



**RISING STARS
SYMPOSIUM 2021**

A Satellite Meeting of The International Conference on Molecular Magnetism 2021

10th & 11th June 2021



**ICMM2021
MANCHESTER**

We welcome you to the **Rising Stars Symposium** of ICMM2021. This satellite meeting is an online pre-conference event that will last for a day and half, commencing on the morning of Thursday, 10th June (UTC+1, UK time).

The focus of this meeting is to provide opportunities for early career researchers to present their research and to network with their peers in the broad fields of molecular magnetism and functional molecular materials and devices. Whilst the broad themes of this symposium are in the synthesis, characterisation and calculations of magnetic materials and molecular magnets, we welcome scientists from the wider community to take part, as for example from areas including electronic devices, electronic conductors, ionic conductors, surface science, supramolecular self-assembly, MOFs and synergistic materials. We aim to be inclusive of all early career researchers, considered to be anyone between postgraduate and established career stages.

We hope you enjoy the invited talks and flash presentations provided by some of the most promising early career researchers in the field of molecular magnetism.

The organising committee of the Rising Stars Symposium 2021

Dr Floriana Tuna

Dr Daniel Reta

Dr Helena Shepherd

Programme at a Glance

UK (UTC+1)	Japan (UTC+9)	USA (UTC-7)	Thursday 10 th June	Friday 11 th June
07:25			Welcome	
			Chair: Guillaume Chastanet	Chair: Jürgen Schnack
07:30	15:30	23:30	Itziar Oyarzabal	Irina Kuhne
07:50	15:50	23:50	Mauro Perfetti	Victor Garcia Lopez
08:10	16:10	00:10	Dimitris Alexandropoulos	Le Tuan Anh Ho
08:30	16:30	00:30	Claudio Bonizzoni	Alessandro Chiesa
09:10 – 09:40 FLASH PRESENTATIONS	17:10 – 17:40	01:10 – 01:40		Peng-Bo Jin
				Simone Chicco
				Isaac Alcon
				Kubandiran Kolanji
				Diana Plesca
			Chair: Alessandro Lunghi	Chair: Eva Rentschler
10:00	18:00	02:00	Giulia Serrano	Krishna Kaushik
10:20	18:20	02:20	Georgios Velkos	Jakub Zakrzewski
10:40	18:40	02:40	Jon Kragsskow	Catalin Maxim
11:00	19:00	03:00	Aman Ullah	Juan-Ramon Jimenez
11:40 -12:10 FLASH PRESENTATIONS	19:40 – 20:10	03:40 – 04:10		Maciej Korzynski
				Selena Lockyer
				Lorenzo Tesi
				Thomas Lohmiller
				Closing remarks
			Chair: Carolina Sañudo	
18:00	02:00	10:00	Xuanyuan Jiang	
18:20	02:20	10:20	Veascheslav Vieru	
18:40	02:40	10:40	Alena Sheveleva	
19:00	03:00	11:00	Nathan Yutronkie	
19:40 – 20:10 FLASH PRESENTATIONS	03:40 – 04:10	11:40 – 12:10	Gemma Gransbury	
			Vijay Parmar	
			Colin Gould	
			James Durant	
			Yan Duan	
			Chair: Joe Zadrozny	
20:30	04:30	12:30	Pierre Dechambenoit	
20:50	04:50	12:50	Angelos Tsanai (A. B. Canaj)	
21:10	05:10	13:10	Kieran Hymas	
21:30	05:30	14:30	Sandhya Singh	

Detailed Programme, Thursday 10th June

Start time (UK, UTC+1)	Speaker	Title
07:25		Welcome to the Symposium
Session 1, Chair: Guillaume Chastanet		
07:30	Itziar Oyarzabal	A redox-active coordination chemistry approach to magnetic and/or conductive materials
07:50	Mauro Perfetti	Trends in magnetic anisotropy: the f^{n+7} effect
08:10	Dimitris Alexandropoulos	Magnetic materials based on rare earth porphyrin building blocks
08:30	Claudio Bonizzoni	Resonant and Dispersive Spectroscopy of Molecular Spin Ensembles through Planar Microwave Resonators
Session 2, Chair: Alessandro Lunghi		
10:00	Giulia Serrano	The magnetism of single molecule magnets at the interface with a type I superconductor
10:20	Georgios Velkos	Dy ₂ O-Clusterfullerenes: Strong Magnetic Anisotropies and Fullerene-Dependent Single Molecule Magnetism
10:40	Jon Kragoskow	Vibronic coupling in a 4f qubit
11:00	Aman Ullah	Theoretical insights into spin-electric couplings & vibronic relaxation pathways in clock-like molecular spin qubit: [Ho(W ₅ O ₁₈) ₂] ₉ ⁻
Session 3, Chair: Carolina Sañudo		
18:00	Xuanyuan Jiang	Vertical tunnel heterojunctions of molecular magnets
18:20	Veascheslav Vieru	Theoretical analysis of aromaticity in a triplet benzene dianion complex
18:40	Alena Sheveleva	Probing NO ₂ Adsorption and catalysis of MOFs via EPR
19:00	Nathan Yutronkie	The Design and Construction of Three-Dimensional Magnetic Exchange Networks from Bisdithiazolyl Radical Building Blocks
19:40 – 20:10 FLASH PRESENTATIONS	Gemma Gransbury	Valence Tautomerism in Bis(dioxolene)-Bridged Dinuclear Cobalt Complexes: Correlating Two-Step Transitions with Redox and Mixed-Valence Properties
	Vijay Parmar	Probing relaxation dynamics in Dy-Aryloxide Single-Molecule Magnets
	Colin Gould	Magnetism and electronic structure of divalent lanthanide metallocene complexes
	James Durant	Cyclobutadienyl Chemistry of the Rare-Earth Elements
	Yan Duan	Data mining, dashboards and statistics: a powerful framework for the chemical design of molecular nanomagnets
Session 4, Chair: Joe Zadrozny		
20:30	Pierre Dechambenoit	How to promote large magnetic exchange and spin delocalization using redox-active π bridging ligand
20:50	Angelos Tsanai (A. B. Canaj)	Slow Magnetic Relaxation in High Performance Macrocyclic Dysprosium (III) Single-Molecule Magnets
21:10	Kieran Hymas	Simulating the Rich Spin Dynamics of Magnetic Molecules: From Molecular Spintronics to Single-crystal Magnetisation
21:30	Sandhya Singh	Spin crossover in Iron(II) dinuclear helicates & tetranuclear cages

Detailed Programme, Friday 11th June

Start time (UK, UTC+1)	Speaker	Title
Session 5, Chair: Jürgen Schnack		
07:30	Irina Kuhne	Investigation on ligand substituent effects on Mn(III) Spin Crossover Complexes
07:50	Victor Garcia Lopez	Spin-crossover self-assembled monolayers
08:10	Le Tuan Anh Ho	Magnetization relaxation in weakly exchange coupling <i>3d-4f</i> Single-molecule magnet system: a perspective theoretical viewpoint
08:30	Alessandro Chiesa	A molecular qubit sensor of chiral-induced spin selectivity
09:10 – 09:40 FLASH PRESENTATIONS	Peng-Bo Jin	A Study of Cation-Dependent Inverse Hydrogen Bonds and Magnetic Exchange-Couplings in Lanthanacarborane Complexes
	Simone Chicco	Controlled coherent dynamics of [VO(TPP)], a prototype molecular nuclear qubit with an electronic ancilla
	Isaac Alcón Rovira	Controlling Pairing of π -Conjugated Electrons in 2D Covalent Organic Radical Frameworks via In-plane Strain
	Kubandiran Kolanji	Singlet and Triplet Ground State Spin-dimers on Nitroxide Free-radicals Connected with Aromatic π -Conjugated Systems
	Diana Plesca	Unexpected Light-Induced Thermal Hysteresis in Matrix Embedded Low Cooperative Spin Crossover Microparticles
Session 6, Chair: Eva Rentschler		
10:00	Krishna Kaushik	Reversible Photo and Thermo-induced Spin-State Switching in a heterometallic $\{5d-3d\}$ W_2Fe_2 Molecular Square Complex
10:20	Jakub Zakrzewski	Functionalization of Yb(III) molecular nanomagnets using cyanido metal complexes
10:40	Catalin Maxim	Chirality driven self-assembly in copper(II) coordination polymers
11:00	Juan-Ramon Jimenez	Mixed Valence M_4Fe_4 (M = Co, Mn) Molecular Cages encapsulating cations: solution and solid-state electronic properties
11:40 - 12:10 FLASH PRESENTATIONS	Maciej Korzynski	Surface deposition of a single-molecule magnet with improvement of the dynamic magnetic properties
	Selena Lockyer	The control of J-coupling via rotaxane methodology
	Lorenzo Tesi	High Frequency EPR: New Tools for Investigating Thin Layers of Molecular Magnets
	Thomas Lohmiller	Accurate Determination of Spin-Spin Interactions in CoII Single-Chain Magnets and Antiferromagnetic CuII Complexes by THz-EPR
	Closing remarks	

Invited Talks – Abstracts

Session 1: Thursday 10th June

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

Itziar Oyarzabal^{1,2,3}, Panagiota Perlepe^{1,4}, Kasper S. Pedersen^{1,5}, Corine Mathonière^{1,4}, Rodolphe Clérac¹

¹Centre de Recherche Paul Pascal, Pessac, France. ²BCMaterials, Basque Center for Materials, Applications and Nanostructures, Leioa, Spain. ³Ikerbasque, Basque Foundation for Science, Bilbao, Spain. ⁴Institut de Chimie de la Matière Condensée de Bordeaux, Pessac, France. ⁵Technical University of Denmark, Lyngby, Denmark

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

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

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

References: (1) P. Perlepe, I. Oyarzabal, A. Mailman, M. Yquel, M. Platunov, I. Dovgaliuk, M. Rouzières, P. Négrier, D. Mondieig, E. A. Suturina, M.-A. Dourges, S. Bonhommeau, R. A. Musgrave, K. S. Pedersen, D. Chernyshov, F. Wilhelm, A. Rogalev, C. Mathonière, R. Clérac, *Science* **2020**, *370*, 587; (2) K. S. Pedersen, P. Perlepe, M. L. Aubrey, D. N. Woodruff, S. E. Reyes-Lillo, A. Reinholdt, L. Voigt, Z. Li, K. Borup, M. Rouzières, D. Samohvalov, F. Wilhelm, A. Rogalev, J. B. Neaton, J. R. Long, R. Clérac, *Nat. Chem.* **2018**, *10*, 1056; (3) K. S. Pedersen, P. Perlepe, L. Voigt, M. Kubus, I. Oyarzabal, D. N. Woodruff, S. E. Reyes-Lillo, M. L. Aubrey, B. Vignolle, P. Négrier, F. Wilhelm, A. Rogalev, J. B. Neaton, J. R. Long, R. Clérac, *in preparation*.

Trends in magnetic anisotropy: the f^{n+7} effect

Matteo Briganti¹, Eva Lucaccini¹, Laura Chelazzi², Samuele Ciattini², Lorenzo Sorace¹, Roberta Sessoli¹, Federico Totti¹, Mauro Perfetti¹

¹Department of Chemistry, University of Florence, Florence, Italy. ²Centre of Crystallography, University of Florence, Florence, Italy

The magnetic anisotropy of the second half of the LnDOTA (H₄DOTA= tetraazacyclododecane-N,N',N'',N'''-tetraacetic acid) series is considered a benchmark in molecular magnetism.[1-5] The anisotropy of the full LnDOTA series (Ln = Ce to Yb) is here unravelled combining torque magnetometry measurements and ab initio calculations. [6] This allowed extending the trends previously noticed in the second half of the series,[2] to the full series.

Thanks to this bird-eye view, a yet unnoticed correspondence has been identified: the *anisotropy reference frame* (i.e. the easy, intermediate and hard direction) of derivatives differing by 7 f-electrons coincides (Figure 1). However, the low-temperature *magnetic anisotropy shape* of some couples is *not* the same (e.g. Pr is easy plane and Dy is easy axis, see Figure 1). We found that the origin of this discrepancy is a subtle competition between the Hund's rules and the Aufbau principle. We also deliver a general way of explaining this phenomenon based on the filling of the f-orbitals.

This trend seems to be generally applicable to low symmetry 4f-complexes, that constitute most of the lanthanide molecules reported so far. Moreover, it allows to save computational power and provides a convenient shortcut to determine the magnetic anisotropy of poorly magnetic ions (e.g. Sm³⁺ and Eu³⁺), which are difficult to investigate experimentally.

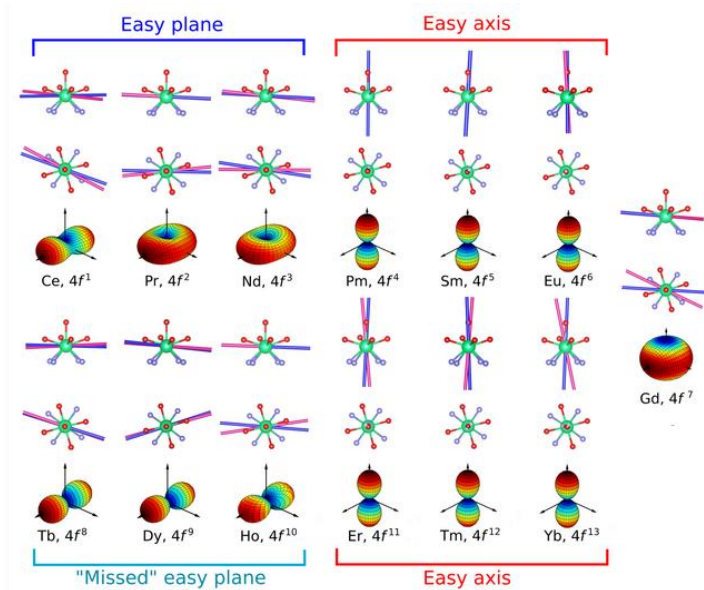


Figure 1. Experimental (pink) and theoretical (blue) orientation of the easiest axis of LnDOTA. The 3D coloured shapes are the calculated susceptibility tensors at 2 K and 1 nT.

References:

[1] Cucinotta et al., *Angew. Chem.* **2013**. [2] Boulon et al., *Angew. Chem.* **2013**. [3] Chilton et al., *Nat. Comm.*, **2013** [4] Briganti et al., *submitted*, **2021**. [5] Car et al., *Chem. Comm.* 2011. [6] Briganti et al., *Chem. Sci.* **2019**.

Magnetic materials based on rare earth porphyrin building blocks

Dimitris I. Alexandropoulos,¹ Jeff M. Van Raden,² Michael Slota,¹ Simen Sopp,¹ Harry L. Anderson,^{*2} and Lapo Bogani^{*1}

¹ Department of Materials, University of Oxford, OX1 3PH, Oxford, UK ² Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Oxford, OX1 3TA, UK

Porphyrin oligomers constitute a thriving area of research, particularly as model systems for light harvesting, catalysis, and molecular electronics. In the latter case, porphyrin tapes are promising candidates as they often possess exceptionally strong π -conjugation and a shallow length-dependence of the single-molecule conductance [1]. Diamagnetic porphyrin tapes, containing zinc(II), have been thoroughly investigated, however there have been few studies of the magnetic properties of tapes hosting paramagnetic metal centers.

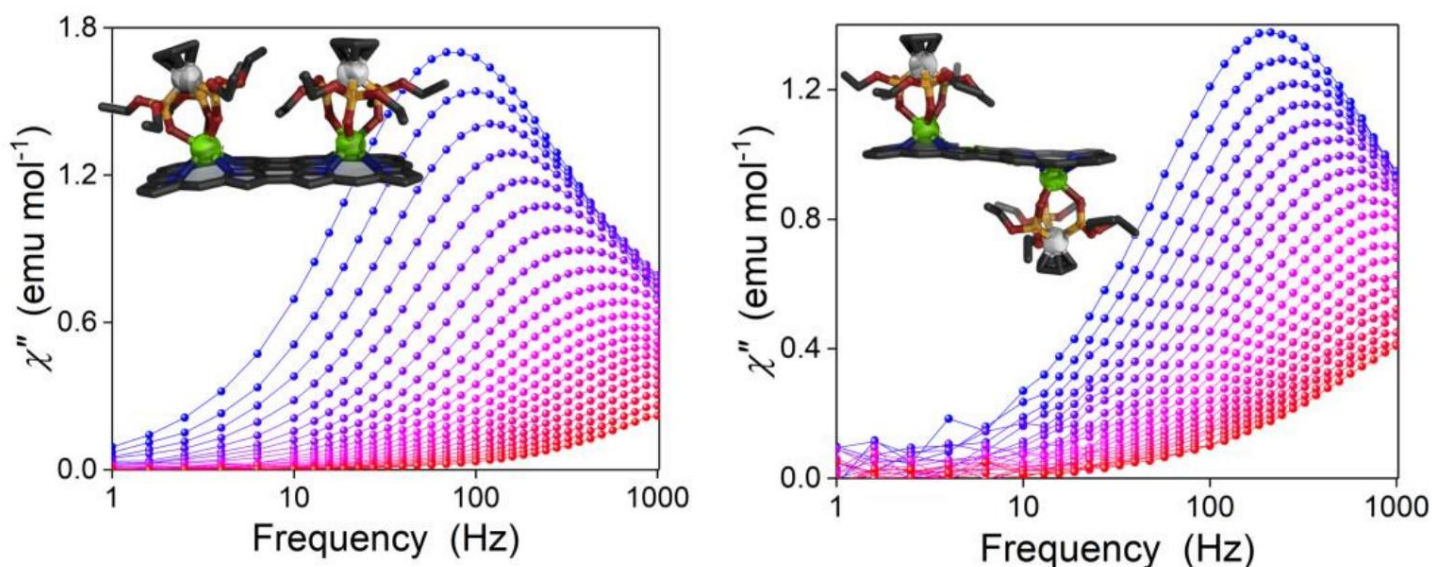


Figure 1. Frequency dependence of the out-of-phase (χ'') signal for the rare earth porphyrin complexes that will be discussed.

Herein, we investigate fused porphyrin rare earth dimers, as models for longer tapes with multiple metal centers. The synthesis and characterization of two stereoisomeric binuclear metal complexes: the syn isomer, in which both lanthanide metal centers are on the same face of the π -system and the anti isomer, in which the metals are on opposite faces, is reported.

References:

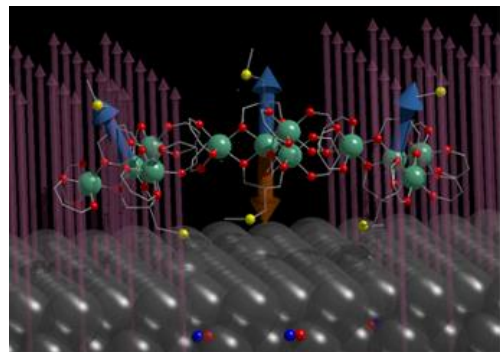
[1] A. Tanaka, A. Osuka, Chem. Soc. Rev. 44, 943–969 (2015).

The magnetism of single molecule magnets at the interface with a type I superconductor

Giulia Serrano¹, Lorenzo Poggini², Matteo Briganti³, Andrea Luigi Sorrentino¹, Giuseppe Cucinotta³, Niccolò Giaconi¹, Luigi Malavolti⁴, Brunetto Cortigiani³, Danilo Longo⁵, Edwige Otero⁵, Philippe Saintavit⁶, Sebastian Loth⁴, Alessandro Vindigni⁷, Francesca Parenti⁸, Anne-Laure Barra⁹, Andrea Cornia⁸, Federico Totti³, Matteo Mannini³, Roberta Sessoli³

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Recently, physical phenomena interesting for spintronic applications have been found by coupling magnetic materials and superconductors.¹ For example, molecular spins deposited on superconductive surfaces led to the observation of localized magnetic states, known as Yu–Shiba–Rusinov bound states,² or enhanced molecular spin lifetimes.³ The interaction with superconductors could then open an interesting perspective also for SMM control, then renewing the interest in using these molecules as nanosized building blocks for spintronic applications.⁴ Here I will present a route for controlling the magnetism and quantum features of diverse SMM systems through superconductive surfaces. SMM films are deposited on the surface of superconductors and investigated by combining scanning tunneling microscopy, photoemissions techniques, and synchrotron experiments. Thanks to these studies,⁵ it is revealed that the transition of the substrate to the superconducting state strongly affects the magnetization of Fe₄ SMMs complexes that locally switch from a blocked magnetization state to a resonant quantum tunnelling regime.⁶ Additionally, by using another archetypal SMM system, the TbPc₂ complex, it is found that molecular films can be used to detect the magnetic hysteresis of the superconducting substrate that is caused by the different topology of superconducting domains when the substrate enters or exits from the superconducting state.⁷ These innovative studies open interesting perspectives for controlling SMMs in spintronic devices as well as for their use as local probes for superconducting materials.



References:

- [1] Linder, J. et al., Nat. Phys., **11**, 307 (2015).
- [2] Malavolti, L. et al., Nano Lett., **18**, 7955 (2018).
- [3] Heinrich, B. W. et al., Nat. Phys., **9**, 765 (2013).
- [4] Gatteschi, D. et al., *Molecular Nanomagnets*, Oxford University Press, (2006).
- [5] Financial support by the EU Commission through the FATOPEN project FATMOLS (GA 862893).
- [6] Serrano, G. et al., Nat. Mater., **19**, 546 (2020).
- [7] Serrano, G. et al., *in preparation*.

Dy₂O-Clusterfullerenes: Strong Magnetic Anisotropies and Fullerene-Dependent Single Molecule Magnetism

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Fullerenes possess the unique property to stabilize various atomic species inside their empty space. When lanthanide ions are encapsulated, the endohedral fullerene can transform into a single molecule magnet [1]. Particularly, the bonding situation between two Dy³⁺ ions and one O²⁻ ion inside the carbon cage, results to the new class of Dy₂O-clusterfullerenes. Presence of O²⁻ ion in short distance from Dy³⁺ ions (≈ 2 Å) imposes very strong axial anisotropy to the latter [2]. We report on three different Dy₂O-clusterfullerenes: Dy₂O@C₇₂, Dy₂O@C₇₄ and Dy₂O@C₈₀. All three exhibit high blocking temperature of magnetization and broad hysteresis [3]. Dy-Dy magnetic coupling is characterized by the competing exchange and dipolar interactions. In Dy₂O@C₇₂, ferromagnetic coupling prevails while in Dy₂O@C₈₀ the antiferromagnetic does. In case of Dy₂O@C₇₄, exchange and dipolar contributions cancel each other leading to effectively decoupled Dy moments and appearance of zero-field quantum tunnelling of magnetization (see below).

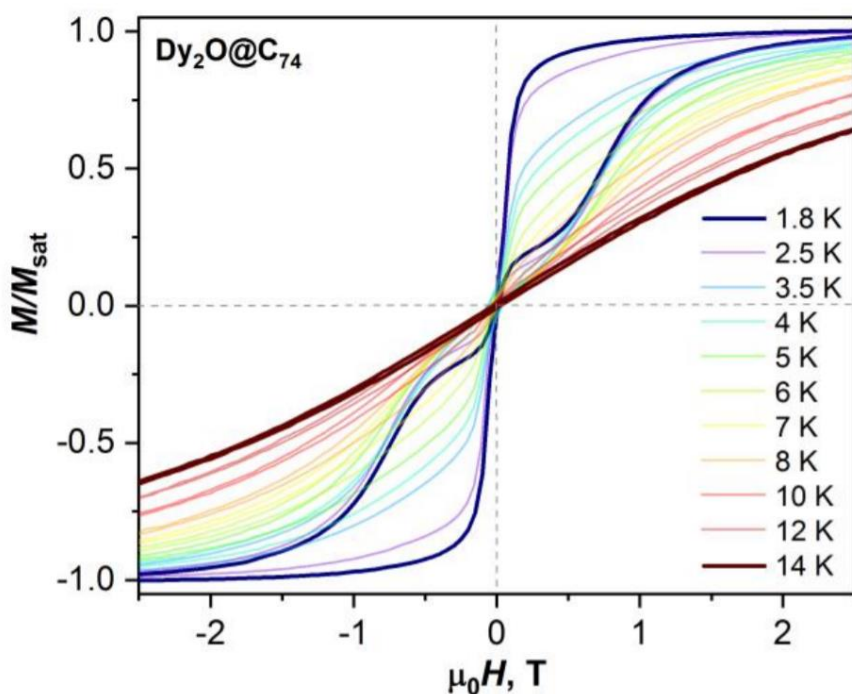


Figure. Magnetic hysteresis curves of Dy₂O@C₇₄ below blocking temperature ($T_B=14$ K)

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

References:

- [1] A. A. Popov, S. Yang and L. Dunsch, Chem. Rev., 113, 5989 (2013) [2] W. Yang, G. Velkos., A. A. Popov, Adv. Sci., 6(20), 1901352 (2019) [3] G. Velkos, W. Yang, A. A. Popov, Chem. Sci., 11(18), 4766-4772 (2020)

Vibronic coupling in a 4f qubit

Jonathan Marbey^{1,2}, Jon Kragoskow³, Christian Buch⁴, Joscha Nehrkorn¹, Mykhaylo Ozerov¹, Stergios Piligkos⁴, Stephen Hill^{1,2}, Nicholas Chilton³

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Vibronic coupling, the interaction between molecular vibrations and electronic states, is a pervasive effect that profoundly affects chemical processes. In the case of molecular magnetic materials, vibronic, or spin-phonon, coupling leads to magnetic relaxation, which equates to loss of magnetic memory and loss of phase coherence in molecular magnets and qubits, respectively. The study of vibronic coupling is challenging, and most experimental evidence is indirect. Here we employ far-infrared magnetospectroscopy to probe vibronic transitions in a Yb^{III} molecular qubit directly. We find intense signals near electronic states, which we show arise due to an “envelope effect” in the vibronic coupling Hamiltonian, and we calculate the vibronic coupling fully *ab initio* to simulate the spectra. We subsequently show that vibronic coupling is strongest for vibrational modes that simultaneously distort the first coordination sphere and break the C₃ symmetry of the molecule. With this knowledge, vibrational modes could be identified and engineered to shift their energy towards or away from particular electronic states to alter their impact. Hence, these findings provide new insights towards developing general guidelines for the control of vibronic coupling in molecules.

Theoretical insights into spin-electric couplings and vibronic relaxation pathways in clock-like molecular spin qubit: $[\text{Ho}(\text{W}_5\text{O}_{18})_2]^{9-}$

Aman Ullah¹, Junjie Liu², Avery Blockmon³, Yan Duan¹, Jose J Baldovi¹, Eugenio Coronado¹, Janice L Musfeldt³, Arzhang Ardavan², Juan Arago¹, Alejandro Arino¹

¹Instituto de Ciencia Molecular, Universitat de Valencia, Valencia, Spain. ²CAESR, Department of Physics, University of Oxford, Oxford, United Kingdom. ³Department of Chemistry, University of Tennessee, Knoxville, USA

Electrical control over spins at the nanoscale provides significant architectural advantages in spintronics devices. To employ magnetic molecules in this context one needs to understand the response of molecular and electronic structures to an electric field. Herein, we study the spin-electric couplings (SEC) in molecular nanomagnet $[\text{Ho}(\text{W}_5\text{O}_{18})_2]^{9-}$, whose spin qubit dynamics are protected against magnetic noise at optimal operating points known as atomic clock transitions. To seek insight into the relationship between applied electrical field (E-field) and clock-transition frequency (δf), we first decompose the molecular distortion attained by E-field into the vibrational basis. And finally calculating the spin-energy spectrum at these electrically induced distortions at *ab-initio* level, we determine the change in δf as function of applied E-field, which ultimately gives a strength of spin-electric couplings (SEC) of order $\sim 10^5 \text{V/m}$, see figure Left. These finding of strong E-field couplings is a step towards coherent spin-photon interface in spintronics devices. [1]

This theoretical effort leaves us in an excellent position to model vibronic coupling, facilitating insights into the relaxation mechanisms in spin qubits and Single Ion Magnets. Our theoretical findings are helpful to comprehend the magnetic-dependent infrared signals experimentally registered for $[\text{Ho}(\text{W}_5\text{O}_{18})_2]^{9-} \cdot 35\text{H}_2\text{O}$ and unravel the vibrational decoherence pathways and provide a strategy for designing molecular spin qubits with improved coherence lifetimes see figure Right. [2]

These outcomes advance the understanding for coherent manipulation of spin information in spintronics devices and further for controlling the dynamics by mitigating the vibronic couplings.

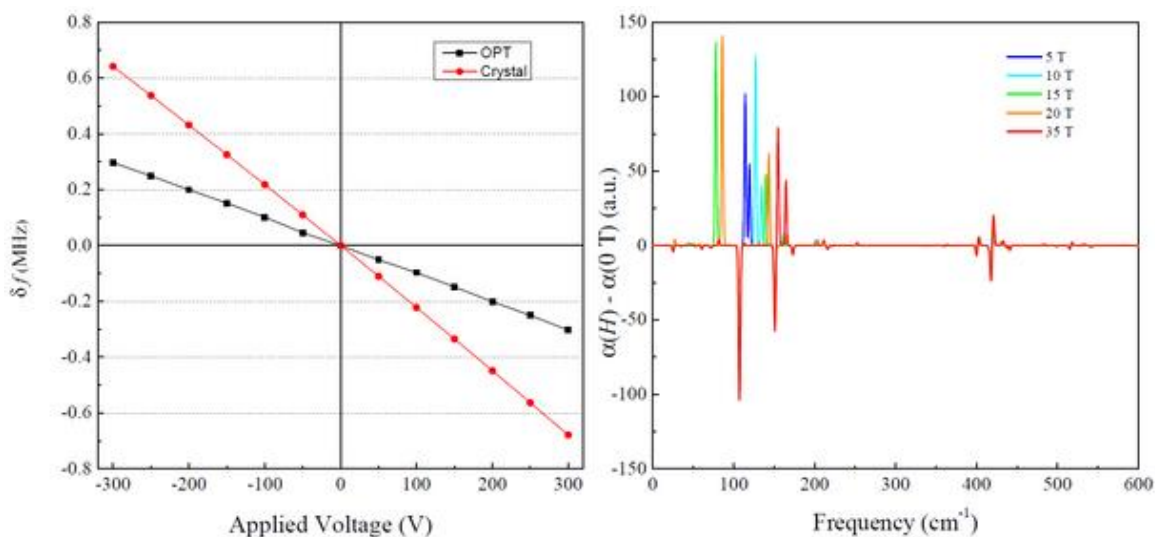


Figure: Left: Change in clock-transition (δf) as a function of the applied voltage (V) in $[\text{Ho}(\text{W}_5\text{O}_{18})_2]^{9-}$, **Right:** magneto-infrared absorption spectrum to show the vibronic relaxation pathways in $[\text{Ho}(\text{W}_5\text{O}_{18})_2]^{9-}$.

1. Liu, Junjie, et al. arXiv preprint arXiv:2005.01029 (2020).
2. Blockmon, Avery L., et al. arXiv preprint arXiv:2102.08713 (2021).

Vertical tunnel heterojunctions of molecular magnets

Xuanyuan Jiang¹, Miguel Gakiya Teruya², John Koptur-Palenchar¹, Michael Shatruk², Arthur Hebard¹

¹University of Florida, Gainesville, USA. ²Florida State University, Tallahassee, USA

The fabrication of vertical devices containing molecular magnets is hindered by the lack of proper top electrodes. Molecular magnet thin films are usually porous, and traditional vacuum sublimated top electrodes can therefore easily penetrate through the films giving rise to pinhole shorts. To overcome this problem, we have employed a soft-landing technique utilizing eutectic-GaIn (EGaIn) which, during application at room temperature as a liquid metal with strong surface tension, does not diffuse into underlying molecular thin films, and is, therefore, a robust top electrode for vertical tunnel junction (VTJ) studies. Using EGaIn counter electrodes, we have fabricated heterojunctions with two different molecules: the spin-crossover (SCO) molecule [Fe(tBu₂qsal)₂] and the anti-ferromagnetic molecule cobalt phthalocyanine (CoPc). In the 20 nm-thick SCO VTJ EGaIn/[Fe(tBu₂qsal)₂]/Pt/Si(100), the SCO transition temperature was marked by a sudden capacitance decrease near 125 K, reflecting a structural change in agreement with bulk SCO magnetization measurements. In the 5 nm-thick single-crystalized CoPc VTJ EGaIn/CoPc/ITO, a pronounced elevated anti-ferromagnetic transition temperature was observed by temperature-dependent magnetoresistance measurements to be above 6 K. We also found that in this heterojunction, the current-voltage characteristics have electric and magnetic field dependence, which may indicate the microscopic electronic and spin states in the molecular magnet multilayers. Among all these measurements, the heterojunctions are not shorted and their electronic and magnetic properties are preserved down to low temperatures. These advantages make EGaIn a promising top electrode candidate for VTJ fabrications. We also anticipate that EGaIn counter electrodes can be used on other single-molecule magnet systems with equal success.

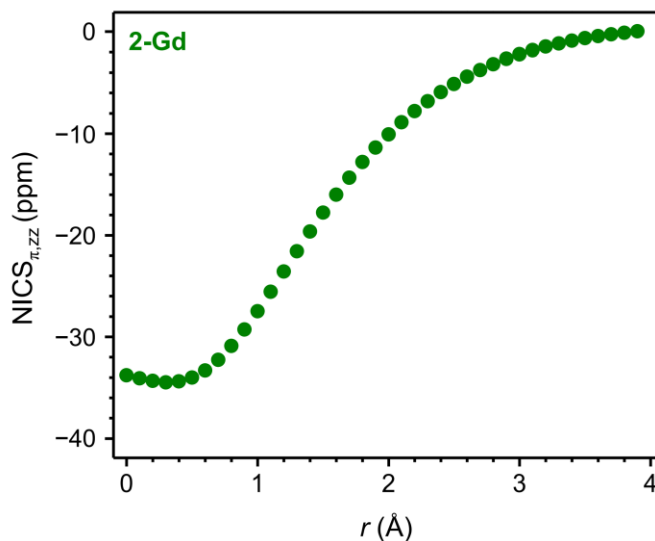
This work was supported by the Center for Molecular Magnetic Quantum Materials (M2QM), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award No. DE-SC0019330.

Theoretical analysis of aromaticity in a triplet benzene dianion complex

Veacheslav Vieru¹

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The presentation will be dedicated to the theoretical analysis of aromaticity in a recently synthesized compound [K(18-crown-6)(THF)₂]₂[Gd₂(BzN₆-Mes)] (BzN₆-Mes = 1,3,5-tris(2',6'-(*N*-mesityl)-dimethanamino-4'-*tert*-butylphenyl)-benzene) that features a triplet ground state. According to the Baird's rule this molecule should be aromatic in the triplet state given that it possesses $4n$ π electrons. Although it might seem easy, making simple ring systems with such an electronic ground state has been challenging since usually such systems undergo Jahn-Teller distortions and end up with a large singlet–triplet gap. In the compound under study the diradical dianion is stabilized through creation of a binucleating ligand that leads to a constrained inverse sandwich structure and direct magnetic exchange coupling. BS-DFT calculations predict an antiferromagnetic exchange in the Gd³⁺ congener that makes the triplet state to become the molecular ground state. Nucleus-independent chemical shift calculations together with the Harmonic oscillator model of aromaticity predict that this compound is aromatic which agrees with the Baird's rule.



References

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Probing NO₂ Adsorption and catalysis of MOFs via EPR

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Metal-organic frameworks (MOFs) are a particular class of 2D/3D porous coordination polymers made of inorganic metal nodes connected via organic linkers. Over the past decade, they have emerged as enabling materials for a wide variety of sustainable technologies. However, the considerable problem that does not allow applying these materials in the industry is the lack of stability under aggressive media or the catalytic process. The synthesis of new MOFs with desired properties is complicated by little understanding of the structure-property-activity relationship. The current study aimed to address this gap to improve our current understanding of MOF materials by Electronic Paramagnetic Resonance (EPR) Spectroscopy.

Many MOFs are magnetically active materials due to the presence of transition metal ions in the structure and formation/adsorption of organic or inorganic radicals; therefore, EPR is a powerful tool to reveal guest-host interactions and structural changes under gas adsorption and catalysis. Working in collaboration with the MOF group in Manchester, we successfully applied CW and Pulse EPR Spectroscopy for series of MOFs with outstanding properties suitable for sustainable technologies.

This presentation will discuss: (i) the first EPR studies focusing on the reversible adsorption of NO₂ in an ultra-robust MFM family MOFs including determining thermodynamic parameters of adsorption and structural characterization of adsorption sites [1]; (ii) application of EPR spectroscopy revealing the catalytic mechanism of efficient benzylic C-H oxidation under mild conditions over a robust metal-organic framework, MFM-170, with redox-active {Cu₂(II)(OOCR)₄} paddlewheels [2]; (iii) characterization of the active catalytic sites of MOF based electrodes for electrochemical CO₂ reduction [3].

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The Design and Construction of Three-Dimensional Magnetic Exchange Networks from Bisdithiazolyl Radical Building Blocks

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Pyridine-bridged bisdithiazolyl (BP) radicals are among a class of stable radical building blocks towards the design of molecular magnetic materials. Through resonance stabilization and the steric influences resulting from their beltline substituents, BP radicals have been shown to afford self-assemblies that generate three-dimensional magnetic networks through pairwise exchange interactions. To this end, the *N*-methyl-4-phenylpyridine-bridged bisdithiazolyl radical (PhBPMe) has been synthesized, crystallizing in two phases: the α -phase in the trigonal space group $P3_121$ and the β -phase in the orthorhombic space group $Pca2_1$. In the crystal structure of the β -polymorph, radicals assemble into corrugated herringbone arrays of slipped π -stacks, from which the beltline substituents restrict radical-radical close contacts to within two-dimensional motifs. However, in the α -phase, these substituents contribute to the arrangement of π -stacks into spiral motifs about 3_1 axes that propagates radical-radical interactions in three dimensions. Variable temperature magnetic susceptibility measurements on the β -phase indicate strong antiferromagnetic coupling while weaker but predominantly antiferromagnetic interactions are observed in the α -phase. Moreover, a three-dimensional antiferromagnetic state ordering below 8 K is observed for the α -phase. This presentation will discuss the selective isolation of each crystalline phase along with their corresponding magnetic behaviour, as analyzed with high temperature series expansion methods and further supported through density functional theory broken symmetry calculations.

How to promote large magnetic exchange and spin delocalization using redox-active π bridging ligand

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Magnetic properties usually result from cooperative effects between the spin carriers. The choice of the linker between the spin carriers is therefore crucial as it will mediate the communication and interactions between them. Using redox-active bridging ligands is particularly attractive as they are able to favor electronic conductivity, provide multistability and allow a certain tuning of the magnetic properties by simple oxidation or reduction.

Through a comparative study of prototype dinuclear M(II) complexes $[M_2(\text{tphz})(\text{terpy})_2](\text{PF}_6)_4$ (M = Co or Ni) containing a redox-active bridging ligand (*tphz* = *tetrapyridophenazine*) (Figure),¹ we will discuss how the electronic configuration and the oxidation states of both the metal centre and the ligand affect the strength of the magnetic exchange / spin delocalization. In particular, besides the obvious interest of stabilizing the bridging ligand at a radical form, we will see and explain how the careful selection of the metal ion based on its electronic configuration is the key step to promote the strongest possible magnetic coupling.

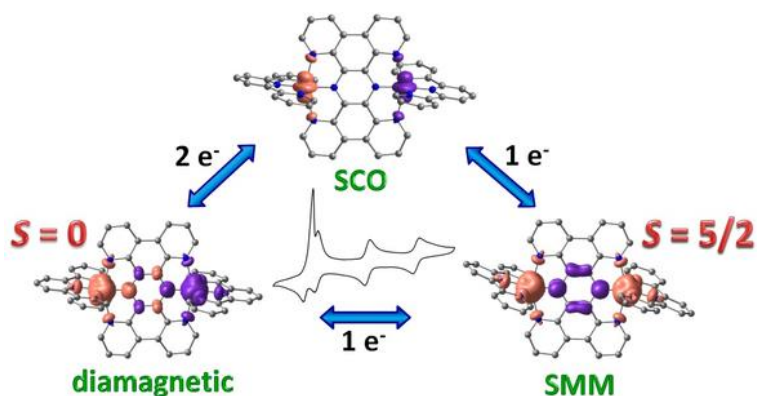


Figure. Crystal structure and computed spin density of $[\text{Co}_2(\text{tphz})(\text{tpy})_2]^{n+}$ ($n = 4$ top, $n = 3$ right, $n = 2$ left). Hydrogen atoms, solvents and counteranions are omitted.

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Slow Magnetic Relaxation in High Performance Macrocyclic Dysprosium (III) Single-Molecule Magnets

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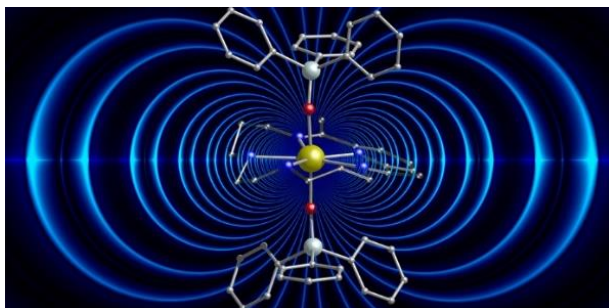
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The field of nanoscale magnetic materials has captivated the interest of chemists, physicists and materials scientists because of their promising quantum properties which can revolutionize information technology. Single Molecule Magnets (SMMs) are molecules that exhibit a measurable slow relaxation of their magnetisation by showing a bistable ground state [1]. These nanoscale magnetic materials have been suggested as very attractive candidates for advanced quantum-based devices [2]. However, the potential application of Single Molecule Magnets in data storage, quantum computing and spintronics requires the ability to function at more elevated temperatures (currently the record stands at 80 K) [3], be stable under ambient conditions and not suffer chemical modifications under heat or air. After the pioneering work of Ishikawa et al., reported in 2003 on the terbium bis-phthalocyanine SMM, lanthanide based SMMs have played a great role in the progress of molecular magnetism[4].

In this work I will present an elegant synthetic strategy, reported for the first time, towards the improvement of the magnetic behaviour of novel dysprosium SMMs using macrocyclic ligands [5-6].



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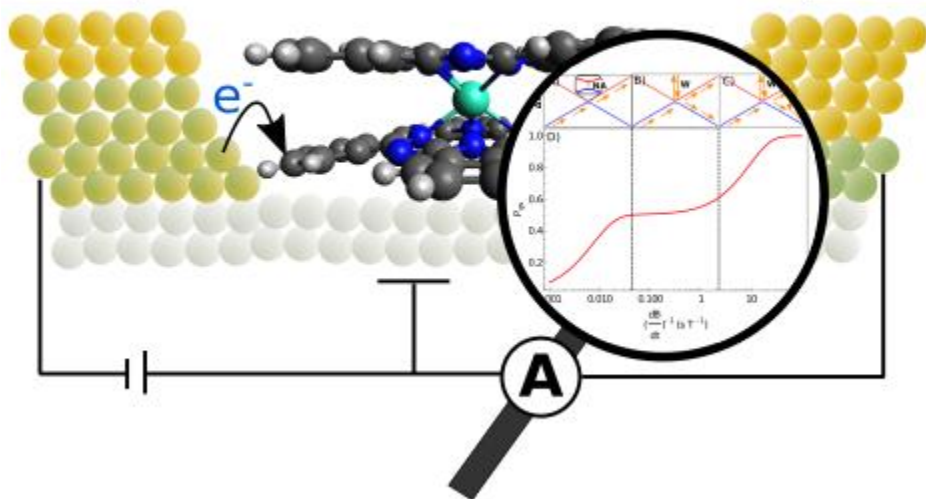
Simulating the Rich Spin Dynamics of Magnetic Molecules: From Molecular Spintronics to Single-crystal Magnetisation

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For the implementation of molecular magnets in future nanoscale technologies, the ability to manipulate and read-out their quantum spin states is pivotal. Accordingly, a microscopic modelling of their slow relaxation in response to magnetic perturbations becomes indispensable. For instance, quantum master equation simulations performed by our group, for the magnetic hysteresis of MDy₆ heterometallic complexes, have proven instrumental in demonstrating the exotic ferrotoroidic coupling between intramolecular Dy₃ sub-units and its signature in single-crystal microSQUID measurements^{1,2}.

Electrical conductance read-outs of molecular spintronics set-ups also provide direct access to single-molecule magnet (SMM) spin dynamics when triggered by an external magnetic perturbation³⁻⁵. Using the adiabatic quantum master equation approach, we investigated the origin of the characteristic electric current response of three archetypal SMM-based spintronics devices subjected to resonant³, quasi-static⁴ and driving⁵ magnetic fields. After being subjected to pulses of coherent, resonant radiation, we show that Rabi oscillations between the entangled spin states of a SMM-spintronics set-up manifest as damped oscillations in time-averaged electric current measurements through the device³. In addition, our latter models capture the idiosyncratic conductance features for experimentally-realised TbPc₂ molecular spin-transistor⁴ and molecular spin-valve⁵ set-ups. Thus, we are able to predict and expound detailed microscopic mechanisms for the manifestation of SMM quantum spin dynamics in conductance read-outs based on their slow relaxation in the presence of quite different magnetic perturbations and a continuous electrical measurement. In addition, an application of our formalism to simulate the single-crystal hysteresis of novel molecules displaying ground state toroidal moments will be presented.



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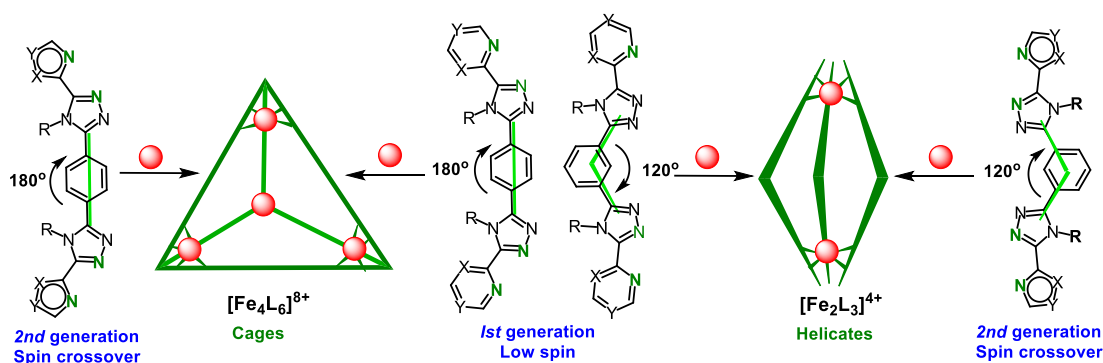
Spin crossover in iron(II) dinuclear helicates and tetranuclear cages

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Iron(II) spin crossover (SCO) materials have been widely studied as molecular switches with a wide variety of potential applications, including as displays, sensors, actuators or memory components.¹

Most SCO materials have been either monometallic or polymeric, and it is only relatively recently that chemists have really started to focus on linking multiple metal centres together within the one, discrete, molecule in an effort to enhance the SCO properties.² Similarly, monotopic **Rat** (azine-triazole) ligands have mostly generated mono- and polynuclear Fe(II) complexes, with 67 SCO-active complexes out of the total of 143 reported.³ Herein, new families of *ditopic Rat* ligands, providing two bidentate *azine/azole*-triazole binding pockets connected by appropriate spacers have been designed and made. These successfully direct the self-assembly of dinuclear helicates and tetranuclear tetrahedral cages (Figure),⁴ and have then been fine-tuned⁵ to generate *SCO-active* helicates $[\text{Fe}_2\text{L}_3]^{4+}$ and cages $[\text{Fe}_4\text{L}_6]^{8+}$. The development of the design, synthesis, structures, fine-tuning of ligand field strength, and trends in redox and SCO-behaviour of these families, will be presented and discussed.



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

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

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Spin-crossover self-assembled monolayers

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Spin crossover (SCO) complexes are a perfect example of molecular bistability. They can be switched in a reversible way between two distinct states by different external stimuli such as light, temperature, pressure, etc... Moreover, reversible changes of physical properties may take place, which make SCO materials promising candidates for many applications such as sensors, memories or spintronic devices.

Prior to the integration of SCO complexes in spintronic devices, deposition on solid surfaces without losing their SCO properties should occur. Most of the research regarding deposition of SCO complexes is focused on ultrahigh vacuum deposition of thermally evaporable neutral complexes onto metal surfaces. Herein we propose a simpler approach based on self-assembly of the molecules onto surfaces from solution.

To reach this goal, SCO Fe(II) complexes based on tridentate ligand bis(pyrazol-1-yl)pyridine functionalized with a carboxylic acid group were obtained. These family of ligands has led to homoleptic and heteroleptic SCO compounds with interesting SCO properties in the bulk [1]. However, deposition of such molecules onto metal oxide surfaces by wet-chemistry protocols, have been unsuccessful due to the lability of Fe(II). Thus, X-ray absorption spectroscopy (XAS) and X-ray Photoelectron Spectroscopy (XPS) confirmed the instability of the complexes [2]. To improve these results, we have prepared a family of SCO Co(II) complexes with tridentate ligands based on the terpyridine ligand containing carboxylic acid groups for grafting on different surfaces (see Figure for an example). Magnetic characterization of the bulk compounds have revealed interesting SCO properties such as reverse, abrupt and hysteretic SCO. On the other hand, preliminary XPS and XAS results of the deposited complexes suggest that they are stable on the surface and that SCO properties are preserved.

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Magnetization relaxation in weakly exchange coupling 3d-4f Single-molecule magnet system: a perspective theoretical viewpoint

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In this talk, we discuss on the magnetization relaxation in the binuclear complexes where a transition metal is in weak exchange coupling with a strong anisotropic lanthanide ion. Roles of the ligand field, exchange interaction in facilitating/hindering the relaxation will be elaborated. From this, an analysis on the main relaxation mechanism, dominant relaxation path, and effective blocking barrier for this family of complexes will be provided. A [Fe^{III}Dy^{III}] binuclear complex is given as an example to demonstrate our theoretical viewpoint.

A molecular qubit sensor of chiral-induced spin selectivity

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Artificial magnetic molecules are very promising systems to realize qubits with remarkable coherence, which can persist even at room temperature. Moreover, the possibility to chemically design their properties make it possible to functionalize them to couple with other sub-units. These features make molecular nanomagnets suitable to realize quantum sensors able to probe peculiar features at the molecular scale.

Here we propose the use of a molecular spin sensor, combined with time-resolved electron paramagnetic resonance (TR-EPR), to assess the nature of chiral-induced spin-selectivity (CISS)¹. This intriguing phenomenon, in which spins are filtered (even at room temperature) after charge displacement through chiral systems, is widespread in different fields, from catalysis to enantio-separation, spintronics, long-range electron transfer, and bio-recognition. Understanding the origin of CISS is fundamental to exploit it in biological and technological applications. However, an unambiguous experiment directly probing the nature of the filtered wave-function is still lacking.

We address this issue by studying electron transfer processes in radical-pairs linked by a chiral bridge and using a qubit sensor to assess the final polarization of the acceptor. Our approach exploits the flexibility of Chemistry in synthesizing molecular qubits coherent even at room temperature (based e.g. on VO or Ti³⁺), that can be easily functionalized to be coupled to a radical pair².

We demonstrate by numerical simulations of TR-EPR experiments that the qubit spectrum provides clear signatures of the final state of the system. A similar approach based on NMR is also considered. In addition, we propose a pulse sequence to transfer the (possible) polarization of the acceptor to the qubit.

These results have important implications on spintronics and quantum computation, where polarization at high temperature could be an important tool to initialize and readout qubits.

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Reversible Photo and Thermo-induced Spin-State Switching in a heterometallic {5d-3d} W₂Fe₂ Molecular Square Complex

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

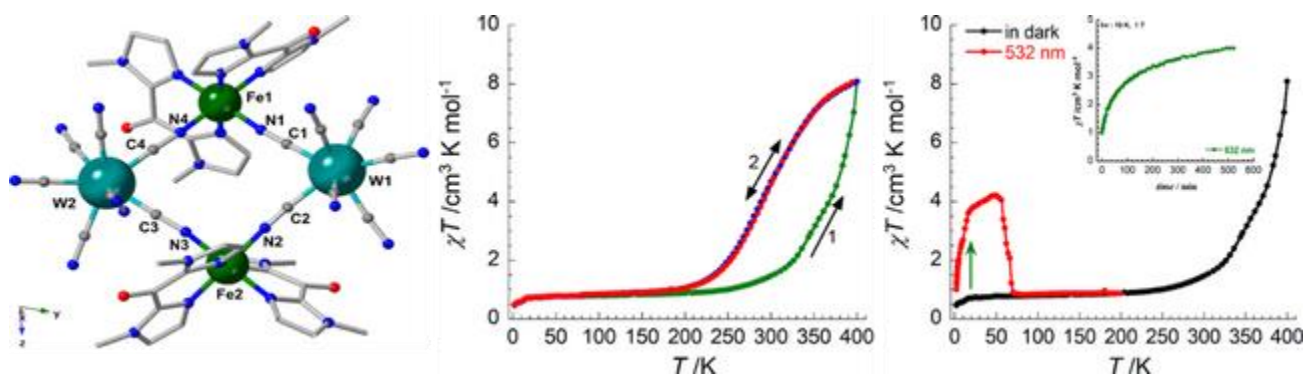


Figure 1: Perspective view of the W₂Fe₂ square complex (left); Temperature dependence of the cT product for the complex at 10000 Oe (middle); cT vs T curve under 532 nm light irradiation (right)

Recently, we have designed a molecular square complex [HNBu₃]₂{[W(CN)₈]₂[Fe(bik)₂]₂}×6H₂O×CH₃OH incorporating octacyanometallate building block [W(CN)₈]³⁻ with Fe(II) metal center and explored the structural, optical, (photo)magnetic and electrochemical properties.³ The complex shows reversible spin-state switching, thermo-induced SCO at near room temperature and photo-induced spin-state switching with $T_{LIESST} = 70$ K under light irradiation at low temperature.

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Functionalization of Yb(III) molecular nanomagnets using cyanido metal complexes

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In the current state of the art devoted to magnetic molecular materials, trivalent lanthanide ions are considered as most promising candidates for the construction of single-molecule magnets (SMMs).¹ Among them, Dy(III)-based systems were successfully involved in achieving high-temperature SMMs, even exceeding the temperature of the liquid nitrogen.² On the other hand, Yb³⁺ ions are characterized with only moderate magnetic anisotropy but are known to exhibit strong near-infrared luminescence, which is often applied for magneto-optical correlations.³ Moreover, their relaxation dynamics often lack the typical Orbach relaxation pathway, thus Yb(III)-based systems are great candidates for the studies concerning the control over Raman relaxation route.⁴ Over the last few years, in our groups we have prepared several Ln-based coordination systems acting as luminescent molecular nanomagnets. We have taken advantage of cyanido metal complexes, which constrain lanthanide coordination geometry, and serve as molecular antennae for efficient sensitization of f-f-centred luminescence.⁵ In this talk, we will briefly present the obtained Yb(III)-based systems, show strategies towards fruitful implementation of the desired magnetic, optical and electronic functionalities, and discuss recent results concerning modulation of Raman relaxation through crystallization solvent and cyanido metal complex exchange.

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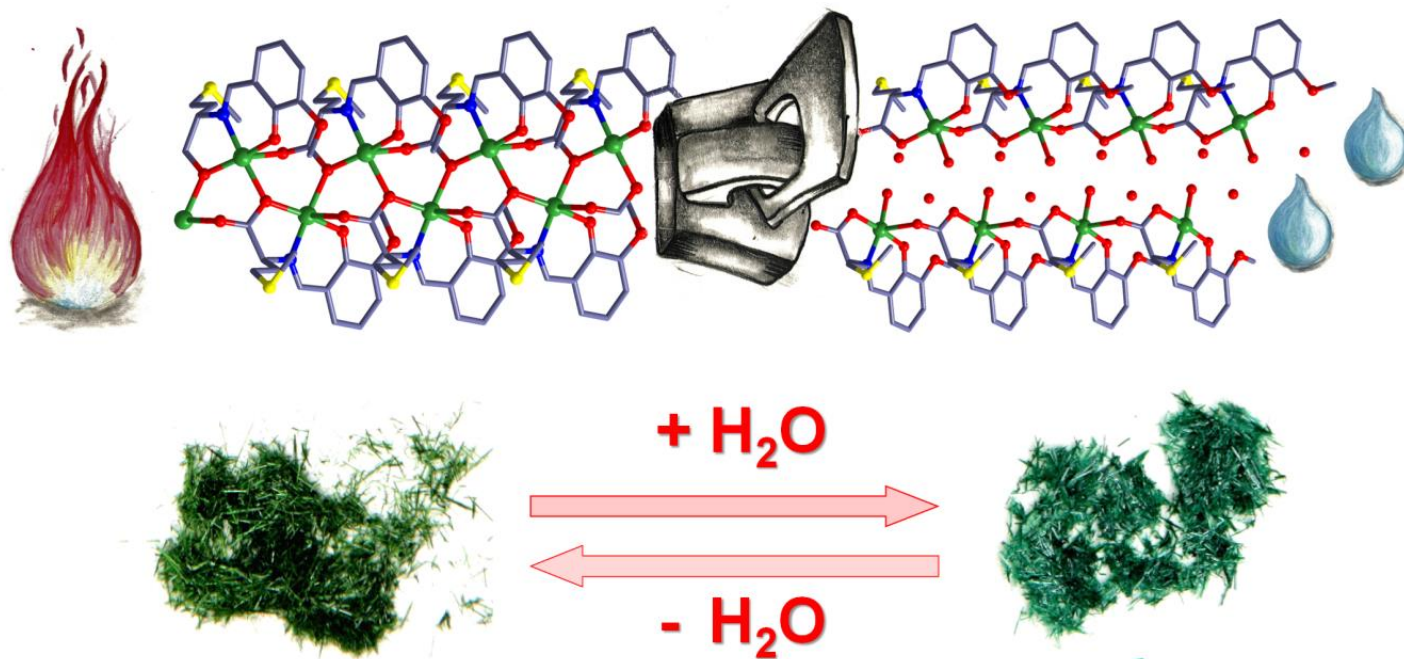
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Chirality driven self-assembly in copper(II) coordination polymers

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The most employed strategy for introducing the chiral information into a metal-ion based network consists of choosing of an enantiomerically pure ligand. In this respect, the usage of natural amino acids as chiral precursors is a simple and practical alternative. Moreover, the preservation of amino acid moieties within the resulting ligand can afford both an increased denticity and different kinds of hydrogen bonds that play a critical role in the self-assembly process. Following this idea, we present herein a chiral monodimensional copper(II) complex based on L- or D-amino acid-containing tridentate Schiff ligand. The dihydrated form, undergoes a single crystal to single crystal transformation to the dehydrated helical double chain, that generates significant changes in magnetic behaviour. [1] These complexes constructed from enantiopure Schiff-base ligands have been employed as metalloligands towards mercury(II) ions. The nature of the heterometallic Cu^{II}-Hg^{II} complexes (coordination polymers or oligonuclear species), resulted from the reactions of the copper(II) complexes with HgCl₂ or HgI₂, is different. The enantiopure metalloligands lead to chiral coordination polymers, ¹ $[\{Cu(R-/S\text{-valmet})(H_2O)\}_2HgCl_2] \cdot 5H_2O \cdot CH_3OH$ and ² $[\{Cu_2(R-/S\text{-valmet})_2(\mu\text{-}H_2O)(H_2O)_2\}HgI_2] \cdot 4H_2O$. The reaction of the racemic mixture of the metalloligands with HgX₂ affords discrete complexes: $[\{Cu(R,S\text{-valmet})(H_2O)_2\}_2HgCl_2] \cdot 2H_2O$ and $[\{Cu(R,S\text{-valmet})(H_2O)(CH_3OH)\}_2Hg_2I_4]$. [2]



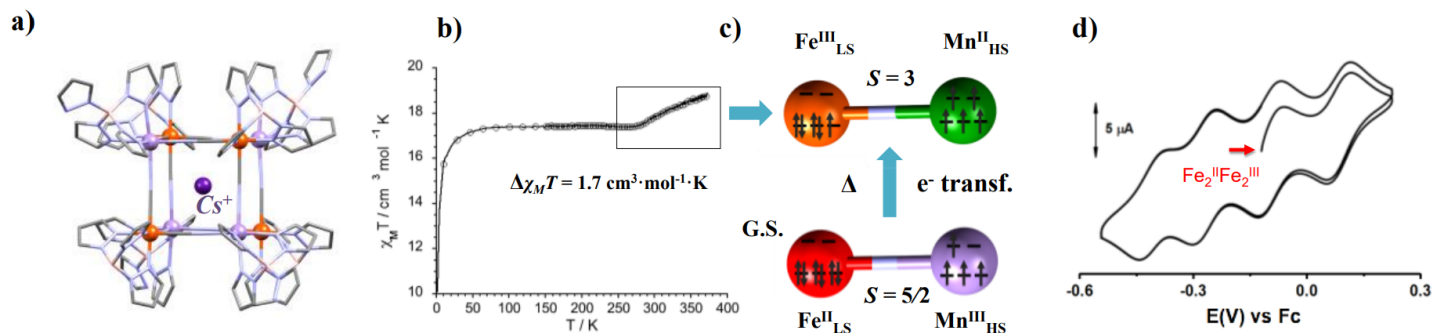
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Mixed Valence M_4Fe_4 ($M = Co, Mn$) Molecular Cages encapsulating cations: solution and solid-state electronic properties

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The versatility of the molecular chemistry has allowed the synthesis of a large number of well-defined zero dimensional (0D) molecular entities mimicking the magnetic properties observed in Prussian Blue Analogues (PBAs) [1,2]. For instance, the molecular analogs of the well-known Co-CN-Fe PBAs have been recently explored and these studies have provided a considerable improvement in our scientific understanding of the electronic behavior in these systems [3]. Appealing electronic properties were also observed in Mn-CN-Fe PBAs [4], but up to date, no molecular analogs showing such properties were reported. Within this context, we will discuss in this presentation the solid and solution electronic properties of a family of mixed-valence $\{Fe-CN-Co\}_4$ and $\{Fe-CN-Mn\}_4$ molecular cages encapsulating different alkali ions [3, 5].



a) Structure of $CsCFeMn$ (Fe: orange, Mn: light violet, Cs: purple; N: blue, C: gray, B: pink; H atoms are omitted for clarity) b) Temperature dependence of the $\chi_M T$ product of fresh $CsCFeMn$ under an applied magnetic field. c) scheme of the spin-state change under heating d) cyclic voltammetry of $CsCFeMn$ (0.97 mm, 100 mVs^{-1} , $0.1 \text{ M } n\text{-Bu}_4\text{NPF}_6$ in acetonitrile, Pt-mesh working electrode, and Pt-wire counter electrode)

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Flash Presentations – Abstracts

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

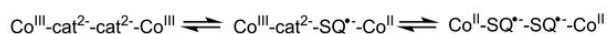
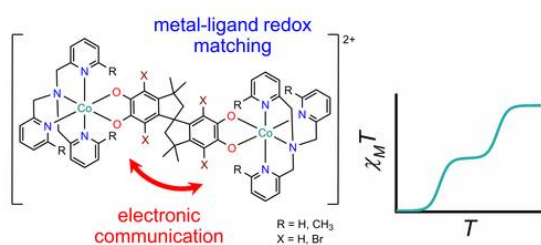
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Switchable molecular materials have a reversible physical response to external stimuli with potential applications in sensors, displays and high density data storage. Of particular interest are discrete compounds that can be reversibly switched between three or more states, enabling ternary data storage, multi-switchable displays and more complex logic processes in molecular electronics and spintronics.

One such reversible molecular transition is valence tautomerism (VT), the stimulated intramolecular electron transfer between a redox-active metal and a redox-active ligand. In cobalt-dioxolene complexes, electron transfer is accompanied by a cobalt spin transition, resulting in states with distinct structural, spectroscopic and magnetic properties. The complex $[\{Co(Me_2tpa)_2\}_2(spiro)]^{2+}$ (Me₂tpa = bis(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine; spiroH₄ = 3,3,3',3'-tetramethyl-1,1'-spirobi(indan)-5,5',6,6'-tetraol) is the only bis(dioxolene)-bridged dinuclear cobalt complex to display a two-step VT transition, which occurs between three electronic states: {Co^{III}-catecholate-catecholate-Co^{III}}, {Co^{II}-semiquinonate-catecholate-Co^{III}} and {Co^{II}-semiquinonate-semiquinonate-Co^{II}}.¹ This work elucidates the requirements for a two-step VT interconversion and how the sensitivity to bridging and ancillary ligands can be exploited to achieve a chemically tunable system.

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



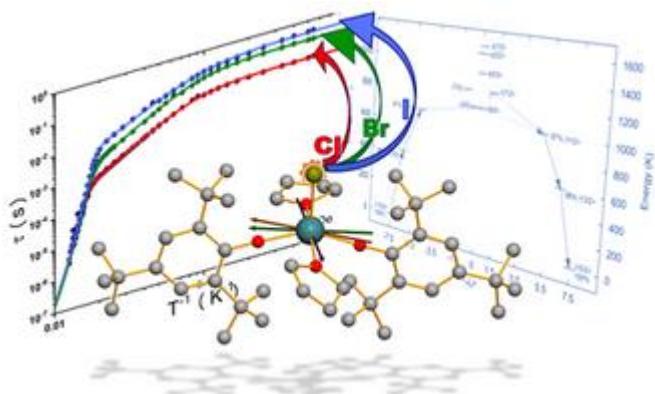
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Probing relaxation dynamics in Dy-Aryloxy Single-Molecule Magnets

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Complexes of certain d-block and f-block ions can retain magnetisation over long periods giving rise to Single-Molecule Magnet (SMM) properties. SMMs could be utilised for technologies such as high-density data storage, quantum computers and molecular spintronics. They were discovered three decades ago but have remained technologically unfeasible as they only operate around impractical temperatures. Some recent remarkable advancements have reignited the research field with new ideas towards making high-temperature SMMs.¹ The latest design approach of high-performing SMMs requires a single Dy centre bound by uniaxial anionic ligands (ideally a two-coordinate Dy complex). The characteristic advantages of aryloxy ligands in realising low-coordinate high-performing Ln SMMs have been demonstrated.² Herein, the role of aryloxy ligands and their resultant crystal field on the physical properties of SMMs is investigated. The synthesis, magnetic behavior and ab initio computational studies of families of Dy SMMs of coordination number (CN) 5, [Dy(OMes*)₂(THF)₂X] (Mes*=2,4,6-*t*Bu-phenyl; X= Cl (1), Br (2), I (3)) with the Dy centres in distorted square pyramidal geometries, and CN4, [Na(THF)₆][Dy(OAd*)₂Cl₂] (4) (Ad*=2,6-Ad-4-*t*Bu-phenyl) and [Na(THF)₆][Dy(OMes*)₃X] (Mes*=2,4,6-*t*Bu-phenyl; X= Cl (5), BH₄ (6)) with the Dy centres in distorted tetrahedral geometries, are presented. Complexes 1-3 show magnetic reversal barriers (U_{eff}) > 1200 K, with a trend in the rate of Quantum tunnelling of magnetisation as 1>2>3, whilst the Orbach and Raman relaxation processes remain unchanged.³ The magnetic relaxation rate is 4<5<6 among the CN4 series, with 4 showing a high U_{eff} (950 K) owing to its bis-aryloxy ligand configuration.



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Magnetism and electronic structure of divalent lanthanide metallocene complexes

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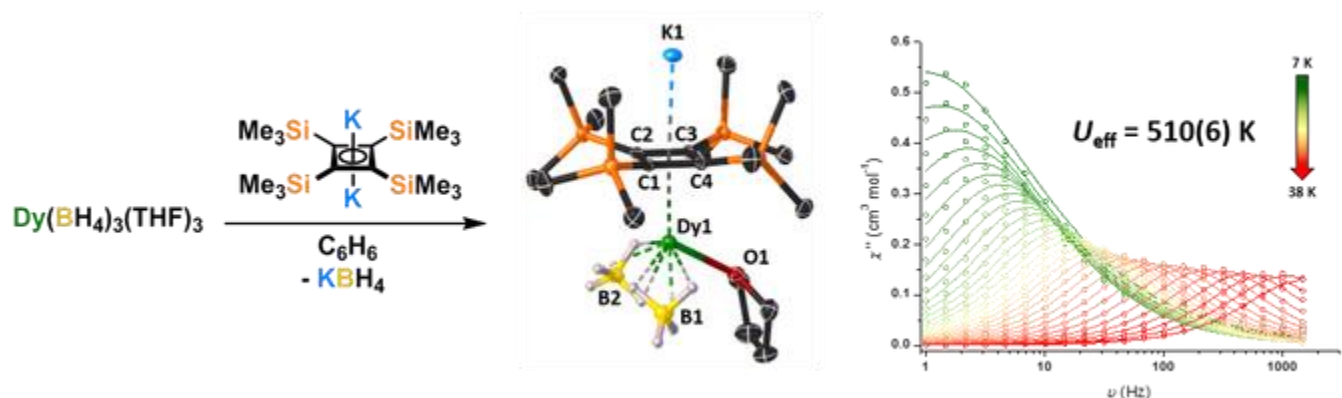
Compounds containing lanthanide(III) ions are the subject of extensive research in the field of single-molecule magnetism, yet molecules containing lanthanide(II) ions remain relatively unexplored. This paper will describe the magnetic properties of $\text{Ln}(\text{Cp}^{\text{iPr}5})_2$ ($\text{Ln} = \text{Tb}, \text{Dy}$; $\text{Cp}^{\text{iPr}5}$ = pentaisopropylcyclopentadienyl) and related lanthanide(II) metallocene complexes with an emphasis on how the unique $4f^n5d^1$ electron configuration influences single-molecule magnet behavior. In particular, comparison of $\text{Tb}(\text{Cp}^{\text{iPr}5})_2$ with its trivalent counterpart, $[\text{Tb}(\text{Cp}^{\text{iPr}5})_2][\text{B}(\text{C}_6\text{F}_5)_4]$, reveals that lanthanide reduction significantly enhances both the thermal barrier to magnetic relaxation and the 100-s magnetic blocking temperature, resulting in the largest values yet observed for a non-dysprosium compound. Intriguingly, strong $5d/6s$ mixing in $\text{Ln}(\text{Cp}^{\text{iPr}5})_2$ gives rise to a rare $j-j$ coupled electronic structure, which causes the coercive magnetic field measured for $\text{Tb}(\text{Cp}^{\text{iPr}5})_2$ in hysteresis measurements to increase as the temperature is raised from 2 to 30 K, in opposition to the trend that is typically observed for single-molecule magnets. Synthesis and magnetic characterization of related terbium(II) metallocene complexes reveals that ligand modification can switch the electronic coupling scheme from $j-j$ to the traditional $L-S$ scheme, resulting in nearly an order of magnitude increase to both the magnetic relaxation time at 2 K and the coercive magnetic field. Furthermore, hysteresis measurements demonstrate that the coercive magnetic field decreases monotonically with increasing temperature for the $L-S$ coupled compounds. In sum, this paper will illustrate the potential utility of lanthanide(II) ions in the design of next-generation single-molecule magnets, describe the unique electronic structures that can arise in such species, and discuss the relationship between electronic structure and magnetic properties.

Cyclobutadienyl Chemistry of the Rare-Earth Elements

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Cyclic p-conjugated organic ligands are widely used in rare-earth organometallic chemistry, and our group in particular has shown that cyclopentadienyl (Cp) ligands are extremely effective in the synthesis of high-performance single-molecule magnets (SMMs). These remarkable magnetic properties are due to the strong axial ligand field that the monoanionic Cp⁻ ligands provide, with recent results including the record-breaking SMM [Dy(Cp^{iPr5})(Cp*)][B(C₆F₅)₄]. Our attention is now focusing the introduction of a dianionic axial ligand, which should produce a stronger crystal field and improve the SMM properties. To this end, we have employed the cyclobutadienyl ligand [C₄(SiMe₃)₄]²⁻ introduced by Sekiguchi *et. al.* to transition metal chemistry, but which is largely unexplored in f-element chemistry, save for our initial studies. Therefore, our investigations into the fundamental coordination chemistry of the cyclobutadienyl ligand with lanthanides and the reactivity of these complexes are presented herein, in addition to the SMM properties of exemplar systems.



Data mining, dashboards and statistics: a powerful framework for the chemical design of molecular nanomagnets

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Data science is revolutionizing our society, but the impact of cheminformatics is still limited mostly to drug discovery and bulk materials science, partly because of the limited number of high-quality datasets. This work is a contribution to what has been termed as the third generation computational chemistry: statistically driven design, applied to a hot topic within Coordination Chemistry, namely Single Ion Magnets. Two decades of research have increased the operating temperature in lanthanide based molecular nanomagnets from liquid helium to liquid nitrogen. This recent convulsion has also had a deep impact on the sister field of molecular spin qubits. However, most of the work has been guided by serendipity, oversimplified theories and chemical intuition which makes this work extremely timely. Herein, we provide state-of-the-art inferential statistical analysis to a body of over 1400 published experiments with the goal of drawing chemical design conclusions on the key parameters which govern magnetic memory in molecular nanomagnets. This statistical study represents the first quantitative and data-supported verification/refutation of several widely held "chemical intuitions" to connect the chemical structures with the physical properties of this kind of coordination complexes. Our analysis shows that the effective energy barrier derived from an Arrhenius equation displays a better than expected correlation with the magnetic memory and that the chemical family, the lanthanide ion and the coordination elements are the three key variables for chemical design. Crucially, we provide an unprecedented dataset and a powerful interactive dashboard for visualizing the collected data, a singular feat in the use of data science for Chemistry, to the best of our knowledge.

A Study of Cation-Dependent Inverse Hydrogen Bonds and Magnetic Exchange-Couplings in Lanthanacarborane Complexes

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Xi'an Jiaotong University, Xi'an, China

Ten lanthanacarborane complexes were synthesized to study the rare $B-H^{\delta-}\cdots M^{n+}$ inverse hydrogen bonds (IHBs). The average bonding energy of $B-H^{\delta-}\cdots Ln^{3+}$ is theoretically determined to be larger than 24 kJ/mol, which is comparable to moderately strong hydrogen bonds (21 ~ 56 kJ/mol). In addition to NMR and IR, magnetometer was used to study the exchange-coupling interaction via such $B-H^{\delta-}\cdots Ln^{3+}$ IHBs in detail and the coupling constant is determined to be -2.0 cm^{-1} , which is strong enough to compare with single-atom bridged dysprosium(III) complexes. Two imidazolin-iminato incorporated complexes have shown energy barrier for magnetization reversal larger than 1000 K and the exchange-biasing effects are evident. Moreover, the bonding strengths of $B-H^{\delta-}\cdots M^{n+}$ IHBs are cation-dependent. If $M = Na$ the $B-H^{\delta-}\cdots Na^{+}$ bonding energy is reduced to 14 kJ/mol, and the dimerization process is no longer reversible. The exchange-biasing effect is also disappeared. We believe such a finding extends our knowledge of IHBs.

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

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

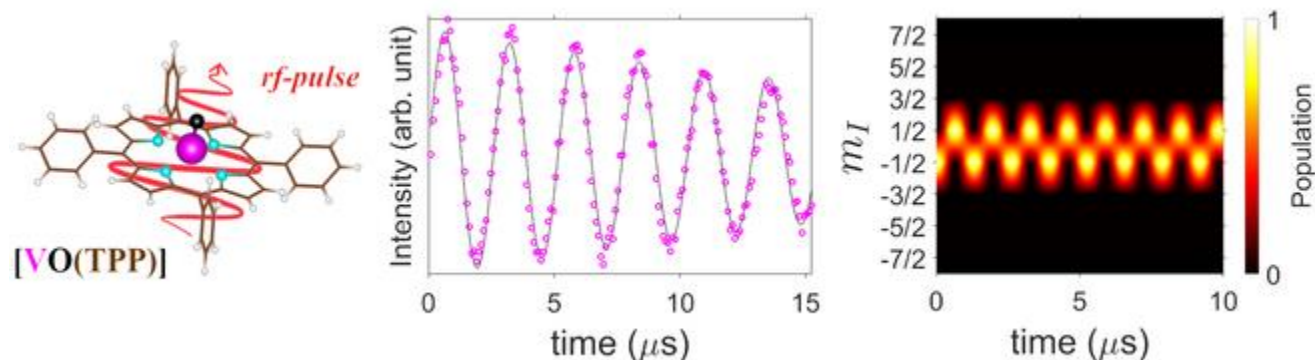


Figure 1 Experimentally induced Rabi oscillation between subsequent nuclear states (centre) and simulated evolution of nuclear state populations (right).

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Controlling Pairing of π -Conjugated Electrons in 2D Covalent Organic Radical Frameworks via In-plane Strain

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Controlling the electronic states of molecules is a fundamental challenge for future sub-nanoscale device technologies.[1] π -conjugated bi-radicals are very attractive systems in this respect as they possess two energetically close, but optically and magnetically distinct, electronic states: the open-shell antiferromagnetic/paramagnetic and the closed-shell quinoidal diamagnetic states.[2] While it has been shown that it is possible to statically induce one electronic ground state or the other by chemical design,[3,4] the external dynamical control of these states in a rapid and reproducible manner still awaits experimental realization. Here I will present our recent work[5] where, via quantum chemical calculations, we have demonstrated that in-plane uniaxial strain of 2D covalently linked arrays of radical units leads to smooth and reversible conformational changes at the molecular scale that, in turn, induce robust transitions between the two kinds of electronic distributions. Our results pave a general route towards the external control, and thus technological exploitation, of molecular-scale electronic states in organic 2D materials.

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Singlet and Triplet Ground State Spin-dimers on Nitroxide Free-radicals Connected with Aromatic π -Conjugated Systems

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Here, we describe design, synthesis, structural and magnetic studies of nitroxide free-radicals connected with aromatic π -conjugated systems. The weakly antiferromagnetic (AFM) coupled spin-dimers to be used for Bose-Einstein condensation (BEC) in the solid state organic magnetic materials. The mixed phenyl and thiophene oligomers are selected for π -conjugated systems and nitronyl nitroxide (NN) is chosen as a spin unit.¹ Moreover, planar π -bridge such as benzo[1,2-*b*:4,5-*b'*]dithiophene derivatives were selected for π -conjugated systems with good π -stacking and substituted with nitronyl- and imino-nitroxides as spin units.^{2,3} The works mostly focused on examination of the spin-spin interaction between the spin centers, which can be related to the energy difference between singlet and the triplet state: $DE_{ST} = 2J$. The exchange interactions were calculated by different DFT methods and upon using molar magnetic susceptibility measurements yielding χ_{mol} vs temperature T curves which were fitted to the Bleaney-Blowers equation providing the experimental exchange interactions. In addition, the mono NN substituted donor π -core such as 4-phenyl-4H-dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP-Ph) derivatives of the molecules were designed, and synthesized. Upon one electron oxidation, these molecules offered radical cationic high spin molecules with triplet ground state. The spin-spin of interaction between NN and radical cation were calculated by DFT.⁴ All the new molecules were characterized by HRMS analysis, the diamagnetic molecules were characterized by NMR and the paramagnetic molecules by well resolved EPR spectra combined with simulation. The final compounds were investigated by optical spectroscopy and crystallized to obtain X-ray structures, which is very important for explaining their magnetic behavior (magneto structural correlation). Further, the bulk magnetic susceptibilities were examined by SQUID in cooperations.

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

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

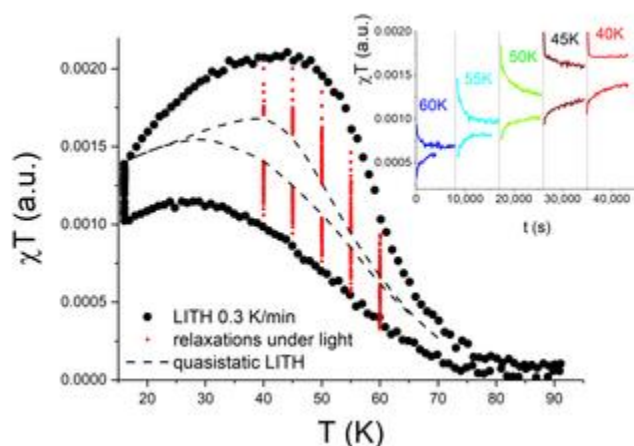


Figure: Light-induced thermal hysteresis for $\text{Fe}(\text{phen})_2(\text{NCS})_2$ microparticles embedded in glycerol (black circles experimental data; red circles partial relaxation under light; dotted line: profile of the real LITH curve as a guide for the eye). (inset) Partial relaxation curves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

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Surface deposition of a single-molecule magnet with improvement of the dynamic magnetic properties.

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Over the last 30 years a tremendous progress has been made in understanding the design principles for assembly of high-performing single-molecule magnets (SMMs). This is epitomized by the record-setting performance of the organodysprosium complexes featuring substituted cyclopentadienyl (Cp) ligands. In contrast to the advances in the realm of molecular SMMs, their surface deposition, a prerequisite for device application, received much less attention and still constitutes a major scientific challenge. This is due to the sensitivity of magnetic properties to small changes in the electronic structure and geometry of the parent complex caused by the interaction with the surface of the supporting material. While the typical approaches to surface deposition of SMMs focus on minimizing the changes to the coordination environment of the parent complex, the erosion of their magnetic properties is a prevalent issue.

In this talk I will describe the surface deposition of the classical (COT)Dy(Cp*) (COT = cyclooctatetraenide, Cp* = pentamethylcyclopentadienide) SMM system using partially dehydroxylated silica as a platform. The surface silanol moieties react with the investigated complex, which leads to a partial substitution of the organometallic ligands for the siloxide anchorages. Despite the extensive changes in the first coordination sphere, the resulting grafted organometallic species not only retain hysteretic behavior, but also exhibit substantial increase in the magnetization relaxation time. Such unique behavior is ascribed to the specific electronic structure of the surface siloxide moiety, which can be thought of as Cp surrogate based on the frontier orbital symmetry considerations.

The control of J-coupling via rotaxane methodology

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Supramolecular chemistry enables complex arrays to be assembled, which can be used to bring together similar and dissimilar spin systems. Through careful design, g-engineering approaches can be used to tune multi spin systems that maintain the unique identity of each individual spin.

Here we show the control of supramolecular adducts and exchange coupling between paramagnetic spin systems, via an organic template that dictates both aspects.

High Frequency EPR: New Tools for Investigating Thin Layers of Molecular Magnets

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Molecular Magnets (MM) are transition metal or lanthanide based molecules that are susceptible to the application of magnetic fields. The slow magnetic relaxation that can be observed at low temperature even after removing the magnetic field makes them appealing for high-density information storage applications (Single Molecule Magnets, SMM).[1] Moreover, their quantum coherence times of the order of microseconds up to room temperature make them attractive for quantum technologies (Molecular Spin Qubits, MSQ).[2] However, the easiest way to realize new devices based on these emerging technologies is to deposit and incorporate thin layers of MM on a surface. In this respect, parallel to the investigation of bulk materials, researchers started to deposit MM on surface and study them by Scanning Probe Microscopy as well as synchrotron based techniques. This has led to develop new methods to access structural, magnetic and dynamic information of thin layers of MM. Here, we present a 2D resonator for High Frequency Electron Paramagnetic Resonance (HFEP) spectroscopy based on plasmonic metasurfaces. This resonator focuses the THz magnetic field in a nanoscale confined area, which results in EPR signal enhancement when dealing with thin layer samples. Thanks to plasmonic metasurface resonators, HFEP enter among the fundamental tools for the investigation of MM on surface.[3] This work is part of our FET-OPEN PETER project, whose main purposes will be outlined in my presentation.[4]

[1] Gatteschi, D., Sessoli, R., Villain, J., *Molecular Nanomagnets*. Oxford Univ. Press: **2006**.

[2] Tesi, L., *et al. Chemical Science* **2016**, *7*, 2074; Bader, K., *et al. Nature Communication* **2014**, *5*, 5304.

[3] Tesi, L. *et al. Submitted*.

[4] www.peter-instruments.eu

Accurate Determination of Spin-Spin Interactions in Co^{II} Single-Chain Magnets and Antiferromagnetic Cu^{II} Complexes by THz-EPR

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Exchange-coupled multi-nuclear complexes play a crucial role as molecular magnets and spin qubits. Knowledge of their zero field splittings (ZFS) and exchange interactions are essential for their characterization. Frequency-domain Fourier-transform (FD-FT) THz-EPR is ideally suited to study spin systems with interactions up to hundreds of wavenumbers. Although determination of dominant exchange interactions by EPR is typically not possible, as $\Delta S_t = 1$ transitions are forbidden, anisotropies from *e.g.* ZFS may grant them sufficient probability for detection. Here, we demonstrate the power of FD-FT THz-EPR for in-depth characterization of spin systems of multi-nuclear molecular magnets.

In a newly synthesized class of 1D Co^{II}-based, thiocyanate-bridged spin chains, some of which behave as single chain magnets (SCMs), intra- and interchain couplings could be provided [1-3]. In addition, we determined the local ZFS of the Co^{II} ions from transitions to the second Kramers doublet for the first time in such spin chains [4]. Tensor anisotropies and orientations could be obtained based on the combination of simulations and *ab initio* theory. Implications of these findings for SCM properties are discussed.

Furthermore, we analyse the spin-spin interactions in two ferromagnetically coupled Cu^{II} dimers, relevant as models for exchange-coupled trinuclear Cu^{II} spin qubits. Detection of the partially allowed triplet-singlet transition allows for detailed determination of both exchange and Dzialoshinsky-Moriya interactions, which can be related to the respective bonding angles.

[1] M. Rams, A. Jochim, M. Böhme, T. Lohmiller, M. Ceglarska, M.M. Rams, A. Schnegg, W. Plass, C. Näther, *Chem. Eur. J.* 2020, **26**, 2837.

[2] M. Böhme, A. Jochim, M. Rams, T. Lohmiller, S. Suckert, A. Schnegg, W. Plass, C. Näther, *Inorg. Chem.* 2020, **59**, 5325.

[3] A. Jochim, T. Lohmiller, M. Rams, M. Böhme, M. Ceglarska, A. Schnegg, W. Plass, C. Näther, *Inorg. Chem.* 2020, **59**, 8971.

[4] T. Lohmiller et al., *in preparation*.

