



	Experiment title: Structural properties of MOFs loaded with photochromic molecules	Experiment number: CH-3776
Beamline: BM01B	Date of experiment: from: 12.06.2013 to: 17.06.2013	Date of report: 26.02.2014
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 organic-inorganic hybrid materials that offers a crystalline nature with an ordered pore structure. Potential applications are predicted in the fields of gas adsorption and separation, separation of liquids and heterogeneous catalysis.^[1] In the last years we have studied the embedment of larger functional molecules like photochromic azo dyes into MOF host materials. Under illumination with light of suitable wavelengths, azobenzene (AZB) isomerizes reversibly between its *trans* and *cis* isomers. In this current project we investigated the embedment of perfluoroazobenzene (*pF*-AZB), octafluoroazobenzene (*oF*-AZB), and tetrafluoroazobenzene (*tF*-AZB) as photochromic guest molecules. For these molecules the switching process had already been studied in solution.^[2-4]

The former investigation of the photochromic behavior of the AZB@MOF systems revealed that AZB@MOF-5, AZB@MIL-68(Ga), and AZB@MIL-68(In) can be switched from the thermodynamically more stable *trans* to the *cis* isomer by illumination with UV light, whereas for AZB@MIL-53(Al) no switching could be detected.^[5] In former investigations (CH-3381) these findings were explained by structural investigations of AZB@MIL-68(Ga) and AZB@MIL-53(Al) using high resolution synchrotron powder diffraction data obtained at 120 K (ESRF, BM01B). It was found that steric hindrance within the smaller pores of MIL-53(Al) is the reason for the non-photochromic behavior of AZB@MIL-53(Al).

In the current project high resolution synchrotron powder diffraction data of the following compounds were collected at room temperature and 120 K: AZB@MIL-53(Ga), *tF*-AZB@MIL-68(Ga), *tF*-AZB@MIL-68(In), and *tF*-AZB@MIL-53(Al). All patterns were indexed and the obtained cell parameters were refined by the *Le Bail* method using the program *Jana2006*.^[6] For AZB@MIL-53(Ga), the laboratory powder diffraction pattern shows noticeable similarities to the pattern of AZB@MIL-53(Al). However, the high resolution powder diffraction pattern recorded at BM01B revealed a doubling of two unit cell axes as compared to the unit cell of AZB@MIL-53(Al). When cooling to lower temperatures, a phase transition from the orthorhombic space group *Cmcm* (No. 63) to the monoclinic space group *P2₁/c* (No. 14) occurs. This result indicates a slightly different arrangement of the AZB molecules within the channels of MIL-53(Ga),

obviously due to its slightly larger pores. Presumably due to the larger unit cell with 16 formula units of $AZB_x@MIL-53(Ga)$, the structure solution algorithm in the program Superflip^[7] did not converge. However, the lozenge shaped channels of the MOF framework are visible in the resulting electron density map. The electron densities as obtained from Superflip as well as the *Le Bail fit* of $AZB@MIL-53(Ga)$ (120 K) are shown in Figures 1 and 2 and the refined unit cell parameters of $AZB@MIL-53(Ga)$ (room temperature and 120 K) and – for comparison – the unit cell parameters of $AZB@MIL-53(Al)$ are given in Table 1.

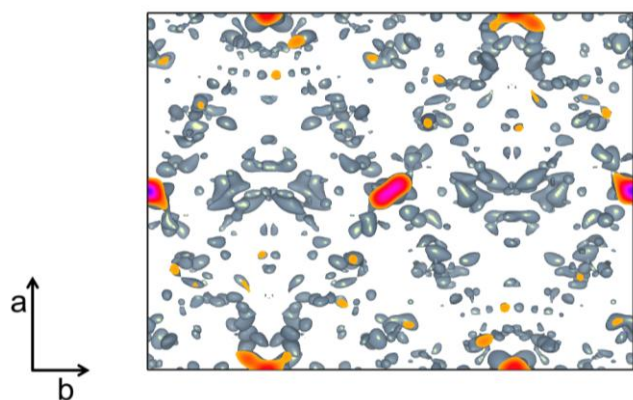


Fig. 1: $AZB@MIL-53(Ga)$; electron density as obtained by the charge flipping algorithm in *Jana2006*.

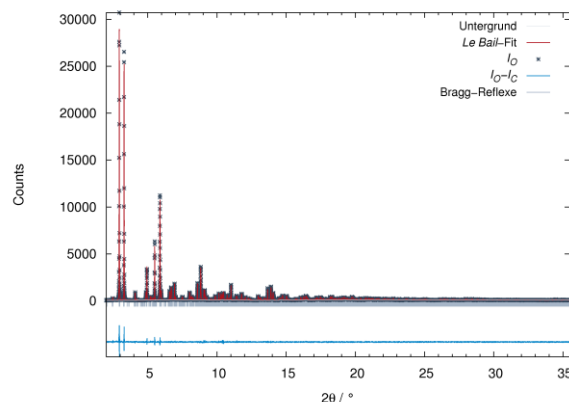


Fig. 2: $AZB@MIL-53(Ga)$; *Le Bail fit* (SG: $P2_1/c$, R_p/wR_p : 0.0611/0.0912, GOF : 1.28).

Tab. 1: Cell parameters obtained from the *Le Bail fits* of $AZB@MIL-53(Ga)$ (room temperature and 120 K) compared to the known unit cell parameters of $AZB@MIL-53(Al)$ (120 K),^[5] BDC = 1,4-benzenedicarboxylate.

	$AZB@MIL-53(Ga)$ (RT)	$AZB@MIL-53(Ga)$ (120 K)	$AZB@MIL-53(Al)$ (120 K) ^[5]
Formula unit	$AZB_x@Ga(OH)(BDC)$		$AZB_{0.5}@Al(OH)(BDC)$
SG (No.), Z	<i>Cmcm</i> (63), 12	$P2_1/c$ (14), 12	<i>Pnma</i> (62), 4
$a / \text{Å}$	13.4899(2)	17.6258(2)	17.2258(3)
$b / \text{Å}$	24.6349(5)	23.7559(3)	6.6385(1)
$c / \text{Å}$	17.3654(3)	13.4896(1)	12.0690(3)
$\beta / ^\circ$	90	90.975(1)	90
$V / \text{Å}^3$	5770.9(2)	5647.5(1)	1380.13(6)

Similarly, the unit cell parameters of *tF*- $AZB@MIL-68(Ga)$, *tF*- $AZB@MIL-68(In)$, and *tF*- $AZB@MIL-53(Al)$ were determined using *Le Bail fits* within *Jana2006*.^[6] In *tF*- $AZB@MIL-68(Ga)$, no phase transition between room temperature and 120 K was observed, whereas a phase transition from SG *Cmcm* (No. 63) to *Pnma* (No. 62) is likely to occur in *tF*- $AZB@MIL-68(In)$. In *tF*- $AZB@MIL-53(Al)$, a temperature dependent breathing of the MOF lattice was observed, as the *a* and *c* axes shrink, whereas the *b* axis increases with decreasing temperature.

Additionally, first studies of the diffraction patterns of *tF*- $AZB@MIL-53(Al)$ under illumination with green laser light (532 nm, Raman laser) were carried out. The refined cell parameters show small changes after the light induced *trans*→*cis* transformation of the embedded *tF*- AZB molecules. But as the ground state already contains 63 % of the *cis* isomer, as known from IR experiments, only small deformations of the network have been expected. Thus, these results are very promising taking into account that, as the experiments were carried out in glass capillaries, probably only small parts of the sample were illuminated by the laser light. In future experiments a reflection geometry and alternating illuminations with 532 nm (*trans*→*cis*) and 405 nm (*cis*→*trans*) laser light shall be used to amplify these effects and to give a more detailed insight into light induced structural changes of *tF*- $AZB@MIL-53(Al)$.

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