Spin crossover behavior in Luminescent Lanthanide Single Molecule Magnet

PhD founding in chemistry proposed to the University of Rennes 1 with an ERC contract

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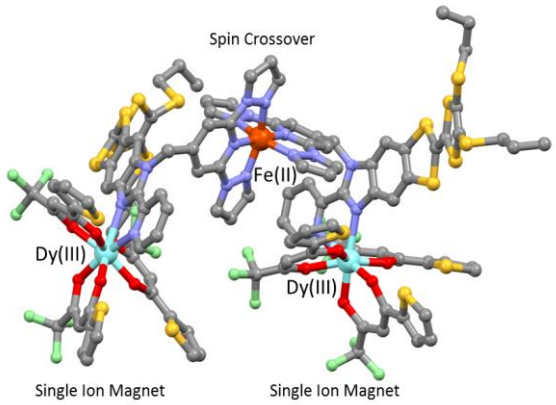
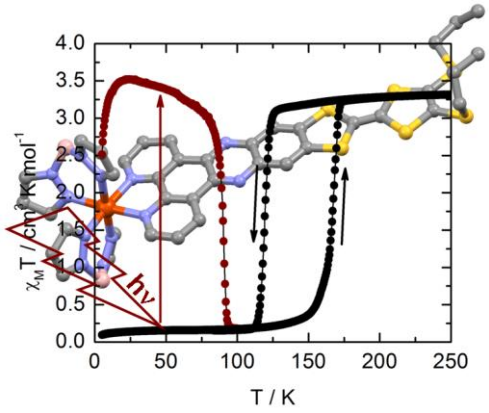
Molecules are the smallest stable elements of matter conceivable and represent in a sense the smallest functionalisable entities. We are now engaged in the miniaturization race in which molecules will play a predominant role. The design and the elaboration of functional molecules is challenging and stimulate the entire community of chemists. In the last twenty years, scientists have proceeded to the elaboration of functional molecules with peculiar and unique properties. We can give two significant examples: 1) The magnetic information can be stored on one single molecule, the so-called Single Molecule Magnets (SMMs) 2) the spin state of molecules can be changed by an external stimulus which can be a temperature variation, a modification of the pressure, a change of the external magnetic field or a light irradiation (spin crossover phenomenon, SCO). In molecular magnetism, lanthanide complexes have attracted much attention during the last decade because they can be successively employed to produce Single Ion Magnets (SIMs) or SMMs. In SIM, the magnetic anisotropy of a single lanthanide ion is responsible of the hysteresis loop of the magnetic moment of one complex while SMM may involve several metallic centres. In addition, lanthanides possess specific luminescent properties with an emission ranging from the visible to the near infrared spectral range. The SCO phenomenon is well known since 80 years. The most studied complexes are based on iron(II) because the spin state changes from a diamagnetic low spin (LS) to a paramagnetic high spin (HS) but can be observed for other transition metals such as Co(II), Fe(III)…





The aim of this proposal is to confer multiple properties to a single isolated complex which may display simultaneously **Single Ion Magnet** (SIM), **Spin Crossover** (SCO) behaviours and **Near Infrared luminescence** thanks to the controlled insertion of both Ln(III) and M(II)/M(III) ions into the molecule. The student will have to perform the synthesis of new organic tetrathiafulvalene-based ligands able to coordinate both 4f and 3d metal ions. He/She will perform the coordination reaction as well as the crystallization of the heterobimetallic 3d/4f complexes. It thus requires a motivated student with a good knowledge in **organic synthesis** and **coordination chemistry** with some interest for this multidisciplinary project (chemistry, crystallography, physics, magnetism, theory… The University offers French courses for foreigners and hosts an international Erasmus Mundus program. Students should obtain their PhD degree within the 3 years of the financial support (**starting date October-December 2017**). Rennes is a medium size French city less one hour and half away from Paris, offering a relaxing life style with many cultural and sport activities.

Selected recent publications of the group in relation with the subject of the thesis:

1) T. T. da Cunha *et al. J. Am. Chem. Soc* **2013**, 135, 16332.
2) F. Pointillart *et al. Acc. Chem. Res.* **2015**, 48, 2834.
3) F. Pointillart *et al. Dalton Trans.* **2016**, 45, 11267.
4) S. Speed *et al. Inorg. Chem. Front.* **2017**, 4, 604.