2014 French-Irish International Workshop on Magnetism and Electronic structure

FIMAG2014

UCD School of Chemistry & Chemical Biology
University College Dublin
19-20 May 2014
Welcome to the 2014 French-Irish International Workshop on Magnetism and Electronic Structure, FIMAG2014. We propose that this be the first of a new series of biannual meetings to alternate between France and Ireland to celebrate cooperation between the two countries in magnetism research. Both have a long history of distinguished contribution to the field and we wish to build on this by providing a forum for discussion and collaboration to grow and flourish.

We thank the Cultural Service of the French Embassy in Dublin for seeding new cooperations via a funding scheme which resulted in the establishment of this workshop. We also thank all other agencies and institutions who have made this meeting possible through their generous support, they are listed in full overleaf.

Finally we sincerely thank you all for your support of this workshop and for the many interesting and diverse abstracts which you have submitted. We hope you enjoy the meeting and look forward to your feedback on how to best proceed with future symposia.

Grace Morgan

&

Annie Powell, SFI Walton Fellow at University College Dublin, 2014
ACKNOWLEDGEMENTS

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Science Foundation Ireland
University College Dublin
The Royal Society of Chemistry - Republic of Ireland Local Section.
The Institute of Physics in Ireland
The Cultural Service of the French Embassy in Ireland
The National University of Ireland
Monday, May 19

09:30-10:30  Registration and Poster Organisation - 2nd floor landing, Science East

09:45-10:30  **Welcome Reception and Presentation to Ambassador of France in Ireland by Chancellor of the National University of Ireland – 2nd floor landing, Science East**

**Lecture Programme – Intel Theatre (Theatre E), Science Hub**

10:30-11:00  Prof. Michel Verdaguer (University Pierre et Marie Curie) France
*Some magnetic moments with molecules, from copper acetate to Horizon 2020*

11:00-11:20  Prof. Martin Albrecht (Univ. College Dublin) Ireland
*A synthetic approach to rationally modulate magnetic properties*

11:20-11:30  Ms. Michelle Harris (Univ. College Dublin) Ireland
*Symmetry Breaking and Spin Crossover in Manganese(III) Complexes*

11:30-11:45  **Coffee**

11:45-12:15  Prof. Jürgen Schnack (Universität Bielefeld) Germany
*Yes, we can! Advanced quantum methods for the largest magnetic molecules*

12:15-12:35  Dr Liviu Ungur (KU Leuven) Belgium
*Ab initio investigation of electronic and magnetic properties of [Ln(COT)$_2$]$^-$ and Ln$_3$(COT)$_3$ systems. Why [Er(COT)$_3$]$^-$ is a much better SMM than [Dy(COT)$_3$]$^-$?

12:35-12:45  Ms Irina Kühne (Karlsruhe Institute of Technology) Germany
*From two tetranuclear {Cu$^{II}$/Dy$^{III}$}$_2$ cluster to an octanuclear {Cu$^{II}$/Dy$^{III}$}$_4$ cluster showing Single Molecule Magnet behaviour from field accessible states*

12:45-12:55  Dr Manase Ako Ayuk (KIT/UCD) Germany/Ireland
*All-round Robustness of the Mn$_{19}$ Coordination Cluster System: Experimental Validation of a Theoretical Prediction*

12:55-14:00  **Lunch**

14:00-14:30  Prof. Hans-Jörg Krüger
*Spin-crossover in cobalt(II) complexes as a means of switching organic ligands from a closed-shell to an open-shell state*
14:30-14:40 Dr Helge Müller-Bunz, (Univ. College Dublin) Ireland
*Crystallographic Phase Transitions: Experimental Difficulties in Triggering and / or Observing them*

14:40-15:10 Dr Cédric Desplanches (ICMCB) France
*Fe(III) Spin-crossover Complexes and Light : uncommon features*

15:10-15:20 Dr Abhishek Mondal (KIT/UCD) Germany/Ireland
*On/Off- Photoswitch in a cyanide-bridged 3d-5d molecular system*

15:20-15:35 Dr Jonathan Kitchen (Univ. of Southampton) UK
*Spin-Crossover in Soft Materials: An introduction to Langmuir based techniques for surface immobilisation of SCO complexes*

15:35-15:50 **Coffee**

15:50-16:20 Prof. Yann Garcia (Université Catholique de Louvain) Belgium
*Tailoring N-salicylidene derivatives and azole based ligands for thermo- and photochromism applications*

16:20-16:40 Mr. Anthony Fitzpatrick (Univ. College Dublin) Ireland
*Geometric Modulation of the Jahn-Teller Distortion in Manganese(III)*

16:40-17:00 Dr Patrick Rosa (ICMCB) France
*Properties of thin and ultrathin films of sublimable spin crossover complexes*

17:00-17:30 Prof. Kamel Boukheddaden (UVSQ) France
*Photo-control of the high-spin low-spin interface inside the thermal hysteresis loop of a spin-crossover single crystal: experience and theory*

17:30-18:00 Dr Valérie Marvaud (Université Pierre et Marie Curie) France
*A Promising Route to Multi-Functional Magnetic Compounds*

18:00-19:30 **Wine Reception and Poster Session**

19:30-20:30 Optional attendance at Dublin Institute of Advanced Studies Statutory Lecture
Professor Freeman Dyson, Institute of Advanced Studies, Princeton
*Are Brains Analog or Digital?*
Theatre D, Science Hub

20:30-22:30 **Workshop Dinner, Stillorgan Park Hotel**
Tuesday, May 20:

09:30-10:00  Prof. Hans-Benjamin Braun (Univ. College Dublin) Ireland
Topological effects in Nanomagnetism: From Perpendicular Recording to Monopoles

10:00-10:20  Dr Solveig Felton (Queen’s University Belfast) Northern Ireland
Lorentz Transmission Electron Microscopy Study of Three Dimensional Artificial Spin Ice

10:20-10:30  Dr Jill Guyonnet (Univ. College Dublin) Ireland
Ferroic domain walls as disordered elastic interfaces

10:30-11:00  Prof. Stefano Sanvito (CRANN/TCD) Ireland
Finding new magnets and finding them fast

11:00-11:20  Coffee

11:20-11:30  Dr Sharali Malik (Karlsruhe Institute of Technology) Germany
Structural modification and Self-Assembly of Nanoscale Magnetite Synthesized in the Presence of an Anionic Surfactant

11:30-12:00  Prof. Jean-Marc Greneche (LUNAM Université du Maine) France
Magnetic nanoarchitectures investigated by $^{57}$Fe Mössbauer spectrometry

12:00-12:30  Dr Anne-Laure Barra (LNCMI Grenoble) France
HF-EPR study of small heterometallic spin clusters

12:30-13:00  Dr Francis Pratt (Rutherford Appleton Laboratory) UK
Dipolar-driven Magnetic Ordering in the Single Molecule Magnet System Fe$_{19}$ studied using $\mu$SR and Monte Carlo Simulation

13:00-14:00  Lunch

14:00-14:30  Prof. Marty Gregg (Queen’s University Belfast) Northern Ireland
Ferroelectrics inspired by Ferromagnetism: Searching for Ferroelectric Vortices and Domain Wall Devices

14:30-14:45  Dr Brian Rodriguez (Univ. College Dublin) Ireland
Characterising Local Ferroelectric and Magnetic Properties of Multiferroic Heterostructures by Scanning Probe Microscopy
14:45-15:00 Dr Lynette Keeney (Tyndall National Institute) Ireland
*Magnetic Field-Induced Ferroelectric Switching in Multiferroic Aurivillius Phase Thin Films at Room Temperature*

15:00-15:15 Dr Andrea Droghetti (CRANN/TCD) Ireland
*Electronic transport in 2D and 3D topological insulator nanostructures*

15:15-15:30 Dr Remo Hügli (Univ. College Dublin) Ireland
*tba*

15:30-15:50 **Coffee**

15:50-16:10 Dr Peter Nockemann (Queen’s University Belfast) Northern Ireland
*Switchable Paramagnetism and Thermochromism of Cobalt(II) in Thiocyanate Ionic Liquids*

16:10-16:30 Dr Kasper Pedersen (Univ. of Copenhagen) Denmark
*Cool surprises with fluoride-bridged molecular magnetic architectures*

16:30-16:40 Prof. Marilena Ferbinteanu, (Univ. of Bucharest) Romania
*Advancing into the new paradigms of molecular magnetism by case studies. A chemist's perspective on the magnetic anisotropy*

16:40-17:00 Dr Ghenadie Novitchi (LNCMI Grenoble) France
*NMR Study of Ligand Exchange and Electron Self-exchange Between Oxo-centered Trinuclear Clusters*

17:00-17:30 Prof. Annie Powell (KIT/UCD) Germany/Ireland
*Cyclic Coordination Clusters incorporating Fe-4f building blocks*

17:30 **Meeting Close**
Oral Abstracts
Some magnetic moments with molecules, from copper acetate to Horizon 2020

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Molecular magnetism was born recently\(^1\)\(^{-6}\). Relying on molecular and quantum chemistry, physics, it is controlling better and better ligand fields, exchange interactions, anisotropies to synthesize and understand new materials. In this brief presentation, we recall some cornerstones and pioneers and then present recent developments and new trends.\(^7\)\(^{-8}\).

Using also some of our own work, we try to show how the discipline is moving from the understanding of simple model systems\(^9\) to the mastering of increased complexity\(^10\) and multifunctional systems presenting magnetism, magnetochiral dichroism, multiferroicity to the control of the tiny (nano...), molecules on surfaces, the unique molecule and Beyond an often useful serendipity, this demands more and more rational approaches and highly efficient collaborations. Time is probably coming for "being more and more eager to export towards other disciplines our original approach to magnetism, and to learn from others how to find new challenging areas to develop" (D. Gatteschi, ICMM 2008). We suggest therefore to involve more systematically the molecular spin and its specificity in new science, reactivity, photonics, spintronics, biology or medicine. Is it still possible in the new frame of Horizon 2020?

References
Switching of magnetic properties is the key concept underlying modern data processing and storage. Spin-crossover materials effectuate such a switching process and have the added benefit to be defined on the molecular scale, thus providing an attractive avenue for miniaturization of magnetically bistable materials.[1] However, ensembles of molecules have to operate in concert to produce a usable signal. One of the major challenges in this domain therefore is the induction of a high degree of cooperativity between these switchable molecular entities, as only cooperative and concerted changes produce an abrupt transition and eventually hysteretic behavior. However, predicting and tailoring of spin crossover has been rather erratic as many of the supramolecular effects remain speculative.[2] We therefore aimed to modulate these interactions in solution and at the liquid-air interface in an attempt to control the supramolecular arrangement of active entities and to control spin crossover.[3] We will specifically discuss our progress in functionalizing a variety of $\text{Na}_2\text{O}_2$-hexadentate ligands with various molecular recognition sites,[4] which indeed induces cooperativity and a remarkably high control of the spin crossover event. (see Figure).

References
Symmetry Breaking and Spin Crossover in Manganese(III) Complexes

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Spin crossover (SCO) molecules comprise a promising class of compounds for application in memory devices. A hysteretic transition pathway and hence molecular bistability i.e. having two electronic states under the same set of conditions is essential in promoting a memory effect and considerable efforts have been expended to develop systems with wide hysteresis loops close to room temperature. Triggers for SCO include temperature, pressure or light. In contrast to Fe and Co there are few examples of SCO in Mn$^{III}$. Mn$^{III}$ is a particularly interesting candidate for SCO as it has a pronounced Jahn-Teller (JT) effect in the high spin (HS) state. We have shown the importance of ligand flexibility in promoting Mn$^{III}$ SCO where population of d$_{x^2-y^2}$ on switching to HS requires elasticity in the xy plane. To date this system type has promoted gradual SCO profiles and we have shown that anion modulation and substituent modulation play a pivotal role in Mn$^{III}$ SCO. We have also reported the first example of a Mn$^{III}$ compound with an abrupt and complete thermal spin transition and opening of an 8 K hysteresis window.$^{[1]}$ We now report here two types of symmetry breaking which have not been observed in the case of Mn$^{III}$: one driven by the resolving of disorder in the BPh$_4^-$ anion$^{[2]}$ and the other driven by the spin-active cation which also drives Jahn-Teller and spin state ordering and opening of a hysteresis loop.

References


Yes, we can! Advanced quantum methods for the largest magnetic molecules

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In this presentation I would like to address two issues: How can we evaluate magnetic observables of truly large anisotropic magnetic molecules and how can we determine the magnetic properties of molecular clusters that are deposited on metallic surfaces?

Numerical strategies to evaluate magnetic observables of few-spin systems usually rest on heavy use of group theoretical methods (e.g. MAGPACK). Such methods are restricted to small enough Hilbert space dimensions. Fortunately, approximate and very accurate methods such as the Finite Temperature Lanczos Method (FTLM) have been developed with which huge molecules with Hilbert space dimensions of up to $10^{10}$ can be modelled [1]. This will be demonstrated for a ring of 12 Mn$^{III}$.

The key question for deposited molecules is whether and how their magnetic properties are modified when deposited on a metallic substrate. In such scenarios the amount of Kondo screening is not a priori known, and interpretation of the data, e.g. XMCD or spin-flip inelastic electron tunnelling spectroscopy, is complicated. In this contribution we demonstrate that one can evaluate observables of the deposited molecular cluster under certain model assumptions by means of the Numerical Renormalization Group method. We show for several fundamental setups such as single anisotropic spins [2] as well as interacting few-spin systems [3] how the magnetization curve is modified due to an exchange interaction with the electrons of the conduction band.

References
Ab initio investigation of electronic and magnetic properties of \([\text{Ln}(\text{COT})_2]\) and \(\text{Ln}_2(\text{COT})_3\) systems. Why \([\text{Er}(\text{COT})_2]\) is a much better SMM than \([\text{Dy}(\text{COT})_2]\)?

Liviu Ungur

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Remanence and coercivity are the basic characteristics of permanent magnets. They are also tightly correlated with the existence of long relaxation times of magnetization in a number of molecular complexes, called accordingly Single-Molecule Magnets (SMMs). Up to now hysteresis loops with large coercive fields have only been observed in polynuclear metal complexes and metal-radical SMMs. On the contrary, mononuclear complexes, called Single-Ion Magnets (SIM), have shown hysteresis loops of butterfly/phonon bottleneck type, with negligible coercivity and, therefore, with much shorter relaxation times of magnetization. The presentation will describe a mononuclear \(\text{Er}\) complex showing hysteresis loops with large coercive fields, achieving 7000 Oe at \(T = 1.8\) K and persists till ca. 5K, while the hysteresis loops are open until 12K. Ab initio investigation of these ions using CASSCF / RASSI / SINGLE_ANISO computational strategy, reveals the origin of the strong magnetic blocking capability of the \(\text{Er}\) compound, and also the reasons why \(\text{Dy}\) equivalent shows no magnetic blocking at all. Theoretical investigation of \(\text{Er}_2(\text{COT})_3\) sandwich compound reveals the unusual strong exchange interaction between \(\text{Er}\) ions, promoted by the conjugated \(\square\) - orbitals of the middle \(\text{COT}^2\) ligand.

References
From two tetranuclear \{\text{Cu}^{	ext{II}}\text{Dy}^{	ext{III}}\}_2\} cluster to an octanuclear \{\text{Cu}^{	ext{II}}\text{Dy}^{	ext{III}}\}_4\}_2\) one showing Single Molecule Magnet behaviour from field accessible states

I. A. Kühne\textsuperscript{[1]*}, N. Magnani\textsuperscript{[2]}, V. Mereacre\textsuperscript{[1]}, W. Wernsdorfer\textsuperscript{[3]}, C. E. Anson\textsuperscript{[1]}, and A. K. Powell\textsuperscript{[1,2]}

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The ongoing exploration of copper-lanthanide based complexes has resulted in several systems with interesting structural and magnetic properties\textsuperscript{[1]-[4]} and in particular that Cu-Dy pairs have recently been proposed as a potential building block for high-performance SMMs because of their relatively strong ferromagnetic coupling\textsuperscript{[5]}.

We report herein three different structures based on a \{\text{CuDy(vanox)(Hvanox)}\}_2^{2+}\) building block and their magnetic properties. Both \{\text{Cu}_2\text{Dy}_2\} complexes (1)+(2) doesn’t show any AC-signal, while the \{\text{Cu}^{	ext{II}}\text{Dy}^{	ext{III}}\}_4\}_2\) cluster (3) shows unusual SMM behaviour which we can understand by calculating the energy spectra and with the aid of the data obtained for the Y(III). This analysis leads to a model for spin arrangements which are accessible through application of magnetic fields and explain the unusual shape of the hysteresis observed. This type of behaviour offers prospects in the area of spintronics as well providing a fascinating system for study.

\textbf{Fig. 1:} Molecular structures of [Cu\text{Dy}_2] (1)+(2) and [Cu\text{Dy}_4] (3).

\textbf{References}
All-round Robustness of the Mn\textsubscript{19} Coordination Cluster System: Experimental Validation of a Theoretical Prediction

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Previously we reported the Mn\textsubscript{19} aggregate \([\text{Mn}^{III}\text{Mn}^{II}(\mu_4-O)_{8}(\mu_3-N_3)_{8}(HL_{Me})_{12}(MeCN)_{6}]\text{Cl}_2\cdot10\text{MeOH} \cdot \text{MeCN} \ (1)\) \(\text{(H}_3L_{Me} = \text{6-bis(hydroxymethyl)-4-methylphenol) in which all the 19 Mn}^{II}/\text{Mn}^{III} \) are ferromagnetically coupled, leading to a record spin ground state \(S = 83/2.\)\(^{[1]}\) At the time, we postulated that the ferromagnetic interactions within 1 were largely mediated by the end-on \((\mu_3-N_3)\) ligands. However, DFT calculations suggested that in fact the oxido \((\mu_4-O)_{2}^{-}\) ligands play the dominant role in these interactions rather than the azides.\(^{[2]}\) To test this theoretical prediction, we have successfully synthesised the coordination clusters \([\text{Mn}^{II}_{19}(O)_{8}(HL_{Me})_{12}(\mu_3-\text{Cl})_{6}(\mu_3-\text{OMe})_{2}(\text{MeOH})_{3}(\text{MeCN})_{3}]\text{Cl}_2\cdot2\text{H}_2\text{O} \cdot 5\text{MeOH} \cdot 5\text{MeCN} \ (2)\) and \([\text{Mn}^{II}_{19}(O)_{8}(HL_{Me})_{12}(\mu_3-\text{Br})_{7}(\mu_3-\text{OH})(\text{MeCN})_{6}]\text{Br}_2\cdot16\text{H}_2\text{O} \cdot 11\text{MeOH} \ (3)\) in which the eight \((\mu_3-N_3)\) ligands in \(1\) have been replaced by either six \((\mu_3-\text{Cl})\) and two \((\mu_3-\text{OMe})\) \(2\) or by seven \((\mu_3-\text{Br})\) and one \((\mu_3-\text{OH})\) \(3\).

Experimental and theoretical studies confirm that achieving the maximum possible ground spin state of \(S_T = 83/2\) for the Mn\textsubscript{19} system is insensitive to replacement of its eight \((\mu_3-N_3)\) ligands by \((\mu_3-\text{Cl}, \mu_3-\text{Br,} \mu_3-\text{OH or} \mu_3-\text{OMe})\), substantiating that the ferromagnetic interactions are indeed mediated mainly by the internal \((\mu_4-O)\) ligands. ESI-MS studies reveal that the molecular structure and oxidation state of \(1\) and its Mn\textsubscript{18}Y analogue are also robust, being maintained both in solution and in the gas-phase.

**References**


Spin-Crossover in Cobalt(II) Complexes as a Means of Switching Organic Ligands from a Closed-Shell to an Open-Shell State

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Valence tautomerism has often been studied in cobalt dioxolene complexes where temperature- or pressure-induced intramolecular electron transfer reactions within low-spin cobalt(III) catecholate complexes result in the formation of high-spin cobalt(II) semiquinonate complexes. Using tetraazamacroyclic di(tert.-butyl)diazapyridinophane (L-N₄tBu₂) as the auxiliary ligand in octahedral cobalt dioxolene complexes, it is possible to generate complexes where the low-spin cobalt(II) semiquinonate state can be obtained. Thus, with 3,5-di(tert.butyl)semiquinonate (dbsq₁) the pseudooctahedral cobalt(II) semiquinonate complex [Co(L-N₄tBu₂)(dbsq)]⁺ can be prepared, which displays temperature-induced spin crossover from a low-spin cobalt(II) to a high-spin cobalt(II) state.

Employing deprotonated 3,3'-dihydroxy-[1,1'-bi(cyclohexylidene)]-2,2',5,5'-tetraene-4,4'-dione (H₂sqsq) as bridging tetraoxolene unit, the respective dinuclear cobalt(II) complex [{Co(L-N₄tBu₂)}₂(µ-sqsq)]²⁺ is generated. It can be demonstrated that this complex exhibits a gradual temperature-induced spin-crossover of the cobalt(II) ions which is accompanied by a change of the electronic state of the bridging ligand (see reaction above). Hence, at high temperatures the electronic structure of the complex is best described to arise from two high-spin cobalt(II) ions which are bridged by a diamagnetic closed-shell quinonoidal ligand with a double bond between both rings. In contrast, at low temperatures the complex contains two low-spin cobalt(II) ions which are bridged by an open-shell ligand where two semiquinonate radical units are linked by a single bond. To the best of our knowledge, this type of switching of the electronic state of an organic moiety triggered by a metal-based temperature-induced spin-crossover process is documented here for the first time and opens up new ways to manipulate spin interactions.

References
Crystallographic Phase Transitions: Experimental Difficulties in Triggering and / or Observing them

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Crystallographic phase transitions are not always easy to trigger, and not in all cases easily detected. This talk is about the difficulties connected to such transitions.\textsuperscript{[1]} There will be some discussion of experimental details and procedures, as well as examples of predicted transitions which could not be found.

Reference

Fe(III) Spin-crossover Complexes and Light: uncommon features


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Spin-crossover is a well-known phenomenon for first row-transition metals. Octahedral transition metals having $d^n$ configuration, with $4 \leq n \leq 7$ can be observed to be low spin (LS) at low temperature and high spin (HS) at high temperature. At low temperature, a metastable HS state can be populated by irradiation: this is the so-called LIESST effect. It opens the possibility to store information by light on a single molecule. Unfortunately, the life-time of this metastable state is often very short above 100 K.

Most of the spin crossover complexes exhibiting LIESST effects are Fe(II) complexes and it has long been thought that Fe(III) would never exhibit long-lived photo-induced HS state. In this talk, a few Fe(III) compounds presenting LIESST effect will be presented, some of these complexes presenting also symmetry breaking effects\cite{1} and co-existence with ferromagnetic properties\cite{2}.

![Fig.](image)

Fig.: Fe(III) complex presenting two-step thermal spin transition as well as two step LIESST effect.

References


On/Off - Photoswitch in a cyanide-bridged 3d-5d molecular system

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The rational design of molecular materials that exhibit tunable optical and magnetic properties through the application of external stimuli could be used as molecular switches, memories and sensors. The cyanide-based chemistry gives access to many molecular-based switches.1) Most of them are based on the {Fe-Co} Prussian Blue Analogues (PBAs). Switching property of these molecules are governed by either through photo-induced electron transfer or through photo-induced spin crossover (or LIESST effect).

Very recently, we explore the use of cyanide-based 5d metal complex to build new switchable systems. Indeed, octacyanometallate-based compounds have proven to be suitable systems to expand the family of photomagnetic materials.2) Photo-induced electron transfer has been observed in {Mo-Cu} and {W-Co} compounds involving the valence state conversions MoIV-CuII ⇔ MoV-CuI and WIV-CoIII ⇔ WV-CoIII. The W-Co pair is of particular interest as the photomagnetic effect can induce a strong change in the magnetic properties, the {WIV-CoIII} diamagnetic pairs being converted into {WV-CoII} paramagnetic ones.

Up to now, few photomagnetic {W-Co} systems have been reported, and all of them are two- or three-dimensional materials.3) Although some discrete {W-Co} complexes have been obtained, none of them were known to exhibit photomagnetic effect. Here we are presenting a novel discrete {W-Co} photomagnetic molecule. The octacyano building block [W(CN)8]3- have been used towards [CoII(L)2(S)2]2+ complex for achieving the desired compound [[W(CN)s]3[Co(bik)2]2]+[Co(bik)3]2H2O 13CH3 CN (bik = bis(1-methylimidazol-2-yl)ketone). It consists of an anionic hexanuclear unit, [[W(CN)s]3[Co(bik)2]2]2+, a paramagnetic counter cation, [Co(bik)3]2+, and crystallization solvent molecules. It exhibits a thermally induced electron-transfer coupled spin transition between the two states: CoIIIHS-WV ⇔ CoIIILS-WIV near ambient temperature and also shows photomagnetic effect at 20 K upon irradiating with 808 nm laser light.4) The reversibility of the photo(magnetic) effect has also been observed when the photo-induced metastable paramagnetic state was subjected to irradiation with 532 nm laser light.


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Spin-Crossover (SCO) compounds have long been plugged as potential candidates for applications in areas such as memory storage, molecular electronics, sensors and display devices.[1,2] In order for such applications to be realised SCO active compounds require immobilisation onto/into suitable media. Generating soft materials such as Langmuir-Blodgett films, Gels, Dendrimers, Liquid Crystals amongst others is one approach researches have employed to fabricate such SCO devices.[1] This tutorial style lecture will focus mainly on the practical aspects of Langmuir, Langmuir-Blodgett and Langmuir-Schaefer techniques for coordination chemistry applications and will include very brief introductions to the techniques, the types of systems that are required and different approaches researches in the field have taken to introduce amphiphilicity to coordination compounds.

References
TAILORING N-SALICYLIDENE DERIVATIVES AND AZOLE BASED LIGANDS FOR THERMO- AND PHOTOCHROMISM APPLICATIONS

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Iron(II) spin crossover (SCO) materials belong to an attractive class of switchable functional solids with spin state that can be reversibly triggered by temperature or pressure.\textsuperscript{[1,2]} Although the origin of the SCO phenomenon is molecular, its cooperative manifestation depends on an efficient coupling between active species in the crystal lattice through covalent and supramolecular interactions.\textsuperscript{[3]} In this context, numerous synthetic systems have been developed,\textsuperscript{[1]} in particular coordination polymers with 1,2,4-triazole and tetrazole building blocks.\textsuperscript{[4]} Using a ditopic 1,2,4-triazole-tetrazole ligand, we recently obtained a mononuclear iron(II) neutral complex, with coordinated water molecules, which was screened for sensing abilities for a wide spectrum of chemicals and to evaluate the response function toward physical perturbations. Interestingly, the complex detects methanol among alcohols. The sensing process, which involves an unexpected spin state change, is visually detectable, fatigue-resistant, selective, and reusable, as demonstrated by both \textsuperscript{[5]}Fe Mössbauer and diffuse reflectance spectroscopies.\textsuperscript{[5]}

The possibility to photoaddress the spin state of these materials is another interesting challenge. In this context, unprecedented photomagnetic/chromic properties at room temperature were discovered for the CP \textsuperscript{[6]}[Fe(BM-4TP)\textsubscript{2}(NCS)\textsubscript{2}]:2MeOH including a diarylethene ligand.\textsuperscript{[6]} More recently, we could revisit the optical-structural properties relationship for \textit{N}-salicylidene heterocycles derivatives affording a new range of solid state thermochromic and photochromic switches operating at room temperature.\textsuperscript{[7]} These molecules were included as ligands in mononuclear\textsuperscript{[8]} and oligomeric SCO complexes.\textsuperscript{[9]} For the dinuclear \textsuperscript{[9]}[Fe\textsubscript{2}(Hsaltrz\textsubscript{3})(NCS)\textsubscript{4}]:4MeOH, with Hsaltrz = \textit{N}-salicylidene-4-amino-1,2,4-triazole, the abrupt SCO phenomenon at \textit{T}1/2 ~ 150 K was tracked by temperature dependence fluorescence spectroscopy for the first time in the crystalline state, thus opening new sensing perspectives, e.g. in thermometry.\textsuperscript{[9]} Non coordinated \textit{N}-salicylidene aniline sulfonate anions were included in mononuclear complexes,\textsuperscript{[10]} and their photochromic properties recently evidenced.\textsuperscript{[11]} A wide range of hybrid materials is expected, for instance blends made from such anionic derivatives and a polyampholyte matrix.\textsuperscript{[12]}

References

Geometric Modulation of the Jahn-Teller Distortion in Manganese(III)

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High spin (HS) Mn$^{III}$ in an octahedral field exhibits a strong Jahn-Teller (JT) effect, Figure 1, which can confer considerable magnetic anisotropy or directionality. Magnetic anisotropy and its effect on the overall assembly of spins has been widely exploited in the design of single molecule magnets.$^{[1]}$ We are particularly interested in exploring the JT distortion in Mn$^{III}$ for two reasons: i) Previous work using strained tridentate ligands yielded a competing coordination mode in which we believe JT plays an integral part;$^{[2]}$ ii) in our previous spin crossover complexes,$^{[3-5]}$ the JT distortion in the HS form is non-classical: we have typically observed a HS axial compression (equatorial elongation), presumably due to the relative ordering of the orbitals in the low spin (LS) state which would place the d$^{x^2-y^2}$ lower in energy than d$^{z^2}$, Figure 2.

The effect of ring substituents, anion choice and solvation are all evident on: i) the coordination mode which is adopted and its effect on the JT axis and magnetic properties, and ii) the ability of the Mn(III) ion to spin cross.

References
Properties of thin and ultrathin films of sublimable spin crossover complexes.

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The ultimate limit of miniaturization is the single molecule, the smallest composite unit allowing control of size, shape and properties. Much work has been undertaken lately on the design at the molecular level of spin crossover systems to manage and store data in a binary format, thanks to the possibility of commuting thermally and/or optically the spin state of such systems. In order to integrate such materials in functional devices at the nanoscale, the understanding of the behaviour at the molecular level of a spin transition complex in strong interaction with its environment, be it a polymeric matrix or a surface, is imperative. Ultra-High Vacuum evaporation techniques can be used to prepare whether high-purity thin and ultra-thin films, or isolated molecules on a well-defined surface, objects crucial for such studies. We will present some of our results on thin films and ultrathin films,[1] and more particularly the thermal and photoswitching of isolated spin crossover molecules on a conducting surface of gold.[2]

References
Photo-control of the high-spin low-spin interface inside the thermal hysteresis loop of a spin-crossover single crystal: experience and theory.

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We investigated single crystals of the dinuclear iron(II) compound \([\{Fe(NCSe)(py)_2\}_2(m-bppy)]\), which exhibit a thermal spin transition with hysteresis near 100 K. The robust character of the crystals made possible the investigation of both on-cooling and on-heating processes. We observed well-defined transformation fronts\[^1\] between macroscopic high spin (HS) and low-spin (LS) phases during the thermally-induced phase transition. The fronts are almost linear in shape, and propagate through the entire crystal at constant velocity (see Fig.1). The interface orientation was ~ constant during the process and its measured propagation velocity typically was ~ 1 and 10 µm/s for the on-cooling and on-heating processes, respectively. The videos of the spin transition processes will be shown in real (or accelerated) time.

The second part of the talk will be devoted to the photo-control of the HS/LS interface dynamics using the light as an external stimulus.

Using microscopic models\[^2, 3\] combining the elastic (volume change) and the electronic (spin state change) degrees of freedom involved in the spin transition phenomenon, we succeeded to simulate the experimental data and to explain the physical origin of the stable front orientation as well as the front dynamics.

References
A PROMISING ROUTE TO MULTI-FUNCTIONAL MAGNETIC COMPOUNDS

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The design and the synthesis of hetero-tri and hetero-tetra-metallic complexes is a real challenge in coordination chemistry, but also a promising route to multi-functional magnetic compounds. This presentation intends to point out some recent achievements in the field of single molecule magnets and photo-switchable high spin molecules,[1,2] viewed as new precursors for functional hetero-poly-metallic compounds.

As part of the general interest in photo-switchable nanomagnets, a large family of Molybdenum-Copper complexes has been obtained including multi-metallic clusters, such as MoCu₄, MoCu₆, Mo₃Cu₄ or Mo₆Cu₁₃, whose magnetic properties might be modified by light. Our strategy demonstrates the relevance of using polynuclear complexes with terminal cyanide ligands as valuable photo-active building blocks for the rational design of hetero-poly-metallic photo-switchable supramolecular architectures.

Following the concept “polynuclear complexes as ligand”, we succeeded in getting hetero-tri-metallic complexes (i.e. NiMo₂Cu₇, Mo₂Cu₂Mn or Mo₂Cu₁Tb₄) [3,4,5] and hetero-tetra-metallic compounds (i.e. Mo₂Cu₂Tb₂Ni or Mo₂Cu₂Tb₂Ru).[6] All these compounds behave as single molecule magnets or photo-switchable high spin molecules, opening the way for photo-switchable single molecule magnets.

References
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How topology affects magnetism - harddisks, spin currents and monopoles

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Similar to knots in a rope, the magnetization in a material can form particularly robust configurations. Such topologically stable structures include domain walls, vortices and skyrmions which are not just attractive candidates for future data storage applications but are also of fundamental importance to current memory technology. For example, the creation of domain wall pairs of opposite chirality delimits the thermal stability of bits in present high anisotropy perpendicular recording media. The ever increasing demand for higher data storage density forces us to understand topological defects at ever decreasing length scales where thermal and quantum effects play an increasingly important role.

As an example, it will be shown how the thermal domain wall nucleation affects the design of current and future magnetic harddisks. A particular challenge is the understanding of the “no man's land” between macroscopic magnetization phenomena and quantum magnetism of atomic clusters. It is shown that geometric quantization via Berry’s phase can bridge these two regimes. As an important consequence it will be shown how the chirality of a classical domain wall translates into quantum spin currents which in turn can be used for information transport. All concepts will be illustrated by state of the art experiments, which encompass the techniques of polarized neutrons and synchrotron x-rays. The final part of the talk will discuss how magnetic monopoles emerge as topological defects in densely packed arrays of nanoislands which effectively interact as dipoles, a system also known as artificial spin ice. In contrast to conventional thin films, where magnetization reversal occurs via nucleation and extensive domain growth, magnetization reversal in 2D artificial spin ice is restricted to an avalanche-type formation of 1D strings. These objects constitute classical versions of Dirac strings that feed magnetic flux into the emergent magnetic monopoles. It is demonstrated how the motion of these magnetic charges can be individually controlled experimentally pave the wave for simple logic operations.

References
Lorentz Transmission Electron Microscopy Study of Three Dimensional Artificial Spin Ice

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Frustration, i.e. the inability to simultaneously satisfy all interactions, occurs in a wide range of systems such as glasses, neural networks and water ice\textsuperscript{1} making systems where the frustrated properties can be measured of fundamental scientific interest. One such type of model system is ‘spin ice’\textsuperscript{2}, where the atomic magnetic moments are frustrated due to geometrical constraints; this type of magnetic ordering was originally found in pyrochlore crystals at very low temperatures. In two-dimensional artificial spin ices the atomic moments are replaced with ferromagnetic islands with lengths of order 100 nm, which act as miniature bar magnets\textsuperscript{3}. This allows a number of the interesting properties of the canonical spin ices, such as emergent magnetic monopoles\textsuperscript{4}, to be reproduced. However, going from three to two dimensions leads to a change in either symmetry or connectivity at each vertex, which changes some aspects of the frustrated system. It is therefore of interest to study three-dimensional artificial spin ice systems. Here we show that three-dimensional inverse opal nanostructures of ferromagnetic permalloy produce Ising spin states with the same symmetry and connectivity as the pyrochlore lattice. Using Lorentz transmission electron microscopy we directly image the micromagnetic state, observing spin ice behaviour.

References

Ferroic domain walls as disordered elastic interfaces


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Propagating interfaces phenomena include fluid invasion in porous media, flame fronts, cracks, and domain walls in ferroic materials. Although these systems have very different microscopic descriptions, they share identical physics at the macroscopic scale and can be described under the unifying framework of disordered elastic systems (DES).[1] The rough morphology and complex response to driving forces of DES obey universal scaling laws which depend on the competition between elasticity and pinning by the disordered medium.

Understanding the formation and propagation of domains in ferromagnetic and ferroelectric domain walls is technologically critical in increasingly more miniaturized devices. In this context, DES theory offers a complementary approach to study the role of defects on domain wall static and dynamic behaviour.[2,3]

Ferroelectric domains of nanometric dimensions can be created and imaged in ferroelectric samples using the very sharp tip of an atomic force microscope (AFM). Here, we present a study of the statics and dynamics of AFM-engineered domains in ferroelectric Pb(Zr0.2Ti0.8)O3 thin films with different defect densities. Because both the AFM tip and the surface charges of a ferroelectric are affected by the environment, we carried these measurements in ultrahigh vacuum (UHV) and ambient conditions. In samples with low defect density, domain walls present a smooth configuration in both conditions and significantly higher propagation rates in ambient. In contrast, higher-defect density samples show rougher domain walls in UHV and slow propagation rates in both environments. These observations are compatible with DES numerical simulations of 1D domain walls under varying disorder and dipolar interaction magnitude.

Fig. 1: Ferromagnetic (a) and ferroelectric (b) domain walls, (c) 2D disordered elastic interface.

References
Finding new magnets and finding them fast

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Magnetic materials underpin a vast and diverse range of modern technologies, going from data storage to energy production and use. However, the choice of magnets for mainstream applications is limited to a few dozens and the development of a new high-performance magnetic compound is a long and often unpredictable process. Here we describe a systematic pathway to the discovery of novel magnetic materials for multiple applications, which demonstrates an unprecedented throughput and speed up in the discovery process. We have constructed a massive electronic structures library for Heusler alloys containing 236,945 prototypical compounds. We have then filtered those alloys displaying magnetic order and identified magnets with specific electronic properties, such as half-metallicity and large magnetization density. Finally we have established whether these can be fabricated at thermodynamical equilibrium. In particular, we have carried out a full stability analysis for intermetallic Heuslers, i.e. for Heusler alloys made only of transition metals. Among the possible 36,540 prototypes we have identified 249 thermodynamically stable materials, with only 21 being magnetic. For the stable intermetallic magnetic Heuslers we have estimated the magnetic ordering temperature, \( T_c \), by performing a regression calibrated on the experimental \( T_c \) of about 60 known Heuslers. Our work paves the way for large-scale design of novel magnetic materials at unprecedented speed.

Our computational strategy comprises of three main steps [1]. Firstly, we construct a massive database containing the computed electronic structure of potential novel magnetic materials. In particular we consider Heusler alloys, a prototypical family of ternary compounds populated with several high-performance magnets [2]. A rough stability analysis, based on evaluating the enthalpy of formation using as a reference those of the parental single phase compounds, provides a first screening of the database. The elemental enthalpy of formation, however, is not a precise measure of the thermodynamical stability of a material, since it does not describe decomposition into the competing binary compounds. Such analysis requires the computation of the electronic structure of all possible binaries associated to the given Heusler alloy. This is our second step and it is carried out here only for intermetallic Heuslers, for which an extensive binary database is available [3]. Finally, we discuss the magnetic order of the resulting stable magnetic intermetallic Heuslers and, via a regression trained to available magnetic data, we estimate their \( T_c \).

References

STRUCTURAL MODIFICATION AND SELF-ASSEMBLY OF NANO SCALE MAGNETITE SYNTHESISED IN THE PRESENCE OF AN ANIONIC SURFACTANT

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Many biological and industrial processes are crucially dependent upon the absorption of surfactants from an aqueous phase onto a solid surface. At the heart of this physical chemical process is the alteration of the interface properties caused by the adhesion and aggregation of the surfactant molecules at the solid surface.

Synthesis of magnetite (Fe₃O₄) in the presence of the surfactant sodium dodecyl sulphate (SDS) gives rise to a variety of nanoscale morphologies, some of which look remarkably similar to magnetite found in organisms, suggesting that similar processes may be involved. So, taking our inspiration from biology, where templates produce magnetite of defined shapes and sizes, we have been interested in investigating how surfactant molecules can similarly influence nanoscale magnetite formation e.g. Figure 1.

Figure 1. Mesoporous nanocrystallites form with diameters of 40-100 nm and a morphology similar to the widely reported truncated dodecahedral shape seen in certain magnetotactic bacteria [1]. In addition to its “biogenic signature” this mesoporous nanomagnetite could be useful for targeted drug delivery [2].

In this paper, we report structural modification and self-assembly of magnetite in the presence of the anionic surfactant SDS. SDS is commonly used to mimic hydrophobic binding environments such as cell membranes [3], and has recently been used to study the folding and thermal stability of cytochrome c (cyt c) a biologically important electron transfer system [4].

References
Magnetic nanoarchitectures investigated by $^{57}$Fe Mössbauer spectrometry

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It is now well established that the development of nanotechnology which usually refers to the manipulation and self-assembly of atomic species or molecules requires first a high control and a fine reproducibility in designing and elaborating functional nanostructures. In addition, among the different classes of nanomaterials, the magnetic nanostructures can be applied in various fields such as GMRs, MRI contrast agents, nanocareers for drug delivery, magnetic hyperthermia fluids, recording media or photocatalyst.

In this topic, an important step remains the preparation of magnetic nanoparticles and then their functionalization or their subsequent organization to get magnetic nanoarchitectures with enhanced tunable physical properties.

Studying these magnetic nanostructures needs several complementary techniques to well understand their whole structural and magnetic properties. In addition to diffraction techniques (X-ray, EXAFS, SAXS, GISAXS, …), microscopies (transmission electron microscopy, atom force microscopy, …), static and dynamic magnetic measurements as well as XMCD, $^{57}$Fe Mössbauer spectrometry appears as also an excellent tool because this local probe technique should first discriminate surface and bulk effects in addition to oxidation and spin states of Fe species and then contribute to follow the hyperfine magnetic properties and their dynamics in correlation with superparamagnetic relaxation phenomena.

After reviewing the main features characteristics of the different nanostructures allowing thus the relevant parameters to be distinguished, we illustrate from selected examples based on nanostructured powders, nanoparticles, functionalized nanoparticles, hollow nanoparticles and assemblies of particles how both the selectivity and the local probe character of $^{57}$Fe Mössbauer spectrometry contribute to investigate in situ local atomic order and magnetic properties. In addition, we report some numeric modelling results, showing how Mössbauer spectrometry and Monte Carlo and/or ab initio calculations are complementary approaches.
HF-EPR study of small heterometallic spin clusters

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Molecules showing slow relaxation of the magnetization at low temperature, known as Single-Molecule Magnets (SMM), are attracting continuing interest in molecular magnetism. Slow relaxation results from a large spin ground state S associated to an Ising type magnetic anisotropy, leading to the presence of a barrier to the reversal of the magnetization. Axial anisotropy terms govern the height of the barrier whereas transverse magnetic anisotropy terms influence the quantum tunneling of the magnetization. HF-EPR spectroscopy has demonstrated to be a key tool to provide precise information on the magnetic anisotropy of SMM and thus to understand the dynamics of their magnetization.

Fe₄ complexes with a propeller-like structure, of formula [Fe₄(L)₂(Hdpm)₆], are providing an important class of SMM displaying synthetic flexibility and ease of functionalization (Hdpm = 2,2,6,6-tetramethyl-heptane-3,5-dione), where L stands for the tripodal bridging ligand. Here we present HF-EPR studies performed on heterometallic complexes related to the Fe₄ family. HF-EPR spectra at low temperature have been collected on polycrystalline samples of several complexes (HF-EPR spectra recorded at 230 GHz on a Fe₃Cr sample are displayed in the figure) in order to understand the origin of the SMM zero-field splitting (zfs) parameters, with a special focus on the single ion contribution to the global zfs.
Dipolar-driven Magnetic Ordering in the Single Molecule Magnet System Fe$_{19}$ studied using $\mu$SR and Monte Carlo Simulation

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Antiferromagnetic ordering at 1.2 K in the single molecule magnetic nanodisc system Fe$_{19}$ has been detected using implanted muons as a local magnetic probe$^{[1]}$. This molecular system has the large spin value $S=35/2$ $^{[2]}$. Two distinct groups of muon sites are identified from the two component muon spin relaxation data, reflecting sites near the magnetic core that are strongly coupled to the electronic spin of one molecule and sites distributed around the periphery of the molecule that are more sensitive to intermolecular spin correlations. Dipole field calculations and Monte Carlo simulations confirm that the transitions in Fe$_{19}$ are consistent with magnetic ordering driven by interactions between molecules that are predominantly dipolar in nature. The triclinic crystal structure and off-axis easy spin direction of this system gives the dipolar field a significant component transverse to the easy spin axis and the parallel component provides a dipolar bias closely tuned to the first level crossing of the system. These factors enhance the quantum tunnelling between levels, thus enabling the system to avoid spin freezing at low temperatures and efficiently reach the dipolar ordered state. This favourable bias condition also applies for the Fe$_{17}$ system, but notably not for the well known Fe$_8$ system.

References


Ferroelectrics Inspired by Ferromagnetism: Searching for Ferroelectric Vortices and Domain Wall Devices

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In 1921, as part of a landmark study on piezoelectricity, Valasek noted that the polarisation-electric field response in Rochelle Salt was distinctly hysteretic. The loops were so strongly reminiscent of those seen in ferromagnetism, that he classified the newly discovered phenomenon as “ferroelectricity”, despite the fact that it was in no way related to the presence of iron. Since then, many aspects of ferroelectric and ferromagnetic behaviour have been found to be strongly analogous to each other. Given the relative maturity of the two fields, a rich source of inspiration for ferroelectrics research can often be found by considering the latest and most exciting discoveries in ferromagnetism.

In this talk, two magnetics-inspired topics will be discussed:
(i) the search for topologically interesting dipole patterns, such as vortices and skyrmions, in nanoscale ferroelectrics;
(ii) the quest for the kinds of control over domain wall injection and movement that have been developed for race-track memory and domain wall logic, as applied to ferroelectrics.

As we will see, despite slow progress, new discoveries have been made: for example, flux-closure patterns have now been unequivocally observed [1, 2], perhaps acting as a precursor to true dipole vortex formation, and control of domain wall injection and motion has been realised through design of inhomogeneity in the electric field during switching [3].

References
Characterising Local Ferroelectric and Magnetic Properties of Multiferroic Heterostructures by Scanning Probe Microscopy

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Multiferroic\textsuperscript{[1]} materials are actively studied as a route to harness magnetoelectric coupling and enable a range of applications whereby magnetism can be controlled by an electric field.\textsuperscript{[2]} Single phase, room temperature multiferroics are rare,\textsuperscript{[3]} leading to a variety of approaches to prepare composite multiferroic materials.\textsuperscript{[4]} Scanning probe microscopy-based characterisation techniques are well-suited to probe both ferroelectric and magnetic properties of such heterostructures, given the sensitivity of the techniques to both short and long range tip-sample interactions. Here, we briefly discuss the use of piezoresponse force microscopy and magnetic force microscopy to probe ferroelectricity and magnetism, respectively, in several multiferroic heterostructures.

In the first example, local ferroelectric polarization switching is studied using piezoresponse force microscopy in self-assembled multiferroic BiFeO\textsubscript{3}–CoFe\textsubscript{2}O\textsubscript{4} nanostructures prepared by pulsed laser deposition.\textsuperscript{[5]} In the second example, piezoresponse and magnetism are probed in several nanocomposite configurations comprising Pb(Zr,Ti)O\textsubscript{3} and CoFe\textsubscript{2}O\textsubscript{4}, which are prepared by pulsed laser deposition through thin nanoporous anodic aluminum oxide masks.\textsuperscript{[6]} Finally, more recent work-in-progress aimed at designing a composite multiferroic material through a sol-gel based method to create porous templates will be discussed.\textsuperscript{[7]}

References
Magnetic Field-Induced Ferroelectric Switching in Multiferroic Aurivillius Phase Thin Films at Room Temperature

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With the seemingly inexorable increase in the use of devices designed to access the internet for an ever increasing series of applications there is a constant need for data storage technologies with higher densities, non-volatility and lower power consumption\textsuperscript{[1]}. Single-phase, room temperature magnetoelectric multiferroic materials are of considerable interest for such applications\textsuperscript{[2]}. However, materials that are both multiferroic and magnetoelectric at room temperature are very unusual\textsuperscript{[3]}. By inserting magnetic ions into Aurivillius phase, layer-structured ferroelectric materials, we have synthesised thin films of average composition Bi\textsubscript{6}Ti\textsubscript{2.8}Fe\textsubscript{1.52}Mn\textsubscript{0.68}O\textsubscript{18} (B6TFMO) by a chemical solution deposition process on c-plane sapphire substrates\textsuperscript{[4]}. Piezoresponse force microscopy (PFM) demonstrates room temperature ferroelectricity. Superconducting quantum interference device (SQUID) magnetometry reveals a distinct room temperature ferromagnetic signature (M\textsubscript{s} = 0.74emu/g, H\textsubscript{c} = 7mT at 300K) in the films. The results of a careful microstructural analysis of the materials will be discussed. This investigation, coupled with the use of a statistical analysis of the data, allows us to conclude that ferromagnetism does not originate from unobserved second phase ferromagnetic inclusions, with a confidence level of 99.5%. Direct PFM evidence of the switching and formation of a ferroelectric polarisation induced by a change in magnetic field within individual Aurivillius phase grains will be presented\textsuperscript{[4]}. This is the first report of such an effect occurring in a genuine single-phase material at room temperature in thin film form. This room temperature single phase magnetoelectric multiferroic material is currently being optimised and assessed for device-level performance and could find application in a wide range of new or improved devices to potentially meet future industry requirements in high density memory applications.

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References

Electronic transport in 2D and 3D topological insulator nanostructures

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Topological insulators are a recently discovered class of materials displaying unique electric and magnetic properties [1]. A consequence of the non-trivial topology of their band-structure is the presence of edge states at the interface with a topologically trivial system. These states have a linear dispersion with spin-linear momentum locking. The topological phase is usually associated to a symmetry of the system, specifically, in the cases here described, the time-reversal invariance.

We show that, as expected, for 2D model systems, the peculiar properties of the topological edge state translate in a perfect transmission even in the presence of defects. This is due to the complete suppression of backscattering. A similar result is also found when investigating the effect of potential barriers, in the form of step edges, on the scattering properties of the (111) surface of the prototypical 3D topological insulator Bi$_2$Se$_3$ [2]. Here, however, other scattering processes, which do not entail a complete spin and momentum reversal, are allowed. We believe that these results can help to interpret recent experiments.

Finally, we investigate the effect of a magnetic impurity on an edge of a 2D topological insulator. We found that, at high temperature, the edge states are not protected against backscattering anymore as the time-reversal symmetry is broken and the system leaves the topological phase. However, at a characteristic low temperature, the magnetic impurity becomes Kondo screened and the topological properties of the system are restored so that perfect ballistic transmission is recovered.

References
Switchable Paramagnetism and Thermochromism of Cobalt(II) in Thiocyanate Ionic Liquids

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Magnetic ionic liquids (ILs) have intrinsic para- or ferromagnetic properties without the need of adding magnetic particles, hence avoiding difficulties arising from maintaining stable suspensions.[1][3] These magnetic properties can originate from the anion, the cation or both. For example, ionic liquids containing magneto-active metal complex anions, such as 1-methyl-3-butylimidazolium tetrachloroferrate(III) [C₄MIM][FeCl₄], have been reported.[4]

Solutions of cobalt(II)thiocyanate in 1-methyl-3-alkyl-imidazolium thiocyanate ionic liquids have been investigated and show reversible switching of the speciation of cobalt(II) from tetrahedral \([\text{Co(SCN)}_4]^{2-}\) at RT to octahedral \([\text{Co(SCN)}_6]^{4-}\) co-ordination at temperatures around -40 °C. This temperature-dependent change in co-ordination is accompanied by a reversible change in colour (blue to red) and by a significant change of the paramagnetic moment of these liquid materials at -40 °C. This effect is also cation-dependent; the ionic liquid provides a reservoir for the anions to reversibly co-ordinate to Co²⁺ in this system.

\[
\begin{align*}
\text{NCS}^- & \quad \text{NCS}^- \\
\text{SCN}^- & \quad \text{NCS}^- \\
\text{NCS}^- & \quad \text{NCS}^- \\
\text{NCS}^- & \quad \text{NCS}^- \\
\text{SCN}^- & \quad \text{NCS}^- \\
\text{SCN}^- & \quad \text{NCS}^-
\end{align*}
\]

\[\text{[C₄mim]₂[Co(SCN)]₄} + 2 \text{SCN}^- \rightleftharpoons \text{[C₄mim]₄[Co(SCN)]₆}\]

References
Cool surprises with fluoride-bridged molecular magnetic architectures

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While oxygen and nitrogen are ubiquitous as bridging ligators in molecule-based magnetic systems, fluoride is much less explored and studied in this respect. Here, examples of new approaches to molecular, 1-D, and 3-D magnetic systems based on fluoride linkages between transition metals and between transition metals and lanthanide ions will be discussed. Assembly of polynuclear lanthanide complexes employing kinetically robust fluoride complexes has proven a convenient route to small heterometallic clusters. By this route, the first examples of unsupported fluoride bridges between paramagnetic transition metals and lanthanide ions have been synthesized. The propensity of fluoride for linear bridging also aids in bringing topological control into the synthesis of 3d-4f clusters \cite{1,2}. The resulting, structurally simple, systems have allowed for modeling of the magnetic properties 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. Extension of the strategy to encompass 5d-fluoride complexes with intriguing magnetic properties, including coupling strengths, which exceed those of analogous cyanide-bridged systems, will also be presented \cite{3}.

References
Advancing into the new paradigms of molecular magnetism by case studies. A chemist’s perspective on the magnetic anisotropy.

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The magnetic anisotropy is a running paradigm of the nowadays molecular magnetism, stirring interest both from academic point of view, since it has intricate mechanisms, and also for application purposes, its understanding serving to design systems behaving as magnets at molecular and nano-scale levels. In an early stage, it was regarded as a sort of *deux ex machina*, being conceptually acknowledged, but having few technical clues to it, being primarily an object from the physicist’s world, impenetrable to simple chemical intuition. In the recent years, the studies aiming to conquer this territory have become increasingly numerous and insightful.[1]

Placing on equal footing the experimental and theoretical deals, we had our own contribution of rationales in this quest,[2-4] offering new keys for this major keyword, by approaching several case studies and proposing useful new tools of analysis, such as the polar maps of state-specific magnetization functions. The main focus is devoted to the f-type complexes, rationalizing the magnetic anisotropy as function of Ligand Field features, as suggested in Fig.1. Regarding the theory as valuable complement to the experiment, we claim pioneering advances in performing the first ab initio approach of the lanthanide molecular complexes, encompassing, with the help of hints from chemical intuition, several technical difficulties related to the non-aufbau nature of the electron configuration of the f-type complexes.

References

![Fig. 1: Synopsis of magneto-structural analysis of a system based on [Er(NO$_3$)$_3$(H$_2$O)$_4$] units: a) the chain structure; b) the polar map of groundstate magnetization function; c) the color map of the Ligand Field potential.](image-url)
NMR Study of Ligand Exchange and Electron Self-exchange Between Oxo-centered Trinuclear Clusters

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Ligand substitution and electron transfer reactions are two of the widely investigated processes in coordination chemistry. Most of these investigations are focused on mononuclear compounds and comparatively little work is available for coordination clusters. In this communication the ligand exchange and electron self-exchange reactions for labile paramagnetic carboxylate clusters ([Fe^{III}_{2}MO(Ac)_{6}L_{3}]^{n+} M=Fe^{III}(1), Fe^{II}(2), Co^{II}(3), Ni^{II}(4) L=Rpy) was analysed by dynamic NMR spectroscopy. The variable temperature line-shape NMR analysis of solutions of each cluster showed that these exchange reactions occur with $D$ limiting dissociative mechanisms. Due to the slow ligand exchanges at the NMR time scale on the homovalent Fe^{III}_{2}O (1) cluster, individual signals for the mixed ligand cluster could be observed. The electron self-exchange rate between 1 and 2 has been followed simultaneously with the ligand exchange on 2. The equilibrium constant for the formation of the precursor to the electron-transfer and the free energy of activation contribution for the solvent reorganisation to reach the electron transfer step have been considered the same for both compounds. The populations of different spin states in Fe^{III}_{2}O (1) and Fe^{III}_{2}Fe^{II}O (2) are correlated with rate of electron self-exchange reaction.

References


Cyclic Coordination Clusters incorporating Fe-4f building blocks

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Coordination clusters contain finite numbers of metal ions enclosed within a shell of ligands. The special case of cyclic coordination clusters can be understood in terms of finite chains of metal ions which are “joined up” to give a ring structure. We have recently been investigating ring systems which contain Fe ions as well as ions from the 4f series. In addition, we have been using the racemic form of the ligand Me-teaH₃ (see figure) and discover some intriguing chiral separations on such cyclic systems. [1]

Furthermore, in terms of the electronic properties in such a cyclic system, where the metal ions are cooperatively coupled in some way, unusual electronic structures can result. Results on the system [Fe₁₀Ln₁₀(Me-teaH)₁₀(Me-tea)₁₀(NO₃)₁₀] reveal that the electronic structure is critically dependent on the nature of the 4f ion with showing femtosecond timescale events within the cyclic cluster and a hopping electron transfer mechanism between individual clusters. [2]

References
Poster Abstracts
Magneto Structural Correlation in Atypical Mn(III) Schiff Base Complexes

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Spin Crossover (SCO) is a phenomenon that can be observed in first row d4-d7 transition metal ions in an octahedral field.1 This allows switching between low spin (LS) and high spin (HS) electronic states by perturbation of the system using external stimuli such as temperature (thermal spin transition), light (LIESST effect) or pressure. MnIII is a d4 ion and previously reported complexes from our group2,3 have utilised a ligand system with a flexible polyamino backbone, which has led to some cases of hysteretic spin transitions.4

HS MnIII in an octahedral field exhibits a strong Jahn-Teller (JT) effect which can confer considerable magnetic anisotropy or directionality. This property has been widely exploited in design of single molecule magnets.5,6 We were interested to explore the magnetic anisotropy in SCO MnIII, particularly because the JT distortion in the HS form is non-classical: we have typically observed a HS axial compression (equatorial elongation), presumably due to the relative ordering of the orbitals in the LS state which would place the dx2−y2 lower in energy than dz2. The addition of strain on the flexible ligand backbone is also explored, leading to the formation of trigonal prismatic complexes, Fig. 1.

![Fig 1: Effects of distortion on Mn(III) Schiff base complexes](image)

References

Competing Coordination Modes in Manganese(III) Schiff Base Complexes

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High spin d4 metal ions in an octahedral field undergo a geometrical distortion known as the Jahn-Teller effect. This distortion lowers the overall energy of the complex as the degeneracy usually seen in the electronic ground state is removed. This effect is usually manifest in an elongation along certain metal-ligand bonds due to the population of the now non-degenerate antibonding orbitals. In the majority of cases population of the dz2 orbital occurs, leading to an axial elongation and a loss of Oh symmetry.

The pairing of this electronic effect with a geometrically constraining ligand has produced an interesting case of competing coordination modes where tridentate ligands will either adopt a tris- or bis-dentate coordination mode with solvent filling the coordination sphere, Fig. 1. These complexes have been isolated with a 50:50 co-crystallisation of the [bis-tridentate] and [bis-bidentate+solvent] modes.[1] These complexes could be useful candidates for molecular switching.[2-4] Presented here is the structural characterisation of four new complexes showing varying coordination modes and the Raman spectra of these four complexes as well as the Raman spectra of the three previously published complexes showing co-crystallisation of two modes.

Fig. 1: Diagram showing competing coordination modes in Mn(III) with chelating ligands

References
Two-Step Spin Crossover in Manganese(III) Complexes

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Spin crossover (SCO) molecules comprise a promising class of compounds for application in memory devices. A hysteretic transition pathway and hence molecular bistability i.e. having two electronic states under the same set of conditions is essential in promoting a memory effect and considerable efforts have been expended to develop systems with wide hysteresis loops close to room temperature. Triggers for SCO include temperature, pressure or light. In contrast to Fe and Co there are few examples of SCO in Mn$^{III}$. Mn$^{III}$ is a particularly interesting candidate for SCO as it has a pronounced Jahn-Teller (JT) effect in the high spin (HS) state. We have shown the importance of ligand flexibility in promoting Mn$^{III}$ SCO where population of d$_{x^2-y^2}$ on switching to HS requires elasticity in the xy plane. To date this system type has promoted gradual SCO profiles and we have shown that anion modulation and substituent modulation play a pivotal role in Mn$^{III}$ SCO. We have also reported the first example of a Mn$^{III}$ compound with an abrupt and complete thermal spin transition and opening of an 8 K hysteresis window.$^{[1]}$ We now report here two types of symmetry breaking which has not been observed in the case of Mn$^{III}$. One driven by the resolving of disorder of the normally passive BPh$_4^{-}$ anion$^{[2]}$ and the other driven by the cation. This occurs through the breaking of hund’s rule which drives Jahn-Teller and spin state ordering. The transition also occurs with the presence of a hysteresis loop.

References


Spin crossover vs $\pi-\pi$ stacking in a family of $[\text{Fe}(\text{H}_2\text{B}(\text{Pz})_2)L]$ complexes

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The abrupt switch between high spin (HS) and low spin (LS) state in spin crossover (SCO) system is an indication of strong cooperativity.$^{[1]}$ It might result in a hysteresis which is desirable from an application point of view.$^{[2]}$ The cooperativity is a function of a crystal lattice and can be derived from hydrogen bonding, $\pi-\pi$ interactions and van der Waals forces. Strong cooperativity can be achieved by the increase of mechanical coupling between spin centres.$^{[3]}$

In order to systematically investigate how the large surface contact areas and extended $\pi-\pi$ interactions will influence magnetic properties the family of $[\text{Fe}(\text{H}_2\text{B}(\text{Pz})_2)L]$ complexes (Fig.1) has been synthesised, where L is an aromatic ligand based on dipyridoquinoxaline backbone differing in number of arene rings. The relationship between crystal packing and magnetic properties will be discussed.

References

Fig. 1: Fe(II) complexes of dihydrobis(1-pyrazolyl)borate with aromatic moieties based on dipyridoquinaxaline.
Multifunctional magnets as probes: sensing chemical processes through magnetometry


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The interplay of a wide range of properties in multifunctional molecular magnets have the potential to be utilised as a probe for sensing chemical processes in the solid state and in solution.

First, a new discrete [V_{16}O_{38}(CN)]^{9−} cluster, which displays the until-now unknown 8−charge on the cluster shell and is the first to encapsulate the cyanide anion, has been synthesised and characterised by IR and UV/Vis/NIR spectroscopy, electro-chemistry, magnetic susceptibility measurements.[1] Bond valence sum analysis of K_{9}[V_{16}O_{38}(CN)]∙13H_{2}O confirms that this new member of the polyoxovanadate series is a mixed-valence complex with intervalence charge transfer bands arising from intra-metal interactions with a small degree of electronic delocalisation. Given the marked differences in magnetic interactions between clusters form the literature with different oxidation states, the redox properties of this cluster indicate a method of magnetic detection of redox reaction. Interesting possibilities exist for the incorporation of this unit into higher dimensionality framework structures where the redox, optical and magnetic properties can be exploited and tuned.

Second, a porous Ni(II) metal-organic framework (MOF) where solvation of the metal centre results in changes to the magnetic properties of the Ni(II) ion allowing us to decouple the pore and metal solvation processes through magnetometry, while giving an independent colourimetic response.[2]

Figure: a) [V_{16}O_{38}(CN)]^{9−} cluster displaying encapsulated cyanide; b) time-dependent susceptibility measurement of the solvation of Ni(II) centres.

References
Tailoring the Self-Assembly and Magnetic Switchability of Fe(III) Complexes

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Molecular entities that possess two magnetically stable states are presumed to be the key component for the next generation of data storage and processing devices. As abrupt transitions with a hysteresis loop are desired for device operations, rational approaches towards tailoring the magnetic activity of spin crossover (SCO) systems are of current interest. Supramolecular principles, via the incorporation of molecular recognition sites, may be exploited to induce cooperative SCO behaviour both in solution and in multilayered systems.

Herein we present a new class of sal₂(trien) iron(III) complexes (Fig. 1) which incorporate dialkylurea groups of various lengths at the sal₂(trien) backbone. These modifications have a negligible effect on the spectroscopic and electrochemical properties of the iron(III) centres, but affect their spin-crossover behaviour and assembly into Langmuir-Blodgett films. We will discuss the impact of these synthetic modifications on the magnetic bistability of these supramolecularly tailored complexes both in solution and at the air-liquid interface.

Figure 1: UV-visible absorption spectra for the high-spin (HS) and low-spin (LS) states; (inset) general structure of Fe(III) SCO complexes.

References
Linear and nonlinear stationary ac response of the magnetization of nanomagnets in the presence of thermal agitation and spin-transfer torques

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Thermal fluctuations of nanomagnets driven by spin-polarized currents are treated via the Landau- Lifshitz-Gilbert equation generalized to include both the random thermal noise field and the Slonczewski spin-transfer torque term. The statistical moment method [1] for the study of out-of-equilibrium time independent observables of the generic nanopillar model of a spin-torque transfer (STT) device subjected to thermal fluctuations is extended to the stationary time dependent observables arising from applied a.c. field. The virtue of our solutions is that they hold for the most comprehensive formulation of the generic nanopillar model, i.e., for arbitrary directions of the external field and spin polarization and for arbitrary free energy density, yielding the STT switching characteristics under conditions otherwise inaccessible. The dynamic magnetic susceptibility is determined for an a.c. field of arbitrary strength.

References
Spin crossover (SCO) is a phenomenon characteristic of d$^4$ – d$^7$ transition metals, and since its discovery SCO complexes have been rigorously studied due to their potential applications in data storage, display devices and thermosensitive MRI contrast agents. In light of this, a number of SCO complexes of iron(II) have been prepared using ligands based on 2,6-di(pyrazolyl)pyridine (3-bpp) derivatives. An isomer of 3-bpp, 2,6-di(pyrazol-1-yl)pyrazine (1-bpp), has played a large part in spin crossover research and has been substituted on every position$^{[1]}$, and so a main focus of this project has been to synthesise their corresponding 3-bpp isomers in an effort to compare their SCO behaviour. Firstly 3-bpp was substituted at the pyrazole 5 position, and various substituents which incorporate steric bulk, inductive effects, electron withdrawal and hydrogen bonding capabilities in an effort to manipulate the spin transition. Second, the pyrazole NH position was alkylated in an effort to imitate isostructural complexes of 1-bpp which proved to exhibit interesting SCO effects$^{[2]}$. Various salts of these complexes using relatively non-coordinating anions have been studied by X-ray diffraction, SQUID measurements and NMR, and it has shown that their behavior is not in fact analogous to their 1-bpp counterparts in that they remain high spin even at low temperatures. This in itself is interesting and has been attributed to a mixture of subtle steric and electronic effects which manifest itself both in solution and the solid state.

References

A Theoretical Study of the Magnetic Properties of Benzotriazinyl-based Molecular Materials

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The rationalization of the magnetic properties of organic radicals is a challenging issue. In those materials, the exchange coupling constants ($J_{AB}$) values are often highly sensitive to small structural distortions caused by thermal effects, thus introducing a notable dependence of its strength on temperature.(1) This fact hinders the interpretation of the magnetic behaviour and evinces the well-known drawbacks(2) of the usual fitting procedures to extract the $J_{AB}$ values from temperature-dependent magnetic data. To aid in this purpose, theoretical methods have been demonstrated to be extremely helpful when a rigorous modelling is carried out.

Herein, we present a theoretical study of the magnetic properties of two benzotriazinyl-based molecular materials, (see Figure). These systems belong to a new family of organic radicals that has raised interest in the last few years.(3) First, high-level $ab$ initio calculations support the usage of DFT to describe the magnetic exchange interactions on those systems. Second, variable-cell geometry optimizations evince the importance of the thermal expansion on the strength of the $J_{AB}$ values and allow us to reproduce the magnetic susceptibility with notable accuracy. Third, Carr-Parrinello Molecular Dynamics simulations reveal the effect of the vibrational motion on the $J_{AB}$ values and uncover the different nature of the structural disorder found in the X-Ray crystal structures. Finally, we present a deep study of the valuable magneto-structural correlations for this family of radicals showing π-slipped staking.

References
Chiral domain wall profiles and magnetization reversal rates in finite-sized magnetic nanoparticles.

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Superparamagnetism, a phenomenon where thermal fluctuations drive transitions across energy barriers separating anisotropy minima in nanoscale magnets, limits the storage density of conventional magnetic memory devices. A detailed understanding of the mechanisms of magnetic switching and reversal rates in magnetic nanoparticles is thus critical for the continued improvement of magnetic memory devices, and for harnessing novel spintronic devices.

Here we present an analytically solvable model describing the energy density of a magnetic nanoparticle deposited on an in-plane magnetized thin film substrate. Our model is used to elucidate the formation of size-dependent chiral spin spirals in such systems, which have been seen in recent experiments.[1] Our formulation allows for an analytical determination of both the spiral profile and the energy density of the domain wall in finite length, significantly extending past work which considered similar structures in infinite length nanowires.

As information may potentially be stored in the two chiral states of the spin spirals we then consider their stability with respect to small fluctuations. We find that in the limit of vanishing external field, the operators describing fluctuations about these finite spiral structures may be described by a Schrödinger-type equation which allows us to determine an exact eigenbasis for the thermal fluctuations about our magnetization profile and so to determine the switching rate.

Reference
How strong is the magnetic field exhibited by lanthanoid dimers?

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An infinite lattice of antiferromagnetically coupled lanthanoid would cancel their magnetic moments and such a solid would not be considered a magnet. In SMM chemistry oxo-bridged lanthanoid dimers are a common motif. Although those lanthanoids are often antiferromagnetically coupled they can exhibit slow relaxation of the magnetization with high energy barriers and blocking temperatures. Nevertheless the cancellation effect of the magnetic fields is unknown, raising the question after the strength of the magnetic field exhibited by such a magnet. For this reason we investigated two different centrosymmetric Fe\textsubscript{4}Ln\textsubscript{2} clusters that both contain Ln\textsubscript{2} units surrounded by strongly antiferromagnetically coupled Fe\textsubscript{2} moieties. Although [Fe\textsubscript{4}Ln\textsubscript{2}(\mu\textsubscript{3}-OH)\textsubscript{2}(n-bdea)\textsubscript{4}(piv)\textsubscript{6}(N\textsubscript{3})\textsubscript{2}] (1) \textsuperscript{11} and Fe\textsubscript{4}Ln\textsubscript{2}(\mu\textsubscript{4}-O)\textsubscript{2}(piv)\textsubscript{6}(NO\textsubscript{3})\textsubscript{2}(EtOH)\textsubscript{2}(pdea)\textsubscript{4} (2) both contain the same metal arrangements. In 1 the lanthanoids are antiferromagnetically coupled in 2 the coupling is ferromagnetic. The magnetic field created by both lanthanoid dimers is measured by \textsuperscript{57}Fe Mößbauer spectroscopy in the form of a Zeeman splitting induced on the nuclear spin states of the Fe\textsuperscript{III} nuclei (fig. 1).

References

Nano-Assembly of Spin Crossover Complexes

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Bulk Complex          Nanowires of Complex

Figure 1. Plots of $\chi_MT$ vs. T for the bulk powder and the templated Fe(III) SCO nanowire sample.

Functional molecular switches have gained considerable interest for their potential technological applications. As a result the miniaturization of these functional molecular materials has been explored, to identify if there is any change to their physical properties on this scale. Spin crossover (SCO) complexes possess two distinct electronic states, a high spin and low spin configuration.\(^1\) These states are switchable in response to external stimuli such as temperature, pressure or light. A unique property that can occur in SCO systems is cooperativity.\(^2\) This effect can lead to a hysteresis loop which is vital for the integration of SCO complexes into devices.

The dimensional reduction of SCO complexes has been observed to have an effect on the magnetic behaviour of the materials. This is a result of the electronic bistability being related to the collective behaviour of the SCO centres in the crystalline lattice. We have shown that the SCO properties were retained for Fe(III) SCO complexes as seen in Figure 1.\(^3\) Here, we now probe SCO properties of Mn(III) complexes at the nanoscale. The successful preparation of a series of nanoassemblies was achieved with Mn(III) SCO complexes, including nanoparticles, nanowires, nanofibers and nanocrystals.

References:
Spin Soliton Excitations in Quantum Antiferromagnets and Dynamical Structure Factors for Neutron Scattering

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Quantum spin chains represent a paradigm for exploring truly quantum phenomena: quantum phase transitions, quantum fluctuations, frustrated spin configurations are just some of the interesting and novel properties that these systems can exhibit. Quantum spin chains are also gateway candidates to an avenue of increasing data storage density in the form of spintronics, in which 'spin currents' play a central role.

Here we investigate the interplay between low-lying excitations in antiferromagnetic quantum spin chains and spin currents, and how such excitations can be measured by spin polarised neutrons. We consider compounds such as CsCoBr₃ whose low energy excitations are described by the anisotropic $XXZ$ Heisenberg model.[1] In particular, we compute the dynamical structure factor for spin soliton pair creation and spin soliton scattering, which can be directly compared to neutron scattering data.

Our results demonstrate that spin soliton pair creation and spin soliton scattering can be distinguished by neutron scattering. Our findings also illustrate that the thermally-activated spin soliton scattering leads to a dominant longitudinal response,[2] while the soliton pair creation leads to a strong (transverse) spin wave response.[3] In addition to this, calculations include both sets of excitations being in the presence of an external transverse magnetic field.

References