Switchable Molecular Magnetic Materials: Journey from 3D network to ultimate miniaturization and future application.

Abhishake Mondal[a,b] Matias Urdampilleta[a,b] and Rodolphe Clérac[a,b]

[a] Le Centre National de la Recherche Scientifique (CNRS), Centre de Recherche Paul Pascal (CRPP), UPR 8641, F-33600 Pessac, France; [b] University of Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France.
Email: abhi04juchem@gmail.com, mondal@crpp-bordeaux.cnrs.fr.

The design of **switchable molecular magnetic materials (SMMMs)** has become an important topic in the field of material science,[1] offering rich potential application for future molecular electronic devices, information storage/processing, molecular switch, high-density recording media and molecular sensors.[2] A variety of external stimuli such as temperature, pressure and light excitation have proved to be efficient in inducing electronic changes (e.g. charge transfer and/or spin state conversion). The molecular systems, which can provide access to room temperature bistability and photomagnetic effects, are among the most promising **SMMMs**.

The cyanido-based chemistry has been particularly fruitful and, for more than twenty years, a large number of cyanide-bridged polymetallic systems have been synthesized through rational choices of cyanido-based building blocks. These systems exhibit interesting properties, such as single-molecule magnets (SMMs) and single-chain magnets (SCMs) behaviours,[3] spin crossover (SCO),[4] electron-transfer process,[5] and photoinduced magnetism.[6]

Since last six years, we started to explore the "complex as ligand" strategy for designing low dimensional SMMMs. For example, we already reported discrete $\{Fe_4\text{-}Co_4\}$[5] and $\{Fe_2\text{-}Co_2\}$[5] molecular model compounds of the well-known photomagnetic Prussian Blue analogues (PBAs).[7] Very last year, we have prepared lowest possible unit of PBAs; a dinuclear Fe-Co complex $[(L)Fe^{III}(CN)_3Co^{II}(L')]+$ (L' = pentadentate N- donor ligand; L = tridentate N- donor ligand). Combined structural, magnetic and photomagnetic studies reveal that this compound also exhibits SMMs, SCO and metal-to-metal electron transfer properties that could be triggered by application of magnetic field, light and temperature.

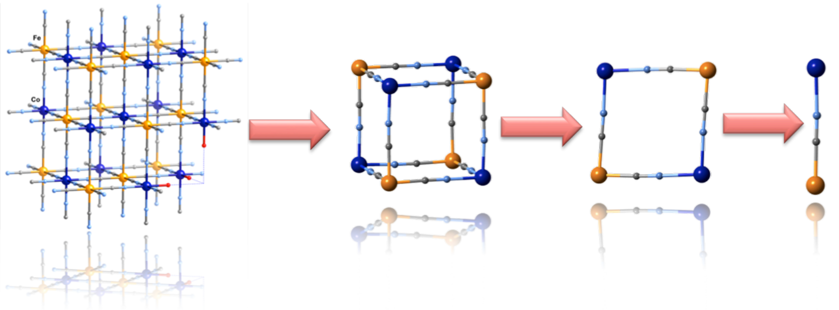

Fig 1. Schematic view of the 3D Fe-Co PBAs, $(Fe_4\text{-}Co_4)$, $(Fe_2\text{-}Co_2)$ and (Fe-Co) molecular unit (left to right).

We are also interested in Molecular electronic for fabrication of flexible, low cost and multifunctional devices. Herein, I will present an original molecular device made of a Micro-Electro-Mechanical Systems (**MEMS**)[8] functionalized with above mentioned SMMMs. Their change of volume at the magnetic transition alters the device's mechanical properties resulting in a change of the resonance frequency. We thus demonstrate the electronic read-out of a mechanical molecular switch that can be activated using temperature or light. Our results open up prospects of new flexible devices for data storage, sensing or (photo)switching, which is very original and rare in current material science domain.

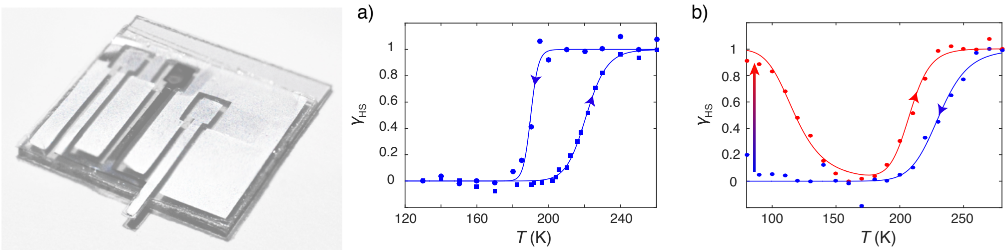

Fig 2. Schematic view of a MEMS cantilever (left), thermo-induced SCO (a) and photo-induced SCO obtained from the MEMS cantilever (b).

References:

[1] *Dalton Trans.*, **2010**, *39*, 4653 and *Chem. Soc. Rev.*, **2011**, *40*, 3053. [2] B. L. Feringa Molecular Switches, **2001,** Wiley-VCH, Germany. [3] R. Lescouëzec et al., *Coord. Chem. Rev.*, **2005**, *249*, 2691; K. R. Dunbar et al., *J. Am. Chem. Soc.* **2007**, *129*, 8139; J. R. Long et al., *J. Am. Chem. Soc.* **2008**, *130*, 2884. [4] J. A. Real et al., *Coord. Chem. Rev.* **2011**, *255*, 2068. [5] R. Clérac et al., *J. Am. Chem. Soc.*, **2008**, *130*, 252; A. Mondal et al., *J. Am. Chem. Soc.*, **2013**, *135*, 1653**;** R. Clérac et al., *J. Am. Chem. Soc.*, **2014**, *136*, 16854. [6] A. Dei *Angew. Chem. Int. Ed.* **2005**, *44*, 1160; A. Bleuzen et al., *Inorg. Chem.*, **2009**, *48*, 3453; S. I. Ohkoshi *Acc. Chem. Res.* **2012**, *45*, 10, 1749. [7] O. Sato et al., *Science*, **1996**, *272*, 704. [8] P. H. Ducrot et al., *Sci. Rep.* **2016**, *6*, 19426.