



	<b>Experiment title:</b> Structural properties of photochromic spiropyranes embedded in porous MOFs	<b>Experiment number:</b> CH-4346
<b>Beamline:</b> BM01B	<b>Date of experiment:</b> from: 24.06.2015 to: 29.06.2015	<b>Date of report:</b> 27.10.2015
<b>Shifts:</b> 12	<b>Local contact(s):</b> H. Emerich	<i>Received at ESRF:</i>
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## Report:

Metal-organic frameworks (MOFs) are a class of organic inorganic hybrid materials that offer a crystalline nature with an ordered pore structure leading to various potential applications. The embedment of functional molecules into MOFs has recently become a new interesting field of research. MOFs were used as hosts for photoresponsive molecules, e.g. stilbenes<sup>[1]</sup>, spiropyranes<sup>[2]</sup>, diarylethenes<sup>[3]</sup> as well as azobenzenes and their fluorinated derivatives<sup>[4-6]</sup>. For the latter we found isomerization rates up to 100% upon irradiation representing a significant improvement compared to the pure solids. Besides that, it was possible to solve several crystal structures of azobenzenes embedded in MOFs from high-resolution synchrotron powder data (CH-3776). Thus, it was possible to get a very first insight 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.<sup>[5]</sup> Recently, we have started to investigate spiropyranes as another class of photochromic guest molecules, which have been intensively studied since their discovery in 1952.<sup>[7]</sup> Spiropyrane dyes consist of two  $\pi$ -systems linked by a tetrahedral spiro carbon. Upon photoinduced modulation the stable closed and rather nonpolar spiropyrane (SP) form transforms to an open, highly polar merocyanine (MC) form that exists in a charge-separated zwitterionic and a quinoidal form.<sup>[8]</sup> Photochromic behavior of spiropyranes has been intensively studied in the liquid phase, but investigations in the solid state have been rarely reported. The photoinduced transformation requires steric freedom, which is not given in a pure solid. To avoid steric hindrance and intermolecular interactions (that may cause *quenching* e.g.), separation of spiropyrane molecules is obligatory, which is achieved by embedding them into (porous) solid matrices like MOFs. We synthesized four SP@MOF-systems: SP@MIL-53(Al), SP@MIL-68(In), SP@MIL-68(Ga) and SP@MOF-5 (SP= 1,3,3-Trimethylindolino-6-nitrospiropyrane). Investigations of the photochromic behavior

revealed that in all cases irradiation with UV light induces switching from SP to MC inside the different MOF pores.<sup>[9]</sup>

During this beam time high resolution powder diffraction data of all four compounds were collected at room temperature and 120 K. The patterns of SP@MIL-68(In), SP@MIL-68(Ga) and SP@MOF-5 were indexed and refined by the *Le Bail* method using the program *Jana2006*.<sup>[10]</sup> Some results are summarized in Table 1.

**Tab. 1:** Cell parameters obtained from *Le Bail* fits of SP@MIL-68(Ga), SP@MIL-68(In) and SP@MOF-5 at RT and 120 K.

Temperature / K	SP@MIL-68(Ga)		SP@MIL-68(In)		SP@MOF-5	
	298	120	298	120	298	120
SG (No.), Z	<i>Cmcm</i> (63), 12	<i>Cmcm</i> (63), 12	<i>Cmcm</i> (63), 12	<i>Cmcm</i> (63), 12	<i>Fm-3m</i> (225), 8	<i>Fm-3m</i> (225), 8
a / Å	21.079(3)	21.070(2)	21.8500(5)	21.8612(4)	25.7687(5)	25.7415(4)
b / Å	36.707(4)	36.680(2)	37.4227(8)	37.3897(7)	a	a
c / Å	6.7422(5)	6.7415(4)	7.2295(1)	7.2276(1)	a	a
V / Å <sup>3</sup>	5217(1)	5210.2(7)	5911.5(2)	5907.7(2)	17114.5(4)	17057.0(3)
V(Lit.) / Å <sup>3</sup>	5240(2) <sup>[11]</sup> (298 K)		5933.8(2) <sup>[11]</sup> (298 K)		16913.2(3) <sup>[12]</sup> (213 K)	
R <sub>p</sub> / wR <sub>p</sub>	0.2046 / 0.3254	0.1232 / 0.1713	0.1667 / 0.2484	0.1114 / 0.1544	0.2056 / 0.3234	0.1343 / 0.1811
GOF	0.91	0.93	0.97	1.16	0.89	0.99

Compared to the empty MOF<sup>[11]</sup> the cell volume of SP@MIL-68(In) and SP@MIL-68(Ga) is decreased. The shrinking of the unit cell might be caused by attractive guest-host interactions. However, the cell volume of SP@MOF-5 is increased, which might be induced by repulsive interactions between the spiropyrene and the host matrix. Further investigations on the exact localisation of the spiropyrene molecules inside the cavities to explain this behaviour is under way. This is obligatory to determine the occurring host-guest interactions and the resulting photochromic behaviour in more detail.

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