

NEW SENSORS BASED ON THERMO AND PHOTOSWITCHABLE IRON(II) SPIN CROSSOVER MATERIALS

Y. Garcia¹

¹Université Catholique de Louvain, Institute of Condensed Matter and Nanosciences, MOST – Inorganic Chemistry, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium. Email: yann.garcia@uclouvain.be

Iron(II) spin crossover (SCO) materials belong to an attractive class of switchable functional solids with spin state that can be reversibly triggered by temperature, pressure or electromagnetic radiation, [1] and that can be tracked by numerous physical techniques including ⁵⁷Fe Mössbauer spectroscopy [2] and muon spin relaxation [3]. Although the origin of the SCO phenomenon is molecular, its cooperative manifestation depends on an efficient coupling between active magnetic species in the crystal lattice through covalent and supramolecular interactions [4].

In this context, iron(II) 1,2,4-triazole 1D coordination polymers have attracted great interest as their abrupt spin transition (ST) is generally associated to both hysteretic and spectacular thermo-chromic effects, thus providing a basis for their potential use in thermal display, memory devices and sensors [5]. Various applications were proposed ranging from smart bank cards and temperature overheating alert systems [6], cold channel tracking sensors [7] and more recently functional paints. The nature of intrachain interactions can be mediated by the triple ligand bridge between iron centres and intramolecular H-bonding in some cases. Interchain interactions are also to be considered in these materials [8], but the role of the anionic sublattice dynamics on the ST mechanism of these compounds, which was probed by ¹¹⁹Sn Mössbauer spectroscopy, is not to be neglected too [7] to tune their magnetic properties. Gas sensing associated to a colour and spin state change is also another appealing facet of these functional materials [6].

Size reduction as well as an effective deposition on suitable surfaces is desirable for implementation of SCO materials into devices. In a unique approach under green technology, we recently introduced an inner epidermis of onion bulb (*Allium cepa*) [9] as a novel support to grow single crystals of desired size and for thin film processing of SCO materials. This radical approach differs from the classical one using conventional supports like glass, quartz, Si-wafer and so on. As a proof of concept, we selected an illustrious thermo-chromic iron(II) complex, [Fe(1-propyl-tetrazole)₆](BF₄)₂ (**1**), whose thermally and light-induced spin transition has been very well documented [e.g. 1]. Non-conventional method of 'seeding' and capillary deposition as well as dip coating were employed for crystal growth and thin film processing of **1**, which was probed by AFM on both abaxial and adaxial sides of the membrane [10]. The nature of the deposition was explained thanks to a detailed ⁵⁷Fe Mössbauer investigation [11].

Unprecedented photomagnetic properties at room temperature were recorded for the photochromic coordination complex [Fe(BM-4TP)₂(NCS)₂·2MeOH including a diarylethene ligand, whose origin were explained thanks to ⁵⁷Fe Mössbauer spectroscopy at variable temperature [12]. More recently, we have revisited the optical-structural properties relationship for *N*-salicylidene *N*-heterocycles derivatives affording a new range of solid state thermo-chromic and photochromic switches operating at room temperature [13]. These molecules were included in mononuclear coordination complexes as a proof of concept [14] as well as in oligomeric SCO complexes [15,16]. For the dinuclear iron(II) complex, [Fe₂(Hsaltrz)₅(NCS)₄·4MeOH, with Hsaltrz = *N*-salicylidene-4-amino-1,2,4-triazole [16], the abrupt ST phenomenon occurring at ~ 150 K could be tracked by temperature dependence fluorescence spectroscopy for the first time in the crystalline state, thus opening new sensing perspectives, e.g. in thermometry.

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- [1] P. Gütllich, Y. Garcia, H. Spiering, *Magnetism: From Molecules to Materials IV*, Wiley-VCH 8 (2003) 271.
- [2] (a) P. Gütllich, Y. Garcia, *J. Phys. Conf. Ser.*, 217 (2010) 012001. (b) P. Gütllich, Y. Garcia, Eds. Y. Yoshida, G. Langouche, Springer (2012, in press).
- [3] Y. Garcia, S. J. Campbell, J. S. Lord, P. Gütllich, *Inorg. Chim. Acta* 361 (2008) 3577.
- [4] Y. Garcia, V. Niel, M. C. Muñoz, J. A. Real, *Top. Curr. Chem.* 233 (2004) 229.
- [5] Y. Garcia, V. Ksenofontov, P. Gütllich, *Hyperfine Interact.* 139/140 (2002) 543
- [6] Y. Garcia, P. J. van Koningsbruggen, E. Codjovi, R. Lapouyade, O. Kahn, L. Rabardel, *J. Mater. Chem.* 7 (1997) 857.
- [7] Y. Garcia, V. Ksenofontov, S. Mentior, M. M. Dîrtu, C. Gieck, A. Bhatthacharjee, P. Gütllich, *Chem. Eur. J.* 14 (2008) 3745.
- [8] M. M. Dîrtu, C. Neuhausen, A. D. Naik, A. Rotaru, L. Spinu, Y. Garcia, *Inorg. Chem.* 49 (2010) 5723.
- [9] J. Schönherr, *J. Expt. Botany* 57 (2006) 1.
- [10] A. D. Naik, L. Stappers, J. Snauwaert, J. Franssaer, Y. Garcia, *Small* 6 (2010) 2842.
- [11] A. D. Naik, Y. Garcia, *Hyperfine Interact.* (2012, in press).
- [12] Y. Garcia, V. Ksenofontov, R. Lapouyade, A. D. Naik, F. Robert, P. Gütllich, *Opt. Mater.* 33 (2011) 942.
- [13] (a) F. Robert, A. D. Naik, B. Tinant, R. Robiette, Y. Garcia, *Chem. Eur. J.* 15 (2009) 4327. (b) F. Robert, A. D. Naik, F. Hidara, B. Tinant, R. Robiette, J. Wouters, Y. Garcia, *Eur. J. Org. Chem.* (2010) 621.
- [14] F. Robert, A. D. Naik, B. Tinant, Y. Garcia, *Inorg. Chim. Acta* 380 (2012) 104.
- [15] (a) F. Robert, A. D. Naik, Y. Garcia, *J. Phys. Conf. Ser.* 217 (2010) 012031. (b) F. Robert, A. D. Naik, Y. Garcia, *Möss. Eff. Data Ref. J.* 34 (2011) 200.
- [16] Y. Garcia, F. Robert, A. D. Naik, G. Zhou, B. Tinant, K. Robeyns, S. Michotte, L. Piraux, *J. Am. Chem. Soc.* 133 (2011) 15850.