Inorganic Ireland Symposium 2023

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INORGANIC IRELAND SYMPOSIUM 2023

Time	Presenter	Title
	Session 1, *Chair: Aidan McDonald/Constantina Papatriantafyllopoulou*	
9.00	Wolfgang Schmitt, *plenary*	*Synthetic Approaches to Nanoscopic Molecular Capsules and Related Framework Structures: Metallo-supramolecular systems for redox catalysis*
9.30	Peter Dunne	*Hollow and Plant-like Copper Sulfide Microstructures Grown from Colloidal Sulfur Seeds*
9.50	Wei Zhang	*A Microfluidic Approach for Tuneable Synthesis of Gold Nanostructures*
10.10	Bob Baker	*Insights Into The Solution Structure Of Hydrated Uranium And Thorium Ions From Neutron Scattering Experiments*
10.30	Foteini Dimakopoulou	*Novel Mixed-Ligand Metal-Organic Frameworks and Coordination Polymers for Environmental Applications*
10.50	**Coffee/Posters**	
	Session 2, *Chair: Celine Marmion*	
11.10	Susan Quinn	*Resolving Light-Activated Processes of DNA Bound Transition Metal Polypyridyl Complexes Containing Nitrile Probes*
11.30	Joseph Byrne	*Carbohydrate-functionalised metal complexes: targeting pathogens for therapeutic and sensing applications*
11.50	M. Rosa Fernandez-Pison	*Highly Stable α,α-Diimine Silver(I) Catalysts that Incorporate CO_2 into Alkynes Frameworks*
12.10	Thorfinnur Gunnlaugsson, *ICI David Brown Award*	*Tails of two endeavours! The application of lanthanides and Ru(II) in the formation of luminescent supramolecular systems*
12.50	**Lunch/Posters**	
	Session 3, *Chair: Aidan McDonald*	
14.00	Tobias Kramer	*Stability and C–H bond activation reactions of palladium(I) and platinum(I) metalloradicals*
14.20	Zoi Lada	*Towards the investigation of Spin Crossover (SCO) systems*
14.40	Manting Mu	*Cooperative Effects in Sodium-based Bimetallic Complexes for Selective Metalation Reactions of Aromative Substrates*
15.00	Cian Clarke	*Targeted Assembly of Novel Molecular Complexes from Ligands with Synthetic Precedence*

15.20	Paul Dingwall	*Investigating The Mechanism and Origins of Selectivity in Palladium-Catalysed Carbene Insertion Cross-Coupling*
15.40	**Coffee/Posters**	
	Session 4*, Chair: Grace Morgan*	
16.00	Paul O'Dowd	*Synthesis and Biological Evaluation of Clinically Relevant Click-Fuctionalisable Pt(II)-Anticancer Complexes*
16.20	William Daly	*Copper Complexes and their unexplored geometry using N,N-disubstuted-N'-aceylthiourea ligands.*
16.40	Lewis More-O'Farrell	*GA(III) SIDEROPHORE COMPLEXES - A METALLO-TROJAN HORSE STRATEGY TO TACKLE ANTIMICROBIAL RESISTANCE*
17.00	Celine Marmion, *Plenary*	*Multi-Targeted Metallodrugs Rationally Designed to Overcome the Evolving Paradigm of Drug Resistance*
17.30	**Drinks/Poster Session**	
19.00		End

Plenary/Award Lecture Abstracts

Tails of two endeavours! The application of lanthanides and Ru(II) in the formation of luminescent supramolecular systems

Thorri Gunnlaugsson

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The development of novel targeting molecules and their self-assembly into larger functional structures and materials using metal directed synthesis has become a major area of research within supramolecular chemistry.[1-2] In this lecture, which is in two parts, we present some of our work carried out in TCD over the years in this area of research, where we demonstrate how the combination of ligand design and the use of either *f*-metal or *d*-metal ions, respectively (or in combination), can result in the formation of both functional as well as purely beautiful self-assembly structures and materials. In the first part of this lecture, lanthanide ions, such as Eu(III), Sm(III) and Tb(III), will be employed in the formation and study of self-assembled luminescent complexes, di-metallic helicates, soft-materials and cross-linked polymers.[3-4] While in the latter half, the focus will be on the use of Ru(II) polypyridyl complexes and their application as luminescent DNA targeting binders, cellular imaging and theranostic agents.[5-6]

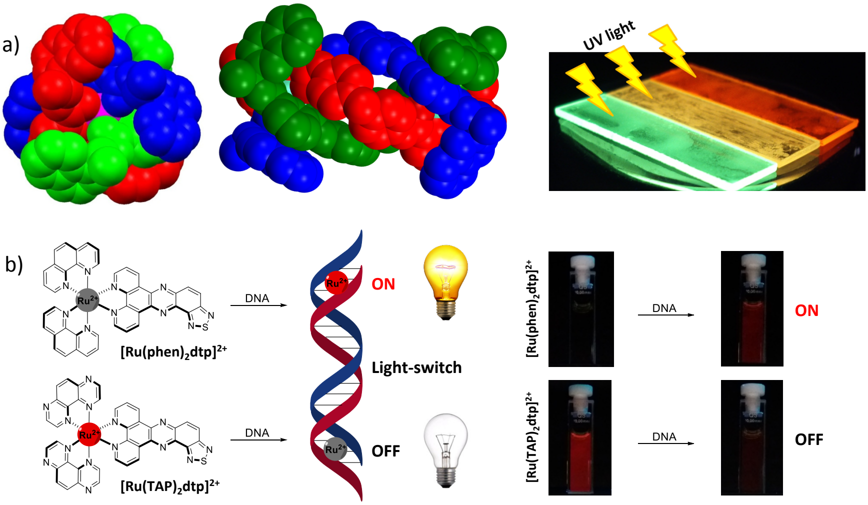

Figure: a) The X-ray crystal structures of a chiral self-assembled lanthanide bundle and a triple stranded di-metallic helicate, and the formation of a luminescent soft-material using Tb(III) (green), Eu(III) (red) and the combination of both (orange). **b)** Example of two Ru(II) polypyridyl complexes where the MLCT emission is either switched '*on*' or '*off*' upon binding to DNA.

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[2] Aramballi J. Savyasachi, *et al. Chem*, 2017, **3**, 764–811.
[3] Dawn E. Barry, *et al. Inorg. Chem.*, 2020, **59**, 2646-2650
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[5] Sandra Estalayo-Adrián, *et al. Dalton Trans.*, 2020, **49**, 14158-14168
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Multi-Targeted Metallodrugs Rationally Designed to Overcome the Evolving Paradigm of Drug Resistance

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Drug resistance is a major health challenge with antimicrobial resistance threatening the very core of modern medicine globally.[1] Cancer drug resistance is also fast emerging as another serious threat.[2] The ability to fine-tune the properties of metal complexes has led to innovative metallodrugs with the capacity to truly break the drug resistance paradigm.

Our group has rationally designed and developed a series of multi-targeted platinum, ruthenium and copper complexes, all of which have shown potential to overcome cancer and anti-microbial drug resistance. We have achieved this by targeting multiple biological pathways, thereby blocking the development of intracellular escape mechanisms essential for cancer or bacterial cell survival. More specifically, we have advanced a new series of complexes incorporating clinically used drugs (such as Vorinostat, Belinostat (histone deacetylase inhibitors), Ciprofloxacin (antibiotic)) or derivatives thereof as ligands.[3-6] A summary of our drug design strategies and our metallodrugs which have been designed to specifically overcome cancer and anti-microbial drug resistance will be presented. Those that have formed the basis of fruitful industrial collaborations will also be highlighted.

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Synthetic Approaches to Nanoscopic Molecular Capsules and Related Framework Structures: Metallo-supramolecular systems for redox catalysis

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The use of highly extended organic ligands is a common synthetic path to molecular cages, capsules and extended 3D structures with large voids. Tritopic benzene-trisethynylbenzoate (BTEB) ligand derivatives yield highly augmented Metal-Organic Frameworks (MOF) and molecular species in which rotations about acetylene moieties lead to stereoisomeric topologies. Particularly noteworthy are Metal-Organic Polyhedra, $[Cu_{36}(\textit{m}\text{-BTEB})_{24}(H_2O)_{28}(DMF)_8]$, with cross-sectional diameters of *ca.* 5 nm.[1] The structures are composed of composed of Archimedean and Platonic bodies, whereby multiple sub-cages provide distinctive binding sites through labile coordination solvent molecules. The latter also facilitate linkage of the molecular entities into 1D polymers and 3D networks. Related supramolecular synthesis concepts use π-cation interactions to form nanoscopic hybrid polyoxovanadate cages whilist managanese-based metal-organic materials can be applied for (photo)electro-catalytic water oxidation achieving onset-potentials of as low as 255 mV and current densities of 10 mA cm^{-2} at 482 mV.[2-4]

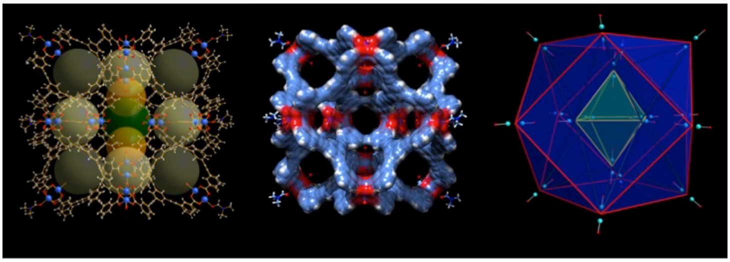

Figure 1. Structure of $[Cu_{36}(\textit{m}\text{-BTEB})_{24}(H_2O)_{28}(DMF)_8]$ in ball-stick, space-filling and topological representation, respectively.

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Lecture Abstracts

Insights into the solution structure of hydrated uranium and thorium ions from neutron scattering experiments

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The solution structure of actinides is an important topic that is difficult to study in detail.[1] We report a study on a 1.0 M Uranyl Chloride solution that has been determined by the EPSR modelling of a combination of neutron scattering and previously reported EXAFS data. The experimental data shows an equilibrium in solution between $[UO_2(H_2O)_5]^{2+}$ and $[UO_2Cl(H_2O)_4]^+$ with a stability constant of 0.23 ± 0.03 mol^{-1} dm^{-3}. The data also show, for the first time in solution, that the uranyl ion is a very poor hydrgen bond acceptor, but the coordinated waters show enhanced hydrogen bond ability compared to the bulk water. Further experiments on the increasing $[Cl]^-$ concentrations of hydrated uranyl chloride will be discussed. To expand the results to other oxidation states, $[UCl_4(H_2O)_x]$ has been studied and again equilibria noted and stablility constants extracted from the modelling. Finally, hydrated $ThCl_4$ and $ThBr_4$ have been studied using the same technique and inner spere vs outer sphere equilibria have again been noted.

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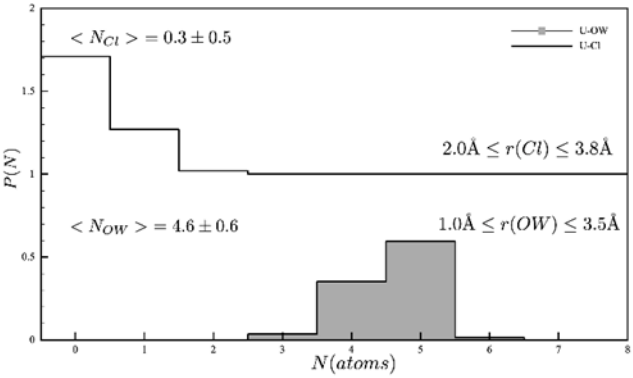

Carbohydrate-functionalised metal complexes: targeting pathogens for therapeutic and sensing applications

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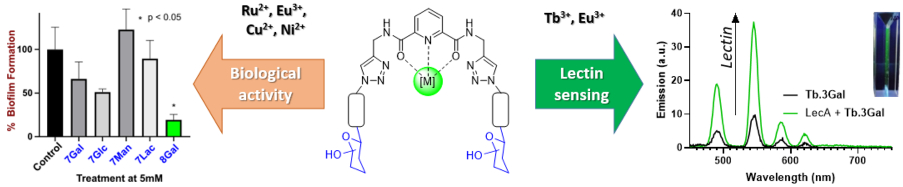
Carbohydrates confer metal complexes with many properties beneficial for biological inorganic chemistry, including well-defined stereochemistry and water-solubility. Moreover, targeted selective interactions with biomolecules, such as carbohydrate-binding proteins, offer pathways for potential therapeutic and diagnostic applications. Carbohydrate–protein interactions are often key to the pathology of bacterial infections;[1] targeting the lectins of *P. aeruginosa (PA)* with glycoconjugates has recently become an area of increasing interest.[2] While various multivalent glyconconjugate approaches are reported, use of metal coordination chemistry in design of lectin-targeting compounds is underexploited. Carbohydrate-functionalised coordination-complexes can exploit properties of both carbohydrates and metals to address healthcare challenges.

We have synthesised Ru(II)-centred glycoclusters, whose ability to inhibit *PA* biofilm formation was found to be dependent on the identity and presentation of the carbohydrate motif.[3a] Several examples of carbohydrate-functionalised complexes with *d*- and *f*-metal ions also inhibit fungal adhesion by *C. albicans* or demonstrate *in vitro* antimicrobial activity against *PA*, further demonstrating therapeutic promise of these systems. Building on this effective platform, we designed and developed related luminescent lanthanide(III)-centred glycoclusters, which show reproducble 'switch-on' sensing behaviour in the presence of several lectins. The relative selectivity of the proteins for different monosaccharide motifs determines whether the sensing response occurs with several analogous emissive complexes. These systems have micromolar affinity for bacterial lectin LecA, and studies are ongoing with other lectins of different selectivities to establish the scope of this sensing paradigm.[3b]



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Targeted Assembly of Novel Molecular Complexes from Ligands with Synthetic Precedence

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The unique properties of molecular complexes have impelled their applications in therapeutics, catalysis, and supramolecular chemistry.[1] Despite their prevalence, rational design of coordination compounds still proves challenging owing to the cost and complexities associated with synthesis. Computational exploration of the vast chemical space that these compounds inhabit provides an opportunity to facilitate and accelerate this design process. In this presentation, we introduce a modular and versatile workflow (*Fig.1*) to enable the generation of bottom-up molecular databases from a library of *ca*. 50,000 ligands extracted from the Cambridge Structural Database (CSD).[2] The workflow includes a method for assigning formal charges to each ligand based on previous work by Duan et al.[3] In addition, a series of filters are implemented to enable users to target ligand properties of interest, including atomic composition, charge and coordinating atom types. Novel molecular complexes with the desired topology are then assembled based on a user-specified set of instructions using the user-curated set of unique ligands. Since each extracted ligand originates from an entry within the CSD, there exists synthetic precedence for the ligands of each assembled molecular complex. Ultimately, we envisage this automated workflow being employed to direct exploration of chemical space and to accelerate molecular discovery through applications in high throughput screening.

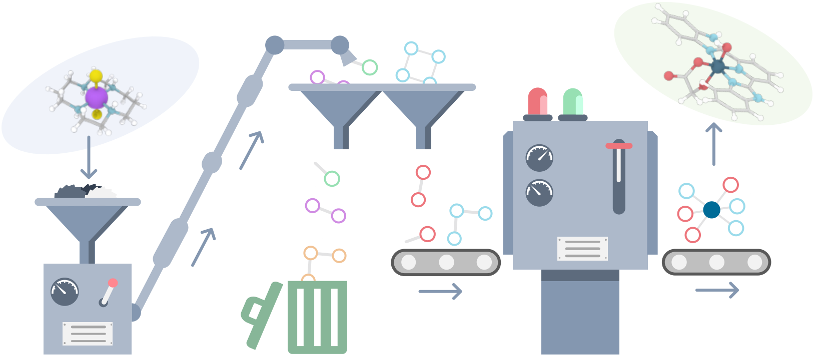

Figure 1: General workflow. Ligands are extracted and curated based on user-selected filters. Novel molecular complexes are assembled and stored.

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Copper Complexes and their unexplored geometry using N,N-disubstuted-N’-aceylthiourea ligands.

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The synthesis, molecular structure investigation and applications of several new complexes of Copper(II) with nine N,N-disubstituted-N’-acylthiourea (HL) ligands. An in depth look at the structural geometry and factors affecting the *cis* or *trans* nature of each compound.[1,2] Factors that were explored include hydrogen bonding, dihedral angles, energy levels and steric bulk of alkyl side chains.

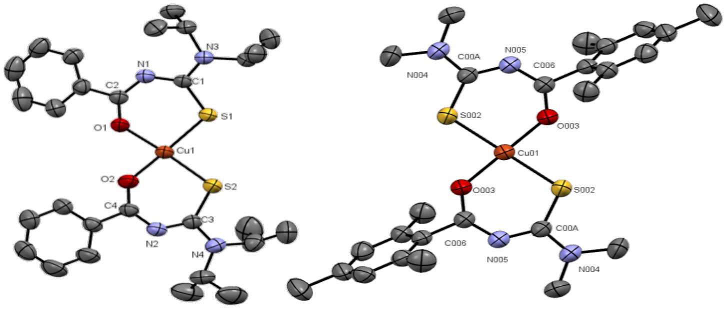

Figure 1 crystal structure of a cis (left) and *trans* (right) geometry copper(II) complex. Hydrogens have been omitted for clarity.

N,N-disubstituted-N’-acylthiourea metal complexes have seen use in multiple applications. In this study the applications focused on include materials deposition and antimicrobial capabilities.

Thermal analysis for stability and volatility was explored.[3] The best results for each geometric isomer was carried forward for proof of principle thermal Chemical Vapour Deposition experiments.

Antimicrobial testing was performed in conjunction with COADD. The results showed a promising future for dual application compounds.

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Novel Mixed-Ligand Metal-Organic Frameworks and Coordination Polymers for Environmental Applications

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2-pyridyl oximes and alcohols are ligands that have the capability to link a large number of metal ions, leading to high nuclearity species. They also favour ferromagnetic exchange interactions between the metal centers, forming clusters that can act as single molecule or single chain magnets. Even though the use of such ligands has shown significant results in the field of metal cluster chemistry, their use for the synthesis of metal-organic frameworks (MOFs) and coordination polymer synthesis has not been fully explored.

With this in mind, we initiated an investigation into the ability of combining such ligands with a variety of polycarboxylic linkers to yield new MOFs and/or coordination polymers. Herein, we describe the synthesis and characterisation of novel species based on this ligand mixture Fig.1).[1-4] Their crystal structures and physical properties (magnetism, photoluminescence) are discussed in detail. The ability of representative examples to encapsulate metal ions from aqueous systems is also discussed.

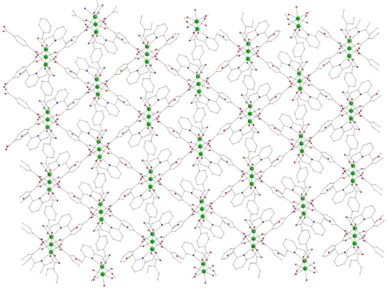

Fig. 1. Representation of the crystal structure of a mixed-ligand Mn MOF.[4]

References:

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Investigating The Mechanism and Origins of Selectivity in Palladium-Catalysed Carbene Insertion Cross-Coupling

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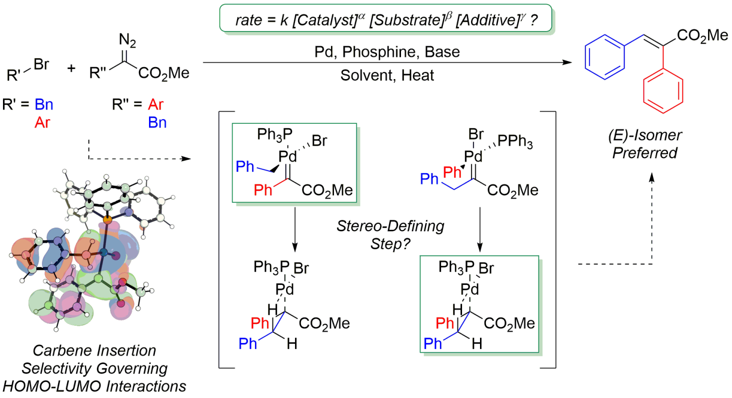

It is only relatively recently that diazo compounds have emerged as a new cross-coupling partner in palladium catalysis.[1] To date, few mechanistic studies have been reported, with the reaction assumed to proceed via a Heck-like mechanism through a palladium carbene intermediate. There has also been no investigation surrounding selectivity, particularly in the formation of tri-substituted alkenes. Selectivity has been widely assumed to originate during β-hydride elimination,[2] despite the major experimental product arising from the more sterically encumbered transition state. Here, we report a recently published,[3] in-depth mechanistic study of palladium-catalysed carbene coupling for the formation of 1,1,2-substituted alkenes using kinetic studies, in situ NMR spectroscopy, and ESI-MS, as well as theoretical insights to determine the origin of high (*E*)-selectivity. Our results allow us to propose as a general model for selectivity in palladium-catalysed carbene insertion reactions with a pendant migratory group and can mechanistically account for previously unexplained selectivities reported in the literature.

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Hollow and Plant-like Copper Sulfide Microstructures Grown from Colloidal Sulfur Seeds

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The formation of complex, biomimetic structures from ostensibly simple inorganic systems has been a source of fascination for centuries. This is exemplified by chemical gardens, in which non-equilibrium precipitation processes result in micro- and nanotubular morphologies driven by diffusion, osmosis, and convection effects.[1] The aesthetics of these systems were the major source of fascination in their early years, however such systems have seen a recent resurgence in interest, as the hollow structures obtained are envisaged as likely adsorbents, catalysts, sensors and fuel cell components.[2] Furthermore, these biomimetic structures have been identified as potential biomarkers for early life; however significant efforts must be made in this area to ensure that potential abiotic origins be considered as alternative pathways to such biosignatures.[3]

Here we report on the synthesis of hollow, framboidal, and plant-like copper sulfide grown from colloidal sulfur seeds in a simple, and wholly inorganic process by reacting sulfur colloids with a copper salt solution a range of morphologies may be achieved. Varying copper to sulfur ratios allow hollow covellite (CuS) microspheres, complex framboidal-type morphologies, cracked microspheres, "germinating seeds", and copper sulfide tendrils to be obtained. It is posited that these varied and complex morphologies result from a nominally simple process — surface crystallisation inducing internal pressures — analogous to that observed in the freezing of water droplets.

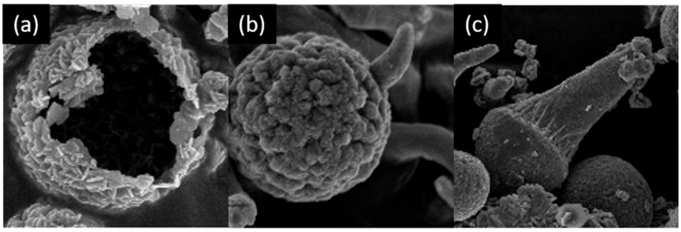

Figure 1: Copper sulfide microstructures grown from colloidal sulfur seeds; (a) hollow microsphere, (b) budding sphere, (c) grown tendril.

References:

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Highly Stable α,α-Diimine Silver(I) Catalysts that Incorporate CO_2 into Alkynes Frameworks

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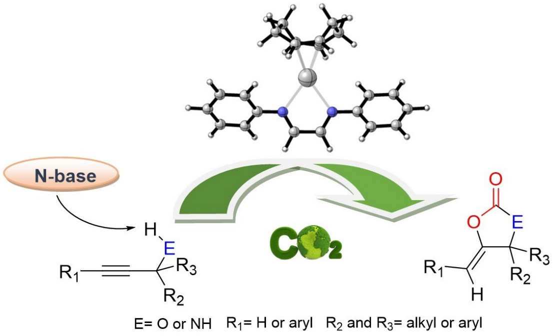
Carbon dioxide is a potentially valuable and highly accessible C1 feedstock. However, the application of this ubiquitous gas in industrial processes is comparably limited due to thermodynamic restraints and general inertness towards C-activation. This work addresses the development of novel room temperature stable cationic silver(I) complexes supported by *N,N'*-chelating α,α-diimines, that demonstrate high alkynophilicity. These complexes are highly efficient in incorporating CO_2 into organic alkynes frameworks,[1,2] affording cyclic carbonates and carbamates under mild conditions. The unusual high stability of these silver(I) pre-catalysts was accomplished by employing a η^2:η^2-chelating *cis*-cyclo-octadiene which was predicted through DFT calculations and compared to the corresponding Cu(I) and Au(I) analogues. The ability of these novel α,α-diimines silver(I) complexes to catalyse the incorporation of CO_2 into a propargylic alcohols/amines and the subsequent cyclisation was evaluated using a variety of terminal and internal alkynes substrates was evaluated in the presence of different non-nucleophilic nitrogen bases. All reactions were performed at 25 ºC under 1 to 6 bars of CO_2 pressure affording the corresponding α-alkylidene cyclic products, which are employed as precursors for drugs and polymers. This family of catalysts shows high conversion at atmospheric CO_2 pressure, using 1-5 mol% catalyst loading. The reaction pathway proved was fully modelled with DFT/solvent corrections, showing the deprotonation of the propargyl alcohols or amines as the rate limiting step.



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Stability and C–H bond activation reactions of palladium(I) and platinum(I) metalloradicals

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Palladium and platinum complexes are among the most versatile transition metal catalysts employed in a wide range of chemical transformations in contemporary organic synthesis. Specifically, they find utility in the activation of C–H bonds,[1] typically realised through concerted oxidative addition involving diamagnetic +II/+IV redox couples. The organometallic chemistry of paramagnetic derivatives of Pd and Pt is much less developed, especially with reference to the advances being made with d^9-complexes of nickel.[2] In 2016, the Chaplin group demonstrated the facile and reversible one-electron oxidation of $M(PtBu_3)_2$ (M = Pd, **1**; Pt, **2**, **Figure 1**) using cyclic voltammetry.[3] Subsequent reaction of **1** with $[Fc][PF_6]$ enabled isolation of paramagnetic $[Pd(PtBu_3)_2][PF_6]$ **3**$[PF_6]$ and revealed stability for prolonged periods of time. Under the same conditions, however, the corresponding Pt(I) metalloradical **4**$[PF_6]$ could not be isolated and instead a 1:1 mixture of Pt(II) metallocycle **5**$[PF_6]$ and Pt(II) hydride **6**$[PF_6]$ was observed. This outcome corresponds to *net* radical oxidative addition of a $C(sp^3)$–H bond across two transient Pt(I) metalloradicals. Using DFT calculations jointly with experiment we were able to demonstrate that the mechanism associated with cyclometallation of **4** follows a *monometallic* radical oxidative addition pathway, resembling radical rebound mechanism of metal-oxo complexes.[4]

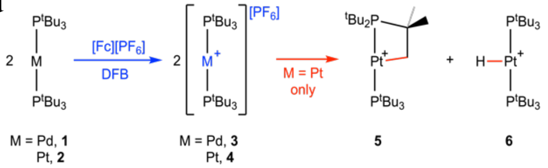

Figure 1. One-electron oxidation of $[M(PtBu_3)_2]$ and subsequent reactivity.

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Towards the investigation of Spin Crossover (SCO) systems

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3d coordination complexes exhibiting Spin Crossover (SCO) behaviour present an intriguing testbed to look for different phenomena in condensed matter. Even though the recognition of SCO phenomena in iron-based dithiocarbamato complexes dates back to the early twentieth century, the number of publications and projects concerning the SCO phenomenon continues to grow.[1-2] SCO or spin-transition (ST) materials are switchable metal complexes where the switching process between the high- (HS) and low-spin (LS) states is induced by external perturbations, such as change in temperature, pressure or by light irradiation. The unique properties of SCO materials as bistable molecular systems means they are useful in a variety of applications including sensors, electronic memories and in opto-electronics. Over the course of a spin transition, the metal-to-ligand bond lengths change significantly, thereby changing the bond order and consequently the force constant of the vibrations (f) and the low-frequency vibrational spectrum and the M-L bond stretches in particular. Phase transitions in solid samples can be readily detected by Raman spectroscopy due to the changes of selection rules as a function of the crystal symmetry. In the case of coordination complexes exhibiting SCO behaviour, temperature dependent Raman spectroscopy plays a significant role, exhibiting important features such as high sensitivity and structure characterization, while molecular structure modifications can also facilitate the determination of ΔS occurring during SCO event. Existing studies mainly focus on the recording of the Raman spectrum and not the complete monitoring of the SCO event, while recent efforts are dedicated for the complete monitoring of the SCO phenomenon. During this talk we will briefly analyze different aspects of temperature dependent Raman spectroscopy for the investigation of recently discovered SCO systems.

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GA(III) SIDEROPHORE COMPLEXES - A METALLO-TROJAN HORSE STRATEGY TO TACKLE ANTIMICROBIAL RESISTANCE

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In 2019, 4.95 million deaths were associated with the global rise in antimicrobial resistance (AMR). Lower respiratory infections were associated with more than 1.5 million deaths. This highlights the urgent need to develop novel antibiotics as AMR is reported to be one of the leading causes of death worldwide.[1] Recently, *Aspergillus fumigatus* (***A. fumigatus***) was classified by the WHO as a "priority one pathogen" which poses a serious threat to human health.[2] *A. fumigatus* is the most common fungus isolated from cystic fibrosis (CF) patients. This is of high concern as invasive aspergillosis is associated with a mortality rate of between 40 and 90% in the immunocompromised.[3] The antimicrobial properties of metals have been well known for centuries, with many metal-based compounds playing important clinical roles as therapeutics and diagnostic agents. Bacteria have a high demand for Iron (Fe) as it plays a vital role in DNA synthesis and oxygen metabolism. Ga^{3+} shares many chemical and physical properties to that of Fe^{3+} and is well known to exhibit antimicrobial properties.[4] Targeting bacterial siderophore Fe-uptake systems is an effective strategy to enhance the intracellular delivery of toxic payloads.[5] Ga citrate is showing promise in an ongoing clinical trial for the treatment of multidrug resistant P. aeruginosa in patients with CF.[6]

A Novel series of Ga(bipy) catecholate complexes has been successfully designed, synthesised and fully characterised by EA, NMR, IR, Mass spectroscopy and X-ray crystallography. Antimicrobial studies, including proteomic analysis, have demonstrated $[Ga(bipy)_2(2,3Dhba_{-2H})][NO_3]$ GaS1 exhibits promising fungicidal activity against *A.fumigatus*. An inhaled formulation of this novel complex has been developed for both nebulisation and dry powder inhalation. Studies are currently on-going to investigate the efficacy of the formulated compounds in an *in-vitro* lung model. This novel complex could be a promising adjuvant therapy for the treatment of *A.fumigatus* infections in cystic fibrosis patients.

The abstract should be maximum 1 page

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Cooperative Effects in Sodium-based Bimetallic Complexes for Selective Metalation Reactions of Aromative Substrates

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Heterobimetallic systems utilising the cooperativity of a highly polar alkali-metal amide and a lower polar metal amide (e.g. Al, Zn or Fe) have emerged as a powerful class of reagents for the selective deprotonation of arenes.[1] In this oral presentation, I will show our recent theoretical insights on the importance of the bimetallic partnership between [Na(HMDS)] and [M(HMDS)$_2$] (M = Fe^{II} or Co^{II}, HMDS = hexamethyldisilazide) which explain why the deprotonative metalation of pentafluorobenzene does not proceed experimentally with neither Na nor M amides alone.[2] An unexpected reaction pathway uncovering the cooperativity of Na and Fe^{II}/Co^{II} in a synchronised manner will be conveyed during the presentation, together with the key roles that Na and M play in this reactivity.

In addition, I will present how this newly found knowledge has led to the rational design of novel NaFe complexes with [Na(TMP)] (TMP = 2,2,6,6-tetramethylpiperidine), allowing the ferration of less activated substrates such as anisole and toluene (Fig. 1a), as confirmed by experimental studies.[2] Furthermore, I will shed light on the unique doubly ortho-F selectivity in the formation of the square planar complex [Na$_2$Co^{II}(C$_6$F$_5$)$_4$],[3] through portraying reaction pathways and stability investigations performed via activation strain, natural energy decomposition, Bader and non-covalent interactions (NCIs) analyses (Fig. 1b).[4] Together, the cooperative effects between Co and Fe in these bimetallic systems will be discussed. Overall, these novel bimetallic systems provide direct regioselective C–H metalations at room temperature, which quantitatively produces the desire metalation product.

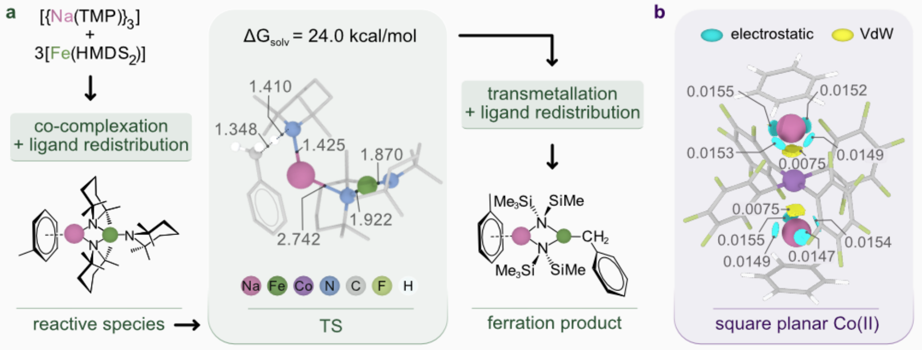

Figure 1. a) Ferration of toluene with equimolar [Na(TMP)] and [Fe(HMDS)$_2$]. b) Bader analysis and NCIs (isovalue = 0.07) on the square planar complex [Na$_2$Co^{II}(C$_6$F$_5$)$_4$].

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Synthesis and Biological Evaluation of Clinically Relevant Click-Fuctionalisable Pt(II)-Anticancer Complexes

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Platinum (Pt)-based drugs such as cisplatin, carboplatin and oxaliplatin play a very important and well-documented role in treating cancer, and are employed in nearly 50% of all anti-cancer regimens today. The primary mechanism of Pt-based drugs has long been associated with their ability to cross-link nuclear DNA; the Pt-DNA adducts interrupt transcription, generate DNA perturbation damage responses and ultimately induce apoptosis. Despite this, reports in recent years have highlighted that different mechanisms may be at play.[1] Moreover, the clinical effectiveness of Pt anti-cancer agents is commonly hampered by toxic side-effects and both intrinsic and acquired resistance mechanisms.[2]

There has therefore been a continued drive to develop novel classes of more effective and better-tolerated Pt(II) and Pt(IV) drug candidates. A better understanding of the precise cellular activity of Pt complexes is needed to achieve this goal.[3] The development of innovative azide-alkyne click based techniques to functionalize Pt(II) and Pt(IV)-based complexes is anticipated to greatly aid this enterprise. Click chemistry is widely used throughout synthetic chemistry and chemical biology, showing tremendous versatility whilst being atom-efficient and in some cases bioorthogonal.[4]

The synthesis of novel Pt(II) click-functionalisable complexes will be presented alongside their use as probes to study the mechanisms of action associated with clinically relevant Pt drugs.

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Resolving Light-Activated Processes of DNA Bound Transition Metal Polypyridyl Complexes Containing Nitrile Probes

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Photoinduced processes triggered by DNA bound metal polypyridyl complexes can be exploited for applications in photodynamic therapy and DNA imaging and diagnostics. We have extensively studied the excited state dynamics of these processes for intercalating ruthenium dppz (dipyridophenazine) polypyridyl complexes bound to DNA.[1-3] While the phenanthroline (phen) light-switch complexes can signal the presence of DNA, the tetraazaphenanthrene (TAP) complexes can cause photodamage by participate in direct one-electron photo-oxidation of guanine, which is sensitive to the local DNA environment and the binding orientation. In addition, the use of osmium can extend the optical window into the NIR.[4,5] In this talk I will share some recent results on DNA binding polypyridyl systems and show time-resolved methods, including time-resolved infrared (TRIR) complemented by structural and computational studies, can be used to identify the binding site of photoactive metal complexes in solution, and to monitor sensitized DNA photo-oxidation. In particular, I will highlight the use of infrared nitrile probes as powerful probes of excited state processes in DNA systems.

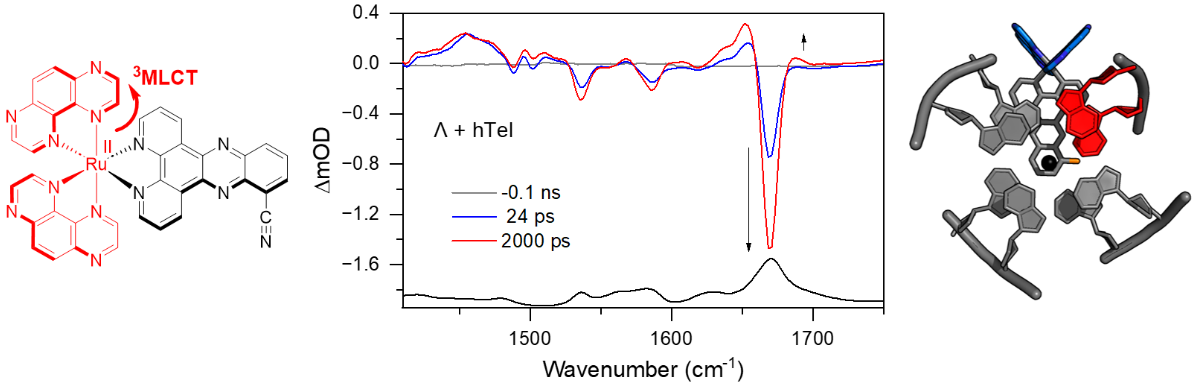

Figure 1: (Left) Structure of quadruplex binding $[Ru(TAP)2dppz\text{-}10\text{-}CN]^{2+}$ (Middle) TRIR spectra recorded with time. (Right) Site of guanine photo-oxidation in quadruplex DNA.

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A Microfluidic Approach for Tuneable Synthesis of Gold Nanostructures

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Nowadays it becomes inevitable for human beings to be exposed to nanostructures with distinctive complex shapes. Gain more depth knowledge regarding the nanoscale shape features regulated biological pathways becomes imperative not only for safety purposes, but also for the design of better nanocarriers for medical treatments. The work presented here introduces a microfluidic approach to achieve the synthesis of nanostructures along shape space trajectories of biological interests.

Inductive navigation by microfluidic synthesis of gold nanostructures along shape space trajectories of biological interests.

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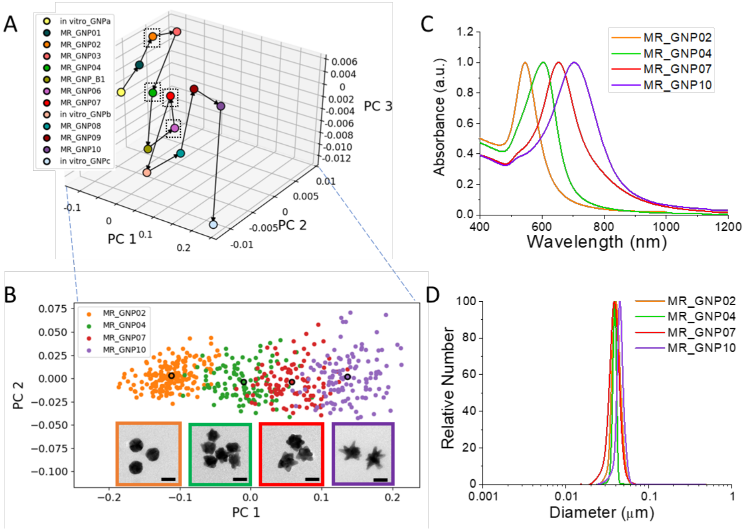

Poster Abstracts

REDOX AND SPIN STATE PREFERENCES IN MANGANESE MODEL COMPLEXES

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Manganese is an important and biologically active element involved in a number of redox enzymes (e.g., catalase, peroxidase, superoxide dismutase)[1] and in the oxygen-evolving center (OEC) of photosystem II.[2] This has stimulated interest in its properties and reactivity, especially in oxidation states II, III, and IV. Lord et al.[3] raised the question of electron transfer between the Mn(II) and Mn(IV) redox states via either the spin quintet or spin triplet forms of the intermediate Mn(III), Figure 1. Studying some uncommon low-spin Mn(III) compounds, with the help of X-ray crystallography and electrochemical, spectroscopic, and magnetic methods, they suggest a greater component of reaction pathway via a high-spin intermediate.

Our group has been interested in the spin states and oxidation states of manganese in hexadentate chelates with an N4O2 donor set embedded in chelates with different numbers and positions of connecting methylene groups, Figure 2. Our results show that the Mn(III) redox form is preferred and that spin crossover is sometimes possible in the solid state. The data also show that many examples can also be stabilized in the Mn(II) and Mn(IV) forms under ambient conditions. An important question is: does compression in the Jahn-Teller orbital direction of the high spin state have a role in determining access to more than one spin state and does this affect the redox window? This will be explored and compared among more constrained and elastic frameworks with smaller or greater number of carbons in the tetraamine backbones.

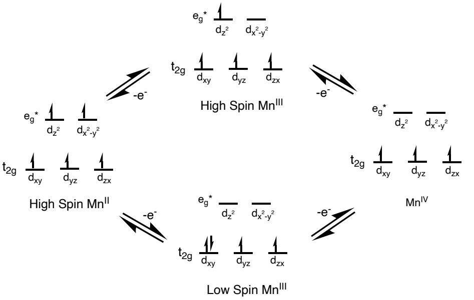

Figure 1. Proposed electron transfer steps for oxidation/reduction reactions going from Mn(II) to Mn(IV) through Mn(III).

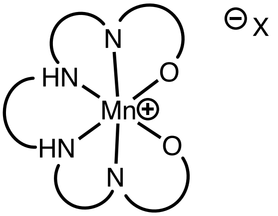

Figure 2. General structure of studied manganese hexadentate ligands.

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Chirality in ternary and quaternary I-III-VI luminescent nanocrystals: the role of the chemical composition on the transfer of chirality

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The introduction of chiropticol properties in inorganic nanomaterials has stimulated a large scientific interest in the last years due to the for the promising properties suitable for a broad range of applications such as: photonics, sensing, catalysis and nanomedicine.[1,2] Among the most investigated chiral nanomaterials, chiral semiconducture quantum dots QDs are of large interest due to their outstanding optical properties. During the last decade the scientific activities have been mainly focused on the investigation of the chirality in Cd-based binary QDs (e.g. CdS, CdSe, CdTe and their core-shell systems).[3] Recently, we reported the first observation of chirality in a I-III-VI ternary QDs and we successfully characterized the role of the chemistry at the ligand-nanocrystal interface in the chiral induction.[4] At the moment, our attention is extended toward the effect of the nanocrystals chemical composition on the transfer of chirality. The oprtical properties of ternary and quaternary I-III-VI QDs (absorption and photoluminescence) are known to be strongly affected by the nanocrystals chemical composition[5,6] and our investigations have proved that this behaviour is also observed in the case of the particle chirality. Moreover, our observations are not limited to a specific system but are still valid for multiple ternary and quaternary I-III-VI QDs in the family of the silver, copper and indium chalcogenide phases.

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DFT Insights into the Mechanism of Enantioselective Synthesis of Homoallylic Alcohols from Ortho-Vinyl and Ortho-Alkynyl Benzaldehydes via Asymmetric Allylboration.

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Abstract

Asymmetric allylboration of aldehydes is a valuable method for the synthesis of homoallylic alcohols, which are important building blocks in the synthesis of chiral drug compounds. Among all the available asymmetric allylation methods, Chiral phosphoric acid (CPA) catalysed allylboration is regioselective and proceeds rapidly.[1] CPA catalysed synthesis of homoallyl alcohols from Ortho-vinyl[2] and Ortho-alkynyl[3] benzaldehyde substrates was reported recently. We applied Density Functional Theory (DFT) calculations to understand the enantioselectivity of allylboration and account for the high enantiomeric excess *(ee)* observed in ortho-vinyl benzaldehydes. Our DFT calculations were performed using the M06-2X functional and the def2-TZVPP basis set. Our DFT results provide a detailed mechanistic understanding of the enantioselectivity in the asymmetric allylboration of aldehydes. Topology analysis using AIM theory revealed that the energetically favourable conformer promotes hydrogen bonding and dispersion interactions which are responsible for the high enantioselectivity observed for O-vinyl benzaldehydes compared to O-alkynyl benzaldehydes.

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Towards Phosphorus Cations as Main Group Catalysts

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Dependence on an ever-dwindling supply of transition metals (TMs) for their catalytic ability necessitates research into the development of candidates based on more-abundant elements[1]. Phosphenium cations, divalent phosphorus centres with a positive charge, have been shown to be effective main group catalysts in reactions such as reductions and hydroborations and are of interest for their potential in Frustrated Lewis Pair (FLP) chemistry[2]. The aim of this work is to determine the catalytic viability and potential scope of a number of phosphenium cations through the synthesis and subsequent analysis of catalytic candidates, with the view to provide viable alternatives to their well-established and widely employed TM counterparts.

Bis(arylimino)acenaphthene (Ar-BIAN, Figure 1 left) ligands are rigid, redox noninnocent diimines. Insertion of phosphorus into the ligand through reaction with phosphorus trihalides and subsequent anion exchange affords the isolated phosphenium cation (Figure 1 right)[3]. These are elements of a particular subset of phosphenium cations refereed to as N-heterocyclic phosphenium cations (NHPs) characterised by the formation of a 5 member aromatic ring.

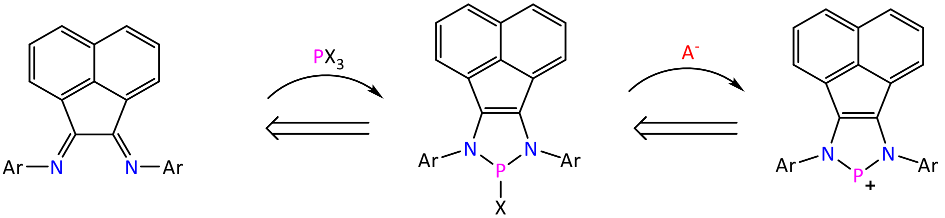

Figure 1: Insertion of phosphorus centre into bis(arylimino)acenaphthene (Ar-BIAN) ligands and isolation of the phosphenium cation

In this project the Ar-BIAN ligands were synthesised, phosphenium cations isolated and their reactivity against a number of substrates was investigated. It is hoped that this work will add to the library of existing phosphenium cations, as well as provide the reactivity studies required for the determination of their catalytic viability.

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MnFe2O4 @SiO2@CeO2 Core-Shell Nanostructures for Applications in Water Remediation[1]

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Removal of dye pollutants from wastewater is among the most important and emerging needs in environmental science and engineering. The main objectives of our work is to develop new magnetic core-shell nanostructures and explore their use for potential removal of pollutants from water using an external magnetic field. Herein, we have prepared magnetic core-shell nanoparticles that show dye pollutant adsorbent properties. These are composed of a manganese ferrite magnetic core coated with silica, to protect the core and enable further functionalisation, then finally coated with ceria, which is shown to be an effective adsorbent. The magnetic core-shell nanostructures have been synthesized by a modification of the solvothermal synthesis. The nanoparticles were fully characterised at each stage of the synthesis by powder x-ray diffraction (pXRD), transmission electron microscopy (TEM), vibrating sample magnetometer (VSM) and Fourier transform infrared spectroscopy (FTIR). These particles were found to be effective in removing methylene blue (MB) dye from water, which was validated by UV-visible (UV-vis) spectroscopy. These particles can be quickly removed from solution using a permanent magnet and then can be recycled after being placed in the furnace at 400 °C to burn off any organic residues. The particles were found to retain their ability to adsorb the pollutant after several recycles and TEM images of the particles after several recycles showed no change in the morphology. This research demonstrated the capacity of magnetic core-shell nanostructures to be used for water remediation.

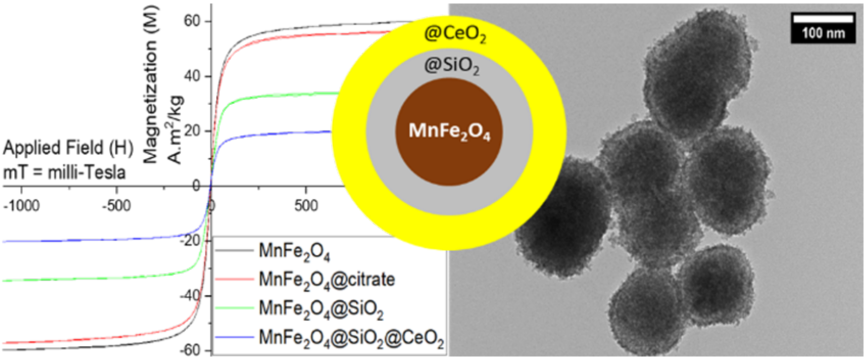

Figure 1: Magnetic core-shell nanoparticles are synthesised, characterised and used for methylene blue removal from water. They can be magnetically extracted and show no reduction in efficiency after several recycles.

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Chiral 2D MoS_2 nanostructures via a bottom-up approach

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The main goal of our work is to develop bottom-up synthesised chiral transition metal dichalcogenide (TMD) 2D nanomaterials. It is expected that this research will give greater insight into chiral induction in, and improve chiroptical properties of, the nanostructures by controlling their size and morphology. This work involved the preparation of MoS_2 nanosheets of few-layer thickness by bottom up chemical synthesis, using the well-documented hot injection method. Chiral functionalisation of these nanosheets was carried out via ligand exchange using enantiopure chiral molecules (e.g. cysteine, penicillamine) to replace the achiral ligands (oleylamine and oleic acid). The structure, morphology and optical properties of these functionalised nanomaterials have been investigated in detail. It is expected that these new nanomaterials will find a range of potential applications in chiroptical sensing and photonics.

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Mapping the Controlled Hydrothermal Synthesis of Materials with Principal Component Analysis

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As a simple, versatile, and green synthetic method hydrothermal (and solvothermal) techniques have seen a surge in interest in recent years, being applied to a wide variety of functional materials and offering control over composition, phase, size and shape.[1] Despite its growing importance the technique remains largely a "black box" as it requires sealed pressurised vessels, such that *in-situ* monitoring is restricted to synchrotron-based experiments.[2] As a result, gaining insights into hydrothermal reaction mechanisms, and thus design of reaction systems to achieve desired product characteristics commonly requires exhaustive empirical testing with the concomitant demands on characterising and analysing obtained products *ex-situ*. These analyses are frequently complex, time-consuming, and require a great deal of operator knowledge, representing an obstacle to materials discovery or process optimisation. Here we show that the statistical method of Principal Component Analysis (PCA) may be readily applied to laboratory powder X-ray diffraction data acquired from the extensive screening of hydrothermal reaction conditions.[3] This is demonstrated in the case of cerium dioxide, CeO_2, which is known to exhibit size- and shape-dependent catalytic properties. PCA was applied to CeO_2 diffraction patterns simulated with varied unit cell parameters and crystallite sizes to provide a theoretical framework for the interpretation of PCA of real data. Combined analysis of the simulated and real data easily reveals trends emerging from the variation of reaction conditions such as precursor choice, temperature, and time on key material properties such as size and shape.

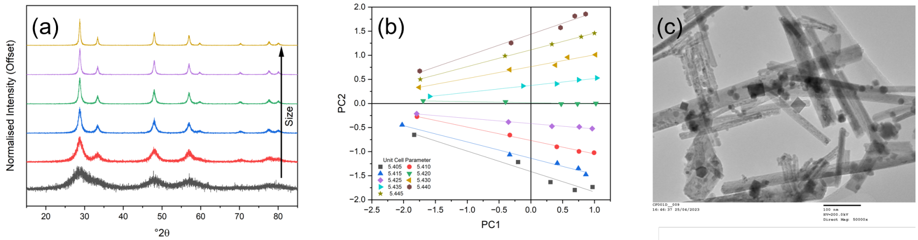

Figure 1: (a) Simulated CeO_2 X-ray diffraction patterns with increasing size, (b) Principal Component Analysis of simulated patterns, and (c) CeO_2 nanostructures obtained from hydrothermal synthesis.

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Synthesis, Characterisation & DNA Binding Interactions of Ru(II) – Pteridinyl Complexes

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G-quadruplexes (G4) are non-canonical DNA structures composed of stacked guanine tetrads, with influence over transcription regulation and act as potential therapeutic targets for cancer treatment.[1] Ruthenium polypyridyl complexes have been extensively investigated as biomolecular probes due to their versatility and favourable photophysical properties.[2] In this work, two new ruthenium(II) polypyridyl complexes containing an extended pteridinyl ligand, with end groups capable of facilitating hydrogen bonding interactions, have been synthesised, characterised, and their interactions with double-stranded and guanine-rich DNA have been evaluated.[3] Tuning of the ancillary ligands (phen *vs.* TAP) allows access to luminescent probe and photo-oxidation functionality respectively.[4][5] These complexes have been synthesised with a view to profile their hydrogen bonding interactions and binding specificity to G4 structures.

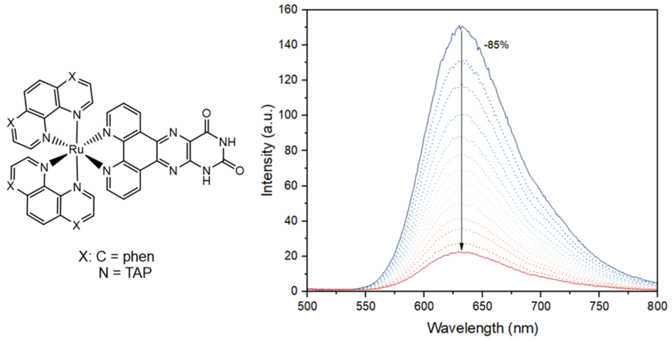

Fig. 1: Structure of representative complex and emission titration of complex *vs.* Poly(G) single stranded DNA, exhibiting emission quenching behaviour

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New Routes to Spin State Switching in Mn^{III}

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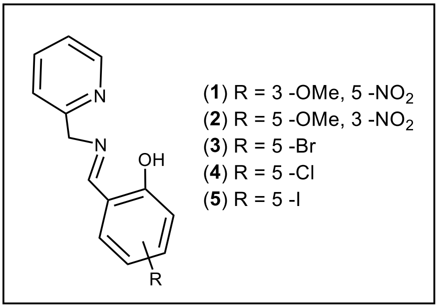
Great interest is being shown in molecular compounds whose physical properties can be controlled with light.[1] Transition metal complexes that exhibit spin-crossover behaviour (SCO) are particularly well suited for this purpose, as a spin transformation can be triggered by photoinitiation.[2] Until now, such LIESST behaviour has been mostly observed for iron(II)-based complexes, with a few iron(III) examples but none for manganese(III).[3] Considering that manganese(III) also exhibits SCO behaviour[2,4], our group is interested in synthesizing novel manganese(III) complexes to investigate their potential LIESST behaviour. To this end we are extending our ligand range to include pairs of tridentate systems with a rigid N_2O^- donor set. This is different from current ligand types for manganese(III) SCO which are usually Schiff bases with $N_4(O^-)_2$ donor sets, where we were already able to observe thermal spin state switching. [2,4] Here we present our results with the new tridentate ligands which included examples with electron-withdrawing groups, **Figure 1**. **Figure 2** shows the orbital population of a manganese(III) ion for the low spin (LS) and the high spin (HS) state and the axial compression in the S = 2 state.



(**1**) R = 3 -OMe, 5 -NO_2
(**2**) R = 5 -OMe, 3 -NO_2
(**3**) R = 5 -Br
(**4**) R = 5 -Cl
(**5**) R = 5 -I

Figure 1 Structure of the used Schiff Base.

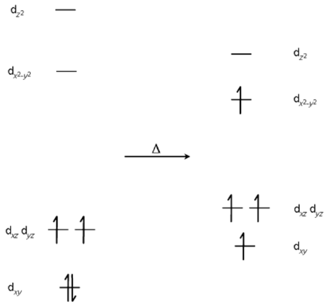


Figure 2 Orbital population of Manganese (III).[2]

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Hydrothermal synthesis of carbon dots from Irish seaweed and seaweed derivatives

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Due to the increase in global renewable energy generation and the need for reduction in greenhouse gas emissions we find ourselves in the energy transition of the century wherein the demand for green, sustainable energy materials is rising. Carbon dots are considered a new and green nanomaterial, applicable for energy generation technologies, including photovoltaics.[1, 2] In this research the potential of seaweed and seaweed derivatives as feedstocks for the hydrothermal formation of carbon dots was explored.[3] Hydrothermal conversion of local kelp and Irish moss and seaweed derivatives, led to the formation of fluorescent chemical species emitting blue photoluminescence under UV illumination. Photophysical analysis of UV-vis and Fluorescence spectra of the fluorescent species confirmed the excitation dependent photoluminescent behaviour expected and reported for carbon dots, with maxima of the excitation and emission wavelengths at 360 nm and 448 nm, respectively. Structural characterisation by TEM, XRD and NMR confirmed fluorescent amorphous carbon, confirming the presence of carbon nanodots in dispersion. The fluorescence of the carbon dots produced was concluded to originate from molecular fluorescence due to the complex conjugated aromatic structure and heteroatoms present in the carbon nanodots. Aggregation of the fluorescent content was observed by eye, DLS and TEM and is explained by instability and impurities in the sample. Overall, seaweed and seaweed derivatives are concluded to be a viable feedstock for hydrothermal synthesis of carbon dots.

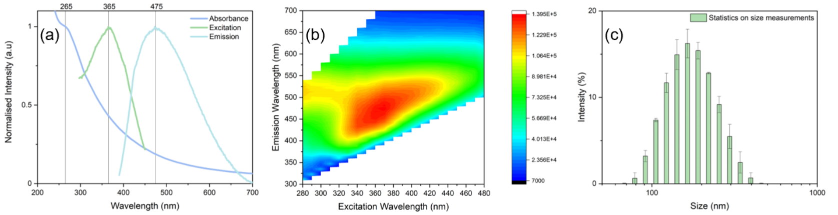

Figure 1: Characterisation of hydrothermally synthesised carbon dots from kelp including (a) absorbance, excitation and emission spectra, (b) photoluminescent map, (c) size by dynamic light scattering.

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Synthesizing Metal Organic Frameworks as potential drug carriers

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Metal Organic Frameworks are a class of highly structured materials, made from metal ions and organic linkers, whose applications vary from biomedical i.e., drug delivery to environmental. [1] These frameworks have a wide range of different characteristics including large surface areas, magnetism, tuneable pore sizes and high stability.[2] For these reasons, metal organic frameworks have proved themselves to be highly promising in the field of drug delivery as drug molecules can be loaded into the material and released in the body at the site of infection.[2][4]

In this project, a metal organic framework with MOF-74 topology has been synthesized with the ability to be used in the treatment of tuberculosis. The MOF-74 analogues are also highly capable of forming mixed metal MOF's, which has been explored further in this project due to the possibility of multiple metals improving the biocompatibility and therapeutic ability of MOFs.[3] Tuberculosis is one of the leading causes of death in the world, and with the rise of drug resistant strains, it is important to put focus on developing a route that overcomes these issues.

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Self-assembly and luminescence of chiral Eu(III) triple stranded helicates

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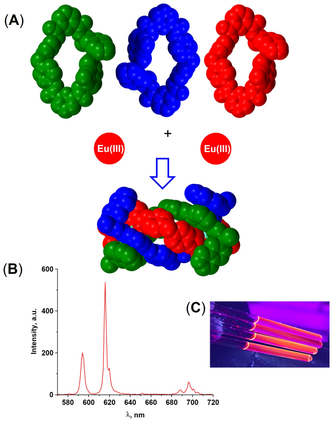

Figure 1. (A) Self-assembly of Eu(III) helicates showing the crystal structure of **L** and $\mathbf{Eu_2L_3}$; (B) Eu(III)-centred emission of $\mathbf{Eu_2L_3}$ (λ_{ex} = 283 nm) and (C) its emission in CH_3CN solution under UV light (λ_{ex} = 365 nm).

The interest to luminescent lanthanide(III)-based triple-stranded di-metallic helical motif systems stems from their structural organisation resembling biological molecules and their potential use as materials in bio-, electronics or environmental applications.[1] Since the ligand design principles leading to the formation of the helical structures with *d*-metal ions were established researchers also investigated the formation of analogous structures with lanthanides. In our research group we based the ligand design on connecting two chiral half-helicate ligands either (*S*) or (*R*) 6-((1-(naphthalen-2-yl)ethyl)carbamoyl)picolinic acid through 4,4'-methylenedianiline spacer following on the previously discovered data.[2] In the current work we investigated the formation of di-metallic Eu(III) triple stranded helicates (Figure 1) in the solution using NMR, mass-spectrometry, luminescence spectroscopy as well as single crystals X-ray crystallography techniques in the solid state.

This work was supported by the SFI AMBER Center [12/RC/ 2278_P2].

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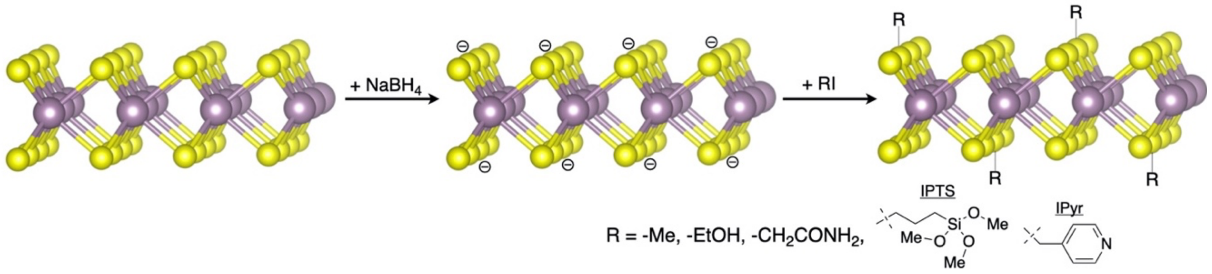
Negative doping in semiconducting 2H-MoS_2 and surface functionalisation

Molybdenum disulfide (MoS_2) is a graphene-like, layered material with semiconducting properties that is naturally present in the Earth's crust. However, the incorporation of the 2D-MoS_2 into multi-component devices had been challenging due to the hydrophobicity and intentness of the surface.[1,2] Here, liquid phase exfoliated 2H-MoS_2 was reacted with $NaBH_4$, which resulted in a mild reduction of the surface and introduction of the negative doping within the material (n-2H-MoS_2) as identified by the zetapotential and emission spectroscopy measurements. At the same time, emission and absorption spectroscopies confirmed the preservation of the semiconducting phase of 2H-MoS_2. A thorough characterisation of the material with XPS, pXRD, TGA, DRIFT and Raman spectroscopies did not reveal any signs of functionalisation, deterioration, or phase transition. n-2H-MoS_2 displayed a very different dispersibility in common solvents compared to pristine 2H-MoS_2, favouring mediums with a high dielectric constant capable of stabilisation of the charge at the electrical double layer.

The potential of integration of 2H-MoS_2 into more complex devices has also been demonstrated by the functionalisation of n-2H-MoS_2 with various organohalides.[3] This has allowed for the incorporation of functionalities of varying chemistry like methyl, hydroxyl, amide, methoxysilane and pyridine. Covalent tethering of new functionalities was identified by TGA, DRIFT, pXRD and Raman spectroscopy.



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Design of bifunctional hybrid ultramicroporous materials

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Crystal engineering is the branch of chemistry that explores the design, properties, and applications of crystals and is illustrated by the prominence of porous coordination networks (PCNs), including metal–organic frameworks (MOFs) and hybrid coordination networks (HCNs).[1] HCNs consist of both inorganic and organic ligands, and their ultramicroporous (<7 Å) variants are known as Hybrid Ultramicroporous Materials (HUMs).[2] HUMs provide three levels of compositional modularity that enable tailored pore environments driven benchmark gas separation performances, often facilitated by energy-efficient recyclability and easy scalability. Among sorbents relevant to the separation of commodity chemicals, combining strong electrostatics (from anionic/inorganic pillars with exposed electronegative atoms) and right pore size (from organic ligands) gives an edge to HUMs. For example, in 2013, Nugent *et al*. synthesized SIFSIX-3-Zn (SIFSIX = $SiF_6^{2-,}$ 3 = pyrazine) with a pore size of 3.84 Å, which was the first foray into HUMs setting a trace carbon capture benchmark.[3] Thanks to the crystal engineering of this generation-1 HUM prototype, generation-2 variants, SIFSIX-3-Ni and SIFSIX-18-Ni-β (18= 3,3′,5,5′-tetramethyl-1*H*,1′*H*-4,4′-bipyrazole) soon found relevance in direct CO_2 capture from air, under dry and humid conditions, respectively.[4] With the use of bespoke azolate and pyridyl ligands, crystal engineering of HUMs is paving the way for us to fine-tune the narrow pores' functions. It is particularly important to control pore and surface hydrophobicity signatures by harnessing the right azolate/pyridyl/mixed ligands, which offer just the right pore size and pore chemistry to the HUMs they afford. In light of the literature, we set out to investigate the adsorptive separation of mixed pyridyl-pyrazole-based HUMs, which remain understudied. Our strategy is to advance the adsorptive gas/vapor separations in modular families of bifunctional HUMs, by synergizing "*the best of both Worlds*" from both types of linker modalities: pyridyl and pyrazole. The prototypal example of a mixed pyridyl-pyrazole-based HUM is shown below.

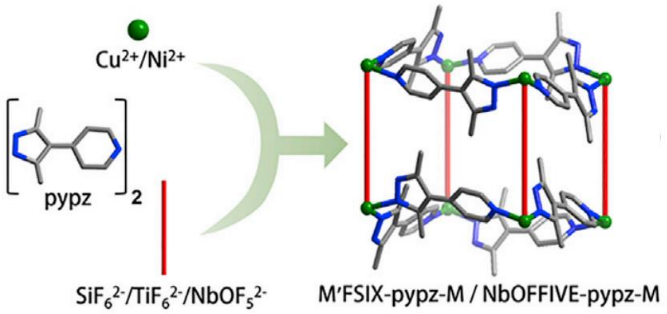

Fig. 1. Schematic illustration of the synthesis of a mixed pyridyl-pyrazole functionalized HUM.[5]

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Controlled Release of Doxorubicin by Smart pH-responsive Metal-Organic Framework – OnG1

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Metal-organic frameworks (MOFs) have attracted considerable attention in recent years because of their applicability in the environmental, industrial and biomedical fields. To circumvent the main problems associated with cancer therapy of high toxicity and side effects, in combination with the poor drug uptake and low stability of the contemporary drug carriers, the exploration of novel multifunctional non-toxic drug carriers has become a hot topic. A family of porous materials, that has the potential to overcome the limitations of chemotherapeutics and contemporary drug carriers, are MOFs. [1,2]

Herein, we report a new biocompatible MOF based on a multitopic elongated carboxylate linker, [Zn4O(L'H3)]n (OnG1). UV-vis, FTIR and TGA, studies indicated that OnG1 exhibits an exceptionally high doxorubicin (Dox) adsorption capacity (1735 mg Dox/g OnG1) with pH-controlled release. Toxicological assessment of the organic linker, OnG1 and Dox@OnG1 was performed using the HDF cell line. Both the organic linker and ONG1 are non-toxic at concentrations of 0.5—1 μM, which is the administered dosage of Dox. The cytotoxic effect of Dox@OnG1 revealed that the MOF is capable of a protective effect on healthy cells by reducing the toxicity of Dox compared to its nonencapsulated form.

Magnetic hyperthermia treatment is an innovative approach in cancer treatment. Despite MOFs being well-established as drug carriers, the exploration of a combining MOF derived chemotherapy and magnetotherapy from magnetic nanoparticles (MNPs) remains an unexplored research area. [3] MNP@OnG1 was isolated and characterised by IR, UV-Vis, TGA and SEM/EDX. The Dox encapsulation ability of the MNP@OnG1 composite was investigated (349 mg DOX/g MNP@OnG1) and characterised by UV-vis.

Acknowledgements

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AERIAL OXIDATION OF TRANSITION METAL SCHIFF BASE COMPLEXES VIA DIOXYGEN ACTIVATION

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Dioxygen activation in cobalt complexes has been well studied and uses for the phenomenon have been found in several different fields such as biomimetics,[1] sustainable energy storage by water splitting[2] and catalytic oxidation of organic substrates.[3] The mechanism of uptake of molecular oxygen by cobalt complexes has been extensively studied and it has been suggested that O2 may undergo a one electron reduction to forms a superoxide radical which quickly reacts with another cobalt site to form a peroxo dimer.[4] In this study we have investigated the oxidation of Co(II) to Co(III) via dioxygen activation. Our structural and spectroscopic studies suggest that in the binding process two Co(II) ions are oxidized to Co(III) and aerial O2 is reduced to peroxide. It was possible to isolate and characterize a metastable peroxo Co(III) dimer intermediate which is stable at room temperature in the solid state when removed from the mother liquor, Figure 1. We have also studied the formation of the dimer using EPR spectroscopy which suggests the formation of a short-lived superoxide intermediate, Figure 2.

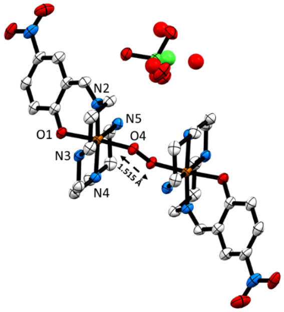

Figure 1: Crystal structure of peroxo complex

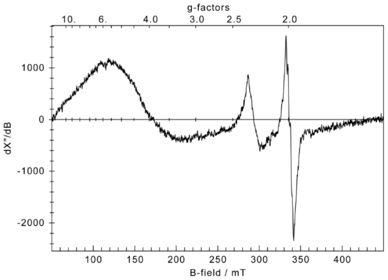

Figure 2: EPR spectrum of reaction mixture at 78K

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Magnetoelectric Coupling 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.

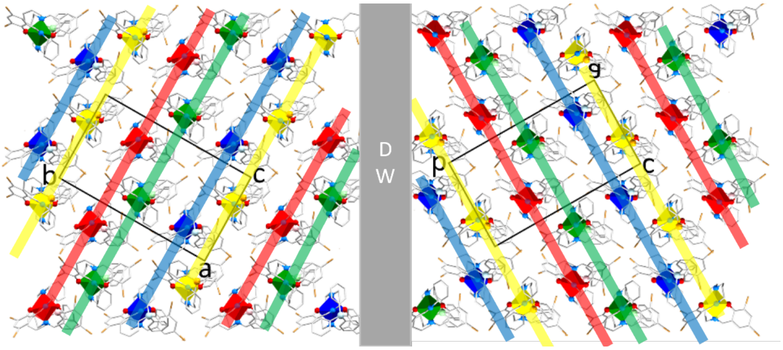

Figure 1. Domain wall formation in the spin-state ordered phase of a ferroelastic Mn3+ complex.gure with caption can be included.

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1,8-Naphthalimide-Based Tröger's Bases for Host-Guest Chemistry

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1,8-Napththalimide-based Tröger's bases (TBNaps) are fascinating chiral molecules that act as rigid V-shaped building blocks in the creation of supramolecular materials (Figure 1). These motifs have found use in applications such as cellular imaging,[1] as therapeutic agents,[2] and in the turn-on fluorescence sensing of volatile organic compounds and of nitroaromatic explosives.[3,4] The potential of TBNaps to be easily structurally tweaked at the *N*-imide position or the "naphthalene" group has been fundamental to the success of these compounds in such a wide breadth of applications. Herein, we present a series of novel TBNap materials, showing how these compounds can play host to a range of neutral and/or charged guests.

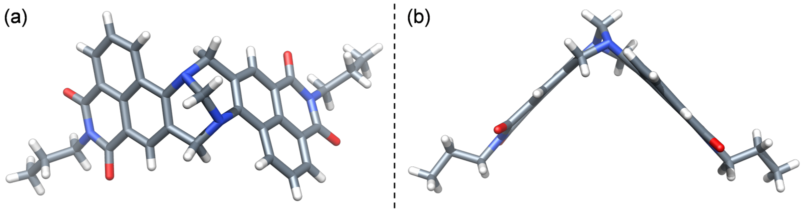

Figure 1. X-Ray crystal structure of *N*-propyl-4-amino-1,8-naphthalimide Tröger's base.[2] (a) "Head-on" view; (b) "side-on" view. Colour code: carbon (grey), nitrogen (blue), oxygen (red), hydrogen (white).

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Luminescent Lanthanide-Directed Self-Assemblies

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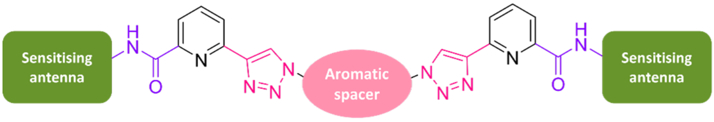
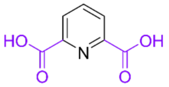
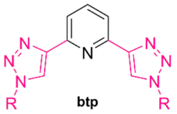
Supramolecular assemblies based on lanthanide coordination are often luminescent, and have shown promise in applications such as sensing, imaging and catalysis.[1] The specific coordination requirements of lanthanide ions determine the resulting supramolecular architecture, so there must be careful consideration when designing ligands for these assemblies. Ditopic terdentate ligands are advantageous in the formation of assemblies such as helicates, cages, grids, and interlocked molecules due to having two distinct binding sites for Ln(III) coordination.[2] The bis-tridentate(1,2,3-triazol-4-yl)-picolinamide (**tzpa**) motif is a combination of the dipicolinic acid (**dpa**) and bis(1,2,3-triazol-4-yl)pyridine (**btp**) motifs, both of which are widely studied in supramolecular chemistry.[3] Here, we examine the self-assembly of a ditopic **tzpa** ligand with lanthanide ions Eu(III) and Tb(III) both in the solution and solid phase with the aim of developing responsive and functional luminescent assemblies.



tzpa



dpa



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A Structural Study of a series of Fe(III) Schiff-Base Complexes

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Certain Fe complexes have been shown to exhibit various switchable properties such as spin crossover (SCO),[1][2] piezoelectricity or ferroelectricity. Fe(III) complexes in particular are appealing as they are resistant to oxidation in air, unlike their Fe(II) counterparts, thus making them more suited for applications. In this study a series of Fe(III) complexes were synthesised with the aim of determining the role of ligand geometry on spin state. The approach was based on a modular ligand design that incorporates a linear tetramine backbone with terminal salicylaldehydes which form a Schiff base. Here the substitution pattern on the salicylaldehyde rings were changed along with the order of ethylene and propylene linkers in the backbone while preserving its length. It was hoped to examine the effect of introducing an element of asymmetry into the tetraamine backbone by changing the linkage pattern from ethylene, propylene, ethylene (232) to ethylene, ethylene, propylene (223). Single-crystal X-ray diffraction (SCXRD) and SQUID magnetometry were used to examine the structural and packing motifs and to determine the spin state of the complexes. In one instance simply changing the backbone from “232” to “223” resulted in a change of spin state for the complexes at 100K, Figure 1.

Fig 1: Octahedra of LS Fe(III) “232” complex (left) and HS Fe(III) “223” complex (right). The LS complex displays much more idealised octahedral geometry.

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APPLICATIONS OF SUBLIMATION IN THE SYNTHESIS AND CRYSTAL GROWTH OF ORGANOSULFONES

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Sublimation has been established as a successful method of producing solvent-free high quality single crystals of several APIs[1–3]. Further applications of sublimation in combined organic synthesis through thermal transformation and crystal growth of organosulfones are currently investigated in this work.

Aromatic sulfones are valuable intermediates in industrial applications and organic synthesis. Diaryl sulfones are of particular importance in pharmaceuticals. Diphenyl sulfone is an intermediate in the synthesis of Dapsone (4,4'-diamino diphenyl sulfone) which is used in the treatment of leprosy[4]. Substituted diaryl sulfones were also found to suppress replication of human immunodeficiency virus type-1 (HIV-1) in vitro[5].

The preparation of 4-phenylsulfonyl biphenyl typically involves multistep reactions that require the use of catalysts and solvents[4]. An in-house low thermal gradient sublimation apparatus[1–3] has shown success in eliminating phenylsulfinic acid from trienes (**1a – 1f**) to produce biphenyls (**2**).

1 was synthesized by reacting [(E)-3-(benzenesulfonyl)allyl]sulfonylbenzene with an equivalent amount of a substituted trans-cinnamaldehyde and 33 equivalents of aluminium oxide to produce a family of substituted derivatives of **2**. In the case of **1a** yellow crystalline needles of the starting compound were transformed into colourless crystalline blocks of the phenyl derivative of 4-phenylsulfonyl biphenyl in quantitative yield.

Controlled thermal transformation and crystal growth through sublimation has proved to be a green method that provides a single-step process for the efficient production of a quantitative yield of organosulfones without the need for solvents, catalysts or further purification.

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Sustainability *and* quality: Hydrothermal injection synthesis of magnetic nanomaterials for medicine

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Magnetic nanomaterials such as the spinel-type oxides, MFe_2O_4 (M = Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}) have emerged as key materials in nanomedicine, with highly tuneable properties, accessed by varying composition or surface modification with functional ligands.[1] Their biomedical applications such as magnetic hyperthermia, an adjuvant to cancer therapies, require the nanoparticles to be water-dispersible, biocompatible, and possess sufficiently high magnetic saturation.[2] As such, control of these properties is essential in the synthesis of these materials. While there are many examples in the literature of ways to obtain iron oxide nanoparticles, there is a happy medium between synthetic control and sustainability that has not yet been realised by any one technique in particular. The present work aims to provide a comparison of some of the most commonly employed synthetic techniques for producing nanoparticles for this application; assessing each method interms of both synthetic control of material properties as well as compliance with green chemistry principles. In doing so, this poster presentation will introduce the promising capabilities of a new technique — a novel, custom-built hydrothermal injection reactor — designed to combine the green sensibilities of traditional hydrothermal synthesis with the synthetic control of the popular hot injection and thermolysis methods. A variety of spinel ferrites have been targeted by each of these synthetic techniques, each characterised by powder X-ray diffraction, electron microscopy, and magnetometry, before narrowing in on cobalt ferrite ($CoFe_2O_4$) – a hard ferromagnet which offers high chemical stability and good saturation magnetisation. It has been found that hydrothermal injection synthesis allows the formation of $CoFe_2O_4$ nanoparticles with size, monodispersity, surface capping, and magnetic properties comparable to those obtained by conventional thermolysis, but with the added green credentials of hydrothermal processing. Thus, this poster will showcase a new sustainable route to magnetic nanoparticles with suitable properties for use in nanomedicine – bringing green chemistry to this rapidly expanding field.

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HOMOCHIRAL Mn^{3+} SPIN-CROSSOVER COMPLEXES: A STRUCTURAL AND SPECTROSCOPIC STUDY

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Spectroscopic data on a Mn^{3+} spin-crossover complex with Schiff base ligand 4-OMe-$Sal_2$323, isolated in crystal lattices with five different counterions were investigated. Complexes of [Mn(4-OMe-$Sal_2$323]X where X= ClO_4^- (1), BF_4^- (2), NO_3^- (3), Br^-(4) and I^- (5), crystallized in the chiral orthorhombic space group $P2_12_12$. The chirality in (methanol) solution was confirmed via circular dichroism (CD) spectroscopy on single-crystals of high-spin complex[1] (1) at room temperature, each measurement recorded on a solution of one crystal, Figure 1). This revealed a 2:1 ratio of enantiomers in the chiral conglomerate, and solution CD measurements on the same sample in methanol to show that it is stable toward racemization. Solid-state UV-vis absorption spectra on high-spin complex (1) and mixed S=1/S=2 sample (5) reveal different intensities at higher energies, in line with the different electronic composition. The statistical prevalence of the homochiral crystallization of $[Mn(4\text{-OMe-}Sal_2323)]^+$ in five lattices with different achiral counterions suggests that the chirality may be directed by the 4-OMe-$Sal_2$323 ligand which could be useful in combining the functions of SCO and chirality.[2] Complexes measured by SQUID magnetometry on polycrystalline samples revealed a range of thermal evolution profiles in the solid state with stepped crossovers in complexes 3 and 5.

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