Les journées scientifiques
de l'Association Française de Magnétisme Moléculaire
JAM^2 2022

Dourdan
22 au 24 novembre 2022

mardi 22 novembre		mercredi 23 novembre		jeudi 24 novembre	
		9:00	TUTORIEL Amélie BORDAGE X-ray Absorption Spectroscopy : Information at the local scale	9:00	TUTORIEL Talal MALLAH The 2022 Nobel Prize in Physics
		10:00	Hélène BOLVIN LCPQ	10:00	Corina RODRÍGUEZ-ESTEBAN BCMaterial ICMCB
		10:25	pause	10:25	pause
		10:55	Nicolas CLAISER CRM2	10:55	Fabrice POINTILLART ISCR
		11:20	Marius HERVE IPR	11:20	Nathan J. YUTRONKIE CRPP
		11:45	Rebecca RODRIGUES DE MIRANDA ICMCB	11:45	Idris TLEMSANI ICMMO
		12:10	Shiteng MI LCC	12:10	clôture
				12:20	déjeuner
12:30	déjeuner	12:35	déjeuner et disscusion		
14:00	introduction				
14:10	TUTORIEL Christophe BUCHER Electron-Triggered Metamorphism in Metal-Organic Architectures				
15:10	Abhijit ADAK CRPP				
15:35	Léo LA DROITTE ISCR	15:30	Guillaume CHASTANET ICMCB		
16:00	Nour-El-Islam BELMOURI GEMaC	15:55	Grégoire DAVID ISCR		
16:25	pause	16:20	Longfei WANG CRPP		
16:55	Gautier DUROUX ICMCB	16:45	Damian PALIWODA LCC		
17:20	Emmelyne CUZA IMAP	17:10	Sabrina GRENDA LMI		
17:45	Grégory BALTHAZAR ICMMO	17:35	café et POSTERS		
18:10	Francisco Javier VALVERDE-MUÑOZ IPR				
18:35	Buqin XU IPCM				
19:00	apéritif et dîner	19:00	dîner		
		20:30	Réunion Conseil d'administration		

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Tutoriels

X-ray Absorption Spectroscopy : Information at the local scale

Amélie BORDAGE

ICMMO, Université Paris-Saclay, CNRS, Bât. Henri Moissan, 17 Avenue des Sciences, 91400 Orsay, France

For the last 30 years, synchrotron-based spectroscopic techniques have proven to be priceless for the study of molecular compounds and their derivatives. In particular, X-ray Absorption Spectroscopy (XAS) has significantly contributed to the enrichment of their structure-property relationships. XAS has indeed the main advantages to be chemically selective and to be able to probe almost all the periodic table. It gives access to a wide range of structural, electronic and magnetic properties, since we can choose which electron is excited (1s, 2p,…) and so which states are probed. Experiments can be designed to characterize reference materials/states in different conditions of pressure/temperature/etc, to monitor in situ spin crossover or charge transfer,… Furthermore, this spectroscopy can be applied to bulk materials, thin films, nanoparticles, … which makes it a very versatile tool.
In a first part, the principle and the different information that can be obtained will be explained, as well as the different ways to extract this information. The different experimental possibilities (setups, types of samples,…) will also be presented. In a second part, I will present some examples of results obtained on molecular compounds thanks to XAS. The theoretical possibilities related to XAS will be briefly mentioned but not detailed.

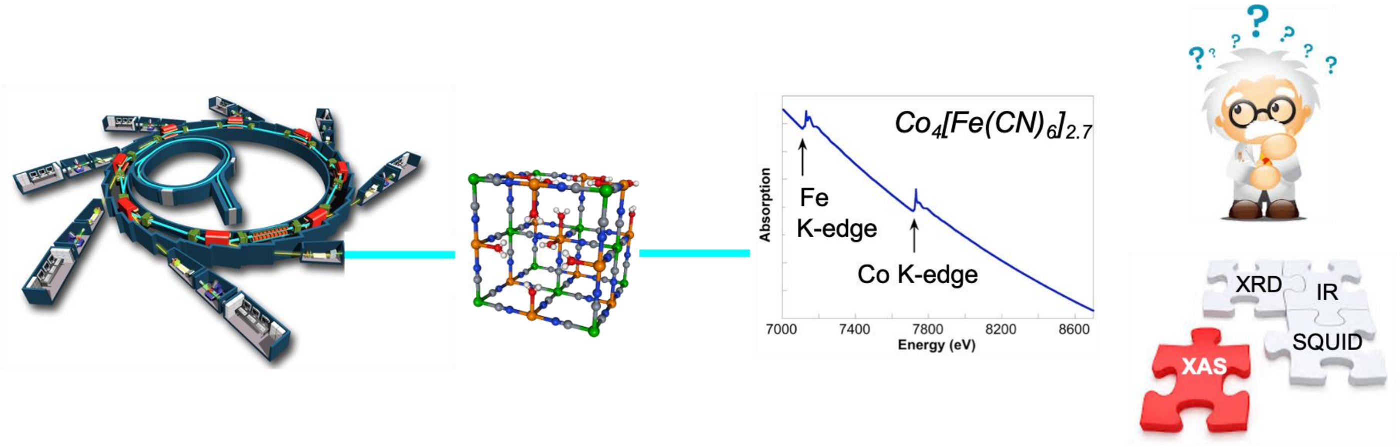


Figure: *Schematic summary of the tutorial*

Acknowledgments: I thank my co-workers at ICMMO Anne Bleuzen and Giulia Fornasieri, all the PhD students and beamline scientists involved in the different projects, as well as the ANR for funding (Project *MagDiDi*, no. ANR-17-CE29-0011) and SOLEIL/ESRF synchrotrons for provision of beamtime.

References (Generalities, history and examples of results) :

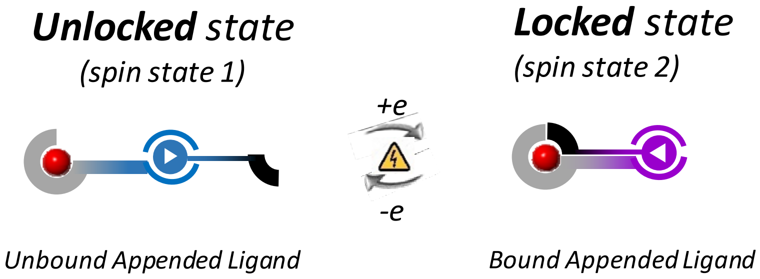
1. C. Garino et al. (2014) Coordination Chemistry Reviews 277-278 :130-186
2. V. Briois et al. (2000) L'Actualité Chimique Mars:31-40
3. R. Stumm von Bordwehr (1989) Ann. Phys. Fr 14:377-466
4. A. Bordage et al. (2018) Journal of the American Chemical Society 140 :10332-10343
5. A. Bordage and A. Bleuzen (2020) Radiation Physics and Chemsitry175:108143
6. C. Mathonière et al. (2022) Chem. Comm. 10.1039/d2cc04246k
7. S. Jafri et al. (2019) Journal of the American Chemical Society 141:3470-3479
8. S. Zerdane et al. (2018) European Journal of Inorganic Chemistry 2018 :272-277

Electron-Triggered Metamorphism in Metal-Organic Architectures : From Responsive Self-Assembled Materials to Spin-State Switching

S. Al Shehimy, O. Baydoun, E. Dumont, D. Frath, F. Chevallier, C. Bucher

Univ Lyon, ENS de Lyon, CNRS UMR 5182, Laboratoire de Chimie, F-69342 Lyon, France
christophe.bucher@ens-lyon.fr

The ability to control the structure and properties of molecular materials has emerged in the past decade as a major scientific objective that is mainly motivated by exciting foreseeable applications in nanoscience. Enormous technologic interests are for instance at stake in being able to devise molecular objects that could respond to external stimuli by changes in structure and function. To achieve these objectives, our group has been focusing over the past few years on the development of tailor-made electron-responsive molecular or supramolecular systems involving metal ions and electrogenerated organic π-radicals as key responsive and/or assembling elements. Our contribution in this area ranges from the development of discrete rotor-or tweezer-like molecules to supramolecular assemblies whose mechanical movements or whose macroscopic properties can be controlled by electrical stimuli. In recent years, controlling molecular motions has also emerged as a promising approach for the development of molecules exhibiting switchable magnetic states, the underlying idea being that modifying the structure of a molecular system could induce drastic modifications of its magnetic properties. From a practical standpoint, these ambitious objectives have so far mainly been addressed with coordination complexes using light as an input signal [1, 2] In contrast, far less progress has been made in these directions with electron-responsive systems even though electrochemistry stands as a particularly attractive trigger in the perspective of applications in solid-state devices or to avoid risks of bleaching associated to high energy light irradiations. In this context, we have recently focused on the development of molecular systems for which large amplitude movements actuated by electron transfer can be used to control the magnetic state of magnetically active metalloporphyrin centers.
Following our previous works on redox-responsive mechanoreactive (supra)molecular architectures [3-6], we will detail in this presentation some of our most recent achievements along these lines including a recent strategy wherein the local environment and the electronic configuration (High Spin versus Low Spin states) of a nickel porphyrin can be determined with an electric trigger enabling to control the nature and number of coordinated ligands [7].



REFERENCES

1.Doistau, B.; Benda, L.; Hasenknopf, B.; Marvaud, V.; Vives, G., *Magnetochemistry* **2018**, 4 (1), 5.
2.Dommaschk, M.; Peters, M.; Gutzeit, F.; Schütt, C.; Näther, C.; Sönnichsen, F. D.; Tiwari, S.; Riedel, C.; Boretius, S.; Herges, R., *J. Am. Chem. Soc.* **2015**, 137 (24), 7552.
3.Iordache, A.; Retegan, M.; Thomas, F.; Royal, G.; Saint-Aman, E.; Bucher, C., *Chem. Eur*. J. **2012**, 18, 7648
4.Kahlfuss, C.; Denis-Quanquin, S.; Calin, N.; Dumont, E.; Garavelli, M.; Royal, G.; Cobo, S.; Saint-Aman, E.; Bucher, C., *J. Am. Chem. Soc*. **2016**, 138, 15234
5.Chowdhury, S.; Nassar, Y.; Guy, L.; Frath, D.; Chevallier, F.; Dumont, E.; Ramos, A. P.; Demets, G. J.-F.; Bucher, C., *Electrochim. Acta* **2019**, 316, 79.
6.Kahlfuss, C.; Chowdhury, S.; Carreira, A. F.; Grüber, R.; Dumont, E.; Frath, D.; Chevallier, F.; Eric Saint, A.; Bucher, C., *Inorg. Chem.* **2021,** *60* (6), 3543.
7.Al Shehimy, S.; Baydoun, O.; Denis-Quanquin, S.; Mulatier, J.-C.; Khrouz, L.; Frath, D.; Dumont, É.; Murugesu, M.; Chevallier, F.; Bucher, C., *J. Am. Chem. Soc.* **2022,** *144* (39), 17955,

The 2022 Nobel Prize in Physics

Talal MALLAH

[1]*Institut de Chimie Moléculaire et des Matériaux d'Orsay, Université Paris-Saclay, 17 avenue des Sciences, 91405 Orsay, France*

I will first present the main fundamental concept of Quantum Mechanics, Superposition through two examples: superposition of positions[1,2] and superposition of the electronic spin that will serve to define the quantum bit (qubit). Then, I will present the Einstein-Podolsky-Rosen (EPR) thought experiment[3] and introduce the second fundamental concept of Quantum Mechanics: Quantum Entanglement that is necessary to implement quantum gates for quantum information. Next, I will present the Bell inequality and show (without calculation) that it is violated for a physical system if superposition is assumed to be present.[4] Finally, I will explain in a simple manner the experiment reported in 1982 by Alain Aspect[5] (Nobel Prize 2022 in Physics) that showed (i) the violation of the Bell inequality and (ii) the *quantitative* correlation between photon polarizations as predicted by quantum mechanics, therefore, demonstrating that the concepts of superposition and entanglement are operative in quantum systems.
The presentation will include as little mathematics as possible.

References:

1. R. Feynman, The concept of probability in Quantum Mechanics, Berkeley Symposium on Mathematical Statistics and Probability, 533-541 (1951).
2. Y. Y. Fein, Ph. Geyer, P. Zwick, S. Pedalino, M. Mayor, S. Gerlich, M. Arndt, Quantum superposition of molecules beyond 25 kDa, Nat. Phys., 15, 1242-1245 (2019).
3. A. Einstein, B. Podolsky, N. Rosen, Can Quantum-Mechanical Description of Physical Reality Be Considered Complete? Phys. Rev. Lett. 47, 777-780 (1935).
4. J. S. Bell, On the Einstein Pololsky Rosen Paradox, Physics, 1, 195-200 (1964).
5. A. Aspect, Ph. Grangier, G. Roger, Experimental Realization of Einstein-Podolsky-Rosen-Bohm *Gedankenexperiment*: A New Violation of Bell's Inequalities, Phys. Rev. Lett. 49, 91-94 (1982).

Présentations orales

Communication orale ☒ par affiche ☐

Tuning the electronic properties of two-dimensional coordination networks via axial ligand substitution and its post-synthetic modification

Abhijit ADAK,[1] Panagiota PERLEPE,[1,2] Laura VOIGT,[3] Itziar OYARZABAL,[1,4] Nathan YUTRONKIE,[1] Dandan LOU,[1] Andoni ZABALA,[1] Aaron MAILMAN,[5] Mathieu GONIDEC,[2] Pierre DECHAMBENOIT,[1] Corine MATHONIERE,[1] Mathieu ROUZIERES,[1] Fabrice WILHELM,[6] Andrei ROGALEV,[6] Charlie Mc MONAGLE,[7] Dmitry CHERNYSHOV,[7] Rasmus Tang CHRISTIANSHEN,[8] Michael BAKER,[8] Mariusz KUBUS,[3] Kasper S. PEDERSEN,[1,3] Rodolphe CLERAC[1]

[1]Univ. Bordeaux, CNRS, CRPP, UMR 5031, 33600 Pessac, France ; [2]Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, 33600 Pessac, France; [3]Department of Chemistry, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark; [4]BCMaterials, UPV/EHU Science Park, ES-48940 Leioa, Spain and IKERBASQUE, Basque Foundation for Science, 48009 Bilbao, Spain; [5]University of Jyväskylä, FI-40014 Jyväskylä, Finland; [6]ESRF – The European Synchrotron, 38043 Grenoble, France; [7]Swiss-Norwegian Beamlines at the European Synchrotron Radiation Facility, F-38000 Grenoble, France; [8]Univeristy of Manchester, Manchester, UK

Email: abhijit.adak@u-bordeaux.fr

Molecule-based magnets are at the forefront of fundamental research, as these magnetic materials offer a means to synthetically tune their physical properties that are not accessible to traditional inorganic-based magnets. A new ground has been laid in this field through the coordination of redox-active Cr(II) with pyrazine (pyz) bridging ligands affording $Cr(pyz)_2Cl_2$, a 2D coordination network with remarkable physical properties displaying a ferrimagnetic ordered state below 55 K and conductivity up to 32 mS cm^{-1} at room temperature (RT).[1] These extraordinary properties stem from an intrinsic one-electron reduction from the Cr^{II} ion to one of the neutral pyrazine ligands, which subsequently transforms the 2D network into a highly delocalized system. The post-synthetic reduction of the 2D $Cr(pyz)_2Cl_2$ network generates a material that retains magnetic hysteresis up to 515 K.[2] In the pursue of enhancing these properties through chemical tunability, we herein present the synthesis and characterization of $Cr(pyz)_2I_2$ 2D-network and its post-synthetic reduction. Replacement of the chloride ligands for its larger congener iodide leads to $Cr(pyz)_2I_2$ (Figure 1) which orders antiferromagnetically below 27 K. The complete post-synthetic reduction of $Cr(pyz)_2I_2$ generates a ferrimagnet with a critical temperature around 570 K, while bearing a larger coercive field compared to that of its reduced chloride analogue (~ 9770 Oe vs. 7500 Oe at 300 K, respectively).

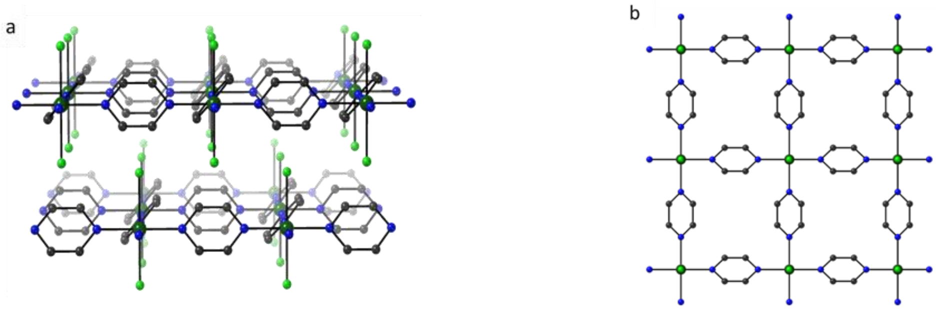


Figure 1. *X-ray diffraction single crystal structure of $Cr(pyz)_2I_2$: (a) Perspective view on the staggered stacking of layers perpendicular to the c-direction, (b) Fragment of the layer structure of $CrI_2(pyz)_2$ shown along the I–Cr–I axis (crystallographic c-direction). Color code: dark green, Cr; light green, I; blue, N; dark grey, C.*

Acknowledgments:

This work was supported by the University of Bordeaux, the Région Nouvelle Aquitaine, the ANR (HiPerMagnet project; ANR- 20-CE07-0022), the CNRS and the ESRF.

References:

1. K. S. Pedersen *et al.*, *Nat. Chem.*, **2018**, 10, 1056-1061.
2. P. Perlepe *et al.*, *Science*, **2020**, 370, 587–592.

Communication orale ■ par affiche ☐

Photo-switching of surface species in cobalt-iron Prussian blue analogues nanoparticles

Grégory BALTHAZAR[1], Anne BLEUZEN[1], Giulia FORNASIERI[1], Amélie BORDAGE[1]

[1]Equipe Chimie Inorganique, Institut de Chimie Moléculaire et des Matériaux d'Orsay, Université Paris Saclay, Orsay, FRANCE

Cobalt-iron Prussian blue analogues (PBAs) are coordination polymer with the chemical formula $C_xCo_4[Fe(CN)_6]_{(8+x)/3}$ (C are alkali cations contained within interstitial sites of the structure). They can exhibit thermo and/or photo-magnetic effects when the amount and nature of alkali cations are well adjusted. These properties make them interesting candidates for information storage applications.

RbCoFe ($Rb_2Co_4[Fe(CN)_6]_{3.3}$) and CoFe ($Co_4[Fe(CN)_6]_{2.7}$) are cobalt iron PBAs, which have been well studied in the powder form made of monocrystalline particles with dimensions of several hundred nm. RbCoFe, mainly made of Co^{III}-NC-Fe^{II} linkages, exhibits a photo-magnetic effect due to a photo-induced charge transfer transforming the $Co^{III}Fe^{II}$ diamagnetic pairs into $Co^{II}Fe^{III}$ ferrimagnetic ones. CoFe, mainly made of Co^{II}-NC-Fe^{III} linkages, exhibits no photo-magnetic effect since it contains no photo-magnetic $Co^{III}Fe^{II}$ pairs.[1]

First studies showed that 5 nm cobalt iron PBA particles present a core-shell structure where shell species can differ from core ones chemically as well as structurally.[2] At this scale the core of NanoCoFe is made of $Co^{II}Fe^{III}$ pairs resembling those forming the corresponding powder (CoFe), while the shell is made of $Co^{II}Fe^{III}$ species having a structure different from that of the core. NanoRbCoFe is made of $Co^{III}Fe^{II}$ core pairs also resembling those forming the corresponding powder (RbCoFe), while the shell is made of the same $Co^{II}Fe^{III}$ species as the shell of NanoCoFe.

NanoRbCoFe present a photo-magnetic effect different from the effect observed in the bigger particles. The behaviour of the core species resembles that of RbCoFe but the shell species also undergo a photo-induced transformation.

In order to better understand the behaviour of the surface species, the magnetic properties of NanoCoFe were investigated at low temperature under irradiation and compared to those of CoFe. This study showed that a photo-magnetic effect is observed in NanoCoFe whereas the magnetization of CoFe remains unchanged under irradiation.[3]

Here we will present these particular photo-switching properties: the conditions in which they were observed in nm sized systems and the species involved.

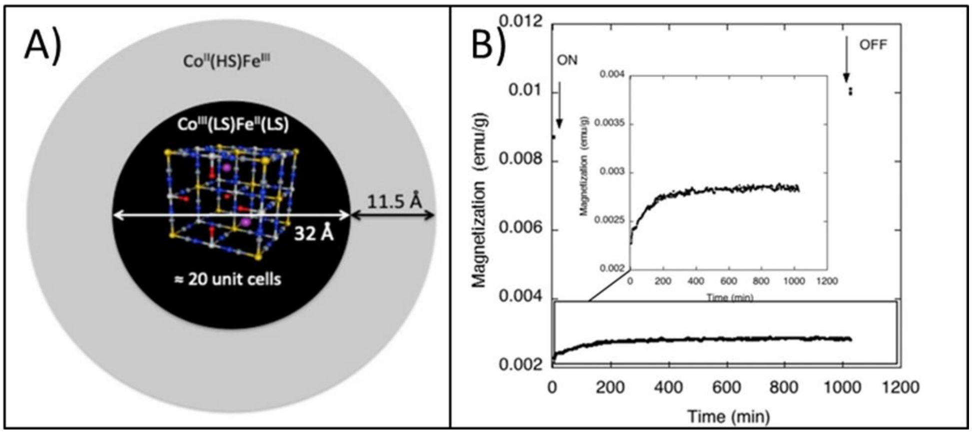


Figure: (A) *Schematic representation of the core-shell structure of NanoRbCoFe, (B) Time dependence of the magnetization of NanoCoFe under irradiation at 10 K.*

References:

1. Escax et al., 2001. J. Am. Chem. Soc 123, 12536–12543
2. Bordage et al., 2018. J. Am. Chem. Soc 140, 10332–10343
3. Bleuzen et al., 2020. Chem2, 2020, 4-1

Communication orale ✕ par affiche ☐

Mechanical reaction diffusion equations to simulate the spin-crossover transition in single crystals

Nour-El-Islam BELMOURI[1*], Nicolas DI-SCALA[1], Kamel BOUKHEDDADEN[1],

1 Université Paris-Saclay, Versailles Saint Quentin en Yvelines, GEMaC, CNRS, 45 Avenue des Etats Unis, F- 78035 Versailles Cedex, France
** Email: nour-el-islam.belmouri@uvsq.fr*

We present a new theoretical approach allowing the study of the spatiotemporal properties of spin-crossover solids, accounting for the spatial fluctuations of high-spin (HS) fraction [1], temperature [2] including lattice mechanical deformation accompanying the spin state changes. The formalism is based on reaction diffusion equations (RDE), derived from n the expansion of the free energy with respect to the gradient of the HS fraction. The expression of the free energy also takes into account for the spin-lattice coupling, which is included the effective ligand energy which depends on the lattice degrees of freedom as it results from the development of the electro-elastic model [3]. The obtained equations [4] of motion involve those of the average local HS fractions and lattice positions, with their own timescales. While the electronic part is solved using finite difference or runge Kutta, the structural part is treated with molecular dynamics at $0K$. We simulate the thermal transition and isothermal one inside the hysteresis, we show that the spin lattice coupling in the way we introduce it, reproduces quantitatively the process of nucleation, growth, and propagation of the HS fraction regardless of the spin-spin interaction, we deeply investigate the effect of molecular dynamics on the spin transition and we introduce light and several external stimuli (constant and/or periodic), leading to self- organized stationary or dynamical equilibrium states.

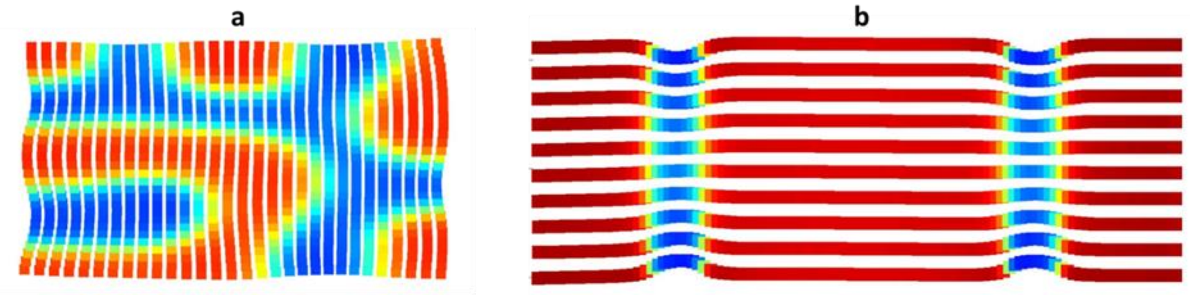


***Figure:** images of auto-organized spin stats. **(a)** in a case where we illuminate the sample with a constant intensity of light. **(b)** in a case where we apply a sinusoidal force on both sides of the sample.*

References:

1. M. Paez-Espejo, M. Sy, F. Varret, and K. Boukheddaden, Phys. Rev. B **89**, 024306 (2014)
2. M. Sy, D. Garrot, A. Slimani, M. Paez-Espejo, F. Varret, and K. Boukheddaden, Angew Chem **128** 1787 (2016)
3. A. Slimani, K. Boukheddaden, F. Varret, and H. Oubouchou Phys. Rev. B **87**, 014111 (2013)
4. N. Belmouri, N. di Scala and K. Boukheddaden (in preparation).

Communication orale ☒ par affiche ☐

Paramagnetic NMR in actinide complexes: experiment and modeling.

Hélène Bolvin[1], Md. Ashraful Islam[1], Matthieu Autillo[2], Claude Berthon[2]

[1]Laboratoire de Chimie et de Physique Quantiques, Université Toulouse 3, France
[2]CEA, DES, ISEC, DMRC, Univ Montpellier, Marcoule, France.

Paramagnetic NMR (pNMR) measures the NMR chemical shift of paramagnetic complexes compared to their diamagnetic counterpart. This shift may be split into *dipolar* terms, arising from the magnetic dipolar interaction between the metal center and the NMR active nucleus, and the *contact* term, due to the spin delocalization leaking from the paramagnetic center towards the ligand[1].

In this presentation, we will illustrate the diversity of information provided by pNMR chemical shifts measured on different nuclei of the ligands coordinated to actinide cations, the so-called Actinide Induced Shifts (AIS).

On one hand, when the dipolar term is dominant, the AIS gives access to the magnetic susceptibility tensor. Further, the temperature dependence allows to determine the energy levels and magnetic parameters of actinyls cations[4]. We will show that in some cases, the AIS provides structural information, as it is the case in biological molecules.

On the other hand, when the contact term is dominant, the AIS allows an experimental determination of the spin densities of the ligands, and the hyperfine contact constants of the NMR active nuclei. This allows to access to the degree of covalency in the actinide – ligand bonding [5,6].

In lanthanide complexes, pNMR chemical shifts are efficiently modeled using crystal-field theory, but due to the larger covalent effects in actinide complexes, those models do not apply to actinide complexes. This will be shown by analyzing the trends of the crystal-field parameters in two series of actinide complexes[2,3]. We will show how ab initio CAS based and DFT methods are complementary tools to the experimental data in order to unravel the dipolar and contact contributions.

References:

1. M. Autillo, L. Guerin, T. Dumas, M. S. Grigoriev, A. M. Fedoseev, S. Cammelli, P. L. Solari, P Guilbaud, P. Moisy, H. Bolvin, C. Berthon *Chem. Eur. J.* **25**, 4435 (2019).
2. J. Jung, M. A. Islam, V. L. Pecoraro, T. Mallah, C. Berthon, H. Bolvin *Chem. Eur. J.* , **25**, *15112 – 15122* (2019).
3. M. Autillo, Md. A. Islam, J. Jung, J. Pilmé, N. Galland, L. Guerin, P. Moisy, C. Berthon, C. Tamain, H. Bolvin *Phys. Chem. Chem. Phys.* **22**, 14293 (2020)
4. M. Autillo † , Md. A. Islam † , J. Héron, L. Guérin, E. Acher, C. Tamain, M. C. Illy, P. Moisy, E. Colineau, J. C. Griveau, C. Berthon, H. Bolvin *Chem. Eur. J.*, **27**, *7138* (2021).
5. L.. Martel, Md. A. Islam, K. Popa, J. F. Vigier, E. Colineau, H. Bolvin, J. C. Griveau *J. Phys. Chem. C*, **125**, *22163–22174* (2021).
6. M. A. Islam, M. Autillo, L. Guerin, C. Tamain, P. Moisy, H. Bolvin, C. Berthon submitted

Nanohybrides commutables : de la synthèse à la caractérisation par microscopie électronique à transmission ultrarapide sur particule unique

Marlène Palluel[1], Yaowei Hu[2], Matthieu Picher[2], Ngoc Minh Tran[3], Nathalie Daro[1], Stephane Mornet[1], Eric Freysz[3], Florian Banhart[2], Guillaume Chastanet[1]

[1] *ICMCB, Univ. Bordeaux, CNRS, Bordeaux INP, UMR 5026, F-33600, Pessac, France. E-mail : guillaume.chastanet@icmcb.cnrs.fr*
[2] *IPCMS, UMR 7504, Université de Strasbourg, CNRS, F-67034 Strasbourg, France.*
[3] *LOMA, Univ. Bordeaux, CNRS, UMR 5798, 358 Cours de la libération, F-33405 Talence, France*

De nombreux phénomènes permettent de stocker des données, comme le changement d'état magnétique dans les matériaux dits à conversion de spin (SCO). Ces derniers peuvent être miniaturisés en nanoparticules, notamment pour leur intégration dans des dispositifs opto-électroniques [1], tout en conservant un effet mémoire crucial pour inscrire une information, notamment par la lumière. Cette photo-inscription requiert de fortes énergies d'irradiation. C'est la chaleur déposée par l'irradiation qui induit un effet de chauffage local et permet la commutation à température ambiante.

Dans ce travail, nous avons souhaité réduire l'énergie d'irradiation nécessaire à cet effet photothermique, en introduisant des nanobâtonnets d'or (70x25 nm) dans les particules commutables pour créer des nanohybrides Au@SCO (200x100 nm, Figure 1). L'excitation de la résonance plasmon de ces particules d'or amplifie l'effet de chauffage local. Cette stratégie a permis de diminuer la puissance d'irradiation d'un facteur 10 000 [2]. Le gain en énergie et en temps de photocommutation a été étudié par mesures optiques résolues en temps ainsi que par microscopie électronique à transmission ultrarapide sur particule unique (UTEM) [3]. Des photocommutations efficaces en 20 ns sont atteintes sur les nanohybrides au lieu de 200 ns sur les nanoparticules de SCO seules. Cette efficacité augmente lorsque le nombre de nanobâtonnets d'or dans la particule SCO augmente (Figure 1).

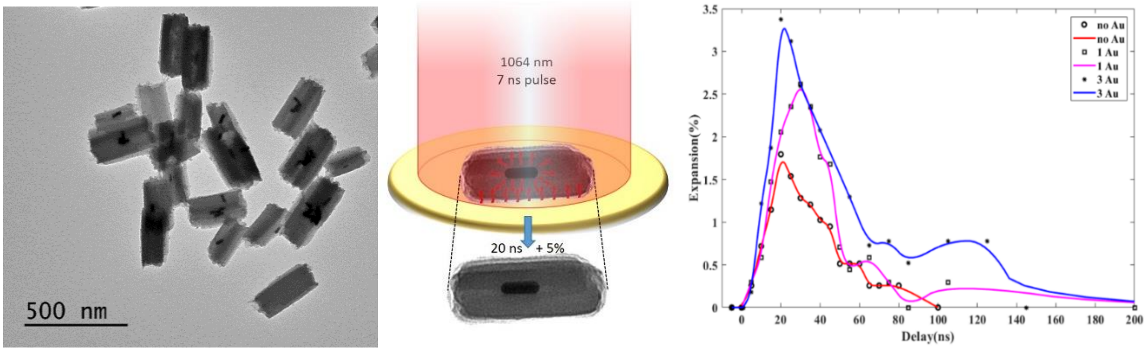


Figure 1 : (gauche) image TEM des nanohybrides Au@SCO; (milieu) principe d'observation de l'expansion d'une particule sous excitation laser pulsée par UTEM; (droite) expansion de la particule en fonction du temps après photo-excitation et du nombre de nanoparticules d'or.

Références :
[1] J.-F. Dayen, N. Konstantinov, M. Palluel, N. Daro, B. Kundys, M. Soliman, G. Chastanet, B. Doudin, *Mater. Horizons,* **2021***, 8*, 2310
[2] M. Palluel, N. M. Tran, N. Daro, S. Buffière, S. Mornet, E. Freysz, G. Chastanet, *Adv. Func. Mater.,* **2020**, *30*, 2000447
[3] Yaowei Hu, M. Picher, N.M. Tran, M. Palluel, L. Stoleriu, N. Daro, S. Mornet, C. Enachescu, E. Freysz, F. Banhart, G. Chastanet, *Adv. Mater*, **2021**, *33*, 2105586

Communication orale ☒ par affiche ☐

Experimental charge density and phase transition studies of a new hybrid perovskite: complementarity between powder, single crystal diffractions and magnetic measurements

Nicolas Claiser[1], Mohamed Souhassou[1], Pierrick Durand[1], Claude Lecomte[1], Dominique Luneau[2], Ahmed S. Abdel-Rahman[3], Seham K. Abdel-Aal[3]

[1]*CNRS, Laboratoire CRM2, UMR CNRS 7036, Université de lorraine, Boulevard des Aiguillettes, BP 70239, Vandœuvre-lès-Nancy, 54506, France*
[2]*Laboratoire des Multimatériaux et Interfaces, UMR 5615, Université Claude Bernard Lyon1, Villeurbanne, 69622, France*
[3]*Physics department, Faculty of Science, Cairo University, Giza 12613, Egypt*

Crystal structure of bis(1,2diaminepropane) di-μ-chloro-bis[diaquadichloromanganate(II)] dichloride, is built as layers of centrosymmetric dinuclear units made of two (MnIICl4(H2O)2)- octahedra (figure 1) sharing one edge along the a direction and distributed in the basal ac plane. These doubly negative charged layers are separated along the b axis positively charged di-amine propane layers. Non-coordinated chloride anions make the electroneutrality and stabilize the structure through hydrogen bonds with coordinated water molecules, and the ammonium groups of organic layers. We modeled the experimental charge density based on high-resolution single crystal diffraction experiment in order to calculate the electrostatic properties of this material, explaining how the electrostatic interactions contribute largely to the stability of the structure.

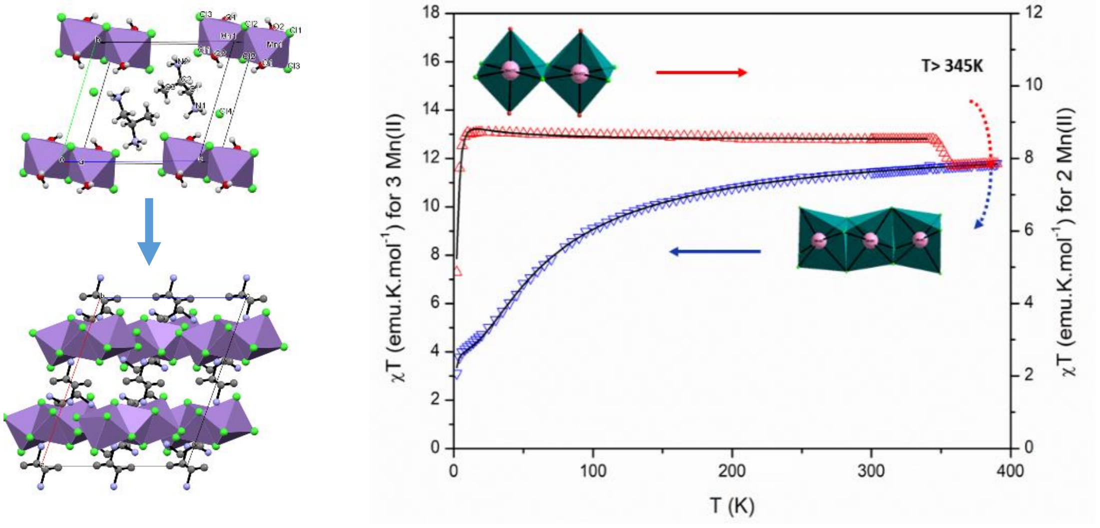


Figure 1. a) 3D view of the structures at 100K before (along the **a** axis) and after (along the **b** axis) high temperature heating. b) Temperature dependence of magnetic behavior.

Differential scanning calorimetry (DSC) reveal 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 show very different magnetic behavior after the transitions. Below 346 K the temperature dependence of the product of the magnetic susceptibly with temperature (□T) is almost constant down to 10K (Figure 1). After heating up to 390 K the □T temperature dependence is no more constant but decrease rapidly with temperature. To understand such a change and using combined powder and single crystal diffraction experiments we investigate the determination of the high temperature resulting structure. This reveals that the dinuclear Mn(II) unit rearrange in trinuclear Mn(II) units with now change. This structural description is according perfectly with simulation of the magnetic behavior.

Communication orale

Volatil organic compounds sensing through hybrid materials design: metal-organic framework and spin crossover complex

CUZA Emmelyne[1*], SERRE Christian[1], TISSOT Antoine[1]

[1] *Institut des Matériaux Poreux de Paris, UMR 8004, CNRS - Ecole Normale Supérieure – Ecole Supérieure de Physique et de Chimie Industrielles, Université Paris Sciences et Lettres*

Metal–organic frameworks (MOFs) are good candidate for sensing small molecules such as VOCs (volatile organic compounds) due to the possibility of modulating the design of the complex assemblies. Over the years many systems have been developed,[1] however they are mostly based on the modulation of the conductivity or the emissive properties of the compounds that comes with limited chemical stability, which prevent them being used in real devices.

In this case, we choose, to avoid the chemical instability, a chemically robust MOF to encapsulate spin crossover (SCO) materials. Already studied in our group with Fe(III) SCO,[2] we decided to focus our attention in using Fe(II) complexes, since they are the most studied in the SCO field. The properties of this materials can be modulated by an external stimuli such light, pression, temperature but also chemicals.[3] It's the later one that is interesting for VOCs detection.

We present here a new hybrid material, composed of MOF-808 Zr(IV)-based mesoporous MOF and a specific Fe(II) complex $[Fe(L)_2].2H_2O$,[4] which show sensitivity and selectivity with some VOCs vapors.

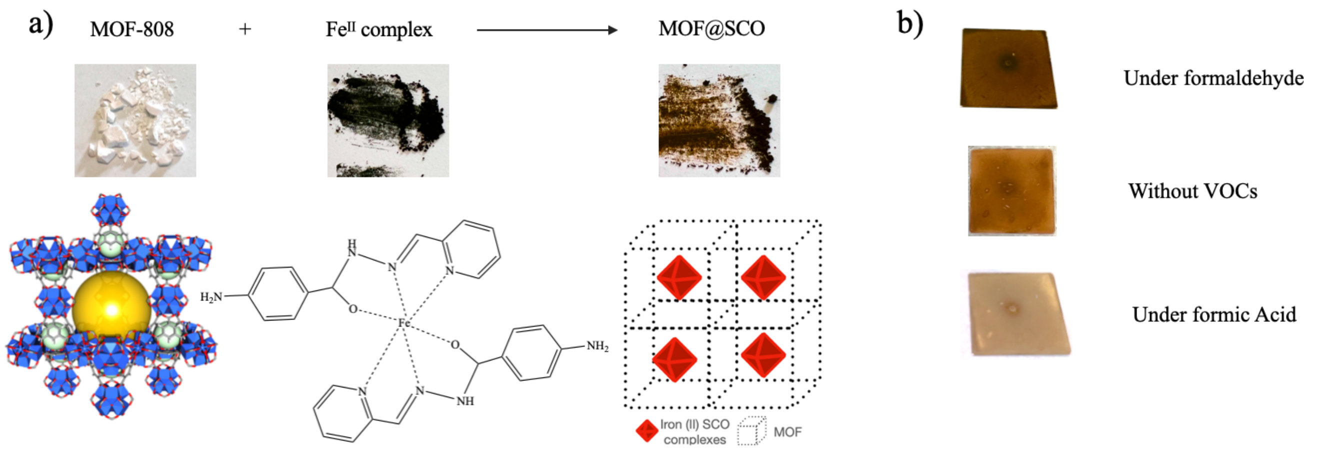


Figure: *a) Loading of SCO Fe(II) complex in MOF-808 b) VOC vapor sensing using a MOF@SCO thin film*

References:

1. a) J. T. Hupp et al., Chem. Rev. 2012, 112, 1105; b) J. Li et al., Chem. Soc. Rev. 2014, 43, 5815
2. a) A. Tissot et al., Chem. Commun. 2019, 55, 194 ; b) F. Moreau et al., J. Mater. Chem. C 2020, 8, 16826
3. a) F. Létard et al., Top Current, 2004, vol. III, 221 ; b) M. Halcrow, Spin-Crossover Materials:Properties and Application, John Wiley & Sons Ltd, 2013, Chapter I-III
4. X.-Q. Chen, Y.-D. Cai, W. Jiang, G. Peng, J.-K. Fang, J.-L. Liu, M.-L. Tong, X. Bao, Inorg. Chem., 2019, 58, 999.

Communication orale ☒ par affiche ☐

Determination of magnetic exchange couplings in KS-DFT: decomposition, *recomposition* method and the role of the spin decontamination

Grégoire DAVID[1], Nicolas FERRÉ[2], Boris LE GUENNIC[1]

[1]*Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, 35000 Rennes, France*
[2]*Aix Marseille University, CNRS, ICR, Marseille, France*

Molecules with remarkable magnetic properties, such as *Single-Molecule Magnets*, have been attracting much attention over the last decades for their potential technological applications as elementary building blocks in Quantum Technologies or Molecular Spintronics.[1] Indeed, molecules have the advantage of being highly versatile, with a possible design of compounds with predefined magnetic properties. In this aim, compounds with multiple magnetic centres, for instance with *f*- and *d*-metal ions or radical ligands, are particularly interesting since the couplings between centres may play a key role in the control of the global magnetic behaviour.[2]

However, the theoretical evaluation of the magnetic exchange couplings J in these systems is particularly challenging. On the one hand, wave-function theory-based methods are the reference approach but their computational cost is most of the time prohibitive in these very large compounds. On the other hand, it is possible to compute these couplings in Kohn-Sham density functional theory (KS-DFT) by means of the broken-symmetry (BS) approach but this strategy is not exempt of important theoretical questions, and among them, one may mention the problem of the spin contamination which is very often neglected.

Whilst KS-DFT is supposed to provide only a numerical evaluation of J, Ferré *et al.* proposed a decomposition scheme based on selective relaxations of the orbitals involved in different mechanisms to extract the main physical contributions to the magnetic exchange coupling: the direct exchange between the magnetic orbitals, the kinetic exchange corresponding to the relaxation of the magnetic orbitals and the spin polarisation of the core orbitals.[3]

In this communication, I will show how the decomposition allows to get valuable insight into the physical mechanisms governing the magnetic exchange couplings in some dinuclear copper compounds.[4] In addition to this powerful rationalisation tool, I will present how this strategy provide a new route to compute couplings in multicentre compounds in a consistent way, the so-called *recomposition* method. This method is applied on a cubane-*like* copper ions-based compound (Figure) and will allow to discuss the importance of the spin decontamination.[4,5]

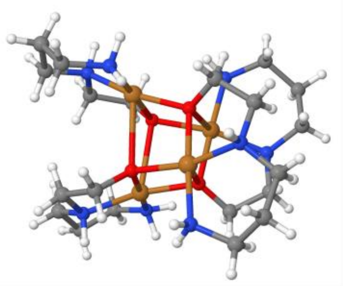


Figure: *Cubane-like compound studied [Cu_4(N-(2-hydroxyethyl)-1,3-propanediamine)$_4$].*

Acknowledgments: G.D. received research funding from the European Union’s 843 Horizon 2020 Research and Program under Marie Skłodowska-Curie Grant Agreement No. 899546.

References:

1. E. Coronado, *Nat. Rev. Mater.*, 5 (2019) 87–104.
2. J. D. Rinehart, M. Fang, W. J. Evans, J. R. Long, *Nat. Chem.*, 3 (2011) 538–542.
3. E. Coulaud, J.-P. Malrieu, N. Guihéry, N. Ferré, *J. Chem. Theory Comput.*, 9 (2013) 3429–3436.
4. G. David, F. Wennmohs, F. Neese, N. Ferré, *Inorg. Chem.* 57 (2018) 12769–12776.
5. G. David, G. Trinquier, J.-P. Malrieu, *J. Chem. Phys.*, 153 (2020) 194107.
6. G. David, N. Ferré, B. Le Guennic, *submitted*

Communication orale ■ par affiche ☐

Chiral nanocomposites: Toward induced magneto-chiral dichroism

Gautier Duroux[1,2], Lucas Robin[2], Reiko Oda[1], Emilie Pouget[1], Elizabeth Hillard[2]

[1] Institute of Chemistry & Biology of Membrane and Nanoobjects (UMR5248 CBMN), CNRS, Bordeaux University, France
[2] Institute of Chemistry of Condensed Matter of Bordeaux (UMR5026 ICMCB), CNRS, Bordeaux University, France

Chirality induction in achiral species is of great interest because it allows access to materials with new exotic properties. Recent work has shown the importance of induced circular dichroism (ICD) in the fabrication of chiral luminescent systems from non-chiral luminophores[1], chiral photonic systems via the helical assembly of gold nanoparticles[2], and sensing systems based on chiral amplification or enantioselective catalysis.

Understanding how ICD works is crucial for the preparation of effective chiral systems. In this work we propose to study the origin of ICD via the fabrication of magneto-chiral nanocomposites by associating different achiral and magnetic species with chiral silica nanohelices. Such objects could lead to the first observation of induced magneto-chiral dichroism (IMChD), MChD being considered to be cross effect between circular dichroism (CD) and magnetic circular dichroism (MCD). In this presentation we will describe our trials in maximizing ICD and MCD in these nanocomposites, using a variety of paramagnetic species.

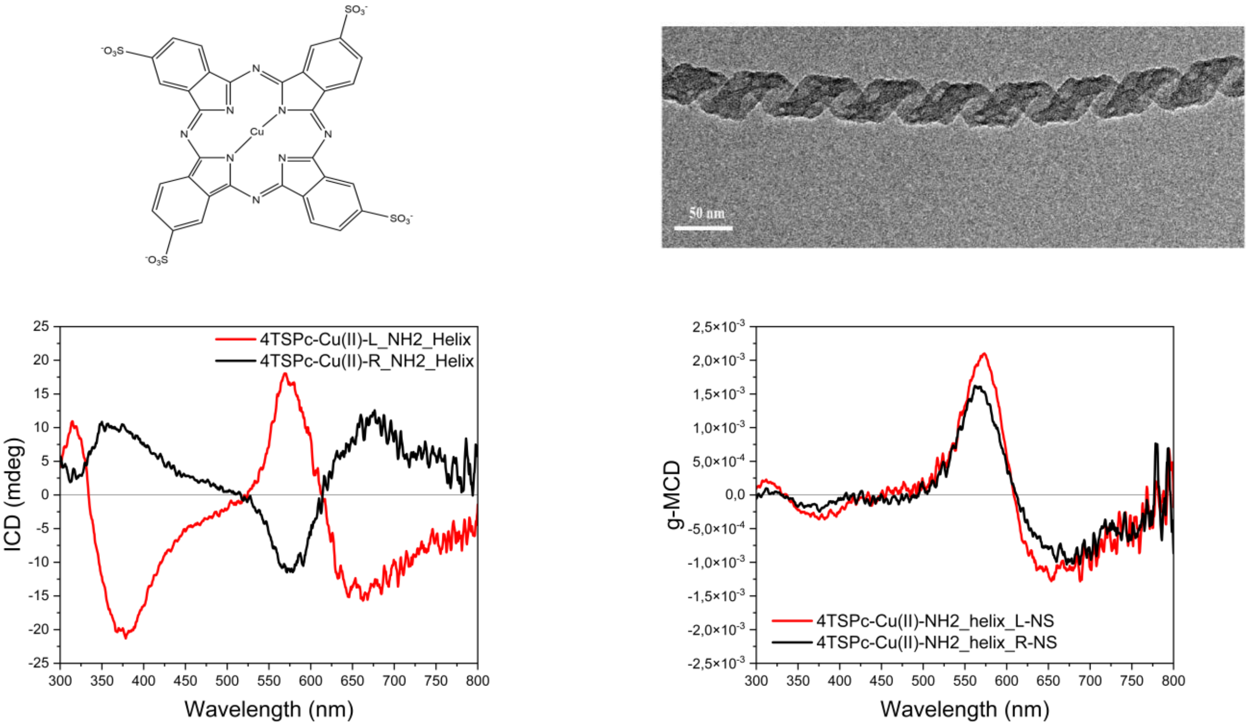


Figure: *4-TSPcCu(II) molecule (top left corner), TEM image of silica nanohelix covered with 4TSPc-Cu(II) (top right corner). Corresponding ICD spectrum (bottom left corner). Corresponding MCD spectrum (bottom right corner).*

References:

1. P. Liu, Y. Battie, M. Decossas, S. Tan, E. Pouget, Y. Okazaki, T. Sagawa, R. Oda, ACS nano, 2021, 15, 16411-16421.
2. J. Cheng, G. Le Saux, J. Gao, T. Buffeteau, Y. Battie, P. Barois, V. Ponsinet, M-H. Delville, O. Ersen, E. Pouget, R. Oda, ACS nano, 2017, 11, 3806-3818.

Communication orale ☒ par affiche ☐

Functionalized Borazine Derivatives by Nitroxide Radicals: Synthesis and Magneto-Structural Properties

Sabrina GRENDA[1], Bérangère TOURY[1], Antonio BARBON[2], Dominique LUNEAU[1]

[1]*Laboratoire des Multimatériaux et Interfaces (UMR 5615) - Université Claude Bernard Lyon 1 - Villeurbanne (France)*
[2]*Electron Paramagnetic Resonance (EPR) Group – University of Padova – Padova PD (Italie)*

Borazine ($B_3N_3H_6$) are heterocyclic boron-nitrogen compounds, well known as the "Inorganic benzene" due to its B-N bond which is isoelectronic and isostructural to the C=C bond [1-3]. However, because of the low aromatic character within the molecule compared to benzene, electronic properties are different, with a charge density mainly located on nitrogen atoms [4]. This makes the BN-core an electron-withdrawing group.

In the frame of an ongoing PhD work, a borazine derivative has been functionalized by free nitroxide radicals, which has never been reported, to our knowledge [5]. The aim of this work is to study the effect of the BN-core on the delocalization of the unpaired electrons carried by the nitroxide functions. During the first year of our thesis we have been able to isolate N,N',N"-(tris(4-Bromophenyl))-B,B',B"-tris((2,6-dimethyl-4-(N-tert-butyl-N-oxyamino)phenyl) borazine (Borazine-B-Tris-Nitroxide). The crystal structure was determined from X-ray diffraction on single crystal (Table 1) and highlight the evidence of three nitroxide radicals (Figure 1). The study of the magnetic properties in the solid state of this system has been carried out by SQUID magnetometer measurements and in the solution by EPR measurements. These studies suggest ferromagnetic intramolecular interactions within the BN-core resulting in a ground state spin S=3/2 combined with intermolecular antiferromagnetic (AF) interactions in the solid state.

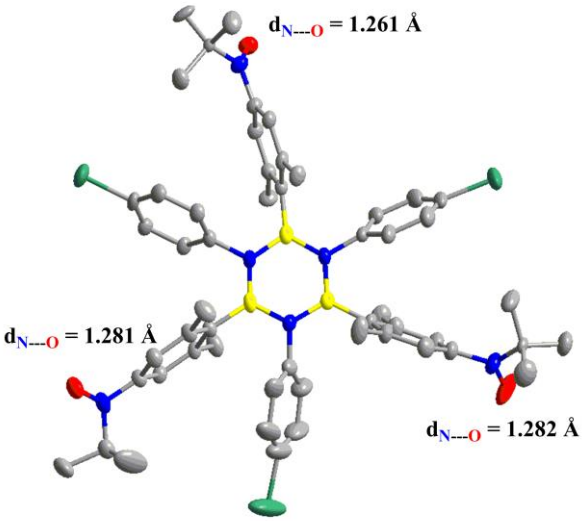


Figure 1 : Crystal structure of Borazine-B-Tris-Nitroxide

Table 1: Crystallographic data for borazine-B-tris-nitroxide

Formula	$C_{54}H_{63}B_3Br_3N_6O_3$
M.W. (g.mol^{-1})	*1116.23*
Crystal system	*Triclinic*
Space Group	*P-1*
a (Å)	*13.0934(11)*
b (Å)	*16.1798(11)*
c (Å)	*16.2429(11)*
α (°)	*104.851(6)*
β (°)	*112.965(7)*
γ (°)	*106.498(7)*
Z	*2*
V (Å^3)	*2762.8(4)*

References:

1. M.M. Lorenzo-Garcia and D. Bonifazi, *CHIMIA*, **2017**, 71(9), 550-557.47
2. H. Oubaha, N. Demitri, J. Rault-Berthelot, P. Dubois, O. Coulembier and D. Bonifazi, *J. Org. Chem.*, **2019**, 84, 9101-9116.
3. F. Fasano, J. Dosso, C. Grazia Bezzu, M. Carta, F. Kerff, N. Demitri, B.L. Su and D. Bonifazi, *Chem. Eur. J.*, **2021**, 27, 4124-4133.
4. R. Boese, A.H. Maulitz, P. Stellberg, *Chem. Ber.*, **1994**, 127(10), 1887-1889.
5. I. Neogi and A.M. Szpilman, *Synthesis*, **2022**, 54, 1877-1907.

Communication orale X par affiche ☐

Non-reversible Photoinduced Phase Transition in the RbMnFe Prussian Blue Analogue Studied by Streaming Crystallography

Marius Hervé[1], Ievgeniia Chaban[1], Gaël Privault[1], Shintaro Akagi[2,3], Elzbieta Trzop[1], Céline Mariette[1,4], Alix Volte[4], Yves Watier[4], Matteo Levantino[4], Hiroko Tokoro[2,3], Shin-ichi Ohkoshi[3,5], Eric Collet[1,3]

[1]Univ. Rennes, CNRS, IPR (Institut de Physique de Rennes) – UMR 6251, F-35000 Rennes, France
[2]Department of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8577, Japan
[3]DYNACOM IRL2015 University of Tokyo - CNRS - UR1, Department of Chemistry, 7-3-1 Hongo, Tokyo 113-0033 - Japan
[4]European Synchrotron Radiation Facility, F-38000 Grenoble, France
[5]Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Modern ultrafast technologies have opened new perspectives in controlling bistable magnetic materials, where light can be used to switch between different phases and thus different properties [1]. Ultrafast photo-switching within bistability regimes indeed promises enhanced control of bistability down to ultrashort timescales. Among the available bistable materials, Prussian Blue Analogues (PBAs) are cyano-bridged bimetallic compounds with a phase transition based on a charge transfer between two stable states of different spin [2]. Moreover, the electronic charge transfer is coupled to symmetry breaking and large volume change, leading to a wide bistability hysteresis [3].

In this work, we followed the multiscale dynamics of the photoinduced phase transition within the thermal hysteresis of RbMnFe PBA micro-crystals (Figure 1) [4,5]. This was made possible by developing a new streaming crystallography method for time-resolved X-ray diffraction studies of non-reversible phenomena. Our results reveal that, above threshold excitation, complete photo-transformation from tetragonal to cubic phases can be achieved down to ultrashort timescales, leading to a permanent photo-induced phase. The out-of-equilibrium and multiscale dynamical behavior results from the coupling of volume strain driven by photoinduced charge transfer and symmetry change [5]. More generally, these results open a broad field of dynamical studies for photo-switching in bistable materials through ultrafast crystallography.

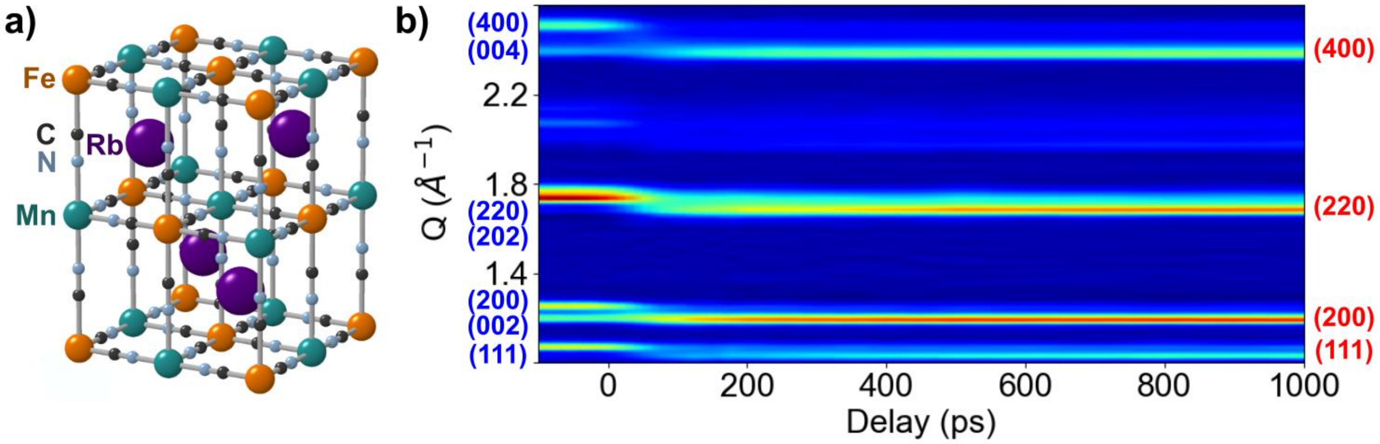


Figure: *a) Structure of the RbMnFe PBA; b) Time-resolved X-ray diffraction pattern of RbMnFe, with (hkl) indices for the initial, tetragonal (left, in blue) and final, cubic (right, in red) phases.*

References:

1. O. Sato, Nat. Chem. **8**(7), 644-656 (2016)
2. H. Tokoro et al., Chem. Mater. **20**, 423-428 (2008)
3. G. Azzolina et al., Phys. Rev. B, **102**, 134104 (2020)
4. G. Azzolina et al., Eur. J. Inorg. Chem. **2019**, 3142-3147 (2019)
5. G. Azzolina et al., J. Mater. Chem. C **9**, 6773 (2021)

Communication orale ☒ par affiche ☐

Organolanthanide complexes: ab initio electronic structures investigation and magnetic properties rationalization

Léo LA DROITTE[1*], Boris LE GUENNIC[1], Olivier CADOR[1]

[1]Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) UMR 6226, 35000 Rennes, France
** email: leo.la-droitte@univ-rennes1.fr*

Single Molecule Magnets (SMMs) are widely studied because of their potential impact in applications such as high-density information storage, quantum computing or spintronics.[1-4] Organolanthanide complexes are a great way to design performing SMMs. However, enhancing the magnetic properties of Ln based SMMs, that is, getting compounds with a slow magnetic relaxation and the highest blocking temperature possible, is a major challenge.[5]

In this work, different design strategies for organolanthanide SMMs are computationally explored, such as the use of cyclooctatetraenyl (Cot) and cyclononatetraenyl (Cnt) large ligands, radical-bridged ligands, or even the seek for a diffuse valence orbital between two lanthanide centres. Recent computational and magnetic measurement results on Ln-Cnt complexes, compounds based on radical-bridged ligands, and derived, will be presented.[6-8]

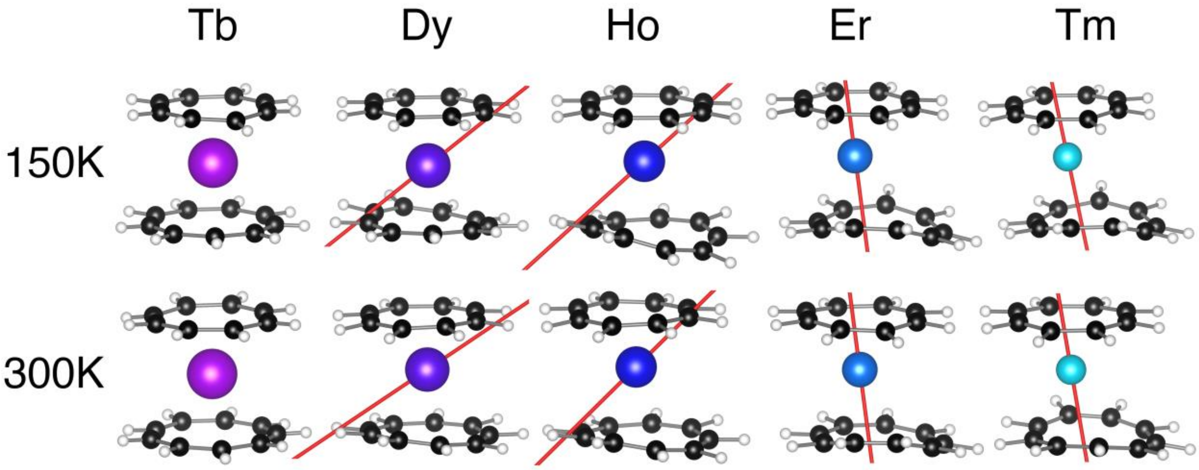


***Figure:** Computed structures of Dy(Cnt)3 (left), [(Cp*2Dy)2(µ-Bbim•)]- (centre) and Dy2(Cnt)3(thf)2 (right).*

References:

1. M. Atzori and R. Sessoli, J. Am. Chem. Soc., 2019, 141, 11339-11352.
2. A. Gaita-Arino, F. Luis, S. Hill and E. Coronado, Nat. Chem., 2019, 11, 301-309.
3. F. D. Natterer, K. Yang, W. Paul, P. Willke, T. Choi, T. Greber, A. J. Heinrich and C. P. Lutz, Nature, 2017, 543, 226-228.
4. A. Candini, S. Klyatskaya, M. Ruben, W. Wernsdorfer and M. Affronte, Nano. Lett., 2011, 11, 2634-2639.
5. Guo et al., Science, 2018, 362, 1400.
6. J. Moutet, J. Schleinitz, L. La Droitte, M. Tricoire, F. Pointillart, F. Gendron, T. Simler, C. Clavaguéra, B. Le Guennic, O. Cador and G. Nocton, Angew. Chem. Int. Ed., 2021, 133, 6107-6111.
7. M. Tricoire, L. Münzfeld, J. Moutet, N. Mahieu, L. La Droitte, E. Moreno-Pineda, F. Gendron, J. D. Hilgar, J. D. Rinehart, M. Ruben, B. Le Guennic, O. Cador, P. W. Roesky and G. Nocton, Chem. Eur. J., 2021, 54, 13558-13567.
8. O. Stetsiuk, L. La Droitte, V. Goudy, B. Le Guennic, O. Cador and G. Nocton, Organometallics, 2022, 41, 133–140.

Communication orale ☒ par affiche ☐

Molecular dynamics simulations of lattice dynamical properties of the spin crossover complex [Fe(pyrazine)][Ni(CN)$_4$]

Shiteng Mi*, Alaa Fahs, Gábor Molnár, William Nicolazzi**, Azzedine Bousseksou

LCC, CNRS & University of Toulouse, 205 route de Narbonne, 31077 Toulouse, France
**E-mail:* *shiteng.mi@lcc-toulouse.fr*
***E-mail:* *william.nicolazzi@lcc-toulouse.fr*

Spin crossover (SCO) materials belongs to the class of smart materials having the ability to reversibly switch from a low-spin (LS) to a high-spin state (HS) under the application of various external and controllable stimuli such as temperature, pressure, magnetic field, light irradiation… At the solid state, the intermolecular interactions between SCO complexes can induce abrupt spin transition curves accompanied by hysteretic behaviours and bistability phenomena. It is now well-accepted that spin transition mechanisms are highly related to the presence of a strong electron-phonon coupling, governing both the molecular switching process and interactions at the macroscopic scale. Thus, the experimental and theoretical investigations of vibrational and mechanical properties as well as their variations upon the spin state change are of paramount importance [1]. In particular, the study of their evolutions with the size reduction is essential for the understanding of switching properties of SCO nanomaterials [2].

In this work, we propose a theoretical investigation of lattice dynamics properties of SCO materials through molecular dynamics (MD) simulations. A new force field for [Fe(pyrazine)][Ni(CN)4] SCO compounds have been built using Raman spectroscopy data[3] and by fitting nuclear inelastic scattering (NIS) experiments[4]. Based on this force field, MD simulations are used to investigate the lattice vibrational properties of both spin states. It is found that the extracted thermodynamical and mechanical parameters are all in good agreement with the corresponding experimental data [4,5]. Most importantly, this new force field successfully reproduces both the low (acoustic modes) and the high (optical modes) frequency parts of the iron partial densities of vibrational states.

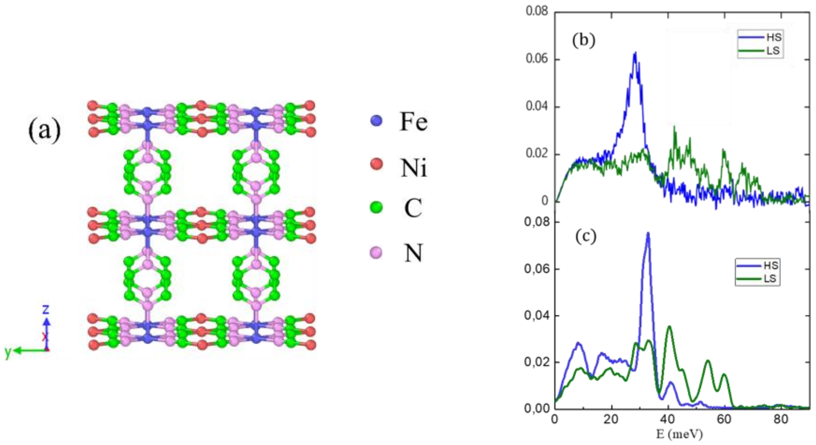


Figure: *(a) 3D schematic representation of the [Fe(pyrazine)][Ni(CN)4] structure. Partial densities of vibrational states in LS and HS states from (b) NIS experiments and (c) MD simulations performed in this work.*

Acknowledgments: this project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement N° 101019522). SM thanks the China Scholarship Council for a PhD grant.

References:

1. G. Molnár et al Annalen den Physik, 531, 1900076 **(2019)**
2. G. Molnár, et al., Adv. Mater. 30, 1703862 **(2018)**
3. G. Molnár, et al., J. Phys. Chem. B 106, 9701 **(2002)**
4. M. Mikolasek, et al., Phys. Rev. B. 96, 035426 **(2017)**
5. G. Felix, et al., Phys. Rev. B. 91, 024422 **(2015)**

Communication orale **X** par affiche ☐

Decoupling Spin-Crossover and Structural Phase Transition in Iron(II) Molecular Complex

Damian PALIWODA[1], Laure VENDIER[1], William NICOLAZZI[1], Gábor MOLNAR[1], Azzedine BOUSSEKSOU[1]

[1]LCC, CNRS & University of Toulouse, 205 route de Narbonne 31077 Toulouse, France

Spin-crossover (SCO) materials are sensitive to external stimuli. SCO transition arouses curiosity because the change of the spin state of metal ion involves appearance of serious structural perturbation related to changes of metal-ligand distances. The interest in Fe(II) spin crossover systems is enhanced by the fact that the spin state can be conveniently switched by changing the temperature, applying pressure, light irradiation or by the action of a chemical agent[1]. Hence, these compounds are considered as materials for potential applications[2] for example in medicinal diagnostic[3], as sensors[4], displays[5] and memory devices[6]. We have recently investigated pressure induced spin-crossover (SCO) transitions in Fe(II) molecular complexes: **(1)** $[Fe^{II}(H_2B(pz)_2)_2(bipy)]$ and **(2)** $[Fe^{II}(H_2B(pz)_2)_2(phen)]$ pz: pyrazole; bipy: 2,2'-bipyridine; and phen: phenanthroline). We have performed a series of high-pressure measurements of **(1)** and **(2)** using wide-opening angle diamond anvil cell (One20DAC) and four-circle Rigaku Synergy-S XtaLab diffractometer equipped with Hypix6000 hybrid pixel Si detector. At normal conditions **(1)** and **(2)** form monoclinic crystals of space group $C2/c$. Both complexes undergo SCO transition when cooled down to 160 K, which is manifested indirectly by abrupt shortening of Fe-N(ligand) distance of about 0.2 Å. While **(1)** remains monoclinic upon further cooling, the low temperature high spin (HS) to low spin (LS) transition in **(2)** is accompanied by the structural transformation from monoclinic C2/c form to triclinic $P\bar{1}$ phase. Compression of **(2)** decouples SCO and structural transition which allows to detect monoclinic LS form, so far undetectable upon cooling[7,8,9].

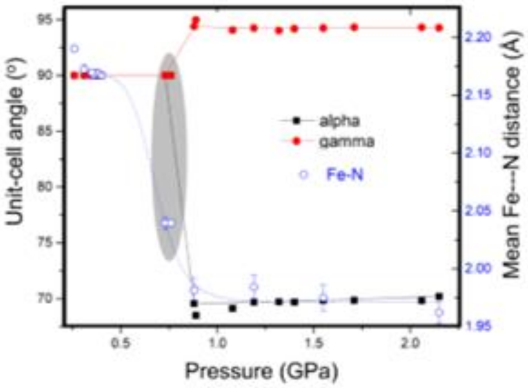


Figure: Unit cell angles α/γ of (2) and av. Fe-N distances in the function of pressure

Acknowledgments: Financial support from regional Nanomat PRRI Project and ERC "E-MOTION" Advanced Grant is gratefully acknowledged.

References:

1. A. B. Gaspar, G. Molnár, A. Rotaru; H. J. Shepherd, *C.R. Chimie*, 2018, **21**, 1095.
2. A. Bousseksou, G. Molnár, L. Salmon, W. Nicolazzi, *Chem. Soc. Rev.* 2011, **40**, 3313.
3. R. N. Muller, L. V. Elst and S. J. Laurent, *J. Am. Chem. Soc.*, 2003, 125, 8405.
4. C. Bartual-Murgui, A. Akou, C. Thibault, G. Molnar, C. Vieu, L. Salmon, A. Bousseksou, *J. Mater. Chem. C,* 2015, **3**, 1277.
5. O. Kahn, C. J. Martinez, *Science*, 1988, **279**, 44.
6. J.-F. Letard, P. Guionneau, L. Goux-Capes, *Top. Curr. Chem.*, 2004, **235**, 221;
7. J. A. Real, M. Carmen Muñoz, J. Faus, X. Solans, *Inorg. Chem.*, 1997, **36**, 3008.
8. A. L. Thompson, A. E. Goeta, J. A. Real, A. Galet, M. Carmen Muñoz, *Chem. Comm.*, 2004, **12**, 1390.
9. D. Paliwoda, L. Vendier, W. Nicolazzi, G. Molnar, A. Bousseksou, *Inorg, Chem.,* 2022, **61**, 15991.

Communication orale ☒ par affiche ☐

Room Temperature Magneto-Chiral Dichroism in Circularly Polarized Luminescent Ytterbium Single-Molecule Magnet

Fabrice POINTILLART[1], Kais DHBAIBI,[1] Maxime GRASSER,[1] Haiet DOUIB,[1] François RIOBE,[2] Olivier MAURY,[2] Stéphan GUY,[3] Bruno BAGUEBARD,[3] Olivier CADOR,[1] Cyrille TRAIN,[4] Boris LE GUENNIC,[1] Matteo ATZORI,[4] Jeanne CRASSOUS[1]

[1] Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France, email: fabrice.pointillart@univ-rennes1.fr
[2] Univ Lyon, Ens de Lyon, CNRS UMR 5182, Université Claude Bernard Lyon 1, Lyon, France
[3] Univ Lyon, Université Claude Bernard Lyon 1, CNRS, UMR 5306, Institut Lumière Matière, 69622 Lyon, France
[4] Univ. Grenoble Alpes, INSA Toulouse, Univ. Toulouse Paul Sabatier, EMFL, CNRS, Grenoble

The design of non-centrosymmetric molecular magnets is of paramount importance since the absence of an inversion centre leads to efficient coupling of electric fields to the molecular magnetic moment,[1] and to magnetochirality,[2] a non-reciprocal effect that can be harnessed by unpolarised light. Such molecular magnets may combine magnetism with other physical properties displayed independently or in synergy leading to an attractive and unusual example of multifunctional materials merging chiroptical, luminescence, and magnetic properties.[3] Lanthanide ions are able to retain their magnetization in a given direction, thus generating a special class of Single-Molecule Magnet (SMM) thanks to their specific magnetic and optical properties.[4] In this context, we developed two new families of enantiopure Ytterbium complexes based on the inherently chiral helicene ligand[5]. Slow magnetic relaxation, Circularly Polarized Luminescence (CPL) and Magneto-Chiral Dichroism (MChD) were investigated for both mononuclear[6] and one-dimensional[7] compounds (Figure). In this communication, the enhancement of the SMM performances and MChD effect in the polymeric structure will be argued thank to the support of ab initio calculations providing a deeper understanding of the underlying factors that govern the physical properties in these multifunctional nanomagnets.[7]

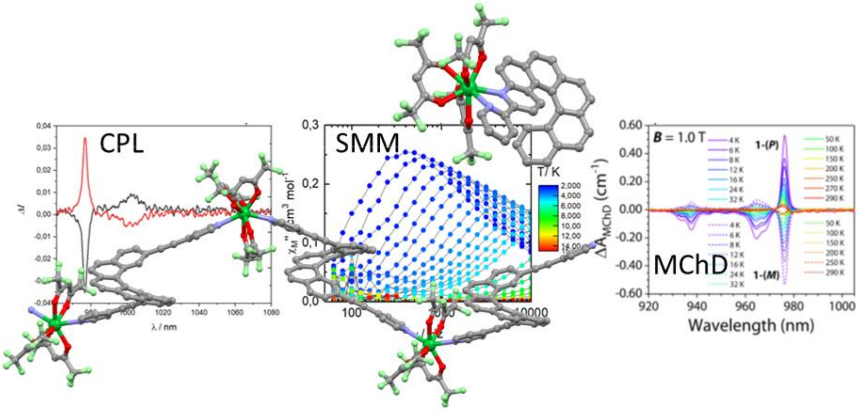


Figure: *Slow magnetic relaxation (SMM), Circularly Polarized Luminescence (CPL) and Magneto-Chiral Dichroism (MChD) behaviours observed in Ytterbium helicene complexes.*

Acknowledgments: The French National Research Agency (ANR-19-CE29-0012-02) and the European Research Council (ERC-CoG Grant Agreement 725184) are acknowledged for financial support.

References:

1. F. Pop, *et al*., *Chem. Rev*. **119**, 8435 (2019).
2. G. L. J. A. Rikken, *et al*.; *Nature*. **390**, 493 (1997).
3. F. Pointillart, *et al*., *Inorg. Chem. Front*. **8**, 963 (2021).
4. D. N. Woodruff *et al*., *Chem. Rev*. **113**, 5110 (2013).
5. K. Dhbaibi et al., *Chem. Rev*. **119**, 8846 (2019).
6. M. Atzori *et al*., *J. Am. Chem. Soc*. **143**, 2671 (2021).
7. K. Dhbaibi, M. Grasser *et al*., DOI : 10.26434/chemrxiv-2022-7k032

Communication orale **x** par affiche ☐

Functionalised spin crossover complexes for thin-film based electronic and spintronic devices

Rebecca RODRIGUES DE MIRANDA[1], Emma BRYAN [2], Mathieu GONIDEC [1], Sandrine HEUTZ [2], Margaux PENICAUD [1], Patrick ROSA [1]

[1] Univ. Bordeaux, CNRS, Bordeaux-INP, ICMCB, UMR 5026, F-33600 Pessac, France

[2]Department of Materials, Imperial College London, South Kensington Campus, United Kingdom

Spin crossover complexes (SCOs) are transition metal complexes that exhibit reversible state switching at ambient conditions, making them promising candidates for molecular electronics and spintronics, for example in memory devices [1]. In iron (II) complexes, switching occurs between a diamagnetic low spin state (S=0) and a paramagnetic high spin state (S=2), and is photo- or thermally-induced. The switching is accompanied by a change in the electronic and magnetic properties, such that molecular junctions of these SCOs exhibit a change in conductance depending on the spin state.

A major advantage of SCO thin-film devices over conventional 2D materials is that the organic ligands can be tailored to add any number of desired properties, such as photoactivity [2] or the ability to self-assemble on a surface [3]. However, the structural and electronic complexity of these molecules mean it can be hard to predict the exact conditions where switching will occur. The goal of my thesis is to control the spin state switching of iron (II) SCCs on surfaces. We aim to perform this tuning in two ways: by functionalising the organic ligands [4], or by changing the 'spinterface' between the molecules and substrate. The latter can be done by varying the substrate material, for instance by using a ferroelectric substrate that can be electrically polarised [5].

First, a library of functionalised iron (II) SCOs is being synthesised and characterised: structurally, electrically and magnetically, both in bulk and as (sub)monolayer films. The effect of the substrate on the spin state switching will be investigated, in particular by using polarisable ferroelectric polymer substrates. As a final step, electronic and potentially spintronic devices will be fabricated from thin films of SCOs.

This research aims to increase our understanding of the spin crossover (SCO) phenomenon at the nanoscale and the subtleties of the spinterface, with the end goal of bringing SCOs closer to technological applications in molecule-based electronics and spintronics.

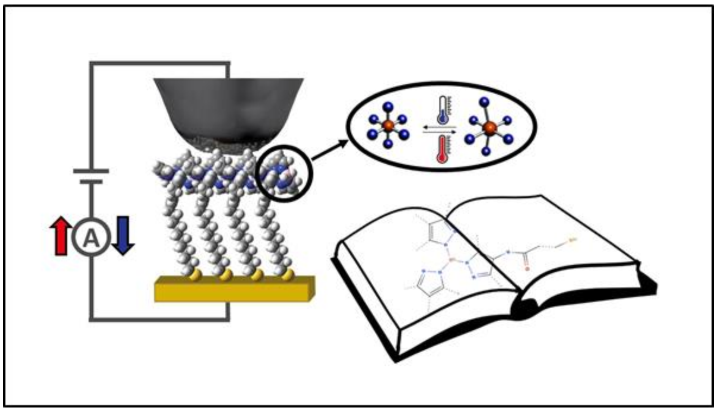


Figure: *Schematic of an electrical measurement on an SCO junction, showing the change in geometry associated with the SCO transition.*

Acknowledgments:

The CNRS-ICL joint PhD programme, the University of Bordeaux, la Région Nouvelle-Aquitaine, and the ERC. Also the chemical analysis, X-ray diffraction and magnetic measurement services of the ICMCB.

References:

1. J.-F. Létard, P. Guionneau, L. Goux-Capes, *Top. Curr. Chem.* **2004**, *235*, 221-249
2. L. Poggini, M. Milek, G. Londi, A. Naim, G. Poneti, L. Squillantini, A. Magnani, F. Totti, P. Rosa, M. M. Khusniyarov, M. Mannini *Mater. Horiz.* **2018**, *5*, 506
3. K. S. Kumar, M. Studniarek, B. Heinrich, J. Arabski, G. Schmerber, M. Bowen, S. Boukari, E. Beaurepaire, J. Dreiser, M. Ruben *Adv. Mater.* **2018**, *30*, 1705416
4. S. Ossinger, L. Kipgen, H. Naggert, M. Bernien, A. J. Britton, F. Nickel, L. M. Arruda, I. Kumberg, T. A. Engesser, E. Golias, C. Näther, F. Tuczek, W. Kuch *J. Phys. Condens. Matter* **2019**, *32*, 114003
5. X. Zhang, T. Palamarciuc, J.-F. Létard, P. Rosa, E. V. Lozada, F. Torres, L. G. Rosa, B. Doudin, P. A. Dowben *Chem. Commun.* **2014**, *50*, 2255

Communication orale X par affiche ☐

Slow Magnetic Relaxation and Luminescent Properties of Mononuclear Lanthanide-Substituted Keggin-Type Polyoxotungstates with Compartmental Organic Ligands

Corina RODRÍGUEZ-ESTEBAN[1,2], Estibaliz RUIZ-BILBAO[3], Beñat ARTETXE,[3] Mathieu GONIDEC,[2] Itziar OYARZABAL[1,4]

[1]*BCMaterials, Basque Center for Materials, Applications, and Nanostructures, Leioa 48940, Spain*
[2] *Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, 33600 Pessac, France*
[3]*Faculty of Science and Technology, University of the Basque Country UPV/EHU, 48080 Bilbao, Spain*
[4]*IKERBASQUE, Basque Foundation for Science, Bilbao 48009, Spain*

In recent years lanthanide-based single molecule magnets (SMM) have been widely studied because of their potential applications; in particular for the development of the future information storage devices[1,2]. A promising design strategy to obtain them relies on the coordinative versatility of POMs. These anionic clusters present some advantageous chemical, structural and electronic features that make them the ideal candidates to design SMMs[3].

In this communication we report the synthesis and magnetic characterisation of a new series of isostructural compounds, namely $K_5[Ln(\alpha\text{-}SiW_{11}O_{39})(H_2L)] \cdot 14H_2O$ (Ln = Sm-Lu, H_2L = N,N'-dimethyl-N,N'-bis(2hidroxy-3-formyl-5-bromobenzyl)ethylene-diamine) (Figure 1)[4]. Considering that POM fragments have been proved to act as antenna ligands to sensitize the emission of the lanthanide ions from the NIR to the visible region[5], we have also performed a complete solid state photophysical study of these complexes, showing the efficient emission of Sm and Eu derivatives in the visible region as well as for Er and Yb analogues in the NIR. On the other hand, magnetic studies have revealed slow relaxation of the magnetization for Gd and Yb derivatives below ~6K.

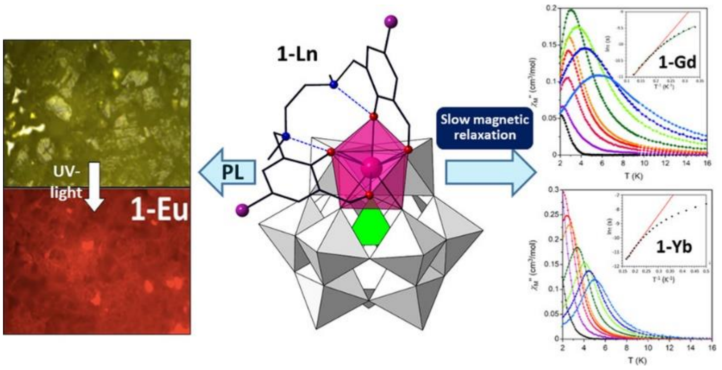


Figure 1. Structure of $[Ln(\alpha\text{-}SiW_{11}O_{39})(H^2L)]^{5-}$ (middle) together with a photograph of the Eu derivative before and after irradiation with UV light (left) and temperature dependence of the out-of-phase magnetic susceptibility for the Gd and Yb derivatives (right).

Acknowledgments: E.R.B. is indebted to EJ/GV for her predoctoral fellowship. I.O. is grateful to the French embassy in Spain for financial support.

References: [1] A. Zabala-Lekuona *et al*., *Coord Chem Rev*. **2021**, *441*, 213984. [2] S. T. Liddle *et al.*, *Chem Soc Rev*. **2015**, *44*, 6655-6669. [3] J. M. Clemente-Juan *et al*., *Chem Soc Rev*. **2012**, *41*, 7464-7478. [4] E. Ruiz-Bilbao *et al*., *Inorg. Chem*. **2022**, *61*, 2428-2443. [5] J. H. Jia *et al*., *Coord Chem Rev*. **2019**, *378*, 365-381.

Communication orale ■ par affiche ☐

Assessing the magnetic relaxation times in a Ni(II) complex: evidence of quantum coherence in zero magnetic field

I. Tlemsani[1*], F. Lambert[1], N. Bridonneau[1], S. Gambarelli[2], T. Mallah[1]

[1] *Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO, UMR 8182), B420 rue du Doyen Georges Poitou, 91400 Orsay, France*
[2] *Laboratoire de Chimie Inorganique et Biologique (UMR-E3 CEA-UJF), INAC, CEA-Grenoble, 17 Ave. des Martyrs, 38054 Grenoble Cedex 9, France*

* email: idris.tlemsani@universite-paris-saclay.fr

In the past few years, the amount of information processed has been constantly increasing, as has the need to solve new problems, both scientific and societal. 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 in the molecular magnet as qubit research 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 long phase memory time T_2. [4]

In this work, we report Electron Paramagnetic Resonance (EPR) spectroscopy studies (cw and pulsed) on a mononuclear Ni(II) complex possessing a distorted octahedral geometry (Figure 1a).[5] CW studies show an Ising type magnetic anisotropy with zero-field splitting spin Hamiltonian parameters D and E equal to -2.35 $\mathrm{cm^{-1}}$ and -0.11$\mathrm{cm^{-1}}$ respectively (Figure 1b). This corresponds to the case where the two $M_S = \pm 1$ are ground levels separated by $2E$, which is consistent with a two-levels system where quantum coherence is possible in the absence of an applied dc magnetic field B_0. EPR studies evidence the presence of a clock transition because experiments in solution show no dependence of T_2 upon deuterating the solvent. We show that the spin-lattice relaxation time T_1 can be enhanced when the molecules are embedded in a rigid matrix that has a larger Debye temperature than the solvent.

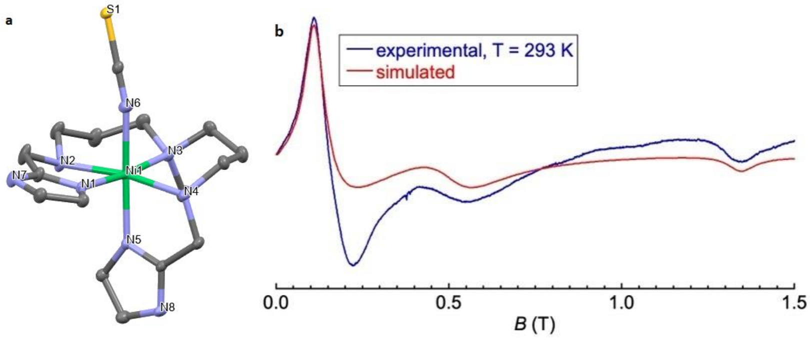


***Figure 1**. View of the molecular structure of [Ni(imdipa)(NCS)]$^+$* (a) *and X-band EPR spectrum at T = 293 K (b).*

References:

1. S. Barz et al., *Nat. Phys.*, **9**, 727-731 (2013)
2. M. N. Leuenberger, et al., *Nature*, **410**, 789-793 (2001)
3. R. Orbach, *Proc. R. Soc. A.*, **264**, 458 (1961)
4. C. A. Collett, et al., *Magnetochemistry*, **5**, 4 (2019)
5. M. Rubín-Osanz et al., *Chem. Sci.*, **12**, 5123–5133 (2021)

Communication orale ☒ par affiche ☐

Ferro-elastic distortion coupled with the spin crossover phenomena in a hysteretic Fe(II) complex

F. Javier VALVERDE-MUÑOZ[1], Abhilash ULHE,[1] Ricardo G. TORRES-RAMIREZ,[1] Elzbieta TRZOP[1], Nathalie DARO,[2] Boris LE GENNIC,[3] Guillaume CHASTANET,[2] Eric COLLET[1]

[1]Institut de Physique de Rennes (IPR), Université de Rennes 1. UMR CNRS 6251, 3500 (Rennes)
[2]Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB), Université de Bordeaux, UMR CNRS 5026, 33600 (Pessac)
[3]Institute des Sciences Chimiques de Rennes (ISCR), Université de Rennes 1. UMR CNRS 6226, 3500 (Rennes)

Symmetry breaking (*SB*) is a relevant feature that can be spontaneously found in some electron labile compounds (e.g. charge-transfer systems, spin-crossover complexes…) which can drastically affect their magnetic response.[1] The origin of the *SB* is mostly associated to the special electronic distribution between bonding and anti-bonding energetic levels within these materials, inducing local distortions that propagate as a cascade effect through the whole crystal lattice. While being still a challenge its rational design from the synthetic point of view, *SB* deserves to be analyzed in deep because seems to be an important source of intriguing physical properties in this class of materials, like the origin of an unexpected hysteresis loop or the appearance of sequential multi-stability.

In this communication will be introduced an extensive structural analysis of the well-known spin-crossover compound $[Fe(PM\text{-}PEA)_2(NCS)_2]$ (**1**), which is of the great interest because it undergoes a very cooperative spin transition coupled with a *SB* that involves the uncommon conversion between a high-symmetry low-spin phase (*Pbcn*) and a low-symmetry high-spin phase ($P2_1/c$), where the ferroelastic distortion occurs at high temperature.[2] We will present how single crystal magnetic and X-Ray diffraction measurements provide key information on coupled *SB* and spin-state conversion. In addition, we will show that DFT calculation and the general Landau theory applied on spin-crossover materials rationalize the overall behavior of this particular material.[3]

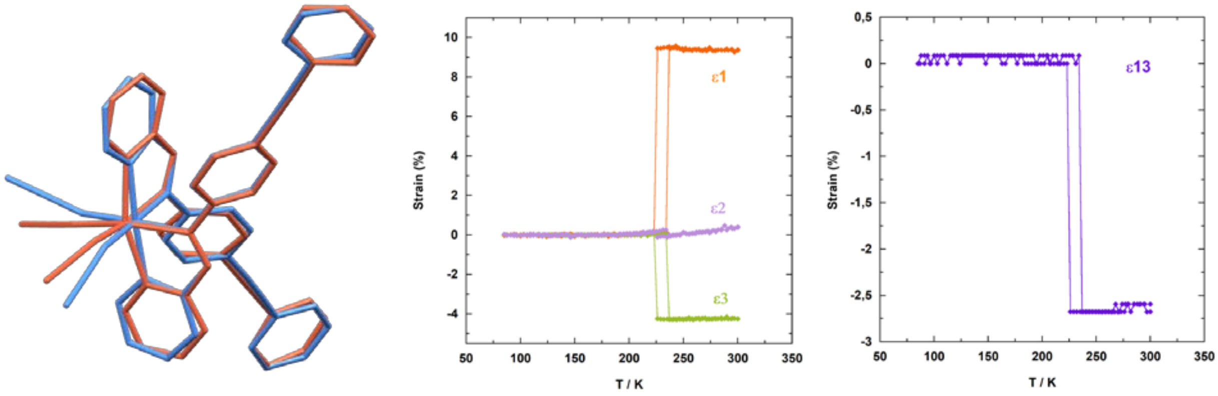


Figure: *Molecular overlap between HS and LS phases in* **1** *complex (left). Non-symmetry breaking (center) and symmetry breaking (right) strain tensors associated with the phase transition in* **1**.

Acknowledgments: The authors acknowledge the financial support from Agence Nationale de la Recherche ANR-19-CE30-0004 ELECTROPHONE. F. J. V-M acknowledges the support of a *APOSTD/2021/359* postdoctoral fellowship from Generalitat Valenciana.

References:

1. a) *Coord. Chem. Rev.* **2015**, *289*, 62; b) *Magnetochemistry* **2016**, *2*, 16.
2. a) *J. Am. Chem. Soc.* **1997**, *119*, 10861; b) *J. Mater. Chem.* **1999**, *9*, 985; c) *J. Phys.: Condens. Matter* **2007**, *19*, 326211; d) *Magnetochemistry* **2016**, *2*, 15.
3. a) *Phys. Rev. B* **2020**, *102*, 134104; b) *J. Appl. Phys.* **2021**, *129*, 085106; c) *Phys. Rev. Materials* **2021**, *5*, 044401.

Communication orale ☑ par affiche ☐

Polymorphism In A Mononuclear Fe(II)-Based Spin-Crossover Complex

Longfei Wang[1], Daniel Rosario-Amorin[1], Mathieu Rouzières[1], Corine Mathonière[1], Rodolphe Clérac[1]

[1] *Université de Bordeaux, CNRS, Centre de Recherche Paul Pascal, UMR 5031, F-33600 Pessac, France*
e-mail: long-fei.wang@crpp.cnrs.fr

Spin-crossover (SCO) compounds are fascinating bistable functional molecules of particular interest due to their potential applications as molecular sensors, switches or memories.[1] In such materials, the d^4–d^7 metal centers under a suitable ligand field can adopt reversible switching between high-spin (HS) and low-spin (LS) states under an external stimuli (e.g., temperature, pressure, light), which can lead to drastic changes to the physical properties of the materials (e.g., magnetic, optical and conductive). Moreover, when cooperative behavior is present between SCO molecules, the presence of elastic interactions between metal centers can vary the population of spin-state species in the crystal lattice at a given temperature upon thermal cycling and result in hysteretic spin transitions.[2] Therefore, controlling the intermolecular interactions (e.g., hydrogen bonding, π–π, van der Waals) and the electronic spin states of SCO molecules are of particular interest towards understanding their effects on the characteristics of SCO transitions (e.g., abruptness, hysteresis and steps). Considering this, the study of SCO behavior in a large family of polymorphs[3] (which is defined as the ability of a substance to exist in two or more crystalline forms) is significantly meaningful, as each polymorphic structure displays variations in molecular conformations and arrangements without changing the molecular structure of the SCO complex. Hence, any changes to SCO behavior can be directly linked to these variations. Herein, we report a series of mononuclear Fe(II)-based SCO polymorphs based on the hydrazone ligand (*E*)-4-methoxy-N'-(pyridin-2-ylmethylene)benzohydrazide (L$^{\mathrm{OMe}}$). Through controlled variations in synthetic conditions (i.e., reagents, temperature, solvent), four polymorphs, labeled as **1*α***, **1*β***, **1*γ***, and **1*σ***, have been successfully prepared. Single-crystal X-ray diffraction measurements of **1*α***, **1*γ***, and **1*σ*** (Figure 1a) reveal the differences between solid-state packing between the polymorphic structures, highlighting changes with respect to the supramolecular interactions and the coordination geometry of the Fe(II) ions. Congruently, magnetic measurements for **1*α***, **1*β***, **1*γ***, and **1*σ*** show changes in SCO cooperativity and transition temperatures (Figure 1b). Thus, this unique polymorphic system offers a model to probe the effect of intermolecular interactions on SCO behavior.

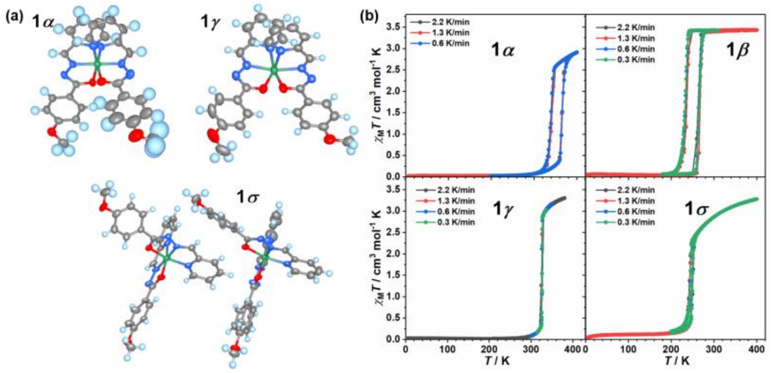


Figure: *Perspective ORTEP views (50% thermal ellipsoids) of the $[\mathrm{Fe}(\mathrm{L}^{\mathrm{OMe}})_2]$ molecules in asymmetric units and the corresponding temperature-dependent χT products for the polymorphs* **1*α***, **1*β***, **1*γ***, *and* **1*σ***.

Acknowledgments:
This work has been supported by the University of Bordeaux, the Région Nouvelle Aquitaine, the ANR (HiPerMagnet project; ANR-20-CE07-0022), and the Centre National de la Recherche Scientifique (CNRS) and the ESRF.

References:

1. O. Kahn, C. J. Martinez, *Science*, **1998**, 279, 44–48
2. H. Spiering, E. Meissner, H. Köppen, E. W. Müller and P. Gütlich, *Chem. Phys.*, **1982**, 68,65–71.
3. J. Tao, R.-J. Wei, R.-B. Huang and L.-S. Zheng, *Chem. Soc. Rev.*, **2012**, 41, 703–737.

Communication orale ☑ par affiche ☐

Partial thermal ETCST under pressure and pressure-induced phase transition of a paramagnetic square $\{[Fe(Tp)(CN)_3]_2[Co(vbik)_2]_2\}(PF_6)_2 \bullet 2CH_3OH$

Buqin Xu[1], Yanling Li[2], and Rodrigue Lescouëzec[1]
1 Sorbonne-université ERMMES, IPCM UMR8232, Paris, France
2 CNRS, IPCM UMR 8232, Plateforme MPBT, Paris, France

Abstract: Molecular magnetic switches are molecules which undergo reversible conversions between two distinct electronic states under external stimuli: temperature, light, pressure···. The change of electronic states can be associated to drastic modification in the magnetic properties but also in the optical, dielectric and mechanic properties. To date, the most investigated molecular magnetic switches are spin-crossover complexes (SCO) and more specifically Fe(II) octahedral. Another class of bistable magnetic compounds have later emerged in which the electronic reorganization involved two cyanide-bridged neighboring metal ions. Here the electronic reorganization often implies a metal-to-metal electron transfer which is coupled to a spin transition on one metal ion (ETCST transition). The effect was first evidence in inorganic polymers (FeCo Prussian Blue Analogs) but strong research efforts have recently been devoted to the design of their discrete molecular analogs. Thus far, the effect of pressure as stimulus has remain scarcely investigated.

Aware of the potential application as sensors and aiming at getting a better understanding of the priezo-induced ETCST process, our group has recently focused its interest on the paramagnetic Fe/Co square compound: $\{[Fe^{III}(Tp)(CN)_3]_2[Co^{II}(vbik)_2]_2\}(BF_4)_2 \bullet 2MeOH$,[1] where Tp = tris(pyrazolyl)borate, vbik = bis(1-vinylimidazol-2-yl)ketone), which shows an abnormal magnetic behaviour under pressure (cooperativity enhance with increasing pressure). For continuing the investigations of the pressure-induced para-to-dia conversion of Fe_2Co_2 square family, here we chose to study the compound $\{[Fe(Tp)(CN)_3]_2[Co(vbik)_2]_2\}(PF_6)_2 \cdot 2MeOH$, which can be considered as a same square complex whose BF_4^- counter-anion is replaced by PF_6^-. The change of the counter-anion here aims at varying slightly the intermolecular interactions.

Here, we show that this new paramagnetic compound $\{[Fe(Tp)(CN)_3]_2[Co(vbik)_2]_2\}(PF_6)_2 \cdot 2MeOH$ presents a different pressure-induced magnetic behaviour compared with the previous one studied. The partial P-induced thermal ETCST is investigated by magnetic measurements, and a phase transition above 1.0 GPa is revealed by high pressure XRD experiments. We also have tried to rationalize the structure-property relationship of those similar square compounds and the main results will be discussed in the presentation.

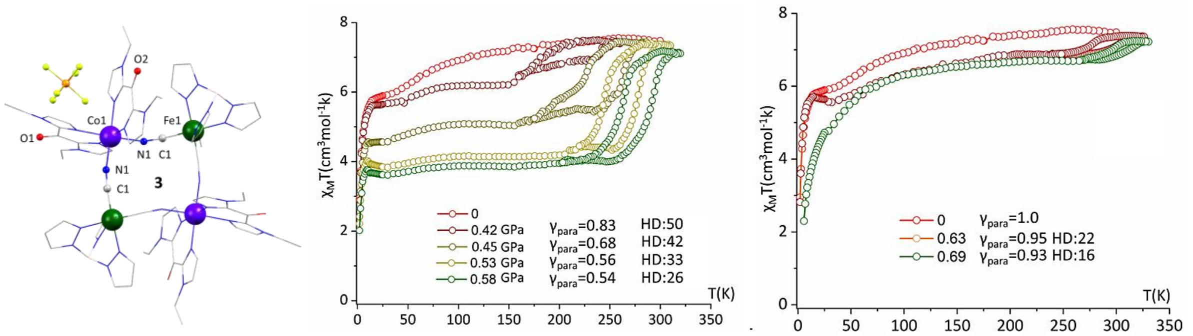


Fig. 1: *The structure at 0 GPa (left), temperature dependence of $\chi_M T$ value under different hydrostatic pressures (middle and right)*

Acknowledgments: Oversea Study Program of Guangzhou Elite Project

References:

1. Li, Y., Benchohra, A., Xu, B, Baptiste, B., Béneut, K., Parisiades, P., Delbes, L., Soyer, A., Boukheddaden, K., et Lescouëzec, R., *Angewandte Chemie International Edition*. **2020**, *vol. 59*(39), p. 17272-17276.

Communication orale ☑ par affiche ☐

Unveiling the structural and electronic versatility of pyrazine in chromium-based coordination systems

Nathan J. YUTRONKIE[1], Dandan LOU[1], Henri BARRY[1], Itziar OYARZABAL[2,3], Aaron MAILMAN[4], Pierre DECHAMBENOIT[1], Mathieu ROUZIÈRES[1], Fabrice WILHELM[5], Andrei ROGALEV[5], Corine MATHONIÈRE[1], Rodolphe CLÉRAC[1]

[1]Université de Bordeaux, CNRS, Centre de Recherche Paul Pascal, UMR 5031, F-33600 Pessac, France
[2]BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, ES-48940 Leioa, Spain
[3]IKERBASQUE, Basque Foundation for Science, ES-48009 Bilbao, Spain
[4]Department of Chemistry, University of Jyväskylä, FI-40014 Jyväskylä, Finland
[5]ESRF-The European Synchrotron, CS 40220, F-38043 Grenoble Cedex 9, France

nathan.yutronkie@crpp.cnrs.fr

Magnetic materials derived from the coordination of metal ions with organic-based ligands offer unprecedented properties for emerging technologies that would otherwise be inconceivable through conventional inorganic-based magnets. At the heart of this continual endeavor is the exploitation of these properties, ideally at or near room temperature, through rationally designed molecular frameworks. Recently, non-innocent bridging ligands, such as pyrazine, have been employed in the construction of two-dimensional networks with Cr^{II} and Cr^{III} metal ions, which has led to the development of ferrimagnetic materials with large coercivity,[1] high ordering temperatures up to 242 °C, and coexisting conductive properties.[2] To further unveil the structural and electronic versatility of this simple ditopic bridging ligand, a series of coordination systems have been crystallized and isolated from reactions between chromium(II) trifluoromethanesulfonate and pyrazine. The structures, elucidated by single-crystal X-ray diffraction, comprise chromium ions bound to pyrazine ligands as either discrete complexes (0D), chain- or ladder-like 1D arrays, or 2D networks with additional solvent and/or triflate ligands completing an octahedral coordination sphere around the metal centers. This presentation will divulge on the methodology to selectively synthesize these coordination solids and corresponding physical properties.

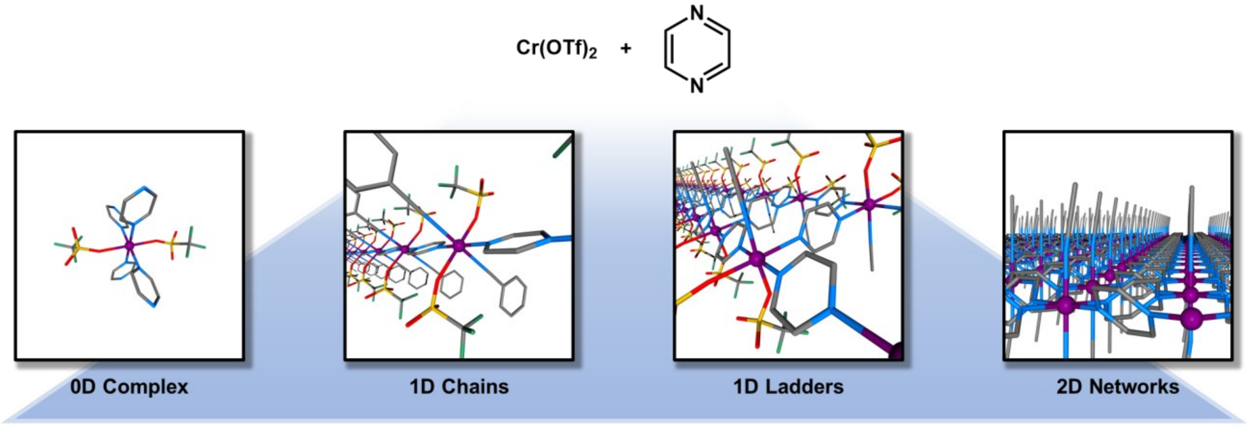


Figure: *Crystal structure views of coordination structures from the reaction of chromium(II) trifluoromethanesulfonate and pyrazine.*

Acknowledgments:

This work was supported by the University of Bordeaux, the Région Nouvelle Aquitaine, the ANR (HiPerMagnet project; ANR-20-CE07-0022, the Centre National de la Recherche Scientifique (CNRS) and the ESRF.

References:

1. P. Perlepe *et al.*, *Science* **2020**, 370, 587.
2. K. S. Pedersen *et al.*, *Nat. Chem.* **2018**, 10, 1056.

Posters

Communication orale ☐ par affiche ⊟

Transition metal K-edge XMCD of Prussian Blue Analogs : Towards quantitative magnetic information

A. Bordage[1], A. Bleuzen[1], A. N’Diaye[1,2], L. Nataf[2], F. Baudelet[2]

[1]ICMMO, Université Paris-Saclay, CNRS, Bât. Henri Moissan, 17 Avenue des Sciences, 91400 Orsay, France
[2]Synchrotron SOLEIL, St Aubin, Gif-sur-Yvette, France

X-ray Magnetic Circular Dichroism is a widely used tool to investigate fundamental properties of matter. On the contrary to $L_{2,3}$-edges of *3d* transition metals (TM), which directly probe the magnetic 3*d* orbitals, the interpretation of TM K-edges XMCD, which probe the delocalized *p* orbitals and offer the advantages to be bulk sensitive and compatible with extreme conditions measurements, remain controversial. To better understand the physical effects at the origin of these TM K-edge XMCD signals and extract quantitative information, we are engaged in their fundamental investigation using Prussian Blue analogs (PBAs) as model compounds. The versatile chemistry of PBAs indeed enables to work with a new experimental approach. We first established the effect of external parameters (temperature, magnetic field) on the XMCD signal and optimized a normalization procedure [1]. We then concentrated on two series of bimetallic PBAs, $A_4[Fe(CN)_6]_{2.7}$ (A=Mn,Co,Ni,Cu) and $A_4[Cr(CN)_6]_{2.7}$ (A=Mn,Fe,Co,Ni) (Fig. 1). They were systematically investigated at the macroscopic scale, especially by SQUID magnetometry, and at the local scale by A, B, Fe and Cr K-edges X-ray absorption spectroscopy and XMCD. The detailed analyses of the XMCD signals of these two series first at the A/B K-edges [2,3] enabled to show that the parameters of the main 1*s*→4*p* contribution (shape, sign, intensity and area) can be related to the magnetic behavior of the probed A^{2+} (B^{2+}) ion (Fig. 2): : (i) the shape to the filling of the 3*d* orbitals, (ii) the sign to the orientation of the magnetic moment, (iii) the intensity of the signal to the total spin number and (iv) the area-under-peak to the Curie constant. A similar analysis was performed at the Fe and Cr K-edges and confirmed all the observations made at the A/B K-edges. This is the first time that the magnetic information contained in TM K-edge XMCD are identified and related to a spectral feature of the signal [2,3]. All these results show that PBA are model compounds particularly well suited to disentangle the information contained in TM K-edge XMCD signals and paves the way to the full understanding of these signals in such molecular systems.

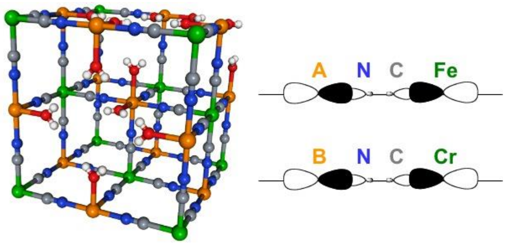


***Figure 1**. Unit cell of the AFe and BCr PBA series*

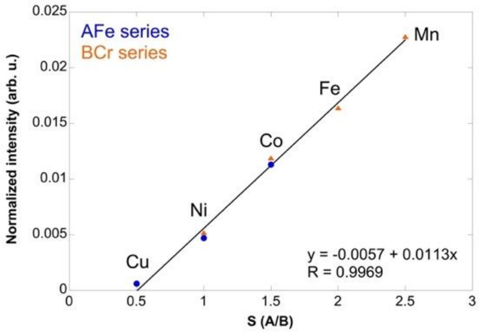


***Figure 2.** Evolution of the intensity of the main 1s⟶4p contribution of the A K-edge XMCD signal as a function of the spin of the A^{2+} ion*

Acknowledgments: The ANR for funding (Project *MagDiDi*, no. ANR-17-CE29-0011) and SOLEIL/ESRF synchrotrons for provision of beamtime.

References:

1. A. N’Diaye et al. (2021) Journal of Synchrotron Radiation 28:1127-1136
2. A. N’Diaye et al. (2022) Inorganic Chemistry 61 :6326-6336
3. A. N’Diaye et al. (2022) ACS Omega 7 :36366-36378

Communication orale ☐ par affiche ☒

Interplay between transition metal K-edge XMCD and magnetism in Prussian Blue Analogs

A. Bleuzen[1], A. N'Diaye[1,2], A. Bordage[1], E. Rivière[1], L. Nataf[2], F. Baudelet[2]

[1]ICMMO, Université Paris-Saclay, CNRS, Bât. Henri Moissan, 17 Avenue des Sciences, 91400 Orsay, France
[2]Synchrotron SOLEIL, St Aubin, Fig-sur-Yvette, France

X-ray Magnetic Circular Dichroism (XMCD) able to probe the magnetic properties of matter at a local level has attracted a growing interest for the study of molecular materials. Nevertheless, the knowledge of the information contained in XMCD signal depends on the probed orbitals. Thus, in the case of first row Transition Metals (TM), it is striking that $L_{2,3}$-edge XMCD has become a well- established technique whereas the interpretation of K-edge XMCD remains at a standstill.

In this context, we are engaged in the development of an original experimental approach based on the use of the versatility of Prussian Blue Analogs (PBA) to better understand XMCD signals at the TM K-edge [1-3]. We present here a combined investigation of two PBA series of compounds ($A_4[B(CN)_6]_{2.7}$; A = Mn, Fe, Co, Ni, Cu; B = Cr, Fe) by K-edge XMCD and magnetometry. This study allows us to propose expressions of the intensity of the main contribution to the XMCD signal (I Calc.), which well reproduce the experimental intensities (I exp.; Figure 1). It thus show that these expressions contain valuable information (i) on the exchange interactions between all involved 3*d* and 4*p* orbitals and (ii) on the local orientation of the magnetic moments carried by the probed element (Figure 2). This new information shed new light on the different macroscopic magnetic behaviors of the studied compounds.

These results pave the way towards a new tool, which could be able to provide valuable information on local orientation of magnetic moments or to better understand the role of exchange interactions between all *d* and *p* orbitals involved in the magnetic properties of TM ions in molecular materials.

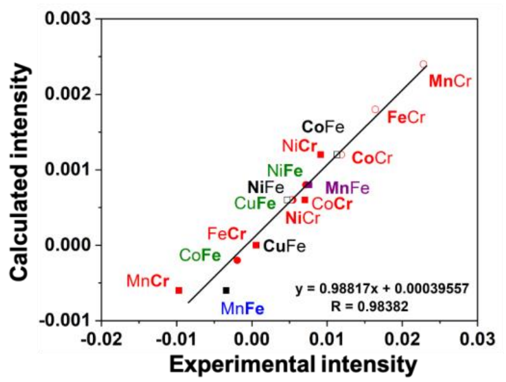


***Figure 1**. Calculated intensity of the main 1s→4p contribution vs. the experimental one at the A and B K-edges*

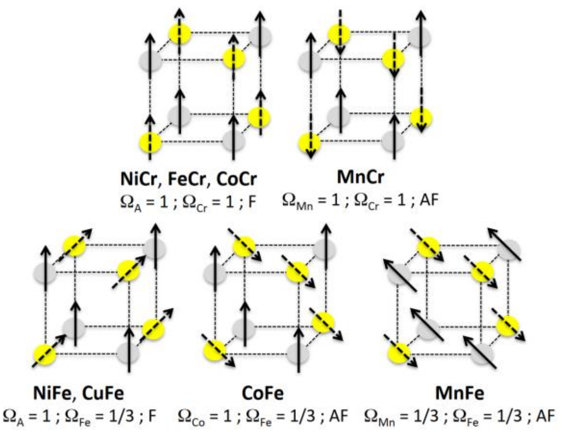


***Figure 2.** Proposed orientations of the magnetic moments for an octant of the PBA structure.*

Acknowledgments: The ANR for funding (Project *MagDiDi*, no. ANR-17-CE29-0011) and SOLEIL/ESRF synchrotrons for provision of beamtime.

References:

1. A. N'Diaye et al. (2021) Journal of Synchrotron Radiation 28:1127-1136
2. A. N'Diaye et al. (2022) Inorganic Chemistry 61 :6326-6336
3. A. N'Diaye et al. (2022) ACS Omega 7 :36366-36378

Electrochemical Modulation of Magnetic Properties in Polynuclear Complexes

Aristide Colin[a], Nathalie Bridonneau[a], François Lambert[a], Nicolas Suaud,[b] Nathalie Guihéry,[b]
Talal Mallah[a]

a. Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO, Université Paris-Saclay, 91400 Orsay
b. Laboratoire de Chimie et Physique Quantique (LCPQ), Université de Toulouse
* email: aristide.colin@universite-paris-saclay.fr

This work deals with the rational design of Ni(II)-based qubits with the purpose of controlling the interaction between three to six qubits by using a redox active central ligand as some examples have been reported **[1]**. These systems are potential candidates as quantum logic gates.

Two complexes based on the same central hexahydroxytriphenylene (HHTP) redox active ligand are studied, one trinuclear and an hexanuclear, that differ by their external ligands. Their redox states are characterized by spectroelectrochemical measurements and for each complex the first oxidation process is successfully performed using I_2 and $AgSbF_6$.

In doing so and with the addition of EPR measurements **[2]**, a switch is observed in both complexes between paramagnetic and diamagnetic states. In the case of the trinuclear complex, the switch occurs from a paramagnetic state where a single electron is present on the central ligand (that magnetically couples the three metallic centers) to a state for which the diamagnetic central ligand isolates the magnetic centers. In the case of the hexanuclear complex the situation is reversed.

Ab initio calculations on a toy model show interesting insights in the electronic structure of the studied species. More precisely, the properties of the HHTP ligand are investigated and allow to explain the experimentally observed properties of the complexes.

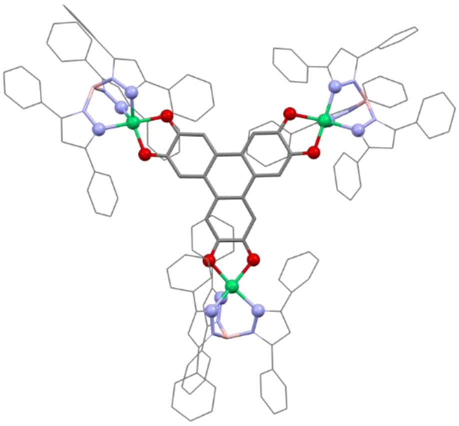


Figure 1 : Crystallographic structure of the trinuclear complex $[Ni_3(HHTP)(HBTp^{(Ph,Ph)}_3)_3]$

References:

[1] Ma, X., Suturina, E.A., Rouzières, M., Platunov, M., Wilhelm, F., Rogalev, A., Clérac, R., Dechambenoit, P., 2019. Using Redox-Active π Bridging Ligand as a Control Switch of Intramolecular Magnetic Interactions. J. Am. Chem. Soc. 141, 7721–7725. https://doi.org/10.1021/jacs.9b03044

[2] Yang, L., He, X., Dincă, M., 2019. Triphenylene-Bridged Trinuclear Complexes of Cu: Models for Spin Interactions in Two-Dimensional Electrically Conductive Metal–Organic Frameworks. J. Am. Chem. Soc. 141, 10475–10480. https://doi.org/10.1021/jacs.9b04822

« Origine de l’orientation de l'interface macroscopique haut spin - bas spin dans les cristaux à transition de spin »

N. di Scala, N. Belmouri, M. Paez Espejo and K. Boukheddaden

Phys. Rev. B **106**, 144107, 2022

Les orientations préférentielles des interfaces macroscopiques haut-spin (HS) et bas-spin (LS) apparaissant dans les cristaux moléculaires à transition de spin au cours de leurs transitions de phase sont expliquées par l’étude d’une version 3D généralisée du modèle électroélastique tenant compte d’un changement anisotropique des paramètres de réseau, a, b et c à la transition. Les investigations sont effectuées à 0 K en analysant le paysage énergétique d’un réseau constitué de deux phases HS et LS séparées par une interface inclinée à orientation variable θ, en fonction du rapport d’anisotropie, $\lambda = \Delta b/\Delta a = \Delta b/\Delta c$, où $\Delta x = x_{HS} - x_{LS}$ est le misfit le long de la direction x (= a, b, c) entre les états HS et LS. Pour les grandes valeurs de $\lambda < 0$, la dépendance en θ de l’énergie élastique totale relaxée représente une structure symétrique en double puits avec deux positions stables θ_{min}, et une orientation instable $\theta_{max} = 90°$. Au-delà d’une valeur critique, $\lambda_C^- < 0$, un seul minimum subsiste à θ = 90°, rappelant ainsi le comportement d’un paramètre d’ordre d’une transition de phase du 2nd ordre. En augmentant λ, ce minimum survit jusqu’à une deuxième valeur seuil $\lambda_C^+ > 0$ au-dessus de laquelle l’énergie élastique récupère une configuration de double puits avec deux nouvelles orientations d’interface préférentielles, mettant en évidence l’existence d’un phénomène de réentrance. Nous démontrons que le comportement de θ_{min} par rapport à λ suit la même classe d’universalité que celle d’une transition de phase de second ordre, pour laquelle nous calculons les exposants critiques β et ν par une analyse de taille finie. Dans l’ensemble, ces recherches révèlent que dans les solides moléculaires commutables présentant une déformation anisotropique de la cellule élémentaire entre les états LS et HS, il existe une orientation de l’interface sans contrainte interne dans le matériau, assurant leur intégrité sur un grand nombre de cycles thermiques ou de charges pendant leur utilisation pratique.

Communication orale ☐ par affiche X

Design of redox-active Cs⊂{Fe_4Ni_4} cyanide-bridged cage complexes bearing monodentate ligands: synthesis, structure and electronic properties

Jana GLATZ [1], Mélodie DONNART[1], Geoffroy GONTARD[1], Yanling LI[1], and Rodrigue LESCOUËZEC*[1]

[1]*Institut Parisien de Chimie Moléculaire, CNRS UMR 8232, Sorbonne Université, 4 place Jussieu F-75252 Paris cedex 5*

In recent years, strong efforts have been devoted to the design and crystallization of molecular models of the cyanido-bridged inorganic polymers known as "Prussian Blue Analogues" (PBA). In this work, we more specifically focus on soluble octametallic complexes that represent an elemental unit of the PBA cubic network. The self-assembly of the tris-cyanido *fac*-$[Fe^{III}(Tp)(CN)_3]^-$ complex and Ni(II) salts is shown to lead to $\{[Fe(Tp)(CN)_3]_4[Ni(S)_3]_4\}^{4+}$ procubes, where the Ni(II) ion is coordinated to labile solvent molecules (S : DMF or CH_3CN). ^1H and ^{133}Cs paramagnetic NMR studies show that (i) the cubic complex is relatively stable during several days in solution, in particular in acetonitrile; (ii) a Cs^+ ion can be inserted inside the cubic cavity as revealed by the presence of strongly shifted paramagnetic signal near -800 ppm at 300 K. The resulting $Cs\subset\{[Fe(Tp)(CN)_3]_4[Ni(S)_3]_4\}^{5+}$ procube shows an enhanced stability as shown by time dependent ^1H and ^{133}Cs paramagnetic NMR spectra collected during several weeks. FT-IR spectra confirm the expected Fe(III) and Ni(II) redox states, with the occurrence of a single characteristic cyanide stretching vibration near 2170 cm^{-1}. The Fe(III) redox state is also confirmed by cyclic voltammetry experiments in acetonitrile, with the occurrence of four pseudo-reversible reduction events that can be assigned to the successive reduction of the four Fe^{III} ions in the Cs-procube. Although these procubes could not be isolated as single crystals, the substitution of the labile coordinated solvent of the Cs-containing procube by N-donor imidazole monodentate ligands allows the crystallization of the novel $Cs\subset\{[Fe(Tp)(CN)_3]_4\text{-}[Ni^{II}(Im)_3]_4\}Cl_3$ cubic complex by slow diffusion of ether in a DMF mother solution. The analyses of this cube demonstrate that in solution in ambient condition Fe(III) centres are gradually reduced to Fe(II). The presence of three chlorides as counterions suggests that the cube can be isolated in the $Fe^{II}_2Fe^{III}_2Ni^{II}_4$ redox state. The presence of at least two Fe(II) ions is actually confirmed by cyclic voltammetry experiment in DMF and FT-IR spectroscopy. An intermediate state $Fe^{II}Fe^{III}_3Ni^{II}_4$ can be identified by isolating fresh crystals (72h) as demonstrated by FT-IR and the magnetic measurements, that also reveal the presence of paramagnetic ferromagnetic interaction between the low-spin Fe^{III} and Ni^{II} ions.

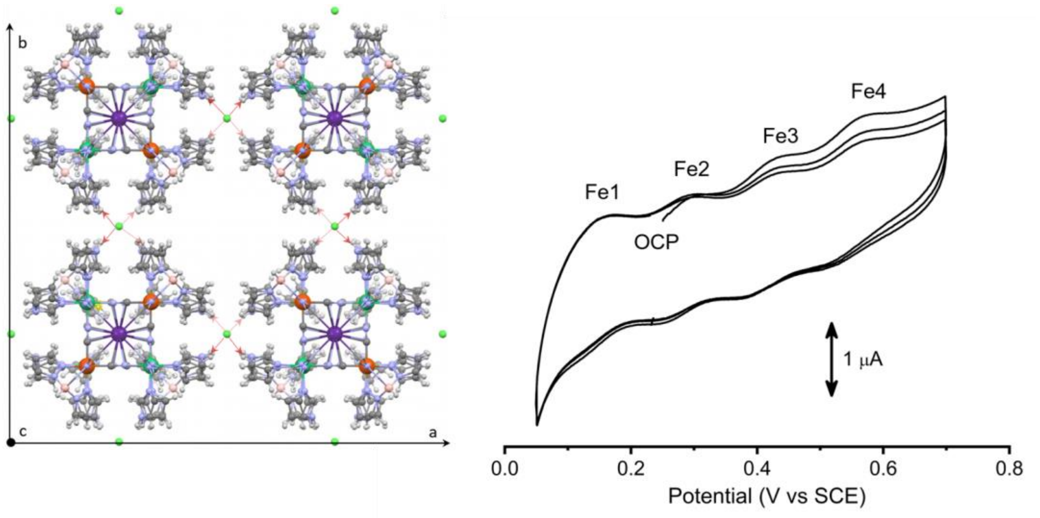


Figure 1: *Crystal packing (left) and redox properties (right) of the* $Cs\subset\{[Fe(Tp)(CN)_3]_4\text{-}[Ni^{II}(Im)_3]_4\}Cl_3$ *cubic complex*

Communication orale ☐ par affiche ✓

Accessing 2D molecule-based magnets through mononuclear building blocks

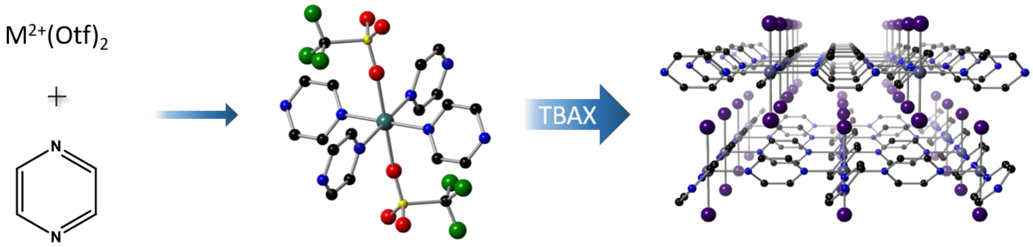
Katia Dujarric[1*], Dandan Lou[1], Nathan J. Yutronkie[1], Abhijit Adak[1], Itziar Oyarzabal[2,3], Aaron Mailman[4], Corine Mathonière[1], Rodolphe Clérac[1]

[1] *Université de Bordeaux, CNRS, Centre de Recherche Paul Pascal, UMR 5031, F-33600 Pessac, France*
[2] *BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, ES-48940 Leioa, Spain*
[3] *IKERBASQUE, Basque Foundation for Science, ES-48009 Bilbao, Spain*
[4] *Department of Chemistry, University of Jyväskylä, FI-40014 Jyväskylä, Finland*

**katia.dujarric@crpp.cnrs.fr*

Molecule-based magnets have shown great interest over the past decades due to their attractive properties[1]. They represent an excellent alternative to the traditional inorganic-based magnets used in modern-day technologies[2]. 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 light, two-dimensional layered structures from the combination of chromium-based precursors and pyrazine (pyz) have recently shown the coexistence of magnetically ordered states[1,3] and electrical conductivity[1,3]. These properties arise from the ability of the chromium(II) centers to reduce one-half of the bridging pyrazine ligands, which affords a highly delocalized network of spins and promotes strong magnetic exchange between paramagnetic centers. To better understand the relationship between the remarkable properties of these systems and their structure, it is crucial to develop single crystals suitable for X-ray diffraction and physical property measurements. Unfortunately, due to the nature of their solvothermal synthesis, crystallization of these coordination solids remains tortuous and factors to control this process are limited.

To circumvent this challenge, a novel building block has been synthesized to generate these 2D networks with greater control of the crystallization process. Here, the mononuclear complex, $Cr^{II}(OTf)_2(pyz)_4$, (OTf = Triflate), has been synthesized (see scheme), enables the exploration of solution-based approaches, while offering a facile means to functionalize the axial positions of the network through anion exchange with the labile triflate moieties. Moreover, following the same synthetic pathway, the mononuclear building block $V^{II}(OTf)_2(pyz)_4$ has also been crystallized for the exploration of vanadium-based networks. This presentation will focus on using this novel building block to synthesize and crystallize two-dimensional magnetic structures.



Scheme: *Synthetic route used to obtain two-dimensional layered structures (right) through the mononuclear building block* $M(OTf)_2(pyz)_4$ *and tetrabutylammonium salts (TBAX;* $X = Cl^-, Br^-$ *or* I^-*).*

Acknowledgments:

This work was supported by the University of Bordeaux, the Région Nouvelle Aquitaine, Quantum Matter Bordeaux, the ANR (HiPerMagnet project; ANR-20-CE07-0022), the Centre National de la Recherche Scientifique (CNRS) and the ESRF.

References:

1. P. Perlepe et al., Science, 370, 587 (2020)
2. J.S. Miller, Mater. Today, 17, 224, (2014)
3. K.S. Pedersen et al., Nat. Chem. 10, 1056 (2018)

Communication orale ☐ par affiche ☒

Organolanthanide complexes: ab initio electronic structures investigation and magnetic properties rationalization

Léo LA DROITTE[1*], Boris LE GUENNIC[1], Olivier CADOR[1]

[1]*Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) UMR 6226, 35000 Rennes, France*
** email: leo.la-droitte@univ-rennes1.fr*

Single Molecule Magnets (SMMs) are widely studied because of their potential impact in applications such as high-density information storage, quantum computing or spintronics.[1-4] Organolanthanide complexes are a great way to design performing SMMs. However, enhancing the magnetic properties of Ln based SMMs, that is, getting compounds with a slow magnetic relaxation and the highest blocking temperature possible, is a major challenge.[5]

In this work, different design strategies for organolanthanide SMMs are computationally explored, such as the use of cyclooctatetraenyl (Cot) and cyclononatetraenyl (Cnt) large ligands, radical-bridged ligands, or even the seek for a diffuse valence orbital between two lanthanide centres. Recent computational and magnetic measurement results on Ln-Cnt complexes, compounds based on radical-bridged ligands, and derived, will be presented.[6-8]

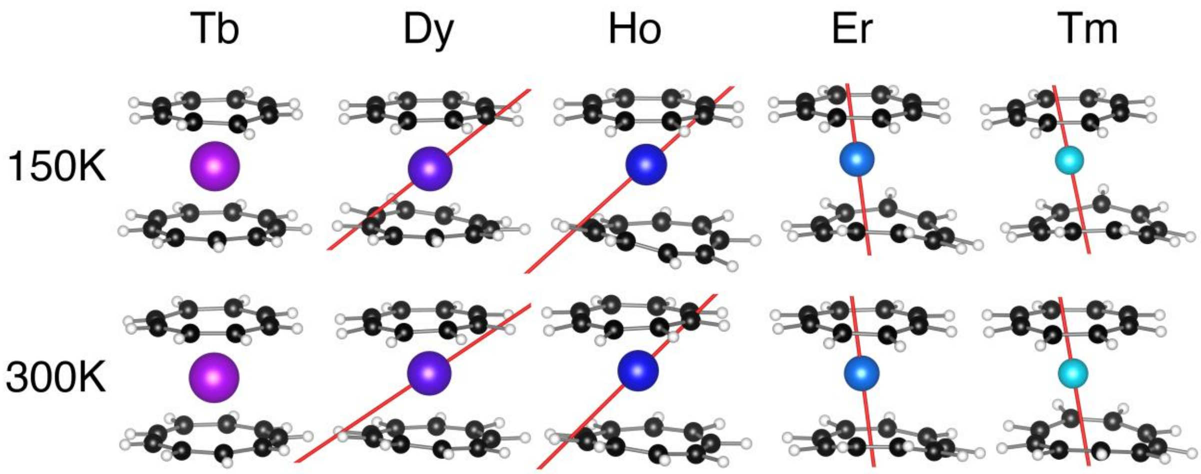


Figure: *Computed structures of Dy(Cnt)3 (left), [(Cp*2Dy)2(µ-Bbim•)]- (centre) and Dy2(Cnt)3(thf)2 (right).*

References:

1. M. Atzori and R. Sessoli, J. Am. Chem. Soc., 2019, 141, 11339-11352.
2. A. Gaita-Arino, F. Luis, S. Hill and E. Coronado, Nat. Chem., 2019, 11, 301-309.
3. F. D. Natterer, K. Yang, W. Paul, P. Willke, T. Choi, T. Greber, A. J. Heinrich and C. P. Lutz, Nature, 2017, 543, 226-228.
4. A. Candini, S. Klyatskaya, M. Ruben, W. Wernsdorfer and M. Affronte, Nano. Lett., 2011, 11, 2634-2639.
5. Guo et al., Science, 2018, 362, 1400.
6. J. Moutet, J. Schleinitz, L. La Droitte, M. Tricoire, F. Pointillart, F. Gendron, T. Simler, C. Clavaguéra, B. Le Guennic, O. Cador and G. Nocton, Angew. Chem. Int. Ed., 2021, 133, 6107-6111.
7. M. Tricoire, L. Münzfeld, J. Moutet, N. Mahieu, L. La Droitte, E. Moreno-Pineda, F. Gendron, J. D. Hilgar, J. D. Rinehart, M. Ruben, B. Le Guennic, O. Cador, P. W. Roesky and G. Nocton, Chem. Eur. J., 2021, 54, 13558-13567.
8. O. Stetsiuk, L. La Droitte, V. Goudy, B. Le Guennic, O. Cador and G. Nocton, Organometallics, 2022, 41, 133–140.

Communication orale ☐ par affiche ☒

Post-synthetic modification mechanism for 1D spin crossover coordination polymers

Yongjian Lai, Alejandro Enriquez-Cabrera, Livia Getzner, Lionel Salmon, Lucie Routaboul, Azzedine Bousseksou
LCC, CNRS & University of Toulouse, 205 route de Narbonne, 31077 Toulouse, France
** email: yongjian.lai@lcc-toulouse.fr*

In the last few years the post-synthetic modification (PSM) has emerged as a very important and efficient tool to chemically modify different materials and to synthesize new species that cannot be obtained otherwise. In this work, the modification of the NH$_2$ functions present on the spin crossover complex (SCO) [Fe(NH$_2$trz)$_3$](NO$_3$)$_2$ was indeed achieved by a PSM methodology. We then confirmed that it is possible to perform quantitative PSM reactions on this solid-state complex. The key factor to obtain this result is the use of a suitable solvent (ethanol or methanol). These two solvents limit the interactions between the particles and separate the polymeric chains of the complex, which allows for an efficient contact of the NH$_2$ functions of the complex with the aldehyde. Note that the use of an unsuitable solvent either leads to no reaction or requires longer reaction times to transform the amine functions into imines. However, in the latter case the resulting compound is not the desired product since the iron II atoms were mostly oxidized to iron III during imine formation. The analysis by transmission electron microscopy confirms that the PSM reaction has a drastic effect on the size and the shape of the nanoparticles and shows that a deterioration of the complex occurs if the reaction time is too long.

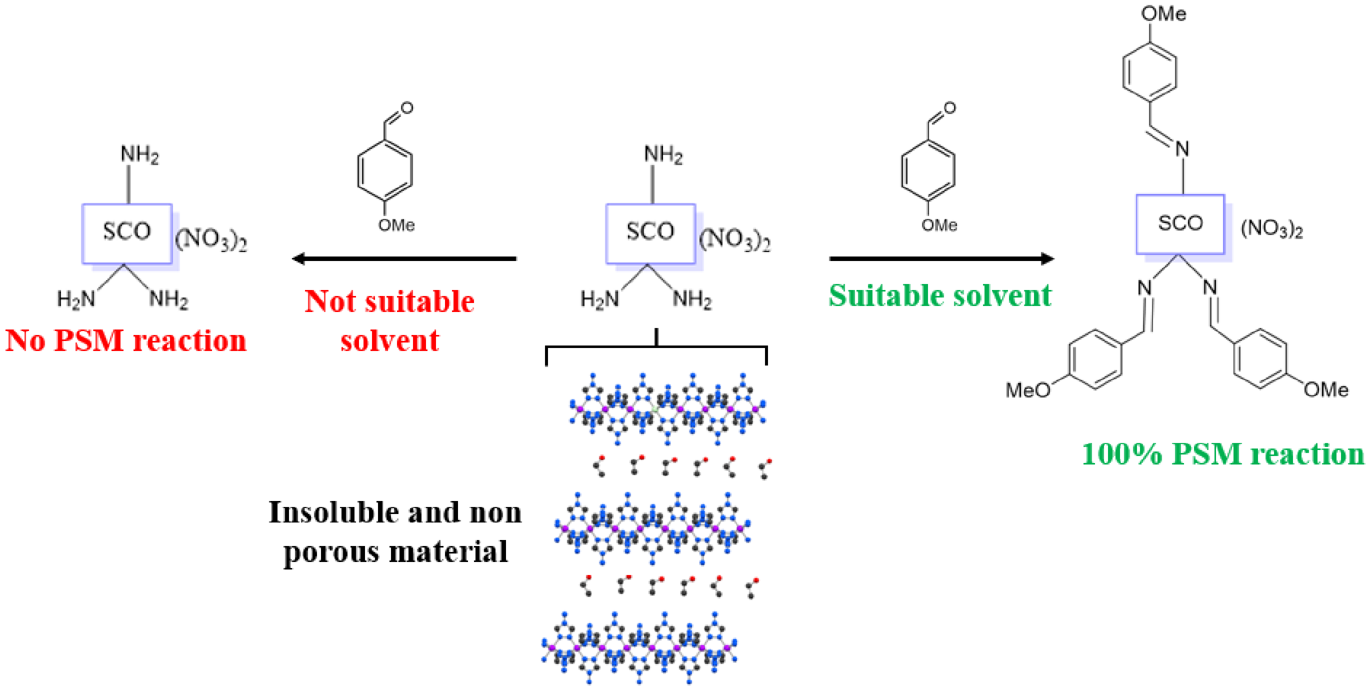


Figure: *Influence of the solvent on the PSM on the [Fe(NH$_2$trz)$_3$](NO$_3$)$_2$ spin crossover (SCO) complex*

Acknowledgments: We thank financial support from the Agence Nationale de la Recherche (ANR-19-CE09-0008-01)

References:

1. New J. Chem., 2022, Advance Article (doi.org/10.1039/D2NJ04015H)
2. Eur. J. Inorg. Chem., 2021, 2000–2016
3. ACS Cent. Sci., 2020, 6, 1046–1057
4. Angew. Chem., Int. Ed., 2014, 53, 10164–10168

Communication orale ☐ par affiche ☑

Fluoride-based magnetic metal-organic frameworks for CO_2 capture and sequestration

Dandan LOU[1], Nathan YUTRONKIE[1], Morgane YQUEL[1], Panagiota PERLEPE[1], Itziar OYARZABAL[2,3], Pierre DECHAMBENOIT[1], Mathieu ROUZIERES[1], Andrei ROGALEV[4], Aaron MAILMAN[5], Kasper S. PEDERSEN[1,6], Corine MATHONIERE[1], Rodolphe CLERAC[1]

[1]Univ. Bordeaux, CNRS, Centre de Recherche Paul Pascal, UMR 5031, Pessac, France. [2]BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain. [3]IKERBASQUE, Basque Foundation for Science, 48009 Bilbao, Spain. [4]ESRF-The European Synchrotron, Grenoble, France. [5]Department of Chemistry, University of Jyväskylä, FI-40014 Jyväskylä, Finland. [6]Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark.

dandan.lou@u-bordeaux.fr

With carbon dioxide (CO_2) being the largest contributor to greenhouse gas emissions, there exists a crucial need in today’s society to effectively capture and sequester atmospheric CO_2 from both environmental and industrial perspectives. Existing carbon capture technologies are simply too expensive to be practical. Meanwhile, the development of new technologies that imprison CO_2 at low concentrations from gas mixtures in an efficient method is still a major challenge faced by researchers. [1,2] Regarding this matter, metal-organic frameworks (MOFs) have been viewed as emerging materials that can be chemically engineered to possess high thermal robustness and appealing physisorption properties in order to greatly improve the energy efficiency of small molecule gas separation. [3] Following this avenue, novel three-dimensional MOFs of the unit formula $Cu(pyz)_2MF_6$ (M = Ti, Ir, Os) with critical pore sizes for CO_2 capture have been synthesized and structurally characterized by single crystal X-ray diffection. By incorporating paramagnetic MF_6 units, the promotion of magnetic coupling between the spin carriers was achieved, which lead to the stabilization of magnetically ordered phases. This presentation will discuss the facile and efficient methodology towards developing these magnetic MOFs and CO_2 absorption studies using these materials.

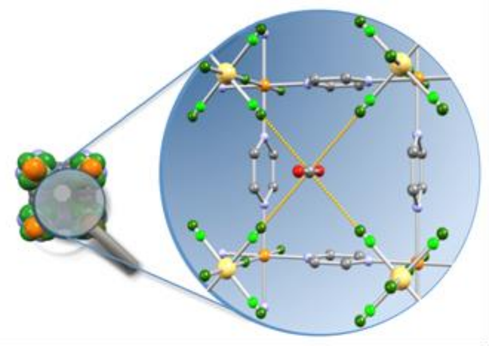


Figure: *View of the porous 3D structure of [$Cu(pyz)_2MF_6$] compounds with imprisoned CO_2 molecules.*

Acknowledgments:

This work was supported by the University of Bordeaux, the Région Nouvelle Aquitaine, Quantum Matter Bordeaux, the ANR (HiPerMagnet project, ANR-20-CE07-0022), the Centre National de la Recherche Scientifique (CNRS) and the ESRF.

References:

1. Shekhah, Y. Belmabkhout, Z. Chen, V. Guillerm, A. Cairns, K. Adil, M. Eddaoudi, *Nat. Commun.* **2014**, *5*, 4228.
2. J. R. Li, J. Yu, W. Lu, L. B. Sun, J. Sculley, P. B. Balbuena, H. C. Zhou, *Nat. Commun.* **2013**, *4,* 1538.
3. D. S. Sholl, R. P. Lively, *Nature* **2016**, *532*, 435.

Communication orale ☐ par affiche ☑

Towards rational tuning of the layer-layer distance in 2D molecule-based magnets

Vincent NADURATA,[1] Mengting SUO,[1] Dandan LOU,[1] Nathan YUTRONKIE,[1] Andrei ROGALEV,[2] Aaron MAILMAN,[3] Corine MATHONIERE,[1] and Rodolphe CLERAC[1]

[1]*Université de Bordeaux, CNRS, Centre de Recherche Paul Pascal, UMR 5031, F-33600 Pessac, France*
[2]*ESRF – The European Synchrotron, CS40220, F-38043 Grenoble Cedex 9, France*
[3]*Department of Chemistry, University of Jyväskylä, FI-40014 Jyväskylä, Finland*

Email: vincent.nadurata@crpp.cnrs.fr

The potential application of tuneable, low density molecule-based magnets in devices remains hindered by low critical temperatures (T_c) and coercive fields compared to state-of-the-art inorganic magnets. In a family of Cr-pyrazine-based two-dimensional (2D) networks, we wish to study how these and other magnetic properties may be modulated by varying the intercalated species in between the 2D layers.

The room-temperature magnet $Li_{0.7}[Cr^{II}(pyrazine^{\bullet-})_2]Cl_{0.7}\cdot 0.25THF$ (THF = tetrahydrofuran) is synthesised via the post-synthetic reduction of $CrCl_2(pyrazine)_2$ via Li(Ac) (Ac = 1,2-dihydroacenaphthylenide, $C_{12}H_{10}^{\bullet-}$).[1] As the distance between the Cr-pyrazine layers is regulated by the Li^+ ions, Cl^- ions, and THF molecules between them, we envisage a rational control of this distance via reduction of the $CrCl_2(pyrazine)_2$ starting material[2] with $Ac^{\bullet-}$ salts of alkali metals with increasingly larger atomic radii. Thus, this work investigates the structural and magnetic properties of $CrCl_2(pyrazine)_2$ reduced by Na(Ac) ($\mathbf{1^{Na}}$) and K(Ac) ($\mathbf{2^{K}}$).

The materials exhibit large T_c and coercive field values comparable to those in the aforementioned Li^+ analogue, with room-temperature hysteresis arising from the anisotropy of the square planar Cr^{II} centres as confirmed via X-ray absorption spectroscopy and X-ray magnetic circular dichroism measurements. Powder X-ray diffraction measurements indicate, however, that although both contain Cr-pyrazine layers in the *ab*-plane, their respective structures differ greatly in the *c*-direction: $\mathbf{1^{Na}}$ is well-ordered in the *c*-direction, due to intercalated Na^+ and Cl^- ions, while $\mathbf{2^{K}}$ is highly disordered in the *c*-direction, potentially due to a lack of intercalated ions. This detailed study of these two contrasting materials sheds light on the importance of intercalated species on the crystallinity of layered materials, and the subsequent effects on the structural and magnetic properties. Additionally, the disorder of $\mathbf{2^{K}}$ in the *c*-direction opens up the attractive possibility of chemically exfoliating these materials via employing even larger alkali metal intercalants,[3] an avenue currently being explored.

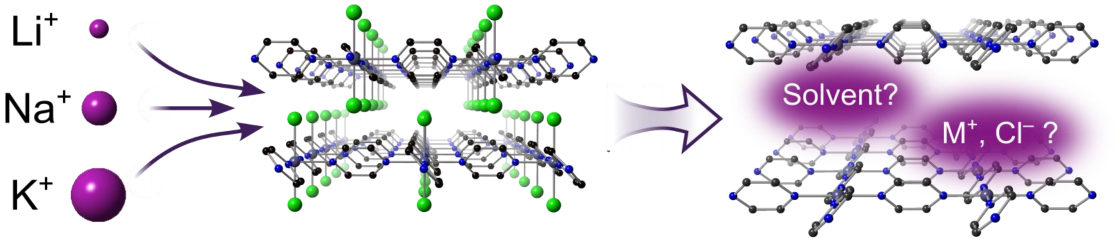


Figure: The reduction of $CrCl_2(pyz)_2$ (left) with various alkali metal salts of $Ac^{\bullet-}$ results in layered room-temperature magnets (right) with varying intercalated structures depending on the alkali metal employed.

Acknowledgments:
This work was supported by the University of Bordeaux, the Région Nouvelle Aquitaine, Quantum Matter Bordeaux, the ANR (HiPerMagnet project; ANR-20-CE07-0022), the CNRS, and the European Synchrotron (ESRF).

References:

1. Perlepe, P., Clérac, R., et al. *Science*, 2020, **370**, 587–592.
2. Pedersen, K. S., Clérac, R., et al. *Nat. Chem.*, 2018, **10**, 1056–1061.
3. Viculis, L. M., Kaner, R. B. et al. *J. Mater. Chem.*, 2005, **15**, 974–978.

Communication orale ☐ par affiche ☑

Modulation of the magnetic properties through a redox-active bridging ligand

Mengting SUO[1], Xiaozhou MA[1], Elizaveta A. SUTURINA[2], Siddhartha DE[1], Mathieu ROUZIERES[1], Mikhail PLATUNOV[3], Fabrice WILHELM[3], Andrei ROGALEV[3], Rodolphe CLERAC[1], and Pierre DECHAMBENOIT[1]

[1]Univ. Bordeaux, CNRS, Centre de Recherche Paul Pascal, UMR 5031, 33600 Pessac, France
[2]Centre for Sustainable Chemical Technologies (CSCT), University of Bath, Claverton Down, Bath BA27AY, UK
[3]ESRF-The European Synchrotron, CS 40220, 38043 Grenoble Cedex 9, France
Email: mengting.suo@crpp.cnrs.fr

Through rational design, a new series of dinuclear complexes $[M_2(\text{tphz})(\text{tpy})_2]^{n+}$ (n = 4, 3 or 2; tphz: tetrapyridophenazine; tpy: terpyridine; M = Co or Ni) (Figure, left) and mononuclear complexes $[\text{Cr}(\text{tphz})(\text{tpy})]^{n+}$ (n = 1, 2 or 3) have been synthesized with the goal to increase and control intramolecular magnetic interactions (Figure, right).[1-3]

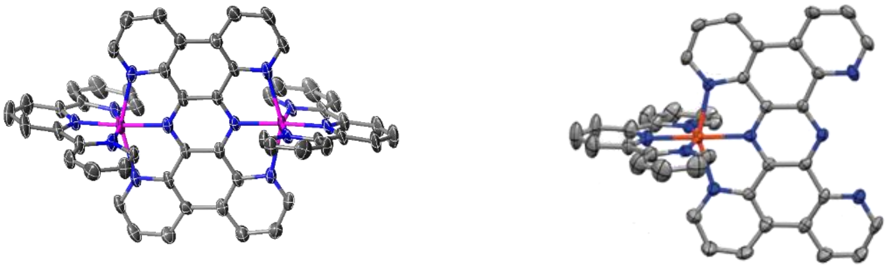


Figure: *Crystal structures of $[\text{Co}_2(\text{tphz})(\text{tpy})_2]^{4+}$ (left) and $[\text{Cr}(\text{tphz})(\text{tpy})]^{3+}$ (right) at 120 K.*

The magnetic properties of these complexes can be tuned reversibly by successive reductions/oxidations of the bridging ligand. In the case of the Co(II) series, the original compound shows a spin-crossover behavior with $T_{1/2} \approx$ 470 K. After a one-electron reduction, the compound behaves as a single-molecule magnet, with a well isolated $S_T = 5/2$ spin ground state. Finally, an overall diamagnetic compound is generated after a further reduction, with a remarkably large intramolecular antiferromagnetic coupling.

For the Ni-based analogues, the once reduced ligand $\text{tphz}^{\bullet-}$ promotes a strong ferromagnetic coupling with Ni(II) ions in contrast to the large antiferromagnetic coupling with Co(II). In its twice reduced form, the bridging ligand affords weak Ni−Ni interactions in marked contrast to the Co(II) analogue as a consequence of the different population of the magnetic orbitals. The comparative study between Ni and Co analogues experimentally evidences the crucial role of the orbital overlaps in the strength and sign of the magnetic exchange.

Additionally, using Cr(III) metal ions instead of Ni(II)/Co(II) ions affords mononuclear complexes. After successive reductions of the pristine $[(\text{tpy})\text{Cr}^{\text{III}}(\text{tphz})]^{3+}$ complex into $[(\text{tpy})\text{Cr}^{\text{III}}(\text{tphz}^{\bullet-})]^{2+}$ and $[(\text{tpy}^{\bullet-})\text{Cr}^{\text{III}}(\text{tphz}^{\bullet-})]^{+}$, the involved magnetic orbitals lead to strong antiferromagnetic interactions between the metal center and the radical spins, affording $S_T = 1$ and $S_T = 1/2$ ground states, respectively.

In conclusion, the redox-active aromatic ligand tphz acts as a very efficient magnetic relay between the metallic spins to these complexes. Meanwhile, tphz also plays the pivotal role of providing magnetic switchability by successive oxidation/reduction.

Acknowledgments:

This work was supported by the University of Bordeaux, the Région Nouvelle Aquitaine, the ANR (HiPerMagnet project; ANR-20-CE07-0022), the Centre National de la Recherche Scientifique (CNRS), and the Chinese Scholarship Council (CSC).

References:

1. X. Ma, E. A. Suturina, S. De, P. Négrier, M. Rouzières, R. Clérac, P. Dechambenoit, *Angew. Chem. Int. Ed*. **57**, 7841 (**2018**).
2. X. Ma, E. A. Suturina, M. Rouzières, M. Patunov, F. Wilhelm, A. Rogalev, R. Clérac, P. Dechambenoit, *J. Am. Chem. Soc.* **141**, 772 (**2019**).
3. X. Ma, E. A. Suturina, M. Rouzières, F. Wilhelm, A. Rogalev, R. Clérac, P. Dechambenoit, *Chem. Commun.* **56**, 4906 (**2020**).

Communication orale ☐ par affiche ■☐

Hetero-poly-metallic architectures: how to achieve multifunctionality

Ingrid Suzana[1], Moritz Malischewski[2], Valérie Marvaud[1]

[1]IPCM-CNRS, UMR 8232, Sorbonne Université, Paris, France,
[2]Fachbereich Chemie, Freie Universität, Berlin, Deutschland.

Design of molecular materials has attracted a great deal of attention in recent years. Owing to their molecular nature, they are associated with soft chemistry routes, light density, optical transparency or tuneable physical properties. More specifically, our interest is focused upon hetero-poly-metallic complexes that have the potential of featuring luminescent, magnetic and photo-switching properties.

Hetero-poly-metallic complexes combining up to four different metallic ions, are obtained according to a smart supramolecular approach that consists in using “complexes as ligands”. In other words, coordination complexes, either mononuclear or polynuclear, are employed as functional precursors for multifunctional assemblies. This method is advantageous as it affords many variations in synthetic parameters, and the properties of the precursors are well established.

Our synthetic strategy essentially relies on oxalate- and cyanide-based coordination chemistry.[1] The key building blocks are original trinuclear complexes that feature high-spin molecule, single-molecule magnet or luminescent properties. And second, paramagnetic oxalates and photo-switching cyano complexes act as structure-directing entities for supramolecular and dendritic assemblies.

To date, we have developed the first multifunctional hetero-tetra-metallic complexes having both magnetic and photo-switching properties. The versatility of the synthetic approach was demonstrated by getting several families of hetero-tetra-metallic complexes, with no less than 18 different compounds.[2] In this presentation, we also report the first instance of metallodendrimers with single-molecule magnet properties, a fascinating tuneable decanuclear architecture.[3]

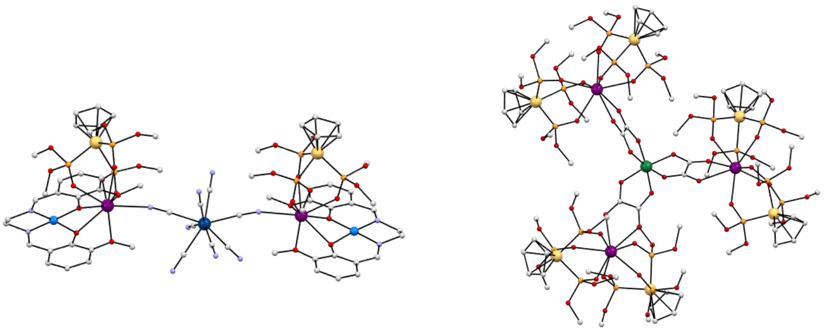


Figure: *X-ray structure of the hetero-tetra-metallic complex MoLnCuCo (left) and the hetero-tri-metallic dendrimer CrLn3Co6 (right) with Ln = Gd, Tb, Dy. Solvent molecules and hydrogen atoms have been omitted.*

Acknowledgments:

References:

1. C. Mathonière, V. Marvaud *et al.*, *Angew. Chem. Int. Ed.*, **2020**, 59, 3117 –3121, M. Malischewski *et al.*, *Angew. Chem.*, **2020**,132, 10605 –10608
2. I. Suzana, J. Forté, J. Von Barbeleden, S. Pillet, V. Marvaud, M. Malischewski, *manuscript in preparation*
3. I. Suzana, S. Rupf, E. Rousset, A. K. F. Rahman, B. Klemke, V. Marvaud, M. Malischewski, *submitted*

Communication orale ■ par affiche ☐

Assessing the magnetic relaxation times in a Ni(II) complex: evidence of quantum coherence in zero magnetic field

I. Tlemsani[1*], F. Lambert[1], N. Bridonneau[1], S. Gambarelli[2], T. Mallah[1]

[1] *Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO, UMR 8182), B420 rue du Doyen Georges Poitou, 91400 Orsay, France*
[2] *Laboratoire de Chimie Inorganique et Biologique (UMR-E3 CEA-UJF), INAC, CEA-Grenoble, 17 Ave. des Martyrs, 38054 Grenoble Cedex 9, France*

* email: idris.tlemsani@universite-paris-saclay.fr

In the past few years, the amount of information processed has been constantly increasing, as has the need to solve new problems, both scientific and societal. 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 in the molecular magnet as qubit research 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 long phase memory time T_2. [4]

In this work, we report Electron Paramagnetic Resonance (EPR) spectroscopy studies (cw and pulsed) on a mononuclear Ni(II) complex possessing a distorted octahedral geometry (Figure 1a).[5] CW studies show an Ising type magnetic anisotropy with zero-field splitting spin Hamiltonian parameters D and E equal to $-2.35\ \mathrm{cm^{-1}}$ and $-0.11\mathrm{cm^{-1}}$ respectively (Figure 1b). This corresponds to the case where the two $M_S = \pm 1$ are ground levels separated by $2E$, which is consistent with a two-levels system where quantum coherence is possible in the absence of an applied dc magnetic field B_0. EPR studies evidence the presence of a clock transition because experiments in solution show no dependence of T_2 upon deuterating the solvent. We show that the spin-lattice relaxation time T_1 can be enhanced when the molecules are embedded in a rigid matrix that has a larger Debye temperature than the solvent.

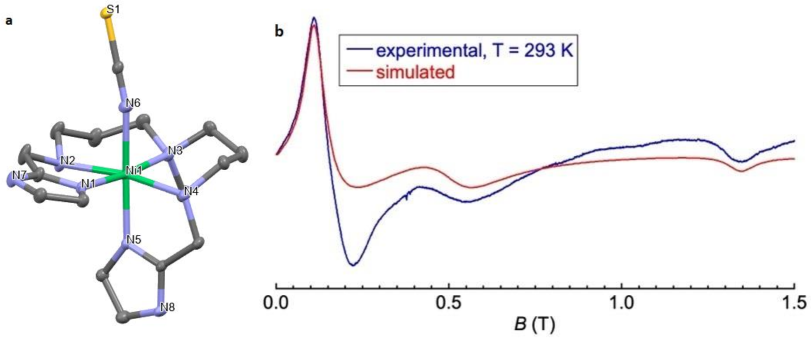


***Figure 1**. View of the molecular structure of [Ni(imdipa)(NCS)]$^+$* (a) *and X-band EPR spectrum at T = 293 K (b).*

References:

1. S. Barz et al., *Nat. Phys.*, **9**, 727-731 (2013)
2. M. N. Leuenberger, et al., *Nature*, **410**, 789-793 (2001)
3. R. Orbach, *Proc. R. Soc. A.*, **264**, 458 (1961)
4. C. A. Collett, et al., *Magnetochemistry*, **5**, 4 (2019)
5. M. Rubín-Osanz et al., *Chem. Sci.*, **12**, 5123–5133 (2021)

Communication orale ☐ par affiche ☑

General Landau theory of non-symmetry-breaking and symmetry-breaking spin transition applied to the analysis of [Fe(PM-PEA)$_2$(NCS)$_2$]

Ricardo G. TORRES[1], Francisco Javier VALVERDE-MUÑOZ[1,2], Elzbieta TRZOP[1,3], Eric COLLET[1,3]

[1]Univ Rennes, CNRS, IPR (Institute de Physique de Rennes), UMR 6251, F-35000 Rennes, France
[2]Instituto de Ciencia Molecular, Departamento de Química Inorgánica, Universidad de Valencia, 46980 Paterna, Valencia, Spain
[3]DYNACOM IRL2015 University of Tokyo - CNRS - UR1, Department of Chemistry, 7-3-1 Hongo, Tokyo 113-0033 - Japan

Phase transitions give rise to different and unique modifications of physical properties in materials. Understanding these changes of state and their origin is of great interest for the further tuning of such properties, through the application of external stimuli, just as temperature, pressure, electric or magnetic fields, and light irradiation.[1,2]

In this sense, the classical Landau theory is a useful tool for the description of different ordering phenomena, taking place during phase transitions, originally through the evolution of symmetry-breaking order parameters, which measure the deviation from the high-symmetry phase.[2] Due to entropy gain, it is the disordered high symmetry phase that is stable at high temperature, in contrast to the ordered low symmetry phase, which is stable at low temperature. In addition, there are many materials, like charge-transfer, spin-crossover, and Mott insulator systems, in which the phase transition is related to an electronic instability without symmetry-breaking. On these cases, the non-symmetry-breaking phase transition should be depicted with the evolution of another order parameter, accounting for the aforementioned electronic instability.[1]

For some materials, like in the case of spin-crossover systems, both, electronic and structural order instabilities may couple. This can result in the widening of hysteresis loops between high- and low- spin phases or in a step-wise evolution of the transition.[3] In order to describe the aforementioned phenomena, the addition of the symmetry-allowed coupling terms to the Landau theory main equation is needed.

In this work, we are interested in the [Fe(PM-PEA)$_2$(NCS)$_2$] system exhibiting a spin transition coupled to a ferroelastic symmetry-breaking. In particular, this system is unusual in the sense that it presents a high symmetry configuration (orthorhombic – Pccn) for the low-temperature low-spin state, while the high-temperature high-spin state is in a low-symmetry phase (monoclinic – $P2_1/c$).[3,4] In this poster, we will show a way to rationalize this unusual behavior within the Landau theory framework, towards the reproduction and understanding of the experimentally observed asymmetric spin-transition hysteresis loop, and coupled changes of spin state and symmetry of the crystal.

References:

1. Azzolina, G., Bertoni, R., Ecolivet, C., Tokoro, H., Ohkoshi, S. I., & Collet, E. (2020). Landau theory for non-symmetry-breaking electronic instability coupled to symmetry-breaking order parameter applied to Prussian blue analog. *Physical Review B*, *102*(13), 1–13. https://doi.org/10.1103/PhysRevB.102.134104
2. Azzolina, G., Bertoni, R., & Collet, E. (2021). General Landau theory of non-symmetry-breaking and symmetry-breaking spin transition materials. *Journal of Applied Physics*, *129*(8). https://doi.org/10.1063/5.0041453
3. Collet, E., & Azzolina, G. (2021). Coupling and decoupling of spin crossover and ferroelastic distortion: Unsymmetric hysteresis loop, phase diagram, and sequence of phases. *Physical Review Materials*, *5*(4), 1–11. https://doi.org/10.1103/PhysRevMaterials.5.044401
4. Guionneau, P., Létard, J. F., Yufit, D. S., Chasseau, D., Bravic, G., Goeta, A. E., Howard, J. A. K., & Kahn, O. (1999). Structural approach of the features of the spin crossover transition in iron (II) compounds. *Journal of Materials Chemistry*, *9*(4), 985–994. https://doi.org/10.1039/a808075e