Session 3

Keynotes lectures
FROM SINGLE-MOLECULE MAGNETS TO MOLECULAR MAGNETIC VORTEXES

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Recent years have witnessed a huge renaissance in the study of the magnetism of lanthanide compounds thanks to the large inherent anisotropy of the metal ions.1 Our recent research efforts focus on the relaxation dynamics and spin feature of lanthanide compounds.2,3 The design and characterization of a series of coordination compounds based on highly anisotropic lanthanide ions will be presented, and their single-molecule magnet (SMM) and single-molecule toroic (SMT) behaviour in terms of relaxation dynamics and spin feature will be discussed.

Figure 1. Structure and spin topology of Dy₆ compound

References


Magnetic relaxation dynamics in dysprosium SMMs

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Following our discovery of relatively high-temperature magnetic hysteresis in dysprosocenium (Figure 1),1 we have been investigating the magnetic relaxation dynamics of various dysprosium-based single-molecule magnets (SMMs) with both experimental and theoretical techniques.2,3 Here we present our recent results in unravelling the competing magnetic relaxation processes at low temperatures, and offer some insights into the origin of the previously pervasive quantum tunneling of the magnetization in high-barrier dysprosium(III) SMMs.

Figure 1. (top) Molecular structure of dysprosocenium. (bottom) Magnetic hysteresis and relaxation rate for dysprosocenium.

References

2 Y.-S. Ding, K.-X. Yu, D. Reta, F. Ortu, R. E. P. Winpenny, Y.-Z. Zheng and N. F. Chilton, Submitted
New Avenues in Lanthanide Single-Molecule Magnets

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Multimetallic rare-earth systems and especially DyIII, ErIII-based materials have sparked much interest in the area of molecular magnetism due to the large intrinsic magnetic anisotropy of the lanthanide ions. When such a unique property is combined with a high spin ground state (S) in a molecular complex, it causes slow relaxation of the magnetization as seen for Single-Molecule Magnets (SMMs). Lanthanide only SMMs are rare due to the difficulty in promoting the magnetic interactions via the overlapping bridging ligand orbitals with the contracted 4f orbital of the ions. Toward the goal of inducing significant magnetic interaction between lanthanide ions and subsequently isolating high-energy barrier SMMs, our research is currently focused on the use of phenoxide bridges as superexchange pathways between spin carriers.1-4 In addition, organometallic lanthanide sandwich complexes provided an alternative approach for understanding intriguing quantum mechanical properties of SMMs.5

Figure 1. Cycloheptatrienyl trianion-based organolanthanide single-molecule magnets

Reticular Chemistry: MOF Design Strategies to Applications

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Demand for functional materials targeted for specific applications is ever increasing as societal needs and demands mount with advancing technology. The building-block approach, whereby at the design stage the desired properties and functionality can be introduced in preselected molecular building blocks (MBBs) prior to the assembly process, has emerged as a prominent pathway for the rational construction of functional solid-state materials.

One class of inorganic-organic hybrid materials, metal-organic frameworks (MOFs), has burgeoned in recent partly years due to effective design strategies (i.e. reticular chemistry) for their synthesis and their inherent [and readily interchangeable] hybrid, functional character.

MOFs have emerged as a unique class of materials amenable to design and manipulation for desired function and application. Several design strategies have been utilized and developed to target viable MOF platforms, from the single-metal-ion MBB approach to the hierarchical supermolecular building block, supermolecular building layer approaches (SBB and SBL, respectively), and recently the merged net approach.

Markedly, highly-connected and minimal edge-transitive nets (with one or two kinds of edge) can be regarded as ideal blueprints for the rational design and construction of MOFs. Here we present the deployment of polynuclear rare earth (RE) clusters as versatile and tunable MBBs for the design and synthesis of MOFs. Our recent research developments permitted the introduction and exploration of various Rare-earth MBBs as highly-connected building units, regarded as net-coded building units (net-cBUs) embedding a unique and precise positioning and connectivity of the net vertex figures.

This inherent built-in information allows access to highly stable and made-to-order porous materials toward applications pertaining to energy and environmental sustainability. Specifically, made-to-order MOFs addressing the energy-intensive separations and gas storage will be discussed.
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Invited lectures
ORGANOMETALLIC QUBITS STUDIED BY PULSED EPR METHODS

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Quantum coherence is a fundamental property of magnetic molecules that enables them to function as quantum bits (or qubits).\(^1\) The lifetime of the qubit must be sufficiently long to enable coherent spin manipulations, preferably at high temperatures.\(^2\) Strategies targeting systems with long memory times are centered around the removal of nearby nuclear spins, regarded as a major decoherence source. However, we recently demonstrated that long memory times up to 4\(\mu\)s are achievable in nuclear-spin rich cyclopentadienyl actinide complexes, \(\text{AnCp}^3\) (\(\text{An} = \text{Th} \text{ or } \text{U}\)).\(^3\) This allowed pioneer measurements of actinide covalency via modern pulsed EPR methods: HYSCORE, ESEEM, ENDOR. Here we focus on another family of cyclopentadienyl complexes, \(\text{LnCp}^3\) (\(\text{Ln} = \text{Y} \text{ or } \text{Lu}\)),\(^4\) for which coherent Rabi oscillations were measured, including at 300 K in a single crystal. Ac magnetic susceptibility data confirmed slow magnetic relaxation at low temperatures, associated with very long spin lattice relaxation times, which were probed by pulsed EPR methods. Despite many \(^1\)H and \(^13\)C nuclei present in the molecules, all electronuclear transitions of the compounds could be coherently manipulated (Figure 1), indicative that the qubit memory time is protected in these systems. Measurements of covalency via 2D HYSCORE spectroscopy will also be discussed.

Figure 1. Echo-detected EPR spectrum (left), and Rabi oscillations (right), for \(\text{Lu(Cp}^3\))K.

References

SINGLE-MOLECULE MAGNETS AND METAL ORGANIC FRAMEWORK: UNITY IS STRENGTH

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A revolution is in progress in the design of single-molecule magnet (SMMs) with the (re)introduction of lanthanides ions as spin carriers.1 We present here such an example with a study that shows that metal-organic frameworks (MOF) can be used as tools to design lanthanide-based SMMs.

In details, we report the study2 of a Dy-based MOF, made of nine-coordinated Dy magnetic building blocks (MBBs) with poor intrinsic SMM behavior. However, the MOF architecture constrains the MBBs into a one-dimensional structure that induces strong Dy-Dy ferromagnetic coupling. The result is an original magnetic object at the frontier between single-chain magnet (SCM) and SMM, owning strong intrachain couplings that cancel quantum tunneling. This compound evidences that bottom-up approach through MOF design can induce spontaneous organization of MBBs to produce unique molecular magnetic material.

Figure 1. Magnetic slow relaxation in a Metal Organic Framework made of chains of ferromagnetically coupled Single-Molecule Magnets

References

SYNTHESIS AND DYNAMIC MAGNETIC PROPERTIES OF RARE-EARTH SANDWICHES

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Single-molecule magnets (SMMs) are coordination compounds that display magnetic memory effects.1 We have a particular interest in metallocene SMMs based on dysprosium, and, over the years, we have reported a few examples of such materials.2 Our work has shown that the [Cp]- ligands provide a strong axial crystal field that enhances the magnetic anisotropy of Dy^3+, leading us to propose that a cation of the type [Cp_2Dy]^+ should be an interesting synthetic target.3 Thus, we and others have described the SMM properties of [Dy(Cpttt)_2][B(C_6F_5)_4] (Cpttt = 1,2,4-tri-tertbutylcyclopentadienyl), which displays a record magnetic blocking temperature of 60 K.4

Having established the design principles required to optimize the SMM properties of dysprosium sandwich complexes, we now turn our attention to the cyclobutadienide ligand, i.e. [Cb]2-. Surprisingly, there were, hitherto, no lanthanide complexes of [Cb]2-, hence investigations of such materials furnish an opportunity for fundamental advances in lanthanide organometallic chemistry. In addition, the greater formal charge and the four-fold symmetry provided by the [Cb]2- ligand provide a new strategy for the development of SMMs, such as the complex illustrated above. Our initial results on such systems will be described.5


REDOX- AND HYDRO-MAGNETIC SWITCHING IN LANTHANIDE-BASED SINGLE-MOLECULE MAGNETS

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The Single-Molecule Magnets (SMMs) fascinated both chemist and physicist communities for the last three decades because of their potential applications in high-density data storage, Quantum computing and Spintronics. Even more challenging is the design of multi-properties SMMs, especially when the switching of one of these properties can be controlled. Such behavior could be open additional applications for switches and sensors but has been rarely achieved in the literature. In this presentation, two examples of magnetic switching will be exposed. Thus, the magnetic switching was highlighted in the Na9[Er(WO18)2]·35H2O4 (Er-1) SMM during the reversible process of dehydration/rehydration. The second example of magnetic switching was observed in the dinuclear complex [Dy2(hfac)6(HSQ-L)]·CH2Cl2 (HSQ-Dy) (where hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate and HSQ-L = 2,2'-benzene-1,4-diylibis(6-hydroxy-4,7-di-tert-butyl-1,3-benzodithiol-2-ylium-5-olate). The complex can be reversibly oxidized into the dinuclear compound [Dy2(hfac)6(H2O)2(Q-L)] (Q-Dy) (where Q-L = 2,2'-cyclohexa-2,5-diene-1,4-diyliendenbis(4,7-di-tert-butyl-1,3-benzodithiole-5,6-dione)) inducing coordination of water molecule to the DyIII ion and its release. HSQ-Dy is a Single-Molecule Magnet with a magnetic relaxation 7000 times slower than for Q-Dy (at 3 K) allowing an “ON-OFF” switch of the magnetic bistability. In other words, the first simultaneous redox and hydro-magnetic switching was achieved. The modulation of the magnetic anisotropy in HSQ-Dy and Q-Dy was quantified by ab initio calculations.

Figure 1. Molecular structures of Er-1 (on the left) and HSQ-Dy (On the right)

References
Radical Bridged Lanthanide Single Molecule Magnet

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Achieving strong exchange coupling in lanthanide system via radical bridges is seen as one of the most efficient routes to high-performance SMMs since the discovery of N$_2$$^-$-radical-bridged lanthanide SMM showing high blocking temperature and strong coercive field. To date, several remarkable nitrogen-based radical examples have been assembled successfully despite the synthetic difficulty, such as N$_2$$^-$, bpm$^-\cdot$, tppz$^-\cdot$, bptz$^-\cdot$, ind$^3\cdot$, HAN$^3\cdot$. They exhibit the robust single molecule magnet (SMM) properties, where in particular quantum tunneling of magnetization is suppressed efficiently. Nevertheless, the in-depth study into crystal field and magnetic interactions of this system is rarely reported via some advanced measurement techniques due to their high air-sensitivity and the complexity from additional spin, which requires the effective collaboration between chemistry and physics researchers. Recently, we reported the detailed investigation on tetraoxolene radical bridged dilanthanide system using HF-EPR, which reveals the significant crystal field splitting and exchange coupling regions in Gd and Tb compounds, respectively. Further work is proceeding to improve the SMM properties.

Figure 1. Typical radical bridges in Ln-SMMs

References


Advances in f-block Metalloccenophane Chemistry: Ln-[1]ferrocenophane Complexes Functioning as Molecular Nanomagnets

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Organometallic compounds featuring one or more lanthanide ion(s) have found ample precedence in areas of homogeneous catalysis and molecular magnetism. Within this field, the chemistry of f-block metalloccenophanes has remained largely unexplored. In this talk, the structural and physical properties of the first isolated mono- and multi-lanthanide-[1]metalloccenophane compounds will be presented. The set of Ln-[1]ferrocenophane complexes, [Ln(Fc)₃(THF)₂Li]⁻ (Ln = Dy³⁺ (1) or Tb³⁺ (2); Fc = [Fe(η⁵-C₅H₅)]₂⁻), have molecular geometries differing dramatically from traditional main-group-[1]metalloccenophanes and both exhibit all of the properties of a soft single-ion magnet. Mononuclear 1 can be utilized as a synthetic building block for the synthesis of the multi-lanthanide-[1]metalloccenophane complex, [Dy₃(Fc)₆(THF)₂Li]⁻ (3). Complex 3 exhibits remarkably strong ferromagnetic interactions between Dy³⁺ centers and hard SMM behavior. These results along with with computational insights into the spin relaxation dynamics of the mono-Ln-[1]metalloccenophane systems will be discussed.

Figure 1. Molecular structures and magnetic properties of anionic [Dy(Fc)₃(THF)₂Li]⁻ (1) and [Dy₃(Fc)₆(THF)₂Li]⁻ (3).

References

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Posters
Covalent or Electrostatic? What DyDOTA can teach us about chemical bonding in f-elements

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Lanthanide ions complexed by polyamino-polycarboxylate chelators form a class of compounds of paramount importance in several research and technological areas, particularly in the fields of magnetic resonance (MR) and molecular magnetism (MM). Gadolinium derivatives are some of the most employed contrast agents for MR-imaging, while, in molecular magnetism, Single Molecule Magnets (SMMs) containing lanthanide ions exhibited record energy barriers to the reversal of magnetization. However, despite several efforts have been done so far, it was not possible to completely understand how the electronic structure, and therefore the magnetic properties of the lanthanide ions, can be influenced by the surrounding ligands. The archetype compound where such effects have been initially claimed to play a subtle influence is the [Na{Dy(DOTA)(H$_2$O)}]·4H$_2$O complex [1]. Indeed, for this SMM, a dependency of the orientation of the principal magnetization axis of the ground Kramers’doublet was predicted by ab initio calculations [1]. This behaviour was investigated as a function of the rotation of the coordinating apical water molecule around the Dy-O$_w$ bond, and an abrupt change of the easy magnetization axis orientation of almost 90° was computed. Successive ab initio studies on the same compound evidenced a puzzling absence of angular dependence of the magnetic properties. To shed some light on these opposite results, the structural models used in literature [1,2] have been critically reviewed and the dependence of the easy axis orientation on the chosen model was highlighted and rationalized. Indeed, magneto-correlations together with a mapping of the electrostatic potential [3] generated by the ligands around the Dy(III) ion through a multipolar expansion has shown i) a non-negligible covalent contribution of the orbitals of water molecule ii) the easy axis’orientation is mainly determined by the electric quadrupolar moments of the ligands.

![Figure 1. Left: \{Dy(DOTA)(H$_2$O)\} complex. Dy, N and O are green, blue and red, respectively. Right: energetic variations envolving the ground and first excited Kramers' doublets as a function of the of apical water molecule’s angle of rotation $\alpha$ around Dy-O$_w$ bond.](image)

References
Isotopes to drive Lanthanide Single-Molecule Magnets

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Lanthanides play an important role in the field of molecular magnetism. Complexes based on these trivalent cations possess strong magnetic anisotropy and high magnetic moment, crucial for enhancing the energy barrier and therefore displaying a slow relaxation of their magnetization and magnetic hysteresis at low temperature, which are the properties making them interesting for their use as Single-Molecule Magnets (SMMs). 1

In the group, special attention has been paid to highly anisotropic dysprosium mononuclear-complexes as ideal candidates to retain the magnetic information in zero field. However, several examples 2,3 show the appearance of a fast relaxation time at sufficient low temperatures in comparison with the energy barrier. This is explained by the existence of intramolecular (hyperfine) and intermolecular (dipolar) interactions that make possible other relaxation pathways. For that reason, effort has been focused in understanding the relation between the magnetic relaxation effects and the contributing interactions, by playing with pure isotopic metal centers and magnetic dilutions. 4

Dysprosium is mainly constituted by four stable isotopes with different nuclear spin: 161Dy and 163Dy, with I=5/2, and 162Dy and 164Dy, with I=0. DyIII-based mononuclear complexes have been synthesized following the previous considerations: 1) isotopic enrichment in order to play with the hyperfine interactions, and 2) magnetic dilution to isolate the molecule from the neighboring complexes. A full dynamic study of the magnetic response has been carried out and the different results have been compared in order to distinguish a similar trend in the magnetic behavior. 4,5

Figure 1. (On the left) X-ray structure of DyIII-Complex with higher anisotropy tensor vectors; (On the right) Temperature dependence of the relaxation time (τ) at 0 Oe for both pure-isotopic (Dy) and magnetic diluted (Dy@Y) complexes.

Field-Induced Dysprosium Single-Molecule Magnet Based on a Redox-Active Tetrathiafulvalene-Based Triad

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Multi-functional molecular materials\(^1\) and in particular, Single Molecular Magnet (SMM) have emerged as new “smart” magnetic materials for future technology development, since their magnetic properties may be combined with other physical features such as luminescence,\(^2\) solvatomagnetism,\(^3\) redox ability,\(^4\) etc… In this context, lanthanide SMM featuring tetrathiafulvalene (TTF) ligands are of outmost importance, not only because the TTF oxidation properties are well identified and led to redox-active lanthanide complexes,\(^5\) but also because this large \(\pi\)-conjugated aromatic ligand provides a way to predict the orientation of the lanthanide magnetic easy axis within the crystal lattice.\(^6\) In this work, we will present the synthesis and the magnetic properties of a dinuclear Dy\(^{III}\) complex comprising a bridging Donor-Acceptor-Donor 1,10-phenanthroline-tetrathiafulvalene ligand (Figure 1) and featuring six independent Dy within the crystal asymmetric unit.\(^7\) This molecular system showed three resolved slow magnetic relaxations (Figure 1) which were assigned to a set of 3 magnetically different Dy centres thanks to SA-CASSCF/SI-SO calculations. Magnetic moment orientations were determined experimentally and theoretically, and were correlated to the molecular stacks within the crystal lattice.

![Figure 1. Molecular structure of one dinuclear complex and the out-of-phase component of the magnetic susceptibility](image)

References