Supporting Information

Sorption behavior of an oriented surface-grown MOF-film studied by *in situ* X-ray diffraction

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Preparation of self-assembled monolayers on gold.

The gold-coated slides (glass slides (76 x 26 mm^2) coated with 10 nm Ti / 100 nm Au by electron-beam evaporation, Advalytix AG) were cut in smaller pieces (10 x 13 mm^2) cleaned in ethanol and methanol. The cleaned gold slides were immersed in a 1 mmol ethanolic solution (6 pieces in 30 ml) of 16-mercaptohexadecanoic acid (MHDA) (90 %, *Aldrich*) and left at RT for 48 h. The SAM-functionalized gold slides were repeatedly washed with ethanol, and stored in fresh absolute ethanol till needed.

Fe-MIL-53 synthesis mixture.

In a glass reactor, 0.2492 g (1.5 mmol) of 1,4-benzenedicarboxylic acid (98 %, Aldrich) were dissolved in 10 ml dimethylformamide (DMF) (p.a., *Acros Organics*). To the clear solution 0.2703 g (1 mmol) $FeCl_3 \cdot 6\,H_2O$ (p.a., *Merck*) was added. The sealed-glass reactor was left for 2 days in a preheated oven at 150 °C. After cooling the synthesis mixture to room temperature, the crystalline product was filtrated and stored for further characterization. The filtrated solution was filled into a glass reactor and left for 5 days in a preheated oven at 150 °C. The clear solution was cooled down to room temperature and used for growth of thin films.

Thin-films growth.

The SAM-functionalized gold-slides were placed upside-down on Teflon®-supports into the previous prepared crystallization solution (3 pieces in 10 ml). The growth step takes place at RT in a closed glass reactor. Immersion times were varied between 16 h to16 d.

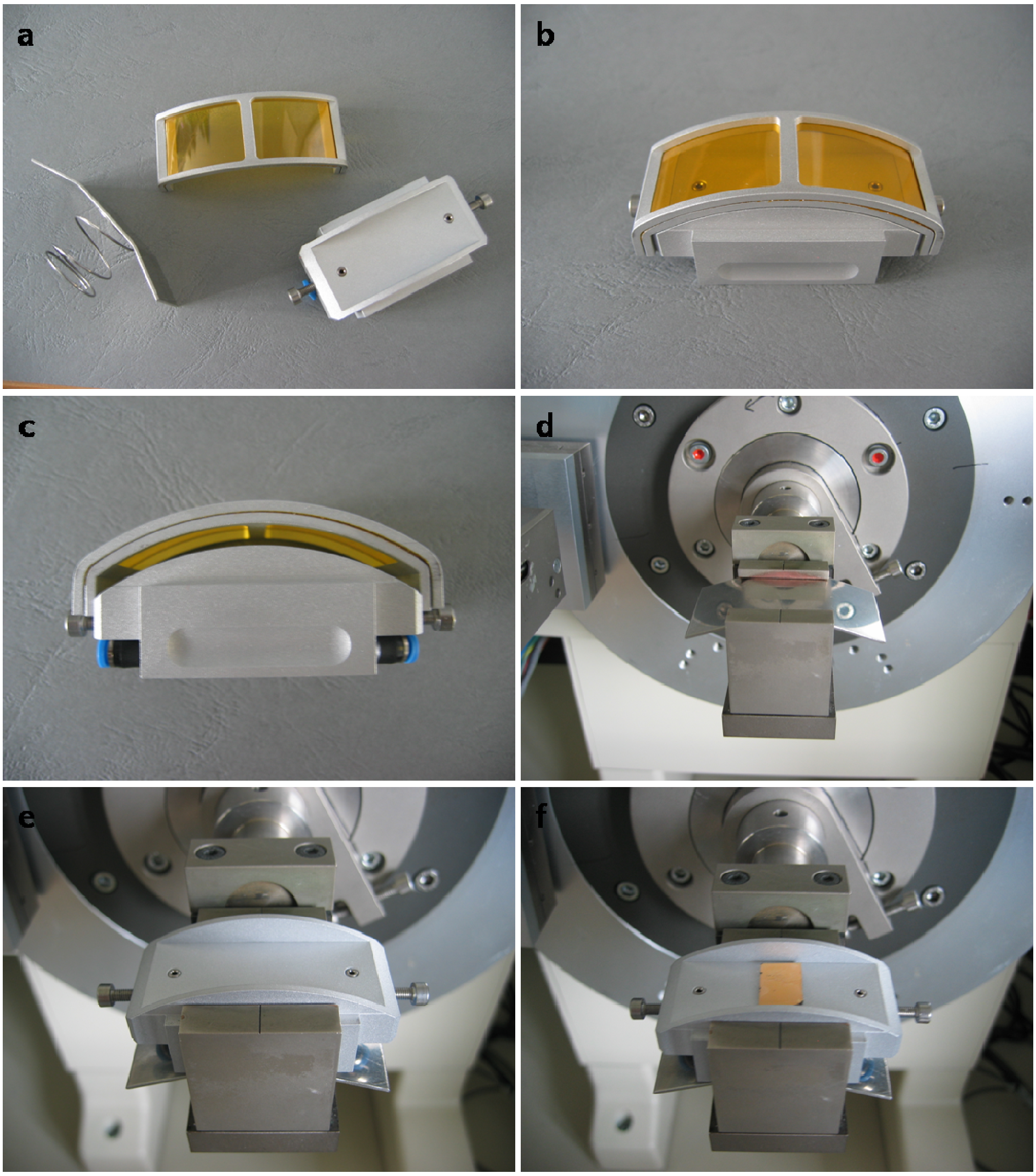

Figure S1. Pictures of sample cell for Sorption@XRD measurements (a-c) and the positioning of the cell into the Scintag XDS 2000 X-ray diffractometer (d-f).

Experimental setup of the flow controlling system

The flow controlling system consists of mainly three parts: the gas flow controller system, the liquid mass flow controller and the controlled evaporation mixer (CEM) (Figure S1).

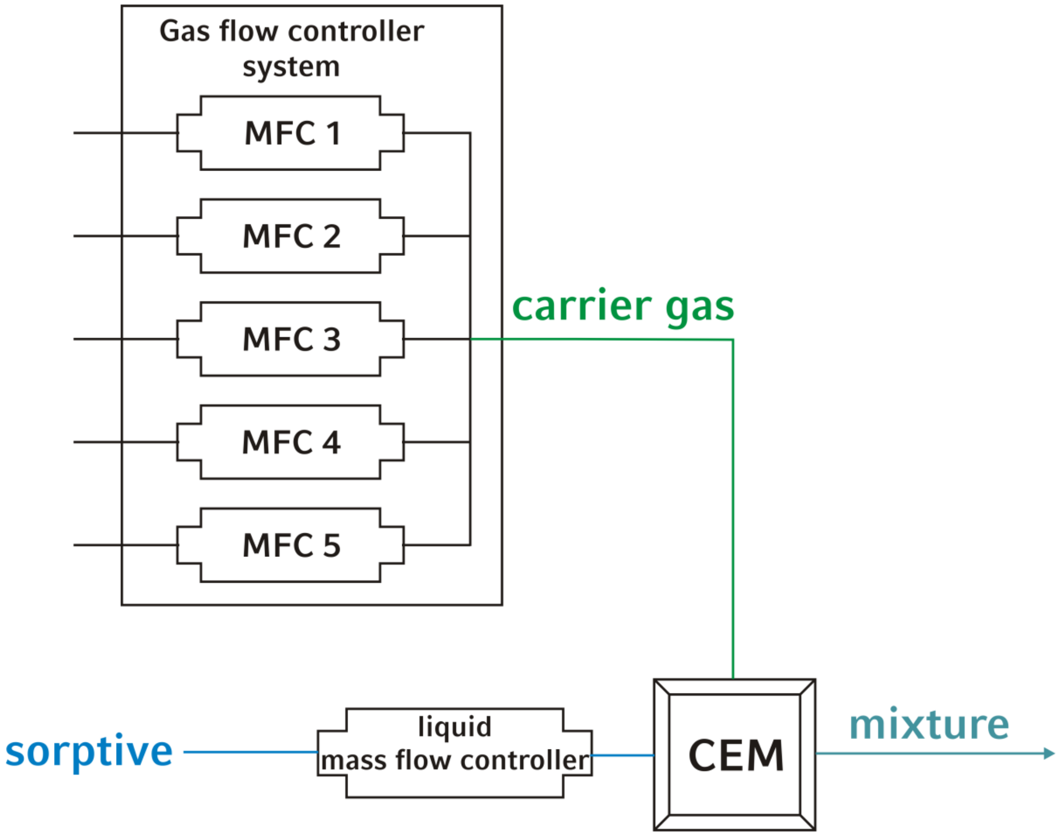

Figure S2. Experimental setup of the flow controlling system employed in this work, consisting of the gas flow controlling system, a liquid mass flow controller and a controlled evaporation mixer (CEM).

The liquid mass flow controller purchased from *Bronkhorst High-Tech, Netherlands* delivers a maximum flow of 1 g/h if water is used as sorptive. The liquid conversion factor to calculate the maximum flow of the particular sorptive is taken from the official *Bronkhorst* web page.[1] In the setup, a reservoir of the particular liquid is connected to the liquid MFC and nitrogen is used to ensure continuous flow from the reservoir to the flow controller.

The central unit, for ensuring the accurate mixing of the carrier gas and the sorptive is the CEM (Label C2, Node 1). In this unit the liquid analyte and the carrier gas are mixed and heated above the specific boiling point of the liquid to ensure a homogeneous mixture of both components.

The settings for the MFCs for the carrier gas and the sorptive were calculated assuming van-der-Waals behaviour to take into account the repulsive and attractive molecular interactions and the non-zero volume taken up by the molecules themselves. Van-der-Waals parameters for the solvents were taken from reference 2.

Table S1. Two theta values of the (002) and (101) reflections and resulting lattice parameters (lp) *a* and *c*. The theoretical value for the reflection position of (100) is calculated and compared to the observed value.

p/p_0	$2\theta_{002}$ / °	d_{002}	parameter *c*	$2\theta_{101}$ / °	d_{101}	parameter *a*	d_{100} (calc.)	$2\theta_{100}$ / ° (calc.)	$2\theta_{100}$ / ° (obs.)
0.00	9.13	9.678	19.357	12.03	7.351	9.176	7.946	11.126	11.15
0.04	9.15	9.657	19.314	11.83	7.475	9.361	8.106	10.905	10.91
0.09	9.15	9.657	19.314	11.74	7.532	9.445	8.179	10.808	10.81
0.14	9.15	9.657	19.314	11.63	7.603	9.550	8.271	10.688	10.69
0.19	9.15	9.657	19.314	11.57	7.642	9.609	8.321	10.623	10.63
0.24	9.15	9.657	19.314	11.53	7.669	9.648	8.355	10.579	10.59
0.28	9.15	9.657	19.314	11.51	7.682	9.668	8.373	10.558	10.57
0.33	9.21	9.594	19.189	10.75	8.223	10.509	9.101	9.710	9.71
0.38	9.21	9.594	19.189	10.73	8.238	10.533	9.122	9.688	9.71
0.43	9.21	9.594	19.189	10.73	8.238	10.533	9.122	9.688	9.69
0.47	9.21	9.594	19.189	10.73	8.238	10.533	9.122	9.688	9.69
0.52	9.21	9.594	19.189	10.73	8.238	10.533	9.122	9.688	9.69
0.57	9.21	9.594	19.189	10.71	8.254	10.557	9.143	9.666	9.67
0.62	9.21	9.594	19.189	10.71	8.254	10.557	9.143	9.666	9.67
0.67	9.23	9.574	19.147	10.69	8.269	10.587	9.168	9.639	9.67
0.72	9.23	9.574	19.147	10.67	8.285	10.611	9.189	9.617	9.63
0.76	9.23	9.574	19.147	10.67	8.285	10.611	9.189	9.617	9.63
0.81	9.29	9.512	19.024	10.3	8.581	11.103	9.615	9.190	-
0.86	9.29	9.512	19.024	10.29	8.590	11.116	9.627	9.179	-
0.90	9.29	9.512	19.024	10.29	8.590	11.116	9.627	9.179	-
0.95	9.29	9.512	19.024	10.29	8.590	11.116	9.627	9.179	-
0.91	9.29	9.512	19.024	10.29	8.590	11.116	9.627	9.179	-
0.87	9.29	9.512	19.024	10.29	8.590	11.116	9.627	9.179	-
0.82	9.29	9.512	19.024	10.29	8.590	11.116	9.627	9.179	-
0.77	9.29	9.512	19.024	10.29	8.590	11.116	9.627	9.179	-
0.73	9.29	9.512	19.024	10.29	8.590	11.116	9.627	9.179	-
0.68	9.29	9.512	19.024	10.33	8.557	11.062	9.580	9.224	-
0.63	9.29	9.512	19.024	10.37	8.524	11.009	9.534	9.268	-
0.58	9.23	9.574	19.147	10.73	8.238	10.538	9.126	9.683	9.67
0.53	9.23	9.574	19.147	10.73	8.238	10.538	9.126	9.683	9.69
0.49	9.23	9.574	19.147	10.73	8.238	10.538	9.126	9.683	9.69
0.44	9.23	9.574	19.147	10.75	8.223	10.514	9.106	9.705	9.71
0.39	9.23	9.574	19.147	10.75	8.223	10.514	9.106	9.705	9.71
0.34	9.23	9.574	19.147	10.75	8.223	10.514	9.106	9.705	9.69
0.29	9.23	9.574	19.147	10.77	8.208	10.491	9.085	9.728	9.73
0.24	9.23	9.574	19.147	10.78	8.200	10.479	9.075	9.739	9.77
0.19	9.23	9.574	19.147	10.79	8.193	10.467	9.064	9.750	9.73
0.14	9.21	9.594	19.189	10.81	8.178	10.438	9.040	9.777	9.810
0.09	9.19	9.615	19.231	10.87	8.133	10.363	8.975	9.847	9.83
0.05	9.17	9.636	19.272	11.71	7.551	9.477	8.207	10.771	10.81
0.00	9.14	9.668	19.336	11.97	7.388	9.231	7.994	11.059	11.15

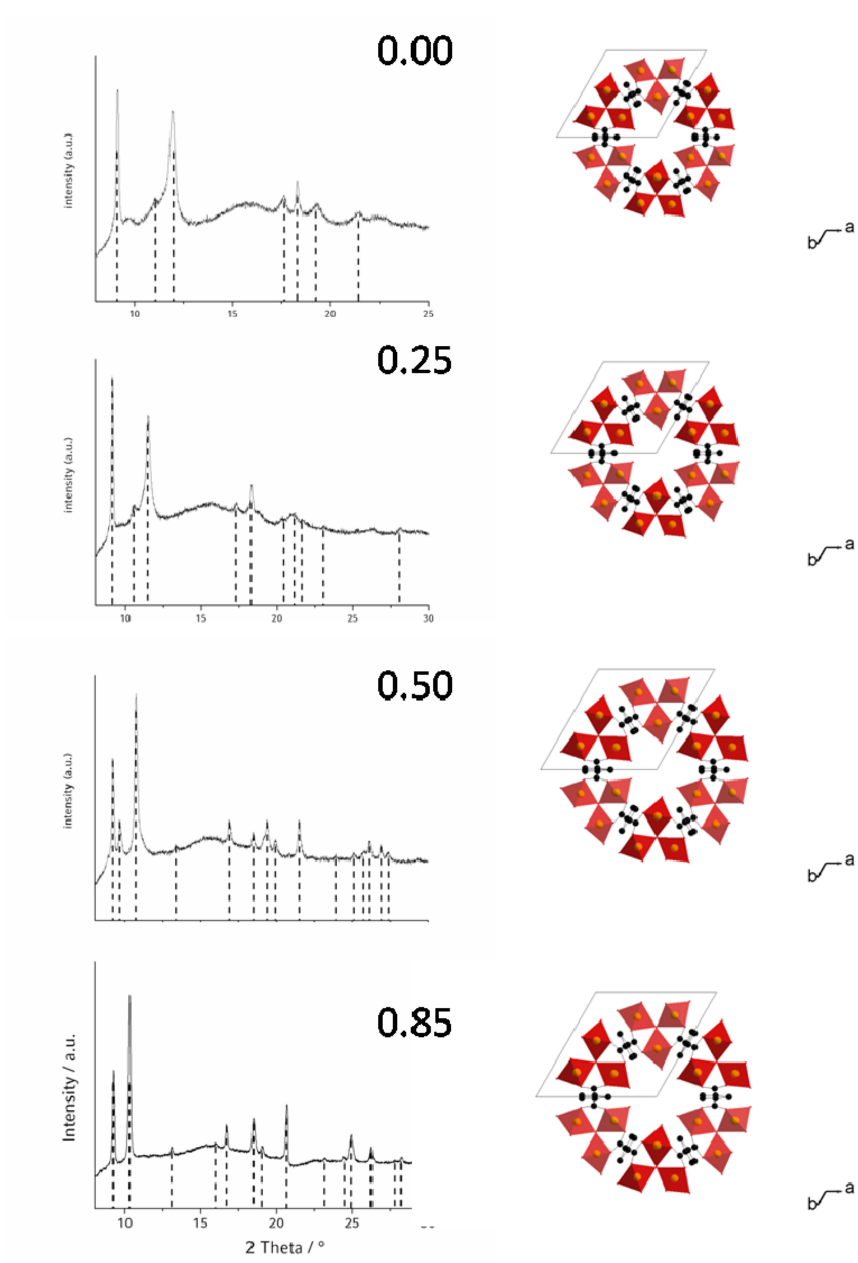

Figure S3. Comparison of the measured X-ray patterns under the given relative pressures with the simulated patterns. Parameters of indexation are given in Table 1. The size of the unit cell as a function of relative pressure is depicted schematically.

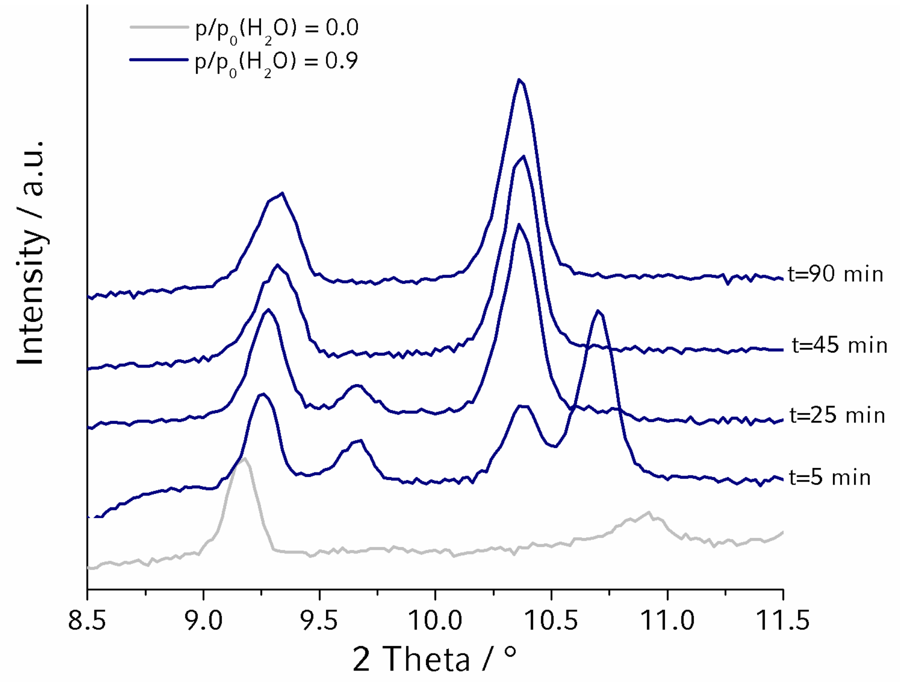

Figure S4. Evolution of structural changes of dry MIL-88B exposed to a relative pressure of water of 0.9.

(1) Bronkhorst FLUIDAT® on the Net. http://www.fluidat.com

(2) Lide, D., *Handbook of Chemistry and Physics*. CRC Press: 2004-2005.