Modern Trends in Molecular Magnetism

(MTMM - 2022)

December 11th-14th, 2022

Department of Chemistry, IIT Kharagpur

Abstract book

Modern Trends in Molecular Magnetism
Department of Chemistry, Indian Institute of Technology Kharagpur
December 11 - 14, 2022
Gargi Auditorium, IIT Kharagpur

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List of Poster Presentations

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2	**Anup Choudhury, Tezpur University** Probing the influence of structural distortion and axial ligands on magnetic anisotropy in a series of chiral pentagonal bipyramidal Co(II) and Ni(II) complexes
3	**Dabasish Deka, Tezpur University** Cyanido bridged heterometallic Co(II)-W(V) aggregates: synthesis, crystal structures and electrochemical analysis
4	**Debasis Pal, IIT Kharagpur** Metal-Organic Frameworks and Coordination Polymers as Strategically Synthesized Proton Conductors
5	**Debopam Sarkar, IISc Bangalore** Reversible Crystal-to-crystal Transformation and Photo and Thermo-induced Metal-to-metal Electron Transfer in Heterobimetallic 2D Network
6	**Garima Bangar, IIT Bombay** Role of spin states and Spin-Coupling in selective adsorption of O2 in the biomimetic Fe-BTTri Metal-Organic Framework
7	**Imran Mondal, IIT Kharagpur** Gold nanoparticles decorated Magnetic-CNT Nanohybrid Heterostructure and Appraisal of their Catalytic Activity through the Reduction of 4-Nitrophenol
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9	**Krishna Kaushik, IISc Bangalore** Reversible Photo and Thermo-induced Spin-State Switching in a series of {5d-3d} Molecular Complex
10	**Mayurika Das, IISc Bangalore** On/Off Photo-Switching And Thermo-Induced Spin Crossover With Cooperative Luminescence In A 2D Iron(II) Coordination Polymer
11	**Moromi Nath, IIT Kharagpur** Thermal Spin Transition in [Co(terpy)2][BF4]2: A Density Functional and Wave Functional Study
12	**Nahid Hassan, IISER Pune** In-Situ Oxidation-Reduction as a Tool to Generate Magnetic Semiconductors
13	**Priya Paul, IIT Kharagpur** Exploration of Multifaceted Applications of Metal Organic Gels
14	**Rajanikanta Rana, IIT Bombay** Deciphering the role of pressure in the magnetization dynamics of lanthanide single molecule Magnets
15	**Rajdeep Paul, IIT Bombay** In Silico Studies of Spin crossover systems on surfaces
16	**Reshma Jose, IIT Bombay** Decisive Role of Spin-States and Spin-Coupling in Dictating Selective O2 Adsorption in Chromium(II) Metal-Organic Framework
17	**Rupesh Kumar Tiwari, IIT Bombay** Modulating Magnetic Anisotropy in Dy(III) Single-ion Magnets Using an Oriented External Electric Field
18	**Sagnik Mondal, IISc Bangalore** Impact of Counteranion on Reversible Spin–State Switching in a Series of Cobalt(II) Complexes Containing Redox-Active Ethylenedioxythiophene Based Terpyridine Ligand
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20	**Sanjoy Sarkar, Tezpur University** Role of Schiff Base Hydrazone Ligands in Self Assembly of Lanthanide Based Aggregates
21	**Santanu Ghora, IIT Kharagpur** Molecules to Material: Synthesis of Transition Metal Phosphide for Electrochemical Energy Applications

22	**Shalini Joshi, IIT Kharagpur** Spin-State Energetics and Magnetic Anisotropy in Penta-coordinated Fe(III) Complexes with Different Axial and Equatorial Ligand Environments
23	**Sounak Ghosh, IISc Bangalore** Bistable Magnetic Materials Based on Self-Assembled Metallosupramolecular [MII4L4] Tetrahedral Cages
24	**Sudip Sarkar, University of North Bengal** Theoretical study of magnetic anisotropy and optical property in doped CrPS4 single layer
25	**Sujit Kamilya, IISc Bangalore** ON/OFF Photo(switching) Coupled with Reversible Thermo-induced Spin-state Change and Single-Crystal-to-Single-Crystal Transformation in a Mixed-valence [Fe2Fe2] Molecular Square
26	**Sukanya Bagchi, IISc Bangalore** Stepwise Spin-State Switching and Effect of Light Irradiation in Manganese(III) Complexes
27	**Supriya Mondal, IIT Kharagpur** Immobilized Polar Sulfone Group Facilitated Flue and Biogas Separations by a Humid-Stable MOF under Dry and Wet Environments
28	T**anu Sharma, IIT Bombay** Charge on nucleus an “underrated player”
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30	**Debolina Mukherjee, IIT Kharagpur** A Highly Selective MOF-based Probe for Turn-on Luminescent Detection of Al3+, Cr3+ and Fe3+ in Solution and Test Paper Strips
31	**Sandip K. Kuila, Parna Pramanik, Rahul Pan, IIT Kharagpur** Ni3-δInSb: Crystal Structure, Electronic Structure and Magnetism
32	**Sreeja Dasgupta, Ayyan Ghosh, IIT Kharagpur** Molecular Ruthenium(III) Complexes with Redox Non-Innocent Ligand Frameworks for Water Oxidation Catalysis
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34	**Abhishek Das, IIT Kharagpur** Origin of the long-range ferrimagnetic ordering in “cubic" Mn(Co)Cr2O4 spinels

Invited Lectures

Graphene Oxide Hybrids with Spin Crossover Materials

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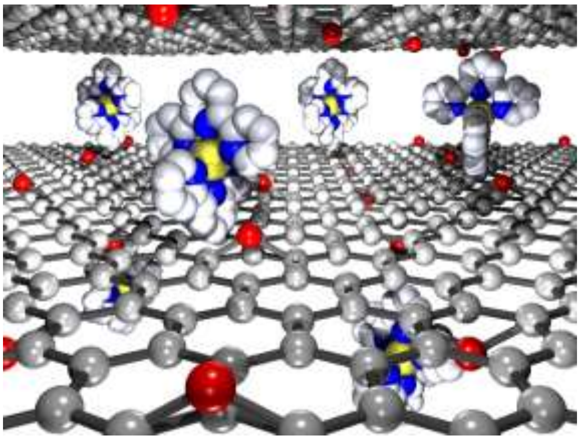
Graphene oxide (GO) is 2D nanosheet, and has many functionality, for example, proton conductivity. The GO has negative charge because GO has many oxygen functional groups such as epoxide group, carboxyl group, hydroxyl group and so on. Therefore, GO is able to combine with positive charge cations such as proton, metal ions, complexes and so on. Furthermore, the hybrids can be prepared by not only electrostatic interaction but also π-π stacking or chemical bonding between epoxy and amine groups. After reduction of GO by hydrazine, UV irradiation or annealing, reduced GO (rGO) can be produced, which shows electrical conduction. After reduction of GO hybrids, rGO hybrids also can be produced. In this study, we focus on GO and rGO hybrids with spin crossover (SCO) cation [FeII(Htrz)$_2$(trz)](BF$_4$). The complex exhibits a unique SCO behaviour depending on counter anions. We succeeded to control the domain size of the SCO complexes on the graphene nano sheet or chemical pressure of the interlayers.



Flexible Organic Field-Effect Transistors-Based Healthcare Sensors

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With the devastating COVID-19 pandemic spreading over the last two years, the need for smart-healthcare technology to take off the pressures on health professionals and provide the patient with much more comfortable yet remote monitoring medical devices becomes paramount. Aligning the flexibility of organic electronic device-based sensors has been found to provide opportunities to develop wearable medical technology, including various diagnostic interventions to replace the existing gold standards with portable, affordable, and wearable devices with remote monitoring capabilities. Developing efficient healthcare sensors becomes essential to innovate such new healthcare technologies. In this seminar, I am going to talk about a few organic field-effect transistors (OFETs) based flexible yet highly sensitive devices, which are developed by integrating selective organic receptor molecules to sense various analytes, such as gas molecules, bio-molecules like blood albumin including deadly virus like SARS-CoV-2, and physical parameters like temperature, pressure, etc. The challenges in fabricating such sensor systems by exploiting chemical, electrical and optical properties will be discussed. I will also touch upon devices developed with spin crossover materials.

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Thermo- mechano-elastic model and lattice dynamics in molecular spin crossover systems

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Spin crossover (SC) molecular magnets, extensively studied due to their potential applications in thermal and pressure sensors, optical displays, actuators or in data storage, are inorganic compounds commutable between two states with different optical, volume, magnetic and vibrational properties: the low spin state (LS) and the high spin state (HS). The experimental studies of SC compounds switched in the last decade from bulk measurements and macroscopic observations to the nanoscale and microscopic approaches. In this context, new and sometimes unexpected behaviours have been documented, which could be only partially described by the classical phenomenological models developed in the last century. Therefore, the development of more complex models, able to reproduce the nucleation and domain propagation within the materials, has proved to be not a whim of some theoreticians, but a necessity, which facilitated the full understanding of observed phenomena and even made premises for further experiments. Here we discuss how the mechano-elastic model[1] and its new version considering thermal effects, can be used for the study of microscopic phenomena, as cluster formation (Figure 1), stability and propagation of elastic waves, for understanding of the behaviour of spin crossover layers on substrates[2], or of evolution of the system after ultrafast photoexcitation[3].

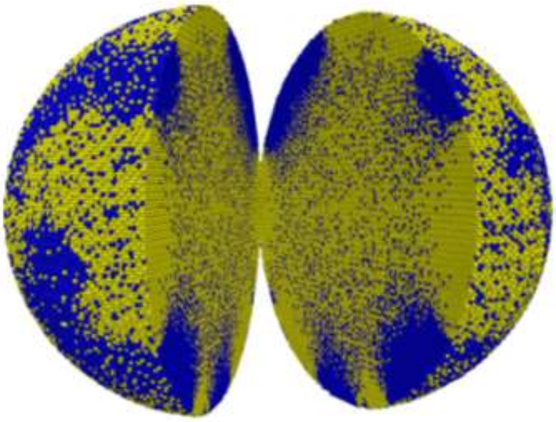

Figure 1: Cluster formation for a large sphere (1.3 million molecules) from several points on the surface and their evolution towards the central part of the sphere. The sphere has been represented cut in order to see how the clusters propagate inside the crystallite. Blue: High spin molecules, yellow: low spin molecules.

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Computational Modelling of Magnetic Phenomena in Frustrated Clusters and Chains, Metal-organic Frameworks and Molecular Systems

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I shall first introduce to the basics of magnetism and magnetic phenomena and how these can be captured accurately using various quantum mechanical modeling methods. I shall discuss our studies on Kagome lattice clusters, wherein employing Heisenberg antiferromagnetic coupling and z-component of Dzyaloshinskii-Moriya (DM) interactions, we find that the spin configuration in Fourier space transforms from (0,0) to $(\sqrt{3},\sqrt{3})$ ordering [1]. I shall talk on spin state of transition-metal@porphyrin, which can be switched on and off by spinterface formation with another graphitic surface. In fact, small molecule and gold STM-tip can precisely modify the conformation and reversibly switch spin state [2]. Next, I shall show the results of our study using linear spin-wave theory and density matrix renormalization group (DMRG) on an alternating spin-1/spin-1/2 chain with nearest and next-nearest neighbour (NNN) antiferromagnetic interactions along with z-component of the DM interactions. Both the AFM NNN interactions and DM interactions introduce strong quantum fluctuations and due to which all the signatures of ferrimagnetism vanishes [3]. We also have studied three Metal-Organic-Framework (MOF) systems, namely, Cu_3Cr_2-MOF, Mn_3Cr_2-MOF and $CuMn_2Cr_2$-MOF. We find that while the pristine Mn_3Cr_2-MOF is ferrimagnetic, the post-synthetically modified Cu_3Cr_2-MOF displays ferromagnetic interactions. On the otherhand, the $Cu_1Mn_2Cr_2$-MOF is found to exhibit interesting magnetic phenomena, reminiscent of meta-magnetism. We collaborated with an experimental group, who found a kink in magnetic susceptibility at 40 K. We have used Ab-initio Molecular Dynamics (AIMD) and Density Functional Theory (DFT) calculations to understand the meta-magnetism, which manifests in temperature dependence of magnetic susceptibility and also in entropy [4]. Towards the end, I shall show some of the results of tunneling versus hopping phenomena in a molecular magnet, Dy_2Gd [5].

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Spin Transition Compounds as Actuators for Inducing Strain in 2D Materials

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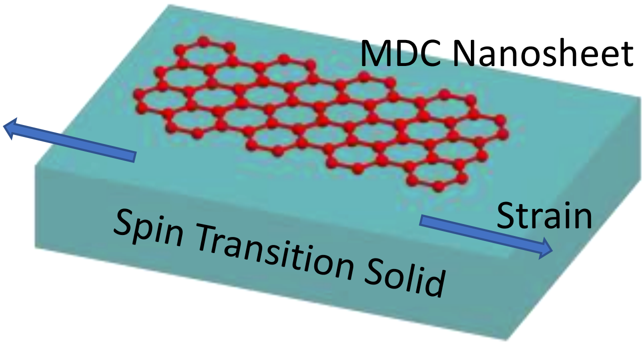
Spin transitions lead to an alteration in the local metal orbital electron distribution, causing large changes in metal-ligand bond distances. As a result, spin transition materials are accompanied by large volume changes, as high as 10-15%, which can be exploited for mechanical actuation. We have previously demonstrated light-actuated strain-induced switching of magnetization in thin film and nanoparticle heterostructures using spin-transition solids such as the Prussian blue analogue $Rb_j[Co_k(Fe(CN)_6)_l]$.[1,2] In more recent work, the concept is extended to using spin transition solids as actuators for inducing strain in 2D materials. Among the interest in 2D materials is their susceptibility to strain which is recognized as a promising parameter to tune optical and electronic properties. Heterostructures formed from metal dichalcogenide (MDC) 2D sheets and spin transition single crystals show the spin crossover event can be used to reversibly strain MDC nanosheets and tune photoemission.



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Quantum Computing with Molecules

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Metal complexes will be proposed to acting as active quantum units for Quantum Computing (QC). We report on the implementation of metal complexes into nanometre-sized (single-)molecular spintronic devices by a combination of isotopologue chemistry, bottom-up self-assembly and top-down lithography techniques. The control of the Hilbert space of the molecular quantum magnets on conducting surfaces/electrodes will be shown and persistence of magnetic properties under confinement in Supramolecular Quantum Devices (SMQD) will be proven. The quantum behaviour (e.g.. superposition) of the metal complexes will be addressed at the single molecule level[1-13] to finally implement a quantum algorithm on a $TbPc_2$-Qudit performing quantum computing operations.[10] Moreover, we will show that that the components of SMQDs as the Quantum Magnet[14] and the graphene sheets[15] can be made from CO_2 guaranteeing a negative Carbon footprint and sustainability of the molecular approach towards QC.

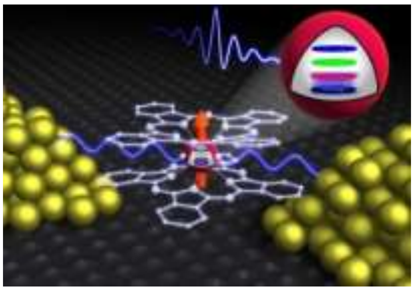

Figure 1 Artistic representation of a Molecular Spin Transistor based on a $TbPc_2$ complex acting as a molecular Spin Qu*d*it.[8]

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Invited Lecture 7

Control of Magnetic and Electric Polarization in Molecular Crystals through External Stimuli

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The design and synthesis of new molecular compounds whose physical properties can be controlled by external stimuli have recently attracted much attention. Various switchable compounds have been developed.[1] An important challenge in the field is the control of the electric polarization of molecular compounds. The change in polarization mostly occurs by ion displacement. When electrons are adopted as the source of the polarization change instead of typical ion displacement and molecular reorientation, faster switching rate, and better durability, and even more interestingly, the photo effect is expected. However, such a fundamental idea, which represents the concept of electronic pyroelectricity (polarization switching via electron transfer), has not been evaluated in non-ferroelectric molecular crystals. We report the electronic pyroelectricity in a valence-tautomeric cobalt complex,[2] a dinuclear [CrCo] complex,[3] and a dinuclear [FeCo] complex.[4] Polarization changes in the [CrCo] complex stem from intramolecular electron transfer between Co and the ligand [2]; $\mathrm{Co^{III\text{-}LS}}$–$\mathrm{dhbq^{3-}}$–$\mathrm{Cr^{III}}$ ⇆ $\mathrm{Co^{II\text{-}HS}}$–$\mathrm{dhbq^{2-}}$–$\mathrm{Cr^{III}}$ (LS = low spin, HS = high spin). Furthermore, photoinduced polarization switching was found to have a time constant of 280 fs by ultrafast pump–probe spectroscopy.[5]

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Quantum Sensing with Nitrogen-Vacancy Spin Defects in Diamond

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Diamond serves as an ideal crystalline host for a variety of point defects due to its qualities such as wide band gap, small spin-orbit coupling and its availability in high quality, isotopically purified single crystals. Among the possible defects, the nitrogen-vacancy (NV) spin defect has been extensively studied as its spin state can be optically initialized and measured at room temperature, and can be manipulated via electron spin resonance by microwave radiation.

The NV center in diamond has been used to measure a number of physical quantities such as magnetic field, electric field, temperature and stress/strain at ambient conditions [1, 2]. Hence, the NV quantum sensor has not only emerged as a powerful magnetometry tool for the study of nanoscale magnetic materials but also as a spectroscopic tool for imaging the charge and strain environments intrinsic to the diamond lattice [3,4]. In this talk, I'll discuss various sensing applications using NV centers.

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Switchable Magnetic Materials Based on Redox-Active Ligand

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The pursuit of smart multifunctional materials with stimuli-responsive magnetic and optical response has drawn escalating interest in both fundamental science and potential applications to switches, sensors, and intelligent devices.[1] Spin Crossover (SCO) materials are ideal candidates for developing smart multifunctional materials and are promising components in nanotechnological devices, for example, in displays, sensors, memory storage units, or actuators.[2] The SCO phenomenon refers to the exchange between two well-defined high-spin (HS) and low-spin (LS) states, mainly occurring in six-coordinated first-row transition metal complexes with d^4–d^7 configurations.[3]

The development of stimuli-responsive flexible coordination polymers (CP) whose porous structures can be reversibly altered in response to the sorption of guest molecules has attracted growing attention. Also, the rational design of stimuli-responsive multifunctional CP by incorporating one or more additional cooperative properties *e.g.,* magnetic, electric, and optical, with the intrinsic properties *e.g.,* permanent and tunable porosity, versatile structural topologies, and physicochemical properties have gained significant attention in recent times.[3] On this aspect, the simultaneous incorporation of both Spin Crossover (SCO) and luminescence properties in CP is challenging but highly attractive as modulation of luminescence signal can signify LS/HS population during the spin-state switching.[4]

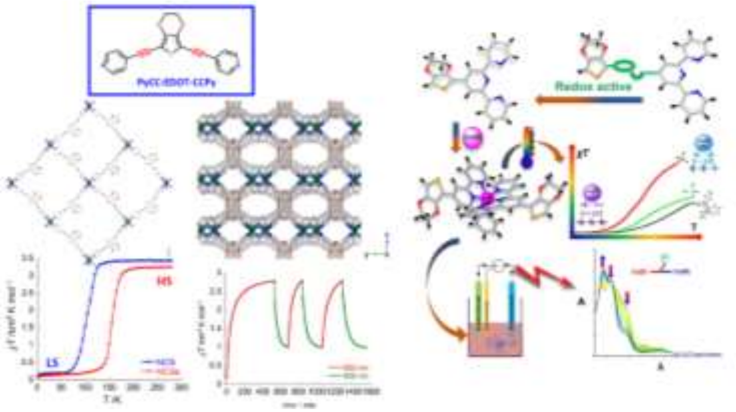

Figure 1: (Left) 2D structural, magnetic, and photomagnetic features of the Fe(II)-based CP; (Right) Structural, magnetic, and spectroelectrochemistry features of the Co(II) monomer with redox-active EDOT-Terpy ligand.

Here, I will discuss the versatility of redox-active Ethylenedioxythiophene (EDOT) based ligand to form a series of 2D CP (**Figure 1** (left)) and monomeric complex (**Figure 1** (right)). The 2D Fe(II)-based CP exhibits cooperative SCO and luminescence properties along with ON/OFF photo-switching behavior.[5] Co(II)-based monomeric complexes exhibit a Spin Crossover between low-spin (LS) ($S = 1/2$) and high-spin (HS) ($S = 3/2$) states modulated by different counter anions.[6] Additionally, we have been able to show a redox stimuli assisted reversible conversion from paramagnetic Co(II) ($S = 3/2$) to diamagnetic Co(III) ($S = 0$) system.

Acknowledgments: We thank the Indian Institute of Science (IISc), the Solid State and Structural Chemistry Unit (SSCU), the Department of Science & Technology-Science & Engineering Research Board (DST-SERB), the Scheme for Transformational and Advanced Research in Sciences (STARS, MHRD) and the Council of Scientific and Industrial Research (CSIR), for financial support.

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Spin Coupling in Diheme Enzyme *MauG* Upon Stepwise Oxidations: Modulation, and Magneto-Structural Correlation

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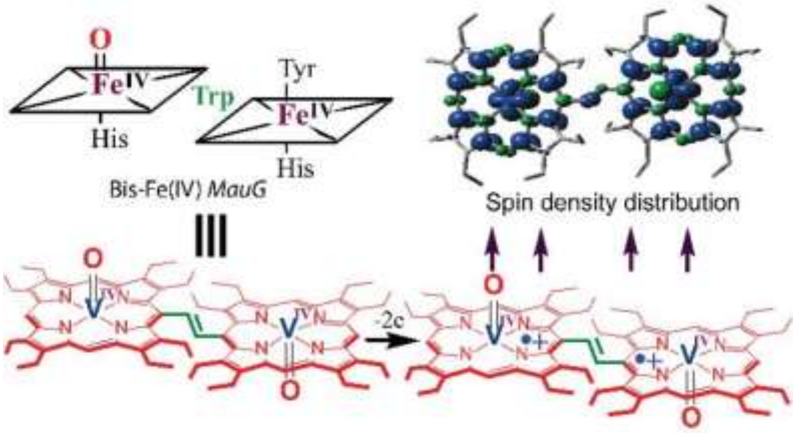
MauG is a terminal enzyme involved in the biosynthesis of the catalytic tryptophan tryptophenylquinone (TTQ) cofactor of methylamine dehydrogenase (MADH). Although two heme units are physically separated in the enzyme, they share electron efficiently behaving as a single diheme unit. A tryptophan residue, positioned midway between the heme centers, has been postulated to act as a bridge for electronic communications. Biomimetic studies of these systems provide valuable information regarding the mechanisms of electron and charge transport behaviors and provide promising platforms for systematic studies of spin coupling to promote long-range communication across the bridge connecting the metalloporphyrin centers. The interchromophore separation and the extent of electronic coupling are the vital factors in the development of electron and charge-resonance phenomena. Using redox-active bridge is particularly appealing as they are able to tune the communication by simple oxidation or reduction acting as a very efficient magnetic relay between the spins. Interaction between the organic radical and paramagnetic metal centre is important machinery for designing functional magnetic materials with desired properties. My talk will highlight our recent activities [1-3].



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Anchoring Cu(II)-Based S=1/2 Kagome Lattices on Functionalized Graphene

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Cu(II)-based atacamite family of minerals have emerged as promising candidates for the investigation of quantum spin liquid (QSL) states. Herein, starting from Cu(I) precursors, we have synthesised phase-pure Cu(II)-based S=1/2 kagome spin lattices at near-ambient conditions. When graphene oxide (GO) was taken along with other reactants, the oxidation of Cu(I) to Cu(II) was accompanied by the reduction of GO to rGO which not only led to the anchoring of various S=1/2 spin lattices onto rGO but also the magnetic exchange interactions were notably modulated by the diamagnetic rGO matrix. Overall, a series of S=1/2 kagome spin lattices are explored, all belonging to the atacamite family of minerals and are known to be antiferromagnetic insulators. Specifically, strongly coupled kagome planes (clinoatacamite), weakly coupled kagome planes (barlowite), and weakly coupled and magnetically isolated kagome planes (paratacamite and herbertsmithite) – were successfully anchored to rGO matrix. The resultant atacamite-rGO nanocomposites were assigned as magnetic semiconductors and electron doping of the kagome spin lattices by rGO is proposed.

Switchable Porous Magnets (3): Paramagnetic O$_2$ mediates magnetic long-range ordering

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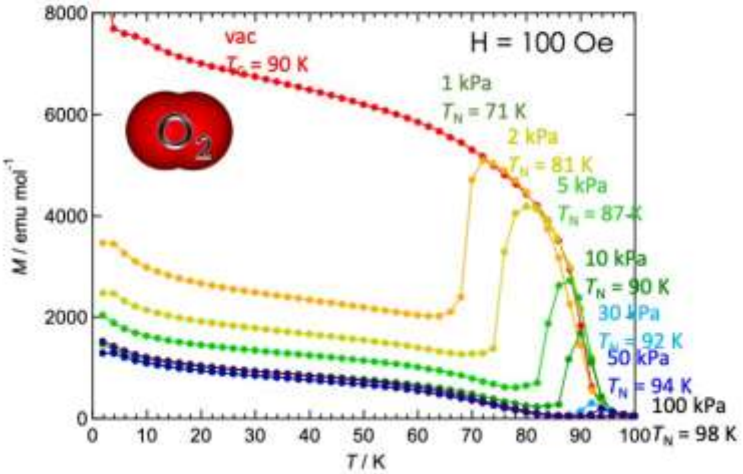
Design of multiply sensing materials whose intrinsic nature is mutually tunable by chemical and physical external stimuli is a pivotal challenge in the field of materials science. A class of electron-conjugated metal-organic frameworks (MOFs) composed of electron-donors (D) and/or –acceptors (A): we call this class of materials as "D/A-MOFs", is one of the favorable candidates for such materials.[1,2] Since the charge transfer (CT) of $D^0A^0 \leftrightarrow D^{\delta+}A^{\delta-}$ is flexible as a function of the combination of the ionization potential of D and the electron affinity of A and the Madelung stabilization of the ionic D^+A^- set, D/A-MOFs are intriguing targets for guest-sensitive functional materials with magnetic, conducting, and their synergistic properties, as well as with their porous nature for gas/solvent sorption or ionic transportation. We have designed such materials in the combinations of paddlewheel-type diruthenium(II, II) complexes ($[Ru_2^{II,II}]$) as D and TCNQ or DCNQI derivatives as A, and demonstrated the rational control of CT in D/A-MOFs to obtain electronic and magnetic functionalities.[2] Among them, magnetic properties of D_2A layered systems containing crystallization solvents or void space between layers are quite sensitive to interlayer environments (e.g., packing structures, interlayer distances, the presence of spins) relevant to guest molecules presented/inserted, as well as the oxidation state of each layer. Here we focus on the adsorption of oxygen (O_2) as a magnetic mediator, in which O_2-dimers inserted between ferrimagnetic layers mediate magnetic long-range ordering.[3,4]



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Chemistry in Confined Nanospace of Molecular Vessels

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Physical and chemical properties of chemical entities in confined nanospace are expected to be different from their usual bulk properties due to restricted rotational and translational motions. This restricted degree of freedom along with other non-covalent interaction/s may allow to stabilize unusual conformations of compounds in confined nanospace of molecular cavity. Our recent efforts on designing chiral molecular flasks including their chiral recognition will be discussed in my lecture. A recently developed strategy on constructing enantiopure cage (Figure 1) without using chiral donor/acceptor will be highlighted in the lecture. My lecture will also focus on the use of confined space for the separation of polyaromatic hydrocarbons by aqueous extraction.

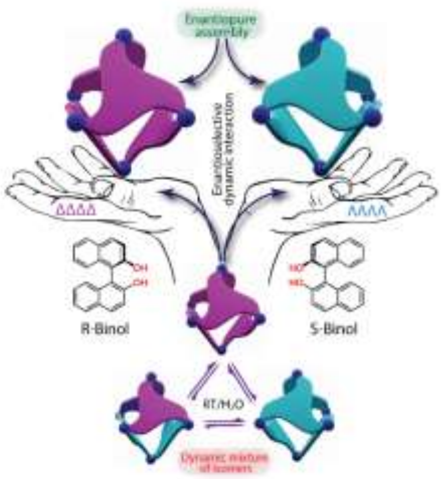

Figure 1 Guest induced enantiopure cage formation.

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Mixed valence Mn^{II}.Mn^{III}, Co^{II}.Co^{III} and heterometallic 3d-4f species offer interesting magnetic outcomes

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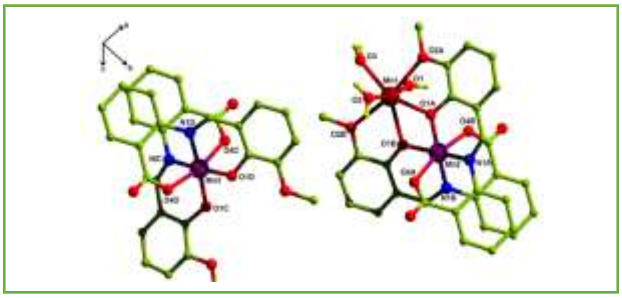
The construction of heterometallic and mixed valence species have witnessed a sweeping growth in the arena of coordination chemistry and magnetochemistry, as evident by a constantly increasing number of publications in this area.[1] The quest for molecular magnetic materials possessing potential applications in information storage, spin−dependent electronics and quantum computing is one of the most challenging topics in chemistry, stimulating new ideas for the development of novel materials. The catalytic development in this direction in the last two decades have been led by single−molecule magnets (SMM) and single ion magnets (SIM).[2] SMMs/SIMs, capable of showing slow magnetic relaxation of molecular origin as a result of an energy barrier to spin reversal of a magnitude sufficient to observe hysteresis at workable temperature − are crucial for their possible uses in molecular devices. In addition to these potential technological applications, the understanding of the fundamental concept including efforts to grasp the design principles and relationship between the molecular structure and the intricate magnetic outcome of a wide variety of Mn$^{II/III/IV}$, Co$^{II/III}$, 3d–4f compositions also serve as the driving force. This knowledge is crucial to synthetic chemists for the tailor-made design of compounds of desirable magnetic properties.

In this lecture, I wish to provide a glimpse of a couple of our laboratory endeavors regarding Mn^{II}-Mn^{III}, Co^{II}-Co^{III}, Ni^{II}-Ln^{III}(Ln = Gd, Tb, Dy, Ho) and Co^{II}-Dy^{III} systems that exhibit promising magnetic characteristics.



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Probing the Origin of Ferro/Antiferromagnetic Exchange Interactions in Cu(II)-4f Complexes

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The mechanistic investigations between Cu(II) and the anisotropic lanthanides (Ln(III)) are not much explored to date. This is due to the complicated energy spectrum which arises due to the orbital angular momentum of anisotropic lanthanides. Interestingly, the exchange coupling J in Ln(III)-Cu(II) systems was found to be antiferromagnetic for < $4f^7$ metal ions and ferromagnetic for $\geq 4f^7$ metal ions, while the net magnitude of J_{Total} strength gradually decreases moving from f^1 to f^{13}. While this is established in several examples, the reason for this intriguing trend is not rationalized. In this lecture, how this challenging task has been overcome by investigating Cu2Ln series with the general molecular formula $[Cu_2Ln(HL)_4(NO_3)](NO_3)_2$, where Ln = La (**1-La**), Ce (**2-Ce**), Pr (**3-Pr**), Gd (**4-Gd**), Tb (**5-Tb**), Dy (**6-Dy**) and Ho (**7-Ho**) and HL = $C_{15}H_{15}N_1O_3$; (2-methoxy-6-[(E)-2'-hydroxymethyl-phenyliminomethyl]-phenolate) is a mono deprotonated tridentate Schiff base ligand. These complexes detailed electronic and magnetic properties will be discussed besides the tentative mechanism of the exchange interaction exist in this series.[1]

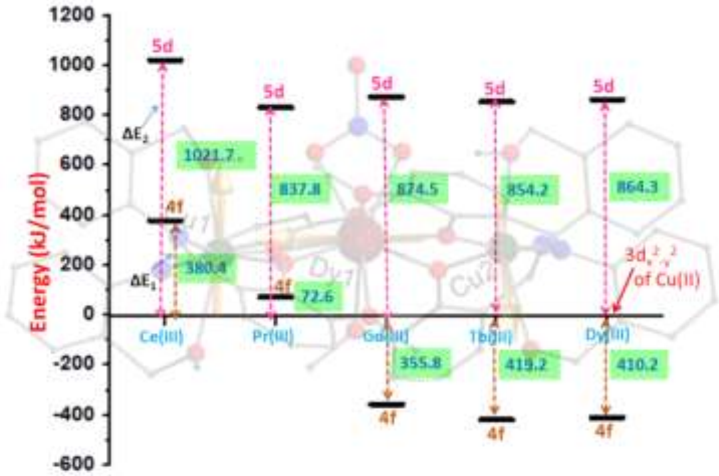

Figure 1. Comparative energies (kJ/mol) of 4f, 5d of Ln(III) and $3d_{x^2-y^2}$ orbital of Cu(II). The energies of Cu(II) $3d_{x^2-y^2}$ are taken as reference for each complexes. The energy differences between 4f(Ln)-$3d_{x^2-y^2}$(Cu) and 5d(Ln)-$3d_{x^2-y^2}$ (Cu) termed as ΔE_1 and ΔE_2, respectively.

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Tailoring spin waves in two-dimensional magnetic materials

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The recent isolation of two-dimensional (2D) magnets offers tantalizing opportunities for spintronics and magnonics at the limit of miniaturization.[1] One of the key advantages of atomically-thin materials is their outstanding deformation capacity, which provides an exciting avenue to control their properties by strain engineering. Herein, we investigate the magnetic properties, magnon dispersion and spin dynamics of the air-stable 2D magnetic semiconductor CrSBr (T_C = 146 K)[2] under mechanical strain using first-principles calculations.[3] Our results provide a deep microscopic analysis of the competing interactions that stabilize the long-range ferromagnetic order and the orientation of the spin in the monolayer.[4] We showcase that the magnon dynamics of CrSBr can be modified selectively along the two main crystallographic directions as a function of applied strain, probing the potential of this quasi-1D electronic system for magnon straintronics applications. Moreover, we predict a strain-driven enhancement of T_C by ~30%, allowing the propagation of spin waves at higher temperatures. Finally, we will also introduce our recent results on the crystal, electronic and magnetic structures of selenized Janus monolayers based on $MnPS_3$ and $NiPS_3$ from first-principles, which predict a drastic enhancement of magnetic anisotropy and the emergence of large Dzyaloshinskii–Moriya interactions, which arise from the induced broken inversion symmetry in the 2D Janus layers. These results pave the way for the development of Janus 2D transition metal phosphorus trichalcogenides and highlight their potential for magnonic applications.[5]

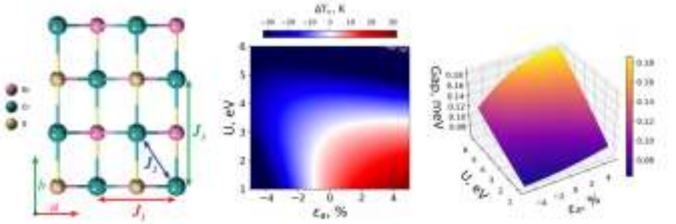

Figure 1. From left to right: (i) chemical structure indicating exchange interactions up to third neighbors, tuning of the (ii) Curie temperature and (iii) gap at Γ-point of the magnon dispersion by uniaxial strain in *a* axis and Coulomb screening.

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Molecular Two-Dimensional Spin-Crossover Materials

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Spin crossover (SCO) complexes are appealing materials for the design of functional molecular devices, due to the large changes in the magnetic, structural, and optical properties that accompany the switching between low-spin and high-spin electronic configurations. In this vein, recent years have brought intensified efforts to translate the abrupt spin-state-switching behavior from the bulk crystalline materials to two-dimensional (2D) thin-film structures. In general, SCO complexes are deposited on solid substrates by vapor sublimation or spin coating, which result, in general in amorphous or semi-amorphous films. The loss of long-range crystalline coherence also leads to weaker cooperativity and less abrupt SCO behavior. To address these challenges, we use an asymmetric ligand that retains the possibility for strong intermolecular interactions on one side of the complex, to preserve the cooperative SCO behavior, and contains bulky tertbutyl (^{t}Bu) groups on the other side, to increase the volatility.[1] The resulting homoleptic Fe(II) complex, [Fe(^{t}Bu$_2$qsal)$_2$], exhibits crystal packing in which layers of neutral SCO molecules are separated by van der Waals interactions between the ^{t}Bu groups. The complex can be easily sublimed at 300 °C and 10^{-4} mbar. Furthermore, the weak interlayer forces allow mechanical exfoliation of this material, all the way to a single molecular layer.[2] We demonstrate that the abrupt hysteretic SCO observed in the bulk crystal is also preserved in the thin films and ultrathin flakes. Moreover, the hysteretic SCO behavior is substantially increased in the thinner flakes. We discuss the possible reasons for the observed behavior and outline further possibilities offered by this unique molecular material.

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Magnetization Reversal in Low-coordinated Single-Molecule Magnets through Spin-Phonon Interactions

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Single-molecule magnets (SMMs) can retain their magnetization along the axis of quantization for a longer period even after switching off the applied magnetic fields. The SMMs have immense potential for high-density data storage and quantum computing device applications. The slow relaxation of the magnetization occurs due to large uniaxial magnetic anisotropy, which increases the barrier height (U_{eff}) of the double-well potential energy surface. The high potential energy barrier could lock the molecular spins in one of the wells. The high-temperature spin locking is the necessity for device applications of the SMMs along with their meaningful fabrications on various substrates retaining the SMMs' properties intact. Spin-reversal through the phonon-assisted quantum tunneling (QT) is the other fundamental challenge leading to the shortcut of the thermal barrier in obtaining SMMs. We have investigated several low-coordinated complexes to estimate the magnetic anisotropy barriers apply multi-reference CASSCF-NEVPT2 calculations.[1-3] In this talk, we will-specifically focus on the magnetic relaxation process through-spin phonon couplings and theoretical and computational challenges associated with it.

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Spectroscopic characterization of multinuclear metallacrown complexes on Au(111) using Inelastic Tunnelling Spectroscopy

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In recent years, the concept of interfaces has emerged in molecular spintronics, showing that the magneto-transport properties of molecular nanodevices are essentially determined by the interface between the molecule and the substrate.[1,2] Spin-flip Inelastic Tunnelling Spectroscopy (SF-IETS) at low temperatures enables the characterization of surface magnetism, especially for molecule/substrate systems that are of potential interest for molecular spintronics. Here we report the use of SF-IETS for the spectroscopic characterization of a multinuclear molecular system with competing intramolecular superexchange interactions. For this purpose, the multinuclear metallacrown system, in detail CuFe$_4$, [Cu^{II}(DMF)$_2$Cl$_2$[12-MC$_{Fe(III)N(Shi)}$-4](DMF)$_6$], and CuCu$_4$, (HNEt$_3$)$_2$Cu^{II}[12-MC$_{Cu(II)N(Shi)}$-4],[3-5] were investigated on Au(111) and the resulting "surface" spin ground states were determined. The spin-flip excitations have been revealed by measuring the local differential conductance spectra in SF-IETS measurements. The molecule-substrate interaction is discussed in detail.

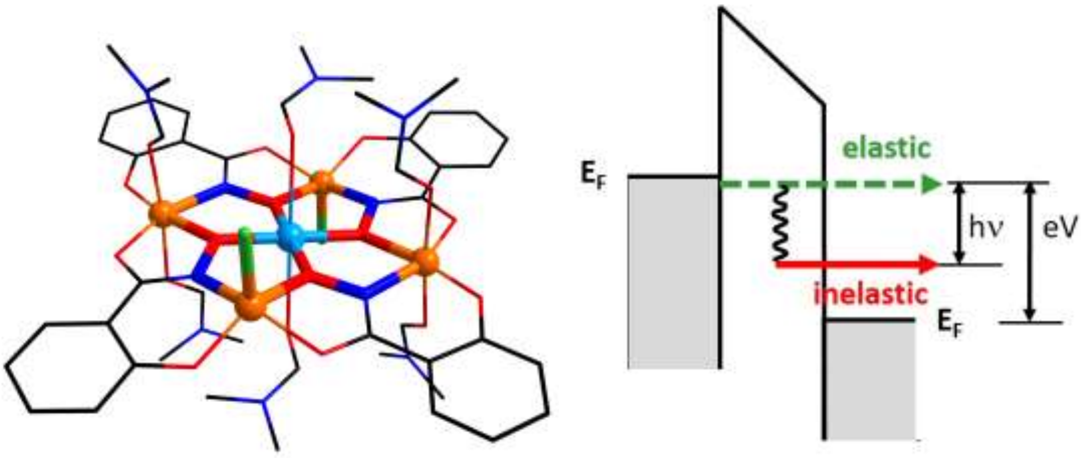

Figure 1: Molecular structure of the CuFe4-metallacrown (left); schematic drawing of an energy band diagram of a tunnel junction (right)

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Synthesis of Stable Radicals and their Counter Ion Dependent Property Modulation

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Synthesis of ambient-stable radicals continues to intrigue researchers for their multifaceted properties.[1,2] In this talk, we will discuss our group's recent progress in the sustainable, green synthesis and isolation of air-stable, colorful organic radical ions.[3] We will also show how the frontier molecular orbitals of these radicals can be tuned to accomplish electron transfer (eT) reactions that were possible only with inorganic reagents.[4]

Next, we will illustrate how the counterions can play a key role in modulating the self-assembling properties of the radicals.[5-7] Here we will discuss how subtle changes in the molecular structure of the radical anions can influence the spin-transition of a counterion endowed with spin crossover property. We will also illustrate how the counterions can play a key role in modulating the self-assembling properties of the radicals. Here we will invoke an unprecedented endergonic eT reaction from a sterically bulky anion, which is pivotal to create new types of soft radical ions. We will pose questions on: How and why such thermodynamically unfavorable eT reactions can happen? What are the types of non-covalent interactions that drive formation of highly organized, rare class of soft radicals?

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Correlating Covalency and Chemical Bonding with Magnetic Anisotropy of Co(II) Complexes: Insights from First Principle Calculations

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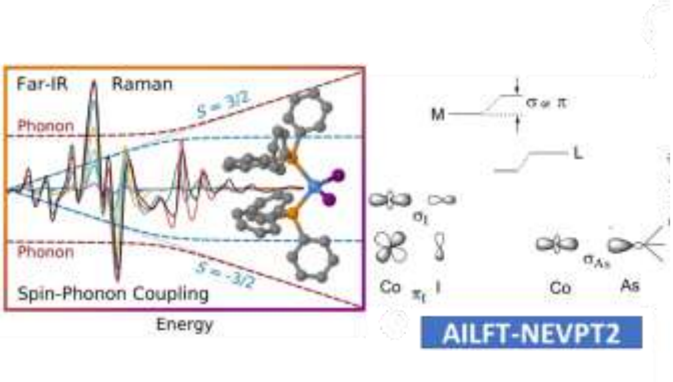
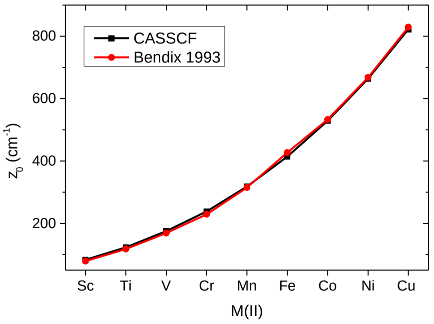
Highly anisotropic mononuclear complexes of the transition metal and lanthanides show a peculiar property of the slow relaxation of magnetization in the absence of the magnetic field and display hysteresis of the molecular origin.[1] These highly anisotropic mononuclear complexes are called Single-Ion Magnets (SIMs), which are highly attractive to explore the quantum effects and have numerous potential applications in information storage devices and molecular spintronics. Of these, Co(II) SIMs are found to be ubiquitous and dominate the 3d SIM family. In fact, due to both the spin and the orbital contributions to the magnetic moment, Co^{2+} ions in various coordination geometries and environments usually have significant magnetic anisotropy. Thus, this metal source is widely used for designing and preparing molecular magnetic materials, including SIMs4 SMMs, single-chain magnets (SCMs), spin-crossover complexes, and magnetic ordering materials.[2]





Computational tools have been instrumental in molecular magnetism, allowing us to precisely predict the sign and magnitude of the spin-Hamiltonian (SH) parameters, developing robust magneto-structural correlations for enhanced properties, to predict the mechanism of the magnetic relaxations.[3] In my presentation, using ab initio-based ligand field theory (AILFT),[4] I will describe the nature of metal-ligand covalency (symmetry adapted and central field covalency) and how it is correlated in fine-tuning the magnetic anisotropy of Co(II) complexes.[5]

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Employing Radicals and Bismuth in Lanthanide Single-Molecule Magnet Design

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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 that can penetrate the core electron density of the lanthanide ions where the 4f spin orbitals lie buried. 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.[1-3] 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.[3]

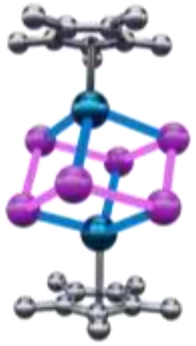

Figure 1. Structure of the $[\mathrm{Cp^*_2Ln_2Bi_6}]^{2-}$ dianion in a crystal of $[\mathrm{K(THF)_4}]_2[\mathrm{Cp^*_2Ln_2Bi_6}]$. Blue, purple, and gray spheres represent Ln, Bi, and C atoms, respectively.

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Electron transport in (hybrid) 2d materials to single molecular junction

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The recent advances in the 2D materials, in particular, the discovery of layered 2D magnet, have shown lot of promises in the field of low dimensional spin based devices. More importantly, the possibility of creating heterostructure helps to incorporate multiple functionalities in the nanoscale devices as well as provides access to study interface induced physical phenomena. In this talk, I will first discuss our electron transport measurement in a 2D metallic Ferromagnet (Fe_4GeTe_2). The magnetization data exhibit a Ferromagnetic transition at ~270K with unusual temperature dependence compared to the conventional Ferromagnet. At ~100K, there is a spin reorientation transition (SRT) where the easy axis changes from in-plane to out of plane. Our transport data indicates that the Hall coefficient changes sign and the magnetoresistance, anomalous Hall magnitude become maximum near the SRT, providing the important role of SRT on the electron transport.

Secondly, I shall focus on the initial results on the hybrid graphene/spin crossover device. Although, spin crossover molecules are common to the community, its implication towards using a memory device and understanding the cooperativity through transport measurements are rather challenging. By incorporating spin crossover nanoparticle on graphene in a three terminal device, we have been able to observe the effect of spin transition by measuring resistance of the hybrid device.

Finally, I will discuss the electron transport measurement through a single molecular junction by capturing a molecule between two metallic electrodes using a mechanically controllable break junction set up. We will discuss our recent results on Au/Ferrocene/Au junction, which exhibits remarkably high conductance (~$0.2G_0$) at room temperature, through resonant transport via direct metal/organometallic coupling. Our set up provides a viable platform to explore single molecular spintronic device.

Molecular Spin Qubits for Quantum Computer and Highly Density Memory Devices Based on Molecular Magnets

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Spintronics, based on the freedoms of charge and spin of the electron, is a key technology in the 21st century. Magnetic random access memory (MRAM), which uses giant magnetoresistance (GMR), has several advantages compared with electronics, such as non-volatile information storage, high operation speeds, etc. Although conventional magnets composed of transition metals are normally used, in our study, we use single-molecule magnets (SMMs) to overcome “Moore`s Limitation”. SMMs are also available for quantum computer, etc. I will talk about the spin qubits and long coherence for quantum computer as well as highly density memory devices such as single-molecule memory device, SMMs encapsulated into SWCNT, and metallic conducting SMMs with negative magnetoresistances.

As for spin qubits and coherence for quantum computer, we will focus on the following three topics:(1)To compare 0D [VO(TPP)] and 3D [VO(TCPP-Zn_2-bpy)] (3D-MOF) to investigate the influence of the spin-lattice relaxation in 0D and 3D lattices. Due to the rigid lattice of 3D-MOF, the Rabi nutation was observed even at room temperature. This is so called crystal engineering method. (2)To compare [VO(TPP) and [CrN(TPP)] to investigate the contribution of the anisotropy of their g-values for the spin relaxation. Due to the large anisotropy of g-values, [CrN(TPP)] shows the short life time. This is so-called g-tensor engineering method. (3)To compare [Ni(cyclam)Cl_2]ClO_4 and TBA[Ni(mnt)$_2$] to investigate the relationship between the different occupied orbitals and spin relaxation. This is so called orbital engineering method.

As for the negative magnetoresistances for highly density memory devices, we have synthesized (BEDO-TTF)$_3$[Co(pmdt)$_2$] (**BO3**) and (BEDO-TTF)$_4$[Co(pmdt)$_2$] (**BO4**). **BO3** show the metallic behaviour around room temperature and M-I transition around 12K. Moreover, **BO3** shows the negative magnetoresistance for the first time by the interaction between conducting electron and SMM.

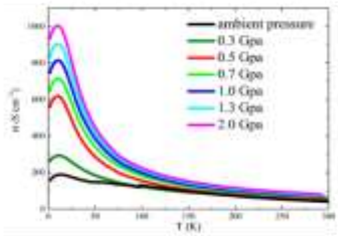

Fig. 1 Electrical Conductivity of **BO3**

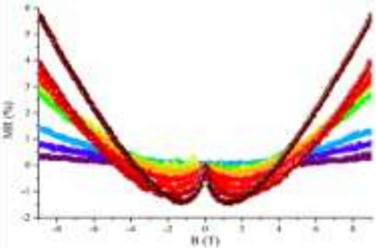

Fig.2 Magnetoresistance of **BO3**

BO4 shows two M-I transitions around 60 K and 6K. The M-I transition around 60K is due to Dirac cone, while it around 6K is due to the antiferromagnetic interaction between the BEDO-TTF and [Co(pmdt)$_2$] single-molecule magnets.

Heterometallic Lanthanide Coordination Complexes for Quantum Technologies

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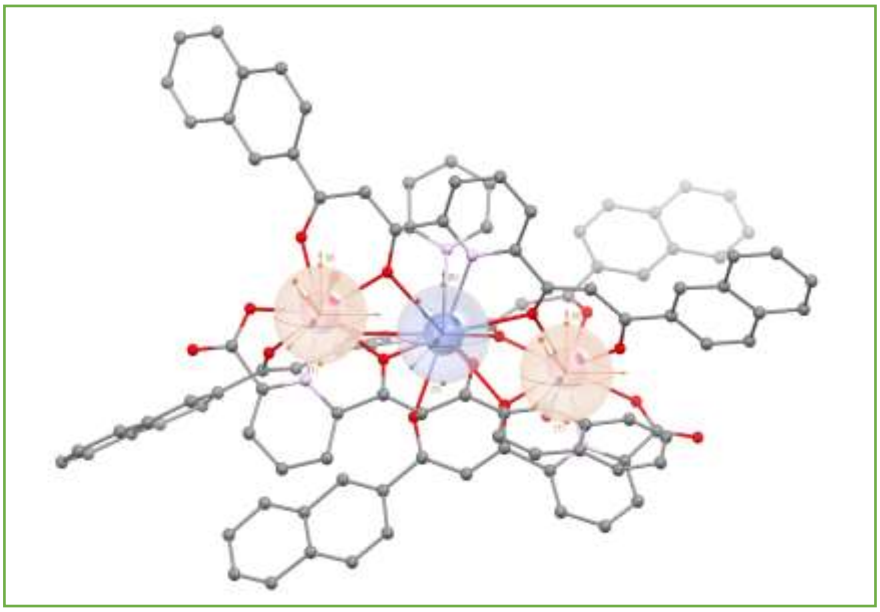
Molecular materials find applications in many crucial areas of technology. For example, molecular electronic spins are potential qubits and qugates in quantum computing.[1-2] Some of their advantages over other technologies are their reproducibility (crucial for a scalable quantum technology) and the versatility of chemical design. The latter enables the preparation of molecules to host several spins, thus embodying various qubits capable to undertake complex tasks. Lanthanides are good spin-qubit candidates in these systems, as they exhibit good coherent properties and a diversity of electronic features. We have designed a ligand-based strategy to synthesize di- or trinuclear lanthanide complexes exhibiting distinct coordination sites within one molecule type. This provides a means of preparing pure heterometallic complexes that can be of the [LnLn'] or the [LnLn'Ln] type, where the nature of the Ln and the Ln' metals can vary extensively.[3-5] Preparation of selective heterometallic complexes in one step is extremely rare and the trinuclear case is unique. The performance of these molecules as multi-qubit quantum gates will be discussed.



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Stimuli-assisted magnetism in two-dimensional (2D) magnets

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Magnetic phase control and room temperature magnetic stability in two-dimensional (2D) materials are indispensable for realizing advanced spintronic and magneto-electronic functions. Our current work employs first-principles based calculations to comprehensively study the magnetic behaviour in several 2D intrinsically magnetic systems, uncovering the impact of strain and electric field on the material. Our studies have revealed that uniaxial strain leads to the feasibility of room temperature ferromagnetism in the 2D-oxychloride system and also detected the occurrence of a ferromagnetic - antiferromagnetic phase transition in the system, which is anisotropic along the armchair and zigzag directions. Beyond such a strain effect, the coupling of strain and electric field leads to a remarkable enhancement of the Curie temperature (Tc) ~ 450 K in CrOCl[1]. Furthermore, the current–voltage (I–V) response showed spin-resolved conductance with 100% spin filtering, conductance fluctuations, characterized by peak to valley ratio and switching efficiency offering high strain assisted tunability[2]. We have extended this work for other members of this family, where interesting magnetic and electronic phase evolution are observed[3,4]. These predictions based on our detailed simulations show the prospect of multi-stimuli magnetic phase control, which could have great significance for realizing magneto-mechanical sensors.

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Electronic Structure and Magnetism of Super-Reduced Uranium

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Oxidation state is one of the most fundamental concepts in chemistry. The discovery of elements in new oxidation states is rare. Pursuing stable compounds containing elements in previously unseen oxidation states is motivated by the insight that can be obtained into bonding, electronic structure and magnetism, and the possibility of using these species for further chemistry. Following the pioneering work of Lappert,[1] the divalent oxidation state is now known for all the rare-earth elements,[2] and several divalent uranium and later-actinide compounds have also been isolated.[3]

Recently, we reported the divalent uranium metallocene $[(\eta^5\text{-}C_5{}^i Pr_5)_2U]$[4] and have since studied its reactivity. Since *trivalent* uranium is well-known as strong reducing agent, the obvious next step was to examine the reactivity of the divalent uranocene towards oxidizing agents. Instead, we examined the reactivity of $[(\eta^5\text{-}C_5{}^i Pr_5)_2U]$ towards reducing agents to determine if it is possible to isolate complexes of the unprecedented Kramers ion uranium(I).[5]

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Ferromagnetically Coupled Singlet Dimers: A Frustrated Magnet

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In this talk we explore the ground state properties of ferromagnetically coupled orthogonal dimers on a two dimensional distorted lattice. In this model ferromagnetic exchange couplings Jx and Jy are along X- and Y-axis and diagonal exchange coupling (J) is antiferromagnetic which forms a strong dimer along the diagonal bond. Possible realization of this model is $(CuCl)LaNb_2O_7$ and the distortion in this system can be due to Cu-Cl bonds. We have noticed the existence of six different phases: dimer stripe (0, π), dimer stripe (π, 0), perfect dimer, dimer spiral along X-direction, dimer spiral along Y-direction and ferromagnetic alignments of the spins in Jx-Jy parameter regime. Phase boundaries of this system are determined based on the correlation functions and gs energies. We also construct the quantum phase diagram in Jx-Jy parameter space.

Engineering Spin Crossover Molecules by Assembly into Nanomaterials

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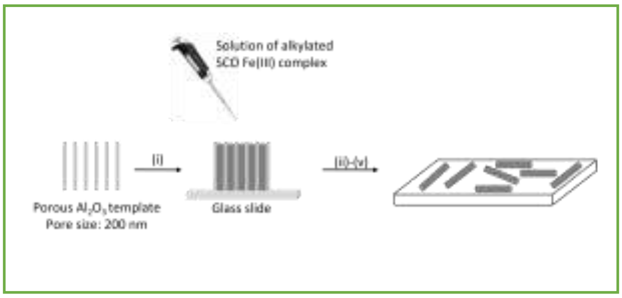
Much effort has been expended in recent years to develop the materials assembly of spin crossover (SCO) complexes and impressive results have been achieved in stabilizing and isolating monodisperse nanoparticles,[1] nanocrystals,[2] thin films,[3] micro- and nanopatterned media,[4] Langmuir-Blodgett surface mono- and multilayers[5] and hysteretic soft media assemblies.[6] The dimensional reduction of SCO complexes has been observed to have an effect on the magnetic behaviour of the materials.[7] This is a result of the electronic bistability being related to the collective behaviour of the SCO centres in the crystalline lattice. We have shown that the SCO properties were retained for Fe(III) SCO complexes.[8] Here, we now probe magnetic, electrostatic and conductive properties of rare SCO Mn(III) complexes at the nanoscale. The successful preparation of a series of nanoassemblies was achieved with Mn(III) SCO complexes including nanoparticles, nanowires, nanofibers and nanocrystals and piezoelectric and conductive properties along and across the wire were probed using conductive AFM.



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Role of Ab initio Calculations in the Development of Molecular Nano Magnets

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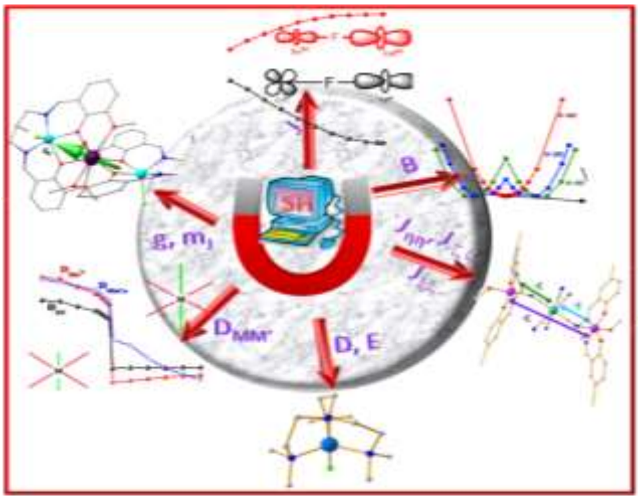
Molecular magnetism is one of the vastly growing research fields with an aim to design the molecules and materials with tunable magnetic and electronic properties.[1] Their synthesis, characterization and implementation as devices which creates lively crossroad among chemistry, physics and material science: a multidisciplinary research field. These molecules have wide spread potential applications ranging from magnetic storage devices, spintronics, Q-bits in quantum computing to magnetic coolants.[2] Single-molecule magnets (SMMs) are the molecules which show slow relaxation of magnetization below the critical temperature and exhibit hysteresis loop similar to classical magnets. SMMs offer key advantage over classical magnets due to their light weight, solubility and multifunctional behavior. Theoretical tools are indispensable in this arena[2] for understanding the observed magnetic properties. The strength of these methods is not only limited rationalization but also to predict novel molecules which can exhibit superior magnetic properties. In this presentation, I will research effort undertaken in our group towards achieving this goal.[2]



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Building Axial Lanthanide Single-Molecule Magnets

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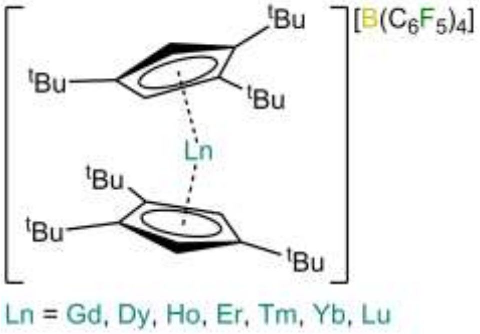
The complexity and richness of synthetic f-element chemistry has attracted increasing attention in recent years. This interest is stimulated jointly by scientific curiosity of a relatively unexplored field and the myriad applications that these elements have found in diverse areas such as organic synthesis, materials science and nuclear fuel cycles.[1] Our research focuses on stabilising lanthanide (Ln) and actinide (An) complexes with unusual coordination geometries and/or oxidation states, which can provide enhanced reactivity and unique physical properties. We mainly utilise bulky bis(silyl)amides and cyclopentadienyls as supporting ligands to stabilise these unusual f-element motifs. Here we will present some recent highlights of this work, focusing on progress made since we reported the first bent Ln(III) complexes containing monodentate ligands (**1**)[2] and the first series of isolated Ln(III) metallocenium cations (**2**),[3-5] which provided record magnetic hysteresis temperatures for the dysprosium analogue in 2017.[3]

(**1**)



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New Spin Liquid Candidate κ-$(ET)_2Cu[Au(CN)_2]Cl$ with Disorder-Free Anion Layer

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Quantum spin liquid (QSLs) have attracted much attention because they are exotic quantum phases of matter where long-range magnetic ordering is suppressed even at low temperature. QSL is thought to be realized by the strong spin frustration in triangular lattice. Several QSL candidates with triangular lattice have been reported in organic conductors so far[1,2]. However, all the reported organic QSL candidates have some disorders in their crystal structures. Such structural disorders have been discussed as one of the key factors for realizing QSL. To evaluate the role of spin frustration in QSL, disorder-free QSL candidates are greatly desired.

Here we report our recent investigation on physical properties of new QSL candidate κ-$(ET)_2Cu[Au(CN)_2]Cl$ (ET = bis(ethylenedithio)tetrathiafulvalene). This is the first organic QSL candidate with disorder-free polyanion layers (Fig.)[3]. This salt has nearly regular triangular lattice and shows no magnetic order down to 0.45 K. This value is at least 1/450 smaller than its exchange interaction J/k_B = 210 K. This new QSL candidate can provide an ideal research platform to investigate a genuine QSL state.

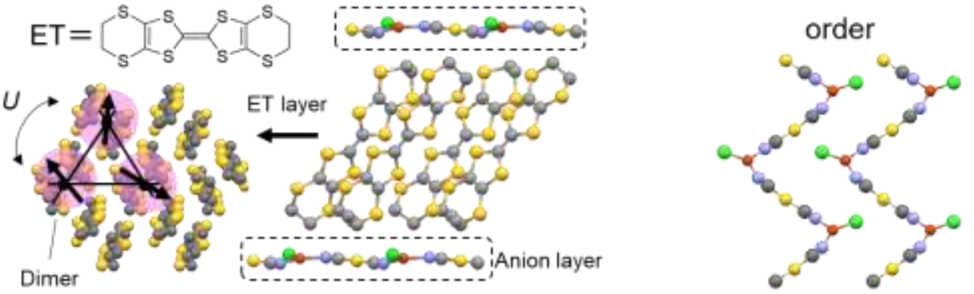

Fig. Crystal structure of κ-$(ET)_2Cu[Au(CN)_2]Cl$

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Spin Crossover and Soft Matter

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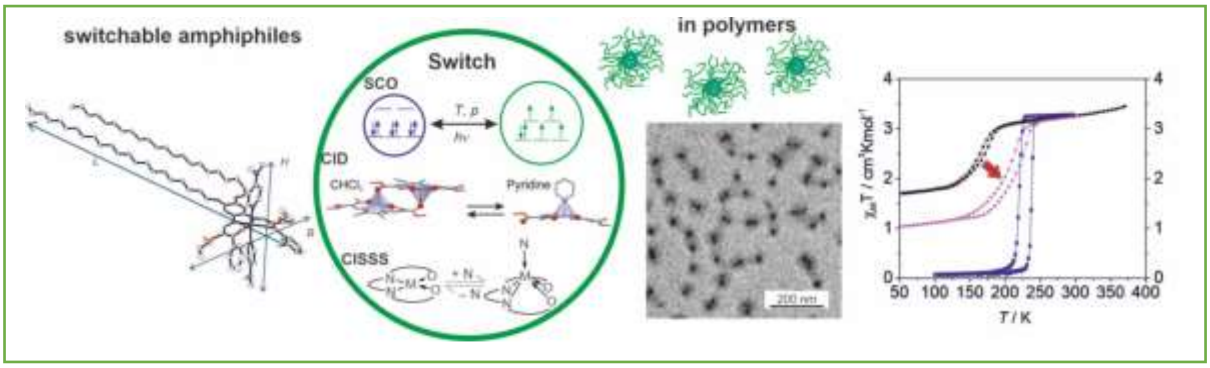
The synthesis of multifunctional materials is generally considered as an important step from basic research to more application-oriented research.[1] One way to realize it are iron(II) spin crossover (SCO) complexes, whose spin state (S = 0 or S = 2) can be switched by a wide range of physical or chemical stimuli.[2] Structural and electronic changes associated with this transition can be exploited for applications e.g. in the field of sensors. In order to realise applications of such switchable molecules, it is important to synthesise nanostructures that can be integrated into composite materials, for example by the utilization of diblock copolymer (dBCP) micelles.[3-5] Alternatively, structured materials can be obtained through the realization of amphiphilic complexes.[6]



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Pentagonal bipyramidal complexes: From magnetic anisotropy to molecular magnets

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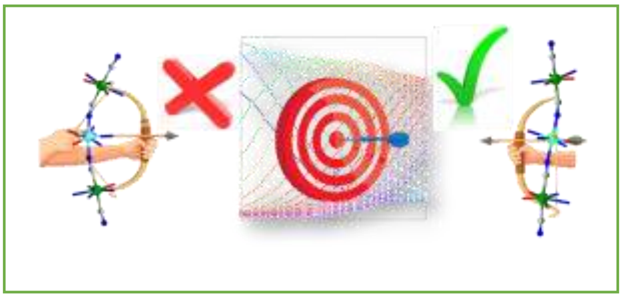
Magnetic anisotropy plays an important role in the behavior of magnetic materials. In this context, seven-coordinated 3d ion complexes with pentagonal bipyramidal (PBP) geometry have been found of great relevance. Small or large ZFS *D* values (up to about +/- 30 cm^{-1}) with a positive or negative sign can be rationally obtained simply by selecting the appropriate metal center;[1] and these complexes can be used as basic units for the construction of heterometallic SMMs and SCMs.[2]

After a short introduction on the magnetic anisotropy in PBP geometry, the use of such complexes for the design of SMM and SCMs will be discussed.



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Converting Fe_2Co_2 Cyanido Squares into Molecular Switches by pressure

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Molecular magnetic switches are complexes, which undergo reversible conversions between two distinct electronic states under external stimuli such as temperature, light, pressure. These changes of electronic states can be associated to drastic modification in the magnetic properties but also in the optical, dielectric and mechanic properties. The most investigated molecular magnetic switches are spin-crossover complexes (SCO), however another class of bistable magnetic compounds have later emerged in which the electronic reorganization involved two cyanide-bridged neighboring metal ions. Here the electronic reorganization often implies a metal-to-metal electron transfer, which is be coupled to a spin transition on one metal ion (ETCST transition). The effect was first evidence in inorganic polymers (FeCo Prussian Blue Analogs) but strong research efforts have recently been devoted to the design of their discrete molecular analogs. To date, the effect of pressure-induced ETCST has remained scarcely investigated on these molecular systems.

Aware of their potential application as sensors, our group has recently focused its interest on the study of FeCo square compound: $\{[Fe^{III}(Tp)(CN)_3]_2[Co^{II}(vbik)_2]_2\}(BF_4)_2{\cdot}2MeOH$,[1,2] (Tp = hydro-tris(pyrazolyl)borate, vbik = bis(1-vinylimidazol-2-yl)ketone), which shows an abnormal magnetic behaviour under pressure (cooperativity enhancement with increasing pressure). In order to better understand this phenomenon, we have started investigating related Fe_2Co_2 square complexes in particular the compound, $\{[Fe(Tp)(CN)_3]_2[Co(vbik)_2]_2\}(PF_6)_2{\cdot}2MeOH$, which show very similar crystal packing as the first square complex. Here, we present our recent results that aim at establishing structure-property relationships.

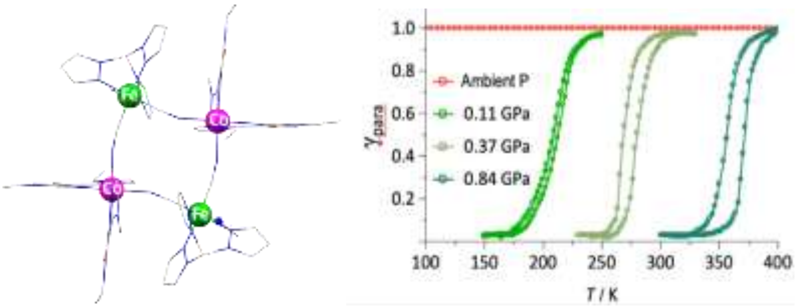

Fig. 1. Structure of $\{[Fe^{III}(Tp)(CN)_3]_2[Co^{II}(vbik)_2]_2\}(BF_4)_2{\cdot}2MeOH$ and thermal variation of paramagnetic compound molar fraction γ_{HS} under different hydrostatic pressures

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GronOR: A massively parallel and GPU-accelerated program for non-orthogonal configuration interaction

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After the initial explorations in the 1980s, non-orthogonal configuration interaction (NOCI) was recognized as an interesting approach for treating electronic structure problems where orbital relaxation plays a fundamental role, e.g., core-hole excitations, metal-to-metal charge transfer excitations and magnetic interactions. However, the method was never applied extensively because of the huge computational cost of releasing the restrictions on the orthogonality of the molecular orbitals. However, recently NOCI is going through a revival, witnessed by the large number of studies that has been published over the last decade. This renewed interest is in part due to the increased computer power, but also to the development of new algorithms and new (faster) variants of NOCI.

Our implementation of NOCI in GronOR [1,2] is based on the use of multi-electron basis functions built in terms of anti-symmetrized spin-adapted products of multi-configurational fragment wave functions. So far, it has been applied to electron and energy transfers in ensembles of molecules to describe singlet fission, magnetic exchange coupling, charge transfer processes [3], but the method is not restricted to these applications.

After a short introduction to the calculation of non-orthogonal matrix elements and the most important characteristics of the implementation in GronOR, we will present the results of a study on the magnetic interactions in some organic radicals showing how NOCI combines accuracy with an intuitive and straightforward interpretation of the mechanisms that govern the coupling between the localized spin moments.

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Chemical tuning of spin clock transitions in molecular monomers based on nuclear spin-free Ni(II)

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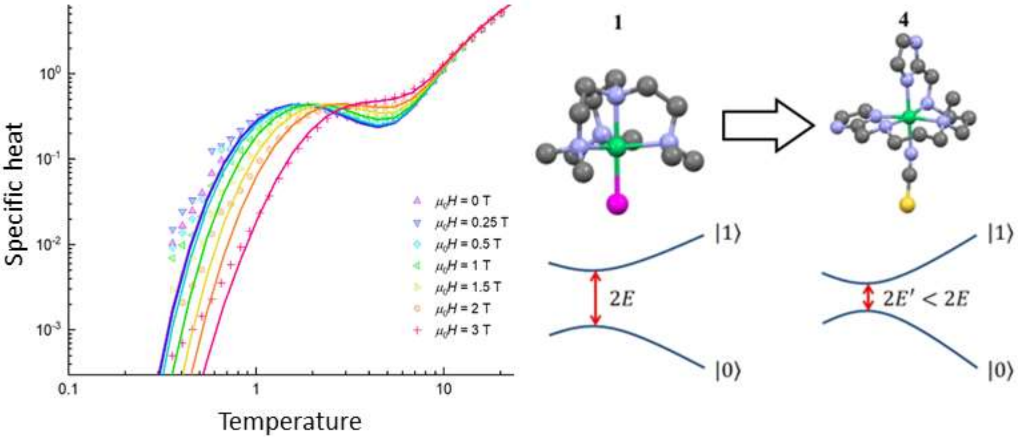
We report the existence of a sizeable quantum tunnelling splitting between the two lowest electronic spin levels of mononuclear Ni complexes. The level anti-crossing, or magnetic “clock transition”, associated with this gap has been directly monitored by heat capacity experiments. The comparison of these results with those obtained for a Co derivative, for which tunnelling is forbidden by symmetry, shows that the clock transition leads to an effective suppression of intermolecular spin-spin interactions. In addition, we show that the quantum tunnelling splitting admits a chemical tuning via the modification of the ligand shell that determines the crystal field and the magnetic anisotropy. These properties are crucial to realize model spin qubits that combine the necessary resilience against decoherence, a proper interfacing with other qubits and with the control circuitry and the ability to initialize them by cooling.[1]



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Mixed 3d-4f Single-Molecule Toroics

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Single Molecule Toroics (SMTs) are defined as molecules that display a toroidal magnetic state that can potentially be used in multiferroic materials, and also in information storage devices and spintronics devices.[1] The observation of toroidal magnetization is dependent on the topology, and it is realized in topologies such as Dy_3 triangles, planar/cubic Dy_4, wheel Dy_6, a snub-square Dy_8, and double Dy_3+Dy_3 triangles.[1] Toroidicity have been mainly observed for Dy^{III} clusters; however, we recently reported SMTs containing Tb^{III} and Ho^{III} ions as well. To enhance toroidicity, we reported {3d-Ln^{III}} complexes connecting two molecular triangles, for example, a heptanuclear cluster containing Cr^{III} linked to two Dy_3 triangles ({$CrDy_6$}) offering a rare phenomenon called ferrotoroidicity.[3] This effect is required for the realization of a ferrotoroidically ordered phase, paving the way for the advancement of multiferroics, which could be addressed using magnetoelectric coupling.[1] Furthermore, we observed such con-rotating ferrotoroidal (FT) ground state behaviour in Tb^{III} and Ho^{III} examples but not in the Er^{III} analogue, extending the possibility of observing toroidal behaviour in non-Dysprosium (III) complexes.[3] We also looked at how to cancel such a toroidal behaviour and the influences that the connecting trivalent ions, counter ions, and solvents have on ferrotoroidal and antiferrotoroidal (AFT) behaviour.[4]

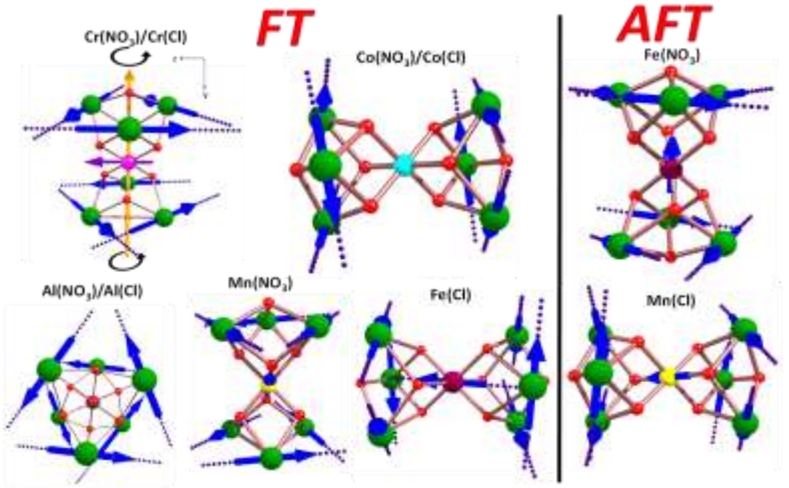

Figure. The Core structure of {M^{III}Dy$^{III}_6$} SMTs in different views along with their computed orientation of the magnetic anisotropy axes in the ground Kramers doublet on each Dy site (blue arrows).

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Poster Presentations

Poster 1

Atomic site preference, electronic structures, and magnetic properties of γ-brass type pseudo-binary Mn_2Zn_{11}–Ni_2Zn_{11} at high Mn-contents

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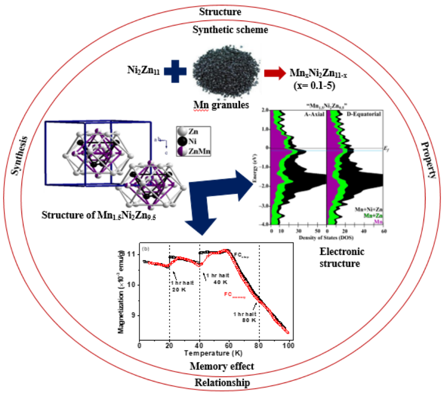
The pseudo-binary $Mn_xNi_2Zn_{11-x}$ (x= 0.1-5) compounds were synthesized using the conventional high-temperature solid-state synthesis method and were characterized by X-ray diffraction, neutron powder diffraction, and energy-dispersive X-ray spectroscopy techniques. The structures were solved in the cubic space group of $I\bar{4}3m$ (217) and are described in close analogy to the Ni_2Zn_{11} parent γ-brass that is based on the 26-atom γ-cluster, consisting of inner tetrahedron (IT), outer tetrahedron (OT), octahedron (OH), and cuboctahedron (CO). For low Mn-content phases (x= 0.1-0.9), OH site is occupied by mixed Zn/Mn, but there is a partial accumulation of Zn at cluster center (CC) with the simultaneous depletion of Zn at IT site. The OT and CO sites remain intact with respect to Ni_2Zn_{11}.[1] In Mn-rich phases (x > 1.1), both IT and OH sites are mixed with Zn/Mn. The OT and CO sites remain intact with respect to Ni_2Zn_{11} throughout the entire homogeneity range.[2] Magnetic properties were studied for the high Mn-content compound, $Mn_{1.5}Ni_2Zn_{9.5}$ by the temperature-dependent zero-field cooled (ZFC) and field-cooled (FC) magnetization, the dc susceptibility, the M(H) hysteresis curves, the thermoremanent magnetization, and the memory effect. $Mn_{1.5}Ni_2Zn_{9.5}$ shows the spin glass magnetism below the spin-freezing temperature of ~58.5 K, originating predominantly from the random distribution of diluted Mn moments.[2]



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Probing the influence of structural distortion and axial ligands on magnetic anisotropy in a series of chiral pentagonal bipyramidal Co(II) and Ni(II) complexes

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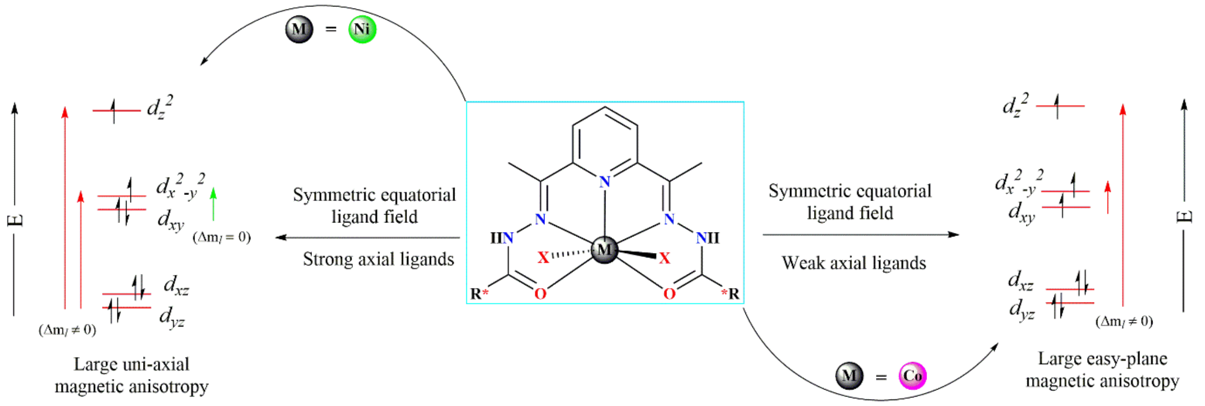
Enhancement of the uniaxial magnetic anisotropy in molecular species has emerged as one of the most prolific strategies to design single molecular magnets[1-2]. Indeed, recent observations of slow relaxation of magnetization in monometallic lanthanide complexes above cryogenic temperatures primarily rely on enhancing the uniaxial magnetic anisotropy by manipulation of ligand field symmetry[3-4]. In comparison to lanthanide ions, the magnetic anisotropy associated with transition metal ions is considerably low due to quenching of orbital angular momentum by crystal field splitting and Jahn-Teller distortion. Nonetheless, the proper choice of ligand field symmetry as well as ligand field environment allows significant enhancement of the uniaxial as well as easy-plane magnetic anisotropy even in transition metal species. During this presentation, systematic analysis of magnetic anisotropy in a series of chiral pentagonal bipyramidal (PBP) Co(II) and Ni(II) complexes synthesized from a series of enantiopure chiral bis-hydrazone ligands will be described. Wave function-based *ab-initio* complete active space self-consistent field (CAASCF) theory calculations have been performed to estimate the nature and magnitude of magnetic anisotropy (*D*). The *D* values are correlated to geometric parameters and based on the results an efficient strategy to enhance *D* value in PBP Co(II) and Ni(II) complexes is proposed.



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Cyanido bridged heterometallic Co(II)-W(V) aggregates: synthesis, crystal structures and electrochemical analysis

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Engineering low dimensional molecular magnetic materials endowed with multifunctionality is currently experiencing renaissance of research interests due to their application in molecular data storage devices, sensors *etc*[1]*.* In this regard, cyanide bridged Prussian Blue Analogues (PBAs) show diverse physical properties such as high T_c ferrimagnetism, thermal phase transition, spin crossover *etc*[2,3]*.* Molecular PBAs derived from Co/Fe pair are extensively studied so far owing to their versatile characteristic of metal-to-metal-charge transfer (MMCT) upon exposure to external stimulant such as light, temperature, pressure, pH, humidity *etc* [4]. However, other bimetallic switchable systems are limited due to their inherent synthetic difficulty and control over the nuclearity. In this direction, we endeavoured to construct cyanide bridged heterometallic Co(II)/W(V) aggregates by employing different capping ligands. Reaction of tridentate *N*-donor capping ligand, Me-TPA and chiral pentadentate planar bis-hydrazone ligand, *R*-daphibh with octacyanidotungstate, $[W(CN)_8]^{3-}$ resulted a discrete pentanuclear cyanide bridged Co(II)-W(V) complex, $\{[Co(MeTPA)]_3\text{-}[W(CN)_8]_2\}$ (**1**) and a cyanide bridged Co(II)-W(V) chiral one dimensional chain $\{[Cs(CH_3CN)(H_2O)][Co(R\text{-daphibh})][W(CN)_8]\}_n$ (**2**), respectively. Upon dissolution in water, compound **2** forms colloidal particles of size less than 10 nm. Further, it can also be recovered from water by evaporation without loss of any structural integrity. During this presentation, the synthesis, characterizations, crystal structures and electrochemical behaviours of **1-2** will be elaborated.

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Metal-Organic Frameworks and Coordination Polymers as Strategically Synthesized Proton Conductors

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Metal-organic frameworks and coordination polymers, as organic and inorganic hybrid crystalline materials have gained tremendous attention due to their high porosity and functionalised pore walls responsible for proton-conduction.[1,2] MOFs and CPs pave the way for the proton-conduction due to their high stability at high relative humidity and high temperature. These materials exhibit comparable proton-conducting ability to that of the commercially available and costly proton-conductor, such as nafion.[2] Continuous water chain inside the channels of MOFs and CPs is the prime factor which is responsible for their high proton conductivity. Moreover, functionalization of organic linkers with different hydrophilic groups ($-COOH$, $-SO_3H$, $-NH_2$, $-OH$) and impregnation of sulphuric acid and phosphoric acid into the cavities of CPs improve the proton conductivity.[3] Recently, our group has successfully designed 3D proton-conducting CP which bears 1D polyhedral water cages having the repeat unit of $(H_2O)_{24}$ with the geometry of the organic molecule pagodane.[4] Coordination polymers of an organic molecule containing pyridine and imidazopyridine moieties with Zn^{II}/Ni^{II} metal salts and uncoordinated 1,5-naphthalenedisulfonate exhibited high to moderate proton conduction at varying temperature and relative humidity.[3] Proton exchange membrane composed of poly(vinylidene fluoride) and amino- and sulfonate-functionalized MOF shows appreciable proton conductivity at 353 K and 98% relative humidity.[2] A Cd(II)-based CP shows very high proton conductivity due to the synergistic effect of sulphate ions and water molecules in the cavity.[5] So here we have shown different aspects of proton conduction by strategically synthesized MOFs and CPs in the direction of future energy applications.

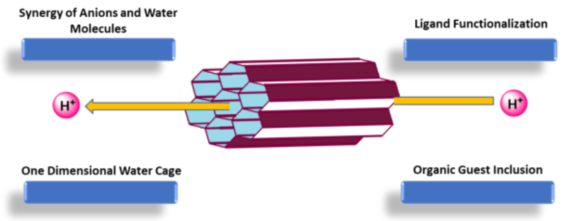

Figure 1. Schematic representation of proton conducting MOFs and CPs.

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REVERSIBLE CRYSTAL-TO-CRYSTAL TRANSFORMATION AND PHOTO AND THERMO-INDUCED METAL-TO-METAL ELECTRON TRANSFER IN HETEROBIMETALLIC 2D NETWORK

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In the modern era of technology, considerable attention has been given to the materials that can reduce the size of electronic devices and can be used for high-density storage devices, quantum computing, spintronics, sensors etc.[1] Room temperature bistable materials, where the properties of the materials can be switched with the sight alternation of external stimuli are desirable for application purposes. In this regard, switchable magnetic materials based on metal-to-metal electron transfer (MMET) are promising and have been explored over the last few years.[2] Amongst them, a particular interest has been given to the materials designed using octacyanometallates ($[M^{IV/V}(CN)^8]^{n-}$ = W, Mo, Re) building blocks that can be used judiciously for the designing of multifunctional magnetic materials. These materials exhibit an enormous range of anticipated physical properties, including long-range magnetic ordering, photomagnetic effect, electro-magnetic properties etc.[3]

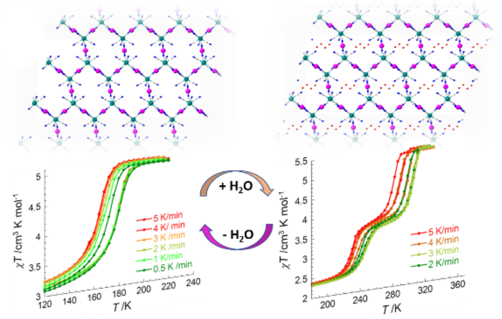

Figure: Crystal structure and χT vs T plot of 2D coordination Networks

Here, I will present the magnetostructural correlation of our recent work based on 2D coordination networks. The novel 2D coordination networks were designed by using octacyanometallates building block and nitrogen donor ligands on 3d metal side. The resulting 2D network uptake moisture and reversibly convert into another form. Detailed (photo)magnetic studies reveal that MMET occured in both the forms togethar with near room temperature large thermal hysteresis loops along with ferromagnetic ordering at low temperature. The novel materials suggest new resource for magnetism in 2D extended corrdination networks.

Acknowledgement: We thank Indian Institute of Science (IISc), Solid State and Structural Chemistry Unit (SSCU) for the research work, Ministry of Education (MoE) for Prime Minister’s Research Fellowship (PMRF) and GARP for financial support.

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Role of spin states and Spin-Coupling in selective adsorption of O2 in the biomimetic Fe-BTTri Metal-Organic Framework

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Biomimetics deals with concepts to create materials, artificial systems, and devices that emulate biological processes. The coordinatively unsaturated iron(II)-based MOF Fe-BTTri ($Fe_3[(Fe_4Cl)_3(BTTri)_8]_2.18CH_3OH$, H_3BTTri = 1,3,5-tris(1H-1,2,3-triazol-5-yl)benzene) has been shown to bind O_2 similarly to hemoglobin and thus, shows exceptional selectivity towards it compared to N_2. It shows the highest reported O_2/N_2 selectivity for any iron-based MOF. Although, a lot of factors come to mind while studying gas adsorption in MOFs such as pore volume, linker length, surface area, and metal ion. However, the role of spin states has not been yet explored. We attempted to find the reasons for this high selectivity using periodic density functional theory. The number of O_2 molecules that could effectively bind to the metal center and the binding energy change depending on the spin state. Our research identified a method of exploiting spin states and their coupling to regulate the MOF's gas adsorption selectivity.

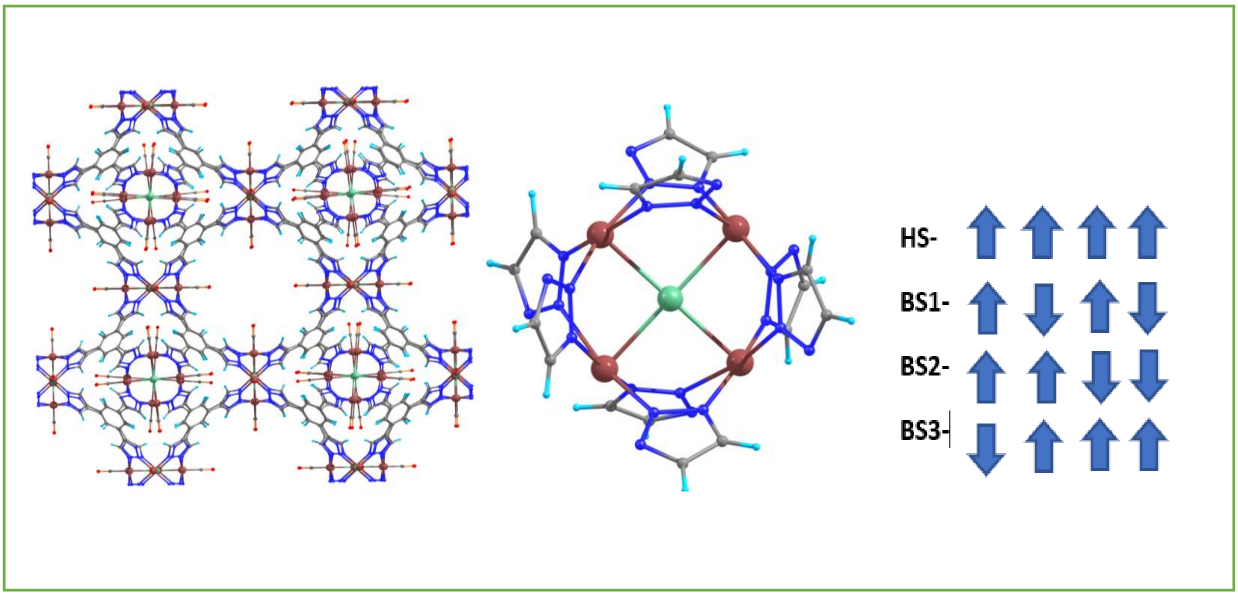

Figure 1. Fe-BTTri MOF (on the left), and a tetramer unit to show possible spin states (on the right)

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Gold nanoparticles decorated Magnetic-CNT Nanohybrid Heterostructure and Appraisal of their Catalytic Activity through the Reduction of 4-Nitrophenol

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A new strategy has been developed for the synthesis of gold nanoparticles decorated magnetite-carbon nanotube nanohybrid (Au-Fe_3O_4-CNT) as the seeds for magnetically recyclable heterogeneous catalysis of 4-nitrophenol reduction. UV light induced ‘click’ chemistry approach has served as the platform for the synthesis of Fe_3O_4-CNT nanohybrid where mechanically and thermally stable CNT is considered as efficient templates for the assembly and tethering of Fe_3O_4 nanoparticles on their surface, onto which positively charged chitosan stabilized AuNPs were immobilized electrostatically. The successfully synthesized heterostructures has been confirmed through XRD (crystallinity) and FTIR spectral analyses. The distinct structural evidence and magnetic property of the formulated nanohybrid have been ascertained using Transmission electron microscopy (TEM) and superconducting quantum interference device (SQUID) analysis respectively and the course of catalytic study was monitored via UV-Visible absorption spectroscopy. The pseudo first order rate constant of 2.00×10^{-3} sec^{-1} for the reduction of 4-Nitrophenol has been affirming the superior catalytic performance of the nanohybrid heterostructures over the similar kind of heterostructures reported earlier. The inkling behind the designing of the heterostructures is the π-π interactions between aromatic ring with the CNT surface enabling their proximity and the attraction of nitro group of 4-nitrophenol to the Au NPs in presence of hydride donor $NaBH_4$ that co-operatively can facilitate the catalytic reduction. Good separation ability and reusability with this formulated distinctive heterostructures can serve as an ideal platform to study various heterogeneous catalytic processes.

Keywords: Magnetite nanoparticles, CNT, Gold nanoparticles, Click chemistry, 4-nitrophenol

Spin-Vibronic Coupling in the Quantum Dynamics of a Fe(III) Trigonal-Bipyramidal Complex

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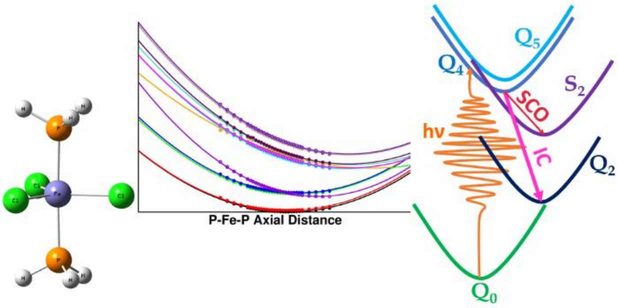
The presence of a high density of excited electronic states in the immediate vicinity of the optically bright state of a molecule paves the way for numerous photo-relaxation channels. In transition-metal complexes, the presence of heavy atoms results in a stronger spin–orbit coupling, which enables spin forbidden spin-crossover (SCO) processes to compete with the spin-allowed internal conversion processes. However, no matter how effectively the states cross around the Franck–Condon region, the degree of vibronic coupling, of both relativistic and non-relativistic nature, drives the population distribution among these states. One such case is demonstrated in this work for an intermediate-spin Fe(III) trigonal-bipyramidal complex[1,2]. A quantum dynamical investigation of the photo-deactivation mechanism in the Fe(III) system is presented using the multi-configurational time-dependent Hartree (MCTDH) approach based on the vibronic Hamiltonian whose coupling terms are derived from the state-averaged complete active space self-consistent field (CASSCF)/complete active space with second-order perturbation theory (CASPT2) calculations and spin–orbit coupling of the scalar-relativistic CASPT2 states[3]. The results of this study show that the presence of a strong (non-relativistic) vibronic coupling between the optically bright intermediate-spin state and other low-lying states of the same spin-multiplicity overpowers the spin–orbit coupling between the intermediate-spin and high-spin states, thereby lowering the chances of spin-crossover while exhibiting ultrafast relaxation among the intermediate-spin states. In a special case, where the population transfer pathway via the non-relativistic vibronic coupling is blocked, the probability of the spin-crossover is found to increase. This suggests that a careful modification of the complex by incorporation of heavier atoms with stronger relativistic effects can enhance the spin-crossover potential of Fe(III) intermediate-spin complexes.



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Reversible Photo and Thermo-induced Spin-State Switching in a series of {*5d-3d*} Molecular Complex

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In the modern era of technology, considerable attention has been given to the materials that can reduce the size of electronic devices and can be used for high-density storage devices, quantum computing, spintronics, sensors etc.[1] Room temperature bistable materials, where the properties of the materials can be switched with the sight alternation of external stimuli are desirable for application purposes. One type of compounds that can exhibit such behavior is Spin-Crossover systems where switching of the magnetic properties originates from their reversible spin-state switching between a low-spin (LS) and high-spin (HS) state upon application of an external stimulus, *e.g.*, temperature, pressure, light irradiation, magnetic and electric field etc.[2] Amongst them, a particular interest has been given to the materials designed using octacyanometallates ($[M^{IV/V}(CN)^8]^{n-}$ = W, Mo, Re) building blocks that can be used judiciously for the designing of multifunctional magnetic materials.[3]

Here, I will present the magnetostructural correlation of our recent work based on octacyanido building block $[W(CN)_8]^{3-}$ with Fe(II) metal center. The novel complexes shows reversible spin-state switching, thermo-induced SCO at near room temperature and photo-induced spin-state switching under light irradiation at low temperature.

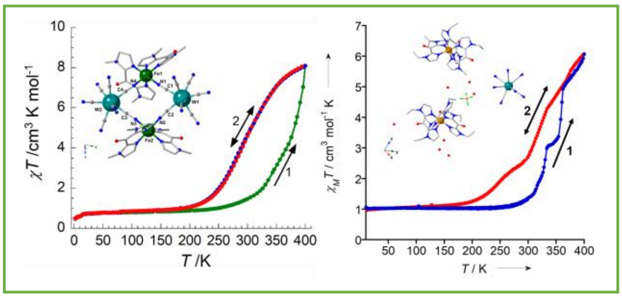

Figure 1. Crystal structure and χT vs T plot of W-Fe molecular complexes

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On/Off Photo-Switching And Thermo-Induced Spin Crossover With Cooperative Luminescence In A 2D Iron(II) Coordination Polymer

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Rational design of stimuli-responsive multifunctional coordination-polymer (CP) by incorporation of one or more additional cooperative properties *e.g.* magnetic, electric, and optical with the intrinsic properties *e.g.* permanent and tunable porosity, versatile structural topologies, and physicochemical properties have gained significant attention in recent times.[1] On this aspect, the simultaneous incorporation of both Spin-crossover (SCO) and luminescence properties in CP is challenging but highly attractive as modulation of luminescence signal can signify LS/HS population during the spin-state switching.[2] As a successful synthetic strategy to improve cooperativity between SCO and luminescent, the direct coupling between the SCO unit and appropriate luminescent organic linkers to form the extended structures is significantly important and challenging to interplay such cooperative properties, which have been rarely investigated in 2D multifunctional CPs.

Herein, we present one 2D CP (**Figure 1**) by introducing $Fe(NCSe)_2$ with a novel EDOT-based ligand which exhibits cooperative SCO and luminescence properties along with ON/OFF photo-switching behavior.[3]

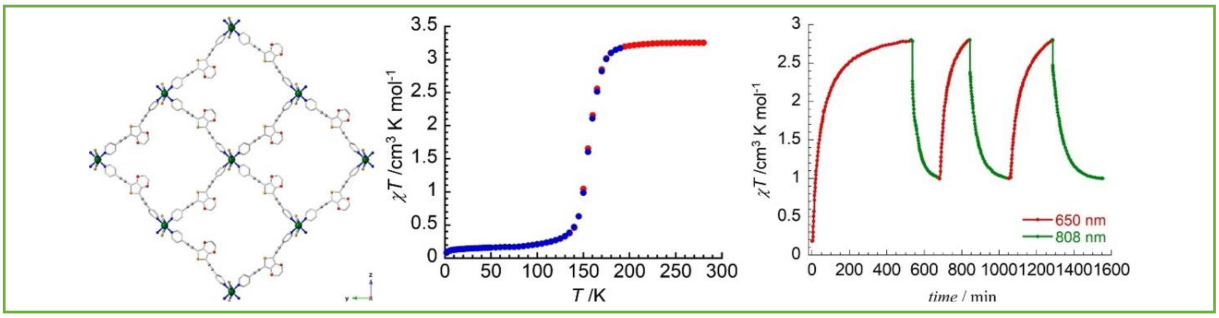

Figure 1: (Left to right) 2D structural, magnetic and photomagnetic features of the CP

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Thermal Spin Transition in $[Co(terpy)_2][BF_4]_2$: A Density Functional and Wave Functional Study

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Magnetic susceptibility studies of $[Co(terpy)_2][BF_4]_2$ show low-spin below 100 K and undergoes a gradual spin-transition on heating at around 270 K [1]. The structure at 30 K shows a pronounced Jahn-Teller distortion and the primary reason for the progress of the spin-crossover is reflected in the subtle changes in the lattice structure as the spin-crossover progresses. In our study, the crystal structures at all temperatures reported in the aforementioned study are taken and analysed using Density Functional Theory (DFT) and wave-function methods to interpret the experimental observations. The variation in the bond and angle parameters of all the structures with temperature show a prominent Jahn-Teller distortion along two of the equatorial bonds while the axial bonds change to the highest extent with temperature. The rigid scan analysis of the same parameters in the two spin-states of Co(II) show that the axial bonds have a notable role in the process of spin-crossover. DFT single-point energy calculations are performed with a range of functionals to mimic the experimental magnetic susceptibility behaviour out of which only B3LYP, B3LYP*, CAMB3LYP and B3PW91 explain the experimental results. CASSCF and CASPT2 calculations including contributions from metal-ligand σ-bonding in the complete active space show the spin-crossover behaviour.

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In-Situ Oxidation-Reduction as a Tool to Generate Magnetic Semiconductors

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Magnetic semiconductors are a special class of materials which allow effective manipulation of charge and spin, and therefore, promising for spintronics applications. Clinoatacamite, a naturally occurring mineral, is found to be a 3D antiferromagnetic insulator. Our reaction involves cuprous chloride (CuCl) and graphene oxide (GO) as precursors where Cu(I) is spontaneously oxidized to Cu(II) (S=1/2) in the form of clinoatacamite [$Cu_2(OH)_3Cl$] with simultaneous reduction of graphene oxide (GO) to reduced graphene oxide (rGO) in one-pot. Successful synthesis resulted in the formation of a stable nanocomposite of phase-pure clinoatacamite nanocrystals embedded in the rGO matrix. The nanocomposite exhibits both the magnetic signatures of clinoatacamite as well as the semiconductivity of rGO – generating a new class of magnetic semiconductors. We also extended this concept of in situ oxidation-reduction reaction to integrate 1D chains of co-ordination polymers of $\{[Mn(CA)(H_2O)_2]H_2O\}_n$ (CA = 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) into rGO matrix.

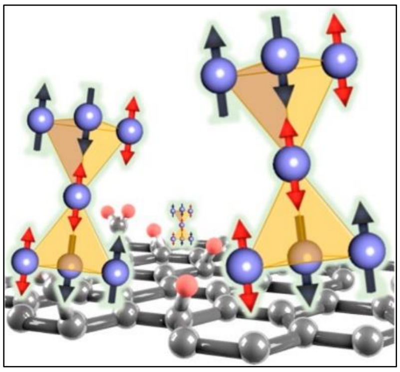

Fig : clinoatacamite-rGO nanocomposite

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Exploration of Multifaceted Applications of Metal Organic Gels

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Metal organic gels (MOGs) are viscoelastic materials formed due to entrapment of solvent molecules in an elastic network mainly linked together by coordination bond present between organic linker and metal ions (Low molecular weight gelators). Along with that some other supramolecular interactions include various noncovalent interactions like hydrogen bonding, coordination bonding, halogen bonding and π-π interaction plays a significant role to hold the network together. [1] The presence of metal ion broadens the possibility of engineering the response of these materials. Bulk production of MOGs is quite easy which drives the interest of the researcher towards exploring various properties of gels. like sustainability, stability, porosity etc. This has led to the use of MOGs in multifaceted applications like catalysis, sensing, gas storage, stimuli responsive devices and drug delivery etc. Numerous works have been published from our group on MOGs utilizing various organic linkers and wide range of transition metals to study many properties like luminescence, sensing, dye absorption, solid state photochemical reactions (Figure 1).[2] In this regard, our group have synthesised pyridyl based MOGs which shows a white light emission along with that it was also used in nitroaromatics sensing [3]. On the other hand, a diketone-based MOG was used as a luminescent based material as well as it shows well response to chemical stimuli (gel to sol transformation) with addition of some external reagents like NH_4OH, and EDTA [4]. MOGs provides a superior platform for photocyclization reaction by maintaining a proper distance between the two unreactive olefins. Our group extensively works in this field and reported pyridyl based amide derived MOGs which undergoes gel state [2+2] reactions, also used for selective gas and dye adsorption [5,6]. In summary, recent works carried out regarding MOGs in our laboratory will be reviewed in this presentation.

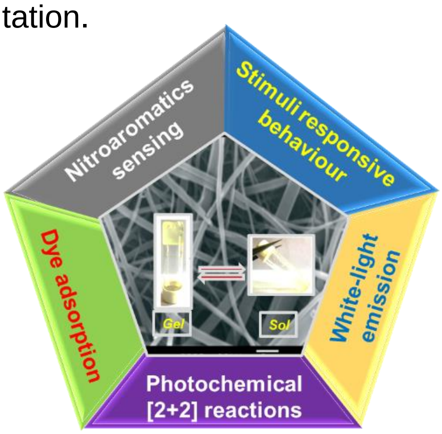

Figure 1. A Schematic representation of different applications of MOGs

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Deciphering the role of pressure in the magnetization dynamics of lanthanide single molecule Magnets

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Presently Lanthanide based single-molecule magnets (SMM) have gained unprecedented interest in the past two decades due to their very large blocking barrier of magnetization reversal (U_{eff}) and blocking temperature (T_B) which are considered to be the figure of merit of an SMM. As the magnetic anisotropy has been reached to its axial limit, the further enhancement of U_{eff} and T_B values with tuning of ligand field strength seems to be impossible. An alternative viable way to increase these parameters is to employ pressure on an SMM. Here, theoretical study based on DFT and CASSCF/RASSI-SO/SINGLE_ANISO calculations can play an important role to design improved SMMs. But, to date only limited studies have been performed due to the complexity in analysing the electronic structure at high pressure. Here, using a combination of pDFT and *ab initio* CASSCF calculations, we have explored a unique way to enhance the barrier height of well-known Ln(III) SIM, $[DyCl_2(THF)_5](BPh_4)\cdot 0.5THF$ **1**, $[Dy(OSiMe_3)Cl(THF)_5]BPh_4.2THF$ **2**, $[Yb(Ph_3PO)_4(I_{0.53}Br_{0.47})(I_{0.38}Cl_{0.62})][I_3]\cdot C_2H_5OH$ **3**. For $[DyCl_2(THF)_5](BPh_4)\cdot 0.5THF$ complex by the application of external pressure, able to make the complex from non-SMM to SMM. Complex $[Dy(OSiMe_3)Cl(THF)_5]BPh_4.2THF$, $[Yb(Ph_3PO)_4(I_{0.53}Br_{0.47})(I_{0.38}Cl_{0.62})][I_3]\cdot C_2H_5OH$, and enhancement of barrier height of 400 cm^{-1}. Our study reveals that with appropriate external pressure direction, the barrier height can be enhanced. Modulation of barrier height with external pressure (non–chemical fine-tuning approach) is going to be a new generation of SIMs.

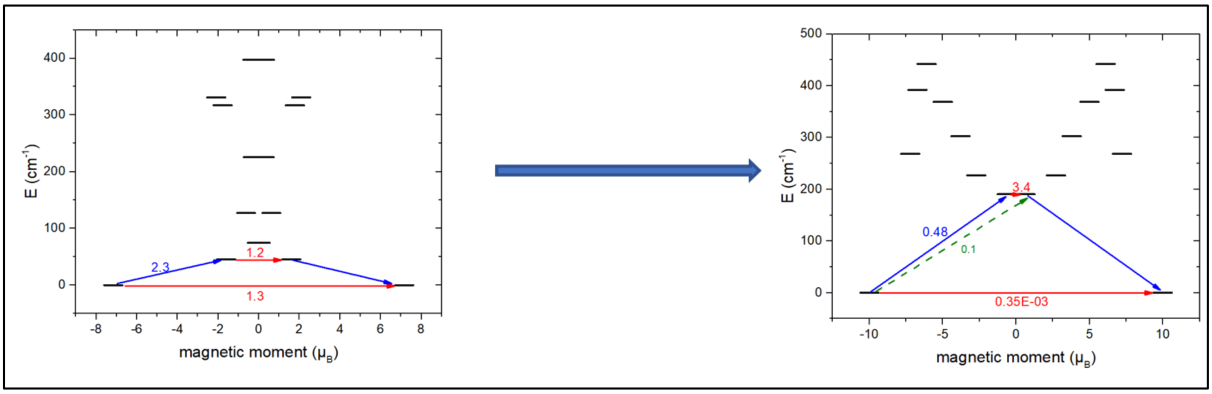

Figure 1. Relaxation mechanism of complex **1**

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In Silico Studies of Spin crossover systems on surfaces

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The use of molecules or molecular assembly for the use of information processing presents one of the best possible objectives for chemists so that they can use a synthetically modified chemical to be found in the industrial application. Although it seems to be a long-term plan but some key aspect is already reported and among those features one of the very important underlying concept seems to be helpful for us is molecular bistability. Molecular bistability can be defined as if the molecular system is found to be stable in two different states and in a given range of perturbation. Among these two states one will be the stable state or ground state and the other will be the meta-stable state. One such example of molecular bistability is named as Spin Crossover (SCO). The SCO complexes are generally found to be transition metal complexes from d^4-d^7 metal ions. The use of the SCO complexes is very much useful in the field of data storage and sensing devices. But for any of the device to work the complex has to grafted on top of a surface which can be metallic or non-metallic in nature. Due to the very low energy barrier between the states of SCO the choice of surface matters a lot during designing a device. Hence, we want to study the binding of the SCO complex with the surface and how the surface reacts to a complex to understand the effect of surface on a SCO complex by doing computational study. In this case the complex Fe $[HB(3,5\text{-}(CH_3)_2pz)_3]_2$ (Fe-pz) has been chosen as it was proved to be stable on the Au (111) surface which is very rare because the Au surface is the most reactive surface to study and it very easily destroys many SCO complexes known prior. By modelling the complex on the surface it was possible to study the system to gain a better understanding on how the surface really react to the SCO systems.

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Decisive Role of Spin-States and Spin-Coupling in Dictating Selective O_2 Adsorption in Chromium(II) Metal-Organic Framework

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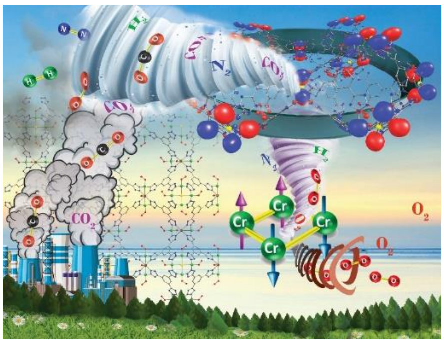

Figure 1: The pivotal role of spin coupling in controlling the gas selectivity

Coordinatively unsaturated Chromium (II)-based $Cr_3[(Cr_4Cl)_3(BTT)_8]_2$ (Cr-BTT; BTT^{3-} =1,3,5-benzenetristetrazolate) metal-organic framework (MOF) has been shown to exhibit exceptional selectivity towards adsorption of O_2 over N_2/H_2. Using periodic Density Functional Theory (DFT) calculations, we attempt to decipher the origin of this puzzling selectivity. By computing and analyzing the magnetic exchange coupling, binding energies, the partial density of states (pDOS), and adsorption isotherms for the pristine and gas bound MOFs $[(Cr_4(X)_4Cl)_3(BTT)_8]^{3-}$ ($X=O_2$, N_2, and H_2), we unequivocally establish the role of spin-states and spin-coupling in controlling the gas selectivity. The computed geometries and gas adsorption isotherms are consistent with the earlier experiments. The O_2 binding to the MOF follows an electron-transfer mechanism resulting in a Cr(III) superoxo species ($O_2^{-\bullet}$) with a very strong antiferromagnetic coupling between the two centers, while N_2/H_2 found to only weakly perturb the metal center. Although the gas bound and unbound MOFs have $S = 0$ ground state (GS), the nature of spin configurations and the associated magnetic exchanges are dramatically different. The binding energy and the number of oxygen molecules that can favorably bind to the Cr center were found to vary with respect to the spin-state with a significant energy margin (47.6 kJ/mol). This study offers a hitherto unknown strategy of utilizing spin-state/spin-couplings to control gas adsorption selectivity in MOFs.

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Modulating Magnetic Anisotropy in Dy(III) Single-ion Magnets Using an Oriented External Electric Field

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Single-molecule magnets (SMMs) are alluring because of their potential applications in storage devices, quantum computing, and spintronics devices. Lanthanide single-ion magnets (SIMs) are promising candidates for SMMs because of their huge barrier height for magnetization reversal (U_{eff}) as well as very high blocking temperature (T_B). Various chemical fine-tuning methods have been explored to obtain large U_{eff}. With numerous mononuclear Dy(III) SIMs reported, it has been stated that the axial limit that controls the U_{eff} has been reached. Here, we have used an oriented external electric field as an alternative non-chemical tool to enhance the axiality and hence the U_{eff} of mononuclear Dy(III) SIMs. Here, we have chosen two types of Dy(III) mononuclear SIMS, first with pentagonal bipyramidal geometry, [Dy(bbpen)X] (X = Cl, **1**;Br,**2**;H_2bbpen=N,N′-bis(2-hydroxybenzyl)-N,N′-bis(2-methylpyridyl)ethylenediamine) and the second with square pyramidal geometry, [Dy(Mes*O)$_2$(THF)$_2$X] (Mes*=2,4,6-tri-tert-butylphenyl) (X=Cl, **3**; Br, **4**; I, **5**). At first, the optimization of the molecule is performed in presence of an electric field and then ab initio CASSCF calculations are performed in presence of the same amount of electric field to capture both structural distortion as well as the effect of the electric field on the magnetic anisotropy of the molecule. In both the complexes [Dy(bbpen)X] and [Dy(Mes*O)$_2$(THF)$_2$X], the electric field is applied along the equatorial Dy-X bond. The X-ray structures of complex **1**, **2**, **3**, **4**, and **5** show the U_{eff} barrier of 492, 792, 764, 800 and 819 cm^{-1} respectively. However, in presence of an electric field, the barrier height for **1**, **2**, **3**, **4**, and **5** increases significantly and is found to be 1013, 1014, 1212, 1021, and 1021 cm^{-1} respectively.

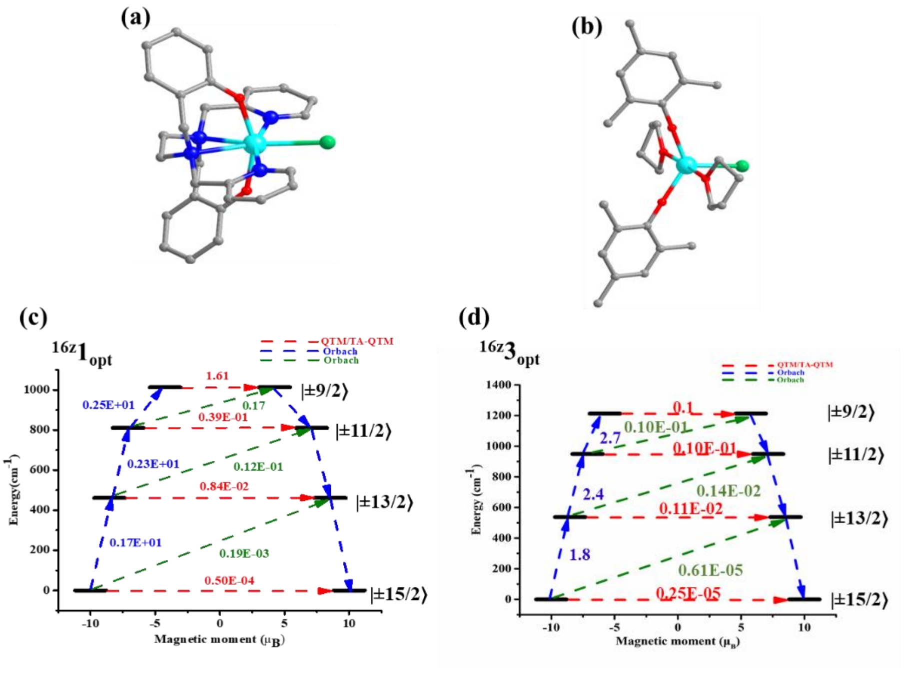

Figure 1. *DFT optimized structures (a)* ***1*** *(b)* ***3*** *(c)* U_{eff} *barrier diagram of* ***1*** *at an applied OEEF of 0.016 au (d)* U_{eff} *barrier diagram of* ***3*** *at an applied OEEF of 0.016 au. Colour code:* Dy^{III} *- cyan, C- grey, Cl- green, O- red and N- blue. Hydrogen atoms are omitted for the sake of clarity.*

Impact of Counteranion on Reversible Spin–State Switching in a Series of Cobalt(II) Complexes Containing Redox-Active Ethylenedioxythiophene Based Terpyridine Ligand

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The low-dimensional switchable molecular-based materials offer a wide range of potential application in future quantum science and technologies.[1] Among them, molecular systems exhibiting Spin Crossover (SCO) phenomenon where the switching of the magnetic properties originates from their reversible spin-state switching between a low-spin (LS) and high-spin (HS) state upon the application external stimuli such as temperature, pressure, light irradiation, electrochemical potential, magnetic and electric field *etc* represent a promising field to provide a potential way to accomplish the molecular spintronic, molecular sensors and nanoscale devices.[2]

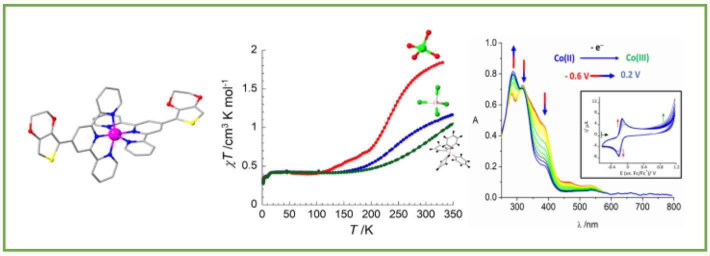

Figure 1: Perspective view of the Co^{2+} complex (left); Temperature dependence of the *c*T product for the complexes at 1000 and 10000 Oe (middle); Solution-state spectroelectrochemistry of the complex (right) and its electropolymerization (right inset).

For the first time, in this work, we have incorporated a redox-active Ethylenedioxythiophene (EDOT) motif in the terpyridine ligand system to explore SCO properties in Cobalt(II) center using three different tetrahedral counter anions (BF_4^-, ClO_4^-, BPh_4^-).[3] Complex with ClO_4^- counter anion exhibits a reversible, gradual, and complete spin-state switching between low-spin (LS) (S = 1/2) and high-spin (HS) (S = 3/2) states. Wherever, complex with BF_4^- and BPh_4^- counter anions show incomplete spin-state switching behaviour. Additionally, we have been able to show a redox-stimuli assisted reversible conversion from paramagnetic Cobalt(II) (S = 3/2) to diamagnetic Cobalt (III) (S = 0) system.

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Manganese-based Spinel Cathode for Aqueous Rechargeable Zinc-Ion Battery

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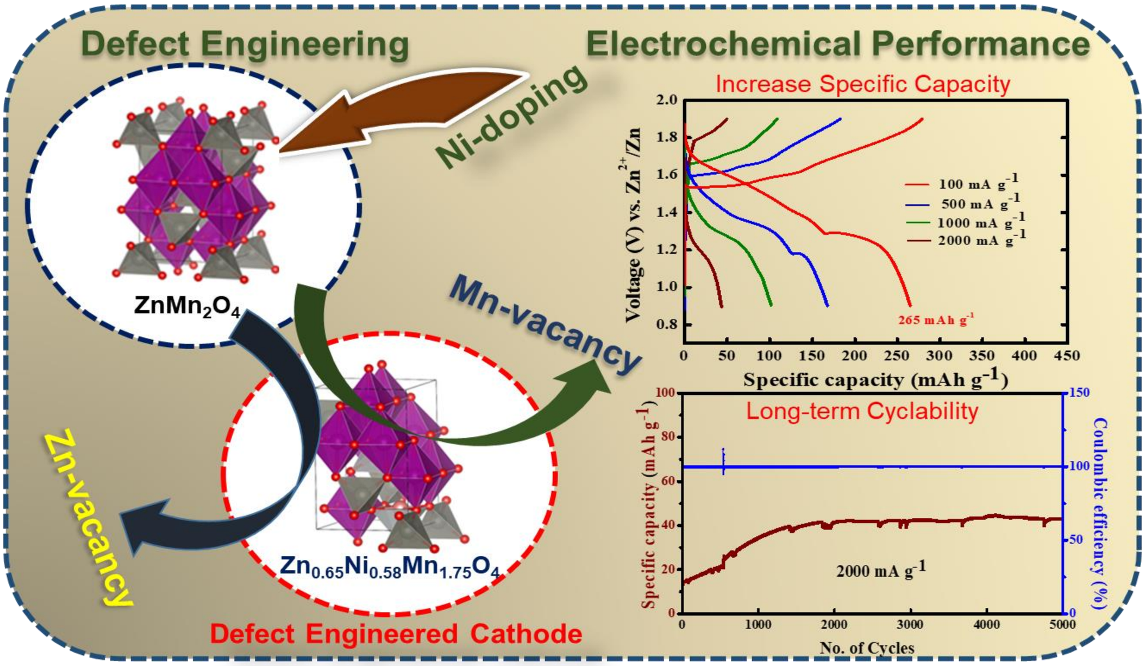
The rational defect engineering of Mn-based spinel cathode materials by metal-ion doping and vacancy creation fosters reversible intercalation/deintercalation of charge carriers and boosts the charge storage performance of aqueous rechargeable zinc-ion battery (ZIB).[1] Herein, we demonstrate the Zn^{2+} ion storage performance of defect-engineered ternary spinel cathode $Zn_{0.65}Ni_{0.58}Mn_{1.75}O_4$. The defect engineering is achieved by Ni^{2+} doping and cation (Mn^{3+} and Zn^{2+}) deficiency. The DFT studies show that the defect engineering modifies the electronic structure and improves the electronic conductivity. $Zn_{0.65}Ni_{0.58}Mn_{1.75}O_4$-based ZIB has very long charge discharge cycling stability with a specific capacity as high as 265 mAh g^{-1} (at 100 mA g^{-1}). Twofold enhancement in the specific capacity is observed after 5000 cycles.[2] The self-discharge studies for a year show that the device retains 63% of the initial performance.



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Role of Schiff Base Hydrazone Ligands in Self Assembly of Lanthanide Based Aggregates

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Lanthanide based magnetic materials have received increased attention due to their relevance in miniaturization of magnetic storage and spintronics devices.[1] Strong uniaxial magnetic anisotropy associated with several lanthanide ions can be attributed to the observation of single molecule magnet (SMM) behaviour along with record high magnetization barrier in mononuclear lanthanide complexes.[2] Multidentate Schiff-base ligands that provide several suitable coordination sites for lanthanide and thereby results in complexes with considerable structural diversity and varied structural topologies.[3] In this regard, C_3 symmetric multidentate Schiff base ligands are of particular interest due to their relevance in accommodating three metal ions in a triangular topology and thereby result in torroidal magnetic materials.[4] Presence of three aromatic carbonyl groups in 1,3,5-triacetylphloroglucinol offers abundant possibilities to construct C_3 symmetric Schiff base ligands with multiple coordination pockets.[5] This led us to explore the reaction of 1,3,5-triacetylphloroglucinol with semicarbazide, mandelic acid hydrazide and benzoic acid hydrazide resulting to the formation of mono-, bis- and tris-hydrazone ligands respectively. Self-assembly of these mono-, bis- and tris-hydrazone ligands with Dy^{III} salts produce a series of mono, di- and tri-nuclear Dy^{III} complexes : $[Dy^{III}(H_2L)(NO_3)(CH_3OH)]\cdot 2CH_3OH$ (**1**) [H_3L= (*E*)-2-(1-(3,5-diacetyl-2,4,6-trihydroxyphenyl)ethylidene)hydrazine-1-carboxamide], $[\{Dy^{III}(L')(H_2O)_2\}_2]\cdot 4CH_3OH\cdot 3H_2O$ (**2**) [H_3L'= *N, N'*-((1*E*,1*E'*)-(5-acetyl-2,4,6-trihydroxy-1,3-phenylene)bis(ethan-1-yl-1-ylidene)bis-(2-hydroxy-2-phenylacetohydrazide)] and $[Dy^{III}_3(H_3ptk(bhz))_2(CH_3OH)_6]\cdot 3Cl\cdot CH_3OH$ (**3**) [$H_6ptk(bhz)$= *N',N''',N'''''*-((1*E*,1*E'*,1*E''*)-(2,4,6-trihydroxybenzene-1,3,5-triyl)tris(ethan-1-yl-1-ylidene))tri(benzohydrazide)]. Magnetic investigation of (**2**) shows the absence of slow relaxation of magnetization. During this presentation the synthesis, crystal structure and characterization of **1-3** will be presented.

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Molecules to Material: Synthesis of Transition Metal Phosphide for Electrochemical Energy Applications

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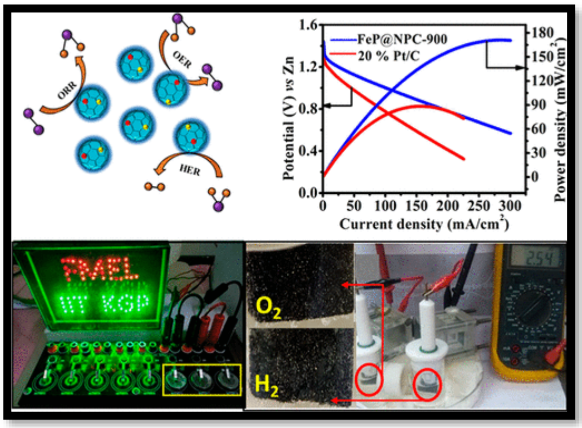
The rational design and synthesis of efficient multifunctional electrocatalysts is of significant interest for energy conversion and storage devices such as metal-air battery and water electrolyzer. The working principle of rechargeable Zn-air battery (ZAB) and water electrolyzer involves oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and hydrogen evolution reactions (HER). The overall efficiency of these devices is limited because of sluggish electron transfer kinetics associated with ORR, OER, and HER. Traditionally Pt-based catalysts are used as state-of-the art catalyst for ORR and HER, and IrO_2/RuO_2 for OER. The high cost and the poor durability are some of the serious concerns associated with traditional electrocatalysts. More importantly, as these catalysts are not bifunctionally active they cannot be used in the rechargeable ZAB or water electrolysers.

Herein, we demonstrate a novel approach for the synthesis of a N, P dual-doped mesoporous carbon-encapsulated transition metal phosphide such as iron phosphide (FeP@NPC) nanostructure for zinc−air battery (ZAB) and alkaline water-splitting applications. FeP@NPC is obtained by the carbothermal reduction of the precursor complex $[Fe(bpy)_3](PF_6)_2$ in the presence of melamine without any traditional phosphidating agent at 900 °C. The ZAB device delivers a peak power density of 190.15 mW cm^{-2}, specific capacity of 785 mA h g_{Zn}^{-1}, and energy density of 706.5 Wh kg_{Zn}^{-1} at 50 mA cm^{-2}. The ZAB exhibits excellent charge−discharge cycling stability for over 35 h with negligible voltaic efficiency loss (0.9%). FeP@NPC-900 also has promising electrocatalytic activity toward water splitting in acidic as well as in alkaline pH. ZAB-powered water electrolyzer is made by integrating two rechargeable ZABs connected in series with the two-electrode water electrolyzer. The ZAB powers the electrolyzer for 24 h without a significant loss in the open-circuit voltage.[1]



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Spin-State Energetics and Magnetic Anisotropy in Penta-coordinated Fe(III) Complexes with Different Axial and Equatorial Ligand Environments

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The penta co-ordinated Fe(III) complex with dimethyl phenyl phosphine (PMe_2Ph) as axial ligand has been investigated in two different conformers, depending on the orientation of the phenyl ring. It is noted that the out-of-plane phenyl ring conformer is more stable than the in-plane conformer in the intermediate spin-state[1]. However, the effective anisotropic barrier for the in-plane conformer is 80 cm^{-1} and the out-of-plane conformer is 42 cm^{-1}. To explore the effect of the ligand field environments on the electronic and magnetic properties of these two conformers, ab initio calculation is performed on $FeCl_3(PMe_2Ph)$ complex with different ligand environments. It is calculated that the strong spin-orbit effect generates large magnetic anisotropy in the complexes. These designed complexes may be used by experimentalists for making highly magnetic anisotropic complexes.

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Bistable Magnetic Materials Based on Self-Assembled Metallosupramolecular [$M^{II}_4L_4$] Tetrahedral Cages

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Potential application of molecular materials in future electronic devices is mainly based on “molecular bistability” that arises switching between two easily accessible electronic spin states of the system *i.e.,* high spin (HS) and low spin (LS) by applying external stimuli *e.g.,* change in temperature or pressure, light irradiation, magnetic and electrical field, presence or absence of a guest molecule *etc*.[1] The design and synthesis of functional materials via supramolecular self-assembly of molecular components is an important aspect in the field of host-guest chemistry.[2] Till date, a very few numbers of metallosupramolecular cages showing bistability are being reported in the literature, mostly based on Fe(II).

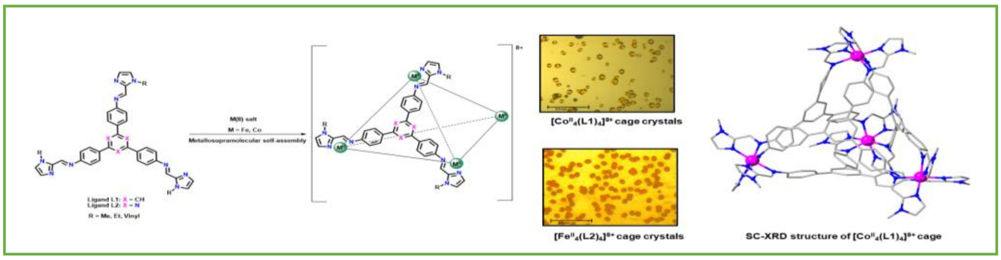

Figure 1: Synthesis Scheme of [$M^{II}_4L_4$]$^{8+}$ cages and Single Crystal XRD structure of [$Co^{II}_4(L1)_4$]$^{8+}$ cage.

In this work, we have synthesized several different tritopic amine ligands (having C3 symmetry), undergoes condensation with N-alkyl-2-imidazolecarboxaldehyde (alkyl: Methyl, Ethyl, Vinyl) using Fe(II) or Co(II) metal salts to obtain the [$M^{II}_4L_4$]$^{8+}$ cages. Among these, [$Co^{II}_4(L1)_4$]$^{8+}$ will be the first ever reported cage to show molecular bistability.[3] The cage has been confirmed by several physical measurements *e.g.,* Mass Spectra, Single crystal X-ray diffraction structure analysis. These types of cages contain a tunable cavity size which can encapsulate different types of guest molecules. By tuning the guest molecules inside the cavity, the magnetic property of the cages can be altered which carries a significant impact in the field of magnetism and host-guest chemistry.

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Theoretical study of magnetic anisotropy and optical property in doped $CrPS_4$ single layer

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Atomically thin layer of ternary transition metal chalcogenides (TTMC) have intrinsic novel properties depending on their composition.[1] By substituting one element in such 2 dimensional layers, the change in physical properties could be explored. In our work we are going to replace one sulfur atom by metal (Li, Ag, Cu) in the 2D layer of TTMC, $CrPS_4$. In this study the bandgap change due the substitution is studied along with spin orbit coupling. The change in magnetic anisotropy and magnetism of the material will be explored. The effect on optical property due to the substitution will be addressed.[2]

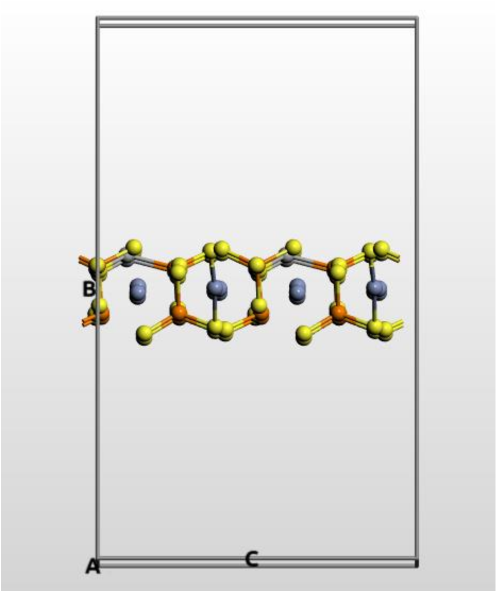

Figure 1. Schematic representation of CrPS4 monolayer.

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ON/OFF Photo(switching) Coupled with Reversible Thermo-induced Spin-state Change and Single-Crystal-to-Single-Crystal Transformation in a Mixed-valence [Fe_2Fe_2] Molecular Square

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From past two decades, a great interest on Prussian Blue (PB), Prussian Blue Analogues (PBAs) and low-dimensional cyanide materials have been manifested due to their exciting physical behaviors.[1-6] One of the most appealing areas of these materials is achieving the spin-state switching accompanied with reversible single-crystal-to-single-crystal (SC–SC) transformation. However, in most cases, high dimensionality and low solubility of these materials obstruct the field of technological application.[3] To overcome such problem, intense research efforts have been directed towards synthesizing the molecular counterparts of PB and PBAs to enhance the solubility and better understand the physical properties with the controlled structural topology.[1-3] Here in this presentation, I will describe a mixed-valence [Fe_2Fe_2]$^{2+}$ molecular square that exhibits reversible thermo- and photo-induced ON/OFF switching.

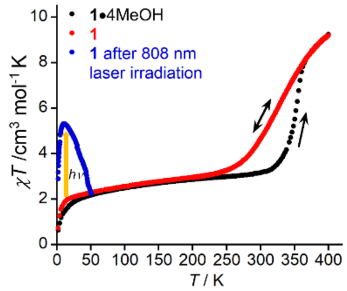

Figure 1. χT vs T plots of **1**•4MeOH and **1** measured at 2 K/min under 2500 Oe external dc magnetic field.

The cyanido-bridged mixed-valence [Fe_2Fe_2] molecular square complex, {$[Fe(pzTp)(CN)_3]_2[Fe(bik)_2]_2$}$[Fe(pzTp)(CN)_3]_2$•4MeOH (**1**•4MeOH) (bik = bis-(1-methylimidazolyl)-2-methanone, pzTp = tetrakis(pyrazolyl)borate) exhibits single-crystal-to-single-crystal (SC-SC) transformation together with spin-state change at high temperature and converted into {$[Fe(pzTp)(CN)_3]_2[Fe(bik)_2]_2$}.$[Fe(pzTp)(CN)_3]_2$ (**1**). Both complexes exhibit thermo-induced spin-state switching behavior in iron(II) centers coupled with the SC-SC transformation where the low-temperature $[Fe^{III}_{LS}Fe^{II}_{LS}]_2$ phase transform into a high-temperature $[Fe^{III}_{LS}Fe^{II}_{HS}]_2$ phase. **1**•4MeOH exhibits abrupt SCO with $T_{1/2}$ at 355 K whereas **1** undergoes through a gradual SCO with $T_{1/2}$ at 338 K. Interestingly, **1**•4MeOH does not show any photomagnetic effect, whereas **1** exhibit ON/OFF photoinduced spin-state switching with T_{LIESST} = 67 K.

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Stepwise Spin-State Switching and Effect of Light Irradiation in Manganese(III) Complexes

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Spin-crossover (SCO) materials have offered an excellent route to the realization of molecular spintronic, sensors, switches, nanoscale devices due to their intrinsic bistable property.[1] Remarkably, stepwise SCO, which shows two or more steps have gained tremendous interest since stepwise SCO produces distinct order associated with intermediate phase-transition.[2] This may significantly improve the information storage capacity due to a more accessible spin-state. Apart from the presence of independent SCO metal centers and/or strong cooperativity which displays SCO at different temperatures and generates non-equivalent SCO sites in the intermediate phase has played a significant role in stepwise SCO. In comparison to well-studied iron and cobalt SCO systems, manganese-based SCO (low-spin (LS) ($t^4_{2g}e^0_g$, $S = 1$, $^3T_1$) to high-spin (HS) ($t^3_{2g}e^1_g$, $S = 2$, ^5E)) in octahedral geometry is less explored, where a complete and stepwise SCO has been rarely reported.

Herein we present mononuclear manganese(III) complexes containing hexadentate chelating ligands which exhibit complete and reversible stepwise spin-state switching behavior without having any symmetry-breaking, rare example in the literature.[3] Additionally, the impact of photo-active ligand on manganese(III) SCO will be discussed which is very unique and probably the first example for manganese(III) SCO systems.

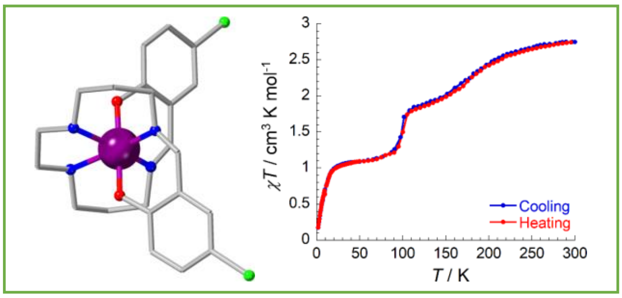

Figure 2: Left: Perspective view of the complex cation in [Mn(5Cl-sal$_2$-323)](BPh$_4$) (1) at 240 K and Right: Temperature dependence of χT product for **1** at 10000 Oe.

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Immobilized Polar Sulfone Group Facilitated Flue and Biogas Separations by a Humid-Stable MOF under Dry and Wet Environments

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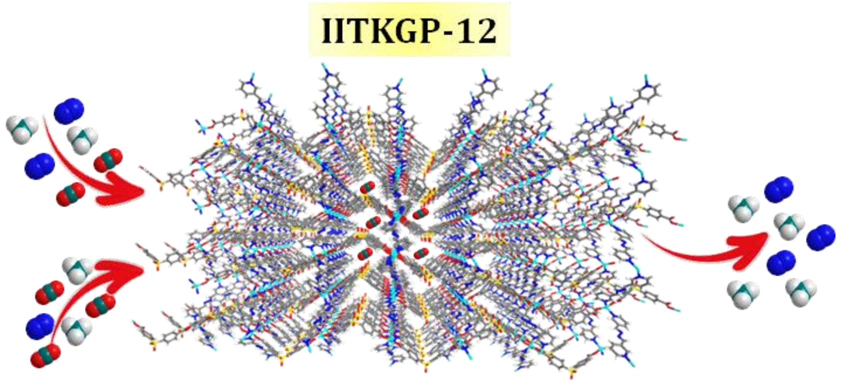
Great efforts have been made toward the separation of CO_2 from flue gas and biogas to mitigate environmental pollution and the demand for renewable fuels, respectively.[1] Having several structural superiority and architectural diversity, the effective design and development of moisture-stable microporous metal−organic frameworks (MOFs) for successful industrial deployment is on demand.[1] Herein, utilizing N, N-donor spacer (L) and a bent organic linker 4,4′-sulfonyldibenzoic acid (H_2SDB) having polar sulfone group ($-SO_2$), a new moisture-stable 2D Zn-MOF, $\{[Zn_2(SDB)_2(L)_2]\cdot 2DMA\}_n$, **IITKGP-12**, has been constructed and employed in challenging flue and biogas separations.[2] The suitable pore channels (4.2 × 6.2 Å^2) decorated with $-SO_2$ moieties triggered such separations *via* preferential binding of polar CO_2 molecules, as verified by grand canonical Monte Carlo (GCMC) simulation. The real-time potentiality was also investigated *via* dynamic breakthrough analysis in both dry and humid conditions. Moreover, the high separation selectivity, easy regenerability, and excellent recyclability made **IITKGP-12** highly promising toward this projected application.



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Charge on nucleus an “underrated player”

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Almost three decades of continuous research in the field of Single molecular magnets has brought many laurels to the area. We have come a long way from discovering $TbPc_2$[1] to achieving a blocking temperature of 80°C[2], and things are moving very fast. All the efforts made in this direction are concerned with the ligand field improvement only. One important aspect that seems to be missed by most of us is the importance of metal ions in achieving anisotropy. It can be clearly understood that the properties of complexes can be changed by varying the oxidation state of the metal ions. In recent years, several bivalent lanthanide-based complexes have been made with almost all lanthanide ions starting from Ce to Lu[3]. Also, experimental and theoretical studies are done on these complexes to establish that these complexes show a far greater magnetic moment than their trivalent counterparts[4]. It leads to our enhanced interest in establishing the SMM properties in tetravalent lanthanide-based SMMs. Although tetravalent lanthanide complexes are not easy to synthesise, a number of Ce(IV) complexes have been studied in the past, and recently Tb(IV) complex was synthesized by Mazzanti and co-workers. This opens to a new world of tetravalent lanthanide complexes. Tetravalent lanthanide complexes will lead to more robust metal−ligand bonds, which will, in turn lead towards a large crystal field. As expected there is increase in the covalency of metal-ligand bond which is confirmed from DFT calculations. This opens the door for tetravalent lanthanide complexes. Theoretical studies based on CASSCF/RASSI-SO/SINGLE_ANISO methods have played a prominent role in the design and development of molecular magnets. Particularly pioneering work related to the development of the relaxation mechanism for simple models such as Dy(III)-O, Dy(III)−$(OH)_2$ and Dy(III)−F helped experimentalists in the design of suitable ligand architecture leading to superior Dy SIMs.

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Step-Economic Construction of Heterobiaryl Ligands

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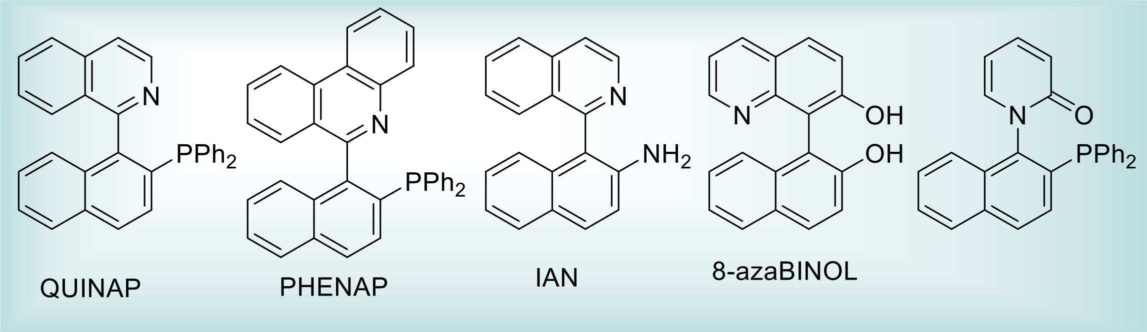
Heterobiaryl motifs are widely present in natural products and pharmaceuticals.[1] They have also been widely employed as preferred ligands in asymmetric catalysis.[2] Among the various type of hetero biaryl scaffolds, the use of heterobiaryls (QUINOL, QUINOX, QUINAP, PINAP, PHENAP, 8-azaBINOL) as ligands having nonequivalent donor atoms is regarded as an innovative method for transition-metal catalyzed transformation.[3] Additionally, they are also widely used in a variety of enantioselective reactions to provide asymmetric induction due to their binding ability with metal ions through their inherent nitrogen and other donor atoms.[4] To access this atropisomeric heterobiaryls scaffold, traditional techniques typically concentrated on the resolution of the racemic axial heterobiaryl backbones. Arguably, one of the simple, direct, and step-economic techniques for the construction of these heterobiaryls would be transition-metal catalyzed site-selective C-H bond functionalizations.[5]



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A Highly Selective MOF-based Probe for Turn-on Luminescent Detection of Al^{3+}, Cr^{3+} and Fe^{3+} in Solution and Test Paper Strips

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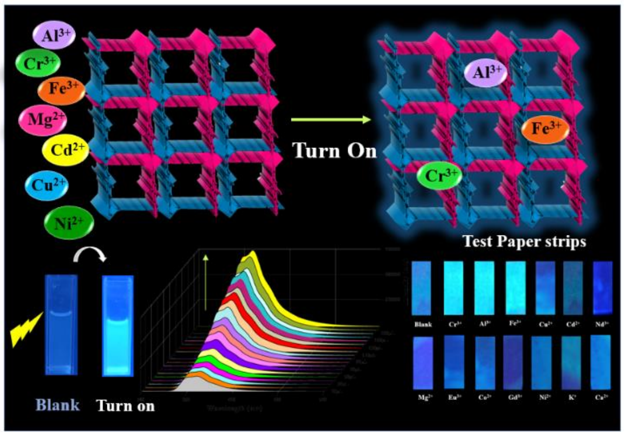
Trivalent metal ions (Cr^{3+}, Al^{3+} and Fe^{3+}) constitute a major section of the environmental pollutants and their excess accumulation has a detrimental effect on health, so their detection in trace quantity has been a hot topic of research. A highly scalable 3D porous Zn-based luminescent metal-organic framework (MOF) has been synthesized by exploiting the mixed ligand synthesis concept. The strategic selection of an aromatic π-conjugated organic linker and N-rich spacer containing the azine functionality as metal ion binding sites immobilized across the pores spaces, have made this MOF an ideal turn-on sensor for Al^{3+}, Cr^{3+} and Fe^{3+} ions with very high sensitivity, selectivity, and recyclability. An in-depth study revealed absorbance caused enhancement mechanism (ACE) responsible for such turn-on phenomena. In order to make the detection process straightforward, convenient, portable, and economically viable, we have fabricated MOF test paper strips (the MOF could be simply immobilized onto the paper strips) for naked eye visual detection under UV light which thus manifests its potential as a real-time smart sensor for these trivalent ions.



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$Ni_{3-\delta}InSb$: Crystal Structure, Electronic Structure and Magnetism

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A ternary phase with the composition $Ni_{3-\delta}InSb$ crystallizing in the orthorhombic space group *Pnma* with lattice constants a = 7.104(3) Å; b=5.200(3) Å and c = 8.2237(2) Å was synthesized by high temperature solid-state synthesis. The crystal structure contains ~20 atoms in its unit cell, that are distributed over 4 crystallographically independent positions (two Ni, one In, and one Sb). The structure can be considered as a ternary substitutional variant of Ni_3Sn_2 (*Pnma*, No. 62), where, In and Sb orderly occupy two Sn sites of Ni_3Sn_2.[1,2] This site decoration pattern of two neighbouring elements, In and Sb is unique and confirmed by first principles total energy and formation energy calculation. The structure can be described by two building units: Ni_2Sb (building unit of Ni_2In) and NiIn (NiAs-type). They alternate in the structure and form an infinite *ac*- slabs (puckered) and the slabs are stacked along [010]. The calculated density of states (DOS) and crystal orbital Hamiltonian population(COHP) explain the stability and bonding characteristics in the structure based on the ordered configuration Ni_3InSb. Detailed magnetic properties of the titled phase are also explored.

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Molecular Ruthenium(III) Complexes with Redox Non-Innocent Ligand Frameworks for Water Oxidation Catalysis

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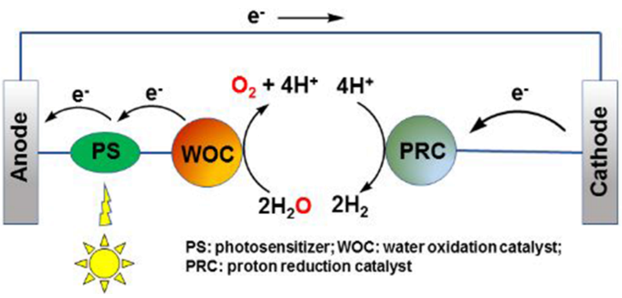
The growing world population and increase in energy consumption led to an urgent need in finding an alternative environmentally friendly energy resource (mainly carbon free). Thus, splitting water into dioxygen and dihydrogen ($2H_2O \rightarrow 2H_2 + O_2$) driven by visible light is a promising, sustainable method to convert solar energy to chemical energy. Although, due to the high kinetic and thermodynamic barrier ($\Delta G^o = +113.38$ kcal/mol) of the water oxidation step ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$), it becomes the bottleneck of the overall water splitting reaction. Nature performs this reaction at Oxygen Evolving Centre in PS II during photosynthesis. Therefore, taking inspiration from nature, an artificial modular system can be developed to produce H_2 from water and sunlight. Here water oxidation catalysts play a significant role in accelerating both multiple electrons and protons transfer as well as in the formation of O-O bond [1,2]. This poster mainly represents new ruthenium complexes as promising water oxidation catalysts to explore the effects of non-innocent ligands on the catalytic activity of water oxidation reaction.



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Tuning Spin-state Switchability in Fe(II) and Co(II)-based Coordination Solids

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The spin-state switchability (*aka* spin-crossover) process involves rearranging electrons within metal d-orbitals from the high-spin (HS) to the low-spin (LS) configuration corresponding to the distribution that yields the maximum and the minimum number of unpaired electrons, respectively. The relative population of the spin states is a function of various external perturbations such as temperature, magnetic fields, external pressure, and light irradiation. The thermal spin-state switching is fundamentally controlled by the zero-point energy difference (ΔE^0_{HL}) between the two spin states and is susceptible to the local tuning of the crystal field. Both long-range and short-range elastic interactions propagate throughout the lattice during spin-state switching due to a significant change in the volume of the ligand coordination sphere that leads to the communication between spin-crossover centers known as *cooperativity*. It is a superposition of two components: short-range, statistically distributed, depends on the shape and distance between neighboring molecules, and long-range, proportional to the average number of HS molecules per unit volume, purely elastic in nature, mediated by the lattice. Therefore, these materials are of current interest in chemistry and materials science because of their intrinsic fundamental properties and potential applications as functional materials for the construction of sensors and memory, and display devices.

In the present work, the tunability in the local crystal field (*i.e.*, Fine tuning of the electronic structure) probed via thermal variation in the spin-state switching behavior in the pure and diluted coordination network of $[Ni_xCo_{1-x}(bpy)_3][LiCr(ox)_3]$, $\{Fe_{1-x}M_x(pz)[Pd(CN)_4]\}$, M = Ni(II), Co(II), Mn(II), Zn(II); $0 \leq x \leq 1$ and $[Fe(pybzim)_3]X_2(XY)$, pybzim = 2-(2'-pyridyl)benzimidazole; X = ClO_4^-, BF_4^-, $CF_3SO_3^-$, XY = ClO_4^-- BF_4^-, will be discussed.

For $[Ni_xCo_{1-x}(bpy)_3][LiCr(ox)_3]$, $0 \leq x \leq 1$, upon increasing Ni(II) contents, the spin transition becomes more gradual and incomplete and eventually becomes temperature-independent for the pure $[Ni(bpy)_3][LiCr(ox)_3]$. Moreover, the thermal spin transition shifts to higher temperatures with increasing Ni contents, clearly establishing its role in stabilizing the LS coordination environment. In the diluted Hofmann-based spin-crossover coordination solids $\{Fe_{1-x}M_x(pz)[Pd(CN)_4]\}$, the variation in the cooperativity in combination with a variation in ΔE^0_{HL} are observed depending upon the relative size, degrees of dilution and the nature of the diluted ions substituted into the networks. Thus, controlling the nature and degree of metal dilution at the cationic site provides a fine-tuned platform for exploring the structure-electronic property correlations. Moreover, the tunability in the local crystal field associated with the alteration of the thermal spin-state switching behavior is further demonstrated by the counter anion variation in the coordination network of $[Fe(pybzim)_3]X_2(XY)$, where X = ClO_4^-, BF_4^-, $CF_3SO_3^-$, XY = ClO_4^-- BF_4^-.

Origin of the long-range ferrimagnetic ordering in "cubic" Mn(Co)Cr2O4 spinels

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Symmetry-lowering structural transition from a cubic to a tetragonal phase in magnetically frustrated AB_2O_4 spinel compounds is generally found indispensable to enable long-range magnetic ordering [1,2]. Intriguingly, $MnCr_2O_4$, and $CoCr_2O_4$, constitute exceptions to the above general rule, as they seem to undergo long-range ferrimagnetic (FIM) ordering within their corresponding cubic phases [3, 4]. We discover that $MnCr_2O_4$ (and $CoCr_2O_4$) undergo a partial glassy magnetic ordering of the spiral-spin components at T_{SP} prior to the long-range ferrimagnetic (FIM) transition, which triggers the onset of structural distortions that lower the local cubic symmetry. In absence of the higher-temperature glassy transition in doped $MnCr_2O_4$, the corresponding FIM ordering is found to be glassy instead of being long-ranged. In magnetic spinel oxides, like $CdCr_2O_4$ and $FeCr_2O_4$, where cubic to tetragonal structural transition [1,5] occurs from either a spin-Jahn-Teller effect or through Jahn-Teller distortions, such a higher-temperature glassy magnetic transition (i.e. above the long-range magnetic ordering) is absent. Our results, thus, clearly elucidate that the symmetry-lowering structural distortions arising at the glassy magnetic ordering at T_{SP} , aided with presence of magnetic A-site ions, play a pivotal role in releasing the geometric-magnetic-frustration in $MnCr_2O_4$ (and also $CoCr_2O_4$) to enable long-range FIM ordering in these systems.

Keywords: Ferrimagnetic, antiferromagnetic, ac susceptibility, spin-frustration.

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Modern Trends in Molecular Magnetism

Department of Chemistry

Indian Institute of Technology Kharagpur

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