AAP China Scholarship Council - CSC 2024

PROJET DE RECHERCHE DOCTORALE (PRD)

Titre du PRD : Responsive Materials based on Molecular Switches

DIRECTION de THESE

Porteuse ou porteur du projet (***doit être titulaire de l'HDR***) :

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Unité de recherche : Code (ex. UMR xxx) et Intitulé : UMR 8232 IPCM

Ecole doctorale de rattachement : ED406 - Chimie moléculaire de Paris Centre

Nombre de doctorants actuellement encadrés : 4 (3 à 50% dont 2 soutenant en 10/2024, 1 à 20%)

CO-DIRECTION de THESE (HDR) ou CO-ENCADREMENT (Non HDR) :

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Unité de recherche : Code (ex. UMR xxx) et Intitulé : UMR 8232 IPCM

Ecole doctorale de rattachement Sorbonne Université : ED406 - Chimie moléculaire de Paris Centre ou autre :

Nombre de doctorants actuellement encadrés : 0

CO-TUTELLE INTERNATIONALE envisagée : ☐ OUI ☒ NON

DESCRIPTIF du PRD :

*Ce texte sera affiché en ligne à destination des candidates et candidats chinois : il ne doit pas excéder **2 pages** doit être rédigé en **ANGLAIS***

Context

The design of switchable molecules and materials that are able to respond to external stimuli and emit specific responses is an attractive research topic for both physicists and chemists. Such bistable systems that can act as molecule-based memories, sensors and switches can actually lead to original nano-devices.[1] In this context, our team have been particularly interested by the design of polymetallic complexes of transition metals that show reversible and repeatable metal-to-metal electron transfer. This particular class of molecular switches is attractive because different stimuli such as light irradiation, temperature, or pressure can lead to drastic changes in various physical properties: optical, magnetic or dielectric ones. For example, in the last years we obtained the first Fe-Mn or W-Co discrete complexes showing thermo-/photo-induced electron transfer leading to a change in magnetic and optical properties.[2-3]

Recently, we have focused our studies on Fe-Co charge transfer complexes in which the photo-, thermo- or piezo-induced electron transfer is accompanied by interesting properties such as photomagnetism.[4-7] Interestingly, we observed that some of our cubic complexes are very stable in solution and show interesting redox properties: up to 9 different accessible electronic states have been observed. Because of these remarkable properties, the switchable Fe4Co4 cubes are attractive building units for the design of responsive materials.[8] Furthermore, we have successively converted by pressure the paramagnetic square complexes (Fe2Co2) into molecular switches.[9]

In this project, we will target at : (i) electronically-active extended frameworks that can show intercalation properties and respond to the insertion of guest molecules by a change in their magnetic and optical signatures. Encouraging preliminary results have been obtained.[7] We now wish to explore the full potentialities of our approach by studying the influence of various guest molecules and physical stimuli on the switchable properties of the materials; (ii) pressure-induced electron transfer of the Fe2Co2 square complexes to probe the fundamental aspects of molecular switching.

Details of the proposal

The Ph.D. work will start with the synthesis and the characterization of switchable cubes and squares bearing anchoring groups at their periphery. The compound will be characterized by standard techniques (NMR, IR and UV-vis spectroscopies). Their switchable properties will be investigated by magnetic, photomagnetic and high-pressure magnetic measurements, and by cyclo-voltammetry (to probe their redox behavior and their electron storage ability). The stability of the cubic complexes in solution will also be investigated by paramagnetic NMR and UV-vis-coupled to cyclovoltammetry. These techniques are all commonly used in our group and will be taught to the student.

The switchable complexes will be further used as polymetallic building units to lead to polymeric frameworks (see scheme below) by reaction of organic linkers with the anchoring groups. This approach has already been validated with one condensation and one addition reaction. The choice of the linkers will allow controlling the nanoporosity of the coordination network and its electronic properties. Then, the composition and structure of the material will be investigated by XRD on single crystal (under ambient or applied pressure) or in powder and by PDF analysis for amorphous phases. Solid-state NMR could also be used if necessary. The answer of the material to different

stimuli (chemical or physical) will be finally investigated. A particular attention will be devoted to host-guest properties of the material. Different aspects of these work will be carried out in the frame of our established collaborations (expert in crystallography, electrochemistry, etc.). This work will be co-directed by R. Lescouëzec and Y. Li from IPCM, in close cooperation with other coworkers from Sorbonne University.

References

[1] Bhushan, Handbook of Nanotechnology, Springer Berlin Heidelberg, Berlin, Heidelberg, 2017; Zhang et al. Chemical Society Rev. 2015, 44, 2998; Lefter et al. Adv.Mat. 2016, 28, 7508.

[2] Jimenez et al. Angew.Chem. 2020, DOI : 10.1002/anie.201916199 ;

[3] Mondal et al. Chem.Eur.J. 2013, DOI : 10.1002/chem.201300661;

[4] Mondal et al. J.Am.Chem.Soc., 2013, DOI: 10.1021/ja3087467 ;

[5] Garnier et al. Chem.Sci. 2016, DOI: 10.1039/c6sc01435f ;

[6] Daffé et al. J.Phys.Chem.Lett. 2018, DOI: 10.1021/acs.jpclett.8b03839

[7] Glatz et al. J. Am. Chem. Soc. 2022, DOI: 10.1021/jacs.2c03421

[8] Xuan et al. J. Mat. Chem. C. 2021, 9, 8882, DOI: 10.1039/d1tc01825F

[9] Li et al. Angew. Chem. Int. Ed. 2020, DOI: 10.1002/anie.202008051

[10] Xu, B et al. submitted

AVIS de l'Ecole Doctorale : Favorable

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