Spin transition at the nanometer scale

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Spin crossover complexes of transition metal ions represent an important class of bistable materials for which switching between the high-spin and low-spin electronic configurations can be obtained by diverse external stimuli such as temperature, pressure, light irradiation, magnetic and electric fields or even the adsorption of gas/vapor molecules [1]. This switching of molecular spin-states is accompanied by a spectacular change of various physical properties. The molecular spin state change in the bulk material gives rise to elastic interactions between the molecules due to the strong electron-lattice coupling, leading to the emergence of various cooperative phenomena, such as first order phase transitions. These cooperative effects are considered as the key properties of these smart molecular systems for future applications in memory and highly efficient switching devices. The recent synthesis of these coordination compounds as nanoparticles, nanowires, thin films and nano-scale assemblies have brought new fundamental questions about the control and the preservation of the cooperativity at the nanometric scale [2-3]. In this presentation I will discuss the development of various top-down and bottom-up methods for the elaboration and patterning of nanometer scale thin films and particles of spin crossover complexes as well as our experimental results concerning size-reduction effects. While the first experimental studies were limited to large collections of nano-objects with a dispersion of sizes and shapes, we put particular emphasis for investigations in which SCO properties of the nano-objects could be clearly correlated with their morphology (see figure). In the course of these investigations we have shown that the memory effect (hysteresis) inherent to the bulk material can be preserved in nano-objects as small as 3 nm. Furthermore, we have evidenced an important matrix effect on the particle properties, which allows one to tune the particle properties by modulating the particle/matrix interface or the matrix properties. Beyond the fundamental aspects, the elaboration of thin films and nano-patterns of spin crossover materials paves also the way towards very promising applications in nano-photonic and nano-electronic devices. The main interest of SCO complexes in this context is that they respond reversibly to various external stimuli and can be therefore used either to detect physicochemical changes in the environment (sensors) or, on the other way around, to control the device properties by an external stimulus (switching and memory devices).

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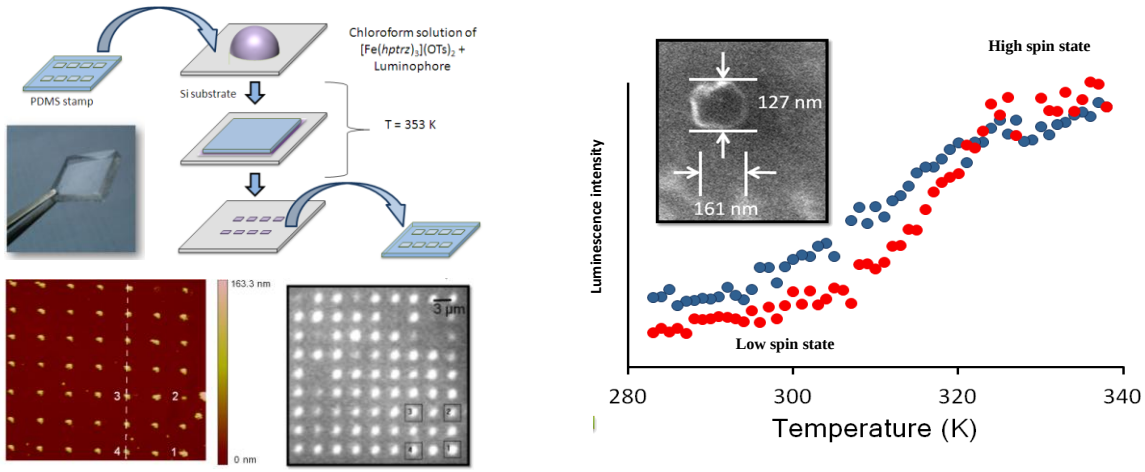
[2] A. Bousseksou, G. Molnar, L. Salmon, W. Nicolazzi, Chem. Soc. Rev. **40** (2011) 3313.
[3] H. J. Shepherd, et al. Eur. J. Inorg. Chem. (2013) 1015.



Left panel: Scheme of a soft lithographic fabrication process for arrays of fluorescent spin crossover nanodots of the complex $[Fe(hptrz)_3](OTs)_2$. The AFM and fluorescence microscopy images of a nano-dot array are also shown with motifs of 370 nm lateral size, 3 µm pitch and a nominal depth of 150 nm. Right panel: Temperature dependence of the luminescence intensity of a single nanodot in the heating (red) and cooling (blue) modes [Quintero et al. J. Mater. Chem. 2012, 22, 3745].