Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

Implementing chemical functionality into oriented films of metal-organic frameworks on self-assembled monolayers

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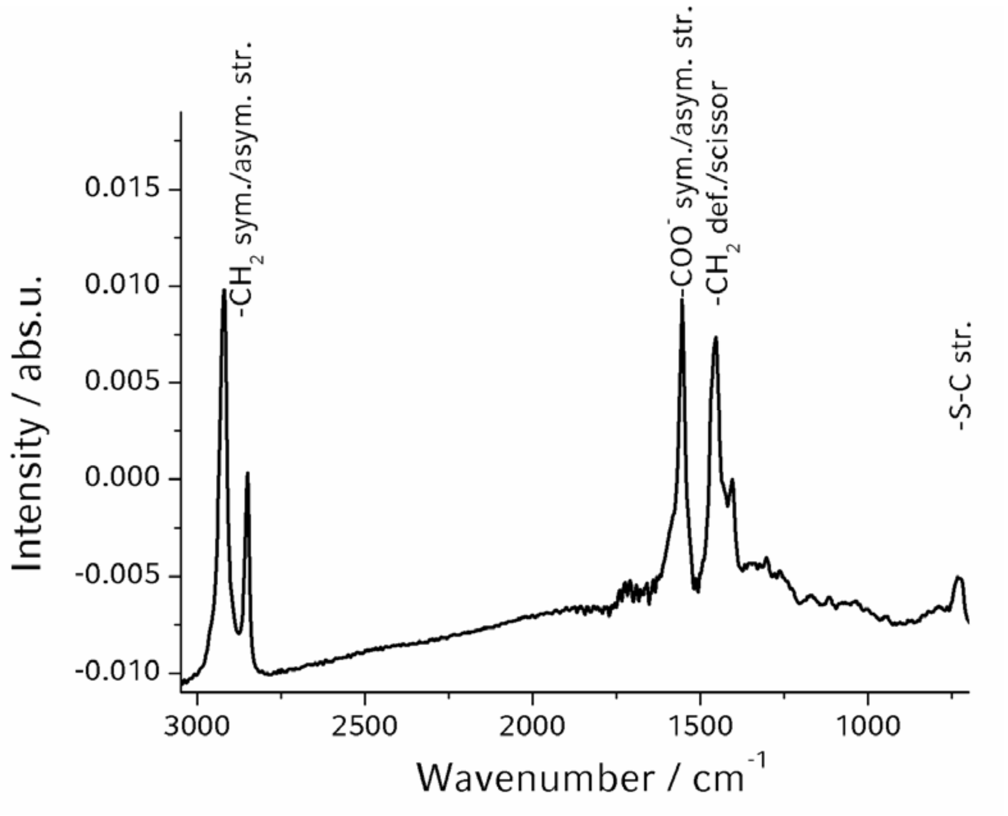

Figure S1: RAIR-spectrum of the MHDA self-assembled monolayer on a gold substrate.

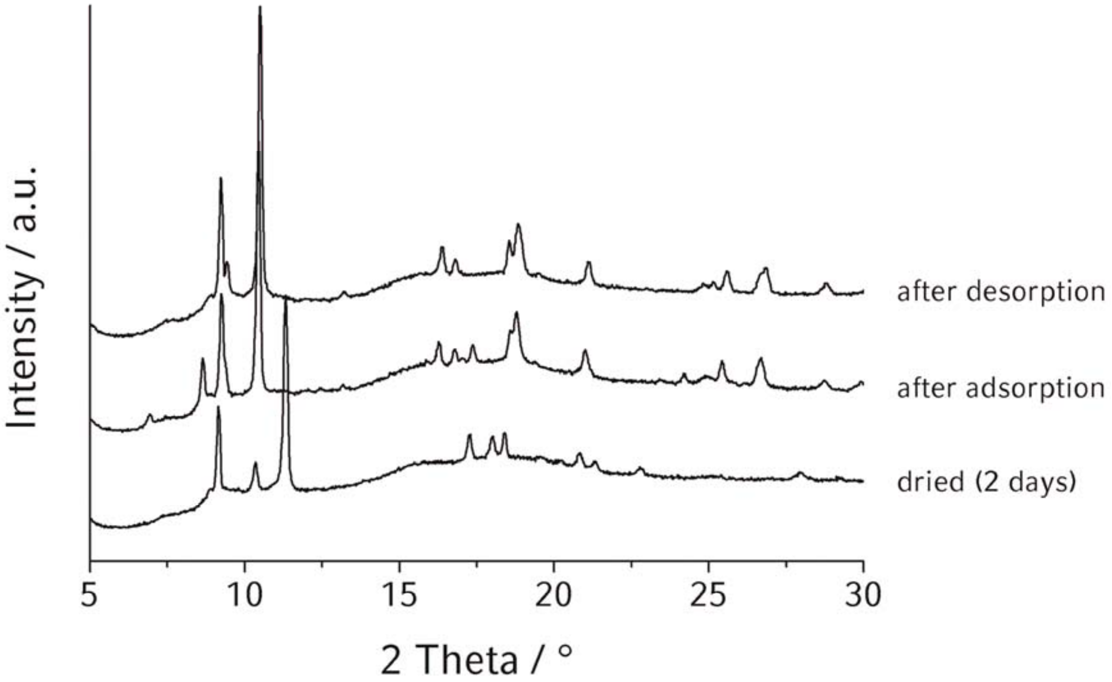

Figure S2: XRD pattern of the ethanolic form of bulk NH_2-Fe-MIL-88B crystals showing the effect of extended drying.

Table S1 Lattice parameter *c* of Fe-MIL-88B after indexing using Werner algorithm for different relative pressures of ethanol.

p/p_0	**2 Theta**	**lattice-parameter *c* / $Å^3$**
0,00	**9,18**	**19,3**
0,02	**9,22**	**19,2**
0,20	**9,23**	**19,2**
0,40	**9,24**	**19,1**
0,60	**9,24**	**19,1**
0,80	**9,25**	**19,1**
0,60	**9,24**	**19,1**
0,40	**9,23**	**19,1**
0,20	**9,22**	**19,2**
0,02	**9,22**	**19,2**
0,00	**9,18**	**19,3**

Table S2 Lattice parameter *c* of NH_2-Fe-MIL-88B after indexing using Werner algorithm for different relative pressures of ethanol.

p/p_0	2 Theta	lattice-parameter *c* / $Å^3$
0,00	9,09	19,4
0,02	9,10	19,4
0,20	9,12	19,4
0,40	9,19	19,2
0,60	9,22	19,2
0,80	9,24	19,1
0,60	9,24	19,1
0,40	9,23	19,2
0,20	9,22	19,2
0,02	9,20	19,2
0,00	9,16	19,3

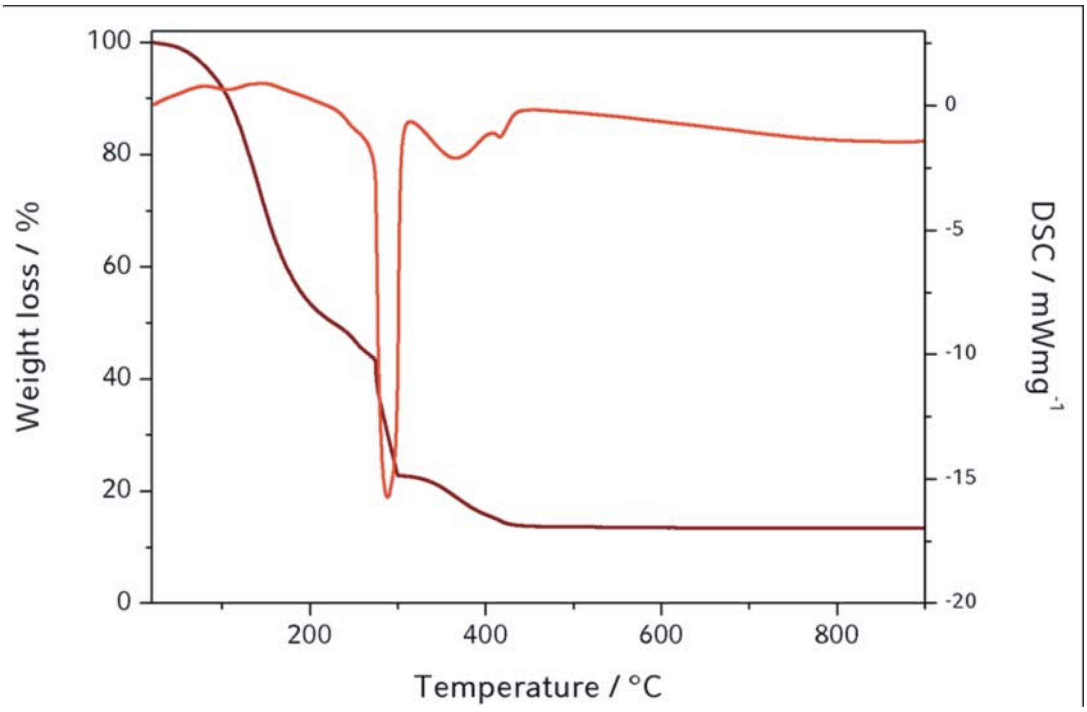

Figure S3: TGA and DSC data of NH_2-Fe-MIL-101. The first step of 56 wt. % in the TGA is assigned to the loss of solvent and water molecules from inside the pores. The decomposition of the organic parts of NH_2-MIL-101 subsequently takes place above 250 °C within two steps, which can also be seen in the differential scanning calorimetry (DSC) in red. These two steps show a weight loss of 30 % and of 70 % corresponding to the crystals with filled pores and those with empty pores, respectively. This 70 % weight loss is in good agreement with the weight fraction of the organic parts of NH_2-Fe-MIL-101 ($Fe_3O(NH_2BDC)_3$), which can be calculated as 75 wt. %.

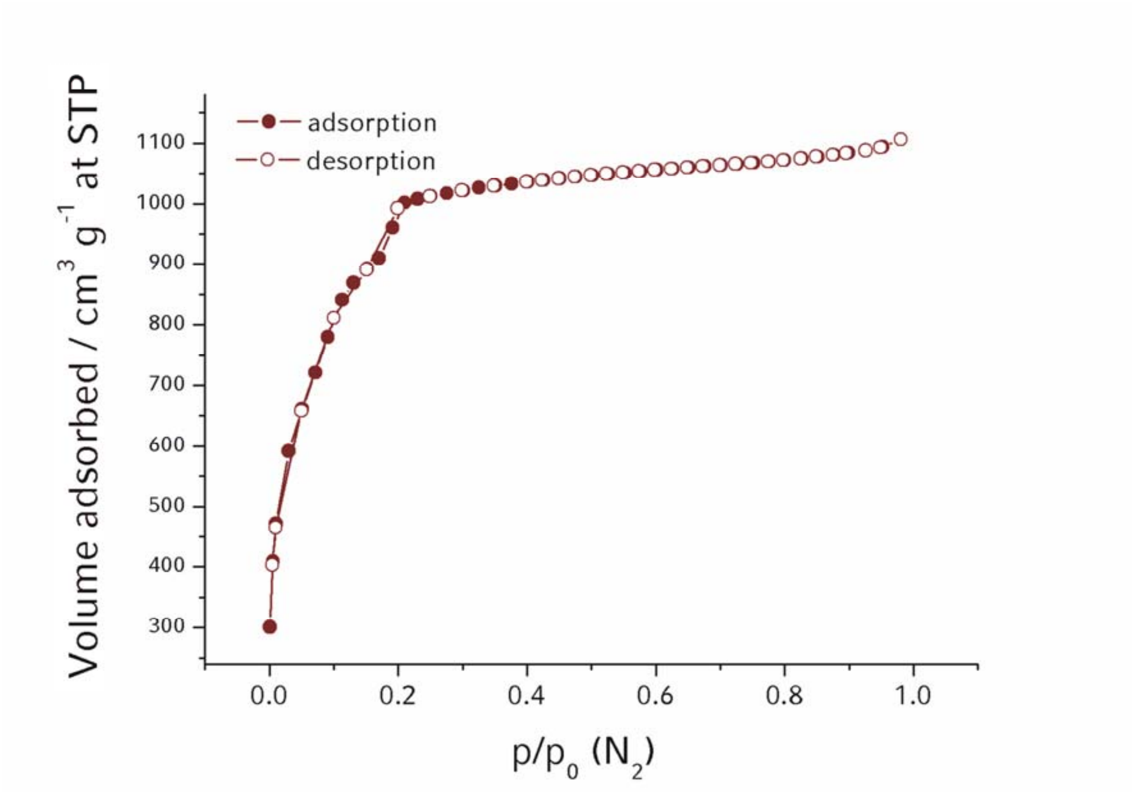

Figure S4: Nitrogen sorption isotherm at 77 K for bulk NH_2-Fe-MIL-101. The Type I isotherm of the amino-functionalized NH_2-Fe-MIL-101 is very similar to the isotherm of the unfunctionalized compound reported in the literature. The shapes of the isotherms are nearly identical, both providing a small step in the adsorption curve at 0.2 p/p_0. The overall adsorbed volume of nitrogen is slightly smaller for NH_2-Fe-MIL-101 than for MIL-101, which can be attributed to the amino groups present in the framework. The fact that the adsorption capacity of the material is only slightly reduced by the amino functionalization is of interest for thin film growth and for possible applications of these functionalized MOF thin films.

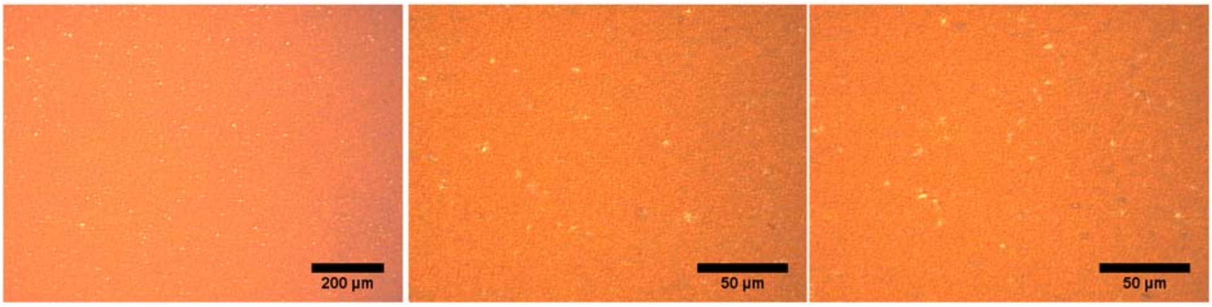

Figure S5: Optical light microscope images of NH_2-MIL-88B thin films with different magnifications (**left**: x10 objective, **middle**: x50, **right**: x50) illustrating the formation of homogeneous and densely packed thin films. No obvious cracks are visible prior to an exposure to vacuum.

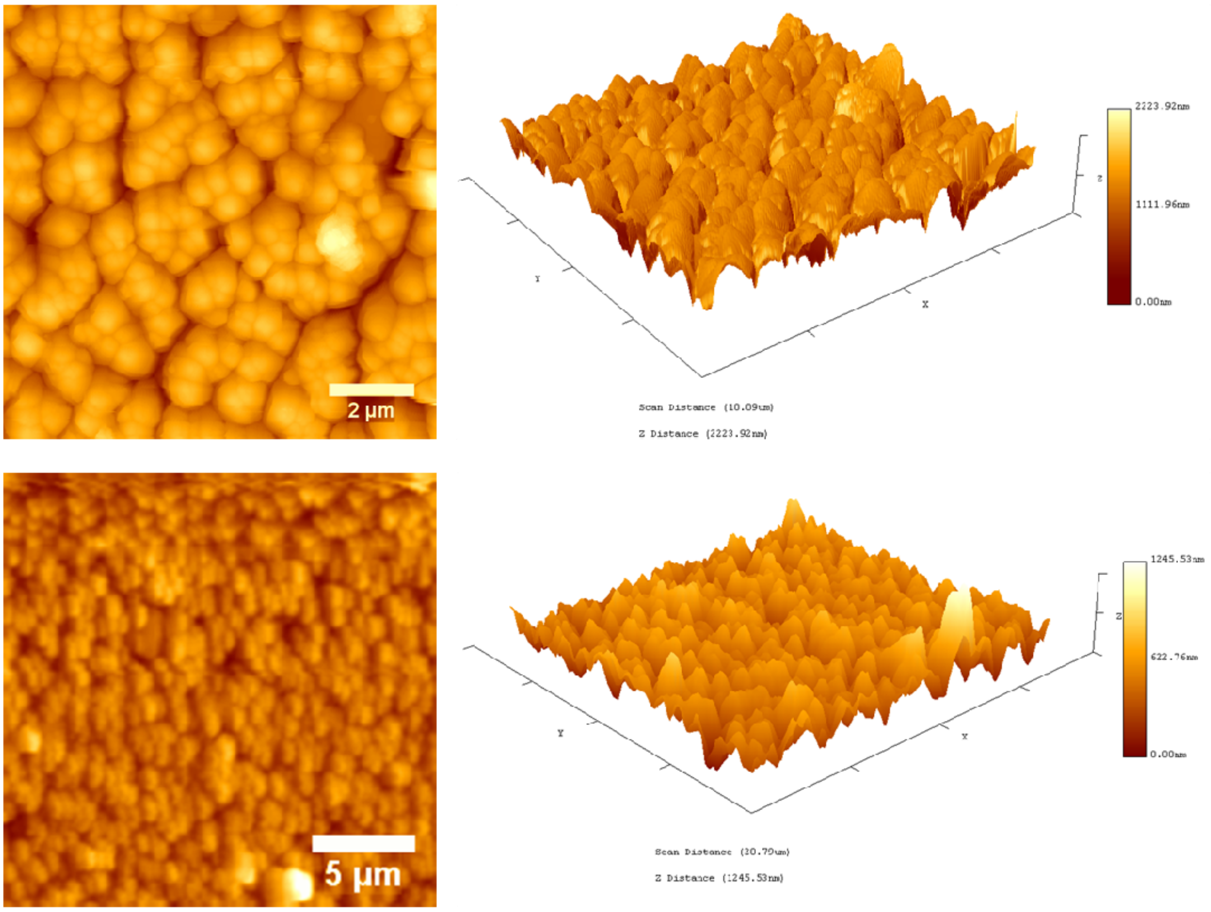

Figure S6: Atomic force micrographs of NH_2-MIL-88B thin films prepared from the batch containing a HCl content of Fe^{3+} : HCl = 1 : 0.5. The AFM images show a rather dense layer of intergrown NH_2-MIL-88B crystals completely covering the gold surface (**left column:** top view image; **right column:** hight field image). AFM pictures are displayed for two differently scaled sections (**top:** 10 µm, **bottom:** 20 µm).

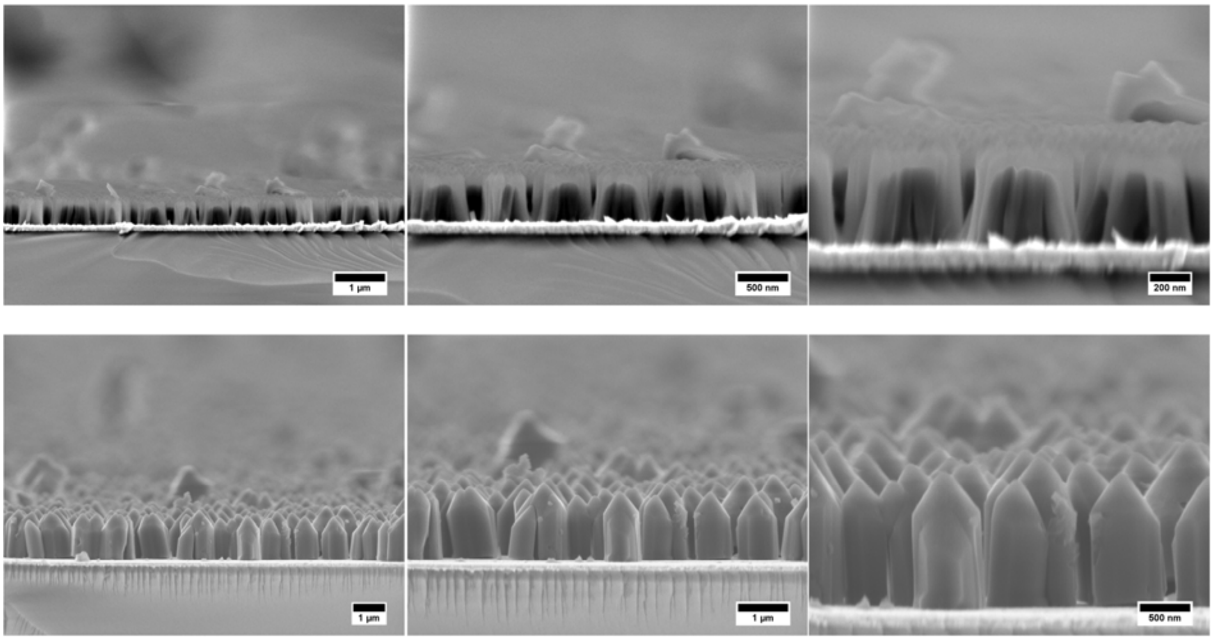

Figure S7: Scanning electron micrographs of NH_2-MIL-88B thin films grown from crystallization solutions with different HCl content (**top:** Fe^{3+} : HCl = 1 : 1; **bottom:** Fe^{3+} : HCl = 1 : 0.5). The immersion time of the substrates in the crystallization solution was 11 days for both samples. The film thickness obviously depends on the different experimental conditions. As revealed by the cross-sections, an almost three-fold thicker layer of NH_2-MIL-88B crystals is obtained for the batch prepared with Fe^{3+} : HCl = 1 : 0.5.

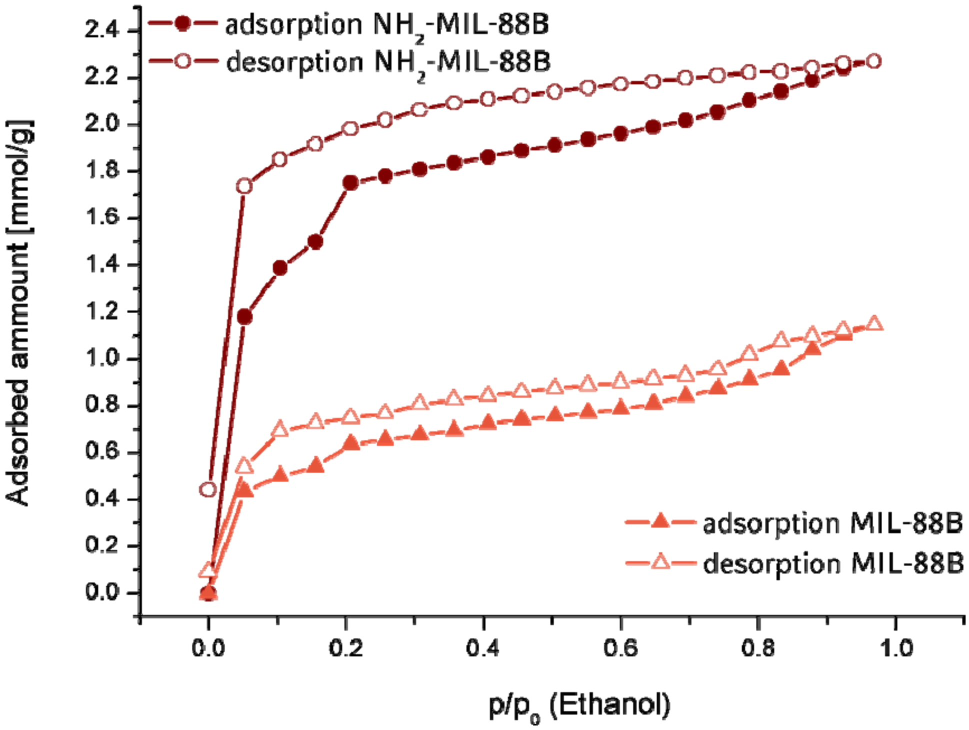

Figure S8: Reproduced sorption experiments showing the ethanol uptake of Fe-MIL-88B and NH_2-Fe-MIL-88B thin films, recorded with a quartz crystal microbalance at room temperature. The adsorbed amount of ethanol up to a relative pressure of 0.16 is almost three times as much as for the unfunctionalized counterpart. The fact that the isotherms are not closing completely is attributed to very long equilibration times for the last desorption step.

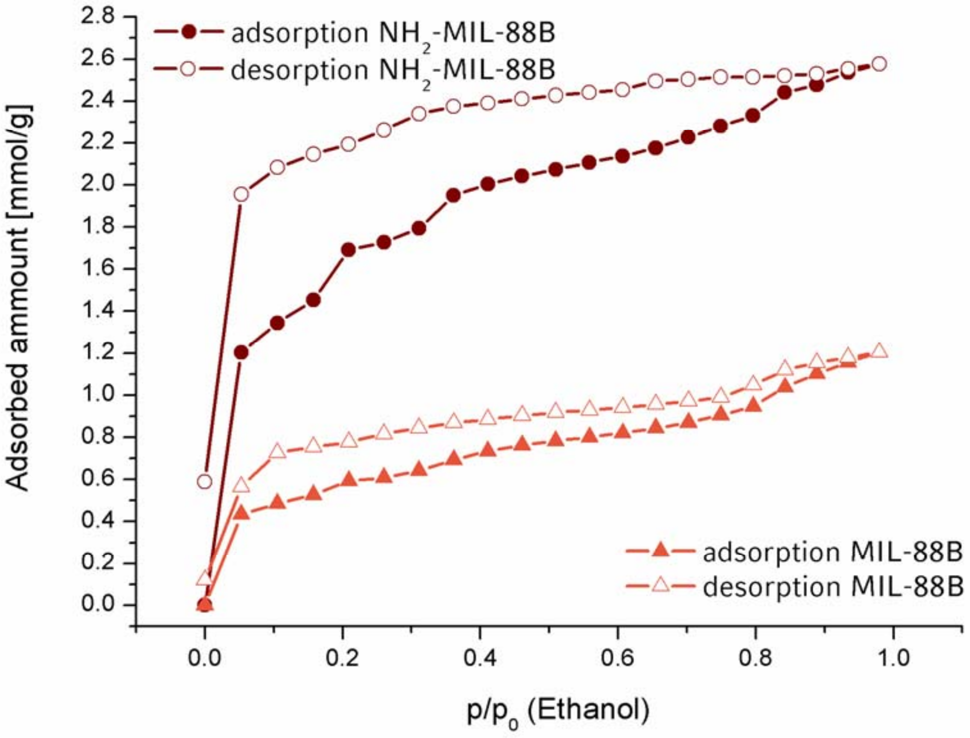

Figure S9: Ethanol sorption isotherms of Fe-MIL-88B and NH_2-Fe-MIL-88B thin films providing evidence for the reproducibility of the quartz crystal microbalance experiment at room temperature. The fact that the isotherms are not closing completely is attributed to very long equilibration times for the last desorption step.