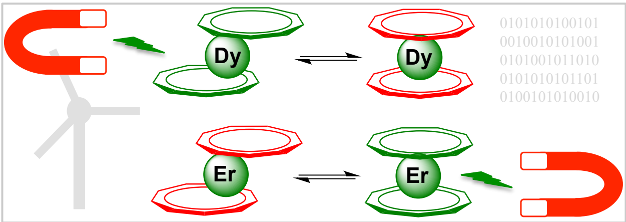
Laboratoire de Chimie Moléculaire
Ecole Polytechnique / CNRS

Advisor : Grégory Nocton
greg.nocton@polytechnique.edu

Linear Sandwich Complexes of Lanthanides: Synthesis and Applications in Magnetism

Rare earth metal ions are strategic elements for the decarbonisation of energy. The technologies that contain these as a resource vary from wind turbines to hybrid electrical motors, mostly because of their performing magnetic properties. Thus, as non-renewable feedstock, the magnet industry developed around them will need to rationalize their use. Important questions are how to miniaturize the magnets and how to recycle them. A good understanding of their chemistry will greatly help to tackle these problems: **the study of their physical chemistry allows the rationalization of their magnetic properties, first step to envision their enhancement, while a good knowledge of their dynamics in solution with various environment (ligands and solvents), helps designing adapted method for their recycling.** The overall methodology proposed herein will come to enforce these great challenges in both aspects: **synthetic methodology in organometallic chemistry for the specific design of performing single-molecule magnets (SMMs) with high blocking temperature.**[1]



We aim at using an underused large monoanionic ligand: the cyclononatetraenyl (Cnt) ligand[2] (Figure above) that is able to undergo hapticity switches depending upon various conditions and constrains. Due to its monoanionic nature, it is adapted with low-valent lanthanides but also with trivalent lanthanide in combination with the well-known dianionic cyclooctatetraenyl (Cot) ligand. We envision **synthesizing a collection of organometallic lanthanides compounds with various lanthanides elements at different oxidation states and with various geometries**, thanks to the large size of the cnt ligand, which allow hapticity switches (Figure above). The synthetic methodology will use original approaches such as solvent-induced isomerization and solvent-induced hapticity switches. **The use of these new methods and the study of the dynamics of the Cnt ligand must be rationalized by adapted characterizations and theoretical studies** (in collaboration). The specific design of these lanthanide compounds with various geometries depending upon the metal center will allow the enhancement of their magnetic properties and in particular their magnetic relaxation properties. **The challenge is to study and rationalize how i) the ligand geometry and ii) the metal physical properties influence the slow magnetic relaxation in the aim to increase the blocking temperature to reach the liquid nitrogen temperature (77 K) and above**. To accomplish this deed, a very good knowledge of the electronic structure is essential. Spectroscopic (luminescence, EPR)[2] and theoretical tools (in collaboration) will be confronted. The candidate will receive appropriate training in inert atmosphere synthesis, X-ray diffraction, RMN of paramagnetic molecules, EPR simulation and magnetism. If the candidate has interest in theoretical methods, it is also possible to receive training for this.

References

1. Xémard, M., Cordier, M., Molton, F., Duboc, C., Le Guennic, B., Maury, O., Cador, O., and **Nocton G.***Inorg. Chem.*, **2019**, *58*, 2872-2880.
2. Xémard, M., Zimmer, S., Cordier, M., Goudy, V., Ricard, L., Clavaguéra, C., and **Nocton G.*** *J. Am. Chem. Soc.*, **2018**, *140*, 14443-14449.
3. Xémard, M., Jaoul, A., Cordier, M., Molton, F., Cador, O., Le Guennic, B., Duboc, C., Maury, O.,Clavaguéra, C., Nocton, G.*, *Angew. Chem. Int. Ed.*, **2017**, *56*, 4266-4271 (back cover)