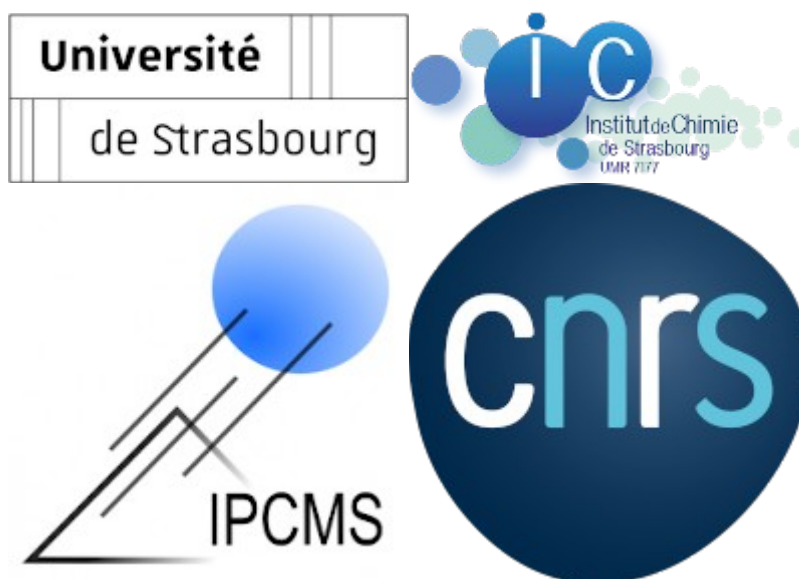


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Programme

Lundi 13 novembre	
A partir de 15h	Accueil des participants
19h30	Apéritif de bienvenue
20h	Dîner

Mardi 14 novembre				
8h45-09h00		Mot d'accueil (G. Rogez / G. Chastanet)		
Inv1	F. Pointillart	09h-10h	C. Pichon	Heptacoordinated complexes : unique playground for molecular magnetism
O1		10h-10h25	K. Dujarric	Designing of 1D and 2D molecule-based magnets through mononuclear building blocks
10h25-11h		Pause		
O2	N. Bridonneau	11h-11h25	M. Suo	Synthesis and characterization of radical-based precursors $M(\text{tpn})(\text{THF})_x$ ($M = \text{Li}^+, \text{Na}^+, x = 1, 2$)
O3		11h25-11h50	S. F. Russi	Electronically active ultra thin-films based on Fe_4Co_4 cyanide cages
O4		11h50-12h15	D. Martinez	Etude des interactions d'échange au sein d'assemblages polymétalliques de Fe(III) et Mn(II)
12h15-14h00		Déjeuner		
Inv2	K. Bernot	14h00-15h	S. Bertaina	Defects in spin chains: a virtual molecular magnet with quantum coherence properties
O5		15h00-15h25	I. Tlemsani	Pulsed EPR study of a clock transition of Ni(II) complex
O6		15h25-15h50	J. Appleton	Using system design to optimize magnetic interactions in porphyrin dimers
O7		15h50-16h15	A. Hoblos	Tunable polaritons using spin crossover molecules
16h15-19h30		Café, posters et photo de groupe		
19h30		Dîner		

Mercredi 15 novembre				
Inv3	H. Bolvin	9h-10h	S. Yalouz	Quantum computing for quantum chemistry
O8		10h-10h25	D. Jankovic	Spins down to electric avenue: electrical addressability of Ln-nuclear spins <i>via</i> ligand field theory for quantum information processing
10h25-11h		Pause		
O9	L. Salmon	11h-11h25	J.-F. Dayen	Interfacial transduction properties of spin crossover/graphene devices
O10		11h25-11h50	A. Trapali	Active spin-crossover/graphene interfaces for bistable electronic devices: molecular systems
O11		11h50-12h15	F. Houard	Exploring supramolecular nanotube deposition through a soft matter perspective for Single-Chain Magnets
12h15-15h		Déjeuner et temps libre		

Inv4	G. Chaboussant	15h-16h	O. Mentré	Some exotic low-D magnetic inorganic systems, frustration vs. magnetic ordering
O12		16h-16h25	Y. Li	Deciphering the unusual pressure-induced electron transfer in the molecular switch $\{[\text{Fe}(\text{Tp})(\text{CN})_3]_2[\text{Co}(\text{vbik})_2]_2\} \cdot (\text{BF}_4)_2 \cdot 2\text{MeOH}$: investigation by synchrotron X-Ray diffraction on single crystal
		16h25-17h	Pause	
O13	A. Bordage	17h-17h25	D.-C. Surgentu	Simple resolution of the standard multispin Hamiltonian in the weak exchange regime
O14		17h25-17h50	P. Roseiro	Modifications of Tanabe-Sugano d^6 diagram induced by radical ligand field: ab initio inspection of a Fe(II)-verdazyl molecular complex
O15		17h50-18h15	R. G. Torres Ramirez	High-temperature symmetry breaking. Experimental and theoretical analysis of $[\text{Fe}(\text{PM-PEA})_2(\text{NCS})_2]$
O16		18h15-18h40	X. Yang	Mechanical properties of composite materials based on mixed-anion $\text{Fe}(\text{NH}_2\text{Trz})_3(\text{BF}_4)(\text{SiF}_6)_{0.5}$ spin crossover complex and polyurethane
O17		18h40-19h05	N. Belmouri	Elastic investigations of the dynamics of cooperative spin states self organization and macroscopic deformation of spin crossover multi-layers
		19h05-19h30	Temps libre	
		19h30	Dîner/banquet	
		21h	Réunion du CA	

Jeudi 16 novembre				
Inv5	L. Lisnard	9h-10h	L. Norel	Control of 4f complexes luminescence and magnetism with organic photoswitches
O18		10h-10h25	R. Rodrigues de Miranda	Spin crossover in self-assembled monolayers for molecular electronics applications
		10h25-11h	Pause	
O19	G. Chastanet	11h-11h25	M. Donnat	New families of cubic molecular switches
		11h30	Déjeuner puis départ (départ de la navette à 13h15)	

Présentations orales

Mardi 14 novembre

HEPTACOORDINATED COMPLEXES : UNIQUE PLAYGROUND FOR MOLECULAR MAGNETISM

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Mots-clés: heptacoordinated complexes; coordination chemistry; single-molecule magnets; single-chain magnets

Résumé: Several chemical strategies have been developed to prepare molecule-based magnets with specific properties (blocking temperatures, coercive fields) and multifunctionalities (photo-, piezo-sensitivity, luminescence, chirality, ...).^[1] All these works highlighted the crucial role of magnetic anisotropy. In 1D, 2D and 3D networks, magnets require an additional control over its strength, its spatial orientation and on the intra- and inter-molecular exchange interactions. Heptacoordinated complexes are adequate platforms to play on these parameters. They are built from pentadentate ligands defining a planar surrounding to metal or lanthanide ions.^[2]

In this tutorial, I will discuss the impact of i) the metallic center (electronic configuration and orbital filling), ii) symmetry and iii) ligand fields on magnetic anisotropy. Their use as building blocks will be illustrated through selected results showing how they give access to heterometallic materials with diverse dimensionalities^[3] and magnetic properties ranging from simple paramagnets, SMMs^[4]/SCMs^[5] to ordered networks^[6] (Figure 1). The influence of chirality in these systems will also be presented.^[6]

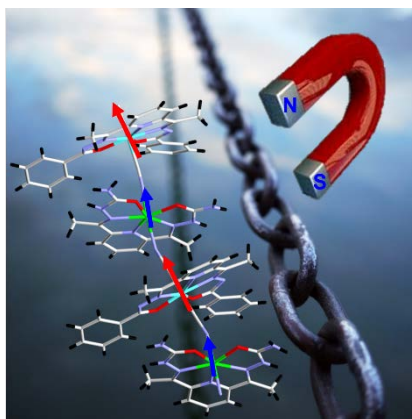


Fig. 1 Illustration of a Single-Chain Magnet built from heptacoordinated complexes.

Références:

1. Sieklucka, B.; Pinkowicz, D., *Molecular Magnetic Materials: Concepts and Applications* **2016**, Wiley-VCH.
2. Sutter, J.-P.; Béreau, V.; Jubault, V.; Bretosh, K.; Pichon, C.; Duhayon, C., *Chem. Soc. Rev.* **2022**, *51*, 3280-3313.
3. Pichon, C.; Duhayon, C.; Delahaye, E.; Sutter, J.-P., *Eur. J. Inorg. Chem.* **2021**, e202100834.
4. Pichon, C.; Suaud, N.; Jubault, V.; Duhayon, C.; Guihéry, N.; Sutter, J.-P., *Chem. Eur. J.* **2021**, *27*, 15484-15495.
5. Pichon, C.; Suaud, N.; Duhayon, C.; Guihéry, N.; Sutter, J.-P., *J. Am. Chem. Soc.* **2018**, *140*, 7698-7704.
6. Jubault, V.; Pradines, B.; Pichon, C.; Suaud, N.; Duhayon, C.; Guihéry, N.; Sutter, J.-P. *Cryst. Growth Des.* **2023**, *23*, 1229-1237.

DESIGNING OF 1D AND 2D MOLECULE-BASED MAGNETS THROUGH MONONUCLEAR BUILDING BLOCKS

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Molecule-based magnets have shown great interest over the past decades due to their attractive properties. They represent an excellent alternative to the traditional inorganic-based magnets used in modern-day technologies.^[1] Indeed, magnetic materials such as inorganic-organic systems, constructed from the coordination of metal ions with organic-based ligands, can give rise to various architectures and dimensionality. Besides promoting long-range magnetic ordering, these systems provide access to unparalleled functionalities that may be difficult to achieve through conventional inorganic-based magnets. In this sense, two-dimensional layered structures from the combination of chromium-based precursors and pyrazine have recently shown the coexistence of magnetically ordered states and electrical conductivity.^[2] To overcome the lack of control encountered with solvothermal synthesis used so far, a new bottom-up synthetic approach involving solution chemistry has been explored. Thereby, a mononuclear compound, Cr^{II}(Otf)₂(pyz)₄, (0D), has been crystallized and isolated from reactions between chromium(II) trifluoromethanesulfonate and pyrazine. This complex, composed of four neutral pyrazines and two trifluoromethanesulfonate groups in axial positions coordinated to the chromium(II) center, has been chosen to form n-dimensional systems with the reaction with halide salts. Several compounds have been synthesized and structurally characterized by tuning reaction conditions. Using this discrete complex in solution, chains (1D) or layered networks (2D) have been obtained. Their magnetic data will be discussed in this presentation.

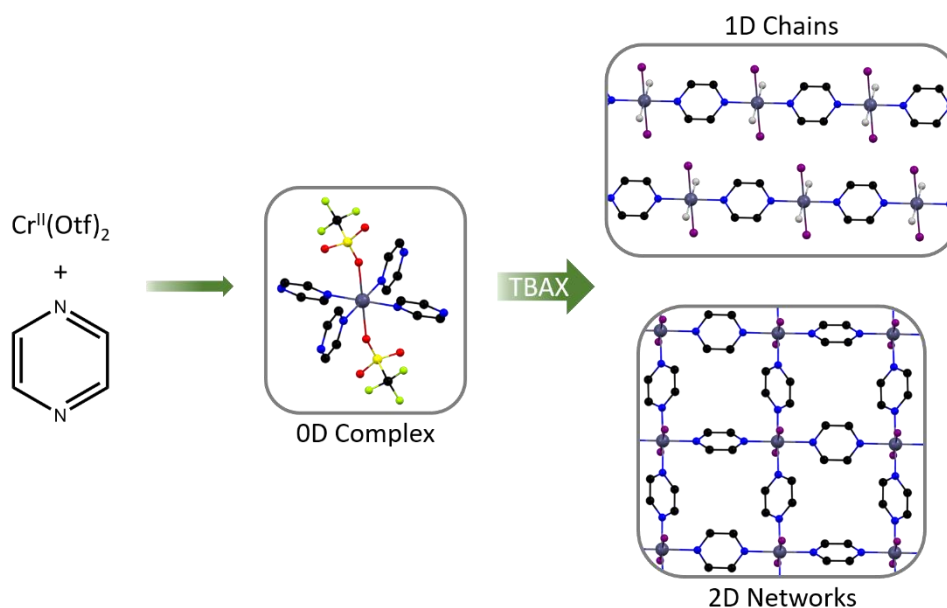


Fig. 1 Scheme of the synthetic route used to obtain one and two-dimensional layered structure using mononuclear building block precursors starting from a chromium(II) trifluoromethanesulfonate salt and pyrazine with TBAX being a tetrabutylammonium halide salt (X = Cl⁻, Br⁻ or I⁻). Dark grey, Cr; Red, O; Black, C; Green, F; Yellow, S; Purple, Halide ion X (Cl⁻, Br⁻ or I⁻) and Light grey, Solvent molecule R (Dimethylformamide (DMF), Dimethylsulfoxide (DMSO)). Hydrogen atoms have been removed for clarity.

References:

1. J.S. Miller, Mater. Today, 17, 224, (2014)
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 and R. Clérac., Nat. Chem. 10, 1056 (2018)

Synthesis and characterization of radical-based precursors $M(\text{tpn})(\text{THF})_x$ ($M = \text{Li}^+, \text{Na}^+, x = 1, 2$)

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Mots-clés: Organonitrile radical, Radical-metal network, Phase change

Résumé: In the past years, various organonitrile radical ligands have been investigated, characterized, and have demonstrated their great potential to construct metal-organic materials with impressive magnetic properties. [1] In particular, the terephthalonitrile radical ($\text{tpn}^{\bullet-}$), which is composed of a benzene ring with two cyano groups in the 1- and 4-positions, could act as an ideal bridging ligand in metal-radical materials. The two nitrile groups could offer a linear coordination geometry and the presence of an aromatic ring would allow the unpaired electron to delocalize over the whole molecule due to the conjugated of the π system with the nitrile group. [2]

For this presentation, we will discuss the synthesis and characterization of two tpn radical-based precursors $M(\text{tpn})(\text{THF})_x$ ($M = \text{Li}^+, \text{Na}^+, x = 1, 2$). The reducing agents lithium 1,2-dihydroacenaphthylenide ($\text{Li}^+\text{Ac}^{\bullet-}$) and sodium metal have been reacted with neutral tpn , leading to $\text{Li}^+(\text{tpn})^{\bullet-}(\text{THF})_2$ (**a**) and $\text{Na}^+(\text{tpn})^{\bullet-}(\text{THF})$ (**b**), which have been characterized by crystallographic, spectroscopic and magnetic susceptibility measurements. The structures of these compounds, as established from single crystal X-ray diffraction data, show that the lithium and sodium ions are bridged by $\text{tpn}^{\bullet-}$ and coordinated with THF, to constitute one-dimensional corrugated chains (Figure, left) and three-dimensional network (Figure, right) respectively. Interestingly, compound **a** shows an intriguing symmetry transformation with a change of temperature. For the magnetic properties, **a** displays paramagnetic behavior as expected and **b** exhibits a diamagnetic ground state due to strong interactions between closely stacked pairs of radical tpn .

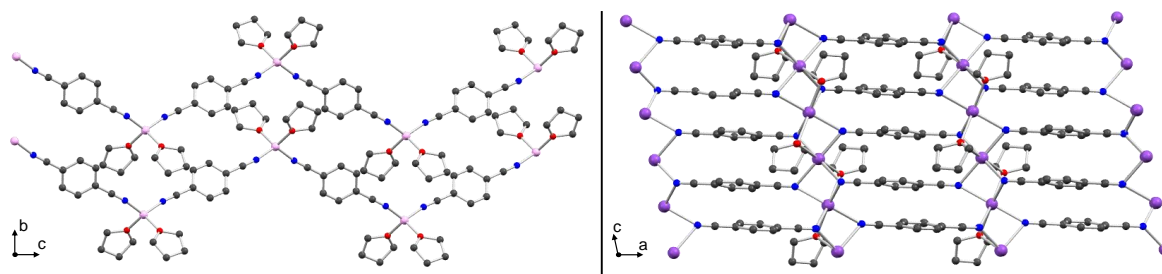


Fig. 1 Crystal structures of **a** (left) and **b** (right) at 120 K, hydrogen atoms are omitted for clarity. Color code: C black, N blue, O red, Li light purple, Na dark purple.

These compounds are attractive not only due to the straightforward synthetic approach of obtaining the organic radicals and isolating them as crystals, but also their potential as prospective precursors in the construction of metal-radical multidimensional magnetic materials.

Acknowledgments:

This work was supported by the University of Bordeaux, the Centre National de la Recherche Scientifique (CNRS), and the Chinese Scholarship Council (CSC).

Références:

1. J. M. Manriquez, G. T. Yee, R. S. McLean, A. J. Epstein and J. S. Miller, *Science*, **1991**, 252, 1415–1417.
2. Q. Deng, S.-J. He, J. Pei, C. Fan, C. Li, B. Cao, Z.-H. Lu and J. Li, *Electrochem. Commun.*, **2017**, 75, 29–32.

ELECTRONICALLY ACTIVE ULTRA-THIN FILMS BASED ON Fe₄Co₄ CYANIDE CAGES

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Emmanuel MAISONHAUTE,³ Laure FILLAUD,³ Nieli DAFTE,⁵ Jan DREISER,⁵ Yanling LI,¹ David
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Switchable molecules, thin films

Prussian blue analogues (PBAs) are well-known 3D inorganic polymers which have been extensively investigated because of their tuneable electronic properties and nanoporosity. However, as they are usually insoluble in organic solvents, it can be difficult to integrate them into microelectronic devices. In this framework, our group developed PBAs on a molecular scale based on FeCo cages which are robust in solution and can be integrated into nanomaterials through simple solution approaches. These compounds are cyanide-bridged $A\{[Fe(Tp)(CN)_3]_4[Co(R^T p)]_4\}$ cubic cages where A=alkali ion, and the metal ions are blocked by tris-pyrazolylborate ligands. As the FeCo PBA parent compound, the system shows switchable properties and the occurrence of a photo-induced metal-to-metal Electron Transfer Coupled to a Spin Transition (ETCST). Moreover, they also show interesting redox behaviour with up to nine accessible oxidation states.^[1]

In this work, with the aim of integrating these switchable molecules into nanodevices, we developed a simple synthetic strategy to obtain electronically active thin film directly onto a conductive substrate. For that, thanks to a modified ^RTp ligand functionalized by a thiophene, two different deposition methods were used: electropolymerization in solution and electrospray ionization in vacuum. Through the first one, the thiophene moiety was used as the electropolymerizable group. Such approach is simple, does not require costly deposition methods and ensures the formation of a film of controlled thickness on different electrodes. In the second one, thiophene served as surface anchoring group to obtain a (sub)monolayer on gold. In both cases, the properties of the cubic units are shown to be maintained in the deposited thin films.^[2]

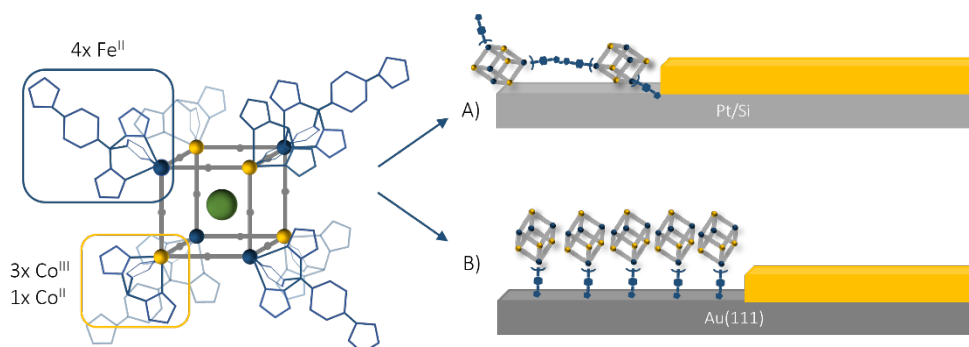


Fig. 1 {Fe₄Co₄} cages deposited on Pt/Si through electropolymerization (A) and on Au(111) via electrospray ionization (B).

1. J. Jiménez, J. Glatz, A. Benchohra, G. Gontard, L. Chamoreau, J. Meunier, A. Bousseksou, R. Lescouèzec, *Angew. Chem. Int. Ed.* **2020**, 59, 8089–8093

2. A. Benchohra, C. Méthivier, J. Landoulsi, D. Kreher, R. Lescouèzec, *Chem. Commun.* **2020**, 56, 6587–6589.

ETUDE DES INTERACTIONS D'ÉCHANGES AU SEIN D'ASSEMBLAGES POLYMETALLIQUES DE Fe(III) ET Mn(II)

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Mots-clés: molécules-aimants; chaînes-aimants; anisotropie magnétique; interaction d'échange.

Résumé: Les complexes d'ions d^5 à d^8 de géométrie bipyramide pentagonale sont caractérisés par de fortes anisotropies magnétiques¹. La construction d'assemblages moléculaires aux propriétés SMM ou SCM à partir de ces composés est permise par la robustesse structurale de ces derniers²⁻⁵. Dans le cadre de mes travaux de thèse, nous avons envisagé l'association de telles briques aux ions 3+ du groupe 8 (Fe^{III} , Ru^{III} , Os^{III}) en géométrie octaédrique ($S = 1/2$) caractérisés par un couplage spin-orbite. Le but est d'évaluer l'effet d'interactions d'échanges anisotropes sur l'anisotropie magnétique d'un édifice supramoléculaire. La linéarité de l'édifice, le recouvrement et la taille des orbitales magnétiques sont autant de paramètres pouvant jouer un rôle dans ces interactions. Lors de cette présentation, nous montrerons que les substituants équatoriaux du ligand pentadente permettent de contraindre la linéarité de complexes trimétalliques [$Fe^{III}_2Mn^{II}$]. Les propriétés magnétiques de chaînes 1D- $[Fe^{III}M^{II}]$ ($M = Mn, Fe$; **Fig. 1**) seront également présentées.

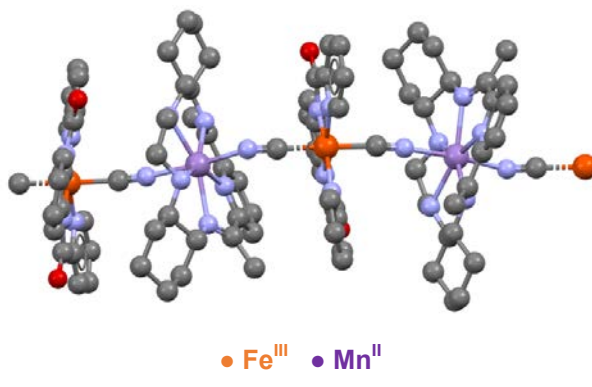


Fig. 1 Structure cristalline de la chaîne 1D- $[(Fe^{III}(bpb)(\mu-CN)_2)\{Mn^{II}(H_2L^{NSRR})\}]$

Références:

1. Sutter, J.-P.; Béreau, V.; Jubault, V.; Bretosh, K.; Pichon, C.; Duhayon, C. *Chem. Soc. Rev.* **2022**, *51*, 3280.
2. C. Pichon, N. Suaud, C. Duhayon, N. Guihéry and J.-P. Sutter, *J. Am. Chem. Soc.*, **2018**, *140*, 7698–7704.
3. Bretosh, K.; Béreau, V.; Duhayon, C.; Pichon, C.; Sutter, J.-P. *Inorg. Chem. Front.* **2020**, *7*, 1503
4. A. K. Bar, N. Gogoi, C. Pichon, V. M. L. D. P. Goli, M. Thlijeni, C. Duhayon, N. Suaud, N. Guihéry, A.-L. Barra, S. Ramasesha and J.-P. Sutter, *Chem. Eur. J.*, **2017**, *23*, 4380–4396.
5. T. S. Venkatakrisnan, S. Sahoo, N. Bréfuel, C. Duhayon, C. Paulsen, A.-L. Barra, S. Ramasesha and J.-P. Sutter, *J. Am. Chem. Soc.*, **2010**, *132*, 6047–6056.

Defects in spin chains: a virtual molecular magnet with quantum coherence properties

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In a perfect dimerized spin chain, the ground state is non-magnetic. A defect, like an end-chain or a stacking fault, will break the translational symmetry and will polarize dozens of spins around it, forming a magnetic pinned soliton [1].

The microscopic structure of such objects is comparable to the SMM V15 : a ground state doublet separated to a quasi-continuum by a gap [2]. While the large number of spins involved should relax the quantum coherence, the strong exchange interaction strongly reduces the decoherence.

In this talk, I will present the quantum coherence of defects in the spin-Peierls chain (o-DMTF)₂Br probed by pulsed electron spin resonance. I will show that the 1D nature of the chain allows the existence of pairs of solitons with a probability of 50% independent to the defect concentration [3].

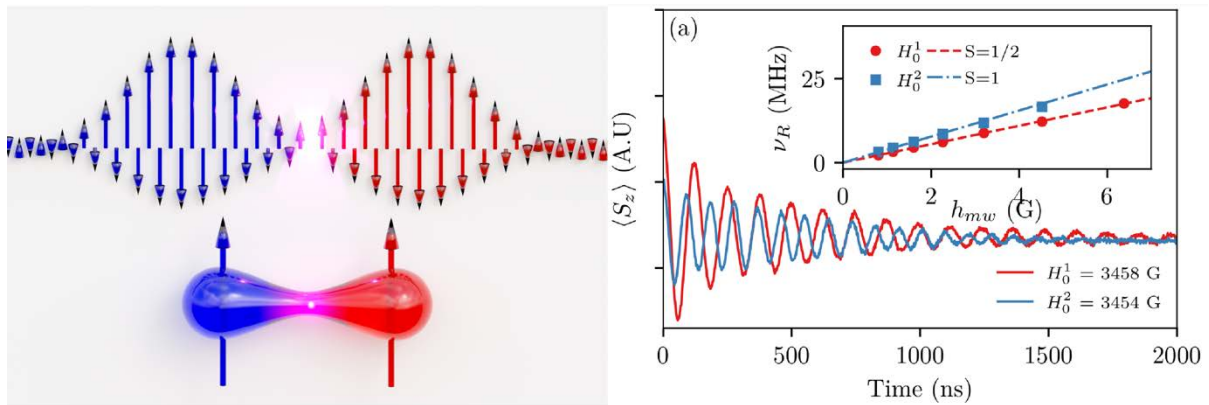


Figure 1: left) Schematic representation of a pair of magnetic solitons pinned to the defect (middle). Right) Rabi oscillations of a single (red) and pair of solitons (blue).

References:

- [1] S. Bertaina, et al., Phys. Rev. B (R) **90**, 060404 (2014).
- [2] J. Zeisner, et al. Phys. Rev. B **100**, 224414 (2019).
- [3] L. Soriano, et al., Phys. Rev. B **105**, 064434 (2022).

PULSED EPR STUDY OF A CLOCK TRANSITION OF NI (II) COMPLEX

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Mots-clés: Cobalt, Clock Transition; Qubit, Nickel, EPR

Résumé:

In the past few years, the amount of information that needs to be treated has been constantly increasing. This led to the proposal of new paradigms in the field of information processing. An emerging field is quantum information that postulates the use of quantum computers based on quantum information storage units called quantum bits (qubits).^[1] Magnetic molecules, due to their flexibility, are attractive candidates to encode spin qubits.^[2] One of the central challenges for molecular magnets to play the role of efficient qubits is to obtain long phase memory relaxation times T_2 . It has been shown that the Debye temperature is the key parameter for the spin-lattice relaxation time T_1 ,^[3] while clock transitions that protect the system from magnetic fluctuations may lead to a long phase memory time T_2 .^[4]

In this work, we report Electron Paramagnetic Resonance (EPR) spectroscopy studies (continuous wave (cw) and pulsed) on a mononuclear Ni(II) complex possessing a distorted octahedral geometry (Figure 1a). CW studies show an Ising type magnetic anisotropy with zero-field splitting spin Hamiltonian parameters D and E equal to -10.1 cm^{-1} and 0.13 cm^{-1} , respectively.^[5] This corresponds to the situation where the two $MS = \pm 1$, separated by $2E$, are the ground levels, which is consistent with a two-levels system that plays the role of a qubit in the absence of an applied dc magnetic field B_0 . We demonstrate, using pulsed EPR study, that T_2 is protected from magnetic fluctuation generated by the spin bath (mainly the H nuclear spins) in the region close to zero magnetic field, demonstrating the effect of the clock transition on T_2 (figure 1.b).

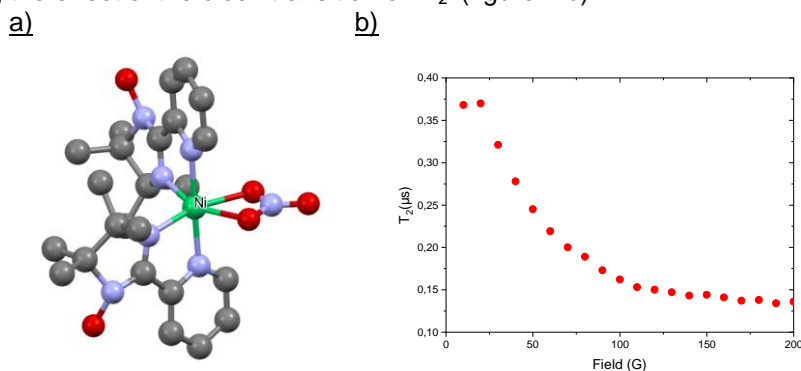


Fig. 1 a) View of the molecular structure of $[\text{Ni}(\text{imidazoline})(\text{NO}_3)]^+$. b) Variation of the coherence time along the magnetic field at 5K in Q band.

References:

1. Barz, S, Fitzsimons, J, Kashafi, E, Walther, P, Nat. Phys. **2013**, 727–731
2. Leuenberger, M., Loss, D., *Nature*. **2011**,410, 789–793
3. Orbach, R, Proc. R. Soc. Lond. A. **1961**, 264, 458–484
4. Shiddiq, M, Komijani, D, Duan, Y, Gaita-Arino, A, Coronado, E, Hill, S, *Nature*. **2016**, 531, 348-351

5. Roger, G, Rebilly, J-N, Barra, A-L, Sorace, L, Blondin, G, Kirchener, N, Duran, M, Van Slageren, J, Parsons, S, Ricard, L, Marvilliers, A, Mallah, T, *Angew. Chem. Int. Ed.* **2005**, 44, 1876-1879

USING SYSTEM DESIGN TO OPTIMISE MAGNETIC INTERACTIONS IN PORPHYRIN DIMERS

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Mots-clés: porphyrins, qubits, EPR, magnetism, coordination chemistry

Résumé: Porphyrins are ubiquitous in nature and their exceptional properties have been exploited by synthetic chemists for decades. Our group is no exception to this, with an optimised porphyrin moiety^[1] possessing an internal and external coordination site (see Figure 1) for formation of high light absorbing, good electronic communicating and magnetically coupled porphyrin dimers.^[2] Such porphyrins can even be self-assembled at a solid/liquid interface.

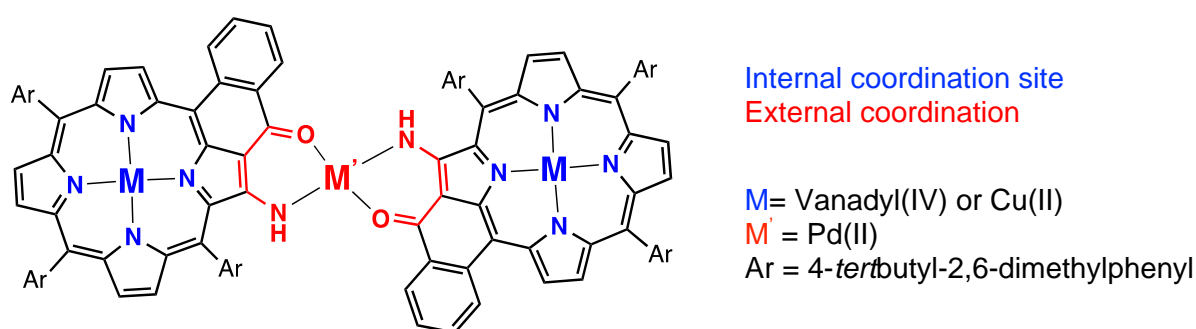


Fig. 1 Dimers assembled from a porphyrin bearing an internal and external coordination site.

On placing a paramagnetic metal at the internal coordination site (Figure 1), porphyrins have also been envisaged as potential candidates for applications in quantum computing^[3] with their robust nature and synthetic availability being highly advantageous.^[4] Rabi oscillations at room temperature have been observed for these porphyrin complexes. Our system design allows for an isotropic exchange coupling close to zero and a weak dipolar interaction, hence two weakly interacting metal ions at the internal coordination site of the porphyrin allows also for such complexes to be envisaged as a 2-qubit system.

Références:

1. S. Richeter, C. Jeandon, J.-P. Gisselbrecht, R. Ruppert, H. J. Callot, *J. Am. Chem. Soc.* 2002, **124**, 6168-6179.
2. J. L. Appleton, N. Le Breton, M. A. Carvalho, J. Weiss, A. K. Boudalis, C. Gourlaouen, S. Choua and R. Ruppert, *Cryst. Growth Des.*, 2023, **23**, 1689–1696.
3. M. R. Wasielewski, *et al. Nat. Rev. Chem*, 2020, **4**, 490–504.
4. S. von Kugelgen, M. D. Krzyaniak, M. Gu, D. Puggioni, J. M. Rondinelli, M. R. Wasielewski, and D. E. Freedman, *J. Am. Chem. Soc.* 2021, **143**, 8069–8077.

TUNABLE POLARITONS USING SPIN CROSSOVER MOLECULES

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Mots-clés: Strong light-matter coupling; Spin crossover molecules; Rabi Splitting; Fabry-Perot Cavity;

Résumé: The field of 'molecular polaritonics', wherein molecular systems are studied under the regime of strong light-matter coupling, has become a topic of intense experimental and theoretical research over the past decade^[1,2,3]. The strong-coupling regime arises when a molecular excitation comes into resonance with a confined electromagnetic mode such as a cavity mode, and a rapid energy exchange (through the exchange of photons) occurs between the optical cavity and the material. If this energy exchange becomes faster than any dissipation process, then the so-called strong-coupling regime is achieved. In this case, new hybrid light-matter states, known as polaritons, are formed, with an energy separation (called Rabi-splitting energy, $\hbar\Omega_R$) being proportional to the coupling strength (Fig. 1a).

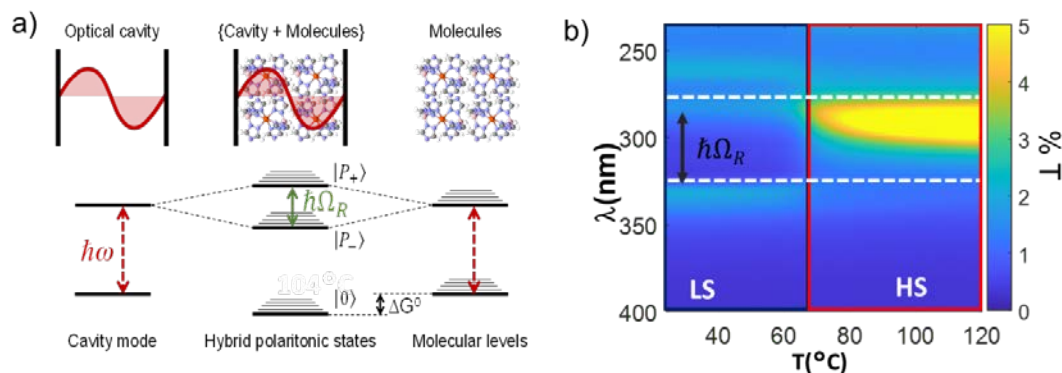


Fig. 1. (a) Energy landscape of a {molecules + cavity} system in strong-coupling regime. The resonance between the molecular excitation and the cavity mode ($\hbar\omega$) leads to the formation of two polaritonic states (P_+ and P_-), separated by the so-called Rabi splitting energy $\hbar\Omega_R$. (b) Transmission spectra of a SCO-based Fabry-Pérot cavity as a function of the temperature, showing the switching between a strong-coupling regime (LS state) and an uncoupled regime (HS state). The dashed lines indicate the absorption maxima of the SCO complex.

In the present study, we demonstrate the possibility of using switchable spin-crossover (SCO) molecules as an active material to activate/deactivate the strong-coupling regime in a photonic nanocavity, and then modulate the cavity resonances^[4]. To this aim, thin films of the [Fe(HB(1,2,4-triazol-1-yl)₃)₂] SCO compound were incorporated into Fabry-Pérot (FP) cavities^[5]. The cavities were designed such that an optical mode falls into the UV wavelength domain, where the SCO material displays intense, spin-state dependent absorption bands, leading to the regime of strong light-matter coupling between the photonic structure and the SCO molecules. As shown in Fig. 1b, in the LS state, an (ultra)strong coupling regime is achieved with Rabi-splitting energies of up to 730 meV. By thermally converting the molecules into their non-absorbing HS state, we show that the coupling strength can be fine-tuned until reaching an uncoupled regime, wherein only a single cavity resonance is observed (Fig. 1b). On the other way around, as the strong-coupling regime can also perturb the molecular ground state (ΔG^0 , see Fig. 1a), further investigations are conducted to study a possible effect of the strong coupling on the spin-transition properties. More generally, the study of strong-coupling phenomena using switchable molecules opens up new avenues for exploring the synergistic effects that can arise from the combination of light-matter hybridization and molecular bistability.

Références:

1. Hutchison J. A., Schwartz T., Genet C., et al., *Angew. Chem. Int. Ed.* 51 (2012) 1592.
2. Törmä P., Barnes W. L., *Rep. Prog. Phys.* 78 (2014) 013901.
3. Ebbesen T. W., *Acc. Chem. Res.* 49 (2016) 2403.
4. L. Zhang et al. *J. Phys. Chem. Lett.* 2023, <https://doi.org/10.1021/acs.jpcllett.3c01136>.
5. Zhang, Yuteng, et al., *J. Mater. Chem. C* 8.24, (2020): 8007-8011.

Mercredi 15 novembre

QUANTUM COMPUTING FOR QUANTUM CHEMISTRY

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Mots-clés: Quantum Computing – Quantum Chemistry – Electronic structure

Résumé:

In quantum computing, solving the electronic structure problem from quantum chemistry is considered one of the most promising applications. Today, lots of efforts are devoted to the development of quantum algorithms in the hope that one day we will be able to access a high-level description of molecular properties at a speed greater than that of any classical computer. But tackling such complex problems with today's quantum devices requires caution, as experimental platforms are still in their infancy and suffer from significant constraints. Until quantum computers are more stable, we will have to adapt our vision of algorithm development.

In this introductory talk, I will describe the state-of-the-art in quantum algorithms for solving the electronic structure problem. Particular attention will be paid to the Variational Quantum Eigensolver: a hybrid classical-quantum method originally developed to target the ground state of molecules. I will then present an extension of this method called SA-OO-VQE¹ that I have recently developed to describe multiple electronic states (ground and excited). Finally, I will discuss some further developments I have made to allow access to nuclear gradients and non-adiabatic couplings², which represent key ingredients in the implementation of numerical quantum dynamics simulations.

Références:

1. Yalouz, S., et al. Quantum Sci. Technol., 2021, 6(2), 024004.
2. Yalouz, S., et al. J. Chem. Theory Comput. 2022, 18, 2, 776–794

Spins Down to Electric Avenue: Electrical addressability of Ln-nuclear spins via Ligand Field Theory for Quantum Information Processing

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Mots-clés: Quantum Information Processing, Single Molecule Magnets, Lanthanides, Stark Effect, Ligand Field Theory, Density Functional Theory

Résumé: Single molecule magnets (SMMs) containing lanthanide ions with large nuclear spins can serve as qubits for quantum information processing when transitions between nuclear spin states can be individually addressed ^[1]. Recent experiments have demonstrated electric addressing of such qubits in TbPc2 ^[2], enabling nuclear spin state control through electric fields rather than magnetic fields. However, a theoretical explanation of the underlying mechanism is still lacking. We hypothesize configuration interaction enabled by odd parity crystal field parameters underlies the effect. We present ligand field atomistic calculations showing significant 4f-5d mixing in some Ln(III) ions in crystal and ligand matrices, confirming the mixed parity ground states needed for electric addressing. Moreover LFDFT (Ligand-Field DFT) has proven successful in capturing spectral profiles and optical properties of two-open shell systems such as f-d transitions in lanthanides ^[3,4]. Combining LFDFT with atomistic calculations allows for the construction of full configuration interaction matrices including crystal field effects, spin-orbit coupling, hyperfine interaction and electrostatic effects that yields energy levels displaying Stark effects forbidden in pure parity states. Our fully ab-initio approach can provide unprecedented insights into the microscopic origins of electrically driven spin transitions, such as the geometry, deformations, strain and composition of the molecule. By elucidating the role of odd ligand fields in mediating the hyperfine Stark effect, this work facilitates the rational design of improved qubit systems for quantum information applications.

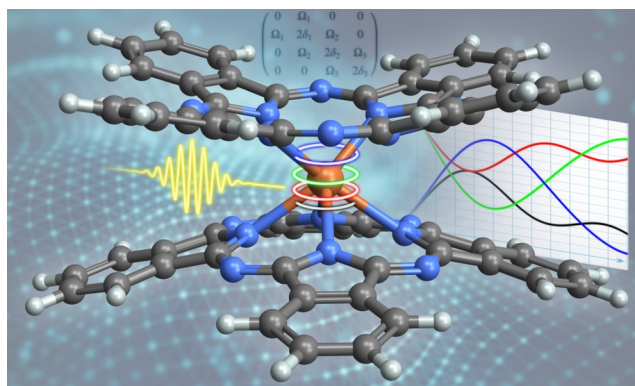


Fig. 1 Artist's rendering of pulse-level addressing of the 4 level qubit in TbPc2

Références:

1. Wernsdorfer, W.; Ruben, M., *Adv. Mat.* **2019**, *31* 1806687.
2. Thiele, S.; Balestro, F.; Ballou, R.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W., *Science* **2014**, *344*, 1135-1138.
3. Ramanantoanina, H. et al., *Phys. Chem. Chem. Phys.* **2015**, *17*, 18547.
4. Borel, A.; Daul, C.A.; Helm, L., *Chem. Phys. Lett.* **2004**, *383*, 584.

INTERFACIAL TRANSDUCTION PROPERTIES OF SPIN CROSSOVER/GRAPHENE DEVICES

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Mots-clés: Interface, LIESST, Spin crossover, van der Waals, optoelectronics, devices.

Résumé: Spin crossover (SCO) molecular materials exhibit a change of magnetic state that can be triggered by several external stimuli, in particular temperature, pressure, electric field and light irradiation. Despite their important potential, their use in multi-functional devices is hampered by several technological locks: (i) optoelectronic devices remain scarce because of complex intricate phenomena into the SCO channel, (ii) the low intrinsic conductivity of SCO material prevents their use for several sensing applications, (iii) optoelectronic switch based on SCO phenomena and operating at room temperature is not yet demonstrated. Here, I will present some of our recent achievements and on-going works illustrating the possibilities offered by SCO-2D materials heterostructures for switchable optoelectronic applications, and how they can unlock these challenges.

First, magneto-opto-electronic properties are shown for a hybrid device constructed from a spin crossover (SCO) thin film of molecular material evaporated over a graphene sensing layer. The principle of electrical detection of the light-induced spin transition (LIESST) and reverse-LIESST effects in SCO/graphene heterostructures is demonstrated at low temperature. [1] The switchable spin state of the molecular film is translated into a remanent change of the conductance of the graphene channel, using two distinct excitation wavelengths to write/erase the two states.

Then, I will present a hybrid device that can be optically switched at room temperature with non-volatile electrical memory effect. For this molecular system, device operation at room temperature is realized, with multi-state stabilization obtained by varying the irradiation intensity or time. [2]

Finally, I will show recent experiments combining impedance spectroscopy and Hall measurements. It provides novel insight into the mechanism(s) for the change of impedance of the graphene layer in proximity with different states of the molecular structure. [3]

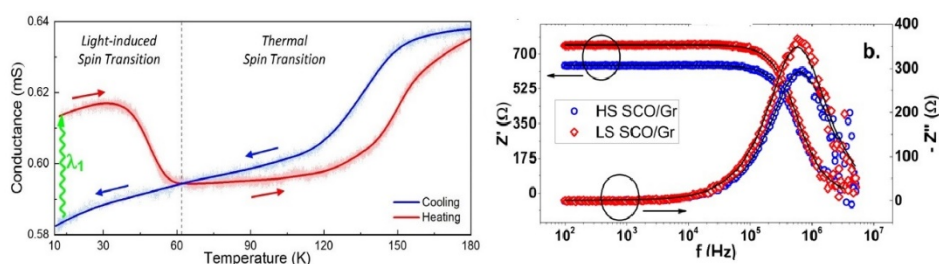


Fig. 1 (Left) Thermal and LIESST SCO transition in SCO/Gr device. (Right) Impedance spectroscopy of SCO spin state in SCO/Gr heterostructure.

Reference :

[1] N. Konstantinov, A. Tauzin, (...) T. Mallah, and J.-F. Dayen, "Electrical read-out of light-induced spin transition in thin film spin crossover/graphene heterostructures," *J. Mater. Chem. C* **9**(8), 2712–2720 (2021).

[2] J.-F. Dayen, N. Konstantinov, (...) G. Chastanet, and B. Doudin, "Room temperature optoelectronic devices operating with spin crossover nanoparticles," *Mater. Horiz.* **8**(8), 2310–2315 (2021).

[3] Krishna Maity, Jean-François Dayen, Marlène Palluel, Nathalie Daro, Guillaume Chastanet, Bohdan Kundys, Bernard Doudin, submitted.

ACTIVE SPIN-CROSSOVER/GRAPHENE INTERFACES FOR BISTABLE ELECTRONIC DEVICES: MOLECULAR SYSTEMS

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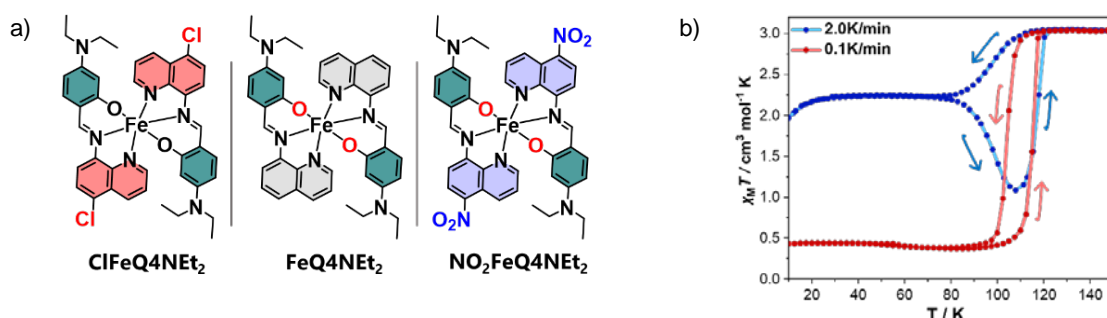
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Mots-clés: Fe(II) Schiff-base complexes; dipolar moment; spin-crossover (SCO), bistability; X-ray absorption spectroscopy studies

Résumé: Spin-crossover (SCO) materials can reversibly switch their spin state upon an external stimulus. This, together with the structural modifications due to the changes in the occupancy of the d orbitals, significantly alters their optical and magnetic properties, electric conductivity, and dielectric constant. Such changes in their physical properties are particularly interesting, yet challenging, for their integration in molecular electronic devices that aim for ultrafast/low-power consumption data storage and information processing.^[1] The challenging nature of this approach lies mainly in the fact that i) molecules exhibit very low conductivity compared to the conventional solid-state materials, ii) the SCO and *a fortiori* the bistability may be lost when downsizing to the nanoscale or to the single molecule level, and iii) the interaction with substrates (metallic, magnetic, etc.) can drastically affect the integrity of the molecular material and its switching properties.^{[2]-[5]} In a quest to tackle these limitations, we designed three new neutral Fe(II) Schiff base complexes tethered with electron-withdrawing and electron-donating groups so as to achieve a local dipolar moment and thus potentially increase their sensitivity towards an applied external electric field (Figure 1a). Magnetic susceptibility measurement experiments in their bulk revealed that the FeQ4NEt₂ material undergoes a thermal SCO transition at around 110 K with a hysteresis loop of 11 K width, which interestingly depends on the temperature's sweep rate (Figure 1b). However, this was not the case for the ClFeQ4NEt₂ derivative, which was locked in its HS state in the whole temperature range. We performed basic Hückel calculations on their ligands and estimated their HOMO-LUMO energy levels and gaps that allow rationalizing the SCO behavior. FeQ4NEt₂ was sublimed under ultra-high vacuum conditions on graphene(Gr)/SiO₂ substrate, and the thermal SCO behavior of the FeQ4NEt₂/Gr/SiO₂ hybrid was examined by X-ray absorption spectroscopy studies.

Fig. 1 a) Fe(II) Schiff base investigated complexes, b) $\chi_M T$ vs. T thermal variation of FeQ4NEt₂ material.



Références

1. Senthil Kumar, K.; Ruben, M., *Coord. Chem. Rev.*, **2017**, *346*, 176-205.
2. Mallah, T.; Cavallini, M., *C. R. Chimie*, **2018**, *21*, 1270-1286.
3. Kipgen, L.; Bernien, M.; Tuczek, F.; Kuch, W., *Adv. Mater.*, **2021**, *33*, e2008141.
4. Iasco, O.; Rivière, E.; Guillot, R.; Buron-Le Cointe, M.; Meunier, J-F.; Bousseksou, A.; Boillot, M-L., *Inorg. Chem.*, **2015**, *54*, 1791-1799.
5. Johannsen, S.; Gruber, M.; Barreteau, C.; Seredyuk, M.; Real, J.A.; Markussen, T.; Berndt, R., *J. Phys. Chem. Lett.*, **2023**, *14*, 7814-7823

EXPLORING SUPRAMOLECULAR NANOTUBE DEPOSITION THROUGH A SOFT MATTER PERSPECTIVE FOR SINGLE-CHAIN MAGNETS

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Mots-clés: Molecular magnetism, Single-Chain Magnets, Lanthanides, Supramolecular, Nanotubes

Résumé: Since their discovery three decades ago, Single-Molecule Magnets (SMMs) have met a huge interest as potential nano-sized elementary units for information storage thanks to their magnetic hysteresis and slow magnetization relaxation.^[1] Observations of these features were extended in one-dimensional polymeric chains called afterwards Single-Chain Magnets (SCMs).^[2] However, the inherent poor solubility of such 1D compounds makes them difficult to isolate on surface, unlike SMMs.^[3]

To bypass the obstacle, we have established a protocol to obtain a new kind of soft-matter magnetic compounds from $Tb(hfac)_3$ ($hfac^-$ = hexafluoroacetylacetonate) and alkoxy phenyl nitronyl-nitroxide (NIT) building blocks.

Depending on the size of the NIT's alkyl tail, either crystals or gels can be obtained, made of helical chains that arrange themselves into close nanotubes. Because of these similar arrangements, slow relaxation of the magnetization of SCM origin and open hysteresis loops have been measured, which is unprecedented for metallogels. We have also demonstrated that such nanotubular structures can be deposited and observed on surface, thanks to enhanced supramolecular interactions.^[4]

This metallogel approach could be a promising way to synthesize new functional materials, taking advantage of the properties of gels.

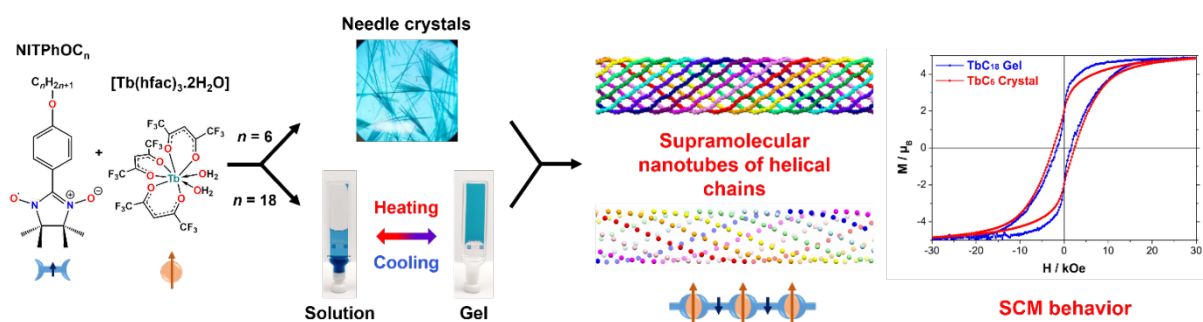


Fig. 1 Schematic representation of the present study, with the initial building blocks, the obtained compounds, their relative molecular organization and hysteresis curves.

References:

- [1] C. Benelli, D. Gatteschi, *Introduction to Molecular Magnetism: From Transition Metals to Lanthanides*, Wiley-VCH, Weinheim, **2015**.
- [2] C. Coulon, V. Pianet, M. Urdampilleta, R. Clérac, in *Molecular Nanomagnets and Related Phenomena* (Ed.: S. Gao), Springer Berlin Heidelberg, Berlin, Heidelberg, **2014**, pp. 143–184.
- [3] (a) A. Cornia, M. Mannini, P. Saintavit, R. Sessoli, *Chem. Soc. Rev.* **2011**, *40*, 3076. (b) R. J. Holmberg, M. Murugesu, *J. Mater. Chem. C* **2015**, *3*, 11986–11998. (c) G. Gabarró-Riera, G. Aromí, E. C. Sañudo, *Coordination Chemistry Reviews* **2023**, *475*, 214858.
- [4] F. Houard, G. Cucinotta, T. Guizouarn, Y. Suffren, G. Calvez, C. Daignebonne, O. Guillou, F. Artzner, M. Mannini, K. Bernot, *Mater. Horiz.* **2023**, *10*, 547–555.

SOME EXOTIC LOW-D MAGNETIC INORGANIC SYSTEMS, FRUSTRATION vs. MAGNETIC ORDERING

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Mots-clés: Inorganic materials, Low-D magnetism, frustration, Idle spin, Spin-Liquid, ordering

Résumé: In this “tutorial-lecture”, I will use some compounds investigated in our laboratory to set the analogy that exists between low-dimensional molecular systems and “pure” inorganic ones. In our approach, magnetic transition metals are surrounded by counter-cations (alkali, alkali-earth) and oxo-anions (PO_4^{3-} , HPO_3^- , SeO_3^{2-} , TeO_3^{2-} ...) which play the role of molecular bridging spacers. It creates original tridimensional edifices in which low-D magnetic units emerge as building units. The possibility to tune M-X-M magnetic exchanges using mixed anionic ligands ($X = \text{O}^{2-}$ and F^- for instance) opens extra potentialities for sizeable behaviors.

In the selected examples, both magnetic frustration and the lattice dimensionality are key ingredients that may harbor exotic phenomena and unconventional states of matter, such as quantum spin liquids (QSLs),^[1] spin ice,^[2] superconductivity,^[3,4] and topological states.^[5] In most 1 or 2 spatial dimensions, the *Mermin-Wagner* theorem states that long-range ordering does not occur at finite temperatures, otherwise that assisted by magneto-crystalline anisotropy. However, in most of the real inorganic such magnetic ordering occurs at low-temperature. However, in some inorganic materials, it exists original intermediate topologies where strongly inner-coupled low-D topologies (chains, layers) are weakly coupled together via frustrated alien-magnetic M' ions, with very ambiguous roles towards the 3D-ordering. I will present such compounds studied at the lab, in which the M' “idle spin” like situation hesitates between a spin-liquid state or very specific magnetic orders. Such examples will be the opportunity to initiate a brief magnetic structure analysis using neutron diffraction data.

In the case of low-D ferromagnetic units, I will also show some possible drastic influence of the magnetocrystalline anisotropy and magnetic domains towards giant coercivity and magnet hardness, a specificity of extended coupled inorganic systems.^[7]

[1] Balents, L. Condensed-Matter Physics: *Nature*, **2016**, 540, 534–535.

[2] Bramwell et al. *Nature*, **2009**, 461, 956–959,

[3] Anderson, P. W. *RVB Theory of High Tc Superconductivity*. In *Novel Superconductivity*; Springer, Boston, MA, **1987**, 295–299

[4] Lee, P. A., *Rep.Prog.Phys.*, **2008**, 71, 012501

[5] Zhang et al. *Phys. Rev.* **2013**. B, 87, 144101, **2013**.

[6] Mentré, O., *Chem. Mater*, *Chem. Mater.* **2023**, 35, 3951–3959.

[7] Mentré. O. *Small Methods*. **2023**, 2300491

Deciphering the unusual pressure-induced electron transfer in the molecular switch

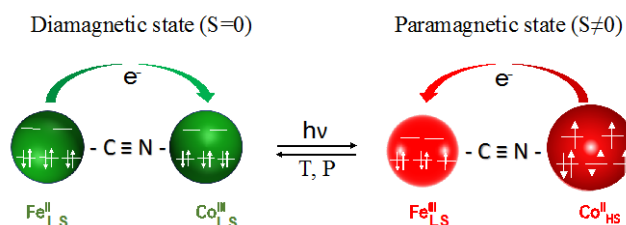
$\{[\text{Fe}(\text{Tp})(\text{CN})_3]_2[\text{Co}(\text{vbik})_2]_2\} \cdot (\text{BF}_4)_2 \cdot 2\text{MeOH}$: investigation by synchrotron X-Ray diffraction on single crystal

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Mots-clés: molecular switches; electron transfer; cyanide-bridged Fe/Co square; hydrostatic pressure; Synchrotron XRD diffraction on single crystal

Résumé: The bistable cyanide-bridged Fe_nCo_n clusters ($n = 1, 2, 4\dots$) have emerged since 2005 as molecular analogues of Fe/Co Prussian Blues. They have attracted growing interests as a new family of molecular switches.¹ The electronic state of these coordination clusters are highly sensitive to various external stimuli. For example, light irradiation, temperature or pressure change, can trigger a reversible intramolecular electron transfer from Fe to Co sites or vice versa in a Fe-CN-Co pairs. The electron transfer is accompanied by a spin transition on the Co site. The phenomenon is called Electron Transfer – Coupled Spin Transition (ETCST), as showed in the schema 1.



Schema 1. The Electron Transfer – Coupled Spin Transition (ETCST) in a FeCo pair.

In this communication, we present the study of a cyanide-bridged square complex, $\{[\text{Fe}(\text{Tp})(\text{CN})_3]_2[\text{Co}(\text{vbik})_2]_2\} \cdot (\text{BF}_4)_2 \cdot 2\text{MeOH}$ (**1**) with Tp = tris(pyrazol-1-yl)borate and vbik = bis(vinylimidazole-2yl)ketone,² which is trapped in a paramagnetic at ambient pressure. The application of hydrostatic pressure transforms it into a bistable molecular switch with unusual ETCST behaviors, with a pressure-induced widening of a thermal hysteresis.³ In order to rationalize this phenomenon, the pressure-induced ETCST of **1** from paramagnetic to diamagnetic state at room temperature has been followed by synchrotron X-Ray diffraction on single crystal (SC-XRD). The structural and geometrical evolution of **1** versus pressure were carefully analyzed, as well as the main types of intermolecular interactions. The variation of unit cell parameters versus pressure of **1** enabled the extraction of linear bulk moduli in the directions of the crystallographic axes, two of which were correlated to the dominant intermolecular interactions. The highest Gruneisen parameter never reported in the literature for **1** indicates its highly anharmonic nature of the lattice potential, which may be responsible for the increasing thermal hysteresis width with increasing pressure.

Références:

1. Nihei M., Chem. Lett., **2020**, 49, 1206-1215.
2. De S., Jiménez J.-R. et al. *RSC Advances*, **2016**, 6, 17456-17459.
3. Li Y., Benchohra A. et al. *Angew. Chem. Internat. Ed.* **2020**, 59(39), 17272-17276.

SIMPLE RESOLUTION OF THE STANDARD MULTISPIN HAMILTONIAN IN THE WEAK EXCHANGE REGIME

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Mots-clés: weak-exchange limit; magnetic anisotropy; proper axis frame of anisotropy; model multispin Hamiltonian; effective Hamiltonian theory; spin-orbit configuration interaction calculations;

Résumé: Simple model Hamiltonians play a pivotal role in bridging quantum mechanical (QM) calculations with magnetic-property experiments, providing a framework for the rational design of single-molecule magnets (SMMs) with magnetic hysteresis closer to room temperature.^[1] The description of magnetic properties in general binuclear complexes is particularly difficult in the weak-exchange regime. This is because, in such a case, the (isotropic) exchange interaction between the localized magnetic moments is weak, much weaker than the local magnetic anisotropies, a pure spin fails to describe the ground electronic state, and the low-energy spectrum is plagued by spin-mixing.^[2]

A pathway for the extraction and rationalization of magnetic properties in the weak-exchange limit is by resolving the standard multispin Hamiltonian (\hat{H}^{MS}). This Hamiltonian takes into account the Heisenberg isotropic exchange and the magnetic anisotropy, among others, and can be validated and resolved by means of QM calculations through the effective Hamiltonian theory.^[3] However, the rigorous extraction of \hat{H}^{MS} in such a procedure may require to introduce high-order anisotropy tensors, such as biquadratic spin-tensors, that are complicated to address.^[4] Furthermore, in absence of centrosymmetry, the choice for a molecular, magnetic proper axis frame (MPAF) becomes less obvious and the fact that the local anisotropy tensors do not align in the MPAF has been overlooked so far.

In this contribution we show how to setup the basis for a consistent use of \hat{H}^{MS} in its simple form to extract and rationalize magnetic properties in binuclear complexes. We provide a simple yet rigorous strategy that always leads to resolution of the model, without relying on assumptions and regardless of the overall point group symmetry. A procedure for defining the MPAF will be presented. The strategy will be showcased for binuclear Co(II) complexes (d^7-d^7) within the framework of two-step, spin-orbit configuration interaction calculations that rely on multiconfigurational complete active-space self-consistent field (CASSCF) wavefunctions and multireference n-electron valence state perturbation theory (NEVPT2) correlated energies.

Références:

1. Gould, C. A.; McClain, K. R.; Reta, D. et al., *Science* **2022**, 375, 198-202.
2. Maurice, R.; de Graaf, C.; Guihéry, N., *Phys. Rev. B* **2010**, 81, 214427.
3. Maurice, R.; Bastardis, R.; de Graaf, C.; Suaud, N.; Mallah, T.; Guihéry, N. *J. Chem. Theory Comput.* **2009**, 5, 2977-2984.
4. Maurice, R.; Guihéry, N.; Bastardis, R.; de Graaf, C. *J. Chem. Theory Comput.* **2010**, 6, 55-65.

MODIFICATIONS OF TANABE-SUGANO D6 DIAGRAM INDUCED BY RADICAL LIGAND FIELD: AB INITIO INSPECTION OF A FE(II)-VERDAZYL MOLECULAR COMPLEX

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Mots-clés: *ab initio*; molecular magnetism; Tanabe-Sugano, radical, *spinmerism*

Résumé: Quantum entanglement between the spin states of a metal centre and radical ligands is suggested in an iron(II) $[\text{Fe}(\text{dipyvd})_2]^{2+}$ compound (dipyvd = 1-isopropyl-3,5-dipyridil-6-oxoverdazyl). Wavefunction *ab initio* (Difference Dedicated Configuration Interaction, DDCI) inspections were carried out to stress the versatility of local spin states. We named this phenomenon *excited state spinmerism*, in reference to our previous work where we introduced the concept of *spinmerism* as an extension of mesomerism to spin degrees of freedom. The construction of localized molecular orbitals allows for a reading of the wavefunctions and projections onto the local spin states. The low-energy spectrum is well-depicted by a Heisenberg picture. A 60 cm^{-1} ferromagnetic interaction is calculated between the radical ligands with the $S_{\text{total}} = 0$ and 1 states largely dominated by a local low-spin $S_{\text{Fe}} = 0$. In contrast, the higher-lying $S_{\text{total}} = 2$ states are superpositions of the local $S_{\text{Fe}} = 1$ (17%, 62%) and $S_{\text{Fe}} = 2$ (72%, 21%) spin states. Such mixing extends the traditional picture of a high-field d^6 Tanabe-Sugano diagram. Even in the absence of spin-orbit coupling, the avoided crossing between different local spin states is triggered by the field generated by radical ligands. This puzzling scenario emerges from versatile local spin states in compounds which extend the traditional views in molecular magnetism.^[1]

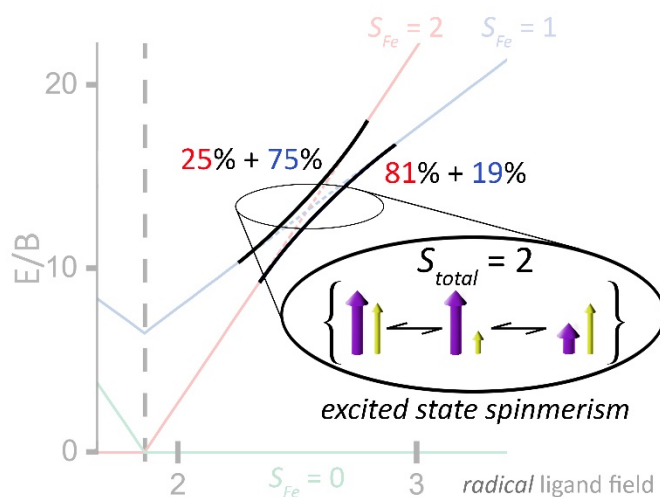


Fig. 1 Based on wavefunction calculations, a manifestation of the mixing of local spin states in excited states, the so-called “*spinmerism*” effect, suggests an extension of the d^6 Tanabe-Sugano diagram in the presence of open-shell radicals.

Références:

1. Roseiro, P; Yalouz, S; Brook, D.J.R; Ben Amor, N; Robert, V, *Inorg. Chem.* **2023**, 62, 14, 5737-5743

HIGH-TEMPERATURE SYMMETRY BREAKING. EXPERIMENTAL AND THEORETICAL ANALYSIS OF [FE(PM-PEA)₂(NCS)₂]

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Mots-clés: Symmetry-breaking, Spin Crossover, Landau theory.

Résumé: Phase transitions commonly result in the appearance of unique physical properties and interesting practical applications. Some materials, as in the case of spin-crossover (SCO) systems, exhibiting a change of electronic state upon application of external stimuli such as temperature, pressure, light irradiation, electric or magnetic fields, may display structural distortions or symmetry-breaking (SB) coupled to the electronic change. This coupling brings the possibility for tailored tuning of ordering-related properties like ferromagnetism, ferroelectricity, or ferroelasticity.^[1]

Nevertheless, due to entropy considerations, the disordered high-symmetry (*hs*) phase is generally the one stable at high-temperature (*HT*), while at low-temperature (*LT*), the ordered low-symmetry (*ls*) phase is the stable one. In this sense, the practical application of this systems is severely limited due to optimal temperature factors.

In this work, we present an experimental and theoretical analysis performed on the SCO system [FE(PM-PEA)₂(NCS)₂]^[2], which shows a highly cooperative and unusual SB at high temperature. It goes from a low-temperature low-spin (*LS*) phase with high symmetry (*LS_{hs}* - *Pccn* space group) to a high-temperature high-spin (*HS*) phase with low-symmetry (*HS_{ls}* - *P2₁/c* space group), see Fig. 1. On one hand, our crystallographic and magnetic studies have shown the coupling between SCO and SB, while DFT calculations have demonstrated a Jahn-Teller molecular instability in the *HS* phase as the origin of the symmetry breaking. To rationalize the behavior of this system, here we also contrast these results in the frame of a Landau theory-based model, which reliably reproduces the experimental observations as it accounts for the coupling between SB and SCO through the volume strain.^[3] This outcome opens the way for the potential development of devices with room temperature ordering-related functionalities.

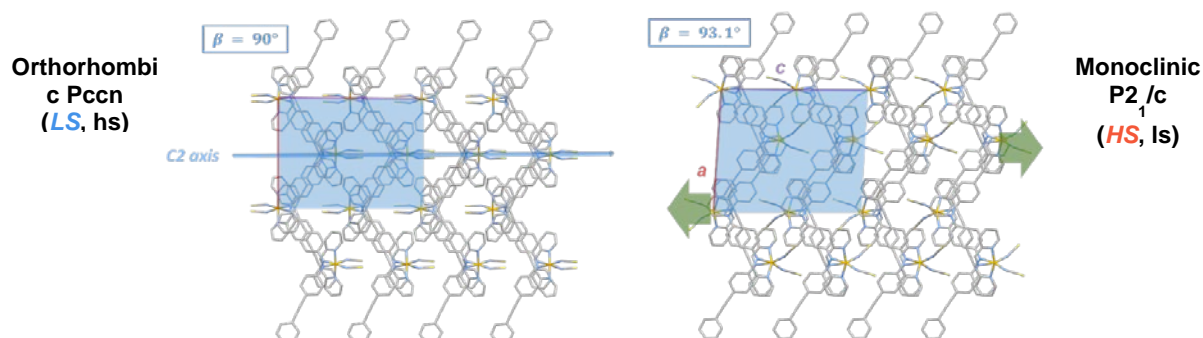


Fig. 1 Symmetry breaking of Fe(PM-PEA) crystal, from the low-temperature low-spin high-symmetry (*LS_{hs}* phase, *Pccn* space group) to the high-temperature high-spin low-symmetry (*HS_{ls}* phase, *P2₁/c* space group). Resulting sliding of the molecular layers and NCS groups torsion due to the loss of the molecular *C2* axis along the *c* direction.

Références:

1. Ohkoshi, et. al. *Angew. Chem.* **2007**, 46(18), 3238-3241.
2. Guionneau, P. et. al. *J. Mater. Chem.* **1999**, 9(4), 985-994.
3. Collet, E., Azzolina, G. *Phys. Rev. Materials.* **2021**,5(4), 1-11.

MECHANICAL PROPERTIES OF COMPOSITE MATERIALS BASED ON MIXED-ANION $\text{Fe}(\text{NH}_2\text{Trz})_3(\text{BF}_4)(\text{SiF}_6)_{0.5}$ SPIN CROSSOVER COMPLEX AND POLYURETHANE

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Mots-clés: spin-crossover materials; polyurethane; composites materials; mechanical measurements; actuators

Résumé: Multifunctional composite spin-crossover materials based on polymers are of great interest since they allow the coupling of the polymer properties to those of the spin-crossover complex^[1]. In this field, the volume change that can occur during the spin-crossover phenomenon can be used to generate interesting actuation properties.^[2-4] In this work, a new pure mixed-anion $\text{Fe}(\text{NH}_2\text{trz})_3(\text{BF}_4)(\text{SiF}_6)_{0.5}$ spin crossover complex is obtained implementing a solid–liquid post synthetic modification (PSM) approach from the $\text{Fe}(\text{NH}_2\text{trz})_3(\text{BF}_4)_2$ parent complex. This compound presents an abrupt spin crossover behavior with a narrow (10 K) hysteresis loop centred just above room temperature (320 K) which makes it very interesting for future integration into devices for various applications^[5]. Composite monolayer films and bilayer devices were prepared by dispersing rod-shaped $\text{Fe}(\text{NH}_2\text{trz})_3(\text{BF}_4)(\text{SiF}_6)_{0.5}$ particles in a Thermoplastic Polyurethane (TPU) polymer matrix using a blade casting method. The coupling of the properties of the complex and the matrix gives rise to interesting mechanical/actuation properties.

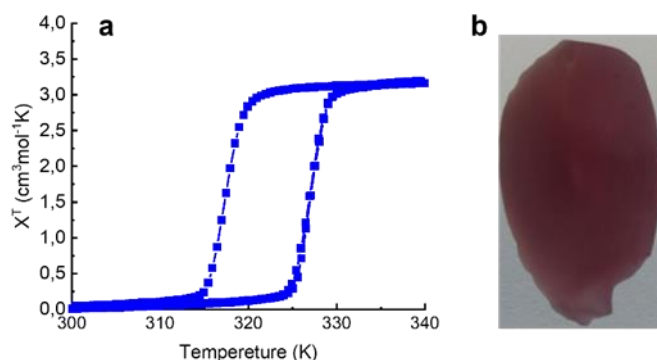


Fig. 1 (a) Thermal variation of the magnetic measurement for $\text{Fe}(\text{NH}_2\text{trz})_3(\text{BF}_4)(\text{SiF}_6)_{0.5}$, (b) $\text{Fe}(\text{NH}_2\text{trz})_3(\text{BF}_4)(\text{SiF}_6)_{0.5}$ @TPU composite film.

Références:

1. Y.-S. Koo et al., *Adv. Mater.* **2014**, 26, 6785–6789.
2. H. J. Shepherd et al., *Nat. Commun.* **2013**, 4, 260.
3. M. Piedrahita-Bello et al., *Mater. Horiz.* **2021**, 8, 3055.
4. Y. Zan et al., *Adv. Intell. Syst.* **2023**, 2200432.
5. Y. Xinyu et al., *Dalton Transactions*, **2023**.

ELASTIC INVESTIGATIONS OF THE DYNAMICS OF COOPERATIVE SPIN STATES: SELF-ORGANIZATION AND MACROSCOPIC DEFORMATIONS OF SPIN-CROSSOVER MULTI-LAYERS

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Keywords: Spin-crossover; 3D modeling; relaxation; elastic anisotropy; frustration; self-organization.

The present work is devoted to the study of 3D switchable spin-crossover (SCO) multi-layers, accounting for elastic frustration effects and elastic anisotropy. The modeling is performed using an adapted version of our electro-elastic model^[1] which includes the lattice volume change at the spin transition. The numerical calculations were made using Monte Carlo (MC) Metropolis for the spin state combined with a semi-analytical method of relaxation of the lattice positions, which revealed to be very efficient in terms of computational time. The 3D character of the simulations allows the molecules to leave the plane of the 2D sheets, thus leading to corrugations and buckling that lead to considerably relax the elastic strain. Various cases of elastic interactions are then studied, among which, those accounting for anisotropic elastic constants and others including an intrinsic elastic frustration in the LS and/or HS states. As a result, multi-stepped relaxation curves are obtained for the temporal behavior of the HS fraction, displaying the emergence of complex self-organizations of the spin states in the plateaus regions. In addition to the usual checkerboard antiferro-like high-spin (HS) low-spin (LS) structures, alternate HS and LS planes organizations were also got, recalling experimental data of Fe-picolyamine compound^[2], which remained an open theoretical problem to date. Use the following notation for references.^[1]

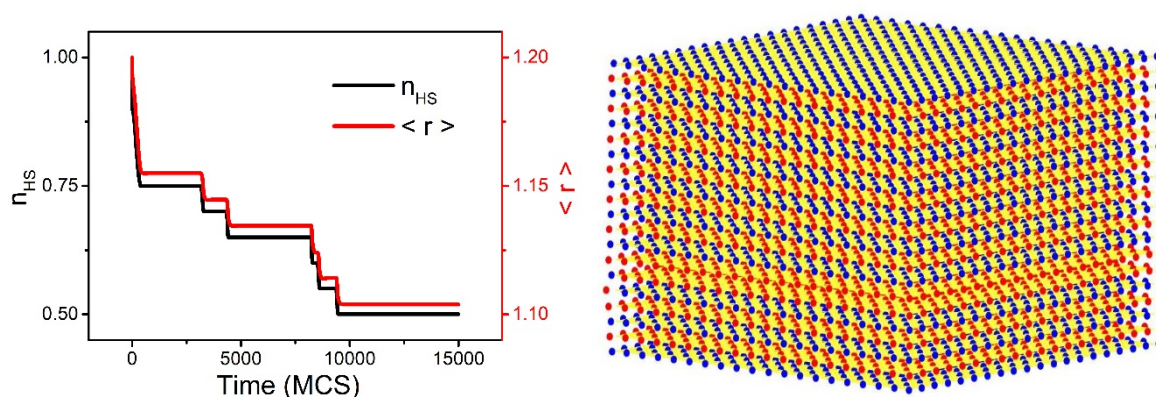


Fig. 1 Example of an isothermal relaxation at 10K starting from the HS state in the case of anisotropic elastic constants and intrinsic elastic frustration in the LS state. On the left, plots of the high spin fraction n_{HS} and the average lattice spacing $\langle r_{ij} \rangle$, as a function of time. On the right, the spatial spin configuration after the relaxation.

Références:

1. Slimani, A; Boukheddaden, K; Varret, F; Oubouchou, H; Nishino, M; Miyashita, S, *Phys Rev B*. **2013**, 87(1), 014111.
2. Chernyshov, D; Hostettler, M; Törnroos, K. W; Bürgi, H. B; *Angew Chem Int Ed*. **2003**, 42(32), 3825-3830.

Jeudi 16 novembre

CONTROL OF 4f COMPLEXES LUMINESCENCE AND MAGNETISM WITH ORGANIC PHOTOSWITCHES

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Mots-clés: Photochromic ligands, lanthanide(III) ions, luminescence, Single-Molecule Magnets

Résumé:

At the heart of various high technology applications, rare earth optical and magnetic properties both find their origin in the fascinating electronic structures of lanthanide(III) ions. Our research deals with the control of lanthanide molecular complexes with light and target either luminescence photomodulation or photomagnetism. In this tutorial presentation, I will introduce several families of organic photoswitches. Understanding which property of the organic switch is affected upon light induced reaction is key to understand ligand design. Indeed, one can target the optical control of luminescent materials with potential applications such as super resolution imaging^[1] or authentication solutions.^[2] The specificities of lanthanide-based emission combined with such light control could lead to innovative solution in the field of bioimaging and smart materials.^[3] I will describe important examples from the literature and then focus on our recent work with photochromic β -diketonate ligands having a dithienylethene ligand, that we could coordinate to a variety of lanthanide ions including NIR or visible emitters in order to understand the photophysical mechanisms at play.^[4] On the other hand, these photoswitchable ligands can also be designed to implement efficient control of Single Molecule Magnets via a contactless and fast external stimulation. Over the years, we have developed several strategies based either on spiropyran ligands,^[5] or the association of highly anisotropic dysprosium complexes and dithienylethene photoswitches (Fig. 1).^[6,7] I hope to show that these strategies are complementary to approach the challenging goal of photoswitchable SMM as well as to describe the current advances in this field of research.

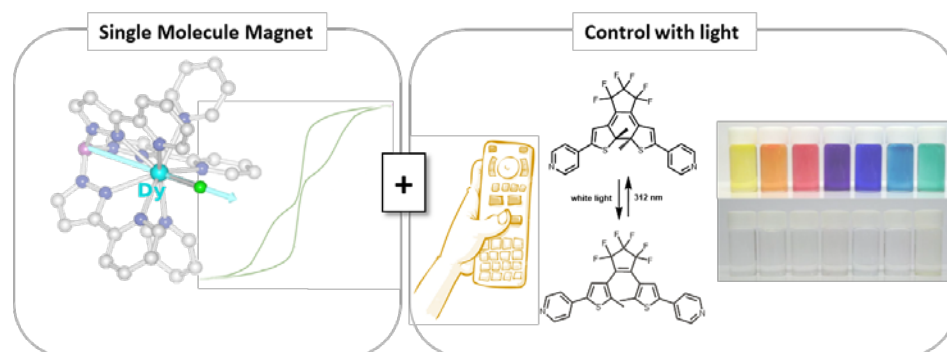


Fig. 1 Schematic view of the strategy used to reach photomagnetic effects with organic photoswitches.

Références:

1. Z.Y.Tian, A.D.Q. Li, *Accounts of Chemical Research* **2013**, 46(2) 269.
2. A. Abdollahi, H. Roghani-Mamaqani, B. Razavi, M. Salami-Kalajahi, *ACS Nano* **2020**, 14, 11, 14417.
3. L. Norel, O. Galangau, H. Al Sabea, S. Rigaut, *ChemPhotoChem* **2021**, 5(5) 393.
4. H. Al Sabea, L. Norel, O. Galangau, T. Roisnel, O. Maury, F. Riobé, S. Rigaut, *Adv. Funct. Mater.* **2020** 2002943.
5. P. Selvanathan, G. Huang, T. Guizouarn, T. Roisnel, G. Fernandez-Garcia, F. Totti, B. Le Guennic, G. Calvez, K. Bernot, L. Norel, S. Rigaut, *Chem. Eur. J.* **2016**, 22, 15222.
6. M. Hojorot, H. Al Sabea, L. Norel, K. Bernot, T. Roisnel, F. Gendron, B. Le Guennic, E. Trzop, E. Collet, J. R. Long, S. Rigaut, *J. Am. Chem. Soc.* **2020**, 142, 931.
7. N. El Beyrouiti, F. Houard, M. Cordier, E. Trzop, S. Rigaut, B. Le Guennic, K. Bernot, L. Norel, *Chem. Commun.* **2023**, DOI: 10.1039/D3CC01037F.

SPIN CROSSOVER IN SELF-ASSEMBLED MONOLAYERS FOR MOLECULAR ELECTRONICS APPLICATIONS

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Mots-clés: Spin Crossover; Molecular Junction; Molecular Electronics.

Résumé: Spin crossover complexes (SCOs) are transition metal complexes that exhibit reversible state switching, often at ambient conditions. In iron (II) complexes, switching occurs between a diamagnetic low spin state ($S=0$) and a paramagnetic high spin state ($S=2$). The switching is accompanied by a change in the electronic properties, such that molecular junctions of these SCOs exhibit a change in conductance with the spin state^[1].

The goal of my thesis is to prepare molecular junctions of these molecules, and to characterise their conductance behaviour in the low spin versus the high spin states. We have prepared a library of functionalised iron (II) SCOs with different spin crossover temperatures and characteristics. With these SCOs we prepare self-assembled monolayers (SAMs) that exhibit temperature- and photo-induced switching. We fabricate molecular junctions using eutectic gallium indium (EGaIn) as a conforming top electrode. This project hopes to bring SCOs closer to applications in molecule-based electronics.

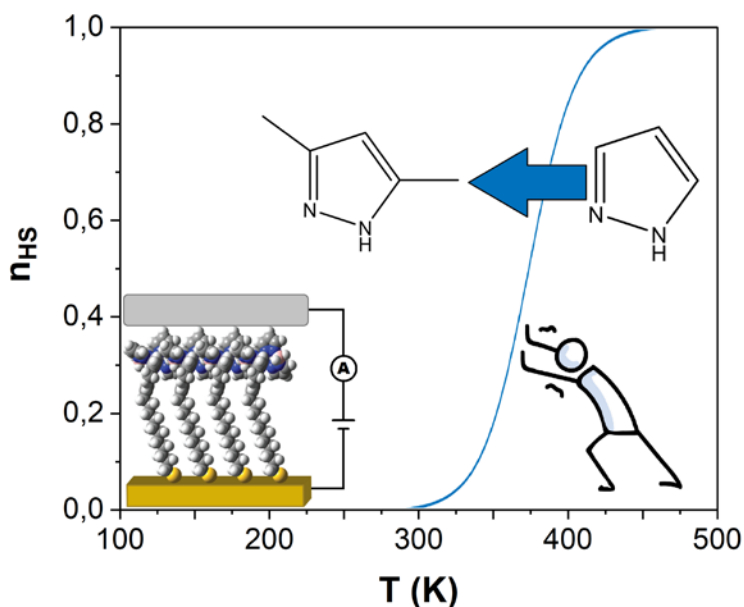


Fig. 1 One way to tune the spin crossover temperature of iron (II) complexes is to change the degree of methylation of the ligands. The goal of this project is to fabricate molecular junctions that are switchable around room temperature, with a less conductive (low spin) state below room temperature and a more conductive (high spin) state above room temperature.

Références:

1. Poggini, L.; Gonidec, M.; González-Estefan, J.; Pecastaings, G.; Gobaut, B.; Rosa, P., *Adv. Elec. Mater.* **2018**, 4 (12), 1800204.

NEW FAMILIES OF CUBIC MOLECULAR SWITCHES

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Mots-clés: Molecular switches ; PBAs, Ligand functionalization, Surface grafting

Résumé:

In recent years, we have been interested in the design of new molecular models of PBAs (Prussian Blue Analogue), aiming for soluble complexes with attractive electronic properties ((photo)magnetic and redox). In this context, multiple cubic cages of general formula $A\Box\{[(M)(L)(CN)_3]_4[(M')(L')_3]_4\}$ have been reported, where the metals (M and M') are linked by cyanides and usually capped by scorpionate ligands (L and L'), and in which a cation A^+ can be inserted.¹⁻² In this communication, we present our recent attempts at exploring the chemical versatility of these systems. More particularly, we aim at incorporating new ancillary ligands that could allow the introduction of reactive groups at the periphery of the cubic units.

We first showed that the reaction of a tris-cyanido *fac*-[Fe^{III}(Tp)(CN)₃]⁻ complex with a metal salt (M' = Ni(II) or Co(II)) leads to a "Pro-cube", where the M' metal is capped by solvent molecules. Interestingly, in certain conditions the procubes can be stable in solution and in powder form, and can be further used in a second step to react with different ligands. For example, capping a Cs⁺□{[Fe(Tp)(CN)₃]₄[Ni(S)₃]₄}⁴⁺ procube with Imidazole (Im) leads to the novel Cs□{[Fe(Tp)(CN)₃]₄[Ni^{II}(Im)₃]₄}Cl₃ cubic complex, which can be crystallized by slow diffusion of ether into the DMF mother liquor.³ We showed that the oxidation states of the Fe ions of the cube evolve over time. An intermediate Fe^{II}Fe^{III}₃Ni^{II}₄ redox state can be crystallized in 72h, before evolving towards the more stable the Fe^{II}₂Fe^{III}₂Ni^{II}₄ redox state, leading to a change of redox and magnetic properties. Furthermore, reacting one equivalent of the monodentate 4-aminopyridine and one equivalent of the bidentate 2,2-bipyridine on a Cs⁺□{[Fe(Tp)(CN)₃]₄[Co(S)₃]₄}⁴⁺ procube leads to the Cs□{[Fe(Tp)(CN)₃]₄[Co^{II}(2,2bipy)(NH₂-py)]₃]₄}·4ClO₄ cube, which also crystallizes by diffusion of ether into DMF, allowing us to probe its properties in the solid state. Moreover, both the monodentate and/or the bidentate ligand can be changed, leading to a wide array of cubes bearing different functions (amino, diazo, thiols...) and with different ligand field. It opens the door to functionalized cubes, which can be used for surface grafting or break-junction analyses.

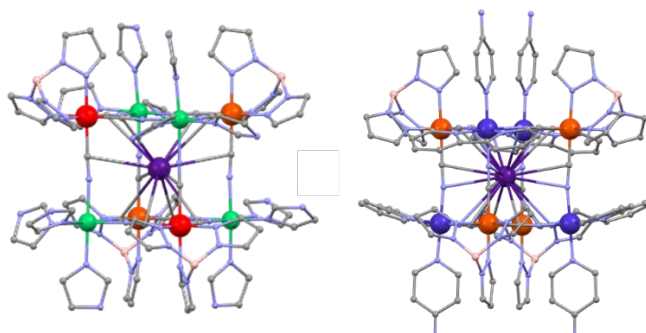


Fig. 1 Crystal structures of Cs□{[Fe(Tp)(CN)₃]₄[Ni^{II}(Im)₃]₄}Cl₃ (left) and Cs□{[Fe(Tp)(CN)₃]₄[Co^{II}(2,2bipy)(NH₂-py)]₃]₄}·4ClO₄ (right)

Références:

1. Jiménez, J.-R.; Tricoire, M.; Garnier, D.; Chamoreau, L.-M.; von Bardeleben, J.; Journaux, Y.; Li, Y.; Lescouëzec, R. *Dalton Trans.* **2017**, *46*, 15549-15557
2. Glatz, J., Chamoreau, L.-M., Flambard, A., Meunier, J.-F., Bousseksou, A., Lescouëzec, R. *Chem. Commun.*, **2020**, *56*, 10950-10953
3. Glatz, J., Donnart, M., Gontard, G., Li, Y., Lescouëzec, R. *Cryst. Growth Des.*, **2023**, *23*, 3, 1709-1717

Posters

RECENT DEVELOPMENTS IN TRANSITION METAL K-EDGE XMCD FOR MOLECULAR MAGNETISM

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Mots-clés: Local magnetism; Prussian Blue analogs; Transition metal; XMCD

Résumé: For the last years, we have been involved in the study of Transition Metal (TM) K-edge X-ray Magnetic Circular Dichroism (XMCD) using Prussian Blue Analogs (PBAs ; $Y_xA_4[B(CN)_6]_{(8+x)/3} \cdot nH_2O$; Y =alkali cation, $x=0-4$, A,B =transition metal) in order to disentangle the physical effects originating these signals in molecular compounds.^[1-4] A tool combining chemical selectivity and bulk sensitivity is indeed missing for the investigation of their magnetic properties. Our experiments first dedicated to the bimetallic $A_4[Fe(CN)_6]_{2.7}$ ($A=Mn,Co,Ni,Cu$) and $A_4[Cr(CN)_6]_{2.7}$ PBAs ($A=Mn,Fe,Co,Ni$) PBAs and more recently to the trimetallic $(Ni_xCo_{1-x})_4[Fe(CN)_6]_{2.7}$ series brought unprecedented information. By analyzing first the A K-edge of the bimetallic PBAs, we could establish that qualitative and quantitative parameters of the main $1s \rightarrow 4p$ contribution to the XMCD signal are related to the magnetic behavior of the absorbing atom: (i) the shape to the filling of the $3d$ orbitals, (ii) the sign to the orientation of the magnetic moment with respect to the applied magnetic field, (iii) the intensity of the signal to the total spin number (S_A) and (iv) the area-under-peak to the Curie constant (C_A).^[2] Additionally, the results at the Ni and Co K-edge of the trimetallic series showed that TM K-edge XMCD is, at the N side of the cyanide bridge, a probe of only the absorbing atom (Ni or Co) and not of the whole sublattice. The analyses of the Fe and Cr K-edges showed that, at the C side of the cyanide bridge, TM K-edge XMCD is a probe of the absorbing atom as well as its interactions with its first magnetic neighbors. We could establish explicit relationships between the intensity and the total spin of the species to which the photoelectron is sensitive;^[3,4] the agreement between the intensity calculated using our expressions and the experimental one is illustrated Fig. 1. Valuable information (i) on the exchange interactions between all involved $3d$ and $4p$ orbitals and (ii) on the local orientation of the magnetic moment carried by the absorbing atom (Fig. 1) were thus proposed. A summary of our previous results on the bimetallic PBAs and the very recent ones on the trimetallic series will be presented, with the new possibilities it offers to molecular magnetism.

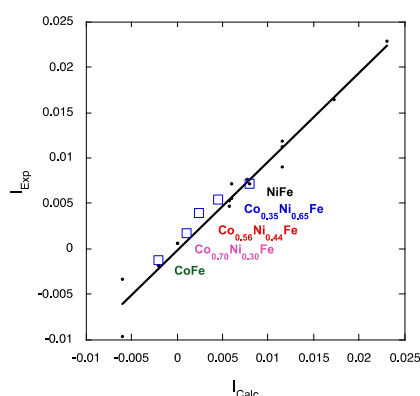


Fig. 1 Experimental intensity (I_{exp}) vs the one calculated using our expressions (I_{calc}) [3-4] for the bimetallic (dots) and trimetallic series

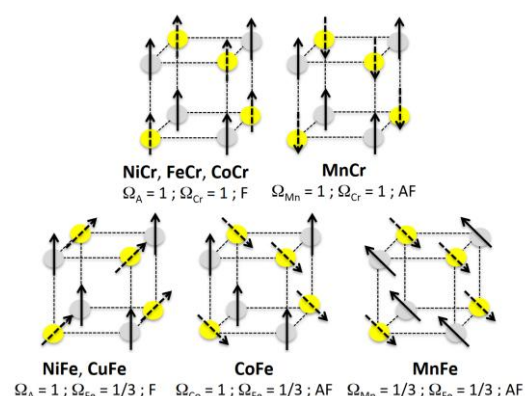


Fig. 2 Proposed orientations of the magnetic moments for an octant of the PBA structure

Références:

1. N'Diaye, A.; Bordage, A.; Nataf, L.; Baudalet, F.; Moreno, T.; Bleuzen, A., *J. Synch. Rad.* **2021**, 28, 1127-1136
2. N'Diaye, A.; Bordage, A.; Nataf, L.; Baudalet, F.; Rivière, E.; Bleuzen, A., *ACS Omega* **2022**, 7, 36366-36378
3. N'Diaye, A.; Bordage, A.; Nataf, L.; Baudalet, F.; Rivière, E.; Bleuzen, A., *Inorg. Chem.* **2022**, 61, 6326-6336
4. N'Diaye, A.; Bordage, A.; Nataf, L.; Baudalet, F.; Rivière, E.; Bleuzen, A., *Submitted*

EXPLORING VALENCE TAUTOMERISM AND REDOX PROPERTIES IN TRINUCLEAR TRIPHENYLENE COBALT COMPLEXES

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Mots-clés: Molecular switches; valence tautomerism; cobalt; hexahydroxytriphenylene

Résumé: Switchable molecules exhibiting reversible changes in their physical properties are highly promising for diverse applications, such as data storage and sensors.^[1] Following our work on Ni₃ complexes,^[2] this study aims at designing trinuclear cobalt complexes based on the tris-bidentate bridging hexahydroxytriphenylene (H₆HHTP) ligand (Fig 1),^[3] capable of displaying multi-step electronic switching. In these trinuclear complexes of general formula [M₃(L)₃HHTP]^{x-}, where M is a transition metal ion and L a tetradentate ligand, seven oxidation states of HHTP^{y-} are theoretically accessible, through reversible oxidations of the catechol (cat) species into semiquinone (sq), and to quinone (q). Using Co(II), the expected switching phenomenon is valence tautomerism (VT) that involves an intramolecular electron transfer between a paramagnetic Co(II) centre and a redox-active semiquinone, leading to the diamagnetic Co(III)-catechol form (Fig 1). The key-point is, therefore, to prepare trinuclear complexes comprising the Co(II)-sq and/or the Co(III)-cat species in order for the switching phenomenon to occur. This can be achieved by adjusting the Co crystal field through the nature of the ancillary tetradentate ligand L, as demonstrated by prior investigations on mononuclear and dinuclear Co complexes.^{[4], [5]} In this work, [Co₃(Me_ntpa)₃HHTP]^{x-} (n = 0-3) complexes have been prepared and characterized both in solid-state and solution. Preliminary experiments revealed that [Co₃(Me₂tpa)₃HHTP]³⁻ undergoes a VT transition at 400K, attributed to the conversion of Co^{II}Co^{II}₂[cat cat sq]³⁻ into Co^{II}Co^{III}[cat sq sq]³⁻ upon heating. However, crude [Co₃(Me₃tpa)₃HHTP]^{x-} displayed a redox-state mixture of Co^{II}₃[sq sq sq]³⁻ and Co^{II}₃[cat sq sq]⁴⁻, with no VT upon cooling. Nevertheless, this compound showed intriguing redox properties, enabling access to all seven redox states of HHTP^{y-}, as supported by cyclic-voltammetry and spectro-electrochemical measurements in solution.

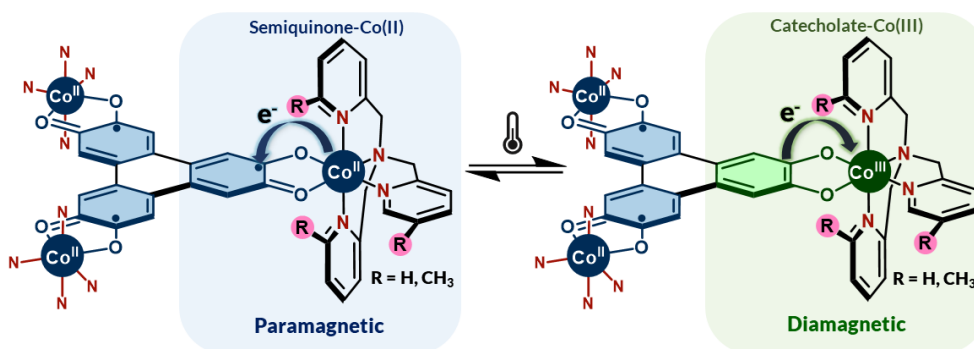


Fig. 1 Valence tautomerism in a [Co₃(Me_ntpa)₃HHTP]³⁻ complex: temperature dependent interconversion between the Co^{II}₃[sq sq sq]³⁻ (left) and Co^{II}Co^{III}[cat sq sq]³⁻ (right) forms.

Références:

1. Kumar, K.; Ruben, M. Emerging Trends in Spin Crossover (SCO) Based Functional Materials and Devices. *Coord. Chem. Rev.* **2017**, *346*, 176–205.
2. Wang, Y.; Lambert, F.; Rivière, E.; Guillot, R.; Herrero, C.; Tissot, A.; Halime, Z.; Mallah, T. *Chem. Commun.* **2019**, *55* (82), 12336–12339.
3. Suenaga, Y.; Inada, H.; Inomata, M.; Yamaguchi, R.; Okubo, T.; Maekawa, M.; Kuroda-Sowa, T. *Chem. Lett.* **2014**, *43* (4), 562–564.
4. Beni, A.; Dei, A.; Laschi, S.; Rizzitano, M.; Sorace, L. *Chem. Eur. J.* **2008**, *14* (6), 1804–1813.
5. Alley, K. G.; Poneti, G.; Robinson, P. S. D.; Nafady, A.; Moubarak, B.; Aitken, J. B.; Drew, S. C.; Ritchie, C.; Abrahams, B. F.; Hocking, R. K.; Murray, K. S.; Bond, A. M.; Harris, H. H.; Sorace, L.; Boskovic, C. *J. Am. Chem. Soc.* **2013**, *135* (22), 8304–8323.

FAR-INFRARED STUDY OF $A_2Co_4[Fe(CN)_6]_{3.3} \cdot nH_2O$ PRUSSIAN BLUE ANALOGUES

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Mots-clés: Prussian Blue analogs; Alkali cation; Photomagnetism; Synchrotron IR spectroscopy

Résumé:

Changes in vibrational modes of materials provide a powerful tool for identifying the species involved in switching mechanisms between two electronic states. These changes enable to elucidate fine structural changes that accompany and sometimes precedes the transitions.^[1-2]

In the present work, a far-infrared study of a A_2CoFe series of Prussian Blue Analogues (PBA) having the chemical formula $A_2Co_4[Fe(CN)_6]_{3.3} \cdot nH_2O$, where A^+ is an alkali metal ion intercalated in the interstitial sites of the well-known face centered cubic structure of PBAs ($A^+ = K^+, Na^+, Rb^+$ and Cs^+), was carried out. The effects of the alkali metal ion nature on the metal-to-ligand vibrations were examined in all electronic states involved in both thermally activated and photo-induced switching properties, revealing a characteristic signature of alkali cations interacting with the $Fe^{II}-C \equiv N$ entities and their non-innocent role in the electron transfer between the $Co^{III}(LS)-Fe^{II}$ and $Co^{II}(HS)-Fe^{III}$ states. X-ray Absorption Spectroscopy (XAS) confirms the far-infrared spectral changes and supports the significant contribution of alkali metal ions in the electron transfers.^[3]

Références:

1. Tokoro, H.; Namai, A.; Yoshikiyo, M ; Fujiwara, R.; Chiba, K.; Ohkoshi, S-I., *Sci. Rep.* **2018**, 8,63
2. Lejeune, J.; Brubach, J-B.; Roy, P. ; Bleuzen, A., *C. R. Chimie* **2014**, 17,534-540
3. Dronova, M. ; Altenschmidt, L. ; Brubach, J-B. ; Roy, P. ; Balthazar, G.; Bordage, A.; Bleuzen, A., In prep.

SPIN CROSSOVER PROPERTIES OF Fe^{II} COMPLEX GROWN ON GRAPHENE SUBSTRATES

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Mots-clés: Spin-crossover, Graphene, X-ray Absorption Spectroscopy, Scanning Tunneling Microscopy

Résumé: Spin-crossover (SCO) molecules exhibit switchable spin states (high spin – HS – and low spin – LS – states) that can be controlled by external stimuli like light, temperature or electric field. This makes them promising molecules for incorporation in devices. Recently ^[1], it has been demonstrated that the spin state of thin molecular films (down to 100 nm) influences the conduction of electrons in graphene. To go to thinner thicknesses, it is of great interest to study this switching property with regards to the substrate in which the molecules are grown on and with respect to film thickness. Here we report a detailed report on the switching properties of the complex FeMPz grown as ultra-thin films on various substrates i.e. monolayer / multilayer graphene, HOPG. XAS measurements give a clear picture of the oxidation state of the central metal atom and thus give an idea of transition of molecules from one spin state to another. Scanning probe techniques (STM, AFM) are used for investigating molecular film growth and evolution.

Références:

1. N. Konstantinov et al., Mat. Chem. C 9, 2712 (2021)

MAGNETO-CHIRAL DICHROISM OF 3d-4f MAGNETIC CLUSTERS

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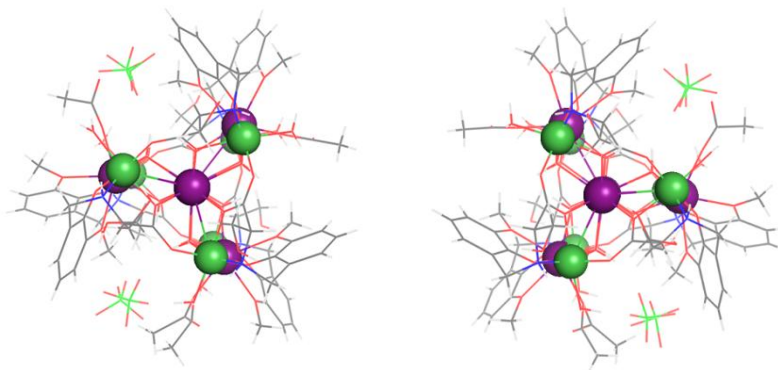
Keywords: Magneto-Chiral Dichroism; Chirality; Lanthanide; Spectroscopy; Magnetism

Résumé: Magneto-Chiral Dichroism (MChD) is a light-matter interaction that features a differential absorption of unpolarized light under a magnetic field by chiral magnetized systems. It depends on the relative orientation of the magnetic field (**B**) and the direction of light propagation (**k**). It also inverts sign for the two enantiomers of chiral systems and it is proportional to their magnetization¹⁻³.

Previously, our group reported MChD studies on **D**- and **L**-{Dy₅Ni₆} magnetic chiral clusters where electronic transitions of each enantiomer in the visible and near-infrared (NIR) region were probed⁴.

Herein, we present the extension of these results to the Erbium analog. It first be noted that systems including this element were never studied by MChD before. **D**- and **L**-{Er₅Ni₆} are isostructural to the Dy parent compounds. In the visible range, we successfully detected and assigned the electronic transitions belonging to both nickel(II) and erbium(III) ions. Furthermore, a strong MChD signal associated to the electronic transition ⁴I_{15/2}–⁴I_{13/2} of Er(III) was detected in the NIR region with similar intensity and reverse sign for the **D** and the **L** enantiomer of the cluster. This, confirms that MChD is highly sensitive to the electric/magnetic-dipole character of the investigated transitions and the magnetization of the sample.

Fig. 1 Crystal structure of **D**-{Er₅Ni₆} (left) and **L**-{Er₅Ni₆} (right)



References:

1. Atzori, M.; Dhbaibi, K.; Douin, H.; Grasser, M.; Dorcet, V.; Breslavetz, I.; Paillot, K.; Cador, O.; Rikken, G.L.J.A.; Le Guennic, B.; Crassous, J.; Pointillart, F.; Train, C., *J. Am. Chem. Soc.* **2021**, *143* (7), 2671-2675.
2. Atzori, M.; Santanni, F.; Breslavetz, I.; Paillot, K.; Caneschi, A.; Rikken, G.L.J.A.; Sessoli, R.; Train, C., *J. Am. Chem. Soc.* **2020**, *142* (32), 13908-13916.
3. Atzori, M.; Breslavetz, I.; Paillot, K.; Katsuya, I.; Rikken, G.L.J.A.; Sessoli, R.; Train, C., *J. Am. Chem. Soc.* **2019**, *141* (51), 20022-20025.
4. Wang, X.; Wang, S.Q.; Chen, J.N.; Jia, J.H.; Wang, C.; Paillot, K.; Breslavetz, I.; Long, L.S.; Zheng, L.; Rikken, G.L.J.A.; Train, C.; Kong, X.J.; Atzori, M.; *J. Am. Chem. Soc.* **2022**, *144* (19), 8837-8847

Photoswitchable nitronyl-nitroxide radical ligands for complexation with lanthanide cations

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Keywords: Photochromism, Stable Radicals, Lanthanide Complexes, Single-Molecule Magnets, Magnetic Anisotropy

Abstract:

Single Molecule Magnets (SMMs) offer unique features that may allow information to be stored with much higher densities, and to be processed at unprecedented speeds.^[1] To use SMM in information storage devices, it would be a great advantage to control the magnetic properties by applying external stimuli such as light.^[2] Some interesting candidates for SMMs, are nitronyl-nitroxide (NIT) radical ligands as they can form complexes with lanthanide cations that exhibit favorable magnetic behaviour.^[3] We target here new photoswitchable NIT ligands in which direct conjugation exist between the radical and the photoswitch, a dithienylethene (DTE).^[4] We hypothesize that photoswitching of these ligands bound to lanthanide cations will lead to similar but more spectacular photomagnetic effects as the recently reported photomodulation of magnetic hysteresis with a diamagnetic pyridyl terminated DTE (Figure 1).^[5]

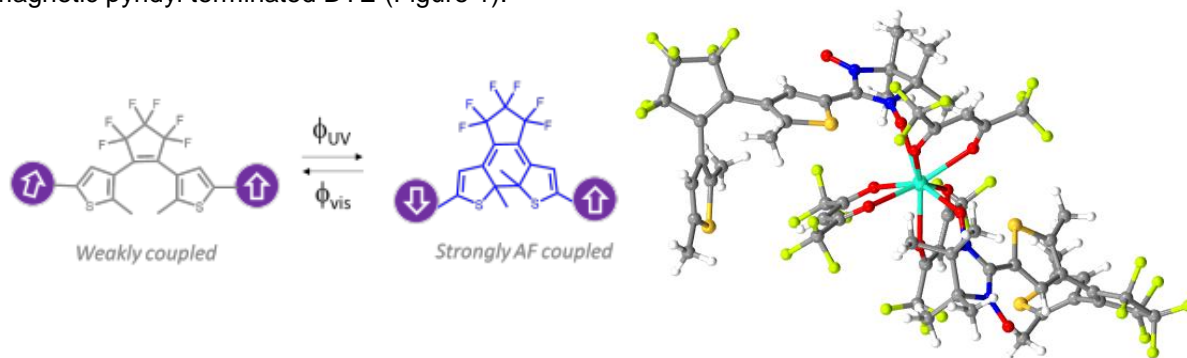


Fig. 1 Photoswitching abilities of the ligand and the impact on the electronic

Fig. 2 XRD structure of a Terbium (III) complex with photochromic NIT radicals

This poster presents a synthetic strategy to synthesize biradical and monoradical NIT ligands and their association with Terbium(III) precursors (Figure 2). The photophysical properties of the ligands and complexes will also be discussed.

Acknowledgments:

I would like to thank Région Bretagne and LUMOMAT for funding this project.

References:

1. Yamashita, M.; Katoh, K.; *Molecular Magnetic Materials: concepts and applications*, **2017**, 4, 79.
2. Zhu, Z.; Li, X.; Liu, S.; Tang, J.; *Inorg. Chem. Front*, **2020**, 7, 3315.
3. Bernot, K.; Bogani, L.; Caneschi, A.; Gatteschi, D.; Sessoli, R.; *J. Am. Chem. Soc.*, **2006**, 128 (24), 7947.
4. Matsuda, K.; Matsuo, M.; Irie, M.; *J. Org. Chem.*, **2001**, 66 (26), 8799-8803.
5. Hojorot, M.; Al Sabea, H.; Norel, L.; Bernot, K.; Roisnel, T.; Gendron, F.; *et al.*; *J. Am. Chem. Soc.*, **2020**, 142 (2), 931.

Towards terephthalonitrile radical-bridged metal-organic molecular architectures

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Organonitrile compounds have received significant attention for their application as organic ligands in coordination polymers and metal-organic frameworks (MOFs), thanks to their potential to mediate strong interactions between neighbouring metal ions via electron delocalisation in π -conjugated systems. Thereby, such networks can exhibit interesting conductive and, or magnetic properties, while retaining relatively large metal-metal distances, leading to lightweight and porous materials in which properties can be modulated using interactions between the framework and guest species within the pores.¹

Terephthalonitrile (tpn) particularly, which is composed of a benzene ring with two cyano groups in the 1- and 4-positions, is a promising candidate, thanks to its ability to form stable radicals,² in which an extra electron, delocalised in the π -conjugated system, facilitates a strong increase in metal-ligand interactions, as has been shown previously in metal-radical materials.³

This presentation will discuss the synthesis and characterisation of two tpn radical (tpn $^{\bullet-}$) salts, which have been obtained by reducing neutral tpn with lithium 1,2-dihydroacenaphthylenide (Li $^+$ Ac $^{\bullet-}$) or sodium metal, leading to Li $^+$ (tpn) $^{\bullet-}$ (THF)₂ (**a**) and Na $^+$ (tpn) $^{\bullet-}$ (THF) (**b**). Establishing their respective structures from single crystal X-ray diffraction data shows that the lithium and sodium ions are bridged by tpn $^{\bullet-}$ and coordinated with THF, forming one-dimensional corrugated chains (Figure, left) and a three-dimensional network (Figure, right). Notably, compound **a** shows symmetry transformation with a change in temperature. Magnetic susceptibility measurements demonstrated paramagnetic behaviour for compound **a**, which is expected for its electronic configuration and a diamagnetic ground state of compound **b**, likely due to strong interactions between closely stacked pairs of tpn $^{\bullet-}$.

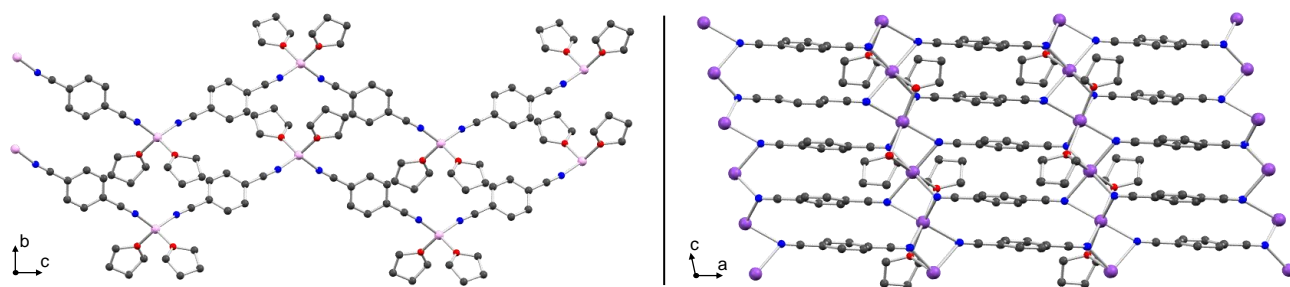


Figure: Crystal structures of **a**(left) and **b**(right) at 120 K, hydrogen atoms are omitted for clarity. Colour code: C black, N blue, O red, Li light purple, Na dark purple.

Acknowledgments:

This work was supported by the University of Bordeaux, the Centre National de la Recherche Scientifique (CNRS), and the Chinese Scholarship Council (CSC).

References:

- [1] Allendorf, M.D.; Schwartzberg, A.; Stavila, V. and Talin, A.A., *Chem. Eur. J.* **2011**, 17: 11372-11388.
- [2] Deng, Q.; He, S.-J.; Pei, J.; Fan, C.; Li, C.; Cao, B.; Lu, Z.-H. and J. Li, *Electrochem. Commun.*, **2017**, 75, 29–32.
- [3] X. Ma, E. A. Sutarina, S. De, P. Négrier, M. Rouzières, R. Clérac, P. Dechambenoit, *Angew. Chem. Int. Ed.* 2018, 57, 7841.

Experimental charge density and phase transition of a new hybrid perovskite: a combination of experimental approaches for a complete description

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The crystal structure of bis(1,2diaminepropane) di- μ -chloro-bis[di-aqua-dichloromanganate(II)] dichloride (1) is built as layers of centrosymmetric binuclear units made of two $(\text{Mn}^{\text{II}}\text{Cl}_4(\text{H}_2\text{O})_2)^-$ octahedra (figure 1) sharing one edge along the **a** direction and distributed in the **a,c** basal plane (P-1 triclinic space group). These doubly negative charged layers are separated along the **b** axis by positive di-amine propane layers. Non-coordinated chloride anions ensure the electroneutrality and stabilize the structure through hydrogen bonds with coordinated water molecules, and to the ammonium groups of organic layers. We modeled the experimental charge density based on a high-resolution single crystal X diffraction experiment in order to calculate the electrostatic properties of this material to understand how the electrostatic interactions contribute to the stability of the structure.

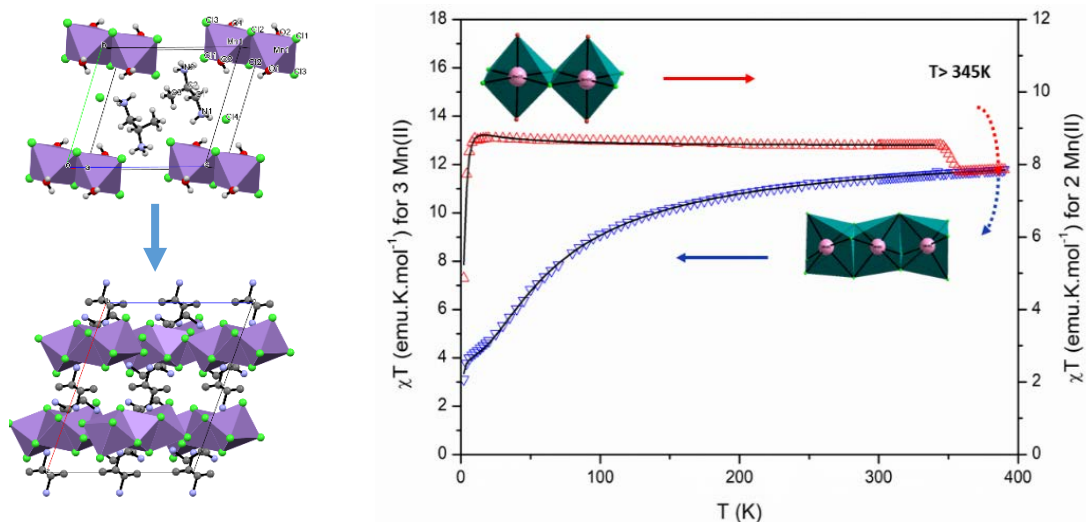


Figure 1. Left: 3D view of the structure at 100K before (along **a** axis) and after (along **b** axis) high temperature heating. Right: Temperature dependence of the magnetic behavior.

Differential scanning calorimetry (DSC) reveals two endothermic peaks attributed to a two-step transition (main peaks at $T = 366$ K and $T = 375$ K) ascribed to the release of the coordinated water molecules. Meanwhile, SQUID magnetometry reveals new magnetic properties after the transitions. Below 346 K the temperature dependence of χT is almost constant down to 10 K (Figure 1). After heating up to 390 K χT rapidly decreases with temperature. As the dehydrated crystals were extremely small, a combination of X-rays and electron diffraction experiments was deemed necessary to solve the structure. Surprisingly the dinuclear Mn(II) cations rearrange into a trinuclear Mn(II) one (figure 1) in a new monoclinic unit cell.

This dehydrated structure allowed a thorough fit of the magnetic behavior. Last, this structural and magnetic transition is reversible on a long time scale (months) leading to the starting hydrated phase as confirmed both by magnetic and X-rays diffraction experiments.

References:

1. Synthesis, crystal structure and phase transitions of novel hybrid perovskite: bis-(1,2-di-amino-propane) di- μ -chloro-bis-[di-aqua-dichloro-manganate(II)] dichloride, S. K. Abdel-Aal, M. Souhassou, P. Durand, C. Lecomte, A. S. Abdel-Rahman and N. Claiser, *Acta Cryst.* (2023). B79, 314-319

X-RAY STRUCTURES AND MAGNETIC PROPERTIES OF COORDINATION DENDRIMERS

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Mots-clés: dendrimers; lanthanides; single-molecule magnets; supramolecular chemistry; coordination chemistry; hetero-polymetallic complexes

Résumé: Developed in the 1980s, dendrimer chemistry has opened up new perspectives in fields as diverse as catalysis, molecular electronics and artificial photosynthesis.^[1] Surprisingly, however, magnetic dendrimers are not common in the literature due to puzzling difficulties in their synthesis and characterization.^[2] In this context, the design of such multimetallic and monodisperse starburst architectures, endowed with magnetic properties, is therefore a real challenge.^[3] Following a supramolecular “complex as ligand” approach, we succeeded in this challenge by carrying out the synthesis, characterization (including X-Ray diffraction) and study of magnetic dendrimers. Our synthetic strategy essentially relies on (i) oxalate-based coordination chemistry as the core of the architecture and (ii) trinuclear complexes, LnCo₂ for the branches (with Ln a lanthanide and Co, the Klaui ligand) that feature single-molecule magnet properties. The combination of these two building blocks allows us to obtain supramolecular and dendritic assemblies. The versatility of this approach makes it possible to anticipate the properties according to the choice of metal cations involved in the structure (single molecule magnets or giant spin values, etc.). Thus, we obtained hetero-tri-metallic magnetic dendrimers, MLn₃Co₆ and ZrLn₄Co₈ (with M=Co or Cr, and Ln=La, Tb, Dy, Er, ...) fully characterized by X-ray diffraction.^{[4],[5]} The magnetic properties are in good agreement with the expected theoretical models. This type of compound could be of great interest for applications in information storage or magnetic refrigeration.

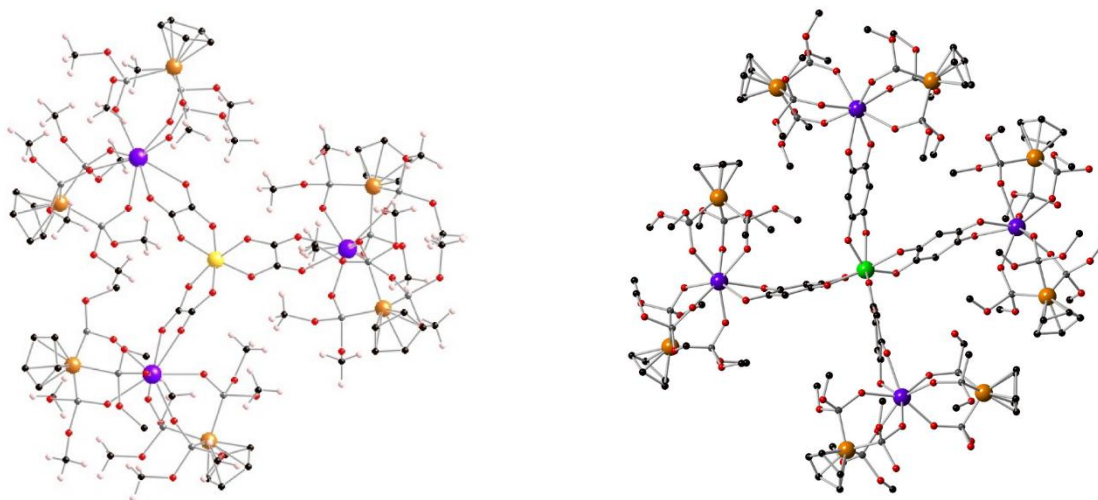


Fig. 1 X-ray structures of magnetic dendrimers: CrEu₃Co₆ and ZrTb₄Co₈

Références:

1. Astruc, D; Boisselier, E; Ornelas, C; *Chem. Rev.* **2010**, *110* (4), 1857-1959.
2. Racja, A; Wongsriratanakul, J ; Racja, S; Cerny, R; *Angew. Chem. Int. Ed.* **1998**, *37* (9), 1229-1232.
3. Suzana, I; Forté, J; Von Barbeleden, J; Pillet, S; Marvaud, V; Malischewski, M, *manuscript in preparation*
4. Suzana, I; Rupf, S; Rousset, E; Rahman, A. K. F.; Klemke, B; Marvaud, V; Malischewski, M, *manuscript in preparation*
5. Pécou, C; Suzana, I; Forté, J; Malischewski, M, *manuscript in preparation*