



	Experiment title: Structural properties of MOFs loaded with optically switchable molecules and complexes	Experiment number: CH-3381
Beamline: BM01B	Date of experiment: from: 28 September 2011 to: 03 October 2011	Date of report: 26 February 2012
Shifts: 15	Local contact(s): Hermann Emerich	<i>Received at ESRF:</i>
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Report:

Metal-organic frameworks (MOFs) are a class of inorganic-organic hybrid materials that offer a crystalline nature with an ordered pore structure. This field is widely explored with respect to gas adsorption/separation and heterogeneous catalysis.^[1] As the embedment of larger functional molecules is less investigated up to now, we have started to incorporate photochromic azo dyes into MOFs as host matrices. Azobenzene (AZB) can be switched with light between the *trans* and *cis* isomers. This process is well studied in solution.^[2] As further photochromic guest molecules perfluoroazobenzene (*f*-AZB) and octafluoroazobenzene (*of*-AZB) were embedded. The investigation of the photochromic behavior revealed that AZB@MOF-5, AZB@MIL-68(Ga) and AZB@MIL-68(In) can be switched from the *trans* to the *cis* isomer by illumination with UV light, whereas AZB@MIL-53(Al) remains unchanged *trans*-AZB after illumination.

In the past it was already shown that nitroprussides retain their optical functionality after embedment in silica xerogels,^[3] but to gain information about the correlation between the structure and the resulting optical properties, knowledge of the arrangement of the guest molecules within the host matrix is essential. With the change of the host material to the crystalline MOF frameworks, we have the opportunity to solve the crystal structures of AZB@MOF systems to get to a more detailed understanding of the underlying interactions between host material and the embedded guest molecules. As the loading of the MOFs is carried out via a gas phase process to avoid the inclusion of additional solvent molecules into the structures, the synthesized photochromic AZB@MOF compounds are only obtained as polycrystalline powders, requiring high resolution powder diffraction to enable the structure solution. To freeze the motion of the guest molecules, all measurements were carried out at 120 K.

From the measured XRPD data three crystal structures were solved and refined up to know: AZB@MIL-53(Al), AZB@MIL-68(Ga) and *f*-AZB@MIL-53(Al). The crystal structure of AZB@MIL-53(Al) and AZB@MIL-68(Ga) are shown in Figures 1 and 3, the plot of the final Rietveld refinement of AZB@MIL-53(Al) is given in Figure 2. The crystallographic data are summarized in Table 1. The structure solution was carried out using FOX.^[4] With the assumption that the structure of the MOF material remains unchanged after embedment of the guest molecules, the atomic positions of MIL-53(Al)^[5] and MIL-68(Ga)^[6] were given and fixed, as well as the distances and angles within the azobenzene molecules. The amount of guest molecules was determined from elemental analysis.

Taking into account the van der Waals radii of MIL-53(Al) and azobenzene it becomes clear that the isomerization process from the *trans* isomer to *cis* azobenzene is sterically hindered in AZB@MIL-53(Al) (Figure 4), which explains the absence of optical switching in this system. In the host material MIL-68(Ga) however azobenzene is accommodated in larger channels, which provide more space to allow an isomerization to the *cis* molecule (Figure 3).

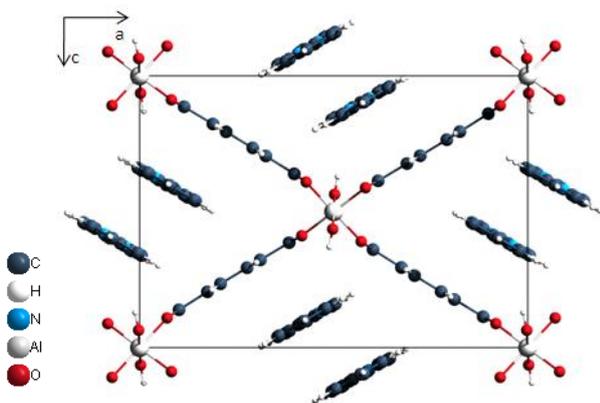


Figure 1. Crystal structure of AZB@MIL-53(Al).

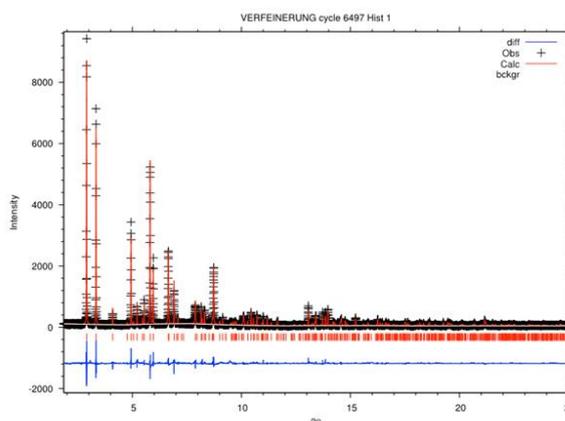


Figure 2. Rietveld refinement of AZB@MIL-53(Al).

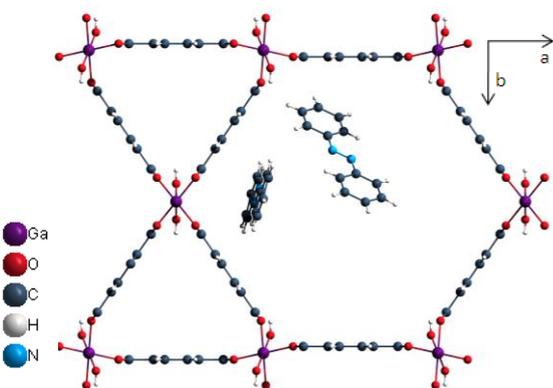


Figure 3. Crystal structure of AZB@MIL-68(Ga). Symmetry equivalent AZB molecules inside the pore are omitted for clarity.

Table 1. Crystal data of AZB@MIL-53(Al) and AZB@MIL-68(Ga).

	AZB _{0.48} @MIL-53(Al)	AZB _{0.57} @MIL-68(Ga)
SPG	P nma (62)	C mcm (63)
a (Å)	17.2258(3)	21.120(1)
b (Å)	6.6385(1)	36.617(3)
c (Å)	12.0690(3)	6.7395(2)
V (Å ³)	1380.13(6)	5212.0(6)
Z	4	12
R _p	9.42	9.73
ωR _p	12.12	12.26
R _{Bragg}	7.12	4.67

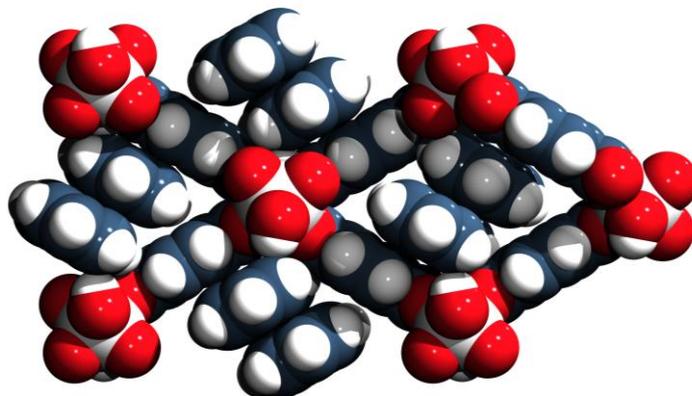


Figure 4. Space filling representation of AZB@MIL-53(Al).

Currently, we are trying to solve more crystals structures of azobenzenes (AZB, *f*-AZB, *of*-AZB) embedded in different MOF hosts. From the knowledge of these structures we will hopefully improve our understanding of the underlying host-guest interactions, which might lead to photochromic materials with optimized properties.

References:

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