SORBONNE UNIVERSITÉ

CHINA SCHOLARSHIP COUNCIL

Appel à projets
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Title of the research project :

Responsive Materials based on Molecular Switches

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Research Unit

Name : Institut Parisien de Chimie Moléculaire

Code *(ex. UMR xxxx)* : UMR CNRS 8232

Doctorate School

Thesis supervisor's doctorate school (candidate's futur doctoral school) : Chimie Moléculaire, ED 406

PhD student currently supervised by the thesis supervisor (number, year of the first inscription) :

Na Li (oct 2020) codir D. Dambournet ; Buqin Xu (oct. 2018) cosup Y Li

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École doctorale

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Buqin Xu (first inscription oct 2018) co-supervisor YL

Joint supervisor :

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Title :

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Research Unit

Name :

Code *(ex. UMR xxxx)* :

École doctorale

Joint supervisor's doctorate school : Or, if non SU :

PhD student currently supervised by the joint supervisor (number, year of the first inscription) :

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ERMMES team

Sorbonne Université / China Scholarship Council program 2021

Responsive Materials based on Molecular Switches

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]

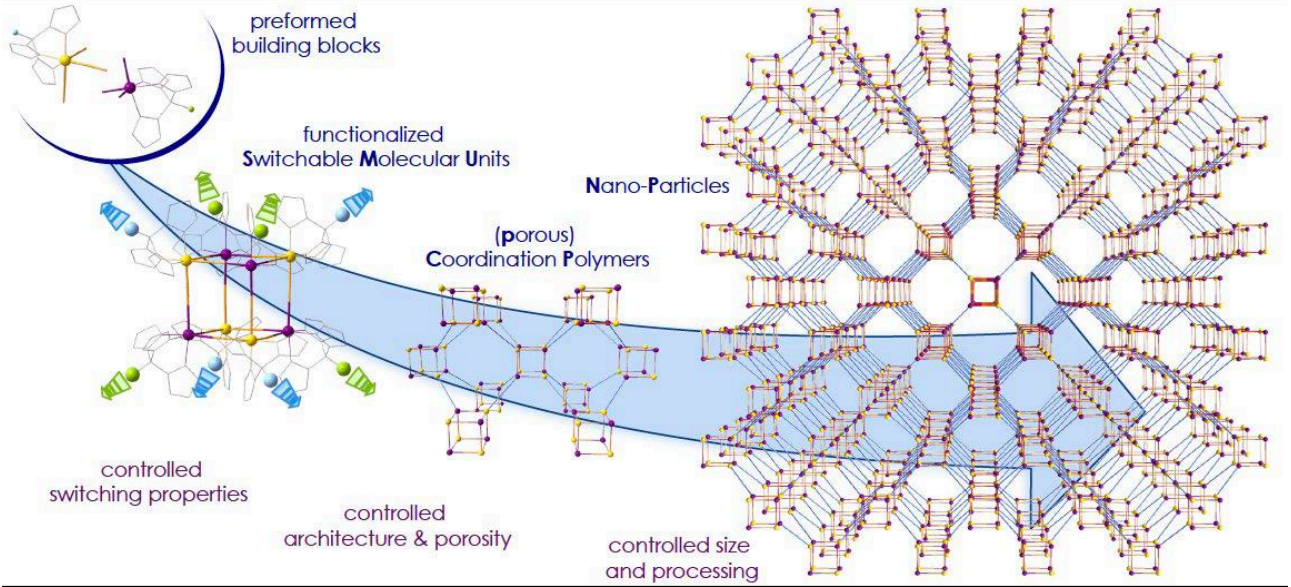
We are also studying Fe-Co charge transfers complexes in which the photo-, thermo- or piezo-induced electron transfer is accompanied by interesting properties such as electrochromism, photomagnetism, *etc*.[4-7] Interestingly, we observed that some of our cubic complexes are very stable in solution and show interesting redox properties: up to 9 different accessible electronic states have been observed. Because of these remarkable properties, the switchable cubes are attractive building units for the design of responsive materials.

In this project, we will target 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,[8] and we now wish to explore the full potentialities of our approach (i) by studying the influence of various guest molecules and physical stimuli on the switchable properties of the materials. The use of these materials in potential applications such as sensing will be more specifically explored.

Details of the proposal

The Ph.D. work will start with the synthesis and the characterization of switchable cubes and squares bearing anchoring group at their periphery. The compound will be characterized by standard techniques (NMR, IR and UV-vis spectroscopies). Their switchable properties will be investigated by magnetometry (to investigate potential photomagnetic effects) and by cyclo-voltammetry (to probe their redox behavior and their electron storage ability). The stability of the complex 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 nano-porosity of the coordination network and its electronic properties. Then, the composition and structure of the material will be investigated by XRD (on single crystal or 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 hostr-guest properties of the material and their potential application in sensing. 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] Li *et al*. *Angew. Chem. Int. Ed.* 2020, DOI: 10.1002/anie.202008051

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

Profile of the applicant

The candidate should have a master in chemistry. He/she should be familiar with standard characterization techniques such as NMR, UV-vis, FT-IR spectroscopy. Ideally, he/she should have some experience in the field of coordination polymers or metal-organic frameworks (their synthesis and characterization through X-ray diffraction). He/she should be highly motivated to participate to a multidisciplinary work that requires to learn different aspects from the synthesis to the material characterization. He/she should be highly motivated and hard worker. He/she should have good communication skills to be able to get involved in a team work. He/she should have a good level in English.

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