NEW ROUTES TO MULTIFUNCTIONAL SINGLE-MOLECULE MAGNETS BY POST-FUNCTIONALIZATION

NOUVEAUX CHEMINS D'ACCES A DES MOLECULES-AIMANTS MULTIFONCTIONNELLES PAR POST-FONCTIONNALISATION

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Nowadays there is an ever-increasing need to find more efficient ways to store digital information. Single-Molecule Magnets (SMMs) or Single-Ion Magnets (SIMs) represent a promising alternative for high-density data storage since they would allow information storage at the molecular level.[1,2] These inorganic entities are metal complexes that individually exhibit the classical properties of a magnet below a critical temperature. In this area, lanthanide complexes have attracted much attention. In SIMs, the magnetic anisotropy of a single lanthanide ion is responsible for the hysteresis loop of the magnetic moment of one complex while in SMMs several metallic centers may be involved. The energy barrier (ΔE), which depends on the total spin (S) and the anisotropy (D) within the metal complex, has to be as high as possible. In addition, lanthanides possess specific luminescent properties with an emission ranging from the visible to the near infrared spectral range.[3]

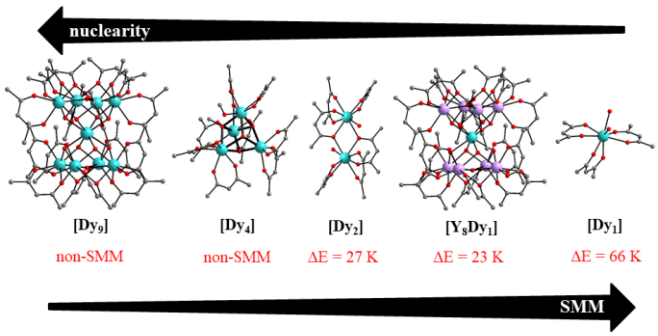

Figure 1. *Correlation between nuclearity control of 4f-complexes and their SMM behavior*

Our recent results have shown that the design of specific metallic unit (nuclearity, number of ligands …) by coordination chemistry route is essential in order to improve SMM properties and to obtain the most interesting ones (see Figure 1).[4-7] For example, different types of organic ligands will lead to different complex nuclearities and then totally different magnetic and/or optic properties. In that sense, the design of the organic moiety that will coordinate 4*f* centers is relevant to improve magnetic and luminescent properties of the final molecular object. We have also shown that by tuning the synthesis conditions (T, pH, solvent …) diverse nuclearities could be obtained in a controlled manner leading to a wide range of properties. However it is delicate to predict the 4*f*-based complex type and its magnetic and/or optic properties when the ligand is modified (before any metal coordination).

In our group, we now focus our researches on the post-functionalization of the organic moiety within the inorganic cluster, after the complex formation by traditional coordination chemistry routes. This post-functionalization by common and simple organic and/or organometallic reactions (Sonogashira coupling for example) or electro-synthesis (forced activation of the reactive function within the complex by selective oxidation or reduction) could bring to the final molecular object additional properties (catalysis, medicinal, storage …) or could improve the already existing properties (see Figure 2). This approach is completely innovative in the coordination chemistry area and should lead to unprecedented results.

The aims of this 3-year PhD project are: (*i*) to synthesize adequate ligands for post-functionalization and metal coordination; (*ii*) construct 4*f* complexes (fixed nuclearity) from these original ligands and study their initial magnetic and/or optical properties, (*iii*) post-functionalize the ligand by organic reactions and/or electro-synthesis, with carefully chosen organic reactants depending on the targeted application; (*iv*) study the final properties of the final molecular objects.

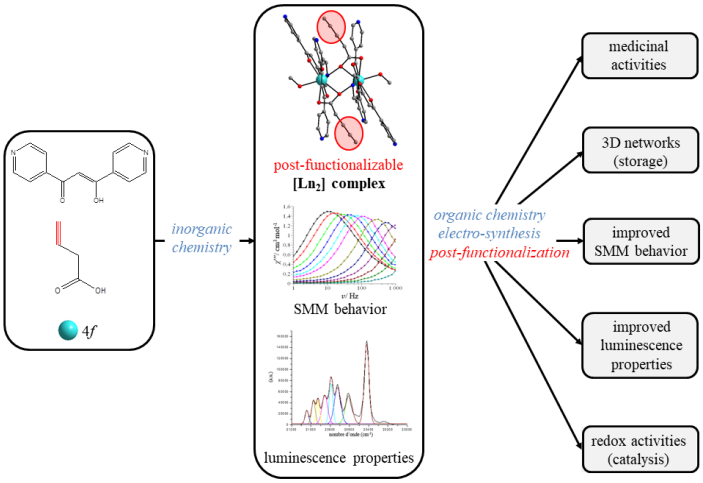

Figure 2. *Example of the strategy that will be fellow during the 3-years PhD project*

Candidate profile:

The research team "*Inorganic Molecular Chemistry and Precursors*" at the Laboratory of Multimaterials and Interfaces (LMI, Lyon) is currently looking for an excellent student to apply for a Doctoral Research Grant at the Ecole Doctorale of the University Lyon 1. A motivated student with a good knowledge in **organic synthesis** (in order to synthesize specific ligands) as well as in **coordination chemistry** (in order to synthesize 4*f* complexes) is required. Interest for a multidisciplinary project (chemistry, crystallography, magnetism, luminescence and electro-chemistry) will be appreciated.

Collaborators involved in the project:

Dr. David Gueyrard (chimie organique), ICBMS Lyon, France
Dr. O. Maury (luminescence), ENS-Lyon, France
Dr. O. Cador (magnetism) and Dr. B. Le Guennic (*ab initio* calculations), University of Rennes 1, France

Selected publications in our group in the topic of Single Molecule-Magnets:

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