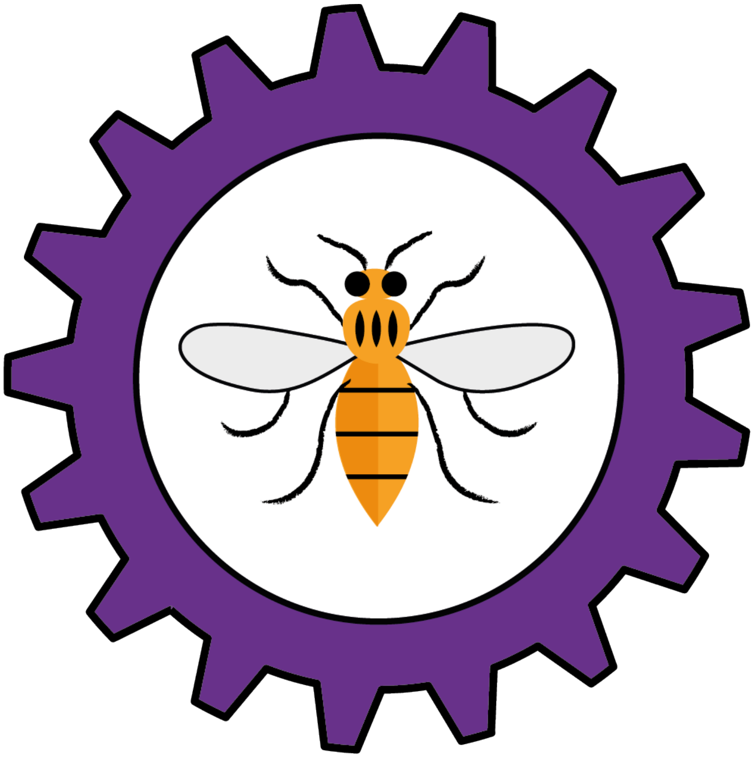

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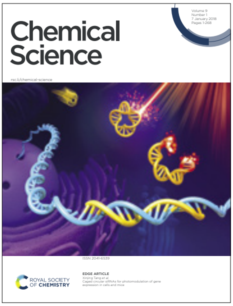

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Prof. Keith Murray: Olivier Kahn Lecture

New examples of lanthanide containing single molecule toroics (SMTs) and of d-f heterometallics

Keith Murray[1], Ivana Borilovic[1], Stuart Langley[2], Kuduva Vignesh[3], Gopalan Rajaraman[4], Jared Ashtree[5], Alessandro Soncini[5], Wolfgang Wernsdorfer[6]

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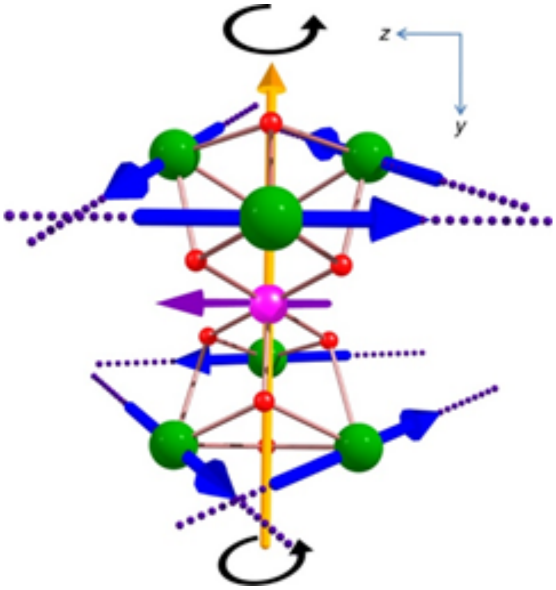
Abstract

Single molecule toroics (SMTs) are a sub topic of single molecule magnets. They generally consist of molecular rings (triangles, squares, hexagons) of lanthanide(III) ions, particularly of dysprosium, but there are recent examples of non-ring systems. The pioneering work by Powell, Chibotaru, *et al*. on μ_3-OH bridged Dy_3 triangles revealed the requisite molecular geometry, the directions of the magnetic moments on each Dy, the nature of magnetisation vs. field plots (often S-shaped) and relevant theory.[1] From a more applied perspective, SMTs offer possible uses in quantum information processing, high-density data storage and as nanoscale devices such as molecular spin valves and spin transistors.

A novel class of “double triangles” of type $[Dy^{III}_6M^{III}(OH)_8(o\text{-}tol)_{12}(MeOH)_5(NO_3)]\cdot 4MeOH$, where M^{III} = Cr,[2] Mn, Fe, Co, Al, o-tol = o-toluate, in which the M^{III} ion bridges the two Dy_3 triangles in a MO_6 coordination environment (see Fig.). The parent Cr^{III} system[2a] showed a rare ferrotoroidal arrangement of the toroidal moments on each triangle. Comparisons will be made[2b] to the new M^{III}-bridged materials which include paramagnetic Mn^{III} and Fe^{III} and diamagnetic Co^{III} and p-block Al^{III}. New theory has allowed simulation of their microSquid hysteresis loops.



1. (a) J. Tang, I. Hewitt, N. T. Madhu, G. Chastanet, W. Wernsdorfer, C. E. Anson, C. Benelli, R. Sessoli, A. K. Powell, *Angew. Chem. Int. Ed.,* 2006, **45**, 1729-1733. (b) L. F. Chibotaru, L. Ungur, A. Soncini, *Angew. Chem. Int. Ed.,* 2008, **47**, 4126-4129. 2. (a) K. R. Vignesh, A. Soncini, S. K. Langley, W. Wernsdorfer, K. S. Murray, G. Rajaraman, *Nat. Commun.*, 2017, **8**, 1023. (b) J. M. Ashtree, I. Borilović, K. R. Vignesh, A. Swain, S. H. Hamilton, Y. L. Whyatt, S. L. Benjamin, W. Phonsri, C. M. Forsyth, W. Wernsdorfer, A. Soncini, G. Rajaraman, S. K. Langley, K. S. Murray, *Eur. J. Inorg. Chem.* 2021, 435-444.

Prof. Ania Jayich: Plenary Lecture

Quantum sensing and imaging with diamond spins

Ania Bleszynski Jayich[1], Maxime Joos[1], Simon Meynell[1], Daipeng Yang[1], Dolev Bluvstein[1,2], Alec Jenkins[1,3], Susanne Baumann[4], Zhiran Zhang[1]
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Abstract

Solid state spin qubits, in particular the nitrogen vacancy (NV) center in diamond, offer a path towards truly nanoscale imaging of condensed matter and biological systems with sensitivity to single nuclear spins. Here I discuss our NV-based magnetic imaging experiments as applied to condensed matter systems, where we have imaged current flow patterns in graphene as well as skyrmions, nanoscale spin textures. A grand challenge to improving the spatial resolution and magnetic sensitivity of the NV is mitigating surface-induced quantum decoherence, which I will discuss in the second part of this talk. Decoherence at interfaces is a universal problem that affects many quantum technologies, but the microscopic origins are as yet unclear. Our studies guide the ongoing development of quantum control and materials control, pushing towards the ultimate goal of NV-based single nuclear spin imaging.

Prof. Daniella Goldfarb: Plenary Lecture

Characteristics of Gd(III) spin labels for the study of protein conformations

Daniella Goldfarb
Weizmann Institute of Science, Rehovot, Israel

Abstract

Gd(III) complexes are currently established as spin labels for structural studies of proteins using pulse dipolar electron paramagnetic resonance (PD-EPR) techniques. This has been achieved by the availability of medium- and high-field spectrometers, understanding the spin physics underlying the spectroscopic properties of high spin Gd(III) (S=7/2) pairs and their dipolar interaction, the design of well-defined model compounds and optimization of measurement techniques. In addition, a variety of Gd(III) chelates and labeling schemes has allowed a broad scope of applications. In this lecture, I will present a brief background of the spectroscopic properties of Gd(III) pertinent for effective PD-EPR measurements and focus on the various labels available to date. I will give a few specific examples of their use in PD-EPR applications and highlight the pros and cons of the labels for particular applications. At the end I will devote a few minutes to in-cell structural studies of proteins using Gd(III), which is an exciting new direction for Gd(III) spin labeling.

Prof. David Leigh: Plenary Lecture

Making the tiniest machines

David Leigh
University of Manchester, Manchester, United Kingdom

Abstract

Over the past few years some of the first examples of synthetic molecular level machines and motors—all be they primitive by biological standards—have been developed. These molecules respond to light, chemical and electrical stimuli, inducing motion of interlocked components held together by hydrogen bonding or other weak molecular interactions. Recently the first programmable systems have been developed, the forerunners of a new technological era of molecular robotics.

Perhaps the best way to appreciate the technological potential of controlled molecular-level motion is to recognise that nanomotors and molecular-level machines lie at the heart of every significant biological process. Over billions of years of evolution Nature has not repeatedly chosen this solution for achieving complex task performance without good reason. In stark contrast to biology, none of mankind's fantastic myriad of present day technologies exploit controlled molecular-level motion in any way at all: every catalyst, every material, every plastic, every pharmaceutical, every chemical reagent, all function exclusively through their static or equilibrium dynamic properties. When we learn how to build artificial structures that can control and exploit molecular level motion, and interface their effects directly with other molecular-level substructures and the outside world, it will potentially impact on every aspect of functional molecule and materials design. An improved understanding of physics and biology will surely follow.

"*Rise of the molecular machines*", *Angew. Chem. Int. Ed*. **54**, 10080 (2015) · "*Sequence-specific peptide synthesis by an artificial small-molecule machine*", *Science* **339**, 189 (2013) · "*An autonomous chemically fuelled small-molecule motor*", *Nature* **534**, 235 (2016) · "*Stereodivergent synthesis with a programmable molecular machine*", *Nature* **549**, 374 (2017) · "*Rotary and linear molecular motors driven by pulses of a chemical fuel*", *Science* **358**, 340 (2017) · "*A catalysis-driven artificial molecular pump*", *Nature*, in press (2021).

Prof. Hiroki Oshio: Quantum Design Lecture

Dynamic Behavior in Metal Complexes

Hiroki Oshio
University of Tsukuba, Taukuba, Japan. Dalian University of Technology, Dalian, China

Abstract

Molecules may have flexible structures with multi-accessible spin and/or oxidation states. In such molecules, the states can be switched by external stimuli and their changes are sometimes observed as dynamic behavior. Flexible molecules have been attached in intense research interests from the view points of fundamental chemistry and potential molecular devices. In this lecture, syntheses and dynamic behavior of single molecule magnet (SMM), spin crossover (SCO), and mixed valence (MV) complexes will be presented.

Invited and Contributed Talks

Functional Magnets Based on Cyanide-Bridged Metal Assemblies

Shin-ichi Ohkoshi
The University of Tokyo, Tokyo, Japan

Abstract

Metal complexes have been extensively studied due to their functionalities. We have reported various functionalities of cyanide-bridged metal assemblies, e.g., light-induced long-range magnetic ordering, ferroelectricity-ferromagnetism, humidity-induced magnetization, light-induced spin-crossover magnetic phenomenon, photoreversible light-induced spin-crossover phenomenon, spin-crossover-induced second harmonic generation, and photoswitching of magnetization-induced second harmonic generation. Herein, I will present cesium detection by THz-light and theoretical prediction of phase transitions, along with a brief introduction on photo-induced spin-crossover magnets.

If a heavy atom is encapsulated in a cage of a porous material, the atom should vibrate slowly and resonate with a low-frequency THz light. In cesium cyanide-bridged manganese-iron framework, the vibration mode of the Cs ion was found to be at 1.4 THz. Such characteristics lead to our proposal of a new non-contact THz-light detection method for Cs ions. In addition, we demonstrated that computer simulations, which combine first-principles electronic structure and phonon mode calculations, can predict a phase transition materials. Furthermore, we will show various multifunctional assemblies such as a single molecule magnet exhibiting superionic conductivity and luminescence thermometry properties.

[1] S. Ohkoshi, et al., ***Nature Chemistry***, 12, 338 (2020). [2] S. Ohkoshi, et al., ***Nature Photonics***, 8, 65 (2014). [3] S. Ohkoshi, et al., ***Nature Chemistry***, 3, 564 (2011). [4] S. Ohkoshi, et al., ***Acc. Chem. Res.***, 45, 1749 (2012). [5] S. Ohkoshi, et al., ***Nature Materials***, 3, 857 (2004). [6] S. Ohkoshi, et al., ***Scientific Reports***, 7, 8088 (2017). [7] Y. Xin, et al., ***J. Am. Chem. Soc.***, 141, 18211 (2019). [8] T. Yoshida, et al., ***Chemical Science***, 11, 8989 (2020). [9] J. Wang, et al., ***J. Am. Chem. Soc.***, 142, 3970 (2020). [10] M. Reczyński, et al., ***Angew. Chem. Int. Ed.***, 60, 2330 (2021).

Phonon-induced magnetic relaxation in Dy-based single-molecule magnets

Elena Garlatti[1,2], Alessandro Chiesa[1,2], Pietro Bonfà[1], Emilio Macaluso[1,2], Ifeany J. Onuorah[1], Vijay S. Parmar[3], You-Song Ding[4], Yan-Zhen Zheng[4], Marcus J. Giansiracusa[3], Daniel Reta[3], Tatiana Guidi[5], David P. Mills[3], Nicholas F. Chilton[3], Richard E. P. Winpenny[3], Paolo Santini[1,2], Stefano Carretta[1,2]
[1]Università di Parma, Dipartimento di Scienze Matematiche, Fisiche e Informatiche, Parma, Italy. [2]UdR Parma, INSTM, Parma, Italy. [3]Department of Chemistry, The University of Manchester, Manchester, United Kingdom. [4]Frontier Institute of Science and Technology (FIST), State Key Laboratory of Mechanical Behavior for Materials, MOE Key Laboratory for Nonequilibrium Synthesis of Condensed Matter and School of Science, Xi'an Jiaotong University, Xi'an, Shaanxi, China. [5]ISIS Facility, Rutherford Appleton Laboratory, Didcot, United Kingdom

Abstract

Understanding the relaxation dynamics of single-molecule magnets (SMMs) is crucial for their application as classical bits. Indeed, the possibility of single-molecule information storage pivots on the magnetic bistability of SMMs with high anisotropy barriers, displaying slow relaxation of the magnetization and molecular hysteresis cycles. However, molecules with similarly high barriers can display very different relaxation dynamics[1]. Hence, this must be explained by a different interplay between relaxation processes, like phonon-driven Raman and Orbach. The study of phonons in SMMs is therefore essential to gain a deeper insight in their magnetic relaxation.

Here we exploit inelastic neutron scattering to measure the phonon Density of States (pDOS) of high-barrier Dy-based systems with very different relaxation dynamics: the record-compound dysprosocenium[2] and two other systems with much worse performances as SMMs, $[Dy(^{t}BuO)Cl(THF)_5][BPh_4]\cdot 2THF$[3] and $[Dy(Mes^{*}O)_2(THF)_2Br]$[4]. In particular, these are the very first SMMs for which the reliability of DFT in calculating the pDOS is demonstrated by comparisons with experimental data[5,6]. We also combine the so-obtained vibrational properties and relaxation measurements with a new theoretical model for the relaxation dynamics of SMMs[5], able to give more physical insight than phenomenological models, but not as demanding as fully ab-initio calculations. Our model explains the temperature-dependence of the relaxation rates of the three compounds, demonstrating that an efficient Raman mechanism considerably worsen the performances of high-barrier SMMs[5,6]. The systematic comparison of these compounds also represent an essential study for the design of higher-performing SMMs.

1. M.J. Giansiracusa, *et al.* Chem. Commun., 2019, 55, 7025.

2. C.A.P. Goodwin, *et al.* Nature, 2017, 548, 439.

3. Y.-S. Ding, *et al.* Nat. Commun., 2018, 9, 3134.

4. V.S. Parmar, *et al.* Chem. Eur. J., 2020, 26, 7774.

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Quantum control of spin in diamond and its application

Jiangfeng Du
University of Science and Technology of China, Hefei, China

Abstract

The science of quantum control lies at the heart of modern physics and promises advanced information processing and sensing technologies. The nitrogen-vacancy in diamond may offer these functionalities because it possesses an atomic-scale electronic spin state that can be used as an individually addressable, solid-state qubit, even at room temperature. In this talk, I will present our recent advancement on controlling this spin system, applying for studying particle physics, and nano-scale magnetic resonance spectroscopy and imaging.

Homo- and heterometallic lanthanide complexes as a single-ion/single-molecule Magnets

Vadapalli Chandrasekhar
Indian Institute of Technology Kanpur, Kanpur, India. Tata Institute of Hyderabad, Hyderabad, India

Abstract

Single molecule magnets (SMMs) are metal complexes that contain one or more paramagnetic metal ions. These can be magnetized below certain temperatures and can retain the magnetization below these temperatures for an indefinite period. This talk will give a brief introduction about the design strategies of SMMs emphasizing the role of magnetic anisotropy in the design and assembly of such complexes. The talk would focus on heterometallic complexes as well as mono- and dinuclear lanthanide complexes. The SMM magnetic properties of these complexes would be presented.

1. Kalita, P.; Ahmed, N.; Bar, A. K.; Dey, S.; Jana, A.; Rajaraman, G.; Sutter, J-P.; Chandrasekhar, V. *Inorg. Chem*. 2020, 59, 6603-6612.
2. Acharya, J.; Ahmed, N.; Flores Gonzalez, J.; Kumar, P.; Cador, O.; Singh, S. K.; Pointillart, F.; Chandrasekhar, V. *Dalton Trans*. **2020**, *49,* 13110-13122.

Coherent Manipulation of an Organometallic Electronic Spin Qubit coupled to a Nuclear Qudit

Matteo Atzori[1,2], Elena Garlatti[3], Giuseppe Allodi[3], Simone Chicco[3], Alessandro Chiesa[3], Andrea Albino[1], Roberto De Renzi[3], Enrico Salvadori[4], Mario Chiesa[4], Stefano Carretta[3], Lorenzo Sorace[1]
[1]Dipartimento di Chimica "U. Schiff" Università di Firenze, Sesto Fiorentino, Italy. [2]Laboratoire National des Champs Magnetiques Intenses, Grenoble, France. [3]Dipartimento di Scienze Matematiche, Fisiche e Informatiche Università di Parma, Parma, Italy. [4]Dipartimento di Chimica Università di Torino, Torino, Italy

Abstract

A distinctive feature of molecular spin systems, compared to other consolidated platforms for quantum computing (QC), is the ease of obtaining single quantum objects featuring more than two levels, so-called qudit. Their multi-level structure can be characterized in detail by exploiting different experimental and theoretical techniques and states encoded in such levels can be manipulated by electromagnetic pulses in the microwave or radiofrequency ranges. This capability of encoding and manipulating the state of a qudit places molecular spins among the most promising platforms for the actual realization of a quantum computer. Indeed, the additional levels available within each logical unit could significantly simplify the implementation of several QC codes, making it potentially achievable in the short term.

We report here[1] a comprehensive characterization of a 3*d* organometallic complex, [V(Cp)$_2$Cl$_2$], (Cp=cyclopentadienyl) which can be considered as a prototypical multi-level nuclear qudit (nuclear spin I = 7/2) hyperfine-coupled to an electronic qubit (electronic spin S = 1/2). This system was chosen in virtue of its uncommon air stability, the possibility of easily obtaining single crystal of relevant size, and the ease of dilution in a diamagnetic isostructural analogue, [Ti(Cp)$_2$Cl$_2$]. By combining complementary magnetic resonant techniques such as pulsed electron paramagnetic resonance (EPR) and broadband nuclear magnetic resonance (NMR), we extensively characterize its Spin Hamiltonian and its electronic and nuclear spin dynamics. Moreover, we demonstrate the possibility to manipulate the qubit-qudit multi-level structure by resonant microwave and radiofrequency pulses, driving coherent Rabi oscillations between targeted electronuclear states. These properties make [V(Cp)$_2$Cl$_2$] a promising candidate to implement qudit-based quantum algorithms and QEC schemes.

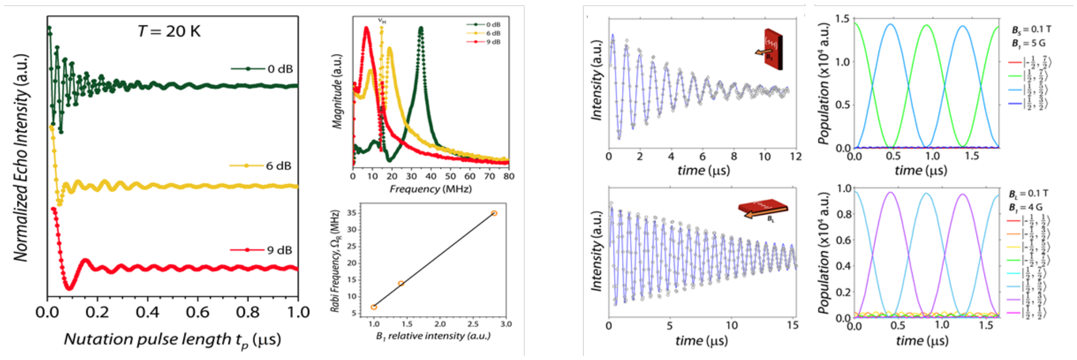

***Figure 1**: Electronic (left) and nuclear (right) Rabi oscillations in [V(Cp)$_2$Cl$_2$]*

[1] M. Atzori et al. *submitted*

Searching for a minimum photon energy quantum for spin state switching in copper-nitroxide based molecular magnets

Sergey Veber[1], Sergey Tumanov[1], Anatoly Melnikov[2,1], Kseniya Maryunina[1], Yaroslav Getmanov[3], Oleg Shevchenko[3], Victor Ovcharenko[1], Matvey Fedin[1]
[1]International Tomography Center SB RAS, Novosibirsk, Russian Federation. [2]Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russian Federation. [3]Budker Institute of Nuclear Physics SB RAS, Novosibirsk, Russian Federation

Abstract

Copper(II)-nitroxide based complexes $Cu(hfac)_2L^R$ ("breathing crystals") exhibit spin-crossover-like (SCO-like) behavior: they can be switched between two magnetostructural states by temperature, light or pressure [1]. Among these external stimuli, using light is, perhaps, most promising for potential applications, and long-lived photoinduced states at cryogenic temperatures have been experimentally evidenced, similar to LIESST in classical iron-based SCO compounds. However, the absorption spectrum of copper-nitroxide compounds is drastically different. If iron-based SCO compounds most often feature well-defined d-d or charge-transfer bands in UV-vis region, copper-nitroxide magnets show poorly resolved broad bands spreading at least to the near IR region (up to ~2000 nm = 5000 cm^{-1}). At the same time, ultrafast photoswitching (<50 fs) and excited state relaxation point out at existence of low-lying excited states [2]. These specifics altogether imply that a very low-energy radiation quanta, far-IR-to-THz range, can possibly induce photoswitching of copper-nitroxide magnets.

Herewith, we report that as low energy as mid-IR is sufficient to switch the breathing crystal $Cu(hfac)_2L^{Pr}$ from ground to excited long-lived state, which was observed at temperature below 10 K with FTIR or EPR detection. Furthermore, Novosibirsk Free Electron Laser (NovoFEL) provides unique opportunity of tunable excitation within 1040-1180 cm^{-1}, yielding solid confirmations of the low-energy photoswitching. Thus, we show that the excitation energy necessary for photoswitching of breathing crystals can be drastically downscaled from UV-vis to mid-IR region (~20 times). At the moment, this is a rather fundamental finding; however, decent advantages of using low-energy quanta may arise in potential applications, as will be considered in the talk.

This work was supported by RSF 17-13-01412.

[1] Coord. Chem. Rev. 289-290 (2015) 341; Angew. Chem. Int. Ed. 47 (2008) 6897.

[2] Angew. Chem. Int. Ed. 40 (2014) 10636; Inorg. Chem. 56 (2017) 11729.

Magneto-Structural Correlations in a Series of Dysprosium Metallocenium Cations and a Neutral Linear Terbium Metallocene Exhibiting High Temperature Magnetic Blocking

K Randall McClain[1], Benjamin Harvey[1], Colin Gould[2], Jeffrey Long[3,4]
[1]Naval Air Warfare Center Weapons Division, Research Department, Chemistry Division, Ridgecrest, USA. [2]Department of Chemistry, Princeton University, Princeton, USA. [3]Department of Chemistry and Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, USA. [4]Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, USA

Abstract

A series of $[DyCp^{x}_{2}]^{+}$ complexes, in which subtle variation of the cyclopentadienyl substituents allows for fine tuning of the ligand field parameters was sought to elucidate structure property relationships for this new class of lanthanide single-molecule magnets. The metallocenium cations $[Dy(Cp^{iPr4R})_2]^+$ (R = H, Me, Et, iPr), which were synthesized by iodide abstraction from corresponding iodide intermediates $Dy(Cp^{iPr4R})_2I$, show a gradual shift in Dy-Cp distances and Cp-Dy-Cp angles across the series. These subtle structural changes are accompanied by large changes in SMM performance, with $[Dy(Cp^{iPr4Me})_2]^+$ achieving the highest blocking temperatures. Alternatively, chemical reduction of the iodide intermediates $Ln(Cp^{iPr5})_2I$ (Ln = Tb, Dy) with KC_8 results in isolation of the neutral linear metallocenes $Ln(Cp^{iPr5})_2$ (Ln = Tb, Dy); the first examples of such species for these elements. Experimental and computational investigation indicates that the extra electron resides in a 6s5d hybrid orbital which enforces the linear geometry. When comparing the neutral metallocenes with their cationic counterparts $[Ln(Cp^{iPr5})^2]^+$ (Ln = Tb, Dy), reduction has strongly opposing effects for Dy and Tb. This results in $Tb(Cp^{iPr5})_2$ having the best performance for any non-dysprosium SMM, with a 100-s blocking temperature of 52 K and thermal barrier of 1205 cm^{-1}.

Spin state transitions as a route to magnetoelectric coupling

Magdalena Owczarek[1], Minseong Lee[2], Wanyi Nie[1], Vivien Zapf[2]
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Abstract

Although known for decades, materials undergoing spin state transitions (SSTs) have recently garnered renewed attention due to the discovery that the transition can provide an attractive alternative route to magnetoelectric coupling. The coupling is attributed to the large involvement of the lattice which, when distorted from the SST, can give rise to the appearance of electric dipoles that can couple to the magnetic field. This discovery has opened a new field of research and, by now, several SST systems with magnetoelectric coupling have been reported[1–4] with operating temperatures of 48–200 K[1,2,3] and 333–338 K[4]. Here we summarize the properties of two Mn(III) compounds[2,3] by way of introduction and we present preliminary results gathered from our efforts to move the magnetoelectric coupling phenomenology closer to room temperature.

[1] Zhang, X.; Palamarciuc, T.; Letard, J. -F.; Rosa, P.; Lozada, E, V.; Torres, F.; Rosa, L. G.; Doudin, B.; Dowben; P. A., The spin state of a molecular adsorbate driven by the ferroelectric substrate polarization, *Chem. Commun*. **2014**, 50, 2255.

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Emerging Spin Physics at Metallo-Molecular Interfaces

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Abstract

When depositing carbon molecular thin films on metallic layers <1 to 10 nm thick, charge transfer and orbital re-hybridisation may lead to changes in the spin physics of both materials. Some of the mechanisms at play on the hybrid system include the formation of an asymmetric magnetoelectric dipole (dubbed π-anisotropy), magnetic hardening and enhanced spin orbit coupling. These result in novel magnetic behaviour, such as spontaneous magnetic ordering in para- or diamagnetic 3d metallo-fullerene interfaces, large magnetic energy products in conventional ferromagnets, spin-singlet to triplet Cooper pair conversion in superconducting multilayers and an increase in the spin Hall angle of heavy metals. These effects will play a key role in the electronic and spin properties of molecular films when grown on, or in contact with metals and other substrates, e.g. when using electric contacts, the response of hybrid spintronic devices and light magnetic metamaterials. Here, I will review some of these results and the potential for future developments.

Electron Spin Echo Envelope Modulation at Clock Transitions in Molecular Spin Qubits

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Abstract

The clock transition (CT) has been shown to be a successful strategy to protect against decoherence for qubits. In this study, we present a joint experimental and theoretical study of Electron Spin Echo Envelope Modulation (ESEEM) around the clock transition in molecular spin qubits. Experimentally, ESEEM spectra have been measured for HoW10, and suppression of this modulation near the CT is clearly demonstrated. To understand this, we build a simple model Hamiltonian of a central spin with an avoided crossing coupled to a nuclear spin bath with a finite number of spins. ESEEM is simulated by exact quantum time evolution, and important experimental characteristics can be captured in simulations. Due to the quadratic energy dependence on magnetic field at the avoided crossing, fluctuations of the spin bath that linearly couple to the central spin do not affect the dynamics of the central spin. Consequently, hyperfine coupling effectively vanishes at the CT, which leads to diminished ESEEM and enhanced coherence.

Polarization and Magnetization Switching via Charge Transfer in Molecular Crystals

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Abstract

The design and synthesis of novel molecular compounds, whose physical properties can be controlled through external stimuli, have attracted considerable attention [1]. Polarization switching mechanism is used in various devices such as pyroelectric sensors and memory devices. The change in polarization mostly occurs by ion displacement. The development of materials, whose polarization switches via electron transfer in order to enhance operation speed, is a challenge [2-4]. We devised a synthetic and crystal engineering strategy that enables the selective synthesis of a [CrCo] heterometallic dinuclear complex with a polar crystal structure, wherein polarization changes stem from intramolecular charge transfer between Co and the ligand [2]; $\mathrm{Co^{III\text{-}LS}}$–$\mathrm{dhbq^{3-}}$–$\mathrm{Cr^{III}}$ D $\mathrm{Co^{II\text{-}HS}}$–$\mathrm{dhbq^{2-}}$–$\mathrm{Cr^{III}}$ (LS = low spin, HS = high spin). The introduction of chiral ligands was paramount to the successful polarization switching in the valence tautomeric compound. Mixing Cr and Co complexes with enantiopure chiral ligands resulted in the selective formation of pseudosymmetric [CrCo] heterometallic complexes. Photoinduced polarization switching was found to have a time constant of 280 fs by ultrafast pump–probe spectroscopy [3].

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Rationalization of the Exchange-Coupling Direction for Mitigating the Quantum Tunneling of Magnetization

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Abstract

Quantum tunneling of magnetization is probably the biggest enemy for obtaining high-performance single-molecule magnets. Though we knew that exchange-coupling can generate a bias field for mitigating the quantum tunneling effect we much overlooked the importance of the exchange-coupling directions. In this talk, we present a dimeric dysprosium(III) complex which has a collinearly aligned exchange-coupling direction and the magnetic anisotropic axes of two pentagonal-pyramidal dysprosium(III) ions, so that the quantum tunneling effect is much reduced compared to those non-collinearly aligned dimeric analogues. This work demonstrates unambiguously that to design a better polynuclear single-molecule magnet it requires the collinearity of the exchange-coupling direction and the magnetic principle axes of the metal centers.

Photoswitchable single chain magnet

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Abstract

Magnetic bistable materials are promising for application in switches and memory devices. It has remained challenging however to devise such systems with switching between magnetic states fast enough to be useful for information storage and processing. Magnetic hysteresis are comparable to elementary binary units (bits). In this work, spin-crossover Fe(II) ions were linked with $[W(V)(CN)_8]^{3-}$ building blocks in alternating W(V)–Fe(II) coordination polymer chains. Under 808-nm-light irradiation magnetic interaction between the paramagnetic high-spin Fe(II) centres and the W(V) centres lead to single-chain magnets with magnetic hysteresis. The paramagnetic high-spin and diamagnetic low-spin states of Fe(II) ions can be interconverted by reversible light-induced excited spin state trapping by alternating between 808- and 473-nm light irradiation. This resulted in the interconversion of the system between a single-chain magnet and a single-molecule one, and also switched the magnetic hysteresis on and off, respectively.

Magnetoelectric effect by the field-induced magnetic quadrupole in the piezoelectric paramagnetic complex

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Abstract

The linear ME effect is known to occur in materials with spontaneously broken time-reversal and space-inversion symmetries, such as multiferroic materials. However, even in a paramagnetic material, breaking of the time-reversal symmetry by *H* can cause the second order ME effect, if its crystal structure is non-centrosymmetric [1]. In this study, we focus on the ME effect in the paramagnetic piezoelectric complex [Mn^{III}(taa)] (H$_3$taa: tris(1-(2-azolyl)-2-azabuten-4 yl)amine). The crystal of [Mn^{III}(taa)] belongs to the piezoelectric cubic point group T_d without the centrosymmetry [2]. The free energy *F* of the second order ME effect of the paramagnetic system with T_d symmetry is written as:

$$F = -\beta(H_xH_yE_z + H_yH_zE_x + H_zH_xE_y) \quad -(1)$$

Here, is the ME susceptibility. Differentiating this *F* by the *E* and *H*, the *P* and *M* are obtained. When the *H* is applied along the [001] axis, the *P* and the *M* are expressed as:

$$\begin{pmatrix} P_x \\ P_y \end{pmatrix} = \begin{pmatrix} 0 & \alpha \\ \alpha & 0 \end{pmatrix} \begin{pmatrix} H_x \\ H_y \end{pmatrix} = \tilde{\alpha} \begin{pmatrix} H_x \\ H_y \end{pmatrix} \quad -(2)$$

$$\begin{pmatrix} M_x \\ M_y \end{pmatrix} = \tilde{\alpha} \begin{pmatrix} E_x \\ E_y \end{pmatrix} \quad -(3).$$

Here, = H_z. The tensor has the same form with the ME tensor, which originates from the q_{xy} type magnetic quadrupole. The magnetic quadrupole is one of the representatives of odd parity magnetic multipole moments, which cause the linear ME effect [3]. Therefore, the second order ME effect in [Mn^{III}(taa)] is considered to originate from the field-induced magnetic quadrupole. To confirm the second order ME effect owing to the field-induced magnetic quadrupole, we have measured the *E*-induced *M* expressed by eq. (3). Figure 1 shows the *E*-induced *M* in the magnetic field parallel to the [001]. The *M* appears perpendicular to the *E*. This behavior agrees with eq. (3). Therefore, the second order ME effect in the T_d point group can be considered to come from the *H*-induced magnetic quadrupole.

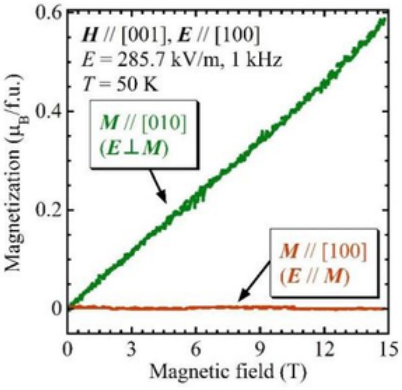

Figure 1. *E*-induced *M* in the *H* // [001]

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How Dimerization of Organic Radicals Leads to Interesting Magnetic Behaviour

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Abstract

Cyclic organic and main-group radicals in which the unpaired electron is delocalized in an extended π-system tend to be thermally and chemically stable, allowing isolation and storage as pure species for extended periods. These planar π-radicals also often exhibit an interesting type of pairwise co-facial interaction, dubbed "pancake bonding." The exacting geometric requirements and the typical enthalpies of pancake bonds are similar to those of hydrogen bonds. Like H-bonds, pancake bonds can be employed to direct crystal packing and design supramolecular architectures.

Recently, we have discovered a series of coordination complexes incorporating thiazyl-based paramagnetic ligands that exhibit pancake bonds in the solid state, but that also undergo crystal-to-crystal phase transitions that rupture the pancake bonds and thus switch the magnetic properties.[1] This has led us to further explore the parallels between H-bonding and pancake bonding at a number of levels, including the design of a thiazyl radical (HbimDTDA) that is capable of both.[2]

Current progress on reversible crystal-to-crystal switching involving rupture of pancake bonds will be presented, with a specific focus on the HbimDTDA system in which a balance between pancake bonding and specific sigma-hole interactions appears to be a primary factor defining the interplay between the diamagnetic and paramagnetic states. The HbimDTDA system exhibits thermal hysteresis of the magnetic susceptibility, associated with the reversible (cyclable) single-crystal-to-single-crystal phase transition. The cooperativity necessary for hysteresis is imparted by a dense network of short intermolecular contacts, including H-bonds.

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Van der Waals 2D lanthanide-based materials: nanosheets and on-surface chemistry

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Abstract

A van der Waals 2D material based on simple carboxylato ligands and lanthanoid ions will be presented. Microwave assisted synthesis has been used to obtain [Ln(MeCOO)(PhCOO)$_2$]. The van der Waals interactions between nanocheest have been calculated for the Dy analogue and are similar to those in graphene.

The material can be easily delaminated into nanosheets with large lateral sizes of several micrometers that can be observed by TEM. We will also report on-surface chemistry on silanized silicon wafers. The nanosheets are anisotropic and can be grown onto a functionalized silicon wafer with homogeneous coverage of the whole surface.

Molecular Magnets: Challenges for Electronic Structure and Some Departures from Simplicity

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Abstract

The size range, possible applications, and fundamental interest of molecular magnets challenges scientists to understand how 50-100 nuclei and 200-1000 electrons can exhibit such simple collective behavior. For example, quantum tunnelling of magnetization, which occurs in broken-spin-symmetry magnetic molecules illustrates the power of density-functional-based pictures for predicting both the magnetic strength of molecules snf the magnetic fields at which quantum tunnelling occurs. Alternatively, the spin-electric effect explicitly challenges the notion that single-determinantal theories can describe this phenomenon. I will review previous work on the Cu_3 molecular magnet and show how the combination of broken symmetry density-functional theory, with simple self-interaction corrections and spin-orbit inclusion, can be used to derive three-spin Heisenberg Hamiltonians that describe the Dzyaloshinskii-Moriya induced splitting of degenerate low-energy Kramers doublets into S=1/2 chiral and anti-chiral pairs. In a more recent example, the $Fe_3O(NC_5H_5)_3(O_2CC_6H_5)_6$ molecule is the first possible spin-electric system based upon spin 5/2 centers. From standard density-functional methods we show that the spin-electric behavior of this molecule may be complicated by the presence of energetically competitive reference states with both high and low local spins (S=5/2 vs. S=1/2) on the Fe^{3+} ions. We provide spectroscopies to deduce the presence of both high- and low- spin states and discuss how the presence of low-energy on-metal-ion excitons can be used to control the magnetism of molecular magnets. A brief summary of other on-metal-ion excitons that we have found to occur in the Mn_3 and Mn_{12}-Acetate molecule will also be provided.

Supported by the M^2QM Energy Frontier Research Center, Grant #: DE-SC0019330, Grant # DE-SC0018331, Texas STARS, & the C. Sharp Clark Cook Physics Chair Endowment.

Quantum Tunnelling of the Magnetisation in Isotopically Enriched Dysprosium Dimers

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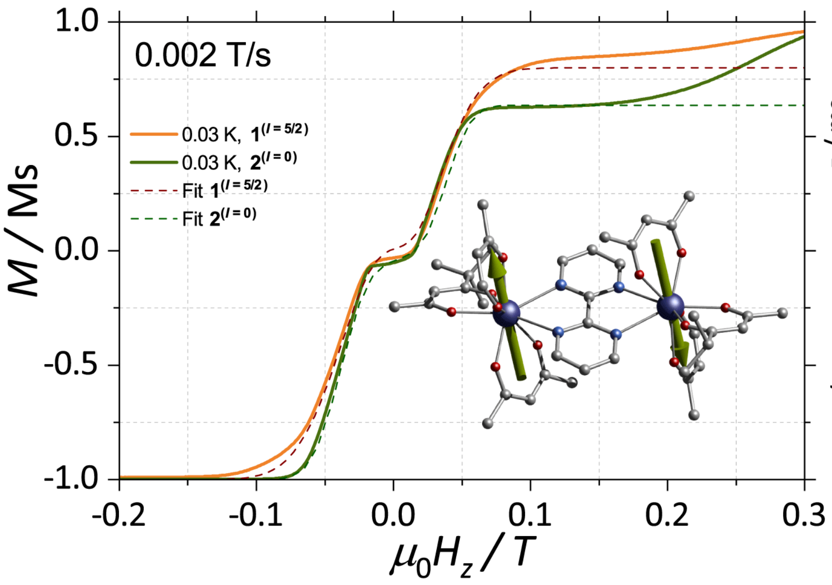
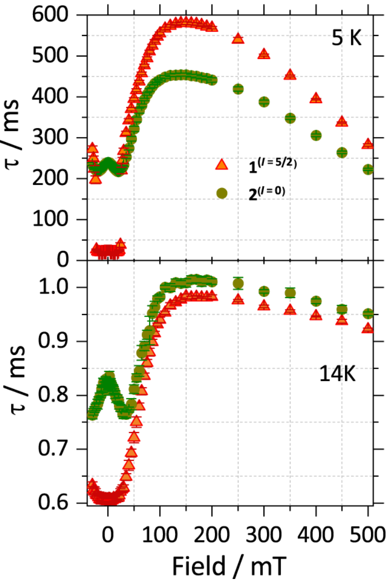
Abstract

Quantum effects play an important role in the magnetic properties of lanthanide Single-Molecule Magnets and are of utmost importance for their possible integration in futuristic applications. An example of the is the Quantum Tunnelling of the Magnetisation (QTM): while QTM is considered a nuisance for data storage devices since it leads to the loss of information, QTM is an essential pre-requisite for the read-out and manipulation of the nuclear states in Quantum Information Processing schemes, as demonstrated in the realization of the Grover's Quantum algorithm. Hence, the comprehension of quantum properties is very important for the implementation of SMMs in practical applications.

In this talk we describe the structure and magnetic properties of two isotopologue dysprosium dimers, i.e. $[(^{163}\mathrm{Dy(tmhd)}_3)_2(\mathrm{bpym})]$ and $[(^{164}\mathrm{Dy(tmhd)}_3)_2(\mathrm{bpym})]$ (tmd = tris(tetramethylheptanedionato) and bpym = bipyrimidine), where the nuclear spin presence or absence clearly affects the relaxation of characteristics of the systems. Through µ-SQUID studies at milli-Kelvin temperatures and alternating current SQUID magnetic measurements, we find significant differences in the magnetic behaviour of both complexes. Whereas simulation of the µ-SQUID hysteresis loops at 30 mK reveal that the tunnelling rates are not affected by the presence of nuclear spin, we find that nuclear spins facilitate the coupling to the phonon bath, hence, enhancing the direct relaxation process; observation reflected in the temperature and field dependence of the relaxation rates.





Optically Gating Spin-States at the Single Molecule Level

Natia Frank
University of Nevada-Reno, Reno, NV, USA

Abstract

Controllable quantum systems are under active investigation for quantum computing, secure information processing, and nonvolatile memory. The optical manipulation of spin quantum states provides an important strategy for quantum control with both temporal and spatial resolution. Challenges in increasing the lifetime of photoinduced magnetic states at T > 200 K have hindered progress toward utilizing photomagnetic materials in quantum device architectures. 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 (λexc = 550 nm) of a spirooxazine cobalt−dioxolene complex induces photo- isomerization of the ligand that in turn triggers a reversible intramolecular charge-transfer coupled spin- transition process at the cobalt center. The generation of photomagnetic states through conversion between a low-spin Co(III)−semiquinone doublet and a high-spin Co(II)−bis-semiquinone sextet state has been demonstrated in both solution and the solid state and is described as a photoisomerization-induced spin−charge excited state (PISCES) process. The high transition temperature (325 K) and long-lived photoinduced state (τ = 10 s at 300 K) are dictated by the photochromic ligand. Theory and ultrafast spectroscopy provides effective modelling of the phenomenon and long-term strategies to further modulate the lifetimes of photomagnetic states for quantum information technologies at the single molecule level.

Single Atom and Molecule Electron Spin Resonance using a Scanning Tunneling Microscope

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Abstract

In this talk, I will present the recently realized combination of electron spin resonance and scanning tunnelling microscopy (ESR-STM)[1], which allows us to address single atoms and molecules on surfaces with unprecedented energy resolution. This novel technique can be used to sense the magnetic coupling between atomic spin centers [2] and to establish magnetic resonance imaging on the atomic scale [3]. It also grants access to the hyperfine interaction between the electron and nuclear spin of different atomic species [4].

Moreover, we could extend this technique recently to electron spin resonance on individual molecules [5]. Here, I will show the behavior of individual iron-phtalocyanine molecules (FePc), which form a S=1/2 when adsorbed on a MgO/Ag surface. Utilizing the high energy resolution of ESR-STM we can elucidate the subtle interplay of exchange and dipolar interaction between different molecules. It allows us also to apply coherent manipulation schemes utilizing pulsed ESR schemes [6]. This opens up a path towards quantum information processing using atomic building blocks, including atoms and molecules.

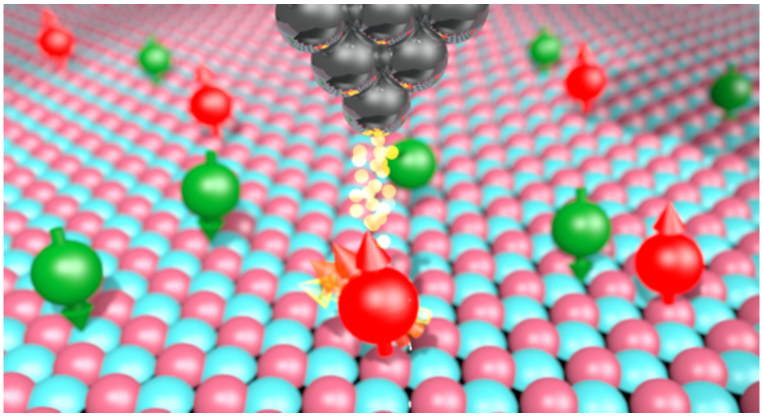

Fig: Artistic representation of single spins on surfaces probed by a scanning tunnelling microscope

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Role of magnetic anisotropy in paramagnetic relaxation enhancement

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Abstract

Nuclear magnetic resonance (NMR) of paramagnetic metal complexes remains a challenging but highly informative analytical technique. The major difficulty is coming from the paramagnetic relaxation enhancement (PRE) that broadens NMR lines beyond detection for nuclei in the vicinity of the paramagnetic centre. However, in some paramagnetic metal complexes the relaxation enhancement is not as dramatic, as shown by a recent example of measured ^{1}H NMR signal of a proton directly attached to an intermediate spin iron(II) at −3560 ppm at 295 K.[1]

We have previously demonstrated that magnetic anisotropy alters both Curie and dipolar relaxation mechanisms in lanthanide complexes especially at low magnetic field.[2] In this work we analyse how magnetic anisotropy alters magnetic field dependence of the PRE. Using *ab initio* theory, Nuclear Magnetic Resonance (NMR) and advanced Electron Paramagnetic Resonance (THz-EPR), we analyse in details PRE and shift data in ^{tBu}*(PNP)Fe–H* complex and show how zero-field splitting can slow down dipolar relaxation (Figure 1).

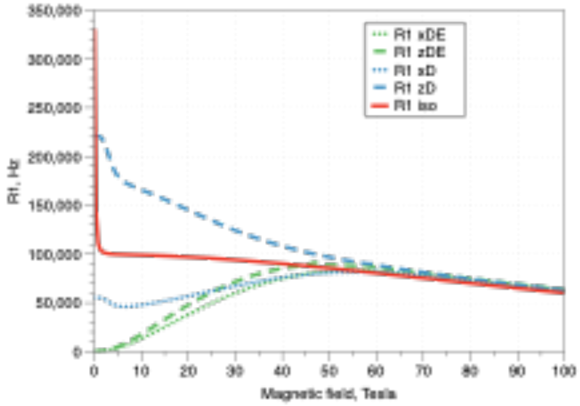

Figure 1. Simulated dipolar longitudinal relaxation rates (R_1) as a function of the magnetic field. The model for a point paramagnetic center with $S = 1$ and ^{1}H located 1.57 Å away either along x-axis (dotted lines) or z-axis (dashed lines). The relaxation profile when no ZFS is present is shown in ***red****, the case of axial ZFS with $D = -56\ \mathrm{cm^{-1}}$ is shown in blue and rhombic ZFS with $E = -13.8\ \mathrm{cm^{-1}}$ is shown in green.*

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Triplet biradical states of phthalocyaninato-terbium(III) multiple-decker complexes captured by paramagnetic NMR analyses

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Abstract

Construction of the extended π-system is one of the main topics in synthetic chemistry. There are two kinds of π-extension, one of which is in-plane extension, and the other being longitudinal extension, so called π-π stacks. Phthalocyaninato multiple-decker complexes composed by lanthanoid and cadmium ions are one rare examples of stacked π-oligomers.[1-2] In addition, oligomers containing terbium ions as the lanthanoid ions are known to show distinct magnetic anisotropy. In this presentation, we will report unusual biradical states and decrease in the magnetic anisotropy of oxidized oligomers proofed by means of ^{1}H NMR analyses and DFT calculations. Because of the strong magnetic anisotropy of Tb(III), the ^{1}H signals show large paramagnetic shift down to -100 ppm. Ligands oxidations results in the decrease in amounts of the paramagnetic shifts, indicating the decrease in the magnetic anisotropy. In addition, there is a large discrepancy between calculated and estimated ^{1}H signals in +2e charged tetramer and pentamer, indicating the triplet biradical states which act as the additional spin source to induce unusual paramagnetic shift. [3]

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Enriching single-ion magnetism: Role of Symmetry and axiality in mononuclear lanthanide complexes

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Abstract

The current frenzy in the field of SMMs is driven by a better understanding of the effects of crystal field (CF) and molecular symmetry on the magnetic properties, especially in the case of mononuclear paramagnetic complexes, apart from other controlling factors. This has led to the advent of highly anisotropic single-ion magnets (SIMs) with magnetic blocking temperatures and anisotropic energy barriers. This talk would summarize our recent research in the light of the emergence of the importance of CF and symmetry in 4f ion based single-ion magnets (SIMs), especially in the context of SIMs with D_{5h} symmetry, apart from commenting on the synthetic efforts adopted to place these metal ions in unusual coordination geometries.

The authors thank Prof. G. Rajaraman and his group for an active collaboration in modelling our systems.

Magnetic Archimedean Tessellations in Coordination Solids

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Abstract

The combination of moderate to strongly reducing metal ions and π-conjugated ditopic linkers has proven to be a feasible approach to realise e.g. electrically conductive magnets and room-temperature molecule-based magnets [1]. Hitherto, these approaches have essentially only focussed on the 3d transition metal ions. In this presentation, we will show how reducing p- and f-block metal ions may be employed to activate ligand redox-activity in a family of magnetic 2D coordination solids. Notably, the higher coordination numbers of the f-block ions result in a variety of structures with 2D tessellations constructed from 5-fold nodes [2]. For instance, the assembly of *trans*-$[\mathrm{LnI_2}]^{+/0}$ (Ln = lanthanide) with closed-shell and open-shell aromatic amines leads to metal-organic framework structures complying with the Archimedean tessellations (= tessellations made from more than one type of polygon; see example in the figure below). Notably, such metal-organic structures have previously only been observed as fragile monolayers on metallic surfaces, that were thought to be necessary for the planarization of the material [3]. These Archimedean tessellation structures verge on quasicrystallinity, and our synthetic strategy may provide a route to elusive quasiperiodic metal-organic frameworks. In this presentation, we will furthermore discuss the magnetic properties of these materials and discuss the prospects for frustrated behaviour in magnetic Archimedean tessellations.

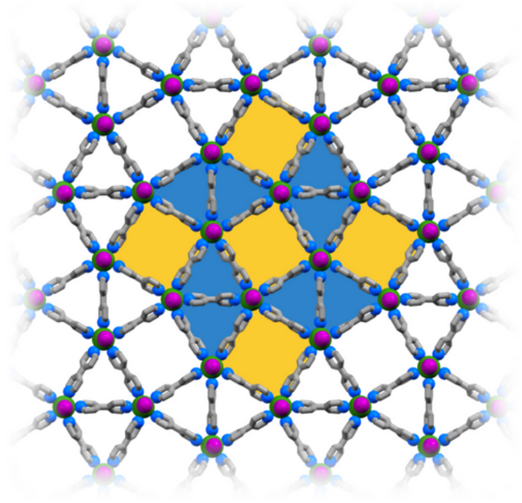

Figure: Single-crystal X-ray structure of $\mathrm{Dy^{III}I_2(bipy)_{3/2}(bipy^{\bullet -})_1}$ highlighting the ideal snub square tiling structure.

[1] See for instance: (a) Perlepe et al. *Science* **2020**, *370*, 587; (b) Pedersen et al. *Nat. Chem.* **2018**, *10*, 1056. [2] (a) Voigt et al. *Nat. Commun.* **2020**, *11*, 4705; (b) Chen et al. *ChemRxiv*, **2021**, DOI: 10.26434/chemrxiv.14529090.v1. [3] (a) Écija et al. *Proc. Natl. Acad. Sci.* **2013**, *110*, 6678; (b) Urgel et al. *Nat. Chem.* **2016**, *8*, 657.

There is more to be done with Chain Magnets.

Miguel Novak[1], Rafael Cassaro[2], Maria Vaz[3]
[1]Physics Institute, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil. [2]Chemistry Institute, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil. [3]Chemistry Institute, Fluminense Federal University, Niterói, Brazil

Abstract

Magnetic Chains have been interesting as model systems for many decades first with rather simple systems and since the beginning of this century became one of the main trends in molecular magnetism after the discovery of slow magnetic relaxation and hysteresis near liquid helium temperatures. Many new systems were synthesized and characterized, theoretical modelling and simulations explained most properties and the blocking temperatures increased significantly. Progress slowed down with the emergence of Single Molecule Magnets of Single Ion with higher temperatures. Difficulties have been pointed and the evolution towards applications seems to have stopped, but as history (superconductors, hard magnets) tells us, new discoveries may take many years but are likely to appear. On the other hand, some issues were left behind without satisfactory solutions. In this talk we will review briefly this story and will present some progress and examples we have been working recently and show that there is still a lot to be done with these systems.

Employing New Radical Ligands in Lanthanide Single-Molecule Magnet Design

Florian Benner, Francis Delano IV, Selvan Demir
Michigan State University, East Lansing, USA

Abstract

The unquenched orbital angular momentum innate to the electronic structures of lanthanide ions such as Tb^{3+} and Dy^{3+}, allow for the construction of large barriers to spin relaxation in mononuclear complexes through matching the ligand field symmetry with the anisotropic electron density distribution of the maximal M_J state. Employing this methodology, we will present the synthesis of lanthanide complexes comprising unprecedented ligand fields that function as new lanthanide-based single-molecule magnets. Another successful approach to improve magnetic blocking temperatures is to generate strong magnetic exchange between lanthanide centers through the employment of radical bridging ligands. If the magnetic exchange coupling is large enough then quantum tunnelling of the magnetization can be attenuated. Here, we will further present the synthesis of new radical-bridged lanthanide single-molecule magnets and describe effective suppression of quantum tunnelling pathways using various organic radical bridging ligands.

Chemistry for the Second Quantum Revolution

Danna Freedman
Massachusetts Institute of Technology, Cambridge, USA

Abstract

Decades of research in molecular magnetism has enabled us to control and understand the fundamental magnetic parameters in molecules. By applying this knowledge towards the field of quantum information science we can develop designer molecular qubits, featuring the inherent structural precision and tunability of synthetic chemistry. Results on designing molecular qubits towards specific applications will be presented, with an emphasis on imbuing molecules with the same optical read-out capabilities as defects in semiconductors, such as the anionic nitrogen vacancy pair defect in diamond. By using an inverse design strategy, we can replicate the electronic structure of NV centers in diamond in transition metal complexes, thereby creating a new class of qubits.

Molecular analogues of magnetic units on ultra-small nanoparticles

George Christou
University of Florida, Gainesville, Florida, USA

Abstract

Molecular chemistry can bring many powerful advantages to the study of nanoscale materials of various kinds, and this area of 'molecular nanoscience' has therefore been a rapidly growing field. The advantages include truly monodisperse (single-size) products and a shell of organic ligation that imparts solubility and crystallinity, allowing structural characterization to atomic resolution by X-ray crystallography. The ligands can usually also be modified as desired, allowing tuning of redox properties and labelling (e.g. ^{2}H, ^{19}F, etc.) for various studies in the solid state and solution, such as NMR spectroscopy. In the molecular nanomagnetism arena, the above advantages have been absolutely crucial in the study of single-molecule magnets (SMMs). They have greatly assisted the synthesis and structural characterization of numerous SMMs, and as single crystals they have also led to the discovery of new quantum physics phenomena important to new 21st century technologies that could not be reliably detected from the study of traditional nanoparticles. In recent years, we have been applying a molecular approach to what we now call 'Molecular Nanoparticles' (MNPs), molecular clusters that represent ultra-small nanoparticles of important metal oxides, either diamagnetic or paramagnetic. Our efforts began with cerium(IV) dioxide, but have since been extended to oxides of bismuth(III), iron(III), and Mn(III, IV), as well as mixed-metal oxides with the perovskite structure, and others. With these successes as a foundation, we are now probing the introduction of surface-bound magnetic units onto these MNPs as a route to molecular analogues of magnetic molecules deposited on surfaces of various types. The syntheses, structures, and magnetic and other properties of a selection of these materials will be described.

How to create giant Dzyaloshinskii Moriya Interactions? Analytical derivation and ab initio calculations on model dicopper(II) complexes

Nathalie Guihéry[1], Mohammed Amine Bouammali[2], Nicolas Suaud[3], Cyril Martins[1], Rémi Maurice[4]
[1]Université de Toulouse 3, Paul Sabatier, Toulouse, France. [2]Université de Toulouse 3, Toulouse, France. [3]Université deToulouse 3, Toulouse, France. [4]SUBATECH, Université de Nantes, Nantes, France

Abstract

This work[1] shows how the on-site first-order spin-orbit coupling can generate giant Dzyaloshinskii-Moriya (DM) interaction in binuclear transition metal complexes. This effective interaction plays a key role in strongly correlated materials, skyrmions, multiferroics, molecular magnets of promising use in quantum information science and computing. Despite this, its determination from both theory and experiment is still in its infancy and existing systems usually exhibit very tiny DM interaction. We derive analytical formulas that perfectly reproduce both the nature and the magnitude of the DM interaction calculated using state-of-the-art *ab initio* calculations performed on model bicopper(II) complexes. We also study which geometrical structures/ligand-field forces would enable one to control the magnitude and the orientation of the Dzyaloshinskii Moriya vector in order to guide future synthesis of molecules or materials. This work provides an understanding of its microscopic origin and proposes recipes to increase its magnitude. We show that i) the on-site mixings of 3d orbitals rules the orientation and magnitude of this interaction, ii) increased values can be obtained by choosing more covalent complexes, iii) huge values (~1000 cm^{-1}) and controlled orientations could be reached by approaching structures exhibiting on-site first-order SOC, *i.e.* displaying an “unquenched orbital momentum”.

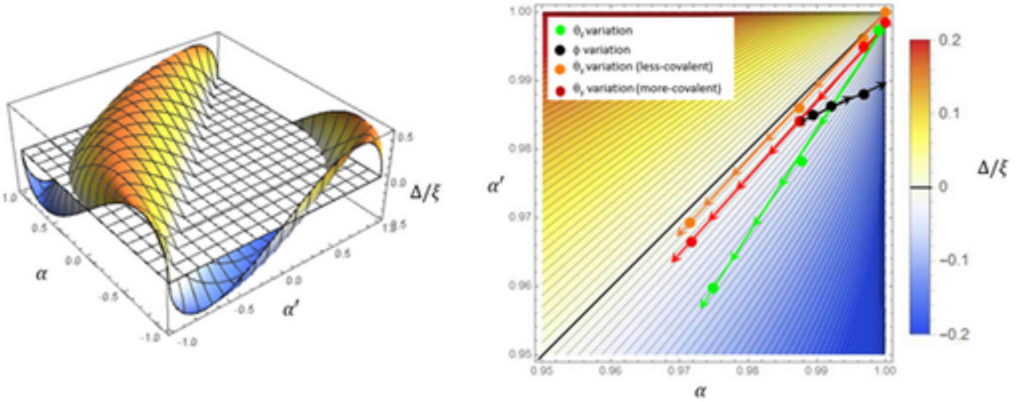

Figure : Surface of the DMI as a function of the mixing orbitals parameters and a portion in the physical region of its contour plot (right). The calculated values obtained for the different studied complexes are also reported (right). Arrows indicate direction towards larger deformations.

[1] Mohammed-Amine Bouammali, Nicolas Suaud, Cyril Martins, Rémi Maurice and Nathalie Guihéry, Journal of Chemical Physics, 2021, in press.

Exploiting material anisotropy to fabricate highly controllable artificial muscles based on spin crossover (SCO) polymeric composites.

Mario Piedrahita-Bello[1], José Elias Angulo Cervera[1], Gábor Molnár[1], Bertrand Tondu[2], Lionel Salmon[1], Azzedine Bousseksou[1]
[1]LCC, CNRS & University of Toulouse (UPS, INPT), Toulouse, France. [2]LAAS, CNRS and University of Toulouse (INSA, UPS), Toulouse, France

Abstract

The development of artificial muscles concerns flexible materials able to deform themselves to move or to adapt their shape to accomplish specific tasks. The development of new actuating materials with novel properties, capable of responding to a variety of needs is thus of great interest in this field. Spin crossover (SCO) materials have been investigated as the basis for actuator systems due to the fact that they present a reversible phase transition accompanied by a significant volume change [1]. The composite approach, where particles of SCO complexes are dispersed in a polymeric matrix, has allowed for the elaboration of conductive actuators [2], micro electromechanical cantilevers [3] and 3D printed actuators [4]. Here we present the development of a highly controllable, electrically driven SCO polymeric actuator. We use a composite approach to confer a P(VDF-TrFE) matrix with novel conductive and actuating properties, and furthermore, by exploiting the anisotropy of the SCO particles, significantly multiply the effect of the volume change of the SCO complexes. This work was supported by the Federal university of Toulouse/Région Occitanie and the Agence Nationale de la Recherche (ANR-19-CE09-0008-01)

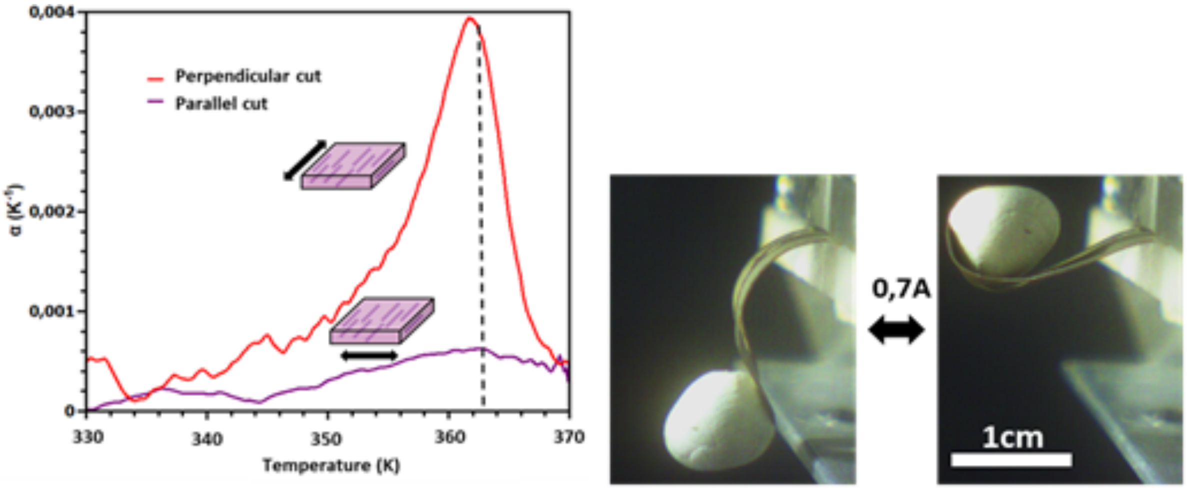

Figure 1. Thermal expansion of a SCO polymeric composite fabricated using anisotropic SCO particles (left). Electrically driven actuation of a spin crossover artificial muscle lifting a mass equivalent to 800% of the actuators weight (right).

1. Shepherd, H. J. *et al. Nat. Commun.* **4**, 1–9 (2013). 2. Gural'Skiy, I. A. *et al. J. Mater. Chem. C* **2**, 2949–2955 (2014). 3. Manrique-Juárez, M. D. *et al. Adv. Funct. Mater.* **28**, 1801970 (2018). 4. Piedrahita-Bello, M. *et al. J. Mater. Chem. C* **8**, 6001–6005 (2020).

Paramagnetic NMR in actinide complexes: dipicolinate complexes as examples

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Abstract

Paramagnetic NMR (pNMR) measures the NMR chemical shift of paramagnetic complexes compared to their diamagnetic counterpart. This shift may be split into a *contact* and a *dipolar* terms, arising from dipolar interaction and spin delocalization, respectively. This spectroscopy provides structural information, on one hand, and information about the degree of covalency, on the other hand. In lanthanide complexes, pNMR chemical shifts are efficiently modelled using crystal field theory, but due to the larger covalent effects in actinide complexes, those models do not apply to actinide complexes. We will show in this presentation how quantum chemistry allows to unravel the two above-mentioned contributions.

This work is based on actinide complexes in different oxidation states formed with dipicolinate ligands and was performed in close collaboration with the group of experimentalists leaded by Claude Berthon at CEA Marcoule (France).

We will discuss:

- the crystal field parameters in the $[\mathrm{An^{IV}(DPA)_3}]^{3-}$ series, and more precisely, the transferability within the series.
- the temperature dependence of the pNMR shifts in $[\mathrm{NpO_2(dpa)_2}]^{2-}$ and $[\mathrm{PuO_2(dpa)_2}]^{2-}$ complexes and how it can be fitted by a two-level model
- the dipolar and contact contributions in the $[\mathrm{An^{IV}(DPA)_3}]^{3-}$ complexes in terms of the magnetic susceptibility tensor of the paramagnetic ion and the spin densities on the nuclei of the ligands.

M. Autillo, et al. Chem. Eur. J. ***25****, 4435 (2019) ;* J. Jung, et al. *Chem. Eur. J. ,* **25***,* 15112 (2019); *M. Autillo, et al Phys. Chem. Chem. Phys.* ***22****, 14293 (2020) ;M. Autillo, et al. Chem. Eur. J.,* ***27****, 7138 (2021).*

Anisotropy-Exchange Resonances as a Mechanism for Entangled State Switching for Two Coupled *S* = 1 Magnetic Particles

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[1]Department of Physics, University of Central Florida, Orlando, USA. [2]Department of Physics, Center for Molecular Magnetic Quantum Materials and Quantum Theory Project, University of Florida, Gainesville, USA

Abstract

Robust control of entangled spin states is important for realizing magnetic molecules as quantum information devices. We present novel resonance conditions of exchange coupling and magnetic anisotropy in coupled magnetic particles for use in quantum information. We explore the three-particle spin model of an $S_1 = 1/2$ particle (e.g., a stationary electron) coupled via exchange interaction to two spin-coupled $S_{2,3} = 1$ particles (e.g., two coupled magnetic monomers) that possess magnetic anisotropy. We show that in the case of $S_{2,3} = 1$ particles, and without the use of an oscillating magnetic field, the coupled particle entanglement states can be prepared, controlled, and read by the S_1 particle. We also show that for particular resonance conditions of the magnetic anisotropy strength D and exchange coupling strength J, the entanglement state switching behavior is maximized and is robust against a range of anisotropic application of the exchange coupling [1].

[1] E. D. Switzer, X.-G. Zhang, and T. S. Rahman, arXiv: https://arxiv.org/pdf/2105.01126.pdf

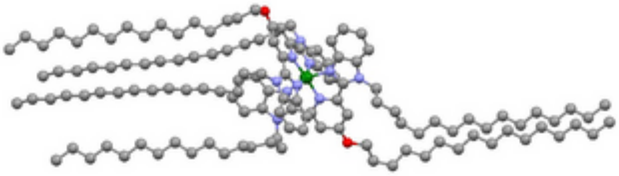
Ferroelectric Spin Crossover Molecules

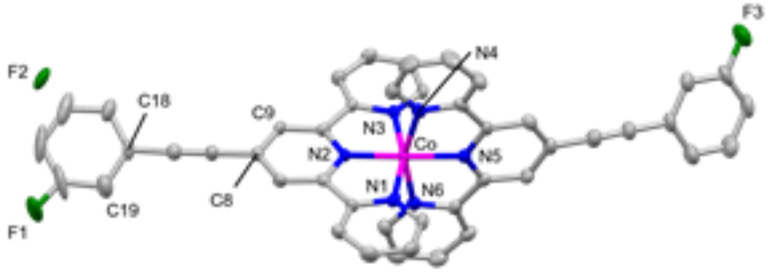
Shinya Hayami
Kumamoto University, Kumamoto, Japan

Abstract

Multifunctional molecular materials exhibiting synergistic coexistence of two or more properties, have received considerable attention over recent years not only for their intrinsic interest but also because of their potential applications that include for information storage, sensors, spintronics and electro-optic devices. One of the more attractive multifunctional molecule-based materials for use in such applications are compounds that exhibit spin crossover (SCO) coupled with the occurrence of another phenomenon (or phenomena), for example, liquid crystalline behavior, electrical conductivity, luminescence and/or non-linear optical (NLO) properties.

We report examples of Ferroelectric SCO $[Fe(3C_{n}\text{-bzimpy})_2](BF_4)_2$ with long alkyl chains and $[Co(FPh\text{-}terpy)_2](BPh_4)_2$ with flip-flop motion fluorophenyl ring.





Two-step valence tautomerism in bis(dioxolene)-bridged dinuclear cobalt complexes

Colette Boskovic[1], Gemma Gransbury[1], Brooke Livesay[2], Matthew Shores[2], Alyona Starikova[3]
[1]University of Melbourne, Parkville, Australia. [2]Colorado State University, Fort Collins, USA. [3]Southern Federal University, Rostov-on-Don, Russian Federation

Abstract

Molecular materials that can be switched between two or more distinguishable states by external stimuli have future applications ranging from materials for sensing and display devices to high density data storage, quantum computing, molecular electronics and molecular spintronics. Of particular interest are species that can be interconverted between more than two states, which are relevant for higher order data storage or complex logic processes. Bis(dioxolene)-bridged dinuclear cobalt complexes provide an avenue toward controlled two-step valence tautomeric (VT) transitions of the form $\{Co^{III}\text{-cat-cat-}Co^{III}\} \rightleftharpoons \{Co^{III}\text{-cat-SQ-}Co^{II}\} \rightleftharpoons \{Co^{II}\text{-SQ-SQ-}Co^{II}\}$ (cat^{2-} = catecholate, $SQ^{\bullet-}$ = semiquinonate). A concerted structural, magnetochemical, electrochemical, spectroscopic and computational study of a series of related cobalt and zinc complexes has allowed elucidation of thermodynamic parameters governing the one- and two-step VT behaviour. Parameters based on the degree of electronic communication within the bis(dioxolene) ligand and, the matching of cobalt and dioxolene redox potentials, provide direct control over two-step switching properties. The resulting ability to chemically tune the VT characteristics confers a clear advantage for dinuclear VT complexes over analogous spin crossover complexes for future applications in devices or materials.

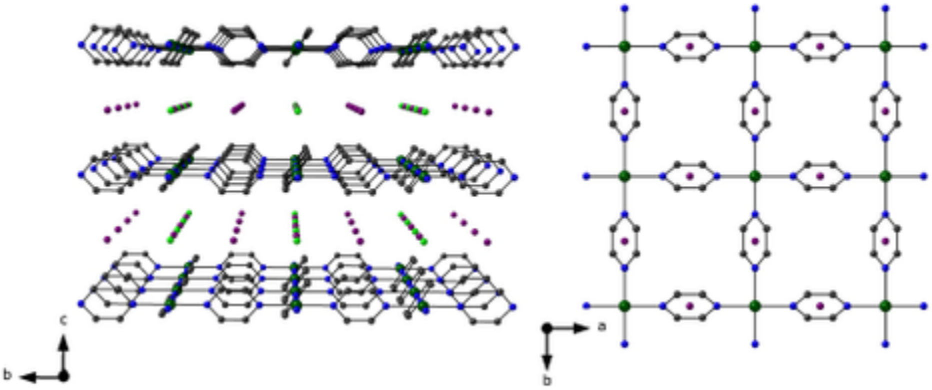
Metal-organic magnets with large room temperature coercivity and ordering temperature up to 515 K

Rodolphe Clérac[1], Panagiota Perlepe[1], Itziar Oyarzabal[1,2], Andrei Rogalev[3], Corine Mathonière[1], Kasper S. Pedersen[1,4], & all the authors of the references [1-3][1]

[1]Univ. Bordeaux, CNRS, Centre de Recherche Paul Pascal, UMR 5031, Pessac, France. [2]Chemistry Faculty, University of the Basque Country, UPV/EHU, Donostia-San Sebastián, Spain. [3]ESRF-The European Synchrotron, Grenoble, France. [4]Department of Chemistry, Technical University of Denmark, Lyngby, Denmark

Abstract

Magnets derived from inorganic materials (e.g., oxides, rare earth and intermetallic compounds) are key components of modern technological applications. Despite extensive success in a broad range of applications, these inorganic magnets suffer several drawbacks, such as energetically expensive fabrication, limited availability of certain constituent elements, high density, and poor scope for chemical tunability. A promising design strategy for next-generation magnets relies on the versatile coordination chemistry of abundant metal ions and inexpensive organic ligands. Following this approach, this lecture will present a general, simple and efficient synthesis of lightweight molecule-based magnets by post-synthetic reduction of pre-assembled coordination networks, $Cr(pyrazine)_2X_2$ (X = Cl or methylsulfonate) incorporating chromium metal ions (in +2 or +3 oxidation states) and pyrazine ligands [1,2]. The resulting metal-organic ferrimagnets feature critical temperatures up to 515 K, and unprecedented 7500-Oersted room-temperature coercivity (see figure below illustrating the structure of $Li_{0.7}[Cr(pyz)_2]Cl_{0.7}$) [3].



This work was supported by the University of Bordeaux, the Région Nouvelle Aquitaine, the CNRS and the ESRF.

[1] K. S. Pedersen, P. Perlepe, M. L. Aubrey, D. N. Woodruff, S. E. Reyes- Lillo, A. Reinholdt, L. Voigt, Z. Li, K. Borup, M. Rouzières, D. Samohvalov, F. Wilhelm, A. Rogalev, J. B. Neaton, J. R. Long, R. Clérac, ***Nature Chemistry*** (2018), **10,** 1056-1061. [2] P. Perlepe, I. Oyarzabal, K. S. Pedersen, P. Négrier, D. Mondieig, M. Rouzières, E. A. Hilllard, F. Wilhelm, A. Rogalev, E. A. Suturina, C. Mathonière, R. Clérac, ***Polyhedron*** (2018) **153**, 248-253. [3] P. Perlepe, I. Oyarzabal, A. Mailman, M. Yquel, M. Platunov, I. Dovgaliuk, M. Rouzières, P. Négrier, D. Mondieig, E. A. Suturina, M.A. Dourges, S. Bonhommeau, R. A. Musgrave, K. S. Pedersen, D. Chernyshov, F. Wilhelm, A. Rogalev, C. Mathonière, R. Clérac, ***Science***, (2020), Vol. 370, **6516**, 587-592.

Quantum Phase Interference in a Fullerene-Based Electron Triplet Molecular Qutrit

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Abstract

High spin magnetic molecules are promising candidates for quantum information processing because their intrinsic multiplicity facilitates information storage and computational operations. However, due to the absence of suitable sublevel splittings, their susceptibility to environmental disturbances and limitation from the selection rule, the arbitrary control of the quantum state of a molecular electron multiplet has not been realized. Here we exploit the photoexcited triplet of C_{70} as a molecular electron spin qutrit with pulsed electron paramagnetic resonance. We prepared the system into 3-level superposition states characteristic of a qutrit and validated them by the tomography of their density matrices. To further elucidate the coherence of the operation and the nature of the system as a qutrit, we demonstrated the quantum phase interference in the superposition. The interference pattern is further interpreted as a map of possible evolution paths in the space of phase factors, representing the quantum nature of the 3-level system.

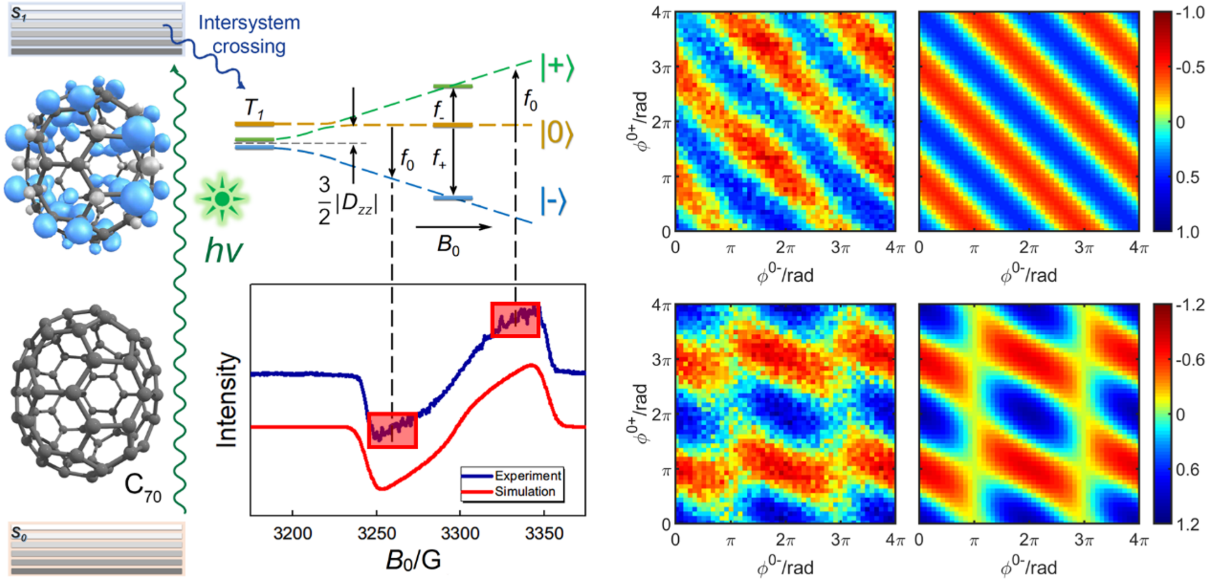

Figure 1. The excited triplet state of C70 is treated as a qutrit, where the 3-levle superposition state is prepared and characterized as quantum phase interference.

Y.-X. Wang, Z. Liu, Y.-H. Fang, S. Zhou, S.-D. Jiang, S. Gao, *npj Quantum Inf.* **2021***, 7,* 32.

Lanthanide Single-Molecule Magnets Constructed with Metallacrown Ligands

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Abstract

Single-molecule magnets (SMMs) exhibit magnetization blocking in the presence of strong magnetic anisotropy. By employing molecular engineering, the blocking barrier can be significantly modified, remaining independent from other external factors such as magnetic field.[1,2] Combining Ising-type magnetic anisotropy with collinear magnetic interactions in single-molecule magnets (SMMs) is a significant synthetic challenge. Herein we report a general assembly strategy to improve the SMM properties, that is, the combination of a metallacrown (MC) and an axially-ligated L−Ln−L motif to construct more regular geometries and introducing negatively charged axial ligands to enhance the magnetic anisotropy.[3,4] Field-dependent oscillation of the magnetization blocking barrier has been firstly observed in the $Ho^{III}F_2[15-MC_{Ni}-5]$ SMM driven by the switch of relaxation mechanisms involving hyperfine interaction. First-principles calculations reveal an activated temperature dependence of magnetic relaxation dominated either by incoherent quantum tunneling of magnetization at anti-crossing points or by Orbach-like processes at crossing points. This mechanism demonstrates that these relaxation barriers can be consecutively switched by increasing the external field, which paves a way for manipulating magnetization dynamics of SMMs using hyperfine interaction.

[1] J. L. Liu, Y. C. Chen, M. L. Tong, Chem. Soc. Rev., 2018, 47, 2431.

[2] M. Feng, Z.-Y. Ruan, Y.-C. Chen, M.-L. Tong, Chem. Commun., 2020, 56, 13702.

[3] S.-G. Wu, Z.-Y. Yuan, G.-Z. Huang, J.-Y. Zheng, V. Vieru, T. Gheorghe, J. Wang, Y.-C. Chen, J.-L. Liu, L. T. A. Ho, L. F. Chibotaru, W. Wernsdorfer, X.-M. Chen, M.-L. Tong, Chem, 2021, 7, 982.

[4] J. Wang, Q.-W. Li, S.-G. Wu, Y.-C. Chen, R.-C. Wan, G.-Z. Huang, Y. Liu, J.-L. Liu, D. Reta, M. J. Giansiracusa, Z.-X. Wang, N. F. Chilton, M.-L. Tong, Angew. Chem. Int. Ed., 2021, 60, 5299.

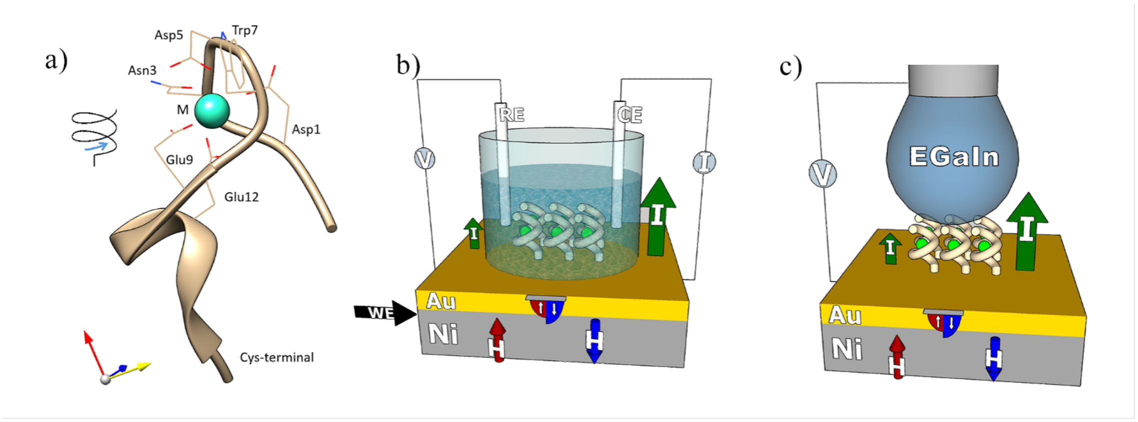
Spin filtering in chiral paramagnetic peptides

Salvador Cardona-Serra, Ramón Torres-Cavanillas, Garin Escorcia-Ariza, Isaac Brotons-Alcázar, Roger Sanchis-Gual, Prakash Chandra Mondal, Lorena E. Rosaleny, Silvia Giménez-Santamarina, Michele Sessolo, Marta Galbiati, Sergio Tatay, Alejandro Gaita-Ariño, Alicia Forment-Aliaga
Institute for Molecular Science, Valencia, Spain

Abstract

Chirality-induced spin selectivity (CISS), whereby helical molecules polarize the spin of electrical current, is an intriguing effect with potential applications in nanospintronics. In this field, the study of the CISS effect using paramagnetic chiral molecules, which could introduce another degree of freedom in controlling the spin transport, remains so far unexplored. To address this challenge, herein, we propose the use of self-assembled monolayers (SAMs) of helical lanthanide-binding peptides. In order to elucidate the effect of the paramagnetic nuclei, monolayers of the peptide coordinating paramagnetic or diamagnetic ions are prepared. By means of spin-dependent electrochemistry, CISS effect is demonstrated by cyclic voltammetry and electrochemical impedance measurements for both samples. Additionally, an implementation of the standard liquid-metal drop electron transport setup has been carried out, demonstrating their suitability for solid-state devices.

In this work, spin filtering enhancement induced by the encapsulated paramagnetic ion has been demonstrated in lanthanide binding peptides. The active role of the paramagnetic ion has been unambiguously confirmed by three independent experimental approaches: cyclic voltammetry, electrochemical impedance spectroscopy and local transport in solid state devices using liquid-metal drop contacts. In the best conditions, a spin polarization *SP* = -70 ± 10 % was achieved with the contribution of complexed Tb^{3+} ions. These findings permit the inclusion of magnetic biomolecules in the CISS field, paving the way to their implementation in a new generation of (bio)spintronic nanodevices.



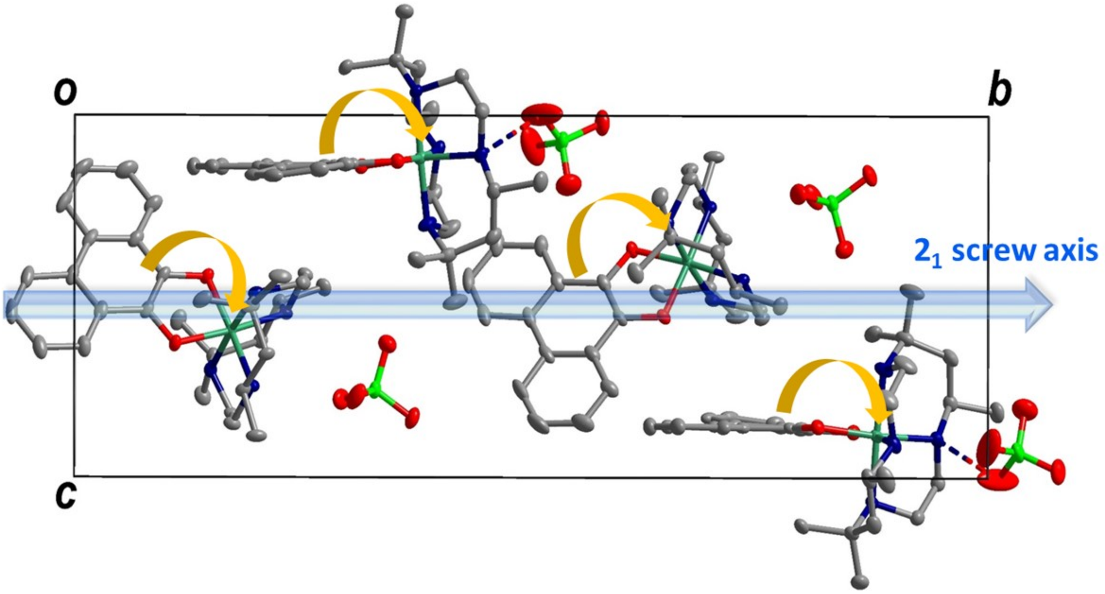
Structure of the MLBTC metallopeptide used for spin filtering studies. **a)** Side view of MLBTC in ribbon representation; arrow shows the right-handed helicity. The aminoacids coordinating the metal ion are tagged. **b)** and **c)** Schemes of spin-dependent transport setups used in this work emphasizing the magnetization of the Ni layer under an external magnetic field and its influence on the empty and occupied density of states, as well as the expected CISS effect.

Molecular Pyroelectricity via Directional Electron Transfer in Valence Tautomeric Complexes

Shu-Qi Wu, Pritam Sadhukhan, Shinji Kanegawa, Osamu Sato
Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka, Japan

Abstract

Pyroelectricity is one of the most efficient ways to harvest energy from heat. Herein, we propose a molecular approach towards constructing novel pyroelectric materials based on valence tautomeric (VT) complexes. A thorough investigation of a mononuclear cobalt complex, [Co(phendiox)(*rac*-cth)](ClO_4)·0.5EtOH (H_2phendiox = 9, 10-dihydroxyphenanthrene, *rac*-cth = racemic 5, 5, 7, 12, 12, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradecane), is illustrated as a proof-of-concept. The complex crystallizes in the polar $P2_1$ space group and exhibits a two-step VT transition. The electron transfer during the VT process is directional, thus can be amplified to a single-crystal level, enabling the repeated observation of two pyroelectric peak currents in the same temperature domain of the VT transition without the application of an electric field. The photo-induced magnetometry and infrared spectroscopy show that the polarization-switching metastable state could be trapped at low temperature, meaning that the Co compound exhibits photo-tunable polarization bistability.[1] Discussion will be extended to a pseudo symmetric dinuclear complex, [(Fe(*RR*-cth))(Co(*SS*-cth))(*μ*-dhbq)](PF_6)$_3$ (H_2dhbq = 2,5-dihydroxy-1,4-benzoquinone). Spectroscopic studies reveal that the compound exhibits a more complicated electronic transition than conventional VT transition. However, pyroelectricity clearly evidences its electron-redistribution nature.



1. S. –Q. Wu, M. Liu, K. Gao, S. Kanegawa, Y. Horie, G. Aoyama, H. Okajima, A. Sakamoto, T. Abe, Y. Shiota, K. Yoshizawa, W. Xu, H. –Z. Kou, O. Sato, *Macroscopic Polarization Change via Electron Transfer in a Valene Tautomeric Cobalt Complex, Nat. Commun.*, **2020**, *11*, 1992.

Exploring magnetism and chirality of monolayers of molecules using X-ray absorption techniques

Matteo Mannini
Dipartimento di Chimica Ugo Schiff, Univesità degli Studi di Firenze, Sesto Fiorentino (Firenze), Italy

Abstract

A growing community is attracted by the interplay between magnetism and chirality, two aspects of nature that this community aims at controlling down to the nanoscale. When operating with molecules as building blocks for spintronics and quantum computation these properties became *crucial* influencing coherence, as well as injection and transport of spin carriers but also *evanescent* because of the detrimental effect of their interaction with surfaces as well as because of the specific fragility of molecules when removed from the protected environment of a single crystal. I will present two cases of study of our recent research activity, where a fragile magnetic system and a chiral organic radical have been assembled on the surface as monolayer deposits using sublimation and wet-chemistry protocol respectively. Their nature has been studied using X-ray absorption spectroscopy flanked by other experimental surface-sensitive techniques. First, I will describe the successful deposition of a monolayer a qubits candidate featuring a remarkable coherence time in frozen-solution,[1] the organometallic (h^8-cyclooctatetraene)(h^5-cyclopentadienyl)titanium, [CpTi(cot)]. I will highlight the difficulties associated with the preparation and analysis of this highly volatile system to extract the information about the arrangement of these molecules on the surface obtained by X-ray natural linear dichroism (XNLD) and their magnetism as extracted from the X-ray circular magnetic dichroism (XMCD).[2] Then I will show how the chirality of a monolayer of enantiopure thia[4]helicene radical cations[3] can be evaluated profiting from the use of the X-ray natural circular dichroism (XNCD) technique.[4]

[1] Camargo, et al. , *Angew. Chem.* **2021**, *133*, 2620.

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Giant spins as magnetic building blocks

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Abstract

We will describe the synthesis and electronic structures of giant-spin, iron-based single molecule magnets which exhibit well-isolated ground states. We will describe how the ground state electronic structures can be manipulated using post-cluster synthetic modifications. Ligand alterations can lead to both anodic and cathodic shifting of the resulting clusters, providing a means for the exploration of charge-transfer salt formation. We will describe how the electronic structures of the clusters are obtained and illustrate possible origins for unquenched magnetic anisotropy.

Photoswitchable Lanthanide Complexes : from Single Molecule Magnets to Anti-Counterfeiting Systems

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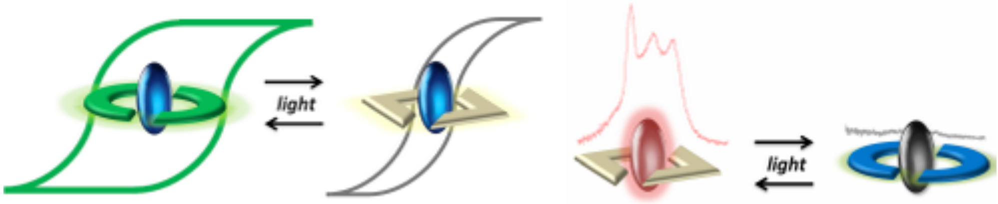
Abstract

At the heart of various high technology applications, rare earth optical and magnetic properties both find their origin in the fascinating electronic structures of lanthanide(III) ions. Our research deals with the control of lanthanide molecular complexes[1] with light and target photomagnetism as well as luminescence photomodulation. Recently, we obtained new air stable complexes having a terminal dysprosium fluoride bond[2] that can serve as highly anisotropic building blocks and are assembled by organic photoswitches into SMM chains showing hysteresis photomodulation.[3] We also explored dinuclear systems in which two dysprosium ions are linked by a photoswitch.[4] Finally we have designed photoswitchable ligands that can be used to modulate lanthanide emission and obtained the first photomodulation of NIR light[5], with interesting potential as anticounterfeiting systems.[6] This communication will thus be focused on the design and synthesis of photoswitchable lanthanide complexes and chosen examples of magnetic or optical properties switching will be presented.



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Fun with lanthanide ligand fields: combining strong axiality with air-stability

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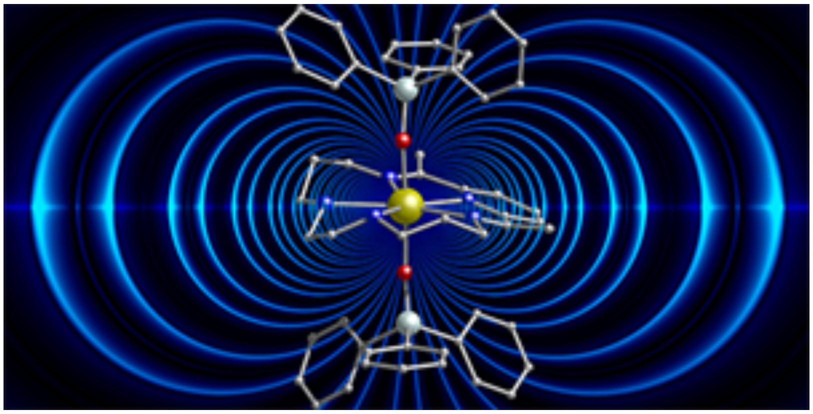
Abstract

Monometallic lanthanide single-molecule magnets (SMMs) with a strong axial crystal field [1] such as ~D_{4d} [2], sandwich type [3-6] and ~D_{5h} [7-10] favour slower relaxation of the magnetization by reducing transverse magnetic anisotropy and promoting relaxation via higher energy m_J states. I will present some of our recent examples of air-stable monometallic lanthanide(III) complexes in different coordination geometries that generate a strong axial crystal field [11-14] and discuss their magnetic behavior.



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Ab initio spin dynamics of SMMs: can we predict the best candidates yet?

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Abstract

Parallel to the outstanding synthetic works on highly axial Dy(III)-based Single Molecule Magnets (SMMs) [1-3], several theoretical approaches aiming at understanding their spin dynamics have been proposed [1,4-6]. Currently, none is capable to account for the whole temperature dependence of the experimental relaxation profiles, making effective design strategies indispensable to keep improving the performance of SMMs.

Here [7] we apply our approach to spin dynamics to the best in class $[Dy(Cp^R)_2]^+$ cations (Cp^R: substituted-cyclopentadienyl) [1-3]. Despite being chemically similar, these systems present very different magnetic properties, making them a perfect testbed to critically assess our method. We find that we correctly reproduce the relative ordering of the relaxation profiles and assign the differences in magnetic properties to molecule-specific crystal field. Also, we predict that *i)* further enhancements to the effective energy barrier U_{eff} seem inconsequential and that *ii)* progress in slowing magnetic relaxation in the Orbach regime could be obtained by engineering the molecular vibrational modes, such that they are off-resonance with electronic transitions, even if U_{eff} barriers are adversely affected.

In summary, this study has allowed us to establish the relative importance of the factors governing magnetic relaxation within the Orbach regime in Dy(III)-based SMMs, confidently propose our approach as a robust tool to predict relative relaxation rates and ultimately provide clear guidelines toward the chemical design of more efficient SMMs.

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Molecular spin qudits: a promising ingredient for quantum computers

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Abstract

The potential to solve problems with large impact on science, society and economy makes the realization of quantum computers one of the hottest topics in current research. The most advanced architectures currently are based on superconducting qubits or ion traps and can already be exploited for interesting proof-of-principle calculations [1]. A promising alternative in the race towards quantum devices is represented by molecular nanomagnets (MNMs). These magnetic molecules are characterized by a sizeable number of accessible low-energy states that can be coherently manipulated by microwave and radiofrequency pulses, thus opening the possibility use them as molecular qudits.

In my presentation, I review some recent results on molecular qudits/qubits. In particular, I show that MNMs can be exploited to define qubits with embedded quantum error correction in single molecules [2,3], thus circumventing the large overhead in the number of physical units required by standard quantum error correction codes. Moreover, I show that molecular qudits can improve the potential for quantum simulations. Then, I briefly report the characterization of promising molecular qudits using broadband NMR. At last, I discuss some recent results on the study of the two main sources of decoherence in MNMs, i.e., interactions with nuclear spins and phonons [4].

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High-field EPR investigation of a potential molecular two-qubit gate based on a cobalt dimer

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Abstract

Quantum information processing (QIP) is key 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 $[Co_2(O_2PBn_2)_3py_4]ClO_4$ 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.

The full ab initio picture of spin-phonon relaxation in molecular crystals of Kramers ions

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Abstract

Achieving a full chemical control of spin lifetime is a central challenge in molecular magnetism, but the success in this area is hindered but the lack of understanding of the details of spin-lattice relaxation.

In this contribution, I will present a parameter-free ab initio strategy able to predict spin-lattice relaxation in molecular magnetic compounds, inclusive of Direct, Orbach and Raman mechanisms[1-3]. The method is based on a combination of the Redfield relaxation theory together with periodic-Density Functional Theory, post-Hartee Fock methods, and machine-learning schemes[4,5], enabling the simulation of realistic systems.

The method is applied to a series of molecular crystals of Kramers ions, including prototypical molecular qubits, such as $S = 1/2$ V(IV) complexes[1,2], and single-ion magnets, such as $S = 3/2$ Co(II)[3] and $J = 15/2$ Dy(III) compounds[6]. Ab initio spin dynamics is able to explain the dependence of spin-lattice relaxation time with respect to temperature for all the investigated compounds, making it possible to individuate the origin of slow relaxation for all the most relevant classes of magnetic molecules. Finally, thanks to the fully-ab initio nature of the method, it is also possible to disentangle all the spin and molecular interactions leading to spin-phonon coupling, making it possible to discuss future directions for this field and possible strategies for the enhancement of spin lifetime in solid-state magnetic molecules.

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Coexistence of proper magnetic and structural incommensurability on $[CH_3NH_3][Ni(COOH)_3]$ compound

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Abstract

In the present communication we describe of the structural and magnetic phase transitions of $[CH_3NH_3][Ni(COOH)_3]$ perovskite-like metal–organic compound. [1] Below T_N the magnetic structure can be described by an unprecedented incommensurate magnetic phase. The structural and magnetic characterization has been performed through variable-temperature single-crystal and powder neutron diffraction. The title compound crystallizes in the orthorhombic *Pnma* space group at room temperature, and below 84 K the appearance of new reflections close to the main reflections suggests the occurrence of an incommensurate phase. The new reflections can be indexed with a wave-vector with an incommensurate component along the *c*-axis ($\mathbf{q} = 0.1426(2)c^*$). The nuclear structure was determined using the super-space group formalism on the *Pnma*(00*g*)0*s*0 space group. This incommensurate phase remains unchanged with the decreasing of temperature up to ca. 2 K.

The magnetic susceptibility data show that $[CH_3NH_3][Ni(COOH)_3]$ compound exhibits an antiferromagnetic behaviour below 34 K. [2] Single crystal and powder neutron diffraction have been used in this work to confirm the long range magnetic order, and the coexistence of nuclear and proper magnetic incommensurability below T_N.[1]

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Manipulating and understanding toroidal ground states in Dy(III) triangles

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Abstract

A non-magnetic ground state is often the result of a vortex, or toroidal, arrangement of spins. Although such systems are well-explored in solid-state physics and chemistry, the molecular realisation of this "dark state" was first identified in a Dy_3 triangle[1] with other examples being increasingly identified. The advantage of such a "dark state" is that information is necessarily preserved since, as the name suggests, the information is hidden, much as it is in the dark matter of the Universe.

Attention will focus mainly on trinuclear systems. and include an exploration of the possibilities offered by using supramolecular synthetic principles. One line of enquiry uses the idea of linking the "simple" Dy_3 triangles into chains and creating multiferroic systems. Even more exciting is the possibility to create toroidal systems where giant triangles of Dy(III) ions are arranged toroidally as we recently described in the largest toroidal molecule so far reported which has two giant Dy_3 triangles sandwiching an antiferromagnetically coupled Fe^{III}_{18} cycle.[,3] Here, the strong coupling between the Fe(III) ions helps to organise the directions of anisotropy axes of the Dy(III) ions.

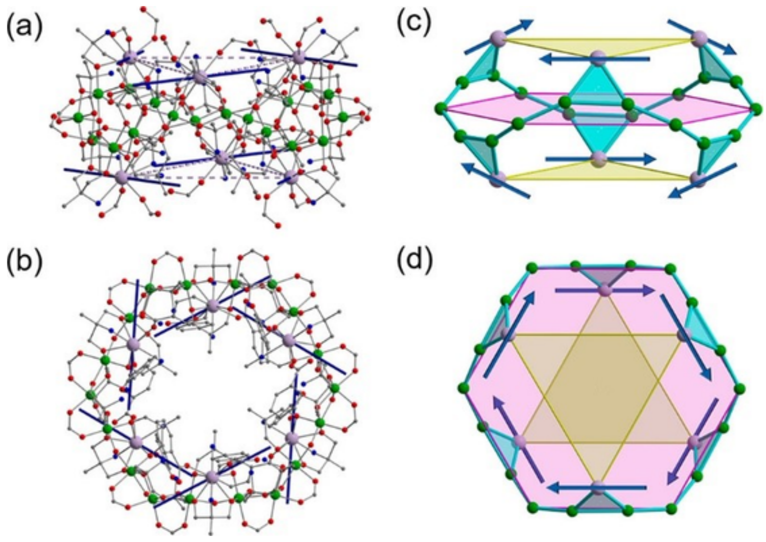

Figure: Views (a) and (b) of the molecular structure (Dy purple, Fe green) and (c) and (d) cartoons of the same view showing the giant toroidal arrangement of the Dy spins.

1. Dysprosium Triangles Showing Single-Molecule Magnet Behavior of Thermally Excited Spin States, J. Tang, I. Hewitt, N. T. Madhu, G. Chastanet, W. Wernsdorfer, C. E. Anson, C. Benelli, R. Sessoli, A. K. Powell, *Angew. Chem. Int. Ed.* 2006, 45, 1729-1733.

2. Inorganic Approach to Stabilizing Nanoscale Toroidicity in a Tetraicosanuclear $Fe_{18}Dy_6$ Single Molecule Magnet, H. Kaemmerer, A. Baniodeh, Y. Peng, E. Moreno-Pineda, M. Schulze, C. E. Anson, W. Wernsdorfer, J. Schnack, A. K. Powell, *J. Am. Chem. Soc.* 2020, 142, 35, 14838–14842.

A Prototype Organometallic Spin Qubit from First-Principles: the [CpTi(cot)] System Investigated *In Silico* on Molecular, Bulk and Adsorbed Scenes

Matteo Briganti[1,2], Luana Carol de Camargo[1], Giulia Serrano[2], Lorenzo Poggini[3], Andrea Luigi Sorrentino[2], Matteo Mannini[2], Jaisa Fernandes Soares[1], Roberta Sessoli[2], Federico Totti[2]
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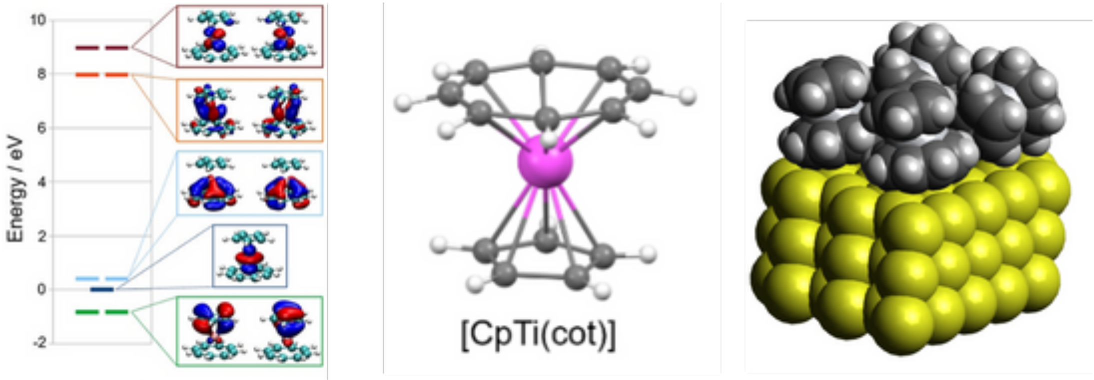
Abstract

In the area of quantum information processing molecular spin systems acquired a prominent role as potential quantum bits (QuBits) due to their wide chemical tunability, easy manipulation by microwave pulses, ability to form 2D ordered arrays [1], as well as the possibility to implement embedded quantum correction [2].



In silico simulations are currently a 'must-have' tool in designing the most promising molecular spin QuBits. As a case study, we investigated the (η^8-cyclooctatetraene)(η^5-cyclopentadienyl)titanium metallorganic mixed sandwich complex, [CpTi(cot)] (see Figure), by multi-level computational methods. Its coherence time T_m was experimentally found to reach 34 μs at 4.5 K; this result represents a remarkable coherence time for a highly protonated molecule [3]. *Ab initio* calculations and theoretical analysis in synergy with experiment were able to identify the main mechanisms governing the decoherence process in frozen solution and in the crystalline phase, paving the way towards improving quantum properties in this class of molecular materials by ligand functionalization and/or crystal engineering of reticular vibrations.

Due to such promising properties, the adsorption of [CpTi(cot)] on metallic surfaces was investigated *in silico*. Periodic density functional theory calculations [4] showed that [CpTi(cot)] can adsorb non-destructively on Au(111) surface in an ordered monolayer, in agreement with scanning probe microscopy (SPM) and X-ray spectroscopy data [4]. These results, along with the accessibility of the semi-occupied non-bonding d_{z2} orbital (see Figure), make the neutral [CpTi(cot)] molecule an ideal candidate for single-qubit addressing on surface and quantum sensing.

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Meltable Spin Crossover Iron(II) Complexes with Strong Cooperative Hysteretic Properties

Francisco Javier Valverde-Munoz[1], Maksym Seredyuk[1], M. Carmen Muñoz[2], José Antonio Real[1]
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Abstract

Iron(II) spin crossover (SCO) complexes switch between the high- (HS) and low-spin (LS) states in response to external stimuli such as temperature, pressure, light, analytes or extrinsic phase transitions. In singular conditions, the SCO event afford excellent examples of molecular bistability conferring memory function to the material. The search for optimal SCO parameters such as equilibrium temperature ($T_{1/2}$) and hysteresis width ($\Delta T_{1/2}$) is a constant motivation in the design of new SCO materials. These parameters can be tuned applying internal "chemical" pressure through isomorphic substitution or applying external hydrostatic pressure but also by chemical design. A first example of systematic chemical control over SCO was based on the "molecular alloy" approach in the 1D polymer $[Fe(Htrz)_{3-3x}(NH_2trz)_{3x}](ClO_4)_2H_2O$.[1] The emergence of robust porous SCO MOFs of the Hofmann-type has more recently afforded new excellent examples of chemical control based on host-guest interactions.[2] Taking into account the well-known intrinsic structural instability of aliphatic groups to induce phase transitions, decoration of a target SCO molecule with aliphatic groups can be an alternative approach to strongly influence over $T_{1/2}$ and $\Delta T_{1/2}$. In this regard, here we will present a reliable approach based on coupling the SCO with reversible crystal-to-liquid phase transitions by chemical design.[3] The resulting meltable iron(II) mononuclear SCO complexes display strong cooperative "forward" and/or "reverse" spin transitions which depend on the precise nature coordination site or the length of the aliphatic chains (Figure 1).

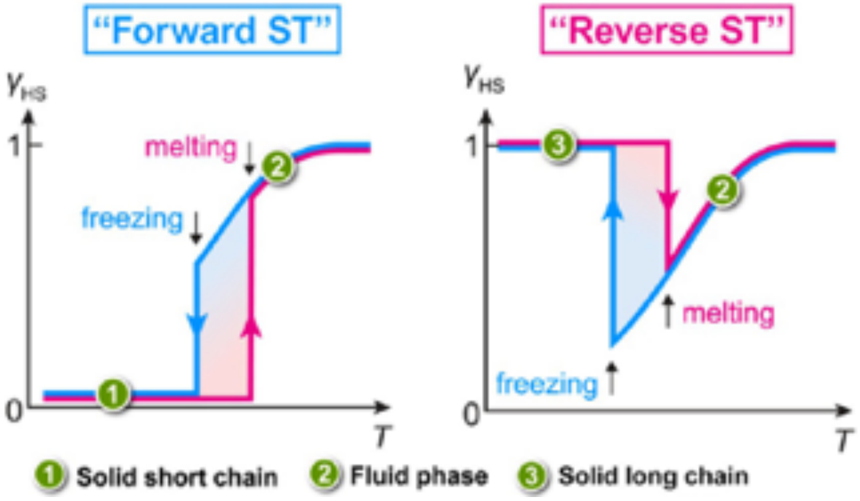

Figure 1. SCO events induced by the coupling between SCO and melting.

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Discovery of Quantum Spin Liquid State in A Two Dimensional Semiconductive Metal-Organic Framework: $Cu_3(HHTP)_2$

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Abstract

The discovery of quantum spin-liquid (QSL) states is attractive to physicists as many unprecedented phenomena could be revealed while the system differs from the semi-classical approaches. Commonly, the QSL states is resulted by the frustrated magnetic interactions of spins that are induced by certain structural topologies of spin centers, such as honeycombs, gyroids and Kagome lattices. On the other hand, the strongly-correlated MOFs have been extensively studied due to their outstanding electrical conductivity, but their magnetic behaviors have yet been carefully examined. With the special topologies, such as honeycomb lattice or 2D Kagome lattice of the spin centers, they could become possible candidates that possessing QSL ground states. In this work, we investigated one of the most well-known 2D semiconductive MOFs, $Cu_3(HHTP)_2$ with a Kagome arrangement of Cu(II) cations, and reported the ultralow temperature physical properties of these MOF. No long-range ordering was observed in the magnetic susceptibility even when the sample is cooled down to 34mK, meanwhile, no anomaly was observed in the specific heat capacity measurement with the temperature down to 65mK. Using the diamagnetic analog, $Zn_3(HHTP)_2$ as a reference of lattice heat capacity, the heat capacity of spins are found to be extremely similar to the theoretically predicted value of a S=1/2 2D Kagome Heisenberg antiferromagnet(KHAF) system. Therefore, these ultra-low temperature results suggested a quantum spin-liquid ground state of $Cu_3(HHTP)_2$ MOF. Further studies on these MOFs have also been conducted, including the high field magnetization behavior and the field suppression of the quantum fluctuations at ultralow temperature.

Phase Switchable Porous Magnets

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Tohoku University, Sendai, Japan

Abstract

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

Crystal-to-Crystal Transformation and Reversible Photo and Thermo-Induced ON/OFF Switching On a 2D Hexagonal Network

Abhishake Mondal[1], Krishna Kaushik[1], Santosh Panjikar[2], Sakshi Mehta[1]
[1]Indian Institute of Science, Bangalore, India. [2]Australian Synchrotron, Victoria, Australia

Abstract

Over the past years, a considerable attention is given to the materials that can reduce size of electronic devices and can be used for high-density information storage, quantum computing and spintronics.[1] A class of materials showing metal-to-metal electron transfer (MMET) is promising in this regard. Octacyanometallates building blocks have been recently applied to judiciously design multifunctional materials which exhibit an enormous range of anticipated physical properties, including long-range magnetic ordering, photomagnetic effect, electro-magnetic properties, *etc*.[3-4]

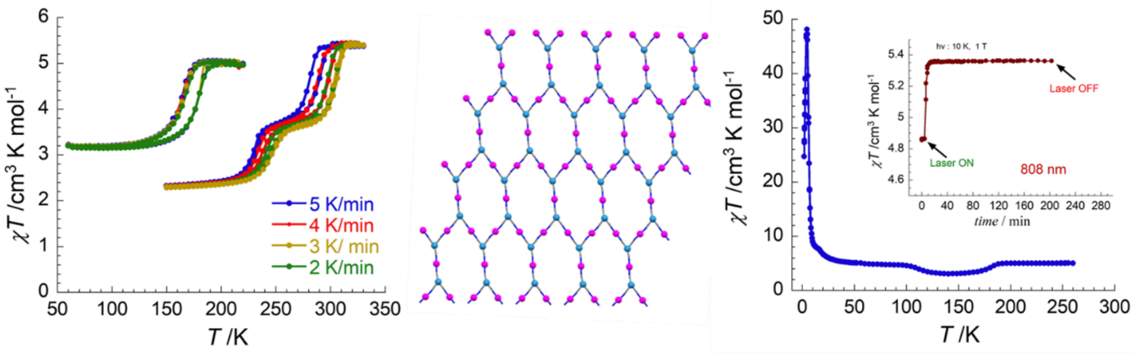

Figure 1: Temperature dependence of the χT product for the complexes (left); Perspective view of the 2D network (middle); χT *vs* T curve under 808 nm light irradiation (right)

In this presentation, I will show our recent development on reversible thermo and photoinduced MMET system which also shows metamagnetic behavior at low temperature.[4] The novel 2-D coordination network was designed by following complex as ligand strategy. The resulting 2D network exhibits many interesting features including Single crystal-to-crystal transformation. Detailed magnetic studies reveal that reversible photo and thermo-induced metal-to-metal ET occurs in both the forms with thermal hysteresis loops along with metamagnetic behaviour at low temperature for the quenched state of first form. The novel materials suggest new resource for magnetism in 2D coordination networks.

We thank, the Indian Institute of Science (IISc), The Science & Engineering Research Board (SERB), Govt. of India for financial support.

[1] Mondal, A. et. al., *J. Am. Chem. Soc.* **2013,** *135* (5), 1653. [2] Arimoto, Y. et. al., *J. Am. Chem. Soc.* **2003,** *125* (31), 9240. [3] Stefańczyk, O. et. al., *J. Appl. Phys.* **2021,** *129* (11), 110901. [4] Mondal, A. et. al., Manuscript under preparation.

Tuning Magnetic Properties in Azido-Bridged Molecular Grids

Zhilin Guo[1,2], Yi-Fei Deng[1], Zoe Pikramenou[2], Yuan-Zhu Zhang[1]
[1]Southern University of Science and Technology, Shenzhen, China. [2]University of Birmingham, Birmingham, United Kingdom

Abstract

Rational design of molecular clusters has received continuous attention in many interdisciplinary fields of sensors, optics, spintronics, catalysis as well as molecular magnetism. In comparison with those closed-shell bridging ligands, which often leads to weak magnetic coupling between the metal centres due to the large spanning distance, the use of free radical bridges is capable of propagating efficient spin exchange beyond the limit of distance and further enhances magnetic interaction with at least an order of magnitude larger due to the direct overlap of orbitals bearing unpaired electrons.

3,6-substituted pyridazine and tetrazine derivatives have been used as coding ligands in assembling a series of polygonal topologies including triangles, squares, and pentagons. However only a few behaved as single-molecule magnets (SMMs). Here we developed a new synthetic route by employing additional azido ions as secondary bridges and prepared a series of Co(II) grid-like SMMs. Remarkably, the successful introduction of tetrazine radicals (bpztz and bptz) into the grid architecture set up much stronger magnetic coupling between the spin carriers and thus better SMM performances were observed. In addition, the Fe(II) counterpart exhibits remarkable spin-crossover behaviour which is first discovered in azido-bridged clusters.

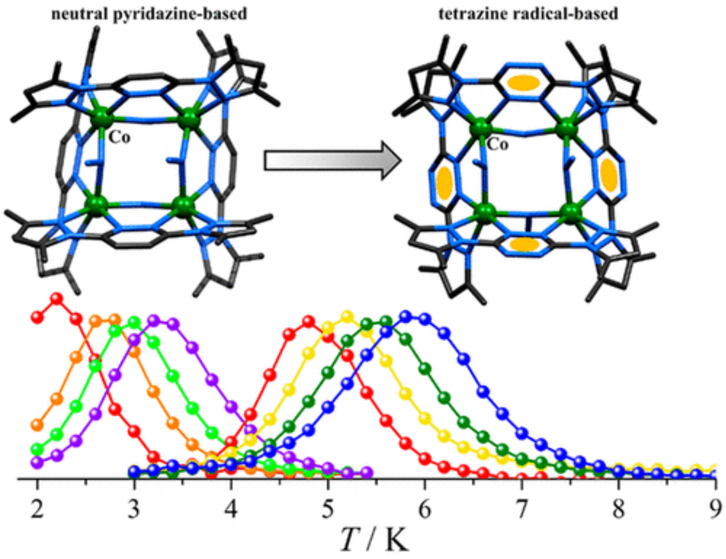

Figure 1. The structures and AC magnetic properties of Co(II) grids.

1. (a) T. J. Woods and K. R. Dunbar et al, *Chem. Eur. J.*, 2015, **21**, 10302-10305; (b) D. I. Alexandropoulos, and K. R. Dunbar et al, *J. Am. Chem. Soc.*, 2017, **139**, 11040-11043; (c) M. A. Lemes, R. Clérac and M. Murugesu et al, *Chem. Eur. J.*, 2018, **24**, 4259-4263. 2. (a) Z. Guo, Y.-F. Deng, Z. Pikramenou, Y.-Z. Zhang, *Dalton Trans.* **2020,***49*, 9218-9222; (b) Z. Guo, Y.-F. Deng, Z. Pikramenou, K. R. Dunbar, and Y.-Z. Zhang, *Inorg. Chem.*, **2021**, *60*, 3651-3656; (c) Z. Guo, Z. Pikramenou, Y.-Z. Zhang et al, *paper under review*.

Spin dynamics in [VO(TPP)] under high-power THz radiation: insights into spin-phonon coupling

Anatoly Melnikov[1,2,3], Stefano Benci[4,5], Fabio Santanni[4], Yaroslav Getmanov[6,3], Oleg Shevchenko[6], Renato Torre[4,5], Roberta Sessoli[4], Matvey Fedin[1,3], Sergey Veber[1,3]

[1]International Tomography Center SB RAS, Novosibirsk, Russian Federation. [2]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russian Federation. [3]Novosibirsk State University, Novosibirsk, Russian Federation. [4]Università degli Studi di Firenze, Firenze, Italy. [5]European Laboratory for Non-Linear Spectroscopy, Firenze, Italy. [6]Budker Institute of Nuclear Physics SB RAS, Novosibirsk, Russian Federation

Abstract

The ability of controllable slowdown or acceleration of spin relaxation in spin-based qubit prototypes is crucial for their practical implementation. In this respect, deep understanding of interplay between spin dynamics and vibrational properties of spin-carrying lattice is of high importance. Transition metal ions, such as V^{IV} and Cu^{II}, grant both long spin decoherence times and flexibility in tuning the vibrational characteristics, thus allowing adjustment of their electronic/magnetic properties. Spin-phonon interaction in oxidovanadium(IV) tetraphenylporphyrin [VO(TPP)] was previously studied in detail [1], showing efficient spin-phonon coupling with ~70 cm^{-1} (~2 THz) absorption band. This makes [VO(TPP)] a candidate of choice for further study of the efficiency of spin-phonon interaction via excitation of relevant vibrational bands.

THz range is probably the last part of electromagnetic spectrum suffering from the lack of bright and tunable light sources. Free Electron Lasers (FELs) are able to overcome this limitation. X-band EPR-endstation developed at Novosibirsk FEL facility allows studying the spin dynamics induced by high-power THz pulses.

Herewith, we report the study of spin dynamics in [VO(TPP)] induced by THz pulses of ~50-100 W power and sub-millisecond duration. The experiments utilize time-resolved continuous wave EPR (THz-pump EPR-probe). THz-induced response of spin system was explored at cryogenic temperatures as a function of THz frequency, THz intensity and applied microwave power. The observed kinetics was rationalized using modified Bloch equations. In order to simulate experimental data, the effects of sample heating, temperature dependence of the spin−lattice relaxation and heat capacity of [VO(TPP)] were taken into account. This described well the "after-pulse" dynamics, but the "on-pulse" kinetics indicated an additional process attributed to THz-induced relaxation. Possible mechanism of THz light interaction with the spin system is discussed.

This work was supported by RSF 17-13-01412.

[1] Yamabayashi, T., et al. JACS. 2018, 140, 12090−12101.

Poster Timetable

Monday 14th June 2021

Session 1.1	19.30 – 19.55 (UK time, UTC+1)

Rm	Abs	Presenter	Title
zoom.us/j/93870750691			
1	316	Leonel Llanos Silva	Ab initio study of the quantum tunelling of magnetization in bimetallic dysprosium single molecule magnets
2	79	Daniel Cutler	Small ligands with giant potential: Building large FeIII-O clusters from simple ligands
3	144	Carmen María Atzin Macedo	Synthesis and spectroscopic characterization of Ni(II), Co(II) and Mn(II) complexes derived from novel Schiff base
4	191	Brittany Grimm	High-Field EPR Study of the Spin-Crossover Transition in a Mn(III) Complex
5	185	Jason Yu	Computational Characterization of Molecular Spin Qubits using Density Functional Theory
6	85	Ashlyn Hale	Large Fe22 and Fe24 clusters: Synthesis, structure, and magnetic couplings via magnetostructural correlations and DFT
7	319	Daniel Lussier	The Structural, Electrochemical, and Magnetic Properties of Diuranium Complexes Containing an Organic, Redox-Active Bridge
zoom.us/j/97439940767			
8	80	Theocharis Stamatatos	Deposition studies of a new {Dy2} single-molecule magnet on graphene-like substrate
9	27	Mark Turnbull	Nearly isotropic AFM spin ladders: Structure and magnetism
10	301	Myron Huzan	Single-ion magnetism in the extended solid-state: insights from X-ray absorption and emission spectroscopy
11	43	Itziar Oyarzabal	A redox-active coordination chemistry approach to magnetic and/or conductive materials
12	148	Rosa Diego Creixenti	A mononuclear spin-crossover complex describing four distinct thermal routes
13	294	Mariana Velho	[Au(dspdt)2]: a conducting neutral bis(1,2-dithiolene) gold complex with a unique crystal structure
14	340	Andreas Kourtellaris	A microporous Co(II) - based 3-D metal organic framework built from magnetic infinite rod-shaped secondary building units
zoom.us/j/91766287448			
15	69	Anne Lüpke	Filling the gap in the metallacrown family: The 9-MC-3 chromium metallacrown
16	295	Jorge Navarro Giraldo	DFT study of Cobalt-based single-molecule magnet deposition on graphene
17	334	Krishnendu Kundu	Massive 9 GHz Hyperfine Clock Transition in a Lu(II) Molecular Spin Qubit
18	158	Aleksandra Pacanowska	Surface Deposition of CN-bridged Magnetic Sponges
19	14	Rubén Turo-Cortés	Reversible guest-induced gate-opening effect observed in spin crossover two-dimensional Hofmann Clathrates
20	115	Maria Sara Raju	Role of Vibronic coupling in the Magneto-Chiral Dichroism of Paramagnetic Complexes Exhibiting Helical Chirality

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<tr><td>2</td><td>182</td><td>Daniel Aravena Ponce</td><td>Choosing between vibrational and Crystal field tuning for improvement of high-performance Single Molecule Magnets.</td></tr>
<tr><td>3</td><td>151</td><td>Lorena Martínez</td><td>Exchange coupling in a thiocyanato-bridged copper(II) chain: computational approach to magnetostructural correlations</td></tr>
<tr><td>4</td><td>193</td><td>Robert Stewart</td><td>Radical-lanthanide ferromagnetic interaction in a Dy(III) bis-phthalocyaninato complex</td></tr>
<tr><td>5</td><td>157</td><td>Michał Magott</td><td>The unexpected impact of humidity on the photoswitching of cyanide-bridged molecular magnets</td></tr>
<tr><td>6</td><td>204</td><td>Elly Daniels</td><td>Synthesis, structural analysis, and magnetic properties of molecular Bi-Mn-oxo and Pb-Mn-oxo coordination cages</td></tr>
<tr><td>7</td><td>307</td><td>Alexandre Vincent</td><td>Lanthanide-Cobalt bis-Dithiolene Compounds Exhibiting Significant Ferromagnetic Exchange and Single Molecule Magnetism</td></tr>
<tr><td colspan="4">zoom.us/j/97439940767</td></tr>
<tr><td>8</td><td>91</td><td>Vassilis Tangoulis</td><td>Spin Crossover Phenomenon and Nano-Topographic Study in Microcrystals and Nanoparticles of 2-D Hofmann-type polymers</td></tr>
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<tr><td>11</td><td>314</td><td>Brenna Cashman</td><td>Toward heavy pnictogen ligated single molecule magnets</td></tr>
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<tr><td>20</td><td>278</td><td>Félix Houard</td><td>Water-dependent crystallization of infinite and finite Single-Chain Magnets</td></tr>
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Tuesday 15th June 2021

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2	179	Raúl Santiago Piera	Tuning magnetism and conductivity in 2D covalent organic radical frameworks via mechanical compression
3	207	Subrata Ghosh	ON/OFF Photo-Switching and Thermo-Induced Spin Crossover with Cooperative Luminescence in a 2D Iron(II) Coordination Polymer
4	259	Richard Collins	Lanthanide SMMs; it's Plane to See
5	107	Yasutaka Kitagawa	Quantum design of ferromagnetic homonuclear bimetallic complexes based on orbital counter-complementarity
6	181	Alessio Nicolini	Tetrairon(II) Extended Metal Atom Chains as Single-Molecule Magnets
7	90	Akito Fujisawa	Anomalous Phase Transition Observed in Nanosize Tetratitanium Heptoxide
8	221	Katarzyna Rogacz	Photochromic dithienylethenes for the construction of photoswitchable quantum nanomagnets
9	231	Kunal Kumar	Effect of lanthanides on magnetic exchange-coupling and second harmonic generation
10	311	Michael Baker	The electronic structure and single-ion magnetism of linearly coordinated Mn(I), Fe(I), Co(I), and Ni(I) doped within lithium nitride crystals quantified by X-ray spectroscopy

zoom.us/j/93990174843

Rm	Abs	Presenter	Title
11	240	Xin-Hua Zhao	Multiple Transition Dynamics: Spin Transition Coupled with Structural Phase Transition
12	168	Simen Sopp	Exceptionally Clean Single-Electron Transistors from Solutions of Pleio-Soluble Molecular Graphene Nanoribbons
13	143	Xin-Yi Wang	Molecular Magnetic Materials Based On $[\mathrm{Mo^{III}(CN)_7}]^{4-}$ Unit
14	315	Masooma Ibrahim	Polyoxometalate-Based High-Spin Functional Clusters
15	28	Jett Tao Janetzki	Predicting Transition Temperature in Valence Tautomeric Molecular Switches: A Computational and Experimental Study
16	132	Pablo Sevilla	Growth of Lanthanide-based 2D MOFs on silicon surfaces
17	150	Mohammad Reza Safari	Towards single-molecule-scale studies of enantioselective adsorption of chiral molecules on ferromagnetic surfaces
18	31	Palmerina Gonzalez Izquierdo	Crystal and Magnetic structures and Dielectric phase transition of the novel Organic-Inorganic Hybrid Halometallate compound: (quinuclidinium)$[\mathrm{FeCl_4}]$
19	209	Alessandro Soncini	Quantum spin toroidicity in molecular spin rings
20	197	Marco Coletta	Biscalix[4]arene-supported metal clusters

Wednesday 16th June 2021

Session 3.1 11.50 – 12.15 (UK time, UTC+1)

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2	255	Kenta Imoto	A pentacyanidonitrosylferrate-based magnetic one-dimensional metal assembly exhibiting photo-induced switching of second harmonic generation
3	50	Nikolaos Konstantinidis	Discontinuous quantum and classical magnetic response of the pentakis dodecahedron
4	98	Athanasios Mavromagoulos	Synthesis and characterisation of CuII-GdIII complexes.
5	106	Yoshio Teki	π-Topology and Ultra-Fast Excited-State Dynamics of Remarkably Photo-stabilized Pentacene Derivative Utilizing Radical Substituents
6	261	Jana Dubnická Midlíková	Development of FTIR spectroscopy in high magnetic fields
7	205	Anatoly Melnikov	Multimodal THz waveguides at EPR endstation of Novosibirsk Free Electron Laser: construction and overall performance
8	46	Xinghui Qi	In-Depth Investigation of Photomagnetic Compounds Based on Octacyanidometallates
9	161	Giang Truong Nguyen	Computational investigation of the magnetization blocking mechanism in exchange-coupled lanthanide single-molecule magnets
10	239	Jonas Braun	Quenching of QTM in Lanthanide Complexes with Semiquinonate Radical Ligands
zoom.us/j/93990174843			
11	111	Yao Binling	A dual-capping tetrazine ligand in favour of both trigonal prismatic geometry and strong magnetic coupling
12	243	Alessandro Chiesa	Molecular spin qudits for quantum simulation of light-matter interactions
13	147	Abinsah Swain	{Ru2Dy2} Butterflies: Examples of 4d-4f Single Molecule Magnets
14	214	Maja Dunstan	Crystal field splitting and exchange interactions in a lanthanoid-semiquinonate complex
15	232	Dominik Czernia	Effect of proton irradiation on magnetic properties of two-dimensional Ni(II) molecular magnet
16	149	Javier Cepeda	MOFs based on cobalt and 2-aminoisonicotinate behaving as field-induced SMMs: developing magnetic sensors
17	169	Jack Neill	Ab initio study of metal-ligand interactions and their role in altering magnetic properties of linear homoleptic two-coordinate transition metal complexes.
18	196	Gabriela Handzlik	Lanthanide complexes with carbo[6]helicene o-quinones
19	269	Emily Payne	Magnetic Exchange in Anderson-Type 3d Transition Metal Clusters
20	217	Diana Plesca	Unexpected Light-Induced Thermal Hysteresis in Matrix Embedded Low Cooperative Spin Crossover Microparticles

Wednesday 16th June 2021			
Session 3.2			12.15 – 12.40 (UK time, UTC+1)
zoom.us/j/93234805108			
Rm	**Abs**	**Presenter**	**Title**
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2	262	Yue Xin	Luminescent Cyanido-bridged DyIII-CoIII Framework Showing Solvent-driven Switchable Single-molecule Magnet Behavior
3	82	Xin-Da Huang	Reversible Cycloaddition Reactions of Dysprosium-Anthracene Compound Following Luminescent and Magnetic Switching
4	244	Daniel Martins	Hyperfine Spectroscopy of Cr7Ni Heterometallic Qubits
5	210	Rie Suizu	Clarification of the origin of the frustration-induced phase transition in reduced diamond lattice
6	18	Mario Falsaperna	Exploring the magnetocaloric effect in the Ln(HCO2)(C2O4) family of Metal-Organic Frameworks
7	279	Asmita Sen	A Computational Assessment on a Series of High-Valent Fe/Mn-oxo/hydroxo Complexes, Revealing the Impact of Inner Electronic Structure on Their Reactivity
8	67	Georgios Velkos	Dy_2O-Clusterfullerenes: Strong Magnetic Anisotropies and Fullerene-Dependent Single Molecule Magnetism
9	249	Olaf Stefanczyk	Photoswitchable high-dimensional octacyanidometallate-based networks
10	183	Simone Chicco	Controlled coherent dynamics of [VO(TPP)], a prototype molecular nuclear qudit with an electronic ancilla
zoom.us/j/93990174843			
11	92	Jing Li	Manipulation of Molecular Qubits by Isotope Effect on Spin Dynamics
12	300	Gemma Gransbury	Valence Tautomerism in Bis(dioxolene)-Bridged Dinuclear Cobalt Complexes: Correlating Two-Step Transitions with Redox and Mixed-Valence Properties
13	251	Magdalena Ceglarska	Magnetic investigations of monocrystalline [Co(NCS)2(L)2]n: new insights into single-chain relaxations
14	224	Maria Brzozowska	High-performance tetrahedral ErIII SMMs.
15	159	Diana Visinescu	Cyanido-bridged {FeIIILnIII} heterobimetallic chains assembled through the [FeIII{HB(pz)3}(CN)3]- complex as metalloligand: Synthesis, crystal structure and magnetic properties
16	171	Zhenxing Wang	Controlling Electron Spin Decoherence in Nd-based Complexes via Symmetry Selection
17	40	Kira Vostrikova	The lanthanide complexes of the tripodal nitroxyl radicals
18	152	Fabio Santanni	Synthesis of a Novel Set of Hydrogen-Free Complexes of 1,3,2-Dithiazole-4-thione-5-thiolate Ligand as Potential Spin Qubits
19	33	Emma Regincos Marti	Study on a family of Ln(III) highly coordinated complexes with a short axial Ln–F bond
20	170	Silvia Gimenez-Santamarina	Towards peptide-based magnetic multistate memristive materials

Posters

14

Reversible guest-induced gate-opening effect observed in spin crossover two-dimensional Hofmann Clathrates

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Abstract

In this work we report a novel family of Spin Crossover[1] (SCO) 2D Hofmann-type coordination polymers (2D-HCP) formulated as $\{Fe(5\text{-}NH_2pmd)_2[M^{II}(CN)_4]\}\cdot H_2O$ [5-NH$_2$pmd = 5-aminopyrimidine, M^{II} = Pt ($\mathbf{1^{Pt}\cdot H_2O}$) or Pd ($\mathbf{1^{Pd}\cdot H_2O}$)]. Both frameworks exhibit a two-step spin transition stemming from the presence of two crystalographically distinct Fe^{II} ions generated by the presence of host-guest interactions. Upon heating up to 400K, the guest molecule is desorbed in a single-crystal to single-crystal process, driving to the corresponding $\mathbf{1^{M}}$ dehydrated counterparts. These desorbed compounds display complete single-stepped SCO curves explained by the existence of a unique type of Fe^{II} center in the bimetallic framework. Furthermore, the activated $\mathbf{1^{M}}$ compounds are able to re-adsorb either molecules of water, even in atmospheric conditions, recovering the original two-stepped SCO behavior or methanol/ethanol which partially block the HS →LS transition of the resulting $\mathbf{1^{M}\cdot MeOH}$ and $1^{M}\cdot\mathbf{EtOH}$ frameworks. Time dependent isotherms have been performed to study the adsorption properties of the activated compounds exposed to different guests. The efficient modulation of the SCO properties through host-guest chemistry, primarily assisted by the tendency of the amino group to form hydrogen bonds, makes the reported 2D-HCP system a powerful platform for the development of future sensor devices.

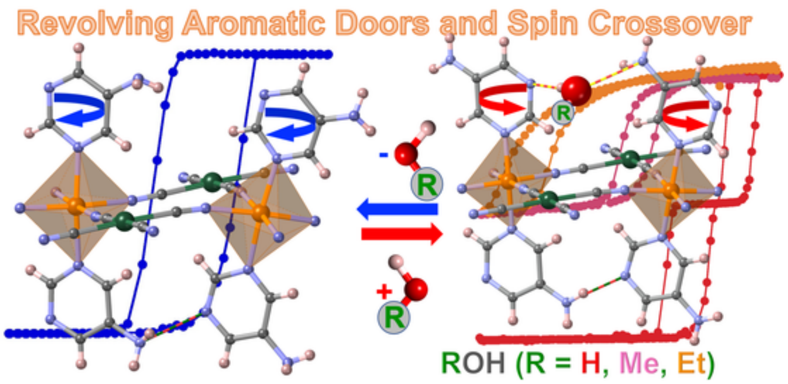

Figure 1. Magnetic properties of the $\mathbf{1^{Pt}\cdot ROH}$ (R = H, Me, Et) derivatives with a superimposed fragment of the **ROH** supramolecular interaction with the host framework. Blue and red arrows indicate the 180º flip of the ligand upon guest adsorption.

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Exploring the magnetocaloric effect in the Ln(HCO_2)(C_2O_4) family of Metal-Organic Frameworks

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Abstract

Low-temperature cooling is a necessary requirement in many areas of fundamental research and applied technologies. Many applications, including quantum computing, spintronics and medical imaging, rely on liquid helium to operate at temperatures below 20 K. In particular, liquid helium ^4He is used for T > 2 K and a mixture of the two isotopes ^3He and ^4He is commonly employed for cooling below this. Liquid helium is costly, expensive and prone to disruptions in supply, so it is necessary to explore efficient and cost-effective alternatives.

Recent work on coordination frameworks have shown compounds, such as Gd(HCO_2)$_3$ and GdOHCO$_3$, having comparable or greater MCEs than $Gd_3Ga_5O_{12}$ (GGG), the benchmark magnetocaloric for cooling below 10 K, with the incorporation of other lanthanides leading to excellent performance above 4 K in low applied fields. Inspired by these results we have synthesised members of the *Ln*(HCO_2)(C_2O_4) family (*Ln* = Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}) that crystallise in the orthorhombic P*nma* space group and feature low-dimensional chains arranged on a distorted triangular lattice. We have studied the magnetic properties and MCE of these materials.

We have found Gd(HCO_2)(C_2O_4) to be an excellent candidate for applications at around 2 K with one of the highest magnetocaloric entropy changes amongst coordination frameworks. Generally, the incorporation of Ising-like cations was previously shown to lead to improved performance at higher temperatures under low applied fields that can be generated more easily using permanent magnets. We have observed this only for Dy(HCO_2)(C_2O_4), in contrast with results found for the *Ln*(HCO_2)$_3$ and *Ln*OHCO3 families of compounds. Neutron diffraction indicates these Ising compounds lack the strong local magnetic correlations found in the related analogues, indicating this negatively affects the optimisation of the MCE performance for these compounds.

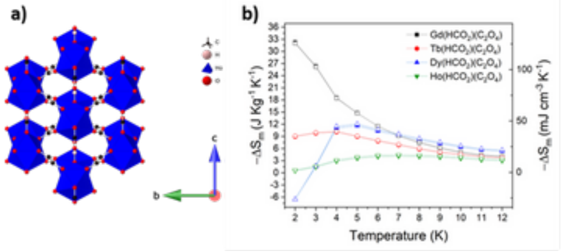

***Fig. 1**: a) Crystal structure of Ho(HCO_2)(C_2O_4) with infinite 1-D chains arranged in a triangular lattice on the bc-plane. b) Maximum entropy change -ΔS_m^{max} for a magnetic field change of 0-2 T for members of the Ln(HCO_2)(C_2O_4) family with filled and hollow symbols representing gravimetric and volumetric -ΔS_m^{max}, respectively.*

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Nearly isotropic AFM spin ladders: Structure and magnetism

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Abstract

The structures and magnetic properties of two AFM spin ladders are presented where both run and rail connections are made via bridging pyrazine ligands. The complexes are *catena*-(bis(3-X-4-pyridone-κ-o)(μ-pyrazine)copper(II)(-μ-pyrazine)diperchlorate ($[Cu(pz)_{1.5}(L)_2](ClO_4)_2$ where L = 3-X-4-pyridone and X = Br (**1**) or Cl (**2**)). **1** and **2** crystallize in the monoclinic space group $P2_1/c$. Due to the bulk of the 3-X-4-HOpy ligands, the ladders are well isolated in the *a*-direction (15.6 Å). The ladders, which run in the *b*-direction, are stacked in the *c*-direction with the separation (7.81 Å) between copper(II) ions caused by the bulk of a semi-coordinate perchlorate ion coordinated in the axial position. The magnetization to 5 T indicates a quantum regime and the magnetic susceptibility down to 1.8 K, for **1** and **2**, is well modeled by the strong-rung ladder model giving nearly isotropic exchange. Theoretical calculations are presented for **2** which are in excellent agreement with experiment.

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Predicting Transition Temperature in Valence Tautomeric Molecular Switches: A Computational and Experimental Study

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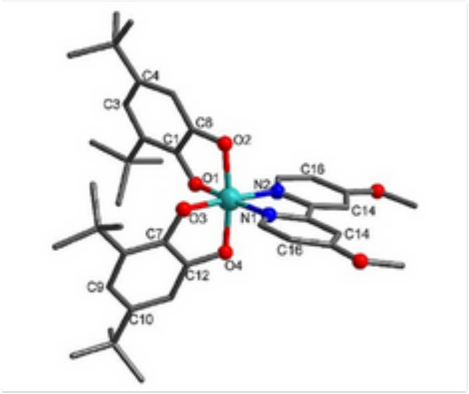
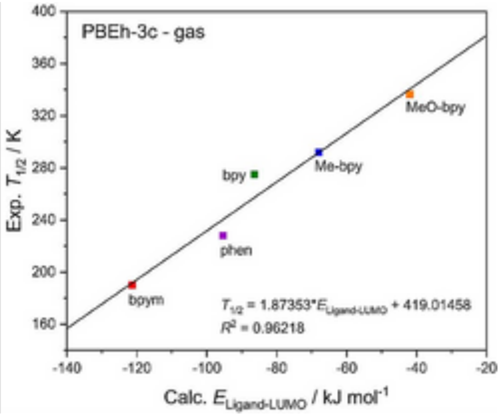
Abstract

A valence tautomeric (VT) transition involves a stimulated reversible electron transfer, accompanied by spin transition, between a redox-active metal-ligand pair. These transitions are mostly commonly seen in cobalt-dioxolene complexes and are potentially important for molecular electronics. In VT complexes with general formula [Co(dbdiox)(dbsq)(N_2L)] (dbdiox = 3,5-di-*t*ert-butyl-dioxolene, in catecholate (dbcat) / semiquinonate (dbsq) form, N_2L = bidentate N-donor ligand), the transition temperature ($T_{1/2}$) between LS-Co(III)-cat and HS-Co(II)-sq changes depending on the N_2L ligand used.

The ability to computationally predict $T_{1/2}$ in VT systems, prior to synthesis, will be a major step toward applicability. We have investigated [Co(dbdiox)(dbsq)(N_2L)] complexes and have synthesized and characterized the new variant [Co(dbdiox)(dbsq)(MeO-bpy)] and determined the $T_{1/2}$ to be 336 K. For a full series of [Co(dbdiox)(dbsq)(N_2L)] complexes, we employed state-of-the-art DFT methods to provide (1) accurate electronic description of the tautomers with precise spin distributions; (2) a method to obtain very accurate relative energies including all physical and environmental effects; and (3) a simple model of correlation between the experimental $T_{1/2}$ (solution) and calculated orbital energies of the ligand. This simple and accurate model, taking less than 15 minutes computational time, will facilitate the future targeted synthesis of VT compounds with desired $T_{1/2}$ values.





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Crystal and Magnetic structures and Dielectric phase transition of the novel Organic-Inorganic Hybrid Halometallate compound: (quinuclidinium)[FeCl4]

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Abstract

The synthesis of complexes based on the combination of organic-inorganic building blocks provides a promising approach in the design of systems with tuneable properties. In this communication, we will present the properties of a new compound based on quinuclidinium and FeCl4 , with formula (quinuclidinium)[FeCl4].[1] Similar compounds containing this quinuclidinium present interesting ferroelectric properties.[2].

The structural characterization shows two phase transitions. The first one, detected in the range from 100 to 300 K, was resolved by single-crystal X-Ray and neutron diffraction. At 300 K, the compound presents the orthorhombic space group Pbc21. At 100 K, the space group is Pbca, with a doubling of the a-axis, related to the rotation of the cations: two different orientations of the counterion are observed in the low temperature phase along the a direction, contrary to the high temperature phase, where it appears only one orientation.

Moreover, this compound presents long-range magnetic order below 3 K. The magnetic structure was solved using single-crystal and powder neutron diffraction data from D19 and D1B instruments (ILL, France), respectively, in the Shubnikov magnetic space group P21’21’21, in which a ferromagnetic component along the c direction is allowed.

The dielectric permittivity data shows a sharp phase transition around 390 K, reaching a maxima of 10^5. This value is giant compared to similar compounds,[2] which could be of interest for electrochemical applications.

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Study on a family of Ln(III) highly coordinated complexes with a short axial Ln–F bond

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Abstract

The recently reported compound $[Dy^{III}LF](CF_3SO_3)_2\cdot H_2O$ (L = 1,4,7,10-tetrakis(2-pyridylmethyl)-1,4,7,10-tetraaza-cyclododecane) displays a strong axial crystal field due to the short Dy-F bond that allows the molecule to behave as a Single-Ion Magnet. Following this discovery, we have further studied the system to identify the magnetic trends within the lanthanide series and now report the structural and magnetic study of a family of complexes with the formula $[Ln^{III}LF]^{2+}$ (Ln(III) = Ce, Pr, Nd, Eu, Tb, Ho, Er, Tm, Yb). The isostructural analogues show a change in space group along the series; bigger lanthanides (Ce(III), Pr(III) and Nd(III)) crystallise in the Pccn space group whilst the smaller ones (Eu(III), Tb(III), Ho(III), Er(III), Tm(III) and Yb(III)) crystallise in the $P2_12_12$ space group. The Ce(III), Nd(III) and Dy(III) analogues show slow relaxation of the magnetization. Due to the short intermolecular distances and the high intrinsic magnetic moments of Dy(III) and Tb(III), ferromagnetic intermolecular interactions can be seen in these analogues. Such interactions can be suppressed by synthesizing magnetically diluted samples using diamagnetic $[LnLpyF]^{2+}$ (Ln=Y or La) hosts. AC magnetic susceptibility data and CASSCF calculations have been employed to describe the magnetic properties of the systems displaying SIM behavior. Considering that studies concerning Ce(III) and Nd(III) complexes that show slow magnetic relaxation are scarce, this study provides insight into the magnetic properties of these less studied lanthanide ions.

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The lanthanide complexes of the tripodal nitroxyl radicals

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Abstract

A series of mononuclear complexes of Ln(III) ions comprising one stable oxazolidine nitroxyl radical were obtained in acetonitrile media starting from nitrates. The compounds, $[LnRad(NO_3)_3]$ (Ln = Y, Eu, Gd, Tb, Dy, Tm, Lu; Rad = 4,4-dimethyl-2,2-bis(pyridin-2-yl)-1,3-oxazolidine-3-oxyl), have a molecular structure. Their coordination polyhedron, LnO_7N_2, is a tricapped trigonal prism (see Fig.1). The extracted value of 23 cm^{-1} for the antiferromagnetic coupling of Gd–Rad established from the DC magnetic and EPR data is a record strength for the complexes of 4f elements with nitroxyl radicals. The terbium derivative displays frequency-dependent out-of-phase signals in zero field, indicating single-molecule magnetic behavior. With an applied field of 0.1 T, an effective barrier of 57 cm^{-1} is found. Surprisingly, for the Eu and Lu complexes a slow magnetic dynamic was observed at 2 K.

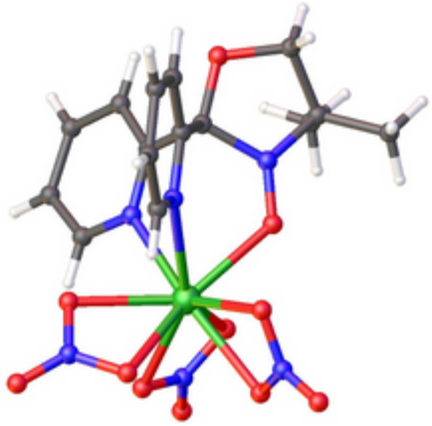

Figure 1. Molecular structure of $[LnRad(NO_3)_3]$. Ln - green, oxygen - red, nitrogen - blue, carbon - grey.

Approaches to the design of new tripodal nitroxides that are promising for improving the magnetic characteristics of complexes will also be discussed.

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Controlling the interactions and conformation of multi-qubit systems using hybrid rotaxanes

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Abstract

Supramolecular chemistry enables complex arrays to be assembled that can bring together similar and dissimilar spin systems. Through careful design, *g*-engineering approaches can be used to tune multi spin systems that maintain the unique identity of each individual spin. We are investigating the interactions between such systems to exploit the electron spin through various EPR techniques.

Here, not only can we achieve control over the electron…electron, spin…spin interaction by altering the distance between two dissimilar spin ½ systems, but also the conformation and stoichiometry of the assembly, by use of supramolecular chemistry.

[2]-, [3]- and [4]-rotaxanes; based upon on the anionic $[Cr_7NiF_8(O_2CBu)_{16}]^-$ ring, which provides a relatively low *g* value of ~1.78, are coupled to a Cu(II) spin ½ motif or a central triangular node $[Ni_2CrF(O_2CBu)_6]$, which both have relatively high *g* values of ~2.1 and ~2.48, respectively.

The weak magnetic interactions for these two, three and four qubit systems have been probed by EPR spectroscopy. In some cases continuous wave EPR can resolve the weak *J*-coupling (where $|2J| << \Delta g u_B B$) where the interactions are such that we observe AX or AX_2 type spectra, and the coupling is shown to be dominated by through-bond rather than through-space mechanisms. Where continuous wave EPR cannot resolve the exchange interactions, coherence times at both components are sufficient for pulsed EPR methods, despite the molecules containing up to 27 paramagnetic ions. Double Electron-Electron Resonance (DEER) is performed to probe the $\{Cr_7Ni\}…\{Cr_7Ni\}$ interactions, and are compared to small angle x-ray scattering (SAXS) measurements to provide a 3 – 298K coverage of the structural conformations.

This work provides a further step towards accessing coherent spin resonance in potential multi-qubit systems incorporating weakly coupled dissimilar spins.

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A redox-active coordination chemistry approach to magnetic and/or conductive materials

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Abstract

It is hard to imagine how technology would have evolved over the years without the extensive use of magnets. These materials have an inorganic origin and constitute the basis of data processing and storage devices among many other applications. Despite their success, they face several drawbacks during their manufacturing and some of them even have a highly polluting origin. This has led to a shift of interest towards metal-organic materials, as apart from benefiting from mild synthetic conditions, they allow to implement more than one useful function in a single material.

In this communication we present a new class of 2D coordination compounds which show high-temperature magnetic order and/or high electrical conductivity at room temperature. The use of non-innocent organic ligands in the presence of paramagnetic metal ions offers many possibilities for the synthesis of high-performance molecule-based materials.

Acknowledgements: I. Oyarzabal is grateful to the Basque Government for a postdoctoral grant. This work was supported by the University of Bordeaux, the Région Nouvelle Aquitaine and the CNRS.

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In-Depth Investigation of Photomagnetic Compounds Based on Octacyanidometallates

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Abstract

Octacyanidometallate based photomagnetic materials containing $[M(CN)_8]^{4-}$ (M = Mo or W) building blocks display in their photo-induced state high relaxation temperatures and high critical temperatures[1]. Two different mechanisms have been proposed to explain the photomagnetic properties of these materials. One is based on a metal-metal charge transfer (MMCT) mechanism between the two metal ions,[2] and the second one is a singlet-triplet crossover exclusively on the molybdenum site.

Herein, a mononuclear octacyanomolybdate, $K_4Mo(CN)_8 \cdot 2H_2O$ (**1**) has been chosen as a primary platform to fully investigate the singlet-triplet crossover behavior on molybdenum (IV).[3] First, based on ground state, CASSCF/CASPT2 and TD-DFT calculations predict the population of the photo-induced triplet state accompanied by the dissociation of one cyanide ligand. Experimental proofs on the photo-induced Mo-C≡N dissociation in **1** have been given by single-crystal X-ray diffraction, reflectivity, UV-Vis, and Infrared spectra measured at 10 K after light irradiation. Actually, an important increase in the magnetic moment was detected after light irradiation. Magnetic anisotropy was identified for the photoexcited state which agrees well with the theoretical calculations. These light-induced modifications could be easily erased with a thermal treatment to 65 K showing the reversibility of the process.

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Discontinuous quantum and classical magnetic response of the pentakis dodecahedron

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Abstract

The pentakis dodecahedron, the dual of the truncated icosahedron, consists of 60 edge-sharing triangles. It has 20 six-fold and 12 five-fold coordinated vertices, with the former forming a dodecahedron, and each of the latter connected to the vertices of one of the 12 pentagons of the dodecahedron. When spins mounted on the vertices of the pentakis dodecahedron interact according to the nearest-neighbor antiferromagnetic Heisenberg model, the two different vertex types necessitate the introduction of two exchange constants. As the relative strength of the two constants is varied the molecule interpolates between the dodecahedron and a molecule consisting only of quadrangles. The competition between the two exchange constants, frustration, and an external magnetic field results in a multitude of ground-state magnetization and susceptibility discontinuities. At the classical level the maximum is ten magnetization and one susceptibility discontinuities when the 12 five-fold vertices interact with the dodecahedron spins with approximately one-half the strength of their interaction. When the two interactions are approximately equal in strength the number of discontinuities is also maximized, with three of the magnetization and eight of the susceptibility. At the full quantum limit, where the magnitude of the spins equals 1/2, there can be up to three ground-state magnetization jumps that have the *z*-component of the total spin changing by $\Delta S^z=2$, even though quantum fluctuations rarely allow discontinuities of the magnetization. The full quantum case also supports a $\Delta S^z=3$ discontinuity. Frustration also results in nonmagnetic states inside the singlet-triplet gap. These results make the pentakis dodecahedron the molecule with the most discontinuous magnetic response from the quantum to the classical level.

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Modulating Magnetic Anisotropy in Ln(III) Single-Ion Magnets using an External Electric Field

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Abstract

Single-Molecule Magnets have potential applications in several nano-technology applications, including high-dense information storage devices and the realisation of this potential application lies in enhancing the barrier height for magnetisation reversal (U_{eff}). Recent literature examples suggest that the maximum values that one can obtain using a ligand field are already accomplished in Ln(III) single-ion magnets. Here we have explored using a combination of DFT and *ab initio* CASSCF calculations, a unique way to enhance the magnetisation reversal barrier using an oriented external electric field in three well-known Ln(III) Single-ion Magnets- $[Dy(Py)_5(O^tBu)_2]^+$ (**1**), $[Er\{N(SiMe_3)_2\}_3Cl]^-$ (**2**) and $[Dy(Cp^{Me3})Cl]$ (**3**). Our study reveals that, for apt molecules, if the appropriate direction and value of electric fields are chosen, the barrier height could be enhanced twice that of the limit set by the ligand field. Application of electric field along the equatorial direction found to be suitable for oblate shaped Dy(III) complexes and electric field along the axial direction found to enhances the barrier height for prolate Er(III) complex. For complex **2** and **3**, the external electric field was able to magnify the barrier height to twice and thrice that of the original complexes. However, moderate enhancement was noticed after the application of the external electric field in the case of complex **1**. This novel non-chemical-fine tuning approach to modulate the magnetic anisotropy is expected to yield new generation SIMs.

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Decisive Role of Spin-States and Spin-Coupling in Dictating Selective O2 Adsorption in Chromium(II) Metal-Organic Framework

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Abstract

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

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Dy_2O-Clusterfullerenes: Strong Magnetic Anisotropies and Fullerene-Dependent Single Molecule Magnetism

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Abstract

Fullerenes possess the unique property to stabilize various atomic species inside their empty space. When lanthanide ions are encapsulated, the endohedral fullerene can transform into a single molecule magnet [1]. Particularly, the bonding situation between two Dy^{3+} ions and one O^{2-} ion inside the carbon cage, results to the new class of Dy_2O-clusterfullerenes. Presence of O^{2-} ion in short distance from Dy^{3+} ions (≈2 Å) imposes very strong axial anisotropy to the latter [2].

We report on three different Dy_2O-clusterfullerenes: $Dy_2O@C_{72}$, $Dy_2O@C_{74}$ and $Dy_2O@C_{80}$. All three exhibit high blocking temperature of magnetization and broad hysteresis [3]. Dy-Dy magnetic coupling is characterized by the competing exchange and dipolar interactions. In $Dy_2O@C_{72}$, ferromagnetic coupling prevails while in $Dy_2O@C_{80}$ the antiferromagnetic does. In case of $Dy_2O@C_{74}$, exchange and dipolar contributions cancel each other leading to effectively decoupled Dy moments and appearance of zero-field quantum tunnelling of magnetization (see below).

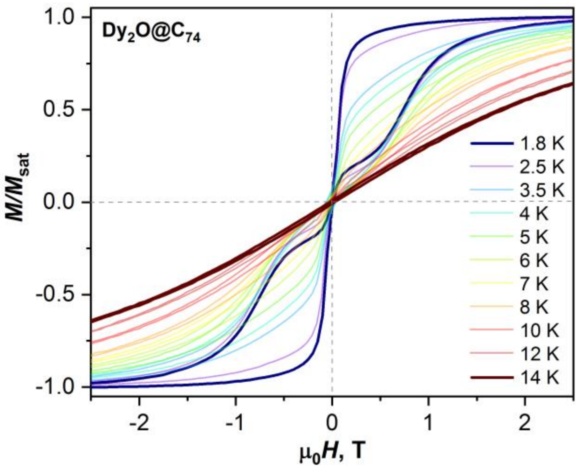

Figure. Magnetic hysteresis curves of $Dy_2O@C_{74}$ below blocking temperature (T_B=14 K)

Although not fully understood yet, our magnetic studies showed that shape and size of the host carbon cage play a very important role on the single-molecule magnetic properties. They influence the Dy-O bond lengths and <Dy-O-Dy angles, and in further extent the sign and strength of the exchange and dipolar interactions.

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69

Filling the gap in the metallacrown family: The 9-MC-3 chromium metallacrown

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Abstract

Metallacrowns (MCs) belong to a continuously developing class of compounds in the field of molecular recognition, catalysis, and magneto chemistry.[1,2] Like their organic crown ether analogs, MCs contain oxygen donor atoms in their repeating units, –[M-N-O]$_n$-, allowing them to coordinate guest ions.

The very first MCs reported by V. Pecoraro in 1989 included complexes showing a 9-MC-3 structural motif. Even then, Pecoraro stated that "[…] it should be possible to form […] metallacrown ethers through synthesis of the kinetically inert Co^{III} or Cr^{III} analogues. We expect that these exchange inert clusters will form the 9-C-3 structure since the metals should be octahedral."[3]

In this work, we now report the missing complex in the MC family. We synthesized and characterized the novel chromium metallacrown (MC) complex {Cr(III)(μ_2-piv)$_3$[9-MC$_{Cr(III)N(shi)}$-3](morph)$_3$}·MeOH (shi^{3-} =salicyl hydroxamate, piv=pivalate, morph=morpholine). The MC with a 9-MC-3 cavity built from kinetically inert Cr^{3+} was synthesized *via* solvothermal reaction. Magnetization measurements reveal a high spin ground state. This first successful Cr^{3+} MC synthesis paves the way for new kinetically and thermodynamically stable MCs for future applications. We are continuing research with the goal of now implementing anisotropic ions in chromium metallacrown cavities.[4]

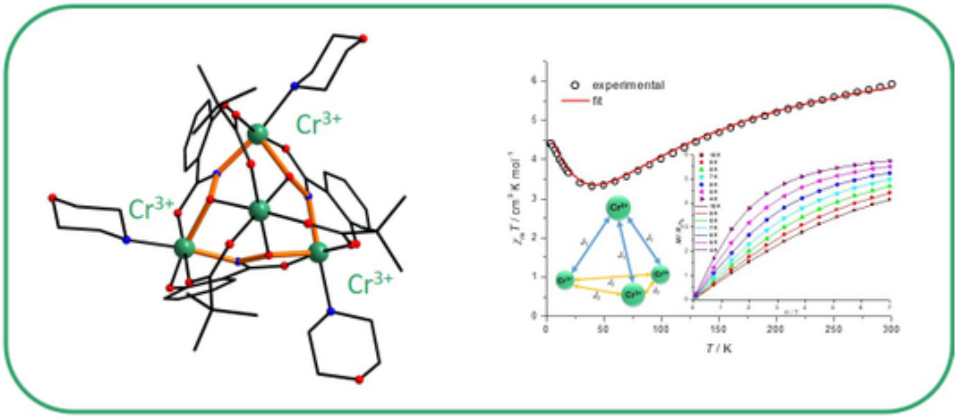

Figure 1 Schematic representation of Cr(III)(μ_2-piv)$_3$[9-MC$_{Cr(III)N(shi)}$-3](morph)$_3$ with susceptibility studies of the complex.

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Facile surface functionalization with luminescent and magnetic lanthanoid Schiff base complexes

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Abstract

The constant evolution of technology requires smaller and more efficient devices. Functional molecules such as single-molecule magnets have been proposed as possible building blocks for the next generation of quantum computers or data storage devices.[1] For this reason, addressing and manipulating single molecules on surfaces is essential and one of the main problems to overcome.[2]

In this work, lanthanoid (europium and dysprosium) complexes with Schiff base ligands have been anchored to a silicon substrate with terminal carboxylate groups via a ligand-exchange reaction—thus, through a chemisorption process. In the europium complex, characteristic luminescence is observed in layers thinner than two nanometers. On the other hand, the magnetic properties of the dysprosium compound could be potentially improved due to a better magnetic anisotropy.

Atomic force microscopy allows us to observe the total and homogeneous coverage of samples independent of their size for both europium and dysprosium compounds and the integrity of the molecules is corroborated by matrix-assisted laser desorption/ionization with a time-of-flight detector (MALDI-ToF).

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Small ligands with giant potential: Building large Fe^{III}-O clusters from simple ligands.

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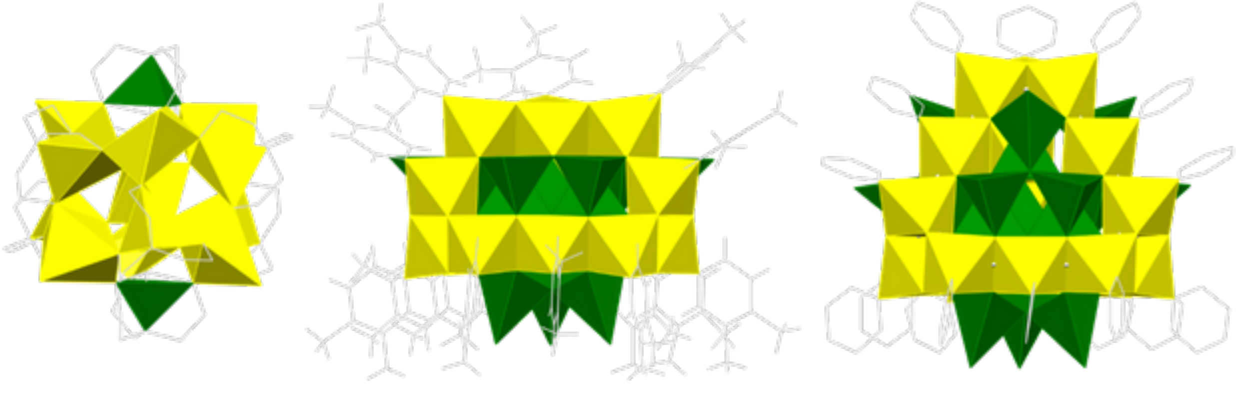
Abstract

Historically, polynuclear Fe^{III}-O clusters have been at the heart of the study of molecular magnetism. From the study of [Fe$^{III}_2$-(μ-O)] dimers detailed magneto structural correlations were developed that can be applied to larger clusters.[1] Larger antiferromagnetic wheels revealed interesting magnetic properties manifesting in stepped magnetisation.[2] The second known single molecule magnet (SMM) was the [Fe$_8$] cluster synthesised by the hydrolysis of the FeCl$_3$(tacn) (tacn = triazacyclononane) monomer.

One particularly interesting aspect of Fe^{III} clusters is their potential to grant access to large ground state spins. Molecules with such properties include the [Fe$_{17/19}$] twin clusters[3] and the [Fe$_{17}$] “molecular magnetite” species’ which show a huge ground state spin of 35/2.[4]

The discovery of such clusters using relatively simple organic ligands has prompted us to speculate that new Fe^{III}-O clusters may be synthesised that can display larger spin ground states and that new geometries may provide a pathway to interesting magnetic frustration effects. Here we present a series of such compounds made using simple organic ligands with nuclearities ranging from 15 up to 34 Fe^{III} ions.



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80

Deposition studies of a new {Dy_2} single-molecule magnet on graphene-like substrate

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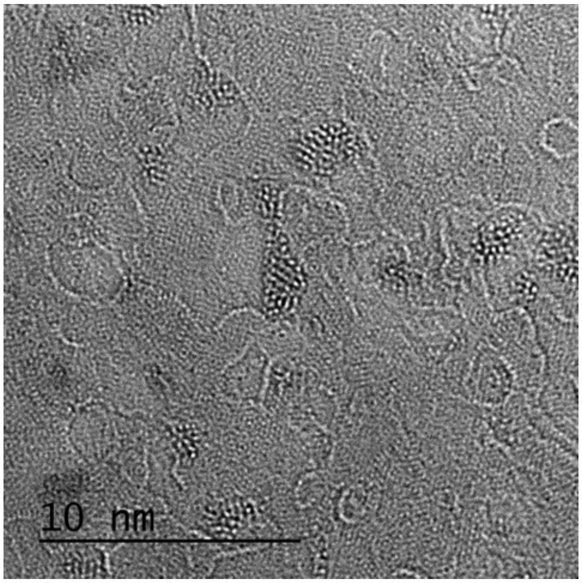
Abstract

Quantum technologies might result in revolutionary improvements in terms of capacity, sensitivity and speed, and will be the decisive factor for success in many industries and markets. Molecular quantum spintronics is a relatively new research area which requires the advanced knowledge of many interdisciplinary fields, such as synthetic chemistry, physics, materials science and theory. The idea is to fabricate molecule-based devices to read and manipulate the spin states of the molecules and carry out basic quantum operations. One of the most appealing schemes involve the synthesis of chemically and structurally stable single-molecule magnets (SMMs), and the study of their interactions with functional substrates (i.e., graphene and carbon nanotubes) to enable surface-state spintronics and electrical spin manipulation. To achieve the fabrication of molecular compounds on a functional surface, two main approaches have been developed, namely the weak- or non-covalent method and the strong- or covalent (chemisorption) method. Non-covalent functionalization is achieved with molecules lacking a specific functional group to react with the surface but having a backbone that induces weak interactions with it (i.e., van der Waals or electrostatic interactions). Covalent linking often requires molecular functionalization and subsequently grafting of the resulting molecules on selected surfaces. We herein present our efforts toward the deposition of a structurally new {Dy_2} SMM on a graphene-like substrate, which include a variety of spectroscopic, physicochemical and electronic microscopy techniques, such as IR, UV/Vis, XPS, Raman, MS, TGA, and HR-TEM. Interestingly, the solid-state material Dy_2@graphene shows frequency-dependent out-of-phase signals at low temperatures, distinctly different than those of the parent {Dy_2} SMM.



81

Symmetry-Breaking and Light Activation in Iron(III) Spin Crossover Complexes

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Abstract

Molecular switches are of great interest for use in a range of future technologies. Spin crossover (SCO) complexes are amongst the best studied of molecular switches as the compounds are easy to prepare and can operate at room temperature.[1] While most SCO complexes are of Fe(II),[2] more recently Fe(III) compounds have been shown to be robust and exhibit strongly cooperative SCO.[3–5] In our continuing interest in iron(III) SCO complexes, we present recent findings on a family of iron(III) spin crossover materials $[Fe(qsal\text{-}X)_2]A\cdot sol$ (qsal-X = halogen substituted quinolylsalicylaldiminate, A = anion, sol = solvent) where a variety of thermal and light-activated SCO profiles are observed.

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Reversible Cycloaddition Reactions of Dysprosium-Anthracene Compound Following Luminescent and Magnetic Switching

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Abstract

Lanthanide complexes are promising multifunctional materials integrating optical and magnetic characteristics.[1] However, synergistically manipulating different physical properties via single-crystal to single-crystal is still challenging. Herein we designed and synthesized one mononuclear compound $[Dy^{III}(SCN)_2(NO_3)(depma)_2(4\text{-}hpy)_2]$ (**1**) featuring pillared-layered supramolecular frameworks composed of two-dimensional hydrogen-bonded network and π-π interacted 9-diethylphosphonomethylanthracene (depma) pairs as pillars. The strong H-bonds in **1** guarantee reversible single-crystal to single-crystal (SC-SC) anthracene-based [4+4] photocycloaddition reaction giving chain-like coordination polymers $\{Dy^{III}(SCN)_2(NO_3)(depma_2)(4\text{-}hpy)_2\}$ (**1UV**). The structural transformation imparts simutaneous switching of intruging photoluminescene and single molecule magnet (SMM) behaviours. The short pseudo-linear O-Dy-O bonds provide **1** with strong axial magnetic anisotropy and, hence, compound **1** shows butterfly-like hysteresis loop up to 5.0 K and highest effective spin-reversal energy barrier of 262 K among all photo-switchable lanthanide-based SMM systems.

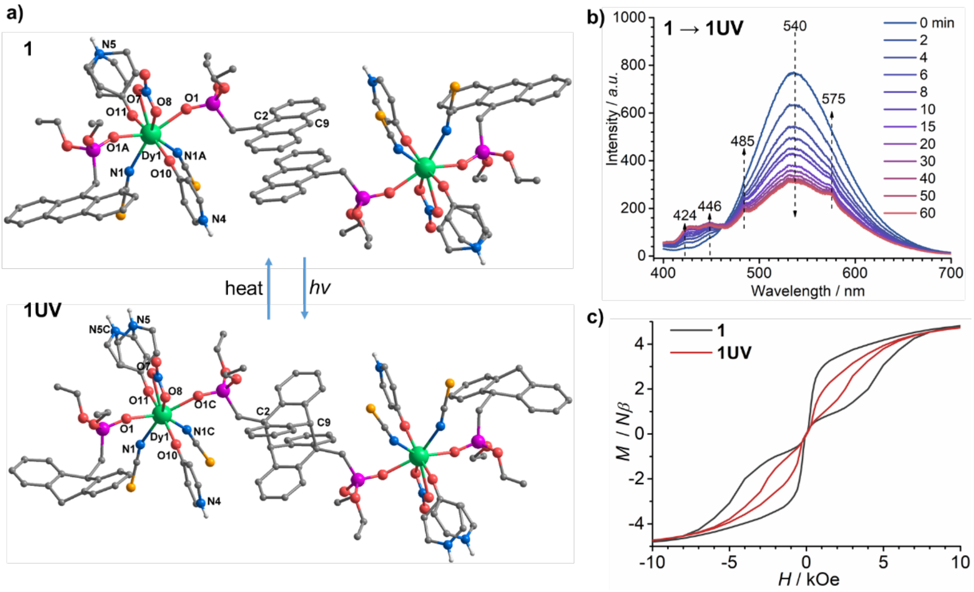

Figure 1. a) The SC-SC structure transformation between **1** and **1UV**. b) The photo-switchable luminescence spectra from **1** to **1UV** under irradiation with 395 nm UV light. c) The butterfly-like magnetic hysteresis loops of **1** and **1UV** at 2 K.

1 X.-D. Huang, G.-H. Wen, S.-S. Bao, J.-G. Jia and L.-M. Zheng, *Chem. Sci.*, 2021, **12**, 929–937.

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Large Fe22 and Fe24 clusters: Synthesis, structure, and magnetic couplings via magnetostructural correlations and DFT methods

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Abstract

The search for synthetic routes to monodisperse magnetic nanomaterials has grown exponentially, coinciding with the demand for the miniaturization of electronic devices. Traditional magnetic nanoparticles have been made by various methods yet suffer from a range of sizes and shapes. As properties are greatly size-dependent at the nanoscale, the "bottom-up" molecular approach offers a complementary route to ultrasmall (1-10 nm) magnetic nanomaterials. It also brings all the benefits of molecular chemistry, such as true monodispersity, crystallinity (allowing structural characterization by X-ray crystallography), and true solubility (vs. colloidal suspensions). Lying at the crux of these efforts is the foray into synthesizing high nuclearity Fe-oxo molecular nanomagnets. Fe-oxo clusters are highly coveted as iron is one of the Earth's most abundant, cheapest metals, bearing relevance to diverse fields such as bioinorganic chemistry, molecular magnetism, and materials science. Despite great efforts towards this end, there is still a need to devise systematic synthetic schemes to families of discrete high nuclearity Fe-oxo clusters, as there are only a few reports in the literature in this size regime. In prior work, our group reported an Fe_{22}-oxo cluster that held the record for many years as the highest nuclearity discrete Fe-oxo cluster. Its synthesis involved an alcoholysis reaction of iron salts in the presence of acetate and *N*-methyl-diethanolamine. The objective of the present work has been to elucidate the synthetic parameters directing the growth of the Fe_{22} cluster to map out the path for the targeted synthesis of increasingly higher nuclearity Fe-oxo clusters. Herein, this systematic synthetic investigation will be presented, along with the detailed structural characterization and magnetic properties of a new Fe_{24} cluster. The exchange coupling parameters (J_{ij}) have also been investigated via complementary use of a magnetostructural correlation for high nuclearity Fe^{III}/O systems, and DFT calculations using broken symmetry methods.

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A smart post-synthetic route towards [Fe_2Co_2] molecular capsules with electron transfer behaviour

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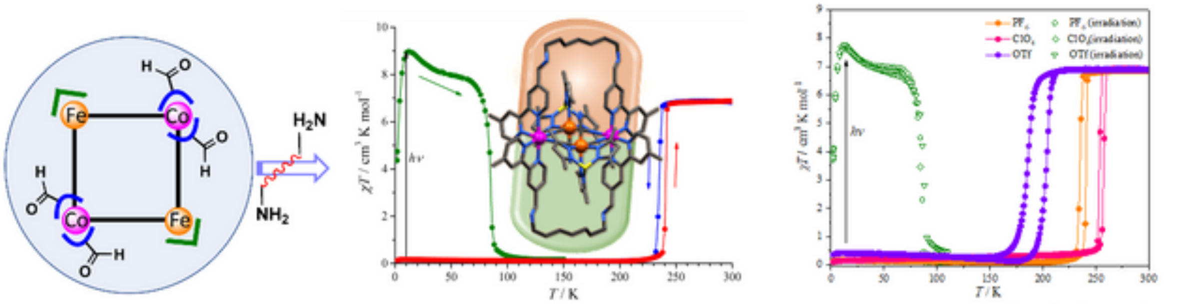
Abstract

The engineering of magnetically switchable molecules due to electron transfer (ET) has been at the forefront of chemical and materials research.[1] Amongst are the cyanide-bridged square-shaped [Fe_2Co_2] complexes, whose electronic structures may be well tuned by modifying the coordination environment of the metal centers as well as manipulating intermolecular interaction through the pre-synthesized approaches using selectively functionalized ligands.[2] Progress notwithstanding, feasible post-engineering strategy towards desired structures and functions remains less explored.[3]

We prepared a series of [Fe_2Co_2] squares decorated with chemical-active aldehyde (-CHO) groups, which may allow feasible introduction of desired functional groups through the simple and effective Schiff-base condensation reactions. For example, these molecules allowed the incorporation of diamines and afforded a series of capsule-like complexes, in which the cyanide-bridged [Fe_2Co_2] square unit is encapsulated by the flexible alkyl chains. Interestingly, the capsules exhibited sharp and complete thermo and photo-induced electron transfer event. Our further studies revealed that the thermally-induced ET events are highly dependent on the types of counter anions, while surprisingly their light-induced metastable states are independent with the anions.



Smart Molecules
Aldehyde-Decorated

Fast ET and bidirectional switching
Switchable Capsules, under review

Counter Anions Dependent/Independent
Switchable Capsules, In preparation.

Figure 1. A smart route to fine-tuning the electron transfer properties based on the aldehyde-decorated [Fe_2Co_2] parent squares.

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Anomalous Phase Transition Observed in Nanosize Tetratitanium Heptoxide

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Abstract

Phase transition phenomena in solid state materials are attracting widespread attention from the viewpoints of both fundamental sciences and practical applications. For example, spin-crossover, charge-transfer, and metal–semiconductor have been aggressively studied.[1,2] Control the phase transition properties by changing the material size is an interesting subject. Here, we focus on the metal-semiconductor phase transition in a coordination compound of titanium and oxide, a tetratitanium heptoxide, and report the anomalous phase transition observed in a nano-sized tetratitanium heptoxide.[2]

Tetratitanium heptoxide, Ti_4O_7, is known to exhibit a two-step phase transition from the charge-delocalized to charge-localized phase (high-temperature (HT) to intermediate-temperature (IT) phase) and the charge-disordered to charge-ordered phase (IT to low-temperature (LT) phase) around 150 K and 130 K, respectively. In this study, we synthesize a nanosize Ti_4O_7 crystal by sintering TiO_2 nanoparticles under a hydrogen flow. Then, nanocrystal Ti_4O_7 shows a one-step phase transition behavior from a charge-delocalized to charge-localized phase (i.e., from HT to IT phase) since the transition from the charge-disordered to the charge-ordered phase is suppressed. Perturbation to the free energy by the surface energy can explain this anomalous phase transition. The present nanoscopic effect, which can control cooperativity in phase transitions, should contribute to develop advanced switching materials.

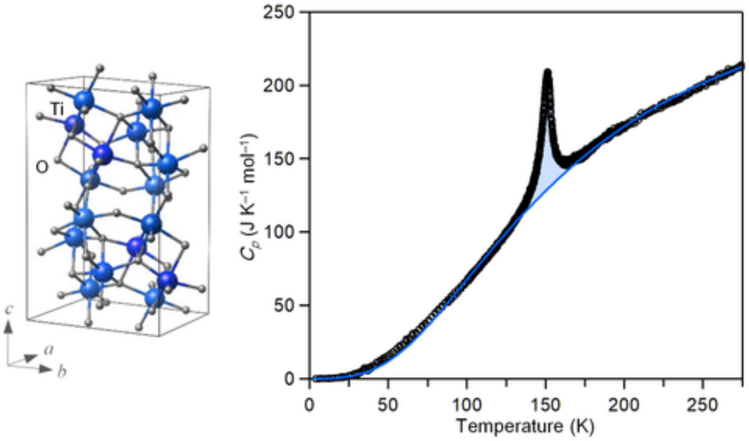

Figure. Schematic crystal structure of Ti_4O_7 (left). Molar heat capacity (C_p) of the nano-sized Ti_4O_7 as a function of temperature (right). A Debye model (blue line) was fitted to the experimental data (circle).

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Spin Crossover Phenomenon and Nano-Topographic Study in Microcrystals and Nanoparticles of 2-D Hofmann-type polymers

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Abstract

The concept of functional nanodevices based on nanoscale Fe^{II} Spin Crossover (SCO) materials appears to be a promising research topic based on the plethora of scientific groups working in this field and the increasing attention in recent years. Due to the unique property of SCO materials of undergoing reversible switching between a high spin state (HS) and a low spin state (LS), new spintronic, electronic, photonic, mechanical devices can be fabricated where the SCO materials will be used for storing and processing information and/or for converting different forms of energy in actuators or sensors.

The case of 2-D SCO Nanoparticles (NPs) remains almost unexplored, especially for systems consisting of ultra-thin 2-D nanosheets as building blocks. Given the interest of the scientific community for alternative chemical approaches of graphene and graphene related products, 2-D SCO NPs provide an ideal platform for further research due to: (i) the highly accessible active sites on the surface; and (ii) the rich synthetic chemistry based on plethora of organic ligands and metal ions. The correlation of the advantages of ultrathin 2-D nanosheets with the downsizing of SCO materials may provide an ideal fabrication protocol for devices with well optimized SCO properties.

We will present the nanofabrication of 2-D Hofmann-type SCO NPs with the formula $[Fe^{II}(2\text{-}mpz)_2Ni(CN)_4]$ (2-mpz = 2-methylpyrazine) along with a detailed magnetic and AFM Topographic study according to which a nano-growth size dependent relationship is revealed with a linear dependence of the aspect ratio vs. the average length of the nanoparticle.

As miniaturisation is one of the hottest topics in technological applications we strongly believe that this kind of characterization is of vital importance for effective deposition protocols of SCO nanoparticles on various substrates.

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Manipulation of Molecular Qubits by Isotope Effect on Spin Dynamics

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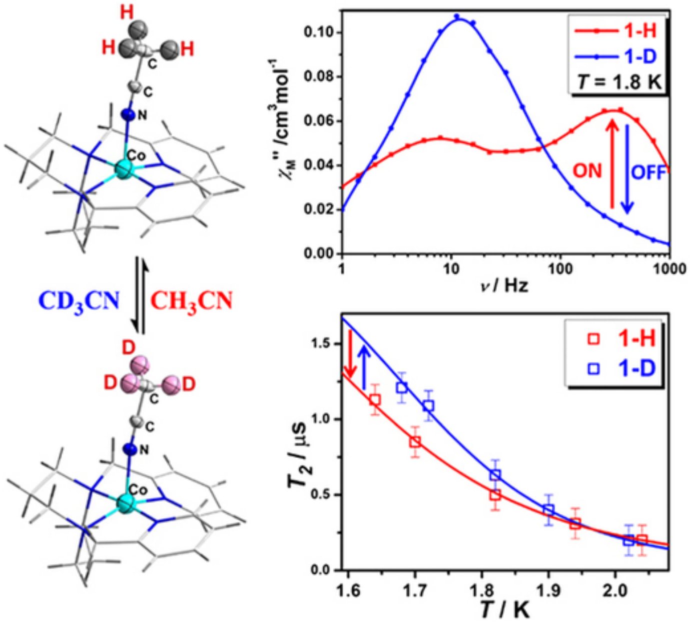
Abstract

Single-molecule magnets (SMMs) and molecule-based spin quantum bits (qubits) are promising candidates for the development of nano-spintronic and quantum computing, which may bring opportunities for the second quantum revolution. Controlling the spin behaviors via external stimuli is a key route to develop molecular spintronics devices. Photon, temperature, pressure, chemicals, and electric field are the possible stimuli. Herein, we report a new method, the isotope effect, to control the spin behaviors in molecule magnet systems. It can not only control the relaxation of magnetization, but also regulate the spin lifetime of quantum coherence. In this theme, we found a couple of low-spin Co(II) complexes, $\{[\mathrm{CoL}](\mathrm{CH_3CN})\}[\mathrm{BPh_4}]_2\cdot\mathrm{CH_3CN}$ (**1-H**, L = 1,5-bis(2pyridylmethyl)-1,5-diazacyclooctane) and its deuterated analog $\{[\mathrm{CoL}](\mathrm{CD_3CN})\}[\mathrm{BPh_4}]_2\cdot\mathrm{CD_3CN}$ (**1-D**), exhibiting the rare ON/OFF switch of double spin relaxation behaviors in the magnetic relaxation as well as the regulation of spin lifetime in quantum coherence at low temperatures. We discuss the mechanisms underlying the formation and the relevance of intramoleculer vibration modes, which give the direct experimental evidence of spin-intramolecular vibration coupling, and also provides a new guidance for ultrafast and electrical control of spin behaviour.



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Theoretical insights into spin-electric couplings and vibronic relaxation pathways in clock-like molecular spin qubit: $[Ho(W_5O_{18})_2]^{9-}$

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Abstract

Electrical control over spins at the nanoscale provides significant architectural advantages in spintronics devices. To employ magnetic molecules in this context one needs to understand the response of molecular and electronic structures to an electric field. Herein, we study the spin-electric couplings (SEC) in molecular nanomagnet $[Ho(W_5O_{18})_2]^{9-}$, whose spin qubit dynamics are protected against magnetic noise at optimal operating points known as atomic clock transitions. To seek insight into the relationship between applied electrical field (E-field) and clock-transition frequency (δf), we first decompose the molecular distortion attained by E-field into the vibrational basis. And finally calculating the spin-energy spectrum at these electrically induced distortions at *ab-initio* level, we determine the change in δf as function of applied E-field, which ultimately gives a strength of spin-electric couplings (SEC) of order $\sim 10^5$V/m, see figure Left. These finding of strong E-field couplings is a step towards coherent spin-photon interface in spintronics devices. [1]

This theoretical effort leaves us in an excellent position to model vibronic coupling, facilitating insights into the relaxation mechanisms in spin qubits and Single Ion Magnets. Our theoretical findings are helpful to comprehend the magnetic-dependent infrared signals experimentally registered for $[Ho(W_5O_{18})_2]^{9-}$ $.35H_2O$ and unravel the vibrational decoherence pathways and provide a strategy for designing molecular spin qubits with improved coherence lifetimes see figure Right. [2] These outcomes advance the understanding for coherent manipulation of spin information in spintronics devices and further for controlling the dynamics by mitigating the vibronic couplings.

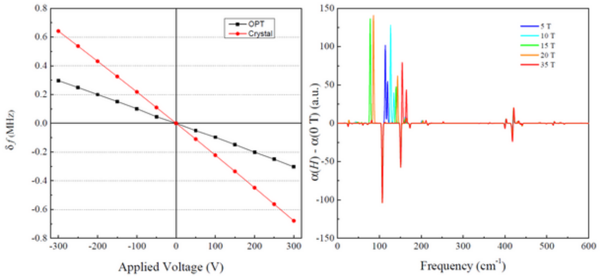

Figure: Left: Change in clock-transition (δf) as a function of the applied voltage (V) in $[Ho(W_5O_{18})_2]^{9-}$ **Right:** magneto-infrared absorption spectrum to show the vibronic relaxation pathways in $[Ho(W_5O_{18})_2]^{9-}$

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Synthesis and characterisation of Cu^{II}-Gd^{III} complexes.

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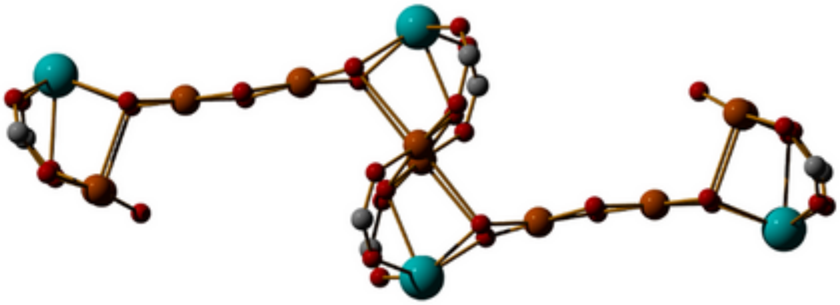
Abstract

3d-4f complexes implementing Gd^{III} ions which enhance the magnetocaloric effect (MCE) are believed to be the most promising pathway for developing ultra-low-temperature coolers, owing to the largest isotropic spin (S=7/2) in the periodic table and the promotion of weak intramolecular interactions [1-2]. We present some results of our study of the Cu^{II}/Gd^{III}/3-methyl-1,3,5-pentanetriol reaction system in combination with various carboxylic acids as co-ligands, and a preliminary study of their magnetic properties.



Metal core of $\{Cu_{10}Gd_4\}$ complex with sea-serpent-like shape [3]. Cyan, Dy; orange, Cu; red, O; grey, C.

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Trinuclear cyano-bridged [Cr2Fe] complexes: to be or not to be a good SMM, just a matter of straightness?

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Abstract

Single-Molecule Magnets (SMMs) attracted interest in the molecular magnetism community for potential applications in data storage or quantum computing.[1] New molecules combining anisotropic units are necessary to understand the factors able to improve their energy barriers and blocking temperatures. In this poster, we will present a serie of trinuclear complexes built from bipyramid pentagonal (heptacoordinated) 3d complexes [2]: an Fe(II) Ising-type anisotropic unit bridged through cyanide to two Cr(III) isotropic entities.[3] The nature of peripheral substituents on the 2,6-diacetylpyridine bis(hydrazine) ligands has a strong effect on the molecular bending. Their impact on the magnetic properties will be discussed on the basis of *ab-initio* calculations.

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π-Topology and Ultra-Fast Excited-State Dynamics of Remarkably Photo-stabilized Pentacene Derivative Utilizing Radical Substituents

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Abstract

Pentacene (Pn) derivatives are intensively studied for promising candidates for organic field-effect transistor, organic thin-film transistor, organic light-emitting diode applications, because of their high hole mobility in solid state. In addition, it is also a promising spin-current transport material useful to the spintronics. However, Pn framework easily decomposes by reacting with oxygen under ambient light. Therefore, the photochemical stability improvement of Pn derivatives are important issue for the material applications. Recently, we reported a new strategy for the photostabilization [1] utilizing the unique excited-state spin dynamics [2] induced by the attachment of the p radical substituent. In this work, we developed this approach and synthesized two novel Pn derivatives having radical- and triisopropylsilylethynyl- (TIPS) substituents (**1*p*** and **1*m***). The photochemical properties of their radical linked systems were evaluated in CH_2Cl_2 under the air-saturated condition by photo-irradiation. They showed remarkable improvement of photostability over 300 times for **1*p*** and 400 times for **1*m*** compared with famous photochemically stable pentacene derivative, 6,13-bis(triisopropyl-silylethynyl)-pentacene. Their solubility in the common organic solvents was greatly improved by the TIPS substituent, which will make the devices fabrication possible using an ink-jet printing technology. Transient absorption spectroscopy was carried out to clarify their excited-state dynamics. It was revealed that the remarkable photo-stabilization of **1*p*** and **1*m*** was due to the ultra-fast intersystem crossing induced by effective p-conjugation between the radical substituent and Pn moiety. The relationship between the p-topology and the photostability will be also discussed based on the excited-state dynamics.

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Quantum design of ferromagnetic homonuclear bimetallic complexes based on orbital counter-complementarity

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Abstract

Single-molecule magnets (SMMs) have attracted much attention as a possible material for high-density memory. To increase the critical temperature (T_c) of the SMM, it is crucial to enlarge a total spin size (S) and/or the size of the (negative) zero-field splitting parameter (D). For example, in recent years, lanthanide ions such as Tb(III) and Dy(III) have been used as spin sources in SMMs to achieve both large values of S and $|D|$ [1,2]. Alternatively, large S values can also be obtained by introducing multiple metal ions into the compounds. We here consider homonuclear bimetallic complexes. In such complexes, the spins on the metal ions must be ferromagnetically aligned or the spin moments on the metal ions cancel each other out. Such intramolecular ferromagnetic interactions are often realized by the orthogonality of magnetic orbitals; however, the magnetic orbitals tend to overlap, resulting in antiferromagnetic interactions. On the other hand, the concept of orbital counter-complementarity has been proposed to explain the ferromagnetic interactions in pyrazole-bridged dinuclear Cu(II) complexes [3]. In this presentation, we demonstrate that this concept can be applied to other metal ions based on density functional theory (DFT) calculations [4,5].

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An In Silico Study of $Gd_2@C_{2n}$ ($15 \le n \le 40$) EMFs: Estimation of Record High Magnetic Exchange and Magnetic Anisotropy

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Abstract

It is very well known that lanthanides does not form covalent bond due to the deeply buried nature of the 4f orbitals which results in very small magnetic exchange between them. To enhance this magnetic exchange, we have encapsulated two Gd atoms inside fullerene cages with reducing cage size ($Gd_2@C_{2n}$; $15 \le n \le 40$) and shown the formation of a covalent bond between two lanthanide ions. The record breaking large antiferromagnetic exchange (computed with DFT/B3LYP) of ca. -63 cm^{-1} has been estimated in $Gd_2@C_{30}$-D_{5h}. The large cage $Gd_2@C_{2n}$, n = 30, 40 leads to the formation of 2c-1e^- Gd-Gd bond but these are unstable due to the presence of one radical in the fullerene cage. In this regard we have estimated the double exchange (B) by state of the art *ab initio* method in stable $Gd_2@C_{59}N$ and $Gd_2@C_{79}N$ which arises due to the 2c-1e^- Gd-Gd bond. The estimated B (434.8 cm^{-1}) and $J_{Gd\text{-}rad}$ (869.5 cm^{-1}) in $Gd_2@C_{59}N$ is found more than two times larger than reported in $Gd_2@C_{79}N$ by us earlier. To explore the magnetic anisotropy in $C_{59}N$ fullerene cage the Gd^{3+} ion has been replaced by anisotropic Dy^{3+} and Tb^{3+} in $Gd_2@C_{59}N$. The *ab initio* CASSCF/RASSI-SO/SINGLE_ANISO/POLY_ANISO calculation reveals record breaking U_{cal} of 1181 and 1532 cm^{-1} in $Dy_2@C_{59}N$ and $Tb_2@C_{59}N$ respectively due the very large $J_{Gd\text{-}rad}$ value which not only quenches the QTM but also increases the blocking barrier. Therefore our study opens up a new avenue in the search for robust SMMs based on lanthanides instead of increasing the axial ligand field.

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A dual-capping tetrazine ligand in favour of both trigonal prismatic geometry and strong magnetic coupling

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Abstract

The pursue of high-performance single-molecule magnets (SMMs)[1] has been a long-standing task over years. The successul strategies include either creating specific coordination geometries for huge axial anisotropy (*D*) or introducing strong intramolecular magnetic exchange coupling (*J*).[2,3] However, systems for marrying both considerations in one molecule are still very limited.[4,5]

Following the above considerations, we synthesized a new dual-capping ligand and prepared a novel tetrazine-bridged dinuclear Co(II) complex, in which the distorted TPR-Co(II) ions and tetrazine radical are strongly antiferromagnetically coupled ($J = -60\ \text{cm}^{-1}$). Remarkably, this complex exhibited much higher effective energy barrier of 69 cm^{-1}. Further ongoing optimization of the local TPR geometry may lead to the significant increment of the SMM performance.

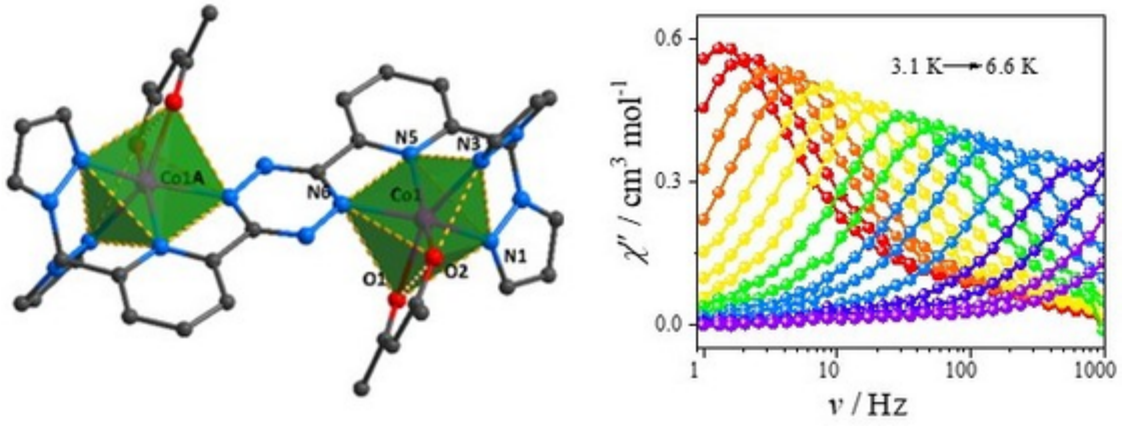

Fig. 1 The structure (left) and out-of-phase ac magnetic susceptibility at 1500 Oe dc field (right) of **1**.

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Role of Vibronic coupling in the Magneto-Chiral Dichroism of Paramagnetic Complexes Exhibiting Helical Chirality

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Abstract

Magneto-Chiral Dichroism (MChD), is the differential absorption of unpolarised light by a chiral medium in the presence of a magnetic field aligned parallel or antiparallel to the propagating wavevector of light.**[1,2]** The interest in this phenomenon is driven by its possible technological application in optical readout of magnetic data and the origin of homochirality on earth.**[3]** Although now it has been reported and studied in different molecular systems, the understanding of the microscopic factors which influence the phenomenon is necessary in order to optimize the MChD signals and attain the aforementioned goals. It was shown that spin-orbit coupling and vibronic coupling plays a decisive role in the intensity of MChD signals.**[5, 6]** In the study presented, the Magneto-Chiral behaviour of a Ni(II) based complex exhibiting helical chirality introduced by the enantiopure 1,2-cyclohexanediamine ligand is compared with the previously reported ethylenediamine analogue.**[6]** This allows to outline the influence of a more rigid ligand in the first coordination sphere of the complex and how this changes the contribution of vibronic coupling and thus influences the overall MChD signal. Moreover, the substitution on Ni(II) by Cr(III), Co(II) and Cu(II) allows to clarify the role of the metal ion onto MChD.

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Supramolecular Assemblies of [n]-Rotaxanes as Potential Quantum Logic Gates

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Abstract

The heterometallic $[Cr_7NiF_8(CO_2{}^tBu)_{16}]^-$ ring ($\{Cr_7Ni\}$) is a spin ½ system and can therefore be considered a two-state qubit [1]. When two spin ½ systems are coupled through a third S=½ component, this can afford a quantum logic gate. The assembly of $\{Cr_7Ni\}$ is templated about an ammonium cation through H···F bonding interactions. Carefully designing the ammonium thread through use of terminal, bulky groups leads to the assembly of a mechanically interlocked [2]-rotaxane. The stoppers can be decorated with metal-coordinating groups such as pyridine, allowing the S=½ [2]-rotaxanes to be coupled to additional spin centres, including single ions or polynuclear clusters, linking varying numbers of qubits in one assembly [2,3]. The [2]-rotaxane ligands are highly tuneable with excellent control over physical properties. Altering the acid employed during ring synthesis can significantly change the solubility of the complex. Varying the thread length can alter the interaction strength between qubits, whilst modifying the ligand stopper can strongly influence magnetic properties, for example by controlling the Jahn-Teller axis alignment of the S=½ d^9 Cu(II) cation should that be used to couple [2]-rotaxanes.

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What dictates structural changes in a Mn-Ln SMM system using N-methyldiethanolamine?

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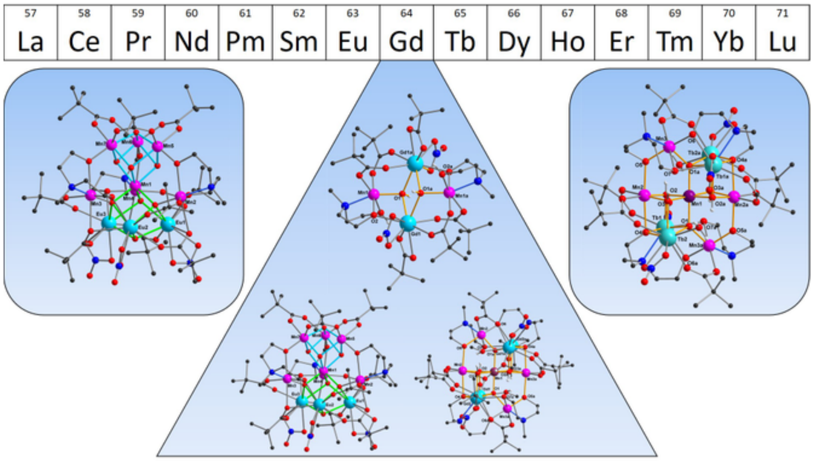
Abstract

In this assisted self-assembly approach starting from the well-known[1] $[Mn_6O_2(Piv)_{10}(4\text{-}Me\text{-}py)_2(PivH)_2]$ cluster a family of Mn-Ln compounds spanning the whole series of lanthanides was synthesised. In general compounds incorporating the later lanthanides are magnetically more interesting due to their anisotropy and high spin values. In fact, very few magnetically interesting examples have been reported from the left side[2]. Particularly Sm(III) should be of interest since it has the same spin as Dy(III), but has a prolate rather than oblate anisotropy ellipsoid. Here we report that the Mn_7Ln_3 system is observed for the left hand side, while on the right hand side only the Mn_5Ln_4 SMM system has so far been identified[3]. Gd(III) represents a special case since it shows both structural types plus representing the first identified example of a Mn_2Ln_2 butterfly system.

Recently, tuning of the reaction conditions made it possible to obtain the different structural types across the whole series, providing fascinating systems for further studies.



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Investigation on ligand substituent effects on Mn(III) Spin Crossover Complexes

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Abstract

The phenomenon of spin crossover in metal complexes is known since the early 1930s, and has since then attracted a lot of interest. Through their possible hysteretic effects, potential applications of these molecules include their use as molecular switches in data storage and in displays. At low temperatures, it is energetically favorable for spin crossover compounds to be in a low-spin state, and by application of an external stimulus, such as heat, light, pressure or applied magnetic field, it is possible for the spins to occupy the energetically higher orbitals, resulting in a high-spin state of the molecule. While the SCO phenomenon is rather common in Fe(II), it is still rather rare in Mn(III). We have developed a ligand system that promotes SCO in Mn(III) and have synthesized various complexes using Schiff base ligands with different substituents on the salicylaldehyde: nitro groups in para- and ortho- position,[1] methoxy groups in the meta-position,[2] methyl groups in the ortho-position[3] and bulky naphthaldehyde groups[4]. We investigated their different magnetic behavior and structural features using also different counterions to understand this additional influence. DFT calculations were able to correctly describe the energetics of intermediate spin/high spin transitions in the complexes.

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Growth of Lanthanide-based 2D MOFs on silicon surfaces

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Abstract

We have developed a procedure to graft lanthanide-based carboxylate 2D metal-organic frameworks (MOFs) of formula [Ln(MeCOO)(PhCOO)$_2$] to functionalized silicon surfaces. The silicon wafers are functionalized with carboxylate terminated silanes to ensure a covalent interaction between the first layer of the 2D MOFs and the Si surface. The silanized samples are then immersed in a solution containing the synthetized 2D MOF. Results indicate that the silicon wafers were evenly covered by few monolayers of the lantanide-based material followed by a growth in a trabecular fashion. The thickness and morphology of the deposited material can be controlled by tuning the concentration of the solution and the growth time, as shown by ellipsometry and contact-angle measurements combined with SEM images. The magnetic characterization of the thickest microcrystalline-like grafted samples were similar to those of the bulk, showing the success of our method for preparing on-surface material with unaltered magnetic properties. These newly developed surfaces could be used in electronics and sensor applications.

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Theoretical study on the difference in single-molecule electron conductivity of paddlewheel-type binuclear Cr(II) complexes between antiferromagnetic and ferromagnetic states

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Abstract

A microfabrication technology for the integrated circuit (IC) has been steadily developing, and a current process node size of transistors has become smaller than 10 nm [1]. However, It has been predicted that conventional silicon-based devices reach the limit of miniaturization, so that molecular electronics have attracted much attention in the field of nanotechnologies. Usually, electronic devices are the aggregate of elements such as switches, wires, and diodes, while these elements are replaced to single-molecules in the molecular electronics. A lot of experimental and theoretical studies have been performed for the single-molecule electron conductivity to realize such molecular devices [2-5]. Among the many candidates for such molecular conductor, we aim to find molecules that can play both the roles of wire and switch because they have a potential for the single-molecular transistor. Especially, we have focused on extended metal atom chains (EMACs). The EMACs, which consist of one-dimensionally aligned transition metal ions with the organic bridging ligands are expected to be the smallest wires. Moreover, our group has suggested that the conductivity can be changed by applying magnetic field, because some of them have localized spins on metal ions [4, 5]. In this study, therefore, we investigate the difference in the electron conductivities between antiferromagnetic and ferromagnetic states on the paddlewheel-type binuclear Cr(II) complexes that are the smallest unit of EMACs in detail by quantum chemical calculations. We also examined the effect of the axial ligands to obtain design guidelines of the molecular transistors using metal complexes.

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Slow Magnetic Relaxation of a Hybrid Inorganic-Organic Ytterbium Complex

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Abstract

Molecular Magnets attracted great attention to the development of new magnetic materials. In this scenario the use of Lanthanide based coordination compounds have given birth to second generation of Single Molecule Magnets, and those with single centre are the so-called Lanthanoid Single Ions Magnets (Ln-SIMs) [1]. Different types of complexes can be obtained depending on the nature of ligands used, for example sandwich lanthanide lacunary polyoxometalates formed rigid compounds compare to complexes formed by only organic ligands, thus the dynamic magnetic properties depend directly on the geometry that the ligands can have [2]. Therefore, the combination of rigid ligands and a flexible organic ligand can modify and improve the dynamic magnetic properties of this hybrid inorganic-organic Ln^{III} complexes [3].

Dy^{III} SIMs are among the most reported systems with either organic or inorganic ligands but compounds with the combination of both types are quite scare. Therefore, Yb^{III} complexes with SIMs behaviour are practically inexistent.

In this work, it is present the study of the relaxation dynamics using ac susceptibility measurements of the mononuclear complex, $[NBu_4]_3[YbH(PW_{11}O_{39})(phen)_2]$, where phen = phenanthroline. The results show that the relaxation process is observed only under an applied dc field.

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Ligand Tuning in Cobalt Complexes for Valence Tautomerism

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Abstract

Molecules that can switch between distinguishable stable states by application of an external stimulus have promise in the development of new functional molecular materials. Those that display valence tautomerism (VT) are promising candidates for such materials as the stimulated electron transfer between a ligand and a metal is accompanied by a change in their magnetic, optical and structural properties.[1] Cobalt-dioxolene complexes are well studied examples of VT however alternative N-donor based redox-active ligands with cobalt have been comparatively unexplored. A promising candidate for investigation is the bis(aryl-imino)acenapthene (Ar-BIAN) ligand family, which has been shown to induce VT in vanadium and ytterbium complexes. [2-4]

Here we present the preparation and in-depth study of a series of homoleptic octahedral Co(II) complexes with Ar-BIAN ligands in different oxidation states. The impact on the electronic structure has been investigated through redox tuning of the Ar-BIAN ligand via variation of the aryl substituents. The understanding of the electronic structure of Co-BIAN systems obtained in this study will facilitate the design of new VT systems.

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Molecular Magnetic Materials Based On $[\mathrm{Mo^{III}(CN)_7}]^{4-}$ Unit

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Abstract

Cyanometallate precursors have been intensively investigated for their great potential for their controllable syntheses and fascinating magnetic properties. Of all the known cyanometallates, $[\mathrm{Mo^{III}(CN)_7}]^{4-}$ unit is very attractive because of the strong and anisotropic exchange coupling between the $\mathrm{Mo^{III}}$ and the CN- bridged metal centers. This anisotropic exchange coupling is very promising for the construction of the high performance single-molecular magnets as have been confirmed experimentally and theoretically[1]. During the past several years, our lab is dedicated to study the $[\mathrm{Mo^{III}(CN)_7}]^{4-}$-based molecular magnetic materials and several breakthroughs have been obtained. The representative results include the following: the first $[\mathrm{Mo^{III}(CN)_7}]^{4-}$-based single-molecule magnet (SMM) with records energy barrier and blocking temperature for a cyanide-based SMM [2], the first one-dimensional compound based on the $[\mathrm{Mo^{III}(CN)_7}]^{4-}$ unit [3], a series of 3D $[\mathrm{Mo^{III}(CN)_7}]^{4-}$ based compounds of 3D magnetic ordering [4-6], and the reversible on-off switching of SMM behavior achieved by crystal-to-crystal transformation between the Mn2Mo and Mn4Mo2 clusters [7]. Recently, we have also succeeded in the construction of a high energy barrier SCM[8] (Figure 1) and a series of 4f-$[\mathrm{Mo^{III}(CN)_7}]^{4-}$ complexes. Their structures and magnetic properties will be presented.

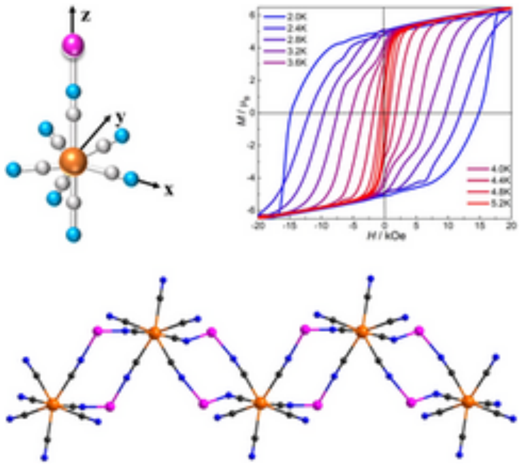

Figure 1. The structure of the $[\mathrm{Mo^{III}(CN)_7}]^{4-}$ and the 1D chain motif of the SCM, together with the hysteresis loop measure from 2.0 to 5.2 K.

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Synthesis and spectroscopic characterization of Ni(II), Co(II) and Mn(II) complexes derived from novel Schiff base

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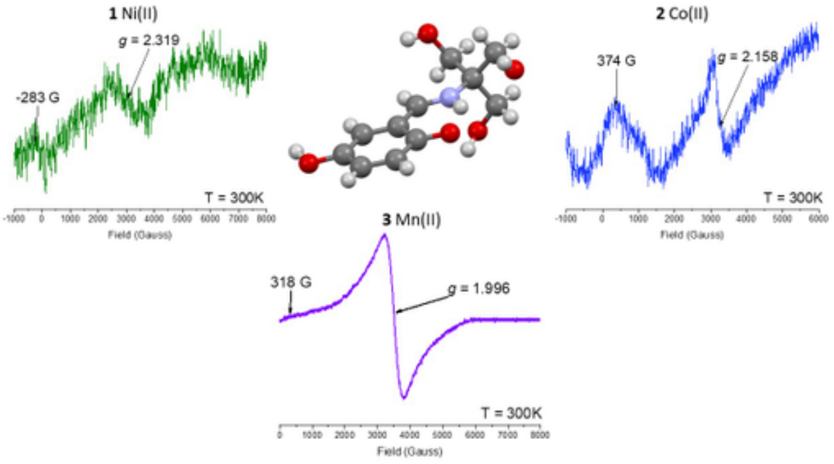
Abstract

The low soluble Ni(II) **1**, Co(II) **2** and Mn(II) **3** Schiff base complexes derived from the novel ligand 2-(((1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)imino)methyl)benzene-1,4-diol were synthesized and characterized by UV-Vis, FT-IR and EPR spectroscopic measurements. The UV-Vis spectrum of **1** exhibited two *d-d* bands at 414 and 540 nm corresponding to $B_{1g} \rightarrow A_{1g}$ and $B_{2g} \rightarrow A_{1g}$ transitions suggesting a square planar geometry around the metallic center, **2** showed two *d-d* bands at 520 and 1055 nm corresponding to ${}^4T_1(F) \rightarrow {}^4T_1(P)$ and ${}^4T_1(F) \rightarrow {}^4T_2(F)$ transitions characteristic of octahedral geometry. Compound **3** did not show *d-d* transitions, suggesting a Mn(II), *s* = 5/2 with octahedral geometry. The FT-IR spectra of **1**-**3** complexes showed typical vibrational transitions of the Schiff base, which are shifted to lower frequencies. The FT-IR information of the complexes showed that nitrogen-azomethine group, selected oxygen-aromatic ring and the tripodal part of the ligand were coordinated to metallic ions without deprotonation. The ESR spectra were measured for **1**-**3** at X-band at 300 and 77 K. The *g* quantifiable values of **1**-**3** were typical of Ni(II), *s* = 1, Co(II) and Mn(II), *s* = 1/2; although, others spin and oxidation states should be present under the line enveloping due to the width of the spectra. The linewidth showed an increase at 77 K, informing us that the dipolar interactions are predominated. The areas ratio (A_{300K}/A_{77K}) for all complexes suggest an antiferromagnetic exchange interaction. All ESR spectra showed zero field splitting ‹444 G. The whole information obtained by the spectroscopy studies revealed that the structures of **1**-**3** have low symmetry and strong magnetic interactions.



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$\{Ru_2Dy_2\}$ Butterflies: Examples of 4d-4f Single Molecule Magnets

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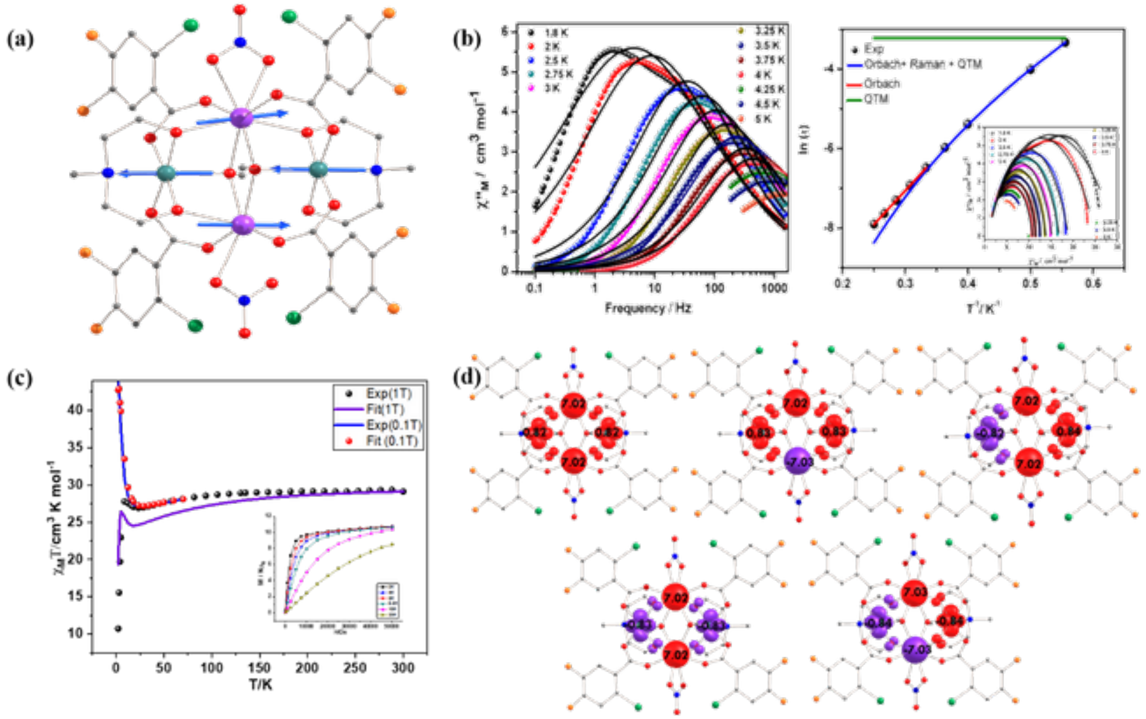
Abstract

Strong magnetic exchange between constituent metals plays a significant role in determining the blocking temperature (T_B) for single molecule magnets.[1] The tetranuclear $\{M_2Ln_2\}$ 'butterfly' complexes provide good examples for studying 3d-4f exchange with M being a first row transition metal ion.[2] Over the last decade several examples of 3d-4f systems were reported with both diamagnetic and paramagnetic 3d ions. The diamagnetic 3d ions such as Co(III) when combined with Ln^{III} such as Dy^{III} are known to be excellent for increasing U_{eff} barrier height, while the paramagnetic 3d ions increase the exchange between 3d-4f ions leading to increases in T_B.[3a,3b] The first 4d-4f butterfly SMM with a $\{Ru_2Dy_2\}$ core was reported in 2015 by Murray et al.[4] The work reported here is an extension of this system aimed at increasing the SMM property. Three new complexes were synthesized by changing the ligand environment around the metal ions, characterized crystallograpically and their magnetic properties were studied along with computational methodologies to understand their magnetic dynamics. It has been found that slight changes around the coordination environment of the Ru and Dy ions can enhance or destroy the SMM property of such butterflies.



$\{Ru_2Dy_2\}$ Butterflies: Examples of 4d-4f Single Molecule Magnets

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A Mononuclear Spin-Crossover Complex Describing Four Distinct Thermal Routes

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Abstract

The spin crossover (SCO) is a fascinating phenomenon that concerns any d^4-d^7 transition metal complex due to their ability to reach to different spin states, depending on the energy of the t_{2g} vs. e_g orbital splitting in relation to that for for pairing two electrons within one d orbital.[1] The origin of this transition ismolecular, but structural phase transitions (SPTs) influence greatly the behaviour within crystalline structures due to different effects of cooperativity. Coordinating tris-imine like ligands with Fe (II) produces a dense network of intermolecular interactions ideal to crystal breathing phenomena and solid-state transformations.[2, 3] The heteroleptic complex, $[FeL(bpp)](ClO_4)_2$ (**1**; L and bpp are tris-imine ligands) is an ideal robust systems that allow making a connection between SCO and SPTs through single X-ray diffraction (SCXRD). Magnetometry and SCXRD measurements unveil a succession of SCO and crystallographic phase transformations never seen before.[4] Starting form a fresh crystal of 1 (a mixed spin state HS-LS) containing one molecule of acetone per Fe center (1·ac), a fully HS (1α phase) state is reached upon warming. This crystallographic phase converts into another one (1β) upon cooling and featuring a LS state. Warming of 1β induces a new SCO coupled to another crystallographic phase transition, 1β→1γ (HS-LS). This last phase cycles thermally between the HS-LS and the LS states through superimposable pathways. We present here four different thermal SCO routes that give rise to four different magnetic responses within a range of temperatures near to ambient conditions.

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MOFs based on cobalt and 2-aminoisonicotinate behaving as field-induced SMMs: developing magnetic sensors

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Abstract

The multifunctionalization of metal-organic frameworks (MOFs) has recently become one of the main research strategies of inorganic and materials chemistry to guide the construction of materials with sensing capacities [1,2]. In particular, the rapid detection of toxic species in environmental and ecological systems is gaining increasing interest because of the large overlap between residential and industrial areas, which causes many diseases in human being [3]. For instance, solvents classified as volatile organic compounds (VOCs) are air and water pollutants and cause severe environmental problems [4]. In this regard, MOFs are good candidates to drive the detection of VOCs owing to their functionalized pore surface, since host-guest interactions may provide a reversible change in a property [5].

In this work, a metal-organic framework based on cobalt(II) ions and 2-aminoisonicotinate (2ain) ligands, namely, $\{[Co(\mu\text{-}2ain)_2]\cdot DMF\}_n$, is evaluated for its capacity to provide distinct magnetic properties depending on the solvents crystallized in the lattice. The crystal structure consists of an open diamond-like topological 3D framework that leaves huge voids, which allows crystallizing two-fold interpenetrated architecture that still retains significant porosity. Magnetic measurements performed on the compound reveal the occurrence of field-induced spin-glass behavior characterized by a frequency-independent relaxation. Solvent-exchange experiments lead successfully to the replacement of lattice molecules by DMSO and MeOH, which, on its part, show dominating SMM behavior with low blocking temperatures but substantially high energy barriers for the reversal of the magnetization.

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Towards single-molecule-scale studies of enantioselective adsorption of chiral molecules on ferromagnetic surfaces

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Abstract

The interplay between electron spin and handedness of chiral molecules, discovered only in recent years, leads to chirality-induced spin selectivity (CISS), which manifests itself in the observations that (i) electrons are spin-polarized when passing through a layer of enantiopure molecules, reaching spin polarization values exceeding 60% at room temperature [1] and (ii) the adsorption of chiral molecules on ferromagnetic surfaces is enantioselective [2]. CISS effects are thus promising for future spintronic devices, the separation/selection of enantiomers, and applications in chemical sensor technology. Although the number of reported experiments successfully demonstrating the CISS effect in various scientific fields is steadily increasing, the theoretical background is not yet sufficiently clarified. Most theoretical explanation attempts still have some shortcomings to fill the large gap between the experimental and theoretically calculated spin polarization values and the chirality-dependence of the adsorption energy. We aim to bridge this gap by performing low-temperature spin-polarised scanning tunnelling microscopy and spectroscopy (STM/STS). We look at individual chiral molecules adsorbed under ultrahigh vacuum conditions on single-crystalline ferromagnetic and non-magnetic metal surfaces to obtain insight into the microscopic properties of these model systems that can serve as input for theoretical modelling. Here, we report on heptahelicene adsorbed on two-monolayer-thick Fe films on W(110), which is a well-known magnetic model system that exhibits out-of-plane magnetized domains. Simultaneously imaging the magnetic domain structure of the Fe film and the chirality of individual heptahelicenes paves the way to a statistical analysis of the preferred adsorption configuration of molecular chirality and local magnetization direction. STM/STS data obtained under such well-defined conditions should provide a suitable basis for future insightful electronic structure and transport calculations on CISS.

We acknowledge Karl-Heinz Ernst for providing racemic heptahelicene molecules.

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Exchange coupling in a thiocyanato-bridged copper(II) chain: computational approach to magnetostructural correlations

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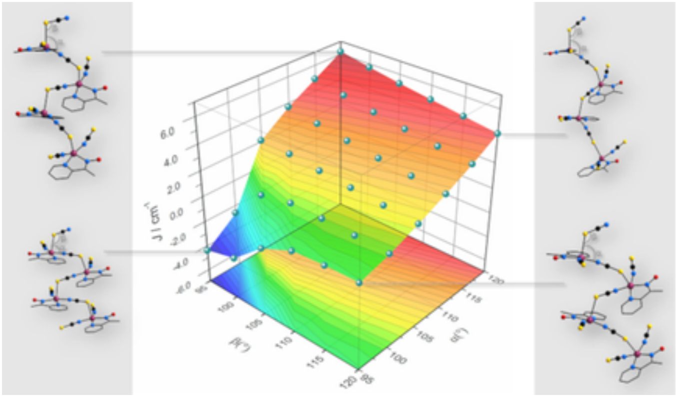
Abstract

The study of the magnetic properties of low-dimensional molecular materials has been an exciting field of research for chemists and physicists for many years, due to their ability to display interesting phenomena as spin-Peierls transitions or multiferroicity, or as simple models of quantum magnetism. Chemists have managed to develop a straightforward way to obtain new low-dimensional molecular materials through the synthesis of coordination polymers. By careful selection of adequate metal centers and ligands it can be possible to design and prepare different molecular structures with the sought dimensionality. When this is accomplished, it turns out to be extremely useful to improve our understanding of fundamental magnetic phenomena, and as positive feedback aimed at the rational synthesis of new materials with desired specific functions.

In this work we report the synthesis and magneto-structural characterization of two new copper(II) compounds with thiocyanato and methyl(2-pyridil)ketone oxime (mpkOH), namely [Cu(NCS)(mpkO)(mpkOH)] (**1**) and [Cu(μ-NCS)(NCS)(mpkOH)]$_n$ (**2**). Compound **1** is a mononuclear complex that crystallizes as discrete units. Conversely, compound **2** is a single equatorial-axial end-to-end thiocyanato bridged polymeric chain of Cu(II) with the oxime as a co-ligand. The coordination geometry around the Cu(II) centers is square pyramidal for **1** and slightly distorted square pyramidal for **2**. The magnetic susceptibility data for **2** reveal weak intrachain antiferromagnetic coupling, with J value −0.74(3) cm^{-1} and g = 2.10(1). The application of computational tools to a binuclear model of **2** allowed us to unveil the structural basis that modulates the magnetic behavior of this type of thiocyanato-bridged Cu(II) chains. The results suggest that although small values of J are expected, stronger ferromagnetic interactions could be favored by including co-ligands that trigger a squared-based pyramidal-to-trigonal bipyramidal distortion of the coordination polyhedra.



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Synthesis of a Novel Set of Hydrogen-Free Complexes of 1,3,2-Dithiazole-4-thione-5-thiolate Ligand as Potential Spin Qubits

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Abstract

Performing qubits are characterized by a coherence time (T_m) long enough to allow the storage and the manipulation of the information within quantum algorithms. Molecular systems showing peculiar magnetic properties, such as coordination compounds based on the first row's transition metals, have been extensively investigated as potential electronic spin-based *qubits*. Indeed, molecular systems present numerous key features such as i) long T_m over a wide temperature range,[1] ii) a set of addressable electronic and nuclear levels appealing for quantum error correction,[2] and iii) sufficient stability for being adsorbed on surfaces for the realization of physical hardware.

A novel set of metal complexes of the 1,3,2-Dithiazole-4-thione-5-thiolate (dttt$^-$) ligand with Cu^{II} or Ni^{II} ion is proposed here (Fig.1).[3] Moreover, a complete study of static and dynamic magnetic properties of pure and magnetically diluted compounds by continuous wave and pulsed EPR is reported.

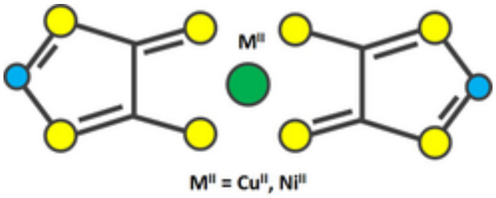

Figure 1. Sketch of the structure of [M(dttt)$_2$] complexes (S = yellow, N = blue, C = grey, M^{II} = green).

The obtained molecules satisfy fundamental requisites: they do not contain hydrogen atoms (thus fulfilling the nuclear spin economy principles proposed so far),[4, 5] and they are neutral (a fundamental prerequisite for controlling their deposition on surfaces by the physical vapour deposition technique). Moreover, [Cu(dttt)$_2$] could be an excellent candidate to perform quantum error correction algorithms by exploiting both electronic and nuclear levels.

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Layered Lanthanide Phosphonates Ln(2-qpH)(SO_4)(H_2O)$_2$ (Ln = La, Ce, Pr, Nd, Sm, Eu): Structures, Magnetic and Luminescent Properties

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Abstract

Three different series of layered lanthanide phosphonates, namely, α-Ln(2-qpH)(SO_4)(H_2O)$_2$ (Ln = Nd, Sm, Eu) (**α-Ln**), β-Ln(2-qpH)(SO_4)(H_2O)$_2$ (Ln = Pr, Nd, Sm, Eu) (**β-Ln**) and γ-Ln(2-qpH)(SO_4)(H_2O)$_2$ (Ln = La, Ce, Pr, Nd, Sm, Eu) (**γ-Ln**) (2-qpH_2 = 2-quinolinephosphonic acid), have been synthesized and investigated. The structures of **γ-Ln** have been determined by single-crystal X-ray crystallography, and **α-Ln** and **β-Ln** were proven to be isostructural with **α-Dy** and **β-Dy** previously reported by our group based on elemental analyses, IR spectra and powder X-ray patterns. Three types of compounds crystallize in monoclinic $P2_1/c$ (**α-Ln**), triclinic P_1 (**β-Ln**) and orthorhombic *P*bca (**γ-Ln**)space groups, respectively. Magnetic studies reveal a field-induced slow relaxation of the magnetization at low temperature is found for compounds **γ-Ce**, **α-Nd** and **β-Nd**. Furthermore, fluorescence measurements reveal Eu derivative shows four characteristic Eu(III)-centered emission bands at 582, 591, 618, 650, 700 nm under excitation at 350 nm.

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The unexpected impact of humidity on the photoswitching of cyanide-bridged molecular magnets

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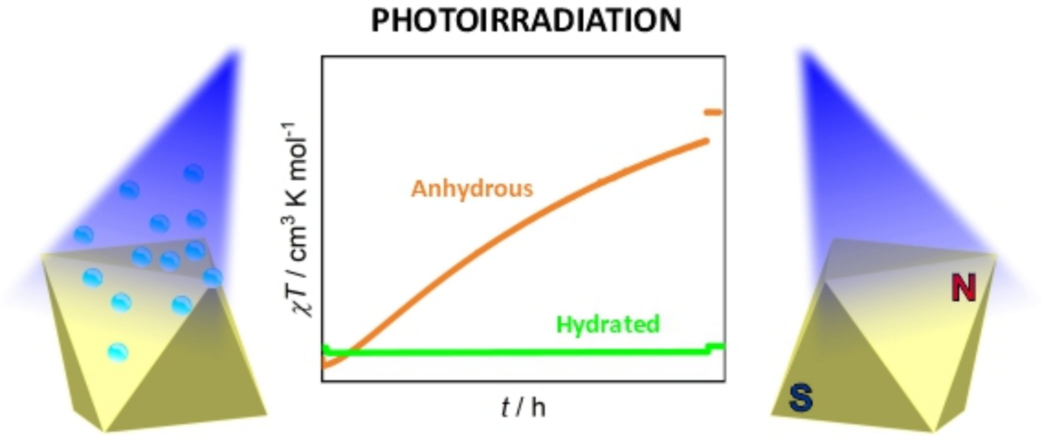
Abstract

The influence of guest molecules on the magnetic properties of microporous magnets is their inherent feature unparalleled by any metallic or ceramic magnet.[1] This effect is even more astounding in the case of porous photomagnets, where absorption of colourless gases (such as water vapours) significantly alters their response to visible light irradiation. We have observed this "photomagnetic sponge" behaviour for the first time in the cyanide-bridged $\{[Mn^{II}(imidazole)(H_2O)_2]_2[W^{IV}(CN)_8]\cdot 4H_2O\}_n$ framework. Its fully hydrated form is completely non-responsive to visible light, while the anhydrous compound shows a very strong photomagnetic effect when irradiated using blue light. The complete photoconversion results in a photo-induced ferrimagnet characterized by the T_c of 93 K.[2] This reversible behaviour cannot be attributed to the negligible changes in the UV-vis spectra upon water adsorption/desorption. Also the water-induced breathing-like structural transformations cannot be solely responsible for the disappearance of the photomagnetism in the fully hydrated phase, as the isostructural molybdenum analogue remains photomagnetic.[3] In order to further study and understand the phenomenon of the "photomagnetic sponges" we prepared cyanide-bridged frameworks accommodating even more water molecules: trimetallic coordination polymers based on a photomagnetic Mo-Pt-Mo spacer[4] and the Mn_2W framework[5] that mimics the topology of MOF-74.[6]



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Surface Deposition of CN-bridged Magnetic Sponges

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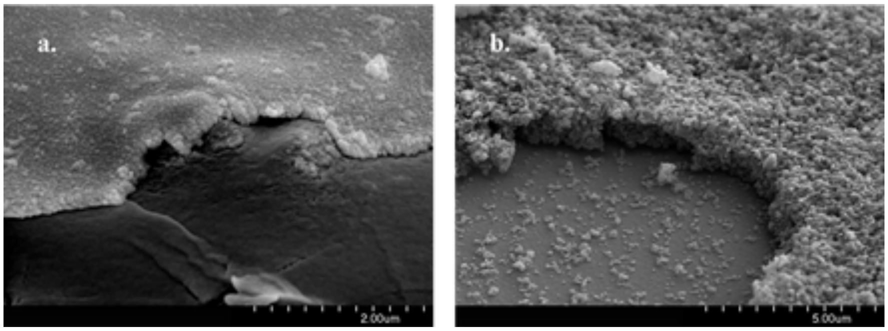
Abstract

Many potential applications of molecular magnets require deposition of these materials on surfaces. Various methods, including Langmuir-Blodgett, vapour deposition, spin- and dip-coating as well as electrochemical techniques, were employed in the studies on the formation of thin films for several classes of molecular magnetic materials [1]. However, in the group of CN-bridged coordination polymers the surface deposition was studied almost exclusively for Prussian blue analogues (PBAs). While PBAs, thanks to high connectivity, usually show higher temperatures of magnetic ordering, hybrid organic-inorganic CN-bridged assemblies offer a wider range of desirable properties. The possibility of inducing structural and magnetic changes by the sorption of guest molecules is one of such features, since porous magnets and magnetic sponges are potential chemosensitive switches.

In our recent study we have focused on two isostructural coordination polymers $\{[\mathrm{Ni(cyclam)}]_3[\mathrm{M(CN)}_6]_2\}_n$ (M = Cr, Fe; cyclam = 1,4,7,11-tetraazacyclotetradecane) characterized by reversible changes in structure and magnetic properties upon sorption or desorption of small molecules [2]. Deposition of selected compounds on a specific surface was carried out using two techniques from aqueous solutions: sequential growth method where the polymer structure was built up gradually on the substrate and dip-coating method based on physical adsorption. The obtained thin films are characterized by homogenous layers of limited thickness, especially in the sequential growth method. The magnetic sponge-like properties of the bulk materials are retained in the thin films, which show very similar reversible water sorption characteristics and the structures may appear in various pseudo-polymorphic forms by changing relative humidity.



SEM images of the produced thin films obtained by (a) sequential growth deposition and (b) dip-coating method from suspension.

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Cyanido-bridged {$Fe^{III}Ln^{III}$} heterobimetallic chains assembled through the [Fe^{III}{$HB(pz)_3$}$(CN)_3$]$^-$ complex as metalloligand: Synthesis, crystal structure and magnetic properties

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Abstract

Homo- and heteroleptic cyanido-metallates were intensively exploited as metalloligands for the design of new cyanido-bridged heterobi- or trimetallic complexes, the investigation of their magnetic behaviour shedding more light on the intramolecular magnetic exchange interactions between d/d'/f spin carriers.[1] Poly(pyrazolyl)borate(tricyano)metallates with three coordination sites blocked with a pyrazolyl borate type ligand and three terminal cyanide groups, disposed in a *fac* arrangement, were particularly suitable to assemble heterometallic cyanido-bridged low-dimensional compounds. The polymetallic complexes assembled from *fac*-[Fe^{III}{$HB(pz)_3$}$(CN)_3$]$^-$ complex and including d/f paramagnetic centers are very rare, all examples showing discrete square-shaped structures [$HB(pz)_3^-$ = hydrotris(pyrazol-1-yl)borate].[2] We report here the first examples of single cyanide-bridged {$Fe^{III}Ln^{III}$} heterobimetallic chains resulting from the use of the low-spin [Fe{$HB(pz)_3$}$(CN)_3$]$^-$ complex as an angular connector against lanthanide(III) ions partially blocked with the bidentate bdpo ligand ([Ln = Gd, Tb, Dy, Ho, bpdo = 2,2'-bipyridine-*N*,*N'*-dioxide). The neutral chains exhibit a unique zig-zag motif in which Ln^{III}-Fe^{III}-Ln^{III} angular assembling units are alternatively perpendicular to each other. The analysis of the cryomagnetic measurements of Gd^{III} derivative through a chain approach with regular alternating classic (S_{Gd} = 7/2) and quantum (S_{Fe} = 1/2) local spins revealed the occurrence of a net weak antiferromagnetic interaction between the low-spin iron(III) and gadolinium(III) ions mediated by the single cyanide bridge.

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Computational investigation of the magnetization blocking mechanism in exchange-coupled lanthanide single-molecule magnets

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Abstract

Combining the on-site strong magnetic anisotropy and strong inter-site exchange interaction represents an important step towards the next generation of single-molecule magnets (SMMs). However, this objective has remained troublesome owing to the complication of adding strong exchange interaction on top of the already complicated interplay between spin-orbit coupling and crystal-field effect. Herein, we report a computational investigation of a family of N_2^{3-}-radical-bridged dilanthanide complexes.[1] By *ab initio* methods,[2] their magnetic blocking behaviors are successfully characterized, allowing to elucidate the origin of the two blocking barriers observed experimentally. In addition, a detailed analysis of exchange wave functions explains why the blocking barrier of the **Tb** complexes is roughly twice as large as that of the **Dy** analogues, a fact which appears to be a general trend exhibited in this family of compounds. [3]

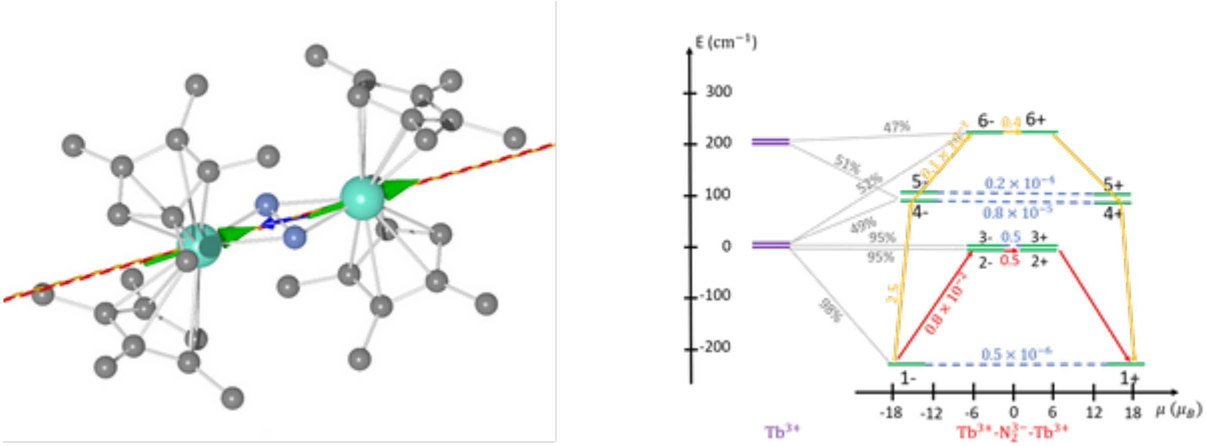

Figure 1: Molecular structure (left) and magnetization blocking barrier (right) of $[(Cp_2^{Me4H}Tb)_2\ (\mu\text{-}N_2^{\circ})]^-$.

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Qualitative insights on molecular design oriented towards spin dynamics: spin relaxation and spin excitation

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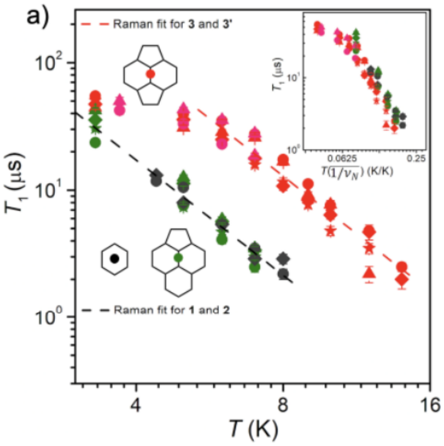
Abstract

Modelling the relation between molecular structure and spin dynamics is an open problem for the chemical design of molecular spin qubits and molecular nanomagnets. Quantum chemistry tools are routinely applied to individual systems but it is still challenging to extract qualitative, general insights. I will discuss recent progress on this question, focusing on two aspects of the problem: spin relaxation and spin excitation.

On spin relaxation, we will focus on endohedral metallofullerenes Eu@C_{2n} (2n = 74-90), which are exceptional molecular spin qubit model systems due to their beautiful simplicity. Pulsed EPR experiments on frozen CS_2 solution allowed us to study the influence of the binding site on T_1 spin-lattice relaxation times. We found the thermal evolution of T_1 can be simply normalized dividing by the vibrational frequencies of the involved modes to produce overlapping plots (Fig. 1). This piles up upon recent experimental and theoretical results demonstrating the role of individual vibrational modes in spin relaxation.[1] It has been possible to obtain further qualitative insights on molecular nanomagnet design and the role of non-Orbach processes by employing a statistical-based approach.[2

On spin excitation, we will focus on the possibilities of molecular design of clock transitions (CTs) for the electrical control of molecular spin qubits. At CTs, the spin states are protected from magnetic noise and present an enhanced quantum coherence. Unfortunately, these optimal points are intrinsically hard to control since their transition energy cannot be tuned by an external magnetic field. However, we found that geometric distortions, either due to chemical pressure or due to an electrical field, constitute a promising avenue.[3] Recent experimental results also support these findings.[4]



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Host-guest induced magnetic features in dia/paramagnetic coordination capsules.

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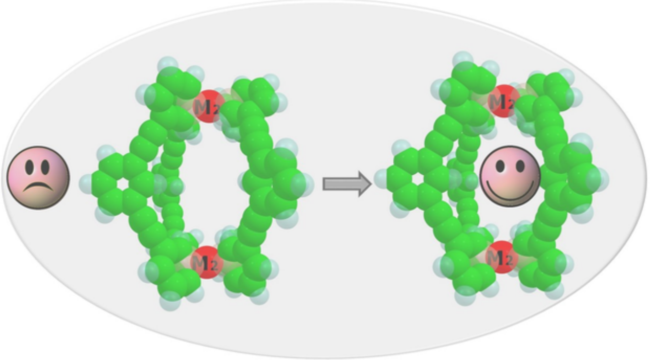
Abstract

The host-guest chemistry of coordination capsules offers a novel route to the modular construction of magnetically interesting species.[1] Relatively simple coordination chemistry ensures a possibility of a variety of different dia/paramagnetic metals can be employed in the host framework, with the nature of encapsulated guest controlled *via* cavity size, charge, host-guest interactions, and hydrophobicity.[2] This, in turn, is governed by the design of the organic ligand, with numerous analogues amenable through standard organic chemistry. Exohedral functionalization of the ligand framework should also be straightforward, allowing, for example, tuning of solubility and targeting specific substrates for surface deposition.[3] Here, we have demonstrated the encapsulation of the highly anisotropic paramagnetic guest molecule/ion (M1) inside the cavity of a dia/paramagnetic $[(M2)_2L_4]^{4+}$ based capsules which induces a magnetic exchange between the M1 and M2 ions/centres, transforming the magnetic properties of the cage. Although guest encapsulation has been observed to change the magnetic properties in other porous materials such as MOFs, on all such occasions, this is due to the guest changing the geometry of the metal ion and not through the introduction of new magnetic exchange pathways. The ability to switch "on" and "off" magnetic exchange interactions in any molecular species has enormous potential for use in various applications ranging from magnetic switching and sensing to electron-spin based quantum information processing.



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Exceptionally Clean Single-Electron Transistors from Solutions of Pleio-Soluble Molecular Graphene Nanoribbons

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Abstract

Only single-electron-transistors with a certain level of cleanliness, where all states can be properly accessed, can be used for quantum experiments. Carbon-nanotubes have revealed their vibrational, spin and quantum coherence properties only after being suspended across trenches. [1,2] Such clean devices remain unachieved for graphene nanostructures: molecular graphene nanoribbons [3,4] provide the necessary structural control, but suffer from poor solubility, similar to carbon-nanotubes. Here we show how the chemical functionalization of nanoribbons enormously enhances the solubility, and suppress bundling to yield extremely sharp single-electron features, typical of ultra-clean transport devices, but achieved directly from solution and without suspension. Franck-Condon blockade is clearly visible, and very strong electron-vibron coupling is identified with transverse bending modes. These results open the path to the investigation of ultra-clean electronic devices made of atomically-precise graphene elements, thus allowing electronic access to their spin, vibrational and topological effects.

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Ab initio study of metal-ligand interactions and their role in altering magnetic properties of linear homoleptic two-coordinate transition metal complexes.

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Abstract

Linear, two-coordinate transition metal complexes can possess remarkable magnetic properties characteristic of single ion magnets (SIMs). In this work we use multireference *ab initio* computational methods to give insight into how magnetic properties of two-coordinate transition metal complexes vary with metal, oxidation state, ligand type and geometry for series of known and model systems.

Of the models tested, Co(II) with carbene, alkyl, thiolate, aryl and phosphine ligands all maintain a doubly degenerate ground state and near maximal anisotropy of the ground Kramers' doublet effective g'-tensor (0, 0, 12) (Figure 1). In contrast to Co(II), Fe(I) complexes feature a doubly occupied d_{z2} orbital due to stabilization by 4*s*-3d mixing with alkyl, amid, aryl, thiolate and alkoxide ligands, and hence, they can only retain a singly degenerate ground state. The only models with a non-degenerate ground state are Fe(I) bis-carbenes and Fe(I) bis-phosphines due to stabilization of dxz and dyz orbitals via π-backbonding (Figure 1). Rotating carbene, amide, thiolate and alkoxide ligands results in the splitting of d_{xz} and d_{yz} orbitals due to anisotropy of the π-bonding interactions. Overall M(II) ions show more potential for SIM synthesis as they tend to retain higher easy-axis anisotropy and higher first excitation energy than M(I) ions with different ligand types and geometries. Conclusions made for model systems hold for most known two-coordinate $3d^7$ complexes, of which $Co(C(SiMe_2ONaph)_3)_2$, $[Fe(N(SiMe_3)_2)_2]^-$ and $[Fe(C(SiMe_3)_3)_2]^-$ are confirmed SIMs. Of a series of $3d^3$ to $3d^9$ amido model complexes, none maintain a doubly degenerate ground state and only Cr(II), Fe(II), Fe(I), Co(II), Ni(II) and Ni(I) maintain singly degenerate ground states as d_{z2} is doubly occupied for $3d^7$-$3d^9$ and M(I) systems obey the Aufbau principle.

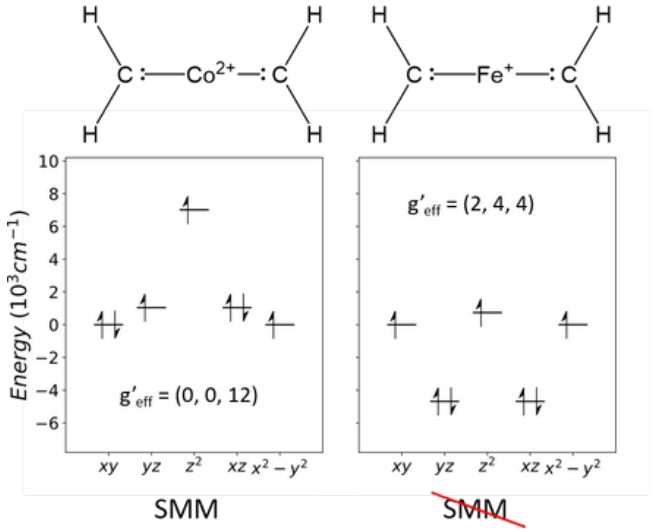

Figure 1 Molecular structure, d-splitting and effective g'-tensors of $[Co(CH_2)_2]^{2+}$ (left) and $[Fe(CH_2)_2]^+$ (right).

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Towards peptide-based magnetic multistate memristive materials

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Abstract

Molecular materials can display memristivity and even excel in some aspects compared with traditional inorganic materials due to (i) their chemical versatility, (ii) possible miniaturization of the system thus energetic cost, and (iii) low-cost processability. Recent results on metallopeptides demonstrating the interaction between paramagnetic ions and the chirality induced spin selectivity effect (CISS) hold particular promise for developing fast (ns–µs) operation times. [1] We will discuss the progress so far in the exploration of magnetic biomolecules for the design and preparation of molecular memristors exploiting the spintronic potential for the design of multistate memristors with a controlled- and indeed, programmable-nanostructure. Among the challenges in the field, a major highlight is the difficulty in modelling the spin dynamics in these complex systems, but at the same time, the use of inexpensive methods has already allowed progress in that direction. We will show that paramagnetic peptides offer a path for tuning the memristive voltage-current pinched hysteresis loop in terms of slope, area, and response to driving voltage frequency merely by changing the peptide sequence. [2]

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Controlling Electron Spin Decoherence in Nd-based Complexes *via* Symmetry Selection

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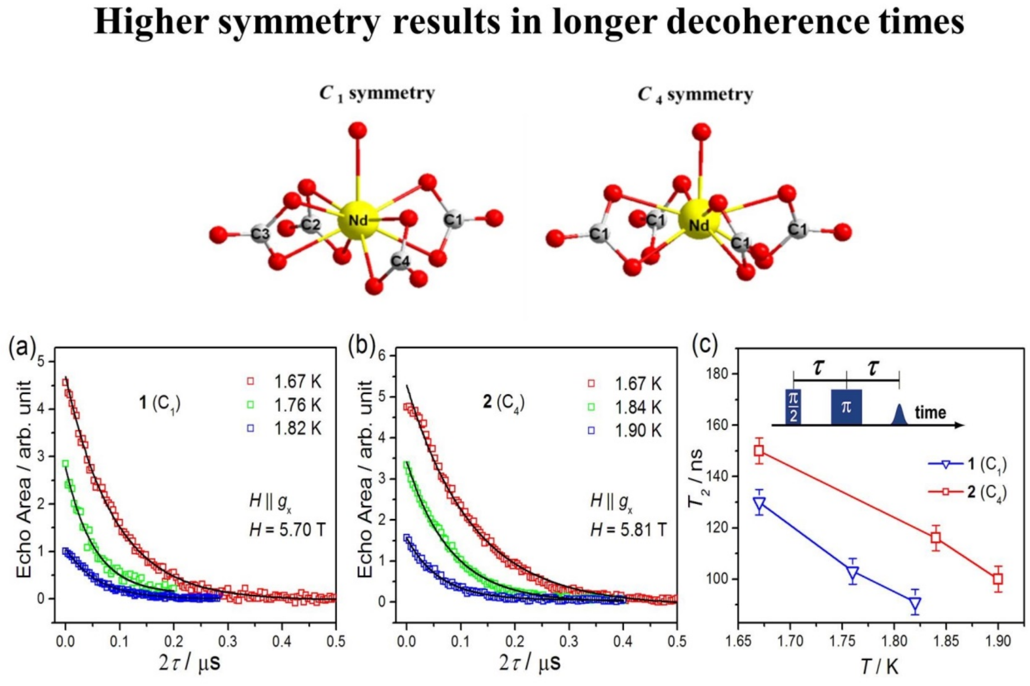
Abstract

Molecular symmetry is a fundamental concept in chemistry, as it can be used to predict or explain many of chemical and physical properties of a molecule, such as its dipole moment, allowed spectroscopic transitions, and the design strategy of single-molecule magnets and molecular ferroelectrics. Though previous studies have shown that the local symmetry of spin carrier plays a crucial part in spin-lattice relaxation process, its role in spin decoherence is still unclear. Herein, two nine-coordinated capped square antiprism neodymium moieties $[Nd(CO_3)_4H_2O]^{5-}$ with slightly different local symmetries, C_1 *vs.* C_4 (1 and 2), are reported, which feature in the easy-plane magnetic anisotropy, and show spin decoherence without magnetic dilution using 240 GHz Pulsed EPR. Based on experiment results and the first principle calculations, our work demonstrates that the symmetry is also an important factor to develop potential qubits with the improved performance, and higher symmetry results in longer decoherence times. This discovery provides a specific design criteria to develop potential qubits with improved performances.



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Reversible Photo and Thermo-induced Spin-State Switching in a heterometallic {5d-3d} W_2Fe_2 Molecular Square Complex

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Abstract

Switchable molecular-based materials have been representing an amazing class of systems offering a large range of desired physical properties with enormous potential application in quantum science and technologies.[1] One type of complexes that can exhibit interesting Spin-Crossover behaviour, where the switching of the magnetic properties originates from their reversible spin-state switching between a low-spin (LS) and high-spin (HS) state upon the application of an external stimulus, *e.g.*, temperature, pressure, light irradiation, magnetic and electric field etc.[2] Importantly, SCO occurring at around or above room temperature is desirable for developing SCO-based electronics and spintronics devices amiable for the practical use.

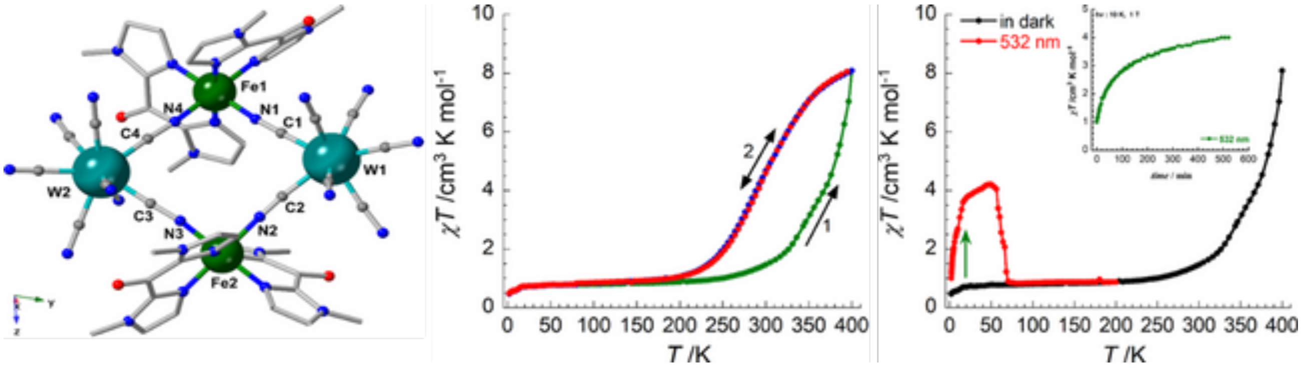

Figure 1: Perspective view of the W_2Fe_2 square complex (left); Temperature dependence of the *cT* product for the complex at 10000 Oe (middle); *cT vs* T curve under 532 nm light irradiation (right)

Recently, we have designed a molecular square complex $[HNBu_3]_2\{[W(CN)_8]_2[Fe(bik)_2]_2\}\times 6H_2O\times CH_3OH$ incorporating octacyanometallate building block $[W(CN)_8]^{3-}$ with Fe(II) metal center and explored the structural, optical, (photo)magnetic and electrochemical properties.[3] The complex shows reversible spin-state switching, thermo-induced SCO at near room temperature and photo-induced spin-state switching with T_{LIESST} = 70 K under light irradiation at low temperature.

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Lanthanide Single Molecule Magnets with azahelicenes

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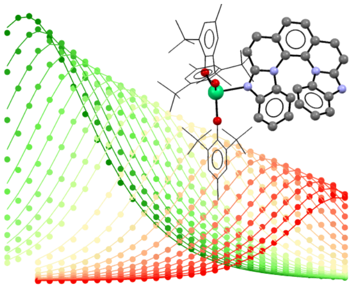
Abstract

Merging magnetic properties with other physical characteristics in a single material is one of the main trends in the field of molecular materials nowadays and the incorporation of chirality into the structures of high performance Single Molecule Magnets (SMMs) is one of the emerging topics. This task, however, is very challenging because of potentially disruptive influence of additional ligands on the slow magnetic relaxation. Herein we present the structural and magnetic properties of two new SMMs: [Er(BHT)$_3$(azahelicene)] and [Yb(BHT)$_3$(azahelicene)] (BHT = 2,6-di-*tert*-butyl-4-methylphenol, azahelicene = benzo[4,5]imidazo[1,2-a]benzo[4,5]imidazo[2,1-*k*][1,10]phenanthroline). The addition of the azahelicene to the parent SMMs[1,2] did not 'destroy' the slow magnetic relaxation because of the weak ligand field character of the N-atoms of the azahelicene. The ligand was prepared in a facile two-step synthesis and has exceptionally high specific rotation as compared to chiral molecules based on asymmetric carbons.[3] This opens possibilities for the observation of strong chirality-related properties as circularly polarised luminescence or magneto-chiral dichroism. Up to this day there are just a few examples of lanthanide complexes with helicene ligands,[4] therefore, the properties of compounds with such strongly chiral ligands are certainly worth exploring.[5,6]



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Tuning magnetism and conductivity in 2D covalent organic radical frameworks via mechanical compression

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Abstract

Triarylmethyl radicals (TAM) can be employed to grow 2D covalent organic radical frameworks (CORFs) in a π-conjugated hexagonal pattern.[1] These materials can be seen as the natural extension of graphene towards more complex chemical structures. Strikingly, contrary to graphene, hexagonal TAM-CORFs do not exhibit a diamagnetic semimetallic phase but a correlated antiferromagnetic Mott insulator (AFMI) band structure.[1,2] From a structural point of view, TAM-CORFs exhibit out-of-plane atoms and thus have a small finite thickness. Here, we show that the twist angles of aryl ring linkers in 2D TAM-CORFs are highly sensitive to out-of-plane compression. Therefore, compression is shown to be capable to modulate the internode π-overlap and electronic coupling and thereby tune the electrical, magnetic, and optical properties. By means of projecting our hybrid DTF results onto a Hubbard's model Hamiltonian, we showed[3] that TAM-CORFs are correlated electronic systems, in which applied modest out-of-plane compression can shift the AFMI state towards a transition to a graphene-like semimetallic state. This work establishes 2D CORFs as a class of versatile materials to advance the understanding of low dimensional correlated electronic systems.

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Tetrairon(II) Extended Metal Atom Chains as Single-Molecule Magnets

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Abstract

Iron-based extended metal atom chains (EMACs) are potentially high-spin molecules with axial magnetic anisotropy and thus candidate single-molecule magnets (SMMs). We herein compare the tetrairon(II), halide-capped complexes $[Fe_4(tpda)_3Cl_2]$[1] (**1Cl**) and $[Fe_4(tpda)_3Br_2]$ (**1Br**), obtained by reacting $Fe_4Cl_8(thf)_6$, or $FeBr_2(thf)_2$, with $[Fe_2(Mes)_4]$ and N^2,N^6-di(pyridin-2-yl)pyridine-2,6-diamine (H_2tpda) in toluene, under strictly anhydrous and anaerobic conditions (HMes = mesitylene).[2] Detailed structural, electrochemical and Mössbauer data are presented along with direct-current (DC) and alternating-current (AC) magnetic characterizations. DC measurements revealed similar static magnetic properties for the two derivatives, with $\chi_M T$ at room temperature above that for independent spin carriers, but much lower at low temperature. The electronic structure of the iron(II) ions in each derivative was explored by *ab-initio* (CASSCF-NEVPT2-SO) calculations, which showed that the main magnetic axis of all metals is directed close to the axis of the chain. The outer metals, Fe1 and Fe4, have an easy-axis magnetic anisotropy ($D = -11$ to -19 cm^{-1}, $|E/D| = 0.05$-0.18), while the internal metals, Fe2 and Fe3, possess weaker hard-axis anisotropy ($D = 8$-10 cm^{-1}, $|E/D| = 0.06$-0.21). These single-ion parameters were held constant in the fitting of DC magnetic data, which revealed ferromagnetic Fe1-Fe2 and Fe3-Fe4 interactions and antiferromagnetic Fe2-Fe3 coupling. The competition between super-exchange interactions and the large, noncollinear anisotropies at metal sites results in a weakly magnetic non-Kramers doublet ground state. This explains the SMM behavior displayed by both derivatives in the AC susceptibility data, with slow magnetic relaxation in **1Br** being observable even in zero static field.

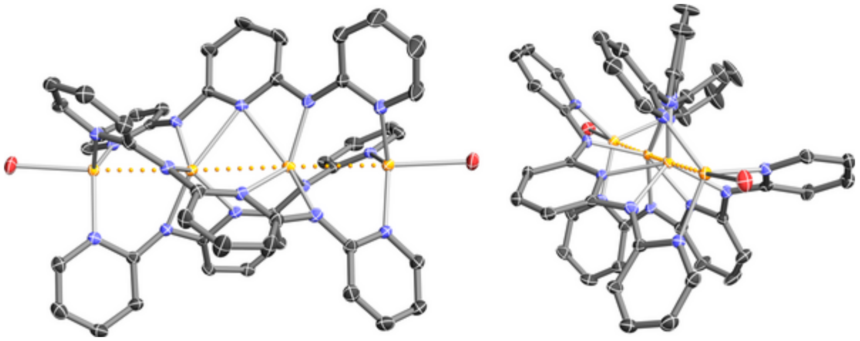

Figure 1. Molecular structure of **1Br**.

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Choosing between vibrational and Crystal field tuning for improvement of high-performance Single Molecule Magnets.

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Abstract

For many years, the central target for the development of new Single Molecule Magnets with higher blocking temperatures (T_B) was the promotion of a stronger ligand field. Together with a coordination environment compatible with uniaxial magnetic anisotropy, this strategy allows to significantly enhance the effective demagnetization barrier. As SMMs improve, vibrational tuning is gaining interest as another avenue to reach the same objective.[1-3] In this presentation, we analyze several literature examples of current high-performance SMMs to evaluate the potential impact of further crystal field and vibrational tuning in their blocking temperatures.[4]

SMMs with higher blocking temperatures (between 50-70 K) are not expected to benefit strongly from vibrational tuning. Thus, promotion of crystal field strength remains as a central strategy for this group. On the other hand, some examples with lower T_B can be significantly improved by this vibrational tuning. Thus, the best tuning strategy depends on the target system.

Finally, we analyze a recently proposed, hypothetical SMM.[5] According to our ab initio method, this system is promising to achieve SMMs with large T_B. In sum, our analysis provides a simple method to identify the most effective tuning approach for improving existing SMMs and a way to assess the potential of hypothetical SMM candidates.

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Controlled coherent dynamics of [VO(TPP)], a prototype molecular nuclear qudit with an electronic ancilla

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Abstract

Vanadyl-based (VO) molecules belong to the class of magnetic molecules characterized by an almost isotropic spin S=1/2 state and long phase memory time T_2[1]. In this work we demonstrate that [VO(TPP)] (TPP=tetraphenylporphyrinate), thanks to the combination of the electronic and nuclear (I=7/2) spin states, can be exploited as multilevel unit (called qudit) for implementing quantum computation algorithms. [2] In fact, we prove the ability to create coherent superposition of nuclear spin states by radio frequency pulses. We use broadband Nuclear Magnetic Resonance on the ^{51}V nuclei to determine the parameters of the coupled electro-nuclear spin Hamiltonian and nuclear spin-coherence times. [2,3] The latter are very competitive with other qubit-qudit systems, thus making this complex suitable for manipulation without significant coherence losses. We then demonstrate that the small quadrupolar contribution of Vanadium nucleus is not a limiting factor for the addressability of single nuclear transitions. In fact, by properly tuning the applied field, we met a condition in which the transverse hyperfine interaction up to second-order perturbation theory yields an effective quadrupolar splitting between nuclear states. The ability to coherently manipulate this qubit-qudit system with radiofrequency pulses is demonstrated by inducing monochromatic Rabi oscillations between subsequent nuclear states and by simulations made by numerically solving Lindblad equation for the system density matrix. Together with long coherence times, this ability is mandatory for the development of quantum computation algorithms and quantum error correction schemes.

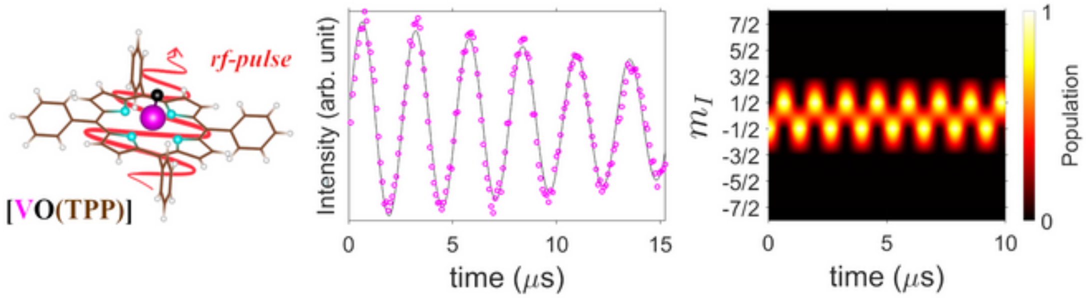

Figure 1 Experimentally induced Rabi oscillation between subsequent nuclear states (centre) and simulated evolution of nuclear state populations (right).

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Computational Characterization of Molecular Spin Qubits using Density Functional Theory

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Abstract

Molecular spin qubits have the potential to greatly improve current quantum computing technologies due to their high degree of structural tunability, which in turn enables fine control over their electronic and magnetic properties via targeted chemical design. Despite challenges in maintaining quantum coherence, progress has been made towards extending phase memory times through engineering compounds with clock transitions (CTs), avoided level crossings which are particularly robust against magnetic noise.

Recently, Kundu et al. reported the synthesis and characterization of three novel rare-earth compounds: $[La(OAr^*)_3]^{1-}$, $[Lu(NR_2)_3]^{1-}$, and $[Lu(OAr^*)_3]^{1-}$ (OAr* = 2,6-Ad_2-4-t-Bu-C_6H_2, R = $SiMe_3$), which possess one unpaired electron residing in a hybrid orbital with $5d_z/6s$ character (DOI:10.26434/chemrxiv.14399333.v1). These compounds were found to have desirable magnetic properties, with $[Lu(OAr^*)_3]^{1-}$ in particular possessing a record hyperfine interaction (~ 9 GHz) which facilitates large hyperfine clock transitions and comparatively longer magnetic relaxation times than conventional EPR transitions.

In this poster, I present the role of quantum chemistry calculations in enabling the understanding of the above molecular qubit series. All-electron density functional theory calculations including relativistic corrections are found to successfully reproduce experimentally observed trends in both the hyperfine and quadrupole interactions for $[La(OAr^*)_3]^{1-}$, $[Lu(NR_2)_3]^{1-}$, and $[Lu(OAr^*)_3]^{1-}$. Furthermore, DFT calculations reveal new design principles for molecular qubits by demonstrating how modulation of metal *s*-orbital character in the HOMO can drastically affect the molecular spin density, and thus the hyperfine splitting and subsequent occurrence of clock transitions. I detail the DFT methodology used to study these new systems, examining the level of relativistic treatment and dynamic correlation necessary to achieve useful predictions at reasonable computational cost. Finally, limitations of the current approach, along with future opportunities for application to quantum materials and technologies are discussed.

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A Ring of Rotaxanes

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Abstract

One challenge in the development of molecular devices is a requirement for multiple components to be linked together. Using supramolecular chemistry, large complexes can be synthesised via Lewis acid and bases, where the resulting assembly can be controlled through simple ligand design and displacement. By using supramolecular compounds containing interlocked species; defined as rotaxanes, the molecular components can be brought together whilst controlling the spin…spin interaction for paramagnetic species. This allows the strength of the interaction between spin components to be engineered as required.

A series of [7]-rotaxanes have been synthesised through coordination of six hybrid organic-inorganic [2]-rotaxanes with the general formula $[RH][Cr_7NiF_8(O_2CtBu)_{16}]$, where RH is a secondary ammonium thread, to a Lewis acidic dodecanuclear Nickel complex. The [2]-rotaxanes displace labile THF ligands on the $[Ni_{12}(chp)_{12}(O_2CMe)_{12}(H_2O)_6(THF)_6]$ metal cluster using a Lewis basic pyridyl group located on the ammonium thread. Four supramolecular molecular assemblies have been structurally characterised using single crystal XRD and SAXS experiments. This allows for a comparison to show how the molecular geometries vary depending upon the structure of the organic thread used in the crystal structure, and in free solution. Q-band continuous wave EPR experiments show the individual components are able to maintain their identity, for which pulse EPR experiments are then able to probe how the relaxation of the phase memory (Tm) and spin-lattice relaxations (T_1) times are affected for the four molecules.

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Nanotubes of Prussian blue and its Cr analog obtained by electrodeposition method

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Abstract

Prussian blue (PB) and Prussian blue analogs (PBAs) are one of the best-known groups of molecular magnets, especially due to their functional properties (sorption capacity, photomagnetism). The numerous methods of synthesizing samples in various forms (bulk, thin films, nanoparticles) create a possibility for interesting research, for instance, the investigation of the influence of the size reduction on their magnetic properties.

In this work, we report the synthesis and physicochemical characterization of the nanotubes composed of Prussian blue ($Fe^{III}Fe^{II}$) and its Cr analog ($Fe^{II}Cr^{III}$). The samples were prepared by template-assisted electrochemical deposition. The porous polycarbonate (PCTE) membranes covered by a thin film of Au were used as the working electrode in a three-electrode electrochemical cell. The samples were fabricated inside the PCTE membranes of different pore sizes: 50, 80, 100, and 200 nm.

The analysis of scanning electron microscope (SEM) microphotographs confirmed that nanotubes of cylindrical shape with outer diameters from 50 to 200 nm were obtained for both samples. The measurements of magnetic properties showed that synthesized materials are ferromagnets with critical temperatures T_c around 4 K and 20 K for $Fe^{III}Fe^{II}$ and $Fe^{II}Cr^{III}$ respectively. These T_c values are comparable to those observed for bulk as well as thin films. This work also covers the relationship between nanotubes' diameters and the coercive field values.

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High-Field EPR Study of the Spin-Crossover Transition in a Mn(III) Complex

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Abstract

Spin crossover (SCO) transitions occur in complexes of octahedrally coordinated $3d^4$ to $3d^7$ transition metals and can be induced via changes in temperature and pressure, or via the application of light, strain, magnetic or electric fields as external perturbations. A Mn-323 complex was investigated, which exhibits a complete transition from a high spin (HS) (S=2) state to a low spin (LS) (S=1) state below a relatively sharp transition. ($T_{1/2}$= 51 K; with <10 K hysteresis). In some SCO complexes, it can be too costly to convert all sites within a crystal from HS to LS, so a crystal may sometimes convert only half of the sites in a highly ordered manner resulting in mixed phases. Due to the inhomogeneity of these mixed phases, such complexes can often be quite difficult to characterize experimentally. Thus, an advantage to studying this Mn^{3+} complex is the 100% HS to 100% LS transition at a relatively low temperature, which allows for a more straightforward characterization of both spin states at temperatures amenable to study using Electron Paramagnetic Resonance (EPR) spectroscopy. The zero-field splitting (ZFS) in Mn^{3+} is dominated by spin-orbit coupling (SOC), as is generally the case for d block transition metals, which admixes crystal field states, giving rise to magnetic anisotropy. This is manifested in the anisotropic *g*-tensor and ZFS parameters, *D* and *E*, employed in the effective Spin Hamiltonian. Using continuous-wave high-field (0 – 14.5 T) powder EPR spectroscopy the ZFS parameters were characterized for both the LS (D = +20.28 cm^{-1}) and HS states (D = +5.66 cm^{-1}, E = +1.31 cm^{-1}).

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Molecule-based metal-organic magnets with large coercivity and ordering temperatures up to 242°C

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Abstract

Inorganic materials such as pure metals, metal oxides and intermetallic compounds, have been widely implemented as room-temperature (RT) magnets in a large number of modern-day technological applications including information storage devices, household appliances, medical equipment, etc. Despite their impressive performances in these applications, inorganic magnets suffer several drawbacks, including high energy consuming fabrication (e.g., for SmCo and AlNiCo) limited access to elemental resources (e.g., in the rare earth–based magnets NdFeB and SmCo), and lack of chemical tunability. Coordination chemistry offers a promising approach for the design of next-generation magnets, as the construction of molecule-based materials affords almost unlimited possibilities for the tuning of the physical properties. On the basis of this strategy, the post-synthetic reduction of preassembled coordination networks, composed of chromium metal ions and pyrazine linkers, leads to the appearance of **magnetization hysteresis up to 515 K** with a coercive field of 7500 Oe at RT for $Li_{0.7}[Cr(pyrazine)_2]Cl_{0.7}\cdot 0.25(THF)$. This compound consists of a two-dimensional network made of Cr^{II} ions and radical pyrazines with layers of Li^+ and Cl^- ions and THF intercalated in-between the planes. It should be noted that before the discovery of this compound, there was not a single metal-organic compound that exhibited magnetic hysteresis loops with coercive fields of more than a few Oersted at RT.

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Radical-lanthanide ferromagnetic interaction in a Dy(III) bis-phthalocyaninato complex

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Abstract

Lanthanide complexes bearing radical organic ligands display a unique magnetic coupling mechanism between the delocalized spin density of the radical on the ligand and the localized 4f moment of the lanthanide ion. This mechanism can be used to mediate magnetic coupling to normally isolated lanthanide ions, a highly desired property for spintronics applications and quantum information technologies. In this study high-field/high-frequency Electron Paramagnetic Resonance (EPR) measurements were performed on a dysprosium bis-phthalocyaninato metalorganic complex, $Dy(Pc_2)$, to investigate the interaction between the radical ligand and the Dy(III) ion. Double-axis rotation measurements on a single crystal reveal the existence of two molecular orientations within the unit cell, the easy-axis nature of the Dy(III) moment, and enable measurement of the strength of the magnetic coupling between the ion and the radical.

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Lanthanide complexes with carbo[6]helicene *o*-quinones

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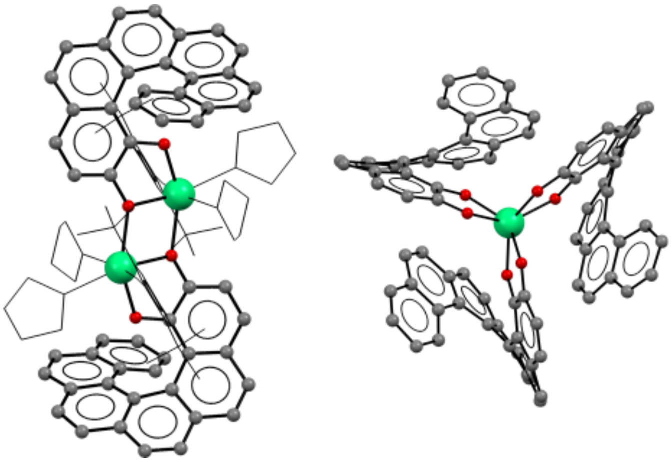
Abstract

Helicenes are fascinating compounds with axial chirality and unique chiroptical properties. Their optical rotation is two order of magnitude larger than that for compounds with chiral carbon atoms. Therefore, the strong chirality of helicenes encourages their exploration as ligands.[1,2] Besides properties arising from the chirality itself (like circularly polarised luminescence), helicene complexes may exhibit even more fascinating features arising from the combination of chirality with other properties like magnetism, i.e. magneto-chiral dichroism.[3] Lanthanide complexes with helicenes as ligands are vastly underexplored and requires therefore extensive experimental and theoretical investigation.

Herein, we report the structural and magnetic characterization of two helicene complexes of erbium(III): a dimer bridged by two helicene catecholate dianions (L) - $[Er(L)(BHT)(THF)_2]_2$ (BHT = 2,6-di-*tert*-butyl-4-methylphenol) and a mononuclear complex coordinated by three helicenes – $Li_3[Er(L)_3]Cl_{1.5}\cdot3(THF)$ (Li^+ cations, Cl^- anions and THF molecules are ommited in the picture for clarity). These complexes constitute the first examples where [6]helicene *o*-quinones[4] are used as ligands (according to CSD database). The dimer exhibits slow magnetic relaxation typical for field-induced SMMs with a butterfly-type magnetic hysteresis. Its slow magnetic relaxation is mainly driven by a Raman relaxation process. The mononuclear complex does not show slow relaxation of magnetization because of the presence of at least one semiquinone radical anion as a ligand in the structure.



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Biscalix[4]arene-supported metal clusters

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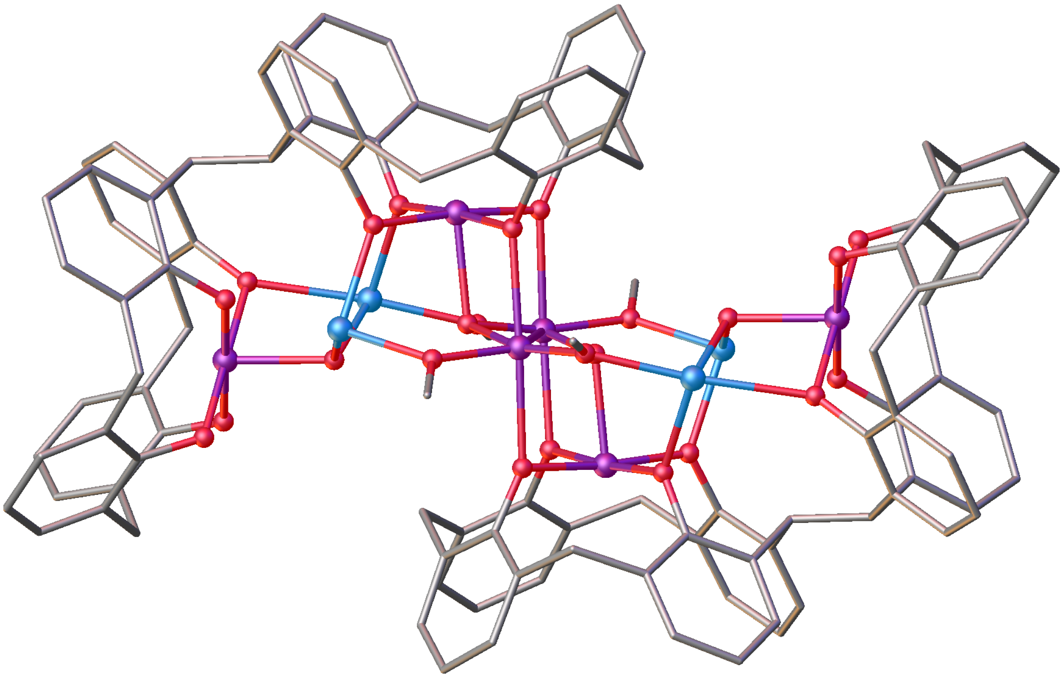
Abstract

Calix[4]arenes (C[4]s) are versatile platforms for the assembly of 3*d* and 3*d*/4*f* polymetallic clusters with fascinating magnetic properties, nuclearities and topologies.[1] Synthetic modification at the methylene bridge offers a unique opportunity to influence / control the cluster-forming chemistry of the C[4] platform by linking two C[4]s directly (2,2'-biscalixarene or BisC[4] hereafter) or through a tether, either flexible or rigid. The conformational properties of BisC[4], coupled with the availability of 8 phenolic O-atoms in close proximity to each other, represents a very attractive platform for the magnetochemist in order to synthesise polymetallic clusters of paramagnetic ions, investigate their magnetic properties and carry out magneto structural correlations. In our exploratory work we have investigated the ion-binding properties of BisC[4], obtaining a plethora of novel polymetallic clusters featuring topologies in agreement with the empirical binding rules established for C[4] and interesting magnetic properties.[2]



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Probing relaxation dynamics in Dy-Aryloxide Single-Molecule Magnets

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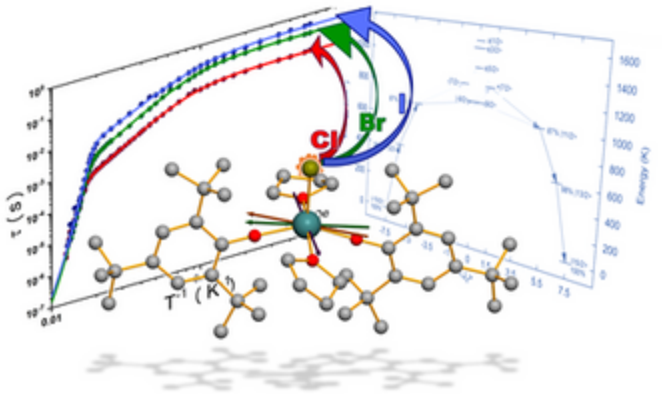
Abstract

Complexes of certain d-block and f-block ions can retain magnetisation over long periods giving rise to Single-Molecule Magnet (SMM) properties. SMMs could be utilised for technologies such as high-density data storage, quantum computers and molecular spintronics. They were discovered three decades ago but have remained technologically unfeasible as they only operate around impractical temperatures. Some recent remarkable advancements have re-ignited the research field with new ideas towards making high-temperature SMMs.[1] The latest design approach of high-performing SMMs requires a single Dy centre bound by uniaxial anionic ligands (ideally a two-coordinate Dy complex). The characteristic advantages of aryloxide ligands in realising low-coordinate high-performing Ln SMMs have been demonstrated.[2] Herein, the role of aryloxide ligands and their resultant crystal field on the physical properties of SMMs is investigated. The synthesis, magnetic behavior and ab initio computational studies of families of Dy SMMs of coordination number (**CN**) **5**, $[Dy(OMes^*)_2(THF)_2X]$ (Mes*=2,4,6-*t*Bu-phenyl; X= Cl (**1**), Br (**2**), I (**3**)) with the Dy centres in distorted square pyramidal geometries, and **CN4**, $[Na(THF)_6][Dy(OAd^*)_2Cl_2]$ (**4**) (Ad*=2,6-Ad-4-*t*Bu-phenyl) and $[Na(THF)_6][Dy(OMes^*)_3X]$ (Mes*=2,4,6-*t*Bu-phenyl; X= Cl (**5**), BH_4 (**6**)) with the Dy centres in distorted tetrahedral geometries, are presented. Complexes **1**-**3** show magnetic reversal barriers (U_{eff}) > 1200 K, with a trend in the rate of Quantum tunnelling of magnetisation as **1**>**2**>**3**, whilst the Orbach and Raman relaxation processes remain unchanged.[3] The magnetic relaxation rate is **4**<**5**<**6** among the **CN4** series, with **4** showing a high U_{eff} (950 K) owing to its bis-aryloxide ligand configuration.



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Synthesis, structural analysis, and magnetic properties of molecular Bi-Mn-oxo and Pb-Mn-oxo coordination cages

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Abstract

Molecular chemistry has afforded a wide variety of aesthetically pleasing topologies. One relatively popular structure has been the cage. A cage compound as defined by IUPAC is a “polycyclic compound with the shape of a cage.” This broad definition allows for many structures to be defined as a having cage topology, e.g., the bimetallic Zintl structures to the Keggin structures of polyoxometalates. The perovskite repeating unit can also be described as a cage of B cations encapsulating an A cation. In our group, the use of manganese, with its various stable paramagnetic oxidation states (II-IV), in metal-oxo-carboxylate chemistry has led to numerous clusters with fascinating structural features and intriguing physical properties, e.g., magnetism, however, few of these complexes have had cage structures. Over the last decade, our group has been working to prepare a family of heterometallic Mn-oxo coordination cages through high temperature methods. Many of these complexes have displayed structural relevance to the perovskite manganite, AMnO3. Although considerable effort has been made in the development of heterometallic manganese clusters, few clusters reported contain manganese and heavy main group metals such as bismuth or lead. Herein, we present the recent efforts towards the development of Bi-Mn-oxo and Pb-Mn-oxo coordination cages. The preparation, structural analysis, and magnetic studies for these heterometallic heavy metal Mn-oxo clusters will be described.

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Multimodal THz waveguides at EPR endstation of Novosibirsk Free Electron Laser: construction and overall performance

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Abstract

Terahertz (THz) frequency range, located midway between microwaves and visible light, is a spectral window with many technical applications and fundamental research problems. There are several difficulties limiting the progress in the THz science. One of them is the strong attenuation of THz radiation in waveguides, caused by high losses due to the finite conductivity of metals and the high absorption coefficient of dielectrics. Although many THz waveguides have been proposed to date, there is still no unified solution and a certain compromise is often required for a specific application. The waveguide design becomes even more complicated when strict space constraints are imposed, as in the case when it is necessary to introduce THz radiation into the cryogenic probehead of the Electron Paramagnetic Resonance (EPR) spectrometer – one of the endstation at Novosibirsk Free Electron Laser (NovoFEL) facility.

Herein, we report the design and fabrication of the THz waveguides used at the X-band EPR endstation of the NovoFEL facility. Experiments carried out at the EPR endstation are aimed to investigate the impact of THz radiation on the spin system of different single molecular magnets and organic radicals. The proposed metal-coated multimodal hollow waveguides are quartz tubes with an outer diameter of 8 mm and an inner diameter of 6 mm, tapering to 2 mm at one end. The inner surface of the waveguide is coated with silver and the total length of the waveguide is 60 cm. The waveguides transmit THz radiation in a wide frequency range of 1.4 to 33.5 THz with transmission losses of ~4.5 dB/m at 1.4 THz and ~11.7 dB/m at 33.5 THz. The proposed design is versatile and flexible, which allow them to be used for other setups with different spatial constraints and requirements.

This work was supported by RSF 17-13-01412.

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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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Abstract

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 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]

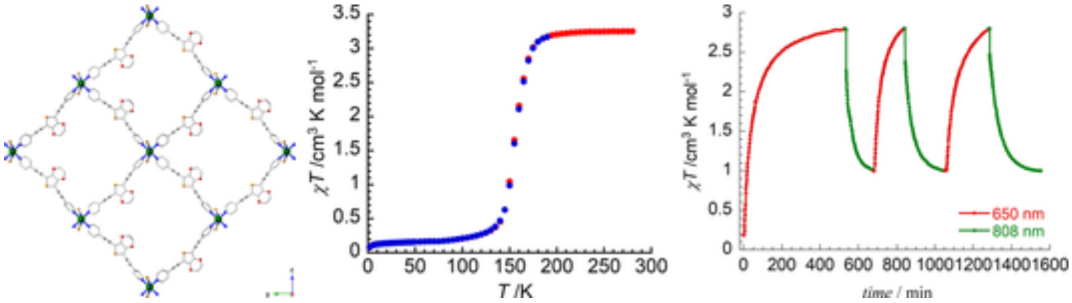

Figure 1. Left: 2D network showing [4x4] square-grid*,* Middle: Temperature dependence of χT product*, and* Right: Plot of χT vs time under cycles of successive irradiation with 650 nm and 808 nm at 10 K and 10000 Oe field for the CP**.**

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Quantum spin toroidicity in molecular spin rings

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Abstract

We will discuss the origin of molecular toroidal states in spin rings [1-3], both in the strong spin-orbit limit [1-4,8,9], and in the weak spin-orbit coupling regime [5-7] where they arise as a consequence of spin frustration and the quantum tunneling of the scalar spin chirality. We will also discuss toroidal states in heterometallic $M^{III}Dy_6$ double triangles (M=Cr, Fe, Mn, Co, Al) [8,9] resulting from the con-rotating coupling, or *ferrotoroidic coupling [8],* of two toroidal Dy_3 rings, and by direct simulation of their hysteretic spin dynamics in a sweeping magnetic field [8,9], we will expose the disparate signature of magnetic, toroidal and ferrotoroidal states on the shape of the measured hysteresis of the magnetization.

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Clarification of the origin of the frustration-induced phase transition in reduced diamond lattice

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Abstract

A cyclic thiazyl radical, bpBDTDA, exhibits unique spatially inhomogeneous phase transition accompanied with dimerization in a stepwise fashion. The unit cell in the high-temperature phase above 359 K consists of four regular π-stacking columns, which are connected by intermolecular S···S and S···N contacts between the thiazyl radical moieties. Below 359 K, three of the four stacking columns exhibit structural transitions toward zigzag chain structures, formed by an alternating dimerization between the radial moieties, while one column maintains the uniform π stacking. In the low-temperature phase below 306 K, the last column finally exhibits the radical dimerization toward a zigzag chain structure. We found that this phase transition is caused by a frustration inherent in a reduced diamond lattice by measuring the X-ray diffuse scattering measurements, THz-TDS measurements, and theoretical calculation. In this talk, we report the origin of this phase transition interpreted by line graph theory.

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Design of Thiocyanido-bridged Fe^{II}-Hg^{II} Frameworks Revealing Chirality, Spin-crossover and Photomagnetism

Guanping LI, Olaf Stefanczyk, Shin-ichi Ohkoshi
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Abstract

Numerous aspects of spin-crossover (SCO) materials such as syntheses, structures, and physicochemical properties have been vigorously researched in last decades.[1] In this content, the goal of our work is to design and characterize the high dimensional thiocyanido-bridged SCO compounds **1-3** based on iron(II) ions with $[Hg(SCN)_4]^{2-}$ anions and 2-, 3-, and 4-acetylpyridines(2-, 3-, and 4-acpy) respectively. Crystals of compound **1** ($\{[Fe(2\text{-acpy})][Hg(SCN)_4]\}_n$) have interesting chiral character due to formation of two mirror-image 3D thiocyanido-bridged networks. Crystals of $\{[Fe(3\text{-acpy})_2][Hg(SCN)_4]\}_n$ (**2**) consist of 2D folded-layers. For compound **3** $\{[Fe(4\text{-acpy})_2][Hg(SCN)_4]\}_n$, 3D network is built of two symmetry-independent tetragonal-distorted octahedral $[Fe(4\text{-acpy})_2(NCS)_4]$ units and it crystallizes in the non-centrosymmetric orthorhombic space group $Pna2_1$. It shows temperature-dependent structural parameters owing to changes of spin states of Fe^{II} ions. All three crystals are found to have fully occupied quintet paramagnetic high-spin(HS) state in two Fe^{II} sites at 300 K. When cooling down, products of temperature and magnetic susceptibility ($\chi_M T$) values for crystal **1** and **2** remain constant down to 50 K and they gradually decrease below this temperature, which can be addressed to Zeeman effect on the high spin Fe^{II} sites. In the case of crystals of **3**, it revealed partial SCO effect with $T_{1/2}$ = 103 K owing to the formation of low-spin state for one Fe^{II} ion ($S = 0$, $t_{2g}^6e_g^0$) and high-spin state for another Fe^{II} ion ($S = 2$, $t_{2g}^4e_g^2$). The Light-Induced Excited Spin-State Trapping (LIESST) effect can be observed for crystal **3** with 473, 532, 658 and 1064 nm lights, which can be further testified by temperature-dependent UV-Vis, IR and THz spectra.

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Modelling Magnetic Molecule Based Molecular Spin Transistor

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Abstract

Transistors are the main component of an electronic circuit. In standard electronics, electrons are manipulated and send through different device components to transport, read or write information. However, only the charge of the molecule is exploited in electronics but not the intrinsic spin components. The spin-up and spin-down components of the electrons interact differently with molecules possessing unpaired electrons and this very nature of the physics been exploited to build spintronics devices.[1{a,b}] Molecular spin transistor has been modelled by placing a magnetic molecule between two gold electrodes and studied their transport properties computationally.[2] The structure, geometry and magnetic properties of a molecular magnet at the electrode interface were studied by using DFT calculation. DFT-NEGF methodology has been implemented to study the transport properties.[3] The device possesses larger conductivity in high-spin state than in low-spin state. Furthermore, it behaves as a perfect spin filter device giving β-polarized current.

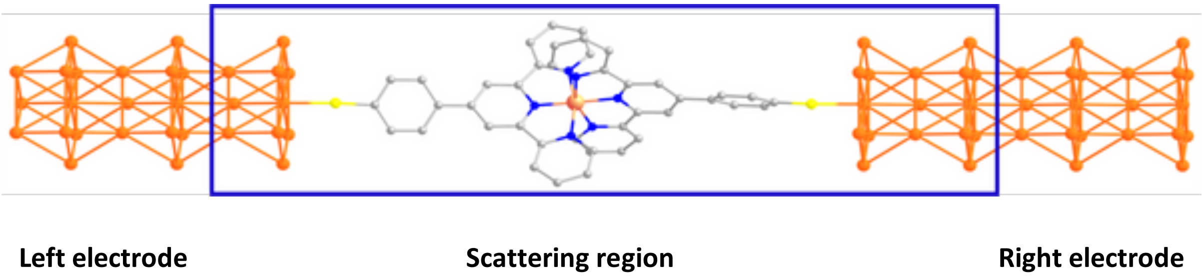

Figure 1. Molecular junction device. Colour code: Golden Yellow Au; light yellow Co; Yellow S; Navy Blue N; Grey C.

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Crystal field splitting and exchange interactions in a lanthanoid-semiquinonate complex

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Abstract

Single-molecule magnets retain their magnetization at low temperatures, with potential applications in quantum processing, molecular spintronics, and high-density data storage. The current best performing SMMs are complexes of the late trivalent lanthanoid (Ln) ions.[1] The energy barrier to reversal of magnetization stems from the crystal field (CF) splitting of the ground spin-orbit coupled *J* state, which can be tuned by appropriate choice of ligands. Aside from efforts to improve Ln-SMMs by increasing the energy barrier to magnetic relaxation, magnetic exchange coupling of the Ln(III) with another metal or organic radical can also modulate SMM behavior. Magnetic coupling can decrease the efficiency of quantum tunnelling of magnetization in zero-field, allowing thermally activated relaxation processes. The contracted nature of the 4f orbitals afford weak exchange coupling with lanthanoid(III) ions, which is difficult to quantify using conventional magnetometric techniques due to the large orbital angular momentum contribution in ions other than Gd(III). Inelastic neutron scattering is well suited to the measurement of CF splitting and exchange interactions in lanthanoid(III) complexes, however it is relatively underutilised compared to other techniques.[3]

Here we present a spectroscopic and computational study of an erbium(III)-semiquinonate complex, [ErTp$_2$dbsq], with antiferromagnetic exchange known for the Gd(III) analogue.[4] We have experimentally determined the magnitude of the magnetic coupling in the Er analogue, along with determining the CF splitting using a combined magnetometric, neutron scattering and electronic structure calculation approach.

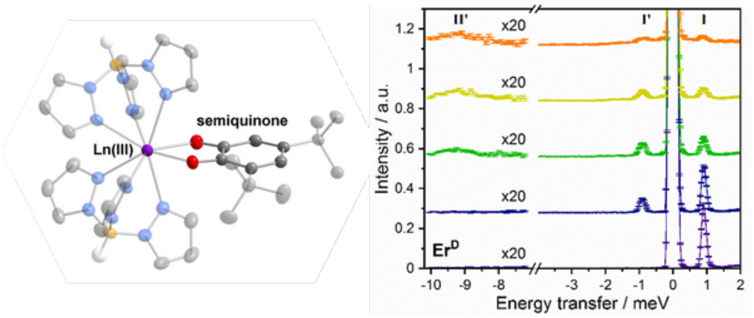

Figure 1: Structure of [ErTp$_2$dbsq] (left) and INS transitions in Er analogue (right)

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Unexpected Light-Induced Thermal Hysteresis in Matrix Embedded Low Cooperative Spin Crossover Microparticles

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Abstract

The embedding of spin-crossover micro- or nanocrystals in various surroundings dramatically changes their functionalities based on first-order spin transitions. [1] The dampening of their internal cooperativity, together with introducing a new kind of interactions occurring at interfaces between spin-crossover particles and their environment, results in spectacular effects, as an enhanced hysteresis with non-cooperative transitions. In this work, we deal with the influence of the embedding matrix on the light-induced thermal hysteresis (LITH) in the case of spin-crossover microparticles of $Fe(phen)_2(NCS)_2$. Despite the low cooperativity of this compound, the competition between the continuous photoexcitation towards the metastable high spin state and the relaxation down to low spin ground state leads to a light-induced thermal hysteresis, with a quasi-static width of around 10 K (see figure). [2] This unexpected hysteresis is explained by considering a switch-on/cutoff mechanism of the particle–matrix interactions in the framework of a mean-field approach based on negative external pressures, with Gaussian distributed variations and of Ising-like and mechanoelastic model with various interactions with the environment. Additional first-order reversal curves measurements and corresponding calculated distributions are in line with relaxations under light and confirm the existence of a non-kinetic LITH.

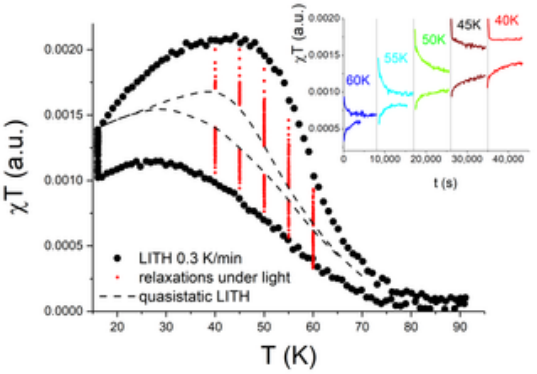

Figure: Light-induced thermal hysteresis for $Fe(phen)_2(NCS)_2$ microparticles embedded in glycerol (black circles experimental data; red circles partial relaxation under light; dotted line: profile of the real LITH curve as a guide for the eye). (inset) Partial relaxation curves under light starting from the two hysteresis branches, showing the existence of a quasi-static real hysteresis.

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"Photochromic dithienylethenes for the construction of photoswitchable quantum nanomagnets"

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Abstract

Dithienylethenes (dte) are photochromic molecules undergoing reversible photocyclization upon UV/vis irradiation (Figure 1a). Both dte forms (open and closed) are thermally stable and the photoswitching is robust. They can be easily modified to accommodate various functional groups and are commonly used for the construction of functional photoswitchable materials including molecular magnets.[1]

The goal of the presented research is to combine photoswitchable dithienylethenes with low-coordinate lanthanide complexes such as [Er^{III}(BHT)$_3$] (BHT = 2,6-di-*tert*-butyl-4-methylphenoxide) or [Dy^{III}(BBPEN)]$^+$ (H$_2$BBPEN = N,N′-bis(2-hydroxybenzyl)-N,N′-bis(pyridin-2-ylmethyl)ethylenediamine)[2] to obtain photoswitchable quantum nanomagnets. We are focusing on the preparation of three dte ligands, equipped with carboxylate (**dte1**), pyridyl (**dte2**) or aryloxide (**dte3**) functional "arms" (Figure 1). Herein we present the crystal structure, photochromism and magnetic properties of {[Er^{III}(BHT)$_3$](dte$_3$)[Er^{III}(BHT)$_3$](dte$_3$)[Er^{III}(BHT)$_3$]} oligomer **Er$_3$(dte3)$_2$** (BHT = 2,6-di-tert-butyl-4-methylphenolate; **dte3** = 1,2-Bis(2-methyl-5-pyrid-yl)thie3-yl)perfluorocyclopentene). The reported compound is a trinuclear linear complex, where bispyridyl dithienylethenes (**dte3**) act as molecular bridges. The terminal Er^{III} are four-coordinate and pseudo-tetrahedral, while the central one is five-coordinate and trigonal bipyramidal. The distance between the two thiophen carbon atoms, that are responsible for the photocyclization, is 3.79 Å which enables photo-induced **dte3** cyclization in the solid state. The yellow crystals of **Er$_3$(dte3)$_2$** undergo photoisomerization upon UV irradiation accompanied by a color change to blue.

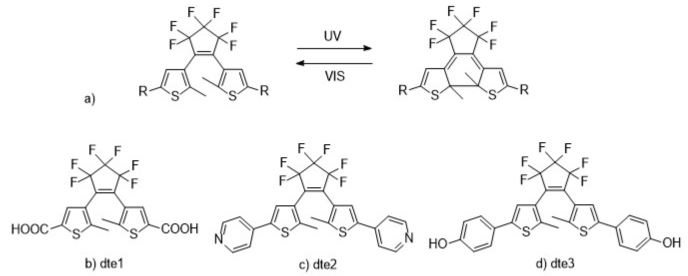

Figure 1. The photocyclization of dte-type ligands (a) and the structural formulae of **dte1** (a), **dte2** (b) and **dte3** (c).

This work was financed by the Polish National Science Center within the Preludium Bis 2019/35/O/ST5/00647

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IN SEARCH OF Co_3^{II} BASED ZERO FIELD SMMs BASED ON TRIPODAL LIGANDS

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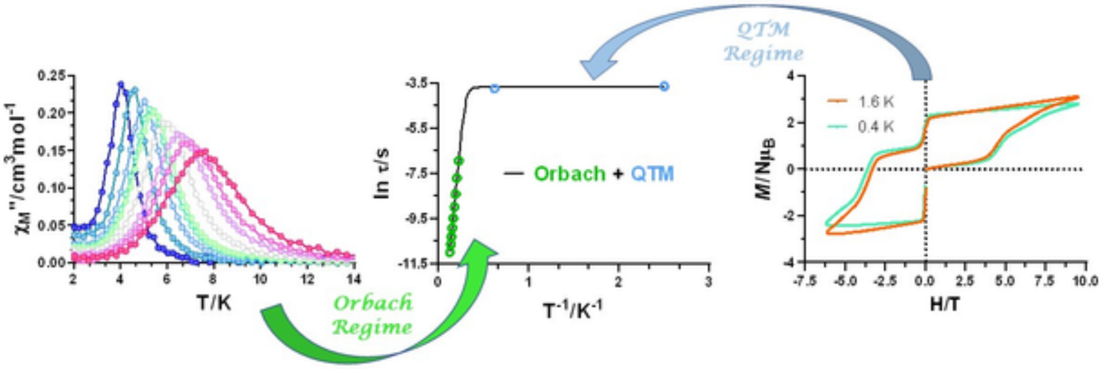
Abstract

The Co(II) ion possesses a non-integer spin ground state (Kramers ions) and their complexes can have strong magnetic anisotropy depending on the geometry. In this regard, low coordination number Co(II) complexes exhibiting weak ligand fields, that favour sizable values of the orbital angular momentum, commonly present a strong magnetic anisotropy. Because these two features favour the SMM behaviour, the predominance of mononuclear Co(II) complexes with such a type of behaviour, is not unexpected. In fact, recently, two-coordinated linear Co(II) complexes have been reported with effective energy barriers as strong as 450cm^{-1}.[1] It is worth noting that, among Co(II)-SIMs, those prepared from tripodal ligands generally show trigonal prismatic geometry, negative anisotropy (D<0) and zero-field SMM behaviour.[2] In view of this, we decided to synthesize a previously reported trigonal ligand, H_3L(1,1,1-tris[(salicylideneamino)methyl]ethane), that contains an inner N_3O_3 pocket and might be suitable to produce trigonal prismatic Co(II) mentioned mononuclear complexes with SIM behavior.[2] Here we report the synthesis, characterization and magnetic properties of a mononuclear diamagnetic complex, [Co(μ-L)]·MeOH, and a trinuclear paramagnetic complex $[Co_3(\mu\text{-}L)_2]$. *Ac* measurements under zero applied *dc* field, hysteretic behaviour and pulse magnetization measurements are reported, observing that the trigonal prism coordination environment around the Co^{II} ion or the strong enough exchange interactions allowed us to observe zero field SMM behaviour for the trinuclear compound. Additionally, we suggest an additional use for pulse magnetization measurements to obtain further information on the QTM regime.



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High-performance tetrahedral Er^{III} SMMs.

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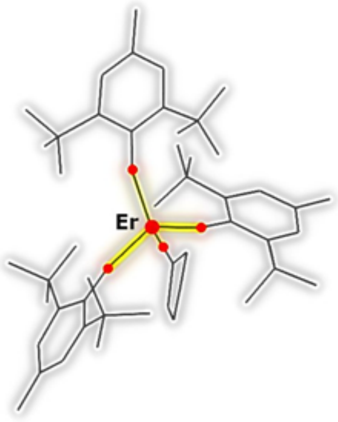
Abstract

Discovery and characterization of new high-performance single molecule magnets (HP-SMMs) is a hot topic in the field of molecular magnetism. Currently the best candidates for HP-SMMs are lanthanide complexes. However, they require a carefully designed coordination sphere which poses the biggest challenge in this vein of research.

In this contribution we present a series of new pseudo-tetrahedral Er^{III} complexes with exceptionally slow magnetization dynamics:[1] $[Er^{III}(TTBP)_3(THF)]$ (**1**) ($TTBP^-$ = 2,4,6-tri-tert-butyl-phenolate), $[Er^{III}(TTBP)_3(TEMPO)]$ (**2**) (TEMPO = 2,2,6,6- tetramethylpiperidine 1-oxyl) and $[Er^{III}(BHT)_3(THF)]$ (**3**) (BHT^- = 2,6-di-tert-butyl-4-methylphenolate). These compounds are designed based on the concept of Rinehart and Long taking advantage of the prolate-shaped electron density of Er^{III}.[2] The slow relaxation of the magnetization of the tetrahedral **1** and **3** is controlled mainly by the Raman-like relaxation mechanism which still allows the observation of the waist-restricted magnetic hysteresis loops at 1.8 K. The reported pseudo-tetrahedral SMMs are compared with the hexa-coordinate pseudo-octahedral Er^{III} complex: $[Li(THF)_2]_2[Er^{III}(N_3N)Cl_2]$ (**4**) (N_3N = tris(N-trimethylsilyl-2-amidoethyl) amine; $[(Me_3SiNCH_2CH_2)_3N]^{3-}$) which shows significantly faster relaxation of the magnetization. Additionally, the effect of substitution of the apical THF molecules in **1** by a radical ligand TEMPO (2,2,6,6- tetramethylpiperidine 1-oxyl) is also studied and it was demonstratd that the radical molecule coordinated to Er^{III} in a monodentate fashion completely disrupts the slow magnetization dynamics demonstrated by the parent complex **1**.



This work was financed by the Polish National Science Center within the Sonata Bis project 2016/22/E/ST5/00055

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First-Principles Spin Dynamics Under Terahertz Irradiation

Andrea Albino[1], Sergey Veber[2], Anatoly Melnikov[2], Matvey Fedin[2], Fabio Santanni[1], Stefano Benci[3], Lorenzo Sorace[1], Renato Torre[3], Alessandro Lunghi[4], Federico Totti[1], Roberta Sessoli[1]

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Abstract

One of the main limitations towards the use of molecular electron spins as qubit are the possible sources of relaxation of the spin state by interaction with the lattice environment. The Vanadyl tetraphenylporphyrinate (VOTPP) molecule was widely studied [1,2] because it exhibits the expected electronic and structural features to behave as a molecular spin qubit combined with other technologically relevant physical properties for a suitable processability and incorporation of these materials in real devices.

This work aims to investigate theoretically the effects of THz radiation on VOTPP spins. Preliminary but already promising results have been obtained on this system at the Novosibirsk Free Electron Laser (NovoFEL) facility with the combined EPR-THz setup described in [3]. In this perspective the spin-phonon coupling interaction of VOTPP is here addressed by means of periodic-DFT and all-electron DFT calculations, as depicted in previous works [4]. This modelization leads to the quantitative evaluation of spin-phonon contribution to the relaxation time and direct demonstration of the effects of single modes of vibration on the spin states. A new computational strategy is then introduced to address the effects of bright THz radiation, resonant with a lattice excitation, over the isolated ½ spins in the VOTPP paramagnetic crystal placed in a static magnetic field. The success of this project will provide a theoretical support to the correlations between spin-relaxation and phonons leading to a significant increase of our knowledge on the processes occurring in the solid state at the molecular scale.

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Effect of lanthanides on magnetic exchange-coupling and second harmonic generation

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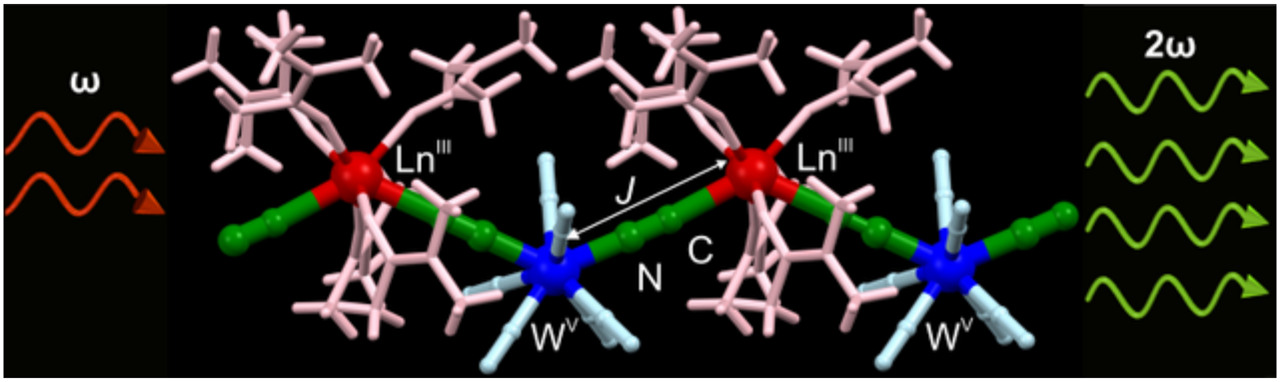
Abstract

Researchers around the globe have been studying cyanido-bridged systems for its multifunctionalities.[1] Inspired by this, The one–dimensional zigzag cyanido–bridged coordination polymers have been prepared as a result of self–assembly of rare–earth ions with octacyanidotungstate(V) in the presence of *N*,*N*–dimethylacetamide (dma). All compounds crystallized in the non–centrosymmetric space group $P2_1$ with molecular formula of $[\mathrm{RE}^{\mathrm{III}}(\mathrm{dma})_5][\mathrm{W}^{\mathrm{V}}(\mathrm{CN})_8]$ (RE = Gd (**1**), Tb(**2**), Dy(**3**), Ho(**4**), Er(**5**), Tm(**6**), Yb(**7**), Lu(**8**) and Y(**9**)). Each compound has been characterized by various techniques like UV-VIS, IR etc. showing the phase and elemental purity. Isostructurality of compounds have been applied in the determination of correlations between their magnetic exchange coupling and second harmonic generation (SHG) properties with diverse structural parameters. Modelling of paramagnetic behaviour of **1** – **7** with CASSCF calculation yielded magnetic coupling constants of 1-5 cm^{-1}. Calculated exchange coupling constants are the largest for **1**, **2**, **3** and **5** among **1** – **7**. All compound exhibit SHG behaviour because of non–zero elements of the second-order susceptibility tensor (χ_{ijk}): χ_{zxx}, χ_{zyy}, χ_{zzz}, χ_{zxy}, χ_{yyz}, χ_{yzx}, χ_{xyz} and χ_{xzx} for the $P2_1$ space group. SH signals were measured for the powdered samples. All materials have SH susceptibilities ranging from 4.7 × to 9.4 × esu. The maximum SH light intensity has been observed for Dy(III)–containing complex **3** with value of 9.4×10^{-11} esu (around 9.4% of potassium dihydrogen phosphate (KDP) utilised as a standard reference. Compounds with smaller ionic radii (**6** – **8**) exhibit much weaker SH signal compared those with large ionic radius, the same dependence trend has also been translated in to SH intensity *vs*. Ln(III)–Ln(III) distance.



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Effect of proton irradiation on magnetic properties of two-dimensional Ni(II) molecular magnet

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Abstract

The broad capability of the molecular magnetic materials emerges from the variety of available systems with unique properties that can be altered by external stimuli such as temperature, pressure, light irradiation, or sorption of guest molecules. Although not popular in the field of molecular magnetism, **ion irradiation** is the other approach for **tailoring the material's parameters**. Energetic particles expose solids to the high-density local energy deposition, leading to non-linear and threshold effects that may create new materials with novel properties.

In particular, the irradiation-induced defects may **give rise to the magnetism** in initially non-magnetic materials and **modify the magnetic properties** of a system with a non-zero magnetic moment, especially when strong magneto-structural correlations are present. The studies of the response of thin films and bulk samples to ion irradiation show there is a possibility to alternate such parameters as the critical temperature, g-factor, or coercivity by energetic particle deposition. However, no systematic studies can be found regarding the effects of ion irradiation on molecular magnetic materials.

Here we examine the magnetic properties of **2D coordination polymer** based on nickel sulfate and a 1,3-phenylenediamine ligand that was **irradiated with 1.9 MeV protons** using fluences ranging from $5\cdot10^{13}$ $p\cdot cm^{-2}$ to $2\cdot10^{15}$ $p\cdot cm^{-2}$. The samples irradiated with the high fluence showed an increase in magnetization saturation up to 200 percent and the reduced coercive field to even 10 percent of the reference level. Simultaneously, the critical temperature remained the same (T_c = 24.5 K) regardless of the received radiation dose. The IR spectroscopy showed that the **overall structure of the studied compound was preserved** after proton irradiation, and only minor changes are present in the local structure.

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Quenching of QTM in Lanthanide Complexes with Semiquinonate Radical Ligands

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Abstract

Much recent emphasis in the research on single molecule magnets (SMMs) has focussed on reducing the frequency of through-barrier processes for lanthanide systems which avoid the summit of the energy barrier.[1,2] In a dimeric Dy compound with four phenanthrene semiquinonate radical ligands it was found that the dipolar interaction between the Dy-centres quenches quantum tunnelling from the ground state (QTM) as relaxation pathway. Analogues have been synthesised using other Ln^{3+} ions (Pr-Lu), as well as by employing alternative ligands or co-ligands. The influence of the different Ln ions and their intrinsic anisotropy as well as different ligands on the quenching of QTM can be systematically explored.

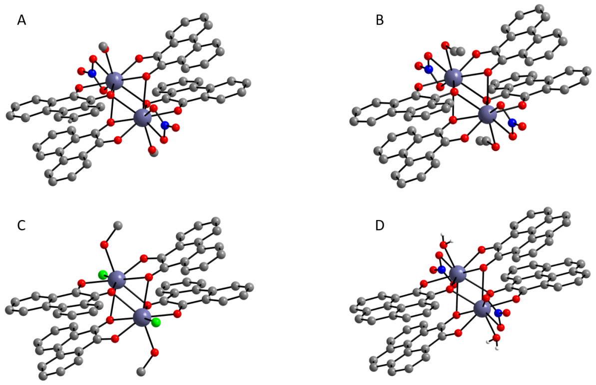

Figure 1: A) [Ln(phsq)$_4$**(MeOH)$_2$**(NO$_3$)$_2$] with Ln = Pr-Lu (without Pm); B) [Ln(phsq)$_4$**(EtOH)**$_2$(NO$_3$)$_2$] with Ln = Dy, Ho; C) [Ln(phsq)$_4$(MeOH)$_2$**(Cl)**$_2$] with Ln = Dy; D) [Ln**(pysq)**$_4$(H$_2$O)$_2$(NO$_3$)$_2$] with Ln = Dy. Highlighting the changing component in each compound. phsq = phenanthrene semiquinone radical, pysq = pyrene semiquinone radical.

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Multiple Transition Dynamics: Spin Transition Coupled with Structural Phase Transition

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Abstract

Switchable molecules with magnetic bistability have attracted a broad interest for their potential applicatility in the new generation of memory and swtiching devices [1]. However, the engineering of magnetic multistability with wide thermal hysteresis remains a major challenge. As one of typical bistable materials, the spin transition complexes such as spin crossover or metal-to-metal charge transfer complexes have been extensively studied, however only very few exhibited both multi-step and wide hysteresis. In addtion, some unusual molecular solids were recently found to exhibit clear non-spin magnetic bistability triggered by structural phase transition (SPT) [2]. These findings may allow the incorporation of both spin and non-spin transitions in one system, and their possible synergy may lead to very unusual properties.

With these considerations in mind, we explored a family of tetradentate ligands decorated with aromatic rings of different sizes, which fortunately meet the needs of both SPT and cooperative π-π interactions [3]. Remarkably, we have prepared a unique cyanide-bridged $\{Fe^{III}_2Fe^{II}\}$ complex showing three-step magnetic transitions and wide thermal hysteresis, originating from both spin and SPT-induced non-spin transitions.

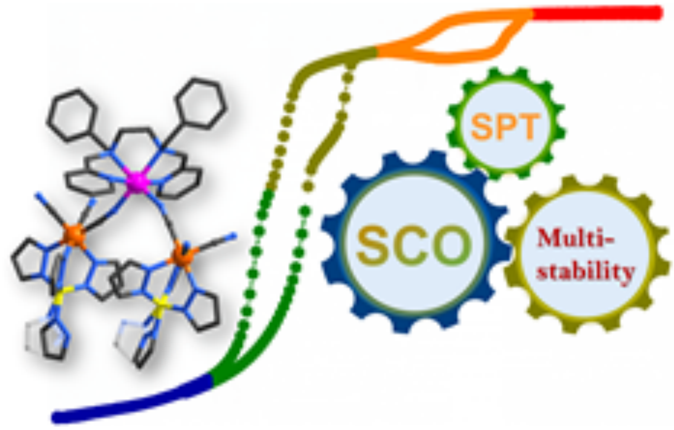

Figure 1. Structure and magnetic property of cyanide-bridged $\{Fe^{III}_2Fe^{II}\}$ complex.

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Molecular spin qudits for quantum simulation of light-matter interactions

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Abstract

Quantum computers are emerging as a disruptive technology which promises to solve problems impossible for any classical device. However, current realizations based on two-level elementary units (qubits) are noisy and only enable approximate small-size calculations. Alternative routes must be explored, to simplify complex algorithm and implement error-correction schemes[1].

Molecular spin systems provide a solution to both these issues[1,2]. Indeed, their multi-level energy structure, combined with their chemical tunability, can be exploited to design a platform based on multi-level building-blocks (qudits)[2], which can also be made robust against decoherence. We exploit these peculiarities to drastically reduce the number of objects and of control operations, compared to a qubit-based architecture. To exemplify the boost in computational power provided by these systems, we focus on a paradigmatic application: quantum simulation of light-matter interactions.

In particular, we use a transition-metal dimer consisting of a spin ½ coupled to a spin S>1 to encode the states of an atom and of a photon field. By directly exploiting the 2S+1 qudit levels we simulate atom-photon interactions in a non-trivial range of parameters up to strong and ultra-strong coupling, much more efficiently than by using a multi-qubit register[3]. Indeed, our scheme significantly reduces both the hardware overhead and the complexity of manipulations and allows us to extract ground state and dynamic properties of the target system.

The effectiveness of the proposed approach is shown by simulating the system dynamics under the sequence of microwave/radiofrequency pulses implementing the proposed procedures and using parameters of existing molecular systems.

[1] A. Chiesa et al., J. Phys. Chem. Lett. 11, 8610 (2020)

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Hyperfine Spectroscopy of Cr_7Ni Heterometallic Qubits

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Abstract

The families of Cr_7Ni heterometallic rings are vastly studied in the literature in the context of quantum information processing (QIP). The archetype molecule consists of an octagon of seven chromium(III) and one nickel(II) ions bridged by eight fluoride and sixteen carboxylate ligands, with an alkyl ammonium counteranion at the centre acting as a template. These molecules are green in colour and referred to as "green rings". Introduction of *N*-ethyl-D-glucamine (Etglu) into the structure of the Cr_7Ni ring generates another family of molecules, often termed "purple rings" (A). These display a coordination vacancy at Ni offering flexibility to functionalise the rings. Thanks to an isolated S = ½ ground state, both systems show potential as spin qubits. In this work, we use 2D HYSCORE (Hyperfine Sublevel Correlation) spectroscopy to evaluate the interaction of the electron spin with the nitrogen-14 nuclei on templates. A representative spectrum (B) and its simulation with $|A_x^N| = 5.3$, $|A_y^N| = 5.0$ and $|A_z^N| = 4.8$ MHz, and a quadrupole constant of $e^2qQ/h = 2.9$ MHz is presented. On the contrary, the related green rings show little evidence of electron spin transfer to the ammonium groups.

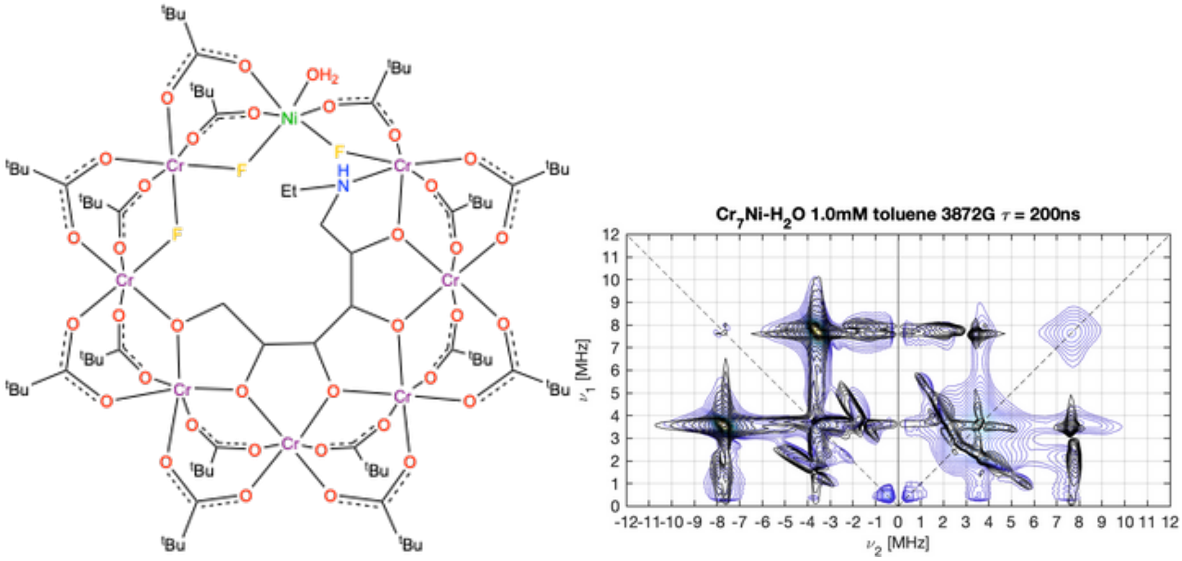

Figure 1. A) Chemical structure of the "purple" ring $[Cr_7NiF_3Piv_{15}Etglu\text{-}H_2O]$ (1) and B) its X-band ^{14}N HYSCORE spectrum in blue and simulation in black.

G. A. Timco, E. J. L. McInnes, R. G. Pritchard, F. Tuna and R. E. P. Winpenny, *Angew. Chemie Int. Ed.*, 2008, **47**, 9681–9684.

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Photoswitchable high-dimensional octacyanidometallate-based networks

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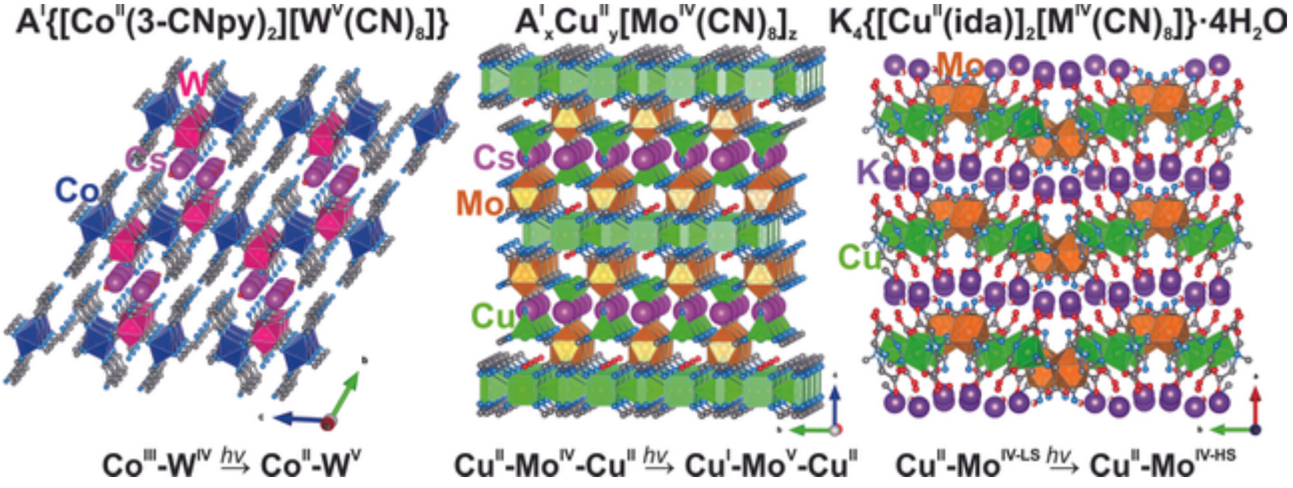
Abstract

The development of new photomagnetic materials (compounds demonstrating the evolution of their magnetic and other physicochemical properties in response to external stimuli with light) is one of the most expanding areas of molecular magnetism. These assemblies are likely to be suitable for use in the construction of advanced detectors, high-density data carriers and energy conversion devices. So far, one of the greatest successes in this field concerns magnetic cyanido-bridged metal compounds, especially, high-dimensional octacyanidometallate-based networks [1].

In this presentation, we will gather and systematize the latest knowledge on photomagnetic effects in two- and three-dimensional cyanido-bridged $\mathrm{Co^{II}\text{-}[W^{V}(CN)_8]}$ and $\mathrm{Cu^{II}\text{-}[Mo^{IV}(CN)_8]}$ networks. We will pay special attention to the recent works on two-dimensional $\mathrm{A^{I}\{[Co^{II}(3\text{-}CNpy)_2][W^{V}(CN)_8]\}}$ layers, where $\mathrm{A^{I}}$ = alkali metal ions and 3-CNpy = 3-cyanopyridine, exhibiting an electron-transfer-coupled spin transition with wide thermal hysteresis and photoinduced spontaneous magnetization with long-range magnetic ordering and large magnetic hysteresis loops [2]. Moreover, we will also describe a similar effect of photoinduced long-range magnetic ordering in three-dimensional $\mathrm{A^{I}_{x}Cu^{II}_{y}[Mo^{IV}(CN)_8]_z}$ coordination polymers [3]. Finally, we will indicate the challenges related to construction of photomagnetic $\mathrm{Cu^{II}\text{-}[M^{IV}(CN)_8]}$ systems with organic ligands on the example of two-dimensional $\mathrm{K_4\{[Cu^{II}(ida)]_2[M^{IV}(CN)_8]\}\cdot 4H_2O}$ (M = Mo, **1**; W, **2**) assembly [4], $\mathrm{ida^{2-}}$ = iminodiacetate, and we will give you some tips on how to be successful in preparing new photomagnetic materials.



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Magnetic investigations of monocrystalline $[Co(NCS)_2(L)_2]_n$: new insights into single-chain relaxations

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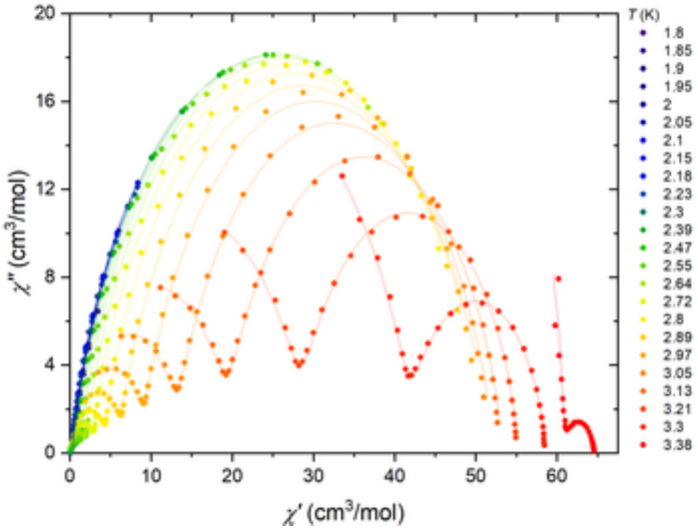
Abstract

Slow relaxation of magnetization is a well-known phenomenon observed in many different molecular systems, including Single-Chain Magnets (SCMs). Relaxations of a single chain in such systems are a nontrivial issue, especially in SCMs based on Co(II) ion. For them, the conventional approach assuming the energy barrier $2\Delta_\xi + \Delta_A$ for the two-wall process and $\Delta_\xi + \Delta_A$ for single-wall process seems to be inappropriate, as the Δ_A value does not correspond to the energy levels in a single Co(II) ion. Therefore, we present a modified approach, which was successfully used to explain the SCM relaxation process in the monocrystalline sample of $[Co(NCS)_2(4\text{-}(3\text{-phenylpropyl})pyridine)_2]_n$ coordination polymer. Its magnetic properties prove an almost Ising-type magnetic anisotropy with a magnetic easy axis nearly along Co-N_{ligand} bond, as predicted by single-ion ab initio calculations. Contrary to the powder sample, for the single crystal, two different magnetic relaxation processes are observed (as visible in the Argand plot). Despite the system is ferromagnetically ordered at T_c = 3.39 K, one of the processes displays a crossover of the relaxation time, indicating SCM behavior. The second process we tentatively assign to spin-wave excitations. The origin of SCM relaxation we explain basing on micromagnetic Monte Carlo simulations. To support the investigations of the SCM behavior, a magnetically diluted counterpart $[Co_xCd_{1-x}(NCS)_2(4\text{-}(3\text{-phenylpropyl})pyridine)_2]_n$ (x = 0.013) is used. To correctly analyze the SCM behavior it is crucial to include the proper relaxation pathways of Co(II) single spins. [1]



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A pentacyanidonitrosylferrate-based magnetic one-dimensional metal assembly exhibiting photo-induced switching of second harmonic generation

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Abstract

Noncentrosymmetric materials are extensively studied due to their unique optical properties. Our laboratory have reported noncentrosymmetric cyanido-bridged bimetal assemblies showing second harmonic generation (SHG).[1,2] In this work, we prepared a Dy-[$Fe(CN)_5(NO)$] one-dimensional metal assembly, [$Dy(phen)_2(NO_3)(H_2O)$][$Fe(CN)_5(NO)$]·$3H_2O$ (phen = 1,10-phenanthroline), and investigated the nonlinear optical properties.[3] The target compound was obtained as orange-colored crystals by reacting an aqueous solution of $Na_2[Fe(CN)_5(NO)]$ and $Dy(NO_3)_3$ with a methanolic solution of phen. The obtained compound possesses an orthorhombic structure with $Pna2_1$ space group and a cyanide bridged one dimensional chain structure. The $\chi_M T$ value shows 13.9 K cm^3 mol^{-1} at 300 K due to a paramagnetic Dy^{III}. Upon cooling, the $\chi_M T$ value gradually decreases below 50 K due to the depopulation of the excited *mJ* states. SHG measurements using a femtosecond pulsed laser (wavelength: 1040 nm) showed that the detected 520-nm light intensity is quadratically proportional to the fundamental light power. The analyzer angle versus SH intensity shows that the output SH light is polarized along the crystallographic *c*-axis direction. Furthermore, by irradiating 473-nm laser, the SH intensity is increased to 5 times the intensity before irradiation. Successive irradiating with 804-nm light reduces the SH intensity. The observed photoreversible switching of SHG is caused by the photoinduced linkage isomerism of the iron nitrosyl sites, i.e., Fe–NO ↔ Fe–ON, confirmed by photo-irradiation experiments on IR spectra.

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Lanthanide SMMs; it's Plane to See

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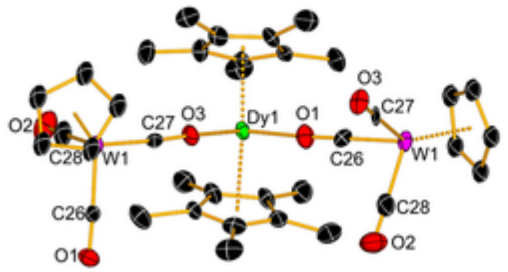
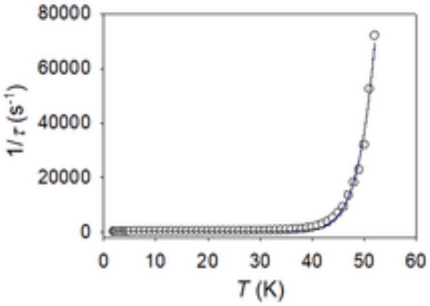
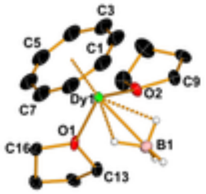
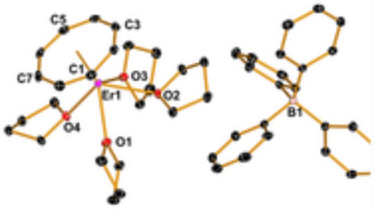
Abstract

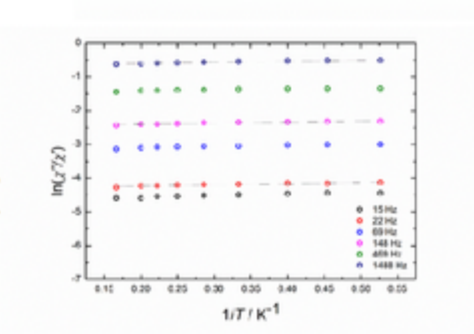
Lanthanide organometallic complexes have consistently demonstrated their applicability in SMMs, with much focus on maximising ligand effects in the appropriate plane for a given metal. The synthesis and magnetic characterisation of new complexes furthers the collective understanding and will improve future design efforts.











Research investigating and understanding the effects of ligands, including bridging ligands, will be essential for the realisation of functional devices. Presented here is work that has focussed on the utilisation of carbonyl bridges paired with a heavy transition metal, alongside the exploration of THF/pyridine as solvato ligands and their effects on the magnetic properties of the complexes. . Finally, the developement of easy to handled building blocks based around cycloocatetraene ligand, have been used to synthesis a new selection of anti-bimetallic complexes.

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Development of FTIR spectroscopy in high magnetic fields

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Abstract

We live in the digital era when the growing need for smaller and more energy-efficient devices has made higher density data storage one of the most important technological quests. With dimensions close to a nanometer and the ability to store one bit of information, molecules called Single-Molecule Magnets (SMMs) give a possibility to move the data storage technology forward. For the investigation of SMMs, spectroscopic techniques, such as Electron Paramagnetic Resonance (EPR), are essential due to their ability to probe molecular and electronic properties directly. However, because of systems with large zero-field splitting, Fourier Transform Infrared (FTIR) spectroscopy in the high magnetic field is needed in order to access fundamental transitions in SMMs. We propose FTIR spectroscopy in high magnetic fields as a very important tool in the characterization of numerous materials, including SMMs. This method allows studying EPR of SMMs with very large zero-field splitting, mainly based on transition metal complexes[1] or lanthanides[2] that cannot be studied by common EPR systems since they do not provide experimental access to the magnetic resonance transitions. It also presents an ideal experimental technique that can probe band structure and elucidate electronic properties of novel 2D materials, such as graphene[3]. The method of FTIR spectroscopy in high magnetic fields will be mediated by a compact FTIR magneto-spectroscopic setup built at CEITEC BUT. It consists of the FTIR spectrometer coupled to the 16 Tesla cryogen-free superconductive magnet. The FTIR magneto-spectroscopic setup will allow us to perform a variety of magneto-optical measurements in the infrared (IR) and terahertz (THz) spectral range.

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Luminescent Cyanido-bridged Dy^{III}-Co^{III} Framework Showing Solvent-driven Switchable Single-molecule Magnet Behavior

Yue Xin[1], Junhao Wang[1], Mikolaj Zychowicz[2], Jakub J. Zakrzewski[2], Koji Nakabayashi[1], Barbara Sieklucka[2], Szymon Chorazy[2], Shin-ichi Ohkoshi[1]

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Abstract

Benefitting from a diversity of interesting physical properties in magnetism, optics, electricity, and porosity, cyanido-bridged metal assemblies are great candidates for the promotion of multifunctional materials including photomagnetism, photoluminescent single-molecule magnet (SMM), humidity-sensitive magnetism and so on.[1] Introducing lanthanide(III) ions into cyanido-bridged networks has been proven as a promising method for exploration in both luminescence and magnetism,[2] together with switchability based on porosity.[3] In this regard, we present switchable photoluminescence and SMM behavior of cyanido-bridged Dy-Co assembly $\{[Dy^{III}(H_2O)_2][Co^{III}(CN)_6]\}\cdot 2.2H_2O$ (**1**), with its dehydrated phase $\{Dy^{III}[Co^{III}(CN)_6]\}$ (**2**) based on reversible dehydration/hydration process.[4] Different from no observation of slow magnetic relaxation in **1**, the generation of Dy^{III} single-molecule magnet behavior in **2** is resulted from a solvent-driven symmetry change from pseudo-D_{4d} to D_{3h} on Dy^{III} center through dehydration. Simultaneously, the solvent-driven process can also greatly amend the ratio between the intensities of $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ electronic transitions, leading to a color-tunable photoluminescent emission between nearly white (**1**) and bright orange (**2**). These changes were validated to be fully reversible upon the following rehydration. Furthermore, the Orbach-type of slow magnetic relaxation contributed from the axial crystal field of Dy^{III} complex in **2**, was confirmed by crystal field analysis based on *dc* magnetic data and photoluminescence.

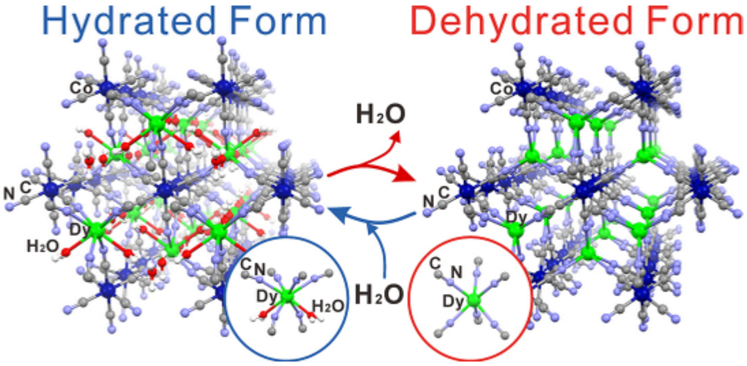

Figure. The reversible change between the three-dimensional coordination structures.

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Magnetic Exchange in Anderson-Type 3d Transition Metal Clusters.

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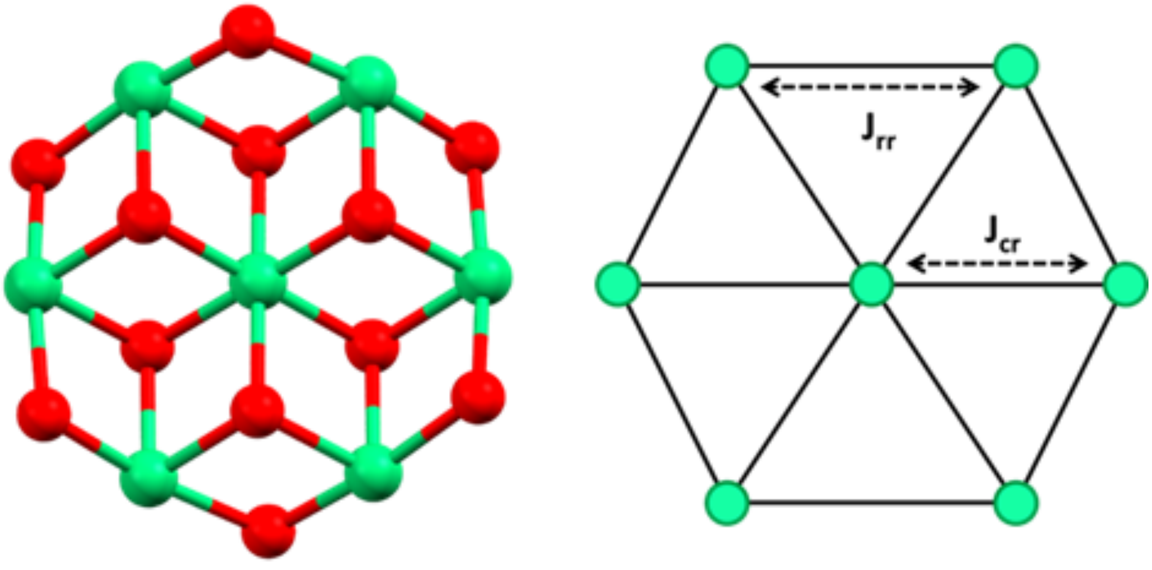
Abstract

Complexes containing triangular arrangements of paramagnetic metal ions have long been of interest in the field of molecular-magnetism, in particular, where those ions are coupled antiferromagnetically leading to the observation of geometric spin-frustration.[1-3] One such triangle-containing structure type is the Anderson wheel, which consists of seven iso-planar metal ions arranged as a centred hexagon (figure 1). Examples of both hetero- and homometallic 3d transition metal Anderson-type cores have proven highly stable and modifiable allowing for the synthesis of a series of related wheels. Here, we present such a family of Anderson wheels, which have been subsequently analysed, and their magnetic properties investigated via experiment and calculations to better elucidate their relevant underlying magneto-structural correlations.



Typical M_7 Core Structure

Simplest Available Coupling Scheme

Figure 1. Left: Generic M_7 Anderson wheel core (where M = green, and bridging atoms = red). Right: The simplest available magnetic coupling scheme for such a core.

1. J. Schnack, *Dalton Transactions*, 2010, **39**, 4677-4686. 2. V. O. Garlea, S. E. Nagler, J. L. Zarestky, C. Stassis, D. Vaknin, P. Kogerler, D. F. McMorrow, C. Niedermayer, D. A. Tennant, B. Lake, Y. Qiu, M. Exler, J. Schnack and M. Luban, *Physical Review B*, 2006, **73**. 3. O. Kahn, *Chemical Physics Letters*, 1997, **265**, 109-114.

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Multiscale out-of-equilibrium dynamics in spin-crossover molecular materials described by a three thermalisation scales model

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Abstract

Here we study the behavior of spin crossover molecules after ultrafast irradiation, by taking into account the different evolution of spin and lattice temperatures. Typical experiments showing the response of a spin crossover system to a femtosecond laser excitation indicate the increase of the high-spin fraction subsequent to photoexcitation in two steps. The first step is known as the "elastic step" and is determined by the spreading of elastic interactions, while the second step, is called "the thermal step" and is due to the heat diffusion inside the sample. By denoting as "lattice temperature" (T_L) the temperature which corresponding to all vibration modes and as the spin state temperature (T_S) the temperature implying only the breathing vibration modes which participates in the switching probabilities, the energy transfers and "temperatures" can be summarized as: (i) Light towards excited molecules which results in photo-excited molecules, (ii) Excited molecules towards neighboring lattice: **first** thermalisation. T_S of photoexcited molecules and T_L are equal (iii) Lattice towards spin state: **second** thermalisation: T_S of all molecules and T_L are equal (iv) System -> bath: **third** thermalisation: the temperature of the ensemble reaches the temperature of the bath. In order to discuss both elastic and thermal step in the framework of an unique model, we use here a modified mechanoelastic model, which was previously applied previously to simulate the elastic self-amplification alone. In this model, the elastic interactions between molecules, represented as rigid spheres, are mimicked by springs. When a molecule changes its state, its volume varies, which will result in an elongation or a compression first of its closest springs, determining the change in position of molecules and a propagation of the initial perturbation.

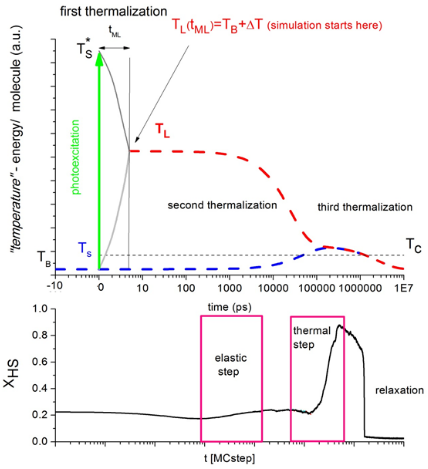

Figure (up) Schema for the behaviour of the system after ultrafast photoexcitation; (down) Simulations using the mechanoelastic model.

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Magnetic interactions in lanthanide dimers: The role of the bridging ligand

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Abstract

Lanthanide complexes have long been seen as promising candidates for making Single Molecule Magnets (SMMs) with high blocking temperatures, because of their potential for high barriers for reversal of the magnetic moment.

Several cases of polymetallic lanthanide complexes have showing interesting SMM properties in the properties are known in the literature.[1-4]

In order to make design criteria to optimize the properties of such clusters, it is necessary to know more about the nature of the magnetic interactions between lanthanide ions. Specifically whether it is dominated by dipolar or superexchange.

In order to investigate the influence of the ligand bridges on intermetallic magnetic interactions a series of dimers of erbium guanidinate complexes bridged by different ligands (Cl^-, Br^- or H^-) has been studied by combination of EPR spectroscopy and CASSCF calculations.[5]

Rich EPR Spectra are observed for all of these dimers and in some cases they can be interpreted using only dipolar interaction in others this interpretation might be insufficient.

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Single-Chain Magnet behaviour in infinite and finite hexanuclear molecules

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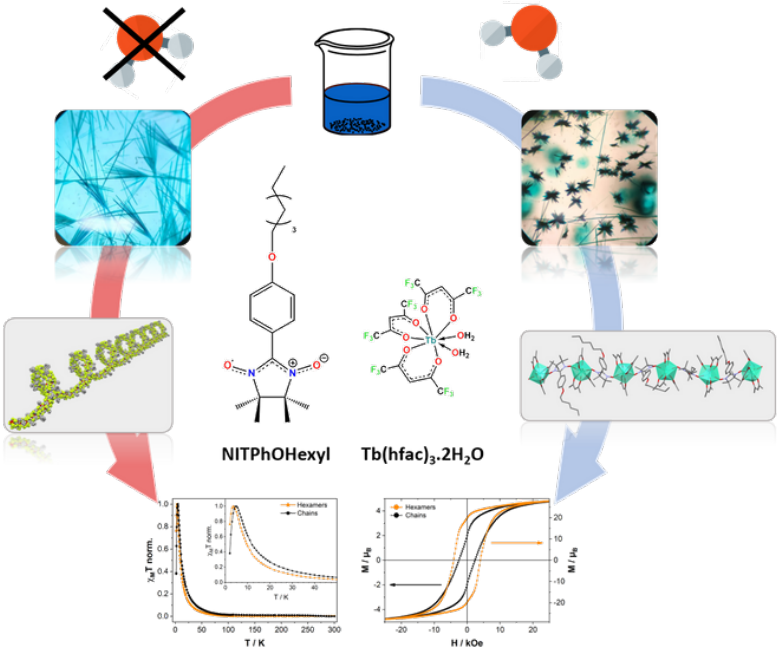
Abstract

Single-Chain Magnets (SCMs) hold a special place among the molecular-based magnets, by their inherent 1D topology and magnetic behaviour. Indeed, lowering the temperature leads to local couplings of the alternating spins that propagate along the chain. The relaxation dynamics related to this correlation phenomenon permit to maintain a magnetization and therefore allow SCMs to act as a magnet.

Herein, we report the synthesis of two lanthanide radical-based SCMs, with a strongly anisotropic magnetic centre, the $Tb(hfac)_3$ (hfac- = hexafluoroacetylacetonate), and an aliphatic bridging nitronyl nitroxide radical, the NITPhOHexyl (2-(4'-hexyloxyphenyl)-4,4,5,5-tetramethylimidazolin-1-oxyl-3-oxide). By monitoring the crystallization conditions, we have shown that we can selectively obtain either an infinite chain or a finite hexanuclear complex.

The infinite chain, because of the flexible aliphatic tail of the radical, grows as a chiral helical coordination polymer generating honeycomb-like nanotubes with an inner diameter of 4.5 nm. However, the presence of water molecules during the crystallization step leads to a linear hexanuclear complex, double-bridged by H-bonding water molecules to form a pseudo chain. Surprisingly, if a magnetic SCM behaviour was expected for the chain, we have demonstrated that the finite hexanuclear complex share similar properties, usually observed only for infinite molecules.



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A Computational Assessment on a Series of High-Valent Fe/Mn-oxo/hydroxo Complexes, Revealing the Impact of Inner Electronic Structure on Their Reactivity

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Abstract

The involvement of multideterminant character in regulating the reactivity of transition metal-dependent bio-mimic catalysts is gaining attention in recent years. In some of the high-valand Mn^{IV}=O species, it is shown that a high-lying ^4E state, arising from a transfer of an electron from occupied e(δ_{xz}, δ_{yz}) orbital to the unoccupied $b_1(\delta_{x^2-y^2})$ orbital, crosses the $^4B_1$ state, responsible for the high reactivity of these complexes towards C-H activation process.[1] In this direction, we have explored the dependency of the catalytic reactivity on the extent of mixing of ground-state configuration with other electronic excited states by studying a series of metal-oxo/hydroxo species, namely, $[M^{II}H_3buea(OH)]^{2-}$, $[M^{III}H_3buea(O)]^{2-}$, $[M^{III}H_3buea(OH)]^{-}$, $[M^{IV}H_3buea(O)]^{-}$, $[M^{IV}H_3buea(OH)]$ and $[M^{V}H_3buea(O)]$ (M = Mn/Fe) towards dihydroanthracene (DHA) employing a combination of the DFT and ab initio calculations. While energetically close-lying electronic states cannot be defined well by a single determinant approach, CASSCF method gives a better perspective of all states. Our calculations reveal an intense mixing of ground-state configuration with the various electronic excited states in Mn^{III}=O, Mn^{IV}=O, Mn^{V}=O, Fe^{II}-OH, and Fe^{V}=O species, generating more than one ground state configurations, and the states with a higher contribution of the electronic excited states tend to determine the rate of the reaction. Moreover, these excited state contributions are affected by the structure of the secondary coordination sphere of the $[H_3buea]^{3-}$ ligand; removal of the hydrogen bonding interactions tends to lower these mixing and results in lower reactivity.

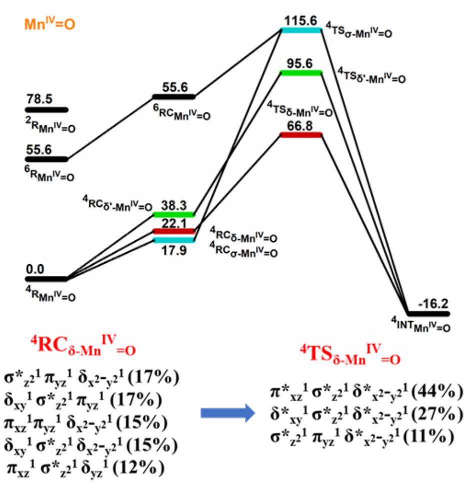

Figure 1: B3LYP-D3 computed energies for the C-H bond activation of 9,10-dihydroanthracene (DHA) by $[Mn^{IV}H_3buea(O)]^-$ showing the lowest energy configuration below.

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Investigating origins and control of slow magnetic relaxation in Ni(III) octahedral complexes

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Abstract

Our interest is to use synthetic design and modulation of coordination environments to tease apart the small forces involved in controlling magnetic properties of mononuclear 3d complexes. In recent years, there is growing interest in the slow magnetic dynamics of $S = ½$ systems especially, due to its applicability in quantum qubit design. While ions like Cu(II) and V(IV) are extensively studied, their nuclear and electronic spins couple to provide accessible pathways towards magnetic relaxation. We are the first group to study octahedral $S = 1/2$ Ni(III) complexes, where the absence of significant nuclear-spin prevents the hyperfine coupling that can speed up magnetic relaxation.[1] Our findings showed that when complexed with oxygen-containing axial ions, such as NO_3^-, slow magnetic relaxation is active but is quenched when complexed with nitrogen-containing ions, such as SCN^-.

Our current efforts focus on further anion modulation and change of the primary and secondary coordination environments of Ni(III) octahedral systems, toward demystifying the origin and controls of slow magnetic dynamics. We have expanded the scope of the axial ions to include ClO_4^-, HSO_4^-, and SO_4^2. The mononuclear complex salts allow us to study the effect of non-covalent interactions on the relaxation dynamics, whereas the sulfate salt leads to 1D chains, which gives us the opportunity to study the effects of covalent interactions.

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Twistable dipolar aryl rings as electric field actuated conformational molecular switches

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Abstract

The ability to control the chemical conformation of a system via external stimuli is a promising route for developing molecular switches. For eventual deployment as viable sub-nanoscale components that are compatible with current electronic device technology, conformational switching should be controllable by a local electric field (i.e. E-field gateable) and accompanied by a rapid and significant change in conductivity. In organic chemical systems the degree of π-conjugation is linked to the degree of electronic delocalisation, and thus largely determines the conductivity.

In this contribution, we will present the results of first principles calculations of the prototypical biphenyl based molecular system in which the dihedral angle between the two rings determines the degree of conjugation. In order to make this an E-field gateable system a net molecular dipole was created by asymmetrically functionalising one ring with electron withdrawing or electron donating substituents. In this way, the application of an E-field interacts with the dipolar system to influence the dihedral angle, thus controlling the conjugation. For all considered substituents conformational energy profile as a function of E-fields and the minimum E-field required to induce a barrierless switching event were obtained for each system. We further extracted the estimated switching speeds, conformational probabilities at finite temperatures, and the effect of E-field on electronic structure. These results allowed us to assess which factors are most important in the design of efficient gateable electrical molecular switches.[1]

Once checked the viability of this type of molecular switches, a biradical made of two perchlorotriarylmethyl (PTM) radicals and a difluorobenzene as a linker has been computationally studied. This model system has demonstrated that the antiferromagnetic exchange coupling between the spins of the PTMs can be tuned by means of an E-field-induced reorientation of the dipolar linker.

[1] K. Jutglar, et al. *Phys. Chem. Chem. Phys.*, **2021**, 23, 3844

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Controlled intra-lattice electron transfers in tetraoxolene-bridged two-dimensional layers by temperature and guest molecules

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Abstract

Exploring new systems, which exhibit switchable magnetic properties upon the applications of external stimuli, is an important subject in the field of materials science. The studies of the thermally driven electron transfer (TDET), resulting in the generation of charge distributions and new spin sets, has attracted great attention and been reported in the metal complexes such as neutral-ionic transition, metal-to metal electron transfers and valence tautomerism. In this work, we report on tetraoxolene-bridged two-dimensional honeycomb layer, $(NPr_4)_2[Fe_2(Cl_2An)_3]\cdot 2(acetone)\cdot(H_2O)$ (**1**), where Cl_2An^{n-} = 2,5-dichloro- 3,6-dihydroxy-1,4-benzoquinonate, exhibiting charge variations attributed to the occurrence of the TDET behavior.

Slow diffusion of water/acetone solution containing constituent building blocks yielded dark and hexagonal single crystals of **1**. Structural analyses revealed that **1** is typical honeycomb network constructed by Fe ions and Cl_2An^{2-} ligands , and the crystallization solvent molecules were in the hexagonal pores inside layers and interlayer space. Interestingly, variable temperature X-ray measurement and magnetic measurements showed anionic layers of **1** exhibit the TDET between $[(Fe^{2+})_2(Cl_2An^{2-})_2(Cl_2An^{\bullet 3-})]^{2-}$ and $[(Fe^{2+})(Fe^{2+})(Cl_2An^{2-})(Cl_2An^{\bullet 3-})_2]^{2-}$ species with the significant bond distance changes ($T_{1/2a}$ = 236 K). Furthermore, **1** showed single-crystal-to-single-crystal transformation associated with release of crystal solvent molecules to form desolvated compound **1-d**. In the magnetic measurements, **1-d** showed two-step TDET behavior ($T_{1/2b}$ = 317 K, $T_{1/2c}$ = 354 K) through an intermediate phase. The reversible phase transformation between **1** and **1-d** could be realized by solvation/desolvation treatments, which provides wide scope for new multi-switchable molecular materials. Furthermore, the $T_{1/2a}$, $T_{1/2b}$ and $T_{1/2c}$ values were modulated by acceptor-site doping.

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Magnetic properties of novel mononuclear Re(II) complexes with azole-type ligands

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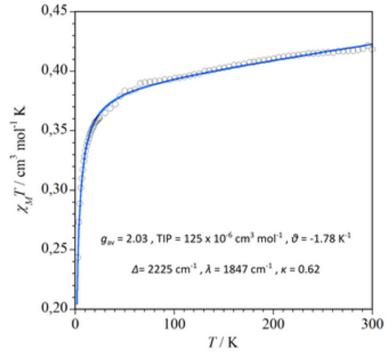
Abstract

Our research group has made incursions into the least-known chemistry of rhenium(II). Literature shows that Re(II) mononuclear complexes are attractive in molecular magnetism due to high magnetic anisotropy due to a significant spin-orbit coupling, turning them a potential source for discovering new molecular magnets[1]. In this work, we present the characterization and crystal structure analysis of three stable Re(II) mononuclear complexes of general formula $NBu_4[Re(NO)Br_4(L)]$ [L = pyrazole(Hpz), imidazole (Him) and 1,2,4-triazole (Htri)]. The crystal structure of these complexes contains NBu_4^+ cations and mononuclear $[Re(NO)Br_4(L)]^-$ units. These new complexes could act as building blocks for high nuclearity clusters with interesting magnetic properties. This work is in progress in our lab.

Moreover, we examined the magnetic properties of the compounds over the temperature range of 2-300K. The thermal dependence of χT in all of them is in line with one unpaired electron and a large temperature-independent paramagnetic contribution (TIP). We study their variable-temperature magnetic susceptibility data through a deep analysis of the influence of the ligand field, the spin-orbit coupling interaction (λ), axial distortion (Δ), covalence effects (κ), and the antiferromagnetic intermolecular interactions (ϑ) as variable parameters. Also, the large TIP values can be related to the low-lying levels that arise from the interplay between the low-symmetry crystal field, spin-orbital, and vibronic interactions. Finally, we compare those previously reported in related examples[2,3].



Thermal dependence of χT for the $(NBu_4)[Re(NO)Br_4(Hpz)]$ complex

Acknowledgements: PEDECIBA, CSIC and ANII for financial support.

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[Au(dspdt)$_2$]: a conducting neutral bis(1,2-dithiolene) gold complex with a unique crystal structure

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Abstract

The so called Single Component Molecular Metals (SCMM) are single neutral species that display a metallic behaviour arising from the molecular interactions in the solid state, and offer the possibility of being multifunctional, combining in the same material several physical properties. The first SCMM, which were reported in 2001, were the neutral bis(1,2-dithiolene) transition metal complexes [Ni(tmdt)$_2$] (tmdt: trimethylenetetrathiafulvalenedithiolate) [*Science*, 2001, 291, 285–287] and [Au(α-tpdt)$_2$] (α-tpdt: 2,3-thiophenedithiolate) [*Chem. Eur. J.*, 2001, 7, 511–519]. These two complexes were triggers for the preparation of a series of molecular metals based on a single neutral species.

Here we present a derivative of [Au(α-tpdt)$_2$], the neutral [Au(dspdt)$_2$] (dspdt: 2,3-dihydro-5,6-selenophenedithiolate), [*Dalt. Trans.*, 2020, 49, 13737–13743] which replaces the thiophene ring for a dihydroselenophene moiety, which could improve the intermolecular interactions and thus the transport properties. This neutral gold complex revealed, in single crystal, a semiconducting behaviour with a relatively high room temperature electrical conductivity of 0.1 S cm^{-1} and low activation energy of 95 meV. This behaviour arises from its unprecedent crystal structure that is composed by interacting dimer and trimer columns. To the best of our knowledge, this was first time that a mixture of dimer and trimer columns is observed in these gold complexes.

The electronic band structure, which was determined using an extended Hückel approach, shows that the interaction between chains of dimers and trimers leads to a combination of mixed trimer and dimer parallel bands considerably split and partially overlapping, with the Fermi level crossing four central bands.

This new mechanism to high electrical conductivity may explain the conducting metallic properties observed in other neutral gold complexes with smaller ligands, such as [Au(α-tpdt)$_2$].

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DFT study of Cobalt-based single-molecule magnet deposition on graphene

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[1]Central European Institute of Technology, CEITEC BUT, Brno, Czech Republic. [2]Brno University of Technology, Brno, Czech Republic. [3]Palacký University, Olomouc, Czech Republic. [4]Slovak University of Technology in Bratislava, Bratislava, Slovakia

Abstract

Single-molecule magnets (SMMs) are versatile systems that can be integrated into electronic devices. A way to perform such integration is by depositing SMMs onto a solid-state material, combining the magnetic properties of the SMM with the electronic, spintronic, and magnetic properties of the substrate. In the present work, we study the adsorption of Co-based SMMs onto graphene at density functional theory (DFT) level, analyzing the adsorption energies, charge transfer, electronic structure, and geometric changes of the systems before and after deposition. We discuss how the geometrical changes induced on SMMs by adsorption could change their magnetic properties, encoded by the *g*-tensor and spin Hamiltonian terms E and D; how magnetic properties can be predicted by CASSCF-NEVPT2** methods, and how they can be experimentally determined by high-field electron paramagnetic resonance (HFEPR) spectroscopy. By studying a particular system, we predict that the mentioned geometrical changes of the molecule can induce small changes in the g-factor but greater ones in E and D.

**complete-active space self-consistent field N-electron valence second-order perturbation theory

Key words: Single-molecule magnets; SMMs; graphene; deposition on surfaces; DFT; CASSCF; HFEPR

Reference: Hrubý J., Vavrečková Š., Masaryk L., Sojka A., Navarro-Giraldo J.*, Bartoš M., Herchel R., Moncol J., Nemec I., and Neugebauer P. Deposition of Tetracoordinate Co(II) Complex with Chalcone Ligands on Graphene. *Molecules* **25**, 5021 (2020).

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Valence Tautomerism in Bis(dioxolene)-Bridged Dinuclear Cobalt Complexes: Correlating Two-Step Transitions with Redox and Mixed-Valence Properties

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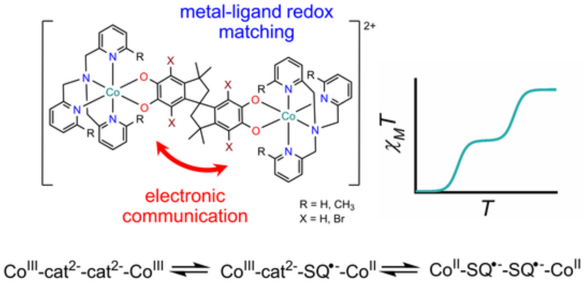
[1]University of Melbourne, Melbourne, Australia. [2]Colorado State University, Fort Collins, USA. [3]Southern Federal University, Rostov-on-Don, Russian Federation

Abstract

Switchable molecular materials have a reversible physical response to external stimuli with potential applications in sensors, displays and high density data storage. Of particular interest are discrete compounds that can be reversibly switched between three or more states, enabling ternary data storage, multi-switchable displays and more complex logic processes in molecular electronics and spintronics. One such reversible molecular transition is valence tautomerism (VT), the stimulated intramolecular electron transfer between a redox-active metal and a redox-active ligand. In cobalt-dioxolene complexes, electron transfer is accompanied by a cobalt spin transition, resulting in states with distinct structural, spectroscopic and magnetic properties. The complex $[\{Co(Me_2tpa)_2\}_2(spiro)]^{2+}$ (Me_2tpa = bis(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine; $spiroH_4$ = 3,3,3′,3′-tetramethyl-1,1′-spirobi(indan)-5,5′,6,6′-tetraol) is the only bis(dioxolene)-bridged dinuclear cobalt complex to display a two-step VT transition, which occurs between three electronic states: $\{Co^{III}$-catecholate-catecholate-$Co^{III}\}$, $\{Co^{II}$-semiquinonate-catecholate-$Co^{III}\}$ and $\{Co^{II}$-semiquinonate-semiquinonate-$Co^{II}\}$.[1] This work elucidates the requirements for a two-step VT interconversion and how the sensitivity to bridging and ancillary ligands can be exploited to achieve a chemically tunable system.

We present four related dinuclear cobalt complexes with distinct electronic structures and VT behaviour: two-step VT, one-step one-electron VT, incomplete VT, and temperature-invariant states.[2] Electrochemistry and DFT calculations have allowed elucidation of the thermodynamic parameters governing the one- and two-step VT behaviour. The VT transition profile is rationalised by the degree of electronic communication within the bis(dioxolene) ligand and the matching of cobalt and dioxolene redox potentials. We have further probed the strong limit of acceptable bis(dioxolene) electronic communication by studying the ligand mixed-valence properties in a zinc(II) analogue complex.



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Single-ion magnetism in the extended solid-state: insights from X-ray absorption and emission spectroscopy

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[3]University of Augsburg, Augsburg, Germany

Abstract

Large single-ion magnetic anisotropy is observed in lithium nitride doped with iron. The iron sites are two-coordinate, putting iron doped lithium nitride amongst a growing number of two coordinate transition metal single-ion magnets (SIMs). Uniquely, the relaxation times to magnetisation reversal are over two orders of magnitude longer in iron doped lithium nitride than other 3d-metal SIMs, and comparable with high-performance lanthanide-based SIMs. To understand the origin of these enhanced magnetic properties a detailed characterisation of electronic structure is presented. Access to dopant electronic structure calls for atomic specific techniques, hence a combination of detailed single-crystal X-ray absorption and emission spectroscopies are applied.

Extended X-ray absorption fine structure (EXAFS) and angular dependent single-crystal X-ray absorption near edge spectroscopy (XANES) measurements determine Fe(I) dopant ions to be linearly coordinated, clean of stoichiometric vacancies, and occupying a D6h symmetry pocket with an exceptionally short Fe-N bond length (1.873(7) Å). It is proposed that this structure protects dopant sites from Renner–Teller vibronic coupling and pseudo Jahn–Teller distortions, enhancing magnetic properties with respect to molecular-based linear complexes. The Fe ligand field is quantified by L2,3-edge X-ray absorption spectroscopy (XAS) from which the energy reduction of $3d_{z2}$ due to strong 4s mixing is deduced. We deduce variable temperature L_3- edge XAS can be applied to quantify the J = 7/2 magnetic anisotropy barrier, 34.80 meV (~280 cm-1), that corresponds with Orbach relaxation via the first excited, $M_J = 5/2$ doublet. These results demonstrate that dopant sites within solid-state host lattices could offer a viable alternative to rare-earth bulk magnets and high-performance SIMs, where the host matrix can be tailored to impose high symmetry and control lattice induced relaxation effects.

Huzan M. S., *et al.* DOI: 10.1039/d0sc03787g

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Lanthanide-Cobalt bis-Dithiolene Compounds Exhibiting Significant Ferromagnetic Exchange and Single Molecule Magnetism

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Abstract

We have synthesized and characterized heterobimetallic compounds $(Cp^*{}_2Ln)_2(Co(pdt)_2)$ (Ln = Y^{3+}, Gd^{3+}, Dy^{3+}) and $[K(18C6)][(Cp^*{}_2Ln)_2(Co(pdt)_2)]$ (Ln = Y^{3+}, Gd^{3+}). $(Cp^*{}_2Ln)_2(Co(pdt)_2)$ features two $[LnCp^*{}_2]^+$ fragments bridged by a dianionic cobalt (II) bis-(stilbenedithiolate) while $[K(18C6)][(Cp^*{}_2Ln)_2(Co(pdt)_2)]$ features an unprecedented trianionic cobalt (I) bis-(stilbenedithiolate) bridge. Dc magnetic susceptometry performed on the Gd congeners of each compound revealed significant Gd-Co exchange interactions of +11.46 cm^{-1} for $(Cp^*{}_2Gd)_2(Co(pdt)_2)$ and +7.8 cm^{-1} for $[K(18C6)][(Cp^*{}_2Gd)_2(Co(pdt)_2)]$. Ac magnetic susceptometry carried out on $(Cp^*{}_2Dy)_2(Co(pdt)_2)$ revealed the suppression of quantum tunneling of magnetization through this exchange interaction, with the resultant slow magnetic relaxation being fully Raman in character. $(Cp^*{}_2Dy)_2(Co(pdt)_2)$ additionally exhibited open loop hysteresis up to a temperature of 4 K. These results in conjunction with the those of high-field EPR spectroscopy and DFT calculations suggest that transition metalloligands can maintain strong exchange interactions with adjacent lanthanide centers while simultaneously adopting geometries which reinforce magnetic anisotropy. The results for $[K(18C6)][(Cp^*{}_2Ln)_2(Co(pdt)_2)]$ demonstrate that $S > 1/2$ bridges can be more easily accessed using metalloligands than with organic radicals and that these $S > 1/2$ metalloligands can exhibit exchange coupling strengths with lanthanide ions on par with those observed with organic radicals.

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The electronic structure and single-ion magnetism of linearly coordinated Mn(I), Fe(I), Co(I), and Ni(I) doped within lithium nitride crystals quantified by X-ray spectroscopy

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Abstract

The doping of metal ions within extended crystalline solids provides an alternative method to explore single-ion magnetism relative to coordination chemistry approaches. Lithium nitride is proven to be an excellent host for studying the single-ion magnetism of dopants. Dopants, from Mn(I) through to Cu(I) can be hosted, occupying a linearly coordinated position between nitride ions[1]. The basic magnetic properties of the transition metal dopant series include easy-plane (Mn, Co) and easy-axis (Fe and Ni) magnetic anisotropy[2]. Fe doped lithium nitride has proven to be a remarkable single-ion-magnet, exhibiting a magnetic coercivity field exceeding many rare-earth-based permanent magnets with a hysteresis that persists up to 16 K[3]. Angular dependent single-crystal, $L_{2,3}$-edge X-ray absorption and magnetic circular dichroism are used to quantify the ligand-fields and spin-orbit coupling of this transition metal series, while also revealing the presence of strong 3d-4s mixing (Fig. 1). The results provide a comprehensive interpretation of the magnetism for the series[4]. Resonant inelastic X-ray scattering measurements on Fe doped-lithium nitride show that 3d-4s hybridised excited states can be directly accessed and the spin-flip excitations of the anisotropy barrier are spectroscopically within reach[4]. Together a comprehensive insight into the electronic structure, bonding and magnetism of linearly coordinated single-ion magnets are obtained. There are far fewer examples of extended solid-state single-ion magnets than molecular-based systems. However, there are seemingly many opportunities to expand this research and the element sensitivity of X-ray spectroscopies are ideally suited for their precise characterisation.

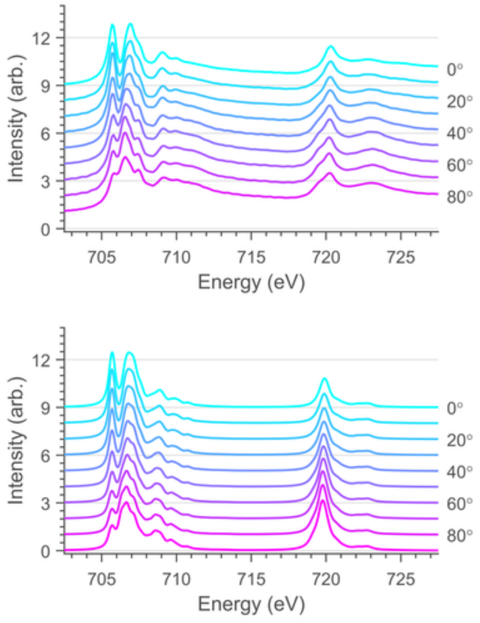

Figure 1. Single-crystal angular dependent $L_{2,3}$-edge XAS of Fe doped lithium nitride (top: measured spectra, bottom: simulations.)

[1] M. S. Huzan, *et al.* Chem. Sci., 2020, 11, 11801. [2] A. Jesche, *et al. Phys. Rev. B* 2015, 91, 18040(R). [3] A. Jesche, *et al.* Nat. Commun., 2014, 5, 3333. [4] in preparation.

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Toward heavy pnictogen ligated single molecule magnets

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Abstract

In transition metals, careful coordination of heavy diamagnetic donors has the potential to enhance the spin-orbit coupling character of light 3d paramagnetic centers, while in lanthanide based systems heavy main group atom based ligands offer possible routes toward enhancing axiality or altering local vibrational modes. To those ends, we have focused on ligands containing bismuth, the largest of the pnictogens and the heaviest stable element. Its poor donor strength and propensity for shedding or rearranging its bonds have traditionally rendered bismuth a less attractive donor atom than its lighter analogs. To date, there are no crystallographically characterized complexes containing a formal bond between bismuth and a paramagnetic transition metal center (one complex containing a long-range Bi—Mn2+ interaction has been reported) and only a handful of mixed bismuth–lanthanide molecular species. Additionally, we have sought not only the synthesis of bismuth ligated complexes, but also the synthesis and characterization of the series of analogous complexes ligated by the lighter pnictogens (P, As, Sb) so as to form a more complete picture of the interplay of donor size and donor strength down the periodic table. Though the synthesis of complexes featuring such interactions presents a unique set of challenges, it also offers the opportunity to not only expand our knowledge of the coordination chemistry of bismuth and other heavy pnictogens but to better elucidate the role of such large main group donor atoms in the electronic and vibrational landscapes of magnetic systems.

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Polyoxometalate-Based High-Spin Functional Clusters

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Abstract

The advantages of using molecules as functional materials mainly lies in the facile manipulation of chemical composition, so that the physical and chemical properties can be fine-tuned. Nano-sized polyoxometalate (POM) molecules retain exceptional properties particularly in highly symmetrical cage structures.[1] Recently, we reported an entirely new class of POM-based hybrid structure $[\{(GeW_9O_{34})_2Dy^{III}_3(\mu_2\text{-}OH)_3(H_2O)\}_6\{Co^{II}_2Dy^{III}_3\text{-}(\mu_3\text{-}OH)_6(OH_2)_6\}_4]^{56-}$ {**$Dy_{30}Co_8$**}, which exhibits a hollow tetrahedron cage structural pattern with six $\{(GeW_9O_{34})_2Dy^{III}_3\}$ units as linkers and four $\{Dy^{III}_3Co^{II}_2\}$ clusters as nodes of the giant tetrahedron. This compound shows *Single Molecule Magnet (SMM) behavior.*[2] This unique family of POM provides a platform for variation/replacement of paramagnetic ions that cause significant changes in the magnetic behavior of the clusters.[3] The zero {**$Dy_{30}Co_8$**} molecular aggregates allows to tune the magnetic exchange couplings by varying the spins in linkers and nodes of the tetrahedron which opens up new possibilities for multifunctional POM–based materials with an unmatched range of physical and chemical properties. The oral communication will be about the Magntocaloric Effect (MCE) properties and the use of POMs as high-field contrast agents for emerging high-field Magnetic Resonance Imaging (MRI) applications.

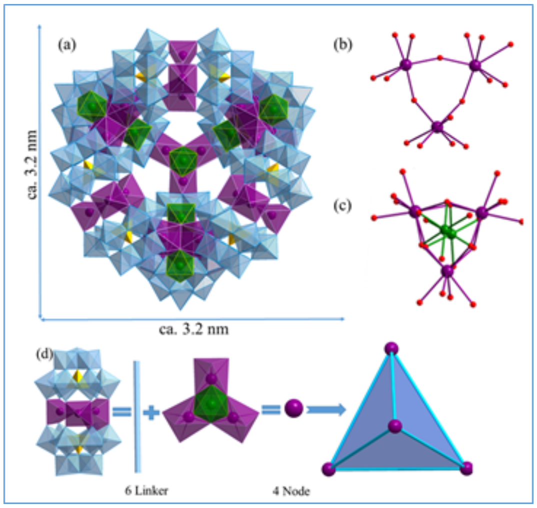

Figure a) $Dy_{30}Co_8$. b) $\{Dy^{III}_3(OH)_3(OH_2)\}$ core in linker. c) Heterometallic node $\{Co^{II}_2Dy^{III}_3(\mu_3\text{-}OH)_6(OH_2)_6\}$. d) The building blocks of **$Ln_{30}M_8$**. Color code: WO_6 blue, GeO_4 yellow, CoO_6 green, DyO_n violet, Dy = violet, O = red, Co = green

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Ab initio study of the quantum tunelling of magnetization in bimetallic dysprosium single molecule magnets.

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Abstract

Single molecule magnets (SMM) have attracted a lot of attention in the field of the development of new spintronic technologies such as high-density data storage devices and molecular cubits. Thus, several efforts have been put in rationalize how to maximize the magnetic anisotropy, which is the origin of the slow magnetic relaxation required to preserve the spin orientation when a magnetic field is applied. At the moment, dysprosium-based SMM with an operative temperature above liquid nitrogen have been synthesized through fine design of the ligand field surrounding metal center, where the limit of the desired axiality seems to be reached. In this way, other factors determining magnetic relaxation have been considered, such as the coupling of a radical ligand or the inclusion of exchange interactions between the anisotropic centers.

In this work, a set of reported binuclear dysprosium compounds which quantum tunneling of the magnetization time (t_{QTM}) can be extracted from the temperature dependence of the magnetic relaxation time have been chosen to understand the influence of the exchange interactions in the relaxation mechanism. t_{QTM} values have been computed from a methodology developed in our group involving multi-configurational ab initio calculations. The obtained results highlight the difference in the magnetic relaxation through quantum tunnelling of the uncoupled picture of each dysprosium center and the coupling of the spins of both dysprosium atoms of the bimetallic molecules.

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The Structural, Electrochemical, and Magnetic Properties of Diuranium Complexes Containing an Organic, Redox-Active Bridge

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Abstract

The incorporation of redox-active organic ligands to bridge two or more lanthanide ions has been a particularly powerful strategy for designing single-molecule magnets with large barriers to magnetic relaxation; in such systems, the strength of the magnetic exchange interaction between the metal ions and a ligand-based radical establishes the magnitude of the relaxation barrier. As such, one potential--and heavily unexplored--route to increase the relaxation barrier in these systems is to pursue actinide-based radical-bridged complexes, as the more radially diffuse 5f orbitals can, in theory, lead to stronger magnetic exchange interactions than what can be achieved in the lanthanides. However, the redox-activity of uranium ions can make the isolation of such species challenging, as the redox processes involving uranium can compete with ligand-based redox processes.

In this presentation, we will describe our synthesis of diuranium complexes with the multi-electron bridging ligand 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz), which, on the basis of cyclic voltammetry and X-ray crystallography studies, allows for the isolation of up to six different redox states, including two diuranium(IV) radical-bridged complexes, as well as a uranium(III/IV) mixed-valence complex. Changes in the metal or ligand oxidation states in these complexes are reflected by changes in their structural, spectroscopic, and magnetic properties; the single-molecule magnet properties of the radical-bridged and mixed-valence complexes will also be discussed, along with the nature of their magnetic ground states, which have been studied by means of X-band EPR.

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Massive 9 GHz Hyperfine Clock Transition in a Lu(II) Molecular Spin Qubit

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Abstract

In this presentation, we demonstrate chemical control of the degree of s-orbital mixing into the spin-bearing d-orbital associated with a series of spin-½ La(II) and Lu(II) molecules. Increased s-orbital character reduces spin-orbit coupling and enhances the electron-nuclear Fermi contact interaction. Both outcomes are beneficial in terms of the development of robust molecular spin qubits: the former reduces spin-lattice relaxation, while the latter gives rise to a record molecular hyperfine interaction for Lu(II) that, in turn, generates a massive 9 GHz hyperfine clock transition. Indeed, the hyperfine interaction is so strong that it becomes necessary to deploy high-field (W-band) EPR techniques to accurately quantify the zero-field hyperfine splitting for these $S = ½$ species. Moreover, measurements performed at multiple frequencies additionally reveal a very strong nuclear quadrupole interaction in the case of Lu(II). Meanwhile, pulsed EPR studies in the 9.11 to 9.5 GHz range reveal at least an order of magnitude increase in phase memory time, T_m, at the clock transition. These findings suggest new strategies for development of molecular quantum technologies, akin to trapped ion systems.

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A microporous Co(II) - based 3-D metal organic framework built from magnetic infinite rod-shaped secondary building units

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Abstract

Metal organic frameworks (MOFs) is a class of porous materials that has attracted tremendous research attention over the past decade for many reasons. These include their intriguing crystal structures and interesting physical properties that lead to potential applications in a series of areas including gas storage and separation, catalysis, sensing, magnetism[1], etc. Particular attention has been devoted to multifunctional MOFs combining two or more interesting properties. [2]

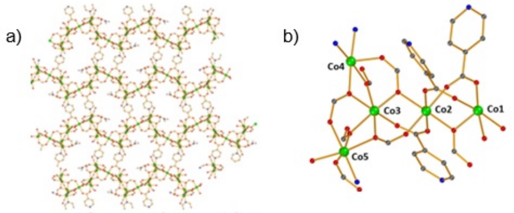

Figure 1. Representations of the a) 3D porous structure and b) Co_5 repeating unit of Co_5-INA.

Recently we have been investigating the synthesis of new MOFs based on polytopic pyridyl carboxylate ligands. These have been proven to be excellent ligands for the construction of multidimensional coordination polymers due to the ability of their N donor atoms to bind most of the metal ions and the high bridging capability of their carboxylate groups. We will discuss the synthesis, characterization and properties of a new MOF **$\{[Co_5(INA)_3(HCOO)_7(DMF)(H_2O)$**$]\cdot 2DMF\cdot 4H_2O\}_\infty$ denoted as [**Co_5-INA**] (INA^- = the anion of isonicotinic acid). **Co_5-INA** exhibits a rigid 3D porous structure that is based on a rod secondary building unit (SBU) which consists of Co_5 repeating units with a unique Co/O core. **Co_5-INA** shows a BET area of 264.5 m^2g^{-1} and CO_2 uptake of 1.96 mmol g^{-1} at 273 K/1 bar. Magnetic measurements revealed that it displays a spin canting behavior with a spin glass relaxation process at ~5.0 K.[3] This work was supported by the Cyprus Research and Innovation Foundation Research Grant "EXCELLENCE/1216/0076" which is co-funded by the Republic of Cyprus and the European Regional Development Fund

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