Fully funded PhD position available:

DFT-DRIVEN SYNTHESIS OF HIGHLY PERFORMANT PHOTOSWITCHABLE MATERIALS

Host laboratory: Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB)
Research group: Switchable Molecules and Materials
**Host University:** Université de Bordeaux, France
Contract duration: 36 months
Keywords: Spin Crossover, DFT calculations, Artificial Intelligence (AI)

Context of the research project

Molecular magnetism aims at synthesizing new magnetic objects based on coordination complexes to ultimately be able to **process information on a single molecule level**. The richness of coordination chemistry makes it possible to consider polyfunctional compounds which combine their magnetic properties with other properties: photomagnetism, thermochromism, chirality, electrochromism, etc.

Photoinduced spin crossover is particularly attractive as it offers the possibility of ultrafast (femtosecond) switching. This is the case of the LIESST effect (Light-Induced Excited Spin-State Trapping) which consists in irradiating the absorption band centered on the metal (*d-d* transitions, MLCT, LMCT) so as to populate a metastable state and thus changing the molecule from a low spin (LS) state to a photo-induced metastable high spin (HS) state. This HS state only has a substantial lifespan below a limit temperature noted T(LIESST). This value of T(LIESST) is determined by photomagnetic measurements as described in figure 1 below.
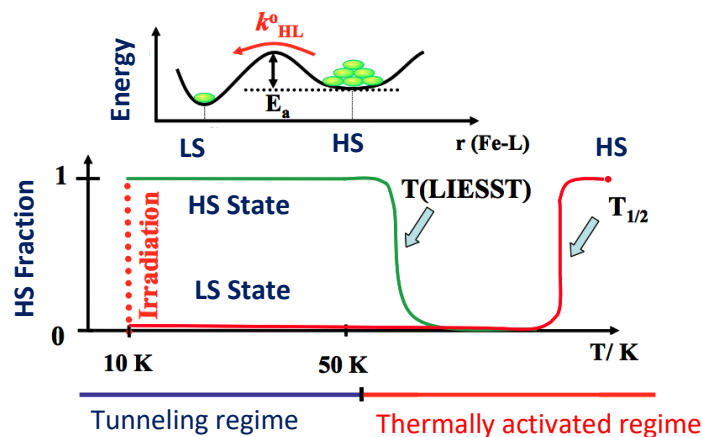
***Figure 1**: principle of measurement of the T(LIESST). The compound is irradiated at 10 K. After stopping the irradiation, the temperature is then increased at a constant rate set at 0.3 K/min. The inflection point of the HS to LS relaxation gives the T(LIESST)value.*


Currently, this value of T(LIESST) remains too low (less than 200 K) to consider applications. If one wishes to increase the temperature T(LIESST), the mechanisms that preside over the relaxation of the photo-induced metastable state must be studied further. A primordial element seems to be the distortion of the coordination sphere during the transition, which must be as large as possible. The current PhD project targets the increase of the T(LIESST) temperature by tuning the coordination sphere distortion of some iron(II) complexes.

Objectives

To achieve room temperature photoswitching using LIESST effect, the coordination sphere distortion improvement is targeted by tuning the coordination number at the metal site. It is based on previous results obtained on **complexes based on macrocyclic ligands**. The overall involvement of the coordination sphere distortion on the lifetime of the photo-induced state will be further explored applying **"machine learning" tools to spin crossover**.

A macrocyclic compound, studied for the first time by Sato, has a high T(LIESST) of 132 K. This complex (figure 2 a) has the particularity of **changing coordination during** the change of spin state, going from coordination 6 in low-spin configuration to coordination 7 in high-spin configuration. This change in coordination was observed by X-ray diffraction measurements (Figure 2b). Basically this corresponds to a large variation in distortion of the coordination sphere, in connection with the high T(LIESST).

By tuning the ligand (substitution of oxygen atoms by nitrogen atoms and addition of flexibility within the ligand, figure 2 c)) high T(LIESST) values were obtained. In the frame of this project, new macrocyclic ligands will be studied in order to search for the same type of systems presenting a bond break during spin crossover. The objective is clearly to study the influence of the strength of the metal-ligand bond on the T(LIESST) by replacing the oxygen by sulfur atoms as well as by changing the axial anionic ligand. In addition, we could play on the flexibility of the ligand by modifying its aliphatic part. The collaboration with photo-crystallographers will be important to determine the structures under irradiation and to determine the role of this coordination/decoordination on the stability of the photo-induced state.
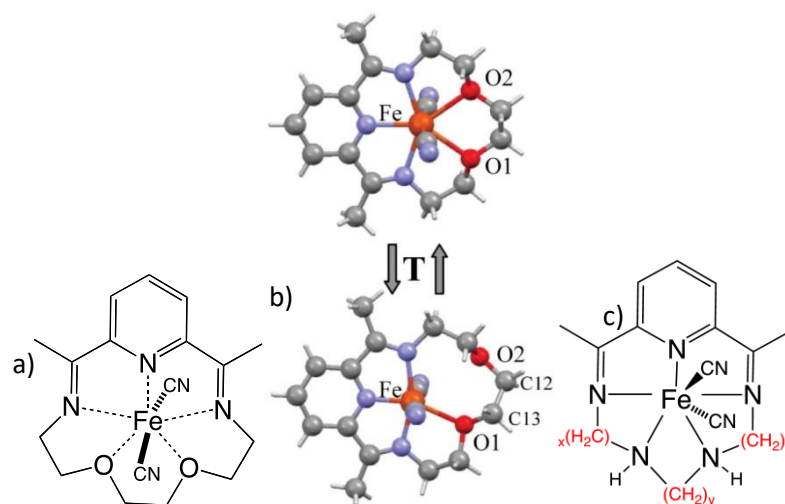
Figure 2: a) on the left: diagram of the macrocyclic compound [Fe(L$_{222}$N$_3$O$_2$)(CN)$_2$]·H$_2$O; b) in the middle: illustration of the change in coordination of the compound; c) on the right: general formula of a series of analogous compounds.

The existence of a decoordination within these new compounds could be anticipated before the synthesis of corresponding ligands. **DFT calculations** were indeed able to correctly account for the geometries of the HS and LS states of the complex with two oxygen atoms in the ligand. **The first step** of the PhD project is to screen the effect of various ligands on the occurrence of coordination number change using DFT calculations. The most interesting compounds will then be synthesized and studied.

The second step of the project will focus on **database analysis *via* "machine learning"**. Machine learning aims to correlate the properties of molecules with descriptors that can be either experimental or calculated using DFT methods. Secondly, these descriptors are correlated with non-calculated experimental properties in order to give a predictive aspect to the study. Indeed, many factors influence the spin crossover, including the temperature T(LIESST). These factors can be the nature of the counterion(s), the nature of the crystallization solvent and its quantity, the crystalline stacking and the elastic and electrostatic interactions that it generates, the presence of structural phase transition, etc. It is therefore difficult to draw correlations between the chemical nature of the molecule and its physical properties in the solid state. Despite current computational methods, it remains very difficult to predict the properties of spin crossover complexes in the solid phase. One way to try to obtain such correlations taking into account certain intermediate parameters would be the use of "machine learning". This will be explored in collaboration with expert in this field.

Candidate profile

We are looking for a candidate with a master's degree in chemistry with a strong interest in making functional molecular systems to study their physico-chemical properties. Knowledge of synthetic chemistry is a must, and knowledge of DFT calculations and Machine Learning would be a clear advantage for this project, even if dedicated training will be provided.

Autonomy, intellectual curiosity and ability to work in a team will be important. Good oral and written communication skills and English proficiency would be a plus for the dissemination of the results (publications, conferences…).

Working environment

The project is funded by a "young HDR" grant.
The student will be hosted mainly at ICMCB in the Switchable Molecule and Materials group. The team has fully equipped labs for chemical synthesis and chemical characterization of the compounds as well as full access to ICMCB facilities like powder, single crystal and surface diffractometers, chemical characterization (NMR, FT-IR, CHNS microanalysis, ICP-OES), magnetometry (SQUID and VSM) and thermal analysis (TGA and DSC).
DFT calculations can be performed on the Curta cluster of the University of Bordeaux. In the frame of the IRP MALCOM (MAchine Learning in COnsensed Matter chemistry) funding is available for stays at the University of Louvain la Neuve (collaboration with Prof. Gian-Marco Rignanèse, specialist in Machine Learning applied to materials)

Funding

Starting date: No later than October 2023
Contract duration: 36 months
Remuneration: ca. 2000 €/month gross (ca. 1600 €/month net)

To apply

Interested candidates are invited to send a CV, motivation letter and contact details of two referees to Cédric Desplanches: cedric.desplanches@icmcb.cnrs.fr