

Book of Abstracts

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Harnessing the Magnetic Properties of Rare Earth Elements for Photochemical Reactions

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Rare-earth (RE) elements make possible everything from consumer electronics to renewable energy and are considered essential to a clean-tech-driven economy. Separation and purification of RE elements using solvent extraction are challenging due to their similar chemical and physical properties. The intrinsic magnetic properties, instead, vary significantly across the 4f block and are a promising handle to develop novel separation methods. Herein, we exploited the spin dependence of photochemical reactions involving magnetic intermediates. In particular, we explored the effect of RE-ions with different spin strengths on the interconversion between singlet and triplet states which drives the photolysis of benzyl glycine. This work provides fundamental principles to design photolabile ligands to prepare RE complexes and their reactivity harnessing both magnetism and light.

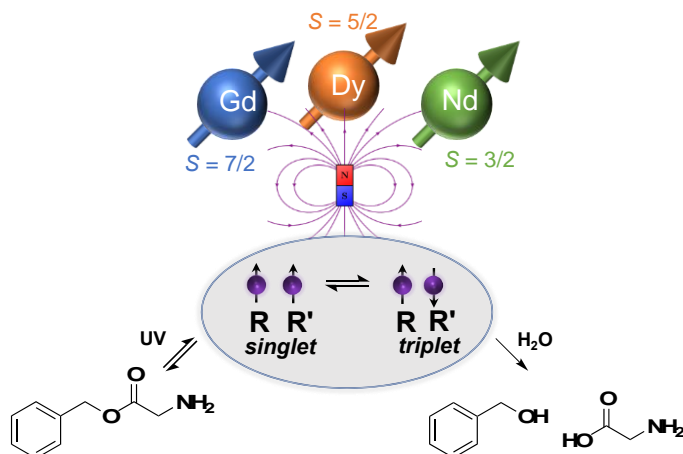


Figure. Graphical abstract

A thorough analysis of Green's function approach to computation of isotropic exchange couplings

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Computation of magnetic exchange coupling constants is important for a growing number of areas, including spintronics, magnetic memory storage, and novel molecular magnet design. Determining exchange coupling for high-nuclearity complexes is not possible experimentally, and thus, computational methods are needed to make predictions. The most widely used methods compute the differences in total energies of a set of magnetic configurations, but the cost and difficulty increase steeply as more centers are added. Thus, it is desirable to have a black-box method that involves only a single state. Recent work¹ has adapted the use of approximate Green's functions from the solid-state community for use on molecules. The Green's function approach provides a far more efficient route to calculate isotropic magnetic exchange couplings, as it only requires the calculation of one state. However, large-scale tests have not yet been performed. Thus, we assess the ability of the Green's function approximation for exchange coupling calculations to reproduce the standard broken-symmetry energy difference approach for transition metal complexes. To accomplish this, we have selected a variety of heterodinuclear, homodinuclear and polynuclear systems containing 3d transition metal centers and computed the couplings with both the Green's function and energy difference methods.

We found that the Green's function approach is shown to have mixed results for the cases tested. For dinuclear complexes with larger strength couplings the Green's function method is unable to reliably reproduce the energy difference values. However, for weaker dinuclear couplings, the Green's function approach reproduces broken-symmetry energy difference couplings. In polynuclear cases, the Green's function approximation worked remarkably well, apart from a few qualitatively wrong predicted couplings.

[1] Steenbock, T.; Tasche, J.; Lichtenstein, A. I.; Herrmann, C., *J. Chem. Theory Comput.*, **2015**, 11, 5651-5664.

Fine-tuning dipolar interactions through bridging ligand identity and coupling angle modulation

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As the field of molecular magnetism develops, many possible mechanisms have been illuminated as contributors to magnetic relaxation. At temperatures too low to allow for over-barrier or vibronically coupled relaxation, the predominant mechanism for the single-ion lanthanide molecular magnets is reduced to processes involving the lowest energy crystal field state of the ground spin-orbit manifold. Weak intermolecular coupling terms often perturb the energies of these states and induce faster relaxation than expected. Intramolecular coupling between magnetic centers can suppress these interactions by decreasing the probability of transitions induced by small or transient state mixing terms. Control and stability of the spin wavefunction is of high importance to advancing molecular magnetism goals in quantum information and spin-based electronics, and thus predictable design is a vital yet daunting challenge.

As a step in this direction we build from the established premise that the COT²⁻ ligand is consistently able to stabilize uniaxial Ising-type magnetic anisotropy in the Er³⁺ ion along the metal-centroid vector. This premise allows a tangible method to translate spin-space models into molecule design using classical principals for axial moments. Extending from this, ErCOT-derived polynuclear complexes have a useful structural handle to predict and direct the individual centers' anisotropies; therefore, they are ideal for tuning the through-space dipolar coupling mechanism. We have carefully modified the magnetic environment as enforced by the bridging ligands across two series of complexes. In one, we show the lengthened relaxation when moving from an inversion-symmetric arrangement of anisotropy axes to a collinear one. In the other, we maintain an inversion-symmetric bridging motif and modify the crystal field strength of the bridging ligands, noting the effect of both coupling strength and single-ion properties of the individual magnetic centers.

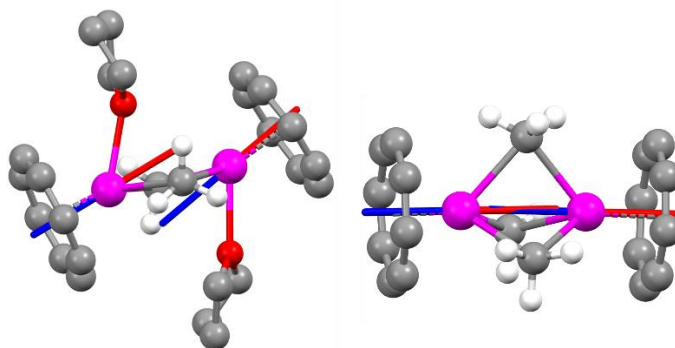


Figure. [ErCOT(μ-CH₃)THF]₂ and [(ErCOT)₂(μ-CH₃)₃]⁻, illustrative of the transition from parallel anisotropy axes to collinear arrangement of anisotropy axes (which are pinned to the Er-COT vector)

Creating Molecular Analogues of α -RuCl₃ for Studies of Kitaev-type Interactions

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Quantum spin liquids (QSL) are an intriguing class of materials that preserve magnetic fluctuations and non-zero magnetic entropy even at very low temperatures (theoretically, down to 0 K).¹ A model QSL system is α -RuCl₃ with a quasi-two-dimensional honeycomb lattice. Such a structure is described theoretically by the Kitaev model, which shows that an important ingredient of the QSL behavior is the difference in the three exchange constants at each metal ion center.² We are interested in investigating molecular analogues that mimic the magnetic exchange topology seen in α -RuCl₃, as such systems could provide new physics with regard to magnetic phenomena in molecules. To achieve this goal, we are focusing on oxalate-bridged metal clusters (Figure 1), where a central magnetically anisotropic metal ion is connected to peripheral metal ions capped by multidentate organic ligand to avoid the growth of extended structures. We report initial results from the synthesis and structural and magnetic characterization of a model tetranuclear cluster, [Ni(cyclen)]₃[Cr(C₂O₄)₃](ClO₄)₃, and discuss further steps to achieve analogous clusters for investigation of Kitaev's interactions.

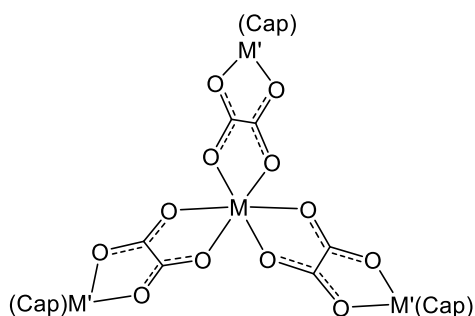


Figure 1. Schematic molecular structure of the tetranuclear oxalate-bridged complex.

[1] Kitaev, A. *Ann. Phys.* **2008**, 321, 2-111.

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Unconventional magnetoelectric coupling in chiral magnet [Cu(pym)(H₂O)₄]SiF₆·H₂O

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We combined variable temperature infrared spectroscopy, magneto-infrared spectroscopy, and high field polarization measurements to reveal unique magnetoelectric coupling in the $S = 1/2$ chiral magnet [Cu(pym)(H₂O)₄]SiF₆·H₂O up to 75 T. An applied magnetic field induces magnetostriction in the system which in turn leads to piezoelectricity. This results in changes to the measured polarization with applied magnetic field – an unconventional magnetoelectric. These effects are observed with magnetic fields as low as 2 T making this material a great candidate for spintronic devices.

Post-Synthetic Modification of 4-(2'-benzimidazolyl)-1,2,3,5-dithiadiazolyl in the Pursuit of Molecule-Based Materials

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In recent decades, research in the design of molecule-based materials with technologically relevant properties has gained much attention. Molecule-based materials provide the opportunity for the incorporation of attractive functionalities such as solubility, volatility, and conductivity via careful selection of structural features. In the pursuit of such materials, our group specializes in the design of 1,2,3,5-dithiadiazolyl (DTDA) radicals for use as paramagnetic ligands. Coordination of DTDA radical ligands to metal ions can result in strong exchange coupling between metal- and ligand- based moments, increasing the net magnetic moment and providing a pathway for coupling between coordination centers. DTDA radicals are known to demonstrate desirable properties such as magnetic bistability,^[1] and magnetic ordering.^[2] Tunability of materials properties can be achieved by careful incorporation of various functional groups. Our recent advances in post-synthetic modification to our DTDA radical ligand, 4-(2'-benzimidazolyl)-1,2,3,5- dithiadiazolyl (HbimDTDA) will be presented.

References

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- 4 Fatila, E. M.; Maahs, A. C.; Mills, M. B.; Rouzières, M.; Soldatov, D. V.; Clérac, R.; Preuss, K. E. *Chem. Commun.* **2016**, *52*, 5414-5417.

A Whole New World of Cobalt/Oxo Cluster Chemistry

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Cobalt-oxo cluster chemistry has been under exploration for many years and has led to an array of clusters of various nuclearities with relevance to bioinorganic chemistry, magnetism, and catalysis. Molecular chemistry provides immense control over the synthesis of magnetic and catalytic molecules; this can be utilized as a powerful resource in the investigation of quantum and catalytic properties, which are vital to next-generation technologies. The molecular nature of these monodisperse materials allows for their study by a variety of techniques, including Electron Paramagnetic Resonance (EPR) spectroscopy, magnetometry, electrochemistry, and single-crystal X-ray crystallography. Although cobalt-oxo-carboxylate chemistry has afforded numerous clusters, the utilization of chelating or polydentate ligands in such chemistry has been relatively little explored. Recently, N,O-containing polydentate ligands have emerged as attractive groups to investigate in cluster chemistry as many bioinorganic compounds have such polydentate ligation. Various binding modes can be achieved using these ligands leading to new structural topologies with interesting effects on the magnetic, catalytic, and surface chemistry of clusters. We have therefore begun to investigate the use of triethanolamine (teaH₃), and a more rigid ligand, 8-hydroxyquinoline (hqn) in Co^{II} and/or Co^{III} cluster chemistry in the search for new clusters with interesting structural features and physical properties. The synthesis, structure, and magnetic properties of new cobalt clusters with teaH₃ and hqn will be discussed.

First-Principles Calculation of Charge Carrier Mobility in graphene with adsorbed magnetic molecules using Complex Band Structure

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Using the Quantum Espresso suite, we compute charge carrier mobility in graphene from the complex band structure as a function of temperature due to phonon scattering and scattering from adsorbed magnetic molecules. Carriers with finite lifetimes due to scattering may be represented by generalized Bloch states with complex energies. Our method determines the constant complex potential that must be added to a perfect crystal to induce the scattering effects seen in a crystal with defects, which can be deduced from a series of complex band calculations. The mean scattering lifetime is computed from the imaginary part of this complex potential, and the carrier mobility is obtained from the scattering lifetime using the Boltzmann transport theory. Mobility is calculated for different magnetic molecule configurations to demonstrate that mobility measurements may be used to detect and distinguish different magnetic molecules. This work was supported as part of the Center for Molecular Magnetic Quantum Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award DE-SC0019330.

[1] Andrew Brooks, Tao Jiang, Shuanglong Liu, Duy Le, Talat S. Rahman, Hai-Ping Cheng, and Xiao-Guang Zhang, Phys. Rev. B 103, 245423 – Published 17 June 2021

Tight-binding Scattering Solution for Electron Mediated Entanglement

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

Unusual long-range ferromagnetic exchange interactions in a family of Ce/Mn/O clusters from comproportionation

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Ce/Mn mixed-metal oxides are employed for a wide range of important applications including the catalytic wet oxidation of organic and inorganic pollutants, as a room temperature diluted ferromagnet in spin-based devices, and as the dielectric material at the interface of semiconductor technologies. To study this class of materials, Ce/Mn-oxo chemistry has been extensively developed via a molecular bottom-up approach and a variety of clusters of different nuclearities have been reported. Among them, Ce_2Mn_3 and Ce_3Mn_5 [1], synthesized by 'reductive aggregation' of MnO_4^- with MeOH, exhibit unusual long-range ferromagnetic exchange interactions between Mn ions well separated by diamagnetic Ce^{IV} ions. These are, however, the only Ce/Mn-oxo clusters that have been identified to date as displaying this interesting property. We have therefore sought to expand this family and have employed a comproportionation procedure, as this offers enhanced control over the oxidation levels of the metal ions in the isolated product. In this presentation, we shall describe two new products with similar structures as the previously reported compounds but with different metal oxidation states. The detailed syntheses, crystal structures, and magnetic study of these clusters will be described, as well as the origin of the long-range ferromagnetic interactions.

[1] Das Gupta, S.; Stewart, R. L.; Chen, D.; Abboud, K. A.; Cheng, H.; Hill, S.; Christou, G. *Inorg. Chem.* **2020**, 59, 8716–8726.

Exploring Magnetic Properties of Organometallic Complexes with Carbenes

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In molecular magnetism, a major goal is to develop fine synthetic control over individual metal centers' magnetic properties. One method to achieve this is to explore ligand and bonding motifs in organometallic complexes to manipulate coupling between metal centers. Two metals that have been foundational in this respect have been iron and cobalt due to their natural abundance, extensive library of compounds with notable magnetic properties, and well-described reactivity. Carbenes, able to be tightly tuned to isolate advantageous electronic properties, are a useful ligand motif to this end. Considering this system, we seek to understand the effects of varying degrees of sigma donation and pi acceptance. With these factors in mind, we decided to explore the magnetic properties of iron and cobalt with cyclic(alkyl)(amino)carbenes (cAACs; see figure). cAACs provide strong sigma donation to stabilize low coordinate systems and good pi acceptance to stabilize electron rich metal centers; these factors allow for more possibilities for synthetic tuning to allow probing bridging motifs to maximize coupling between metal centers.

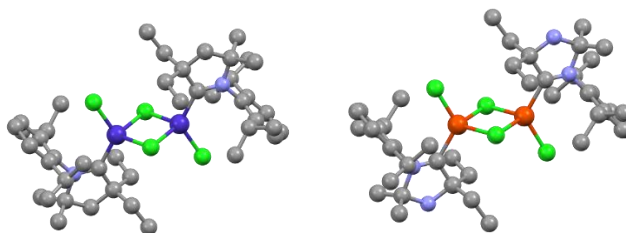


Figure. [Co(cAAC)Cl₂]₂(left) and [Fe(cAAC)Cl₂]₂(right).

Dzyaloshinskii-Moriya Interaction-Induced Magnetoelectric Coupling in a Tetrahedral Molecular Spin-Frustrated System [1]

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Using a combined first-principles calculation and a direct diagonalization of the quantum spin Hamiltonian, we investigate magnetoelectric coupling in the single-molecule magnet $\text{Mn}_4\text{Te}_4(\text{PEt}_3)_4$. The system shows tetrahedral spin frustration. Our studies based on density functional theory find that an electric dipole moment can emerge from various non-collinear spin configurations. The form of the spin-dependent dipole is determined to be consistent with that in non-centrosymmetric magnets driven by the Dzyaloshinskii-Moriya interaction. With the spin Hamiltonian parameterized by first-principles results, we obtain eigenvalues and eigenstates and compute the partition function. We then quantify the magnetoelectric (ME) coupling by calculating the response of thermal averages of the electric susceptibilities to the external magnetic field, and the response of magnetic susceptibilities to the external electric field. Quadratic relations are observed. Our analysis shows that with the sensitivity of current experimental techniques, ME couplings in this systems are detectable in experiments.

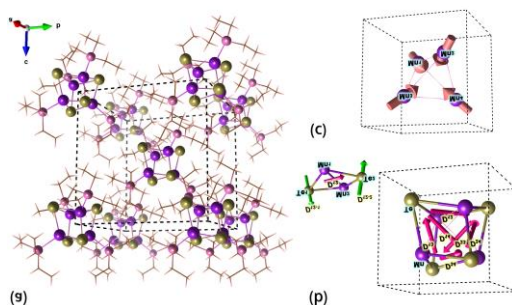


Figure. Figure 1. (a) The crystalline phase of $\text{Mn}_4\text{Te}_4(\text{PEt}_3)_4$. Purple: Mn, dark yellow: Te, pink: P. (b) The DM vectors and (c) the axis of magnetic anisotropy in $\text{Mn}_4\text{Te}_4(\text{PEt}_3)_4$.

[1] arXiv:2111.03793

Giant Magnetic Anisotropy in a Trigonal Ni(II) Complex

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The trigonal bipyramidal Ni(II) complex, Ni[(Me₆tren)Cl]PF₆, has a ground state spin of $S = 1$ with a giant first-order axial magnetic anisotropy. By studying the angle-dependence of the EPR spectra of a single crystal sample, we can gain unique insights into the stability of the orbitally degenerate ground state of this molecule. In particular, such studies may provide signatures of Jahn-Teller-type structural distortions, leading to a lowering of the trigonal symmetry and a reduction in the overall magnetic anisotropy [1,2]. In the false color image below, the EPR peak position associated with the transition within the isolated ground $m_S = \pm 1$ quasi-doublet is plotted as a function of polar and azimuthal angles over the surface of a sphere, revealing the highly axial nature of the magnetic anisotropy tensor; the red arrow depicts the orientation of the magnetic easy-axis and the red colored region denotes the hard-plane. We do not find any clear evidence for a breaking of the trigonal symmetry in spite of the fact that the overall anisotropy scale is reduced relative to expectations for the orbitally degenerate case. This suggests that measurements at higher magnetic fields may be needed. Finally, we note that the parallel mode EPR transition within the ground $m_S = \pm 1$ quasi-doublet displays a giant 69 GHz clock transition, which could be of interest for quantum information applications.

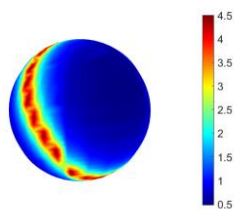


Figure. Magnetic field position of the ground state EPR transition as a function of field orientation.

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The use of pyrazole and its derivatives in Mn-oxo cluster chemistry

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The synthesis of novel polynuclear Mn clusters has been an active field of research in coordination chemistry over the past few decades due to their relevance to bioinorganic chemistry and molecular magnetism. Many synthetic procedures to high nuclearity Mn clusters have been developed by the community, with three particularly prominent approaches: comproportionation, reductive aggregation, and aerial oxidation. Chelating and/or bridging ligands such as carboxylates, oximates, and pyridyl alcohols are also commonly used in reaction systems to arrest the growth of the Mn-oxo core and yield polynuclear molecular clusters. Over the past several years, our group has been exploring the reactions of various chelating/bridging ligands with preformed Mn clusters with the hypothesis that the fragmentation and rearrangement of the starting materials will induce the aggregation of the Mn ions into new high nuclearity clusters. While bridging pyrazolate ligands have been primarily used in the synthesis of late transition metal complexes, their utilization in Mn-oxo cluster chemistry has been very limited in comparison. In this work, we will describe recent efforts in developing a family of high nuclearity Mn-oxo clusters from reactions using pyrazole and its derivatives. The synthetic methods, structural analyses, and magnetic studies of three new high nuclearity Mn-oxo clusters will be presented.

Coherent Sub-Terahertz Spin Pumping from an Insulating Antiferromagnet

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Emerging phenomena, such as the spin-Hall effect (SHE), spin pumping, and spin-transfer torque (STT), allow for interconversion between charge and spin currents and the generation of magnetization dynamics that could potentially lead to faster, denser, and more energy efficient, non-volatile memory and logic devices. Present STT-based devices rely on ferromagnetic (FM) materials as their active constituents. However, the flexibility offered by the intrinsic net magnetization and anisotropy for detecting and manipulating the magnetic state of ferromagnets also translates into limitations in terms of density (neighboring elements can couple through stray fields), speed (frequencies are limited to the GHz range), and frequency tunability (external magnetic fields needed). A new direction in the field of spintronics is to employ antiferromagnetic (AF) materials. In contrast to ferromagnets, where magnetic anisotropy dominates spin dynamics, in antiferromagnets spin dynamics are governed by the interatomic exchange interaction energies, which are orders of magnitude larger than the magnetic anisotropy energy, leading to the potential for ultrafast information processing and communication in the THz frequency range, with broadband frequency tunability without the need of external magnetic fields.

I will present the first evidence of sub-terahertz coherent spin pumping at the interface of a uniaxial insulating antiferromagnet MnF₂ and platinum thin films, measured by the ISHE voltage signal arising from spin-charge conversion in the platinum layer. The ISHE signal depends on the chirality of the dynamical modes of the antiferromagnet, which is selectively excited and modulated by the handedness of the circularly polarized sub-THz irradiation (see figure). Contrary to the case of ferromagnets, antiferromagnetic spin pumping exhibits a sign dependence on the chirality of dynamical modes, allowing for the unambiguous distinction between coherent spin pumping and the thermally-driven, chirality-independent spin Seebeck effect. Our results open the door to the controlled generation of coherent pure spin currents with antiferromagnets at unprecedented high frequencies.

This work has been primarily supported by the Air Force Office of Scientific Research under Grant FA9550-19-1-0307.

[1] Priyanka Vaidya, Sophie A. Morley, Johan van Tol, Yan Liu, Ran Cheng, Arne Brataas, David Lederman, and Enrique del Barco, "Subterahertz spin pumping from an insulating antiferromagnet" *Science* 368, 160-165 (2020) / Work highlighted in the Journal by a perspective article: Spin pumping gathers speed, by Axel Hoffman, *Science* 368, 135-136 (2020)

Magnetic Hysteresis in Dinuclear Lanthanide Single-Molecule Magnets

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Lanthanides are qualified candidates for the design of single-molecule magnets owing to their large magnetic moments and high magnetic anisotropy that stem from strong spin-orbit coupling of the 4f orbitals. By employing lanthanide ions such as Tb(III) and Dy(III) which possess intrinsically large orbital angular momentum, substantially higher spin-reversal barriers and blocking temperatures can be attained. One effective methodology to increase blocking temperatures of multinuclear compounds is to generate strong magnetic exchange between lanthanide centers using radical bridging ligands. In the event of large magnetic exchange coupling, undesirable relaxation pathways such as quantum tunneling of the magnetization can be suppressed. Here, the generation of new radical ligands and their use in the synthesis of radical-containing single-molecule magnets will be discussed. A second 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 present the first lanthanide bismuth cluster single-molecule magnets, Figure 1 [1].

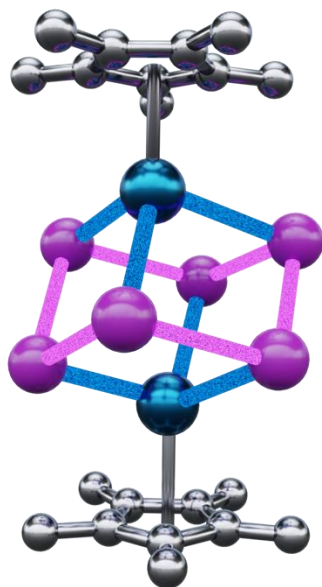


Figure 1. Structure of the $[\text{Cp}^*_2\text{Ln}_2\text{Bi}_6]^{2-}$ dianion in a crystal of $[\text{K}(\text{THF})_4]_2[\text{Cp}^*_2\text{Ln}_2\text{Bi}_6]$.

Blue, purple, and gray spheres represent Ln, Bi, and C atoms, respectively.

[1] Peng Zhang, Florian Benner, Nicholas F. Chilton, Selvan Demir, *Chem*, **2022**, 8, 717-730.

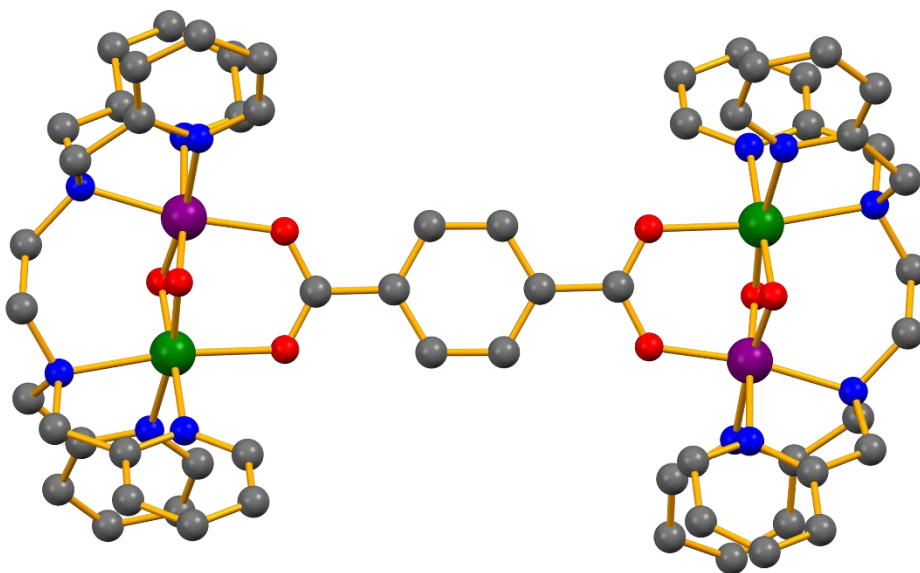
Covalently-linked Dinuclear Manganese-oxo Complexes

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Supramolecular chemistry has been used to link magnetic molecules together in the interest of creating arrays of molecular qubits. An advantage of using supramolecular chemistry is that it provides tunability between magnetic centers, thus providing a pathway to control the magnetic interactions between molecules. In the past decade, our group has exploited the use of supramolecular principles to covalently link systems of single-molecule magnets (SMMs) to create solution stable oligomers of molecular nanomagnets. Other research has demonstrated that the use of supramolecular frameworks of covalently-linked heterometallic rings acting as two-level systems could be potentially used as arrays of programmable qubits when controllable linkages are implemented. Recently, a new direction of supramolecular chemistry has been developed in our group to covalently link magnetically distinct units that function as two-level systems, applying the same techniques developed in linking SMMs, to achieve our own controllable system of molecular qubit arrays in the future. Our strategy uses simple mixed-valence dinuclear manganese-oxo complexes as our two-level system, with covalent linkage achieved through a single-substitution site. We have found through electrochemical and magnetic studies that by varying the organic linker between our new metal center, the two-level state of each respective manganese-oxo complex within the linked system is retained, and the strength of the interaction between them is altered.



Well-Defined Heterometallic Framework Architectures of Molecular Qubits

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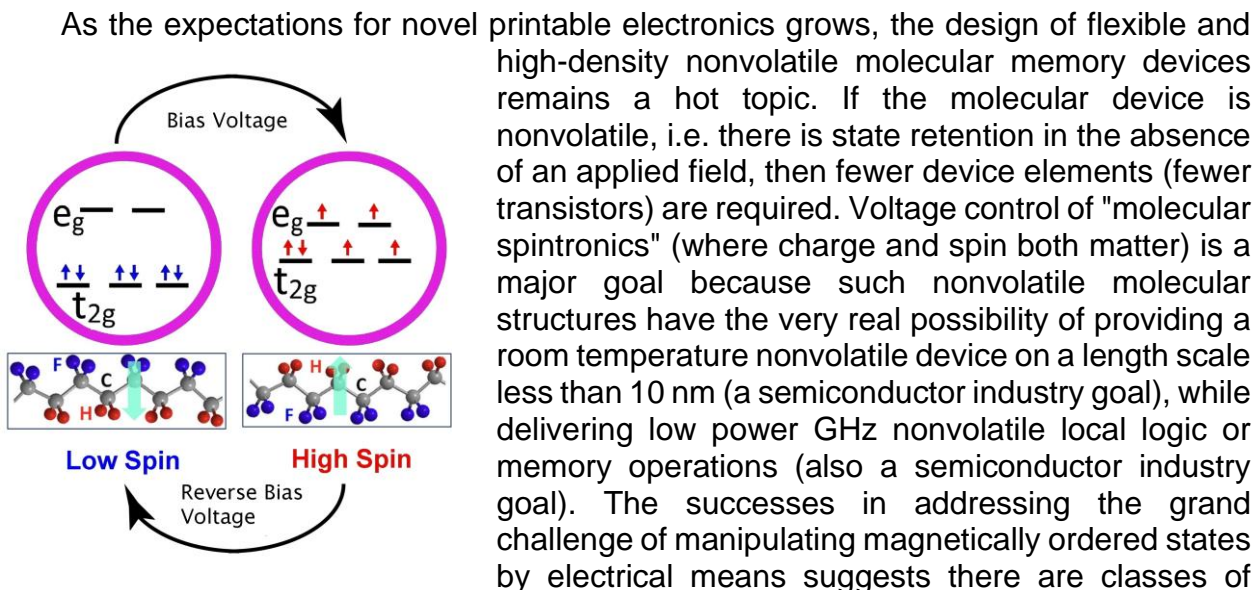
In the rapidly growing area of quantum information science, chemical synthesis and framework chemistry are powerful approaches to enable the bottom-up creation of novel modular quantum materials. The atomic-scale precision and tunability of quantum molecular building blocks coupled to bottom-up assembly and scale-up offered by crystalline hybrid materials, such as metal-organic frameworks (MOFs), is promising pathway to achieve large scale organized assemblies of qubit centers. The MOF chemistry not only allows one to achieve an atomically precise arrangement of identical qubits into scalable networks but also provides the additional benefits of reproducible qubit fabrication and tunability of qubits by chemical design.

In this work, we utilized the framework chemistry to incorporate selected molecular building blocks, which are characterized by long coherence times, inside a MOF matrix. We have demonstrated that the developed approach for incorporation of qubit centers inside porous scaffolds results in maintaining of their coherence times. Moreover, we demonstrated that the modulation of MOF coherence times can be achieved as function of qubit center nature, metal node modification, and/or density of incorporated qubits. Thus, the developed strategy opens a novel approach for development of framework architectures for quantum information.

Is there a route to a competitive molecular multiferroic electronic device?

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molecules suitable for novel spintronics.

While much in its infancy, molecular spintronics has now been shown to be possible. The spin crossover (SCO) phenomenon, in 3d transition metal compounds, through the manipulation of interfacial chemistry, can be exploited to create voltage-controlled isothermal changes in the electronic structure. This has been shown for the Fe (II) spin crossover complexes interfaced with molecular ferroelectrics. This nonvolatile isothermal voltage controlled switching, at room temperature, is evident in both spectroscopy and transport studies of thin film bilayer devices [1,2]. This comes at a lower energy cost and at faster speeds and far less fabrication complexity than the currently commercially available nonvolatile memory (from Everspin, Toshiba and others) based on magnetic tunnel junctions. If the molecular system(s) can be made into an ink, then printable electronics is a very real possibility. Even better, the fact that molecular device fabrication is possible at room temperature from solution, means that 3 dimensional memory arrays are possible - if the power dissipation is small.

But there are challenges still to be addressed. Just the same, in just the past 2 years, the key problem of the high device impedance has now been addressed though chemistry. The key take away point is that molecular nonvolatile room temperature "memory" devices have been realized and new developments in chemistry should lead to better molecular nonvolatile electronic devices.

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Dynamical effects and critical field of spin crossover complexes

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Spin crossover molecules exhibit a spin state transition from low spin state to a high spin state under external stimulus. This spin state change can be observed by magnetometry and spectroscopy. By measuring the magnetic moments with respect to temperature, there are indications the finite temperature effects even without a spin state transition. Most of the magnetic moment measurements show a decrease in the total magnetic moment at temperatures beyond the spin transition temperatures which suggest that there are other finite temperature effects beyond the change in spin state. We performed a temperature dependent X-ray Magnetic Circular Dichroism (XMCD) studies on two different spin crossover molecules, [Co(SQ)₂(4-CN-py)₂] complex [1] and [Fe{H₂B(pz)₂}₂(bipy)] complex to study the behavior of the spin and orbital moments separately in the high spin state of these very different spin crossover molecules. The field dependent XMCD study for the Co spin crossover complex and [Fe{H₂B(pz)₂}₂(bipy)] both indicate that a critical field is required for the orbital moments become evident. Furthermore, thin films of [Fe{H₂B(pz)₂}₂(bipy)] show some evidence of magnetic anisotropy. The conclusion is that there is an anisotropy barrier for the magnetic moments. This has important implications. Either the molecules adsorb on surfaces with a preferential orientation or cooperative effects play a significant role in the magnetic anisotropy of otherwise paramagnetic molecular thin films. The magnetic anisotropy likely can be exploited to improve device functionality in spintronic devices made from like molecules.

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Simulating computationally complex magnetic molecules with Heisenberg-like Hamiltonians

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I will discuss work that I have done in modeling magnetic molecules using computational methods that include both quantum Monte Carlo (QMC) methods and matrix diagonalization methods. These methods – and their strengths and limitations – are discussed in Ref. 1. QMC methods allow the simulation of quantum systems with very large numbers of energy levels, such as the $\{\text{Ni}_{21}\text{Gd}_{20}\}$ cage shown in the figure, which was introduced in Ref. 2. I am also interested in the development of user-friendly software for simulating quantum systems, such as the FIT-MART software introduced in Ref. 3.

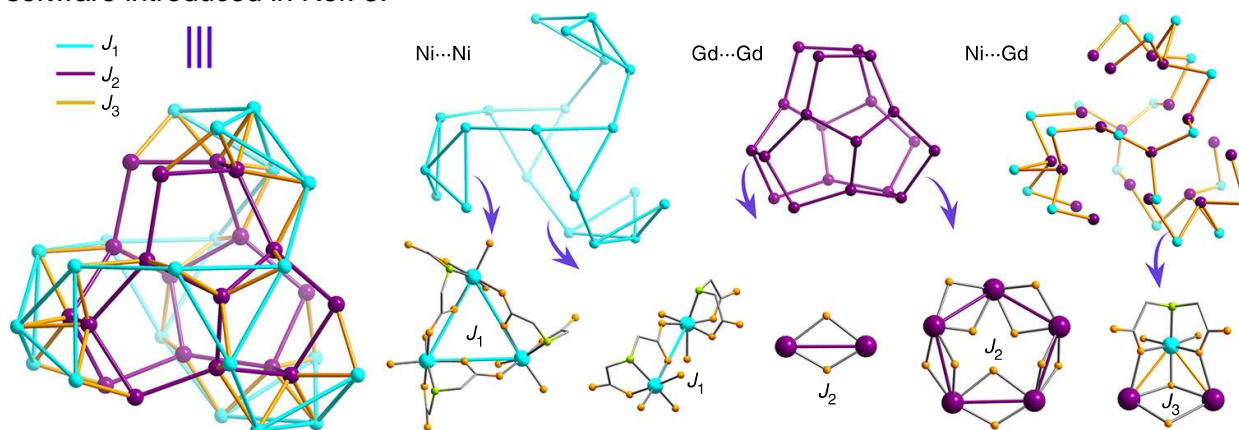


Figure. Structure, and magnetic coupling of the $\{\text{Ni}_{21}\text{Gd}_{20}\}$ cage from Ref. 2. Non-magnetic ligands have been removed for clarity.

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Competing Exchange Interactions and Multiferroic Behavior of a Molecule-Based Magnet

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Multiferroic behavior sensitively depends on the microscopic interactions between spins. The molecule-based magnet $(\text{NH}_4)_2\text{FeCl}_5(\text{H}_2\text{O})$ exhibits a complex magnetic-field or pressure versus temperature phase diagram with three multiferroic phases observed by magnetization [1], neutron diffraction [2-3], and Raman spectroscopy [4] measurements. Both FE I and FE II phases contain spin cycloids with electric polarization \mathbf{P} along the a axis produced by the inverse Dzyaloshinskii-Moriya interaction. Above the spin-reorientation transition at roughly 4 T, the spins form a canted antiferromagnetic state and \mathbf{P} rotates to the c axis. The electric polarization in the FE III phase is believed to be caused by p - d orbital hybridization.

We evaluate the magnetic interactions in the low-field FE I by comparing inelastic neutron scattering spectra of a single crystal with a simple Heisenberg model containing five exchange interactions mediated by intermolecular hydrogen and halogen bonds. Two competing exchange interactions in every bc plane produce a cycloid with spins in the ac plane, helicity $\mathbf{S}_i \times \mathbf{S}_j$ along the b axis, and ordering wavevector $\mathbf{Q} = (0,0,0.23)$ *r.l.u.* along c . We obtain excellent agreement between theory and the inelastic neutron-scattering spectra.

After including higher-order onsite anisotropic spin interactions to produce the large high-order anharmonic components observed in the FE I phase from neutron diffraction experiments, we predict [6] the transition from the incommensurate FE I state to an intermediate FE II state with commensurate wavevector $\mathbf{Q} = (0,0,0.25)$ *r.l.u.*. By emphasizing the importance of the higher-order spin anisotropic interactions, our work provides a general framework to understand multiferroic materials with rich phase diagrams.

*Supported by the Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering.

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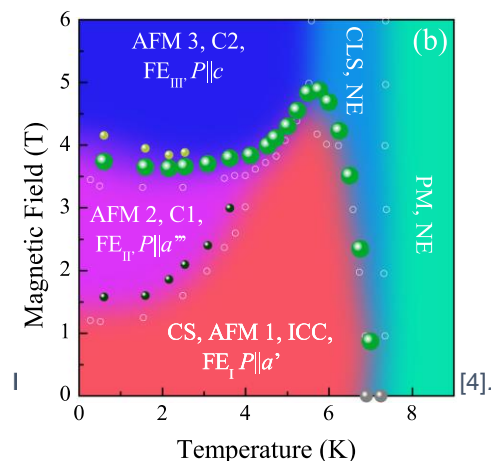
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High BxT: Tunable In-field Synthesis and Characterization Above Room Temperature

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Figure 1. The High BxT system at UF Physics.

The High BxT Station at the University of Florida Physics Department is a newly developed instrument that combines a resistive-heater with a variable-field, 400 MHz NMR (9.4 T max), 89 mm bore superconducting magnet to enable cutting-edge in-field experiments above room-temperature. The cryogen-immersed magnet is protected from stray heat by our custom designed and manufactured cooling jacket insert which holds the vertically-oriented furnace plus extra insulation (**Fig. 1**). The High BxT system will be used to probe the effects of applying a high B or B ∇ B field on the properties and phase identity of samples at high temperatures, as well as the largely unexplored opportunities for materials design and discovery that they offer. This poster details the design, applications, and planned future development of this system. As an example, we present results from the flux growth of ferromagnetic Co from a molten-flux [1]. The high Curie temperature of Co (1115 °C) [2] means that single crystal may be grown out of a molten flux directly in the ferromagnetic state, where the effect of an applied field will be maximized. Samples grown this way show a clear morphological dependence on the presence of an applied field. Ongoing work aims to determine the effect of these differences on properties and to develop a magnetometry insert.

This work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Advanced Manufacturing Office award number DE-EE000913. The views expressed herein do not necessarily represent the views of the U.S. Department of Energy or the United States Government. The MagLab facility supported by NSF DMR-1644779 and the State of Florida, and CLB and MWM participation in this meeting is also supported by NSF DMR-1708410.

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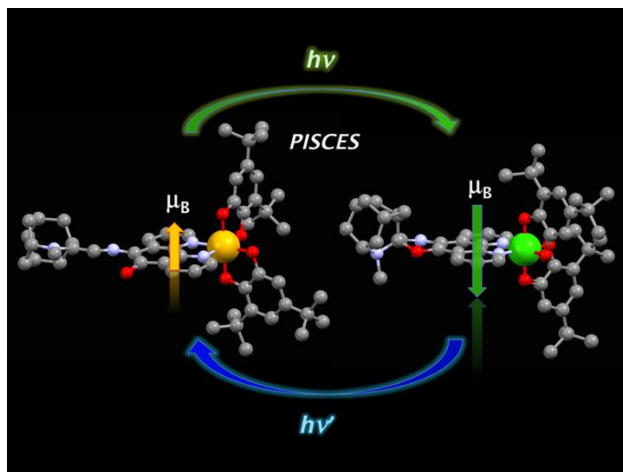
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The Role of Charge Transfer in Spin-State Gating in Transition Metal and Organic Spin systems

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Abstract: Controllable quantum systems are under active investigation for quantum computing, secure information processing, and nonvolatile memory. (i) The role of coordination complexes as spin-based qubits is explored. The optical manipulation of spin quantum states provides an important strategy for quantum control with both temporal and spatial resolution. Here we demonstrate reversible light-induced magnetization switching in an organic thin film at device operating temperatures of 300–330 K. By utilizing photochromic ligands that undergo structural changes in the solid state, the changes in ligand field associated with photoisomerization modulate the ligand field and in turn the oxidation and spin state of a bound metal center. Green light irradiation ($\lambda_{\text{exc}} = 550$ nm) of a spirooxazine cobalt–dioxolene complex induces photoisomerization of the ligand that in turn triggers a reversible intramolecular charge-transfer coupled spin-transition process at the cobalt center. The high transition temperature (325 K) and long-lived photoinduced state ($\tau = 10$ s at 300 K) are dictated by the photochromic ligand. Theory and ultrafast spectroscopy provides effective modeling of the phenomenon and long-term strategies to further modulate the lifetimes of magnetic states in these systems for quantum information technologies at the single molecule level. (ii) The role of hydrogen bonding and slipped stack π – π interactions in the magnetic and electrical behaviour of amino functionalized benzotriazinyl radicals as spin $\frac{1}{2}$ systems is explored. The magnitude and sign of π – π interactions are modulated as a function of protonation state, in which significant “long-bonds” are observed between the radical cation form leading to strong AFM exchange. The deprotonated state on the other hands presents ferromagnetic and semiconductor behaviour. The electronic structure factors controlling both magnetic and electrical behaviour in these systems are discussed.



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Asymmetric Ligand Design for Volatile and Exfoliable Spin-Crossover Complexes

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Spin crossover (SCO) in transition metal complexes leads to large changes in the magnetic, structural, and optical properties of the material, due to drastic difference in the characteristics of the low-spin and high-spin electronic configurations. These large changes render SCO materials appealing targets for applications in sensors, nanothermometers, memory devices, etc. Minutuarization of electronic devices has caused an increased interest in the preparation of thin or ultrathin structures based on SCO complexes. The central challenges in these studies are the ability to deposit the SCO complex by vapor sublimation, spin coating, or exfoliation, and the preservation of the SCO behavior in the ultrathin structure. 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 uses bulky tertbutyl (tBu) groups on the other side, to increase the volatility. We show that an Fe(II) complex, Fe[(tBu)₂qsal]₂, exhibits crystal packing in which layers of neutral SCO molecules are separated by van der Waals interactions between the tBu groups. As a result, the complex easily sublimates at 300 °C and 10⁻⁴ mbar. Furthermore, the weak interlayer forces make it possible to exfoliate this material mechanically to a single molecular layer. We demonstrate that the abrupt hysteretic SCO observed in the bulk crystal is also preserved in the thin films and ultrathin flakes. The differences in the behavior of the bulk sample and thin-film structures will be also discussed.

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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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Applications of Advanced Electron Paramagnetic Resonance Techniques to Lanthanide and Actinide-Based Coordination Complexes

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Electron Paramagnetic Resonance (EPR) methods have been used extensively to unravel the origin of physical properties in transition metal coordination complexes. Despite this success few studies have applied EPR techniques to actinide-containing compounds. At the same time our understanding of bonding and the relationship between physical and electronic/magnetic properties in actinides remains anemic compared to the rest of the periodic table. Here, we present on our efforts using continuous wave- and pulse- EPR methods to probe the magnetic properties of lanthanide and actinide-based coordination complexes. We will discuss some of our experimental results, capability development, and computational efforts to understand the magnetic properties of f-element coordination compounds.

Continuous-Wave High-Field Powder EPR Investigation of the Spin-Crossover Transition in a Mn^{3+} Complex

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Spin Crossover (SCO) occurs in octahedrally coordinated $3d^4$ to $3d^7$ transition metal complexes when perturbed with an electric field, magnetic field, pressure, optical irradiation, or a change in temperature. In this investigation, a Mn^{3+} complex, which undergoes a complete transition from a high (HS) $S = 2$ state to a low spin (LS) $S = 1$ state below a sharp transition ($T_{1/2} = 51$ K; with < 10 K hysteresis), was studied using continuous-wave high-field powder Electron Paramagnetic Resonance (EPR) Spectroscopy. For d-block transition metals, zero-field splitting (ZFS) is dominated by spin-orbit coupling, which admixes crystal field states. This gives rise to magnetic anisotropy and can be characterized via the g -tensor and the ZFS (D and E) parameters employed in the effective spin Hamiltonian. In some SCO complexes an inhomogeneous mixture of different phases from incomplete transitions may be observed, making it much more difficult to experimentally characterize the magnetic anisotropy in each phase. Thus, with the advantage of studying a complex exhibiting a complete SCO transition around temperatures amenable to study using EPR, the ZFS parameters were obtained for both the LS ($D = + 21.23 \text{ cm}^{-1}$, $E = + 2.275 \text{ cm}^{-1}$) and HS states ($D = + 5.66 \text{ cm}^{-1}$, $E = + 1.31 \text{ cm}^{-1}$)

Connecting Molecular Electronic Structure and Electron Spin Relaxation for Quantum Information Science

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Quantum devices based on molecules afford unique potential in miniaturization, spatial localization, and tunability through the methods of synthetic chemistry. Unpaired electrons constitute a platform for implementing a quantum bit (qubit), the smallest unit of quantum information processing. However, spin relaxation destroys the quantum coherences needed to process information and constitutes a significant barrier to attaining room temperature quantum devices. While spin relaxation times have been rationalized using the Debye model, key assumptions are incompatible with the structure of molecular materials, and the model fails to yield meaningful predictions for slowly-relaxing, highly coherent molecules. This talk will describe our ligand field electron spin dynamics research, including a pedagogical component within physical inorganic chemistry, which has provided a molecular paradigm to quantitatively evaluate and understand temperature-dependent electron spin relaxation. These analyses elucidate the specific vibrational modes driving decoherence in the T_1 -limited regime and the critical spin-phonon coupling, chemical bonding, and symmetry factors leading to room temperature coherence.

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

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

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

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Structure-Property Studies of Paramagnetic Niobium Carbenes and Amides.

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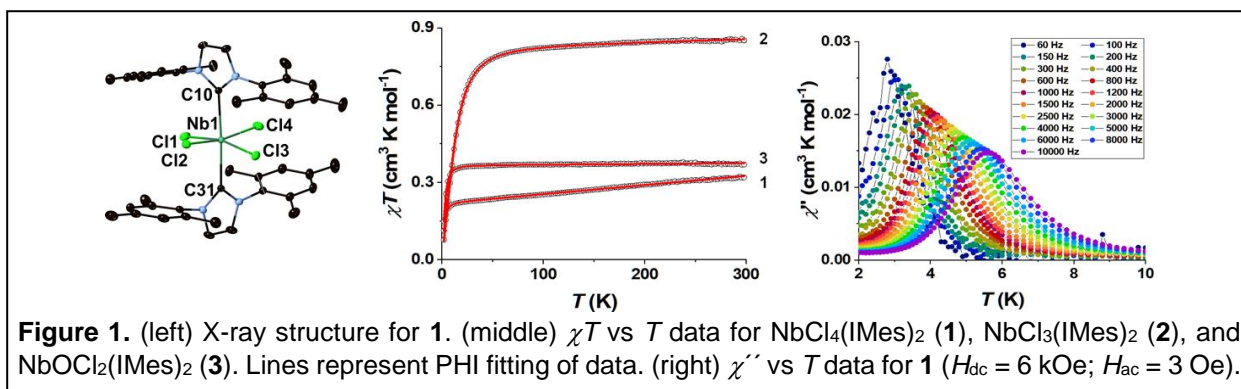
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Transition metal *N*-heterocyclic carbene complexes find extensive use in catalysis, medicinal, materials, and surface science applications. While numerous paramagnetic 3*d* complexes are known comparatively fewer 4*d* and 5*d* analogues have been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

Another approach exploits control of spin-lattice relaxation by minimizing thermally populated excited state spin levels particularly in the absence of ligand-centered nuclear spins. Among these are several V^{IV} ($S = \frac{1}{2}$) complexes where long relaxation times are often observed offering the prospect of a tunable spin-qubit platform for molecule-based information storage applications. A survey of the chemical literature indicates that niobium(III,IV) complexes are underexplored in comparison to their 3*d* congeners, with most reports being limited to cyanide, pyridyl, phosphine, and phosphine oxide derivatives. Among these are $Nb^{IV}X_4(py)_2$ ($X = Cl, Br, I$) complexes whose magnetism deviates from spin-only behavior [e.g., $\mu_{eff}(\mu_B) = 1.37$, Cl; 1.26, Br; 1.05, I] where small *g* parameters ($g \leq 1.58$) are also found, suggesting halide bonding and orbital contributions may be important. In this presentation, we will describe recent efforts to develop a modular approach using *N*-heterocyclic carbene (Figure 1) and amido ancillary ligands for the deliberate preparation of complexes, whose magnetic properties are tuned via ligand steric demand and donor strengths.



Emergent Quantum Critical Phenomena in a Low-dimensional Molecular Antiferromagnet $\text{C}_9\text{H}_{18}\text{N}_2\text{CuBr}_4$

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Quantum magnets have proved to be fertile ground for studying new types of quantum many-body states. Of particular interest are critical quantum phenomena near quantum phase transition that occurs at zero temperature between distinct ground states by tuning a nonthermal control parameter. In this talk, I will first introduce neutron scattering technique as a powerful tool to probe exotic quantum phenomena in quantum spin systems. After that, I will present neutron scattering studies on a novel low-dimensional spin-1/2 coupled ladder molecular antiferromagnet (dimethylammonium)(3,5-dimethylpyridinium) CuBr_4 ($\text{C}_9\text{H}_{18}\text{N}_2\text{CuBr}_4$), abbreviated as DLCB. I will show that DLCB is close to a quantum critical point in two dimensions at zero field and ambient pressure [1]. Moreover, in conjunction with theoretical calculations, our results show the exotic quantum effects in spin dynamics include evidence of the field-induced spontaneous ($T=0$ K) magnon decay in an applied transverse magnetic field [2] and observation of Higgs-like amplitude mode [3], which is characterized by amplitude fluctuations of the order parameter and roughly analogous to Higgs boson in particle physics. Our work provides much-needed experimental insights to the understanding of these intriguing quantum many-body effects in low-dimensional antiferromagnets.

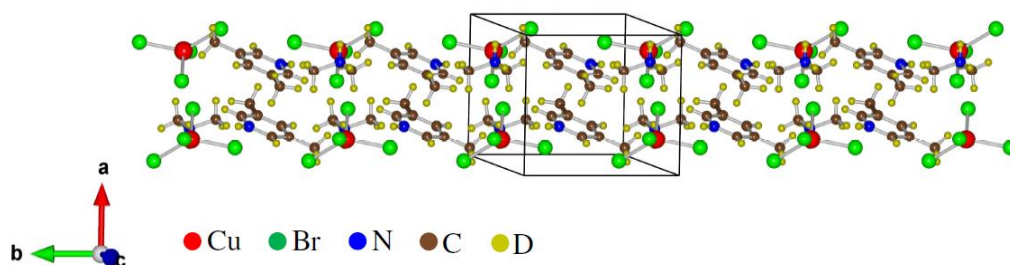


Figure: Crystal structure of $\text{C}_9\text{H}_{18}\text{N}_2\text{CuBr}_4$ projected along the crystallographic c -axis to show the stacking of discrete DMA⁺($\text{C}_2\text{H}_8\text{N}$) and 35DMP⁺ ($\text{C}_7\text{H}_{10}\text{N}$) cations. Outlined is a nuclear unit cell. Nearest-neighbor and next-nearest-neighbor contacts between bromide ions suggest that CuBr_4^{2-} anions form two-leg ladders along the crystallographic b -axis.

- [1] Hong *et al.*, Phys. Rev. B **89**, 174432 (2014).
- [2] Hong *et al.*, Nat. Commun. **8**, 15148 (2017).
- [3] Hong *et al.*, Nat. Phys. **13**, 638 (2017).

Structural Diversity of Lanthanide *n*-nitrotrispyrazolylborates and their Potential as Luminescent Single-Molecule Magnets

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The lanthanides (Ln), owing to their desirable, intrinsic opto-electronic and magnetic properties, have found applications in a wide variety of modern technologies, such as bioimaging agents and magnetic devices. These properties include their long radiative lifetimes, narrow emission bands ranging from UV-visible to the near-IR, unquenched orbital angular momentum and large spin-orbit coupling, all of which are a direct result of their shielded *f*-electrons and chemical environment. The judicious pairing of organic ligands with lanthanides allow for intimate control of their chemical environment and tunability of the optical and magnetic properties of the resultant Ln-materials. Lanthanide trispyrazolylborates (Tp⁻), are of particular interest, as LnTp_x systems display sensitized luminescence, single-molecule magnet properties and have been developed into a model system for studying the electronic structure of *f*-block elements. A relatively understudied aspect of this class of materials are lanthanide pyrazolylborates functionalized with strongly electron-donating or withdrawing groups and the introduction of which presents the opportunity to tune the chemical environments and subsequent properties of the resultant complexes. This work details the synthesis, crystal structures and photophysical properties of a new class of lanthanide materials, with asymmetric, functionalized Tp⁻ ligands, *n*-nitrotrispyrazolylborates (n-NO₂Tp⁻) where *n* = 3 or 4, featuring the lanthanides in a variety of chemical environments. Lanthanide 3-nitrotrispyrazolylborates (3-NO₂Tp⁻) can generate up to 5 different structural types, ranging from monomers to dimers or tetramers, which all feature an additional binding site in the oxygen of the NO₂-group, whereas the 4-nitrotrispyrazolylborates (4-NO₂Tp⁻) are nine-coordinate D_{3h} complexes, similar to the non-functionalized LnTp₃ complexes. Optical measurements, in tandem with computational analysis, indicate that sensitization of Ln³⁺ luminescence *via* nitrotrispyrazolylborates involves multiple intra-ligand charge transfer (ICT) transitions and that only 3-NO₂Tp⁻ is good sensitizer for most lanthanides. The variable nuclearity and chemical environments afforded by the reported compounds allow us to study how substituent effects influence both the luminescence and magnetic properties of Ln-materials and may be a useful platform to probe magneto-luminescent properties. By establishing trends in these materials, this work will inform the rational design of Ln-based luminescent single-molecule magnets.

Probing the Spin Transition of Molecular Magnets in a Vertical Tunnel Junction

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In this work, the spin transition in manganese phthalocyanine (MnPc) thin films was studied by the differential conductance measurements in a vertical tunnel junction. We fabricated a heterostructure Eutectic GaIn/H₂Pc (1nm)/MnPc (1nm)/NiCo₂O₄ (001)/MgAl₂O₄ (001) where the eutectic GaIn (EGaIn) works as a soft-landing non-magnetic top electrode, the NiCo₂O₄ works as a ferrimagnetic bottom electrode and the 1nm H₂Pc works as a protective layer. The conductance transition and its magnetic field dependence (inset) through the junction is established in the figure. The bias voltage (ΔV) where the conductance transition happens indicates the energy gap between the ground state and the excited state due to the superexchange coupling in MnPc multilayers. This energy gap is qualitatively like those seen in STM measurements on CoPc molecules [1]. These preliminary data suggest a spin transition associated inelastic electron tunneling spectroscopy which measures (to our knowledge for the first time) quantum states in molecular magnets without using bulky STM probes as electrodes.

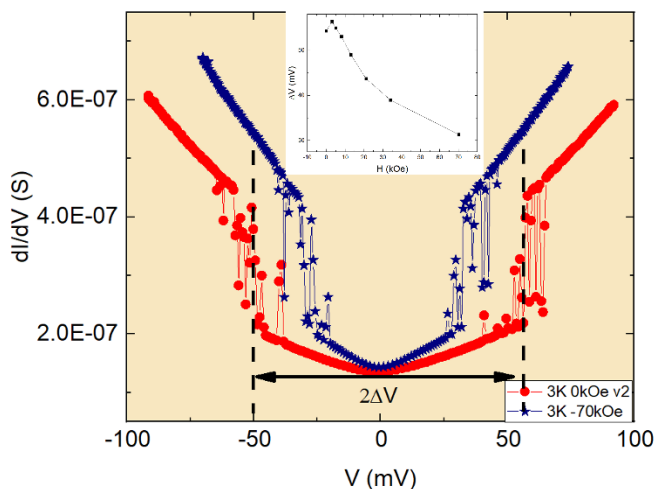


Figure. Conductance transition and its magnetic field dependence (inset) through the Eutectic GaIn/H₂Pc (1nm)/MnPc (1nm)/NiCo₂O₄ (001)/MgAl₂O₄ (001) heterostructure.

Synthesis of Mn–oxo clusters as ‘molecular nanoparticles’ of important manganese oxides

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The capability of Mn-oxo clusters to be the source of so many types of magnetic molecules, from single-molecule magnets to giant Mn_{70} and Mn_{84} torus-shaped clusters of ~4 nm dimensions, has stimulated us to develop new synthetic routes to so-called ‘molecular nanoparticles’ (MNPs) of important Mn oxides. MNPs are clusters that possess the same structure as a bulk metal oxide, and can thus be considered ultra-small nanoparticles of that material in molecular form. Using the ‘reductive aggregation’ developed by our group in which a high oxidation state MnO_4^- source is reduced by MeOH in the presence of excess carboxylic acid, leading to aggregation to a Mn-oxo cluster, we previously reported a family of Mn_{12} and Mn_{16} products with various topologies and interesting structural and magnetic properties. Until recently, reductive aggregation had not been explored in heterometallic chemistry, but our group recently had success in synthesizing a family of Mn_5Ce_3 clusters using this method. In the present work, we have extended this work to Mn/Ba and Mn/Bi heterometallic chemistry and have synthesized various Mn-oxo clusters which are molecular nanoparticles of different Mn-oxides that are widely used for catalytic, industrial, and medical applications. The current status of this work will be described.

Massive 9 GHz Hyperfine Clock Transition in a Molecular Spin Qubit

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Electron spins in molecules have been proposed as potential qubits in quantum computers, enabling chemical tunability of their quantum nature and potential for scaleup via self-assembly. We demonstrate chemical control on the degree of s-orbital mixing into the spin-bearing d-orbital associated with a series of spin-half ($S = 1/2$) La(II) and Lu(II) molecules. Increased s-orbital character reduces spin-orbit coupling and enhances the electron-nuclear Fermi contact interaction. In one particular Lu(II) complex, we have observed an enormous hyperfine interaction (^{175}Lu , $I = 7/2$) for a molecular system, $A_{\text{iso}} = 3467$ MHz (more than 1200 G), which, in turn, generates a 9 GHz clock transition.¹ The large magnitude of this hyperfine interaction necessitated high-field W-band EPR to fully characterize the electron-nuclear spin Hamiltonian parameters. Meanwhile, pulsed X-band EPR studies reveal an order of magnitude increase in phase memory time, T_m , at the clock transition. These findings suggest new strategies for the development of molecular quantum technologies, akin to trapped ion systems.

[1] K. Kundu, J. R. K. White, S. A. Moehring, J. M. Yu, J. W. Ziller, F. Furche, W. Evans, S. Hill. *Nature Chemistry*, **2022**, <https://doi.org/10.1038/s41557-022-00894-4>

Two Views of Terbium: in Tetravalent Lanthanide Complexes and in a Trivalent Exchange-Coupled, Triangular SMM

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In this talk, I will present my groups recent synthetic, spectroscopic (electronic absorption, EPR, XAS), and magnetic studies of tetravalent lanthanide (praseodymium and terbium) complexes and discuss periodic changes in bonding and single-ion properties as a function of oxidation state. I will also present our studies of isomeric hetero-tetrametallic, exchange coupled clusters in which varying the symmetry of the central trivalent lanthanide ion tunes the relaxation dynamics. Lastly, I will demonstrate some Matlab based rapid processing and analysis software for thermomagnetic data from PPMS and MPMS platforms developed in my group.

Development of a Magnetostructural Correlation for Polynuclear Mn^{III}/oxo Clusters

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Since Mn^{III}/oxo clusters continue to play an important role in molecular magnetism research, the accurate determination of the pairwise Mn₂ exchange interactions (J_{ij}) within these clusters remains a crucial objective. Traditional experimental and computational methods, such as fits of experimental data by matrix diagonalization or density functional theory (DFT) approaches, frequently fall short of providing reliable J_{ij} values for high nuclearity clusters, especially ones with low symmetry. Similar problems in Fe^{III}/oxo clusters previously led our group to develop a magnetostructural correlation (MSC) specifically for polynuclear Fe^{III}/oxo clusters, to serve as an independent means to estimate the exchange interactions. We have since used Fe^{III}/oxo MSC with satisfying success to rationalize the magnetic properties of clusters of various nuclearities and also to provide reliable input values for fitting of experimental magnetic data to minimize overparameterization problems and false fits.^[1]

In contrast, the available MSC models for Mn^{III}/oxo clusters have been limited to dinuclear complexes or clusters of a specific higher nuclearity.^[2] Therefore, we initiated a search for a new and general MSC for polynuclear Mn^{III}/oxo clusters, using the angular overlap model we used for the Fe^{III}/oxo MSC but also realizing that the effect of the Mn^{III} Jahn-Teller distortion also had to be incorporated. In this presentation will be described **(i)** the development of a semiempirical MSC that estimates the pairwise Mn₂ J_{ij} values using the Mn-O-Mn bond lengths and bond angle; and **(ii)** the use of this MSC to rationalize ground state spin (S) values of various clusters, analyze the presence of any spin frustration effects, and provide reliable input values for fits of experimental magnetic data.

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[2] Zhang, Y.; Luo, C. Theoretical Study of Magnetostructural Correlations in a Family of Triangular Manganese(III) Complexes. *Dalton Trans.* **2009**, 5627-5636.

First Principle Resonant Raman Intensity Calculations of Single-Molecule Magnet Dimers ($[\text{Mn}_3]_2$)

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Resonant Raman scattering happens when the laser energy is close to or coincident with an electronic transition of the irradiated sample. Only the vibrational modes involving nuclear motions corresponding to the atomic displacement during the electronic transition are enhanced. Therefore, resonant Raman spectra of the same molecule at different spin quantum state have different enhancement, which makes it possible to identify spin quantum state of single-molecule magnets (SMMs) by resonant Raman spectra. By using Density Functional Theory, we calculate optimized structures of AFM and FM Single-Molecule Magnet Dimers ($[\text{Mn}_3]_2$) in electronic ground state and excited states. We apply first principle resonant Raman scattering theory [1] and calculate resonant Raman spectra of $[\text{Mn}_3]_2$ in different spin quantum states. We compare the calculated resonant Raman spectra to the nonresonant Raman spectra also calculated from first-principles.

[1] Yue Yu, Jun Jiang, Liangbo Liang, Georgios D. Barmparis, Sokrates T. Pantelides, and X.-G. Zhang, submitted.

Density functional theory calculations of single-molecule magnets $\text{Co}_3(\text{SALPN})_2(\text{O}_2\text{CCH}_3)_2\cdot\text{R}_2$

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In search of candidate magnetic molecular systems that emulate Majorana zero modes, we perform density functional theory (DFT) calculations for Co trimers $\text{Co}_3(\text{SALPN})_2(\text{O}_2\text{CCH}_3)_2\cdot\text{R}_2$, where R is an OCH_2 , OCHNH_2 , or $\text{OCHN}(\text{CH}_3)_2$ solvent molecule. The three Co atoms form a one-dimensional chain, and each Co atom exhibits axial spin with $S=3/2$. We extract the exchange coupling constant and the local axial and rhombic zero-field splitting (ZFS) parameters based on DFT total energies. According to our calculations, the ratio between the exchange coupling constant and the local axial ZFS parameter is 7.3 for the end Co atoms and 5.7 for the center Co atom; the local magnetic easy axis of the center Co atom differs from that of an end Co atom by 42.9 degrees. These results provide a starting point for mapping the spin-3/2 Hamiltonian to an effective spin-1/2 Hamiltonian, which indicates the existence of Majorana zero modes. We will also analyze the d-orbital occupation matrix and discuss the necessity to control it for obtaining reliable results.

This work was supported as part of the Center for Molecular Magnetic Quantum Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award No. DE-SC0019330. Computations were done using the utilities of National Energy Research Scientific Computing Center, and University of Florida Research Computing systems.

[1] Hoffman *et al.*, arXiv:2110.12019 (2021).

High-Field EPR Investigation of a Potential Molecular Two-Qubit Gate Based on a Cobalt Dimer

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Quantum information processing (QIP) is critical to overcoming classical computational limitations such as factoring, quantum modelling and secure communication. Key to this is the assembly of quantum gates comprised of multiple qubits. The current leading systems include trapped ions or defects in solids, such as NV centres in diamond. However, the lack of control over the distribution of spin centres limits the scalability of such platforms. In recent years, coordination chemistry has yielded an alternative “bottom-up” design approach which enables precise tailoring of the quantum properties of individual spins and the coupling between them. The necessary characteristics of molecular spin qubits are dictated by the function of quantum gates. In its simplest form, a two-qubit gate can perform a controlled-NOT (c-NOT) or SWAP operation. The c-NOT gate performs a phase inversion on the target qubit depending on the state of the control qubit, while the SWAP gate exchanges the states of the two qubits. In both cases, it is crucial to independently address the qubits whilst knowing the state of the other. To fulfil the first criteria, inequivalent spin centres are used, and to ensure the second criteria without undermining the first, the spins must be weakly coupled.

To address these challenges, we propose the compound $[\text{Co}_2(\text{O}_2\text{P}^{\text{Bn}})_3\text{py}_4]\text{ClO}_4$ with asymmetric coordination of the Co(II) ions. Using unique high-field vector magnet capabilities, we performed a detailed angle-dependent electron paramagnetic resonance (EPR) spectroscopy study. Features corresponding to the Co(II) ions with octahedral or tetrahedral coordination could be independently identified and the magnitude of the weak exchange coupling was extracted. This work both presents a suitable candidate for multi-spin qubits and details a methodology for characterizing the magnetic properties of such compounds. This is critical in the development of molecular spin qubits that will overcome the current challenges of QIP.

Synthesis and magnetic properties of some functionalized trispyrazolylborate complexes of iron and cobalt

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We will present on a family of NO₂-, NH₂- and I- substituted complexes based on the rigid, air-stable and sublimable bis(trispyrazolylborate)metal (II) (Tp⁻) = trispyrazolylborate) framework, with a special attention given to the complexes of iron and cobalt. The iron complexes display thermal spin crossover properties in solid state and solution, while the cobalt complexes show are SMMs under applied field. These two series of complexes with magnetic bistability have potential applicability in sensors, processing units and information storage devices.

Direct exchange reactions between NO₂- and I-pyrazole and the trispyrazolylborate ligand or unfunctionalized [(Tp)₂Fe] and [(Tp)₂Co] complexes were developed to give access to a variety of NO₂- and I-complexes. The NH₂-functionalized derivatives were obtained through the reduction of nitro groups. I will show how the variation of the nature, position and number of the functionalities impacts the electronic and steric properties of the ligands and in turn the magnetic properties of the complexes in the solid state and in solution. Our systematic investigation, including XRD, electrochemistry, IR, UV-vis spectrometry, SQUID and paramagnetic NMR, helps disentangle the electronic and steric effects of substitution. Based on this investigation, we expect that further modifications of the ligand backbone can be used to tune the molecular properties and adapt the complexes to a desired working environment.

Dimensional reduction of Ni(II) quantum magnets

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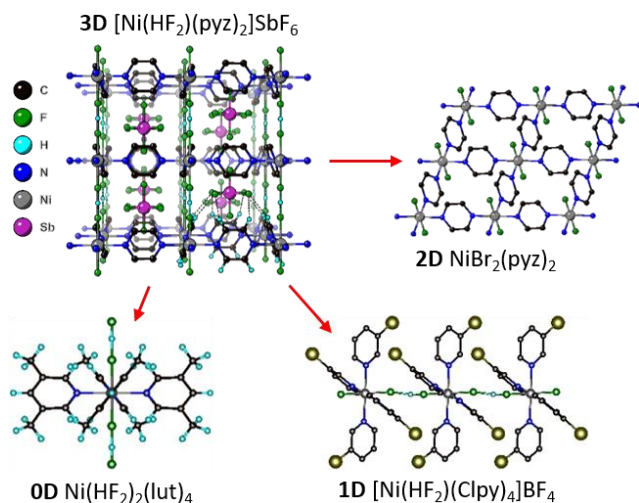
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We are exploring *strong* F...H...F bonds and are particularly interested in: (1) promoting the self-assembly of multi-dimensional molecule-based solids; (2) fostering magnetic superexchange interactions between quantum spin species, such as Ni(II) ($S = 1$) ions; and (3) experimental strategies to extract interaction parameters that describe these systems via simple model Hamiltonians.

The d_{z^2} and $d_{x^2-y^2}$ orbitals of $3d^8$ Ni(II) ion are half-occupied thus allowing multiple superexchange pathways including Ni-F...H...F-Ni (J). Moreover, large and positive zero-field splitting (D) of the Ni(II) $^3B_{1g}$ ground-state occurs for NiN_4F_2 coordination spheres. For $[Ni(HF_2)(pyz)_2]SbF_6$ (pyz = pyrazine) and, more generally for any polycrystalline quantum magnet in which D and J compete, we show that quantifying the Hamiltonian parameters is not feasible from bulk magnetic susceptibility alone, but rather requires a unique combination of experimental techniques.¹

To further understand the magnetic behavior of such compounds, we apply *dimensional reduction* (Figure) by synthesizing: 2D $NiX_2(pyiz)_2$ square lattices ($X = F, Cl, Br$ and I),² Q1D $[Ni(HF_2)(3-Clpy)_4]BF_4$,^{3,4} and mononuclear $NiX_2(3,5-lutidine)_4$ ($X = HF_2, F \cdot H_2O, Cl, Br, I$).^{5,6} Each represents an isolated subset of $[Ni(HF_2)(pyz)_2]SbF_6$, leaving independent characterization of key magnetic parameters (i.e., D , J , and J') to be made and compared to those of the bulk parent.



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Figure. Dimensional reduction scheme for $[Ni(HF_2)(pyrazine)_2]SbF_6$.

Facile and green fabrication of magnetic composite of MOFs for use as a photocatalyst under visible light irradiation

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Fe_3O_4 nanoparticles are robust, non-toxic, and reusable photocatalysts. However, agglomeration of Fe_3O_4 nanoparticles and their low bandgap limit their photocatalytic performance. On the other hand, it has been demonstrated that the band structure of ZIF-8 can be tuned by cobalt as a dopant to activate it under visible light. In this project, we aim to synthesize a ZIF- Fe_3O_4 composite material that can photodegrade waste dye under visible light.

All of our synthesis methods are facile and green. Fe_3O_4 nanoparticles were prepared with a fast participation method. Cellulose as green and abundant material is used to reduce the agglomeration of Fe_3O_4 nanoparticles. Co-doped ZIF-8 as a water-stable visible light photocatalyst was prepared with a one-pot, fast, cost-effective, and environmentally friendly method. The synthesized materials are characterized by XRD, FTIR, and SEM.

The photocatalytic activities of as-prepared samples were evaluated by photodegradation of methylene blue (MB) under visible light irradiation of a 20 W LED. Photodegradation of Co-ZIF-8 was considerably higher than ZIF-8 which confirms that our doping strategy was successful. Both Co-doped ZIF-8 and the Co-ZIF-8@MCC@ Fe_3O_4 exhibited similar and remarkable photocatalytic activity under visible light (97% removal of MB). The mechanism of photodegradation of MB by Co20%-ZIF-8@MCC@ Fe_3O_4 was also studied. The magnetic composite was successfully recycled and reused several times, the reduction in photodegradation of MB was relatively negligible.

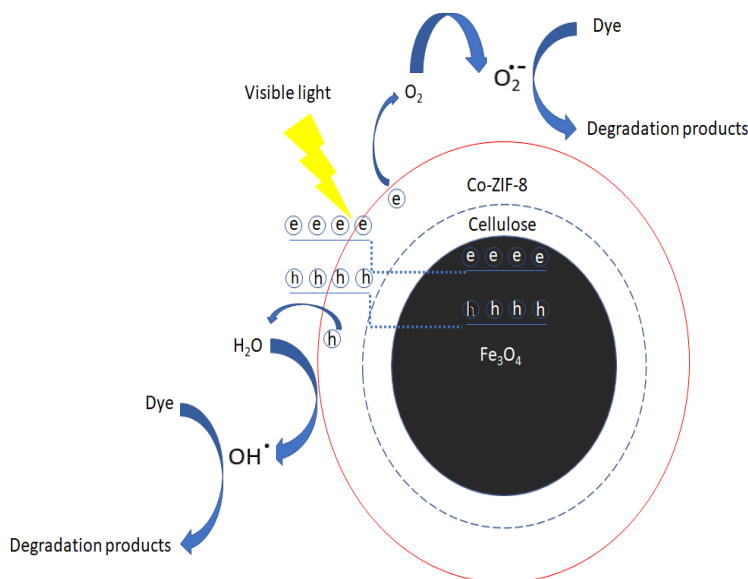


Figure. Fe_3O_4 @MCC@Co-doped ZIF-8 as photocatalyst for photodegradation of MB.

Organic-based Antiferromagnets and Artificial Antiferromagnets

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The study of organic-based magnetically ordered materials has focused on non-compensated magnets, e.g., ferro- and ferrimagnets. Compensated magnets are antiferromagnets, but they have not received much attention, although they are fascinating as well as rich in physical properties. $\text{Mn}[\text{Mn}(\text{CN})_4]$ is like Prussian blue, except that each metal ion site is tetrahedral, not the canonical octahedral for Prussian blue, and adjacent nearest neighbor spin sites are $S = 5/2$ and antiferromagnetically couple leading to compensated antiferromagnet.

More complex materials of $\text{AMn}_3(\text{CN})_7$ and $\text{A}_3\text{Mn}_5(\text{CN})_{13}$ ($\text{A} = \text{NR}_4$) stoichiometry form ferrimagnetic layers that couple antiferromagnetically via a $\mu\text{-CN}^-$ leading to an antiferromagnetic ground state and are artificial antiferromagnets. $\text{A}_2\text{Mn}_3(\text{CN})_8$ in contrast to $\text{AMn}_3(\text{CN})_7$ forms a layered structure and is a ferrimagnet.

$\text{Mn}(\text{TCNE})[\text{C}_4(\text{CN})_8]_{1/2}$ (TCNE = tetracyanoethylene) possesses ferrimagnetic layers bridged by -NCCCN- moieties and also order as an artificial antiferromagnetic. In contrast, $\text{Mn}(\text{TCNE})_{3/2}(\text{I}_3)_{1/2}$ possesses similar ferrimagnetic layers, but is bridged by $S = 1/2$ $[\text{TCNE}]^-$, and orders as a ferrimagnet.

Besides providing an overview of antiferromagnetic behavior, the chemistry and magnetochemistry of these systems will be discussed.

Slowing Magnetic Relaxation with Open-Shell Diluents

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Abstract: Strategies for slowing magnetic relaxation via local environmental design are vital for developing next-generation spin-based technologies (e.g. quantum information processing). This research demonstrates a technique to do so via chemical design of a local magnetic environment. We show that embedding the open-shell complex $(\text{Ph}_4\text{P})_2[\text{Co}(\text{SPh})_4]$ in solid-state matrices of the isostructural, open-shell species $(\text{Ph}_4\text{P})_2[\text{M}(\text{SPh})_4]$ ($\text{M} = \text{Ni}^{2+}$, $S = 1$; $\text{M} = \text{Fe}^{2+}$, $S = 2$; $\text{M} = \text{Mn}^{2+}$, $S = 5/2$) will slow magnetic relaxation for the embedded $[\text{Co}(\text{SPh})_4]^{2-}$ ion by three orders of magnitude. Magnetometry, EPR, and computational analyses reveal that integer spin and large, positive zero field splitting (D) values for the diluent produce a quiet local magnetic field which slows relaxation rates for the embedded Co molecules. These results may enable the investigation of magnetic systems for which strictly diamagnetic congeners are either synthetically inaccessible or are not isostructural.

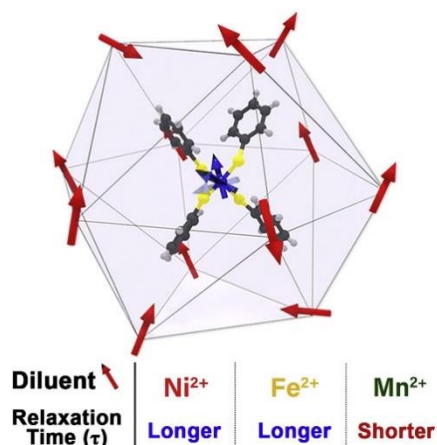


Figure 1. Graphical abstract for presentation research.

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Assessment of the Influence of Self-interaction Error on predicting Magnetic Exchange Coupling Constants using Three Self-interaction Correction Methods

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Accurate theoretical determination of magnetic exchange couplings (J) is necessary to describe the strength and nature of the coupling, especially for large, multicenter magnetic complexes where experimental measurements become challenging. Although density functional theory (DFT) provides a computationally efficient [alternative](#) among electronic structure methods, self-interaction error (SIE) could impact the accurate prediction of J couplings. Here, the role of removing SIE in evaluating J couplings is benchmarked using three self-interaction correction (SIC) methods, namely, Perdew-Zunger-SIC (PZ-SIC) [1], the orbitalwise scaled SIC (OSIC) [2], and the local scaling (LSIC) [3] methods. Both spin-projected and non-projected Js for representative cases of different magnetic interactions, including H-He models, organic radical molecules, and chlorocuprate, are assessed. Our results reveal that PZ-SIC performs well for systems dominated by single-electron regions, while the overcorrection of the J is observed in most complexes. In contrast, LSIC shows better estimations compared to PZ-SIC in the set of organic systems and chlorocuprate. Also, there are two significant takeaways drawn from this study. First, both density and energy corrections are needed to improve the J prediction. Second, SIC methods must be chosen with care for practical applications since each method shows different performance in [different](#) cases.

Acknowledgement: *This work was supported by the US Department of Energy grant DE-SC0018331*

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Generating Magnetic Anisotropy Through Exchange and Ligand Fields

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This presentation will discuss two different approaches that share the common goal of generating magnetic anisotropy in 4f-based complexes. The first part will discuss our group's recent results concerning the utilization of new heterocycles as ligands for lanthanide ions to generate high-performance single-molecule magnets (SMMs). The second part of the talk will focus on how fairly strong magnetic coupling between lanthanides can be achieved in the absence of open-shell bridging ligands, yielding exciting new SMM platforms.

Using nanoparticle-molecule conjugates to host photogenerated spin-correlated radical pairs

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Photoexcitation in donor-acceptor molecular systems can generate charge-separated states composed of two previously spin-paired electrons that reside on spatially separated sites. These spin-correlated radical pairs have unique properties that make them promising as qubit candidates in quantum information applications. They exist in well-defined quantum states at moderate temperatures, can have long decoherence times, and when hosted by molecular or supramolecular structures are highly tailorable via bottom-up synthesis. The current work explores using molecule-nanoparticle conjugates to host photogenerated spin states, such as these spin-correlated radical pairs. This talk will present cases in which the nanoparticle (e.g. CdSe) is photoexcited and charge transfer occurs to a surface bound molecule [1]. It will also discuss cases in which a molecular dye is photoexcited, and charge transfer occurs to a linked ZnO nanoparticle (Figure 1). The photophysics of these nanoparticle-molecule conjugates are measured using both steady-state and time-resolved photoluminescence spectroscopy as well as transient absorption spectroscopy. In both cases optical spectroscopy shows that long-lived (>100 ns) charge separated states are generated. These charge-separated states are then analyzed using laser-induced transient electron paramagnetic resonance spectroscopy to fully characterize the spin dynamics of the photogenerated spin-correlated radical pairs.

In both systems, we find that photogenerated spin states in nanoparticle-molecule systems offer a route to creating well-defined, or at least polarized, spin states at moderate temperatures.

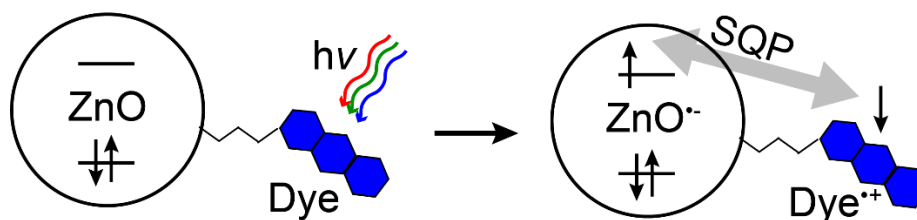


Figure 1. Schematic of photogenerated spin-correlated radical pair (or spin qubit pair, SQP).

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Intuitive Control of Low-Energy Magnetic Excitations via Directed Dipolar Interactions in a Series of Er(III)-Based Complexes

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The field of molecular magnetism continually seeks further understanding and control of magnetic states to advance future quantum technology. For lanthanide single-molecule magnets, spin-orbit coupling and crystal field effects have been fairly well understood, however, coupling methodologies between magnetic centers are still under investigation to improve magnetic behaviors and increase relaxation times. The dipolar coupling regime is rarely evoked as a prominent proponent of coupling between magnetic spins, however, this work will elegantly demonstrate the tenacity of the dipolar coupling model in suppressing QTM relaxation pathways and elongating relaxation times at low temperatures.

To facilitate our study, we present a series of mono-, di-, and tri-nuclear erbium-based single-molecule magnets based on the Er-COT building block. Magnetic experiments on these complexes are coupled with detailed *ab initio* computational studies to discern the role and effects of dipolar coupling on relaxation behaviors and allow us to better understand how to control low-lying quantum states generated through a dipole coupling interaction of the ground Kramers doublets. Furthermore, due to the highly anisotropic nature of our magnetic units, we are able to offer a predictive model of though based on two crystallographically derived geometric parameters. This allows us to extend these findings to offer intuitive paradigms for synthetic exploration.

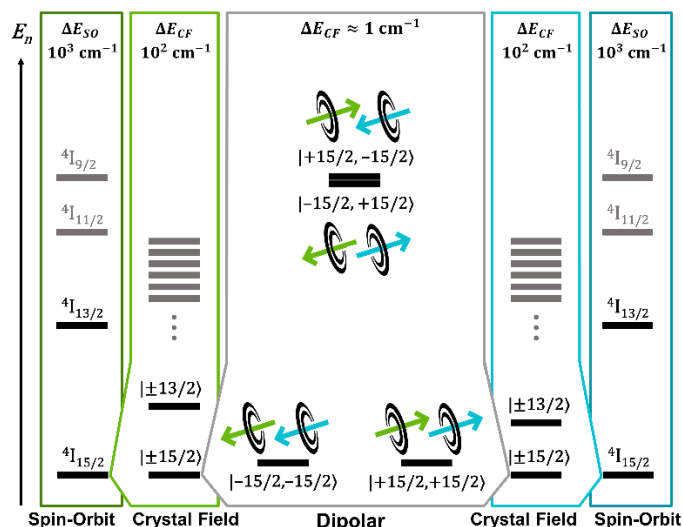


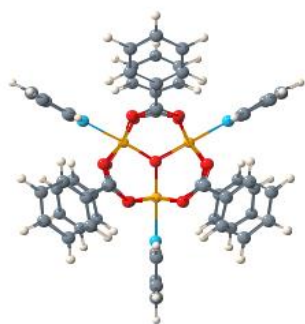
Figure 1. Idealized perturbative scheme for a dinuclear interaction between two magnetic centers, each with the general electronic structure of the Er-COT unit.

Molecular Magnets: Models for Qubits, Quantum Sensors and Protons (?)

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$$R_Q \equiv \begin{pmatrix} \frac{1}{3} & -\frac{2}{3} & -\frac{2}{3} \\ -\frac{2}{3} & \frac{1}{3} & -\frac{2}{3} \\ -\frac{2}{3} & -\frac{2}{3} & \frac{1}{3} \end{pmatrix}$$

The size range, possible sensing applications, and fundamental interest of molecular magnets attracts interdisciplinary physical scientists and challenges them to understand how 50-100 nuclei and 200-1000 electrons can exhibit a range of rather simple collective electromagnetically-driven behaviors such as resonant tunneling of magnetization and spin-electric effects. I will review how DFT can be used to explain both phenomena and then turn to more recent cases where both behaviors occur with modest changes in mechanical, chemical or electromagnetic environment. In one example - the $\text{Fe}_3\text{O}(\text{NC}_5\text{H}_5)_3(\text{O}_2\text{CC}_6\text{H}_5)_6$ molecule - using standard density-functional methods we show that the spin-electric behavior of this molecule could be more interesting due to energetically competitive reference states with high and low local spins ($S=5/2$ vs. $S=1/2$) on the Fe^{3+} ions and, further, that single-spin anisotropic behavior also arises. We also find that similar behavior exists in the Mn_3 molecular magnet and in the Mn_{12} -Acetate molecular magnet [2]. For the case of Mn_3 , it was determined that an $S=2$ to $S=1$ transition can occur and that axial pressure might be

a means for driving the transition. Similarly we find that such spin-flip excitonic transitions can occur in Mn_{12} -Acetate. Finally, as a curiosity, I discuss the rather unusual point-group symmetry in many triangular molecular magnets, which includes a set of point-group rotation matrices that are similar to those that appear in elementary particle wavefunctions. Supported by the M²QM Energy Frontier Research Center, Grant # DE-SC0019330, Grant # DE-SC0018331, Texas STARS, & the C. Sharp Clark Cook Chair in Physics Endowment.

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Bayesian optimization of molecular properties via ligand substitution

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The discovery of novel materials and molecules with magnetic properties desirable for use in device fabrication can be greatly expedited via the use of quantum chemical computational methods such as Density Functional Theory (DFT) which allow systems to be examined at hugely reduced cost compared to experimental synthesis and measurement. However, the large number of possible candidates available for exploration combined with the nontrivial cost of their examination using the more precise methods available still demands that resources be expended in an economical manner. In this work, we apply a Bayesian Optimization (BOpt) process to two sets of DFT-generated data of molecules containing transition metals to determine the resource savings that the process would generate when optimizing certain molecular properties. We minimize the HOMO-LUMO energy gap in a database of 641 Manganese based coordination complexes with elements consisting of various combinations of planar-arranged ligands and the ferromagnetic-antiferromagnetic (FM-AFM) ground state energy difference in a database of 1081 Cobalt dimer based Single-Molecule magnets (SMM) with elements consisting of a static core region and different combinations of capping ligands. We compare the behavior of several acquisition functions: probability of improvement (PI), expected improvement (EI), and upper confidence bound (UCB). We also employ a non-constant mean function which is based on a Bayesian posterior generated by a partial data set. We find that for these discrete data sets the all three acquisition functions reliably enable sampling of molecules with low HOMO-LUMO gap and FM-AFM energies with much less resource expenditure than Monte-Carlo or brute force methods, though the degree of savings depends on the data set.

Chemistry and Topology of Competing Interactions in Tetravalent Lanthanide Oxides

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Rare-earth-based insulating magnets are of broad interest because of their strong spin-orbit coupling (SOC) and inherent anisotropy. In the traditional picture, the SOC multiplet is split by the crystal electric field (CEF) which acts as a second order perturbation on the Hund's rule ground state multiplet. Overall, metal-ligand bonds are not very covalent in trivalent lanthanides and an ionic picture often prevails. By changing the oxidation state of the lanthanide from +3 to +4, however, the metal-ligand bond becomes much more covalent (4*f*-2*p* hybridization). This change makes leads to SOC and CEF in tetravalent lanthanides (Ln⁴⁺) to be of comparable energy scales and requires an intermediate coupling model.¹

In this presentation, I will describe our studies towards understanding the topology of competing interactions in tetravalent lanthanides and its effects on single-ion and collective behaviour of these materials. In order to understand the ground state electronic structure of Ln⁴⁺ ions, CEF measurements using INS and FIRMS were carried out on a series of Ln⁴⁺ oxides with primary focus on Pr⁴⁺.⁴ Pr⁴⁺ with 4*f*¹ electronic configuration is isoelectronic to Ce³⁺. Based on our recent investigations on Na₂PrO₃, the first CEF level was identified at 230 meV with a substantial antiferromagnetic exchange interaction ~ 1.2 meV (typically 0.3-0.5 meV for Ln³⁺) both of which have been attributed to enhanced 4*f*-2*p* hybridization.^{2,3} The series of Pr⁴⁺ oxides allow us to tune the CEF by changing the local symmetry (CEF ranges from 160 meV to 230 meV based on the local symmetry). A point charge model using Stevens operators in the intermediate coupling limit was developed to extract the ground state wavefunction of Pr⁴⁺ single-ion. Due to competing CEF and SOC interactions, ground state has contributions from different excited states. Evidence of 4*f*-2*p* hybridization in Pr⁴⁺ and consequences of increased covalency on single-ion properties, exchange interactions, and collective behaviour in Pr⁴⁺ oxides will be shown using a combination of *M*_{4,5} edge and O *K*-edge XAS and XMCD spectroscopies. With these observations, I will establish a cohesive model to understand the electronic structure of Ln⁴⁺ materials and for developing applications of these properties in functional magnetic materials including qubits.

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Screening the Cambridge Structural Database (CSD) for Spin Cross-over Materials

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Spin cross-over (SCO), commonly observed with first row d^4 through d^7 transition metal complexes in an octahedral ligand geometry, is when the complex changes spin state due to an external stimulus, such as pressure, temperature, light, or magnetic field. Discovering SCO materials for their potential applications in electronic devices requires techniques which allow efficiently identify SCO candidates. In this work, we screen the Cambridge Structural Database (CSD) and apply machine learning (ML) to identify spin cross-over (SCO) materials. We assemble a dataset by first selecting 1200 materials from CSD, then performing Density Functional Theory (DFT) calculations to determine their spin states and the energy at each state. Using this dataset with DFT calculated properties, we train Gradient Boosting (GB) classifier and regressor to predict: (i) number of d electrons of the metal center at its oxidation state in the complex, (ii) the spin of ground state, (iii) the range of SCO energy (ΔE_{SCO}), and (iv) the value of ΔE_{SCO} , where predicting the range of ΔE_{SCO} directly targets SCO materials. We show excellent performance in predicting number of d electrons and the spin of ground state. We demonstrate high efficiency in identifying SCO materials using the classifier predicting the range of ΔE_{SCO} compared to DFT calculations. We identify 218 SCO materials with ΔE_{SCO} within 0-0.5 eV.

Fine-Tuning the Electron Spin Wavefunction with Magnetic Dipoles

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Many of the models forged in molecular magnetism over the last 60+ years and SMM research over the last 30 years are optimized for maximizing the energy separations between angular momentum states. Redirecting these models toward new challenges in quantum information science and spin-charge interaction offers an exciting possibility to expand the palette of viable materials of interest for synthetic magnetochemists while also contributing to new fields. To do this effectively, however, will benefit from a more intuitive means of controlling the spin wavefunction at small energy scales where the dominant interactions are often difficult-to-predict or transient low-symmetry and dipolar effects.

The lanthanides have led to many advances of fundamental importance to SMMs through the highly predictable nature of the spin-orbit (SO) and crystal field (CF) Hamiltonian terms. These perturbations can be considered as design parameters using the f-electron count and coordination environment on $E = 10^3$ and 10^2 cm^{-1} orders of magnitude, respectively. Coupling to vibrational modes has been shown to highly important to modeling the relaxation of many molecules, yet its effects are difficult to predict a priori and the energy scale of importance has a strong overlap with that of the CF tuning perturbation. Missing from this picture are robust methods for tuning the wavefunction in the 10^0 cm^{-1} range. Importantly, this range is capable of mixing wavefunctions without significantly disturbing the well-established single-ion manifold previously established by the SOC + CF formalism. This talk will focus on use of highly predictable local dipolar coupling as a mechanism to generate state interactions with the potential for *a priori* knowledge of the resulting density matrix.

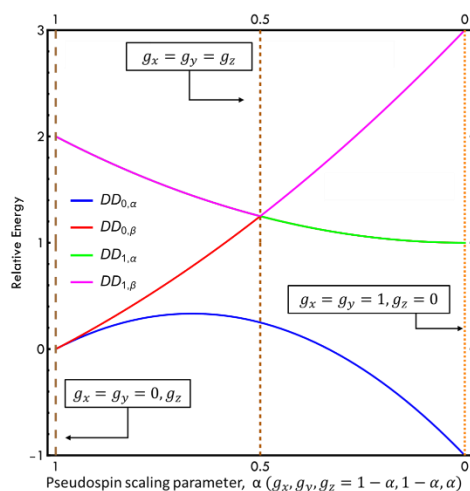


Figure 1. Representative energy diagram for two identical pseudospin $\frac{1}{2}$ states interacting via the magnetic dipole-dipole interaction as a function of the initial state anisotropy.

Pulsed 94 GHz EPR for Spin Population Transfer in a Gd³⁺ Molecular Crystal

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Gd³⁺ is an $S = 7/2$ ion that possesses a half-filled $4f^7$ electron occupancy, with no first order orbital angular momentum. Consequently, the $2S + 1 = 8$ spin levels are minimally mixed and can typically be considered quite pure, with very weak zero-field splitting expected. For these reasons, Gd³⁺ has been proposed as a $d = 8$ level qudit system approximating 3 coupled qubits (i.e., $d = 2^3 = 8$), with each $\Delta m_S = \pm 1$ transition being fully allowed via EPR, permitting spin state manipulation using resonant microwave pulses.^{1,2} To access this proposed application, the pulsed EPR spectrometer must meet several requirements. These include: (1) sufficient power to achieve wide bandwidth excitation capable of accessing multiple spectrally separated spin transitions; (2) nanosecond time resolution with a high degree of control over the pulse waveform shaping; and (3) sufficient detection sensitivity for studying small samples with low spin concentrations. The 94 GHz quasioptical HiPER spectrometer at the National High Magnetic Field Laboratory meets all of these requirements and additionally allows for *in situ* single crystal rotation. Using this unique spectrometer, we have demonstrated dynamic population transfer within the $^8S_{7/2}$ ground manifold of a Gd³⁺ coordination compound, paving the way towards implementation of simple quantum logic operations within a $d = 8$ molecular spin qudit.

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A Synthetic and Spectroscopic Investigation of Polynuclear, Oxo-Bridged Iron Clusters

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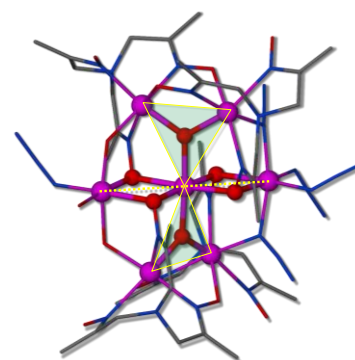
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Polynuclear metal complexes comprising of oxo-bridged iron sites are widespread and have found many important applications in catalysis and magnetism. This poster will present the structural and spectroscopic characterization of a heptanuclear iron cluster and the field-dependent ⁵⁷Fe Mössbauer investigation of a family of tetranuclear iron clusters.

We have synthesized and isolated a [Fe₇] cluster supported by a redox-active ligand, tris-(2-hydroxyl-iminopropyl)-amine. The structure of this complex was elucidated using X-ray crystallography, which revealed a topology of two corner-sharing triangles with the common site incorporated in a linear trinuclear cluster (see the figure on the right). The triangular motifs are expected to give rise to unusual magnetic interactions, such as spin frustration. To elucidate the electronic structure of this cluster, we have performed a detailed EPR and field-dependent Nuclear Gamma Resonance (Mössbauer) spectroscopic investigation. These studies revealed that all iron sites adopt a high-spin iron(III) configuration. Moreover, the field-dependent Mössbauer spectra exhibit a hyperfine splitting pattern indicative of spin frustration.



Most recently, we have investigated a series of tetranuclear iron complexes inspired by the active site of the oxygen evolving complex of photosystem II. These clusters incorporate an unusual Fe(III)-oxo group stabilized by hydrogen bonding. Our field dependent Mössbauer studies have allowed us to monitor not only the changes induced by the reversible protonation of the oxo group, but also those caused by the variations in the oxidation state of different iron sites.

Molecular Approach to Ultra-Small Iron Oxide Nanoparticles

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Iron oxide nanomaterials have attracted a lot of research interest for numerous applications such as magnetic data storage, biosensing applications, targeted drug delivery, and contrast agents in magnetic resonance imaging, among others. These technological and biomedical applications require an overall narrow particle size distribution, as it influences the structural characteristics and, thus, electronic and chemical properties. Therefore, control over the nanoparticle synthesis to produce truly uniform particle sizes is an extremely important objective in this and other areas of nanoscience. However, the polydispersity of traditional nanoparticles has long been a challenge in nanoscience research. While synthetic methodologies to produce uniform-size nanoparticles have improved through the years, a single synthesis still produces a range of particle sizes. The fact that no two nanoparticles are the same has hindered the study of the size, shape, and surface-dependent properties. Therefore, the ultimate dream remains to synthesize truly uniform nanoparticles, identical in size and shape, and which can be structurally characterized to atomic precision. This research work discusses a molecular 'bottom-up' approach that targets the synthesis of ultra-small (<3 nm) iron oxide nanoparticles as molecular clusters, their structural and magnetic characterization.

Massive 116 GHz Crystal-Field Clock Transition in a Tetragonal Molecular Ho(III) Complex

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Molecular lanthanide complexes are promising candidates for development of next-generation quantum technologies [1]. In particular, high-symmetry structures can give rise to well-isolated crystal-field quasi-doublet ground states, i.e., quantum two-level systems that may serve as a basis for spin qubits. More importantly, recent work has shown that the coordination environment around the lanthanide can be tailored to produce an avoided crossing, or clock transition within the ground doublet, where the first-order sensitivity to fluctuations in the local magnetic field is suppressed, leading to significantly enhanced coherence times [2]. Here, we employ single-crystal high-frequency electron paramagnetic resonance (EPR) spectroscopy to interrogate a new molecular Ho(III) complex. An axial coordination environment with four-fold symmetry gives rise to a ground state $m_J = \pm 8$ crystal-field quasi-doublet with a massive 116 GHz clock transition, where m_J denotes the projection of the $J = 8$ spin-orbital moment associated with the Ho(III) ion. These states are further split into eight ($2I + 1$) sub-levels due to the hyperfine interaction with the $I = 7/2$ nuclear spin (100% natural abundance). We assess the prospects for carrying out coherent (pulsed) high-frequency EPR spectroscopy of this molecule.

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A Spectroscopic and Theoretical Investigation of High-spin Ferrous Complexes Supported by S- and Se-based Ligands

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This presentation will focus on the electronic structures of two pseudotetrahedral high-spin ferrous complexes, $[\text{Fe}(\{\text{EP}^i\text{Pr}_2\text{N}\}_2)_2]$ where E = S (**1**) and Se (**2**).¹ These compounds were investigated using high-frequency and -field EPR and field-dependent ^{57}Fe Mössbauer spectroscopies. Our studies revealed quintet ground states characterized by moderate but negative zero-field splitting (ZFS) parameters D . Our theoretical analysis of the hyperfine and spin Hamiltonian parameters revealed that the orbital ground states have a predominant (x^2-y^2) character admixed with $\sim 10\%$ (z^2). Interestingly, replacing the S-containing ligands of **1** by their Se-containing analogues in **2** leads to a smaller ZFS. An extensive series of *ab initio* CASSCF calculations revealed that the ligand spin-orbit coupling plays a marginal role in determining the magnetic anisotropy of these compounds. Instead, the $(x^2-y^2)^\beta \rightarrow (xy)^\beta$ excitations yield a large negative contribution, which dominates the ZFS of both compounds, while the different energies of the $(x^2-y^2)^\beta \rightarrow (xz)^\beta$ transitions are the predominant factor responsible for the variation of D values. The electronic structures of these compounds will be contrasted with those of other iron-sulfur sites, including that of reduced rubredoxin, by considering a D_2 -type distortion of the metal centers.

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Probing spin-phonon coupling in magnetic materials using magneto-Raman spectroscopy

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Combining spectroscopy with one or more external parameters such as low temperature, high pressure, and high magnetic fields, allows us to probe interplay between spin, charge, orbital and lattice degrees of freedom. Recently, we employed magneto-Raman spectroscopy on two different kinds of metal-organic magnetic materials to probe spin-phonon coupling. Spin-phonon coupling plays an important role in several magnetic materials including single-molecule magnets and molecular qubits. In the first compound $\text{Co}^{\text{II}}(\text{acac})_2(\text{H}_2\text{O})_2$ (acac = acetylacetonate) which is a molecular magnet, we were able to show for the first-time, distinct couplings of g phonons of and its deuterated analogs with zero-field-split, excited magnetic/spin levels (Kramers doublet (KD)) of the $S = 3/2$ electronic ground state. The couplings are observed as avoided crossings in magnetic-field-dependent Raman spectra with coupling constants of $1\text{--}2\text{ cm}^{-1}$ [1]. The second compound is the multiferroic metal organic framework $[(\text{CH}_3)_2\text{NH}_2]\text{Co}(\text{HCOO})_3$ belonging to the family of MOFs comprised of methylammonium ($\text{A} = (\text{CH}_3)_2\text{NH}_2$) and metal ($\text{B} = \text{Co}, \text{Cu}, \text{Fe}, \text{Mn}, \text{Ni}$) cations with a formate ($\text{X} = \text{HCOO}_3$) anion. Several efforts have been made to understand the exchange interactions in these functional materials including magnetization at high magnetic fields up to 60 T and infrared spectroscopy at magnetic fields up to 35 T. In the infrared studies under applied magnetic fields, it was concluded that Co complex adopts a different mechanism for facilitating saturation of magnetic states by involving formate stretching distortions unlike other complexes in the family that use the formate bending mode. We were able to unambiguously identify that formate bending mode around 800 cm^{-1} is in fact involved in the magneto-elastic coupling in $[(\text{CH}_3)_2\text{NH}_2]\text{Co}(\text{HCOO})_3$ using magneto-Raman spectroscopy at magnetic fields up to 31T [2].

This work has been performed at the user facilities in the National High Magnetic Field Laboratory (NHMFL), Tallahassee. The NHMFL is supported by the National Science Foundation through NSF/DMR-1644779 and the state of Florida. The project is also funded by DoN HBCU/MI program award # N000141713061.

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Predicting Magnetic Properties of Lanthanide-Based Single-Ion Magnets from Ab Initio Electronic Structure Calculations

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Lanthanide-based single-ion magnets (SIMs) are promising building blocks for the development of new materials with applications in high-density magnetic memory, spintronics, quantum sensing, and quantum computing. All these applications require SIMs with stable and controllable magnetic properties, which originate from the electron spin of lanthanide ions. Spin relaxation is responsible for the loss of magnetization in high-density memory applications, while spin decoherence is related to the loss of quantum information in qubits used in quantum sensing and computing. We will describe our theoretical and computational efforts to understand the factors affecting the electron spin relaxation and decoherence in lanthanide complexes and to determine the design criteria for multifunctional lanthanide-based SIMs with useful opto-magnetic properties. The focus will be on the complexes with the terpyridine ligands and different lanthanide ions in the gas, solution, and crystal phases. High-level ab initio electronic structure calculations showed that in the gas phase these complexes are characterized by a significant ligand field anisotropy. In the crystal phase, the anisotropy is reduced due to a more symmetric ligand coordination. These small changes in the ligand coordination can lead to significant variations in the electronic structure and affect the magnetic properties of these lanthanide complexes.

Physical properties of chiral magnet $M_{1/3}\text{TaS}_2$

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Exotic physical phenomena are bound to happen in chiral magnets, since broken space inversion, mirror symmetry and time reversal symmetry often accompany new physical phenomena. For example, the Dzyaloshinskii Moriya (*DM*) interactions, allowed by the lattice chirality, could bring about a twist between the magnetic moments and lead to various novel chiral magnetic structures (e. g., magnetic chiral solution and Skyrmion lattice). So far, very few chiral magnets have been discovered. Recently, we successfully synthesized single crystals of $M_{1/3}\text{TaS}_2$ ($M = \text{Cr, Co and Ni}$) which are new chiral magnet candidates. $M_{1/3}\text{TaS}_2$ crystallizes in a non-centrosymmetric chiral hexagonal space group $P6_322$ with M atoms intercalated between 2H-stacked TaS_2 layers. Strong *DM* interactions may exist in $M_{1/3}\text{TaS}_2$ and induce novel physical properties. In this work, we will discuss the novel magnetic structures, bulk magnetic susceptibility and magneto transport properties of $M_{1/3}\text{TaS}_2$.

Teaching Nuclear Spins to Act Like Electronic Spins

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The development of next-generation quantum bits hinges on the satisfaction of multiple different criteria in the system. For example, a candidate molecular spin must be (i) addressable, (ii) initializable, (iii) capable of entanglement with other spins, and (iv) have a robust and long-lived spin superposition.^{[1],[2]} In practice, however, a given candidate qubit system only meets some of the criteria, not all. Thus, new design strategies that enable a given qubit candidate to realize more of the requirements for quantum applications are necessary.^[3]

We have begun study on a strategy of “quantum mimicry” to enable molecular spin systems to satisfy more of the above criteria. As the proof of concept to be discussed, we study the intersection of nuclear spin coherence with electron-spin properties in molecular systems. Nuclear spins have robust spin superpositions, yet their environmental sensitivity is weak. In contrast, electronic spins are strongly environmentally sensitive, yet have short-lived superpositions. Our guiding hypotheses are that (1) ligand design can transduce environmental sensitivity into metal-ion nuclear spins and (2) hybrid molecular systems of magnetic nuclei and electrons will enable nuclear spins to “mimic” the environmental sensitivities of electron spins while retaining the robust spin coherence of magnetic nuclei. The long-term capabilities afforded by such systems would be molecular systems for quantum sensing and biomedical applications. In this talk, I will discuss our recent reported and unreported results in the area^{[4],[5]} and understanding how electron spin conversion processes enable ^{59}Co nuclear spins to “mimic” the temperature sensitivities of the electron paramagnetic resonance signals of unpaired electrons.

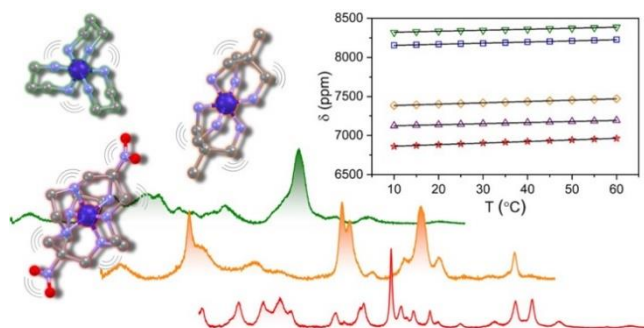


Figure. Graphical depiction of topics to be discussed: metal complexes, variable temperature ^{59}Co NMR, and vibrational spectroscopic analyses.

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Spin decoherence due to Ampere field fluctuation from acoustic phonons

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We compute the decoherence time of electron spin under the magnetic field produced by phonon motion of the ions. By using the linear dispersion relation in elastic medium, the magnetic field due to acoustic phonon motion and time correlation function of magnetic field are calculated numerically. We then solve the Redfield equation of motion for the reduced density matrix, which yields the decoherence time of electron spin from the time correlation function of the magnetic field. The calculations are carried out for both in NV center and in semiconductor quantum dots. The NV center result of SiC shows the onsite field dominate the decoherence time. The quantum dot calculation of GaAs, InSb and InAs shows all atoms in dot contribute.

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Two-dimensional spin bistable molecules

Presenter: Xiao-Xiao Zhang, Assistant Professor
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The successful isolation of two-dimensional (2D) crystals through mechanical exfoliation has led to numerous scientific breakthroughs and paved avenues for next-generation nanoscale devices, with the majority of these studies focused on inorganic van der Waals crystals. In this talk, I will present characterization of the mechanically exfoliated Fe-based magnetic molecules down to the monolayer thickness. These molecular are bound by anisotropic van der Waals interactions into 2D assemblies, and can be exfoliated into single-crystalline flakes similar to inorganic atomic crystals. With reducing thickness, we observe a substantial increase in the spin-state transition thermal hysteresis, which suggests the important roles of substrate and interlayer coupling in molecular systems. Our results establish molecular solids with strong anisotropy of intermolecular interactions as precursors to a novel class of 2D materials, affording new possibilities for designing hybrid organic-inorganic heterostructures and devices.

Probing local magnetic ordering with neutron total scattering

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Neutron diffuse scattering is a powerful technique for probing local magnetic ordering and reverse Monte Carlo modeling is one of the typical approaches for rebuilding nucleus and magnetic ordering models from experimental data. Two representative studies will be presented here concerning the application of neutron diffuse scattering for local magnetic ordering studies. In the first study, a detailed structure analysis for the site-diluted $\text{Sn}_x\text{Fe}_{4-x}\text{N}$ ($x=0.25, 0.41$ and 0.88) has been carried out through complex modeling of the neutron total scattering data [1]. We present quantitative evidence showing the local ferromagnetic cluster size extending to ~ 8 Å on average when $\text{Sn}_{0.88}\text{Fe}_{3.12}\text{N}$ undergoes the spin-glass transition (the other two not showing such a transition). The modeling methodology used in this work involving the corefinement of the nuclear and magnetic structure in both real and reciprocal space can potentially be applied generally to explore a variety of spin-glass material problems. In the second study, neutron diffuse scattering was employed to explore the inter- and intra-layer magnetic couplings in a 2D vdWs system – $\text{Fe}_{5-x}\text{GeTe}_2$. RMC modeling and post-analysis indicates weakening magnetic anisotropy which could be attributed to orbital quenching as the result of local symmetry breaking.

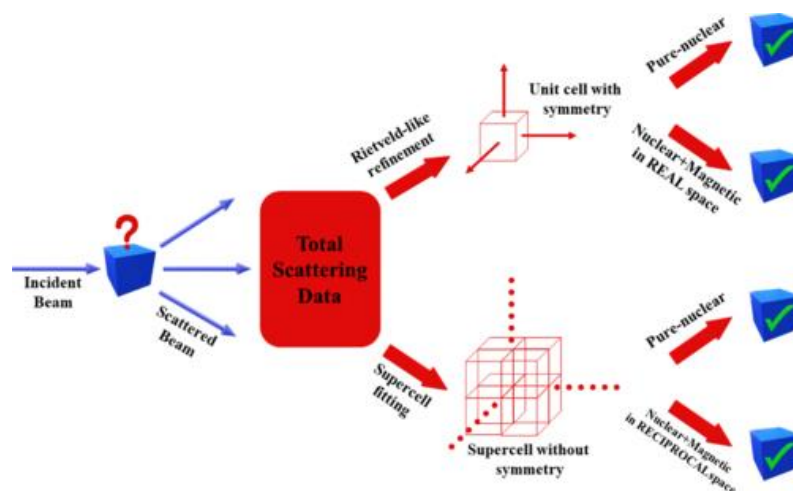


Figure. 1. Illustration of common approaches for neutron total scattering data analysis.

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