



	Experiment title: Breathing of flexible MOFs with embedded photochromic molecules upon UV illumination	Experiment number: CH-4646
Beamline: BM01B	Date of experiment: from: 26.04.2016 to: 03.05.2016	Date of report: 08.02.2018
Shifts: 21	Local contact(s): Hermann Emerich	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Heidi Schwartz*, Verena Gramm*, Uwe Ruschewitz* Department of Chemistry, University of Cologne, Greinstraße 6, D-50939 Köln, Germany		

Report:

Photochromic molecules are an interesting class of compounds, as upon light illumination their structures change leading to different optical properties of ground and excited state. This behaviour has been well investigated in solution, but in solids the switching is hindered due to sterical hindrance in close packed structures. To employ photochromic molecules in functional materials, e.g. data storage devices, they are typically embedded in amorphous hosts like polymers or thin films thereof. The embedment of such molecules in porous MOFs (metal-organic frameworks) is a quite new approach, which was reviewed by us recently.^[1] Among the known photochromic molecules spiropyrans have been intensively investigated since their discovery in 1952.^[2,3] Upon UV light irradiation, the closed, colourless and non-polar spiropyran form converts into its open, polar and strongly coloured merocyanine form. As both, the spiropyran and merocyanine form, differ markedly from each other with respect to shape and size, their embedment in MOFs is a straightforward approach to transfer their unique photo-physical properties to solid materials, as these guests are spatially well separated inside a porous MOF matrix. Metal-organic frameworks (MOFs) are well-known hybrid materials, which consist of inorganic nodes, i.e. metal ions or metal-oxo clusters, and organic linkers connecting them to a three-dimensional network with “potential” voids.^[4] For azobenzene and fluorinated derivatives we have already shown that this approach is successful to obtain materials with improved photochromic properties.^[5,6] Notably, we were able to solve several crystal structures of azobenzenes embedded in selected MOFs from high-resolution synchrotron powder diffraction data (CH-3776). Thus, we obtained very first insights into the host-guest interactions in these systems and the influence of the MOF’s pore size on the photochromic properties of the embedded molecules.^[5,6]

Since the photo-transformation of spiropyrans requires even more space than that of azobenzenes, we expected that light induced transformation of spiropyrans inside a MOF should have an effect on the solid state structures

of breathing MOFs like MIL-53.^[7] For our experiments, we synthesized SP@MOF-5 (**1**), SP@MIL-68(In) (**2**), SP@MIL-68(Ga) (**3**) and SP@MIL-53(Al) (**4**) (SP= 1,3,3-trimethylindolino-6-nitrospiropyrane) and investigated them by means of high-resolution synchrotron powder diffraction. Unfortunately, for MIL-53(Al) we found that the spiropyran molecules are mainly adsorbed on the MOF's surface, so that no light-induced transformation of the crystal structure of SP@MIL-53(Al) was observed upon illumination with light.

In Table 1 the results of the high resolution powder diffraction investigations on compounds **1-3** are summarized and compared with the results of the respective solvent-free MOFs (all patterns recorded at room temperature). To obtain reliable lattice parameters the patterns of **1-3** were refined using the *Le Bail* method. Comparison of loaded and unloaded MOFs reveals repulsive (increase of unit cell volume upon loading) interactions for **2** and **3** and attractive interactions (decrease of unit cell volume upon loading) for **1**. For **4** only negligible changes of the unit cells and reflection intensities were found, which indicated that no loading of the MOF pores with SP had taken place.

Table 1. Results of *Le Bail* fits of high-resolution synchrotron powder diffraction data of compounds **1-3** compared with the unit cell volumes of the respective unloaded MOFs.

	1	2	3
T/K	298	298	298
GOF	0.80	0.97	0.91
R _p	0.186	0.167	0.205
wR _p	0.291	0.248	0.325
V/Å ³	17111.8(3)	5911.5(2)	5217(1)
V/Å ³ (unloaded MOF)	17156.0(4)	5901.1(2)	5197.0(7)

Nonetheless, we fully characterized all four SP@MOF-systems by a combination of XPS and different spectroscopic methods. Depending upon the host matrix we found differing absorption properties of the excited states (merocyanine forms). This solvatochromic behaviour very much resembles that of spiropyrans dissolved in solvents of varying polarity (see Figure 1). Thus, we claim that MOFs can be regarded as “solid solvents” for such dye molecules. These results have recently been published.^[8]

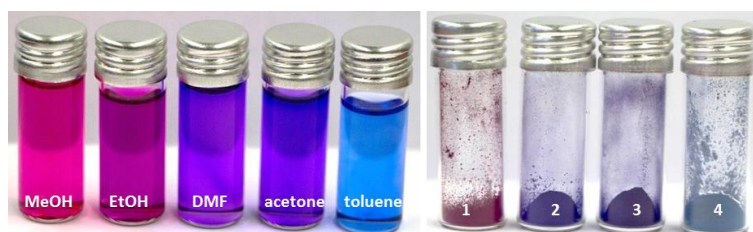


Figure 1. Left: photography of merocyanine dissolved in solvents with different polarities after irradiation with UV light ($\lambda = 365$ nm, 1 min); right: photography of **1-4** (from left to right) after irradiation with UV light ($\lambda = 365$ nm, 1 min).

References

- [1] H. A. Schwartz, U. Ruschewitz, L. Heinke, *Photochem. Photobiol. Sci.* **2018**, submitted.
- [2] E. Fischer, Y. Hirshberg, *J. Chem. Soc.* **1952**, 4522.
- [3] O. Chaudé, R. Rumpf, *C. R. Hebd. Seances Acad. Sci.* **1953**, 236, 697.
- [4] S. R. Batten, N. R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O'Keefe, M. P. Suh, J. Reedijk, *Pure Appl. Chem* **2013**, 85, 1715.
- [5] D. Hermann, *PhD Thesis*, University of Cologne, **2013**.
- [6] D. Hermann, H. Emerich, R. Lepski, D. Schaniel, U. Ruschewitz, *Inorg. Chem.* **2013**, 52, 2744.
- [7] T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Férey, *Chem. Eur. J.* **2004**, 10, 1373.
- [8] H. A. Schwartz, S. Olthof, D. Schaniel, K. Meerholz, U. Ruschewitz, *Inorg. Chem.* **2017**, 56, 13100.