Self-Assembler Monolayers of molecular complexes for molecular electronics

Patrick ROSA

Univ. Bordeaux, CNRS, Bordeaux-INP, ICMCB, UMR 5026, 87 avenue du Dr. A. Schweitzer F-33600 Pessac, France

ABSTRACT

Spin crossover complexes (SCOs) are transition metal complexes that exhibit reversible state switching, often at ambient conditions. In iron (II) complexes, switching occurs between a diamagnetic low spin state (S=0) and a paramagnetic high spin state (S=2). The switching is accompanied by a change in the electronic properties, such that molecular junctions of these SCOs exhibit a change in conductance with the spin state.[1] Ultrathin films of those complexes have thus high potential to become the active layer for switches and memristors in molecule-based electronics. Preparing such ultrathin films has been done so far mainly through PVD techniques,[2] limiting thus seriously the potential molecules (neutral, low-weight,…) and offering limited control on the films morphology, when transport measurements require continuous films[3]. We have circumvented this issue by using complexes enabling chemical grafting, in order to prepare Self-Assembled Monolayers (SAMs). Indeed SAMs enable chemically specific modifications of a surface and find increasing application in standard electronics. We have prepared a library of functionalised iron (II) SCO complexes with different spin crossover behaviours in the bulks, and prepared SAMs characterized physically and chemically by a variety of surface techniques (ToF-SIMS, PM-IRRAS, XPS, XANES/XMCD) evidencing temperature- and photo-induced switching on Au and Cu substrates. We are now fabricating molecular junctions using eutectic gallium indium (EGaIn) as a conforming top electrode.

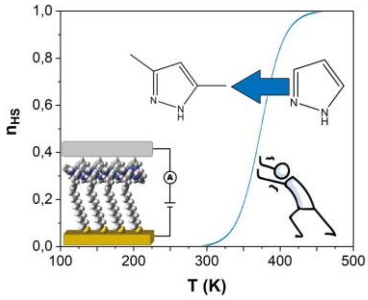

Fig. 1 Tuning the SCO temperature is possible by playing upon steric hindrance around the transition metal

The CISS effect (Chirality-Induced Spin Selection) has raised considerable interest[4,5] due to its potential to generate currents with very high spin polarizations, far above cryogenic temperatures. Theoretical studies show that spin-orbit coupling (SOC) should play an important role in CISS, but fail to predict the scale of the effect by several orders of magnitude. We have undertaken efforts towards systematic, rational studies across series of molecular systems designed specifically to ascertain the relative influences of the different molecular properties on the CISS effect. Some very preliminary elements will be discussed.

REFERENCES

1. L. Poggini, M. Gonidec *et al.*, *Adv. Elec. Mater.* **4**, 1800204 (2018).
2. M. Kelai, V. Repain *et al.*, *J. Phys. Chem. Lett.* **12**, 6152−6158 (2021).
3. Margaux Pénicaud, *Incorporation de complexes à conversion de spin dans des dispositifs d'électronique moléculaire*, Ph. D. thesis, Unversity of Bordeaux (2023).
4. C. D. Aiello, J. M. Abendroth *et al.*, *ACS Nano*, **16**, 4989 (2022).
5. F. Evers, A. Amnon *et al.*, *Adv. Mater.*, **34**, 2106629 (2022).

Patrick Rosa is a CNRS scientist in the Switchable Molecules and Materials (SMM) group at the Institute of Condensed Matter Chemistry of Bordeaux in Pessac. After graduating at École Polytechnique in Paris, he obtained a PhD in Molecular Chemistry on the phosphorus analogues of 2,2'-bipyridine and their coordination chemistry. He did a first post-doctoral contract with Prof. Geoffroy at the Physical Chemistry department of the University of Geneva, Switzerland, on EPR spectroscopy, and a second postdoctoral contract under Prof. Roberta Sessoli in Prof. Gatteschi's group at the Univeristy of Florence. He joined ICMCB as a permanent CNRS researcher at CNRS in 2004, where he was habilitated at the start of 2016. Current research interests cover a broad area: spin crossover complexes, their chemistry, shaping as thin films or ceramics, and physical characterization under external constraints (light and pressure most particularly); chirality and its use in molecular complexes, and studies of chiroptical properties and the CISS effect. He is currently leading an European consortium on the application of spin crossover molecular complexes into barocaloric refrigeration. His academic accomplishments include 86 articles in international peer reviewed journals with more than 2000 citations, participations to 3 book chapters, and 2 patents.