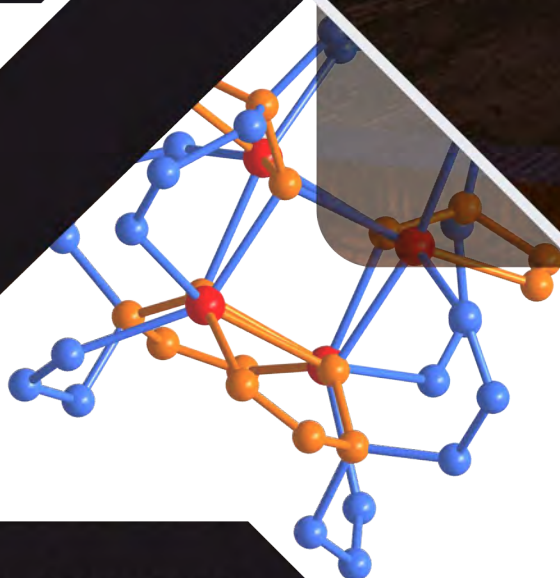
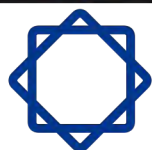




ECMM2015

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September 6th - 10th 2015

ZARAGOZA (SPAIN)

MEETING AT A GLANCE



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	Sunday 6	Monday 7	Tuesday 8	Wednesday 9	Thursday 10	
08:00 - 08:30		Registration				
08:30 - 09:00		Opening Ceremony				
09:00 - 10:00		P1 E. Coronado	P2 W. J. Evans	P3 C. Serre	P4 P. Gambardella	
10:00 - 10:30		IO1 J. P. Sutter	IO6 M. Evangelisti	IO10 L. Chibotaru	IO14 K. Inoue	
10:30 - 11:00		Coffee Break	Coffee Break	Coffee Break	Coffee Break	
11:00 - 11:30		IO2 G. Molnar	IO7 T. Mallah	IO11 R. Lescouezec	IO15 C. Gómez	
11:30 - 12:00		IO3 S. Triki	IO8 J. M. Rawson	IO12 R. Tamura	IO16 W. van der Wiel (Kai Wang)	
12:00 - 12:15		O1 M. Perfetti	O11 F. Luis	O17 D. Buergher	O29 G. Serrano	
12:15 - 12:30		O2 G. Chastanet	O12 M. Yamashita	O18 E. Ruiz	O30 K. Pedersen	
12:30 - 12:45		O3 M. Mito	O13 A. Ghirri	O19 A. Chiesa	O31 R. Westerström	
12:45 - 13:00		O4 J. Olof Johansson	O14 M. D. Darawsheh	O20 D. Ruiz-Molina	O32 G. Mínguez	
13:00 - 13:15		O5 T. Makarova	O15 G. Chaboussant	O21 A. Tissot	O33 O. Cespedes	
13:15 - 13:30		O6 I. Ratera	O16 C. Mathonière	O22 F. Totti	O34 J. Baldoví	
13:30 - 15:00			Lunch	Lunch	Lunch	Closing Ceremony
15:00 - 15:30			IO4 A. Forment	OKIA Award Ceremony	IO13 R. Layfield	
15:30 - 15:45			IO5 A. Ardavan	OKIA Lecture	O23 G. Lorusso	
15:45 - 16:00					O24 A. Majcher	
16:00 - 16:15			O7 S. Gao		O25 N. Aliaga-Alcalde	
16:15 - 16:30			O8 C. Saenz de Pipaon		O26 B. Le Guennic	
16:30 - 16:45		O9 J. van Slageren	IO9 J. I. Pascual	O27 A. Powell		
16:45 - 17:00		O10 E. Darbinean		O28 L. Catala		
17:00 - 17:45		Flash (3 min) FL1 - FL15	Flash (3 min) FL16 - FL30	Industrial Session and eCMM Promoted Industrial Round Table		
17:45 - 18:30						
18:30 - 19:00	Registration	Poster Session PS1	Poster Session PS2	EIMM General Assembly		
19:00 - 19:30						
19:30 - 20:00						
20:00 - 20:30	Welcome Reception			Conference Dinner		
20:30 - 21:00						
21:00 - 21:30						





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ID: P1, 2015-09-07 09:00

Molecular nanomagnets

(Plenary (only for plenary speakers))

Not strictly molecular magnetism

Eugenio Coronado¹

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Molecular Magnetism has been a source of new chemistry, new physics and new materials in the last 20 years. However, the future of this area will be strongly determined by the connections it will be able to establish with other emergent areas of current interest. In this talk I will show three of these connections. The first is the crossing of Molecular Magnetism with Metal-Organic Frameworks and other coordination polymers. This provides unique examples of multifunctional stimuli-responsive materials, in which the magnetism can be tuned by the application of a chemical or a physical stimulus [1, 2]. The second concerns the coupling of Molecular Magnetism with Molecular Electronics and Spintronics. As a result, a new field namely Molecular Spintronics is emerging in which magnetic molecules and molecular materials can be used as components of new electronic structures to afford a second generation of spintronic devices [3], which can be made smaller and smaller to reach the single molecule limit, thus providing the opportunity of exploiting also the quantum nature of the spins [4, 5]. The third concerns the intersection with graphene and other 2D materials. In this last context, Molecular Magnetism can be a source of magnetic molecules that can be organized and addressed on these surfaces, as well as a useful source of single magnetic layers that can expand the electronic properties already observed in this class of low dimensional materials (which are mainly based on semiconducting and conducting materials) [6].

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ID: P2, 2015-09-08 09:00

Molecular nanomagnets

(Plenary (only for plenary speakers))

Exploratory Synthetic f Element Chemistry and Its Connection to Single-Molecule Magnets

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This lecture will describe single-molecule magnet chemistry from the perspective of a synthetic f element chemist. The origins of the exploratory research that led to the syntheses of single-molecule magnets like $(C_5Me_5)Er(C_8H_8)$ and $[K(18\text{-crown-6})(THF)_2]\{[(R_2N)_2(THF)Ln]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)\}$ will be presented and evaluated in terms of current synthetic approaches to new single-molecule magnets. Syntheses of improved versions of these complexes will also be discussed, as well as some of the synthetic challenges encountered in developing f-element-based single-molecule magnets.



High valence Metal Organic Frameworks: from synthesis to potential applications

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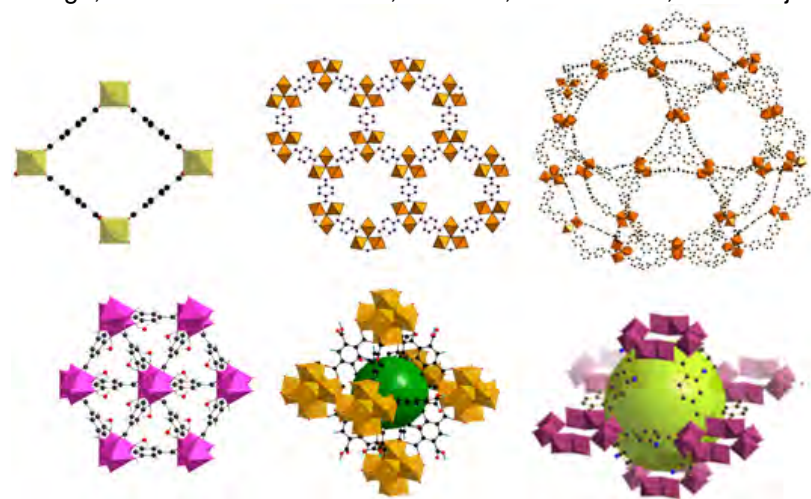
Metal Organic frameworks (MOFs) are of interest for many potential applications due to their tunable porosity, composition and structural features [1]. Among them, some are still at the laboratory level (e.g. biomedicine [2]) while others are currently evaluated at a pilot scale such as purification, separation or gas storage [3]. However, their sometimes fragile character in the presence of water, often rules out their practical use. It was shown recently that the chemical stability of MOFs depends mainly on the strength of the metal-ligand bonds, increasing thus for a given coordination number, with the charge of the metal cation.[4] This strongly justifies to develop new porous stable MOFs based on tri- or tetra-valent transition metal cations such as Fe³⁺, Al³⁺, Cr³⁺ or Ti⁴⁺/ Zr⁴⁺. [5, 6] However, such metals, out of acidic conditions, form easily metal oxides, or a very fast chemical reactivity making hard the control of their synthesis, which typically limits their use in the MOF field. We will report here our recent results in terms of synthesis/structure (Figure), [7] as well as their most significant properties in domains such as separation, catalysis [6, 7, 8] or biomedicine. [9, 10]

Figure : stable porous MOFs based on high valence cations

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ID: P4, 2015-09-10 09:00

Molecular nanomagnets

(Plenary (only for plenary speakers))

Molecular magnets on surfaces: tune, couple, induce

Pietro Gambardella¹

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* *Pietro Gambardella, pietro.gambardella@mat.ethz.ch*

Metal-organic complexes at surfaces are widely investigated for developing multifunctional spintronic devices. While solid-state substrates provide both support and electrical contact to the molecules, the interaction between the molecular orbitals and substrate electronic bands strongly affects the chemistry and magnetic properties of such complexes. In this talk, I will present an overview of the different ways in which the magnetic moment of metal-organic molecules at surfaces can be modified and, to a certain extent, tuned by controlling charge transfer from the substrate, molecule-molecule interactions, and extrinsic doping. The same factors will be shown to have a strong influence on the coupling between single-molecule magnets and ferromagnetic or antiferromagnetic substrates. Finally, I will discuss the possibility to induce slow relaxation of the magnetization in single metal ions in appropriate surface coordination environments.



Anisotropic Heptacoordinate Transition-Metal Complexes: Single-Ion-Magnets and Ising-Type Building Units

Arun K. BAR¹, Céline PICHON¹, Jean-Pascal SUTTER¹

1) Coordination Chemistry Lab of CNRS (LCC), Toulouse (France)

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Uni-axial zero-field splitting parameter (D) in conjunction with spin ground state plays crucial role in governing the energy barrier for magnetization reversal in molecule-based magnets. However, it has long been challenging for chemists to rationally control the single-ion magnetic anisotropy by chemical design. Recent investigations revealed that deviation from hexa-coordination and adaptation of non-conventional coordination geometry can induce significantly large magnetic anisotropy in mononuclear complexes with appropriate 3d transition metal ions. Interestingly, association of such Ising-type anisotropic mononuclear complexes with paramagnetic metallo-ligands could lead to polynuclear systems with large spin ground state as well as high energy barrier for magnetic relaxation. We have been considering hepta-coordinate 3d transition metal ions as anisotropic building units.[1] In this paper, we will discuss the magnetic features of such mononuclear complexes (Fig.) and their use for the construction of heterometallic single-molecule magnets.

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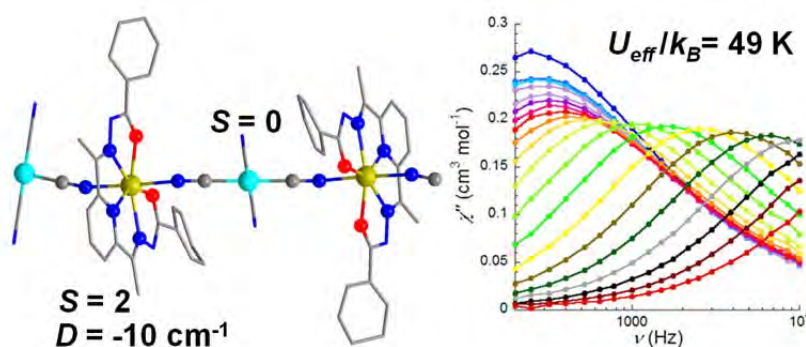


Figure : Solid state organization and out-of-phase magnetic susceptibility feature for a Fe(II) centre in D_{5h} surrounding.



Switchable magnetic materials and optical magnets
(Invited (only for invited speakers))

Spin crossover nanomaterials: from fundamental questions towards applications

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In the past decade, investigation of nano-objects displaying spin transition has attracted much attention [1-2]. In our group we explored different chemical [3-7] and lithographic [8-11] approaches for the organisation of spin crossover complexes at the nanometer scale. In addition we developed various experimental methods [12], based on scanning probe microscopy [13-14], fluorescence [11, 15-16] and surface plasmon [17-19] spectroscopies to analyse their physical properties. Based on these experimental tools as well as theoretical modelling, our attention has been focused more recently on the rationalization of finite size effects [7, 20-25] and possible applications of these bistable nano-objects as sensors [11, 15, 26-28], actuators [29-31] and photonic [17-19] or electronic [32-33] switches. In spin crossover compounds, size effects may lead to a loss of the hysteresis, a shift of the transition temperature or the occurrence of an incomplete transition [1-2, 20]. We successfully explained a major part of these experimental observations by considering the spin-state dependence of the surface energies in the frame of a nanothermodynamical model [21-25]. As a consequence the most important parameter to describe size effects seems to be actually not the size of the object itself, but the surface-volume ratio as well as the physico-chemical properties of the interface between the spin crossover particle and its environment. Since the bistability depends mainly on the strength of the elastic interactions, we have also investigated the lattice dynamics of spin crossover nanoparticles and especially the acoustic phonon modes by Mössbauer spectroscopy and nuclear inelastic scattering (ESRF) techniques [7, 21, 24]. As expected, we observed in each case significant lattice stiffening when going from the high spin to the low spin phase. In addition, rather unexpectedly, a stiffening of the particles was detected at the extreme size reduction limit (~1-5 nm), which we correlated with the reappearance of hysteresis in ultra-small particles.

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Switchable magnetic materials and optical magnets
(Invited (only for invited speakers))

Magnetic Switching in Polycyanide-Based Coordination Polymers

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Spin crossover (SCO) materials are one of the best representative examples of molecular switchable materials. The goal nowadays is to design SCO materials with perfectly controlled magnetic and photo-magnetic behaviours in a rational chemical synthetic strategy. Up to now, numerous SCO materials have been synthesized and described in the literature, but it has never been investigated the potential impact of using anionic organic ligands, connecting the active metal centers, on the switching properties (hysteresis width, abruptness of the transition,...). The use of such anions in combination with neutral appropriate co-ligands is a very promising and appealing strategy for obtaining molecular architectures with different topologies thanks to their ability to coordinate and bridge metal ions in many different ways.

In this context, our group is interested in the design of new series of switchable materials using organic or inorganic polycyanide anions as ligands [1,2]. The presence of several potentially coordinating CN groups, their rigidity and their electronic delocalization allows the synthesis of original coordination polymers exhibiting magnetic transitions such as SCO behaviour [1] or *spin-Peierls-like* transition [2].

Here we report an overview of the results based on some of these polycyano ligands, showing their rich coordination chemistry and their crucial role in the design of molecular materials exhibiting unusual magnetic and photomagnetic behaviours.

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ID: IO4, 2015-09-07 15:00

Molecular nanomagnets

(Invited (only for invited speakers))

Magnetic Imaging and Manipulation of Molecular-based Nanoparticles on a Surface

Alicia Forment-Aliaga¹, Elena Pinilla-Cienfuegos¹, Samuel Mañas-Valero¹, Susmit Kumar¹, Eugenio Coronado¹, Laure Catala², Talal Mallah²

1) Instituto de Ciencia Molecular (ICMol). Universidad de Valencia 2) Institut de Chimie Moléculaire et des Matériaux d'Orsay CNRS, Université Paris Sud

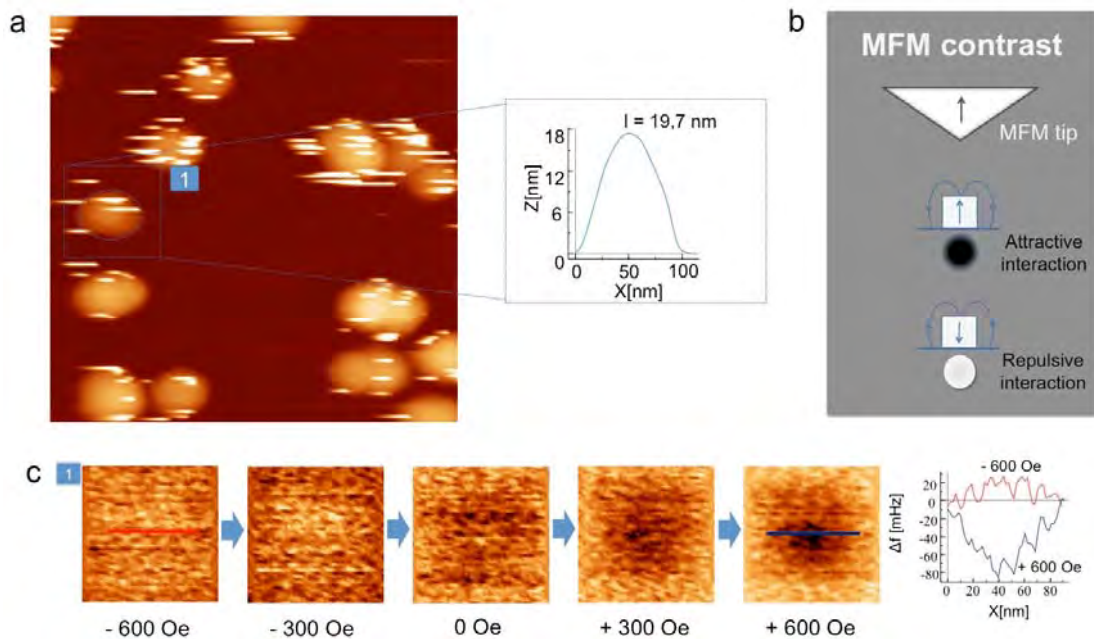
* Alicia Forment-Aliaga, alicia.forment@uv.es

In the race towards the miniaturization in nanoelectronics, magnetic nanoparticles (MNPs) have emerged as potential candidates for integration in ultra-high density recording media. Before their implementation in real devices is reached, two challenges have to be overcome: a precise organization on surfaces and a reliable characterization and manipulation of their individual magnetic behavior. In this scenario, molecular-based materials open the possibility to design new tailor-made MNPs with variable composition and sizes, which are benefited by the intrinsic properties of these materials. As model, bimetallic, cyanide-bridged nanoparticles of the family of Prussian blue analogues (PBA)[1] have been chosen because their reproducibility and size tunability permit the control of the magnetic structure to be around the single domain limit. Moreover, their bare and anionic nature can be used to attach them onto surfaces and to reach 2D structuration with high accuracy by means of local oxidation nanolithography or soft-lithography methods, fulfilling the first of the two aforementioned challenges.[2]

Until now, the magnetic properties of molecular-based MNPs have been deeply studied in bulk because they present low Curie temperature (T_C) and weak magnetic signal that have complicated an individual and detailed characterization and manipulation. In this presentation we will show that it is possible to achieve high resolution of their individual magnetic state through Low Temperature Magnetic Force Microscopy (LT-MFM) under low-noise conditions. This technique has permitted us to resolve the magnetic response of individual PBA-MNPs deposited on a surface and to correlate the topography of every single nanoparticle with the individual magnetic signal under the influence of small magnetic fields (Figure 1).[3] This way, we have step by step imaged the reversal magnetization processes[4] involved in different PBA-MNPs: coherent rotation, curling or even vortex state formation and annihilation. Thus, we demonstrate that the vortex spin structure, including its vortex core, can be observed and manipulated in small objects of nanometric size (25 nm nanoparticles) by means of LT-MFM, achieving the second challenge mentioned before.

Figure 1: a) Topographic image of PBA-MNPs dispersed on silicon, with the height profile of one them (1). (Image size: 500 x 500 nm²). b) Schematic representation of the magnetic contrast in MFM. c) Set of magnetic force images of nanoparticle 1 in (a) (Image sizes: 114 x 114 nm²) at different external magnetic fields applied and corresponding frequency shift profiles.

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ID: IO5, 2015-09-07 15:30

Molecular nanomagnets

(Invited (only for invited speakers))

Engineering coherent interactions in molecular nanomagnet dimers

Arzhang Ardavan¹

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Proposals for systems embodying condensed matter spin qubits cover a very wide range of length scales, from atomic defects in semiconductors all the way to micron-sized lithographically-defined structures. Intermediate scale molecular components exhibit advantages of both limits: like atomic defects, large numbers of identical components can be fabricated; as for lithographically-defined structures, each component can be tailored to optimize properties such as quantum coherence. We have demonstrated what is perhaps the most potent advantage of molecular spin qubits, the scalability of quantum information processing structures using bottom-up chemical self-assembly. Using Cr₇Ni spin qubit building blocks, we have constructed several families of two-qubit molecular structures with a range of linking strategies. For each family, long coherence times are preserved, and we demonstrate control over the inter-qubit quantum interactions that can be used to mediate two-qubit quantum gates.



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ID: IO6, 2015-09-08 10:00

Molecular nanoscience

(Invited (only for invited speakers))

Cool molecules

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The recent progress in molecule-based refrigerant materials is reviewed. Advanced applications in cryogenics and future perspectives are also discussed.



Magnetic Anisotropy and Single Molecule Magnet behavior in trigonal bi pyramidal mononuclear Co(II) complexes

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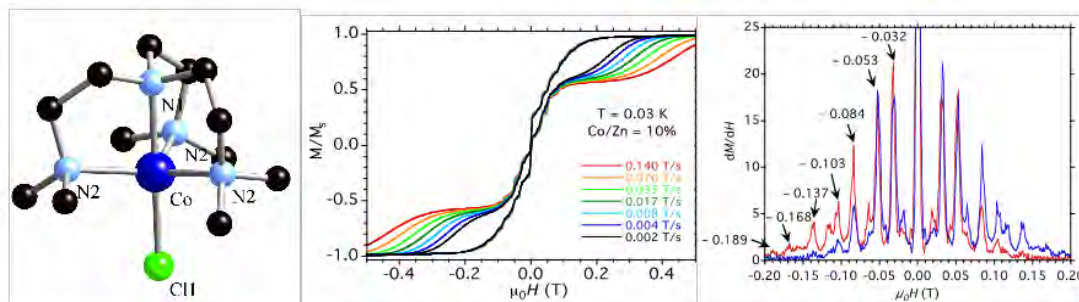
One of the challenges in the field of molecular magnetism is to design stable molecular complexes based on transition metal ions possessing a blocking of the magnetization in the absence of a static magnetic field. This is a requirement if such molecules are to be used as single quantum bits for quantum information processing.¹

Trigonal bipyramidal mononuclear Co(II) ($S = 3/2$) complexes of the general formula $[\text{Co}(\text{Me6tren})\text{X}](\text{ClO}_4)_2$ (Me6tren is a tetradentate ligand) possess all the characteristics to present a blocking of the magnetization and an opening of the magnetic hysteresis loop at low temperature (Figure 1).² The effect of the nature of the axial ligand X that has a structural and an electronic influence on the magnitude and the nature of the magnetic anisotropy will be discussed. The role of the transverse anisotropy in the case of these Kramers doublets ions will be discussed also.

Figure 1. (left) view of the molecular structure of the $[\text{Co}(\text{Me6tren})\text{Cl}]\text{ClO}_4$ complex; (middle) magnetic hysteresis loop of a diluted single crystal of $[\text{Co}(\text{Me6tren})\text{Cl}](\text{ClO}_4)$ and (right) derivative of the central part of the $M = f(\mu_0 H)$ loop showing the hyperfine coupling between the electronic and the nuclear ($I = 3/2$) spins of Co(II).

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ID: IO8, 2015-09-08 11:30

Photo-induced magnetism

(Invited (only for invited speakers))

Recent advances in dithiadiazolyl radicals: From photoswitchable materials to composites.

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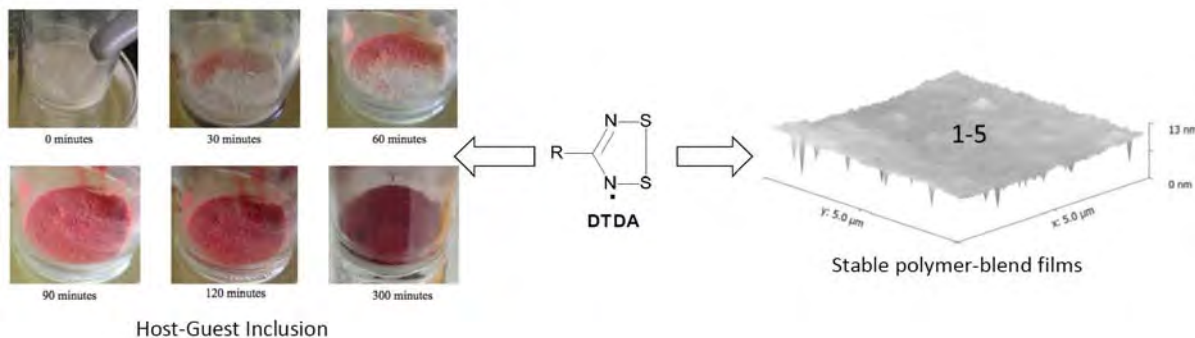
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The field of S/N and related Se/N radicals has contributed significantly to the fields of molecule-based magnetism and molecular electronics, with examples of high T_c magnets, conductors, semi-conductors, photo-conductors and spin-switching materials.[1]

The first half of this talk will focus on recent developments in dithiadiazolyl (DTDA) radical chemistry in which we have incorporated chromophores into the R-substituent (Scheme 1) which offer the potential to generate photo-switchable states, long-lived excited states and access polyradicals.

The second half of the talk focuses on composite materials in which DTDA radicals are included into both metal-organic frameworks such as MIL-53(Al) or polymeric matrices. Notably the later provide thin films with significant air and moisture stability.

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MAGNETIC MOLECULES ON THE SURFACE OF A SUPERCONDUCTOR

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Magnetism and superconductivity are phenomena that cannot simultaneously exist in the same region of a material: weak applied magnetic fields are expelled from the superconductor, while strong magnetic fields destroy the superconducting properties. An interesting playground to study the interplay between both phenomena are magnetic impurities on a superconductor. Using scanning tunnelling spectroscopy, we investigate interactions, and excitations of individual paramagnetic molecules on a superconducting lead Surface.

For the case of sizeable coupling between magnetic moment and quasiparticles at the lead substrate, we observe localized states in the superconducting energy gap [1,2,3]. These bound states reflect the weakening of the superconducting pairing (Figure right) and allows us to track the local destruction of superconducting phenomena by magnetic impurities [4].

By simply adding passive end groups to the molecular ligands the interaction with the environment can be reduced, and coupling with substrate quasiparticles vanishes. In this scenario, inelastic tunnelling processes mediate spin excitations between states with different magnetic anisotropy. The presence of the superconductor electrodes enhances the energy resolution and allows us to track slight modification of magnetic anisotropy in response to tip-induced variations of their ligand field (Figure right and refs.[5,6]).

An interesting outcome found when low energy spin excitations on superconductors is that they may survive for nanoseconds [5], a much larger time scale than on normal metal surfaces. This is interpreted as due to the depletion of electronic states within the superconducting energy gap at the Fermi level, which prohibits pathways of energy relaxation into the substrate.

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ID: IO10, 2015-09-09 10:00

Modelling and theory

(Invited (only for invited speakers))

Quantum chemistry study of exchange interaction in lanthanide complexes

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Lanthanide-based compounds are in the focus of current research, being viewed as perspective materials for potential applications in spintronics, memory storage and quantum computing. The complexity of magnetic properties of lanthanides is determined by strongly anisotropic exchange interaction which is by far more involved than in transition metal complexes [1]. In particular, it deviates drastically from Heisenberg exchange interaction which gives the main contribution to magnetic coupling between transition metal ions. This complicates much the experimental extraction of exchange parameters in lanthanide complexes.

In this presentation the application of quantum chemistry based approaches for the investigation of exchange interaction in lanthanide complexes will be discussed. Complexes with strongly axial lanthanide ions, which are of primary importance for applications, are considered in detail. It is explained, in particular, why in this case the description of exchange interaction is greatly simplified and can be recast within the Lines model [2]. The application of *ab initio* and DFT calculations to the description of exchange anisotropy in pure lanthanide and mixed lanthanide – transition metal complexes is shown also for materials requiring a description going beyond the Lines model, such as the N₂³⁻-radical-bridged lanthanide complexes [3].

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ID: IO11, 2015-09-09 11:00

Photo-induced magnetism

(Invited (only for invited speakers))

The [FeIII(Tp)CN]3⁻ complex : a versatile building block for the preparation of functional magnetic molecules

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Cyanide chemistry has been broadly used to prepare molecule-based magnetic materials. The most emblematic examples of cyanide-based systems are likely the Prussian blue analogues (PBAs). These inorganic polymers that are readily obtained by using hexacyanometallates precursors can show a variety of interesting magnetic behaviour depending on the nature of the metal ions and the stoichiometry of the PBAs. Inspired by this work, we prepared in 2002 a mixed cyanide-scorpionate iron(III) building block [FeIII(scorp)(CN)3]⁻ ($S = \frac{1}{2}$) in order to prepare low dimensional parent compounds of the PBAs with original architecture and interesting properties (SMM behaviour, photomagnetic effect, etc.). Here, the scorpionate blocking ligand allows a decrease of the coordination ability of the building block and the obtention of lower dimensional systems. Because of the great versatility of the scorpionate chemistry, it is also possible to tune the electronic properties of the precursor and the resulting properties of the polynuclear complexes.

In this presentation we will focus on the use of the [Fe(Tp)CN]3⁻ building block. We will present some experimental investigations that allowed us to probe the magnetic properties of this complex at the atomic scale. We will also give some examples of swichable magnetic molecules, high nuclearity systems or slow relaxation molecules that have been prepared using this building block.



Unique Magnetic Properties of Chiral All-Organic Radical Liquid Crystals

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Since 2004 we have reported the preparation and magnetic properties of chiral rod-like all-organic liquid crystalline (LC) radical compounds with a stable chiral cyclic nitroxide unit in the mesogen core, which can show a variety of chiral and achiral LC phases over a wide temperature range (Fig. 1a).^{1,2} Consequently, we could discover a unique magnetic phenomenon, referred to as "positive magneto-LC effects", a generation of spin glass-like inhomogeneous ferromagnetic interactions (average $J > 0$) induced by low magnetic fields in the various LC phases (Fig. 1b).³

Here I talk about the following electric and magnetic properties which these chiral nitroxide radical compounds exhibited in the chiral LC phases.

- (1) Ferroelectricity in the chiral smectic C (SmC*) phase (Figure 1a)²
- (2) Positive magneto-LC effects induced by weak magnetic fields (Figure 1b)³
- (3) Magneto-electric effects in the ferroelectric and ferromagnetic LC phase at high temperatures (Figure 1c)⁴

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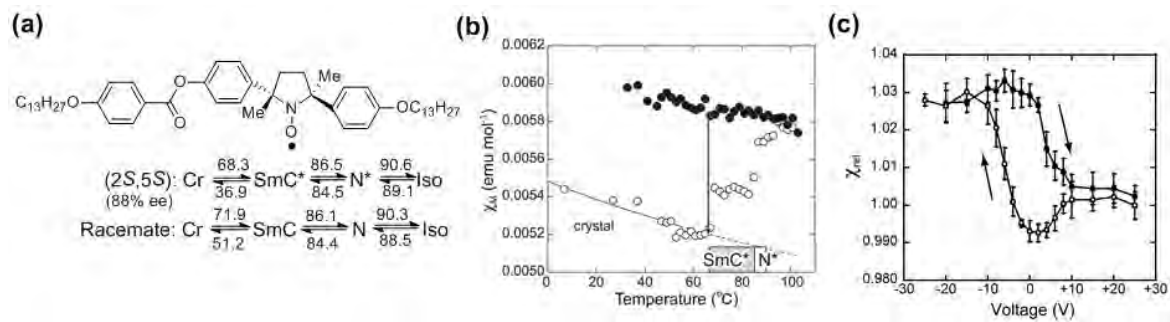


Figure 1. (a) Chiral LC radical compounds. (b) Porstive magneto-LC effects. (c) Electric field dependence of relative paramagnetic susceptibility (χ_{rel}).



Pnictogen Chemistry as a Design Tool in Molecular Magnetism

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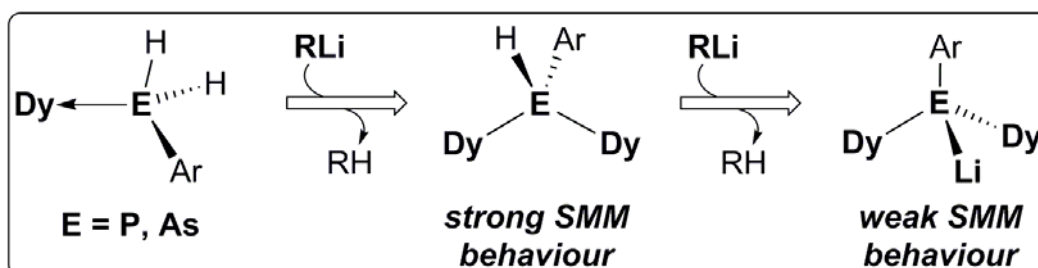
Rare earth metal compounds containing soft heteroatom donor ligands have attracted considerable interest in recent years. The combination of M³⁺ cations with heavy p-block donor atoms results in a so-called hard-soft “mismatch”[1] that can lead to unusual bonding properties and to distinct reactivity. Within this context, rare earth complexes of anionic phosphorus donor ligands have been extensively studied. Some analogous chemistry with anionic arsenic ligands is known, but such compounds are still very rare. The use of P- and As-donor ligands in the design of lanthanide single-molecule magnets (SMMs) is, however, entirely unknown.[2,3]

In this lecture, the dynamic magnetic properties of a series of dysprosium ring systems with phosphide, phosphinidene, arsenide and arsinidene ligands (Figure 1) will be described.[4-6] The experimental studies are complemented by ab initio calculations, which have enabled us to construct a model for the magnetic anisotropy and magnetization relaxation mechanisms in our SMMs. The theoretical model also provides insight into how SMMs with larger anisotropy barriers may be designed, and selected new systems with antimony-based ligands will also be presented.[7]

Figure 1.

Acknowledgements: Financial support from the ERC, the UK EPSRC, EU Marie Curie Actions, and the Royal Society is gratefully acknowledged.

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State-of-the-Arts and Future of Chiral Magnets

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By quantum mechanics, particles behave as linear waves with quantum phase. The coherent quantum phase control is one of the key issues to create for new stage of materials. The quantum phase coherence easily lost in centro-symmetric crystal, but protected in non centro-symmetric crystal. This protection coming from difference topological number of systems. Chirality is commonly found in nature, from particle physics to molecular chemistry, and one of the non centro-symmetric systems. It is characterized by a reflection asymmetry that we are most familiar with in terms of our left hand being the mirror opposite of our right hand. When this kind of handedness appears in the structure of atoms or molecules in a solid, it affects the way that the magnetic moments of unpaired electrons organize themselves through the Dzyaloshinskii-Moriya (DM) interactions[1-3]. In a symmetric structure, these interactions cancel out, but in a chiral lattice they do not. The DM interactions stabilize a screwlike helical arrangement of the magnetic moments, but they must compete with ferromagnetic exchange, which tries to align all the magnetic moments in the same direction.[4] The result is a helical magnetic arrangement with a winding period of several tens or hundreds of nanometers, which is much longer than the lattice constant. Therefore, even though the chiral properties depend on the symmetry of the lattice, they can be understood and manipulated at the mesoscopic level, independently of the structural details. The properties of these magnetic arrangements are similar to that of chiral liquid crystals. Both materials have helical structures, and they both contain extremely stable excitations called solitons. Solitons are nonlinear excitations that behave like particles, maintaining their shape and energy as they propagate, as exemplified by tsunamis that travel across entire oceans. In chiral magnets, solitons take the form of one-dimensional kinks or two-dimensional vortices called skyrmions[5]. These solitonic excitations are stabilized by temperature and magnetic fields. They are extremely robust and can be manipulated by electric currents or even condense to form a regular lattice, such as the lattice of skyrmions found in MnSi and other related systems [5]. In this paper, we would like to introduce how can stabilize chiral magnetic structures by the structural chirality.

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Advantages of anilate-type ligands to prepare new multifunctional molecular materials

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Anilate-type ligands ($[\text{C}_6\text{O}_4\text{X}_2]^{2-}$ = dianion of the 3,6-disubstituted derivatives of 2,5-dihydroxy-1,4-benzoquinone, $\text{H}_4\text{C}_6\text{O}_4$) are quite old ligands that have been used for many years to prepare dozens of 0D, 1D, 2D and 3D compounds with different metal ions.^[1] However, until very recently,^[2] their use to prepare extended structures (1D, 2D and 3D) was limited to homo-metallic derivatives presenting non magnetic ground states due to the antiferromagnetic coupling mediated by the bridging anilate-type ligands.

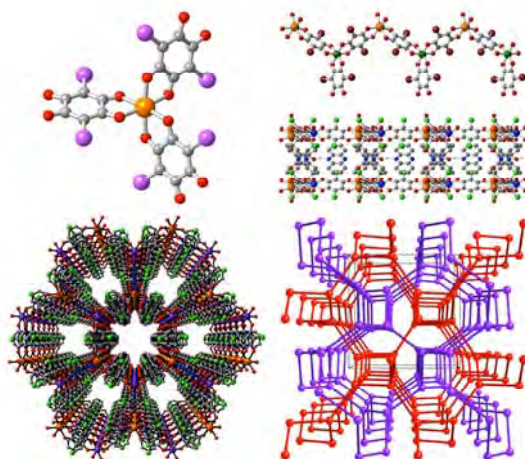
Given the similarity of the anilato and oxalato ligands, we can anticipate that the well known hetero-metallic 2D honeycomb and 3D (10,3)-gon lattices that have been prepared with oxalato in the last twenty years, might also be prepared with anilato-type ligands.

Here we present our recent results obtained using anilato-type ligands to prepare a plethora of materials with different dimensionalities as: (i) a family of 0D chiral tris(anilato)metalate anions $[\text{M}^{\text{III}}(\text{C}_6\text{O}_4\text{X}_2)_3]^{3-}$ (M^{III} = Fe, Ga, Mn and Cr; X = Cl, Br and NO_2) where the cation plays a key role to obtain chiral crystals. (ii) 0D SCO compounds presenting LIESST effect and a unusual modulation of the transition temperature with X and with the presence/absence of a water molecule. (iii) 1D ferrimagnetic hetero-metallic chains. (iv) Unprecedented heterometallic 2D hexagonal structures with vacant sides (peanut-like structures). (v) 2D hexagonal honeycomb layered ferrimagnets with tunable critical temperatures and even with chirality and porosity.^[2] (vi) 2D honeycomb $[\text{M}^{\text{I}}\text{M}^{\text{III}}(\text{C}_6\text{O}_4\text{X}_2)_3]^{2-}$ lattices.^[3] (vii) a 3D interpenetrated anilato-based 10,3-gon networks.^[3]

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Spinterfaces – Spin transport through Co and C₆₀ hybrid interfaces

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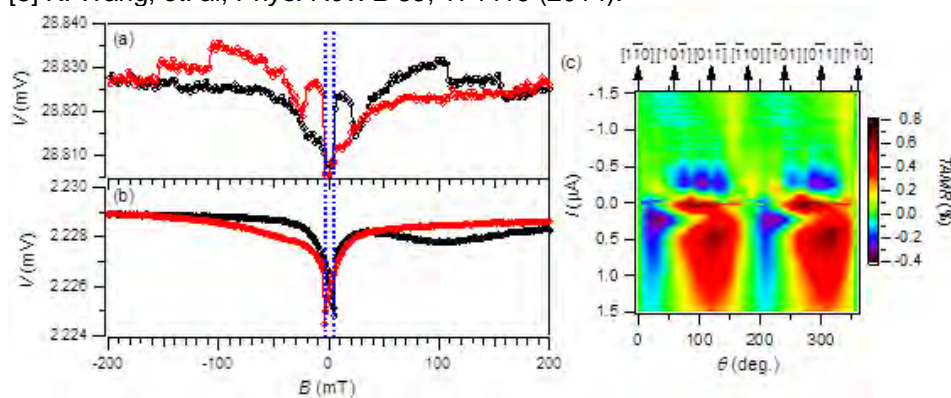
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An intriguing phenomenon between ferromagnetic surfaces and organic semiconductors results in the formation of hybrid interfacial states. Such interfacial electronic energy states with distinct magnetic properties, mainly due to spin-polarized electron transfer from ferromagnets. Spin-dependent transport through such tailored interfaces can be significantly influenced by these hybridization effects.[1] Here, we report spin transport measurements for devices containing interfaces between epitaxial face-centered-cubic (fcc) cobalt (Co) and non-magnetic fullerenes (C₆₀). In one heterojunction, a C₆₀ molecular layer is directly grown on a Co electrode, and is capped with an AlO_x tunnel barrier and an Al top contact [sapphire(substrate)/Co(8 nm)/C₆₀(4 nm)/AlO_x (3.3 nm)/Al (35 nm)]. Since only one ferromagnetic contact (Co) appears, tunneling anisotropic magnetoresistance (TAMR) determines the effects. The TAMR of Fig.1(a) shows distinctly different magnetic switching behavior than that observed in anisotropic magnetoresistance (AMR) measurements of the Co/C₆₀ bi-layer (see Fig.1 (b)). Fig.1 (c) reveals a two-fold symmetric TAMR upon rotating an in-plane 800 mT magnetic field. A maximum TAMR ratio of 0.7% at 0.5 μ A was measured at 5 K, which is markedly different from that of devices based on fcc-Co without C₆₀ [2,3]. We believe these phenomena can be attributed to the magnetic coupling between Co and the newly formed Co/C₆₀ hybrid interfacial states, which is expected to bring some interesting functionalities for organic spintronic applications.

Figure 1. (a) TAMR measured at 5 K for the sapphire/Co(8 nm)/C₆₀(4 nm)/AlO_x (3.3 nm)/Al (35 nm) junction, (b) the in-plane AMR for the Co/C₆₀ bi-layer, and (c) TAMR measured at 5 K upon rotating a 800 mT magnetic field over an in-plane angle θ .

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ID: 01, 2015-09-07 12:00

Instrumentation

(Oral)

Torque magnetometry: a unique experimental tool to characterize magnetic anisotropy

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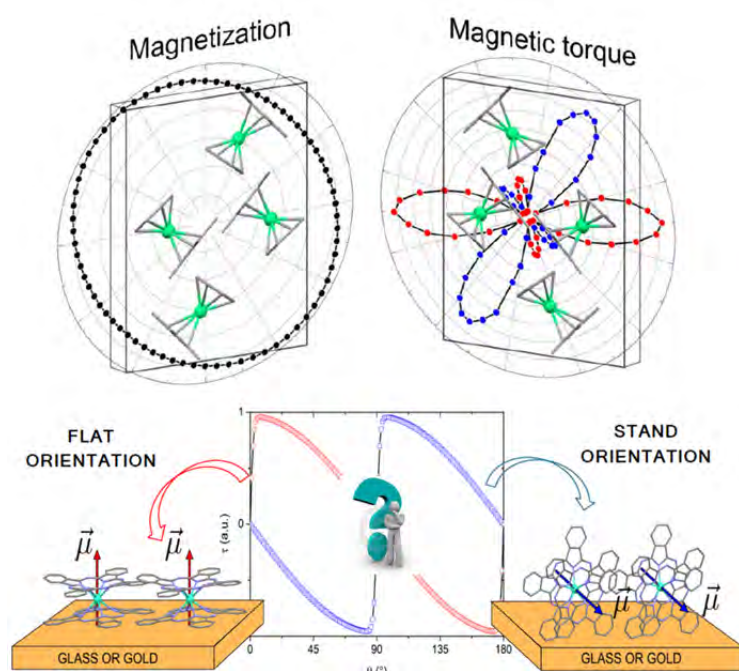
Mapping the orientation and strength of magnetic anisotropy of mono- and polynuclear complexes is currently a hot topic in molecular magnetism. This is because a precise picture of the magnetic anisotropy of each metal ion in a polynuclear complex is mandatory to understand the magnetic behaviour and to rationally design new single molecule magnets. Despite large theoretical efforts were made in this field¹⁻⁴, the experimental techniques that can give this precious information are still scarce. Single crystal magnetometry was revealed to be useful but mainly in few crystalline c systems⁵⁻⁷. Torque magnetometry based on capacitive cantilevers is a simple but powerful technique very sensitive to magnetic anisotropy, that can efficiently flank other experimental and theoretical approaches. We studied a large number of complexes, mainly based on heavy lanthanide ions and developed a protocol to efficiently fit torque data and obtain anisotropy orientation⁸ and Crystal Field parameters^{9,10}, even in case of molecules with multiple orientation in the crystal (Fig. 1, top). An accurate fit of the torque data allows the complete disentanglement of all the contribution coming from the magnetic ions inside complex clusters. Moreover torque magnetometry was proved to be useful to investigate layers, with thickness of the order of few nanometers, of magnetic molecules on different substrates (Fig. 1, bottom). This study allowed a detection of the organization of this molecules on surface, an information generally achievable only with synchrotron light. We present here some recent intriguing studies on spin systems solved using torque magnetometry.

For the results presented here, we acknowledge the financial contribution of the ERC through the AdG MolNanoMaS (267746).

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**Towards Hidden Phases in Switchable Molecular Materials: Control of the Overlap
Between the Low Temperature Metastable HS State and the Thermal Hysteresis**

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In recent years, molecular optical switches have attracted considerable attention as they hold great promises in molecular electronic and photonic devices. The reversible photo-switch of the magnetic states^[1] is widely studied in spin-crossover systems able to exhibit high-spin (HS) ↔ low spin (LS) conversion under thermal perturbation. This has led to the introduction of the T(LIESST) measurement to estimate the limit temperature above which the photoinduced HS metastable state is erased.^[2] The creation of a database^[3] allowed to increase T(LIESST) value from 60 K to 130 K for pure iron(II) SCO materials^[4] and 180 K in molecular cluster.^[5] This opens the opportunity to study the particular situations where the metastable HS state reaches, and even overlaps, the thermal spin-crossover regime.^[6,7]

In this presentation we will show several examples of such overlap obtained by rational metal dilution approach in both spin-crossover compounds and Prussian blue analogues. Experimental and theoretical studies will be presented in cooperative systems and the observation of hidden phases will be discussed.

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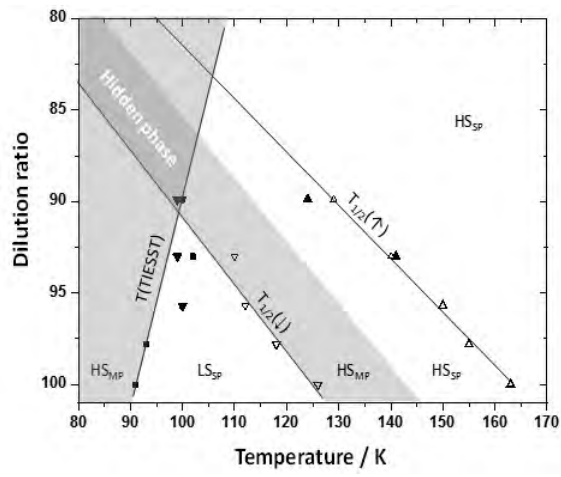


Figure: pseudo phase diagram of the evolution of $T(LIESST)$ and the thermal spin-crossover temperatures in warming and cooling modes as function of metal dilution ratio. It shows the clear overlap of the thermal hysteresis and the photo-induced state giving rise to hidden phases.



Magnetic diagnostics of chiral crystals using nonlinear magnetic responses

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Magnetic response against ac magnetic field (H) yields wealthy physical information on dynamics of magnetic domains as well as phase transition. Long-ranged magnetic order is insensitive against the change in the frequency (f) of the ac field, whereas small magnetic domain exhibits critical slowing-down as a function of f .

Thermal stability of magnetic domain can be observed by the heat capacity measurement reflecting the magnetic entropy, whereas it yields no information on magnetic dynamics. Transmission electron microscope is a direct approach to observe the magnetic domains, whereas has no time resolution enough to detect the response against the change in the magnetic field in fast time scale. On the other hand, the periodic response of magnetization M under H is useful for "magnetic diagnostics" on the magnetic domain formation. We pay much attention to the higher-order magnetic response ($M_{n\omega}$, $n \geq 2$). In particular, the third harmonic $M_{3\omega}$ reflects the breaking of spatial reversal symmetry of the magnetic moments, and it is useful to investigate the nature of magnetic domains. For instance, we have observed prominent $M_{3\omega}$ responses in a chiral metal-complex magnet [1, 2], a helical magnet [3], and magnetically networked single molecule magnets [4, 5]. In chiral crystals that we focus herein, the development of magnetic domains assisted by the relativistic spin-orbit Dzyaloshinskii-Moriya (D-M) interaction often exhibits a glassy feature, resulting in the appearance of "giant $M_{3\omega}$ response". Indeed, $M_{3\omega}$ is related to the shape of the M - H hysteresis, and its response is physically connected with magnetic nonlinearity in a nonlinear-spring model, which can explain the movement of domain walls.

Thus, by unearthing valuable $M_{n\omega}$ response in ac magnetic response carefully, we could find out unique magnetic behavior near the magnetic ordering temperature. Further the approach of magnetic diagnostics also yields a physical knowledge for whether a magnetic nanoparticle has any magnetic correlation with neighboring nanoparticles or not.

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Ultrafast Spin Dynamics in the V-Cr Prussian Blue Molecule-Based Magnet

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Switching the physical properties of functional materials to metastable states using external perturbations is of great interest for future electronic and information storage technologies. In order to achieve fast switching, ultrashort laser pulses are promising excitation sources. Femtosecond spectroscopy is currently the only technology able to function beyond 1 THz, therefore well adapted for investigating the main mechanisms involved in a switching process. The recent advances in ultrafast magneto-optical (MO) techniques open up an exciting possibility to study dynamics of magnetic phenomena occurring in metallic films or nanostructures on an unprecedented timescale [1–3].

We report the first ultrafast magneto-optical study of thin films of the V^{II/III}/Cr^{III} Prussian Blue Analogue (PBA), which is a molecule-based magnet. The V^{II/III}/Cr^{III} PBA is a cyanometallate coordination polymer and has a rock-salt-type structure [4,5]. The films were excited with 60 fs, 400 nm laser pulses, which spectrally overlapped with the broad ligand-to-metal (LMCT) bands in the UV. A white-light continuum spanning 480 – 690 nm and generated by the fs laser was used to monitor the changes in transmission and MO signal (Faraday rotation and ellipticity) as a function of time delay between the pump and probe (Fig. 1a). Measurements were carried out at 50 and 300 K and in ± 0.5 T external magnetic fields in order to separate the optical and magnetic dynamical response.

The probe spectrum overlaps with the metal-to-metal charge-transfer (MM'CT) band (Fig. 1b). As seen in Fig. 1c, we observe a fast initial increase in the transmission, which decays on two timescales, viz. 0.8 and 4 ps. The local change in spin populations shows up at short times in the MO contrast of both the Faraday rotation and ellipticity whereas the longer decay is due to the heating of the lattice and subsequent recovery of the magnetisation (Fig. 1d–e). The spectral dynamics of the magneto-optical signals are different, indicating a complex transfer of momentum in the excited state inducing both magnetic circular dichroism and magnetic birefringence. As will be further detailed, these results show the large potential of Femtomagnetism (magnetic studies at the femtosecond time scale) for studying and monitoring molecular magnets.

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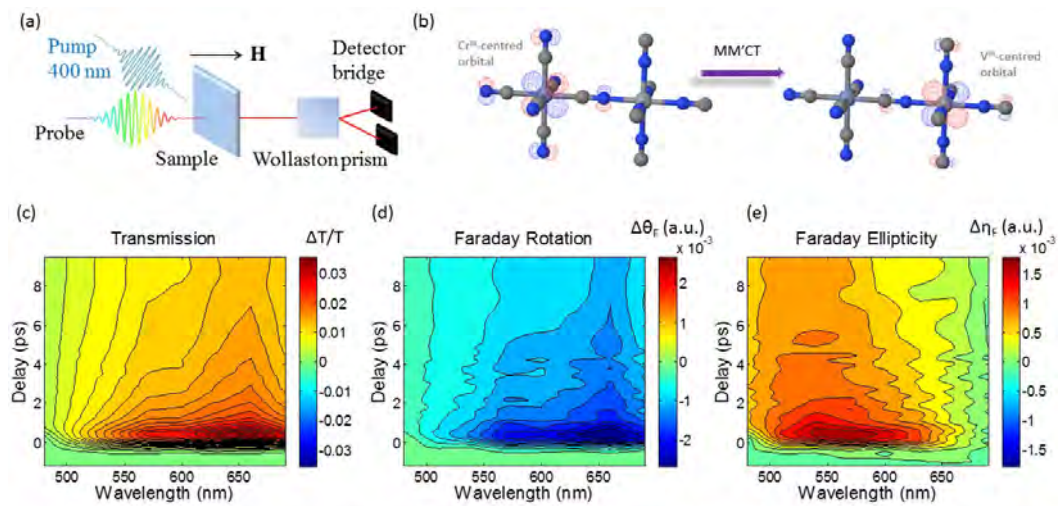


Figure 1: (a) Experimental setup [1]; (b) The white-light probe measures changes related to the MM'CT transition; (c) Change in transmission as a function of wavelength and time delay between pump and probe pulses; (d) Change in Faraday rotation angle ($\Delta\theta_F$) and (e) Faraday ellipticity ($\Delta\eta_F$).



Graphene zigzag junction as a two-leg organic spin ladder

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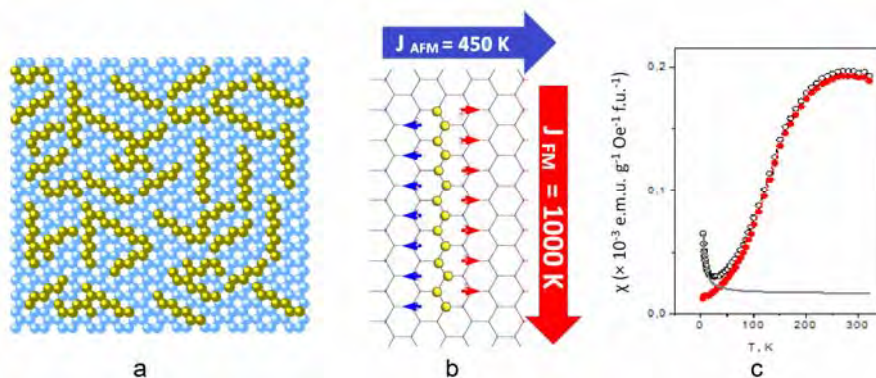
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Attempts to make graphene magnetic by introducing localized states at zigzag edges have failed so far, presumably due to structural instability of torn zigzags. We have synthesized a material containing zigzag graphene junctions, namely, two graphene regions separated by a stable monoatomic zigzag chain of fluorine atoms (Fig. 1a). Thus, the fluorine chain serves as chemical scissors that cut the graphene plane in the sense that the lattice sites that are occupied by CF groups become unavailable to the p-electron system. This “cut” creates two edges that are separated by a nearly impenetrable CF-nanoridge. Graphene bipartite lattice consists of inequivalent a and b sublattices. In the case of a zigzag edge, one expects a set of localized spin states in sublattice a on one side of the nanoridge and sublattice b on the other side. The edge spins are ferromagnetically ordered within each of the zigzag interfaces whereas the spin interaction across the nanoridge is antiferromagnetic (Fig. 1b).

Our experimental data agree with this physical picture, and the magnetic susceptibility vs temperature exhibits behaviour typical of quantum spin-ladder system with ferromagnetic legs and antiferromagnetic rungs. The ground state of this material is singlet and the existence of excitation gaps is suggested by the temperature dependence of the static magnetic susceptibility (Fig. 1c). Spin susceptibility diverges at low temperatures, and the cT product at the maximum is a quarter of the theoretical value. The exchange coupling constant along the rungs is measured to be 450 K, strong enough to consider graphene with zigzag junctions as a candidate for a room temperature spintronics material.

Figure 1. a: Structure of graphene plane with zigzag junctions; b: zigzag junction as a spin ladder with ferromagnetic legs and antiferromagnetic rungs; c: magnetic susceptibility, as-measured data are shown with open circles, data with Curie contribution subtracted are shown with solid circles.





Switchable magnetic materials and optical magnets
(Oral)

Towards self-doping molecular systems based on radical donor-acceptor molecules

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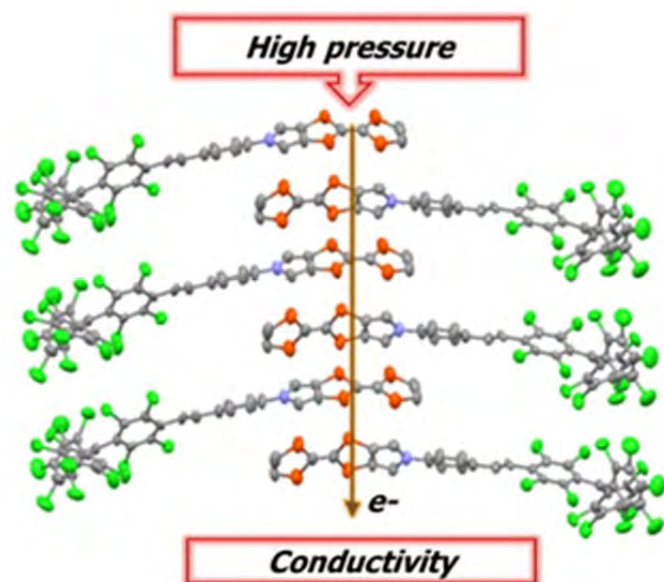
Organic molecules containing electron donor (D) and electron acceptor (A) units linked by pi-conjugated bridging groups are worthy of attention for the investigation of intramolecular electron transfer (IET) phenomena and associated bistability phenomenon [1]. Recently, we have reported a radical D-A dyad based on a tetrathiafulvalene (TTF) electron pi-donor connected to polychlorotriphenylmethyl (PTM) radical electron acceptor that exhibits bistability [2-4]. Nevertheless, crystals of this molecule are insulating because of the lack of a proper packing of TTF subunits.

Advanced supramolecular engineering techniques have been exploited to attain crystalline materials of this family of compounds exhibiting a molecular packing with a complete segregation of the donor and acceptor fragments forming homostacks of the TTF subunits; a prerequisite for attaining electronic conductivities.[5] In accordance with the intrinsic softness of such crystals its structure is affected by external stimuli, like pressure and temperature, which dramatically alter their physical properties. Indeed, preliminary experiments showed that these crystals exhibit conductivity upon the application of high pressures due to such a self-doping process. Raman spectroscopy has been used to corroborate the intramolecular charge transfer under high pressure with the observation of the TTF-cation formation.

This result opens the possibility to obtain materials with a precise control of the coupling between the mobile electrons along the TTF stacks and the (semi)localized electrons on the PTM radical residues exhibiting interplay between the electronic transport and the magnetic properties.

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Organometallic Single-Ion Magnets

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The single-molecule magnets (SMMs) are attracting the increasing interest due to their potential applications in high density information storage, quantum computing, molecular spintronics, and magnetic refrigeration. This field provides scientists a possible access into the crossover of the classical and quantum world, and a wonderful model to study the fascinating magnetic properties between microscopic and macroscopic materials.

After the milestone discovery of the first single-molecule magnets (SMMs) Mn12ac, many new SMMs were structurally and magnetically characterized. The most studied systems are mainly conventional coordination compounds with polynuclear structures. From 2011^[1-5], we explored a series of organometallic sandwich molecules, Cp*LnCOT (Cp* = C₅Me₅⁻, pentamethylcyclopenta-dienide; COT = C₈H₈²⁻, cyclooctatetraenide; Ln = Dy³⁺, Ho³⁺, Er³⁺), which behave as single-ion magnets, into the field of molecular nanomagnets. It opened a door of SMMs to the chemists in organometallic chemistry. Recently, we found some new sandwich and half-sandwich lanthanide organometallic molecules could also show the slow relaxation of magnetization. We hope these systems can provide new understandings of slow magnetic relaxation and new clues on the design and synthesis of molecular nanomagnets.

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Switchable magnetic materials and optical magnets
(Oral)

Spin crossover in a polyanionic Fe^{II} trimer with T_{TIESST} >250 K

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Spin crossover (SCO) compounds appear especially suited for applications as stimuli-responsive molecular switches for multifunctional materials, memories, electrical circuits or display devices [1-3]. Our group is particularly interested in the search for anionic SCO complexes to increase their processing capabilities when incorporated into hybrid materials. In this line, reaction of the polysulfonated triazole ligand L = 4-(1,2,4-triazol-4-yl) ethanedisulfonate with iron(II) salts in water yields the trimeric species [Fe₃(μ-L)₆(H₂O)₆]⁶⁻. This polyanion can be isolated from solution as the dimethylammonium salt, where a complex hydrogen bonded network connects anions, cations and solvent molecules in the solid state.

This compound shows a thermally induced spin transition for the central Fe position in the trimer above room temperature, with T_{1/2}(↑) = 400K and T_{1/2}(↓) = 310K. This is among the widest robust thermal hysteresis found for SCO materials. In addition, this material shows extremely slow dynamics what allows easy thermal quenching of the metastable high spin (HS) state via slow cooling, even at rates as slow as 5K/min. Once it is trapped, the HS state remains metastable. Thermal energy is not able to promote relaxation into the low spin (LS) ground state below 215 K, with characteristic T_{TIESST} = 250 K, the highest temperature ever observed for thermal trapping in a spin crossover compound. The isothermal relaxation curves from the thermal trapped state to the low spin state show sigmoidal behavior, suggesting high cooperativity. From these data, an activation energy above 6000 K is estimated for this relaxation process.

Since SCO phenomena is very sensitive to changes in the crystal packing, we have substituted the dimethylammonium cation by methatesis for a variety of other cations such as benzidine, cesium or sodium. This allows tuning the magnetic properties of the compound. The thermal hysteresis width ranges from 90K to 54K, and the T_{TIESST} can be increased up to 280K. The dynamics of the transition are also affected, with materials exhibiting thermal trapping of the HS state at cooling rate as slow as 0.3K/min.

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Quantum coherence in molecular nanomagnets

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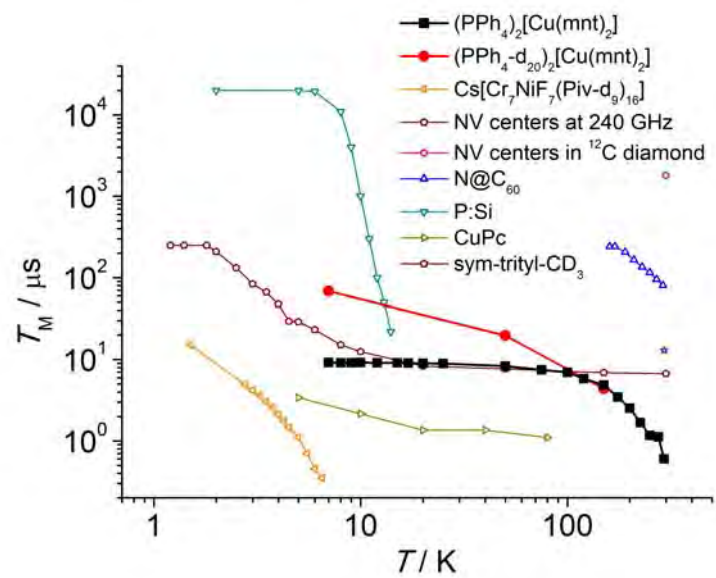
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Molecular nanomagnets have been proposed as prime quantum bit candidates. Quantum computing promises to enable calculations that will forever remain intractable with conventional computers. In principle, any two-level system will function as a qubit. One of the decisive quantities which determine the usefulness of a particular system is the ratio of the quantum coherence time and the time needed for a single quantum operation. The latter is given by electronics constraints, thus only the former can be optimized by chemical means. The quantum coherence time is the lifetime of an arbitrary superposition state, and corresponds to the time available for the quantum computation. The advantage of molecular systems is that their properties may be tuned continuously and almost without limitations by chemical synthetic means. This feature is especially useful, given the fact that quantum computing only becomes competitive if networks of hundreds of interacting qubits can be generated. In that respect, the fact that molecules have been shown the ability to form long-range ordered arrays on surfaces is also beneficial.

However, thus far, quantum coherence times have been less than astounding, with the current record 15 μ s at 1.5 K. We have recently shown that single ion systems (i.e., mononuclear complexes) can display much longer coherence time. Thus, we have found coherence times of up to 68 μ s at 7 K for $(\text{PPh}_4\text{-d}_{20})_2[\text{Cu}(\text{mnt})_2]$ and even at room temperature, the quantum coherence time is almost a microsecond.[1] Thus, the quantum coherence time exceeds that of prime competitors, such as diamond NV centres and phosphorus dopants in silicon in certain conditions. In this presentation, we will show published results,[1 – 4] as well as new results on single-qubit systems, two-qubit systems and on triangular qubits featuring antisymmetric exchange interactions. The last of these were predicted to be addressable by means of microwave electric fields, which would enable local control.

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Rational Functionalization of Molecular Materials Towards Magnetic Liquids and Liquid-Crystals

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Single-molecule magnets (SMMs) appear to be promising molecular units for the development of future integrated nanodevices, such as molecular transistors, single-molecule spin-valves, quantum computers, "nanosquid" junctions, or magnetic random access memories.¹ The potential use of these molecular materials in such devices requires a close and facile control of their organization.

The organization of SMMs has been reported on surfaces, in mesoporous materials or by coordination chemistry,² but another promising strategy towards their eventual use is the development of molecular systems with self-organization abilities.³ Liquid crystalline phases are one of the best examples of self-assemblies in which order coexists with fluidity.⁴ Thus, by synthesizing SMM materials with liquid crystalline properties (Figure) we can: (i) isolate and protect the magnetic cores by an organic shell, (ii) organize, align and orient the magnetic unit o keep their easy axis in the same direction, and (iii) improve the processability for future applications.

In this communication, we will discuss on the synthesis and characterization of new $[\text{Mn}_{12}\text{O}_{12}(\text{L})_{16}(\text{H}_2\text{O})_4]$ complexes (where L^i are based-carboxylate mesogenic ligands). We applied two strategies of functionalization: (a) the functionalization of peripheral ligands with strongly lipophilic groups (long alkyl chains), and (b) the grafting of a mesomorphic promoter through a flexible aliphatic spacer. All the complexes preserve the SMM behavior of the parent $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4]$ compound and exhibit interesting mesogenic properties. By varying the chain density around the rigid core, it was possible to stabilize thermotropic cubic mesophases with different symmetries while smectic mesophases with hexagonal 2D organization were obtained using a regioselective functionalization strategy.

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Figure 1. Schematic representation emphasizing the benefits of ligand functionalization in SMMs: (left) functionalization with ligands possessing strongly lipophilic groups (long alkyl chains) can protect and isolate magnetic cores from contacts between them; (right) the self-organization of liquid crystalline phase can help to orient, align, and organize SMMs.



Spin dynamics of Dy₂ molecular clusters deposited onto micro-SQUID sensors

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The application of single molecule magnets in quantum information technologies necessarily involves a rational integration of these molecules into solid state devices, such as SQUIDs or superconducting resonators [1,2]. An intriguing question is then how the loss of crystal order and the interaction with the substrate affect the relevant magnetic properties. Here, we report the results of ac susceptibility measurements performed, down to very low temperatures ($T > 13$ mK), on thin layers of the Dy₂ analogue of a series of asymmetric molecular clusters that have been proposed as candidates for the realization of 2-qubit gates [3,4].

The molecules are integrated into a μ -SQUID susceptometer by means of Dip Pen Nanolithography. This technique enables the structuration of the molecules on the most sensitive areas of the sensor without the need of any previous functionalization of neither the molecule nor the substrate, while controlling the number of molecular units deposited on each array [5]. Frequency-dependent susceptibility data measured on 4 and 20 molecular layers thick films are compared with similar results obtained for bulk polycrystalline samples. The analysis of these experiments provides direct information on the single-ion magnetic anisotropies and the intra-molecular coupling between the two lanthanide spins, which are crucial ingredients for the realization of a CNOT gate. The results show that the molecular Dy₂ units largely remain intact at the surface, in sharp contrast with a similar study performed on Mn₁₂ clusters that revealed dramatic changes in the spin dynamics [6]. Low-nuclearity lanthanide magnetic clusters are robust against distortions caused by the molecule-substrate interactions and thus might provide suitable building blocks for the development of a scalable quantum architecture.

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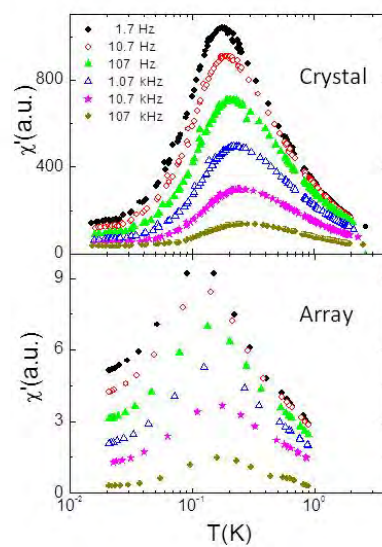
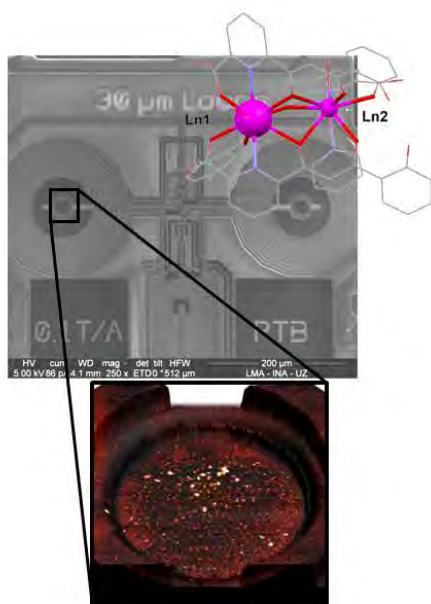
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Molecular spintronics
(Oral)

Frontier of Quantum Molecular Spintronics Based on Single-Molecule Magnets: Giant Magnetoresistance and Tunneling Magnetoresistance

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In order to realize the quantum molecular spintronics such as giant magnetoresistance, tunneling magnetoresistance, and field effect transistors, we have used single-molecule magnets.

For this purpose, we have synthesized the conducting SMM such as $[\text{TbPc}_2]\text{Cl}_{0.6}$. The hysteresis is observed below 10K. This SMM shows the negative magnetoresistance below 8 K. As for the second strategy, we try to input/output one memory into/from double-decker Tb(III) SMM (TbPc_2) by using the spin polarized STM. In this research, we have observed Kondo peak by using STS for the first time. We have succeeded in controlling the appearance and disappearance of Kondo peak by the electron injection using STS, reversibly. This is considered as the first single-molecule memory device. As for the third strategy, we have made the Field Effect Transistor devices of SMMs. The DyPc_2 device shows the ambipolar behavior, while the TbPc_2 device shows the p-type behavior. As for the fourth strategy, we have made doping of Cs atoms onto Pc_2Y , where Kondo peaks have not observed by coupling between the radical of Pc and 6s electron of Cs atom to make a singlet pair, while other Pc_2Y sites show Kondo peak due to the radicals. As for the fifth strategy, we have succeeded to write the letters of T and U, which are the initials of Tohoku University. As for the sixth strategy, we have evaporated TbPc_2 SMM on the magnetic Co surface, and by using the magnetic Cr tip, we have observed the giant magnetoresistance (GMR=200 %) for the first time. Finally, we have evaporated the Co film and TbPc_2 on Au surface, and by using the magnetic Cr tip, we have observed the tunneling magnetoresistance (TMR) with the double butterfly structure for the first time.



YBCO microwave resonators for strong collective coupling with spin ensembles

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In the strong coupling regime, the coherent transfer of information between microwave photons and spin ensemble can be achieved. Experimentally this can be done by means of high quality factor superconducting resonators, provided that the spin-photon coupling rate exceeds both the decay rate of the resonator and the linewidth of the EPR transition. Molecular nanomagnets, thanks to their favorable transitions and engineerable dephasing rates, are appealing in this context [1]. Their manipulation however requires strong magnetic fields that are not compatible with conventional superconducting resonators [2].

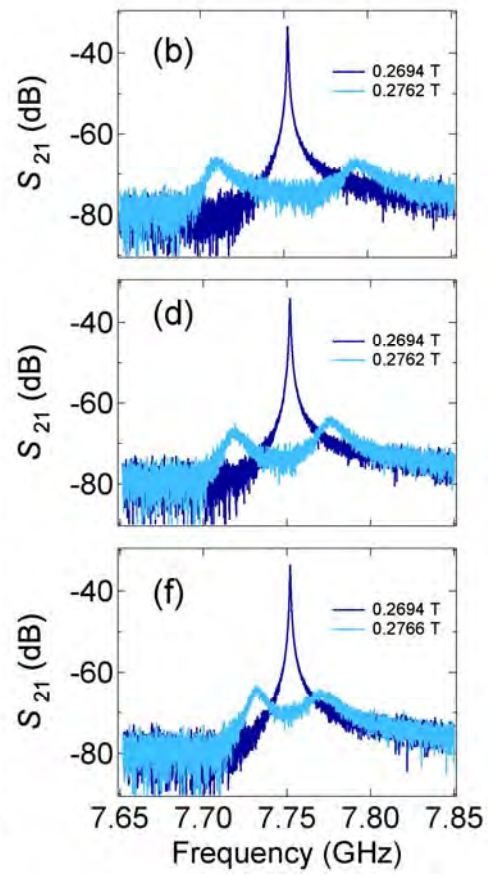
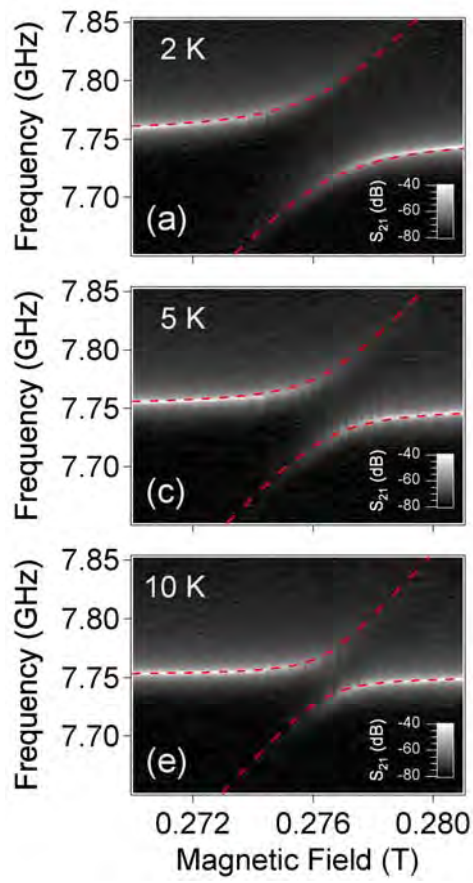
Coplanar microwave resonators made of 330 nm-thick superconducting YBCO have been fabricated and tested in a wide temperature (T , 2-100 K) and magnetic field (B , 0-7 T) range [2]. We show that the measured quality factors (Q_L) significantly exceeds 10^4 below 55 K and slightly decreases for increasing fields, remaining 90% of $Q_L(B=0)$ for $B=7$ T and $T=2$ K.

These features allow the coherent coupling of resonant photons with spin ensembles at finite temperature and magnetic field. To demonstrate this, collective strong coupling was achieved by using the spin ensemble of a DPPH organic radical placed at the magnetic antinode of the fundamental mode (Fig. 1): the in-plane magnetic field is used to tune the spin frequency gap splitting across the single-mode cavity resonance at 7.78 GHz, where clear anticrossings are observed with collective coupling rate as high as 39 MHz at $T=2$ K, which is shown to scale as the square root of the number of active spins in the ensemble.

We discuss potential candidates among molecular magnets that show relevant features for the observation of the strong coupling with the microwave field.

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Switchable magnetic materials and optical magnets
(Oral)

Guest, Light and Thermally Modulated Spin Crossover in [Fe(II)₂] Supramolecular Helicates

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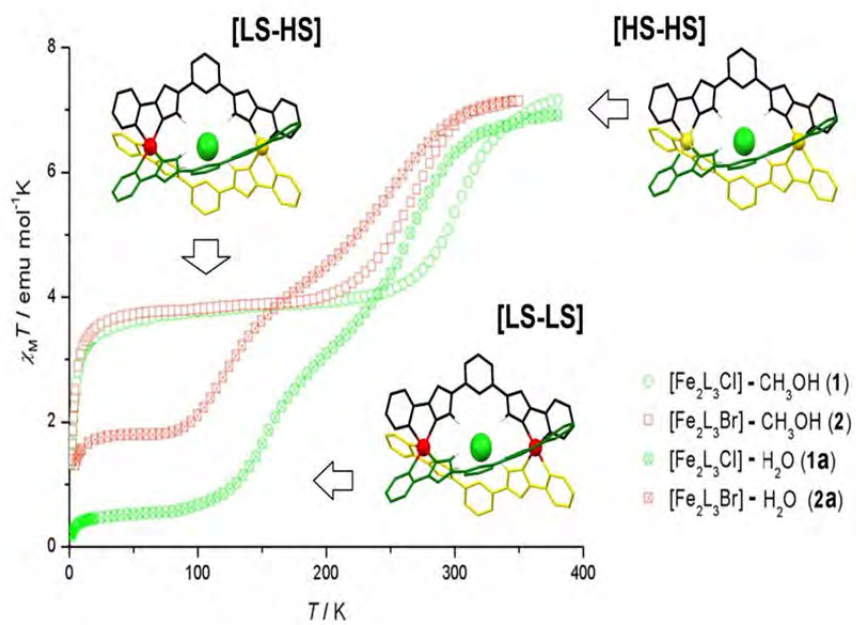
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The search of molecular functional materials is of great interest for many future applications. An important class of molecules is made up by those that can switch their properties by means of external stimuli.¹⁻³ The self-assembly of a ditopic bis-(pyrazol-pyridyl) ligand H₂L with Fe(II) leads to a triple-stranded helicate capable of encapsulating halide anions in its cavity, which can exhibit three different spin states accessible through different types of external stimuli; thermally, chemically and optically. The non-centrosymmetric molecules [X₂Fe₂(H₂L)₃] \cdot X \cdot (PF₆)₂ \cdot 5CH₃OH (X= Cl, **1**; Br, **2**) exhibit two Fe(II) ions with distinct properties, thus leading to two different ordered spin states, [LS-HS] and [HS-HS], that can be accessed by controlling the temperature, near ambient conditions, as evidenced through single crystal X-ray diffraction (SCXRD) and magnetometry. The change from Cl⁻ to Br⁻ shifts the transition down by approximately 50 K. The solvent MeOH molecules can be exchanged by water through single-crystal-to-single-crystal (SCSC) processes leading to now centrosymmetric compounds [X₂Fe₂(H₂L)₃] \cdot X \cdot (PF₆)₂ \cdot 1.5H₂O (X= Cl, **1a**; Br, **2a**), which feature a [LS-LS] third magnetic state at low temperatures, in addition to the other two previously seen, giving rise to a two-step full spin crossover. The three states were characterized by SCXRD, which shows that the intermediate [LS-HS] is not ordered as a consequence of the crystallographic disorder of the otherwise, two distinct Fe(II) centers of each molecule. At low temperature, the transformations [LS-HS] \rightarrow [HS-HS] (compounds **1** and **2**) and [LS-LS] \rightarrow [LS-HS] (compounds **1a** and **2a**) can be realized using green radiation, via the LIESST effect.

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Molecular nanoscience
(Oral)

Small Angle Neutron Scattering (SANS) studies of magnetic Prussian-Blue analogue nanoparticles $\text{CsNi}[\text{Cr}(\text{CN})_6]$

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Small-Angle Neutron Scattering (SANS) is a technique able to probe the morphology and spatial organization of nano-objects, dispersed in solution or embedded in solid matrices, from a few nanometers up to the μm range. One major asset of this technique is its sensitivity to the chemical contrast between the nano-objects and the medium. Moreover, neutrons are sensitive to the magnetic induction so that SANS enables to probe not only the magnetization of the particles but also the induced stray fields. We performed SANS and neutron diffraction studies on coordination nanoparticles (CNP's) based on cyanide-bridged networks embedded in CTA or PVP polymer matrices. These magnetic nanoparticles, of the Prussian-Blue analogue form $\text{Cs}_x\text{Ni}[\text{Cr}(\text{CN})_6]$, present magnetic properties which are size and concentration dependent [1,2]. After an initial study of the structural properties through the determination of the geometrical form factors and structure factors as a function of concentration and matrix type, we investigate the super-paramagnetic behaviour below ca. 90K under magnetic field [3]. The difference between the SANS signal under ZFC and FC is shown to be proportional to the spherical magnetic form factor $\text{FM}(q)$ of the particles and to the internal magnetization $M(T)$ described by a Langevin expression. The present results evidence the possibility, thanks to SANS, to describe the individual spatial magnetization process of nanoparticles.

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Rational Design of a Photomagnetic Chains: Bridging Single-Molecule Magnets With Spin-Crossover Complexes

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The rational design of molecule-based systems displaying tunable optical and/or magnetic properties under external stimuli has received a great deal of attention recently. This interest is driven by the potential applications in the high-performance molecule-based electronic devices in the area of recording media, switches, sensors, and displays. As examples, Fe(II) complexes and cyanido-bridged compounds notably demonstrate the concomitant change in magnetic and optical properties by thermally and light-induced spin crossover or metal-to-metal electron transfer respectively [1,2].

The foregoing remarkable properties in the cyanido-bridged networks prompted many researchers to design new photomagnetic compounds through a building-block approach [3]. In this presentation, we will present recent systems that we obtained with the association between Fe(II) spin crossover units and Mn(III) Single-Molecule Magnets through cyanido bridges. The optical reflectivity and photomagnetic experiments reveal that the photomagnetic properties of the Fe(II) unit is kept after its coordination to the acceptor Mn^{III}/saltmen complexes, allowing to switch "on" and "off" the magnetic interaction between the photo-induced Fe^{II} HS unit ($S = 2$) and the Mn(III) ions [4]. To the best of our knowledge, one of the reported compounds represent the first example of a coordination network of Single-Molecule Magnets linked by spin-crossover units inducing thermally- and photo-reversible magnetic and optical properties.

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Electronic Structure and Structural Integrity of Single Adsorbed Double-Decker Phthalocyanine Molecules

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We study the early-lanthanide double-decker phthalocyanine complex NdPc₂ adsorbed on metal surfaces by scanning tunneling microscopy/spectroscopy (STM/STS) at 4 K and state-of-the-art density-functional theory (DFT) calculations to understand the impact of the molecule-substrate interaction on the electronic and transport properties.

The NdPc₂ molecules were home-made and *in-situ* evaporated onto Cu(100), Au(111), and a 1-2 monolayer (ML) thick Fe film on W(110). The latter is a model system with in-plane and out-of-plane magnetization for 1 and 2 ML Fe thickness, respectively. A significant fraction of the NdPc₂ decomposes upon adsorption into two single-decker Pc with a strongly substrate-dependent decomposition probability. Surprisingly, the most reactive Fe/W(110) surface shows the lowest decomposition probability, whereas there are no intact NdPc₂ on the least reactive Au(111) surface. STS-spectra indicate a stronger *intramolecular* bonding in the NdPc₂ chemisorbed on Fe/W(110) than on Cu(100). We attribute these findings to substrate-dependent partial charge transfer from the substrate to the Pc ligands, which strengthens the intramolecular electrostatic bonding [1].

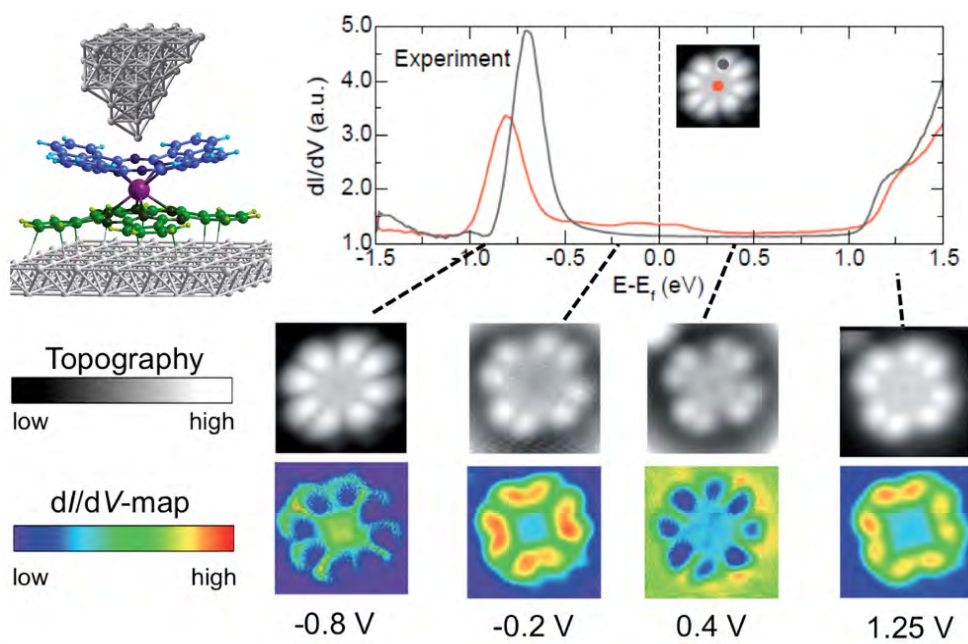
For the NdPc₂/Cu(100) system we record energy-dependent topography and differential conductivity (dI/dV) maps as well as $dI/dV(V)$ curves at different sites on the NdPc₂ molecule (see Figure). Spatially and energetically resolved orbitals compare well with DFT calculations allowing identifying them with specific electronic states of the molecule-substrate complex. We find that the electric field between STM tip and sample must be taken into account to properly describe the molecular-like electronic states associated with the upper Pc ligand, which are barely coupled to the substrate and therefore highly susceptible to the electric field. With increasing field strength they shift for both field polarities away from the Fermi level until they hybridize with the Nd 4*f*-orbitals, where they are pinned and measured in STS [2]. Furthermore, we demonstrate for the first time that the spin-polarized Nd 4*f*-states are involved in the charge transport through NdPc₂ on Cu(100) [2]. In contrast to the Tb³⁺ ion in the previously studied late-Ln analogue TbPc₂ [3,4], the Nd³⁺ ion has a larger ionic radius with more delocalized 4*f*-electrons and, thus, stronger hybridization with the Pc ligands. Thereby, the 4*f*-orbitals become accessible to transport experiments, while largely maintaining the relative energetic positions of spin-up/-down states and hence the magnetic moment [2]. This result opens up prospects for electrical manipulation and detection of the molecular spin state, providing the basis for all-electrically controlled device concepts in molecular spintronics.

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Large Magnetoresistance at Room Temperature in a Single-Molecule device

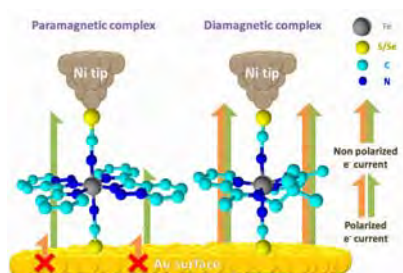
Eliseo Ruiz¹, Daniel Aravena¹, Ismael Díez-Perez¹, Albert C. Aragonès¹, José Antonio Real², Zulema Acís-Castillo², Josh Hihath³, Jorge I. Cerdá⁴

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Controlling the spin of electrons in nanoscale electronic devices is one of the most promising topics toward devices with rapid and highly dense information storage. The interface magnetism or spinterface resulting from the interaction between a magnetic molecule and a metal surface, and vice versa, has become a key ingredient to engineering nanoscale molecular devices with novel functionalities. Here, we present a single-molecule wire displaying large (>10000%) magnetoresistance based on STM measurements. The molecular device is built by trapping individual spin crossover Fe(II) complexes between one Au and one ferromagnetic Ni electrode at room conditions. Large changes in the single-molecule conductance are measured when the electrons flow from the Au to either an α -up or a β -down spin-polarized Ni electrode, the latter case being at least 100-fold more conductive than the former. The current flowing through such an interface appears to be strongly spin-polarized, thus resulting in the observed magnetoresistance effects depending upon the magnetic Ni polarization direction. DFT calculations have been performed to gain some insights in the mechanism of such magnetoresistance effect.

The observed large magnetoresistance switching is achieved at near-zero bias voltage, which implies the use of very small currents and low power consumption. Thus, we will present an example of strong magnetoresistance in a single-molecule device at room temperature. The key ingredients to generate magnetoresistance in a single-molecule device are: (i) engineering a hybrid electrode/molecule interface that results in spin-polarized states. This spinterface is responsible for the polarization of the current flowing through the single-molecule contact. (ii) The electronic structure of the magnetic molecule should be appropriate, as the high-spin Fe^{II} complexes, to favor transport through one of the channels. (iii) The use of a spin-polarization ferromagnetic electrode on one side of the single-molecule junction that acts as electrons *sink*. The observed magnetoresistance is then controlled depending upon the direction of the electrode magnetic polarization. The observation of strong magnetoresistance effects in a single-molecule device opens up a new door for the design and control of spin-polarized transport in nanoscale molecular devices at room temperature.





Switchable magnetic materials and optical magnets
(Oral)

Molecular nanomagnets with switchable coupling for quantum simulators

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The physical implementation of quantum simulators is a major technological target of current research. Suitably engineered supramolecular complexes of molecular nanomagnets (MNMs) have been theoretically proposed as excellent candidates [1, 2].

Here we report the study [3, 4] of a family of pairs of antiferromagnetic Cr₇Ni rings linked through Ni and Co complexes and we show that these can be exploited for proof-of-principle experiments of quantum simulation. Qubits are encoded in the Cr₇Ni ground multiplet, which behaves at low temperature as an effective $S=1/2$. The ion interposed between the qubits is used as a switch of the effective qubit-qubit interaction, thus allowing us to implement scalable single-qubit rotations and two-qubit gates such as Controlled-Z and Controlled-NOT.

To achieve this we define the computational basis within the low-energy subspace where the switch is frozen into its $M = -S$ state. In a field of few Teslas the states are practically factorized and within the computational subspace the exchange switch-qubit interaction is equivalent to a renormalization of the magnetic field felt by the two rings. Hence, within this subspace it is possible to implement high-fidelity single-qubit rotations by EPR pulses resonant with low-energy gaps. Conversely, two-qubit Controlled-phase gates can be implemented by temporarily bringing the switch to a state where it is into its $M = -S+1$ state.

The magnetic couplings and crystal field anisotropy are engineered by coordination chemistry in order to fit the requirements of the scheme. Several Cr₇Ni-Ni-Cr₇Ni variants with different geometry (Fig.1-a) are studied by means of a recently-developed [5] DFT approach and their spin Hamiltonian is deduced systematically. In addition, a Cr₇Ni-Co-Cr₇Ni variant has been characterized by means of Q- and W-band EPR spectroscopy.

The present family of compounds is characterized by the correct hierarchy of interactions to implement sequences of quantum gates and to simulate interesting physical models, such as the transverse field Ising model reported in Fig.1-b (for the Ni variant). We find that the combination of the anisotropic nature of the Co-ring exchange and the perpendicular arrangement of the two rings which makes the two qubits significantly inequivalent. This allows us to address each of the two qubits separately and makes this complex well suited for the implementation of CNOT gates and for the quantum simulation of antisymmetric Hamiltonians.

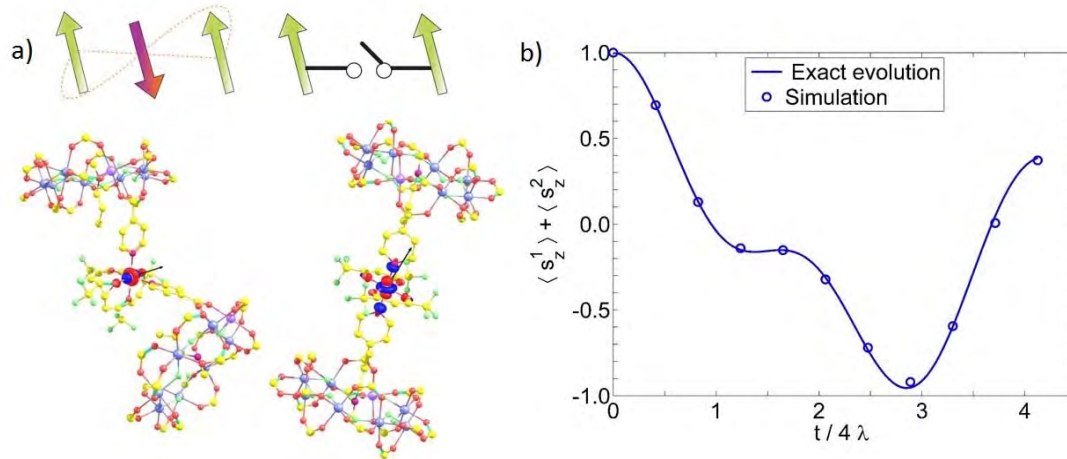
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ID: O20, 2015-09-09 12:45

Molecular nanoscience
(Oral)

Polymer-based nanostructures as robust spin transition platforms

Daniel Ruiz-Molina¹, Fernando Novio¹, Fabiana Nador¹, Pablo González¹, Nuria Vazquez¹, Jordi Hernando²

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The idea of developing magnetic molecular switchable materials into real functional electronic devices with low-cost and scalable techniques appeared with the emergence of the field several years ago. Today, even though great advances have been done with this aim, the promise of a functional device working at the micro-/nanoscale and at room temperature has unfortunately not fully completely materialized yet, as their use still strongly depends on the fabrication methodology of a robust device that can be handled and integrated without compromising their functionality.

Here we propose the use of polymeric-based platforms or matrices for the development of such robust switchable structures exhibiting reproducible results independently of the dimension - from macro to micro-/nanoscale- and morphology -from thin-films to nanoparticles and nanoimprinted motives.

To demonstrate the validity of our approach we have selected different families of valence tautomeric (VT) complexes properly selected to fulfil the challenges related with their integration into devices since the occurrence of valence tautomerism and, if so, the temperature at which it takes place have been found to be very sensitive to a variety of parameters (crystallinity, intercalation of solvent molecules, properties of the surrounding matrix, etc). This leads to an overwhelming lack of reproducibility in valence tautomeric behavior when transferring VT complexes between different media (e.g. from solution to the solid state), which has become one of the greatest roadblocks to their use in high added-value applications.

Related references of this work:

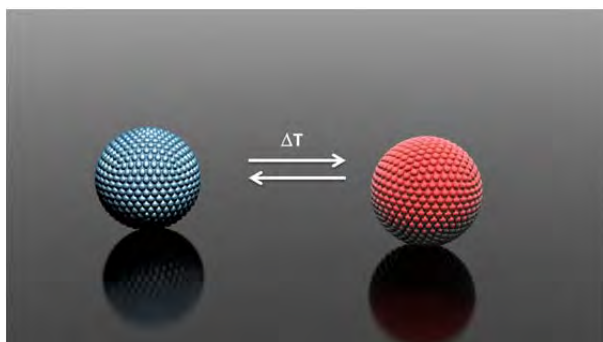
Adv. Func. Mat. 2015, in press.

Chem. Eur. J. 2015, in press

SCIENTIFIC REPORTS | 3 : 1708 | DOI: 10.1038/srep01708

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ID: O21, 2015-09-09 13:00

Switchable magnetic materials and optical magnets
(Oral)

Photoswitching dynamics of spin-crossover nanocrystals

Antoine Tissot², Teresa Delgado¹, Laure Guénée³, Céline Besnard³, Andreas Hauser¹

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Spin-crossover molecular materials are prototypes for photoactive and bistable solids, and thus their switching properties stimulate a lot of interest for fundamental and applicative goals, such as molecular switches and information storage. Precise control of their spin-state may be achieved by wavelength selective irradiation via the Light-Induced Excited Spin State Trapping (LIESST) effect.¹ Within the past few years, a lot of work has been dedicated to the synthesis of spin-crossover coordination-polymer-based nanoparticles in order to understand the effect of the size reduction on cooperative effects during the thermal spin transition.² Our aim is to elaborate switchable nano-objects, particularly by focusing on the effect of size reduction on their photoswitching dynamics.³

The spin transition dynamics has been studied on Fe(pyrazine)Pt(CN)₄ micro- and nano-objects. 4D electron microscopy has been used to probe individual nanocrystals, evidencing a photodriven thermal spin transition that strongly depends on the nanoparticle surroundings.⁴ Moreover, synchrotron powder X-Ray diffraction studies have revealed that a quantitative photo-induced conversion from the low-spin (LS) state into the high-spin (HS) state, based on the LIESST effect, can be achieved at 10K in a microcrystalline powder and in nanocrystals. Time-resolved measurements evidence that the HS→LS relaxation proceeds by a two-step mechanism with microcrystals: a random HS→LS conversion at the beginning of the relaxation is followed by a nucleation and growth process, which proceeds until a quantitative HS→LS transformation has been reached.⁵ Finally, the influence of size reduction on this switching mechanism will be presented.

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Characterization of Molecular Magnets on Surfaces by DFT: $[\text{Fe}_4(\text{Ph-C}(\text{CH}_2\text{O})_3)_2(\text{dpm})_6]$ on Au(111)

Federico Totti¹, Silviya Ninova¹, Alessandro Lunghi¹, Guglielmo Fernandez-Garcia¹, Roberta Sessoli¹

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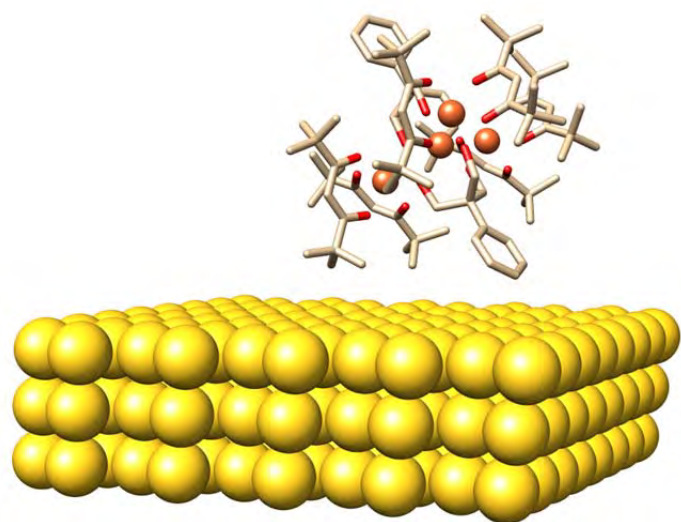
New ibrid nonostructures confirm to be a very hot research topic since they can boost, for instance, the data storage and new sensors technology development. In particular, since their magnetic behavior could be moduled by electro-magnetic fields, the possibility that the spin state of molecular nanomagnets could be set through electric fields can represent a key possibility to develop miniaturized high density memory units.

The quantum-mechanical calculations have become extremely important for the project, synthesis, characterization and rationalization of such complex new materials. The study of the $[\text{Fe}_4(\text{Ph-C}(\text{CH}_2\text{O}_2\text{O}_3)_2(\text{dpm})_6]$ adsorbed on gold. $\{\text{Fe}_4\}@Au(111)$, represents a step to the control of the nanoscale organization of SMMs to be integrated into molecular spintronic devices [1]. A preferential orientation of $\{\text{Fe}_4\}$ complexes on a surface is, therefore, mandatory and a lot of chemical tailoring work to achieve such results is still under study. The system is actually modeled through a no reconstructed Au(111) surface with three layers for a total of 240 gold atoms with the SMM on top of it. The calculations were performed within the P-GPW/revPBE+D3 approach. [2,3,4].

*This research has been supported by the European Research Council through the Advanced Grant MolNanoMaS.

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Gadolinium formate grown on Si surface for cryogenic magnetic refrigeration

Giulia Lorusso¹, Eva Natividad¹, Marco Evangelisti¹, Olivier Roubeau¹

1) Instituto de Ciencia de Materiales de Aragón (ICMA)

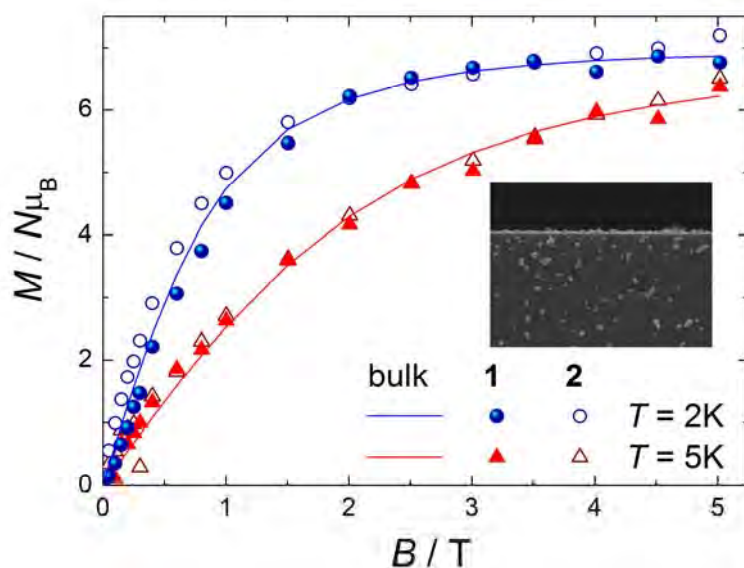
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Recently, we found that the Metal-Organic Framework (MOF) material with formula $\text{Gd}(\text{OOCH})_3$ shows an extraordinarily large magnetocaloric effect (MCE), comparing favorably with conventional magnetic refrigerants for liquid-helium temperatures, such as the benchmark Gadolinium Gallium Garnet. [1]

Here, we target a step forward toward the integration and exploitation of $\text{Gd}(\text{OOCH})_3$ in a micron-sized device for on-chip local refrigeration. Taking advantage of synthetic and technological strategies already developed for MOF materials, we have grown $\text{Gd}(\text{OOCH})_3$ nano-crystals on Silicon surface by using pre-functionalization with Self-Assembled Monolayers of two thiols: MUDA (1) and MHDA (2). Thorough topographic, structural and chemical characterization by AFM, FESEM, XPS and out-of-plane X-Ray diffraction allows to confirm the successful growth of $\text{Gd}(\text{OOCH})_3$ and indicates a preferential orientation along the 110 crystallographic axis. Finally, we present SQUID magnetization measurements which confirm that the magnetic properties, and so the corresponding MCE, of the arrays of $\text{Gd}(\text{OOCH})_3$ nano-crystals on the Si surface are unchanged with respect to the bulk parent material.

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A detailed magnetic study of the $\text{Fe}_{9-x}\text{Co}_x[\text{W}(\text{CN})_8]_6$ clusters ($x = 0 - 9$)

Anna Majcher¹, Robert Podgajny², Szymon Choraży², Jan Stanek¹, Wojciech Nogaś², Michał Rams¹, Marcin Kozieł², Ewa Juszyńska-Gałązka³, Barbara Sieklucka²

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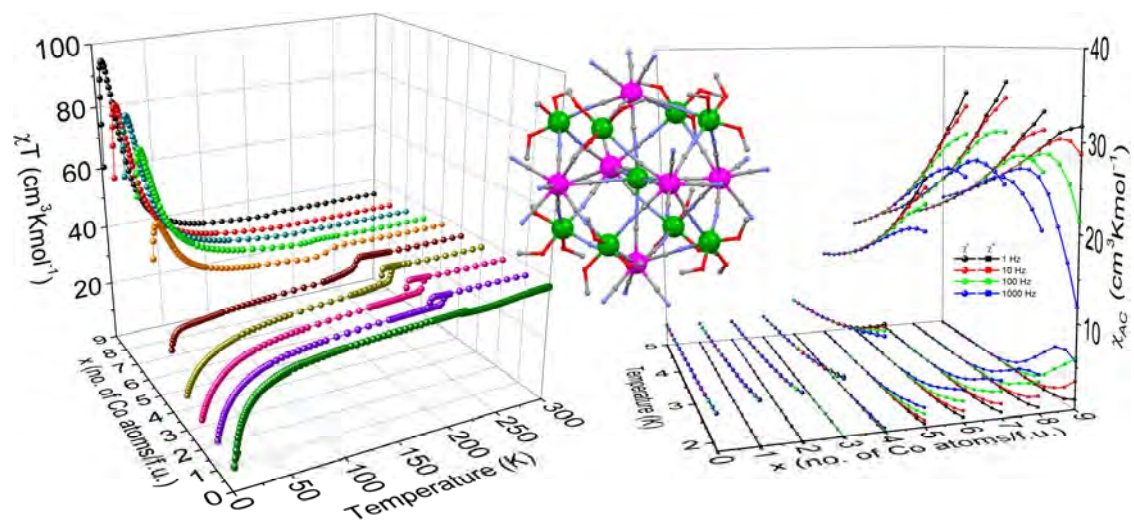
A thorough study of the magnetic properties of a series of $\text{Fe}_{9-x}\text{Co}_x[\text{W}(\text{CN})_8]_6$ clusters ($x=0-9$) is presented. The discussed system, with the controllable x parameter, shows a strong dependence of magnetic properties on Co/Fe stoichiometry.

For high Fe concentrations ($x = 0 - 4$), the clusters exhibit sharp structural phase transitions at relatively high temperatures (around 211, 207, 206, 197 and 183 K for $x = 0, 1, 2, 3$ and 4, respectively), which has already been reported for one of the compounds ($x = 3$)^[1]. The transitions are reversible and occur with significant thermal hystereses (with widths of 6, 14, 17 and 11 K for $x = 0, 1, 2$ and 3, respectively; no hysteresis was observed for $x = 4$). In the case of $x = 0$ (Fe_9W_6) the transition is induced by the $^{\text{HS}}\text{Fe}^{\text{II}}\text{W}^{\text{V}} \rightarrow ^{\text{HS}}\text{Fe}^{\text{III}}\text{W}^{\text{IV}}$ electron transfer (in the decreasing temperature mode) with a possible partial contribution of spin crossover on the central Fe atom: $^{\text{HS}}\text{Fe}^{\text{II}} \rightarrow ^{\text{LS}}\text{Fe}^{\text{II}}$. In the case of $x = 1 - 4$ the transitions are caused by two simultaneous processes: the previously mentioned $^{\text{HS}}\text{Fe}^{\text{II}}\text{W}^{\text{V}} \rightarrow ^{\text{HS}}\text{Fe}^{\text{III}}\text{W}^{\text{IV}}$ electron transfer and an electron transfer with additional spin crossover on the Co centres: $^{\text{HS}}\text{Co}^{\text{II}}\text{W}^{\text{V}} \rightarrow ^{\text{LS}}\text{Co}^{\text{III}}\text{W}^{\text{IV}}$. In the case of rising temperature the exact opposite process takes place. For $x = 5$ and 6 the transition gradually disappears (see Fig. 1 on the left). The occurrence of the transitions was confirmed by other techniques (XRD, ^{57}Fe Mössbauer spectroscopy, DSC measurements).

For the increasing concentration of Co centres within the cluster ($x = 5 - 9$), another effect emerges: the clusters start to show a frequency dependence of the AC susceptibility at low temperatures (Fig. 1 right), which implies the occurrence of slow magnetic relaxations. The AC data vs. frequency taken at a series of temperatures were fitted using the Cole-Cole model, which delivered a thorough characterisation of the relaxations. The obtained α parameter, which describes the distribution of the relaxation times, was within the range $\alpha = 0.4-0.7$.

The clusters under discussion are extremely interesting considering their stoichiometry-dependent behaviour which provides a useful tool for controlling both the DC and AC magnetic properties.

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Molecular nanomagnets
(Oral)

Mononuclear 3d/4f (Easy Plane & Easy Axis) Single Molecule Magnets containing Curcuminoids and their Prospects in Molecular Electronics

Núria Aliaga-Alcalde¹, Raúl Díaz-Torres², Arántzazu González-Campo³, Olivier Roubeau⁴, Simon J. Teat⁵, E. Carolina Sañudo², Alessandro Sorrenti³, Ferry Prins⁶, Enrique Burzuri⁶, Herre S. J. van der Zant⁶

1) ICREA (Institució Catalana de Recerca i Estudis Avançats)-ICMAB/CSIC 2) Facultat de Química/Universitat de Barcelona 3) ICMAB-CSIC (Institut de Ciència dels Materials de Barcelona) 4) Instituto de Ciencia de Materiales de Aragón (ICMA)/CSIC and Universidad de Zaragoza 5) Advanced Light Source/Lawrence Berkeley National Laboratory Berkeley 6) Kavli Institute of Nanoscience/Delft University of Technology

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The realistic use of the bottom-up approach in areas as nanoscience and nanotechnology requires the implementation of well-developed equipment, capable of providing stimuli (and analyses of the outcome) together with the development of molecules with tailored properties (eg.: magnetic, electronic, fluorescent,...) suitable for such studies (capable of providing the outcome).^[1] Therefore, the design and complete understanding of the molecular systems, that later can be addressable by external stimuli, directly associates with the progress on the above areas.

In this regard, we do direct our efforts to integrate straightforward functional coordination compounds in the related fields of molecular nanomagnets and molecular electronics.^[2] These molecular materials are designed building blocks where the final features correspond to the sum of the metallic (3d/4f centers) and organic features.

The organic groups selected for such enterprise are Curcuminoids (CCMoids) which, by definition, are molecules that relate to a natural product named Curcumin (CCM). CCM and CCMoids are been fully studied as anticancer, antimutagenic, antioxidant and antiinflammatory agents. However, much less is known about their application in other fields of research.^[2]

Here I present a family of mononuclear Co^{II}/Dy^{III}/Yb^{III}-9Accm coordination compounds with emphasis on the increasing relevance of such metals in the area of molecular magnetism.^[3,4] All these species present SMM behavior in the presence of an external magnetic field with positive and negative D values. Studies in solution and solid state of the latest show their different luminescent properties, where the ligand 9Accm acts as a fluorophor and/or antenna allowing fluorescence in the visible and/or Near-IR regions. Preliminary nanostructuration studies of all the compounds on HOPG and Si(100) surfaces show the great affinity of these systems toward graphite substrates elucidating their possible use as components in carbon based nanodevices.^[4]

The above coordination compounds are being studied toward their implementation in graphene electronic devices. Preliminary results achieved with the free ligand, 9Accm,^[3] and a Cu^{II}-9Accm coordination compound,^[5] have shown the potential application in molecular electronics.

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ID: O26, 2015-09-09 16:15

Modelling and theory
(Oral)

***Ab initio* inspection of magnetic exchange coupling in nitronyl-nitroxide radical-based lanthanide complexes**

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1) Institut des Sciences Chimiques de Rennes UMR 6226 CNRS-UR1, Université de Rennes 1, 35042 Rennes Cedex, France 2) Departamento de Química Física, Universidad de Sevilla, Profesor Garcia Gonzalez s/n, 41012 Sevilla, Spain 3) UEB, INSA, ISCR, UMR 6226, 35708 Rennes Cedex, France

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The use of lanthanide ions in extended magnetic networks is limited by the internal character of the 4f orbitals and the consequent poor involvement in the magnetic exchange.¹ Nevertheless, when interactions are mediated by magnetically non-innocent ligands like nitronyl-nitroxide radicals they can be significant also at relatively large distance and give rise for example to single-chain magnet behavior.^{2,3}

Studies on smallest molecular entities (i.e. monomers of the corresponding chains) has already highlighted the importance of 4f single ion anisotropy⁴ in the overall behavior of the chains⁵ however little is known about the mechanism and the pathways at the origin of the magnetic coupling.

In this framework we focused our attention on monomers of general formula $[Y^{III}\text{-Rad}]_2$ where "Rad" is a family of four closely related nitronyl-nitroxide radicals. *Ab initio* calculations based on the CASSCF/DDCI methodologies⁶ allow us i) evidencing the importance of through-space magnetic exchange interactions in the overall magnetic behavior of these complexes and ii) understanding the mechanisms at the origin of the various magnetic exchange paths.⁷



Nano-Cyclic Molecular Magnets

Amer Baniodeh ¹

1) Institute of Nanotechnology (Karlsruhe Institute of Technology)

* Annie Powell, annie.powell@kit.edu

Coordination clusters have recently been systems contain finite properties a cyclic system numbers of metal ions enclosed within a shell of ligands. The special case of cyclic coordination be understood in terms of finite chains of metal ions to give a ring structure. We which contain Fe(III) ions as well as ions from the 4f series. In addition, we intriguing chiral separations on such cyclic systems.[1]

Furthermore, in terms of the electronic, where the meta which are "joined up" I ions are cooperatively way, usual electronic structures can result. Results on the system-for example- $[\text{Fe}_{10}\text{Ln}_{10}(\text{Me-teaH})_{10}(\text{Me-tea})_{10}(\text{NO}_3)_{10}] \{\text{Nd}, \dots, \text{Lu and Y}\}$ reveal that structure is critically dependent on the nature of the 4f ion (Kramer or non-Kramer) with showing femtosecond timescale events within the cyclic cluster and a hopping tran between individual clusters.[2]

These clusters can which are "joined up" have up to 3nm diameter and behave in some cases as nanoparticles but also as molecular materials. The system is ferromagnetic (for Gd analogue with a record $S_T = 120/2$) with applications. All these properties record magnetic effect. The Tb and Dy analogues show single molecule magnetic behaviour. The c are photo reductive and effect on magnetism when irradiate it with laser. In addition, they are stable in we demonstrated that they can be used as Magnetic Agents (MRT applications). mentioned properties could be confirmed and even in one molecule.[3, 4] Being Single Molecule Magnet is a very iant target of nano-magneto-scientists toward quantum computing and data storage and of nano-toroidal as well as can be presented other exg examples of chiral toroidal ring possible applications of this clusters and their SMM properties in this talk.

Biography

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Amer Baniodeh has completed his PhD degree doing his habilitation aiming with *Suma Cum Laude* by Prof. Annie K. Powell at Karlsruhe Institue of Technology in October 2012 at Institute Chemistry and a principal investigator at Institute for Nanotechnology and full professor carrier.

ADVANCED FUNCTIONAL MATERIALS

LANTHANIDES

On page 6450, A. K. Powell, A. H. Unterwiesing, K. Goll, and co-workers report an investigation of both intra- and intermolecular electron transfer processes in a family of rare-earth metal (REIII)–pyridine–oxadiazole–diolates. Photo-induced intramolecular electron transfer proceeds via radical formation on the oxadiazole bridge. Intermolecular transport is rationalized using a hopping model. In both cases, the lanthanide part of the lanthanide site is important.



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Molecular routes to magnetic nanoparticles
(Oral)

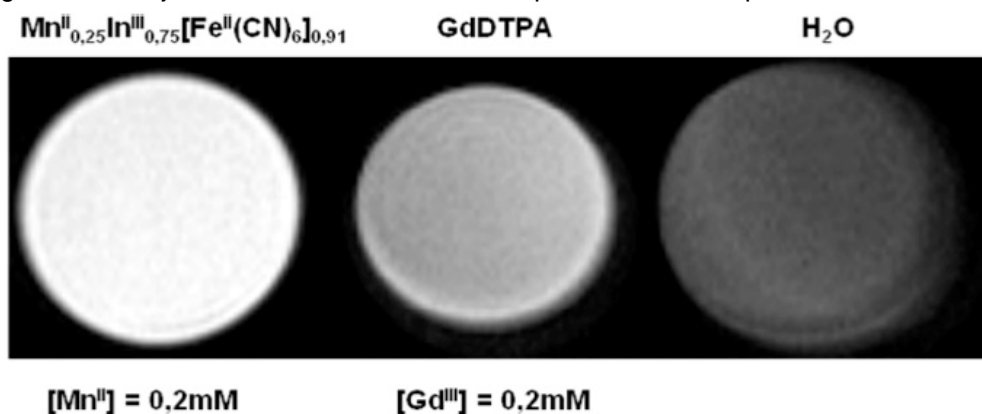
Contrast agents based on Prussian blue analogues

Gabriella PAUL¹, Yoann PRADO¹, Lucie SANCEY², Olivier TILLEMENT², Lucie VANDER ELST³, Sophie LAURENT³, Robert MULLER³, Talal MALLAH¹, Laure CATALA¹

1) LCI, ICMMO, Université Paris Sud, France 2) LPCML, UMR 5620 CNRS, Université Lyon 1, France 3) NMR and Molecular Imaging Laboratory, Université Mons Hainaut, Belgique

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Coordination chemistry offers the possibility to tailor in metal-based coordination networks platforms at the nanoscale for diagnosis or biomedical applications. This communication will focus on nanoparticles and core shells of Prussian blue analogues (PBA) based on Mn^{II} and Gd^{III} that can be tuned at will, with an excellent control over size and protected by biocompatible polymers. Large relaxivities have been observed at very low Mn^{II} and Gd^{III} content, due to a location of these active ions at the periphery of the particles. The advantages offered by these original nano-objects will be discussed and compared to recent reports in the literature.





Spin spectroscopy of molecular nanomagnets with a radio frequency scanning tunneling microscope

Stefan Müllegger¹, Stefano Tebi¹, Reinhold Koch¹

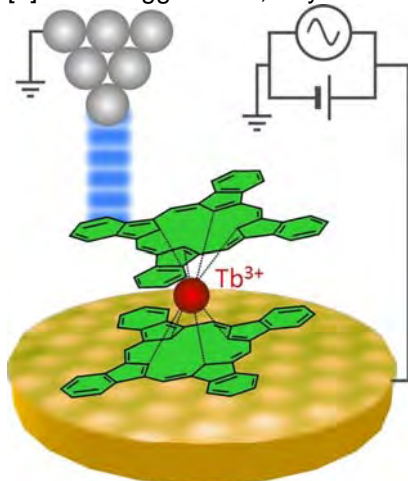
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The aim of this work is to combine the analytic power of magnetic resonance methods with the unrivalled spatial resolution and manipulation capability of the scanning tunneling microscope (STM). For this purpose, we have modified a commercial low temperature STM with a dedicated radio-frequency (rf) generation and detection system. Our STM is capable of adding a variable ac modulation between 10 MHz and 4 GHz to the dc tunneling current [1]. The frequency of the ac component is tuned into resonance with low-energy (micro-electronvolt) transitions of the sample under investigation, in particular, spin transitions under a static external magnetic field of the order of 10 mT. The response signal is the dc tunneling conductance between the STM and the rf-excited sample obtained at different excitation frequencies. With our novel technique, we have studied single molecules of the archetypal terbium double-decker single molecule magnet adsorbed on Au(111) at 5 K. We demonstrate the successful resonant spectroscopy of the complete manifold of nuclear and electronic magnetic transitions of single quantum spins in single magnetic molecules within the experimental bandwidth [2]. In particular, we achieve sub-nanometer spatial resolution combined with single-spin sensitivity. The method of resonant radio-frequency scanning tunneling spectroscopy (rf-STs) offers, atom-by-atom, unprecedented analytic power and spin control, which may impact diverse fields of nanoscience and nanotechnology.

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Switchable magnetic materials and optical magnets
(Oral)

Constructing Multidimensional Spin-Architectures from $[\text{MF}_6]^{x-}$ Modules

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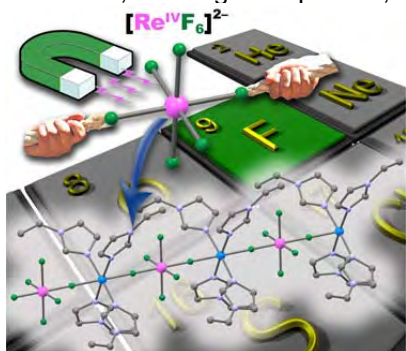
Diffuse orbitals and large magnetic anisotropy resulting from strong spin-orbit coupling make complexes with central ions from the 4d and 5d series interesting modules for magnetic materials [1]. Herein, we present the synthesis, characterization and properties of several homoleptic fluoride complexes, $[\text{MF}_6]^{x-}$, of the heavier transition elements ($\text{M} = \text{Ru}, \text{Re}, \text{Os}, \text{Ir}, \dots$) and uranium, and their incorporation into bimetallic (porous) magnetic networks. The preponderant linearity of $\{\text{M}-\text{F}-\text{M}'\}$ motifs is a viable way to acquire structure-directing control over the myriad of possible outcomes of chemical reactions involving metal-ion centers.[2] Combining principles from solid-state chemistry (e.g. F_2 and HF_2^- melt fluorinations) with “softer” coordination chemistry principles provides a possibility to explore novel types of molecular materials based on metal-ion modules that cannot be prepared by traditional solution chemistry routes, including many $[\text{MF}_6]^{x-}$ systems.[3] The close-to-octahedral symmetry of $[\text{MF}_6]^{x-}$ units largely conserves orbital angular momenta, and the spin and orbital momenta have been quantified by X-ray magnetic circular dichroism spectroscopy, and provide for peculiar magnetic properties, including slow paramagnetic relaxation. Conclusively, our results reveal structurally simple, robust and strongly magnetically anisotropic $[\text{MF}_6]^{x-}$ complexes of the heavier transition elements to be unique, convenient building blocks for magnetically interesting, molecular systems.

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Ferro- and antiferromagnetic super-exchange coupling: The role of the ligands in the $\text{Dy}_2\text{ScN@C}_{80}$ and $\text{Dy}_2\text{TiC@C}_{80}$ endofullerene nanomagnets

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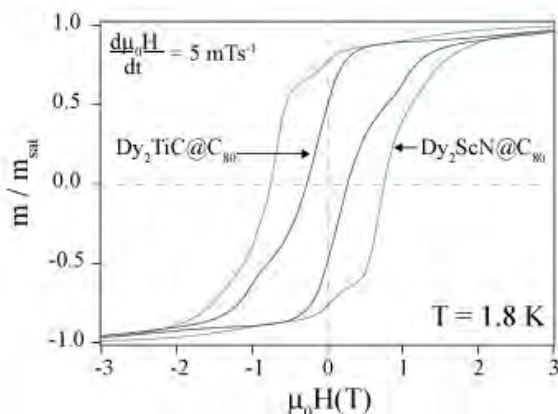
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Endofullerenes [1] represent a new family [2] in the class of lanthanide-based single molecule magnets [3]. A fascinating example is the dysprosium-scandium-nitrogen based $\text{Dy}_n\text{Sc}_{3-n}\text{N@C}_{80}$ ($n = 1-3$) series, where the entrapped cluster combines diamagnetic Sc^{3+} and/or paramagnetic Dy^{3+} species at the corners of a triangle with a central N^{3-} ion. The ligand fields, mainly from the N^{3-} ion, results in an axial anisotropy where the magnetic easy axis is directed along the corresponding Dy-N bonds. Additionally, for the polynuclear Dy clusters ($n=2,3$), the central N^{3-} ion mediates a superexchange coupling that, in combination with the dipolar interactions, leads to a ferromagnetically coupled ground state with blocking of the magnetization ($n=2$), or frustration ($n=3$) [3].

Here we compare $\text{Dy}_2\text{ScN@C}_{80}$ with $\text{Dy}_2\text{TiC@C}_{80}$. Both behave as single molecule magnets with 100 second blocking temperatures of 5.5 K [2] and 1.8 K, respectively. From analogy to $\text{Lu}_2\text{TiC@C}_{80}$ [4] the endohedral TiC sub-unit is expected to be diamagnetic. However, the magnetisation curves of $\text{Dy}_2\text{TiC@C}_{80}$ indicate a lower exchange and dipolar coupling, which in turn suggests antiferromagnetic exchange for the latter. This opens new opportunities for single molecule magnets, in particular the relative simplicity and knowledge of the structures should open doors for testing of theories on super-exchange in dipolar fields.

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Magnetization curves from $\text{Dy}_2\text{ScN@C}_{80}$ and $\text{Dy}_2\text{TiC@C}_{80}$ recorded at 1.8 K using SQUID at a field sweep rate of 5 mT s⁻¹.



Dynamic magnetic MOFs

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Metal-organic frameworks (MOFs) have attracted much attention in the last 20 years due to the wide range of applications and physical properties, caused by the unlimited combination of organic ligands and metal centres. Here we present three different magnetic phenomena that have been incorporated into MOFs providing examples of different dynamic magnetic MOFs:^[1] i) spin-crossover phenomena; ii) magnetic cooperativity; iii) magnetic relaxation.

First, we present a family of Fe^{II} coordination polymers which shows spin-crossover behaviour and selectively separates different mixtures of gases.^[2] Despite the lack of permanent channels, these coordination polymers effectively trap a wide range of gas molecules into the internal cavities due to the flexible and dynamic nature of the framework. The presence of spin-crossover centres permits elucidating the strength of the interaction between the gas molecules and the framework, the strongest response being found for CO₂.

Secondly, we combine magnetic cooperativity and gas sorption and show that the chemisorption of gaseous HCl molecules by a non-porous one-dimensional coordination polymer instigates drastic modifications in the magnetic properties of the material, switching from strong antiferromagnets to ferromagnets upon gas sorption.^[3] These conversions result from profound structural changes, involving cleavage and formation of covalent bonds caused by the removal/addition of ligands from the framework itself, but with no disruption of crystallinity.

Finally, we describe the formation of a MOF with nodes that have single-molecule magnet (SMM) behaviour,^[4] which has been achieved by using mononuclear lanthanoid analogues, also known as single-ion magnets (SIMs). The incorporation of bulky polyoxometalates (POMs) into the cavities of the SIM-MOF has been done by anion exchange, which do not interfere with the slow magnetic relaxation.

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Emergent Magnetism in Metallo-Molecular Interfaces

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Although some rare earths like Gd can exhibit magnetic ordering at relatively high temperatures, only three elements are ferromagnetic at room temperature: the transition metals iron, cobalt and nickel. The origin for the ferromagnetic ordering in these metals is found in the Stoner criterion: the product of the density of states with the exchange integral must be greater than unity for spontaneous ordering to emerge.[1] Previously, we have shown that it is possible to alter the properties of ferromagnetic metallic thin films via molecular coupling and charge transfer. [2] Here, we demonstrate that it is also possible to alter the density of states of non-ferromagnetic materials, such as copper and manganese, in order to generate magnetic ordering at room temperature. This effect is achieved via coupling between metallic thin films and C₆₀ molecular layers of several nm. The emergent ferro-state can exist over several layers of the metal before being quenched at large sample thicknesses by the bulk metal properties. While the induced magnetisation is easily measurable by magnetometry, low energy muon spin spectroscopy [3] provides insight into the magnetic distribution, indicating localized spin-ordered states at and close to the metallo-molecular interface. Density functional theory simulations suggest a mechanism based on changes in the density of states and exchange integral of the metal atoms due to electron transfer. [4,5] This opens novel paths to design magnetic metamaterials using abundant, non-toxic elements. Charge transfer at molecular interfaces can be controlled via, for example, gate voltages or band matching, and then be used to control spin polarisation or magnetisation in devices for electronic, power or computing applications. [6,7]

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Benchmarking the capabilities of state-of-the-art theoretical approaches in single-ion magnets

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Lanthanide single-ion magnets (SIMs) have excited researchers working in molecular magnetism over the past decade due to their attractive physical properties. The magnetic and quantum properties of SIMs depend primarily on the anisotropy of a single ion, which results from a strong spin-orbit coupling and an adequate ligand field. In spite of the theoretical efforts to fully understand their behaviour, modelling the magnetic and spectroscopic properties of *f*-element complexes still remains an open problem. Commonly, these systems have been explained by crystal field theory, which unfortunately requires the determination of a large number of crystal field parameters (CFPs). [1] A different strategy involves the direct calculation of CFPs and all the observables using the real structure of the compounds. These predictive methods include Complete Active Space *ab initio* calculations (CASSCF and CASPT2) [2] and effective electrostatic models, such as the *semiempirical* Radial Effective Charge (REC) model [3].

In this contribution, we present a series of new SIMs that are used as model systems to test the predictive capabilities of these predictive standard tools in the field. Because the theoretical description of SIMs is rarely validated, we take advantage of the spectroscopic studies [4] and angular dependence of the single-crystal magnetic susceptibility carried out on these complexes [5]. In this process, we also study the thermal structure effects in a *b*-diketonate SIM, whose structure has been determined by single crystal X-ray diffraction at different temperatures, using both approaches.

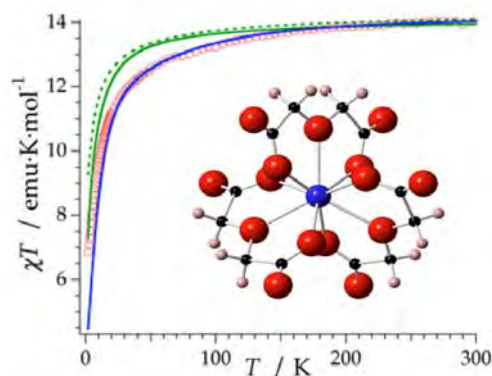
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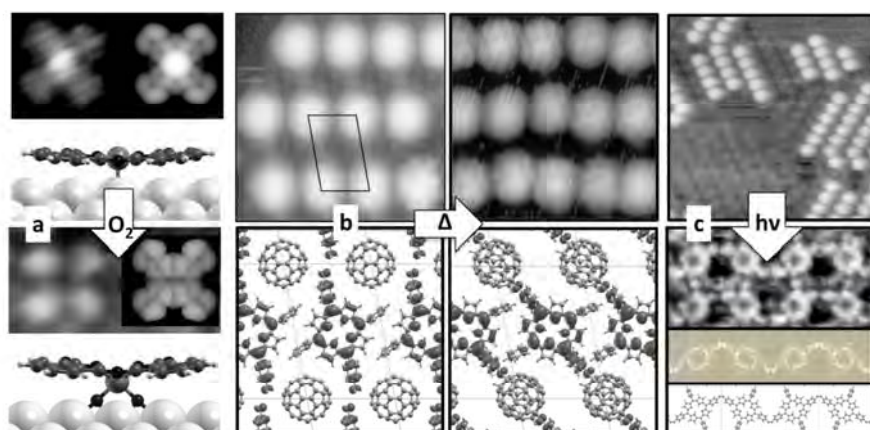
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Molecular electronics
(Poster)

Spectroscopic and Magnetic studies of different reduced states of the molybdenum Keggin

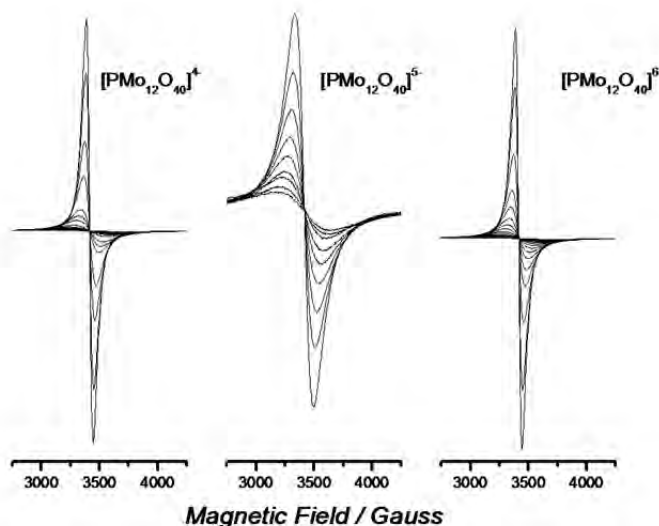
Carolina Aliaga¹, Francisco Fernandez-Vidal⁴, Javier Gonzalez-Díaz⁴, Verónica Paredes-García², Evgenia Spodine Spodine³, Diego Venegas-Yazigi¹

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Polyoxometalates (POMs) belong to an extensive family of inorganic polyanions obtained by condensation of polyhedral metal-oxygen units. Keggin, in 1933 [1] informed the first study of a 12-phosphotungstic acid structure. As the chemistry of molybdenum and tungsten are similar, molybdenum Keggin is also obtained. Considering the interesting properties of their reduced forms, some studies employing EPR shown that the hyperfine structure was only detectable at very low temperatures [2]. In the present work we studied the delocalization phenomena as a function of the interaction of the Keggin with the solvent. We performed this study in glass phase. The different mixed valence states are achieved by electro-synthesis.

Single crystal of compounds mono- bi- and three electron-reduced steps were X-ray characterized. UV spectra of the studied POMs showed a ligand to metal charge transfer transition (LMCT) for the oxidized and reduced states. The reduced states have inter-valence charge transfer transitions in the range between 550 and 1200 nm. The EPR in polycrystalline samples are shown Figure 1.





CARBONATE WINDMILLS – EFFECTIVE FIXATION OF CO₂ INTO NOVEL DISCRETE COORDINATION ENTITIES

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Chemical transformation and activation of CO₂ are considered as a long-standing challenges of the scientific community in order to reduce global warming and use the captured CO₂ as an inexpensive chemical feedstock.¹ Great efforts are dedicated by researchers for the development of metal-organic frameworks (MOFs) capable to absorb atmospheric carbon dioxide thanks to the existence of pores and high specific surface areas within their structure.² As possible alternatives for MOFs one may consider coordination compounds containing *in situ* formed carbonate ligands by fixation of CO₂ in basic media. Those kinds of compounds offer an inexhaustible source of possibilities thanks to the great variety of potential carbonate coordination modes. However, examples where carbonate ligands build the entire skeleton of the structure are still rare.^{3,4}

Here we present four novel homo- and heterometallic pentanuclear coordination assemblies with general formulae [M₅(CO₃)₄(py)₁₄]CO₃; M=Ni, Co] and [M₄M'(CO₃)₄(py)₁₂]NO₃; M=Ni, Co, M'=Na]. A common structural feature of these units is the almost perfectly planar metal-carbonate core with a square arrangement of the metal ions. This structural peculiarity comes from the very rare coordination mode of carbonate anion (μ^3 -O:O, O': O'') which is now observed for the first time in Co(II) and Na(I) systems. Easy and highly effective synthesis of the described entities as well as their long-term stability makes them suitable candidates for prolonged storage of CO₂. The properties of these compounds will be discussed following crystallographic, spectroscopic, magnetic and thermodynamic studies.

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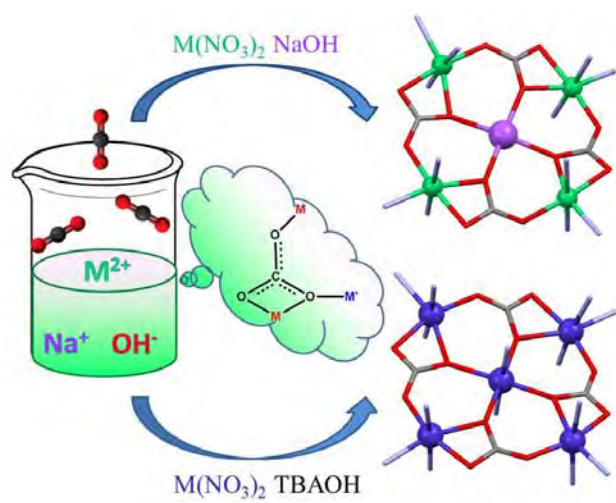
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Molecular nanomagnets
(Poster)

TOPOLOGY AND SITE SELECTIVITY IN HYDROXO-DIKETONATO BASED MOLECULAR CLUSTERS: MAGNETOSTRUCTURAL CORRELATIONS

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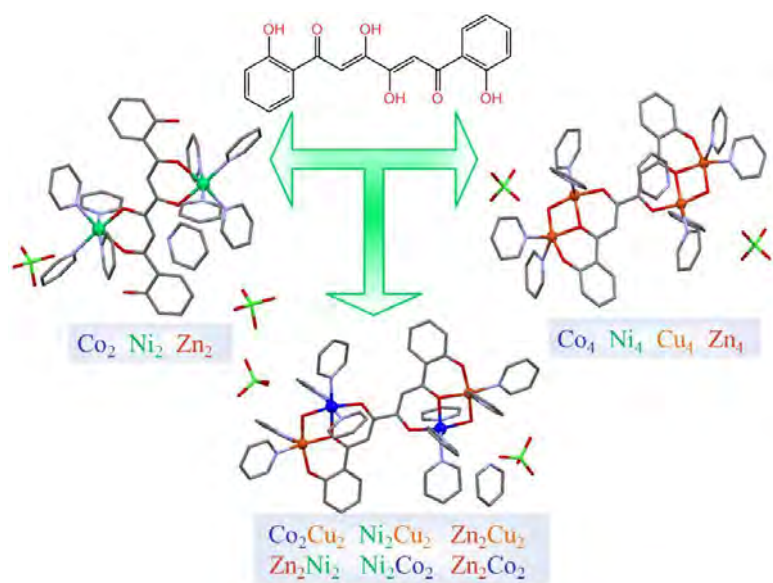
An ambitious pursuit of novel multifunctional materials with desired properties has led to the prolific discovery of exciting systems and fundamental scientific knowledge in the recent years. Particularly important progress is taking place in the arena of coordination chemistry, which has proven to be inexhaustible spring of tools in formation of metallo-organic structures embodying diverse physico-chemical properties and synthetic strategies.

The family of *bis*- β -diketone ligands represents an example of sophisticatedly engineered molecular platforms for controlled construction of polynuclear coordination molecules where according to number, size and separation of the coordination pockets, metal ions can be aligned into weakly coupled molecular cluster pairs, linear arrays, metallamacrocycles or cage clusters.¹ We have designed a new flexible ligand, 1,6-di(2-hydroxyphenyl)-1,3,4,6-hexanetetron (H₄L) which has been employed in the preparation of a family of structurally related dinuclear [M₂(H₂L)(py)₆₋₈](ClO₄)₂ or tetranuclear ([M₄(L)(OH)₂(py)₈₋₁₀](ClO₄)₂ and [M₂M'₂(L)(OH)₂(py)₈₋₁₀](ClO₄)₂) coordination clusters of 3d transition metals (M, M'=Co, Ni, Cu, Zn). The nuclearity of these clusters is controlled directly with the degree of deprotonation of the ligand and the amount of the hydroxide co-ligands while their metallic composition is defined exclusively by the nature and stoichiometry of metal ions employed in synthesis. Transoid conformation of the ligand defines the topology of these entities as two separate pairs of coordination pockets oriented in opposite directions. Analysis of the crystal structures has revealed site-selective metal composition originated from favoring different coordination geometries.² Additionally, a correlation is observed between the measured metal-ligand bond distances and the stability of the coordination compounds predicted from the Irving-Williams series. Magnetic studies reveal antiferromagnetic coupling between spin carriers which will be discussed, quantified and rationalized taking into account cluster topology, nature of the metal ions and superexchange via different ligand donor atoms.

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Molecular spintronics
(Poster)

Spin Pumping Manipulation of Transport and Spectroscopic Properties of Molecular Films

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In recent years there has been an increased interest in organic spintronics as a result of the long spin lifetimes and in some polymers long spin diffusion lengths of up to 200 nm, as well as applications in flexible electronics and optoelectronics. [1] Taking advantage of this spin coherence, carbon based materials have been used as an active spacer layer in spin injection devices where the thickness of the active layer can be orders of magnitude greater than for inorganic spacer layers while maintaining high magnetoresistance (MR). [2] A range of organic materials have been used for this purpose, among the most successful of which are tris(8-hydroxyquinolino)aluminium (Alq3), phthalocyanines and C₆₀. [3-6] This rapid progress notwithstanding, novel designs of molecular electronics and spintronics need not be limited to standard structures such as spin valves. The rich spectroscopic properties of molecular materials with respect to their inorganic counterparts remain comparatively underused in carbon-based spintronics. [7] Here, we address this problem and seek to prove the first principles of manipulating the physical properties of molecular materials in order to obtain novel or improved functionalities, such as a magneto-vibrational response or enhanced luminescent and transport responses. We do this by using hybrid magneto-molecular bilayers excited at their ferromagnetic resonance (FMR). The generated spin waves can be used to induce a pure spin current, as demonstrated in direct measurements of the inverse spin Hall effect (ISHE) in a PEDOT:PSS system as well as indirectly in PBTBT. [8] On the other hand, spin pumping itself can be used to manipulate the physical properties of the molecules. Applying this technique, we can increase the conductivity of a C₆₀ film by several percent and its luminescence by a factor of 2. The vibrational spectrum of the fullerenes, as measured via Raman spectroscopy, shows remarkable changes in the amplitude and position of Ag and Hg normal modes of vibrations during resonance. These terahertz vibrons are correlated to the applied magnetic DC and RF fields, opening new avenues of research for microwave molecular spintronic devices, magneto-optics and transducers.

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Switchable magnetic materials and optical magnets
(Poster)

INS reveals magnetic excitations in a thermal spin transition material [Mn³⁺(pyrol)3tren]

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Spin-transition phenomena found in some organo-metallic compounds are promising examples of molecular systems where magnetic bistability may be tuned and controlled by external stimuli like temperature, light or pressure. Their magnetic properties (in Low-Spin and High-Spin states) and interplay with structural properties are crucial information to address questions related to potential applications, like transition kinetics, magneto-structural correlations, quantum transitions between spin-states, etc. As a prototypical case, we have investigated by Inelastic Neutron Scattering (INS), neutron diffraction and magnetometry the magnetic properties of the spin-transition mononuclear complex [MnIII(pyrol)3tren] [1] in both high-spin (HS, S=2) and low-spin (LS, S=1) states. The system presents an abrupt Spin-Transition around 46.5K with a small hysteresis, characteristics of a collective transition process. In the HS phase, the INS spectrum at 56K and zero-field show several peaks which have been properly assigned to transitions within a Zero-Field Split (ZFS) S=2 state. The D and E parameters are derived with excellent accuracy and are compared to High-Field EPR [2]. On cooling down through the transition, these low-energy peaks disappear and are replaced by a large single magnetic peak at 4.85meV. Under magnetic field, this peak shifts up and broadens. We argue that the LS state can be described by a genuine S=1 spin-Hamiltonian, despite an unquenched orbital moment (L=1), where the observed peak corresponds to a transition M=0 to Ms=±1 with a large D=+39cm⁻¹ and a small E term. A full Hamiltonian model is proposed based on these first INS results obtained in a thermal Spin-Transition molecular magnetic system

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Digital quantum simulators in a scalable architecture of hybrid spin-photon qubits

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The ultimate quantum simulator will probably be a hybrid device exploiting the best characteristics of distinct physical systems. In particular, spin systems are characterized by long coherence times and wide chemical tunability, whereas photons stored within coplanar waveguide resonators can be locally controlled, while keeping their high mobility [1]. Here we introduce a novel scheme that can potentially realize a universal and intrinsically-scalable digital quantum simulator in a superconducting circuitry architecture [2]. We suggest an array of superconducting resonators as the main technological platform, on which hybrid spin-photon qubits can be defined by introducing strongly coupled spin ensembles in each resonator [3, 4].

One- and two-qubit quantum gates can be easily implemented by independently and simultaneously tuning the resonators modes through external magnetic fields. The mobility of photons across different resonators is exploited to perform two-qubit gates between physically distant qubits. This is done much more efficiently than by sequences of SWAP gates, and makes the class of Hamiltonians which can be realistically addressed much larger. Long-distance operations arise whenever mapping the target system of the simulation onto the register implies two-body terms between distant qubits, including the many-spin terms which implement the antisymmetric nature of fermion wavefunctions.

The time evolution of a generic Hamiltonian is decomposed into a sequence of elementary single- and two-qubits gates, which are combined to mimic the dynamics of the target Hamiltonian. We report our results for the digital quantum simulation of the transverse-field Ising model on 3 qubits, the tunneling of a spin one in a rhombic crystal field and the Hubbard Hamiltonian. The robustness of the scheme is demonstrated by including the effects of decoherence in a master equation formalism. Finally, we show how potentially harmful effects of inhomogeneous broadening of the spin ensemble are circumvented by operating the scheme in a cavity-protected regime. In this respect, high-spin molecules that possess magnetic-dipole transitions whose amplitude is roughly proportional to the spin length are particularly promising to achieve a strong coupling regime.

The proposed setup exploits the best characteristics of distinct physical systems: the long coherence times of the spins and the mobility of photons entering the hybrid encoding. Moreover, on-site tunability and scalability make this architecture extremely appealing and competitive with respect to alternative proposals.

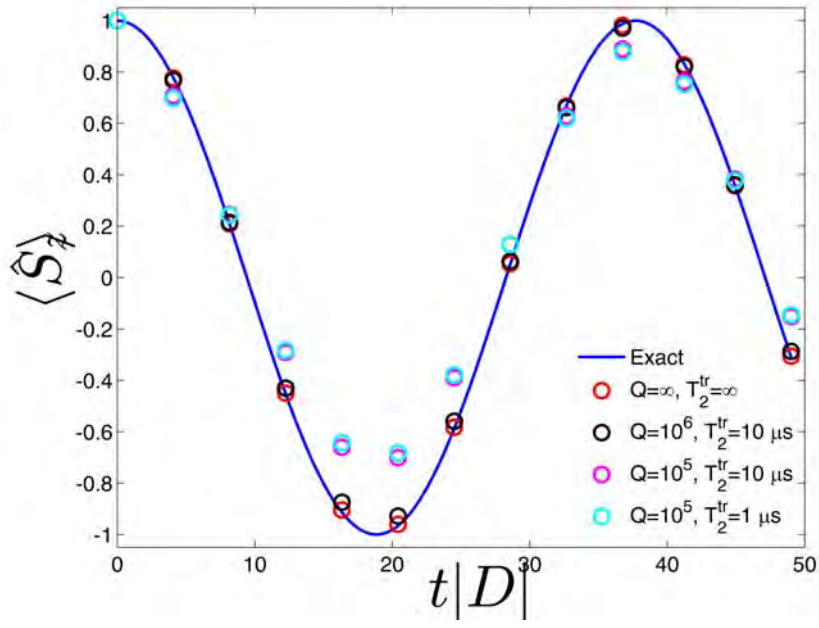
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Switchable magnetic materials and optical magnets
(Poster)

Key role of a water molecule in the hysteresis and T_c of anilate-based compounds with SCO exhibiting LIESST effect

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A hot topic in molecular magnetism is the preparation and characterization of multifunctional materials combining magnetic properties with a second interesting property as spin crossover (SCO), to prepare magnetic switchable materials. In this context, we have combined the cation $[\text{Fe}(\text{3-bpp})_2]^{2+}$ (3-bpp = 2,6-bis(pyrazol-3-yl)pyridine) with magnetic chiral $[\text{Cr}(\text{C}_6\text{O}_4\text{X}_2)_3]^{3-}$ anions ($\text{X} = \text{Cl}$ and Br)^[1] to prepare a new series of compounds formulated as $(\text{NBu}_4)[\text{Fe}(\text{3-bpp})_2][\text{Cr}(\text{C}_6\text{O}_4\text{X}_2)_3] \cdot \text{H}_2\text{O}$ ($\text{X} = \text{Cl}$ and Br). These compounds present the coexistence of the paramagnetic behaviour of the $[\text{Cr}(\text{C}_6\text{O}_4\text{X}_2)_3]^{3-}$ anions with a SCO behaviour in the $[\text{Fe}(\text{3-bpp})_2]^{2+}$ cation with critical temperatures of ca. 145 and 183 K for $\text{X} = \text{Cl}$ and Br , respectively.

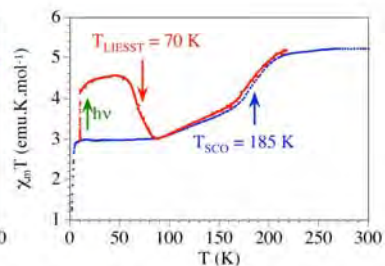
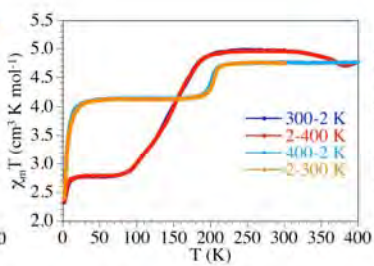
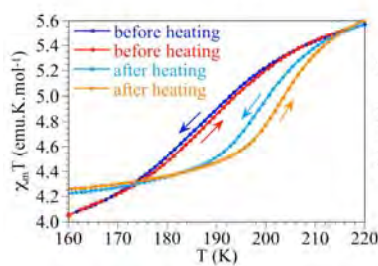
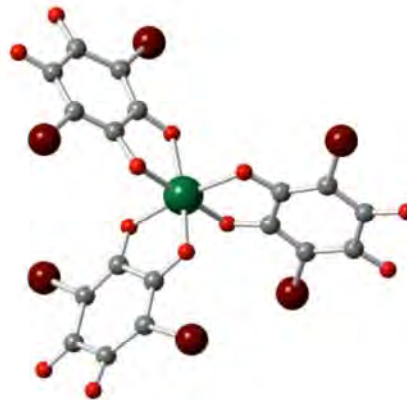
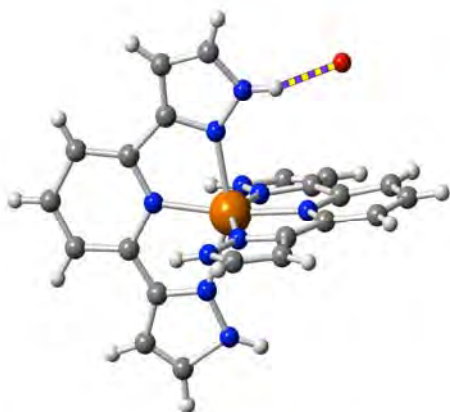
Their X-ray crystal structures show the presence of isolated $[\text{Fe}(\text{3-bpp})_2]^{2+}$ cations and $[\text{Cr}(\text{C}_6\text{O}_4\text{X}_2)_3]^{3-}$ anions with a water molecule H-bonded to one N atom of one of the two 3-bpp ligands of the $[\text{Fe}(\text{3-bpp})_2]^{2+}$ cations. Interestingly, this water molecule plays a key role in the SCO transition temperature and in the hysteresis of this transition. Thus, in the $\text{X} = \text{Cl}$ derivative when the water molecule is removed by heating the sample at 400 K the SCO temperature increases from ca. 145 to ca. 205 K and the dehydrated sample shows a small hysteresis of ca. 3 K, absent in the hydrated form. In the $\text{X} = \text{Br}$ derivative the behaviour is very similar: the removal of the water molecule leads to an increase of the SCO temperature from ca. 183 to ca. 200 K with a hysteresis of ca. 5 K, also absent in the hydrated form. In this communication we explain this unusual, although not novel,^[2] behaviour with a complete crystallographic and magnetic study of both compounds.

We will also present the LIESST effect displayed by these compounds and will show the unexpected indirect modulation of the magnetic properties of the cation (SCO temperature and LIESST effect) with the X group of the anilate-type ligand of the anion.

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2D and 3D anilato-based heterometallic M(I)M(III) lattices: the missing link

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Although crystal engineering of molecular materials is a relatively young discipline, it has already given rise to many materials designed and prepared with an appropriate choice of the precursor molecular building blocks. Most of these materials have been prepared by using well-known coordination chemistry tools: magnetic d- or f-block metal ions and simple anionic ligands as oxalate, one of the most used in the last two decades. In this work, we present a topologically analogous ligand to oxalate: anilate, in which the central C=C moiety is changed by an aromatic ring. This ligand also promotes magnetic coupling, and thus, can be used in the preparation of iso-reticular magnetic networks to those reported for oxalate-based materials, with the advantage of tuning the ordering temperature through variation of the X group.

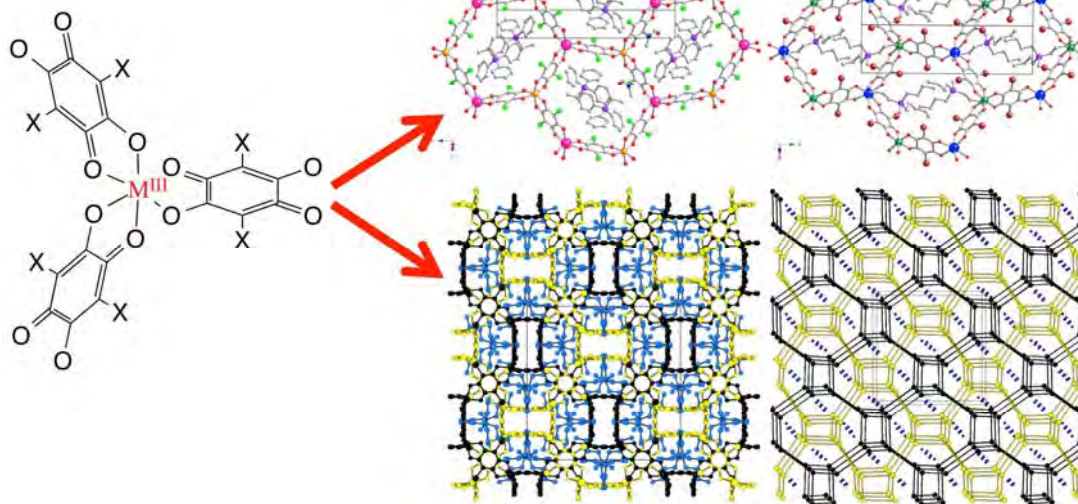
The similar bis-bidentate coordination mode of oxalato and anilato-based ligands is exploited here to create the first examples of 2D and 3D heterometallic lattices based on anilato ligands combining M(I) and a M(III) ions, phases already observed with oxalato but unknown to date with anilato-type ligands.^[1]

These lattices are prepared with alkaline metal ions and magnetic chiral tris(anilato)metallate molecular building blocks: $[M^{III}(C_6O_4X_2)_3]^{3-}$ ($M^{III} = Fe$ and Cr ; $X = Cl$ and Br , $(C_6O_4X_2)^{2-}$ = dianion of the 3,6-disubstituted derivatives of 2,5-dihydroxy-1,4-benzoquinone, $H_4C_6O_4$). The new compounds include three similar 2D lattices formulated as $(PBU_3Me)_2[NaCr(C_6O_4Br_2)_3]$ (**1**), $(PPh_3Et)_2[KFe(C_6O_4Cl_2)_3](dmf)_2$ (**2**) and $(NBu_3Me)_2[NaCr(C_6O_4Br_2)_3]$ (**3**). These three compounds present hexagonal $[M^I M^{III}(C_6O_4X_2)_3]^{2-}$ honeycomb layers with $(PBU_3Me)^+$ in **1**, $(PPh_3Et)^+$ and dmf in **2** and $(NBu_3Me)^+$ cations in **3** inserted between the honeycomb layers. We also present compound $(NBu_3Me)_2[NaCr(C_6O_4Br_2)_3]$ (**4**) which is a 3D polymorph of compound **3**. Interestingly, this polymorphism in the anilato-based networks has not been observed to date in the oxalato-based ones. Compound **4** represents the first heterometallic 3D lattice based on anilato ligands. Although the 3D (10,3)-gon lattice is chiral, in **4** there are two interlocked chiral 3D (10,3) lattices with opposite chiralities and, therefore, compound **4** is not chiral.

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2D honeycomb



3D (10,3)-gon



Hierarchical assembly of TbPc₂ molecules on surfaces

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The contest of assembling single molecule magnets (SMM) on surfaces, intended as the first step toward the development of novel SMM-based technologies, is among the most florid activities of our community, the point of contact between different expertises. In the past we learnt how to functionalise SMM and to chemisorb these molecules to specific surfaces as well as how to maintain their magnetic behaviour at the nanoscale [1] with the development of impressive single molecule based devices using break junctions [2] and carbon nanotubes [3]. However, it became more and more evident that nanostructuration of a SMMs is not an innocent process. In particular in the case Terbium(III) bis(phthalocyaninato) complexes (TbPc₂ hereafter) an erratic behaviour of the magnetization dynamics has been found depending on the specific environment in which TbPc₂ is included [4] as well as on the orientation of these molecules with respect to the substrate and the consequent occurring interactions [5-8]. Alternative approaches for binding these molecules to a substrate must be explored with the aim of extending the skills on SMMs assembling. This requires to find an universal approach exploiting supramolecular chemistry to promote persistent and reversible interactions allowing a more efficient control of the grafting of SMMs to surfaces.

Here we report the formation of monolayer and submonolayer deposits of TbPc₂ on surface via a multiple *H-bonding* hierarchical protocol [9]. A novel heteroleptic Tb-double decker system has been functionalized with a complementary unit with respect to the one present on the pre-functionalised surface allowing the controlled and reversible assembling of the molecules to the surface. According to a synchrotron-based characterization the tested protocol guarantees the conservation of the SMM magnetic properties and promotes a preferential orientation of the assembled molecules. This approach permits the reversible connection of the TbPc₂ to surfaces, independently on the nature of the surface, and envision the possibility to control the distance and the orientation of the TbPc₂ core with respect to the surface and thus to easily tune the interaction between the molecule and the surface by simply playing on the acceptor molecule used to pre-functionalise the surface.

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STM characterization of ordered assemblies of Fe₄ SMMs on Au(111) surface

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Propeller-shaped tetrairon(III) (Fe₄) clusters are one of most studied classes of SMMs. Their stability permits an easy functionalization [1], as required for chemisorption on surfaces [2,3], and UHV-based processing down to the nanoscale [4]. Since Fe₄ systems have anisotropy barriers not exceeding 20 K, studying magnetic relaxation of these complexes at the nanoscale is experimentally challenging. However, sub-Kelvin XMCD experiments evidenced that the typical memory effect, as well as the resonant quantum tunnelling mechanism, survive on Au(111) surfaces [2–4]. This result, which is rare among molecular nanomagnets, has opened the way toward the exploration of the magnetism of an individual SMM via local probes [5,6].

Here we focus on nanostructures obtained by thermal sublimation in UHV and we report the *in situ* low temperature STM characterization of Fe₄ molecules assembled on Au(111) [4,7]. Our morphological investigation revealed that the [Fe₄(L)₂(dpm)₆] (Fe₄Ph) system (Hdpm= dipivaloylmethane, H₃L=2-hydroxymethyl-2-phenylpropane-1,3-diol) can be sublimated on Au(111) forming a 2D lattice with short-range hexagonal order. An accurate image analysis allowed to distinguish between regions where the Fe₄Ph molecules are directly adsorbed on the gold surface from regions where they lie on top of a wetting layer of impurities, presumably deriving from a partial decomposition of the molecule.

These high-resolution STM studies open several perspectives on the local characterization of individual Fe₄ molecules as well as on the realization of ordered SMM arrays and, at the same time, alert to the inherent difficulties in achieving a pure monolayer of SMMs.

We acknowledge the financial contribution of the ERC through the AdG MolNanoMaS (267746)

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New approaches to obtain uranium SMM compounds

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Single-molecule magnets (SMMs) based on actinides compounds are important counterparts in comparison with lanthanide analogues in order to understand the key parameters determining the features and the mechanisms of slow relaxation of magnetization observed at low temperatures and their study became a hot topic in molecular magnetism [1]. Although in a still scarce number, and mainly restricted to mononuclear U(III) species [1-5], these studies could put clearly into evidence effects, such as different ligand environments, magnetic dilution, charge of the co-ligand, and different coordination geometries. The effect of the oxidation state of uranium, which is known to exist in the range +2 to +6, has remained less explored. Besides U(III), only one example based on a mononuclear uranium(V) system has been identified [6] and so far no examples of SMMs based on uranium(IV) have been reported. The U(IV) ion, an f^2 system with a 3H_4 ground state, is a non-Kramers ion, which generally presents an orbital singlet ground state at low temperatures. Lacking the magnetic bistability of the ground state required for slow magnetic relaxation, U(IV) is thus believed not to be a suitable candidate for generating single-ion magnets (SIMs) [7] and, in fact, SIM behavior was explicitly reported as absent in some U(IV) compounds. However, we show how an appropriate choice of the coordination environment and the presence of a radical may circumvent this constraint. In fact, we have demonstrated that the presence of a radical ligand enhances their magnetic behavior inducing the appearance of slow magnetic relaxation under zero static magnetic field [5]. The same principle can be applied to a non-Kramers ion as U(IV) through magnetic exchange coupling with a radical ligand (half-integer spin) in order to produce a Kramers magnetic molecule capable of slow magnetic relaxation. An overview of uranium compounds containing different ligands, bipyridine and azobenzene, radical or non-radical, will be presented in this contribution. The implications of the structural diversity taking into account the U environment will be discussed by a combination of the experimental study of their magnetic behaviour with an analysis considering a full single-ion Hamiltonian under an effective electrostatic model [8].

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Switchable magnetic materials and optical magnets
(Poster)

Slow magnetic relaxation in Erbium(III) complexes with 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione as the primary ligand

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Over the past few years, significant research has been devoted to the development of multifunctional materials which combine a set of well-defined properties for specific technological applications. In this context, lanthanide complexes with organic ligands are excellent candidates due to their interesting magnetic and luminescent properties [1].

We recently reported the synthesis and structure of three Er^{3+} complexes containing a fluorinated β -diketonate ligand, 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione [2]. These new ternary Er^{3+} complexes, which only differ in the neutral ligand, the diimide, emit in the C band transmission window for fibre optic communications. The choice of the ancillary ligand (2,2'-bipyridine, bathophenanthroline or 5-nitro-1,10-phenanthroline) was shown to determine the efficiency of the *antenna effect*, leading to a complete quenching of the ligand-associated visible emission and to an enhancement of the near infrared (NIR) emission in the case of 5-nitro-1,10-phenanthroline.

In this work, the ability of these same ligands to provide an environment for the lanthanide ion that promotes the existence of an anisotropic barrier to magnetization reversal has been probed by measuring the magnetic properties of aforementioned three Er^{3+} highly-coordinated compounds. From this study, and similarly to other previously Er^{3+} β -diketonates reported by us [3, 4], slow relaxation of the magnetization has been found with energy relaxation barriers ranging from 7 to 14.6 cm^{-1} .

In order to find the orientation of the g-tensors for the ground and excited states, we have resorted to CASSCF+RASSI calculations using MOLCAS software [5]. All the eight Kramers doublets have been found to span over an energy window of circa 300 cm^{-1} . From those calculations we have been able to conclude that the magnetic relaxation occurs through the first excited state, only 20-30 cm^{-1} above the ground state.

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Controlled Assembly of Single-Molecule Magnets on Gold Nanorods

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In recent years, the research interest in the field of molecular magnetism shifted from the synthesis and characterisation of Single-Molecule Magnets (SMMs) to the development of protocols for the deposition of SMMs on various surfaces, the detection and manipulation of the magnetic moment of individual SMMs deposited on surfaces and the understanding of the interplay between SMM and surface properties.[1]

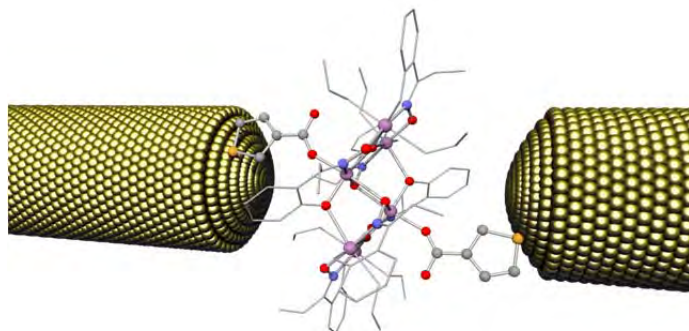
The coupling of SMMs with various nanometre-sized structures is a promising “bottom-up” approach that can be applied in the development of novel molecule-based devices and in the investigation of SMM-substrate interactions.[1,2]

We present our work in relation to the controlled assembly of SMMs on gold nanorods (AuNRs). The choice of AuNRs confers the possibility to obtain two types of hybrid systems. The first one consists of SMM deposition on the surface of AuNRs at monolayer or sub-monolayer coverage. The second target system is characterized by an end-to-end linking of AuNRs via an SMM linker. Moreover, AuNRs functionalized with S-donor groups at their surface, appear to be paramagnetic or even super-paramagnetic.[3] Thus, such SMM-AuNR hybrid systems could exhibit additional exciting magnetic properties due to the interaction of the components.

We use Mn(III) oxime bridged SMMs that we functionalized with appropriate groups to show chemical affinity towards AuNR surface. The assembly is performed in solution. This allows characterization of these systems in solution and/or in bulk solid state by conventional techniques such as SQUID magnetometry, EPR, optical absorption spectroscopy and TEM.

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Molecular nanomagnets
(Poster)

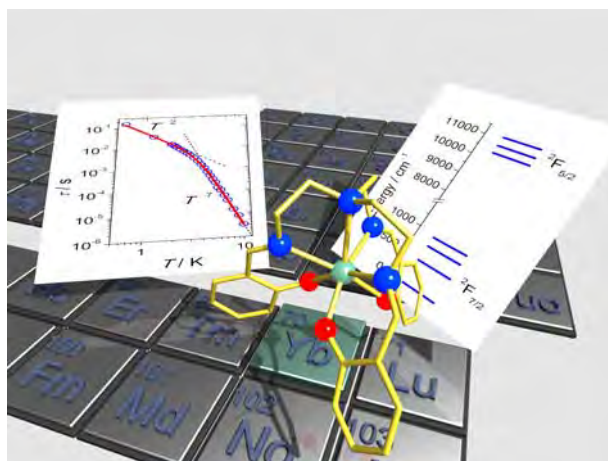
Design of Single-Molecule Magnets: Insufficiency of the Anisotropy Barrier, as the Sole Criterion.

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Determination of the electronic energy level diagram of a trigonal-symmetry mononuclear Yb³⁺ Single Molecule Magnet (SMM) by high-resolution absorption and luminescence spectroscopies reveals that the first excited electronic doublet is placed at more than 400 cm⁻¹ above the ground one. Fitting of the paramagnetic relaxation times of this SMM to a thermally activated Orbach model ($\tau = \tau_0 \times \exp[\Delta_{\text{Orbach}}/(k_B T)]$) affords an activation barrier, Δ_{Orbach} , of only 38 cm⁻¹. This result is incompatible with the spectroscopic observations. Thus, we unambiguously demonstrate, solely based on experimental data, that Orbach relaxation cannot *a priori* be considered as the main mechanism determining the spin-dynamics of SMMs. The present study demonstrates that the general synthetic approach of optimizing SMM behaviour by maximization of the magnetic anisotropy/ligand field associated energy barrier, as the only synthetic parameter to be tuned, is insufficient because it neglects the interaction of the molecular magnetization with its environment. Thus, synthetic procedures need to consider additional design criteria, that address the presence of alternative relaxation processes besides the Orbach one. Along these lines optimization of Raman processes by tailoring of lattice phonon states appear a viable approach to yield both further insights and to optimize SMM behaviour.





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Molecular nanomagnets
(Poster)

Spectroscopic evidence for the enhanced interactions in a lanthanide cluster

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Long awaited applications of molecular magnets critically depend on the enhancement of their blocking temperatures. Molecules containing rare-earth ions are promising candidates because of strong anisotropy and large individual magnetic moments. However, the first polynuclear lanthanide clusters suffered from a low interaction strength between the magnetic moments. An N_2^{3-} radical-bridged dinuclear lanthanide molecular complex, $Ln_2N_2^{3-}$, was recently synthesized to overcome this problem [1], the ternium compound being a single-molecule magnet with a world-record blocking temperature of 14 K [2]. Inelastic neutron scattering data on this molecule, its parent compound $Tb_2N_2^{2-}$ as well as the non-magnetic analogue $Y_2N_2^{3-}$, were recorded at the LET instrument at the ISIS neutron source. In the parent compound we observe ligand field levels at 0.7 meV and 5 meV. In addition to the rich vibration spectrum also seen in the yttrium compound, we observe an excitation at 9 meV in the SMM compound due to exchange coupling between the lanthanide magnetic moments. This presents the first direct evidence of enhancement of interactions in this system. For the simulation of the data we are developing a novel approach which takes into account structural aspects to handle the many ligand field parameters.

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Ferromagnetic cluster spin wave excitations in the high spin molecules Mn_{19} and Mn_{18}Sr

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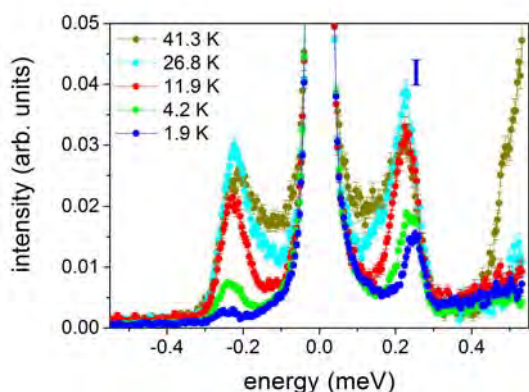
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The ferromagnetically coupled molecule Mn_{19} with its huge high-spin ground state $S = 83/2$ has attracted considerable interest in the past [1]. From the chemistry point of view determining the exchange coupling constants and their comparison to e.g. *ab-initio* result is of interest, while physically it is highly interesting to understand its ferromagnetic cluster spin-wave excitations. The huge Hilbert space and intricate topology of Mn_{19} complicates the analysis of experimental data enormously, and hence the simpler molecules Mn_{10} and Mn_{18}Sr , which can be regarded as model compounds for the exchange couplings in Mn_{19} , were also studied. The inelastic neutron scattering (INS) spectrum in Mn_{10} was previously successfully interpreted in terms of ferromagnetic cluster spin waves [2].

Here we present a detailed study of the magnetic excitations in Mn_{18}Sr and Mn_{19} by INS. For Mn_{18}Sr we determined the magnetic coupling constants from combined least-square fits to the positions of two cold peaks in the measured INS spectra and the temperature-dependent magnetic susceptibility. The magnetic susceptibility was calculated with the Quantum Monte Carlo algorithm [3].

Both Mn_{18}Sr and Mn_{19} exhibit two cold peaks at ca. 3.0 meV and 5.7 meV. However, in Mn_{19} one additional excitation is observed at ca. 0.25 meV (see figure), which is not present in Mn_{10} and Mn_{18}Sr , and shows an unusual behaviour for exchange-only clusters: Both the Stoke's and Antistoke's lines increase in intensity with temperature, and shift in energy, reminiscent to collective excitations. As a result Mn_{19} cannot be treated by a non-interacting spin-wave picture, but requires an inherent many-body description. Mn_{19} is hence a unique example of a magnetic molecule showing both cluster-type and collective-type magnetic excitations.





Spin dependent hybridization between molecule and metal at room temperature through interlayer exchange coupling

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The organic spininterface describes the spin-polarized properties that develop, due to spin-dependent hybridization and charge transfer, at the interface between a ferromagnetic (FM) metal and the molecules of an organic semiconductor [1,2]. The organic spininterfaces were also indirectly observed by the strong coupling that may exist between paramagnetic molecules and the FM substrate [3-6]. However, the study of spininterfaces was so far limited to sublimable molecules deposited in ultra-high vacuum conditions in order to prevent the oxidation of the FM substrate. Alternatively, the strong interaction of the molecules with the FM layer may alter molecular properties, such as spin-crossover [7]. While intercalating a graphene layer [8] is one solution that introduces strong constraints on the FM selection, we investigated the possibility to use interlayer exchange coupling as the mediator of the molecule/FM magnetic coupling.

Using X-ray magnetic circular dichroism (XMCD), we studied the magnetic coupling between manganese phthalocyanine (MnPc) molecules and a Cu(001)/Co FM substrate separated by a wedge-shaped Cu spacer. The XMCD data show that the Mn ion within MnPc molecules can be magnetically coupled to the Co substrate at room temperature when separated by up to 4 ML of Cu. The XMCD intensity evolves in an oscillatory manner with increasing Cu thickness, in agreement with *ab initio* calculations. By decreasing the temperature, we could observe stronger oscillations in the magnetic coupling and this over a much larger Cu thickness range (up to 12 ML). The phase and the periods of the oscillatory coupling is found to be the same than that of the prototypical Cu(001)/Co/Cu/Co system. Finally, we theoretically considered the spintronic performance of a Co/Cu(3ML)/MnPc stack. The calculations reveal a spin-polarization of the density of states in the vicinity of the Fermi level that reaches +74% suggesting thus promising spintronic performance [9].

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Studies of spin crossover thin films with X-ray radiation

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Spin crossover (SCO) complexes are coordination complexes composed of a metal ion surrounded by organic ligands. This numerous family of systems exhibits an intrinsic feature of undergoing spin-state switching of the central metal ion while exposed to external stimulation. High sensitivity of the electronic structure of metallic center to the ligand field enables the switching between its high-spin (HS) and low-spin (LS) state. The switching can be triggered by temperature change, light irradiation or application of electric/magnetic field[1-2]. Recent reports of intact sublimed SCO compounds on surfaces enabled the study of thin films and single molecules in order to reveal microscopic details of the SCO mechanisms[2-3]. In turn, it opens the path towards SCO-based nano devices[3].

Out of a few hundred known SCO materials, only several compounds available for UHV sublimation have been reported. The sublimation ensures intact molecules, contamination-free and good quality thin films fabrication. We present a new sublimable SCO molecule and the result of the successful and spin-crossover preserving thin film fabrication via UHV thermal deposition of $\text{Fe}[\{3,5\text{-dimethylpyrazolyl}\}_3\text{BH}\}_2$ ("FePyrz") (Fig. 1. (left))[4-5]. The morphology and the magnetic properties of the films were characterized by various experimental techniques including SQUID and x-ray absorption spectroscopy. We confirmed that the molecules composing the thin films preserve the SCO phenomenon. Furthermore, we evidenced that the material exhibits light induced excited spin state trapping (LIESST) and that the light radiation can be used to trigger reversible $\text{LS} \leftrightarrow \text{HS}$ switching (Fig. 1 (right))[5]. We believe that these promising outcomes will lead the way to applications (memory storage, sensing) of this interesting material and also enhance the interest of the community in the research over it.

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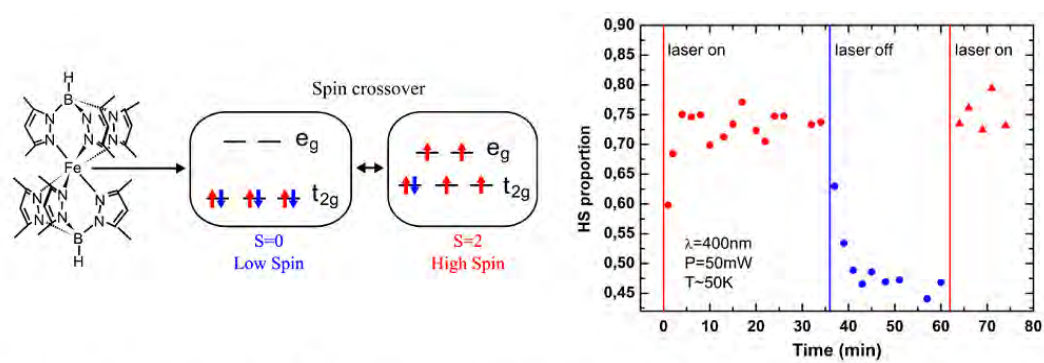


Fig. 1. (left) Structural model of FePyrz. (right) Reversible switching of FePyrz thin film with laser radiation.



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Modelling and theory
(Poster)

Ab Initio Molecular Dynamics of a Single Molecule Magnets on Au(111): evolution of structural and magnetic properties from the bulk to the adsorbed scenario

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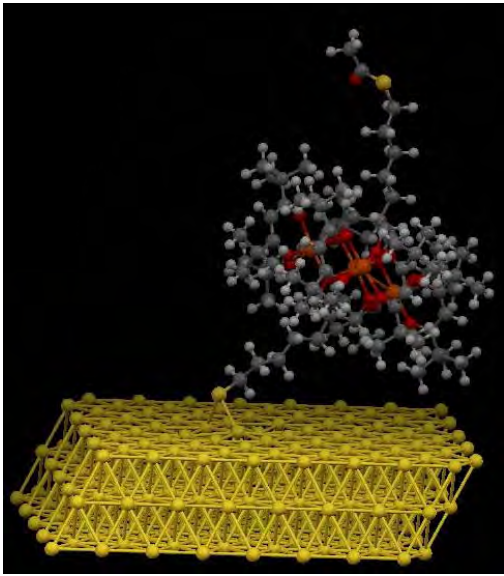
An Ab Initio Molecular Dynamics (AIMD) study of the $[\text{Fe}_4((\text{C}_5\text{H}_{10}\text{SAc})_2\text{-C}(\text{CH}_2\text{O})_3)_2(\text{dpm})_6]$ (Fe_4) adsorbed on gold is presented [1]. The experimental evidence of the retaining of the Single Molecule Magnets (SMMs) properties of Fe_4 once grafted on Au(111) have represented a milestone in the study of molecular spintronic devices [2]. This experimental result challenged both theoreticians and experimentalists to get a detailed understanding of the nature of the interactions between Fe_4 complexes and metallic substrates. In our work we have developed a computational strategy to predict magnetic properties [3] modifications upon grafting. Moreover we have been able to separate contribution coming from molecular structure modifications and electronic interactions with the gold surface, that is of fundamental importance in order to better understand the complex interactions between SMMs and substrates.

The system have been modeled through a no reconstructed four layers slab Au(111) surface with the SMM on top of it, for a total of 580 atoms. The AIMD calculations were performed within the periodic GPW/TPSS+D3 approach. An assessment of magnetic properties have been performed with GGA, GGA+U and Hybrids functional using CP2K and Orca Packages.

*This research has been supported by the European Research Council through the Advanced Grant MolNanoMaS.

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**Isomerism effect on the SCO behaviour in the cyanocarbanion based-systems
[Fe(DPA)₂(A)₂] (DPA = dipyridylamine, A⁻ = Cyanocarbanion)**

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Cyanocarbanions are interesting anionic ligands due to their high electronic delocalization and their cyano groups juxtaposed in such a way that they cannot all coordinate to the same metal ion [1]. In last few years, our group and others have reported several Metal-polynitrile compounds with fascinating molecular structures of different dimensionalities and unusual magnetic properties [1]. Taking into account the crucial role of these anionic ligands, we are interested in using them in combination with other chelating or bridging neutral co-ligands to explore their structural and electronic characteristics in the large field of molecular materials exhibiting the SCO phenomenon which is governed essentially by subtle changes in the structural packing and, therefore, by the nature of the polynitrile ligand [2].

In the last few years, we have reported the first SCO series based on the cyanocarbanions bearing one negative charge and abpt (4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole) co-ligand [2a]. However, in this system, all the complexes display SCO transitions above room temperature, making difficult to reach any structural and electronic informations on the HS state. Thus, in order to better control the transition temperature, we have substituted abpt co-ligand by other chelating co-ligands displaying lower crystal field energies, allowing SCO transition around or below room temperature.

We report herein syntheses, structural characterizations and magnetic properties of new series of formula [Fe(DPA)₂(A)₂] (DPA = dipyridylamine, A⁻ = cyanocabanion).

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ELECTRONIC PROPERTIES OF POLYOXOVANADOBORATES CONTAINING THE $\{V_6O_{18}\}$ AND $\{V_{10}O_{30}\}$ RINGS.

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The family of polyoxovanadoborates (VBO) includes polyanions with close spherical-like structures and with open barrel-like structures, which contain V^{IV} (d^0) and/or V^V (d^1) centers as five-coordinated entities $[VO_5]$ in a square base pyramid coordination geometry. The different connectivities that these polyhedra show within the VBO polyanions structures will determine their electronic properties.

We have been studying the optical and magnetic properties of the close spherical-like clusters $\{V_6B_{20}O_{50}H_n\}$ and $\{V_6B_{22}O_{54}H_{10}\}$, and of the open barrel-like cluster $\{V_{10}B_{24}O_{66}H_8\}$, recently reported in the literature¹. These polyanions have a central $\{V_6O_{18}\}$ and $\{V_{10}O_{30}\}$ ring, respectively; each one condensed to two polyborate crowns (Figure 1). In this work, the magnetic susceptibility measurements and the EPR spectra of the crystalline systems based on the $\{V_6B_{22}O_{54}H_{10}\}$ and on the $\{V_{10}B_{24}O_{66}H_8\}$ are presented. Additionally, the theoretical study of the magnetic behavior of both clusters is included.

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Acknowledgments: The authors acknowledge FONDECYT 1120004 and Basal Project FB0807 for partial financial support, and to the LIA-MIF CNRS 836 International Collaborative Program. **Powered@NLHPC:** This research was partially supported by the supercomputing infrastructure of the National Laboratory for High Performance Computing, NLHPC (ECM-02), Centre for Mathematical Modeling CMM, Universidad de Chile.

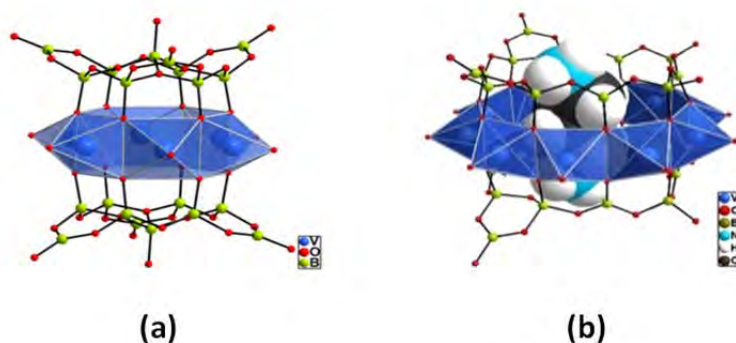


Figure 1. $\{V_6B_{20}O_{50}H_6\}$ cluster (a) and $\{V_{10}B_{24}O_{66}H_8\}$ (b). For the $\{V_{10}B_{24}O_{66}H_8\}$ cluster, an occluded $(NH_3CH_2CH_2CH_2NH_3)$ molecule is shown. The $\{V_6O_{18}\}$ and $\{V_{10}O_{30}\}$ ring are depicted in polyhedral representation.



Subtle Geometrical Effects on Magnetic Anisotropy of Mononuclear Lanthanide Single Molecule Magnets: the Dy(DOTA) Archetype

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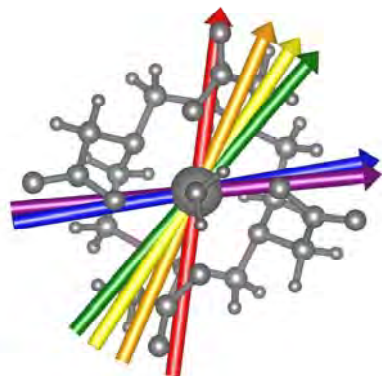
Record energy barriers to the reversal of magnetization were reported for mononuclear Single Molecule Magnets (SMMs) containing lanthanide ions. Indeed, lanthanides present large anisotropy due to the contribution of the unquenched orbital angular momentum of the electrons in the *f*-orbitals. Nevertheless how the electronic structure of the lanthanide ion is influenced by the surrounding ligands has not been completely explained yet. The archetype compound where such effects have been demonstrated to play a subtle influence is the Dy(DOTA)[1]. Indeed, a dependency of the orientation of the principal magnetization axis by the rotation of the coordinating apical water molecule around the Dy-O_w bond was evidenced. An abrupt change of the orientation of almost 90° was computed by Complete Active Space Self Consistent Field (CASSCF) approach with Spin-Orbit State Interaction (RASSI-SO). This computational protocol proved to reproduce the magnetic properties of lanthanide containing single molecule magnets [2].

In this poster we have reconsidered in more detail the water orientation effect in relation to crystal environment. In addition, a mapping of the electrostatic potential generated by the ligands around the Dy(III) ion through a multipolar expansion has been also presented.

We acknowledge the financial contribution of the ERC through the AdG MolNanoMas (267746).

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Enhancing anisotropic energy barrier of lanthanides by exploiting a diamagnetic Zn(II) ion

Apoorva Upadhyay¹, Maheswaran Shanmugam¹

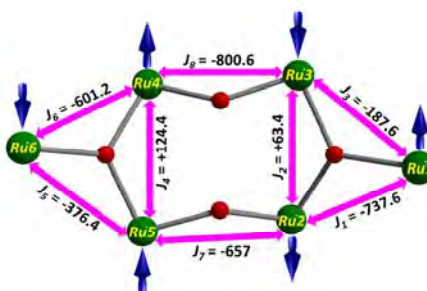
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Unquenched orbital angular momentum constitutes large magnetic anisotropy in lanthanide ions which is evident from the mononuclear terbium phthalocyanin single molecule magnet reported by Ishikawa about a decade ago. Several efforts (such as substituent position on the ligating atom, geometry etc.) been made to enhance the energy barrier of the SMM, however we have shown for the first time by exploiting a diamagnetic zinc ion near vicinity of anisotropic lanthanides increases the effective energy barrier. To this contribution we have synthesized Dy(III) monomer and a heteronuclear dimer of Dy(III)-Zn(II) with molecular formula $[\text{Dy}(\text{HL})_2(\text{NO}_3)_3]$ (**1**) and $[\text{ZnDy}(\text{NO}_3)_2(\text{L})_2(\text{CH}_3\text{CO}_2)]$ (**2**) respectively (where L is a Schiff base ligand namely 2-methoxy-6-[(E)-phenyliminomethyl]phenol). Near fivefold increase in U_{eff} in **2** compared to **1** is rationalized by detailed ab initio calculations. We aim to show the importance of 4d transition metal ions in building SMM, where from largest exchange can be harvested due to the diffused nature of the 4d orbitals. We did present in this poster, one of the largest ruthenium cluster based on carboxylate ligand $[\text{Ru}_6^{\text{III}}(\mu_3\text{-O})_2(\mu\text{-OH})_2((\text{CH}_3)_3\text{CCO}_2)_{12}(\text{py})_2]$, which is registered with largest exchange (800 cm^{-1}) known for any transition metal cluster so far. Theoretical calculations shed light on the origin of largest exchange in this ruthenium cluster.

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What controls Quantum Tunnelling of Magnetization in Ni(II) containing Ln(III) Single-Molecule-Magnets?

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Naushad Ahmed and Maheswaran Shanmugam.

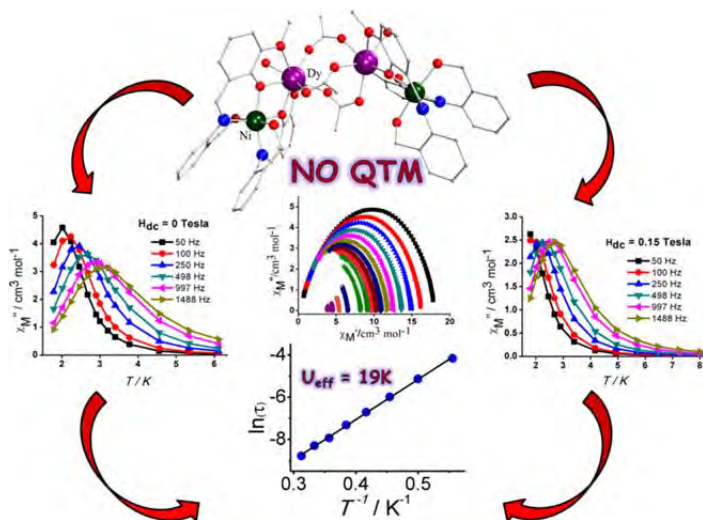
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The unquenched orbital angular momentum in lanthanide constitutes large magnetic anisotropy in these ions which is evident from a monomeric $[\text{Tb}(\text{Pc})_2]^-$ complex. Although ground breaking effective energy barrier reported for $\{\text{Dy}_4\text{K}_2\}$ and other related cluster, blocking temperature still lies well below 10 K range. This is due to Quantum tunnelling of magnetization which is significantly faster than the Orbach process. Several efforts have been made to quench QTM by various means like incorporating free radical systems and transition metal ions which enhance the magnetic exchange interaction resulting QTM suppression. In this line of interest we have isolated $[\text{Ni}_2\text{Ln}_2(\text{CH}_3\text{CO}_2)_3(\text{HL})_4(\text{H}_2\text{O})_2]^{3+}$ complexes where $\text{Ln}^{3+} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$ or Lu with suitable Schiff base ligand (H_2L) namely 2-methoxy-6-[(E)-2'-hydroxymethyl-phenyliminomethyl]-phenolate. Among these complexes, $\{\text{Ni}_2\text{Dy}_2\}$ was found to show out of phase susceptibility signals in which QTM was fully suppressed/quenched to a maximum extent.^{1,2}

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Field-Induced Slow Relaxation in a Monometallic Mn(III) Single-Molecule Magnet

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A current area of interest in molecular magnetism is the study of compounds that show slow relaxation of the magnetisation arising from a single, 3d transition metal (TM) ion in an appropriate ligand field.[1] This approach seeks to maximise the magnetic anisotropy of the 3d TM ion as a means of increasing the barrier to the loss of magnetisation, U_{eff} . This strategy was first demonstrated for Fe(II);[2] however, since then, it has been expanded to include other 3d TM ions, such as Co(II) or Mn(III).[1]

Here we describe the structural, magnetic, and spectroscopic properties of the compound $\text{Na}_5[\text{Mn}(\text{L-tart})_2] \cdot 12\text{H}_2\text{O}$ (**1**, L-tart = L-tartrate, Fig. 1).[3,4] High field EPR measurements show that **1** has negative axial zero-field splitting, and a small rhombic anisotropy. Dynamic magnetic measurements show that an applied DC field is sufficient to suppress quantum tunnelling of the magnetisation, and allow slow relaxation of the magnetisation to be observed.

Fig. 1 A view of the compound $\text{Na}_5[\text{Mn}(\text{L-tart})_2] \cdot 12\text{H}_2\text{O}$.

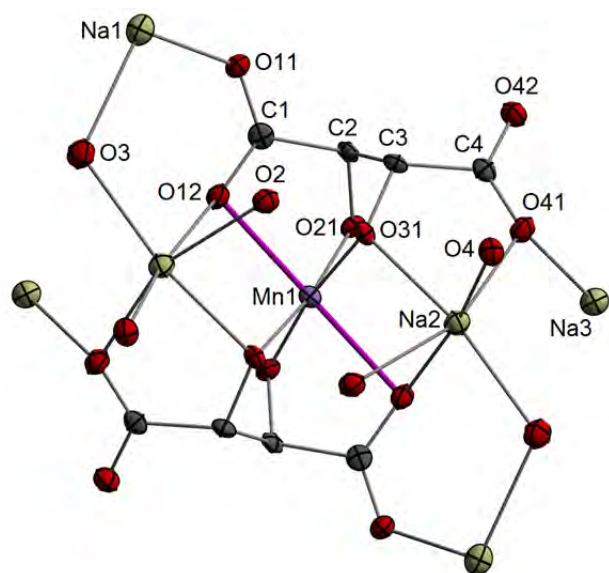
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Construction of Molecular Nanomagnets via d-f Heterometallic Strategy

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Single-molecule magnets (SMMs) and single-chain magnets (SCMs), the most valuable families in the field of molecular nanomagnets, have attracted considerable attention as a result of their unique physical properties and chemically tunable structures. Potential advantages have been provided that using d-f heterometallic approach to create new SMMs and SCMs: large magnetic moment can be achieved by the strong spin-orbit couplings of lanthanide or actinide ions instead of by exchange interactions within polynuclear clusters;^[1] the significant uniaxial anisotropy can be satisfied more easily from single-ion anisotropy rather than that of molecular geometry control;^[2] the moderate magnetic couplings between d and f spin carriers can efficiently suppress zero-field quantum tunneling effects which are often observed in lanthanide or actinide-based complexes and lead to lowering the effective energy barriers for spin reversals.^[3]

It is challenging to rationally design and synthesize d-f heterometallic complexes due to the specific chemical nature of d and f spin carriers, as well as the complicated reaction systems. From the point view of ligands, two main approaches are widely adopted in this field: a) "designed assembly" approach, namely employing the ligands that are elaborately designed to possess different kinds of coordination pockets for both d and f ions; b) "assisted self-assembly" approach, namely introducing suitable co-ligands to assist the self-assembly processes in which lanthanide ions can combine transition metal ions at the presence of multidentate ligands.^[4]

Up to now, a large amount of d-f heterometallic complexes have been obtained and investigated, such as the polynuclear discrete cluster compounds with customer designed organic ligands^[5] and the high dimensional heterometallic frameworks^[6] and so on. These d-f heterometallic complexes are synthesized by using a great range of organic ligands under optimized conditions, exhibiting diverse molecular structures with interesting topologies and various interesting magnetic properties for both theoretical interests and potential applications.

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Study of the Layered Lanthanide Hydroxide series $\text{Ln}_8(\text{OH})_{20}\text{Cl}_4 \cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{Tb}, \text{Dy}, \text{Ho}$ and Er) and the correspondent diluted compounds ($\text{Y}_x\text{Ln}_{8-x}(\text{OH})_{20}\text{Cl}_4 \cdot 6\text{H}_2\text{O}$): from single ion magnets to 2D and 3D interaction effects

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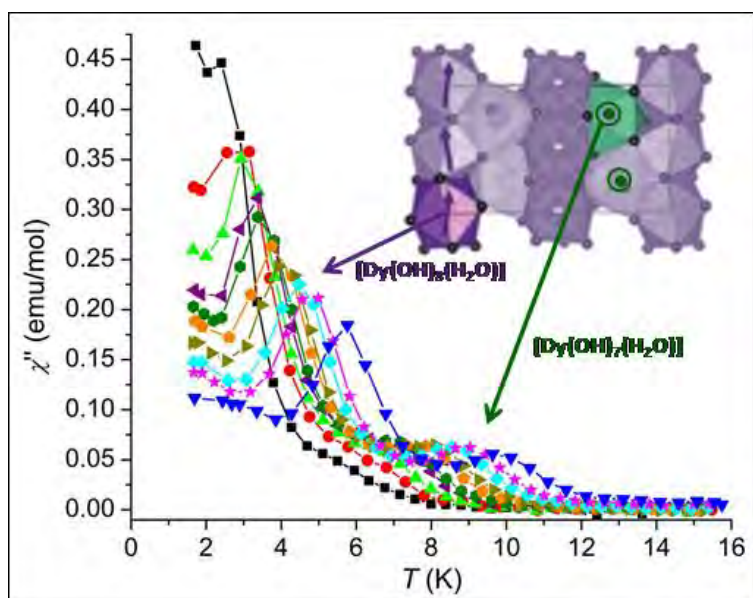
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Layered Lanthanide Hydroxide (LLnH) with composition $\text{Ln}_8(\text{OH})_{20}\text{Cl}_4 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Nd}, \text{Sm-Tm}$ and Y) were originally prepared by Sasaki and co-workers. A host-guest system with pure Ln cations in the layer allowed us to combine the study of lanthanide chemistry with that of layered and intercalated compounds, providing advances in the field of new organic-inorganic hybrid systems that configures these materials as multifunctional materials. These ionic lamellar compounds have recently attracted a large interest in different research fields such as catalysis, drug delivery, optics and luminescence, although their magnetic behaviour has remained essentially unexplored.

In this work the magnetic properties of the layered dysprosium hydroxide material $\text{Dy}_8(\text{OH})_{20}\text{Cl}_4 \cdot 6\text{H}_2\text{O}$ (LDyH) were studied and revealed slow magnetic relaxation behaviour characteristic of single-molecule magnets (SMM), being the first layered lanthanide compound presenting this behaviour. The results obtained support the idea that this slow relaxation probably stems mainly from single ion effects, with the Dy–Dy interactions, although non-negligible, playing a secondary role. In order to verify the influence of these Dy–Dy interactions, the magnetic properties of LDyH, both diluted in the diamagnetic yttrium analogous matrix (LYH:0.04Dy) and intercalated with 2,6-naphthalene dicarboxylate anions (LDyH-2,6-NDC), were studied and compared with the undiluted compound.

The Y diluted compound reveals a SMM behaviour of single Dy ions, with two distinct slow relaxation processes of the magnetization at low temperatures associated with the two main types of Dy sites, 8- and 9-fold coordinated. Only one relaxation process is observed in both undiluted LDyH and intercalated compounds as a consequence of the dominant ferromagnetic Dy–Dy interactions, both intra- and interlayer. All these results are supported by theoretical calculations of crystal field splitting of the Dy levels in different crystallographic sites. These semiempirical calculations using a radial effect charge (REC) model for the crystal field splitting of the Dy levels are used to explain data in terms of contributions from the different Dy sites. From this study, the single ion, 2D and 3D Dy–Dy interaction effects could be put separately into evidence. The ferromagnetic nature of the 2D and 3D interactions in these compounds could also be explained by the orientation of the easy magnetization axes of different Dy sites together with the superexchange (Dy–O–Dy angles) and direct (Dy–Dy) interactions. To the best of our knowledge this was the first time such a clear separation and detailed analysis of different effects has been achieved in a layered lanthanide compound with slow relaxation of magnetization.

This study is being pursued with other Ln ions, namely Tb, Ho and Er. The magnetic characterization of these LLnH and respective diluted compounds in the Y matrix (LYH:xLn) is underway, already showing promising results.





A Flexible Molecular Toolkit for the Directed Synthesis of Heterometallic Molecular Complexes

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The development of new synthetic methodologies towards the assembly of 3d and/or 4f high-nuclearity complexes has been attracted a considerable interest in recent years. The design of these polynuclear complexes has focused the efforts of molecular magnetism since the discovery of the interesting magnetic properties displayed by the first single-molecule magnets (SMMs), and its potential technological applications such as information storage devices, quantum computing, or magnetic refrigerants.^{1,2}

In the last decades several polydentate organic ligands which dispose multiple donor atoms and/or well-defined coordination pockets have been successfully used in the design of heterometallic high-nuclearity clusters.³ Here we propose the use of the flexible ligand 2,2'-(propane-1,3-diyl-diimino)bis[2-(hydroxymethyl)propane-1,3-diol] (H₆L) to control and direct the assembly of the metal atoms in the synthesis of heterometallic polynuclear systems.⁴

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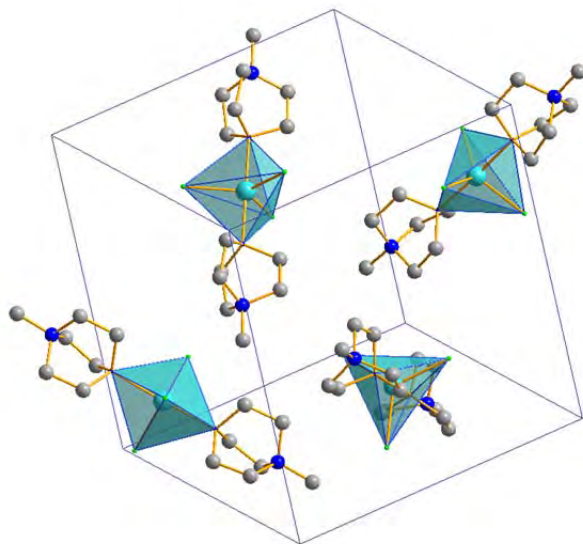
Pushing the Limits of Magnetic Anisotropy in a Monometallic Ni(II) Single-Molecule Magnet

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Monometallic complexes based on 3d transition metal ions in certain axial coordination environments can exhibit appreciably enhanced magnetic anisotropy, which is important for memory applications, due to stabilisation of an unquenched orbital moment. However, competing structural instabilities that reduce this anisotropy need to be minimised through the judicious selection of ligands. Here we report a series of trigonal bipyramidal 3d transition metal complexes where the combination of large ligands in the equatorial positions and rigid, bulky ligands in the axial positions, results in only a small distortion of the structure.





Local structural study of multiferroic GaFeO₃ samples prepared by sol-gel methods

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In the past decade research on the multiferroic nature of the gallium iron oxide has been of interest for several reasons. GaFeO₃ has been intensively studied for its potential applications as a magnetoelectric material [1]. Such a system can be used for switching its electric state vs. magnetic state and vice versa. Moreover GaFeO₃ seems to be promising memory media which allow a simultaneous reading and writing a data [2].

The physical properties, especially magnetism in GaFeO₃, depend strongly on the method of preparation. GaFeO₃ forms a collinear antiferromagnetic ordering along [001] direction [3]. Any disorder of the cation origin leads to more complicated non-collinear structures, such as ferromagnetic [4], canted antiferromagnetic [5] or ferromagnetic [6]. Therefore many efforts have been expended on fabrication of gallium iron oxide by Pechini modification of the sol-gel method. Careful preparation gives the ability to systematically track conditions conducive to filling each crystalline sublattice occupancy.

In the present study a systematic investigation has been conducted on the multiferroic GaFeO₃ samples synthesized in three different scenarios, by changing the initial semi-products and heating procedures. Obtained in this way different disorder in site occupancies was probed by an element specific local structure measurement tool, such as EXAFS, across the magnetic transition temperature by synchrotron-based EXAFS technique both at Ga K-edge (10367 eV) and Fe K-edge (7112 eV) over a wide temperature range from 77 K up to 400 K.

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Switchable magnetic materials and optical magnets
(Poster)

Synthesis and characterisation of new polymeric valence tautomeric complexes.

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Of considerable interest are molecular materials based on systems that can be switched between two or more distinguishable electronic states by applying an appropriate external perturbation. Valence tautomerism involves stimulated intramolecular electron transfer between a redox-active metal centre and a redox-active ligand.¹ The vast majority of complexes that exhibit valence tautomeric transitions are based on a Co-dioxolene systems, in particular incorporating 3,5-di-tert-butylidioxolene ligands.

Herein we report the new family of one-dimensional valence tautomeric coordination polymers [Co^{III}(3,5-dbcate)(3,5-dbsq)(L)] (3,5-dbcate = 3,5-di-tert-butylcatecholate, 3,5-dbsq = 3,5-di-tert-butylsemiquinonate, L = linking N-donor ligand), some members of which undergo thermally and light driven valence tautomeric interconversions.

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Spectroscopic and theoretical investigation of the electronic structure of lanthanoid-polyoxometalate complexes

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Polyoxometalates (POMs), among different ligands that have been used to synthesize lanthanoid-based single-molecule magnets (SMMs), are of particular interest because of their intrinsic diamagnetism and steric bulk, which minimizes intermolecular interactions.¹⁻⁴ Lanthanoid-POM complexes also show a great variety of lanthanoid coordination environments and nuclearity that makes them ideal candidates to explore the effect of the ligand geometry on the electronic structure and therefore on the magnetic properties.⁵ Here we present the preliminary results of a spectroscopic and theoretical investigation of several lanthanoid-POM complexes, some of which exhibit SMM behaviour. The combined information obtained from spectroscopy, magnetometry and calculations has allowed clarification of the electronic structure of the ground state of these molecules.

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Molecular nanomagnets
(Poster)

Magnetic and Luminescence Properties in Multiple Functionalized TTF-based Complexes of Lanthanides.

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On one hand, lanthanide ions are well-known to exhibit large magnetic moments and strong magnetic anisotropy and therefore they are considered good candidates for the elaboration of Single Molecule Magnets (SMMs). And they also possess interesting luminescence properties, emitting light when adequately sensitized by an appropriate ligand.

And on the other hand, Fe^{II} in an octahedral environment is the most studied 3d ion to form complexes that exhibit the Spin Crossover (SCO) phenomenon, changing from the diamagnetic low spin (LS) state to the paramagnetic high spin (HS) state caused by an external stimulus such as temperature, pressure, magnetic field or light irradiation variations.

It has been demonstrated previously in our group that the TTF-based ligands can play the double role of structural agent for SMM¹ behaviour and organic chromophore for an antenna effect.²

So to combine both properties (SMM and SCO) in a single complex we have designed a new two new TTF-based ligands which have been functionalized with two different coordination sites that are specifically suited for Fe^{II} and Ln^{III} ions: i) a benzoimidazole-2-pyridine (bzip) acceptor which may give SMM behaviour when coordinated to Ln^{III},³ and ii) a 2,6-di(pyrazol-1-yl)pyridine (dpp)⁴ moiety or a 5-methyl-2,2'-bipyridine (bpy)⁵ moiety which are well-known for the elaboration of SCO Fe^{II} complexes displaying LIESST effect.

We have already been able to crystallize lanthanide-based complexes with both the designed ligands (figure) and we will present their magnetic and luminescence behaviours.

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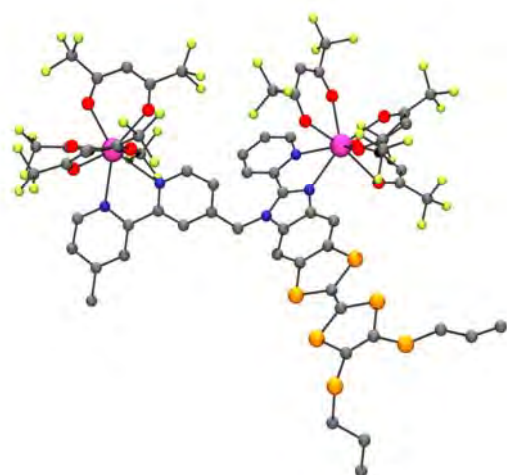
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Figure. Dysprosium complex of the TTF-based ligand with a 5-methyl-2,2'-bipyridine moiety.





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Molecular nanomagnets
(Poster)

Mixed-valence tetranuclear cobalt (II, III) complexes containing curcuminoid ligands

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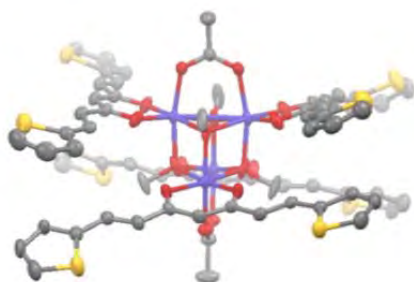
Multifunctional Materials are any material or material-based system which combines two or more properties, one of which is normally structural and the other functional, e.g. optical, electrical, magnetic, thermal etc...^[1] One way to design multifunctional molecular materials is to synthesize different types of complexes having the properties of the organic ligands and the properties of the metals combined. Concerning the ligands, a lot of synthetic efforts are directed to obtain organic p conjugated systems, which are good candidates for molecular optoelectronic devices due to their optical and electronic properties. In parallel, working with paramagnetic metals can also introduce magnetic properties, introducing spin and anisotropy on the system, and in some cases the molecules behaving as Single Molecule Magnets.^[2] This research work is based on the combination of both fields, synthesis and characterization of conjugated organic ligands and their coordination with metals together with the analysis of the properties.

With this aim in mind, this work introduces two p-conjugated ligand with terminal thiophene groups from the family of curcuminoids (CCMoids)^[3] (derived from curcumin (1*E*,6*E*)-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,6-diene-3,5-dione) that exhibit electronic and fluorescent properties due to their conjugated skeleton. Their reaction with mononuclear cobalt salts provided crystals of the first two examples of mixed valence tetranuclear Cobalt (II,III) complexes containing curcuminoid ligands. Preliminary magnetic studies show that at least one of the compounds behave as a Single Molecule Magnet.

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Molecular nanomagnets
(Poster)

Exploring the capabilities of a family of benzotriazole-based ligands using Cobalt (II) halogen salts: Synthetic and magnetic aspects

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Utilization of a series of benzotriazole-based ligands with Cobalt (II) halogen salts has lead to the synthesis of seven new coordination compounds, $[\text{Co}_2(\text{L}^1)_2\text{Cl}_4] \cdot 2\text{MeCN}$ (**1**), $\text{Co}_2(\text{L}^1)_2\text{Br}_4$ (**2**), $[\text{Co}_2(\text{L}^2)_2\text{Cl}_4] \cdot 2\text{MeCN}$ (**3**), $\text{Co}_2(\text{L}^2)_2\text{Br}_4$ (**4**), $[\text{Co}(\text{L}^3)\text{Cl}_2] \cdot \text{MeCN}$ (**5**), $[\text{Co}_2(\text{L}^3)_2\text{Br}_4] \cdot 2\text{MeCN}$ (**6**) and $\text{Co}(\text{L}^3)\text{Cl}_2$ (**7**). Motif and dimensionality of each compound is related to the ligand and halide used in each case. All structures have been characterized by X-Ray crystallography. Synthetic aspects and magnetic properties of certain compounds will be discussed.



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Molecular nanomagnets
(Poster)

Preparation, magnetic properties and transport through bipyrimidine-bridged binuclear complexes

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Molecule magnets have been attracting much scholarly interest due to their potential applications in optoelectronics, information storage, and switching devices. However, before such materials can be used in these applications, a thorough consideration of how both structural and electronic perturbations can affect the magnetic exchange is necessary. In this poster we aim to present a family of binuclear complexes bridged by 2,2'-bipyrimidine (bpm). These complexes with magnetically-active transition metal and lanthanides were synthesized and characterised by chemical analysis, X-ray, i.e., NMR spectroscopies, UV-Vis spectroscopies, Inelastic neutron scattering (INS), and magnetic susceptibility measurements. As shown through our experiments, the inverse of the magnetic susceptibility of this kind of complexes can be fitted by a Curie – Weiss model. Thanks to two possible coordination modes, bpm can act as a terminal or a bridging ligand for the metals. Also an interesting behavior arising from the bridging coordination mode of bpm is that it can mediate electronic interactions between the metal centres. Finally the transport of electrons through the Co₂ and Ni₂ molecules was studied by mechanically controlled break junctions (MCBJs)¹ and scanning tunneling microscopy (STM) experiments.²

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The influence of axial ligation on the structural and magnetic properties of

$\text{Co}_3(\text{dpa})_4\text{X}_2$ complexes (X = F, Cl, Br, I)

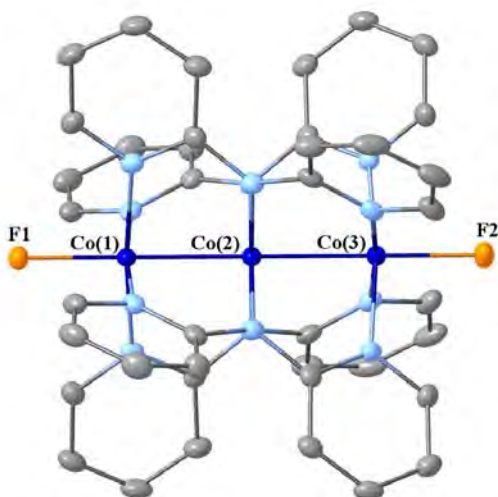
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Since its discovery in 1994,^[1] several studies have been carried out on the linear trinuclear complex $\text{Co}_3(\text{dpa})_4\text{Cl}_2$ (**1**), particularly in terms of its spin crossover (SCO) behavior. These investigations revealed that the trinuclear moiety exists in both symmetrical and unsymmetrical (i.e., *s*-**1**· CH_2Cl_2 and *u*-**1**· $2\text{CH}_2\text{Cl}_2$) forms with respect to the Co–Co distances,^[2] a rare case of bond-stretch isomerism. However, much less work has been done to study the effects of the axial ligands on the structural and magnetic properties of these compounds. In this context, we report the first synthesis of $[\text{Co}_3(\text{dpa})_4]^{2+}$ with iodide and fluoride (Fig. 1) in the axial position. Crystallographic studies on these compounds revealed an unsymmetrical core for $\text{Co}_3(\text{dpa})_4\text{I}_2 \cdot \text{Et}_2\text{O}$ (**2**· Et_2O), with Co–Co distances of 2.299(1) and 2.434(1) Å, and Co–I distances of 2.861(1) and 2.772(1) Å at 120 K. As the temperature is decreased, the $[\text{Co}_3]$ core tends towards a symmetrical geometry. On the other hand, $\text{Co}_3(\text{dpa})_4\text{F}_2 \cdot \text{CH}_2\text{Cl}_2$ (**3**· CH_2Cl_2) is essentially symmetrical with Co–Co distances of 2.325(6) and 2.316(6) Å, and Co–F distances of 2.009(1) and 2.005(1) Å at 120 K, and remains symmetrical down to 85 K. In the previously published $\text{Co}_3(\text{dpa})_4\text{Br}_2 \cdot \text{CH}_2\text{Cl}_2$ (**4**· CH_2Cl_2) compound, symmetry is crystallographically enforced at all temperatures, with a Co–Co distance of 2.3164(8) Å and a Co–Br distance of 2.622(1) Å at 111 K.

Magnetic susceptibility studies on these compounds shows that the nature of axial ligands significantly modifies the spin crossover properties.





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New Materials
(Poster)

Magnetic Properties of New Ordered Bimetallic Phases $M^{I'}_{0.2}Mn_{0.8}PS_3 \times 0.25H_2O$ ($M^{I'} = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}$)

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Among the family of MPS_3 compounds, the $MnPS_3$ phase has been widely studied due to the magnetic properties, since an unusual change from antiferromagnetism in the pristine phase to a spontaneous magnetization is observed when cations such as potassium ions are intercalated [1]. In addition, the obtained potassium intercalate is a useful precursor for further cation exchange reactions, due to the weak interaction of the potassium ions with the lamellar host. These exchange reactions have been traditionally done by stirring for several days at room temperature. Recently the use of microwave radiation has been reported by our group in the preparation of new composites based on MPS_3 lamellar phases [2].

All the bimetallic $M^{II'}_xM^{II}_{1-x}PS_3$ phases reported to date have been obtained mainly by ceramic method. In the present work, the microwave assisted synthesis and the characterization of a new family of bimetallic phases is reported, $M^{I'}_{0.2}Mn_{0.8}PS_3 \times 0.25H_2O$ ($M^{I'} = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}$). The bimetallic phases are obtained from the $K_{0.4}Mn_{0.8}PS_3 \times H_2O$ phase, which has been shown to present ordered distribution of the vacancies [1]. The potassium intercalated phase is made to react with the corresponding nitrate, by a microwave assisted reaction. The obtained materials were characterized by infrared spectroscopy, X-ray diffraction for powder samples, atomic absorption analyses and scanning electron microscope, with an EDXS detector.

All the bimetallic phases are antiferromagnetic, with lower values of the Weiss constant in comparison with that of the pristine $MnPS_3$ phase, and the ferromagnetic behaviour of the potassium precursor is not observed. All analyses and the magnetic behaviour are in agreement with the insertion of the second transition metal ion.

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Fluoride-bridged manganese(III) chains. Three-dimensional magnetic ordering and one-dimensional magnetization dynamics

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Fluoride bridging is a common motif in the solid state structures of many early transition metal fluorides, but despite this apparent affinity for bridging, the use of fluoride as linker in molecular magnetism remains quite a rarity. Based on fluoride's redox-innocence one can have only modest expectations for the strength of the mediated superexchange interaction. However, we have clearly demonstrated the efficacy of fluoride as mediator of magnetic exchange, and surprisingly fluoride can outcompete even cyanide in otherwise similar polynuclear assemblies [1]. Taking fluoride's preference for forming linear bridges into account [2], this anion stands out as a powerful and ultimately simple building block for the rational design of new molecule-based magnetic materials.

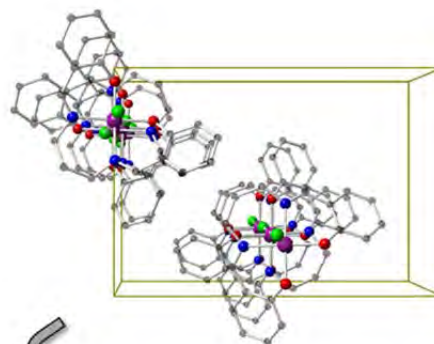
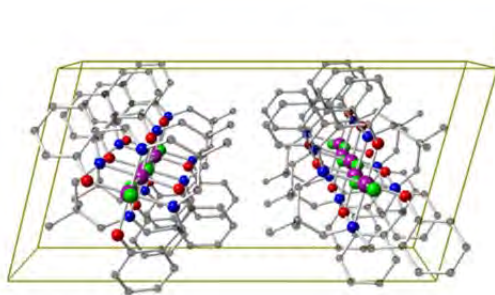
Taking advantage of fluoride's structure-directing properties, coordinatively unsaturated metal complexes can be assembled into higher-dimensionality systems in a controlled fashion. Using the ubiquitous $[\text{Mn}^{\text{III}}(\text{salen})]^+$ -type building blocks ($\text{salenH}_2 = N,N'$ -bis(salicylidene)ethylenediamine), we have tailored one-dimensional systems by exchanging labile ligands along the Jahn-Teller axis of the high-spin $[\text{Mn}^{\text{III}}(\text{salen})]^+$ complexes with fluoride or by simply using MnF_3 as synthon [3]. This is done under surprisingly mild conditions, and playing on the chemically modifiable nature of the salen-type ligands, we have prepared a family of one-dimensional systems bridged solely by fluoride. The overall one-dimensional structural motif is retained throughout the series but the antiferromagnetic intrachain superexchange interactions are highly sensitive to the specific bridging angle. In this way, the structural tunability provides a direct handle for fine-tuning of static magnetic properties.

The magnetic properties are strongly affected by a delicate balance between the large fluoride-mediated intrachain antiferromagnetic superexchange interactions and the pronounced uniaxial single-ion anisotropy characteristic of high-spin manganese(III) systems. The resulting spin canting manifests itself in the low-temperature three-dimensional magnetic ordering of the systems. Despite the preserved one-dimensional motif, the chemical modifications of the salen-type ligands control and greatly alter the crystal packing, and consequently various ordering scenarios have been realized. The spin canting reveals itself, both in canted antiferromagnetically ordered systems showing magnetization hysteresis with large coercive fields ($> 1\text{ T}$), and (canted) antiferromagnetically ordered systems where the slow magnetization dynamics, reminiscent of single-chain magnet behavior, are observed below the ordering temperatures ($\Delta_{\text{eff}} > 50\text{ cm}^{-1}$).

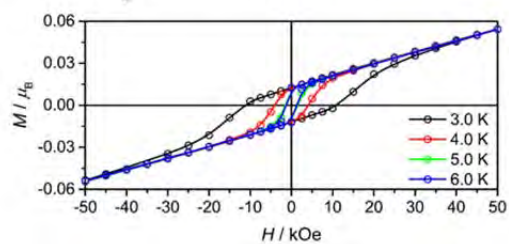
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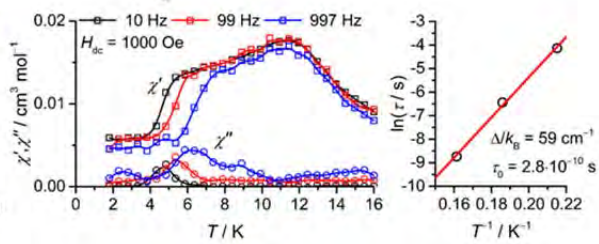
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3D magnetic ordering



1D magnetization dynamics





Synthesis, Structure and Magnetic Properties of Copper(II)-Lanthanide(III) Aminopolyol Complexes

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Since the discovery of the bi-stable magnetic properties of the archetypal single molecule magnet (SMM) Mn_{12} -acetate, there has been a large and ever growing interest in discovering new SMMs and in further developing synthetic strategies to obtain them. This interest is due to these molecules being good test subjects for further investigation of the physics of molecular magnetism, as well as displaying a large array of exciting potential applications within the fields of high density information storage, quantum computing and spintronics.^{1,2}

For a molecule to be classified as an SMM it must display slow relaxation of magnetisation. For this to be the case the molecule must possess a large negative axial anisotropy and a large, well defined spin ground state. One potential avenue to achieving this is to utilise the weak ferromagnetic coupling often seen between Cu(II) and Ln(Gd, Tb, Dy).³ Ferromagnetic coupling within the molecule can lead to larger ground state spin which combined with the large anisotropy of Ln(Tb, Dy) can lead to substantial barriers to reorientation and thus slow relaxation.

We will present new Cu-Ln compounds utilising aminopolyol ligands, which can be used in synthesis as linkers to form large 3d-4f compounds,⁴ and explore their structure and magnetic properties.

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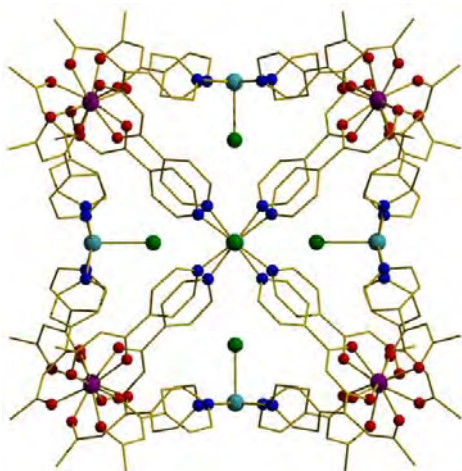
The synthesis of New Heterometallic Coordination Cubes

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A new family of coordination cages, constructed from the metalloligand $[\text{Fe}^{\text{III}}\text{L}_3]$ and various transition metal (II) salts, of general formula $[\text{M}_6(\text{FeL}_3)_8(\text{X})_{12}]$ ($\text{M} = \text{Cu}, \text{Pd}$; $\text{X} = \text{Br}, \text{OTf}$ and $\text{L} = 1$ -(4-pyridyl)butane-1,3-dione) are presented. The metallic skeleton of the cage describes a cube where the corners are occupied by the FeL_3 metalloligands and the square faces are capped by the “naked” M^{II} ions. Computational techniques known in theoretical nuclear physics as statistical spectroscopy are used to interpret the magnetic behaviour, in tandem with EPR spectroscopy. Flexibility in design offers the potential to tune physical properties, since all the constituent parts of the cage can be changed without structural alteration. The corner ions can be any M^{III} ion as long as the precursor ML_3 can be made; the face-capping metal ions can be any M^{II} ion; the 12+ charge on the cage suggests the anions can be varied and can be innocent or non-innocent; and the solvent bonded terminally to the $\text{M}(\text{II})$ ions should be easily replaced allowing attachment of a host of different species and/or the assembly of the cubes into higher order structures. The large internal cavity suggest the cage could play host to different species, including magnetic and/or redox-active guests, exerting control over magnetic exchange between metal ions in the host framework and between the host and guest(s). Post-synthetic exohedral functionalization, and simple changes to ligand design, will also allow for modification of magnetic properties, but additionally can be manipulated to tune solubility, reactivity, stability and substrate specificity.





Switchable magnetic materials and optical magnets
(Poster)

Switchable Spin Crossover Molecules & Materials based on 1,2,4-Triazoles

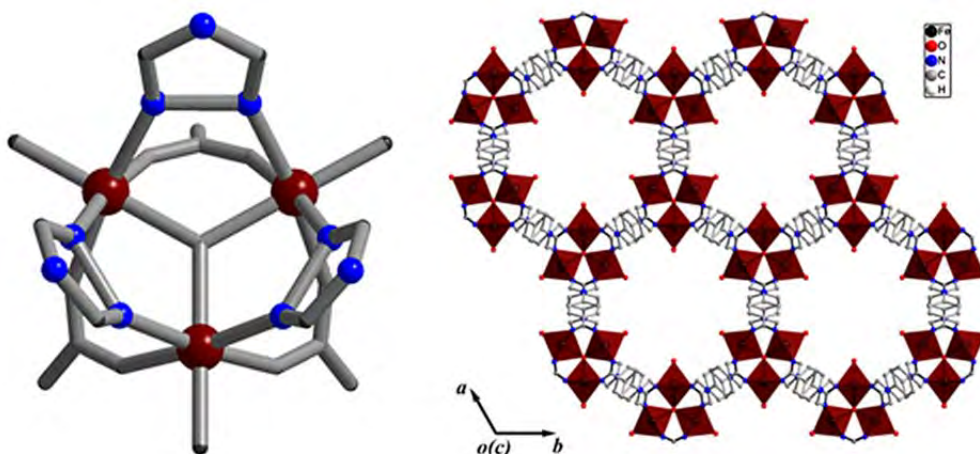
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As one of the two most prospective spin crossover (SCO) systems for potential applications, the 1,2,4-triazole-based ligand has been widely employed for constructing magnetic molecular materials.^[1,2] Used as the organic base to build up switchable coordination compounds, the 1,2,4-triazole (Htrz) and its 4-R-derivatives without substituents at 1- and 2-positions tend to coordinate to metal centers via a bidentate bridging mode, forming either oligo- or polynuclear compounds.^[3] This coincides with the idea of improving abruptness of the SCO compounds by covalently linking the spin crossover centers.^[1] And it allows us to introduce other functional groups into the R-substituent to get the enhancement of intermolecular interactions between adjacent magnetic molecules, and thus getting higher cooperativity.^[4] The promising approach in our project here is the well-designing of the 4-substituent, with the idea to modify the appropriate ligand field that triggers the SCO behavior on one hand, and to link the active magnetic molecules via varieties of non-covalent interactions (H-bonding, p...p, Halogen...Halogen, ... etc.) on the other hand. Series of well-designed ligands and several complexes have been successfully synthesized and characterized. This project is being carried out currently and further investigations of the obtained complexes are undergoing.

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Switchable magnetic materials and optical magnets
(Poster)

Cyanido-bridged di- and trinuclear complexes exhibiting bistable magnetic properties

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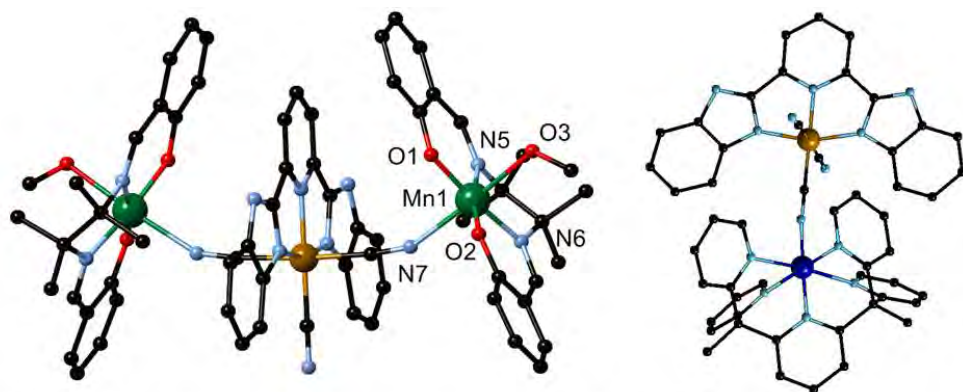
Molecule-based magnets have been widely investigated in the field of molecular magnetism, due to their potential applications such as quantum computing and molecular spintronics.¹ One way to build heterometallic molecular complexes relies on the building block approach using cyanido-bridged complexes.² The design of cyanide building blocks with capping ligands allows the control of the nuclearity, the topology and the dimensionality of the final product. Cyanido-bridged molecular materials have been largely exploited because of the relatively high exchange interaction afforded between metal ions, suitable for the design of single-molecule magnets (SMMs) and compounds with higher dimensionality such as 1D (single chain magnets, SCMs), 2D and 3D extended network.^{2,3} In addition, since the discovery of magnetic and optical bistability in Prussian blue analogues $K_xCo[Fe(CN)_6]_y \cdot nH_2O$, intense research efforts have been devoted lately in order to design switchable discrete heterometallic molecules displaying thermo- and photo-induced intermetallic electron transfer.^{4,5}

In this presentation, we will present two molecules obtained from $TBA_2[Fe(bbp)(CN)_3]$ building blocks (H_2bbp : 2,6-bis(benzimidazo-2-yl)pyridine): a $[Mn_2Fe]$ trinuclear cyanide-based molecule **1** displaying SMM behaviour and a $[CoFe]$ dinuclear electron transfer pair **2**. The synthetic strategy employed and the physical characterization of these compounds will be thoroughly described.

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View of the molecular structure for **1** and **2**. Mn, Fe, Co, C, N, O atoms are in green, yellow, dark blue, black, light blue, red. The solvent molecules and hydrogen atoms are omitted for clarity.



A Dy(III) Metal-Organic Framework Exhibiting Slow Relaxation of the Magnetization

Xue-Jing Zhang¹, Ke Liu¹, Wei Shi¹, Peng Cheng¹

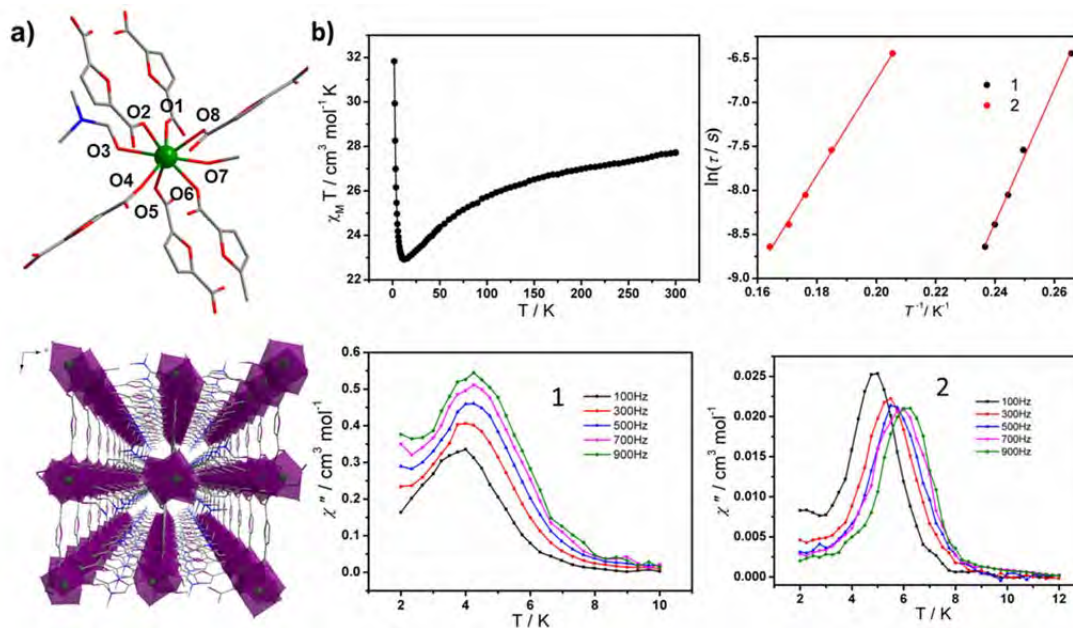
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Recently, magnetic metal-organic frameworks have been largely pursued to obtain new types of molecular magnetic materials.¹⁻⁴ Herein we present a new 3D Dy^{III}-MOF (Fig. 1a) [Dy₂(FDA)₃(DMF)₂(CH₃OH)₂]_n (**1**) and its Y-diluted analogue in a molar ratio of 1:40 (**2**). The $\chi_M T$ value (Fig. 1b) of **1** at room temperature is 27.71 cm³ mol⁻¹ K, which is close to the expected values of 28.10 cm³ mol⁻¹ K for two free Dy^{III} ions (⁶H_{15/2}, $g = 4/3$). And the $\chi_M T$ value increases sharply when the temperature is lowering to 2 K, suggesting the presence of intra-chain weak ferromagnetic interactions. **1** and **2** showed frequency dependence of ac magnetic susceptibilities at zero external fields. The energy barriers of **1** and **2** are obtained by Arrhenius fitting to give the effective energy barrier of 69 K for **1** and 54 K for **2**, suggesting that the dynamic magnetic behaviors of **1** are largely related to the single-ion properties of the eight-coordinated Dy^{III} ions, and the ferromagnetic interactions in the carboxyl-bridged 1D chain also make some contribution to its energy barrier for spin reversal.

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Magneto-structural correlations in bis-(*o*-semiquinonato) Ni(II) complexes

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Metal complexes with *o*-semiquinonate (SQ) ligands are valuable objects for creating components of sensors and switches that are sensitive to external effects. It was shown previously [1, 2], that bis-(*o*-semiquinonate) copper(II) complexes have a specific combination of the intramolecular ferro- and antiferromagnetic exchange interactions between spins of Cu(II) and SQ ligands. And an extra ligand coordinated to the Cu(SQ)₂ produces a dramatic effect on the magnetic properties of the complex by changing the multiplicity of the ground state. Also in pentacoordinated bis-*o*-iminosemiquinonato gallium complexes the character of magnetic exchange interaction between spins of *o*-iminosemiquinone radicals was found to be strongly influenced by the nature of apical substituent [3]. The antiferromagnetic coupling is predominant in case of halogens or NCS anions, whereas in case of alkyl group the triplet ground was observed.

In the present study we investigated an influence of changing uncharged ligands L on the magnetic properties of mixed-ligand complexes Ni(SQ)₂L_n (n = 1, 2). It was found that a Ni–SQ exchange coupling is ferromagnetic and changes slightly with varying L for both types of complexes – with *cis*- and *trans*- coordinated SQ ligands. An SQ–SQ exchange coupling quite the contrary is different for complexes with *cis*- and *trans*- coordinated SQ ligands. Thus the SQ–SQ exchange is usually antiferromagnetic and changes slightly with varying L for *trans*-Ni(SQ)₂L_n. Whereas in *cis*-Ni(SQ)₂L_n the SQ–SQ exchange strongly changes with varying L and may be both ferro- and antiferromagnetic.

The study was financially supported by RFBR (13-03-12401-ofi, 15-03-00488, 15-33-20286, 15-53-10009_RS), MK-247.2014.3, MK-2732.2015.3, RAS and SB RAS.

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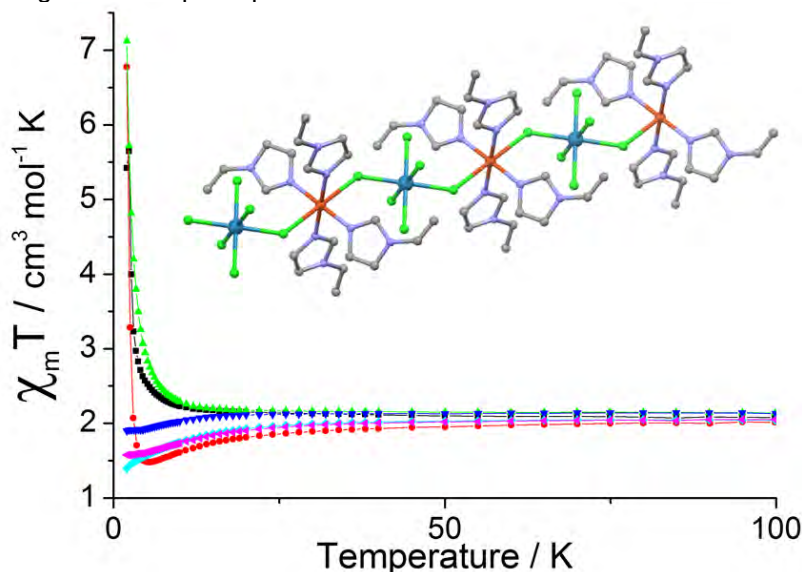
Magnetostructural correlations in a family of Re^{IV} - Cu^{II} chains based on the $[\text{ReCl}_6]^{2-}$ anion.

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The highly anisotropic Re^{IV} -ion has long been employed for the preparation of interesting molecular magnetic materials. Single molecule magnets and single chain magnets have been synthesised containing Re^{IV} . [1,2] The first use of the paramagnetic anion $[\text{ReCl}_6]^{2-}$ as a building block for 1D magnetic systems was reported in 2014 by Martínez-Lillo *et al.* with the system $\{(\text{Cu}(\text{imidazole})_2(2-(2'\text{-pyridyl})\text{imidazole}))[\text{ReCl}_6]\}_n$. [3] Here we present the magnetostructural characterisation of a family of chloro bridged Re^{IV} - Cu^{II} chains based on the $[\text{ReCl}_6]^{2-}$ anion. The chains are of general formula $\{(\text{Cu}(\text{L})_4)[\text{ReCl}_6]\}_n$ with L = imidazole, 1-methylimidazole, 1-vinylimidazole, 1-butylimidazole, 1-vinyl-1,2,4-triazole, and DMF. The structural differences in the chains are significant, with Re – Cl – Cu bond angles of 128 – 152° and Re ... Cu separations of 4.73 ... 5.30 Å. The structural variations induce different magnetic properties, such as antiferromagnetic and ferromagnetic exchange, as well as, ferrimagnetic and metamagnetic behaviour. High pressure studies on these systems reveal unusual structural, magnetic and optical perturbations.





A metallic molecular paramagnet and an unprecedented 3D coordination polymer containing the tris(chloroanilate)ferrate anion

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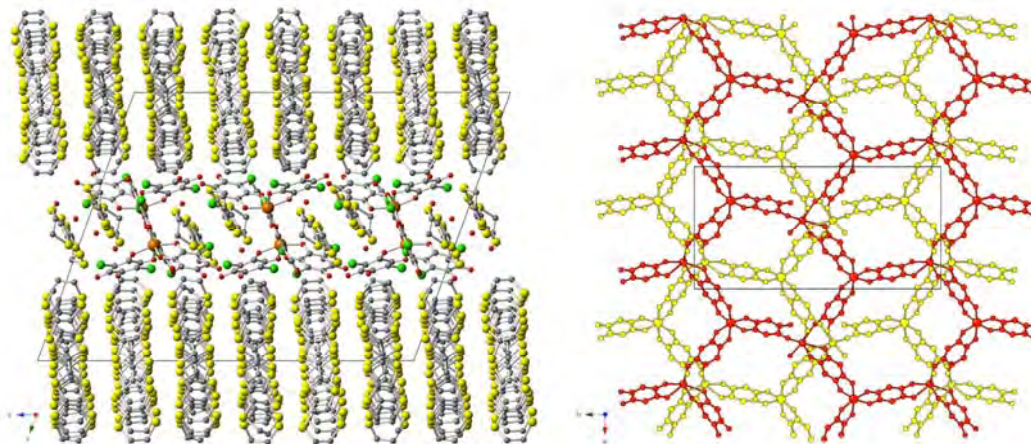
In this communication we will show two different compounds containing the chiral tris(chloroanilate)ferrate anion, $[\text{Fe}^{\text{III}}(\text{C}_6\text{O}_4\text{Cl}_2)_3]^{3-}$.

On one hand, this anion has been combined with the well known organic donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF = ET) to prepare the first radical salt of ET with a tris(anilate)metallate anion.^[1] This salt presents coexistence of the paramagnetic properties of the anion with the conducting properties of the organic ET donor. The salt, formulated as $(\text{ET})_6[\text{Fe}(\text{C}_6\text{O}_4\text{Cl}_2)_3](\text{H}_2\text{O})_{1.5}(\text{CH}_2\text{Cl}_2)_{0.5}$, presents ET layers with an average +0.5 charge and very high electrical conductivity with a quasi-metallic behaviour around room temperature. The magnetic properties are those of the paramagnetic $[\text{Fe}^{\text{III}}(\text{C}_6\text{O}_4\text{Cl}_2)_3]^{3-}$ anion with a zero field splitting (ZFS). This salt is, therefore, one of the few known examples of paramagnetic metals.

On the other hand, the synthesis of this $[\text{Fe}^{\text{III}}(\text{C}_6\text{O}_4\text{Cl}_2)_3]^{3-}$ anion in presence of Na^+ and NEt_3Me^+ cations yields compound $(\text{NEt}_3\text{Me})[\text{Na}(\text{dmf})][\text{NaFe}(\text{C}_6\text{O}_4\text{Cl}_2)_3]$ whose structure consists in 2D hexagonal honeycomb layers formulated as $[\text{NaFe}(\text{C}_6\text{O}_4\text{Cl}_2)_3]^{2-}$ with the NEt_3Me^+ cations inserted in the hexagonal cavities of the anionic layers.^[2] These hexagonal layers are formed by $[\text{Fe}^{\text{III}}(\text{C}_6\text{O}_4\text{Cl}_2)_3]^{3-}$ anions connected through Na^+ cations forming hexagons with alternating Fe^{3+} and Na^+ ions. These hexagonal layers are further connected through $[\text{Na}(\text{dmf})]^+$ cations to generate an unprecedented 3D structure. As in the previous compound, the magnetic properties are those of the paramagnetic $[\text{Fe}^{\text{III}}(\text{C}_6\text{O}_4\text{Cl}_2)_3]^{3-}$ anion with a ZFS.

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Molecular spintronics
(Poster)

Enhanced tunnel magnetoresistance in a single-wall carbon nanotube quantum dot with embedded magnetic molecule

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We analyze the spin-resolved transport properties of a single-wall carbon nanotube quantum dot with embedded magnetic molecule weakly coupled to external ferromagnetic leads. Using the real-time diagrammatic technique in the lowest order perturbation theory with respect to the tunnel coupling, we calculate the current, differential conductance and tunnel magnetoresistance in both the linear and nonlinear response regimes. We show that transport properties greatly depend on internal parameters of both the carbon nanotube and the magnetic molecule. When the nanotube favors the triplet state at equilibrium and the exchange coupling between nanotube and molecule is of ferromagnetic type, we predict an enhanced tunnel magnetoresistance. On the other hand, in the case of antiferromagnetic coupling, the tunnel magnetoresistance can become negative. This behavior of tunnel magnetoresistance is associated with particular spin states being active in transport and nonequilibrium spin accumulation that builds up in the system. In addition, we also study the bias and gate voltage dependence of the Fano factor and find super-Poissonian shot noise in certain transport regimes.



Switchable magnetic materials and optical magnets
(Poster)

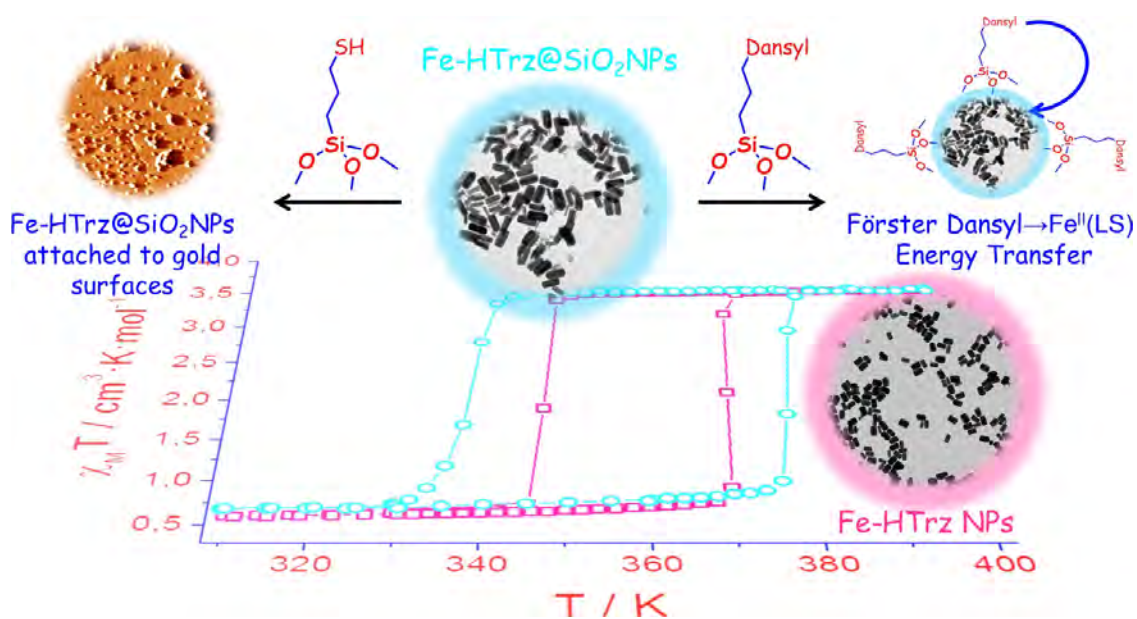
Studies on bifunctional Fe(II)-triazole SCO nanoparticles: time-dependent luminescence, surface grafting and effect of silica shell on the magnetic properties.

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Pure and silica wrapped Fe(II)-triazole (FeHTrz) spin-crossover (SCO) nanoparticles have been prepared following a water-in-oil synthetic procedure. The size and shape can be tuned by controlling the Fe(II) and triazole concentrations in the aqueous phase. The magnetic properties of these nanoparticles are strongly affected by the presence of a silica shell embedding the nanostructured FeHTrz polymer. Whereas bare FeHTrz nanoparticles exhibit abrupt and cooperative spin transition with 24 – 35 K-wide thermal hysteresis loops, for the silica derivatives the hysteresis width increases up to 37 – 42 K. This probes the efficiency of the silica shell to promote interparticle interactions and enhance cooperativity effects. Tomographic studies of the FeHTrz@SiO₂ nanoparticles reveal a core/shell structure with the pure FeHTrz polymer wrapped into a thin shell of pure silica. Taking advantage of the chemical properties of the silica shell, these hybrid nanoparticles were coated with a dansyl derivate fluorophore whose luminescent properties can be adjusted by the spin state of the SCO polymer. Time-dependent luminescent studies reveal the existence of a non-radiative energy transfer (Förster type) between the organic fluorophore and the Fe(II)-low spin ions. These nanoparticles have also been functionalized with thiol groups allowing them to be deposited onto a gold surface in a controlled manner.





Switchable magnetic materials and optical magnets
(Poster)

Novel dinuclear cyanido-bridged molecular complexes exhibiting

SMM, ET and SCO properties

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The design of molecule based magnetic materials is an emerging area of material sciences.¹ Moreover, molecules that exhibit tunable optical and magnetic properties through the application of external stimuli (temperature, pressure, light irradiation, magnetic field etc) has become an important area in the field of material sciences, offering rich future application such as electronic devices, information storage/processing, molecular switch, high-density recording media and molecular sensors.²

The cyanide-based chemistry has been particularly fruitful and, for more than twenty years, a large number of cyanide-bridged polymetallic systems have been synthesized through rational choices of cyanido-based building blocks. Interesting properties, such as single-molecule and single-chain magnets behaviours,³ spin crossover,⁴ electron-transfer process,⁵ and photoinduced magnetism.⁶ In our quest to obtain new molecular systems and concomitantly to reduce the size of these functional materials, we reported a dinuclear complex,⁷ which exhibits switchable optical and magnetic properties depending on its physical state. Very recently we have successfully design a new dinuclear [Fe/Co] complexes exhibiting both thermally and light induced electron transfer in solid state.⁸

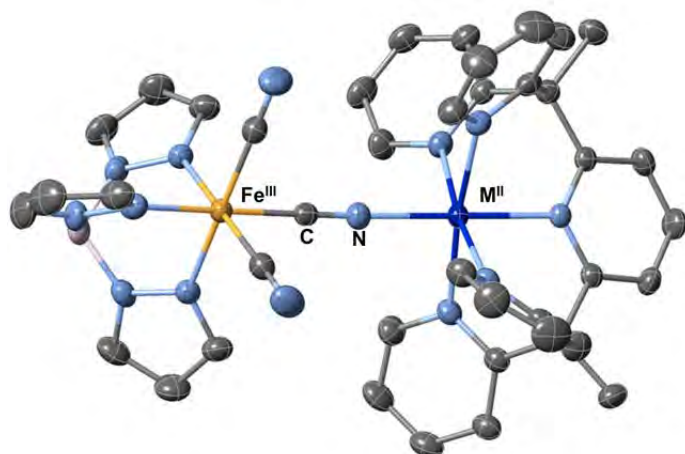
In this presentation, we report novel dinuclear complexes $[(L)Fe^{III}(CN)_3M^{II}(L')^+]$ (L' = pentadentate N- donor ligand; L = tridentate N- donor ligand, $M(II)$ = Co, Ni, Mn), designed by rational building-block approach. Combined structural, magnetic and photomagnetic studies reveal that SMM, SCO and metal-to-metal electron transfer properties could be triggered by application of magnetic field, light and temperature.

Acknowledgements. We thank, the Centre Franco-Indien pour la Promotion de la Recherche Avancée (CEFIPRA), the Centre National de la Recherche Scientifique (CNRS), the Conseil Regional d'Aquitaine, the University of Bordeaux and the Agence Nationale de la Recherche (ANR) for financial support.

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Molecular nanomagnets
(Poster)

Microwave assisted synthesis and nanostructuration of heterometallic 3d-4f nanomagnets

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Microwave assisted synthesis is a useful technique to obtain pure and reproducible homo- and heteronuclear coordination compounds. Moreover, if this synthesis is done without organic solvents, we can include it in green chemistry. These metalorganic structures present characteristic cores that provide them with interesting magnetic properties. Such complexes are called molecular nanomagnets (MNMs) and have been investigated due to their possible application in fields like magnetic coolers or information storage and processing. In order to fabricate devices for this aim, deposition and nanostructuration of these complexes on surfaces is required.

Complexes with 3d metals and lanthanides have been prepared using solvent free microwave assisted synthesis at low temperatures, like the heterometallic Ni_4Ln complexes ($Ln = Tb, Dy, Gd, La$). The tert-butyl groups that decorate the ligands provide the complexes with solubility and a grafting ability onto soft metal or graphite-like surfaces.

We demonstrate the use of solvent free microwave assisted synthesis in coordination chemistry. Grafting ability on HOPG and soft metals is programmed into the MNMs prepared by ligand design. Functionalized nanoparticles and surfaces will be/are studied using some characterization techniques like AFM, XMCD, TEM or DLS.



Heterostructured switchable nanorods

Mauricio López Jordà¹, Damien Garrot², Kamel Boukheddaden², Alexandre Gloter³, Talal Mallah¹, Laure Catala¹

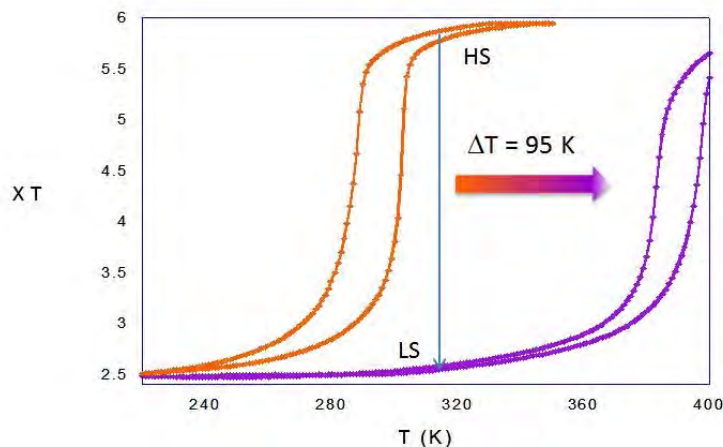
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Microporous 3D metal-organic frameworks represent an interesting class of crystalline molecular materials. Switchable networks based on cyanide bridges like Prussian Blue Analogues (PBA) and Hofmann-like clathrates offer tunable physical properties under external stimuli such as temperature, pressure or irradiation by light. The origin of these phenomena is located at the molecular level with the presence of an "active" metal, which generates either a spin crossover of the metal into the network or a metal-metal charge transfer. The switching of a center/pair affects nearby sites inducing a strong cooperativity and hysteretic response (optical and magnetic) close to room temperature. Furthermore, the microporosity of the clathrate networks allows for the insertion of various molecules within the pores leading to a complete change in optical and magnetic properties of the material.^[1] We will present a new type of heterostructured nanoobjects based on the Prussian Blue Analogue $\text{Cs}[\text{NiCr}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ with high Curie temperatures ($T_c = 90 \text{ K}$)^[2] and the Hofmann clathrate-like coordination compound $\text{Fe}(\text{pz})[\text{Pt}(\text{CN})_4] \cdot x\text{H}_2\text{O}$ (pz = pyrazine) with hysteresis and spin transition at room temperature. Inclusion of different guest molecules within pores of $\text{Cs}_{0.7}\text{Ni}[\text{Cr}(\text{CN})_6]_{0.9} @ \{\text{Fe}(\text{pz})[\text{Pt}(\text{CN})_4]_2\}_4$ nanorods and their effect on the magnetic properties have been studied.

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Magnetic properties of crystalline salts with radical anions of metal-containing and metal-free phthalocyanines

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Metal phthalocyanines are promising compounds for the development of conducting and magnetic materials [1]. It should be noted that functional phthalocyanine compounds were obtained mainly by oxidation up to now. However, some theoretical and experimental works showed that reduced metal phthalocyanines can also show promising conducting and magnetic properties [2].

In this work we have developed a simple method to generate radical anion salts of different metal-containing and metal-free phthalocyanines and studied their magnetic properties [3, 4].

Radical anion salts of phthalocyanines $\{MPc(3-)\}^-$, where $M = Cu^{II}, Ni^{II}, H_2, Sn^{II}, Pb^{II}, Ti^{IV}O$, and $V^{IV}O$, $Sn^{IV}Cl_2$ have been obtained as single crystals by phthalocyanine reduction with sodium fluorenone ketyl in the presence of tetraalkylammonium cations. That provides the first solid-state characterization of molecular structure and magnetic properties of the $[MPc(3-)]^-$ radical anions, containing reduced Pc ligand.

Radical anions with $Ni^{II}, Sn^{II}, Pb^{II}, Sn^{IV}Cl_2$ and $Ti^{IV}O$ have $S = 1/2$ spin state, whereas $[Cu^{II}Pc(3-)]^-$ and $[V^{IV}OPc(3-)]^-$ containing paramagnetic Cu^{II} and $V^{IV}O$ metal centers have two $S=1/2$ spins per radical anion. Most radical anions of metal phthalocyanines are isolated in the crystals and that provides only weak magnetic coupling between spins. Nevertheless, in the complexes with a layered arrangement of phthalocyanines, strong enough magnetic coupling is observed with Weiss temperature of -17 K for $(TBA^+)_2\{[Pb^{II}Pc(3-)]^-\}^-(Br^-)$ and of -57 K for $(Bu_4N^+)\{[Ti^{IV}OPc(3-)]^-\}$. The strongest magnetic interactions were found for $(Et_4N^+)\{[Ti^{IV}OPc(3-)]^-\}C_6H_4Cl_2$ in which phthalocyanine radical anions form layers of closely packed π -stacking dimers. In this case spins are ordered antiferromagnetically before 150 K due to a singlet-triplet transition in the $\{[Ti^{IV}OPc(3-)]^-\}_2$ dimers. Central metal atoms affect strongly EPR spectra of phthalocyanine radical anions. Instead of narrow EPR signals characteristic of metal-free phthalocyanine radical anions $[H_2Pc(3-)]^-$ (linewidth of 0.08–0.24 mT), broad EPR signals are manifested (linewidth of 2–70 mT) with temperature-dependent g-factors and linewidths.

The proposed approach makes it possible to prepare anionic metal phthalocyanines as crystals with different cations and allowing the development of magnetic and conducting phthalocyanine assemblies based on them.

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Luminescence and magnetic studies of $A[Mn_3O(R\text{-salox})_3(O_2C\text{-anthra})_2]$ compounds, A= alkaline cation

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The use of salicylaldoxime ligands and related derivatives to synthesize hexanuclear manganese complexes with general formula $[Mn^{III}_6O_2(salox)_6(O_2CR)_2L_4]$ where L = solvent molecule has been widely studied. It has been established that the magnetic properties in this kind of compounds are mainly related with the substituent of the R-salicylaldoxime ligand.^[1] The use of a fluorescent carboxylate ligand such as anthracenecarboxylate could allow to study the luminescence behaviour of these manganese compounds. The combination of the corresponding magnetic and luminescence properties could make these compounds very interesting in the field of molecular electronics.

Here we present a series of compounds with the typical $\{Mn_3O(R\text{-salox})_3\}$ core where R = H or 3-Me and different alkaline anthracenecarboxylate salts. One of the compounds that we have obtained is $\{Na[Mn_3O(salox)_3(O_2C\text{-anthra})_2(EtOH)_3(H_2O)_4] \cdot 2EtOH\}_n$ shown in Fig. 1. In this case the alkaline metal acts as a link to form chains of $\{Mn_3O(R\text{-salox})_3\}$ units. The aim of this work is to study the impact of the different substituents in the R-salicylaldoxime ligands and the different alkali metals on the luminescence and magnetic properties.

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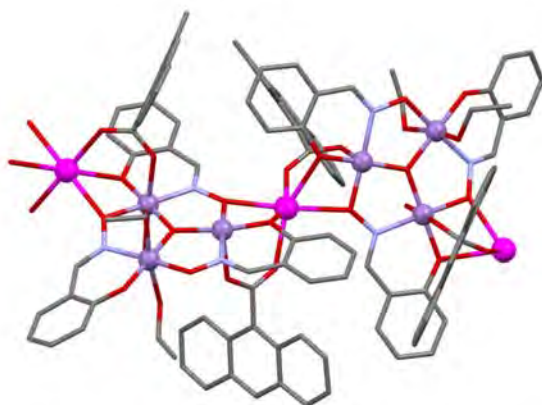


Fig. 1 $\{Na[Mn_3O(salox)_3(O_2C\text{-anthra})_2(EtOH)_3(H_2O)_4] \cdot 2EtOH\}_n$



Magneto-structural characterization of trinuclear mixed valence complex.

Jorge Manzur¹, Mónica Soler¹, Nicolás Farías¹, Andrés Vega², Albert Escuer³

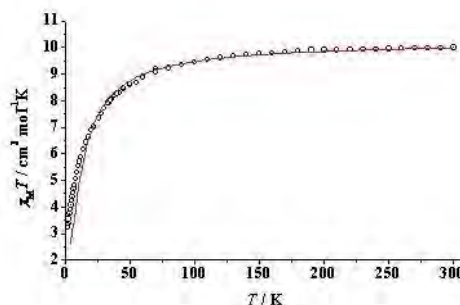
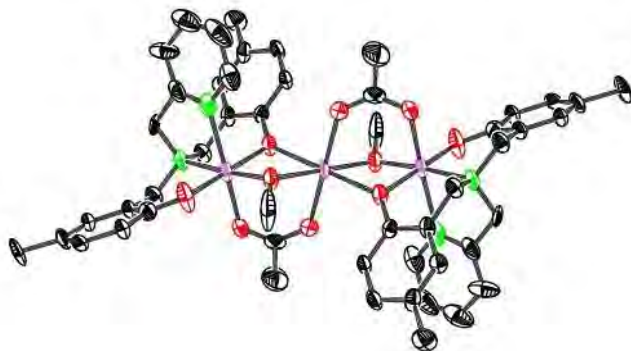
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The chemistry of polynuclear manganese complexes has received a great deal of attention, mainly due to current interest in the design and synthesis of single molecule magnets (SMM) and single chain magnets (SCM), since high nuclearity manganese aggregates display a propensity for large spin ground states; so that they may serve as precursors to molecular materials¹. Many interesting polynuclear manganese complexes have been synthesized by using phenoxo and/or pyridine derived ligands. We are interested in ligands containing both of these two functional groups such as N-(2-pyridylmethyl)-N,N-bis-[2'-hydroxy-5'-methyl-benzyl]-amine (H₂L).

In a previous work², we reported the formation and magnetic properties of tetranuclear Cu(II) complexes and the HL mono-anion: [Cu₂(LH)₂(m⁴-X)Cu₂(LH)₂]³⁺. (X=Cl, Br). In these complexes the copper(II) ions are connected by the HL anion through the phenolate oxygen atom forming a dinuclear unit, while two of them are connected by a halide to give a tetranuclear species. In the present study, a trinuclear mixed valence manganese complex (Mn^{III}-Mn^{II}-Mn^{III}) with the same ligand has been synthesized and its X-ray crystal structure, and magnetic properties have been investigated. The hexacoordinated central Mn^{II} center is bridged to the terminal Mn^{III} centers by one phenoxo, one methoxo and one acetato bridges. The coordination sphere around the Mn^{III} ions presents the same oxygen donor atoms and is completed by the amine and pyridine nitrogens and a terminal phenoxo group of the ligand.

The best fit of the magnetic susceptibility data, as a function of temperature, was obtained using a conventional trinuclear linear model [$H = -2J(S_1S_2 + S_1S_3)$] with $J = -0.79 \text{ cm}^{-1}$ and $g = 1.99$. The ligand reported in this work is a promising candidate for the synthesis of polynuclear metal assemblies, using suitable bridges such as cyano or azide, which may exhibit interesting magnetic properties. We are currently studying its coordination ability towards others metal ions.





Synthesis, structure and magnetic properties of chains made from $[\text{MF}_6]^{2-}$ ($\text{M} = \text{Re}, \text{Zr}, \text{Sn}$) and trinuclear metal-metal bond cobalt clusters

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$\text{Co}_3(\text{dpa})_4\text{Cl}_2$ is a metal-metal bonded "paddlewheel" complex of interest due to its spin-crossover (SCO) properties ($S_{\text{LS}} = 1/2$, $S_{\text{HS}} = 3/2$). Three atoms of cobalt are linearly arranged and are bridged by four 2,2'-dipyridylamide (dpa⁻) ligands with a chlorido ion in each axial position.^[1] This compound was used to synthesize one dimensional coordination polymers using $(\text{PPh}_4)_2[\text{MF}_6]$ where $\text{M} = \text{Re}^{\text{IV}}$,^[2] Zr^{IV} or Sn^{IV} . In this way, we obtained and crystallographically characterized neutral $[\text{Co}_3(\text{dpa})_4\text{MF}_6]_{\infty}$ chains in which the fluorine atom acts as a bridge between the terminal Co ions and the Re, Zr or Sn ions (Figure 1). While the parent compound $\text{Co}_3(\text{dpa})_4\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ demonstrates a gradual, but clear, SCO event above 160 K,^[1] no such increase in the χT product is observed in the one-dimensional compounds. $[\text{Co}_3(\text{dpa})_4\text{ZrF}_6]_{\infty}$ and $[\text{Co}_3(\text{dpa})_4\text{SnF}_6]_{\infty}$ show Curie behavior typical of an $S = 1/2$ system, with $g = 2.36$ and 2.40 respectively. While the diamagnetic $[\text{ZrF}_6]^{2-}$ species mediates weak antiferromagnetic coupling ($J/k_B = -1.0$ K) between the $\{\text{Co}_3\}^{6+}$ units, no significant intrachain antiferromagnetic interactions are found in $[\text{Co}_3(\text{dpa})_4\text{SnF}_6]_{\infty}$. $[\text{Co}_3(\text{dpa})_4\text{ReF}_6]_{\infty}$, possessing the paramagnetic $[\text{ReF}_6]^{2-}$ linker, displays sizable ferromagnetic coupling ($J/k_B = +9.9$ K) between the $\{\text{Co}_3\}^{6+}$ $S = 1/2$ and Re^{IV} $S = 3/2$ units.^[3]

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Acknowledgements: We thank L. Falvello for crystallographic assistance, the Centre National de la Recherche Scientifique (CNRS), the Conseil Régional d'Aquitaine, the University of Bordeaux, and Erasmus Mundus MID program for financial support.

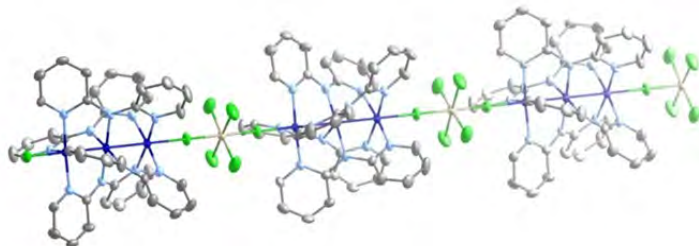


Figure 1. Thermal ellipsoid plot of $[\text{Co}_3(\text{dpa})_4(\text{ReF}_6)]_{\infty} \cdot 2\text{DMF}$. Hydrogen atoms and solvents of crystallization have been omitted for clarity. Ellipsoids are drawn at 50% probability level.



FINE TUNING OF the ENERGY BARRIER OF Dy(III) SIMs

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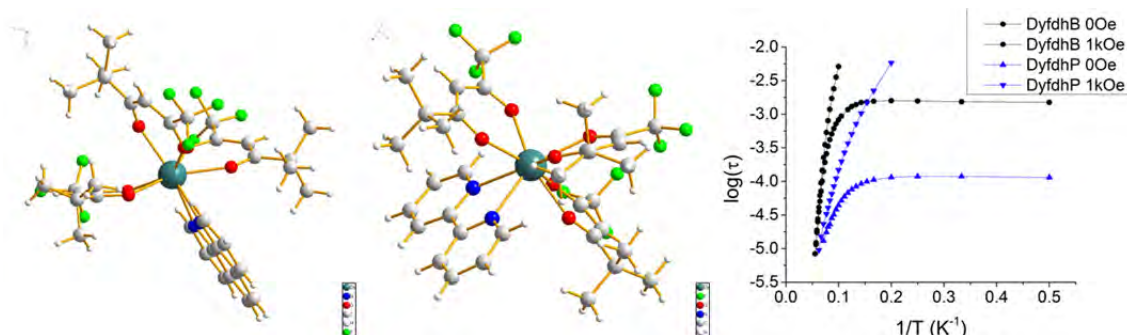
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Recent years, single ion magnets (SIMs) are studied because of the slow relaxation property [1,2]. They are expected as the potential candidate of high density magnetic storage and quantum computing. The mechanics of slow magnetic relaxation is gradually revealed. Among them Orbach process is strongly related to the electron structure, and can be modified by ligand field. In this work, we synthesized two similar lanthanide complexes, in which the lanthanide ion was coordinated by β -diketone (2,2-dimethyl-6,6,6-trifluoro-3,5-hexadione, dfh) and 1,10-phenanthroline or 2,2'-bipyridine ligands. They have 6 oxygen atoms and 2 nitrogen atoms around the lanthanide metal ion in the center with similar bond length, forming a pseudo- D_{4d} coordination structure. The magnetic relaxation behaviors of the two compounds are quite different. Dyfdh₃bpy shows SIM behavior. The alternating current susceptibility shows a temperature dependent process and quantum tunneling relaxation under zero applied field. The fitted energy barrier is 112cm^{-1} at 0Oe and 125cm^{-1} at 1kOe dc field. On the other hand, Dyfdh₃phen with a similar structure has a much lower energy barrier (26.4cm^{-1} at 0Oe and 48.3cm^{-1} at 1kOe) and stronger quantum tunneling. The significant difference between the two compounds may be due to the slight difference in the coordination sphere.

This work was supported by the NSFC and the National Basic Research Program of China.

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Trigonal Bipyramidal Co(II) Complexes: Structures and Magnetism

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Paramagnetic Co(II) ion is an important candidate to construct single-ion magnets (SIMs) for its possible Ising-type magnetic ground state. Three trigonal bipyramidal complexes [CoNP₃X][BPh₄] (**1**), (X = Cl, Br, I) have been synthesized and characterized, all of which crystallized in a triclinic space group *P*-1, and share very similar crystal parameters. The local coordination environments of **1** are nearly C_{3v}.

Variable-temperature dc magnetic susceptibilities were measured on crystalline powders. Both the shape of $\chi_M T$ plots and the non-superposition of the *M* vs. *H/T* plots imply the magnetic anisotropies (*D* = ~ -10 cm⁻¹).

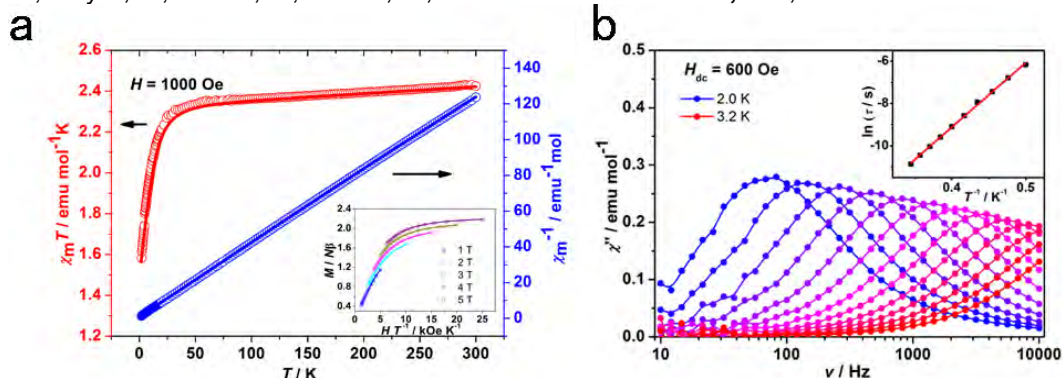
Ac susceptibilities of **1** at various frequencies were measured at low temperature. Under 600 Oe dc field, out-of-phase ac susceptibility (χ'') signals were observed, showing a strong frequency dependence of χ'' below 5 K. Arrhenius plots were used to extract the relaxation barriers, giving the *U*_{eff} values of ~ 30 K, τ_0 of ~ 6×10⁻¹⁰ s, very close to ones of similar Co(II) complexes reported before.¹

Theoretical studies using *ab initio* methods reproduced the susceptibility and magnetization measurements well, giving a deep understanding of the magnetic relaxations and magneto-structural correlations.

* This work was supported by the NSFC and the National Basic Research Program of China.

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Molecular nanomagnets
(Poster)

Functional Hetero-Tri and Hetero-Tetra-Metallic Architectures

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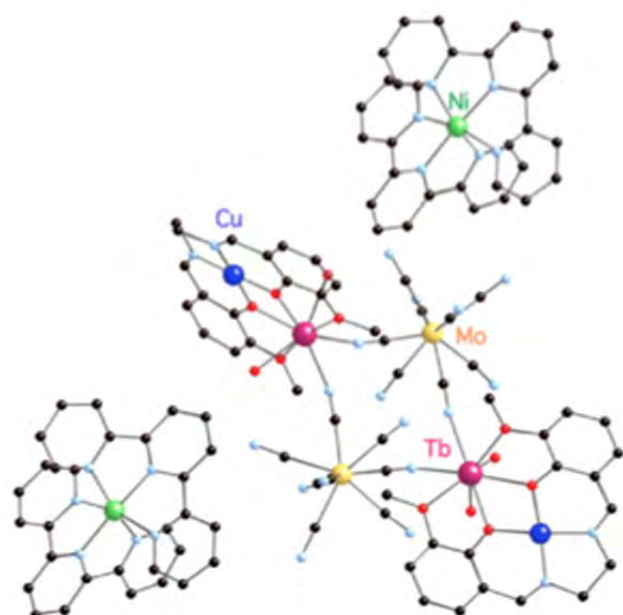
The design and the synthesis of hetero-tri and hetero-tetra-metallic complexes is a real challenge in coordination chemistry and a promising route to multi-functional magnetic compounds. This presentation highlights some recent achievements in the field of single molecule magnets and photo-switchable high-spin molecules^{1,2,3} viewed as new precursors for functional hetero-poly-metallic assemblies.

As part of the general interest in photo-switchable nanomagnets, a large family of Molybdenum/Tungsten complexes has been obtained including multi-metallic clusters, such as MoCu_n (n = 2, 4, 6), MoZn₂ or WZn₂ whose magnetic properties can be modified by light. Our strategy demonstrates the relevance of using these polynuclear complexes with pendant cyanide ligands as valuable photo-active building blocks for the rational design of hetero-poly-metallic photo-switchable supramolecular architectures.

Relying on the concept of "polynuclear complexes as ligands", we succeeded in obtaining a versatile family of hetero-tri and hetero-tetra-metallic complexes (*i.e.* Mo₂Tb₂Cu₂-Ni, MoCuTb-Ru)^{4,5,6}. The next step is to design multifunctional architecture mixing several properties (single molecule magnets, photomagnetism, spin crossover, luminescence...) and if possible to create synergy between them.

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ALKALI-TEMPLATED POLYNUCLEAR LANTHANIDE SINGLE-MOLECULE MAGNETS

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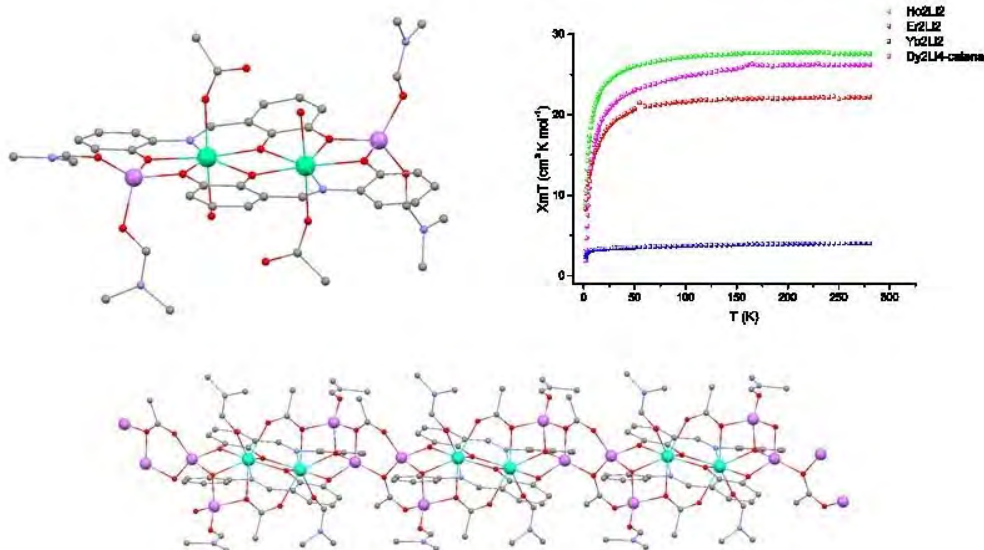
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Due to their inherent highly anisotropic nature, lanthanide ions have attracted during the recent years great attention within the field of molecular magnetism. Researchers have synthesized a large number of mononuclear and polynuclear species that behave as single-molecule magnets (SMM's) [1]. Such systems exhibit slow relaxation of the magnetization in sufficiently low temperatures, a trait that renders them potential candidates for high density information storage devices [2].

Towards this direction we designed a polydentate Schiff-base ligand to employ in the synthesis of such systems. Reaction of the ligand with various lanthanide nitrates and different alkali acetates afforded a number of lanthanide complexes that fall into different families.

We will present some interesting synthetic aspects of the system such as how the nuclearity and structure of the complexes depend on the choice of lanthanide and alkali ions. In addition preliminary magnetic measurements have been performed on the synthesized complexes. We will summarize the static magnetic properties of these systems and we will present details of the dynamic magnetic properties which suggest the presence of slow relaxation of the magnetization at low temperatures for some of the complexes, an indication of SMM behavior.

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Switchable magnetic materials and optical magnets
(Poster)

Spin Transition in Heterospin Complexes $\text{Cu}(\text{hfac})_2$ with (4-methylpyridin-3-yl)-substituted Nitronyl Nitroxides

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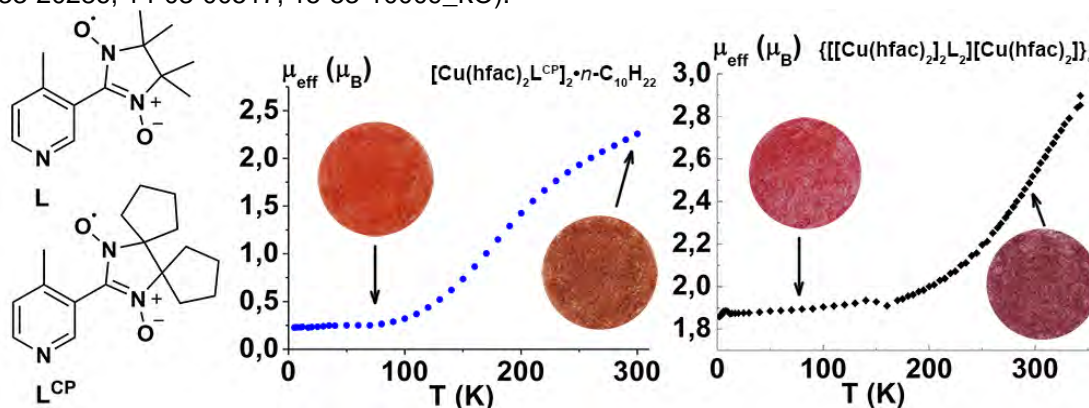
Breathing crystals based on $\text{Cu}(\text{hfac})_2$ complexes with nitroxides showing thermally and light induced spin crossover (SCO) attract significant attention in the field of molecular magnetism.

We succeeded in synthesizing of (4-methylpyridin-3-yl)-substituted nitronyl nitroxides **L** and **L^{CP}**. The main peculiarity of **L** and **L^{CP}** molecules consist in a large dihedral angle between the planes of the paramagnetic fragment $\text{O}^\bullet\text{--N}=\text{C}=\text{N}^\bullet\text{--O}$ and pyridine ring. Inside the solids this angle is equal to 55.2 and 56.1°, respectively. $\text{Cu}(\text{hfac})_2$ reacts with **L** and **L^{CP}** giving rise to dinuclear $[\text{Cu}(\text{hfac})_2\text{L}]_2$, $[\text{Cu}(\text{hfac})_2\text{L}^{\text{CP}}]_2 \cdot \text{Solv}$ (Solv = $n\text{-C}_6\text{H}_{14}$, $n\text{-C}_{10}\text{H}_{22}$, $n\text{-C}_{16}\text{H}_{34}$), tetranuclear $[\text{Cu}(\text{hfac})_2]_4(\text{L}^{\text{CP}})_2$ and polymeric chain $\{[\text{Cu}(\text{hfac})_2]_2\text{L}_2\}[\text{Cu}(\text{hfac})_2]_\infty$ heterospin complexes.

In the 200-250 K temperature range $[\text{Cu}(\text{hfac})_2\text{L}^{\text{CP}}]_2 \cdot \text{Solv}$ solids show SCO phenomenon that is accompanied by a color change from orange to brown when heated and in the opposite direction upon cooling. Included solvent molecules influence weakly on solvates magnetic properties.

The presence of methyl group in the pyridine ring promotes SCO phenomenon in $\{[\text{Cu}(\text{hfac})_2]_2\text{L}_2\}[\text{Cu}(\text{hfac})_2]_\infty$ under ambient temperature, which is accompanied by a color change from red to burgundy when heated.

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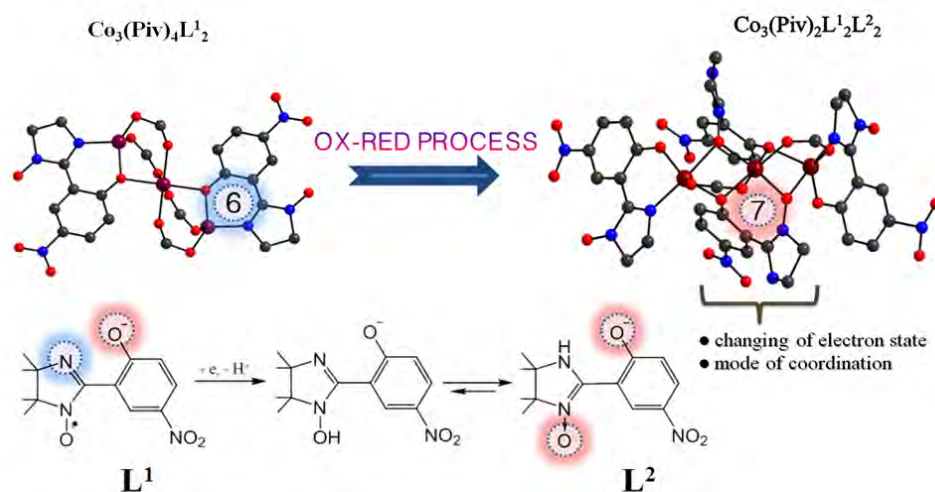
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It was found that $[\text{Co}_2(\text{H}_2\text{O})(\text{Piv})_4(\text{HPiv})_4]$ (where Piv is trimethylacetate), FeCl_3 , CrCl_3 , MnCl_2 reacted with nitroxide HL^1 (2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-1-oxyl) giving rise to the complexes containing both initial imino nitroxide HL^1 and corresponding nitron L^2 simultaneously. We succeeded in synthesizing both mononuclear and polynuclear transition metal complexes containing simultaneously nitroxides and their reduced forms as ligands. Moreover, nitroxide and nitron were coordinated in a different manner by the same metal ion. We named this phenomenon as “red-ox induced change in the ligand coordination mode.” This effect is difficult to reveal without using a stable nitroxide in the reaction. The effect of a change in the ligand function includes a reduction of nitroxyl to hydroxylamine, proton addition, subsequent prototropic rearrangement to nitron, rotation of the 2-imidazoline heterocycle, and a change of coordination atoms^[1]. Thus red-ox process provoked a change not only in the electronic state of the ligand, but also in its coordination mode. Noteworthy, when using $[\text{Ni}_2(\text{H}_2\text{O})(\text{Piv})_4(\text{HPiv})_4]$, we have never observed the formation of complexes containing nitroxides and its reduced forms simultaneously.

The research was supported by RFBR (13-03-12401, 15-03-00488, 15-33-20286, MK-2732.2015.3, 14-03-00517, MK-247.2014.3)

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Molecular nanomagnets
(Poster)

Moving away from serendipity: The construction of novel supramolecular magnetic cages

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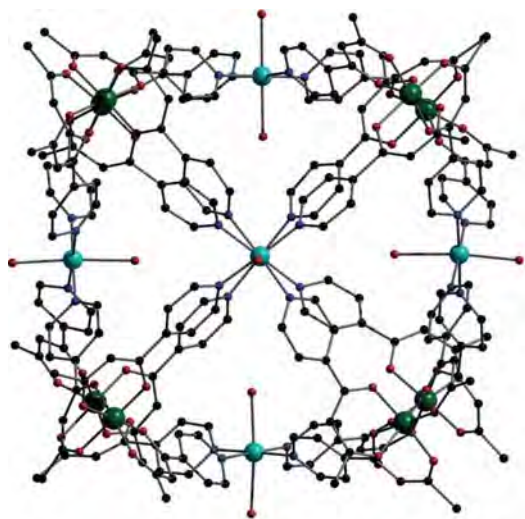
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Synthetic strategies for designing new metallic clusters range from a serendipitous approach, which makes use of coordinatively flexible metal ions and flexible bridging organic ligands as building blocks, to more rational approaches, where rigid ligands contain available donor sites with predesigned orientation preferences. 3D capsules built through rational design, which contain diamagnetic metals and are based on Platonic and Archimedean solids, are particularly attractive within supramolecular chemistry due to their often large internal cavities which can play host to a large array of potential guests. These host-guest interactions have been probed extensively through solution NMR studies and have important roles to play in areas such as photochemistry, catalysis and drug delivery [1]. Surprisingly, there is limited use of paramagnetic metals in the construction of these capsules and an even more limited understanding of their magnetic behaviour [2]. Herein we present the synthetic strategy and magnetic studies of a new series of cubes, based on $[\text{Cr}^{\text{III}}\text{L}_3]$ (HL = 1-(4-pyridyl)butane-1,3-dione) as a paramagnetic building block, which acts as a tritopic donor towards a "naked" M^{II} salt (Co or Cu) [3]. Due to the difficulty of monitoring NMR on paramagnetic entities, current studies are underway that use diamagnetic analogues of the capsules, allowing us to mimic host-guest interactions.

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Using INS to witness entanglement in a pyrazine linked molecular nanomagnet dimer

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The neutron is a key tool for probing the properties of molecular nanomagnets. In particular it helps us to understand the excitations that characterize the microscopic magnetic properties of these systems, in terms of the energy levels and the strength of the interactions.

Being finite spin systems, molecular nanomagnets are perfect test beds for probing quantum dynamics. The tremendous potential of time of flight (ToF) neutron spectroscopy as a technique for investigating these dynamics were recently demonstrated by Baker et al.¹ In a benchmark setting experiment, they utilised a large single-crystal sample of a Cr₈ antiferromagnetic ring. Then together with developments in neutron spectrometer technology; such as detectors sensitive in both the azimuthal and scattering plane positions as well as compounding this with developments in analysis software, they were then able to measure such large volumes of S(Q,E) that they could directly extract the spin dynamics of the system without the need for a model spin-Hamiltonian. This was possible since the amount of information extracted was so large.

We wish to build on this breakthrough and apply it to large spin systems in molecular magnetism, where understanding of the spin dynamics is traditionally inhibited, due to the size of Hilbert space involved. Understanding these dynamics is crucial if molecular nanomagnets are to realise their potential in technologies such as quantum computing.

One of the most promising molecular nanomagnets for implementation in quantum computing is Cr₇Ni, whose $S=\frac{1}{2}$, well separated ground state and slow relaxation time, allow it to behave as a prototypical qubit. One of the requirements for 2 qubit gate operations in QIP (as detailed in the DiVincenzo criteria) is to entangle these spin units. Chemists at the University of Manchester have managed to address this challenge by tying two of these Cr₇Ni spin $\frac{1}{2}$ units together using an organic pyrazine linker. This linker holds the two Cr₇Ni modules very closely together at a distance of 7.027(3)Å (through space).

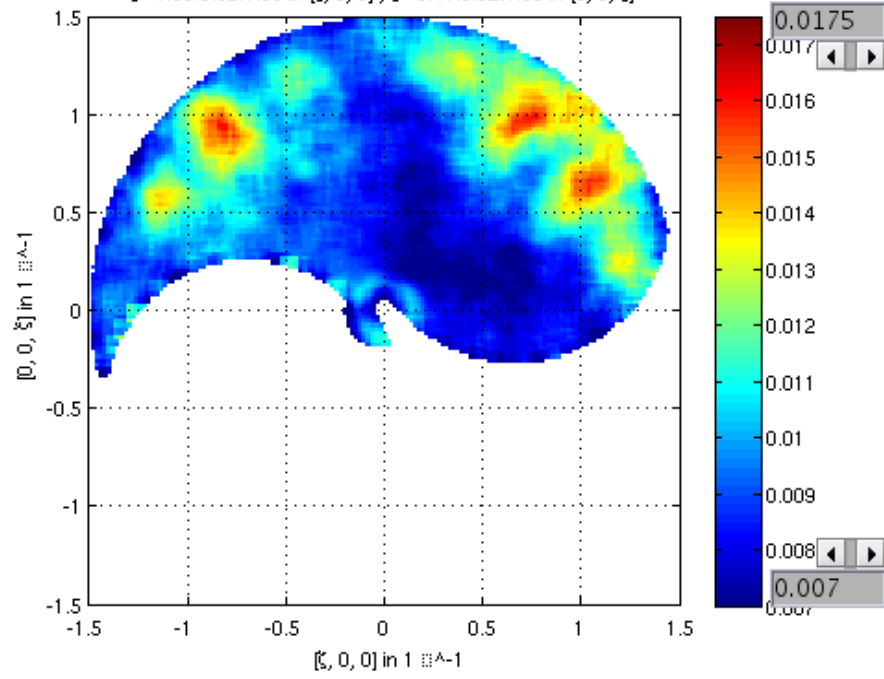
We show that using ToF neutron spectroscopy we have directly observed the presence of this entanglement, manifesting through the modulation in the Q-dependence viewed along the inter-ring axis. This results from the S() dependence in the neutron scattering function for the correlated system. We therefore verify that through organometallic chemistry we can entangle spin units in molecular magnetism and use the neutron to detect this.

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$-0.2 \leq \eta \leq 0.2$ in $[0, -\eta, 0]$, $0.217 \leq E \leq 0.253$

$\xi = -1.59:0.02:1.53$ in $[\xi, 0, 0]$, $\xi = -0.41:0.02:1.59$ in $[0, 0, \xi]$





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Molecular nanomagnets
(Poster)

A synthetic and magnetic overview for a series of Zn^{II}-Dy^{III} complexes with the (*E*)-2-(2-hydroxy-3-methoxybenzylideneamino)phenol motif.

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Four heteronuclear Zn^{II}-Dy^{III} complexes, possessing interesting topologies, formulated as ([Zn₂Dy₂(L1)₄(EtOH)₆]ClO₄·EtOH) (**1**), [Zn₅Dy(L1)₆(OH)]·MeCN·H₂O (**2**), [Zn₄Dy₂(L₂)₄(DMF)₄(CH₃O)₂]·DMF (**3**) ([Zn₂Dy₂(L3)₂(NO₃)₄]·MeOH) (**4**), are synthesised and their structures measured by single X-ray crystal diffraction. All ligands employed in the formation of complexes share the (*E*)-2-(2-hydroxy-3-methoxybenzylideneamino)phenol motif with property enhancing modifications. The synthetic strategy employed explores how the ligands in conjunction with varying solvent system can affect the topology of the resultant compound. Magnetic properties of compounds **1-4** are reported



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Switchable magnetic materials and optical magnets
(Poster)

Hybrid magnetic/conducting composites from spin crossover complexes and spin and organic conducting polymers

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Spin crossover (SCO) compounds have been proposed as molecular switches for multiples applications in electrical circuits, data storage or sensing, taking advantage of their bistability between low spin (LS) and high spin (HS) states controlled by external stimuli (pressure, temperature or light irradiation) [1, 2]. In the case of electrical circuits, the intrinsic insulating character of SCO materials precludes their wide incorporation to most electrical architectures.

Our group has developed an strategy for the exploitation of the unique SCO switching features in conducting materials from the combination of SCO probes into conducting organic conductor polymers. In these hybrids, the spin transition triggers a remarkable change in the resistivity of the organic film, with differences between the HS and LS phases above 100% [3].

In this communication we will report our latest results in this area, showing the multiple applications of this general approach with additional polymer films such as PEDOT:PSS, doped-polythiophene, or doped-polyaniline, etc. At the same time, incorporation of different SCO molecules allows easy tuning of the transition temperatures between liquid nitrogen up to over 400 K.

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Crystal structure studies and full magnetic investigations of a mononuclear 4f polyoxometalate family with single molecule magnet behaviour

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Polyoxometalates (POMs) are a fascinating class of metal-oxo clusters containing transition metal ions, mainly W and Mo, in their high oxidation states. POMs have been widely explored over the last 50 years for various applications in catalysis, for bio-medical and biological features. Indeed, these metal-oxo clusters offer undeniable qualities for future applied devices such as a wide structural and compositional diversity (possible tuning of their electronic structure). The story of molecular magnetism begins with the reports by Sessoli et al.^[1] on the $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$, $\{\text{Mn}_{12}\}$, and the observation of its slow magnetic relaxation process in a molecular material. Over the last two decades the number of reported single molecule magnets (SMMs) did not cease to grow with several examples of 3d, 4f and even mixed 3d-4f complexes.^[2]

Up to now, only 3d and 4f substituted POMs exhibiting single molecule magnet behaviour have been reported to date. The first mononuclear lanthanide complex $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{9-}$ (Ln = Ho, Er) with SMM behaviour was published by Coronado et al. in 2008.^[3] After this breakthrough, similar approaches were extended to the mononuclear family with the Preyssler-type series $[\text{Ln}(\text{P}_5\text{W}_{30}\text{O}_{110})]^{12-}$ (Ln = Tb, Dy, Ho, Er, Tm, Yb) and the Keggin-type structure $[\text{Ln}(\beta\text{-SiW}_{11}\text{O}_{39})_2]^{13-}$ (Ln = Dy, Ho, Er, Yb). Up to now, only three types of mononuclear 4f POM complexes exhibiting SMM behaviour are observed and join the very short list of published polyoxometalates showing this magnetic property.

Here, we highlight^[4] a new isostructural family of 4f mononuclear “sandwich” Keggin POMs with a large variety of lanthanide ions (Ln = Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb). The crystal structure of all new POMs was successfully solved and the full magnetic measurements with alternating current (ac) and direct current (dc) are under investigation. Preliminary results on the $[\text{Dy}(\beta_2\text{-GeW}_{11}\text{O}_{39})_2]^{13-}$ derivative revealed the presence of SMM behaviour. Moreover, careful studies of the Dysprosium coordination geometry show that the Dy^{3+} ion is embedded in a favourable antiprismatic geometry for SMM behaviour.

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New developments in the characterisation of discrete photomagnetic $\text{L-Cu}^{\text{II}}\text{-[M}^{\text{IV}}(\text{CN})_8\text{]}^{4-}$ assemblies

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The design, synthesis and physicochemical characterization of new switchable magnetic materials is one of the major challenges in the pursuit of polyfunctional assemblies.¹ Along these lines, extensive research is related to cyanido-bridged coordination polymers: Prussian Blue Analogs^{2,3} and bimetallic coordination networks constructed of octacyanidometallates.³⁻⁵ Within this family, the $\text{Cu}^{\text{II}}\text{-[Mo(CN)}_8\text{]}^{4-}$ assemblies have been extensively studied for their photomagnetic properties.⁶ We have shown the impact of diverse ligands on the functionality of octacyanidometallate-based assemblies.⁴ Presently, we conduct a study of the influence of ligands on the formation of discrete Cu(II)-Mo(IV) systems, and on the presence and effectiveness of photomagnetic process.

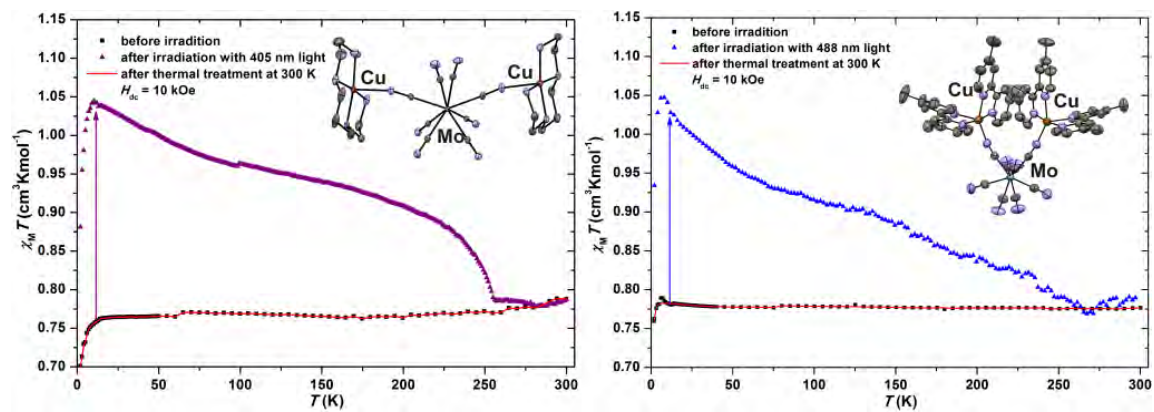
In this presentation, we report several polynuclear copper(II) complexes with N-donors ligands and octacyanidomolybdate(IV) revealing photomagnetic effect. Trinuclear $\text{Cu}_2\text{Mo}^{\text{IV}}$ assemblies with tetradentate polyamines $[\text{Cu}^{\text{II}}(\text{enpnen})_2][\text{Mo}^{\text{IV}}(\text{CN})_8]\cdot 6.75\text{H}_2\text{O}$ (enpnen = N,N'-bis(2-aminoethyl)-1,3-propanediamine) (Figure 1 left) and with bidentate aromatic imines $[\text{Cu}^{\text{II}}(4,4'\text{-dmbpy})_2][\text{Mo}^{\text{IV}}(\text{CN})_8]\cdot 5\text{H}_2\text{O}$ (4,4'-dmbpy = 4,4'-Dimethyl-2,2'-dipyridyl) (Figure 1 right) were distinguished. The structural, spectroscopic, magnetic and photomagnetic properties were investigated for all the assemblies. After irradiations with selected wavelengths, a global increase of the magnetic moment was observed. The initial paramagnetic state of the compounds can be fully recovered by heating the sample above the temperature of relaxation around 250 K (Figure 1). In accordance with these results, the influence of the structure (Cu-Mo distances, Cu-Mo-Cu angles, number of cyanido-bridges and type of interactions between discrete molecules) on the photomagnetic properties was studied.

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Figure 1. Left: The $\chi_{\text{M}}T(T)$ plots for $[\text{Cu}^{\text{II}}(\text{enpnen})_2][\text{Mo}^{\text{IV}}(\text{CN})_8]\cdot 6.75\text{H}_2\text{O}$ before (black squares), after irradiation with 405 nm light (violet triangles) and after thermal treatment at 300 K (red

line). Right: The $\chi_M T(T)$ plots for $[\text{Cu}^{\text{II}}(4,4'\text{-dmbpy})_2]_2[\text{Mo}^{\text{IV}}(\text{CN})_8]\cdot 5\text{H}_2\text{O}$ before (black squares), after irradiation with 405 nm light (blue triangles) and after thermal treatment at 300 K (red line).





**Polynuclear and coordination polymer complexes of Mn(III) metal ions and
thiosemicarbazide derivative ligands**

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In memoriam to Prof. Mihail Revenco

In the last years, considerable efforts have been devoted to the synthesis of coordination compounds of 3d elements with Single-Molecule Magnet (SMMs) properties. In this field, the manganese chemistry of thiosemicarbazide-based ligands has not been much investigated.

Recently we have described an original template reaction of salicylaldehyde S-alkyl-isothiosemicarbazones with 2-formylpyridine molecules which opens an original synthetic approach to design new families of ligands derived from thiosemicarbazide and, hence, new metal-ion coordination complexes [1, 2]. Manganese(II) is not known to be an efficient templating ion for this type of condensation. Nevertheless using Mn(II) precursors, we have been able to successfully synthesize polynuclear manganese complexes. The single crystal X-ray study of these compounds shows the formation of deca- and hexa- nuclear manganese species containing two different ligands. The general formula of these complexes is $[\text{Mn}^{\text{III}}_{10}(\mu_3\text{-O})_4(\mu_2\text{-OH})_2\text{L}^1_2\text{L}^2_4(\text{OC}_2\text{H}_5)_2]\cdot 4\text{C}_2\text{H}_5\text{OH}$ for decanuclear and $[\text{Mn}_6(\mu_3\text{-O})_2\text{L}^1_2\text{L}^2_2(\mu_2\text{-OC}_2\text{H}_5)_4]\cdot 2\text{C}_2\text{H}_5\text{OH}$ for hexanuclear complexes, in which L^1 is an anionic ligand resulting from the double deprotonation of the salicylaldehyde S-methyl-isothiosemicarbazone molecule; and L^2 is a triply deprotonated ligand obtained from the addition of 2-formylpyridine to salicylaldehyde S-methyl-isothiosemicarbazone. For these deca- and hexa-nuclear compounds the dominant antiferromagnetic interaction was observed.

The non alkylated salicylaldehyde thiosemicarbazone in strongly alkaline solutions gives the compounds with composition $\text{Mn}(\text{L})\cdot 3\text{H}_2\text{O}$. The X-ray investigation of its structure demonstrated the formation of a binuclear complex of the composition $[(\text{MnL}_2)(\text{Mn}(\text{H}_2\text{O})_4)]\cdot 2\text{H}_2\text{O}$. Both manganese(II) ions are hexacoordinated. The $\text{O}_2\text{N}_2\text{S}_2$ coordination sphere of Mn1 may be described as distorted trigonal prism, while O_6 geometry around Mn2 ion is an octahedron. The investigation of the magnetic properties of the manganese(II) dinuclear species shows a dominant antiferromagnetic interaction between paramagnetic centers. The compound is not soluble in any solvent in inert atmosphere. In the presence of the air oxygen, the oxidation of the of Mn(II) to Mn(III) and an oxidative dimerization of the coordinated salicylaldehyde thiosemicarbazone anion were detected in methanol solutions. As a result, the formation a new hexadentate bicompartimental ligand coordinated to two different manganese(III) ions by O_2N_4 donor atoms has been observed. The manganese(III) units $[(\text{Mn}_2\text{L})(\text{CH}_3\text{O})_2(\text{CH}_3\text{OH})_2]$ are assembled in polymer *via* μ -oxo bridges provided by methoxy groups coordinated to the metal ions. The coordination of the metal is completed up to square-bipyramidal by methanol molecule coordinated in axial position. Low-temperature magnetic investigations of the polymer indicates a ferromagnetic interaction and a slow relaxation of the magnetization detected by ac susceptibility, confirming the SMM behavior of the complexes.

Mihail D. Revenco, Oleg V. Palamarciuc, Paulina N. Bourash, Janusz Lipkowski, M.Gdanec, Yurii A. Simonov, Rodolphe Clérac, *Inorganica Chimica Acta* 368, 2011, p. 157–164.



New linear trinuclear $Mn^{III}M^{III}Mn^{III}$ ($M = Fe, Ru, Os$) compounds with Single Molecule Magnet behavior

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In memoriam to Prof. Mihail Revenco

In 1993 the discovery of single-molecule magnets (SMMs)¹ opened an exciting field of research. SMMs exhibit magnetic hysteresis on a molecular scale and show quantum phenomena such as tunnelling of magnetization. These properties make them promising molecular candidates for magnetic data storage devices and bits for quantum computing². Coordination chemistry is a key tool to develop the synthesis of magnetic molecule-based materials. Nowadays, rational design of magnetic materials (potentially SMMs) is more widely exploited and enables the design of original systems with a fine controlled arrangement of preformed building blocks with well-defined properties. In this context, cyanidometalate derivatives are interesting metalloligands, as they are known for their efficient coordinating properties in the presence of metallic complexes with substitutable coordinating groups. On the other hand, Mn(III) Schiff base complexes are attractive building-blocks possessing a strong magnetic anisotropy and substitutable axial positions to be connected by donor cyanido-based complexes. The versatility of Schiff base ligands also allows a control of the final structural arrangement together with the physical properties. Among the possible Schiff base ligands, thiosemicarbazide ones possess interesting chelating and coordinating properties for metal ions and in particular manganese ions.³

Here we describe a new family of isostructural linear trinuclear complexes $[NEt_4\{[Mn(L)]_2[M(CN)_6]\}]$ ($M = Fe, Ru, Os$) (Fig.1.a) obtained from anisotropic building-block based on N1,N4-di(salicylidene)S-alkyl-isothiosemicarbazide manganese(III) Schiff base and 3d, 4d and 5d hexacyanometalate complexes. AC susceptibility measurements show that these compounds display slow relaxation of their magnetization at low temperatures. The experimentally observed energy barriers for magnetization reversal were estimated at 19.2, 21.3 and 25.4 K for MnFeMn, MnRuMn and MnOsMn complexes respectively (Fig. 1).

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Figure 1: (a) Crystal structure of the Mn-Fe-Mn. The NEt_4^+ cations and H atoms have been omitted for clarity. (b) Arrhenius plot of the ac magnetic behaviour of the trinuclear Mn-Fe-Mn compound.

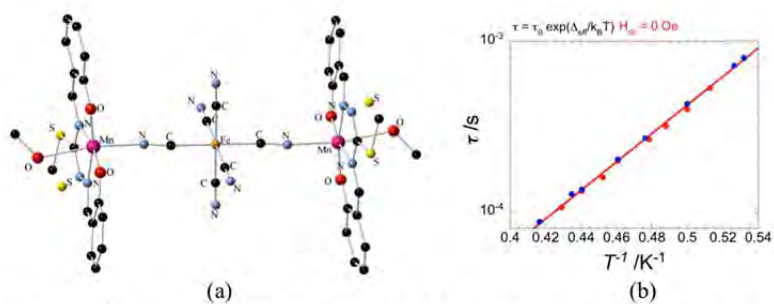


Figure 1: (a) Crystal structure of the Mn-Fe-Mn. The NEt_4^+ counterion and H atoms have been omitted for clarity. (b) Arrhenius plot of the ac magnetic behaviour of the trinuclear compound



Spin canting in a 3D Fe(II) coordination polymer

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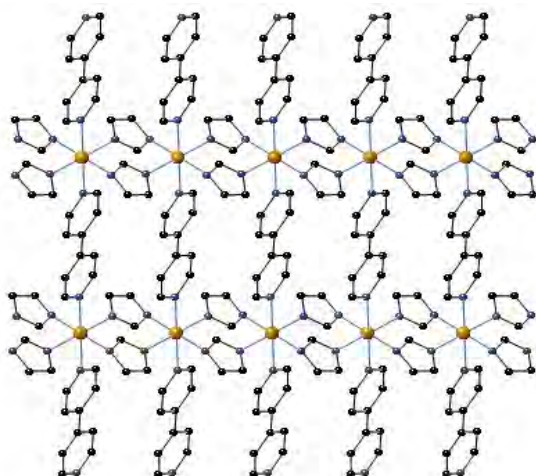
Stimuli-responsive materials for which physical or chemical properties can be tuned by applying an external stimulus are attracting considerable interest in view of their potential applications as chemical switches, memories or molecular sensors. In this sense, magnetic Metal-Organic Frameworks (MOFs) provide numerous examples where the magnetism can be tuned either with a chemical or physical stimuli.⁽¹⁾

The use of a mixture of linkers, typically carboxylates and pyridine-like ligands, has resulted in a plethora of coordination polymers with pillared-layer structure.⁽²⁾ Here we present the combined use of imidazolate and 4,4'-bipyridine to prepare an iron(II) magnetic coordination polymer formulated as $[\text{Fe}(\text{Im})_2(\text{bipy})]$. This compound forms neutral 2D layers in which the Fe atoms are bridged by imidazolate linkers, with the bipy ligands interconnecting the layers to form a 3D coordination polymer. Magnetic measurements (dc and ac susceptibility) reveal that the material magnetically orders at low temperatures ($T_C = 15$ K), likely due to a spin canting. Description imagen:

Figure 1. Crystal structure of the coordination polymer $[\text{Fe}(\text{Im})_2(\text{bipy})]$

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Electronic Structure and Single-Molecule Magnet Behavior in $[\text{ReCl}_4(\text{CN})_2]^{2-}$

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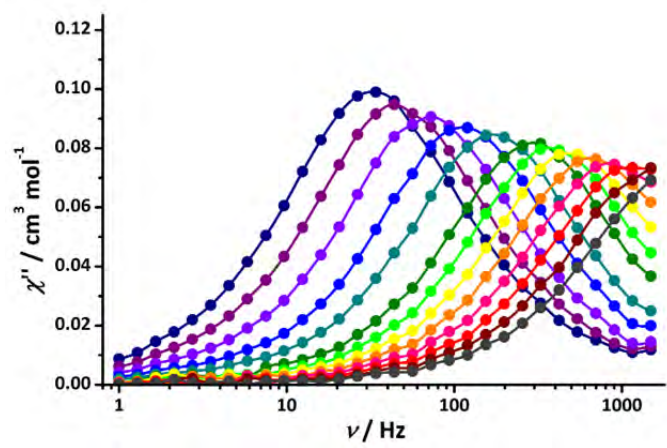
Heavier elements provide enhanced spin-orbit coupling which potentially contributes to the larger magnetic anisotropy for single-molecule magnets (SMMs). Mononuclear 4d and 5d cyano/halogeno complexes are also the capable and useful building blocks to approach single-molecule magnets and single-chain magnets (SCMs).^[1] As an odd-electron ion, according to the Kramers theorem,^[2] Re^{IV} metal ion possesses a ground-state doublet in the absence of magnetic field, regardless of the m_s of the ground doublet. However a large number of published works for Re^{IV} SMMs reports that the effective energy barrier is significantly smaller than the expected energy gap between the two Kramers doublets.^[3]

Herein we present a mononuclear $(\text{Bu}_4\text{N})_2[\text{Re}^{\text{IV}}\text{Cl}_4(\text{CN})_2]\cdot 2\text{DMA}$ displaying SMM behavior with an effective energy barrier of 22 cm^{-1} (32 K), despite a planer magnetic anisotropy, *i.e.* the axial zero-field parameter (D) is positive. This is in agreement with the EPR derived parameters ($D = +11\text{ cm}^{-1}$, $E = |3.2|\text{ cm}^{-1}$),^[1d] suggesting the spin relaxes via the more efficient Orbach-type process.

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Spin-crossover coordination polymers for selective gas sorption

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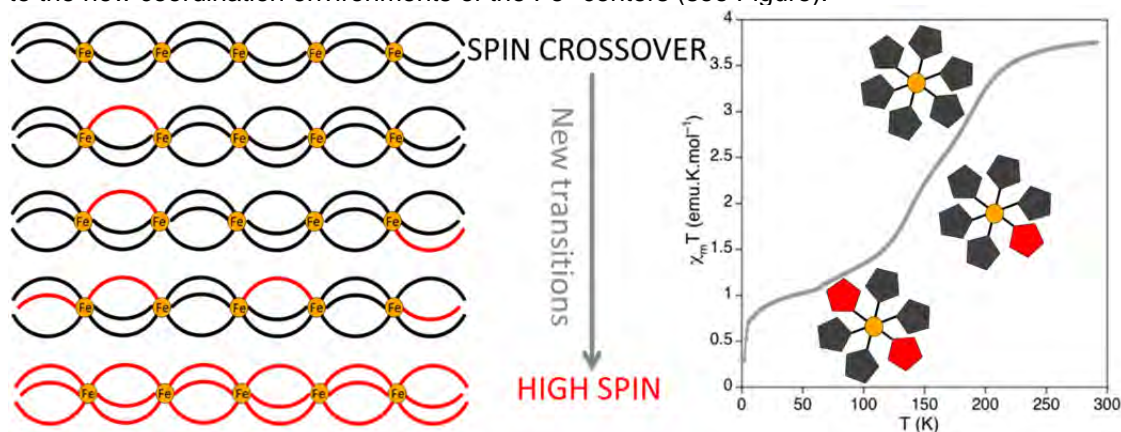
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Since 1990, coordination polymers, also named MOFs (metal-organic frameworks), have been widely developed and have recently become one of the most studied materials. MOFs are compounds extended infinitely in 1D, 2D or 3D structures, formed by metal centers connected by organic ligands through coordination bonds.^[1] MOFs have varied and useful applications such as gas storage (due to the cavities in the crystal structures), sensors, catalysis, enantioselective separation, conductivity, luminescence or the exploitation of magnetic properties. Within magnetic MOFs,^[2,3] those presenting spin-crossover (SCO) phenomena are more interesting since the magnetic change can occur at temperatures of gas sorption. The work presented here focuses in the study of a family of MOFs with spin crossover whose transition temperature can be modified by gas adsorption and other chemical stimuli.

Our group has previously reported the preparation of a SCO coordination polymer that forms infinite chains containing internal cavities of 10 Å diameter, where a CO₂ molecule can be physisorbed^[4]. This CO₂ sorption causes a change in the spin transition, resulting in a shift of T_{1/2} from 200 to 209 K. We have now improved this structure by synthesizing an isomorphous MOF with a larger ligand. Thus, the new compound has a similar structure with discrete voids, but larger in size (232 Å³ vs. 117 Å³). Gas sorption studies show that two molecules of CO₂ can be physisorbed in each void, doubling the result for the original system as expected. The effects on the SCO transition temperature of the increasing number of CO₂ molecules in the voids will also be discussed.

In addition, surface deposition studies have been performed in silicon and quartz. Morphology studies of the substrates using scanning electron microscopy show a complete deposition over the silicon substrate. The deposition is formed by an irregular accumulation of microparticles of the polymer and has a thickness of 400 micrometers.

In a different approach, we have prepared a family of multivariant MOFs to modify the spin transition temperature with the use of a different types of azole organic ligands^[5]. This chemical mixture yields a series of isostructural coordination polymers in which not only a shift in the spin transition temperature occurs, but also new transitions are observed at lower temperatures due to the new coordination environments of the Fe^{II} centers (see Figure).





New Pyridazine-Triazole Ligands for Spin-Crossover

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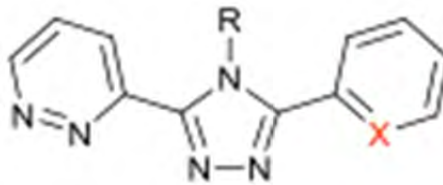
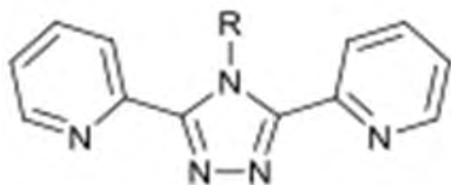
The phenomenon known as spin crossover (SCO), which is the switching between two different electron configurations, high spin (HS) and low spin (LS), has been attracting considerable attention during recent years due to its wide potential in applications, such as data storage devices, optical displays, molecular switches, and sensors.^[1]

Iron(II) complexes of dipyridyltriazole-based ligands, **Rdpt** (Figure, left), with different nuclearities have been investigated by a number of groups^[2] including ours,^[3] revealing a wide range of appealing and interesting results, including spin crossover.^[4] Herein we present the synthesis and properties of selected iron(II) complexes of new pyridazine-based analogues of the **Rdpt** ligands, the **Rpdt** ligands (Figure, right).

Figure. (left) **Rdpt** and (right) pyridazine-based analogue **Rpdt**. X is N or CH.

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3d/4f heterometallic networks. Structure and magnetic characterization

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In recent years, the design and synthesis of 3d/4f heterometallic compounds have been attractive in the synthetic inorganic chemistry, because the unusual architectures and topologies that can be obtained as product of the different coordination characteristics which these cations have, as well as for their potential applications as functional materials in the field of magnetism and luminescent materials, among others [1]. However, the control of the assembly of 3d/4f heterometallic compounds is not easy, being a challenge for the chemists mainly because of the differences in the coordination number and coordination characteristics present for each cation. A synthetic strategy for assembling 3d and 4f ions in an unique structure consists in the use of ligands containing oxygen and nitrogen as donor atoms such as the 4,5-imidazoldicarboxylic acid (H₃IDC), which also present a wide diversity of coordination modes [2,3].

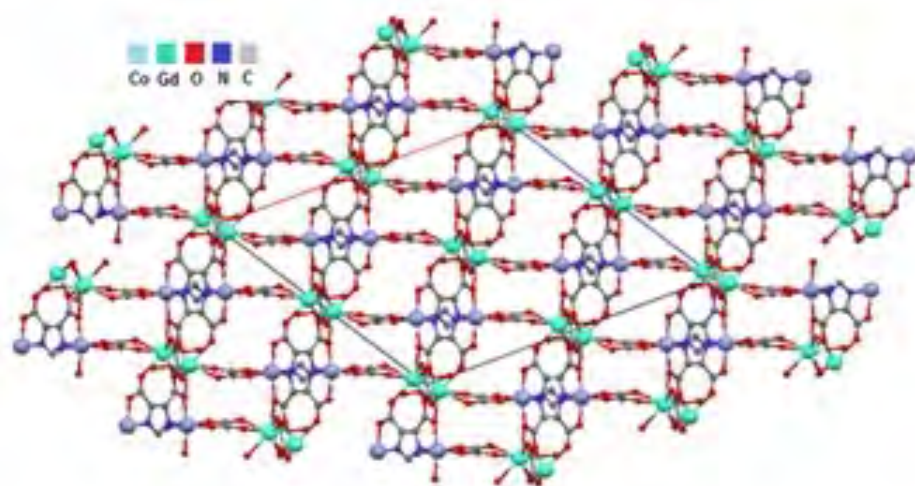
In the present work, the synthesis, structural characterization and magnetic properties of two 3D heterometallic network [Gd₂(H₂O)(C₂O₄)₂Co₂(IDC)₂(H₂O)₂].2H₂O (**1**) and [Gd₂(H₂O)(C₂O₄)Co₂(IDC)₂(C₂O₄)].2.5H₂O (**2**) obtained under solvothermal synthesis are presented. Both structures were assembled considering different metallic precursors, H₃IDC as the main ligand, and oxalate as secondary ligand. Details of the structural characterization and magnetic behavior will be discussed in this work.

Figure 1: Structure of [Gd₂(H₂O)(C₂O₄)Co₂(IDC)₂(C₂O₄)].2.5H₂O

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Acknowledgements: The authors acknowledge financial support from FONDECYT 1130643 and Financiamiento Basal, FB0807. The authors also acknowledge the LIA-MIF 836 International collaborative project. C.C., thanks CONICYT Fellowship.





INVESTIGATING THE MAGNETISM OF RHENIUM(IV):

HETEROMETALLIC – AND HETEROLEPTIC COMPLEXES OF RHENIUM(IV)

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The fact that incorporating 4d/5d metal centers instead of 3d analogues, in SMMs, often lead to new and interesting magnetic properties, has been known for some years now [1]. This is due to the heavier elements' intrinsic characteristics, such as: more diffuse d-orbitals, enhanced spin-orbit coupling leading to larger magnetic anisotropy as well as their structural diversity as compared to 3d systems.

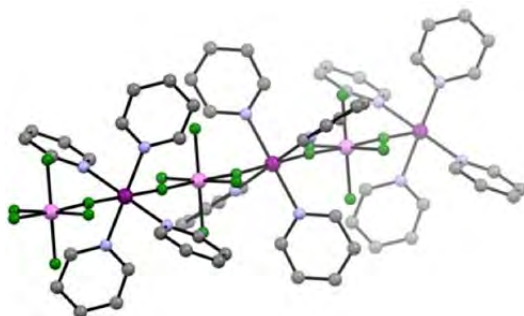
Recently Pedersen et al. demonstrated that ReF_6^{2-} exhibits SMM behaviour [2]. Extensive magnetic studies have been carried out on 1D-systems containing this module and have revealed that fluoride is a much stronger mediator of magnetic exchange interactions between two magnetic centres than cyanide analogues [3]. 1D-systems similar to these, but with changes made to the non-bridging part of the ligand sphere have been prepared and are currently being studied, in order to quantify the effects of local anisotropy on the magnetism of such systems.

Given that the ReF_6^{2-} anion has now been proven as a moderately coordinating building-block, modification of the ligand sphere of Re^{IV} was targeted. This has resulted in heteroleptic systems such as $\text{trans}[\text{ReF}_2\text{Cl}_4]^{2-}$ and the next step will be to incorporate the $\text{trans}[\text{ReF}_2\text{Cl}_4]^{2-}$ module into similar networks, as has been done for the ReF_6^{2-} complex. The former is thought to be much more anisotropic (large D) due to the increase in axial zero-field splitting caused by the mixed ligand sphere. Salts of this ion have been isolated and structurally characterized (Re-F: 1.9340(2)Å; Re-Cl: 2.3648(2)Å). Ongoing efforts towards anisotropic 5d-building blocks will also be presented.

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Two-Dimensional Self-Assembly and Electrical Properties of the Donor-Acceptor TTF-PTM Radical

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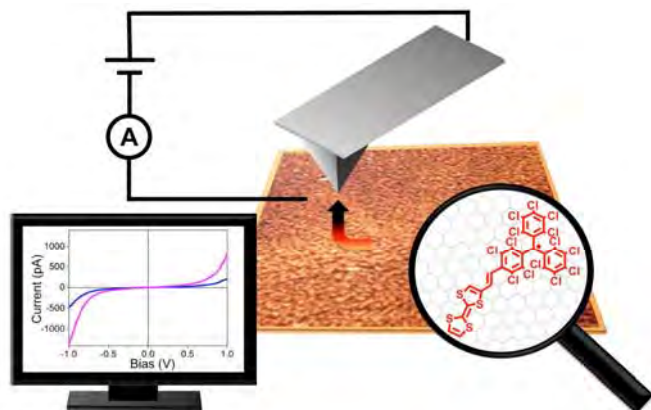
The electron donor-acceptor tetrathiafulvalene-polychlorotriphenyl methyl radical, shows an intricate interplay between its intramolecular electron transfer (IET) from donor (TTF) to acceptor (PTM)¹ and its intermolecular charge transfer (CT) mediated by the TTF subunit in solution giving rise to interesting supramolecular structures²⁻³ including for example, a reversible switch between diamagnetic dimers, observed at room temperature, and paramagnetic monomers at high temperature.⁴ TTF-PTM was recently deposited on highly oriented pyrolytic graphite substrates and its self-assembly has been investigated paying special attention on how both the IET and CT influence its supramolecular structure by scanning probe microscopy. Moreover, temperature dependent X-ray photoelectron spectroscopy and conducting atomic force microscopy revealed both surface-molecule and intramolecular interactions of the prepared nanostructures, which showed asymmetric I-V curves, i.e. electrical rectification.

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Molecular nanomagnets
(Poster)

Synthesis and study of new niobium complexes

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Over the last 30 years, the development of new magnetic functional materials with enhanced performances became a technological necessity, in particular for information recording and storage. Single-molecule magnets (SMMs) and single-chain magnets (SCMs) are classes of metallo-organic compounds, which show superparamagnetic behavior at the molecular scale. Such assemblies are believed to have relevance in information storage at the molecular level. A way to make SMMs and SCMs is to use a "molecular building block" approach. This requires a suitable choice of the molecular component. Various magnetic systems with transition metal ions were studied as potential building blocks for the generation of these molecular nanomagnets.¹

The design and synthesis of 4d and 5d metal-based magnets are of particular interest due to their large magnetic anisotropy (compared to 3d metal ions), their ability to promote large coupling constants between magnetic metal ion centers and the diversity of their d-electron configurations due to their large number of accessible oxidation states. Although polycyanometallates, such as Os(CN)₆³⁻, Mo(CN)₇⁴⁻, W(CN)₈³⁻, Nb(CN)₇³⁻, Nb(CN)₈⁴⁻ were successfully used as building blocks to synthesize SMMs and SCMs,² the dimensionality is usually hard to control.³ For this reason we decided to use suitable "blocking" ligands to block some specific coordination sites around the metal center to allow a better control of the dimensionality. To reach this goal we used in our work "salen-type" ligands which are derivatives of H₂salen (H₂salen = N,N'-bis(salicylidene)ethylenediamine) due to their ability to coordinate with a square planar geometry, letting two axial coordination sites free for the coordination of bridging ligands, such as CN⁻ and SCN⁻ (Fig). Our current research is devoted to niobium complexes. There are very few complexes of niobium with oxidation states +II, +III or +IV, and their magnetic properties are almost never studied, with the exception of the polycyanoniobiate Nb(CN)₇³⁻ and Nb(CN)₈⁴⁻. In this presentation, we will present the synthesis and the characterization of new Nb-based complexes with salen-type ligands which can be used as promising precursors for new molecular nanomagnets.



Magnetic anisotropy transfer from mono- to poly-metallic complexes: a metallo-supramolecular approach.

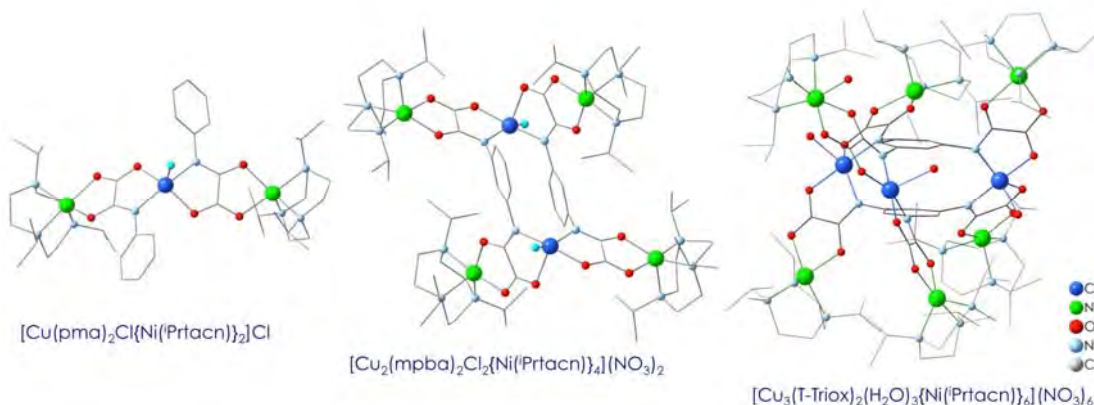
Marion Poncet¹, Geoffrey Gontard¹, Lise-Marie Chamoreau¹, Yanling Li¹, Laurent Lisnard¹, Yves Jouranux¹

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Oxamate ligands have largely proved their appeal for the design of metallo-ligands and the subsequent preparation of multidimensional compounds with controlled architectures where magnetic interactions can be tuned through spin topology and spin polarisation.¹⁻³ Reacting oxamate-based metallo-ligands with additional metallic building-blocks following a “complex-as-ligand” strategy leads to polymetallic molecules with targeted magnetic properties. Using mono-, di- or tri-metallic oxamate-based polydentate complexes (M = Cu^{II}, Ni^{II}, Co^{II}) towards the intrinsically anisotropic unit [M'(iPr₃facn)Cl₂] (M' = Ni^{II},⁴ Co^{II}) led us to the synthesis of tri-, tetra-, hexa-, octa- and ennea-metallic compounds and it was possible to demonstrate that our strategy yields an efficient transfer of the building-blocks' anisotropy to the formed polymetallic compounds.

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Novel inorganic polymers and Metal-Organic Frameworks with multifunctional properties

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The design of homo- and heterometallic coordination polymers is of high interest in crystal engineering [1]. The main interest in this systems arises from their magnetic, luminescence and sorption properties.

Here, we present two families of coordination polymers. The first family is constructed from copper(II) and manganese(II) ions using the oxime multidentate ligand resulted from the reaction of 3-formylsalicylic acid and hydroxylamine [2]. We obtained two heterometallic complexes, $[\text{Mn}\{\text{Cu}_2(\text{L})_2\}_2(\text{H}_2\text{O})_2]$ and $[\text{Mn}\{\text{Cu}_2(\text{L})_2\}_2(\text{H}_2\text{O})_4]$, both with a 2-D structure. Their magnetic properties have been investigated. The second family consists of 3-D coordination polymers constructed from trinuclear $[\text{Cu}_3]$ nodes connected by polycarboxylato anions as spacers (terephthalic acid, isophthalic acid, trimesic acid, 1,2,4,5-benzenetetracarboxylic acid, 1,2,3,4,5,6-cyclohexanhexacarboxylic acid). The crystal structures of the two representative examples from each family are illustrated in Figures 1 and 2.

A.S.D. acknowledges POSDRU 159/1.5/S/ 137750 for financial support.

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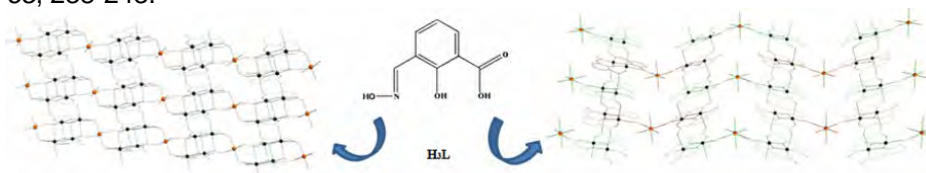


Figure 1.

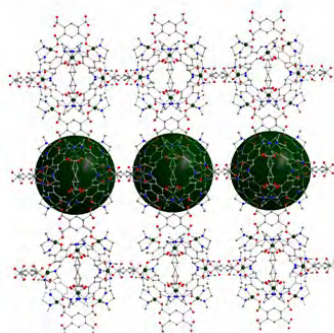


Figure 2.



New Rare Earth Ferrocenoylacetates: Synthesis, Characterizations, and Magnetic properties.

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Metal ion complexes based on β -diketonates have been known for a long time, while their derivatives containing stable organometallic fragments, ferrocenyl in particular, are rare. When these complexes incorporate rare earth elements, there are even less reports [1-3].

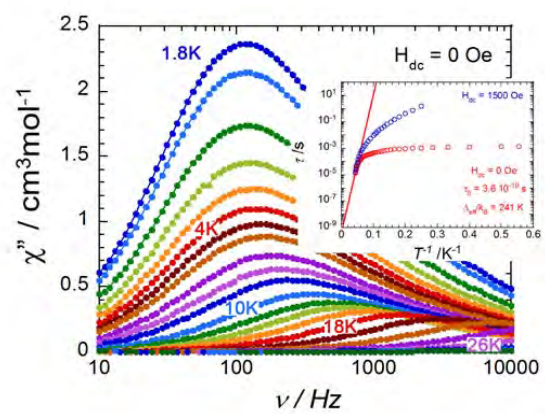
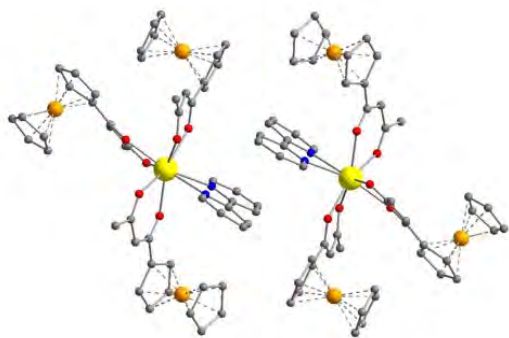
In this work, new rare earth ferrocenoylacetates $[\text{Ln}(\text{FcCOCHCOMe})_3(\text{bpy})]\cdot\text{MeC}_6\text{H}_5$ ($\text{Ln} = \text{Pr}$ (**1**), Eu (**2**) Gd (**3**), Tb (**4**), Dy (**5**), Ho (**6**), Y (**7**); Fc – ferrocenyl, bpy – 2,2'-bipyridyl) and $[\text{Ln}(\text{FcCOCHCOMe})_2(\text{NO}_3)(\text{bpy})]\cdot n\text{MeC}_6\text{H}_5$ ($\text{Ln} = \text{Eu}$ (**8**), $n = 0.5$; Dy (**9**), $n = 1$) were prepared. In the crystal lattice of the isostructural compounds **1-7**, two complexes form quasi-dimeric structure due to stacking interactions between the coordinated bpy molecules (Fig., left). Such stacking is absent in the structures of **8** and **9**.

Thermal decomposition of the compounds was also studied by means of DSC and TGA. According to X-ray powder analysis data, the final products of thermolysis of **1-7** under air contain perovskites LnFeO_3 and garnets $\text{Ln}_3\text{Fe}_5\text{O}_{12}$, therefore these compounds can serve as potential precursors for the functional complex oxides similarly to rare earth ferrocenecarboxylates [4]. DC magnetic susceptibilities for **3-6** and AC susceptibilities for **4-6** were studied. The magnetic measurements on **4-6** revealed the presence of a slow relaxation of the magnetization. For the dysprosium complex **5**, an effective magnetic relaxation energy barrier of 241 K was found (Fig., right). To date, it is one of the highest known value for a mononuclear single molecule magnet based on dysprosium β -diketonate complexes.

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Photo-induced magnetism
(Poster)

Magnetochirality in metal-radical helices: towards new magneto-electric effects

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Chirality and magnetism are directly connected in the interaction between matter and electromagnetic radiation through the magneto-chiral dichroism and birefringence. Magneto-chiral dichroism (MXD), a non-reciprocal effect with different absorption of not-polarized light by systems with opposite chirality in the presence of a magnetic field, is a fascinating phenomenon that has been suggested to be at the origin of homochirality of life on the earth and observed only recently. It is in general very weak, being assumed in first approximation to be related to the product of natural (NCD) and magnetic circular (MCD) dichroism, and only few examples are available in literature with limited information on the factors that originate the phenomenon. The archetypal of Single-Chain Magnets, comprising Cobalt(II) beta-diketonates and nitronyl-nitroxide radicals, spontaneously crystallize in the chiral $P3_1/P3_2$ space groups. A detailed hard X-rays synchrotron investigation of the magneto-chiral effect detected at the 3d-metal K edge in two isostructural molecular helices comprising either isotropic Manganese(II) or anisotropic Cobalt(II) bridged by stable organic radicals have been performed.^[1] The experiments have revealed a strong magneto-chiral dichroism associated with the non-collinear spin structure of the Co^{II} derivative, which is absent in the Mn^{II} analogue. Interestingly, the chiral nature of these molecular helices allows the presence of novel magneto-electric effects. Density Functional Theory calculations, beyond reproducing the magnetic properties,^[2] have in fact revealed^[3] that the electric polarization of the molecular helix is affected by the relative alignment of neighbouring metal and radical spins, opening the perspective of controlling the magnetization dynamics of these one-dimensional structures through the application of an electric field.

The authors acknowledge the financial support of the European Research Council through the AdG MolNanoMaS and of Italian MIUR through FIRB project n° RBAP117RWN.

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New Materials
(Poster)

Thermal, Photonic and magnetic studies of Pyrene-DTDA, phenanthrene-DTDA and Anthracene-DTDA.

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Sulphur-nitrogen radicals form one family of particularly stable radicals which have been used to construct high T_c organic magnets[1]. Conversely Poly-Aromatic Hydrocarbons (PAHs) such as anthracene and pyrene are well known to exhibit remarkable photonic and electrochemical properties[2]. Here we report the synthesis and crystal structures of a series of PAH-DTDAs radicals **1** – **3** as well as probe their thermal stability and polymorphism through DSC, VT-PXRD and single crystal XRD. Such PAH-DTDA systems have been proposed as 'high spin organic molecules' [3] and we have examined their electronic properties through UV/visible, fluorescence and magnetic properties of these different derivatives.

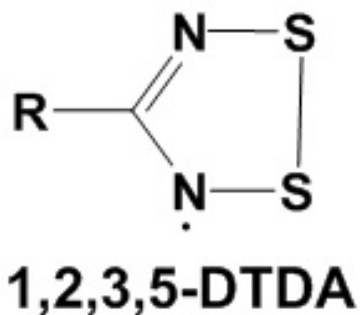


Fig.1. (1 R = Phenanthrene; 2 R = Pyrene; 3 R =Anthracene)



Switchable magnetic materials and optical magnets
(Poster)

Incorporation of alkaline metal cations into a Ni-Nb based structurally flexible molecular magnet

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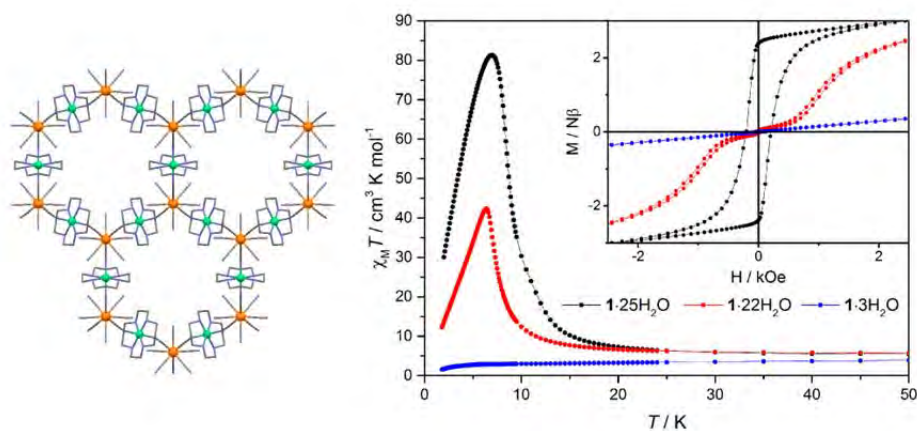
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The flexibility of the coordination framework is crucial in the design of dynamic molecular magnets responsive to the presence of guest molecules. The $\{[\text{Ni}(\text{cyclam})]_2[\text{Nb}(\text{CN})_8] \cdot n\text{H}_2\text{O}\}_\infty$ 3D neutral network [1] is an example of a material exhibiting significant changes in structure and magnetic properties upon dehydration. The reaction between the same building blocks: $[\text{Ni}(\text{cyclam})]^{2+}$ and $[\text{Nb}(\text{CN})_8]^{4-}$ in the concentrated LiCl solution led to the formation of a 2D $\{\text{Li}_2[\text{Ni}(\text{cyclam})_3[\text{Nb}(\text{CN})_8]_2 \cdot n\text{H}_2\text{O}]\}_\infty$ network (**1**), in which negative charge of the CN-bridged Ni-Nb layers is compensated by the presence of Li^+ cations. Compound **1** shows the topology of a honeycomb, similarly to earlier characterised guest-responsive $\{[\text{Ni}(\text{cyclam})]_3[\text{W}(\text{CN})_8]_2\}_\infty$ [2]. The layers in **1** are intersected by channels filled with water and Li^+ ions. The fully hydrated **1**·25H₂O form, which is stable in the presence of solvent, shows ferrimagnetic ordering with $T_c = 8.2$ K. Upon drying in air it reversibly undergoes structural transformation to the **1**·22H₂O phase, which is stable at ambient conditions and exhibits metamagnetic character with $T_c = 6.9$ K and critical field of 1 kOe. Dehydration under vacuum leads to the antiferromagnetic **1**·3H₂O phase with $T_c = 3.0$ K. The transformations between the three hydrates are fully reversible. **1**·3H₂O is rehydrated to **1**·22H₂O when exposed to humid air, and further to **1**·25H₂O by immersion in water. Our recent results show that the incorporation of other cations, like Na^+ , K^+ or Mg^{2+} , into the framework of **1** is also possible. The detailed studies of structural transformations, magnetic and electrical properties of the network are currently under way.

This work is carried out with financial support of the Polish Ministry of Science and Higher Education under the Diamond Grant project (grant no 0195/DIA/2013/42).

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Devices and applications
(Poster)

Quantum signatures of a molecular nanomagnet in direct magnetocaloric measurements

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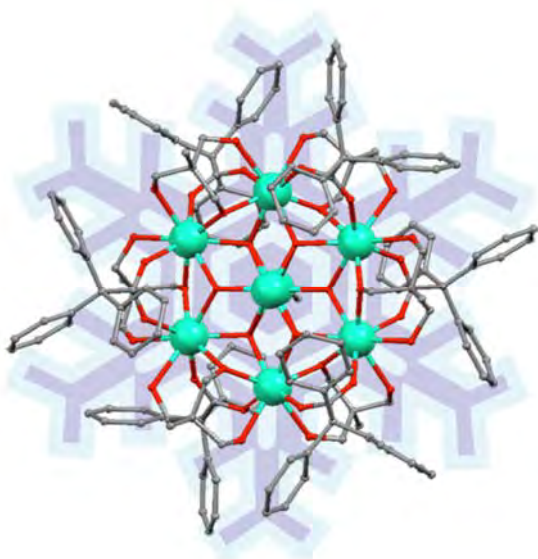
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Geometric spin frustration in low-dimensional materials, such as the two-dimensional kagome or triangular antiferromagnetic nets, can significantly enhance the change of the magnetic entropy and adiabatic temperature following a change in the applied magnetic field, that is, the magnetocaloric effect. In principle, an equivalent outcome should also be observable in certain high-symmetry zero-dimensional, that is, molecular, structures with frustrated topologies. Here we report experimental realization of this in a heptametallic gadolinium molecule.

Adiabatic demagnetization experiments reach about 200 mK, the first sub- Kelvin cooling with any molecular nanomagnet, and reveal isentropes (the constant entropy paths followed in the temperature-field plane) with a rich structure. The latter is shown to be a direct manifestation of the trigonal antiferromagnetic net structure, allowing study of frustration-enhanced magnetocaloric effects in a finite system.

J.W. Sharples, D. Collison, E.J.L. McInnes, J. Schnack, E. Palacios,

M. Evangelisti, *Quantum signatures of a molecular nanomagnet in direct magnetocaloric measurements*, Nature Communications **5** (2014) 5321





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Modelling and theory
(Poster)

Mn₁₂-acetate – finally calculated with the Advanced Finite-Temperature Lanczos Method

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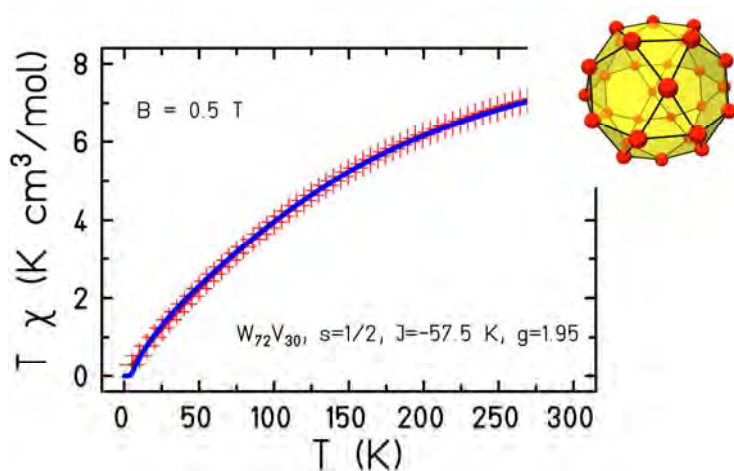
The Finite-Temperature Lanczos Method (FTLM) is a so-called trace estimator. With such a method one can approximate thermodynamic partition functions for very large Hilbert spaces. In this contribution we demonstrate that the magnetization as function of temperature and magnetic field can be evaluated for molecules such as the Keplerate {V₃₀W₇₂} with a Hilbert space dimension of about 10⁹ or the famous Mn₁₂-acetate with a Hilbert space dimension of

10⁸. For the latter we compare various suggestions of parameterizations of spin Hamiltonians with magnetic observables, something that was not possible so far.

After countless efforts to develop numerical strategies that rest on the symmetries of a quantum spin problem, nowadays approximate methods such as FTLM produce approximate results of unprecedented accuracy. In addition they are very easy to program whereas

irreducible representations of SU(2) combined with point groups have been mastered by only a rather small group of experts. We are thus convinced that the theoretical investigation of ever larger magnetic molecules has become feasible now.

O. Hanebaum, J. Schnack, *Advanced Finite-Temperature Lanczos Method for anisotropic spin systems*, Eur. Phys. J. B **87** (2014) 194





Theoretical investigation of a Re^{IV} building block for molecular nanomagnets

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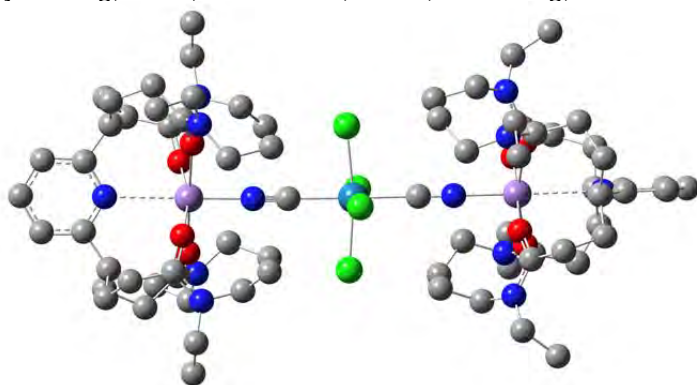
One route to build molecular magnets revolves around the usage of building blocks containing 4d or 5d transition metals that provide large spin-orbit coupling, thus boosting magnetic anisotropy. $\text{trans}[\text{ReCl}_4(\text{CN})_2]^{2-}$ looks particularly promising since it contributes three unpaired electrons as well as two possible linkers to 3d metal centers, which can increase the total spin of the system. It also has a local C_4 symmetric coordination sphere which should minimize rhombicity.

Calculations on DFT level of theory of the building block alone surrounded by two tetrabutylammonium ions find a negative D value, which is in agreement with ligand field theory calculations [1], and a small rhombicity that stems from slight deviations from D_{4h} symmetry. The trinuclear $[(\text{MnPY}5)_2\text{ReCl}_4(\text{CN})_2]^{2+}$ [2] with PY5 being a η^5 pentapyridyl ligand was investigated next, our calculations showing again a negative D value and a considerable rhombicity of 4%. The environment of the Re center is not C_4 symmetric, since the Re-CN-Mn bonds are bent. In a search for a ligand which supports a linear Re-CN-Mn alignment, our calculations found a new PyAm_4 (four diethyl amides attached to pyridine) ligand with this property.

There are two possibilities to form a $[(\text{PyAm}_4)_2\text{ReCl}_4(\text{CN})_2]^{2+}$ complex: A coplanar arrangement of the pyridine rings (**A**) which has approximate C_2 symmetry and a vertical one (**B**) having approximate S_4 symmetry; both structures have virtually the same energy. **A** shows a rhombicity of 2.8%, whereas **B** shows a rhombicity of 0.6%.

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The Hunt For New SIMs

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New and improved molecular nano-magnets (MNMs) have been sought for several decades by physicists and chemists. They are characterised by their effective barrier to the slow relaxation of their magnetisation, U_{eff} , and the temperature below which this occurs, T_B . Since the first MNM the former has increased markedly, though the latter has remained stubbornly low, far from practical liquid nitrogen temperatures. The challenge to improve U_{eff} follows from the equation $U_{\text{eff}} = DS^2$, where D is anisotropy and S the total spin of the compound; perhaps a naïve approach in hindsight. This led to many poly-nuclear species, attempting to increase the total spin of the molecule, such as $\{\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_7\}$, where $S = 83/2$. Conceptually more difficult is the desire to increase D , indeed, Neese and Pantazis¹ demonstrated the fallacy of this approach and suggested a different route to improved MNMs. This is based on the idea that S and D are inversely connected and a better route is to maximise D of small, mono-nuclear compounds, so called Single-Ion Magnets (SIMs).

Transition metal SIMs are attractive targets², with large spin-orbit coupling constants possible. The key is the synthesis of a molecule with an appropriate metal and ligand crystal-field, so giving the desired first-order coupling of spin and orbital angular momentum. The key is the degenerate ground term which is split into its M components by the crystal-field, thus creating a large barrier to spin reversal. We have investigated Ni(II), Fe(II) and Co(II) complexes in geometries which are shown by theoretical calculations³ to give large, and negative D values, using a selection of simple nitrogen and oxygen-based donor ligands and here show their structures and measured slow relaxation behaviour. These are the potential building blocks to new and improved MNMs, starting from the synthetic challenge of smaller SIMs.

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Modelling and theory
(Poster)

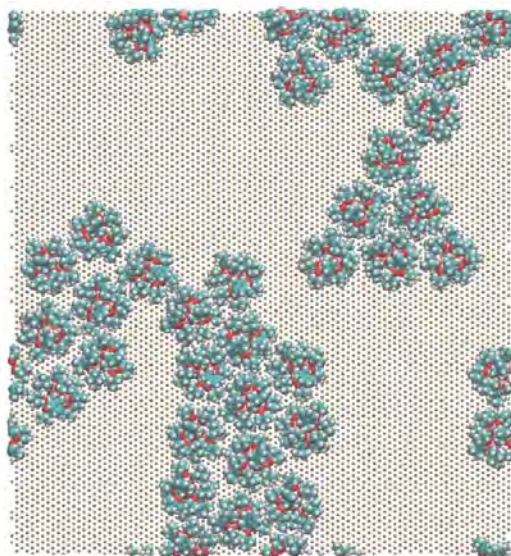
Assessment of a Combined MM and QM Approach for the Study of the Single Molecule Magnet Fe₄Ph adsorbed on Au(111)

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An integrated MM (Molecular Mechanics) and DFT (Density Functional Theory) approach for the modelization of magnetic systems on surface has been developed and applied to study the adsorption of single molecule magnet [Fe₄(L)₂(dpm)₆] (where Hdpm=dipivaloylmethane and H₃L=2-hydroxymethyl-2-phenylpropane-1,3-diol), called also Fe₄Ph, on an unreconstructed surface of Au(111). These kind of systems are useful as model systems for the design of new materials, as spin valves or data storage devices. Indeed, the family of Single Molecule Magnets of the Fe₄ iron star exhibits a slow relation of the magnetization, making them suitable candidates for new technologies based on molecular magnetism. The DFT is the natural tool to study the electronic and magnetic properties, but it becomes unaffordable if the interest lies also in the self-assembly process. We developed a full set of ad hoc classical potentials via the HESS2FF code and direct parametrization of specific interactions, to study the large scale (temporally and spatially) phenomena. The new potentials have been tested on a series of benchmark tests to verify the reliability of the model. With this integrated approach we studied three model systems: a single molecule on surface, the half coverage monolayer and the full coverage monolayer. We identified a stable conformer and achieved important insights on the clusterization process. All the MM results have been tested in comparison with periodic DFT calculations. Moreover we studied the magnetic properties of the new conformer and of a single molecule extracted from the full monolayer, to understand the modification due to the self-assembly process.





3d-4f Single Molecule Magnets from a Ditopic Carbohydrazone based Ligand

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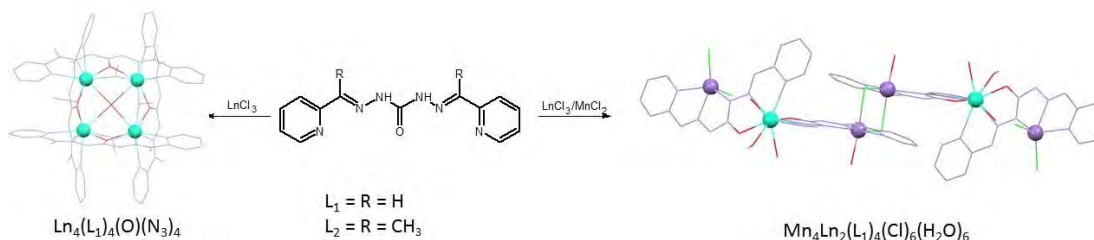
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Self-assembly of polymetallic complexes can be achieved in a programmed approach through the use of polytopic ligands designed to incorporate metal ions in designated pockets but, at the same time, leaving enough coordination unsaturation that self-assembly leads to clusters and grids.^[i] Ditopic pyridyl carbohydrazone based ligands have two potential pockets to accommodate two metals (figure 1). The ligand component responsible for bridging the metal ions in close proximity is the central hydrazine-O atom, which also leads to spin communication between the metal ions. Examples of square μ -O bridged grid complexes are known with transition metals such as $\text{Fe}^{\text{II/III}}$, and Co^{II} ^[ii] and recently with lanthanides (Gd, Tb, Dy, Ho, Tm, Er) where Dy_4 complexes have been reported to display slow relaxation of magnetization.^[iii] In order to synthesise 3d-4f square grids, L_1 was reacted with LnCl_3 ($\text{Ln} = \text{Dy, Gd, Tb, Eu}$) in the presence of MnCl_2 , however instead of Mn_2Ln_4 squares, a series of linear $\text{Mn}^{\text{II}}_4\text{Ln}^{\text{III}}_2$ clusters were generated. Single crystal x-ray studies reveals that all complexes are isostructural and preliminary SQUID magnetic data shows that $\text{Mn}^{\text{II}}_4\text{Dy}^{\text{III}}_2$ is a single molecule magnet.

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ELECTRONIC AND MAGNETIC PROPERTIES OF AN IMIDO-FUNCTIONALIZED MOLYBDENUM LINDQVIST POM.

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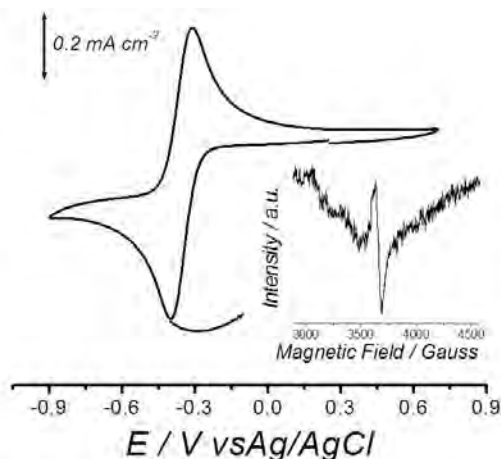
The polyoxometalates (POMs) belong to the family of inorganic polyanions derived from oxides. They present different applications in areas such as magnetism, medicine and catalysis among others. Molybdenum is in its higher oxidation state, thus making the Lindqvist structure a strong electron acceptor species. The functionalization of this compound with an organic amine (R-NH₂) fragment through a covalent Mo-N bond produces a molecule with donor-acceptor characteristics (R-N-POM)¹.

In this work, we present the electronic properties of a novel system based on a molybdenum Lindqvist POM (Mo₆) functionalized with 4-(1H-1,2,4-triazol-1-ylmethyl)aniline. The electrochemistry, UV-visible-NIR and electronic paramagnetic resonance (EPR) studies will be discussed. In figure 1 the EPR spectrum and the cyclic voltammetry of the reduced species are shown.

Reference.

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MONONUCLEAR PENTACOORDINATE COBALT (II) COMPLEXES AS SINGLE MOLECULE MAGNETS

Cyril Rajnák¹, Roman Boča¹

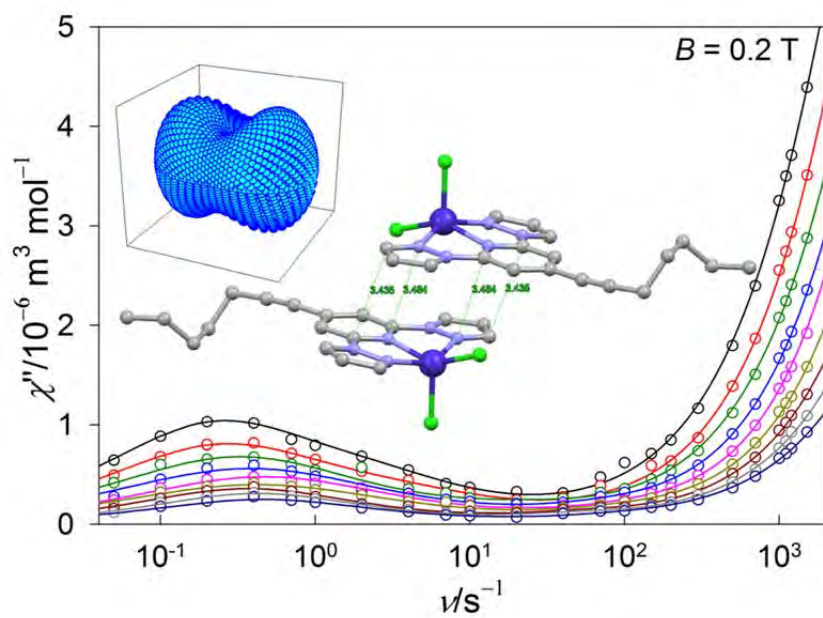
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The class of single-molecule magnets (SMM) could represent one of the key roles for high-density information storage in the future. Therefore, it can be seen rapidly growing interest in this area over the last few years. Existence of magnetic anisotropy is a major cause of slow relaxation of magnetic moment in SMM upon removal from magnetic field¹. This phenomenon is revealed as the magnetic hysteresis. Several of the prepared SMM's were simple tetracoordinate, pentacoordinate and hexacoordinate mononuclear Co(II) complexes. We focused on the pentacoordinate Co(II) complexes as a potential SMM's¹⁻³. For this study we synthesized and characterized sets of mononuclear cobaltous compounds made up from "antennae" ligands. This term we introduced for ligands containing 2,6-bis(2-pyrazolyl)pyridine unit with long alkyl chain in position 4' of pyridine. For instance L^{C0} = 4-iodo-2,6-di-pyrazol-1-yl-pyridine; L^{C7} = 4-hept-1-ynyl-2,6-di-pyrazol-1-yl-pyridine; L^{C10} = 4-dec-1-ynyl-2,6-di-pyrazol-1-yl-pyridine; L^{C12} = 4-dodec-1-ynyl-2,6-di-pyrazol-1-yl-pyridine; L^{C14} = 4-tetradec-1-ynyl-2,6-di-pyrazol-1-yl-pyridine. Five novel pentacoordinate complexes, namely, $[CoL^{C0}Cl_2]$, $[CoL^{C7}Cl_2]$, $[CoL^{C10}Cl_2]$, $[CoL^{C12}Cl_2]$, $[CoL^{C14}Cl_2]$ were isolated as a blue single crystals. The complex $[CoL^{C7}Cl_2]$ with a tridentate antennae-like ligand forms a dimer held by short π - π stacking with head-to-head contacts at 3.4 Å. The DC magnetic susceptibility and magnetization data confirm weak ferromagnetic interaction and a large-magnetic anisotropy, $D/hc = 150 \text{ cm}^{-1}$ and $E/hc = 11.6 \text{ cm}^{-1}$. The system shows superparamagnetic behavior at low temperature that depends upon the applied magnetic field. At $B_{DC} = 0.2 \text{ T}$ a low-frequency peak at the out-of-phase susceptibility is seen ($\nu \sim 0.3 \text{ Hz}$) whereas the second peak appears at $\nu > 1500 \text{ Hz}$ confirming two slow relaxation processes³.

Acknowledgement: The grant agencies (Slovakia: VEGA 1/0522/14, VEGA 1/0233/12, APVV-0014-11) are acknowledged for the financial support. C.R. thanks to grant from the *Fund to support of research at University of Ss. Cyril and Methodius*.

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Synthesis and spectroscopic characterisation of a novel series of hydroxo-bridged decanuclear $[\text{Fe}_8\text{Ln}_2]$ clusters (Ln = Eu, Gd, Tb, and Dy) supported by pyridine-containing β -diketone ligands

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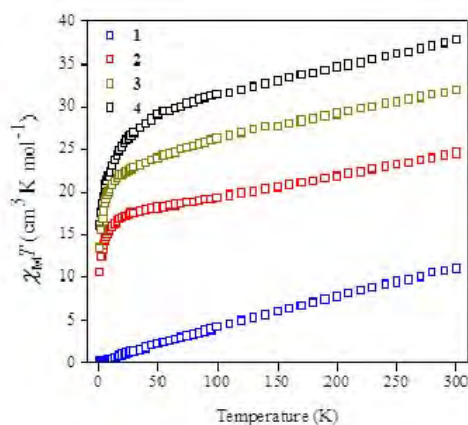
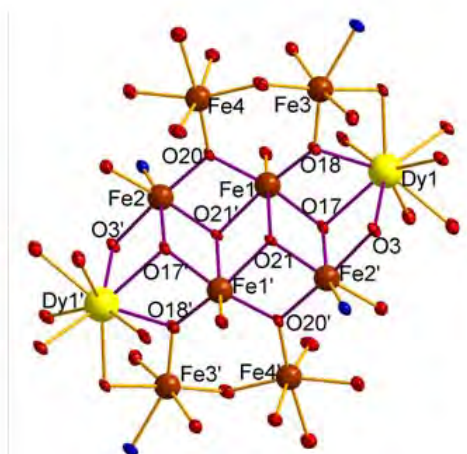
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The structure, magnetism, and Mössbauer studies of a family of $[\text{Fe}_8\text{Ln}_2]$ clusters are reported, where Ln = Eu (**1·Eu**), Gd (**2·Gd**), Tb (**3·Tb**), and Dy (**4·Dy**). Static magnetic studies indicate strong antiferromagnetic interactions between iron centers dominated in complexes **1·Eu-4·Dy** and reveal an $S = 0$ ground state in **1·Eu**. Only **3·Tb** and **4·Dy** exhibit slow magnetic relaxation in $H_{\text{dc}} = 0$ by performing ac susceptibility measurements. Field-induced slow relaxation is observed for **2·Gd** in 5000 Oe bias field and gives an energy barrier of 31.71 K.¹⁻² The Mössbauer spectra collected for **1·Eu** at low temperature confirm the $S = 0$ ground state, while the spectra of **4·Dy** demonstrate the presence of relaxational broadening.

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Extended Metal Atom Chains as Single-Molecule Magnets

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Extended Metal Atom Chains (EMACs) consist in linear arrays of metal ions helically wrapped by four oligopyridylamide (or related) ligands. These compounds have been widely investigated as examples of "molecular wires" and as benchmark systems for the understanding of metal-metal bonding [1].

We herein report that one of the most popular EMACs, namely $[\text{Cr}_5(\text{tpda})_4\text{Cl}_2] \cdot 4\text{CHCl}_3 \cdot 2\text{Et}_2\text{O}$ ($1 \cdot 4\text{CHCl}_3 \cdot 2\text{Et}_2\text{O}$, $\text{H}_2\text{tpda} = N^2, N^6$ -di(pyridin-2-yl)pyridine-2,6-diamine) [2], behaves as a field-induced single-molecule magnet. As depicted in the Figure, the five chromium(II) ions in **1** are arranged in two quadruply-bonded diamagnetic $\{\text{Cr}_2\}$ units *plus* a terminal chromium(II) ion ($S = 2$), with chlorides acting as axial ligands [3]. According to W-band EPR spectroscopy, the terminal chromium(II) ion resides in a quasiaxial environment with $g_x = g_y = 1.990(3)$, $g_z = 1.975(2)$, $D = -1.53(1) \text{ cm}^{-1}$ and $|E/D| = 6(2) \times 10^{-3}$. When no static field is applied, above 1.8 K the compound behaves as an $S = 2$ paramagnet for frequencies up to 10 kHz. However, slow relaxation of the magnetization is detected at 2.5 kOe, with a linear Arrhenius plot from 1.8 to 4.8 K and an anisotropy barrier of 9.2(5) K. This value is within experimental error from the total splitting of the $S = 2$ state (8.81(6) K), suggesting that in-field relaxation follows an overbarrier Orbach mechanism and that $\pm M_S$ states are not severely admixed [4]. Such a genuine overbarrier relaxation is rarely observed in isolated metal ions without first-order orbital angular momentum, like the terminal chromium(II) ion in **1** [5]. In fact, small values of $|D|$ and S normally result in extremely efficient quantum tunneling.

Our studies show that EMAC structures enforce metal ions in an environment suitable for single-molecule magnet behaviour and may consequently be regarded as new target systems in molecular magnetism; we are now looking for more examples of EMAC-based single-molecule magnets featuring different nuclearity, axial ligands and embedded metal ions.

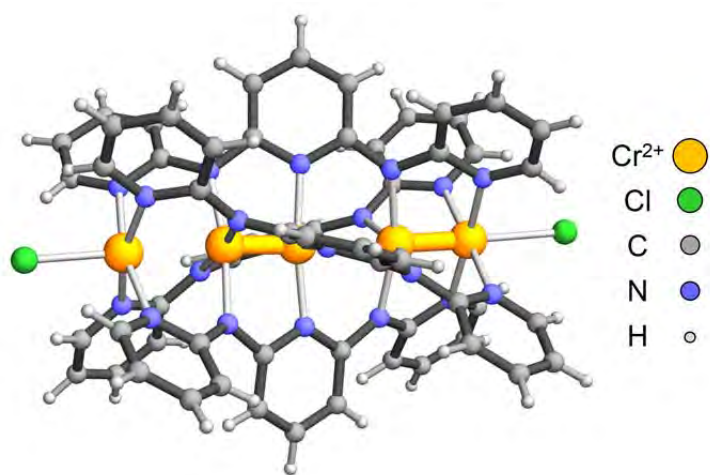
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Switchable magnetic materials and optical magnets
(Poster)

Synthesis and Characterizing Novel Aminium-Radical-Cation-Based-Diradical Magnets

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Magnetic spin materials which have organic-based open-shell molecular structure, like radicals, have been intensely paid attention. They are promising to make big progress in domains of molecule-based magnets, memory device, radical-based batteries, spintronics devices, and molecular spin-based quantum computers. Among these spin radical molecules, diradicals, multi-radicals, poly-radicals and radical-ions attract much more attentions in recent years due to their wide molecular design, structural flexibility, the complexity of their intermolecular interactions and intramolecular interactions^[1-4].

The most important factor of diradicals is the control of the spin state, the singlet state ($\uparrow\downarrow$) (low spin) and triplet state ($\uparrow\uparrow$) (high spin). In this study, we present a new class of diradicals, Aminium-Radical-Cation-Based-Diradicals which have electron donor moieties in the substituted-phenothiazine. **PDTN-1** and **PDTN-2**. Here the donor strength of phenothiazine in the radical should be enhanced by donor substitution for which two thiophene were used to lower the oxidation potential. This design is aim at improving the stability of cationic diradical and to avoid final structure changing to quinone.

Scheme 1. Structure of **PDTN-1** and **PDTN-2**

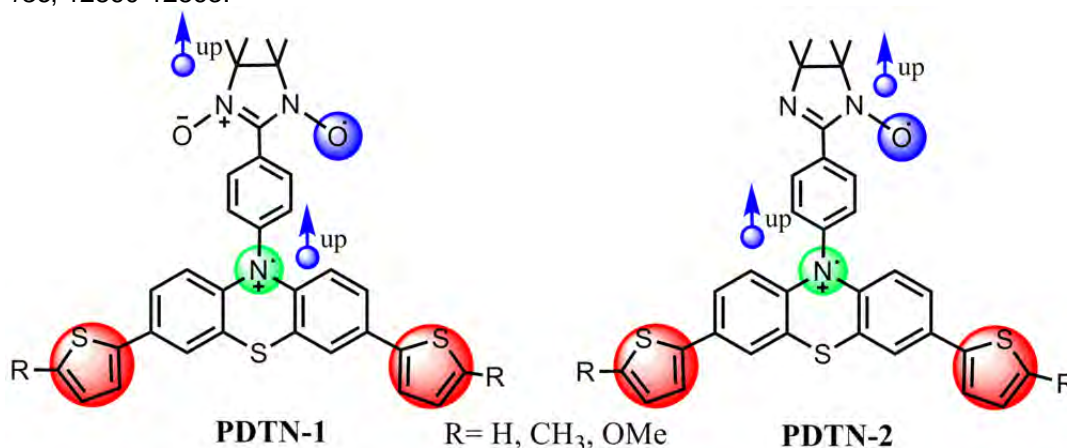
Before we acquire **PDTN-1** and **PDTN-2**, we have already got two structures of phenothiazine with monoradical nitronyl nitroxide and imino nitroxide. Where the first provides a five-line signal in the EPR spectrum, the second one a seven-line signal.

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Molecular nanomagnets
(Poster)

Supramolecular Approach to Magnetic Platonic Solids

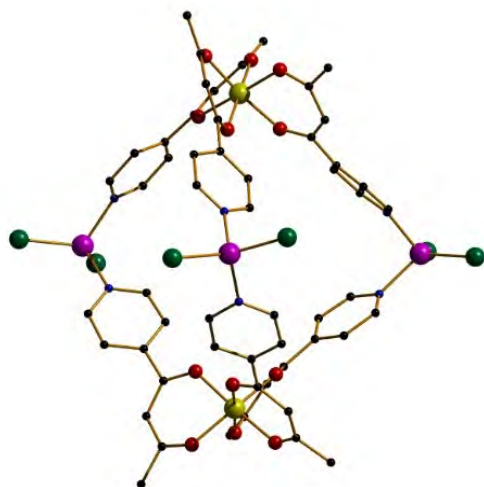
Sergio Sanz¹, Helen M. O'Connor¹, Priyanka Comar¹, Eufemio Moreno Pineda², Kasper S. Pedersen³, Gary S. Nichol¹, Ole Mønsted³, Høgni Weihe³, Stergios Piligkos³, Eric J. L. McInnes², Paul J. Lusby¹, Euan K. Brechin¹

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Coordination-driven self-assembly through the use of strong and directional metal-ligand bonds has been exploited in Supramolecular Chemistry for the construction of 0-3D cages, capsules and porous polymeric materials. The interest in these structures primarily stems from host-guest chemistry, with potential application in catalysis, drug delivery and the stabilisation of reactive intermediates.¹ Although the design of these systems has been extensively studied with diamagnetic metals, only two examples employing paramagnetic metal ions have ever been reported.² Herein we discuss the structures and magnetic properties of heterometallic cages built through the use of pre-made paramagnetic metalloligands and paramagnetic linker units with the appropriate directionality and angularity to access a range of magnetic cages, capsules, and paramagnetic and porous coordination polymers, capable of hosting magnetic guests that will have the potential to exhibit tunable (e.g. switchable) magnetic properties.

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Modelling and theory
(Poster)

Liquid-state paramagnetic relaxation from first principles

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Nuclear magnetic resonance relaxation of diamagnetic compounds in liquid state is typically well-described by the Redfield relaxation theory [1]. The Redfield theory is a good approximation in the regime where the magnitude of the interaction Hamiltonian is weak as compared to the average Zeeman interaction and the time-scale of relaxation is much greater than the time-scale of molecular fluctuations contributing significantly to relaxation. However, in paramagnetic systems the former condition is usually not met, whereas – sometimes – the latter is. We simulate paramagnetic relaxation from first principles by sampling a molecular dynamics trajectory with quantum-chemical calculations, and producing a time series of instantaneous parameters of the spin Hamiltonian, which is, in turn, used to numerically solve the Liouville-von Neumann equation for the time evolution of the spin density matrix. We demonstrate the approach by simulating the electron and nuclear spin relaxation in an aqueous solution of the Ni(2+) ion [2,3]. The spin-lattice (T1) and spin-spin (T2) relaxation rates are extracted from the simulations of the time dependence of the longitudinal and transverse magnetization, respectively. Good agreement with the available experimental data is obtained by the method.

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Molecular nanomagnets
(Poster)

Crown-Ether Dy^{III} Complexes: Synthesis of Theoretically Predicted Single-Molecule Magnets.

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The electron density of Dy^{III} centers is a key magnitude to determine the single-molecule magnet properties. The shapes of ground state electron density for Dy complexes with the maximum mJ values of 15/2 is oblate.¹ From CASSCF calculations, we have seen that the shape of the electron density is affected by the repulsion of the ligand.² Thus, the axial Ising anisotropy of an oblate ion is maximized if the electron density of the ligand is concentrated above the plane that contains the electron density. From the experimental point of view, the choice of neutral equatorial ligand and highly charged axial ligand will favor the accommodation of the oblate electron density in the equatorial plane in order to reduce the metal-ligand electron repulsion. Crown-ether ligands fulfill some of the requirements to synthesize Dy^{III} complexes with high magnetic anisotropy: i) they have all the O-donor atoms close to one plane; ii) donor oxygen atoms are very efficient to coordinate lanthanide centers; iii) such ligands are neutral molecules, thus, the charged ligands could be placed in the axial positions. iv) macrocyclic effect will provide high stability for the metal complexes. Hence, we have the goal to perform the synthesis and characterization of lanthanide complexes with crown-ether ligands. We will focus the communication on Dy^{III} complexes, but also with Tb^{III} and Nd^{III} centers while the 18-crown-6 ligand will be employed to encapsulate the lanthanide centers.

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Tuning and switching the antiferromagnetic interaction in μ -oxalatodicopper(II) complexes by counterions : there is no innocent counterion.

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We are engaged in a long term study of oxalate complexes, from the simplest copper(II) dinuclear units – started with the late O. Kahn - to specially designed multifunctional materials. [1-3] On our way, we discovered the unique influence of the nature of the counterion on the magnetic properties, proposed herein.

We report the preparation and crystal structure determination of five oxalato-bridged dicopper(II) complexes of formula $[\text{Cu}_2(\text{bpy})_2(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)](\text{CF}_3\text{SO}_3)_2$ (**1**), $[\text{Cu}_2(\text{bpy})_2(\text{C}_2\text{O}_4)](\text{PF}_6)_2$ (**2**), $[\text{Cu}_2(\text{bpy})_2(\text{C}_2\text{O}_4)](\text{ClO}_4)_2$ (**3**), $[\text{Cu}_2(\text{bpy})_2(\text{H}_2\text{O})\text{Cl}_2(\text{C}_2\text{O}_4)]$ (**4**) and $[\text{Cu}_2(\text{bpy})_2(\text{NO}_2)_2(\text{C}_2\text{O}_4)]$ (**5**) (bpy = 2,2'-bipyridine and $\text{C}_2\text{O}_4^{2-}$ = oxalate).

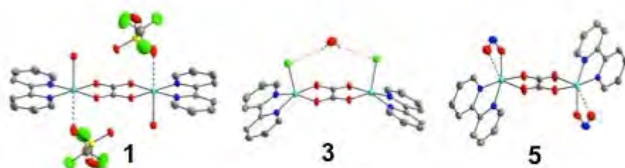
In the five compounds, the oxalate acts as a bis-bidentate ligand bridging the Cu(II) ions and the two bipyridine are terminal ligands. The two nitrogen atoms of bpy are always two of the nearest neighbours of Cu(II). The values of the copper-copper separation across the oxalate bridge vary in the range 5.127(1) - 5.466(1) Å.

The main structural differences for the five compounds are related to the coordination of the counter anions and the surroundings of the copper(II) ions. In **1-4**, the four nearest neighbors of copper are roughly in the plane of the $\text{CuC}_2\text{O}_4\text{Cu}$ unit, whereas in **5**, they are in a plane almost perpendicular to the $\text{CuC}_2\text{O}_4\text{Cu}$ unit. **1-4** present a large intramolecular antiferromagnetic coupling. Using the isotropic Hamiltonian $\mathbf{H} = -J \mathbf{S}_1 \cdot \mathbf{S}_2$, where \mathbf{S}_1 and \mathbf{S}_2 are the spin quantum operators for Cu1 and Cu2, $J = -387 \text{ cm}^{-1}$ (**1**), -385 (**2**), -370 (**3**), -330 (**4**) and -13 cm^{-1} (**5**). This switching of the magnetic exchange coupling when going from **1** to **5**, is due to the anion coordination and is simply explained by the changes in the overlap of the magnetic orbitals through the oxalate bridge, leading to the conclusion that there is no innocent counterion.

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Figure 1 : Perspective view of dinuclear units in compounds **1**, **3** and **5**. Colour code: carbon, grey; nitrogen, dark blue; oxygen, red; halogen (F or Cl), green; copper, light blue.





Porous layered materials based on anilato-type ligands

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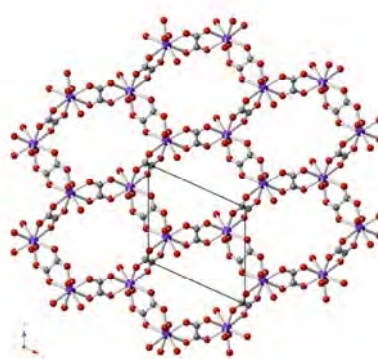
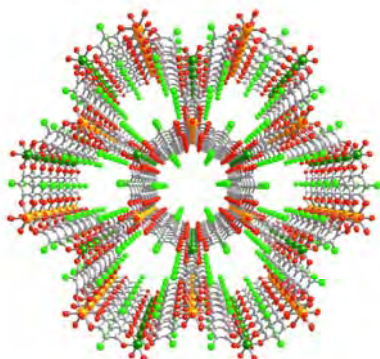
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In this communication we will show the use of anilato-type ligands: $[\text{C}_6\text{O}_4\text{X}_2]^{2-}$ = dianion of the 3,6-disubstituted derivatives of 2,5-dihydroxy-1,4-benzoquinone, $\text{H}_4\text{C}_6\text{O}_4$) to prepare different layered neutral networks formulated as $\text{A}_2(\text{C}_6\text{O}_4\text{X}_2)_3 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}, \text{H}, \text{OH}, \dots$; $\text{A}^{3+} = \text{La}, \text{Nd}, \text{Gd}, \text{Tb}, \text{Fe}, \text{Cr}, \dots$).^[1] We will show the activation of these layers to prepare porous layered materials based on anilato-type ligand in order to insert different solvent and gaseous molecules. The magnetic characterization of this family of layered porous networks will also be presented.

Furthermore, we will show how the use of the $\text{X} = \text{OH}$ derivative, $[\text{C}_6\text{O}_4(\text{OH})_2]^{2-}$, with Tb^{3+} has led to the unexpected synthesis of $\text{Tb}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$. Although in-situ oxalato synthesis catalyzed by Ln^{3+} ions is well known,^[2] this is the first case where the precursor is not a carboxylic acid. We will discuss the possible mechanism for this unexpected synthesis.

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Analysis of the role of peripheral ligands coordinated to Zn(II) and counteranion in rising the anisotropy energy barrier of a series of zero-field Zn-Dy-Zn Single Molecule Magnets

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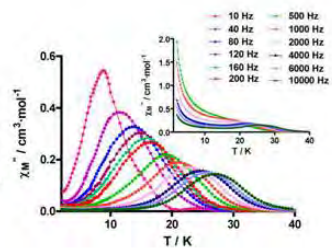
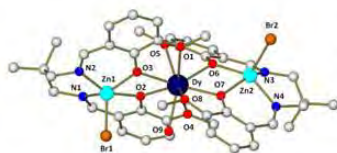
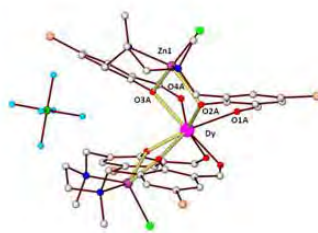
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Lanthanide ions exhibit strong magnetic anisotropy due to the combination of strong spin-orbit coupling and crystal-field effects promoted by the ligand surrounding and therefore are excellent building blocks to be used in the construction of coordination compounds with SMM properties. In fact numerous 3d/4f and 4f (and 5f) mononuclear and polynuclear coordination compounds, most of them containing Dy^{III} ions, have been shown to exhibit SMM behavior. Interestingly, mononuclear and low-nuclearity 4f metal complexes have been shown to possess energy barriers an order of magnitude higher than observed in 3d and 3d/4f polynuclear clusters. The SMM behavior observed for low-nuclearity 4f metal complexes generally is due to the individual Ln^{III} ions rather than to the whole molecule. Moreover, Ln...Ln interactions frequently favors fast quantum tunneling of the magnetization in the ground state, which reduces the energy barrier to an effective value U_{eff} . Nevertheless, when the complex containing paramagnetic Ln^{III} ions is diluted in an isostructural diamagnetic lattice, the Ln...Ln interactions are reduced and the energy barrier (U_{eff}) often increases. Theoretical and experimental studies carried out by us and others have shown that the incorporation of diamagnetic metal ions such as Zn^{II} in a Dy^{III} complex is a good strategy to enhance U_{eff} .

By exploiting these features of the Zn^{II}/Dy^{III} systems and playing with the distribution of donor atoms on the Dy^{III} coordination environment following the guidelines of the simple prolate-oblate electrostatic model, we were able to rationally design Zn-Dy-Zn SMM with two different compartmental ligands and large anisotropy energy barriers (See Figure 1).¹ *Ab initio* calculations support the easy-axis anisotropy of the ground Kramers doublet and predict zero-field SMM behavior through Orbach and TA-QTM relaxations via either the first or the second excited Kramers doublets. In accordance with the experimental results, *ab initio* calculations show, on one side, that, compared to water, the peripheral halide ligands coordinated to the Zn²⁺ ions increases the barrier height, and, on the other side, that the replacement of the counteranion in a Zn-Dy-Zn trinuclear complex provokes a change towards a more symmetric structure where there exists a C₂ axis on the Dy^{III} ion. The presence of the C₂ axis imposes collinearity of the anisotropic axes of the two lowest KDs, so that the thermal activated relaxation is suppressed via the first excited KD and takes place via the second excited state, giving rise to a dramatic increase in the effective energy barrier.

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Molecular nanomagnets
(Poster)

Evaluating linear [CuLnCu] complexes as potential 2 and 3-qubit quantum gates

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An alternative and very promising proposal for the realization of quantum information processing relies on the use of paramagnetic species within molecular entities to embody addressable spin qubits.[1,2] Coordination chemistry provides means to dispose, in a controlled manner, different metal ions within a molecular complex, which are of particular interest to realize multiple qubit structures required for specific qugates.[3,4] We focus here on a series of known linear trinuclear [CuLnCu] complexes [5] that, depending on their composition, can provide the adequate topology for the realization of various 2- and 3-qubit quantum gates. The low temperature static and dynamic magnetic properties and heat capacity of the La and Er analogues were measured and analysed to determine the corresponding energy level schemes. On basis of these, we discuss the potential of these molecules to implement CNOT and CCNOT (or Toffoli) quantum gate operations. The presence of inequivalent g factors of the Cu(II) ions and of a weak antiferromagnetic exchange coupling in [CuLaCu] allows us to propose its use as a CNOT molecular qugate. In [CuErCu], the additional spin states associated with the electronic ground state doublet of Er(III) and its weak antiferromagnetic interaction with both Cu(II) ions give rise to an energy level scheme that is suitable for the realization of a CCNOT gate, which forms the basis for some quantum error correction protocols, as well as of a universal three-qubit processor.

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Multifunctional compounds: spin crossover and chirality

Patrick Rosa¹, Ahmad Naim¹, Elen Duverger-Nedellec¹, Philippe Guionneau¹

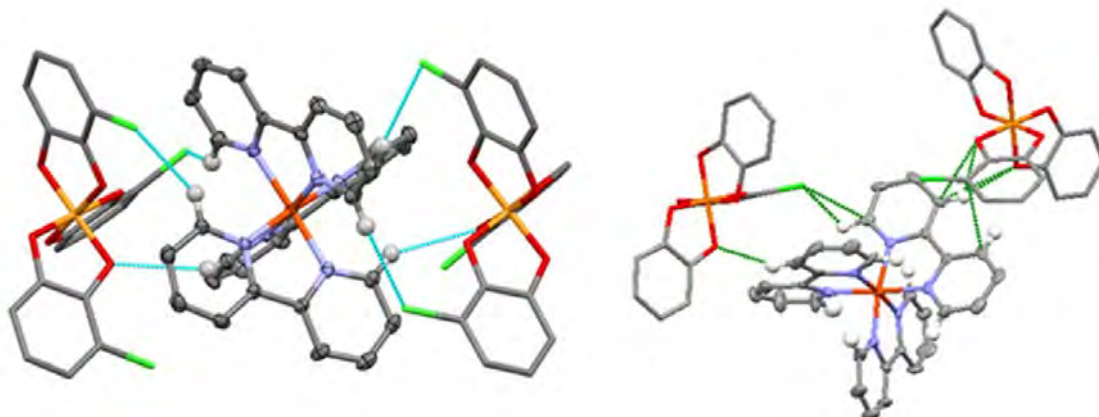
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The synthesis of new spin crossover compounds is interesting fundamentally, for the understanding of the physics underlying the corresponding phase transitions, as much as for the potential technological applications of those compounds. Obtaining non-centrosymmetric magnetic compounds yields interesting subjects for non-linear optical studies (on the effect of unpaired electrons),[1] or for crystallography (see recent evidence on incommensurate spin state ordering).[2]

Various strategies are being currently pursued at ICMCB towards such spin crossover non-centrosymmetric molecular materials. These strategies introduce chirality by playing on the two variables components of the material, the ligands on the transition metal (typically Fe(II) or Co(II)), and the possible counteranions. We will show the results we have obtained recently using the latter approach, with various families of chiral anions, that were used previously mainly for chiral HPLC and/or NMR enantioselective differentiation, rarely for the synthesis of molecular materials, but never for spin crossover compounds: tris(dioxolene) derivative of phosphate(V) (the TRISPHAT family that has been set up by Prof. J. Lacour from Université de Genève)[3] or arsenate(V),[4] adducts of (+)- or (-)-tartrate with As(III) or Sb(III).[5] We will present the new anions we obtained and characterized, together with various examples of Fe(II) complexes cocrystallized with those anions. We will show that the analysis of chiral interactions in the solid state can lead to different conclusions respective to results obtained in solution (NMR, circular dichroism), and that those interactions depend heavily, as much as for the spin crossover phenomenon, on non-covalent intermolecular interactions such as hydrogen bonding. Figure: Anion-cation interactions in (a) [Fe(2,2'-bipy)₃](rac-TRISPHAT)₂; (b) [Fe(2,2'-bipy)₃](Δ-TRISPHAT)₂

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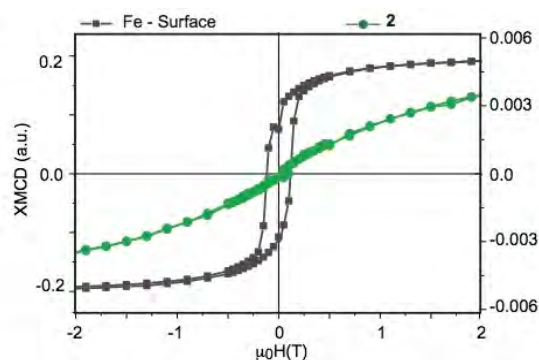
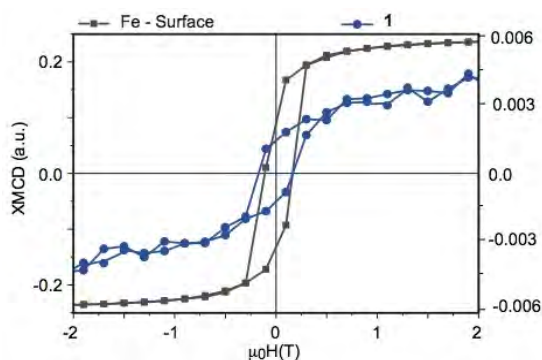
**Molecular control of the magnetic exchange between self-assembled metal-complexes
and ferromagnetic surfaces: towards molecular spintronics**

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Controlling the interface poses a challenge when constructing molecular spintronic devices. This study shows that it is possible to modulate the magnetic response of a system with a molecule and control the interaction between the molecule and the surface *via* the interface. A family of lanthanide complexes was synthesized by the subcomponent self-assembly methodology. Molecular architectures, which were stable in solution and in ambient conditions, were designed by the in-situ formation of ligands around metal ion templates (**1**: Co(II) and **2**: Ni(II)). These molecules display magnetic anisotropy and can be chemically tethered onto ferromagnetic surfaces. Anchoring induced, in the paramagnetic cobalt(II)-containing complex, a magnetic ordering and hysteresis that was studied by X-ray absorption spectroscopy (XAS), X-ray magnetic circular dichroism (XMCD) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). While, we do not observe any coupling with the ferromagnetic electrode for the isostructural nickel(II)-containing complex. This result highlights the fundamental effect that the electronic structure of the metal ion in conjunction with the nature of the organic spacer has on the resulting molecule/electrode interaction.





Reduction of Mn₁₉ Coordination Clusters on a Gold Surface

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The Mn₁₉ molecule [1] features an extremely large spin $S = 83/2$ ground state which originates from the ferromagnetic coupling of its constituent Mn(II) and Mn(III) ions. In view of positioning and addressing single molecules in molecular spintronics applications, and in order to gain a fundamental understanding of the effects of molecule-surface interactions, it is interesting to study such molecules when deposited on surfaces. Previously, methoxy-functionalized Mn₁₉ molecules have been investigated by scanning tunneling microscopy on highly oriented pyrolytic graphite surfaces [2].

In this contribution we present recent results on Mn₁₉(SMe) denoting Mn₁₉ molecules equipped with methylmercapto substituents on the organic ligands, $[\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_7(\text{m}_4\text{-O})_8(\text{m}_3\text{-Cl})_{7.7}(\text{m}_3\text{-OMe})_{0.3}(\text{HL}^{\text{SMe}})_{12}(\text{MeOH})_6]\text{Cl}_2 \cdot 27\text{MeCN}$, ($\text{H}_3\text{L}^{\text{SMe}} = 2,6\text{-bis(hydroxymethyl)-4-mercaptomethylphenol}$), deposited onto Au(111) surfaces from solution [3]. X-ray absorption spectroscopy and X-ray magnetic circular dichroism show that in the submonolayer regime the molecules contain only Mn(II) in contrast to the simultaneous presence of Mn(II) and Mn(III) in the powder sample. The total spin ground state of the molecules in the submonolayer is much lower than $S = 83/2$ of the pristine molecules. We conclude that the electronic structure, molecular geometry and intramolecular exchange coupling are strongly modified upon surface deposition. A sample with coverage of a few layers of Mn₁₉ exhibits the presence of Mn(III) which suggest that a suitable intermediate decoupling layer could prevent the surface induced modifications.

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Switchable magnetic materials and optical magnets
(Poster)

Effect of intermolecular interactions on the nucleation, growth and propagation of like-spin domains in spin crossover materials.

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The nucleation, growth and propagation of like-spin domains in spin crossover materials was investigated during the relaxation process of a metastable HS state at low temperature using an electro-elastic model running on a deformable 2D square lattice. We distinguish the onset of patterns

formation of low-spin domain as the intermolecular interaction is increased passing successively through random dispersion to clustering pattern and ending up with an impressive single macroscopic

domain growth. Attaining and maintaining a single domain configuration through the transition is attributed to the long range character of interactions. Qualitative investigation of the elastic energy, of the propagation of the low-spin domain, and of the displacement field are presented. We demonstrate that as the intermolecular interaction increases the propagation of the like-spin domain slow-down. The deformations are believed as the prolonged effect of the intermolecular interactions that are at the origin of the onset of dispersed, poly and single domains nucleation. Spatial autocorrelation of the deformations analysis is used. We demonstrate that at short distance a significant spatially autocorrelated patterns are detected, and the extent of the autocorrelation decreases with the distance.



Ultrafast spin dynamics in transition metal complexes

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Transition metal complexes with different types of organic ligands offer a large chemical flexibility allowing their controlled synthesis for specific applications. Over the past few years, a number of novel ultrafast experimental tools have emerged, such as ultrafast fluorescence up-conversion^[1] ultrafast X-ray spectroscopies (absorption and emission)^{[2],[3]} and ultrafast photoelectron spectroscopy, that allow the detailed mapping of the intramolecular relaxation pathways among electronic states of same spin (internal conversion, IC), intramolecular vibrational relaxation (IVR) and relaxation among states of different spins (intersystem crossing or ISC).^[4] In particular, regarding the latter, the emerging picture is that spin transitions can occur at extremely short times (down to <30 femtoseconds) and that they do not scale with the spin-orbit coupling constant of the metal considerations structural dynamics density states energetics are also key parameters in spin a href="#_ftn5" title="" data-mce-href="#_ftn5">>[5]^[6]

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Changes in the magnetic behaviour of a 3-D MOF of SMMs induced by pressure and counterion substitution

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The preparation of ordered arrays of SMMs in the crystalline state is of interest for both theoretical and practical reasons.[1] A small number of examples exist of structurally characterized 1-D, 2-D and 3-D polymeric arrays of SMMs.[2] The study of how variations in the environment of the magnetically active entities modulates the magnetic behaviour of the sample can shed light on the nature of the magnetic interactions present.[3] We have previously studied the effects of the counterion on the magnetism of a 2-D polymeric array of SMMs, relating magnetic changes to the structural modifications provoked by cationic substitution.[4]

The isomorphous compounds $\{M_4Co_4(citr)_4[m-Co(H_2O)_4]_2 \cdot 8H_2O\}_n$, $M = K^+, Rb^+$, which crystallize in space group $I4_1/a$, have K^+ and Rb^+ as counterions and a cobalt/citrate ratio of 3:2. Crystals of these compounds present triple interpenetration of equivalent 3-D diamondoid nets composed of SMMs bridged by magnetically active Co(II) units with octahedral coordination geometry. The counterions and free water molecules reside in channels parallel to the crystallographic quaternary axis. According to IUPAC nomenclature [5], these compounds are hybrid MOFs containing SMMs, which present potential voids for solvent and ionic interchange. Their magnetic characterization shows a phase transition to a magnetically ordered phase after the characteristic blocking of the cubane units of the polymeric net. This is, to the best of our knowledge, the first example of the coexistence of a blocking phenomenon and a phase transition for a compound based on cubanes. This can be attributed to the short cubane-cubane distances between interpenetrated nets. A study of the modifications of the magnetic response of the samples induced by chemical changes in the environment of the cubanes, along with those provoked by pressure, is presented in this work.

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Magnetic lanthanoid complexes as molecular spin qubits

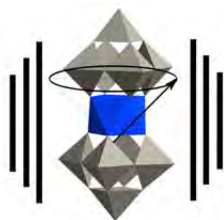
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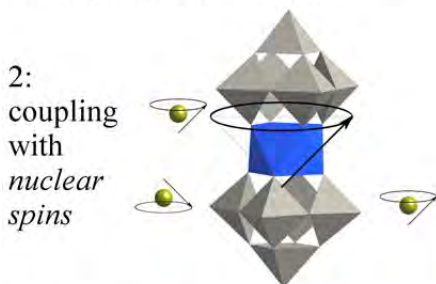
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Magnetic coordination complexes have been proposed as molecular spin qubits, and, in particular, as model systems to study quantum decoherence. We will discuss recent advances in this topic, such as

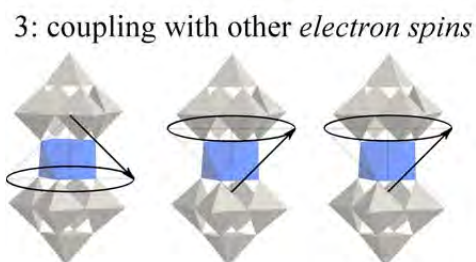
1. the experimental finding of optimal operating conditions in different magnetic polyoxometalates that profit from their electronic and molecular structure to greatly extend quantum coherence,
2. a theoretical proposal for quantum error correction using a single magnetic molecule,
3. a proposal for the complex organization of molecular qubits using biopolymers as a smart scaffold.



1: coupling with *vibrations*



2:
coupling with
nuclear spins



3: coupling with other *electron spins*



Molecular Spintronics with hybrid Quantum Cicuits

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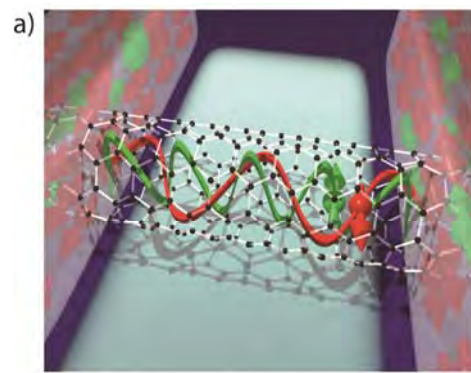
Combination of two or more physical systems, with the goal of harnessing the strength of the constituents is the main motivation towards building hybrid quantum circuits. Here, we explore the coupling between different molecular electronic devices and magnets of different dimensionalities.

Electron transport through carbon nanotubes (CNTs) remains one of the most exciting areas of research in nanoscale condensed matter, due to the interplay of quantum interference, strong electron-electron interactions, and spin-polarized transport [1]. Finite-length NTs, fenced off with tunnel barriers, behave as quantum dots (QDs) and thus show Coulomb blockade (Quantum confinement) and Kondo effect (spin-1/2 electrons in the dot coupled to Fermi sea). Interestingly, the feasibility to attach different electronic orders (for example, ferromagnets) or dimensionalities (3D electrodes, magnetic nanoparticles, Fullerenes, Single molecular magnets) to CNTs allows us to combine nano-electronics with magnetism [2]. Here, we implement for the first time a quantum dot connected to two non-collinear leads. The device acts like a spin-valve with non-collinear magnetic leads, with a finite tunneling magnetoresistance effect. While the linear spin dependent transport displays the usual signatures of electronic confinement, the finite bias magnetoresistance displays a striking antisymmetric reversal in stark contrast with the linear regime. This effect, which can only be understood if electronic interactions are present, is accompanied by a linear dispersion of the zero magnetoresistance point in the bias-field plane. The slope of the dispersion corresponds to an effective gate tunable g-factor ranging from 200 to 700. Such high values cannot be understood in terms of Zeeman or magnetic field induced orbital effects and leads us to conclude that they are evidence for current induced spin precession.

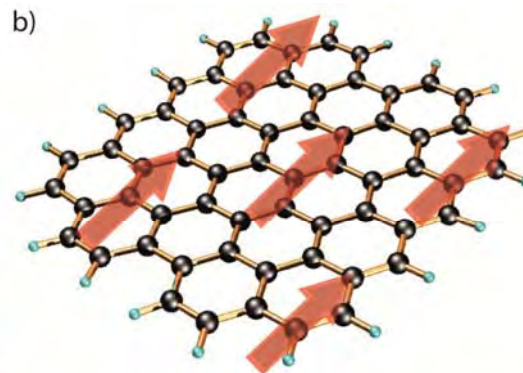
Graphene, a one atom thick graphite layer, with its unique valley structure and Dirac neutrality point separating hole states from electron states, has led to the observation of new electronic transport phenomena such as anomalously quantized Hall effects, and the existence of a minimum conductivity. Graphene might also be a promising material for spintronics and related applications, such as the realization of spin qubits, owing to the low intrinsic spin orbit interaction, as well as the low hyperfine interaction of the electron spins with the carbon nuclei. To explore spin dependent properties of these materials, we have chosen polycyclic hydrocarbon with a singlet biradical ground state which has recently become a hot topic among various studies on p-conjugated systems and it is of importance to understand the fundamental spin transition from singlet to triplet states. The main objective of this work is to graft the magnetic object with 2D layered materials and study their electronic and optical properties in view of spintronic applications.

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Spin Transport through CNT junction



Magnetic molecule - graphene hybrid



**Synthesis, Structure and Magnetic Properties of Chiral Magnetic Materials
using Achiral Ligands and Transition Metals**

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1. Introduction

Molecular magnetic materials with various dimensionality using organic radicals and transition metal ions have been synthesized and reported. Nitronyl nitroxide radicals is expected the diversity of the coordination form, because capable of coordinating two site in metal ions. In general, $M^{II}(\text{hfac})_2(\text{hfac}=\text{hexafluoroacetylacetonato})$ and phenyl nitronyl nitroxide radicals (NIT) with a substituent to form a one-dimensional chain structure and mononuclear structure. This time, our group were synthesized three types of complexes using achiral NIT (Fig.1 (1)~(3)) which introduced methoxy group. In this paper, we would like to report the structure and magnetic properties.

2. Experiment

NIT(1-3) and $Mn(\text{hfac})_2$ mixed EtOH/*n*-heptane = 1:3 solution. Deep green needle crystals or powder were obtained upon stand for a few days at room temperature.

3. Results and Discussion

Crystal Structure. $[1 \cdot Mn^{II}(\text{hfac})_2]$ and $[2 \cdot Mn^{II}(\text{hfac})_2]$ complexes both have one-dimensional chain structures with trans coordinated Mn ion. These complexes crystallizes spontaneous chiral crystallization, with space group of $P6_1$ and $P6_5$ in both cases. The *c*-axis is correspond to the helical axis. For the case of complex 3, powder sample was obtained then the structure and space group were not determined.

Magnetic Properties. Temperature dependence of magnetizations showed a sharp rise at 8.4 K for the polycrystal samples of $[2 \cdot Mn^{II}(\text{hfac})_2]$. The field dependence of magnetization at 1.8 K revealed soft ferrimagnetic behavior. The saturation magnetization value of $3.8 \mu_B$, which is good agreement with theoretical value of $4 \mu_B$ ($5/2-1/2=4/2$) for $[2 \cdot Mn^{II}(\text{hfac})_2]$ —The magnetic easy axis is perpendicular to helical axis.

In this presentation, we would like to discuss the structures and magnetic properties for the complexes.

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Structures and Physical Properties of Octacyano-Bridged Compounds Containing W and Cu

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Magnetic materials belonging to non-centrosymmetric space groups are highly expected to exist Dzyaloshinsky-Moriya interactions that introduce non-collinear magnetic structures, such as chiral helical and/or conical spin structures are expected to show fascinating physical properties. Molecular-based magnetic materials have attracted attention for both the unique physical properties and routes of their synthesis. They have characteristics to be able to synthesize separately racemic and right- and left- handed enantiomers with easily compared with inorganic magnets. In addition, molecular-based magnets are also suitable for observation of dielectric effect, magneto-optical effect and spin current because most of them are transparent and insulators. Especially, Prussian blue analogues are one of the most attractive classes of compounds in this field due to the wide variety of architectures and ease of functionalization by introducing different organic ligands. We try to reveal the particular properties coming from chirality with molecular-based magnets.

Two types of W-Cu cyano-bridged compounds were synthesized used (*R*) or (*rac*)-1,2-cyclohexanediamine ((*R*) or (*rac*)-chxn) as the ligand. They have different structure and magnetic properties each other. The compound which is used (*R*)-chxn is belongs to chiral space group monoclinic C2. One W interacts with four Cu and one Cu with four W by CN. The magnetic susceptibility versus temperature plots showed that the magnetic ordering temperature of this was 5.8 K and the magnetic susceptibility decreased below this temperature. And the existence of the magnetization inflection point became evident of chiral spin structure by the magnetization dependence of the magnetic field. On the other hand, racemic compound consists of hexagonal layers with W and Cu linked by CN. One W interacts with three Cu and one Cu with two W by CNs. The magnetic properties of the racemic compound are antiferromagnetic with $T_N = 2.4$ K and H_{sf} is about 1000 Oe.

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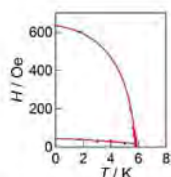


Fig. 1. The phase diagram of *R* compound

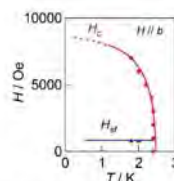


Fig. 2. The phase diagram of racemic compound



THERMOSTABLE DYSPROSIUM SINGLE-MOLECULE MAGNETS

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Single-molecule magnet (SMM) behaviour of lanthanide compounds are attractive, since its complicated electronic structure and rich geometrical symmetry are sensitive to its coordination environment [1]. The general strategy to fine-tune the coordination environment is to vary the ligands' substituent groups [2]. Apart from the high performance of SMM and the multi-functionality [3], the stability is one key factor for fabricating device or organizing on substrates [4].

Following the prior work focusing on the β -diketonate based lanthanide SMMs [5], we designed four new dysprosium (III) compounds $[M\{Dy(8mCND)_4\}(CH_3OH)_2(Me_2CO)_2]_2 \cdot (Me_2CO)_2$ ($M = Na$ (**1**), K (**2**), Rb (**3**), Cs (**4**)) with 8mCND as the N-, O-, chelate ligand. There are four identical ligands coordinated to a Dy (III) ion, and a alkali metal ion is linked to Dy (III) ion through three O atoms from the ligands (Figure 1) except **1**. As the counter ions, the alkali metal ions, barely tuned the coordination environment of dysprosium, and the energy barriers of spin reversal are around 40cm^{-1} and 90cm^{-1} under 0 and 1000 Oe for **2-4**. The energy barrier of **4** was also obtained from photoluminescence of dysprosium at 77 K (Figure 1). After sublimating at about 330°C under high vacuum, the four thermostable compounds $[M\{Dy(8mCND)_4\}]$ ($M = Na$ (**5**), K (**6**), Rb (**7**), Cs (**8**)) were obtained (Figure 1). It is found that Dy—O and Dy—N bonds of **8** are slightly shorter than of **4**, and the coordination polyhedron of **8** is closer to the idealized dodecahedron. Fortunately, slow magnetic relaxation at 0 and 1000 Oe dc field were remained for **5-8** and photoluminescence of dysprosium of compound **8** was observed at 77 K (Figure 1).

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MAGNETISM OF FLUORIDE-BRIDGED CHAINS, RINGS AND POLYNUCLEAR COMPLEXES

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Fluoride is an interesting bridging ligand for the construction of molecule-based magnetic systems. The pronounced preference of fluoride for bridging in a linear fashion allows for control over topologies.^[1,2] Simultaneously, the strong discrimination of fluoride among metal centers allows for selectively targeting the hardest metal ions.^[1] Some examples of new routes to molecular, 0-D, 1-D, and 3-D magnetic systems based on fluoride linkages between transition metals and between transition metals and lanthanide ions will be discussed.^[3,4] Importantly, the electronic structure of the fluoride complexes constituting building blocks for more complicated structures are significantly perturbed by the second sphere interactions with hard metal ions (or protons). In this respect, fluoride differs pronouncedly from the heavier halides. For the construction of heterometallic lanthanide complexes with fluoride bridges, it has surprisingly been found that usage of kinetically robust fluoride complexes is not a prerequisite. These systems have allowed for modeling of the magnetic properties^[5] and for the first quantification of magnetic coupling between 3d and 4f centers across a fluoride bridge. By using the derived magneto-structural correlations, new systems with optimal properties for magnetic cooling have been synthesized and characterized.

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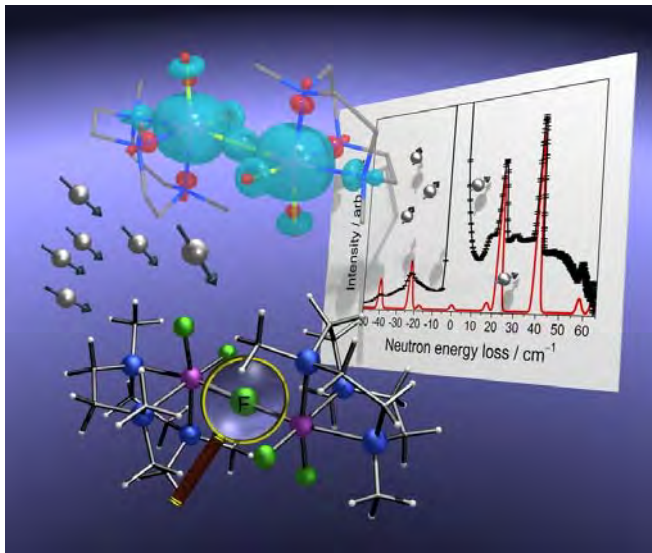
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Tuning the magneto-chemical interaction of spin-bearing molecules with ferromagnetic substrates by use of nitrogen and chlorine spacer layers

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The magnetism of spin-bearing metallo-organic complexes (e.g. square-planar metalloporphyrins and -phthalocyanines) has recently attracted significant attention. Upon adsorption on ferromagnetic substrates such magnetic molecules possess an exchange induced magnetic moment[1] that can be further modified by introducing a spacer layer made of a non-magnetic material such as C, O or Cr [2-4] or by means of a chemical stimulus (i.e. by coordination with ligands like NO, NH₃, CO) [3-5]. In this contribution, N and Cl reconstructed ferromagnetic Co films are used to study the magneto-chemical interaction between Mn- and Fe-tetraphenylporphyrins and the terminated top-most layer of those films. We employ surface sensitive techniques such as X-Ray Photoelectron Spectroscopy (XPS), Scanning Tunneling Microscopy (STM) and Low-Energy Electron Diffraction (LEED) to get insight into the structure and composition of the probed metal/organic interfaces, while X-Ray Magnetic Circular Dichroism (XMCD) spectroscopy provides insight into the magnetic properties of these three layer 'sandwich' systems and the relative magnetization of their components. It is this spectro-microscopy correlation approach combined with DFT+U calculations, which enables us to investigate and understand both, complex on-surface architectures as well as changes in the magnetic interaction strength. We demonstrate, that the latter can be tuned by N or Cl spacer layers introduced between the spin-bearing adsorbate and the ferromagnetic substrate. We report that N and Cl introduce qualitatively different modifications due to the different orbitals involved in the interaction as a consequence of their different electronic structure and reactivity.

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Endohedral metallofullerenes: a versatile platform for molecular magnetism

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The molecules of endohedral metallofullerenes (EMFs) comprise the fullerene cage encapsulating one to three metal ions or a more complex hybrid cluster.^[1] Metal atoms usually donate their valence electrons to the fullerene cage resulting in rather ionic environment, and destabilizing Coulomb repulsion between metal atoms can be balanced by a presence of non-metal atoms bearing negative charges. E.g., in nitride clusterfullerenes $M_3N@C_{80}$ three metal atoms (Sc, Y, lanthanides) bearing a 3+ charge state surround the 3-fold negative charged nitride ion (the charge of the carbon cage is thus 6-). The large negative charge of the nitride ion and its location in the close proximity of lanthanide ions results in the large magnetic anisotropy with quasi-uniaxial ligand field. For the lanthanides with oblate shape of the 4f density (Tb, Dy, Ho, etc) the ground magnetic state has the largest J_z projection and rather large gap to higher energy states,^[2] which results in single molecule magnetism, especially strong for Dy compounds.^[3]

In this contribution we will discuss the effect of molecular structure and environment on the magnetic properties of lanthanide-based endohedral clusterfullerenes. E.g., the nitride cluster composition can be varied using the mixed-metal approach, and various combinations of two or even three metal atom were described for nitride clusterfullerenes. The intracluster exchange and dipolar interactions have dramatic effect on the magnetic properties. The studies of $DySc_2N@C_{80}$, $Dy_2ScN@C_{80}$, and $Dy_3N@C_{80}$ showed different magnetization behaviour, Dy_1 showing the tunneling at zero field, Dy_2 exhibiting remanence, and Dy_3 showing fast relaxation due to magnetically frustrated state.^[3a] Recently we found that in the presence of Ti, the central nitride ion can be replaced by carbon giving $M_2TiC@C_{80}$ molecular composition with double $T=C$ bond.^[4] The Dy analogue exhibit single molecule magnetism, but is softer than isostructural $Dy_2ScN@C_{80}$. Thus, a range of different magnetic phenomena can be realized within one class of compounds. Finally, the fullerene cage has high chemical and thermal stability, thus shielding endohedral magnetic ions and protecting their spin states from the environment. EMF molecules can be sublimed without decomposition, and monolayers of $Dy_2ScN@C_{80}$ on metal substrate retain SMM behavior.^[5]

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Liquid crystalline derivatives of 6-oxoverdazyl

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Open-shell organic systems are becoming increasingly important structural elements of modern materials for spintronics, photomagnetic devices, energy harvesting, and memory and energy storage. In this context, we have been investigating supramolecular assemblies of stable p-delocalized radicals. Recently, we focused on the 6-oxoverdazyl system (**I**), which upon substitution with appropriate wedge-shaped or elongated groups give anisometric disk-like [1,2] or bent-core derivatives [3,4] that exhibit liquid crystalline phases.

Liquid crystals provide a viable approach to engineer the bulk structure of a material either in its fluid state (liquid crystal phase) or as a rigid solid (crystal, soft crystals, or glass from the mesophase). While they are liquid-like and dynamic, liquid crystals also exhibit some characteristics of ordered crystalline solids, e.g. optical, dielectric, and magnetic anisotropy. They exhibit over two-dozen distinct calamitic, discotic, banana and soft crystalline phases providing almost a continuum of molecular order between an ordinary isotropic liquid and a rigid solid crystal. This offers access to a wide variety of dynamic, thermodynamically controlled spatial molecular arrangements and intermolecular, including spin-spin, interactions.

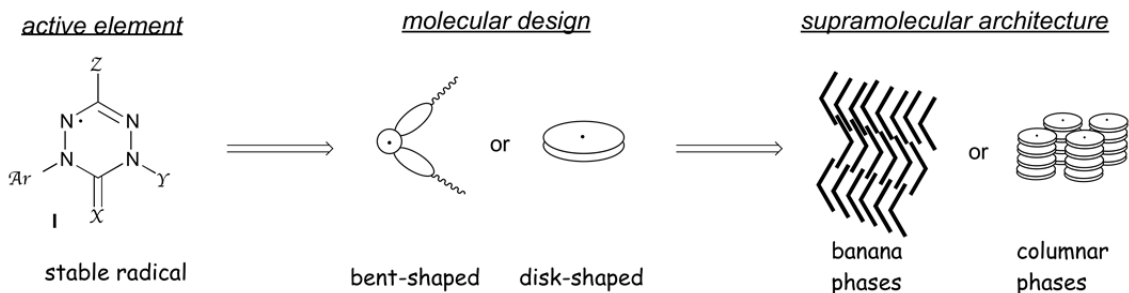
For instance in one series of bent-core mesogens we found rich liquid crystalline polymorphism (including a novel 3D tetragonal phase), ambipolar photoconductivity, and electro-optical effects [3]. In a series of disc-like derivatives of 6-oxoverdazyl magnetization studies (SQUID magnetometer at 200 Oe) revealed paramagnetic behavior in both crystalline and fluid phase. The effective magnetic moment (m_{eff}) in the pristine crystalline phase corresponds to $87 \pm 3\%$ of spins, which increased to $95 \pm 2\%$ at melting to an isotropic phase.

Synthesis, liquid crystalline, photovoltaic and magnetic results for several series of compounds will be presented.

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MULTIDIRECTIONAL MANIPULATION ON LOW DIMENSIONAL CYANIDO-BRIDGED SKELETONS – THE ROUTES TOWARDS NEW MAGNETIC MATERIALS

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The low dimensional cyanido-bridged species gained an extremely strong interest due to the diversity of structural coordination forms and numerous properties, prospective for future applications in data storage and processing. This could be accessible through the controlled manipulation on structural, electronic and magnetic state of the related soft materials. Several important underlying prerequisites, such as magnetic coupling and magnetic anisotropy, spin-crossover (SCO) charge-transfer induced spin transition (CTIST) and light-induced excited spin state trapping (LIESST), linkage isomerism, guest dependent behaviour and other were found and examined [1,2].

Along this line, our presentation will be focused on current information on the organisation of the selected low dimensional cyanide-bridged $M^{II}-W^V$ ($M = Mn, Fe, Co$) species in crystalline phases. We will consequently attempt to describe the modular routes towards novel materials, according to the emerging *synthetic condition – crystal structure – properties* scheme. These include: (i) chiral magnetic sponges, (ii) solid solutions with composition dependent spin distribution and spin phase transitions and (iii) high spin cluster based extended systems for slow magnetic relaxation or magneto-caloric effect.

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Redox-controlled exchange bias in a supramolecular chain of Fe₄ single-molecule magnets and Ru₂ paddlewheels

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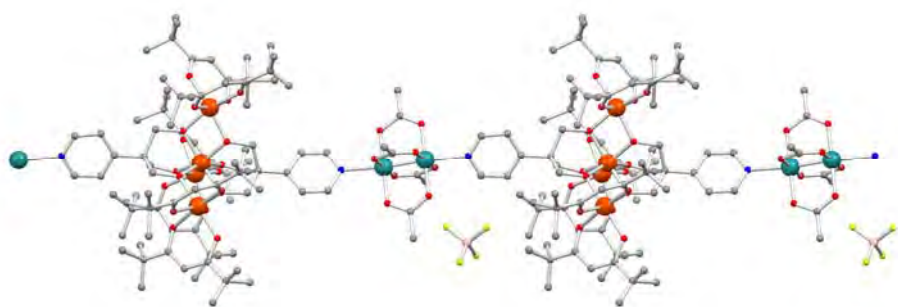
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Single-Molecule Magnets (SMMs) provide nanoscale, chemically-tuneable units displaying magnetic hysteresis and quantum magnetism at the molecular level.^[1] For this reason they have been proposed as components of molecular spintronic devices or as qubits for quantum computation.^[2] Weak coupling between two or more SMMs can be used to enhance their functionality: on one side, each SMM can act as a bias on its neighbour(s), generating a better memory effect; on the other side, entanglement between quantum states is an important resource for quantum information processing.^[2]

Herein we present the fully-controlled assembly of the tetrairon(III) SMM [Fe₄(pPy)₂(dpm)₆] (**1**) with an *S* = 5 ground state^[3] (H₃pPy = tripodal ligand bearing a 4-pyridyl substituent and Hdpm = dipivaloylmethane), into one-dimensional supramolecular structures held together by coordination bonds. **1** acts as a ditopic synthon and reacts with the paddlewheel dimers [Ru₂(OAc)₄(MeOH)₂] and [Ru₂(OAc)₄(THF)₂](BF₄) to give the supramolecular chains [Fe₄(pPy)₂(dpm)₆][Ru₂(OAc)₄](BF₄)_x with *x* = 0 (**2a**) or 1 (**2b**), respectively. Crystal structures of **1**·2EtOH and **2b** (see Figure; colour code: Ru = sky blue, Fe = orange, F = yellow, O = red, N = blue, C = grey, B = pink, H omitted), together with preliminary data of **2a**, will be also shown. Polymers **2a** and **2b** differ in the electron count on the diruthenium bridges, which are both paramagnetic with *s* = 1 and 3/2, respectively. However, at low temperature, the diruthenium(II,II) paddlewheels in **2a** behave as effective *s*_{eff} = 0 spins and act as magnetic insulators. By contrast, the mixed-valent (II,III) bridges (*s*_{eff} = 1/2) in **2b** introduce weak intrachain exchange bias with concomitant enhancement of the remnant magnetization. The detailed analysis of the magnetic hysteresis loops at very low temperature of all compounds will be presented.^[3]

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Slow magnetic relaxation in a Mn(III)-Mn(III) dimer

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Nowadays, the laboratory synthesis of an artificial oxygen-evolving complex (OEC) has been the objective of many synthetic chemists. Particular attention has been given to mixed manganese-calcium compounds aimed to shed light on the tetranuclear arrangement of the manganese centers in the OEC [1]. By 2013 only two Mn/Ca heteropolynuclear complexes were reported in which the manganese ions are in mixed-valence [$\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_{10}\text{Mn}^{\text{II}}_2$] [2] and [$\text{Mn}^{\text{III}}_3\text{Mn}^{\text{II}}$] [3] oxidation states.

In efforts to construct heterometallic mixed-valence Mn-Ca cluster, our attention focussed on using pre-organised [$\text{Mn}_3\text{O}(\alpha\text{-fur})_6\text{Py}_2(\text{H}_2\text{O})$] ($\alpha\text{-fur}$ = $\alpha\text{-furoic acid}$) with the intention of forming a cluster with $\text{Ca}(\text{ClO}_4)_2$ and 2-(hydroxymethyl)pyridine (hmp). The synthesised complex can be described by formula [$\text{Mn}_2\text{Ca}_2(\text{hmp})_6(\text{H}_2\text{O})_4(\text{CH}_3\text{CN})_2](\text{ClO}_4)_3$ (1). Cluster 1 crystallizes in the monoclinic space group C2/c with the cation lying on an inversion centre. The manganese and calcium ions of the [Mn_2Ca_2] core are bridged by six moieties of 2-(hydroxymethyl)pyridine, four molecules of water and two of acetonitrile. The Ca and Mn atoms are seven and six coordinate, respectively. The distance Mn...Mn is 3,297 Å, but Mn...Ca is 3,490 Å. The complex was characterised by different physical-chemical methods: IR, cyclic voltammetry, UV-visible spectroscopy and dc/ac magnetometry.

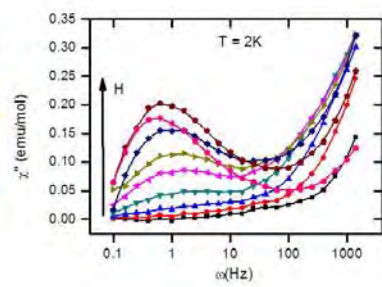
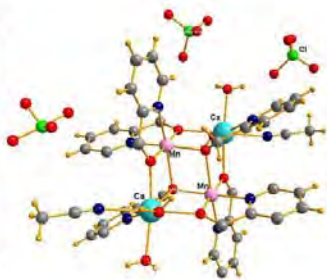
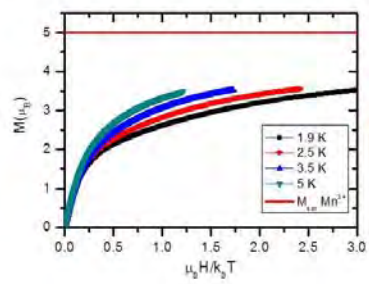
Magnetization measurements as a function of field at different temperatures and magnetic temperature-dependent susceptibility measurements reflect an unique Mn(III) valence state in the whole temperature range, with a dimerization of the Mn ions at low temperatures. Ac magnetization in addition reveals the slow relaxation characteristics of a Single Molecule Magnet (SMM) below 4K. At zero magnetic field, a magnetic relaxation process is observed at high frequencies ($\tau \sim 10^{-5}$ s), while a second low-frequency process ($\tau \sim 0.2$ s) is induced by the application of an external d.c. magnetic field.

Acknowledgements

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Low-temperature thermo-magnetic study of the $\{\text{Fe}_3\text{LnO}_2\}$ “butterfly” molecules

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An extensive study of a particular case of transition metal-Ln molecule-based magnets, the series of $[\text{Fe}_3\text{Ln}(\mu_3\text{O})_2(\text{CCl}_3\text{COO})_8(\text{H}_2\text{O})(\text{THF})_3]$ “butterfly” molecules [1], where Ln(III) represents a lanthanide cation, has been performed. The intracluster interactions and the field-induced spin reorientation of the Ln moment with respect to the Fe_3 subsystem were reported in our previous works [2, 3]. Here, we focus on the magnetization relaxation mechanisms for different Ln substitutions, with the aim of exploring the presence of quantum tunneling phenomena in some of them and their possible application as qubits.

A thermo-magnetic characterization of the series $\{\text{Fe}_3\text{LnO}_2\}$ with Ln(III)= Gd, Dy, Tb, Ho and Lu, and Y as pseudolanthanide has been performed. In order to check the possible existence of slow magnetic relaxation, the heat capacity and dc susceptibility of each compound have been investigated at temperatures down to 0.35 K, while the ac susceptibility has been studied down to the base temperatures, 12 mK and 0.1 K, respectively, of two ^3He - ^4He refrigerators. We discuss the static and dynamic magnetic properties in terms of an effective spin Hamiltonian that includes the intracluster exchange and crystal field interactions.

The interpretation of the ac susceptibility data along with the Mössbauer spectroscopic results has allowed us to conclude that the present butterfly molecules, with the exception of the Gd compound, behave as SMMs, that is, they show slow relaxation in absence of magnetic field. Different rates of spin relaxation are observed depending on the particular lanthanide element and isotope. More specifically, we observe very fast spin fluctuations for Ln=Gd and Y ($f > 10^6 \text{ s}^{-1}$) and slower ones for Ln=Dy, Tb and Ho ($f < 10^6 \text{ s}^{-1}$). The application of an external magnetic field detunes the levels and gives rise to additional relaxation paths, as for example, Orbach processes.

In the $\{\text{Fe}_3\text{LnO}_2\}$ compounds with Ln= Y, Dy and Tb, a very slow process ($\tau \approx 10^{-1} \text{ s}$) is also observed at temperatures above 2 K for the Y and Dy cases and below 2 K for the Tb compound. This is a legitimately slow process that we have tagged as due to direct process, although its origin remains unclear.

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Finite-size effects in spin crossover materials

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In recent years, investigation of nano-objects displaying spin transition has attracted many attention. Indeed, the phase stability and the transformation kinetics are in general highly size-dependent. In spin crossover (SCO) compounds, size effects may lead to a loss of the hysteresis properties, a shift of the transition temperature or the occurrence of an incomplete transition, but also a reappearance of the hysteresis at the extreme size reduction [1].

We successfully explained a major part of these experimental observations by considering the spin-state dependence of the surface energies in the frame of a nanothermodynamical model [2]. As a consequence the most important parameter to describe size effects seems to be actually not the size of the object itself, but the surface-volume ratio as well as the physico-chemical properties of the interface between the SCO particle and its environment. For instance, using Monte Carlo simulations, we predicted that hollow nanoparticles with different sizes, but the same surface-volume ratio should have similar SCO properties [3]. On the other hand, core-shell particles with the same surface-volume ratio, but different core/shell lattice mismatch will exhibit different behaviours [4].

Since the bistability depends mainly on the strength of the elastic interactions, we have also investigated the lattice dynamics of SCO nanoparticles and especially the acoustic phonon modes by elastic and inelastic (ESRF) Mössbauer spectroscopy in order to deduce key parameters such as the Debye temperature, the Young's modulus and the sound velocities for different particle sizes [2,5,6]. As expected, we observed in each case significant lattice stiffening when going from the high spin to the low spin phase. In addition, rather unexpectedly, a stiffening of the particles was detected at the extreme size reduction limit, which we correlated with the reappearance of hysteresis behaviour in ultra-small particles of [Fe(pyrazine){Ni(CN)₄}] [5]. This phenomenon can be explained by the change of intrinsic properties at the nanoscale due to interface-volume mechanical coupling [7]. In particular, a global or a surface stiffening of intermolecular bonds, mimicking surface relaxation or reconstruction, would lead to a global increase of the elastic modulus.

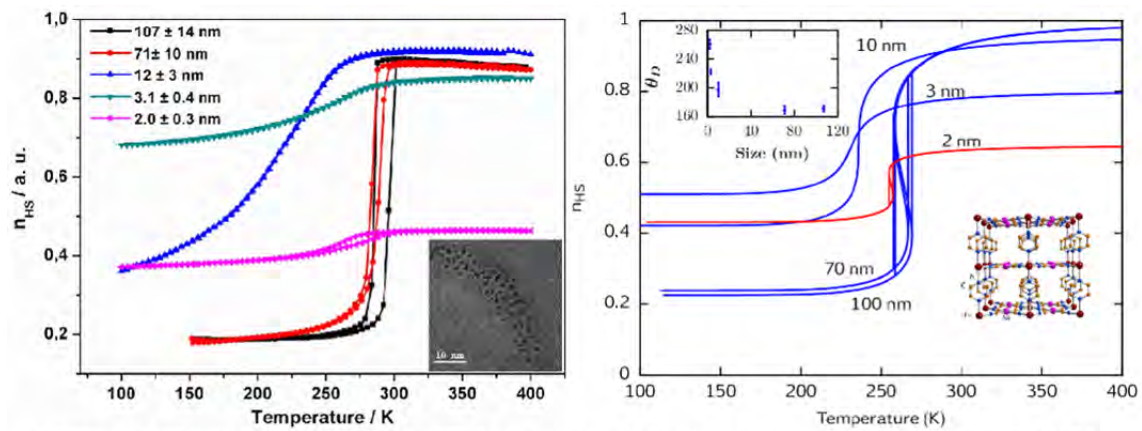
In this presentation we will discuss these recent findings as well as ongoing lattice dynamics simulation results and we will propose a global view of finite-size effects in SCO materials.

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1) Calibrated high spin fraction curves $n_{HS} = f(T)$ for magnetic and Mössbauer measurements of [Fe(pyrazine){Ni(CN)₄}] nanoparticles. Inset: TEM image of 3.1 nm particle. 2) Thermal evolution of the total HS fraction for different sizes of cubic nanoparticles, calculated using a nanothermodynamic core-shell model. Top-inset: Variation of the Debye temperature as a function of the size of the particles. Bottom-inset: Perspective view of the structure of the [Fe(pyrazine){Ni(CN)₄}] complex.



Switchable magnetic materials and optical magnets
(Poster)

XMCD at Fe $L_{2,3}$ edges in three Fe-based precursors of Photomagnetic Prussian Blue Analogues

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The family of Prussian Blue and its analogues, referred as Prussian Blue analogues (PBA), exhibit thermal and photomagnetic bistability. The discovery of these remarkable properties of Prussian Blues (PBs) in 1996 by Sato et al., prompted scientists to design new switchable molecule-based magnets with novel functionalities which offer potential technological applications like energy efficient materials and photoswitchable molecule-based information storage. Over the years, chemists have investigated the synthesis of magnetic and photoresponsive complexes through rational choices of cyanido-based building blocks [1]. The current challenge of designing systems that exhibit bistability at nanoscale requires the deep understanding of the thermally and light-induced electron transfer phenomenon and its driving mechanism. Therefore, advanced characterization techniques like X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) are the excellent tools to probe the change in the macroscopic magnetic properties of PBAs and can give local information about the metal centers existing in the structure. In order to develop molecular nanomagnets with desired photomagnetic properties, the electronic and magnetic structure of the corresponding precursors must be investigated. In this talk, we present our results obtained on three Fe-bearing precursors (see figure 1) which are the building blocks of three photomagnetic Fe/Co Prussian Blue Analogues with cube [2], square [4] and linear dinuclear shape [5].

Element specific XAS and XMCD measurements at Fe $L_{2,3}$ edges were performed on the DEIMOS beamline (SOLEIL, France). In order to achieve detailed interpretation of data and to extract quantitative information XAS and XMCD spectra were modeled using the Ligand Field Multiplet theory (LFM). LFM calculations combined with experiment provided valuable information about the spin and orbit magnetic moments for the three precursors. The magneto-optical sum rules have also been applied to the calculated spectra to address the pertinent question of the applicability of the spin sum rule for Fe^{III} (Low Spin) species. This study is an important step to understand to what extent electronic and magnetic properties of the molecular PBA are inherited from the corresponding precursors to develop better PBA based switchable molecular magnets.

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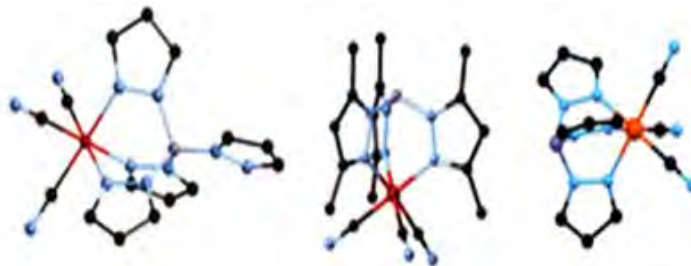


Fig.1 Molecular structures of the complex anions of three Fe(III) precursors, **FepzTp** $[(pzTp)Fe^{III}(CN)_3]^-$ (left) [2], **FeTp*** $[(Tp^*)Fe^{III}(CN)_3]^-$ (middle) [3] and **FeTp** $[(Tp)Fe^{III}(CN)_3]^-$ (right) [5]. Counter-cations, lattice solvents and hydrogen atoms are omitted for clarity. Color scheme: Iron – red, Carbon – black, Nitrogen – Light blue, and Boron – grey.



Coupling Molecular Qubits

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Molecular-spin clusters have been proposed as suitable qubit candidates units for quantum computing. Studies performed on different version of the well-known {Cr₇Ni} wheels have shown promising properties, fulfilling several of the so-called *DiVincenzo* criteria.¹ This system has a spin ground state $S = \frac{1}{2}$ well separated from the first excited multiplet, with reasonable phase memory times. A controlled generation of the entanglement between the qubits is an important requirement.² With this in mind we have obtained two families of {Cr₇Ni} wheels through either functionalization of the {Cr₇Ni} unit with a terpyridine group and its reaction with a cobalt source (Co²⁺) or incorporation of the {Cr₇Ni} into hybrid rotaxane molecules.

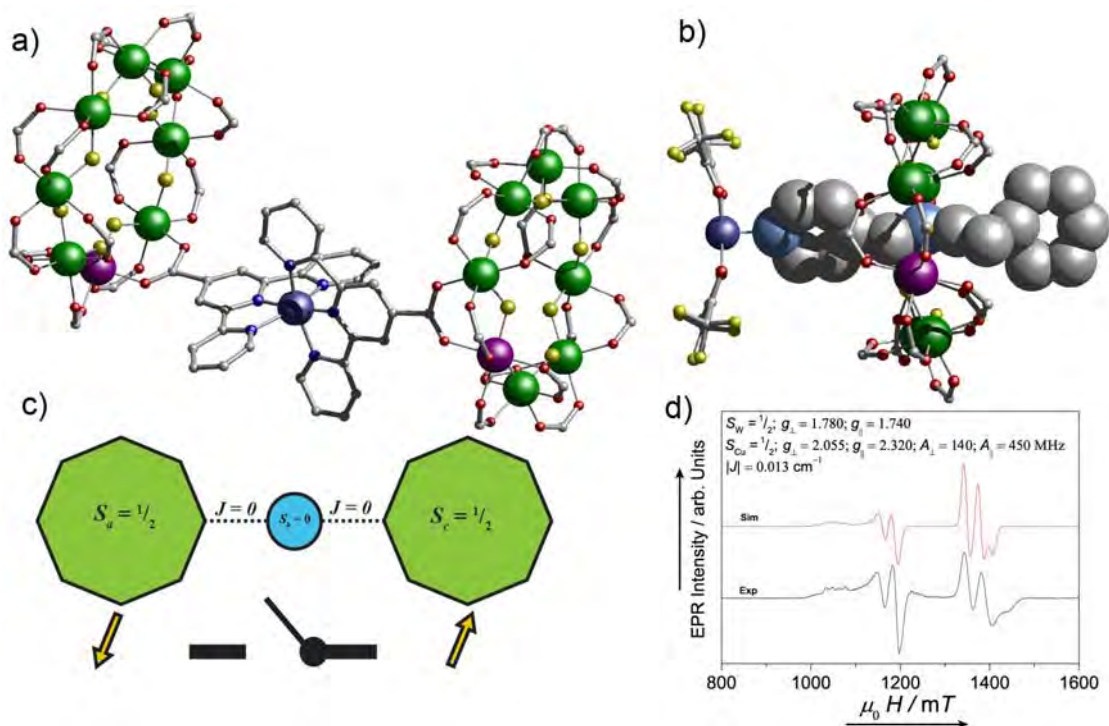
The product of the reaction of the functionalized wheel with a cobalt source consists of two {Cr₇Ni} wheels linked by a redox active low spin Co²⁺ ($S = \frac{1}{2}$) (Figure 1a) whilst [2]rotaxanes and [3]rotaxanes are obtained through the hybrid rotaxane approach, where a {Cr₇Ni} unit is bound through-space to a Cu(II) via an organic thread. Electron paramagnetic resonance (EPR) spectroscopy of the {Cr₇Ni}-Co-{Cr₇Ni} dimer shows a weak but observable interaction, which can be switch off/on through chemical means. Moreover, despite no through-bond pathway between the spin centres of the ring and the single Cu(II) site rich EPR spectra is observed for the hybrid rotaxanes. All systems herein presented represent plausible candidates to perform either $\sqrt{\text{SWAP}}$ or a CNOT gates for their implementation in QC.

Figure 1. a) [Cr₇Ni(μ_2 -F₈)(O₂C^tBu)₁₅(O₂C-tpy)](C₆NH₁₆)₂(Co(ClO₄)₂); b) [PyCH₂NH₂CH₂CH₂Ph][Cr₇Ni(μ -F)₈(O₂C^tBu)₁₆]; c) Schematic representation of the {Cr₇Ni}-Co switch; d) EPR experimental data and simulation for [2]rotaxane. Colours: Cr, green; Ni, purple; Cu, indigo; F, yellow; O, red; C, grey; N, pale blue. H-atoms and ^tBu groups of pivalates omitted for clarity.

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**Mononuclear lanthanide polyoxometalates and heterometallic 3d-4f molecular materials:
crystal structure and magnetic behaviour investigations**

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In 1991, Sessoli & *al.*¹ first reported on the observation of a magnetic bistability phenomenon from a purely molecular origin, in a Mn₁₂ acetate complex. Since this pioneering result, molecules exhibiting a slow relaxation of their magnetization are named single molecule magnets or SMMs and have been widely studied. To observe SMM behaviour two main characteristics are required: **(1)** a large magnetic anisotropy characterized by a large negative value (*D*) and **(2)** a large ground state spin (*S*). Up to now, peculiar attentions have been devoted to the synthesis of 3d and heterometallic 3d-3d' complexes.² But recently, in the search for more efficient SMMs, it has been demonstrated that the incorporation of a highly anisotropic 4f ions into 3d matrices can enhance the SMM properties³ as well as the combination of a highly anisotropic 4f ion with a quite isotropic 3d ion such as Cr^{III} ion to enhance the blocking temperature.⁴ In the quest of new efficient SMMs, two synthetic approaches are currently under exploration in our group: **(1)** synthesis of heterometallic Cr-Ln molecular materials and **(2)** polyoxometalate materials. As metal-oxo cluster materials containing transition metal ions in their higher oxidation state, polyoxometalates or POMs are a virtually inexhaustible reserve of robust and structurally diverse compounds.

In this context we have very recently highlighted a new family of heterometallic Cr^{III}-Ln^{III} complexes.⁵ Crystal structure determinations revealed that the dysprosium and the terbium derivatives crystallize both into two polymorph forms (crystal systems: triclinic and monoclinic). Full magnetic behaviour investigations showed that the Dy^{III} and Tb^{III} complexes exhibit single molecule magnet behaviour. We also herein present a new family of mononuclear lanthanide polyoxometalates [α -Ln(SiW₁₁O₃₉)₂]¹³⁻ (with Ln = Gd, Tb, Dy, Ho and Er).⁶ All POMs crystallize in the triclinic space group *P*-1. The single crystal structures of these five 4f α -silicotungstate are reported here for the first time. dc and ac magnetic susceptibility measurements on all POMs surprisingly revealed that none of these POMs exhibit single molecule magnet behaviour. This observation is in opposition with a report from Coronado & *al.*⁷ on the β -form of the silicotungstate family. Our report and observation shed new lights on the structure-magnetic behaviour relationships.

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Switchable magnetic materials and optical magnets
(Poster)

Room Temperature Control of Spin States in a Thin Film of a Photochromic Fe(II) Complex

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The assembly of monolayers of magnetic molecules is believed to lead to technological breakthroughs in the near future: studies in this field are connected to the possibility to develop new devices for data storage and molecular spintronics¹. A crucial point is the deposition of magnetic molecules that can be achieved by using thermal sublimation process. On this regard, several reports have described the protocols for assembling Spin Crossover molecules (SCO),^[1-5] bistable systems that can be switched via external stimuli, such as temperature,^[6,7] pressure^[8] or light irradiation.^[7,9] Thanks to the reversible alteration of their spin state, the implementation of SCO complexes in molecular electronics, spintronics, memory devices or sensors has been envisaged as an intriguing development of molecular magnetism. Recently, a particular Fe(II) complex, namely the ([Fe(H2B(pz)2)2phen*], pz = 1-pyrazolyl, phen = 1,10-phenanthroline functionalised with a diarylethene moiety; hereafter [Fe-diaryl]), has been reported. Thanks to the photochromic properties of diarylethene-based ligand the Fe-diaryl system has shown the possibility to induce SCO in solution upon light irradiation at room temperature.^[7]

Here we demonstrate that this system can be sublimated in UHV on Au(111) surface while keeping its SCO behaviour up to the thin film level. This work is based on the characterization of 5nm thick deposit molecules through Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), X-ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS). Moreover, characterization through X-ray Absorption Spectroscopy (XAS) and magnetometry of thicker films confirmed the retention of the magnetic behaviour observed in the bulk phase at the nanoscale.

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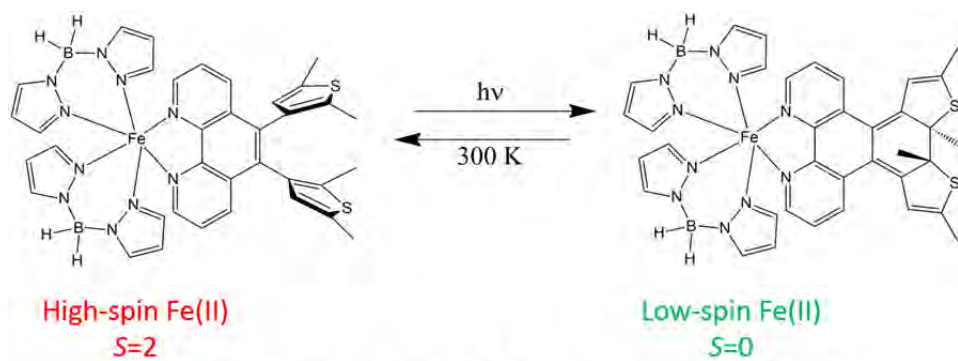


Figure 1. SCO switching with light stimuli for complex [Fe-diaryl].



Pulse EPR study of Cr₇Ni wheels linked by a switch

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To develop quantum computing, the scientific community has to develop systems susceptible to act as quantum bits (q-bit) or quantum gates (q-gates). Such objects need to be : addressable, bistable, robust. The electronic spin is thus a good candidate.[1]

The group of molecular magnetism of the University of Manchester is specialised in the synthesis of Cr₇Ni-based molecular wheels.[2] In these compounds, the odd number of Cr ions and the antiferromagnetic coupling lead to a resultant spin S=1/2.

Associated them with molecular switch, or switchable complexes, we aim at developing compounds with controllable interactions.

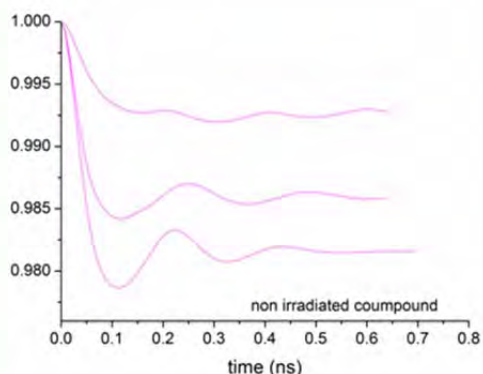
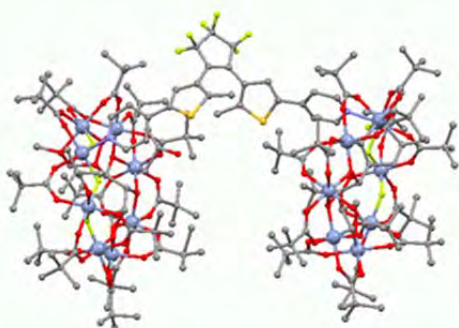
This talk will present the pulsed EPR characterisation of the new compounds synthesised by our group since this technique allows to characterise the intramolecular interactions and relaxations times.

Caption for figure left: 1,2-bis(2'-methyl-5'-(pyrid-4''-yl)thien-3'-yl)perfluorocyclopentene bridging two wheels right: Double Electron Electron Resonance spectroscopy at 2.5K in a 2 mMol.L⁻¹ toluen solution.

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Exchange coupling and anisotropy in lanthanide based molecular systems.

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Claiming pioneering breakthroughs in the computation and analysis of lanthanide-based complexes by state of the art ab-initio tools, with initial focus in the celebrated story of Cu-Gd quasi-general ferromagnetic coupling we deepened the insight in the molecular magnetism of *f*, *f-f* and *d-f* complexes.^{[1],[2]} Thus, the factors determining the opposite behaviour of *d-f* antiferromagnetic interactions were clarified in terms of certain topological demands of the spin distribution on the ligand.

Taking the magnetic anisotropy is a challenging paradigm of the nowadays molecular magnetism, we had our own contribution of rationales in this quest,^{[3],[4]} offering new keys for this major keyword, by approaching several relevant prototypic case studies and proposing methodological advances in the analysis.^[5] Thus we designed a methodology for drawing the so-called state-specific magnetization polar maps, obtained by extracting data from black-box of multiconfigurational spin-orbit calculations, characterizing in a very picturesque and intuitive manner the orientation and extension of local magnetization axes. The ligand field concepts are used to bring together experimental data and theoretical interpretation, in transparent manner.

Case studies from the chemical outcome of our group or literature examples (such as molecular magnets based on endohedral fullerenes) are considered in a large tableau of structure-property correlations dedicated to current issues of molecular magnetism.

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Relaxation Dynamics of the Dy₆ Molecular Ring

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Molecular nanomagnets are good candidates to study quantum effects in finite systems and are promising components for emergent technologies in spintronics and quantum information processing. Recently, the first rare-earth based ring has been synthesized: [Dy(Htea)(NO₃)]6·8MeOH. Dy₆ is predicted to have a non-magnetic ground doublet with a net toroidal magnetic moment, which makes it very interesting for fundamental issues and for the possible applications in quantum computing and information storage [1]. In this work we present an investigation of Dy₆ by means of Muon Spin Relaxation (μ SR), proton Nuclear Magnetic Resonance (1H-NMR) and AC susceptibility measurements. NMR and μ SR are powerful microscopic probes for studying the spin dynamics on an intermediate time scale between macroscopic techniques and neutron scattering. The nuclear spin-lattice relaxation rate (1/T₁) and the muon longitudinal field relaxation rate can probe in fact the fluctuations of the dipolar and hyperfine fields from the molecular spins, thus providing information on the electronic relaxation dynamics beyond the frequency range accessed by AC susceptometry.

AC-susceptibility measurements, aimed at studying the relaxation of the spin system, have been performed as a function of temperature and frequency in zero and applied field. They showed that, at low temperature, the magnetization is characterized by more than one characteristic correlation time, whose values depend strongly on the applied field.

The 1H-NMR and μ SR measurements have been carried out as a function of temperature for different applied magnetic fields. The NMR 1H spectra, studied as a function of the field in the range 0.2-1 Tesla at constant low temperature T=1.35 K, display a sizeable shift of the Larmor resonance frequency and an even larger line width due to a distribution of static internal fields, indicative of a magnetic state of the Dy₆ molecule in an external field.

The ¹H NMR spin-lattice relaxation rate 1/T₁ shows, at all applied fields in the range 0.5-6 Tesla, a strong increase on by lowering T which produces a considerable loss of the echo signal (wipeout effect) below 50-70 K, hampering the study of the low-temperature spin dynamics. To overcome this limitation, μ SR measurements as a function of temperature in zero and in different applied fields have been performed, with the aim of extracting the temperature- and field-dependence of the dominant electronic relaxation time. The μ SR longitudinal field relaxation rate displays a marked peak in the range 20-30 K, whose position depends on the applied field.



Coherent and Relaxation Dynamics in the odd-numbered Cr₉ antiferromagnetic ring probed by Inelastic Neutron Scattering and NMR

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Molecular nanomagnets (MNM)s are spin clusters where magnetic interactions can be engineered at the synthetic level. They represent model systems to investigate fundamental quantum phenomena and they are also promising materials for several technological applications. One of the most important classes of MNMs is that of even-membered antiferromagnetic (AF) rings, like Cr₈ [1], characterized by an almost perfect polygonal structure and by a $S = 0$ ground state. Cr₈-derived heterometallic rings, especially Cr₇Ni, have been shown to be excellent candidates to encode qubits [2].

Now the attention is focusing on closed odd-membered AF rings, since they represent model system to study frustration-induced properties. If the ring has a regular geometry and half-integer local spins, it obeys the definition of degenerate frustration given by O. Kahn [3]. However, significant structural distortions in the geometry of these molecular polygons lead to the removal of frustration, even if there are still competing AF interactions. For this reason, all the odd-membered closed rings with $N > 3$ studied so far [4] cannot be classified as degenerate frustrated. Here we present the characterization of a regular Cr₉ AF ring, which represents the first example of regular odd-membered homometallic ring. In this work we report the investigation of Cr₉ spin dynamics by inelastic neutron scattering (INS) and nuclear magnetic resonance (NMR). The analysis of the INS data leads to an accurate determination of the microscopic Spin Hamiltonian and of the energy-level diagram of the system. The energy spectrum reveals that the investigated Cr₉ ring is an almost perfect example of degenerate frustrated cluster. We also study the phonon-induced relaxation dynamics of Cr₉, which can be probed by NMR through proton spin-lattice relaxation rate $1/T_1$ measurements [5]. At low temperatures Cr₉ relaxation dynamics is characterized by a single dominating rate of relaxation like Cr₈, corresponding to an Orbach inter-multiplet relaxation process, whereas other systems with competing AF interactions show multi-timescale dynamics [6]. On the other hand, at higher temperatures Cr₉ is indeed characterized by multi-timescale dynamics, which set in at rather lower temperature than in other even-numbered parent compounds.

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The effect of crystal packing and Re(IV) ions on the magnetisation relaxation of [Mn₆]-based molecular magnets

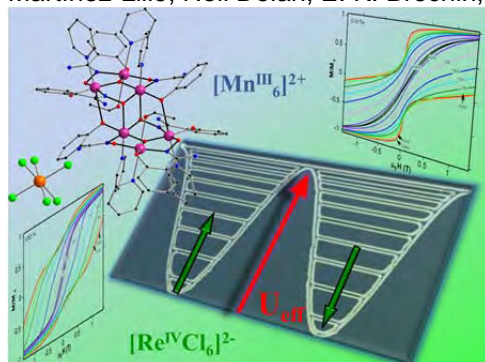
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A large body of work has involved the use of derivatised salicylaldoxime and salicylamidoxime in Mn^{III} coordination chemistry.^{1,2} This has led to the isolation of an extensive family of [Mn^{III}₆] single-molecule magnets (SMMs), many of them possessing spin ground states as large as $S = 12$ and obtaining the largest energy barrier to magnetisation reversal for polynuclear d-transition metal complexes yet reported.¹ Very recently, the cationic salicylamidoxime-based [Mn₆]²⁺ SMM of formula [Mn₆(μ₃-O)₂(H₂Nsao)₆(py)₆(EtOH)₂][ClO₄]₂·4EtOH possessing a $S = 12$ ground state, was reported.² The preparation of this cationic [Mn₆]²⁺ complex opened a plethora of new and appealing synthetic routes that can be easily exploited to obtain advanced, potentially multi-functional, magnetic materials, since the identity and nature of the anion can be deliberately employed to control, for example, solubility, reactivity, stability and substrate specificity, but also because the cationic cluster produced can be charged balanced through the incorporation of anions that bring another physical property or functionality to the material, such as conductivity, luminescence or paramagnetism. Here, we show effect of replacing the diamagnetic ClO₄⁻ anions with the highly anisotropic Re^{IV} ion in the form of [Re^{IV}Cl₆]²⁻, thus generating [Mn₆][ReCl₆] salts. Our initial results suggest that the [Re^{IV}Cl₆]²⁻ anion can a) induce structural distortions of the Mn-N-O-Mn bridges through hydrogen bonding interactions, b) mediate magnetic exchange pathways with the [Mn₆]²⁺ cations and c) provide increased anisotropy to the system.

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Experimental spin- and electron density study of the magnetic exchange interaction in water-bridged transition metal dimers

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In this contribution we have applied unusual approaches to the studies of the nature and strength of the magnetic exchange interaction between the two di-valent transition metal atoms in the general class of water-bridged dimers having the molecular formula $[M_2(OH_2)(O_2C_5H_9)_4(R1)_2(R2)_2]$, where R1 and R2 are neutral ligands (pivalic acid, pyridine, 2- or 3-picoline). This knowledge is notoriously difficult to obtain from magnetic susceptibility data alone, in particular for atoms with significant spin-orbit contributions, and small geometrical changes appear to change the interaction.^[i] The reasons that these compounds have nevertheless been the subject of intense studies are due to the fact that they are mimics of central atomic arrangements within the active sites in important enzymes,^[ii] as well as constituting the smallest possible molecular framework exhibiting magnetic exchange, thus allowing a detailed study of this effect which is otherwise not possible in larger systems.

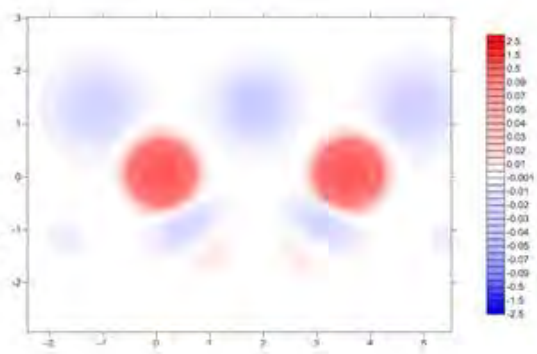
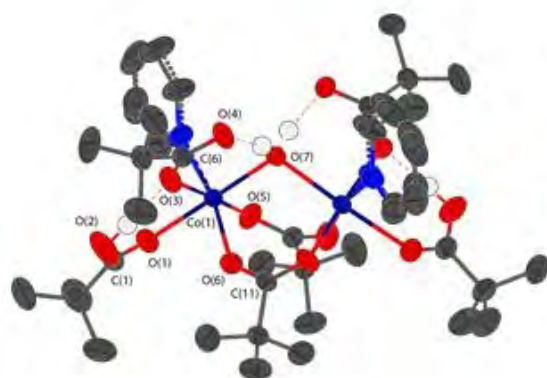
We have recently^[iii] studied the electron density distributions in two water-bridged dimer compounds of the above mentioned type, with R1 being pivalic acid and R2 is pyridine, for both Co and Ni for which a ferromagnetic interaction is found (Figure 1, left shows the molecular structure). Although the study of the total electron density is not directly revealing information about the spin density, it does reveal information about the interatomic interactions, and the major result from that initial study was the clear absence of a direct metal-metal interaction, indicated by a vanishing delocalization index.

In an extension of the electron density work, we have now carried out polarized neutron single crystal diffraction on the same compounds which allows a modeling of the spin density, i.e. the density distribution of the unpaired electrons alone. Preliminary results of the modeling has shown a spin polarization effect (Figure 1, right), showing the opposite signs of the spin density on the Co atoms relative to the bridging oxygen. This is clear evidence of the anticipated superexchange pathway between the metal centers. At the time of writing two spin density experiments are being executed on the Ni-analogue as well as a related Co-dimer, and this presentation will include the combined results of the spin and electron density studies.

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Devices and applications
(Poster)

Actions of weak magnetic fields on signaling molecules in biological systems

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Modified geomagnetic fields elicit the expression of *c-fos* in most of central nervous structures. The expression of this early gene was abolished by inhibiting the MAP kinases pathway, which transduces signals between glutamate membrane receptors and cellular nuclei. This blockage resulted to be maximal when rats were pretreated with calcium blockers previous to geomagnetic fields application. Visually deprived rats, as a model of experimental amblyopia, were subjected to these geomagnetic fields 3 times a day during 1 week. A microarray study of the expression changes of *c-fos* promoted microRNAs in control visual cortex in comparison with amblyopic cortex revealed a lower expression of microRNAs like Rno-let-7b, Rno-miR-330 and Rno-miR-376c and consequently an increased expression of BDNF, Neurotrophin 3 and Synuclein beta, which are the main targets of these microRNAs. These changes were accompanied by nuclear actions like increase of histone acetylation in neurons of the supragranular layers of the visual cortex, which is considered a parameter of visual recovery. Recently we have begun to explore the effects of geomagnetic fields on extraneuronal tissues like the heart. Similar geomagnetic fields were applied during 10 days to swiss mice. Histological examination of the myocardial tissue revealed that after this time, a significant hypertrophy of cardiocytes together with an increase of local blood vessels were detected. It is our purpose in the future to study the effects of geomagnetic fields on memory mechanisms, aversive effects or circadian rhythms changes involved in nervous diseases as well as the use of these fields for the recovery of myocardic ischemic lesions.



***Ab initio* molecular dynamics study of the spin-state dependence of the solution structures of iron(II) complexes**

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The mechanism of the photoinduced low-spin \rightarrow high-spin crossover is intensively being investigated in Fe(II) complexes using ultrafast time-resolved optical, vibrational and X-ray absorption spectroscopies.¹ These studies remarkably accurately inform on the reaction coordinate of the Fe(II) chromophore upon photoexcitation. However, they leave open the questions regarding the structural changes undergone by the ligands and the role of the solvent. To answer these questions, we apply *ab initio* molecular dynamics to the determination of the spin-state dependence of the solution structure of the complexes.² We will present the results recently obtained from the compared study of the low-spin and high-spin aqueous solution structures of the low-spin complexes $[\text{Fe}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{tpy})_2]^{2+}$ (bpy = 2,2'-bipyridine, tpy = 2,2':6',2''-terpyridine).

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Hydrogen-bond mediated exchange coupling in supramolecular Cu(II) chains

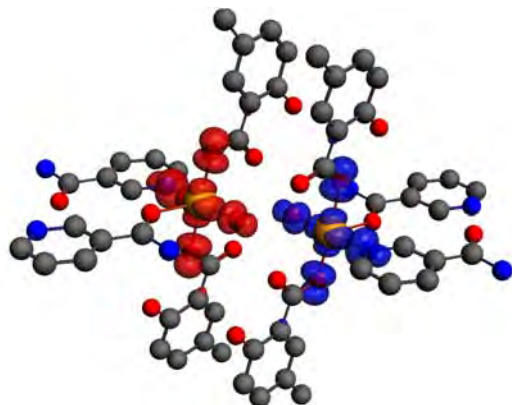
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Besides the traditional notion of the hydrogen-bonds as a powerful sticking agent of the molecules they are being progressively recognized also for their ability to transmit the magnetic exchange interaction. In presented work the magnetism of two new dimeric Cu(II) complexes is analysed, where the H-bonds play a crucial role, namely $[\text{Cu}(\mu\text{-menia})(3\text{-Mesal})_2(\text{menia})(\text{H}_2\text{O})]_2$ (**1**), and $[\text{Cu}(\mu\text{-nia})(5\text{-Mesal})_2(\text{H}_2\text{O})]_2$ (**2**), where *menia* stands for N-methylnicotineamide and 5-*Mesal* for 5-methylsalicylato anion. From the structural point of view the dimers are linked by the H-bonds resulting in a 1D chain supramolecular system. In the analysis of the macroscopic magnetic properties of **1** and **2**, three alternative approaches were tested and discussed, including the finite-ring approach, empirical formula for alternating antiferromagnetic Heisenberg chain and dimer approach. Out of them the system was best described as formed by antiferromagnetic dimers with small additional molecular field interaction. The DFT study on the exchange coupling intensity and its pathway showed that it operates preponderantly at the intermolecular level via the H-bond linkers, making thus a distinction between the molecular and magnetic structure of the system. The parameters extracted from the magnetization fitting and calculated by the DFT approach are mutually in very good qualitative and quantitative accordance. The CASSCF based AIM analysis was employed to discuss the mechanism of the exchange.

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Spin transistors based on single-molecule magnets

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Individual magnetic molecules embedded into electric circuits are envisaged as functional components in the emerging field of molecular spintronics. Single-molecule magnets (SMM), with high spin and high magnetic anisotropy are interesting candidates.

We study three-terminal charge transport through individual Fe₄ SMM. In these transistors, an Fe₄ molecule is linked to two gold electrodes fabricated by self-breaking electromigration of a gold nanowire [1]. A third gate electrode is used to access different redox states of the molecule.

The measurements reveal that the magnetic properties of the molecule are preserved and can be reversibly modified by adding a single electron into the molecule [2,3]. Interestingly, we observe that the current through the molecule can be significantly tuned by the presence of small transverse magnetic anisotropy perturbations [4] and individual vibrational modes of the molecule [5,6]. These two properties are of special relevance to use SMM as memory elements or qubits and opens the door to study quantum properties of the SMM such as quantum tunnelling and quantum interferences at the single molecule level.

As a further step in the control of individual molecular spins, we work on ferromagnetic-functionalized graphene electrodes to inject spin-polarized currents into magnetic molecules.

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**STRUCTURE AND MAGNETIC PROPERTIES OF THE MOLECULAR PEROVSKITE-LIKE
 $\{(\text{CH}_6\text{N})[\text{Co}(\text{CHO}_2)_3]\}_n$ COMPOUND**

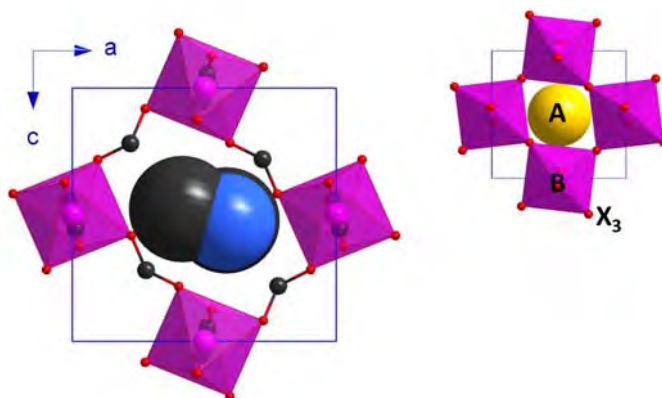
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Magnetic metal-organic frameworks have attracted intense interest in last years, not only from the fundamental point of view, but also from the development of new functional materials. The formate-base complexes are an interesting option to be explored since it generally present perovskite-like metal organic frameworks, where combines a condensed metal network with a notable structural flexibility. These materials generally present a magnetic ordering due to the ability of the of well know formate ligand to mediate ferro- or antiferromagnetic coupling between metal ions depending on the coordination modes of the ligand (syn-syn, anti-anti, syn-anti or monoatomic coordination modes).

The crystal structure phase transition characterization together with the magnetic studies have been carried out on $\{(\text{CH}_6\text{N})[\text{Co}(\text{CHO}_2)_3]\}_n$ (**1**) perovskite-like metal-organic compound [see figure 1] through variable-temperature single crystal diffraction and magnetic susceptibility measurements. The structural studies show a structural phase transition at ca. 196K with a change from *Pnma* space group at RT to *P2₁/c* space group at low temperature. This phase transition has not been reported before and involves the occurrence of a reorientation of the methylammonium ions into the framework as well as a small distortion of the host net. Cryomagnetic studies have shown an overall antiferromagnetic coupling with a long range ferromagnetic order at 7 K which points to the occurrence of a weak spin-canting.





Switchable magnetic materials and optical magnets
(Poster)

Spin-Crossover and crystal structure correlations in a new family of heteroleptic Fe(II) octahedral complexes

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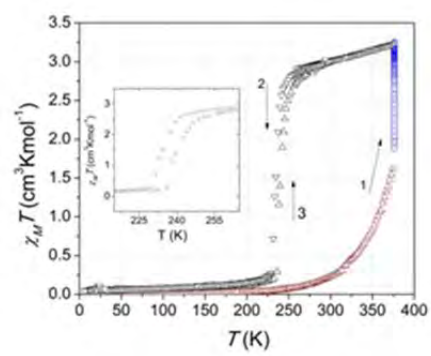
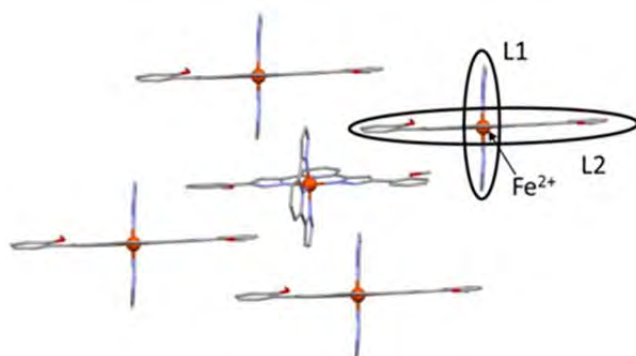
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The spin crossover (SCO) phenomenon in Fe^{II} coordination compounds is one of the most spectacular examples of molecular bistability; these molecules may be switched reversibly between a diamagnetic low spin state (LS, S=0) and a paramagnetic high spin state (HS, S=2).[1] The switching behavior of a SCO compound is related to the cooperativity within the lattice, which is higher as the intermolecular forces increase. Recently our group has demonstrated that, assisted by a dense networks of intermolecular forces, a lattice constituted by the homoleptic Fe(H4L)₂²⁺ (H₄L=2,6-bis-5-(2-hydroxyphenyl)-pyrazol-3-yl)pyridine) discrete complex may suffer a highly abrupt and cooperative spin transition.[2] Moreover, a cohesive and efficient packing (see figure) of the heteroleptic compound [Fe(3bpp)(H₂L)](ClO₄)₂ (3bpp=2,6-bis-(pyrazol-3-yl)pyridine); H₂L= 2,6-bis(5-(2-methoxyphenyl)-pyrazol-3-yl)pyridine) may exhibit crystal-to-crystal transformation processes, accompanied by the lost/absorption of solvent molecules.[3]

Herein, we present the preparation of a new family of heteroleptic [Fe(L1)(L2)](ClO₄)₂ compounds from a plethora of combinations involving the Fe(II) salt and pairs of terpyridine and/or 3bpp derivative ligands. The crystal structures of the obtained samples reveal the preference for the formation and/or crystallization of the heteroleptic [Fe(L1)(L2)]²⁺ cation, which establishes intermolecular bonds with the ClO₄⁻ anions and solvents within the 3D packing.

We discuss here the tendency to form heteroleptic over homoleptic complexes based on mass spectrometry measures and single crystal X-ray diffraction. Our observations reveal that the complex observed in solution is not always the same isolated in the solid state, indicating a balance between electronic and crystal packing effects. These observations have been corroborated by DFT calculations, which agree with the experimental observations. We also discuss the relationship between the SCO behavior and the crystal packing of the presented compounds. A correlation is found with the intermolecular forces within the 3D lattice and, therefore, it is tunable through the chemical nature of the functional groups introduced in the chelating ligands. This relates to the local distortion of the octahedral environment of the iron(II) which ultimately determines the SCO dynamics.

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Switchable magnetic materials and optical magnets
(Poster)

Light-induced phenomena in octacyanido-bridged molecular materials

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Octacyanidometallates are remarkably valuable building blocks in construction of bimetallic cyanido-bridged coordination polymers revealing a wide range of magnetic functionalities including photomagnetism.¹ They are especially promising from the viewpoint of multifunctionality.^{2,3} In this context, we concentrate here on the photomagnetic assemblies and magnetic systems combining chirality and luminescence.

The most spectacular effect exhibited by the photomagnetic molecular materials is a reversible photoswitchability between non-magnetized or paramagnetic state, and the magnetically ordered state. The few reported synthetic routes towards such light-induced magnets are the important achievements in the field of multifunctional molecular materials.⁴ A number of photomagnetic materials exhibiting a change in magnetization after irradiation were prepared, but only a few of them reveal a photoinduced long-range magnetic ordering. Within this family, the light-induced magnetic ordering was found for Cu^{II} – Mo^{IV} systems exploring *charge-transfer* in Cu^{II}-NC-Mo^{IV} linkages.⁵⁻⁸

We focused also our attention on octacyanido-based d-4f coordination polymers as a potential source of magneto-luminescent bifunctionality. Here, we present our latest results in this field: (i) a series of chiral coordination helices^{9,10} and (ii) a series of layered frameworks showing multicolored lanthanide-dependent emission, and the excitation switchable green to red luminescence for Tb-W compound.¹¹

The presented molecular systems open a new perspective in the field of light-induced magnetic materials revealing tunable photomagnetic and magneto-optical properties, as they results from the property of a single coordination networks.

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Dy(LH)₃ complex: a comprehensive magnetic study of a Single Molecule Magnet

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We present here an all-round magnetic investigation on a mononuclear Dy(LH)₃ complex (where the HL is the anion of the N-picolinylidene-N'-salicyloylhydrazine ligand), both experimental and theoretical. The magnetic characterization included static and dynamic magnetization measurements, Torque magnetometry and EPR spectroscopy, while the theoretical study comprised ab-initio calculations with Molcas [1]. The static magnetic properties excluded strong interaction among neighbouring paramagnetic centers but suggested the presence of non magnetic residuals that could not be observed in powder XRD. The study of the AC susceptibility revealed a composite dynamic behavior between 2 and 20 K: the complex, both when pure and diluted (1:10) in the isostructural diamagnetic Y(III) analogue, showed two different relaxation channels in zero and non-zero magnetic static field, the application of an external field allowing to suppress one channel and activating the other [2]. The analysis of the magnetization relaxation rate in zero applied field pointed out, below 15 K, a weaker temperature dependence compared to those measured with a static field. At higher temperature the two magnetic relaxation have a similar temperature trend from 15 K to 20 K, where they then become too fast to be measured. This behavior was analyzed in terms of different processes contributing to the relaxation (Orbach, Raman, direct). In the diluted sample both the relaxation processes turned out to be slower than in the pure sample so that at 2 K the diluted sample exhibited a butterfly shaped hysteresis loop, configuring this as a "real" SMM [3]. The relation of this behavior to the magnetic anisotropy of the complex was then investigated by EPR, showing the complex to be silent, and by torque magnetometry [4] that evidenced the presence of an easy axis of magnetization. The orientation of the anisotropy axis and its degree of axiality are in agreement with ab-initio calculations, which predicted an effective g-factor of almost 20. In addition calculations suggested that the ground state is almost entirely a $|\pm 15/2\rangle$ and that the first excited doublet lies about 200 cm⁻¹ above. These two features explains the absence of an EPR signal and provides useful insight about the possible relaxation mechanisms.

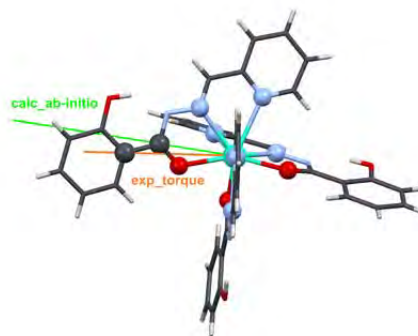
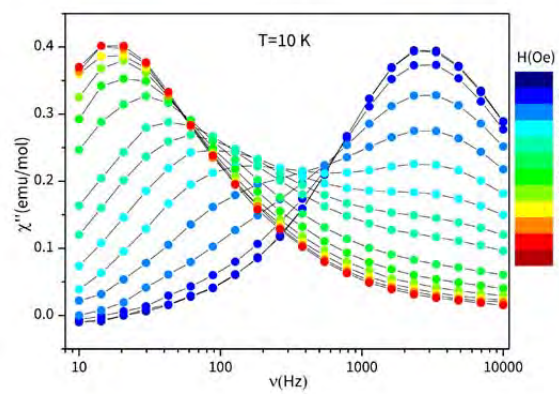
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Single Ion Magnets based on Lanthanoid Quinoline Complexes as building blocks for Molecular Spintronic Devices

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Lanthanoid Single Ion Magnets are coordination compounds with a wide number of attractive physical properties such as slow relaxation of the magnetization and quantum phenomena [1]. Thanks to these features they constitute ideal building blocks of molecular spintronics and quantum computing. This has motivated the deposition of single ion magnets in two dimensions, either as uniform single layers or in some kind of patterns.

Quinoline complexes and in particular Alq_3 stand out as promising molecules since they have been used in several areas of interest related with molecular electronics. The use of lanthanide-quinoline compounds in molecular spintronics is new but has already provided interesting examples [2]. The solution based chemistry of these compounds reveal that they are very sensitive to the synthesis conditions since small changes can lead to the formation of different compounds. For example, substituted quinoline (Rq) ligands can afford either *tris* $[Ln(Rq)_3L_2]$ as well as *tetrakis* complexes $([Ln(Rq)_2(RqH)_2X])$ and $C[Ln(Rq)_4]_n$, where X is a halogen atom and C is a monovalent or divalent cation).

In this work, we present some coordination complexes based in lanthanoid quinolate compounds. They have that have been structurally and magnetically characterized and some of these compounds were found to display Single Ion Magnet behavior. Interestingly, it was found that several complexes can be sublimated in gentle conditions, ensuring that their molecular structures are preserved. This feature make these complexes suitable for their incorporation as spin collector layer of molecular spin valves.

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Acknowledgments

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**Synthesis and magnetic properties of coordination fullerene C₆₀ complexes with cobalt:
from monomers to dimers bonded by bridged cobalt atoms and single C-C bonds**

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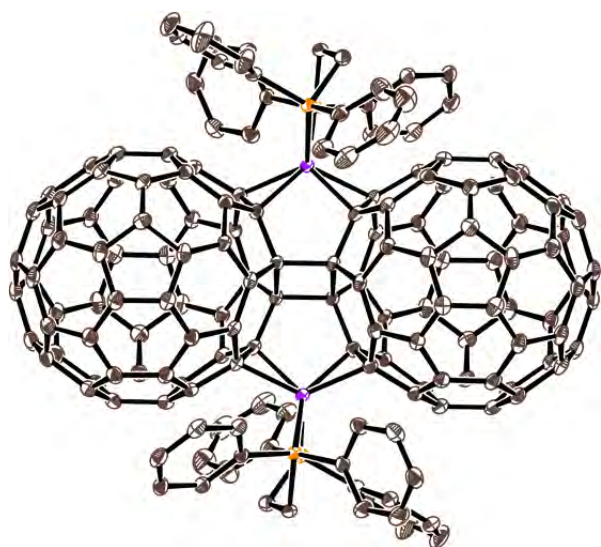
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In this work we report on the structure and magnetic properties of a series of mononuclear and dimeric coordination complexes of fullerene C₆₀ with cobalt in zero oxidation state. Complexes {Co(η^2 -C₆₀)(dppe)(C₆H₅CN)}·C₆H₄Cl₂ (**1**), {Co(η^2 -C₆₀)(dppf)(C₆H₅CN)}·C₆H₄Cl₂ (**2**) [1], {Co(Ph₃P)(C₆H₅CN)(m_2 - η^2 , η^2 -C₆₀)}₂·2C₆H₄Cl₂ (**3**) [2], {Co(dppe)}₂(m_2 - η^2 , η^2 - η^2 , η^2 -[(C₆₀)₂])·3C₆H₄Cl₂ (**4**) [3] were obtained via the reduction of C₆₀ and Co(L)Br₂ mixtures by zinc dust or sodium fluorenone ketyl in *o*-dichlorobenzene (C₆H₄Cl₂) in the presence of benzonitrile (**1-3**) or in pure C₆H₄Cl₂ (**4**) (dppe is 1,2-bis(diphenylphosphino)ethane and dppf is 1,1-bis(diphenylphosphino)ferrocene).

Coordination units in **1** and **2** are mononuclear in which cobalt atoms coordinate to fullerene by η^2 -type. Each cobalt atom is linked with two fullerene units in **3** and **4** by two η^2 -type and in this case cobalt atoms become bridges between two fullerene molecules. These bridges bring fullerenes together in **4** allowing their dimerization with the formation of intercage C-C bonds of 1.571(4) Å length (Fig. 1). In all cases coordination is realized to the 6-6 C-C bonds of C₆₀ (the length of the Co-C bonds is 2.04-2.13 Å).

Optical spectra of **1-4** indicate neutral state of fullerenes in the complexes. Therefore, cobalt atoms are formally in zero oxidation state and have $S = 1/2$ spin state. Complexes **1** and **2** manifest intense asymmetric EPR signals attributed to Co⁰. Effective magnetic moments of **1** and **2** indicate low-spin ($S = 1/2$) state of Co⁰ [1]. Cobalt atoms located at the 5.31-6.45 Å distance in **3** and **4** are bound through the fullerene p-system and that provides effective magnetic coupling between them. Dimers have thermally excited triplet ($S = 1$) state and transfer to diamagnetic singlet ($S = 0$) state at low temperatures. Experimentally determined exchange interaction is $J/k_B = -28.6$ K in **3**. It was shown theoretically that the singlet states were estimated to be more stable than the triplet ones by 28.7 K in **4**. Theoretical calculations show that C₆₀ could work as an effective spin coupler between paramagnetic metals. Such materials can be interesting for the development of molecular magnets and materials combining high conductivity and magnetic ordering. We are grateful to the Russian Science Foundation (Project No. 14-13-00028).

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Molecular nanomagnets
(Poster)

Heterometallic complexes of Mn(III): SMMs by design and models for WOC in Photosystem II

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A reaction system with substituted derivatives of salicylic acid (SALOH₂) has been fine tuned for the preparation of heterometallic complexes containing Mn(III) and an heterometal. The possible metals chosen have been the Lanthanide ions La(III), Gd(III), Dy(III), Tb(III) and Ca(II). These reactions have afforded a family of single-molecule magnets (SMMs) of general formula [cation]_x[Mn₆M'(OMe)₃(OH)₃(SALO)₆(SALOH)₃] (M'=Ca(II), x=1; M'=Ln(III), x=3). The magnetic properties of these complexes show that they are SMMs below 2 K.

The tuning of the reaction by addition of coordinating ligands for the Mn/Ca system has afforded new species with Mn(III)₂Ca(II)₂ core. The Mn(III)/Ca(II) complexes are also of interest as models for WOC in PSII. Preliminary electrochemical data show that these species can be oxidized to Mn(III)Mn(IV)/Ca(II).



Tuning of slow magnetic relaxation in heptacoordinate Co^{II} complexes with pyridine-based macrocyclic ligands

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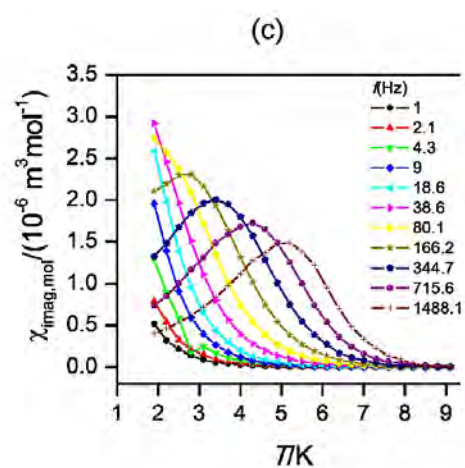
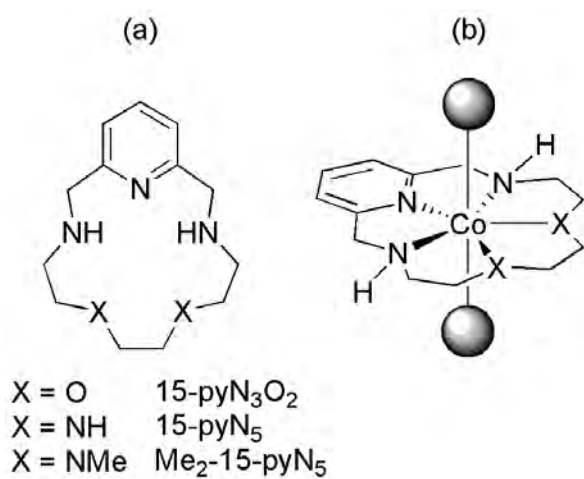
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Recently, heptacoordinate Co^{II} complexes have attained more attention of magnetochemists, because these systems were theoretically predicted and practically proven as magnetically interesting building blocks with a large positive axial anisotropy.¹ Surprisingly, despite this fact, they revealed single-ion magnet (SIM) behavior in a weak external magnetic field.² In this perspective, Co^{II} complexes with 15-membered pyridine-based macrocycle 15-pyN₃O₂ (3,12,18-triaaza-6,9-dioxabicyclo[12.3.1]octadeca-1(18),14,16-triene, Figure 1a) were prepared and systematically studied. Co^{II} is known that in the complexes with 15-membered pyridine-based macrocycles reveals coordination number of 7 and adopts pentagonal bipyramidal geometry (Figure 1b).³ The ligand is coordinated in the planar equatorial plane while two axial positions are opened for coordination of two monodentate co-ligands. In order to tune the magnetic properties of the complexes, the co-ligands in axial positions were varied, and the original chlorido ligands have been substituted by dicyanamide or tricyanomethanide. This dramatic change in the ligand coordination ability resulted in the formation of field-induced 3d-SIM species which may be documented by temperature- and frequency-dependent out-of-phase ac susceptibility (χ'') signals with well-resolved maxima shown in Figure 1c. Additional tuning of the magnetic properties could be done by a structural modification of the macrocyclic ligand. The two macrocyclic oxygen atoms can be substituted by NH or NMe groups (ligands 15-pyN₅ and Me₂-15-pyN₅, Figure 1a) in order to form more symmetric equatorial coordination sphere, which should increase the value of the axial zero-field splitting parameter D according to the theoretical predictions.¹ Detailed comparison of the influence of the nature of the axial ligands as well as structural modification of the macrocycle on the structure and magnetic properties of the obtained complexes will be discussed within the framework of the presentation.

Figure 1 – Structural formulas of the studied ligands 15-pyN₃O₂ (X = O), 15-pyN₅ (X = NH) and Me₂-15-pyN₅ (X = NMe) (a) together with schematic illustration of coordination sphere of Co^{II} complexes with these macrocyclic ligands ((b), sphere = Cl[−], NH(CN)₂[−] or C(CN)₃[−]) and an example of results of ac susceptibility measurements obtained for [Co(15-pyN₃O₂){C(CN)₃}₂] complex at B = 0.2T (c).

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Switchable magnetic materials and optical magnets
(Poster)

The first pressure-induced photomagnet

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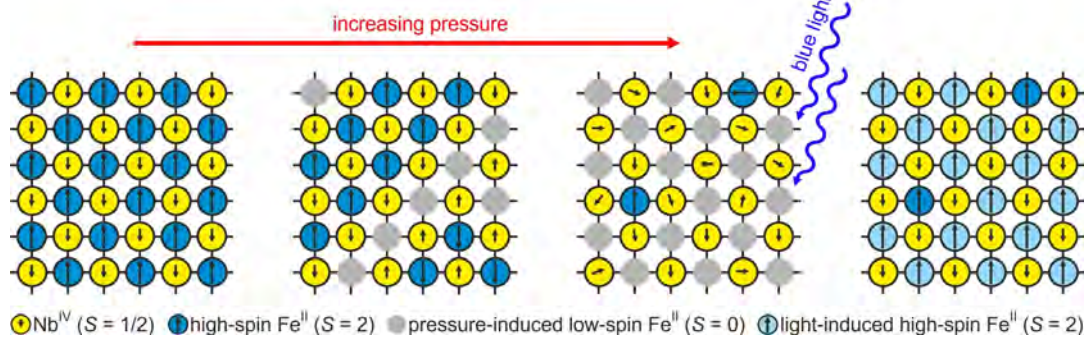
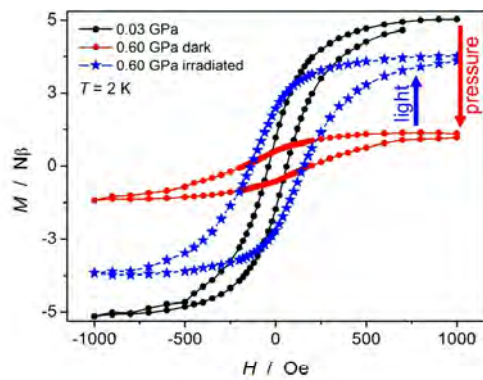
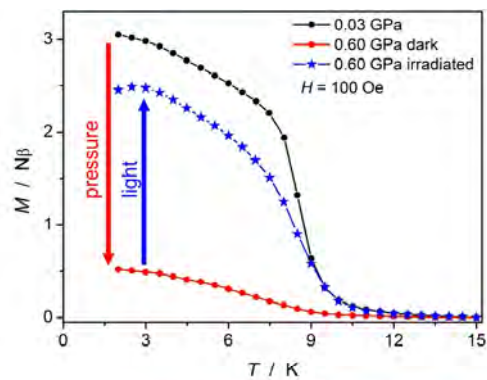
Multifunctional solids are currently a hot topic within the chemistry, physics and materials science due to their application potential. One of the most exciting classes of such compounds are photomagnets, which exhibit light-induced magnetization changes related to the 'generation of magnetic moments' using photons.¹

In the following contribution we will demonstrate that photomagnetism can be enforced in a non-photomagnetic compound by mechanical stress.² The non-photomagnetic cyano-bridged $\{[\text{Fe}^{\text{II}}(\text{pyrazole})_4]_2[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot 4\text{H}_2\text{O}\}_n$ (**FeNb**) coordination polymer³ has been subjected to high-pressure structural, magnetic and photomagnetic studies at low temperature, which revealed a wide spectrum of functionalities including thermal and pressure-induced spin-crossover, piezochromism, switching of the magnetic ordering and the pressure-induced photomagnetic behavior. As a result the first pressure-induced photomagnet has been discovered and characterized (Figure 1) and the high-pressure photomagnetic effect has been recorded for the first time. **FeNb** is a very rare case of a sophisticated multi-switchable material, which is responsive to several different stimuli and their appropriate combinations: temperature, pressure, magnetic field and light.

All structural, magnetic and photomagnetic studies under pressure for **FeNb** are compared with a reference compound - the manganese(II) analogue $\{[\text{Mn}^{\text{II}}(\text{pyrazole})_4]_2[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot 4\text{H}_2\text{O}\}_n$ (**MnNb**) which does not show any of the aforementioned properties except a significant pressure-shift of the magnetic ordering temperature towards higher values.

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UNIQUE CYANIDO-BRIDGED Co/Fe DINUCLEAR COMPLEX: DETAILED CHARACTERIZATION OF THE ELECTRON TRANSFER PHENOMENON

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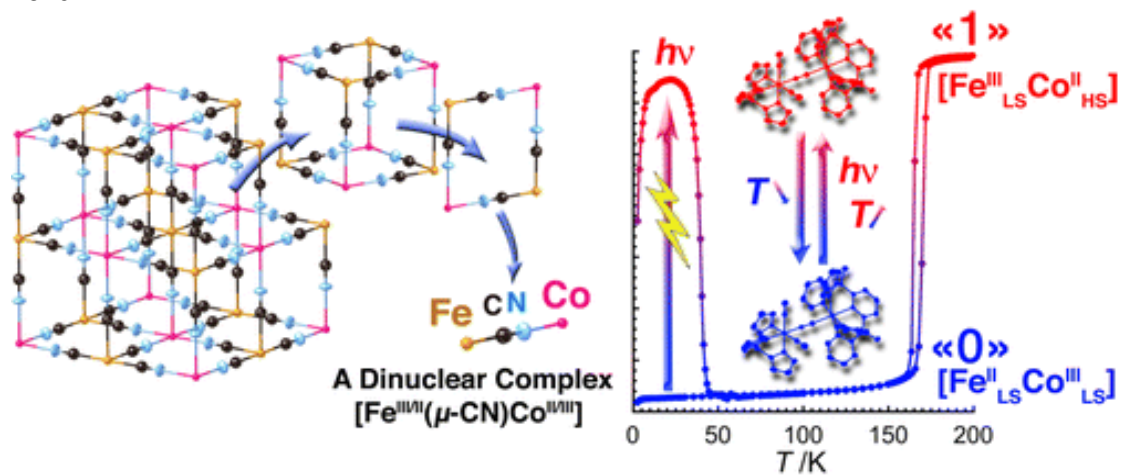
The rational design of molecular systems, which exhibit switchable physical properties as a function of external stimuli (T , E or H , $h\nu$, P , etc.) is a subject of the intense research activity to conceive high-performance molecule-based electronic devices.^{1,2} Over the past decade, chemists have investigated the synthesis of magnetic and photoresponsive complexes through rational choices of cyanido-based building blocks. This approach has been extremely successful, and various molecular architectures have been obtained with remarkable properties such as spin crossover,³ electron-transfer process,⁴ and photoinduced magnetism.^{4,5} In our quest to obtain new molecular systems and concomitantly to reduce the size of these functional molecules, we reported a dinuclear complex,⁶ which exhibits switchable optical and magnetic properties depending on its physical state.

In this presentation, we report a novel dinuclear complex $[(\text{Tp})\text{Fe}^{\text{III}}(\text{CN})_3\text{Co}^{\text{II}}(\text{PY5Me}_2)]^+$ (PY5Me_2 = 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine; Tp = hydridotris(pyrazol-1-yl)borate),⁷ designed by a rational building-block approach. Combined bulk and local techniques (structural, magnetic and photomagnetic studies) reveal that a metal-to-metal electron transfer that can be triggered in solid state by light and temperature is observed for the first time in a dinuclear [Fe/Co] complex.

Acknowledgements. We thank the Centre National de la Recherche Scientifique (CNRS), the Conseil Regional d'Aquitaine, the University of Bordeaux and the ANR for financial support.

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Molecular routes to nanostructured magnets
(Poster)

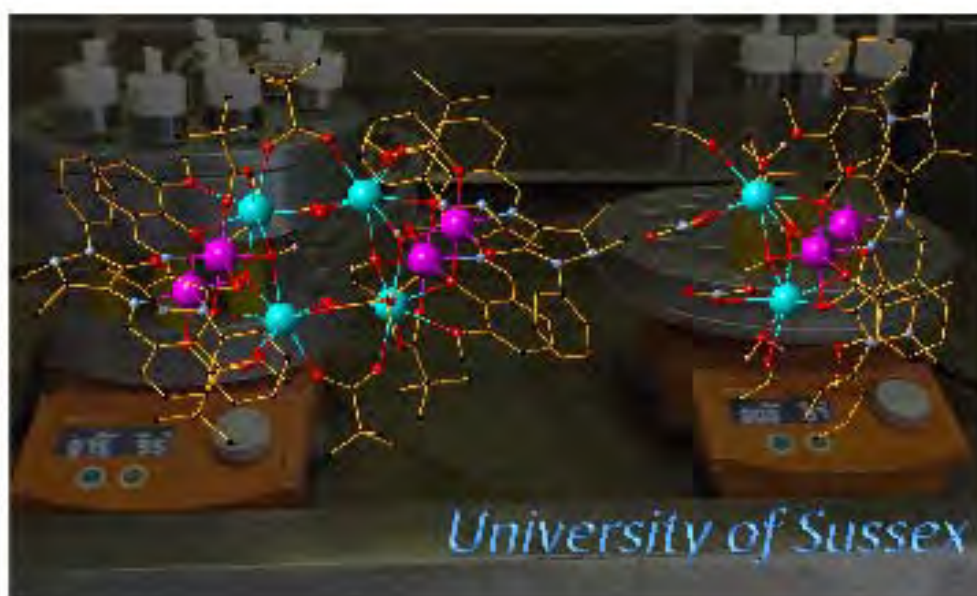
Towards a rational synthesis of high nuclearity Co(II)/Dy(III) Coordination Clusters

Benjamin Berkoff¹, Edward Loukopoulos¹, Alaa Abdul-Sada¹, Graham Tizzard², Simon Coles², Albert Escuer³, George Kostakis¹

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Mixing highly anisotropic metal centres, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, along with a monoanionic schiff base ligand, (E)-4-(2-hydroxy-3-methoxybenzylideneamino)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one HL, in the presence of a co-ligand, pivalic acid, in various solvents results in Coordination Clusters with robust and unprecedented topologies. These show the temperature and reaction time influence on the formation of the final product and suggest rational approach towards the targeted synthesis of an octanuclear $\text{Co}(\text{II})_4\text{Dy}(\text{III})_4$ compound. Magnetic studies of those heteronuclear species are indicative of Single Molecule Magnet (SMM) behaviour.





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Switchable magnetic materials and optical magnets
(Poster)

Design and synthesis of photo-switchable magnetic coordination complexes

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A fascinating goal in coordination chemistry is to manipulate photochemically magnetic properties of complexes, which could find applications in important areas such as that of spin-based quantum computing [1]. Indeed, molecules exhibiting well defined spins separated by a photoswitchable moiety could serve as prototypes of a SWAP quantum gate if the interaction between both spins can be controlled by light irradiation in a similar way as proposed for an electrically controlled spin-based gate [2].

Following the previous idea, we have designed and synthesized a new ligand to assemble pure weakly coupled pairs of heterometallic dimers of the type $[MM'\cdots M'M]$ ($M, M' = \text{Cu, Ni, Zn, Co}$) through site-selective control of different spin carrier metals in a single molecule [3]. We have measured by pulsed EPR techniques the quantum coherence of the spin transitions within each dimer of some of these molecules. In addition, the ligand possesses a photochromic unit [4] able to switch the quantum correlation between both total spins through light. Photocyclization is carried out using UV light and reversed with visible light.

We present the structural, magnetic and optical properties of this new family of compounds and evaluate their potential as prototypes of SWAP quantum gates.

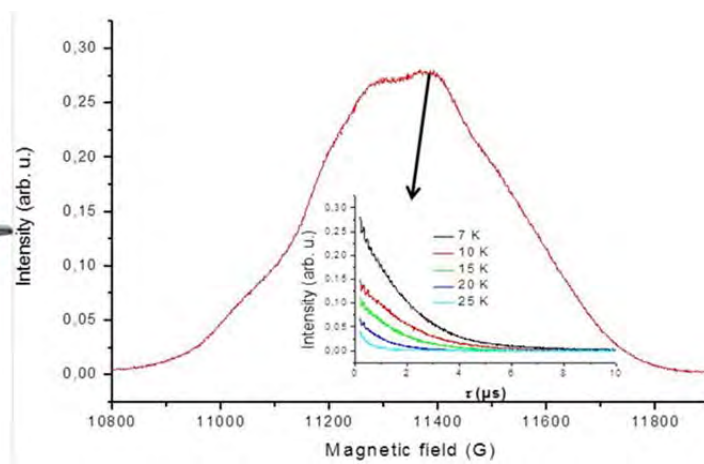
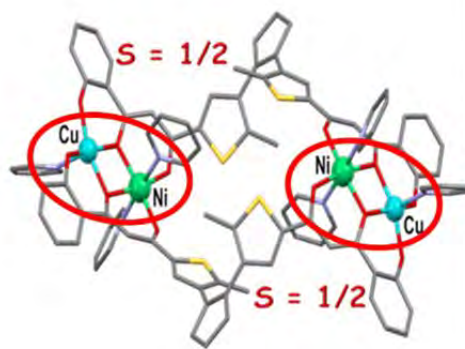
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Fingerprints of Degenerate and Non-Degenerate Spin Centers in Transport and Force Measurements by STM/AFM

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To engineer the magnetism of quantum devices, it is necessary to quantify how the structural and chemical environment of the junction influences the spin. Metrics such as coordination number or symmetry provide a simple method to quantify the local environment, but neglect the many-body interactions of an impurity spin when coupled to contacts. We have utilized the highly corrugated hexagonal boron nitride (h-BN) monolayer to mediate the coupling between a cobalt spin in CoH_x (x=1,2) complexes and the metal contact. While the number of hydrogen controls the total effective spin, the corrugation is found to smoothly tune the Kondo exchange interaction between the spin and the underlying metal. Using scanning tunneling microscopy and spectroscopy together with numerical simulations, we quantitatively demonstrate how the Kondo exchange interaction mimics chemical tailoring and changes the magnetic anisotropy.[1]

These results are complemented by atomic force microscopy measurements on CoH_x spin centers at 1 K. Through simultaneous measurement of the tunnel current and frequency shift as the metallic tip approaches the spin center, we are able to discriminate between degenerate and non-degenerate magnetic states by the decay of the short range forces.[2] For a metallic tip approaching a non-degenerate spin-1 system, the tunnel conductance and the force are strictly proportional. As the tip approaches the degenerate spin-½ Kondo system, the tunnel conductance is proportional to the square of the force. These results set the stage for purely force-based measurements of single spin centers in the absence of inelastic electron tunneling processes.

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Voltage and light control of spin crossover complexes at the molecular scale

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Spin-crossover (SCO) organo-metallic complexes are promising molecules for the development of organic spintronics as they present two spin-states that can be control by external stimuli (light, pressure, temperature or electric field). SCO is usually observed in the bulk, and it is well documented that the environment has a dramatic influence on the observed behavior (transition temperature...). In the context of the miniaturization of devices, it is important to explore the properties of such compounds at reduced dimension and ultimately at the molecular level. Scanning tunneling microscopy (STM) thus offers the unique possibility to probe such materials at the molecular scale. Recent results on molecules deposited on metallic surfaces show the co-existence of the two spin states without large scale ordering (STM and X-ray absorption spectroscopy). [1-4]

In this paper, we study $\text{Fe}^{\text{II}}((3,5-(\text{CH}_3)_2\text{Pz})_3\text{BH})_2$ (Pz= pyrozoly) sub-monolayer on Au(111) at low temperature by STM. The molecules self-organized in a 2D crystal whose lattice parameters correspond to the (0 1 -1) bulk plane. Interestingly, the islands present a super structure depending on the STM bias voltage. We have provided evidences that the two sub-lattices have different electronic properties and our measurements indicate that most probably one sub-lattice corresponds to molecules in the high spin (HS) state and the other to molecules in the low spin (LS) state thus forming a perfectly long-range ordered HS/LS 2D-crystal. We then demonstrate the possibility to induce a higher spin state phase by light illumination and investigate the kinetics of LS to HS conversion as well as the HS to LS relaxation. Our results underline the cooperative behavior of such molecular layers.

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Heterometallic 3d-4f Single Molecule Magnets: Experiment and Theory

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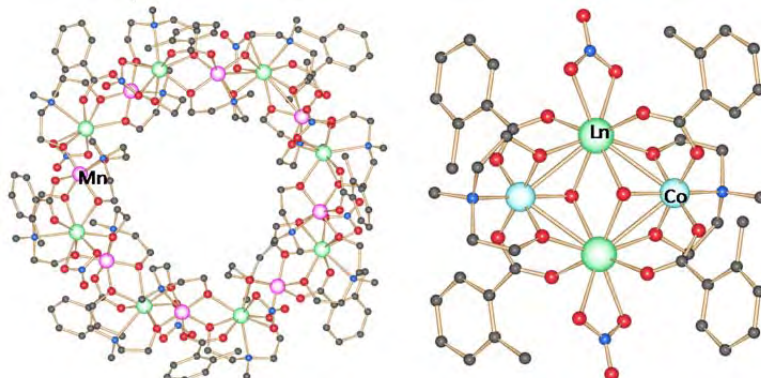
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Complexes which exhibit slow relaxation of magnetization, even in the absence of a magnetic field, are called Single Molecule Magnets (SMMs) and these molecules can act as magnets below their blocking temperature (T_B).^[1] To date, the search for SMMs was based primarily on the use of 3d metal ions.^[2a] Recently, the design and synthesis of heterometallic 3d-4f clusters have caught great attention since the discovery that such complexes are potential SMMs.^[2b-c] We herein report the synthesis, magnetic properties and theoretical studies of a new molecular wheel of core type $\{Mn^{III}_8Ln^{III}_8\}$ and butterfly $\{Co^{III}_2Ln^{III}_2\}$ complexes. The $\{Mn^{III}_8Ln^{III}_8\}$ wheels represent the largest Mn^{III}-Ln^{III} heterometallic wheels thus far reported. A non-zero out-of-phase component is observed for Dy and Y analogue, however, no maxima are observed in AC measurements. The MOLCAS^[3] calculation in line with the experimental prediction and the Dy wheel complex has SMM behavior but slow magnetic relaxation of the molecule is not observed due to the large transverse components (g_x and g_y). The $\{Co^{III}_2Dy^{III}_2\}$ complex is showing maxima in the AC measurements and results the energy barrier of 87K.

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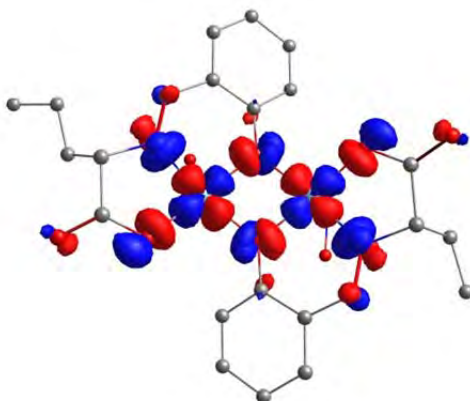
Correlating Magnetic Exchange in dinuclear bis(phenolate) bridged complexes- A Computational Perspective.

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Density functional theory (DFT) calculations have been performed to analyse the magnetic properties of dinuclear $M^{II}-M^{II}$ [$M = Cu, Ni$] bis(phenolate) bridged complexes. Since the study of the exchange interaction on simple building blocks can pave the way for the construction of the polynuclear clusters, we have focused on several dinuclear complexes, especially copper dinuclear complexes which have been reported to have a very strong antiferromagnetic interaction. We mainly emphasize on computing the magnetic exchange interaction J , to probe an origin of the antiferromagnetic exchange and to find a reliable magneto structural correlation for these complexes. Three complexes are selected, in which two metals are antiferromagnetically coupled with the magnitude of coupling J : Cu (II) (-416.0 cm^{-1}) > Cu (II) (-401.0 cm^{-1}) > Ni (II) (-34.9 cm^{-1}). The DFT calculations yield J values of -384.8 cm^{-1} , -375.3 cm^{-1} and -42.8 cm^{-1} for complexes **1-3** respectively and these values are in good agreement with the experimental values. The overlap integral analysis and the calculations reveal that the antiferromagnetic interaction stems from the superexchange interaction between the metal $d_{x^2-y^2}$ orbitals via the phenolate pathway. Extensive magneto structural correlation reveals the importance of the M-O-M bond angle as it tunes the coupling from antiferro to ferro at lower angles. The developed magneto-structural correlations are reliable and can be utilized to understand the magnetic properties of analogous complexes.





Placing a Crown on Dy(III) – Dual Property Ln(III) Molecule-Based Magnets Assembled From Crown Ether Ligands

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Several lanthanide ions display high potential in the field of molecular magnetism due to their large intrinsic anisotropies, which can be enhanced by an appropriate ligand coordination environment; however, many of the ligand systems employed to date require multi-step syntheses and result in complexes which are unstable to air or moisture rendering them unsuitable for practical applications. Our approach has been to make use of the inherent oxophilic nature of lanthanide ions and employ oxygen-rich macrocyclic ligands, such as crown ethers. The use of crown ethers with smaller cavity sizes and Ln(III) salts (Ln = Dy, Tb, Er) has led to the formation of a novel family of half-sandwich type complexes, e.g. **1**. The geometry of these complexes increases the anisotropy of the lanthanide ions employed, affording mononuclear single molecule magnets (SMMs) that exhibit both slow relaxation of magnetization and photoluminescence properties, Figure 1. Interestingly, the magnetic properties of these complexes can be tuned by making small modifications to the size of the crown ether cavity. The syntheses, structural, magnetic and optical properties of selected Ln(III)-crown ether complexes will be presented.

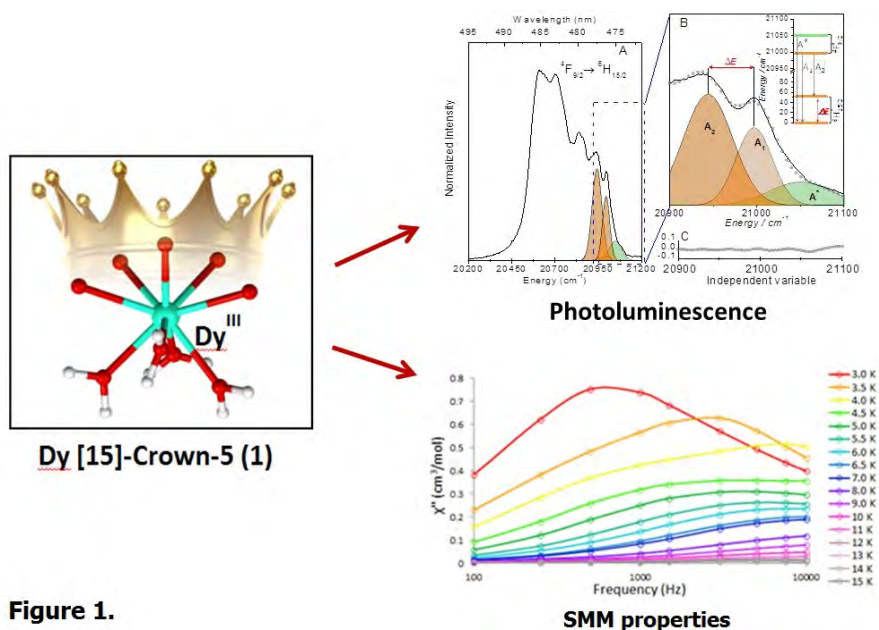


Figure 1.



Heterodimetallic [LnLn'] lanthanide complexes, toward a chemical design of two qubit molecular spin quantum gates

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One of the newest challenges in coordination chemistry has become the preparation of clusters for the implementation and realization of quantum computation as suitable systems to embody quantum bits (qubits) and quantum gates (qugates) in robust and scalable architectures.[\[i\]](#)

A new strategy to synthesize asymmetric heterometallic lanthanide clusters [LnLn'] allows us to use their electronic spins as two inequivalent Qubits. The molecule accomplishes the basis qugate requirements[\[ii\]](#) and could be used for quantum information processing as a CNOT logic operation.

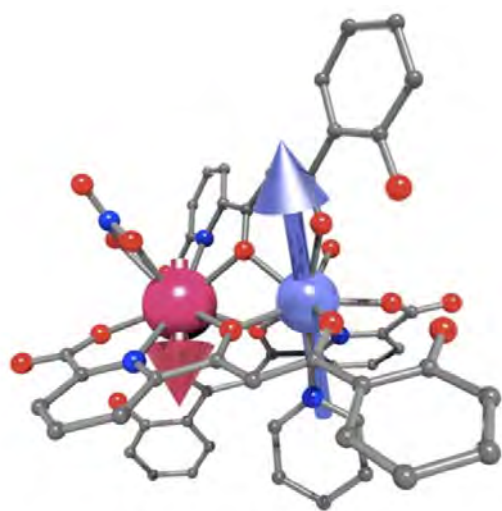
The synthetic versatility of this unique system lets us to choose almost any desired binary combination. Compound [CeEr] is ideal for this proposal. Both ions have a doubly degenerate magnetic ground state and can be addressed individually. Their isotopes have mainly zero nuclear spin, which enhances the electronic spin coherence. The analogues [Ce₂], [Er₂], [CeY], and [LaEr] have also been prepared to assist in showing that [CeEr] meets the qugate requirements.

Through magnetic susceptibility, specific heat, and EPR studies we demonstrate that these molecules represent a step forward in molecular quantum devices. [\[iii\]](#)

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Representation of the CeEr complex
and their different spin orientation



Modeling the states of spin-precession dynamics for the SMM Fe₈ and the ballistic magnonic transport across such molecules between iron leads.

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The single-molecule magnet (SMM) usually referred to as Fe₈ [1], contains eight ions per molecule, each with a commonly attributed spin of $S_{Fe} = 5/2$. These ions present relatively strong nearest neighbor magnetic exchange interactions [2], with six spins aligned up, and two others down [3-4]. The reversal of the magnetization from the direction of one easy-axis to another is impeded by an energy barrier of 25 K [5]. The magnetic properties of Fe₈ have been described hence, at relatively low temperatures, by a fundamental single-molecular spin $S_{mol} = 10$, for which the first excited single-molecular spin state corresponds to $S_{mol} = 9$.

In the present work, we undertake the study of another type of spin states, namely those corresponding to the spin-precession dynamics of the ionic spins. These states may constitute a hyperfine structure of energy levels between the fundamental and excited single-molecular spin states. The system Hamiltonian for treating the precession states is identical in form to that used for the effective single-molecular spin Hamiltonian [5], but is summed over the contributions from the interacting ionic spins; our model takes into account the significant biaxial magnetocrystalline anisotropy [6].

Using the Green's function theory [7], we calculate the spin-precession dynamics hyperfine states, in particular their numbers and energies, over the interval between the energies of the $S_{mol} = 10$ and 9 single-molecular spin states under external fields. Using the computed hyperfine states it is possible in principle to refine the proposed values of the individual spins for the ions, and of the magnetic exchange between the ionic spins, by comparing such computations with experimental data when available, using for example neutron scattering [6].

We also calculate, using the phase field matching theory (PFMT) [8], the ballistic magnonic transport across a row of Fe₈ SMMs, between semi-infinite leads of Fe monoatomic layers. This permits to characterize the localized spin-precession dynamics states of the Fe₈ SMM, and consequently the quality of the single-molecule magnet as a magnonic filter device.

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Rational conception of Dysprosium-based complex featuring different Single-Molecule Magnets

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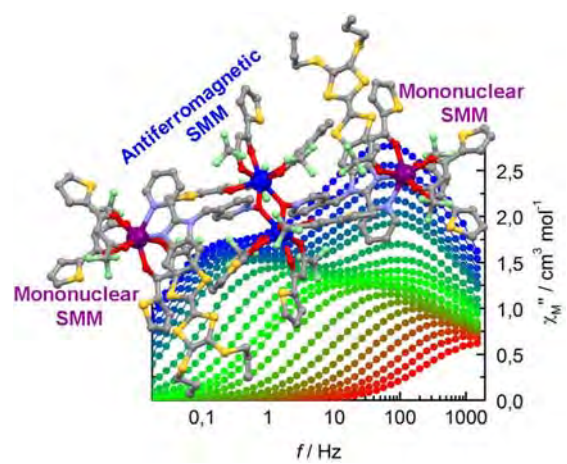
Lanthanide-based Single Molecule Magnets (SMMs) are fascinating objects for both fundamental science and potential applications.¹ The most used lanthanide to elaborate such molecular objects is undoubtedly the Dy^{III} ion. The mononuclear Dy-based SMMs present a large magnetic hysteresis loop but closed in zero field due to the fast relaxation of the quantum effect while the polynuclear Dy-based SMMs present a narrower hysteresis loop but opened in zero field when the magnetic interaction are significant. So, it is natural to try to combine both mononuclear and polynuclear (with significant magnetic interaction) SMMs in the same compound in order to obtain as large as possible magnetic hysteresis loop. To do so, we start from two systems synthesised in our group: i) a binuclear Dy^{III}-based SMM ([Dy(tta)₃(L¹)]₂ with L¹ = tetrathiafulvalene-3-pyridine-*N*-oxide and tta⁻ = 2-thenoyltrifluoroacetate anion)² in which the antiferromagnetic coupling between axial magnetic moment leads to the opening of the magnetic hysteresis loop at zero field which closes in field (double butterfly) and ii) a mononuclear Dy^{III}-based SMM ([Dy(tta)₃(L²)] where L² = 4,5-bis(propylthio)-tetrathiafulvalene-2-(2-pyridyl)benzimidazole-methyl-2-pyridine)³ with hysteresis opened in field only (butterfly). Then during this presentation, it will be exposed how the carefully designed TTF-based ligand L³ (L³ = 2-{1-Methylpyridine-*N*-oxide-4,5-[4,5-bis(propylthio)tetrathiafulvalenyl]-1*H*-benzimidazol-2-yl}pyridine) can guaranty the auto-assembly of the two previously presented systems in a unique molecule. Among other properties, the SMM behaviour of the resulting tetranuclear complex [Dy₄(tta)₁₂(L³)₂]⁴ will be presented and explained.

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High-spin ground state and single-molecule magnet behavior in tri- and hexanuclear iron clusters

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Our laboratory has previously reported the synthesis of formally all-ferrous tri- and hexanuclear iron clusters.¹ In both cases these are subtended by a weak-field hexadentate amine ligand, ^{tb}_SLH₆ (1,3,5-(^tBuMe₂SiNH-*o*-PhNH)₃C₆H₉) and ^HLH₆ ((NH₂-*o*-PhNHCH₂)₃CCH₃), respectively. The mixed valence products resulting from either oxidation or reduction have been chemically isolated and characterized by spectroscopic and magnetic methods. The molecular single crystal structure of the reduced triiron species [(18-crown-6)K(THF)₂][(^{tb}_SL)Fe₃] displays an average contraction of 0.13 Å in the Fe–Fe distances relative to the all-Fe(II). In addition, the reduced species displays a well-isolated *S* = 11/2 ground state up to room temperature. While the nominally all-Fe(II) does not present single-molecule magnet (SMM) behavior at low temperatures, the reduced species exhibits this phenomenon at zero-applied dc fields. The emergence of SMM behavior with regard to electron delocalization is discussed further in this contribution. In the case of the hexanuclear iron clusters, the introduction of itinerant electrons via reduction of the all-ferrous cluster, (^HL)₂Fe₆ (*S* = 6), enhances the ferromagnetic coupling among the six iron sites to achieve ground states of *S* = 21/2 to 11. The singly- and doubly-reduced clusters are isostructural to the parent all-Fe(II) species with only one significant perturbation: the Fe–N(H) bond distances are elongated relative to (^HL)₂Fe₆. The increase in these bonds suggests population of Fe–N(H) orbitals with antibonding character. The latter is rationalized according to a qualitative molecular orbital diagram. Moreover, since no additional ligand is bound to the cluster upon reduction, the increase of the spin ground state is attributed solely to an electronic effect. Furthermore, while the monoanionic hexairon cluster, [(^HL)₂Fe₆][–], exhibits SMM behavior at low temperature; the two-electron reduced species, [(^HL)₂Fe₆]^{2–}, does not present the characteristics of slow relaxation. The latter observations are discussed within the framework of a delocalized electronic structure.

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Exfoliation of oxalate and anilate-based magnets

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Two-dimensional (2D) materials are one of the most appealing topics in chemical science. 2D materials have attracted increasing interest in the last few years due to their unique morphology and properties. Top-down exfoliation approaches have been successfully adopted for preparing nanosheets of many inorganic layered materials. These methods have been extended very recently to 2D coordination polymers or metal-organic frameworks (MOFs).

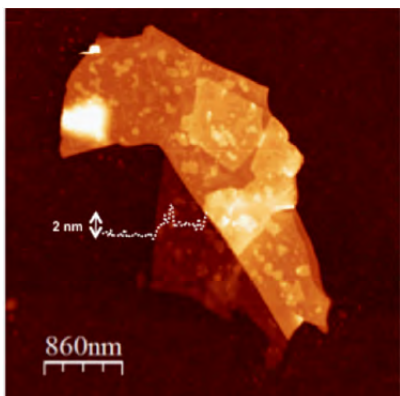
Oxalate-based extended networks of general formula $[M^II M^III(C_2O_4)_3]^-$ have attracted a lot of attention because their 2D anionic networks provide a magnetic functionality and are able to host a wide variety of functional cations. They have provided a rational synthesis of magnetic multifunctional materials combining the long-range magnetic with a second property of interest.¹ Very recently, we have extended this strategy to the larger anilate bis-bidentate bridging ligands, 2,5-dihydroxy-1,4-benzoquinone derivatives of formula $C_6O_4X_2^{2-}$ (X_2An^{2-} ; $X = Cl$ or Br).² One of the main problems of this approach is that the compounds obtained so far are micrometer-sized single crystals or polycrystalline powders, which are difficult to prepare as thin-film structures desirable for applications

In this work, we have prepared a new family of compounds that combine anilate-based anionic networks with small cations such as the spin-crossover complex, $[Fe^III(acac_2-trien)]^+$, or NH_4^+ . The reduction of size of these templating cations together with the increase of size of the anilate ligand have afforded a novel type of structure, in which the cations are placed into the hexagonal channels of the 2D network and not between the layers as usual for this type of compounds. These compounds present a ferrimagnetic ordering at around 10 K.³

The insertion of the cations within the channels of anilate-based networks confers a neutral character to the layers. These layered materials can be exfoliated in atomically-thin layers with heights down to 2 nm by using the well-known Scotch tape method.³ Interestingly, this method can also be successfully used to exfoliate other 2D oxalate and anilate-based compounds, which exhibit the typical alternated cation/anion layered structure. This result shows that the micromechanical exfoliation method, which has been extensively used for exfoliating van der Waals layered solids, can also be useful for exfoliating layered coordination compounds, even when they are formed by ionic components. This method paves the way for new studies and applications such as characterization of the magnetic properties of a single flake by contact methods (MFM, STM) or the processing of the flakes for magnetic devices.

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Supramolecular Organization of 3d Heptacoordinated Complexes: Towards Mononuclear and Heterometallic Molecule-Based Magnets

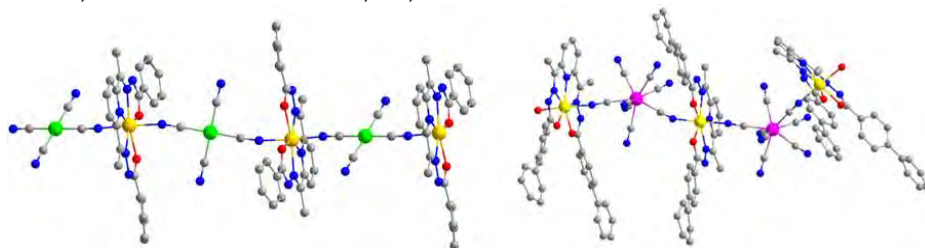
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Single-Molecule Magnets (SMMs) [1] and Single-Chain Magnets (SCMs) [2,3] are fascinating magnetic molecule-based materials displaying at low temperatures slow relaxation of the magnetization and magnetic bistability, required for potential application for data recording and storage on a molecule.[4] The synthesis of mononuclear 3d metal complexes with geometry (two- to octa-coordinated) and ligand field carefully chosen is a promising route to reach significant uni-axial magnetic anisotropy (D) leading notably to the first examples of 3d monometallic complexes displaying SMM behaviors.[5] Hepta-coordinated mononuclear complexes are in this context remarkable anisotropic entities allowing to reach D values ranging between -17 and $+30 \text{ cm}^{-1}$ going from Ni(II) or Fe(II) to Co(II).[6] In the case of Fe(II) complexes, slow relaxation of the magnetization was observed for the first time and reduction of dipolar interactions between the seven-coordinate units with a diamagnetic spacer shed light on the impact of supramolecular organization on the magnetization dynamics (Figure 1 left).[7] In this presentation, the synthesis and magnetic properties of hepta-coordinated Co(II), Fe(II) and Ni(II) complexes will be described. Labile axial positions make them attractive Ising-type building units to design molecule-based nano-magnets. This approach will be illustrated in a second part in which discrete and one-dimensional heterometallic systems (Figure 1), synthesized by association of the hepta-coordinated building blocks with diamagnetic $[\text{Ni}(\text{CN})_4]^{2-}$ and paramagnetic linkers $[\text{M}(\text{CN})_8]^{n-}$, $\text{M} = \text{Mo}^{\text{V}}$, W^{V} , Nb^{IV} , will be discussed.[7]

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T-REX: A Time-of-flight Reciprocal space Explorer for the future European Spallation Source

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We present the proposal of a direct geometry time-of-flight (TOF) chopper spectrometer for the future European Spallation Source (ESS). The instrument is optimized for mapping excitations and fluctuations in a wide dynamic range that extends from 20 μeV to 150 meV in energy transfer and from 0.01 \AA^{-1} to 17 \AA^{-1} in wave-vector transfer. The elastic energy resolution (FWHM) can be freely adjusted in the range from 1% to 3% at 3 meV and from 4% to 8% at 100 meV. The instrument has access to the thermal moderator, thus enabling uncompromised performance for neutron energies between 20 and 150 meV. The neutron guide can be fed with a replaceable extraction system from the cold moderator, which can also serve as a polarizer for cold neutrons, featuring an efficiency of 80-90% in the cold energy range. The core of the novel design is in the chopper system [1], which is specifically designed to make an efficient use of the source long pulse by means of Repetition Rate Multiplication (RRM), and enables one to reach a time resolution of 10 μs (FWHM). A specially developed pulse suppression chopper enables variable acquisition time frames to account for the variable incident neutron energy. Ray-tracing simulations for standard instrument configurations show gain factors around two orders of magnitude compared to simulations of world leading chopper spectrometers. The total instrument length of nearly 170 m enables different means to avoid that the sample area has direct view onto the moderator to provide a very good signal-to-noise ratio.

The science areas to be covered by T-REX include: magnetism, strongly correlated electron materials, functional materials, soft-matter, biophysics and disordered systems. It will implement TOF spectroscopy with Polarization Analysis as a standard option, e. g. for studying the effect of confinement on the magnetic excitations in nano-particles or to uniquely derive the vibrational hydrogen excitations in soft matter through separation of the nuclear spin incoherent scattering. Besides the polarizing extraction system, a ^3He spin filter cell will be used to polarize thermal neutrons. The XYZ polarization analysis will be possible thanks to a specifically developed guide field and the so-called MAGIC Pastis coil layout. A prototype is under construction for the TOPAS spectrometer at the FMR II, which uses a wide-angle banana-shaped ^3He Neutron Spin Filter cell to cover a large range of scattering angles, both in the horizontal and vertical direction.

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New Materials
(Poster)

YBCO nanoSQUIDS applied to the investigation of small spin systems

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We present the realization of ultra-sensitive YBCO nanoSQUIDS based on submicron grain boundary junctions patterned by focused ion beam milling which can be operated in strong magnetic fields. White flux noise down to ~ 50 nF0/Hz^{1/2} has been achieved, yielding spin sensitivities of down to a few μ_B /Hz^{1/2}. Moreover, we demonstrate that magnetic fields up to the tesla range can be applied. Our efforts focus now on the development of reliable techniques for controlling the position of magnetic nano-systems with respect to the SQUID, which ultimately limits the optimum spin sensitivity of the devices. As a proof-of-principle we present the successful deposition and characterization of a Fe-filled carbon nanotube and an individual Co nanopillar close to the YBCO nanoSQUID loop enabling the detection of the magnetization reversal of the particle under different ambient conditions.



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Molecular nanoscience
(Poster)

Biodistribution studies of polymer coated superparamagnetic iron oxide nanoparticles using Magnetic Resonance Imaging

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Magnetic resonance imaging (MRI) is considered as one of the most promising noninvasive diagnostic tools in medical science. Superparamagnetic iron oxide nanoparticles (SPIONs) are inorganic nanomaterials comprising a class of MRI contrast agents. Thus far, several SPIONs preparations have already been used for clinical practice, especially for liver MRI, such as Ferumoxides (i.e. Endorem® in Europe, Feridex® in the USA and Japan) coated with dextran, and Ferucarbutran (i.e. Resovist® in Europe and Japan) coated with carboxydextran.

The magnetic nanoparticles studied here are part of a synthetic platform for SPIONs based on the use of polymers. They are made from biocompatible components, and are stable as a colloidal aqueous fluid in phosphate buffered saline at pH = 7.4. They consist of: 1) hydrophobic polymer [poly(4-vinyl pyridine) (P4VP)] core encapsulating maghemite (γ -Fe₂O₃) nanoparticles, which is densely coated with 2) hydrophilic polymer chains [polyethylene glycol (PEG)] that may contain at the outer end various functionalities such as luminescence, antibodies and molecular thermometry. In the sample used in this work, a part of the PEG chains are functionalized with –COOH groups to provide sites for the anchoring of antibodies to nanoparticle surface so they can be directed to specific targets. The iron oxide nanoparticles in the P4VP core have a diameter of 13 nm. The core and the polymeric coatings have a total hydrodynamic diameter of 163 nm.



High Nuclearity, High Spin Clusters and Single Molecule Magnets from the Use of Diols in Mn Chemistry

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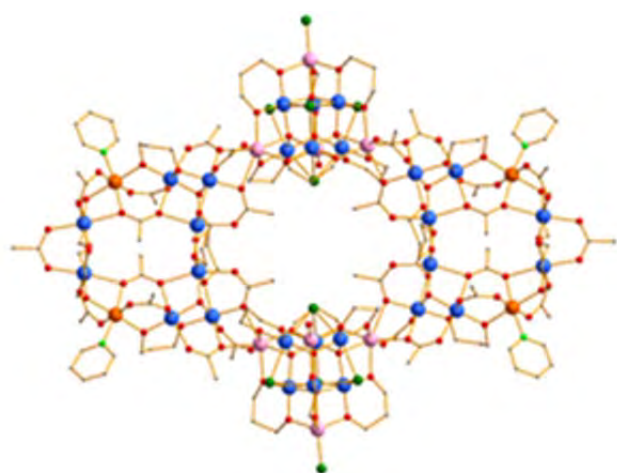
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Single Molecule Magnets (SMMs) represent a molecular approach to nanomagnetism [1] and have been proposed for several technological applications including high-density information storage, molecular spintronics, qubits for quantum computation and magnetic resonance imaging contrast agents. One of the most successful synthetic approaches towards new high spin molecules and SMMs involves the use of chelates containing alcohol groups, since alkoxides are good bridging groups and thus favour the formation of polynuclear products.[2] Recently, we have been investigating the use of 1,3-propanediol (H_2pd) and other diols in Mn carboxylate chemistry.[3] We will report, the synthesis, crystal structures and magnetic properties of a series of new compounds that were prepared from the use of various diols in Mn – carboxylate chemistry, including the families of Mn₁₇ octahedra, Mn₄₀M₄ (M = Na⁺ or Mn²⁺) loops of loops and Mn₃₆Ni₄ 'loop-of-loops-and-supertetrahedra' aggregates.

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Preparation and magnetic properties of all-organic radical liquid crystalline gels

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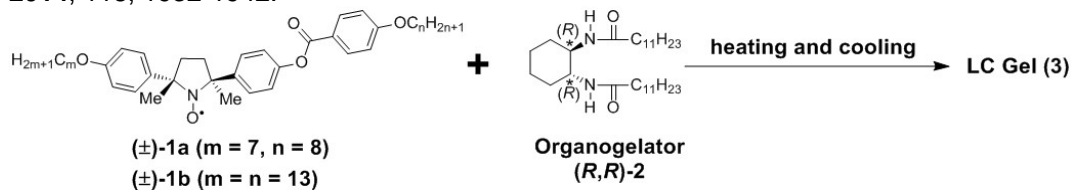
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Abstract :

Previously we reported that chiral all-organic magnetic liquid crystalline (LC) materials (**1**) with a five-membered nitroxide unit in the mesogen core and a negative dielectric anisotropy ($\Delta\epsilon < 0$) exhibited a sort of spin glass (SG)-like inhomogeneous ferromagnetic interactions (positive magneto-LC effects, > 0) induced by weak magnetic fields in the LC phases.¹

In order to gain an insight into the relationship between the positive magneto-LC effects and the LC domain sizes in each LC phase, we have prepared the magnetic LC gels by adding a diamagnetic optically active organic gelator [(*R,R*)-**2**] to racemic all-organic radical compounds [(\pm)-**1a** and (\pm)-**b**]. Generally, LC gels are composed of a network structure of entangled fibers, which are formed by one dimensional (1D) supramolecular association of low-molecular organic gelator molecules, and liquid crystal solvents incorporated by that fiber network. By polarizing optical microscopy, the formed radical LC (chiral nematic) gels (**3**) turned out to consist of random micro domains divided by 1D gelator fibers and the micro domain sizes were dependent on the amount of gelator. By the variable-temperature electron paramagnetic resonance (VT-EPR) spectroscopy, the molecular orientations in the LC gel phases were found to be controlled by the amount of gelator. In this presentation, we will report the effects of organic gelators on the positive magneto-LC effects as well as the molecular orientation in various magnetic LC gels.

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Molecular nanomagnets
(Poster)

**Targeting of a theranostics nanoplatform to breast cancer with the therapeutic antibody
Nimotuzumab**

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Nanostructured materials have been widely studied during the last years. Among them, nanoparticles arise as powerful tools for biomedical applications: they might be large enough to carry several active molecules but small enough to cross biological barriers so that we may think of them as multifunctional nanoplatforms. These may incorporate several tools such as a molecular thermometer, imaging tags (fluorescent, magnetic resonance or radioactive), therapeutic drugs (cisplatin) and biological targeting vectors (antibodies and oligopeptides). Here we describe a multifunctional nanoplatform based on copolymer coated maghemite nanoparticles for magnetic hyperthermia. The SAR value at 20 mT and 96.5 kHz is about 23 W/g and it is due in part to Brownian contribution. The saturation magnetization is 62 emu/g(Fe₂O₃), which is smaller than the average value found for bulk (76 emu/g) as expected for nanoparticles of this size. The out of phase susceptibility presents a maximum around 250 K, but increases above the melting point, and has a maximum at around 3300 Hz, associated with the average hydrodynamic volume of the beads (48 nm). These nanoparticles have been functionalized with the humanized therapeutic monoclonal antibody Nimotuzumab that specifically binds to the epidermal growth factor receptor (EGFR), overexpressed in some types of cancer, and which has been tested in over 20,000 patients. Our experiments highlight the importance of both the amount of antibody and the pH used on the conjugation. The bioactivity of the functionalized nanoparticles has been analyzed by flow cytometry, thanks to the fluorescein anchored to the copolymer, on two breast cancer cell lines. Thus, our nanoplatform has specifically bound to MDA-MB-468 cells, expressing a large amount of EGFR, whereas it has not interacted with the SKBR-3 control cells since they barely express it. The cytotoxicity of the NP-antibody conjugate has been evaluated in comparison with that of the antibody alone.



NOVEL SYNTHETIC ROUTES TO 1,2,4-BENZOTRIAZINYL RADICALS

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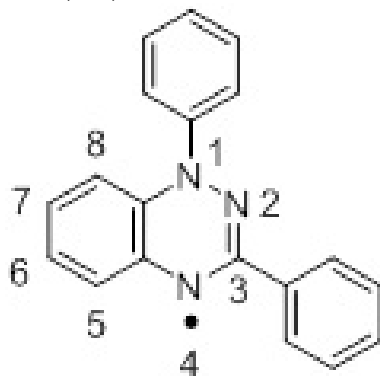
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Although 1,2,4-benzotriazinyl radicals have been known since the late 60s only a few examples of this radical family have appeared in the literature.¹ These radicals have the potential to be used as building blocks for multifunctional materials as they combine optical, transport and magnetic properties.² In order to control their macroscopic properties, structure-property relationships are necessary to be established. This requires the development of new synthetic routes to a range of 1,2,4-benzotriazinyls functionalized at positions C5-C8 of the benzo-fused ring, as well as N1 and C3 of the triazinyl ring. A number of different synthetic routes are presented and critically compared to understand their advantages and limitations.

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Configuration-averaged open-shell ab initio method for lanthanide(III) complexes

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In computational studies of lanthanide single-molecule magnets, the most popular ab initio method today is the CASSCF/RASSI-SO approach. It has been applied with success to compute magnetic properties of several Ln(III) complexes (a recent review is Ref. [1]). The multiconfigurational Complete Active Space Self-Consistent Field (CASSCF) calculations deal with the open-shell structure of the 4f orbitals, and the subsequent state-interaction calculation (RASSI-SO) is used to evaluate the spin-orbit coupling [1]. One drawback of this method is that it is computationally very expensive; a recent review states for example that the current maximum number of spin states that one can afford to include in the RASSI-SO calculation is less than 300 (using the MOLCAS software package) [1]. Given that Dy(III), for example, has a total of 735 spin states this means that a full intermediate-coupling calculation on a mononuclear Dy(III) complex is currently out of reach.

In this contribution we discuss an alternative ab initio approach that is conceptually and computationally simpler than the CASSCF/RASSI-SO approach. The computational cost is in principle reduced to that of a single Hartree-Fock calculation. One advantage of this method is that its computer implementation can benefit from many techniques that have been developed in the past to reduce the computational scaling of Hartree-Fock calculations. This would allow application to larger complexes than currently feasible, and possibly even to polynuclear compounds.

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A Monometallic Lanthanide Bis(methanediide) Single Molecule Magnet with a High Blocking Temperature

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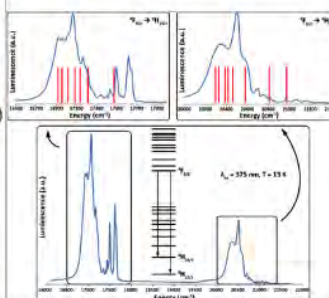
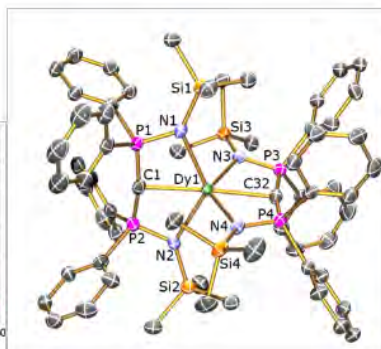
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We report a dysprosium(III) bis(methanediide) single molecule magnet (SMM) where stabilization of the highly magnetic states and suppression of mixing of opposite magnetic projections is imposed by a linear arrangement of negatively-charged donor atoms supported by further weak neutral donors. Treatment of [Ln(BIPMTMS)(BIPMTMSH)] [Ln = Dy, 1Dy; Y, 1Y; BIPMTMS = {C(PPh₂NSiMe₃)₂}-; BIPMTMSH = {HC(PPh₂NSiMe₃)₂}-] with benzyl potassium/18-crown-6 ether (18C6) in THF afforded [K(18C6)(THF)₂][Ln(BIPMTMS)₂] [Ln = Dy, 2Dy; Y, 2Y] (Figure 1a). AC magnetic measurements of 2Dy in zero DC field show temperature- and frequency-dependent SMM behavior. Orbach relaxation dominates at high temperature, but at lower temperatures a second-order Raman process dominates. 2Dy is found to have two thermally activated energy barriers (U_{eff}) of 721 and 813 K, the largest U_{eff} values reported for any monometallic dysprosium(III) complex. Dilution experiments confirm the molecular origin of this phenomenon. Field-cooled/zero-field cooled susceptibility measurements for 2Dy show a clear divergence at 16 K (Figure 1b) and magnetic hysteresis is observed for 10%2Dy@2Y up to 16 K; these two independent techniques confirm the blocking temperature (TB) to be 16 K, which is the highest TB of any SMM. Ab initio calculations suggest that the lowest three Kramers doublets of the ground 6H_{15/2} multiplet of 2Dy are essentially pure, well-isolated | 15/2 _g, | 13/2 _g and | 11/2 _g states quantized along the formal C=Dy=C axis. Thermal relaxation occurs via the fourth and fifth doublets, verified experimentally here for the first time, with calculated U_{eff} values of 742 and 810 K that compare very well to the experimental values. The energy levels derived by calculation are supported by luminescence measurements (Figure 1c). This work validates a design strategy towards realizing high-temperature SMMs. 1

Fig. 1. (a) Structure of 2Dy; (b) Susceptibility of 2Dy; (c) Luminescence spectra of 2Dy.

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Molecular nanomagnets
(Poster)

Coherent spin dynamics in molecular Cr₈Zn rings

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Molecular spin clusters present a large variety of spin states that can be selectively addressed by microwaves at different applied magnetic fields. Controlling and understanding transitions between molecular spin states allows selection of the most suitable ones for qubit encoding. Here we present a detailed investigation of polynuclear Cr₈Zn molecular ring, namely $[(C_3H_7)_2NH_2][Cr_8ZnF_9(O_2CC^tBu)_{18}]$. 241 GHz Electron Paramagnetic Resonance (EPR) spectroscopy has been performed in high magnetic field on Cr₈Zn single crystals. The continuous wave spectra show transitions between pure and mixed states in correspondence to a well-defined anti-crossing. Spin Hamiltonian calculations account for these EPR transitions by properly considering mixing of S states. By means of pulsed spin echo experiments we measured the dephasing time (T_2) down to 1.3 K. The T_2 obtained for the EPR transition to a mixed state is sizably longer (655 ns) than that measured for the transition with conventional selection rules (470 ns). Nutation experiments show coherent spin oscillations and demonstrate that the molecular spin of Cr₈Zn can be successfully manipulated by a suitable sequence of pulses. Overall, these results clarify how different molecular spin states can be exploited as a resource for quantum information processing.