JAM² session 2021

23-25 novembre 2021

Dourdan

Journées scientifiques de l'Association Française de Magnétisme Moléculaire – JAM² session 2021

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PROGRAMME

Mardi 23 novembre 2021

14h00 – 14h10	Introduction des journées scientifiques
14h10 – 15h10	**[Tutorial 1] E. Collet** (Rennes) *When electronic instability couples to symmetry breaking*
15h10 – 15h30	**[O1] E. Cuza** (Brest) *Isomorphism in spin crossover complexes based on tripodal ligand*
15h30 – 15h50	**[O2] M. Pénicaud** (Bordeaux) *Substrate-driven Spin crossover in Fe(II) heteroscorpionate complex*
15h50 – 16h10	**[O3] I. Soroceanu** (Toulouse) *Dielectric relaxation in SCO materials analyzed using the Havriliak-Negami model*

16h10 - 17h00 PAUSE

17h00 – 17h20	**[O4] G. Balthazar** (Orsay) *Effet de la réduction en taille de particules d'analogue du bleu de Prusse sur leurs propriétés de commutation*
17h20 – 17h40	**[O5] L. Curti** (Paris) *Magnetic anisotropy exaltation by a two-step surface functionalisation of superparamagnetic maghemite nanoparticles*
17h40 – 18h00	**[O6] M. Kermarrec** (Brest) *Matériaux commutables viscoélastiques*
18h00 – 18h20	**[O7] G. Paveliuc** (Genève) *Accurate Prediction of the High-spin/Low-spin Energy Difference in Fe(II) Complexes*
18h20 – 18h40	[**O8] I. Oyarzabal** (Bordeaux-San Sebastian) *Orbital Energy Alignment in Early Transition Metal 2D Coordination Solids*
18h40 – 19h00	*Présentation ECMM 2022*

19h00-20h00 Apéritif

20h00 **Dîner**

Mercredi 25 novembre 2021

9h00 – 10h00 **[tutorial 2] G. Nocton** (Palaiseau) *Lanthanides and actinides organometallics*

10h00 – 10h20 **[O10] D. Lou** (Bordeaux) *Fluoride-based magnetic metal-organic frameworks for CO_2 capture and sequestration*

10h20 - 10h50 PAUSE

10h50 – 11h10 **[O11] R. George** (Orsay) *Prussian Blue self-assembled nanochains for theranostics*

11h10 – 11h30 **[O12] V. Jubault** (Toulouse) *Complexes heptacoordinés chiraux de Mn(II) et Fe(II) comme briques de construction de systèmes hétérométalliques linéaires*

11h30 – 11h50 **[O13] M. Tricoire** (Palaiseau) *New linear sandwich complexes of divalent and trivalent lanthanides*

11h50 – 12h10 **[O14] K. Dhbaidi** (Rennes) *Chiral multifunctional molecules based on helicene-lanthanide complexes*

12h30 - 16h00 **Photo de groupe**
Déjeuner

Session poster

16h00 - 17h00 **[Tutorial 3] M. Orio** (Marseille) *Computational EPR Spectroscopy*

17h00 – 17h20 **[O15] M. Kelai** (Paris) *Thermal Bistability of an Ultrathin Film of Iron(II) Spin-Crossover Molecules Directly Adsorbed on a Metal Surface*

17h20 – 17h40 **[O16] Q. Xu** (Paris) *Pressure-Induced Conversion of a Paramagnetic FeCo square Complexes into a molecular switch with Tuneable Hysteresis*

17h40 - 18h00 PAUSE

18h00 – 18h20 **[O17] S. Yergeshbayeva** (Rennes-Gainesville) *Synthesis of Fe^{II} SCO materials with abrupt hysteretic spin transitions*

18h20 – 18h40 **[O18] L. La Droitte** (Rennes) *Ab initio study of organolanthanide Single Molecule Magnets*
functionalisation of superparamagnetic maghemite nanoparticles

18h40 – 19h00 **[O19] K. Magra** (Orsay) *Electrical switching and fluorescence detection of bistable molecular monolayers*

19h00 – 19h30 **Assemblée générale**

19h30 **Dîner**

Jeudi 25 novembre 2021

9h00 – 10h00	**[Tutorial 4] R. Clérac** (Bordeaux) *New Metal-Organic Magnets*
10h00 – 10h20	**[O20] M. Ndiaye** (Versailles) *Pressure-induced multi-step and self-organized spin states in an electro-elastic model for spin-crossover solids*

10h25 - 11h00 PAUSE

11h00 – 11h25	**[O21] N. el Beyrouti** (Rennes) *Ligand-driven light switching of Single Molecule Magnets*
11h25 – 11h50	**[O22] I. Kibalin** (Saclay) *Quantifying magnetic anisotropy using polarized neutron powder diffraction*
11h25 – 11h50	**[O23] I. Suzana** (Paris) *Hetero-poly-metallic complexes: towards multifunctional molecular materials*
11h50	**clôture**

12h00 - Déjeuner

COMMUNICATIONS ORALES

When electronic instability couples to symmetry breaking

Eric Collet[1]

[1] *Univ. Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, F-35000 Rennes, France*

Systems exhibiting electronic instabilities, such as spin state or charge-transfer, may undergo phase transitions related to change of electronic state, stabilized by structural reorganization at the molecular and lattice levels. For many systems, electronic bistability occurs without symmetry change. The non-symmetry breaking order parameter q monitoring the change of electronic state can couple to volume change and drive cooperative phase transitions.

Materials may also exhibit symmetry-breaking phase transitions, of various types such as Jahn-Teller distortion, ligand ordering, spin-state ordering, lattice distortion... The Landau theory of phase transition is relevant for describing such ordering processes through the evolution of a symmetry-breaking order parameter η.

When both phenomena occur, non-symmetry-breaking change of electronic state and symmetry breaking can couple through the volume strain and may occur simultaneously or sequentially. This gives rise to rich phase diagrams and sequences of phases of different natures: continuous, discontinuous, hysteretic, stepwise (Figure below)…

I will present how to use the Landau approach for a relevant description of symmetry-breaking and non-symmetry-breaking electronic bistability. I will show different examples from the literature and discuss how couplings explain various behaviours [1-3]. The tuning of electronic instability with external parameter, such as magnetic field for spin state, allows to take advantage of the coupling for controlling symmetry-breaking properties like ferroelectricity [4].

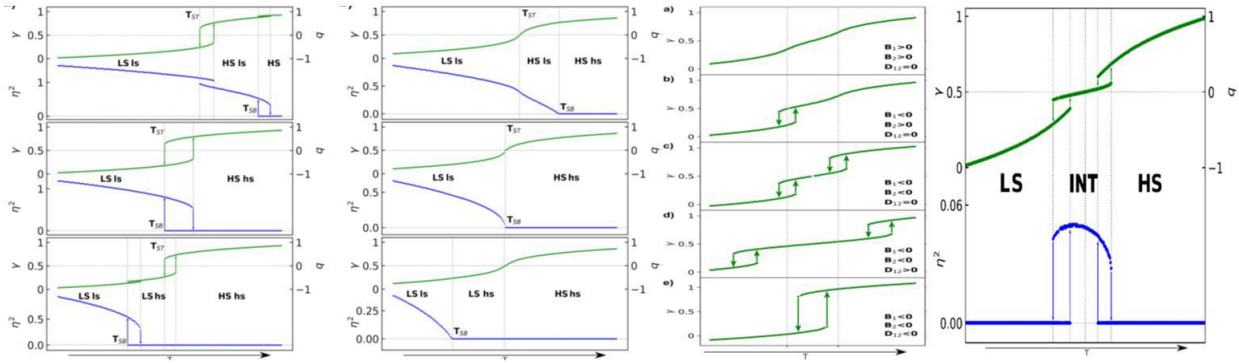


Figure: *phase transition exhibiting evolution of electronic state (green curves) of different natures: continuous, discontinuous, hysteretic, stepwise, coupled or not to symmetry change (blue).*

References:

1. G. Azzolina, R. Bertoni, C. Ecolivet, H. Tokoro, S. Ohkoshi, E.Collet *Landau theory for non-symmetry-breaking electronic instability coupled to symmetry-breaking order parameter applied to Prussian blue analog* **Physical Review B 102**, 134104 (2020)

2. G. Azzolina, R. Bertoni, E. Collet *General Landau theory of non-symmetry-breaking and symmetry-breaking spin transition materials* **Journal of Applied Physics** 129, 085106 (2021)

3. E. Collet, G. Azzolina *Coupling and decoupling of spin crossover and ferroelastic distortion: Unsymmetric hysteresis loop, phase diagram, and sequence of phases* **Phys Rev Materials 5**, 044401 (2021)

4. V.B. Jakobsen, S. Chikara, J.-X. Yu, E. Dobbelaar, C. T. Kelly, X. Ding, F. Weickert, E. Trzop, E. Collet, H.-P. Cheng, G. G. Morgan, V. S. Zapf *Giant Magnetoelectric Coupling and Magnetic Field-Induced Permanent Switching in a Spin Crossover Mn(III) Complex* **Inorganic Chemistry** (2020)

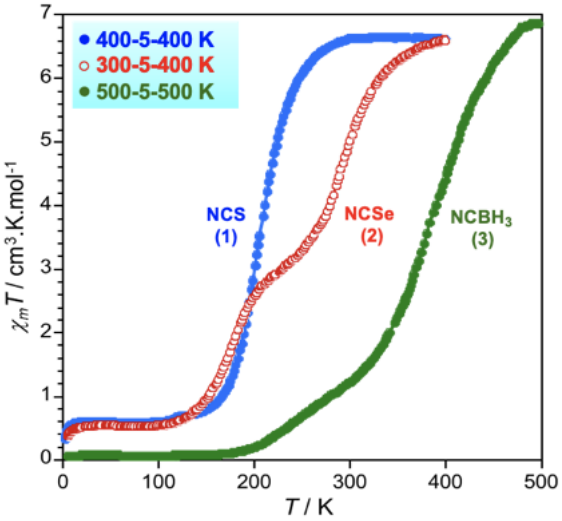
Isomorphism in spin crossover complexes based on tripodal ligand

Cuza Emmelyne[1,2], Conan Françoise[1], Triki Smail[1],
[1]*Université de Bretagne Occidentale UMR-CNRS6521- 6 avenue Le Gorgeu, Brest*
[2]*Ecole Normale Supérieure UMR8004, IMAP, Paris*

In recent years, spin crossover (SCO) complexes are undoubtedly the most studied molecular systems among switchable materials thanks to their several potential applications, in particular for the development of new generations of electronic devices such as memories, molecular sensors and displays.

By far, the major part of the SCO materials, reported up today, are either cationic or neutral, while the number of anionic systems are relatively very scarcely reported, despite their potential interest such as their ability to be associated to cationic functional complexes to design new multifunctional materials. In this context, as part of our ongoing work on new cooperative spin crossover systems, we have reported very recently the first anionic polymorphs complexes $(N(C_2H_5)_4)[Fe(tpCOEt)(NCS)_3]$ based on tris(pyridyl)ethoxymethane ligands (tpCOEt).[1] Both structural and magnetic studies of these compounds revealed the significant impact of the linearity of the N-bound terminal thiocyanato $(NCS)^-$ ligand on the SCO characteristics.[2]

In this contribution we report a magneto-structural relationships of a new series of isomorphic complexes $[Fe(tpCOEt)_2][Fe(tpCOEt)(NCE)_3]_2$, where the ligand field energy can be chemically tuned using the NCE^- (S, Se,BH_3) pseudo-halide anions.[3,4]



Magnetic properties of isomorphic complexes based on tripodal ligand

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1. E. Cuza, C. D. Mekuimemba, N. Cosquer, F. Conan, S. Pillet, G. Chastanet, S. Triki, *Inorg. Chem.*, **2021**, 60, 9, 6536
2. C. D. Mekuimemba, F. Conan, A. J. Mota, M. A. Palacios, E. Colacio, S. Triki. *Inorg. Chem.* **2018**, *57*, 2184-2192.
3. E. Cuza , S.Benmansour, N. Cosquer, F. Conan, S. Pillet , C. J. Gómez-García, S. Triki, *Magnetochemistry*, **2020**, 6(2), 26.
4. E. Cuza, S. Benmansour, N. Cosquer, F. Conan, C. J. Gómez-García, S. Triki, *Magnetochemistry*, **2021**, 7(6), 75.

Substrate-driven spin crossover in Fe(II) heteroscorpionate complex

Margaux PENICAUD[1], Lorenzo SQUILLANTINI[2], Lorenzo POGGINI[2], Juan H. GONZÁLEZ-ESTEFAN[1], Mathieu GONIDEC[1], Matteo MANNINI[2], Patrick ROSA[1], Emilio VELEZ-FORT[3].

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Fe(II) based SCO complexes, showing a diamagnetic and a paramagnetic state, have been proposed to be employed in molecular electronic and in multifunctional spintronic devices. The assembly of SCO molecules on a solid support is the fundamental first step before any device fabrication: for this scope high-vacuum sublimation deposition allows obtaining high quality nanometric films, with a good control of the final thickness[1]. Disadvantages of this approach are that it is limited mostly to neutral SCO complexes, and of those only a few can be heated up to the sublimation temperature without thermal degradation. Moreover, in nanostructured SCO complexes, the interaction with the surface can bring the system in a total or a partial loss of SCO properties, due to a strong interaction with the substrate[2] or due to a partial degradation of the molecular structure[3]. In order to avoid surface effects, using non-metallic, weakly interacting substrates like HOPG might be a winning strategy: indeed, a SCO complex in direct contact with HOPG retaining its switching properties has been reported[4]. We will present the nanostructuration of a "heteroscorpionate"[5] SCO complex, $[Fe(HB(pz)_2(dmpz))_2]$ (pz=pyrazole, dmpz=3,5dimethylpyrazole) that has been sublimated in high vacuum on a HOPG surface and on Gold single crystal (Au(111)).

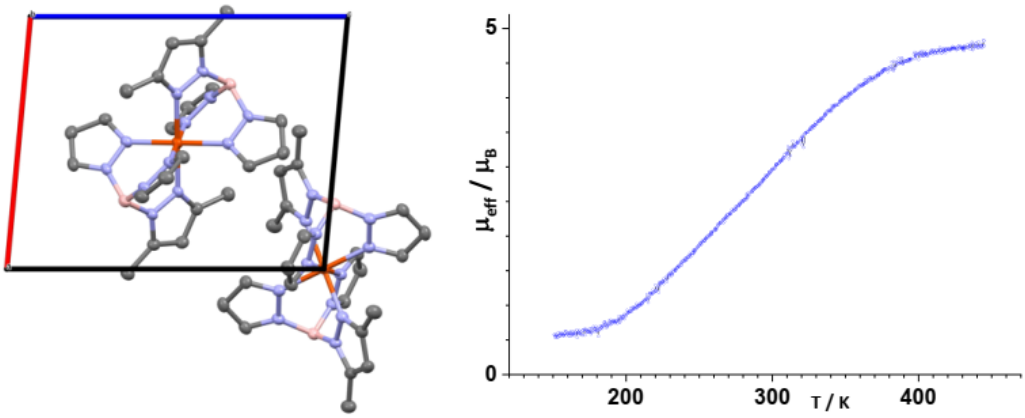

Figure: *Left: crystal structure of [Fe(HB(pz)2(dmpz))2] at 120K observed along* **b** *axis. Right: Magnetic susceptibility measured by Vibrating Sample Magnetometry (VSM) on the microcrystalline powder of the complex.*

Acknowledgments: We fully acknowledge all the ICMCB staff and all the ID32 Beamline staff. Work funded by the Doctoral School of Chemical Science (EDSC, Bordeaux), the French National Research Agency (ANR) Investment for the Future Programme IdEx Bordeaux (ANR-10-IDEX-03-02) and the European Commission MOLSPIN-COST.

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3. T. G. Gopakumar, M. Bernien, H. Naggert, F. Matino, C. F. Hermanns, A. Bannwarth, S. Mühlenberend, A. Krüger, D. Krüger, F. Nickel, W. Walter, R. Berndt, W. Kuch and F. Tuczek, *Chem. - A Eur. J.*, 2013, **19**, 15702–15709.
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5. S. Trofimenko, *Scorpionates The Coordination Chemistry of Polypyrazolylborate Ligands*, 1999

Dielectric relaxation in SCO materials analyzed using the Havriliak-Negami model

Ion Soroceanu[1,2], Simona-Lacramioara Lupu[1], Ionela Rusu[1], Adrian Graur[1], Eugen Coca[1] Mario Piedrahita-Bello[2], Lionel Salmon[2], Gábor Molnár[2], Azzedine Bousseksou[2] and Aurelian Rotaru[1]

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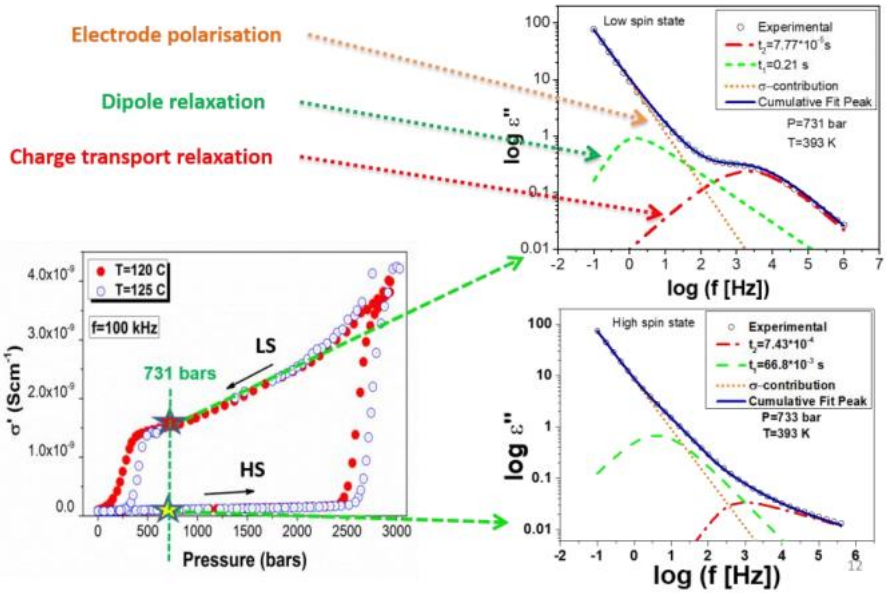
The complex dielectric permittivity of a series of spin crossover complexes, with variable ligand stoichiometry $[Fe(Htrz)_{1+y-x}(trz)_{2-y}(NH_2trz)_x](BF_4)_y \cdot nH_2O$ (x= 0 – 0.3), has been investigated as a function of temperature and pressure in a wide frequency range [1-3]. In each compound, a substantial drop of the conductivity and permittivity is evidenced when going from the low spin to the high spin state, albeit with decreasing amplitude for increasing ligand substitution (i.e. for increasing x). The deconvolution of the dielectric spectra using the Havriliak–Negami equation allowed to extract the dipole and conductivity relaxation times, their distributions as well as the dielectric strengths in both spin states. Remarkably, the permittivity and conductivity changes between the high spin and low spin states are amplified at the corresponding relaxation frequencies.



Fitting the imaginary part of the dielectric permittivity using the Havriliak-Negami model in the low spin and high spin states within the hysteresis region.

Acknowledgments: This work was supported by the European Commission (H2020-MSCA-RISE-2016, No. 734322), the EXCALIBUR project (Contract No. 18 PFE/16.10.2018) and Campus France (Eiffel grant of IS).

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Effet de la réduction en taille de particules d'analogue du bleu de Prusse sur leurs propriétés de commutation

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

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

Les analogues du bleu de Prusse, des polymères de coordination de formule chimique $C_xM_y[M'(CN)_6]_z$ (avec M et M' des métaux de transitions et C cations alcalins contenus dans les sites interstitiels de la structure), peuvent présenter des propriétés de commutation, et donc passer d'un état magnétique à un autre sous l'influence d'un stimulus extérieur. Dans un contexte où la nécessité d'augmenter la densité de stockage de l'information est de plus en plus importante, ces propriétés intrinsèquement moléculaires font d'eux des candidats intéressants pour l'élaboration de nouveaux matériaux commutables.

Les premières études de nanocomposites contenant des particules d'analogue cobalt-fer du bleu de Prusse de 5nm de diamètre ont montré que les nanoparticules de ces composés présentaient effectivement des propriétés de commutation, mais aussi une structure particulière dite cœur-coquille. Les espèces à la surface de la particule diffèrent d'un point de vue chimique et structural des espèces de cœur. Pour les particules habituellement synthétisées (dont la taille est de l'ordre de quelques centaines de nm) les espèces de cœur sont largement majoritaires et dominent les propriétés. Cependant lorsque l'on réduit leur taille, le rapport surface/volume augmente et l'on ne peut plus négliger les espèces de surfaces qui vont certainement jouer un rôle dans le comportement magnétique des particules.

La modification de la composition chimique à la fois du cœur et de la surface des nanoparticules d'analogues du bleu de Prusse cobalt-fer, dans le but d'en déterminer l'influence sur les propriétés de commutation, sera abordée dans le travail présenté.

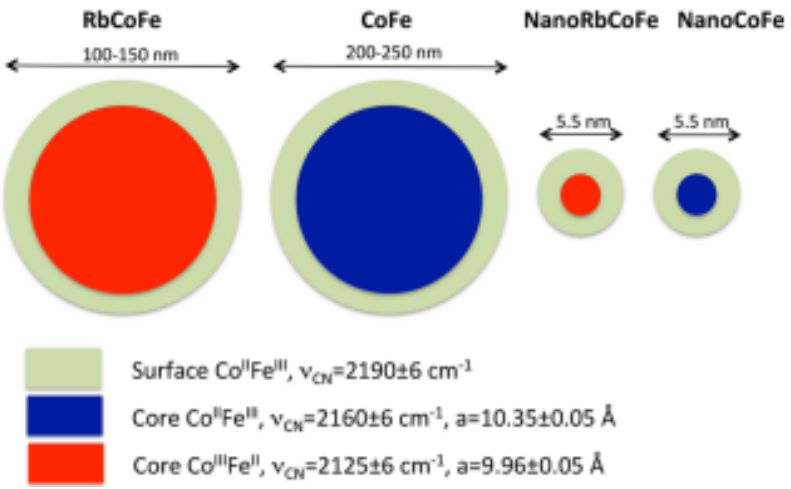

Figure: *Schéma de la structure proposée pour les nanoparticules CoFe* [1]

Références:

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Magnetic anisotropy exaltation by a two-step surface functionalisation of superparamagnetic maghemite nanoparticles

Leonardo CURTI [1], Delphine TALBOT [2], Vincent DUPUIS [2], Edwige OTERO [3], Philippe OHRESSER [3], Christophe CARTIER DIT MOULIN [1], Marie-Anne ARRIO [4], Philippe SAINCTAVIT [3,4], Jérôme FRESNAIS [2], Benoit FLEURY [1] and Laurent LISNARD [1]

[1] *Institut Parisien de Chimie Moléculaire / IPCM, CNRS, Sorbonne Université, 75005, Paris, France.*
[2] *Physicochimie des Electrolytes et Nanosystèmes Interfaciaux / PHENIX, CNRS, Sorbonne Université, 75005, Paris, France.*
[3] *Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, Gif-sur-Yvette, 91192, France.*
[4] *Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie / IMPMC, CNRS, Sorbonne Université, 75005, Paris,France.*

Superparamagnetic iron oxides nanoparticles (SPIONs) have been thoroughly investigated and their properties lead to a plethora of multidomain applications. [1,2] A fine tuning of the magnetic anisotropy (MA), which shapes their properties, appears then essential. To this end, the surface of the nanoparticles represents an attractive playground for coordination chemists considering its strong contribution to the systems MA. [3] Prado et al. [4] demonstrated that the grafting of magnetic complexes to a SPION gives a massive improvement of the magnetic properties, with the only limit being the aggregation of the NPs. To tackle this issue and boost the MA we report here a new approach (Figure): a sequential surface coordination of Co(II) ions and Co(II) complexes to γ-Fe_2O_3 NPs. In this hybrid, an increase in MA is observed if compared to the bare NPs and to the NPs functionalized respectively with Co(II) ions or with Co(II) complexes, proving the efficacy of our approach.

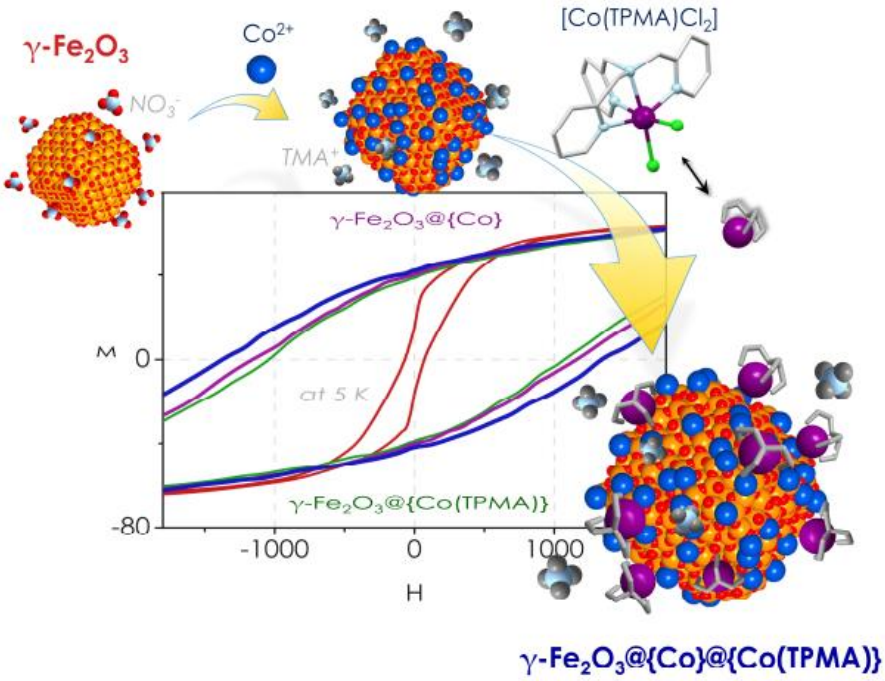

***Figure**: Schematic representation of the two-step surface functionalization of SPIONs and magnetization versus field curves for the different nano systems at 5 K.*

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4. Prado, Y. et al *Nat. Comm*. **2015**, *6*, 10139.

Matériaux commutables viscoélastiques

M. Kermarrec[a], C. Charles[a], T. Aubry[b], J. Ville[b] , C. J. Gómez-García[c], S. Triki[a]

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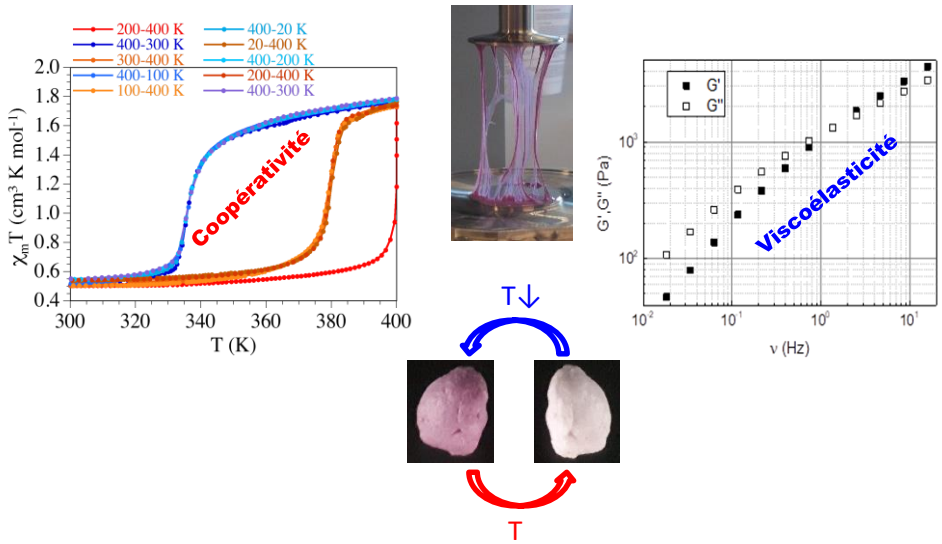
b- Univ. Brest, IRDL,UMR 6027, UBO, 6 Av. V. Le Gorgeu, CS 93837-29 238 BREST Cedex 3.
c- Department of Inorganic Chemistry, University of Valencia, C/José Beltrán, 2, 46980 Paterna (Valencia) Spain

A ce jour, de nombreux matériaux commutables ont été synthétisés et décrit dans la littérature. Un enjeu important de cette famille de matériaux reste la mise en forme pour leurs intégrations dans des dispositifs [1]. Pour ce faire une stratégie explorée dans la littérature consiste à introduire des nanoparticules à transition de spin dans une matrice polymère[2]. Cependant, l'impact des propriétés viscoélastiques et/ou des propriétés physiques (conductivité, luminescence, phénomènes électro- et photo-actifs, …) des polymères organiques sur les propriétés de transition de spin est relativement peu étudié. Ainsi, l'utilisation de nouveaux polymères en présence de polymères de coordination à transition de spin s'est révélée être une stratégie innovante conduisant aux premiers matériaux coopératifs et viscoélastiques.

Lors de cette présentation, nous présenterons des systèmes obtenus à partir de la chaine de coordination $[Fe(Htrz)_2(trz)](BF_4)$ (Htrz = triazole) dispersée dans un polymère organique. L'influence du polymère sur les propriétés magnétiques et l'impact structurant des cristallites sur les propriétés viscoélastiques du système seront discutés.



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Accurate Prediction of the High-spin/Low-spin Energy Difference in Fe(II) Complexes

Gheorghe PAVELIUC, Latévi Lawson Max Daku,

Université de Genève, Sciences II, Quai Ernest Ansermet 30, 1211 Genève, Suisse

Although DFT has proven to provide an efficient framework for the study of SCO systems, a complete characterization of SCO within DFT remains hampered by the inability of available approximate density functionals to accurately predict the HS-LS energy difference ΔE_{HL}. However, from basic thermodynamic considerations, current DFT methods have been shown to give accurate estimates of the variation $\Delta(\Delta E_{HL})$ of ΔE_{HL} in series of complexes of TM ion. Therefore, they can be applied to the accurate determination of ΔE_{HL} in such a series of complexes, provided that its value is accurately known in one case.[1]

The authors report the application of this approach to the determination of the spin-state energetics of a series of homoleptic *tris*-diimine Fe(II) $3d^6$ complexes whose electronic ground states and magnetic behaviors are experimentally well-characterized,[2] using as reference complex $[Fe(NCH)_6]^{2+}$ for which an accurate estimate of ΔE_{HL} based on high-level coupled-cluster calculations is available.[3] Different semilocal and hybrid functionals were used, combined with a large basis set. The CASPT2 method, which also suffers from the TM spin-state energetics issue,[4] was also employed using a minimal (6,10) and the canonical (10,12) active space and two large basis sets. None of the DFT and CASPT2 results obtained for the direct determination of ΔE_{HL} in the studied series of complexes agree with experiments. However the deduced $\Delta(\Delta E_{HL})$ values exhibit a weak dependence on the method used; and in the case of the CASPT2 method, the choice of the ionization potential-electron affinity shift hardly influences the calculated $\Delta(\Delta E_{HL})$ values.For both the DFT and the CASPT2 methods, combining the $\Delta(\Delta E_{HL})$ values with the accurate estimate of ΔE_{HL} in $[Fe(NCH)_6]^{2+}$ gives estimates of ΔE_{HL} in the diimine complexes which are in excellent agreement with experiments. These results contribute to establishing the $\Delta(\Delta E_{HL})$ approach as a powerful tool for the characterization of the spin-state energetics of SCO compounds and for the *in-silico* design of novel complexes.

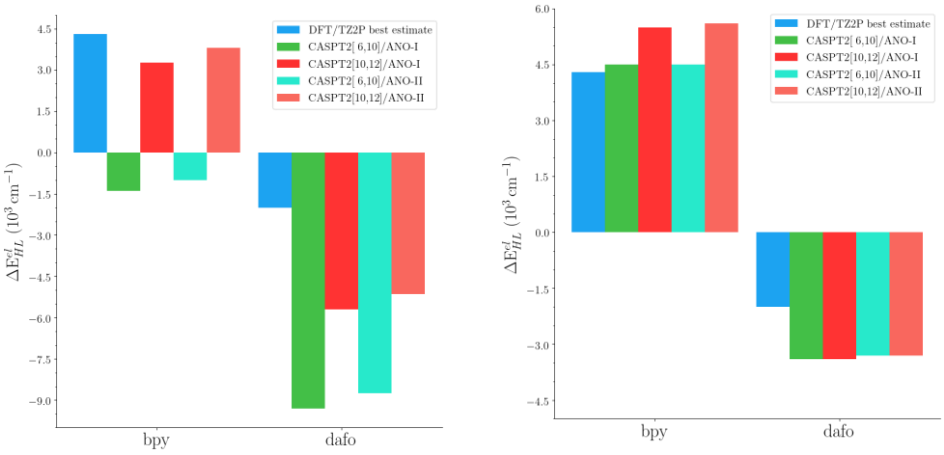

Figure 1: HS-LS energy differences in $[Fe(bpy)_3]^{2+}$ and $[Fe(dafo)_3]^{2+}$ obtained by CASPT2 calculations (Left) and (Right) using the $\Delta(\Delta E_{HL})$ approach

Acknowledgments: The computations were performed at University of Geneva on "Baobab" and "Yggdrasil" HPC cluster(s). The authors thank Thomas Buergi for the financial support given during this project.

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Orbital Energy Alignment in Early Transition Metal 2D Coordination Solids

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Two dimensional (2D) materials, such as graphene[1] and transition metal disulfides[2], have been in the center of immense attention in the last years, due to their extraordinary properties. However, all these materials have certain shortcomings, which hinder their involvement in specific applications and make the design of more advanced, second-generation 2D materials more relevant than ever.

Among the different alternatives, metal-organic networks have gained increasing attention. In such complexes, tuning the orbital conjugation between transition metal ions and bridging organic ligands is key for the engineering of their physical properties and consequently, for the appearance of electrical conductivity and strong magnetic interactions.[3]

In this communication we present the synthesis and characterization of the isostructural 2D coordination solids $TiCl_2(pyz)_2$ and $VCl_2(pyz)_2$ (pyz = pyrazine). Whilst $VCl_2(pyz)_2$ is an electrical insulator, $TiCl_2(pyz)_2$ displays metallic conduction and one of the highest observed electrical conductivity values (~5 S cm^{-1}) for any coordination solid based on octahedrally coordinated metal ions. Nevertheless, $VCl_2(pyz)_2$ displays an unprecedentedly high Néel temperature (~120 K) for a neutral pyrazine-based coordination solid, which is ascribed to a good orbital overlap of the constituents.

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

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Lanthanides and actinides organometallics

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Organometallic complexes of f-elements are an interesting class of organometallic compounds that have been developed in the 1950's and that now concern most of the rare earths in their trivalent and divalent states as well as many of the actinides. The applications for such compounds are numerous for single electron transfer reactivity[1] and small molecules activation as well as because of their optical and magnetic properties, their Single-Molecule-Magnet behavior have impressed with record blocking temperatures.[2] Additionally, very original magnetic behaviors have shed light on their intriguing bonding nature.[3] We will present a short overview of our methodology for the synthesis of organometallic complexes with very original geometry[4] and in which the oxidation state is not trivial to assess because of the development of intermediate valent electronic states.[5] The magnetic data is used as a guide for a better understanding of their bonding and has led to the report of several compounds featuring SMM properties.[6]

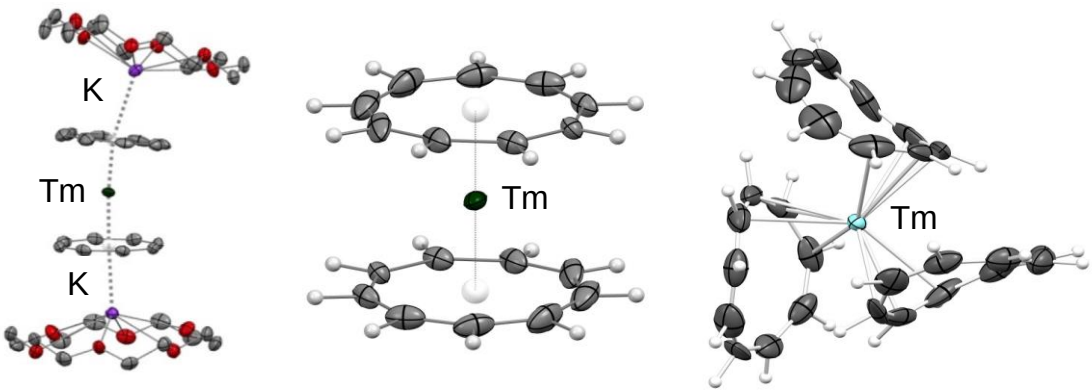

Figure: *Tm organometallic complexes with the Cot (cyclooctatetraenyl) and the Cnt (cyclononatetraenyl) ligand.*

Acknowledgments: Parts of this work have received funding from the ERC under grant agreement No 716314 and from an ANR (French National Research Agency) granted collaborative project (ANR-19-CE07-0019-1).

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

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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 diffraction. 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.

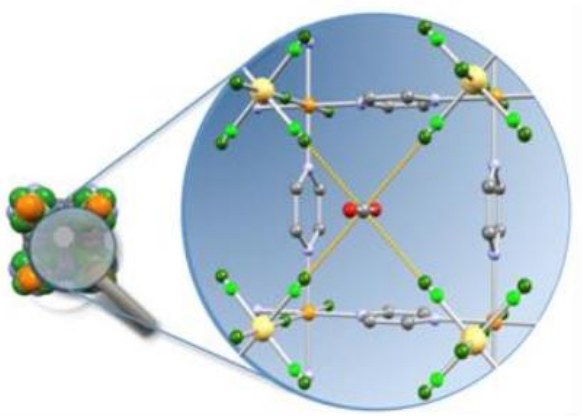

Figure: *View of the porous 3D structure of $[Cu(pyz)_2MF_6]$ compounds with imprisoned CO_2 molecules.*

Acknowledgments:
This work was supported by the University of Bordeaux, the Région Nouvelle Aquitaine, the CNRS and the ESRF.

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Prussian Blue self-assembled nanochains for theranostics

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Cancer is one of the leading causes of death worldwide. Widespread research is being conducted to develop novel and efficient theranostic nanoplatforms. Prussian Blue, the well-known ancient pigment, is an FDA-approved material commonly used for radionucleide decontamination that offers new promising applications in the field of nanomedicine. PB nanoparticles act as photothermal therapeutic (PTT) agents absorbing in the NIR as efficiently as gold-based nanostructures. These microporous ultra-small PB nanoparticles display enhanced T1-weighted MRI contrast and Photoacoustic imaging. [1] A major drawback of using nanoparticles for therapy is that sub-10 nm particles may be prematurely cleared out while larger nanoparticles cannot be renally eliminated and accumulated inside the body, causing side-effects. Our goal has been focused on new activatable self-assemblies of ultrasmall particles that could be retained within the tumor for a longer time compared to the bare 5 nm particles, and may be cleared out.

We report in this communication a surfactant-free green method of creating stable 1D nano-assemblies of ultra-small Prussian Blue nanoparticles around 100 nm in water [2]. These nanoplatforms could be post-coated with different polymers to provide multi-functionality. Anti-cancer drugs like doxorubicin can be loaded onto these assemblies with a high encapsulation efficiency. Moreover, these Prussian Blue nanochains show both temperature and pH –triggered release, that can be used as a the tumor-targeted treatment. This combination of photo-and chemotherapy in these new self-assembled nanochains may be extrapolated to other drugs and therapies. They reveal enhanced MRI contrast as compared to the ultrasmall particles and open interesting perspectives for multimodal theranostics.

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Complexes heptacoordinés chiraux de Mn(II) et Fe(II) comme briques de construction de systèmes hétérométalliques linéaires

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La coordination de ligands pentadentes aux ions d^6, d^7 et d^8 permet l'obtention de complexes de géométrie bipyramide pentagonale caractérisés par de fortes anisotropies magnétiques[1,2]. La robustesse structurale de ces composés permet de les utiliser comme briques de construction d'assemblages moléculaires pouvant présenter des propriétés SMM ou SCM[3–5]. Dans le cadre de mes travaux de thèse, nous avons cherché à implémenter de la chiralité au sein de ces complexes afin de réaliser des nano-aimants chiraux. Pour de telles systèmes chiraux, une synergie entre l'anisotropie magnétique et les propriétés optiques est susceptible de permet l'émergence de propriétés particulières[6,7]. Dans cette présentation, nous illustrerons notre démarche et discuterons quelques édifices 1-D chiraux obtenus (Fig. 1). Les propriétés optiques et magnétiques des composés seront présentées.

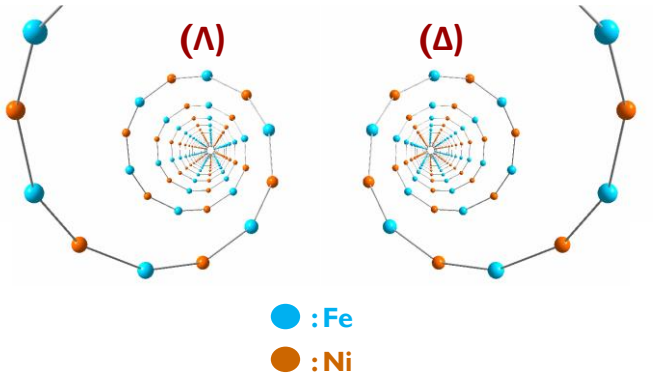

Figure: *Vue de la chiralité moléculaire à l'échelle macroscopique dans les chaînes* $[Fe(L^{R,R})][Ni(CN)_4]$ *et* $[Fe(L^{S,S})][Ni(CN)_4]$

Acknowledgments: Ces travaux ont été réalisés dans le cadre du projet ANR AnisoChirMag soutenu par l'Agence Nationale de Recherche ANR-17-CE07-007.

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New linear sandwich complexes of divalent and trivalent lanthanides

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Many different applications of rare-earth-based compounds originate from their unique physical properties: strong spin-orbit coupling, large magnetization and chore 4f-orbitals.[1] To enhance these properties for specific applications, the synthesis and characterization of new organometallic compounds of divalent and trivalent lanthanides is the key to obtain a larger scope of properties aside to the well-known cyclopentadienyl-based ligands.[2] In the case of f-element based Single Molecule Magnet, Rinehart and Long rationalized the influence of the ligand field tuning on the magnetic anisotropy of such compounds.[3] Following their concept, the record blocking temperature of 80 K was achieved with a close to linear sandwich complexes of Dysprosium.[4] Considering that large aromatic rings, such as cyclooctatetraenyl (Cot) and cyclononatetraenyl (Cnt) ligands were recently presented as interesting tools to prepare linear complexes of lanthanides,[5] this presentation will focus on the synthesis and magnetic characterization of new divalent [$K_2(Cot)_2Tm$] complexes, as well as the (Cot)Ln(Cnt) series (Ln = Tb, Dy, Ho, Er, Tm, Lu), which presents an interesting distortion of the Cnt ligand along with the size of the lanthanide ion.[6]

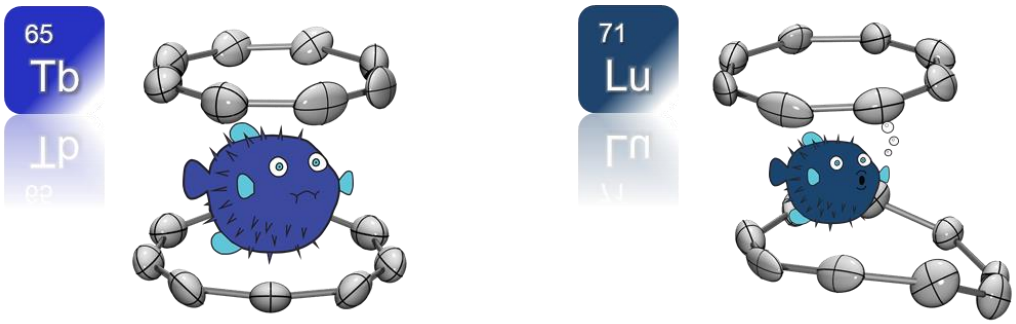

Figure: *Schemed representation of the size-induced hapticity switch in the (Cot)Ln(Cnt) series*

Acknowledgments:
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Chiral multifunctional molecules based on helicene-lanthanide complexes

Kais Dhbaibi[1], Matteo Atzori,[2] Haiet Douib[1], Boris Le Guennic,[1] Cyrille Train,[2] Jeanne Crassous[1], Fabrice Pointillart[1]

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Preparing molecular magnets with additional features such as conductivity, photo-reactivity, and optical properties is an exciting goal for scientists and a key challenge in modern materials science.[1-3] Combining magnetism and chirality in molecules also furnishes a beautiful demonstration of how powerful is the association of physics and chemistry fields to build-up new multifunctional molecules giving rise to new phenomena like the Magneto-Chiral Dichroism (MChD).[4] 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.[5] We reasoned that the combination of chiral organic ligand with a given f element may lead to an attractive and unusual example of SMM molecules merging chiroptical, luminescence, and magnetic properties.[6] Helicenes are polycyclic aromatic compounds with nonplanar screw-shaped skeletons formed by ortho-fused benzene or other aromatic rings, and can be regarded as valuable inherently chiral building blocks for reaching intense chiroptical properties.[7] In this context, a new family of enantiopure helicene-based ligands was prepared and their complexation with various lanthanide ions was performed. Chiral ytterbium complex (Figure 1) allows for the first time the investigation of MChD through NIR light absorption, along with an intense Circularly Polarized Luminescence (CPL) activity in the NIR region.[8]

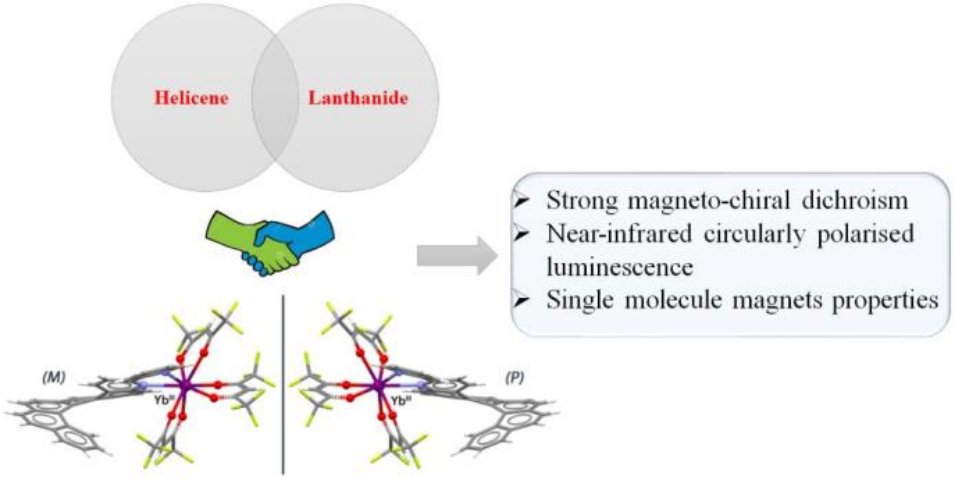

Fig. 1: *Co-existence of SMM, MChD, and CPL properties in enantiopure ytterbium complex based helicene ligand.*

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Computational EPR Spectroscopy

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This tutorial is dedicated to the application of quantum chemical tools based on Density Functional Theory (DFT) combined with the use of Electron Paramagnetic Resonance (EPR) spectroscopy for the characterization of molecular compounds related to bioinorganic chemistry. By combining theory and experiment, we usually aim at determining the structural and the dynamic features of the entities in order to find out the optimal conditions to set up the best model systems for reactivity and catalysis purposes. In addition, such mixed approach allows to establish specific relationships connecting the structures, the properties and the reactivities of the species, which can ultimately serve as a basis for predicting geometries, probing structures (in enzymes) and developing new systems (in catalysis or biochemistry). In this presentation, we will present some practical examples coupling theoretical methods with experimental ones like those involving continuous-wave and pulse EPR techniques to (i) identify unknown species, (ii) rationalize their molecular properties and (iii) determine magneto-structural correlations.

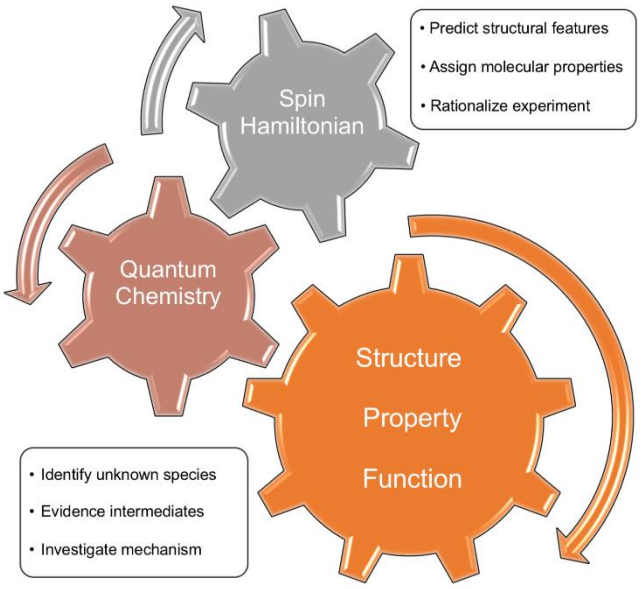

Figure: *Combing quantum chemistry and EPR spectroscopy.*

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Thermal Bistability of an Ultrathin Film of Iron(II) Spin-Crossover Molecules Directly Adsorbed on a Metal Surface

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Spin-crossover molecules are very attractive compounds to realize multifunctional spintronic devices. Understanding their properties when deposited on metals is therefore crucial for their future rational implementation as ultrathin films in such devices. Using X-ray absorption spectroscopy, we study the thermal transition of the spin-crossover compound $Fe^{II}((3,5\text{-}(CH_3)_2Pz)_3BH)_2$ from submonolayer to multilayers on a Cu(111) substrate. We determine how the residual fraction of high spin molecules at low temperature, as well as the bistability range and the temperature of switching, depends on the layer thickness. The most spectacular effect is the clear opening of a 35 ± 9 K thermal hysteresis loop for a 3.0 ± 0.7 monolayers thick film. To better understand the role played by the substrate and the dimensionality on the thermal bistability, we have performed Monte Carlo Arrhenius simulations in the framework of a mechanoelastic model that include a molecule–substrate interaction. This model reproduces well the main features observed experimentally and can predict how the spin-crossover transition is modified by the thickness and the substrate interaction.

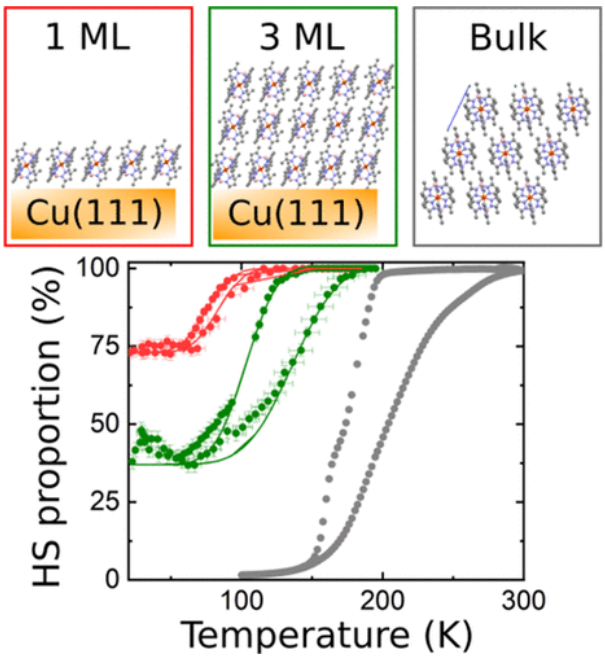

Figure: *Thermal hysteresis (HS as a function of temperature) for 1 ML (red), 3 ML (green) of $Fe^{II}((3,5\text{-}(CH_3)_2Pz)_3BH)_2$ on Cu(111) extracted from XAS. In grey, the bulk behavior measured by magnetic susceptibility.*

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Pressure-Induced Conversion of a Paramagnetic FeCo square Complexes into a molecular switch with Tuneable Hysteresis

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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 compounds: $\{[Fe^{III}(Tp)(CN)_3]_2[Co^{II}(vbik)_2]_2\}(A)_2 \cdot 2MeOH$, where Tp = tris(pyrazolyl)borate, vbik = bis(1-vinylimidazol-2-yl)ketone and A = BF_4, PF_6 and SbF_6) We have shown that these paramagnetic compounds which can be converted into molecular switches upon pressure application. The high pressure XRD results showed slight differences in both square core structure and the intermolecular interaction of three compounds, which surprisingly have led to very different thermal ETCST properties. We have tried to rationalize the structure-property relationship of those compounds and the main results will be presented here.

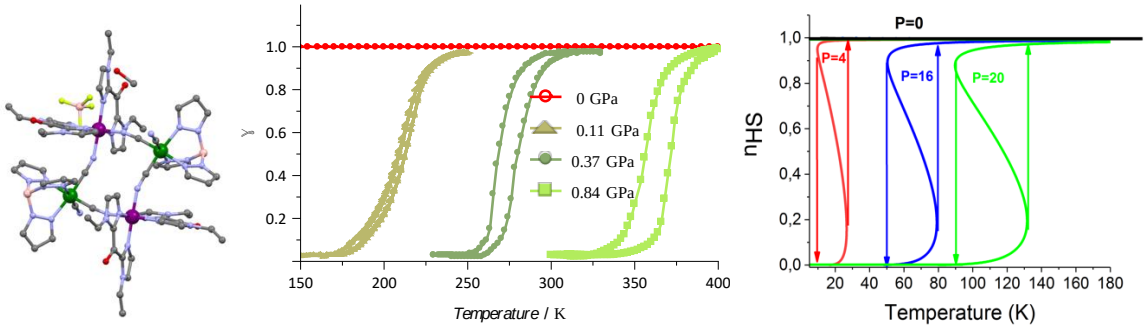

Fig. 1: *The structure at 0.85 GPa (left), thermal variation of paramagnetic $\{Fe^{III}_2Co^{II}_2\}$ molar fraction γ_{HS} for 1 under different hydrostatic pressures (middle) and numerical simulation of thermal hysteresis (right).*

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Synthesis of Fe^{II} SCO materials with abrupt hysteretic spin transitions

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One of the central challenges in the spin crossover (SCO) research is to initiate strongly cooperative interactions known to lead to abrupt spin transitions and thermal hysteresis. One of the strategies to enhance the cooperativity is to design SCO complexes with supramolecular networks such as π-π stacking or hydrogen bonding interactions.

In this work, we report syntheses and characterization of heteroleptic Fe^{II} complexes that display abrupt hysteretic spin transitions. We discuss how the magnetic behavior correlates with changes in the crystal packing and interactions between the π-stacked aromatic substituents in the complexes $[Fe(tpma)(L)](ClO_4)_2$ (tpma = tris(pyridin-2-ylmethyl)amine) with novel π-extended biimidazole-type ligands (L) bearing 2,3-dimethyl-naphthalene-, 6,7-dimethyl-2,3-diphenyl-quinoxaline, and 2,3-dimethyl-anthracene pendant fragments. The complex $[Fe(tpma)(xnap\text{-}bim)](ClO_4)_2$ exhibits an abrupt thermal spin transition at $T_{1/2}$ = 127 K with a narrow 1 K hysteresis loop, as well as a light-induced excited spin-state trapping at lower temperatures. This complex also shows a strong influence of solvation on the SCO behavior. The analogous complexes with the other two ligands show gradual SCO.

Ab initio study of organolanthanide Single Molecule Magnets

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Lanthanide based Single Molecule Magnets (Ln based SMMs) are widely studied because of their potential impact in applications such as high-density information storage, quantum computing or spintronics.[1-4] In order to get performing SMMs, namely compounds with a slow magnetic relaxation and the highest blocking temperature possible, the strategy was to seek to maximize the magnetic anisotropy. Currently, the SMM with the highest blocking temperature is a metallocene-type organometallic compound based on Dy^{III}, and exhibits magnetic hysteresis up to 80K,[5] which represent a goal to exceed.

In this work, organolanthanide complexes with large ligands, such as cyclooctatetraenyl (Cot) and cyclononatetraenyl (Cnt) (8 and 9 carbons cycles), was studied to understand the influence of the ligand geometry on the magnetic properties of the complexes. Recent computational results on sandwich-type complexes and derived will be presented.[6-7]

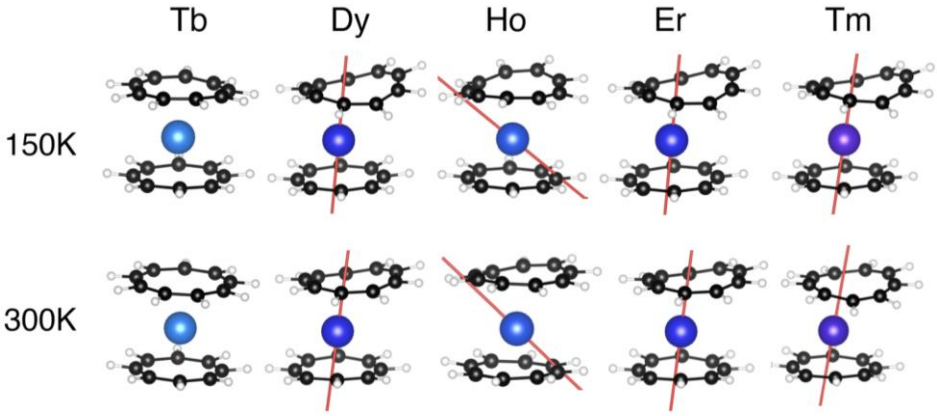

Figure: *Computed structures of Ln(Cot)(Cnt) at 150 and 300 K and ground-state anisotropy axis (not represented for Tb due to planar anisotropy).*

Acknowledgments: The author acknowledges the support of the French Agence Nationale de la Recherche (ANR).

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Electrical switching and fluorescence detection of bistable molecular monolayers

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Some coordination complexes with magnetic properties - spin crossover - have switchable and bistable character which is very attractive for some applications in the field of molecular electronics.[1] The switching between two electronic spin states required stimuli such as temperature, pressure, light or electrical pulse.[2] These systems, a priori miniaturizable down to the individual molecule scale and easily functionalized, can be integrated into molecular-based electronic devices provided that it is possible to control their properties (magnetism, switching, bistability). In this context, our objective is to develop electrically switchable bistable molecular monolayers on conductive ITO (Indium Tin Oxide) surfaces and optically detectable by fluorescence.

Our approach is based on surface functionalization by cobalt complexes bearing luminescent ligand (BODIPY)[3], which could electrochemically switch from paramagnetic form, possibly spin crossover (Co(II)) to diamagnetic form (Co(III)). These functionalized molecules are synthesized, then anchored via covalent binding on conducting subtract ITO by a sequence of reactions.[4] X-Ray photoelectron spectrometry confirmed the formation of Co(II) complexes monolayers. Cyclic voltammetry studies were conducted in solution and after immobilization of complexes on ITO surface to compare their properties. Finally, electro-fluorescence measurements on functionalized surface were performed. These experiments will be presented and discussed.

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New Metal-Organic Magnets

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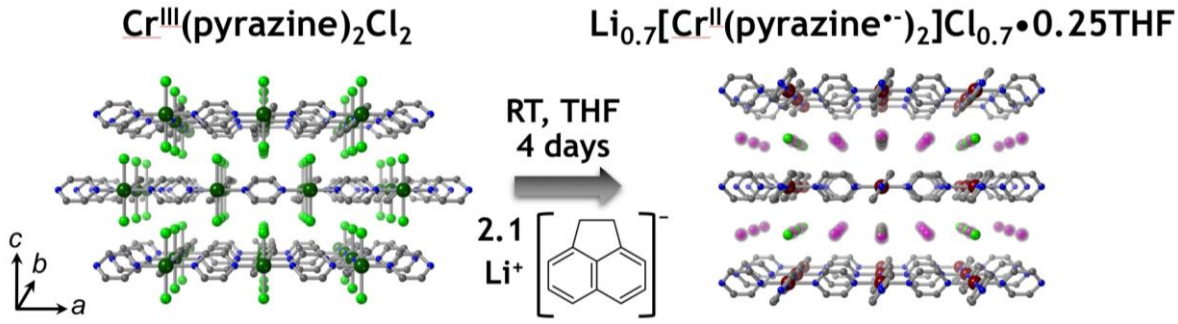
Magnets derived from inorganic materials (e.g., oxides, rare earth and intermetallic compounds) are key components of modern technological applications. Despite extensive success in a broad range of applications, these inorganic magnets suffer several drawbacks, such as energetically expensive fabrication, limited availability of certain constituent elements, high density, and poor scope for chemical tunability. A promising design strategy for next-generation magnets relies on the versatile coordination chemistry of abundant metal ions and inexpensive organic ligands.

Ordered magnets are the result of cooperative effects between magnetic spins. The choice of the linker between the spin carriers is therefore a crucial element to control, as it mediates the communication and interactions between them. The use of a redox-active bridging ligand as a linker is a particularly attractive strategy. By oxidation(s) or reduction(s), it can act as a control switch of the magnetic interactions. While in its diamagnetic state, it mediates usually weak magnetic interactions, in its radical form, it can promote a better spin delocalization inducing large magnetic interactions and in the same time, a good electronic conductivity which could lead to new high T_C conductive magnets. In this presentation, the rational design of new magnetic systems based on redox-active ligands will be discussed and illustrated by (i) paramagnetic dinuclear M(II) complexes, $[M_2(tphz)(tpy)_2](PF_6)_4$ (M = Co or Ni; tpy = terpyridine; tphz = tetrapyridophenazine) [1-3], (ii) a two-dimensional coordination network, $Cr(pyrazine)_2Cl_2$, which is a ferrimagnet and a semiconductor (left part of the figure below) [4,5] and (iii) lightweight molecule-based magnets (right part of the figure below), which feature critical temperatures up to 515 K, and unprecedented 7500-Oersted room-temperature coercivity [6].



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Pressure-induced multi-step and self-organized spin states in an electro-elastic model for spin-crossover solids

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The spin transition materials are known to exhibit a rich variety of behaviours under several stimuli, among which the pressure leads to major changes in their electronic and elastic properties. From the experimental point of view, thermal spin transitions under isotropic pressure showed transformations from (i) hysteretic to continuous transformations where the the hysteresis width vanishes beyond some threshold pressure value; that is the conventional case. In several other cases very pathological and unexpected behaviours emerged, like (ii) persistent hysteresis under pressure; (iii) non uniform behavior of the thermal hysteresis width which first increases with pressure and then decreases and vanishes at higher pressures; (iv) also double step transitions induced by pressure are also often obtained, where the pressure triggers the appearance of a plateau during the thermal transition, leading to two-step transitions, and finally (v) other non-conventional re-entrant transitions, where the thermal hysteresis vanishes at some pressure and then reappears at higher pressure values are also observed. In the present theoretical study, we investigate this problem with an electro-elastic description of the spin-crossover phenomenon by solving the Hamiltonian by Monte Carlo technique. The pressure effect is here introduced directly in the lattice parameters and the elastic constants. By considering pressure-dependence compressibility's, we demonstrate that a large panel of experimental observations can be qualitatively described with this model.

PACS numbers:

Keywords: Spin-Crossover transition, First-order transitions, Pressure effect, Monte-Carlo simulations, self-organization, phase diagrams, elastic interactions, spin models.

Ligand-driven light switching of Single Molecule Magnets

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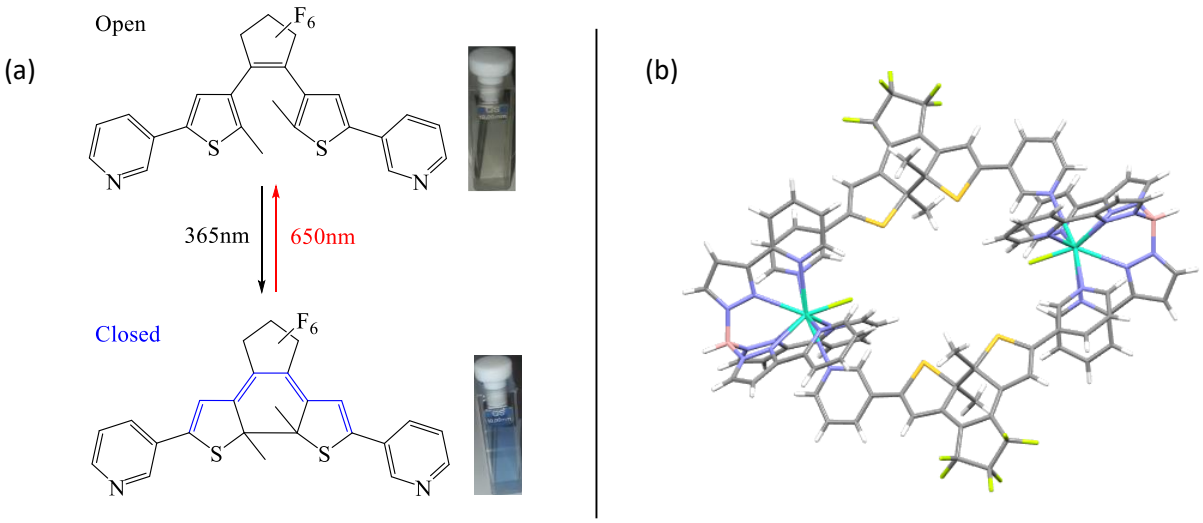
Single Molecule Magnet (SMM) offers unique features that may allow information to be stored with much higher densities, and to be processed at unprecedented speeds. [1] In order to use SMM in information storage devices, it would be a great advantage to control the magnetic properties by applying an external stimuli. Light is fascinating in this purpose due to its easy and contactless application. [2]
The goal of our project is to create an efficient strategy to switch reversibly the molecular magnetic behavior with light, relying on the photochromic abilities of a ligand, and on the recognized influence of the coordination environment on the SMM property.



(a) *Photochromic transformation of a DTE molecule* ***(b)*** *Cationic cage assembled with DTE and Dy-F units*

We aim to control the slow relaxation behavior of dysprosium (III) complexes through the photoisomerization of a dithienylethene (DTE) ligand that is known to show good photo-reversibility and excellent thermal stability for both open and closed forms. [3] In this presentation, I will introduce a supramolecular strategy to photo-switch reversibly the SMM behavior. Our design uses of $[Dy(T_p^{py})F(pyridine)_2]BArF$ (Tppy = tris(3-(2-pyridyl)pyrazolyl)hydroborate) as a building unit because it shows a strong axial magnetic anisotropy generated by a short Dy–(η^1-F) bond. The exchange of the equatorial pyridine ligands in this compound with a ditopic photoactive bispyridyl DTE ligand yields different structures that I will discuss during the presentation. [4]

Acknowledgments: We would like to thank ANR for funding this project.

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Quantifying magnetic anisotropy using polarized neutron powder diffraction

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Magnetic anisotropy is an essential property of primary importance in areas ranging from molecular magnetism and magneto-optics to magnetoelectric transport. It is an inherent characteristic of magnetic materials that describes the response of the magnetization to a magnetic field. Several techniques are currently used to extract information about the bulk magnetic anisotropy; the most well-known are single crystal and torque magnetometry, EPR. However, all these techniques provide information about the bulk anisotropy of material [1].

A powerful alternative method for characterizing magnetic anisotropy is single-crystal polarized neutron diffraction (PND). In this approach, measured flipping ratios are used to fit the atomic magnetic susceptibility tensors for each of the magnetic atoms in the asymmetric unit, which allows one to quantify the magnetic anisotropy at the local level [2]. It is becoming a reference in mapping the magnetic anisotropy at the atomic scale in molecular magnets. However, PND cannot be applied to many highly interesting topics due to the difficulties encountered in growing sufficiently large single crystals. Thus, the step forward is extending this approach to powder samples.

The absence of appropriate data analysis software was one of the main limiting factors in characterizing magnetic anisotropy in powders. For Rietveld analysis of 1D and 2D polarized diffraction profiles, the new software has been developed at LLB (https://github.com/ikibalin/cryspy). It provides an easy way to quantify the local magnetic anisotropy of magnetic materials and opens polarized neutron diffraction to a large community who are not familiar with this technique.

We applied the software to analyze a range of polarized neutron powder diffraction measurements performed at the LLB. The quasiplanar (XY) local anisotropy of Dy ions has been revealed for the first time in the hyperkagomé dysprosium garnet $Dy_3Ga_5O_{12}$ (Fig.1a) [4]. Using a sample of a single-molecule magnet with Co(II) complex, it was shown that the crystallites orient under a high external magnetic field (Fig.1b) [5]. Surprisingly, we found that this preferred field-induced orientation improves the precision of determining the local susceptibility parameters. This shows that polarized neutron powder diffraction opens new opportunities in the studies of local magnetic anisotropy in powders, which is currently inaccessible to other experimental techniques.

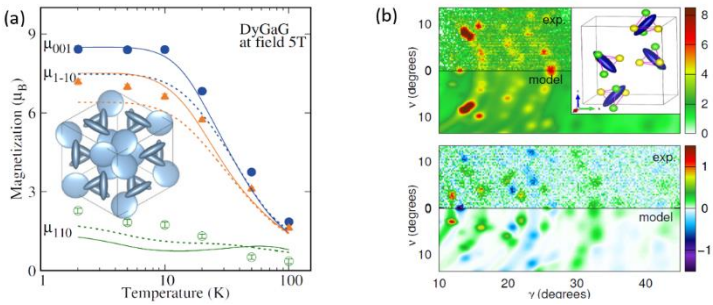

Figure: *(a) Magnetization components versus temperature for DyGaG. (b) Measured and calculated flipping sum (top) and difference (bottom) diffraction patterns collected on* $Co([(CH_3)_2N]_2CS)_2Cl_2$ *at 2K, 5T.*

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Hetero-poly-metallic complexes: towards multifunctional molecular materials

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[2]*School of Molecular Science, University of Western Australia, Perth, Australia*
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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.

To obtain hetero-poly-metallic complexes combining up to four different metallic ions, we adopt a 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 molecular architectures. This method is first advantageous since it affords many variations in synthetic parameters, and second, the properties of the precursors are well established.

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

Employing dinuclear complexes and octacyanometallates as precursors, we have developed hetero-tri-metallic decanuclear squares and hetero-tetra-metallic assemblies that constitute a new class of single-molecule magnets. [1,2] Here, we report the synthesis of several families of hetero-poly-metallic assemblies illustrated below. The magnetic as well as the photophysical properties are also investigated.

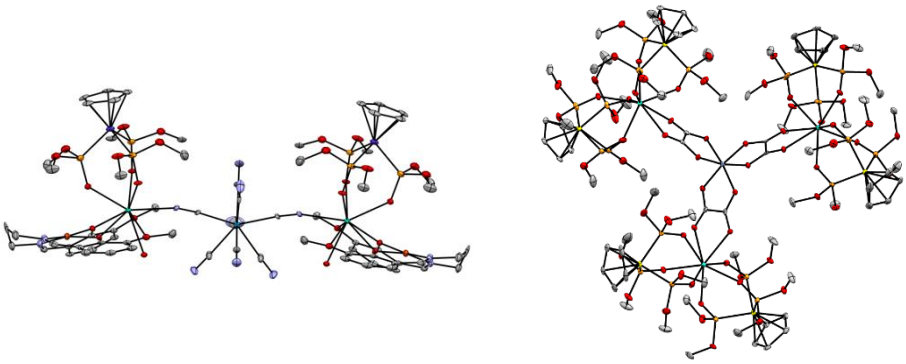

Figure: *X-ray structure of the hetero-tetra-metallic complex $Mo(LnCuCo)_2$ (left) and the hetero-tri-metallic dendrimer $CrLn_3Co_6$ (right) with Ln = Gd, Tb, Dy. Solvent molecules and hydrogen atoms have been omitted.*

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POSTERS

Tuning the electronic properties of two-dimensional coordination networks via 3d-metal substitution

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Molecular spintronics represent an emerging field of research that bridges the quantum spin of an electron with the physical properties of molecules.[1] A quintessential aspect to the design of these molecule-based materials is the ability to control the interactions between the spin-active sites in a predictable manner. This becomes critically important towards the development of molecule-based magnets exhibiting magnetic orders at ambient temperatures. Given the endless possibilities of molecular building-blocks, hybrid blends of metal ions and organic ligands offer untapped potential to tune and explore novel functionalities in future technologies that may otherwise be inconceivable to their inorganic counterparts. Our team recently laid new grounds in this field through the coordination of redox-active $CrCl_2$ with pyrazine (pyz) bridging ligands affording $Cr(pyz)_2Cl_2$, a 2D coordination network with remarkable physical properties. Below 55 K, $Cr(pyz)_2Cl_2$ displays a ferrimagnetic ordered state, and at room temperature, the material exhibits electrical conductivity up to 32 mS cm^{-1}.[2] 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 and simultaneously promotes strong magnetic exchanges between the spin carriers. In the pursue of enhancing these properties through chemical tunability, we herein present the synthesis and characterization of the isostructural vanadium and titanium analogues: $V(pyz)_2Cl_2$ and $Ti(pyz)_2Cl_2$. This presentation will communicate the contrasting nature of the metal ions within these networks and the resulting impact on the magnetic and conductive properties.

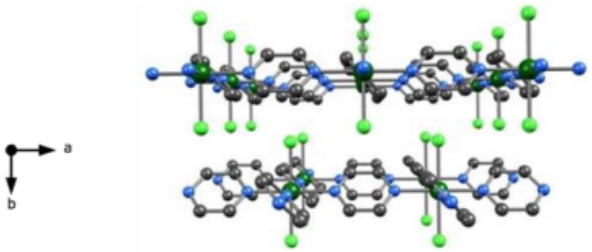

Figure: *Perspective view of the 2D structure of M(pyrazine)$_2$Cl$_2$ (where, M = V and Ti).*

Acknowledgments: This work has been supported by the University of Bordeaux, the Région Nouvelle Aquitaine, the CNRS and the ESRF.

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Magneto-Chiral Dichroism properties of Chiral Prussian Blue Analogues

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Prussian Blue Analogues are among the molecular compounds with the highest magnetic ordering temperatures. The introduction of chirality, by adding a chiral co-ligand during their synthesis, intend to favor the appearance of physical properties linked to chirality, such as Magneto-Chiral Dichroism (MChD). MChD is a differential absorption or emission of unpolarized light that depends on the relative orientation of the magnetization with respect to the direction of light propagation and on the absolute configuration of the system[1]. It is a non-reciprocal manifestation of light-matter interaction. Recently, the absorption and MChD properties of $[Mn^{II}(X\text{-pnH})(H_2O)][Cr^{III}(CN)_6]\cdot H_2O$ (X-pn = (*S* or *R*)-1,2-propanediamine) were thoroughly investigated[2]. MChD signals of opposite signs resulting in perfect mirror images are obtained for opposite enantiomers[2]. According to the attribution of the electronic transitions, the most intense MChD signal were associated to the Mn^{II}, the less intense well-defined low energy signals to the MMCT bands, whereas the very weak contribution is associated to Cr^{III}. MChD properties are currently studied in the $[M_1^{II}(X\text{-pnH})(H_2O)][M_2^{III}(CN)_6]\cdot H_2O$ analogues of $[Mn^{II}(X\text{-pnH})(H_2O)][Cr^{III}(CN)_6]\cdot H_2O$ to investigate the influence of the metal centers onto the MChD properties. By substituting Cr^{III} by Mn^{III}, the role of a higher magnetic anisotropy can be clarified. Powder and single crystal synthesis procedures, physicochemical characterizations (IR and XRD), magnetic and MChD properties measurements of the $[Mn^{II}(X\text{-pnH})(H_2O)][Mn^{III}(CN)_6]\cdot H_2O$ will be presented (Fig. 1).

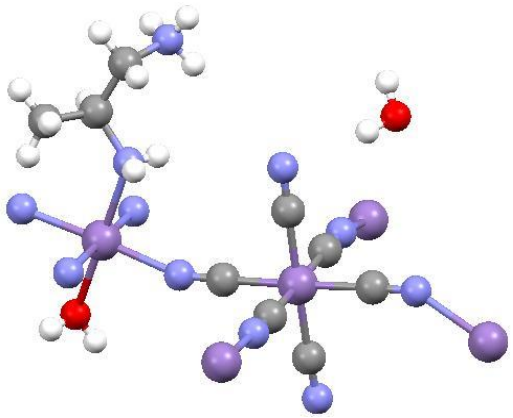

Figure 1: View of the structural moiety. Color codes: violet, Mn; blue, N; red, O; gray, C; white, H.

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Synthesis of cyclononatetraenyl containing complexes as potential new SMM

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Aromatic ligands have been key players in the development of the coordination chemistry of lanthanide ions. Their steric profiles as well as their tunability have allowed for the synthesis of a wide variety of complexes with novel properties and notably, several well -performing single molecule magnets (SMM).[1,2] If five and eight membered ring molecules have been extensively studied, larger aromatic ligand such as the cyclononatetraenyl (Cnt) ion remain underdeveloped. It has recently been shown to be a good ligand to access the neutral sandwich compounds, whether in the divalent state with the lanthanidocene series[3] or even the trivalent state when paired with the more classical cyclooctatetraenyl (cot) ligand.[4] Moreover, the latter series demonstrate its ability to modulate its hapticity in order to properly fit the metallic ions.[5] This can be used as a useful tool in the control of the symmetry, a factor of great importance for the synthesis of SMM.[6] Consequently, the Cnt ligand is used to expand the coordination chemistry of lanthanide complexes with potential magnetic properties. We will show a series of examples of the flexibility of the Cnt ligand in both structural and redox aspects.

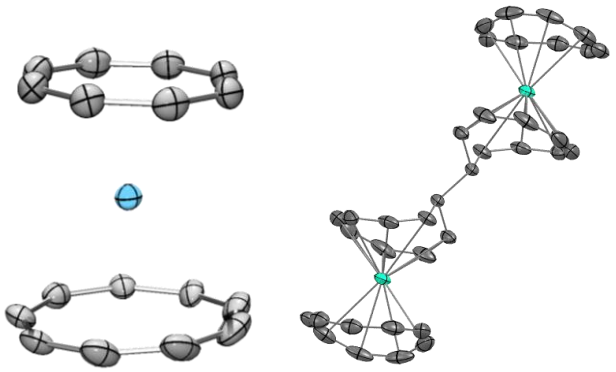

Figure: *X-ray structure of LaCotCnt (left) and Dy_2Cnt_4 (right), carbon atoms are showed in grey, lanthanum in pale blue and dysprosium in green, hydrogens are removed for clarity.*

Acknowledgments: Parts of this work have received funding from an ANR (French National Research Agency) granted collaborative project (ANR-19-CE07-0019-1)

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Investigating the Role of Vibronic Coupling in Magneto-Chiral Dichroism

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Magneto-Chiral Dichroism (MChD), is the differential absorption of unpolarised light by a chiral medium in the presence of a magnetic field aligned parallel or antiparallel to the propagating wavevector of light.[1,2] The interest in this phenomenon is driven by its possible technological application in optical readout of magnetic data and explanation of the origin of homochirality on earth.[3, 4] Although now it has been reported and studied in different molecular systems, the understanding of the microscopic factors which influence the phenomenon is necessary in order to optimize the MChD signals and attain the aforementioned goals. It has been recently shown that spin-orbit coupling and vibronic coupling plays a decisive role in the intensity of MChD signals.[5, 6] In the study presented, the Magneto-Chiral behaviour of a Ni(II) based complex exhibiting helical chirality introduced by the enantiopure 1,2-cyclohexanediamine ligand is compared with the previously reported ethylenediamine analogue.[6] This allows to outline the influence of a more rigid ligand in the first coordination sphere of the complex and how this changes the contribution of vibronic coupling and thus influences the overall MChD signal.

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Magneto-Chiral studies on single crystals.

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Magneto-Chiral Dichroism (MChD) is a magneto-optical effect in which the absorption coefficient of a chiral molecule in an unpolarised light beam changes depending on the orientation of an externally applied magnetic field, parallel or antiparallel, to the direction of light propagation.[1] Theoretically predicted in 1982,[2] this phenomenon has been observed for the first time in 1997.[3] Since then, there have been only a few demonstrations of this effect, mainly in the crystalline state. The proximity to the chiral center and the magnetization of the material appear to contribute to the intensity of the MChD response,[1] but until now, no theoretical calculations have been performed to evaluate the contributions in a quantitative manner.

In the present project, two well-characterized paramagnetic chiral materials, tris(ethylenediamine)nickel(II) nitrate and tris(ethylenediamine)cobalt(II) nitrate, have been selected for study as model compounds (***Fig.1 A***).[4] Enantiopure crystals were obtained by spontaneous resolution during crystallization. These crystals demonstrate very high MChD signals (***Fig. 1 B***), with *g* values up to 10^{-1}. Quantum chemical calculations have been developed to well simulate the spectra, underlining the important contribution of vibronic coupling to the MChD intensity.

Current work in our labs is focused on the development of new families of magneto-chiral crystals to further probe the role of vibronic coupling, as well as spin-orbit coupling and magnetic anisotropy.

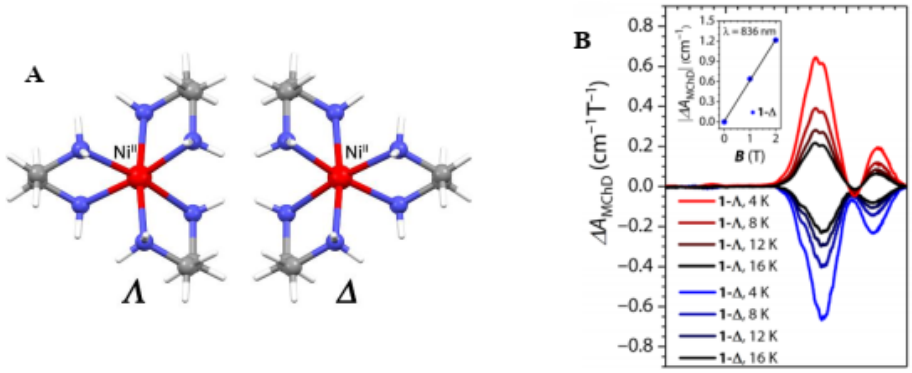

Figure 1. *(**A**) Molecular structure of the investigated systems. View of the molecular structure of Λ-$[M^{II}(dae)_3]^{2+}$ (left) and Δ-$[M^{II}(dae)_3]^{2+}$ (right) (M^{II} = Ni, Co) complex cations. Color codes: red, M^{II}; blue, N; gray, C; white, H. Nitrate anions are omitted for clarity (**B**) Orthoaxial Δ_4MChD spectra for Λ and Δ single crystals for several temperatures. The inset shows the MChD strength as a function of the magnetic field strength; the straight line is a fit.*

Acknowledgments: Thanks to ANR MaChiNaCo and to LAPHIA.

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Lanthanide complexes based on cyclononatetraenyl ligand: synthesis, structure and properties

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Coordination chemistry of lanthanides with aromatic ligands have been largely developed since the first complexes were reported in 1954 with cyclopentadienyl ligand. [1] However, the coordination chemistry of larger aromatic ring (cyclononatetraenyl, *cnt*) still remains undeveloped. Thus, the only very few reports were done during last few years [2, 3]. Having this in mind, we chose the *cnt* ligand for the synthesis of series of Ln-complexes in order to investigate its coordination behavior and magnetic properties of complexes.
The ligand was obtained *via* three-step synthesis, according to the procedure, reported earlier. [4] The series of Ln-based *tris*-complexes $Ln(cnt)_3$, (Ln = Y, Gd-Tm, see Figure) complexes were obtained by the reaction of LnI_3 with Kcnt in toluene and fully characterized. Magnetic measurements are finalizing this work.

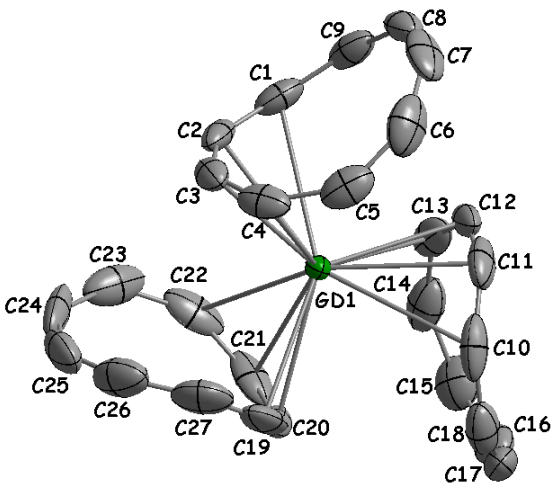

Figure: *Crystalline structure of $Gd(cnt)_3$*

Acknowledgments: ANR RelaxMax project, Thomas Simler, Maxime Tricoire and Nicolas Casaretto are gratefully acknowledged for the help at the beginning of my work.

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Mapping the charge and spin densities in a mixed valence diruthenium(II,III) paddle-wheel complex

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Mixed valence diruthenium(II,III) tetracarboxylate complexes, $[Ru_2(O_2CR)_4X_2]^-$ (X=Cl^-, Br^-,...), with paddle-wheel type structure (Figure 1) are well known for their unique magnetic properties. Indeed, they have a large zero-field splitting ($D \approx 60$ cm^{-1}) and exhibit a resultant high spin state S = 3/2. This is because the three unpaired electrons are spread in the accidentally degenerated π^* and δ^* orbitals[1]. Interestingly, the assemblies of such dimers with hexacyanometalate ions $[M(CN)_6]^{3-}$afford molecule based magnets [2]. This poster presents the mapping of electron density in diruthenium compound $(NBu_4)[Ru_2(O_2CC_3H_7)_4Br_2]$ from high resolution X-ray diffraction (100K) [3] together with spin density mapping from Polarized Neutron Diffraction [4]. This work should contribute to elucidate the occurrence of spin-delocalization of the unpaired electrons in these ruthenium(II,III) dimers from the ruthenium ions to surrounding ligands which until now has been characterized uniquely by MO calculations and 13C NMR spectroscopy[5].

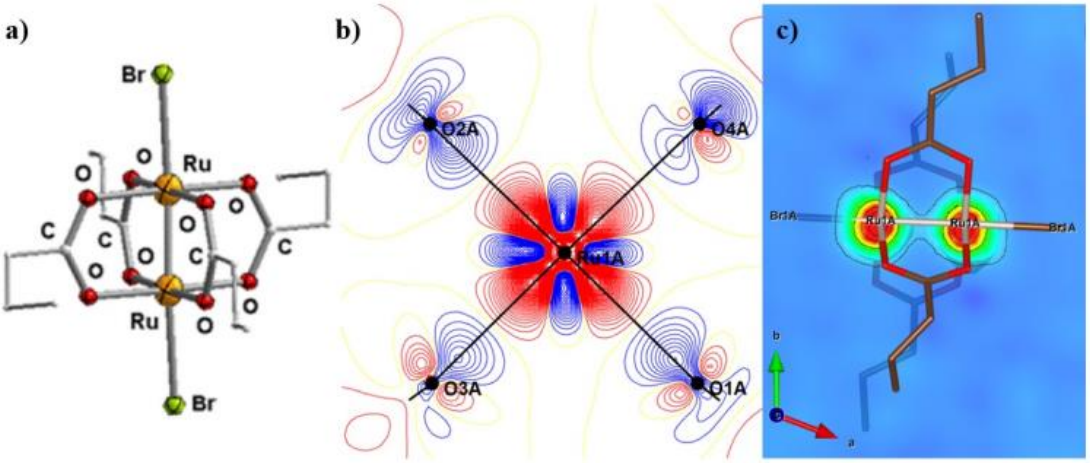

Figure 1: **a)** *Structure of the tetracarboxylate complex.* **b)** *Contour plots of the static deformation electron density in the plane RuO_4. Level line contour interval is 0.05e/Å ^{3} with the positive contour draws as blue solid lines, and the negative ones are red.* **c)** *Contour plots of the static deformation spin density in the (001) plan. Level line contour interval is 0.1μ_B/Å ^{3}. Hydrogen atoms are omitted for clarity.*

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Morphological studies of spin crossover@SiO_2 nanoparticles

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Spin crossover (SCO) iron(II) 1,2,4-triazole-based coordination compounds in the form of SCO@SiO_2 nanoparticles were prepared using a reverse microemulsion technique [1-5]. The thickness of the silica shell and the morphology of the as obtained core@shell nanoparticles were studied modifying ω, the polar phase/surfactant ratio but also, the quantity and the insertion phase (organic, aqueous and micellar phases) of the tetraethylorthosilicate (TEOS) precursor, the quantity of ammonia and the reaction temperature. The morphology of the nanoparticles was monitored by transition electron microscopy (TEM/HRTEM) while their composition probed by combined elemental analyses, thermogravimetry and EDX analyses. The evolution of the spin crossover properties associated with the change in morphology was investigated by variable temperature optical and magnetic measurements.

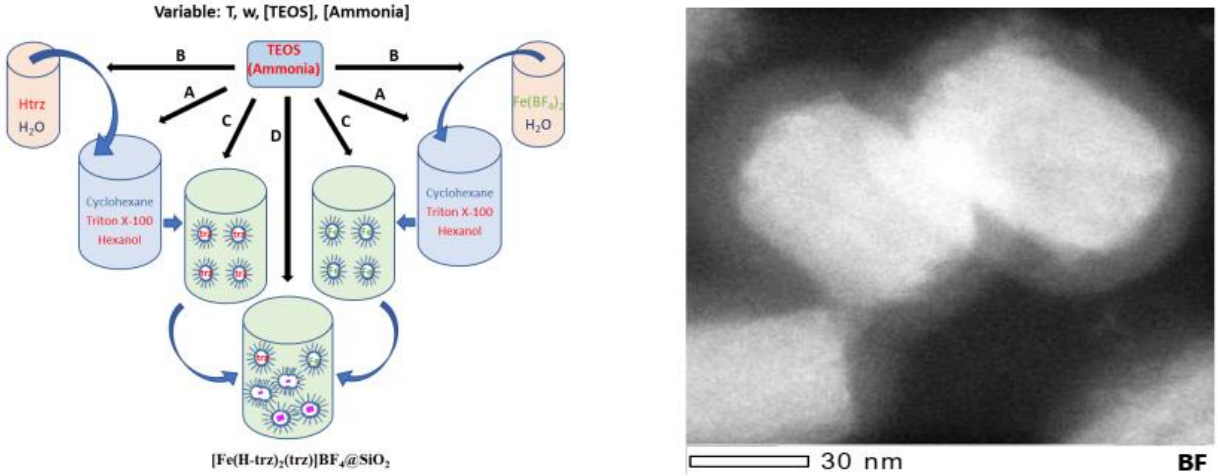

Figure: *Schematic representation of the different synthetic routes and HRTEM image for SCO@SiO_2 core-shell nanoparticles*

Acknowledgments: This work received financial support from the China Scholarship Council (PhD grant of YZ) and from the Agence Nationale de la Recherche (ANR-19-CE09-0008-01).

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Antisymmetric exchange in a real copper triangle

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The antisymmetric exchange, also known as the Dzyaloshinskii-Moriya interaction (DMI), is an effective term in the spin Hamiltonian that emerges in transition metal complexes and ionic solids with adequate symmetric properties. While many theoretical studies have been devoted to the study of symmetric terms in the model Hamiltonian [1], only a few ones concern the DMI. Understanding the origin of DMI requires a couple of explanations because of the subtle interplay between fine electronic interactions and the spin-orbit coupling. In this presentation, we will discuss from theory standpoint the DMI in an synthetized tricopper(II) complex [2], capitalizing on previous methodological studies performed on model complexes [3,4]. We will show that the correct application of the permutation relationship is necessary to explain the outcomes of the *ab initio* calculations, prior to justifying the use of a smaller structural model with only two active copper(II) sites. Finally, we will advocate for further theory/experiment efforts, given the difficulty of determining the DMI from both theoretical calculations and experimental measurements.

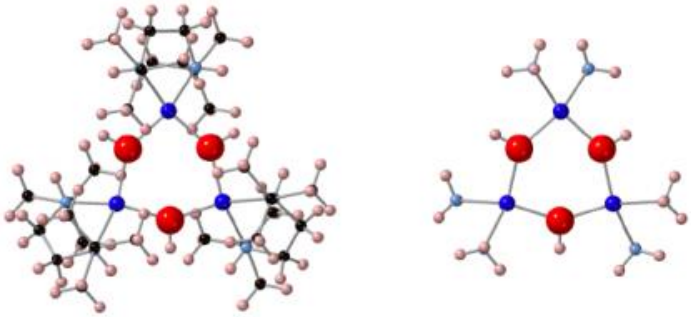

Figure: Ball and stick representations of the two parent structural models with three active copper(II) sites. Color code: dark blue stands for Cu, red for O, light blue for N and light pink for H.

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Shedding light on a new functional spin-crossover molecule: Towards fluorescent spin-crossover sensors

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A big effort has been made during the last years in order to reduce the size of switchable objects to their ultimate dimension and to study their properties on surfaces in order to design devices for classical and quantum information processes.[1–3] However, it is needed to read their information once deposited on surfaces. In order to do so, state-of-the-art fluorescent spin crossover (SCO) molecules are a key road as building blocks for magneto-opto-electronic devices as it is possible to detect the reversible switching between the diamagnetic low spin (LS, S=0) and the paramagnetic high spin (HS, S=2) states induced by various stimuli (temperature, light, pressure or electric and magnetic fields) via the change in the fluorescence emission.[4–6] Here are reported the synthesis and the properties of a new asymmetric Fe(II) complex $[Fe((Naphthalimide\text{-}L_3)_2](BF_4)_2$. S (S = solvent), incorporating an original C-scorpionate chelating ligand L_3 and a fluorescent function Naphthalimide.[4] The molecular material was characterized by single-crystal X-ray diffraction, magnetic and spectroscopic measurements. The 6-coordinated Fe(II) complex, that crystallizes in a solvated form, exhibits a thermal spin crossover centered around 200 K. The Naphthalimide-L_3 ligand shows a fluorescence spectrum in the 340-460nm region that is red-shifted in solid state with respect to the solution. A temperature-dependent fluorescent emission study was carried out with the powder of $[Fe(Naphthalimide\text{-}L_3)_2](BF_4)_2$ encapsulated in a cyanide glue. This experiment shows a strong modulation of the position and the intensity of the emission bands with the temperature which could be a signature of a coupled process between the spin crossover and the fluorescence emission of the complex, if interferences with other structural rearrangements can be ruled out.

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Photoswitchable nitronyl-nitroxide (NIT) radical ligands for complexation with lanthanide cations

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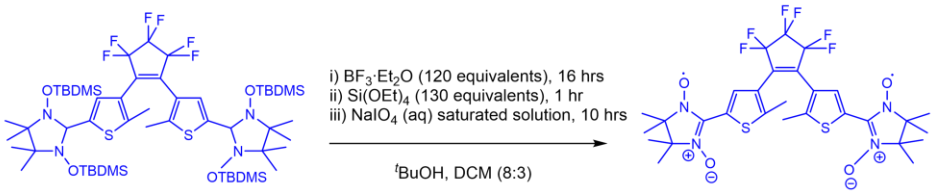
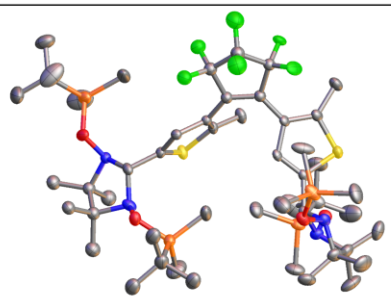
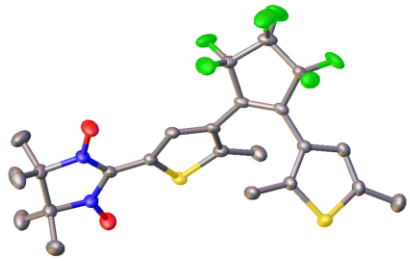
Nitronyl-nitroxide (NIT) radical ligands form complexes with lanthanide cations that exhibit favourable magnetic behaviour [1]. It is possible to photoswitch the spin-exchange interaction between NIT radicals in biradical NIT ligands where the alkyl group spacer is a dithienylethene (DTE) [2]. Our hypothesis is that photoswitching of these biradical ligands bound to lanthanide cations will lead to similar but more spectacular photomagnetic effects as the recently reported photomodulation of magnetic hysteresis with a pyridyl terminated DTE [3].



i) Conversion of the protected DTE biradical precursor into the nitronyl-nitroxide biradical ligand



ii) Crystal structure of the protected biradical precursor



iii) Crystal structure of the monoradical DTE ligand

Here we present the demanding synthesis, EPR and UV-Vis spectroscopy of a symmetrical biradical DTE designed to maximise the intramolecular spin-exchange interaction [4]. Derivatization of the bis-aldehyde precursor failed due to poor solubility, so the molecule was assembled stepwise from protected thiophene bis-hydroxyamines. The synthesis was beset with obstacles including formation of a bis-oxime by-product and steric inhibition of the reaction with perfluorocyclopentene to form the DTE caused by the -OTBDMS protecting groups. Asymmetrical biradical precursors and monoradical DTEs can be prepared in higher yields (iii). Tetrabutylammonium fluoride (TBAF) appeared to cause decomposition of the electron poor hydroxyamine DTEs before they could be oxidized to biradicals. This was resolved by using $BF_3{\cdot}OEt_2$ to remove the protecting group [5] to successfully synthesise the biradical DTE (i and ii).

Acknowledgments:
We would like to thank Région Bretagne and ANR for funding this project.

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Switchable dielectrics: from molecules to functional composites

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Switchable dielectric molecular materials (SDMMs) have gained a growing interest over the last 10 years because of their controllable structure and functional diversity, as well as their technological relevance in electrical or electronic industries. These molecular-based smart materials are envisioned as active components in intelligent devices such as switches, sensors, actuators, and capacitors switchable dielectrics due to their temperature dependent properties, such as ferroelectricity or dielectric transitions.[1] Since September 2018, G2Elab aims at developing a new research activity on the design, synthesis and physico-chemical characterizations of SDMMs. We present here our re-investigation of the textbook case dabcoHBF$_4$ (1,4-diazabicyclo[2.2.2]octane fluoroborate) and its corresponding composites with PVDF (PolyVinyliDene) and PVA (PolyVinylAlcool) polymer matrices.

In SDMMs, the key for obtaining switchable dielectric features lays in the local motional changes (ordered/disordered states) of the cationic and/or anionic components: the dielectric transition between low- and high-dielectric states is directly linked to the motional changes in the polar components between the static and dynamic phases occurring during the phase transition (PT). Among SDMMSs published to date, the textbook case dabcoHBF$_4$ undergoes such a solid-to-solid phase transition at Tc = 107°C (Figure 1). Accurate analysis of polycrystalline samples of dabcoHBF$_4$ prepared as pellet evidenced the role of pressure molding, applied electric field frequency and temperature scanning speed over the thermal hysteresis loop.[3]

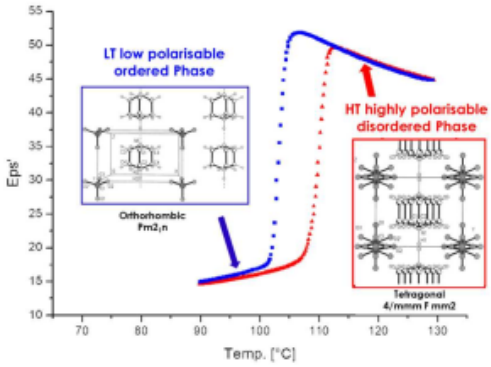

Figure: *Dielectric permittivity (real part) measured in the heated (red) and cooled (blue) modes for dabcoHBF$_4$, together with its low k (ordered) and high k (disordered) phases*

We selected PVDF and PVA as suitable host to incorporate dabcoHBF$_4$ because of their intrinsic polarity favoring uniform dispersion and according to their excellent film-forming ability. We prepared a series of dabcoHBF$_4$@PVDF and dabcoHBF$_4$@PVA composites depending on the loading content whose effect on the structure, crystallinity, thermal stability, and dielectric behavior has been investigated. Flexible composite films with up to 50% of molecular filler exhibits switchable dielectric property, comparable to that of powder-pressed pellet of pure dabcoHBF$_4$, with moderate fatigability. The use of these soft functional materials as dielectric elastomer generator for energy harvesting is currently undertaken in our lab.

Acknowledgments: A. Brzovic thanks the Fédération des Micro&NanoTechnologies (https://fmnt.fr) for M1 financial support

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Voltage-Induced Bistability of Single Spin-Crossover Molecules in a Two-Dimensional Monolayer

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Bistable spin-crossover molecules are particularly interesting for the development of innovative electronic and spintronic devices as they present two spin states that can be controlled by external stimuli. Here, we report the voltage-induced switching of the high spin/low spin electronic states of spin crossover molecules self-assembled in dense 2D networks on Au(111) and Cu(111) by scanning tunneling microscopy at low temperature.
On Au(111), voltage pulses lead to the non-local switching of the molecules from any - high or low - spin state to the other followed by a spontaneous relaxation towards their initial state within minutes.
On the contrary, on Cu(111), single molecules can be addressed at will. They retain their new electronic configuration after a voltage pulse. The memory effect demonstrated on Cu(111) is due to an interplay between long range intermolecular interaction and molecule/substrate coupling as confirmed by mechanoelastic simulations [1].

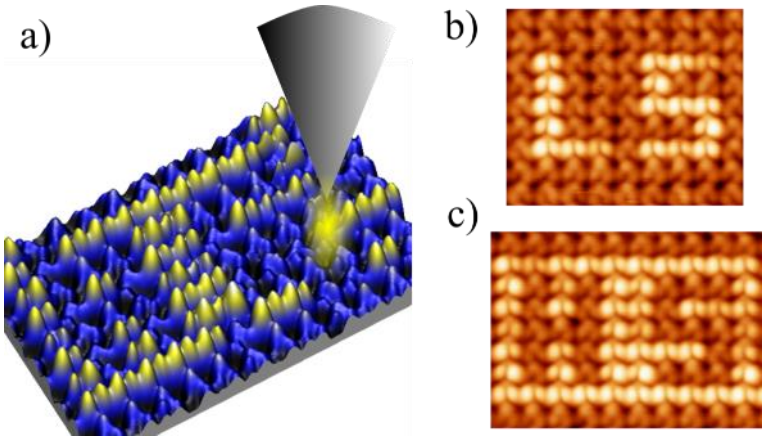

Figure: *a) Scheme of the manipulation by voltage-pulses. b) 10x10nm² and c) 10x12.5nm² topographic images where "LS" and "HS" have been written by voltage pulses (V=0.3 V, I=3 pA).*

Acknowledgments:
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Electrochemical Modulation of Magnetic Properties in Polynuclear Complexes

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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.

A trinuclear and an hexanuclear complexes based on the hexahydroxytriphenylene (HHTP) redox active ligand are studied. Their redox states are characterized by spectroelectrochemical tandem measurements and for each complex the first oxidation process is successfully performed using I_2.

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 observed is from a state where a single electron is present on the central ligand that should magnetically couple the three metallic centers to a state with a diamagnetic central ligand with no coupling between the magnetic centers. In the case of the hexanuclear complex the situation is reversed.

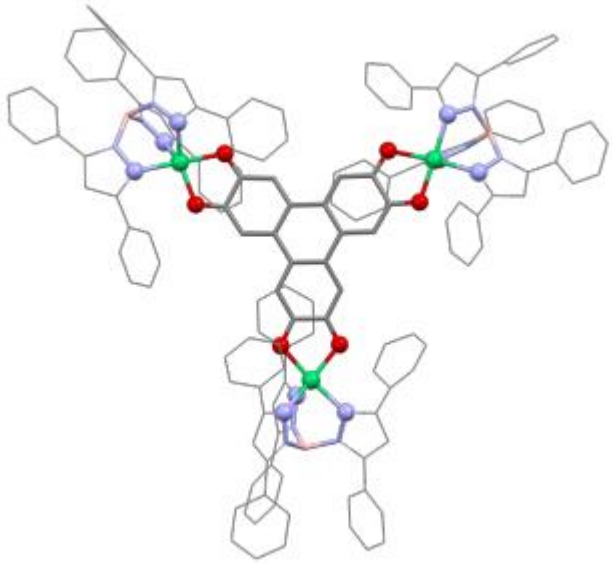

Figure 1 : Crystallographic structure of the trinuclear complex [Ni3(HHTP)(HBTp(Ph,Ph)$_3$)$_3$]

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Rational Design of 3*d*4*f* Heterobimetallic Complexes: Attempts to Associate Spin Crossover and Slow Magnetic Relaxation Behaviors.

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In the last decades, theoretical and experimental studies have demonstrated that the multifunctional molecular materials [1] have a great interest due of their original magnetic properties (single molecule magnet (SMM), spin crossover (SCO)…) as well as synergy between them allowing the observation of new physical properties such as Circularly Polarized Luminescence (CPL), Magnetochiral Dichroism (MChD) , Magnetoelectric Coupling (ME) [1, 2]... In particular, the mixed 3d4f complexes, which combine large magnetic moment and high magnetic anisotropy of the 4f elements with the 3d-4f magnetic interactions, could be suitable candidates.

This work allowed the synthesis of two series of 3d4f complexes thank the association of lanthanide ions to the L_2M (L= N-(2-Pyrazylcarbonyl)-2-pyrazinecarboxamide (dpzca), M= Co (II), Fe (II)) fragment which displayed SCO behavior.[3, 4] The crystallographic structures of these complexes were obtained, showing the important role of the size of metal centers and ancillary ligands (1, 1, 1, 5, 5,5-hexafluoroacetylacetonate (hfac), 2-thenoytrifluoroacetylacetonate (tta) or [3-(heptafluoropropyl hydroxymethylene)-*d*-camphorate] (hfc)) on the nuclearity of the final compounds. Indeed trinuclear, hexanuclear and one-dimensional complexes could be isolated.

Spin state of the 3d transition metal and slow magnetic dynamics were studied and discussed in this communication.

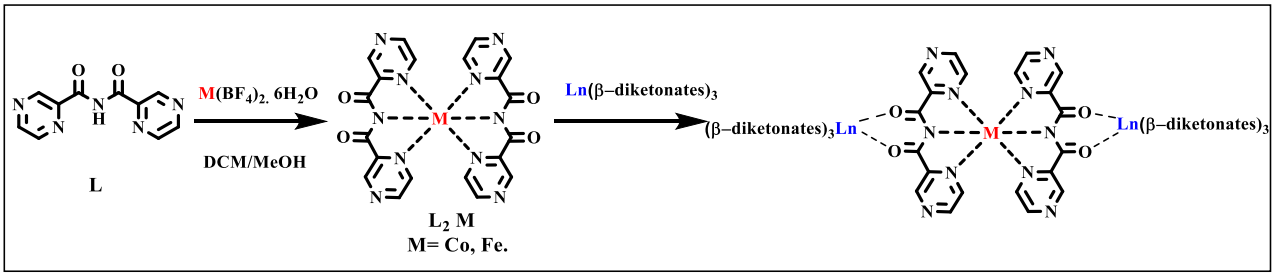

Figure: *details for synthesis of ligand and complexes.*

Acknowledgments:
The University of Rennes 1, CNRS, National Agency of Research (N ° ANR-13-BS07-0022-01) and the European Commission through the ERC-CoG 725184 MULTIPROSMM (project n. 725184) supported this work.

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Antiferromagnetic coupling in porphyrin dimers

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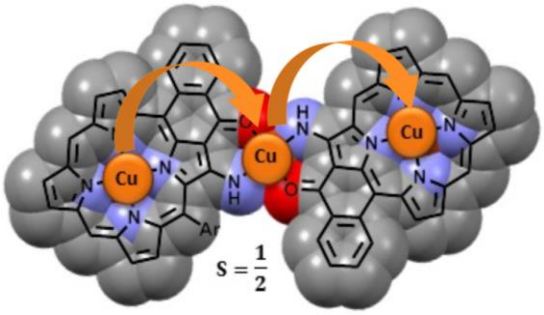
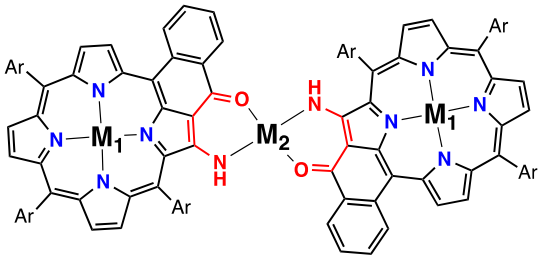
Synthesis of a porphyrin containing both an internal coordination site and an external coordination site is well established in our group. These two coordination sites can be exploited to synthesise a multitude of porphyrin dimers. For this project we have synthesised porphyrins dimers with a paramagnetic metal ion at the internal coordination site be it copper(II) or vanadyl and a paramagnetic or diamagnetic metal ion as a linker by utilising the external coordination site be it copper(II), vanadyl or Pd(II). The optical and magnetic properties of such molecules were then studied.





Antiferromagnetic coupling

For our CuPdCu dimer, we remark a weak magnetic exchange interaction between the two Cu ions, this is expected as the distance between the two sites is large. However, on changing the diamagnetic linker (i.e. the Pd) to a paramagnetic linker in this case Cu we observe a strong magnetic exchange for our CuCuCu dimer hence demonstrating a more efficient exchange and consequently a stronger antiferromagnetic coupling. This strong antiferromagnetic coupling is able to occur as the linking Cu(II) ion is acting as a relay for the magnetic exchange interaction consequently leading to a larger interaction compared to our CuPdCu dimer.

These results therefore demonstrate the necessity of a paramagnetic linker for optimal antiferromagnetic coupling. Similar results presenting this concept of relay for improved magnetic exchange has also been demonstrated for VVV porphyrins.

Symmetry-resolved THz, IR, Raman spectroscopies and DFT calculations study of lattice phonon modes in the spin crossover crystal [Fe(phen)$_2$(NCS)$_2$]

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The spin-crossover crystal complex Fe(phen)$_2$(NCS)$_2$ undergoes a Low spin (LS) to High spin (HS) phase transition driven by temperature, pressure and light. In this compound the relation between phonons modes and photoinduced spin state switching is highlighted by femtosecond experiments [1]. The vibrational entropy difference between the HS and LS states also plays an important role for thermal equilibrium phase transition, as highlighted by Raman and Infrared measurements on Fe(phen)$_2$(NCS)$_2$ powder, interpreted with Density Functional Theory (DFT) calculations of molecular vibrational modes [2]. However, the unit cell of this crystal contains 4 molecules and the combination of their in-phase or out-of-phase vibrations give rise to 609 optical lattice phonon modes with different symmetries, frequency and polarisation dependency [3]. I will discuss lattice phonon modes of Fe(phen)$_2$(NCS)$_2$ crystal by combining polarization-resolved Raman, THz and IR measurements, allowing selective probing of lattice modes of different symmetry. We compare the measurements with DFT calculations of the lattice phonon modes. Modes with similar molecular vibration nature and of different symmetries do not exhibit the same frequency change during the HS-LS conversion (Fig), which adds a higher complexity in the analysis of vibrational entropy.

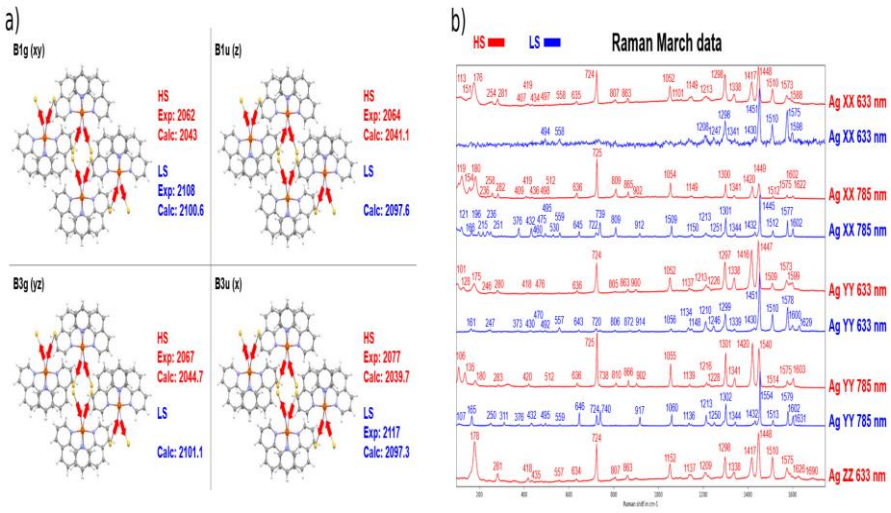

Figure: *Representation of 4 N↔CS vibrational modes in the Fe(phen)$_2$(NCS)$_2$ with their symmetry and frequencies (calculations and measurements in both spin states).*

Acknowledgments:
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Exploring the role of bridging pyrazine ligands in chromium-based one-dimensional coordination polymers.

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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 the 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 versatility of this simple ditopic bridging ligand, four one-dimensional (1D) coordination polymers have been crystallized and isolated from reactions between chromium(II) trifluoromethanesulfonate and pyrazine. The structures, elucidated by single-crystal X-ray diffraction, comprise arrays of chromium ions linked by pyrazine in either chain- or ladder-like arrangements with additional solvent and triflate ligands completing an octahedral coordination sphere around the metal centers. This presentation will divulge on the methodology to selectively synthesize these 1D coordination polymers and corresponding magnetic behaviour, in order to gain insights into the role of pyrazine in extended chromium-based systems.

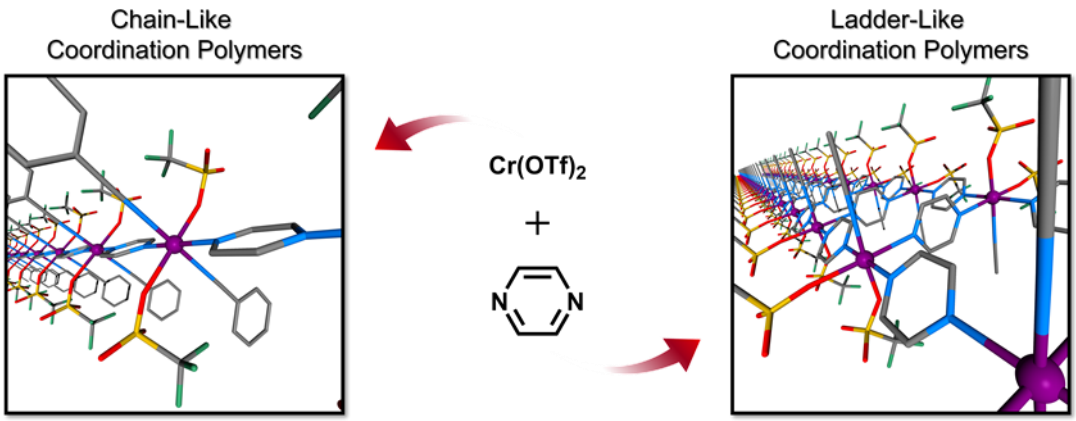

Figure: *Crystal structure views of chain- and ladder-like coordination polymers from the reaction of chromium (II) trifluoromethanesulfonate and pyrazine.*

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

Supercritical CO_2-assisted flow chemistry for processing switchable molecular nanomaterials

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Molecular switches are getting increasingly implemented in functional materials for sensing applications and in molecular electronics. Among this family, the Fe(II) spin crossover (SCO) materials are studied with great interest due to their ability to change their electronic configuration[1,2,3]. The material chosen for this study is an archetypal 1D-polymeric compound based on Fe(II) and triazole ligand. Such materials are close to applications and there is a need to obtain larger quantities of this product and more reliable processes. We address this challenge using an innovative approach based on flow chemistry to synthesize SCO nanoparticles in a reliable one-step process. The continuous system has already been used successfully to get different kinds of materials[4], from polymers[5] to metal-organic frameworks[6], leading to high-quality sub-micrometric, or even nanoparticles.

The use of a continuous flow process instead of conventional batch syntheses, coupled with supercritical fluids, has recently made possible to carry out syntheses in a single step, compared to five usually, without the use of any surfactant and with perfectly mastered sizes and compositions for the $[Fe(Htrz)_2(trz)](BF_4)$ compound[7]. The flow synthesis of nanoparticles will be then extended to other compounds of this family and to the design of heterostructures combining the properties of several materials.

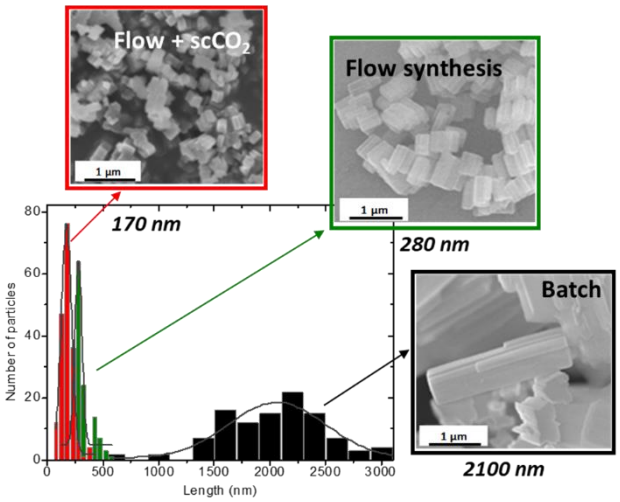

Figure: *Histograms of the lengths of samples 1–3 with their corresponding statistical distributions obtained by TEM, on at least 100 particles and corresponding TEM image* [7]

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8.

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Journées scientifiques de l'association française de magnétisme moléculaire JAM² session 2021

Mardi 23 novembre 2021	Mercredi 24 novembre 2021	Jeudi 25 novembre 2021
	9h00 Nocton	9h00 Clérac
	10h00 O10 Lou 10h20	10h00 O20 Ndiaye 10h20
	PAUSE	PAUSE
Accueil des participants	10h50 O11 George	10h50 O21 El Beyrouti
	11h10 O12 Jubault	11h10 O22 Kibalin
	11h30 O13 Tricoire	11h30 O23 Suzana
12h30	11h50 O14 Dhbaidi 12h10	11h50 clôture 12h10
DEJEUNER	DEJEUNER	DEJEUNER
14h00 Introduction 14h10	POSTERS	14h00
Collet		
15h10 O1Cuza		
15h30 O2 Pénicaud		
15h50 O3 Soroceanu 16h10	16h00 Orio	
PAUSE		
17h00 O4 Balthazar	17h00 O15 Kelai	
17h20 O5 Curti	17h20 O16 Xu	
17h40 O6 Kermarrec	17h40 PAUSE	
18h00 O7 Paveliuc	18h00 O17 Yergeshbayeva	
18h20 O8 Oyarzabal	18h20 O18 la Droitte	
18h40 O9 présentation ECMM 2022	18h40 O19 Magra	
19h00	19h00	
Aperitif	**Assemblée générale**	
DINER	DINER	