3-year PhD position

Structure and dynamics of photosensitive hybrid materials: Method development

General information:

- Funded by Lorraine University d'Excellence (LUE)
- Application open: until occupied
- Starting date: End of 2024
- Thesis directors: Dominik Schaniel & El-Eulmi Bendeif (CRM2 laboratory)

Candidate profile:

- The PhD candidate must be graduated in Physics and or Material Science.
- She (He) must show a strong motivation to carry out both experimental and numerical simulation works in collaboration with different research teams.
- An experience in crystallography, total scattering and numerical simulation would be greatly appreciated
- The candidate must be open-minded and curious, able to learn by her (him) self through bibliographic studies.

Application: Send us as soon as possible (email to dominik.schaniel@univ-lorraine.fr)

- your CV and a motivation letter,
- your Bachelor and Master transcripts,
- Assessment letter from the Master2 internship supervisor
- Possibly recommendation letters.

Selection process:

- 1st step: pre-selection of suitable candidates based on the submitted documents
- 2nd step: audition by a jury (thesis supervisors + external experts) in the form of an interview by Visio conference.

Project description:

Since their emergence in the late 1990s metal-organic frameworks (MOFs) established a new area of research focusing on the design of smart materials, e.g., MOFs have increasingly been applied as hosts for photochromic dyes to form functional switch@MOF composites [1]. These molecules can be reversibly transformed between two or more photoisomers by light irradiation. Since the light induced structural changes cause alterations in absorption properties (color change), dipole moment and/or refractive index, they can be implemented in data storage or memory devices. Since the properties of the guest molecules are determined by their structure and the interaction with the host, adapted characterization techniques are mandatory to draw a full picture of material properties as a function of structure and interaction motifs. However, the greatest challenge lies precisely in the analysis of such crystalline, semi-crystalline, or even dynamic host materials with possibly "liquid-like" dynamic or disordered guest molecules. Since the standard methods for structure analysis fail to describe the system in the necessary detail, it becomes obligatory to advance methods and combine complementary approaches. This problem is even more pronounced, if one desires to study the influence of external stimuli like pressure or light irradiation on the functional properties of the material.

Thus, the main goal of this project is to establish a robust analytical workflow combining experimental and theoretical methods to fully characterize the structure and dynamics of such (partially) disordered host-guest systems to derive the structure-property relationship. By this, optical characteristics of the overall material are linked to the structural properties. The targeted photosensitive guest molecules are either purely organic substances such as spyropyranes or metal-nitrosyl compounds such as $[Fe(CN)_5NO]^{2-}$. Both material classes exhibit photoisomerism and the corresponding changes in the optical properties are of interest in applications [2].

The detailed structural analysis of these functional materials will be performed by using complementary experimental techniques as well as appropriate modelling [3]. Total X-ray scattering combined to pair distribution function analysis (PDF) and EPSR modelling will yield structural information at local and intermediate length scales and, hence, allow the study of ordering effects due to confinement. The complementarity of the methods will be exploited by combining them to form a structural model, which will be further supported by IR and UV/Vis spectroscopic data on the electronic and nuclear structure of the switch@MOF composites. The experimental data will be confronted to results obtained from self-consistent charge density functional tight binding molecular dynamics (SCC-DFTB MD) simulations, which also yield the PDFs and vibrational spectra as well as a detailed description of the binding motifs adopted by the host- guest complex at the atomic scale [4].

The project is conducted within an international partnership with the Institute of General, Inorganic and Theoretical Chemistry of the University of Innsbruck (UIBK, Austria), led by Ass.-Prof. Dr. Heidi Schwartz, expert on design and synthesis of photoswitches@MOFs and Ass.-Prof. Dr. Thomas Hofer, expert in DFTB calculations and MD simulations. During the project, the PhD student is expected to spend some time at the University of Innsbruck to learn about MOF synthesis and to delve deeper into the numerical simulations.

[1] H. A. Schwartz et al., *Photochem. Photobiol. Sci.*, 2018, *17*, 864. [2] D. Schaniel et al., *Adv. Mater.*, 2007, 19, 723. [3] H. Schwartz et al., *Inorg. Chem.* 2017, *56*, 13100; K.-Y. Hsieh et al., *RSC Adv.*, 2013, *3*, 26132 [4] F. R. S. Purtscher, et al, *J. Phys. Chem. C* 2023, *127*, 1560