PhD OFFER
in chemistry and spectroscopy
October 2018 – September 2021

New developments in X-ray absorption spectroscopy dedicated to innovation : The case of molecular memories for high density data storage

I. Summary and key-words

Summary

The increasing demands for improved data storage eventually require a technological mutation. Photoswitchable molecular materials offer appealing perspectives and the goal of this thesis project is to transform this attractive idea into a realistic alternative. Metal-metal charge-transfer inorganic compounds are very interesting candidates but their photoswitching properties are observed at too low temperature to be used in any application. One way to adjust their property is to modulate the fine distortions of their structure. The objective of this interdisciplinary (physics and chemistry) thesis is therefore to elucidate the relationship between slight structural distortions and photoswitching properties in model compounds: Prussian Blue Analogs (PBAs). To reach this goal we will develop a new tool based on the X-ray magnetic circular dichroism (XMCD) at the K-edge of transition metals. PBAs will be first used as model-compounds so that chemistry helps solving physical problems; they will enable to establish a methodology for the quantification of slight structural distortions from TM K-edge XMCD and to deeply understand physical processes originating TM K-edge XMCD. PBAs will then be considered as solutions to the problems currently meet in the area of data storage, this time the physical tools allowing chemistry to answer today's technological challenges.

Mots-clés

Transition metal K-edge XMCD ; Synchrotron radiation; Prussian Blue Analogues ; Structural distorsions ; Photomagnetism

II. Thesis overview

Prussian Blue Analogs (PBAs) are molecular compounds of chemical formula $C_xA_4[B(CN)_6]_y \bullet nH_2O$ (A,B = transition metals ; C = alkali cation). Some of them presents photoswitching properties originating from an electron transfer ; the adressing time, extremely short for this kind of transfer, makes PBAs very good candidates for the future of data storage devices. However, photoswitching properties are mainly observed at low temperature, which hinders their use in applications. Getting around this obstacle, which could be done by deeply understanding the structure-property relationship in PBAs, is one of the main research subject of our team.

Several studies showed that a chemical change in the bimetallic network of the transition metals ($A_4[B(CN)_6]_y$) in photoswitchable compounds usually kills the photoswitching property. On the contrary, slight structural distortions of this network induced by the application of either a physical pressure in a high-pressure cell or a chemical pressure created by the insertion of alkali cations (C) could enable a control of the switching properties. Therefore one way to alter the switching property is to control these distortions.

In the case of these compounds, obtained as powder and whose structure is quite disordered, usual characterization techniques used to investigate the structure of matter cannot quantify the very small structural distortions. So our team works on the development of a new methodogy, that would allow the quantification of small structural distortions from X-ray Magnetic Circular Dischroism (XMCD) signals at the K-edge of transition metals, which is a technique derived from X-ray absorption spectroscopy. First experiments on PBAs demonstrated its sensitivity to small structural distortions induced by a pressure, as well as its relevance to understand and quantify the effects that can modulate the switching properties of PBAs. However, no satisfying quantitative description of these signals exists. Moreover, the physical phenomena originating transition metals K-edge XMCD are not well understood, which slows down the establishment of the new methodology.

The main goal of this thesis is the elaboration of molecular memories with photoswitching properties at room temperature. To reach it, several orientations will be investigated :

1) The PBAs family will be used as model-compounds to disentangle the physical effects originating the XMCD at the K-edge of transition metals and establish the methodology to quantify small structural distortions from these signals. This experimental part belongs to a long-standing collaboration between our team and the team of the ODE team (SOLEIL synchrotron), where all the transition metal K-edge XMCD experiments will be

performed. A theoretical investigation of these signals may be possible, in collaboration with physicits at IMPMC (UPMC, Paris).

2) The stable and metastable photoexcited states of the best known photoswitchable PBAs (Cs2CoFe, Rb2CoFe, Na2CoFe, Rb4MnFe) will be studied by transition metal K-edge XMCD, in order to identify the origin of their different photoswitching properties. This part will also be in collaboration with the ODE beamline team.
3) The structural distortions will be adjusted by chemical ways to control the switching properties of these compounds. Several ways will be investigated to chemically act on the switching properties (insertion of different alkali cations in the PBA 3D-network, change of solvent, insertion of guest-molecules, elaboration of core-shell particles…).

III. Profile, skills and experience

The thesis can be eclined in several aspects : (i) the development of a new methodology derived from x-ray absorption spectroscopy through the use of coordination polymers as model compounds, (ii) the characterization at the atomic scale of (photo)magnetic compounds using state-of-the-art X-ray spectroscopic techniques, (iii) the use of chemical ways to adjust switchable properties. This subject is so at the interface between physics/spectroscopy and chemistry. It implies an experimental part in the laboratory (synthesis, characterization) and on synchrotron (measurements campaigns, data treatment) ; a theoretical part (simulations of X-ray absorption spectra) could also be considered.

The PhD thesis is at the interface between physics and chemistry, with a significant experimental part but also possible developments towards theory and simulations. A master in physics (fundamental or applied), materials science, physical chemistry, inorganic chemistry or great instruments is required. Skills in inorganic synthesis will be appreciated but are not mandatory.

The applicant must be curious, open-minded, autonomous, motivated and have a strong team-spirit.

IV. Informations pratiques

The main PhD advisor will be Anne Bleuzen (professor at University Paris Sud) and Amélie Bordage (CNRS researcher) will be co-advisor.

Contact : Dr. Amélie Bordage (amelie.bordage@u-psud.fr / 01.69.15.70.55)

Institute : Institut de Chimie Moléculaire et des Matériaux d'Orsay (CNRS, Université Paris Sud, Université Paris-Saclay)
Adresse : Université Paris Sud, Bât. 420, Rue du doyen Georges Poitou, 91400 Orsay

Doctorate school : 2MIB (ED 571) — Sciences chimiques : Molécules, Matériaux, Instrumentation et Biosystèmes *(Chemical sciences : Molecules, materials, instrumentation and biosystems)*

Funding : ANR

Starting date : October 2018