effect of different doping percentages of the red emitting Eu³⁺ and the blue-green emitting amino derivative of the ligand into the parent frameworks. We performed a detailed photophysical study on the synthesized materials concerning the observed lifetime of the Eu³⁺ metal center, the measured quantum yields of single (up to 87%) and double-doped materials (up to 17%) and we discuss the probable energy transfer mechanisms that populate the excited states of Eu³⁺. Furthermore we present the fine tuning of the emission of the above mentioned materials as well as the two different ligand-centered emission profiles that occurred (monomer and excimer). Overall this work demonstrates the synthesis, characterization and photophysical behaviour of lanthanide MOFs that emit warm and cold white light with the use of a single emissive lanthanide.

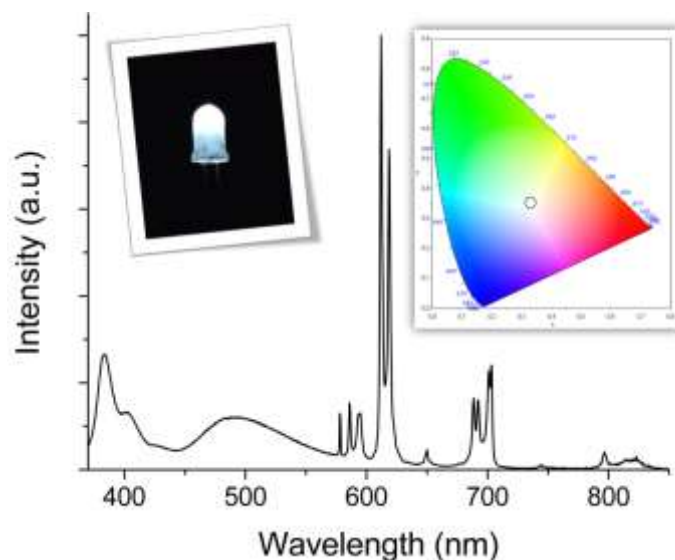


Figure 1. Emission spectrum, chromaticity diagram (right inset) and coated Uv-LED bulb of the white light-emitting material ($\lambda_{\text{ex}} = 365 \text{ nm}$).



The research project was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the “1st Call for H.F.R.I. Research Projects to support Faculty Members & Researchers and the Procurement of High-and the procurement of high-cost research equipment grant” (Project Number: 3371).

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$[\text{Mn}_7\text{Dy}(\text{OH})_2(\text{sacb})_4(\text{OAc})_9(\text{MeOH})_2]_n$: A helical coordination polymer prepared from achiral components

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The reaction of ligand *N*-salicylidene-2-amino-5-chlorobenzoic acid (sacbH₂) with Dy(OAc)₃ and Mn(OAc)₂, all non-chiral components, in a solvent mixture of MeOH and MeCN, and in the presence of NEt₃, gave the helical coordination polymer $[\text{Mn}_7\text{Dy}(\text{OH})_2(\text{sacb})_4(\text{OAc})_9(\text{MeOH})_2]_n$, which could be considered as the wonderland of helical structures. The crystallization indicates a spontaneous resolution process which results in the formation of a conglomerate with the formation of two types of crystals. The structure solution reveals the crystallization of the studied compound in two enantiomeric space groups, P 6₁ 2 2 and P 6₅ 2 2. The architecture of each helix seems to be based on helical design principle of using achiral molecular building blocks to construct a chiral framework [1]. The system gives the opportunity to discuss all the factors that govern the shape and packing of the helices in their structures. The helices present V-shaped coordination mixed metal building blocks with a 2-fold symmetry, which is a strategy used with V-shaped ligands to build helices. Intramolecular hydrogen bond interactions are developed within its building block and also neighboring helices interact through Cl...Cl intermolecular forces. The structure is homochiral, i.e. all helices in both structures are arranged parallel to each other and have the same chirality [2]. Studies indicate that the hexagonal arrangement of helical polymers and especially those which crystallize in both enantiomeric space groups of the studied compounds favor the formation of homochiral structures [3]. The study of helical compounds has attracted the research interest because of their inherent chirality, their relevance and significance to biological processes, for their use in asymmetric catalysis, enantioselective separation, optical activity, chiral magnetism etc. Also, the study of helical coordination polymers is appealing not only for the need to understand, detect and amplified chirality [4] but also for their structural aesthetic characteristics.

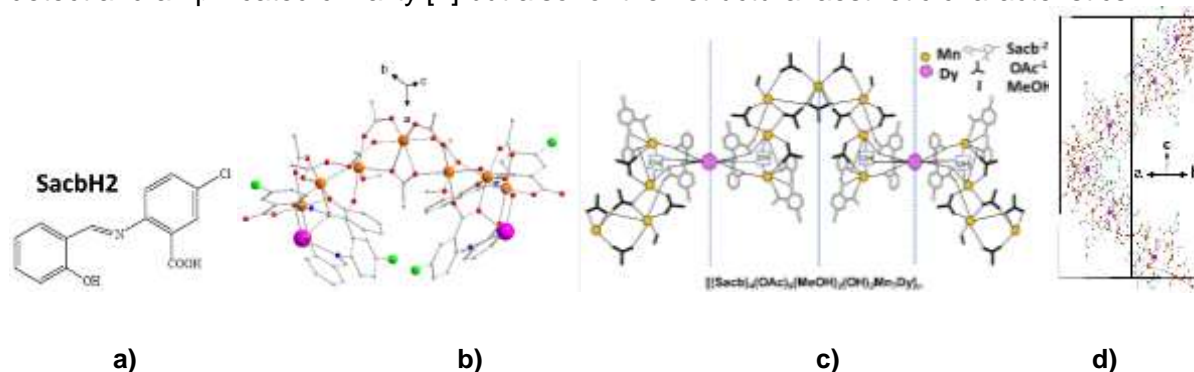


Figure. a) Ligand sacbH₂ b), c) The building unit of the helix in molecular and schematic presentation d) the helix developed along c-axis (Space Group: P 6₁ 2 2).

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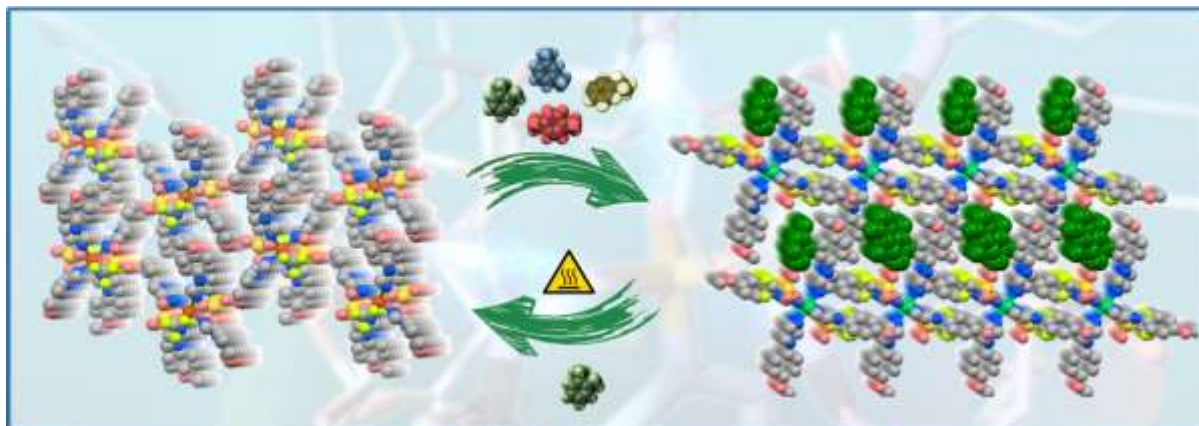
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Crystal engineering of a 'closed to open' transition in an azole-based Werner complex for C8 separation

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In the chemical industry, separation techniques are critical for obtaining pure forms of important chemicals and solvents for commercial or research reasons. The separation of C8 aromatic hydrocarbons, such as ortho-xylene (OX), meta-xylene (MX), para-xylene (PX), and ethylbenzene (EB), is one of the seven industrially critical separation processes "to change the world", because of their widespread use as chemical feedstocks in plastics, fibers, polymers, solvents, and fuel additives ^[1]. Due to their very similar boiling points, it is impractical to separate them efficiently by distillation due to the large number of theoretical plates required ^[2]. Many studies have demonstrated the promise of switching materials, i.e. materials that can undergo a sudden stimulus-driven structural transformation (from a closed to an open phase) caused by adsorption, as energy-efficient materials for separation applications ^[3]. The viability of using 0D metal-organic switching materials such as Werner complexes, as energy-efficient materials for separation of aromatic C8 isomers is investigated in this work. Werner complexes may reversibly switch between a densely packed 'closed phase' and a porous 'open phase' with no structural strain or degradation due to their molecular nature. The sorption characteristics of a new Werner complex constructed from azole-based mono-dentate ligands are shown in this study. The novel Werner complex variations were formed by replacing neutral N-donor equatorial ligands such as imidazoles using crystal engineering principles, and have shown promise in the separation of C8 aromatic hydrocarbons.

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Heterometallic Cu/Ln Schiff base complexes: synthetic efforts, structural characterization and magnetic studies

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Heterometallic 3d/4f complexes have been extensively studied over the years, in order to understand the nature of the magnetic interactions between the metal ions, and also due to their potential impact in technological applications, such as high-density information storage devices, quantum computing, spintronics and magnetic refrigeration. Efforts to synthesize compounds which combine more than one physical properties have been undertaken, thus leading to multifunctional materials, an active area in materials science with expected impact in the development of new technologies and applications. From the synthetic point of view, the proper choice of the metal ions, the organic ligands and the contribution of co-ligands is equally important. Our synthetic efforts to prepare heterometallic Cu/Ln complexes with Schiff base ligands and carboxylato co-ligands, afforded families of complexes with different Cu:Ln ratios, metal topologies and nuclearities. The study of their structural and magnetic properties will be discussed [1-3].

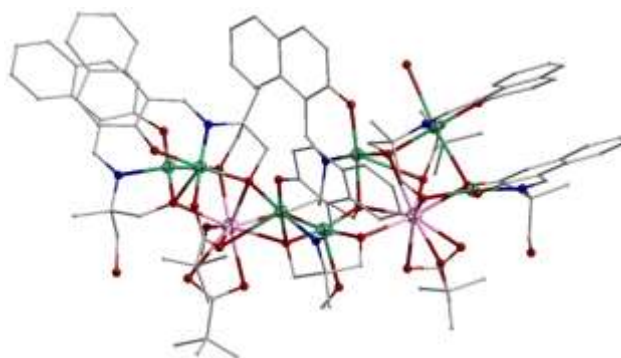


Figure. The molecular structure of a family of {Cu₇Ln₂} complexes.

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Electronic structure and Spin Coupling in a Trinuclear Fe^{III} Cluster Revealed by Combined Spectroscopic, Magnetic and Theoretical Studies.

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The reaction of FeCl₃·6H₂O with 2-acetylpyridine, pyCOMe, in the presence of bicine, N(CH₂CH₂OH)₂CH₂COOH, and MeONa affords the trinuclear complex [Fe₃Cl₄(bicine)(L2)]·Me₂CO·0.2H₂O (**1**) from a Me₂CO/MeOH solution. L2²⁻ = pyCO(Me)CH₂CO(OMe)py is formed in situ. The molecular structure of **1** (Figure 1, left) consists of two corner-sharing [Fe₂O₂] rhombic units, with the two terminal Fe^{III} ions in distorted square pyramidal geometry and the central Fe^{III} in distorted octahedral geometry.

Magnetic measurements indicate that the ferric pairs are antiferromagnetically coupled resulting in an S = 5/2 ground state. The room temperature Mössbauer spectrum from a powder sample of **1** comprises two doublets at a 2:1 ratio attributed to the two different coordination environments of the ferric sites. At liquid helium temperatures (Figure 1) the spectrum comprises two magnetic sextets at a 2:1 ratio indicating that the ferric sites are magnetically distinct. This is consistent with the specific spin coupling scheme imposed by the analysis of the magnetic measurements.

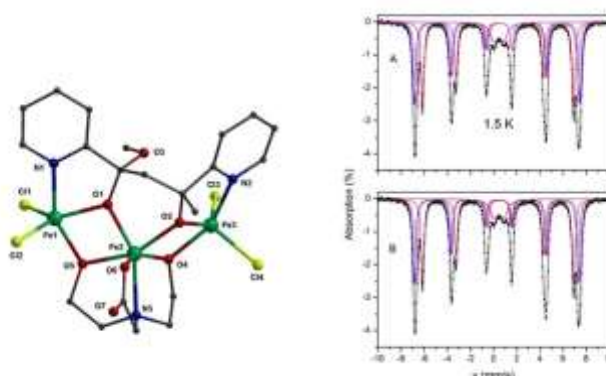


Figure 1. Left: The molecular structure of **1**. Right: The Mössbauer spectrum of **1** at 1.5 K.

Solid lines: Theoretical simulations on the basis of two different models.

A closer examination suggests that the Mössbauer spectra either at room temperature or at liquid helium temperatures (Figure 1, right) can be fitted equally well assuming two different deconvolution approaches. Theoretical methods are applied in order to determine which of the two different models holds for **1**. This approach sheds light on the effect of the coordination environment on the electronic properties of the ferric ions and how this effect is reflected on the Mössbauer hyperfine parameters.

The Pharmaceutical Drug Discovery & Development Process: Breakthrough Psychedelic Drug Therapies for Treatment of Resistant Depression

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Clinical research on the application of psychedelic drugs originated with studies on LSD by psychiatrist Harvey Osmond in the 1950s. Osmond and Aldous Huxley together coined the term psychedelic (literally “mind moving” from the Greek) as a classification for drugs like mescaline (peyote), LSD and psilocybin (magic mushrooms) to confer a state of enhanced mental perception. The psychedelic effects of LSD itself, were originally discovered by inventor Albert Hofmann at Sandoz. This led Sandoz to supply synthetic LSD as well as psilocybin to clinical researchers to study potential applications in psychiatry. In fact, long before LSD became a recreational “hallucinogenic” drug capturing the zeitgeist of the 60s research studies indicated the potential for LSD as a treatment for psychiatric disorders. Osmond’s research indicated that LSD



assisted psychotherapy was an effective treatment for alcoholism in a large sample size of subjects. Timothy Leary a respected clinical psychologist at Harvard in the early 1960s also conducted foundational clinical studies with LSD and psilocybin which were legal drugs at the time. Unfortunately, Leary subsequently played a key role in elevating psychedelics to cult status as a poster child for the 1960s counterculture and “subversive” recreational drug use. With the ensuing “war on drugs” in the early 1970s championed by Nixon, psychedelic drugs became strictly regulated Schedule 1 narcotics and clinical research on the medical applications of psychedelic drugs essentially stopped for the next 40-years.

Fortunately, over the last 15-years clinical research on psychedelic drug applications in psychiatry has mounted a comeback led by a core community of psychedelic specialist clinicians including researchers at Johns Hopkins, the MAPS foundation and the Beckley Institute. These studies have shown that the psychedelics can effectively treat severe psychiatric disorders, most notably major depressive disorder and PTSD, that are not treatable with standard drug treatments (eg SSRI class drugs like Prozac). Psychedelic therapies such as psilocybin represent a paradigm shift for serious psychiatric disorders – away from a daily pill regimen – but rather with periodic therapy that addresses the fundamental circuit disorder of the brain wiring. However, current psychedelic therapies like psilocybin have some safety limitations due to their lack of selectivity for the target 5-HT_{2A} serotonin receptor subtype. To be able to reach broader patient populations, there is a need for improved safety psychedelic drug. This talk will detail the process for bringing a second-generation synthetic psychedelic to a broader population of patients using modern molecular drug optimization and engineering.

Hybrid Magnetic Materials from the Deposition of Single-Molecule Magnets on Graphene-like Substrates

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Quantum technologies might result in revolutionary improvements in terms of capacity, sensitivity and speed, and will be the decisive factor for success in many industries and markets. Molecular quantum spintronics is a relatively new research area which requires the advanced knowledge of many interdisciplinary fields, such as synthetic chemistry, physics, materials science and theory. The idea is to fabricate molecule-based devices to read and manipulate the spin states of the molecules and carry out basic quantum operations. One of the most appealing schemes involve the synthesis of chemically and structurally stable single-molecule magnets (SMMs), and the study of their interactions with functional substrates (i.e., graphene and carbon nanotubes) to enable surface-state spintronics and electrical spin manipulation.^[1] To achieve the fabrication of molecular compounds on a functional surface, two main approaches have been developed, namely the weak- or non-covalent method and the strong- or covalent (chemisorption) method. Non-covalent functionalization is achieved with molecules lacking a specific functional group to react with the surface but having a backbone that induces weak interactions with it (i.e., van der Waals or electrostatic interactions).^[2] Covalent linking often requires molecular functionalization and subsequently grafting of the resulting molecules on selected surfaces. We herein present our efforts toward the deposition of a ferromagnetically-coupled {Ni₇} cluster and a structurally new {Dy₂} SMM on graphene-like substrates (**Figure 1**), which include a variety of spectroscopic, physicochemical and electronic microscopy techniques, such as IR, UV/Vis, XPS, Raman, MS, TGA, and HR-TEM.

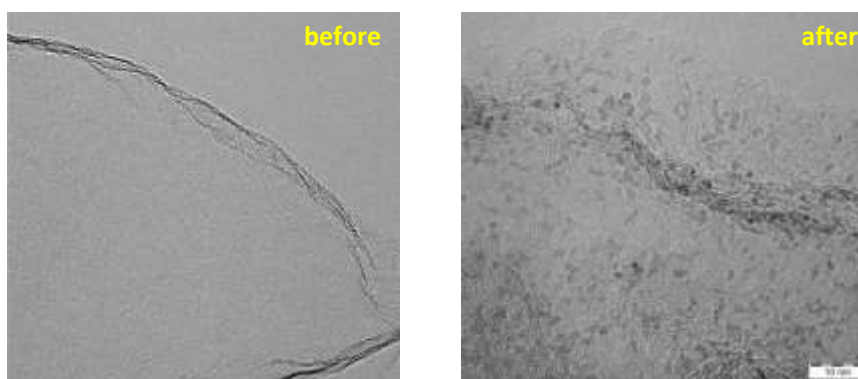


Figure 1. TEM images of the pristine graphene (left) and the {Ni₇}@graphene hybrid material (right).

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Selective laser melting of stainless steel 316L with silica nano-additives: powder processing - consolidation and characterization

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Stainless steel 316L in the form of gas atomized powder was ball milled with SiO₂ nano-additives to produce a feedstock material for consolidation with selective laser melting (SLM) and in turn investigate solidification processes. Ball milling (BM) was performed for different durations to assess the response on powder morphology and microstructure. Scanning electron microscopy indicated the deformation of powder-particles, portrayed in the loss of sphericity and the development of sharp-edged geometries over increasing BM durations at 200 rpm and a 2:1 ball-to-powder weight ratio. An optimal BM duration of 4 h was selected after performing microstructure investigations with X-ray diffraction (XRD) to limit micro-strains and the formation of secondary phases. SLM consolidation was implemented in two steps; initially through the variation of volumetric energy density (E_d) from 91 to 509 J/mm³, and secondly through the employment of scanning strategies with multiple patterns and passes. The response on the depth-to-width ratio of melt pools was illustrated through optical microscopy of etched surfaces, while crystallographic texture evaluation was based on XRD pole figures. It was concluded that a (110) preferred orientation over the building direction is associated with high E_d -values, whereas in-plane alignment reflected variations in scanning strategy. Furthermore, columnar grains were observed with electron backscatter diffraction, while thermal diffusivity was sharply lower with addition the of SiO₂ for temperatures below 300 °C. Finally, electrochemical behavior remained stable in comparison with pure stainless steel 316L, as indicated by potentiodynamic polarization curves.

Acknowledgements

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Towards “Naked” M²⁺ in the Condensed Phase

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Typically, metal complexes consist of the metal center coordinated to neutral, anionic or even sometimes positive ligands. The combination of metal and ligands determines the reactivity of these complexes. For example, complexes with chiral ligands can catalyze enantioselective transformations. On the other hand, metal ions that are only weakly coordinated to the counterion(s) and the solvent can in principle showcase their intrinsic properties. Enhanced Lewis acidity is displayed in lithium salts with weakly coordinating anions (WCAs) such as Li[B(C₆F₅)₄], and the less common +1 oxidation state is stabilized in [Ga(arene)_n][WCA] salts.

The synthesis of M[WCA]₂ salts containing M²⁺ cations is more challenging because the higher lattice energy decreases the solubility in low polarity solvents, and the higher Lewis acidity of the metal center creates additional stability demands from the WCAs. Here, we will present our efforts to generate Zn²⁺ salts with carborate and ammonio-dodecaborate counterions and report the high activity of one of these salts, Zn[HexCB₁₁Cl₁₁]₂, as hydrosilylation catalysts. In addition, we will disclose initial results involving the syntheses of Mg²⁺ and Co²⁺ salts.

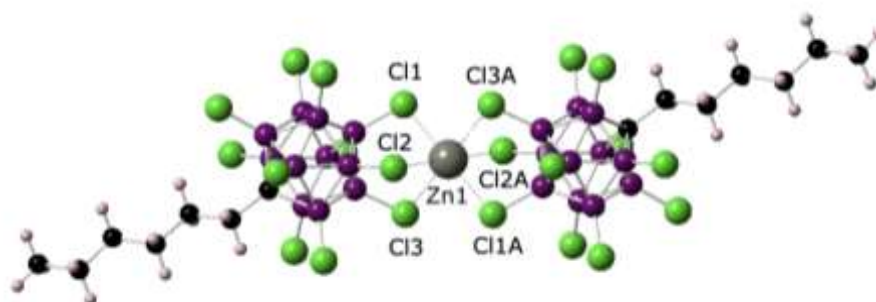


Figure. Crystal structure of Zn[HexCB₁₁Cl₁₁]₂.

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Quantum Crystallography

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This is quite a paradox that a century after introduction of the spherical Independent Atom Model (IAM, 1914 [1]), 99.7% of all ca. 1.5mln known crystal structures have been refined using IAM, which suffers from severe methodological deficiencies. Far better results can be obtained when new approaches of Quantum Crystallography(QCr) utilising aspherical atomic scattering factors are applied. In short, QCr is crystallography beyond IAM. In this contribution, I will present details of aspherical Hansen-Coppens [2] pseudoatom refinement of electron density and the main ideas of Hirshfeld Atom refinement. My lecture will be complemented by several examples of our QCr studies including: (1) Experimental charge density studies of organic dithiadiazolyl radicals, (2) Multipole refinement of electron density in crystals of minerals including minerals under pressure, (3) Hirshfeld Atom Refinement (HAR) refinement of ice VI structure, (4) HAR refinement of H-atom positions in small molecule organic compounds and hydrides, (5) Experimental HAR studies of relativistic effects and electron correlation in gold derivatives.

A century after the Braggs, it is possible to obtain H-atom positions from X-ray diffraction studies which are equally reliable as those from neutron diffraction. It is also possible to get reliable positions of H-atoms in the closest neighborhood of very heavy atoms, to study tiny redistribution of electron density in minerals under pressure, or to estimate consequences of relativistic effects using X-ray diffraction data. So users of X-ray crystallography can do far better than just routinely refining poor IAM model against precise, accurate and very often very dear diffractometer/synchrotron/XFEL X-ray data.

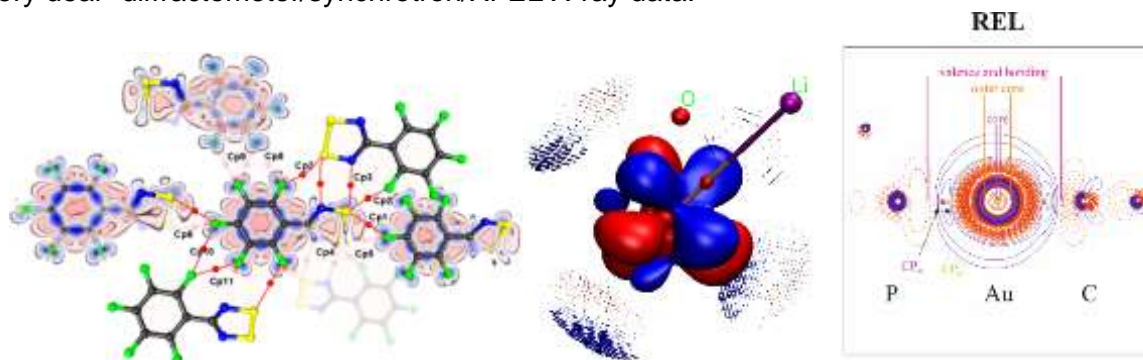


Fig 1. (a) Example of intermolecular interactions in dithiadiazolyl radicals, (b) relocation of electron density at fluorine anion under pressure, (c) relativistic effects at Au atom.

This work was funded by the Polish National Science Centre (NCN) under Opus grant DEC-2018/31/B/ST4/02142 and carried out at the Core Facility for crystallographic and biophysical research to support the development of medicinal products sponsored by the Foundation for Polish Science (FNP).

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Crystal Engineering: Then and Now

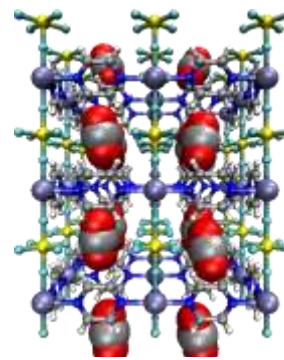
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That composition and structure can so profoundly impact the properties of crystalline solids has provided impetus for exponential growth in the field of *crystal engineering*¹ over the past 30 years. This contribution will address how crystal engineering has evolved from its initial focus upon design (form) to its current emphasis on properties (function). Strategies for the generation of two classes of “task-specific” porous crystalline materials will be presented:

- **Hybrid ultramicroporous materials**, HUMs, offer exceptional control over pore chemistry, pore size and binding energy. New benchmarks for CO₂ or C₂H₂ capture (see Figure) have been observed² thanks to the tight binding sites and strong electrostatics associated with these coordination networks, which remain underexplored when compared to materials such as MOFs.
- **Flexible metal-organic materials**, FMOMs, were once seen as a curiosity but it has recently been recognized that they can offer a possible solution to important gas storage and separation applications, especially when they switch from closed (non-porous) to open (porous) phases.³

Figure. CO₂ capture in a HUM^{2a}



The overall goal of this presentation is to address how and why crystal engineering can offer a paradigm shift from the more random, high-throughput methods that have traditionally been utilized in materials discovery and development. In short, crystal engineering can teach us how to custom-design the right crystalline material for the right application.

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Oxidation of Isodiphenylfluorindine and Synthesis of C3 and C9 Oxo Analogues

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Isodiphenylfluorindine **1a**^[1] reacts with $K_2Cr_2O_7/H^+$ to give 13-oxo-isodiphenylfluorindinium perchlorate **2** (75%), but with PIFA or MnO_2 it gives the zwitterionic and quinoidal cruciform 13,13'-dimers **3** (85%) and **4** (89%), respectively.^[2] The zwitterionic 13,13'-dimer **3** can be rapidly converted with MnO_2 into the quinoidal 13,13'-dimer **4** (100%).^[2] Since isodiphenylfluorindinone **5** and isodiphenylfluorindone **7**, *i.e.*, the C3- and C3,C9-oxo analogues of isodiphenylfluorindine **1a**, that were first postulated 100 years ago, cannot be directly obtained via oxidation of **1a**, an alternative strategy was needed. As such, isodiphenylfluorindinone **5** and isodiphenylfluorindone **7**, were prepared by deprotection of the C3- and C3,C9-benzoyloxy isodiphenylfluorindines **1b** and **1c**.^[3] The isodiphenylfluorindinone bisperchlorate salt **6** was also synthesized.^[3] The structural assignments of all products are supported by spectroscopic data. Their optical and electrochemical behavior is also presented, along with theoretical studies.

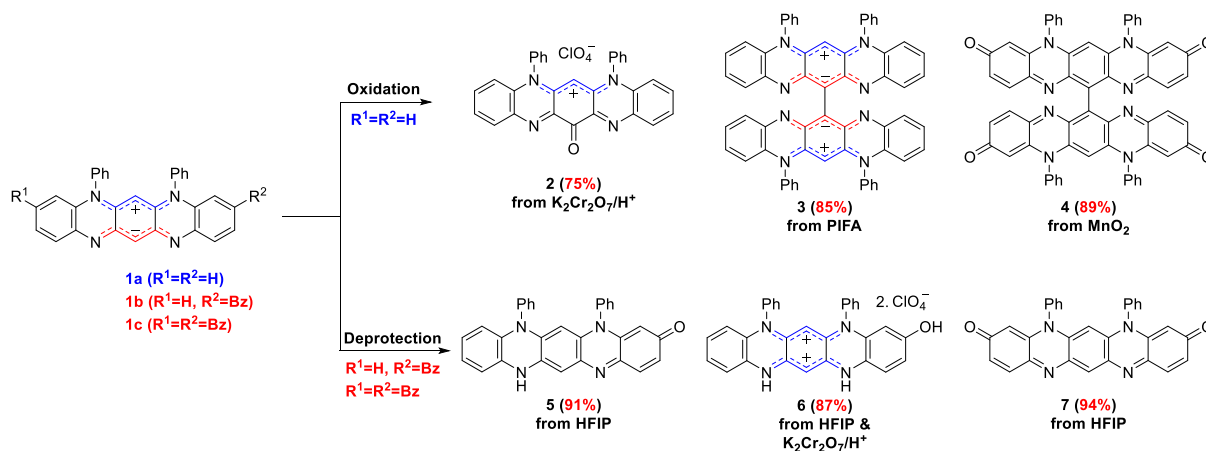


Figure 1. Oxidation and deprotection of isodiphenylfluorindines 1.

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