Structure and dynamics of photosensitive hybrid materials: Method development	
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Since their emergence in the late 1990s metal-organic frameworks (MOFs) established a new area of research focusing on the design of smart materials. In the course of the last years, MOFs have increasingly been applied as hosts for photochromic dyes to form functional switch@MOF composites [1-3]. 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. Among the many known switchable dyes, spiropyrans and spirooxazines are of great potential regarding their combined photochromic and solvatochromic response upon UV light irradiation. 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. As we know how structure is affected by synthesis, we can elegantly impact the optical characteristics by modulating the synthesis strategy. The targeted photosensitive guest molecules are either purely organic substances such as the mentioned 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 [4].

The detailed structural analysis of these functional materials can be performed by using complementary experimental techniques as well as appropriate modelling [5]. These tools will provide information on the local structure and dynamics of the guest molecules as well as short range host-guest interactions, while total X-ray scattering combined to pair distribution function analysis (PDF: Pair Distribution Function) 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 PS@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. The preliminary PDF results (Figure 1) show good agreement with preliminary DFTB calculations and illustrate the potentiality of the chosen approach [6].

The thesis project contains a significant experimental part, consisting in collecting and analyzing total X-ray scattering data from laboratory or synchrotron experiments, such as e.g. the synchrotron sources in France (Cristal beamline at SOLEIL) and abroad MS@SLS. Further complementary experimental techniques employed are solid-state NMR, IR and UV/Vis spectroscopy. An important part of the project is based on molecular simulation for the reconstruction of the different structural models. Furthermore, the potential of X-ray absorption spectroscopy for the characterization of such photosensitive hybrid materials shall be explored.

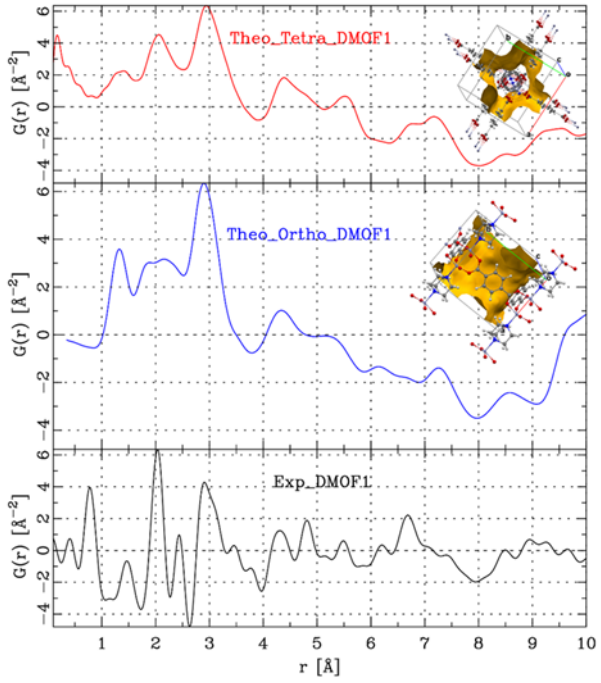

Fig 1. Comparison of theoretical and experimental PDF diagrams for DMOF-1 [6]

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 doctoral 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. The PhD student will also take advantage of the various scientific actions and meetings organized by scientific societies such as the GDR Solvate, the French Crystallographic and Physical Associations to present results and exchange with the different researchers involved in these organizations.

Références :

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3 year PhD position

Funded by Lorraine University d'Excellence (LUE)

Application open from: February 21st 2024 to April 27th 2025

Pre-selection and interviews: Mai 2025

Starting date: October 2025

Candidate profile :

- The PhD candidate must be graduated in Physics, Chemistry 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.