



PROPOSITION DE SUJET DE THESE

Campagne 2019/2020

Date: 12.2018

ÉCOLE DOCTORALE: École Doctorale de Chimie de Lyon-ED 206

TITLE OF RESEARCH SUBJECT /TITRE DU SUJET DE RECHERCHE:

Electro-Mechanical actuation of Spin-Crossover (Supra)Molecular Complexes

Research team/Équipe de recherche: Supramolecular Chemistry & Chemical Biology

http://www.ens-lyon.fr/CHIMIE/recherche/Teams/Chimie_Organique_et_Materiaux_Nanostructures

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Lab Language/ Langue de travail: English, français.

Abstract/Présentation du sujet:

The prospect of **mastering/exploiting molecular motions** has been a powerful source of motivation for chemists ever since the rise of molecular machines initiated in the early 80s.^[1] Under the impulse of a few pioneers, much efforts have been devoted over the years to the development of molecules endowed with metamorphic properties, *ie* for which large amplitude motions can be triggered in response to an external stimulus. These efforts have led to major achievements demonstrating the interest of molecular motions in electronics, analytical chemistry or for the development of molecular machines. In recent years, controlling molecular motions has emerged as a promising approach for the development of molecules exhibiting switchable magnetic states, the underlying idea being that modifying the structure of a molecular system could induce drastic modifications of its magnetic properties. From a practical standpoint, these ambitious objectives have so far mainly been addressed with coordination complexes using light as input signal.^[2] From a magnetic point of view, spin state changes are of interest to the electronic industry, most notably for the development of memory devices^[3] relying on the magnetic bistability of molecular compounds.^[4] The most promising molecular systems reported so far in this field are spin crossover or tautomeric compounds^[5] responding to external perturbations such as variation of temperature, application of pressure, or light irradiation. Such spin crossover process are mostly observed for bulk materials in the solid state, in which intermolecular cooperative effects play important roles for achieving HS/LS transitions. In contrast, well-defined stimuli-triggered spin transitions of “isolated” molecules in solution are relatively rare.

In this context, **this PhD project will aim at developing molecular systems for which large amplitude motions actuated by electron transfer can be used to control the magnetic state of key metallic centers** embedded in the structure. In the strategy detailed below, the local environment and the electronic configuration (High Spin (HS) versus Low Spin (LS) states) of the active metal will be determined with an electric trigger enabling to control the nature and number of coordinated ligands. In more specific terms, a **coordination induced spin state switching** process will be actuated in solution by the mechanical folding and unfolding of isolated molecules triggered at different potential values. The concepts proposed in this PhD project, involving molecular motion as a key driver of magnetic functions, built on the expertise accumulated over the years by the host research group in the development of redox-switchable (supra) molecular systems.^[6] One concept which will be developed is based on the self-locking principle sketched in Figures 1. **It aims at controlling the coordination**

number of a magnetically active metal center upon electric stimulation of a redox responsive molecular hinge that can toggle between an open and a closed position.

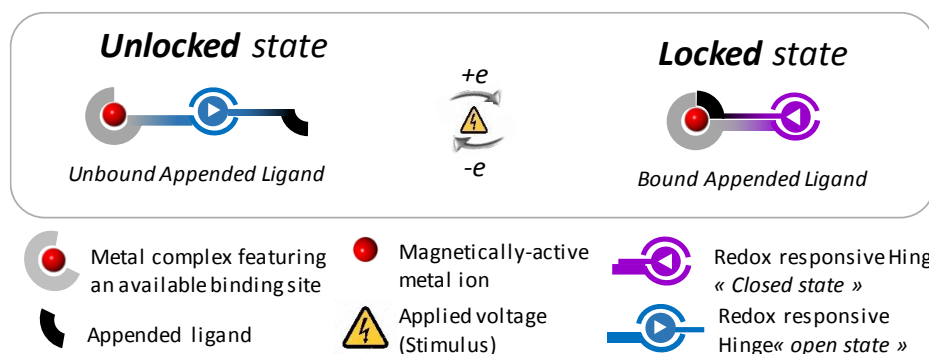


Figure 1. Self-locking principle targeted to achieve a coordination induced spin state switching.

In the unlocked state depicted above, the molecule adopts an elongated conformation: the electronic configuration (LS state) of the central metal is thus imposed by an unfilled coordination sphere. In accordance with the dynamic process depicted in Figure 1, reducing the hinge at a suitable potential will then trigger a mechanical motion of the coordination arm which will toggle to a locked position and promote a modification of the electronic configuration (HS \leftrightarrow LS) of the central metal (locked state, Figure 1).^[4,6] Depending on the metal, this concept of responsive self-locking molecule will be developed either with one or two coordinating arms actuated by electron transfer.

This multidisciplinary project will benefit from the complementary expertise of different partners in the fields of organic chemistry, electrochemistry, computational chemistry and in the design and characterization of coordination complexes endowed with magnetic properties. The applicant will ideally have a multidisciplinary background with a good expertise in organic chemistry.

Keywords/Mots-clés: Organic Synthesis, Supramolecular Chemistry, Coordination-Induced Spin Switching, redox activation; Magnetism, Molecular motions.

References:

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