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Electronic Supporting Information

Comment on "Insight into the reversible structural crystalline-state transformation from MIL-53(AI) to MIL-68(AI)" by A. Perea-Cachero, E. Romero, C. Téllez and J. Coronas, *CrystEngComm*, 2018, **20**, 402

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Chemicals

 $Al(NO_3)_3$ 9H₂O (99.6 %, VWR Chemicals), terephthalic acid (98 %, Merck), N,N-dimethylformamide (>99 %, VWR Chemicals) and AlCl₃ 6H₂O (99 %, Alfa Aesar) were used as purchased without further purification.

Synthesis and activation of MIL-53(AI)

MIL-53(Al) was synthesized as reported in literature¹ with minor modification regarding the synthesis time. 13.29 g of Al(NO₃)₃ 9H₂O (34.72 mmol) was dissolved in 50 ml of deionized water. 2.91 g of terephthalic acid (17.36 mmol) was added to the solution. The synthesis was performed in a teflon-lined 125 ml autoclave which was placed in a preheated oven at 220 °C. After 36 h synthesis time, the autoclave was taken out of the oven and cooled down to room temperature. The sample was isolated by filtration followed by washing with deionized water (3 x 50 ml) and 50 ml acetone.

The synthesis yielded MIL-53*as* (*as synthesized*) with unreacted terephthalic acid trapped inside of the pores. Subsequently, the unreacted linker was removed by extraction² with DMF at 120 °C for 24 h. The sample was filtered off and washed with acetone three times. Finally, the product was placed in a vacuum oven at 150 °C to remove solvent residues.

Synthesis attempt of MIL-68(AI)

The synthesis was performed by following the synthesis protocol reported by Yang et al.³. 1.63 g of AlCl₃ $6H_2O$ (6.68 mmol) and 1.68 g terephthalic acid (10.02 mmol) were dissolved in 100 ml of DMF. The synthesis was performed for 18.5 h at 130 °C in a round bottom flask equipped with a reflux condenser. The sample was filtered off and washed three times with 50 ml of DMF. Finally the sample was dried at room temperature.

This attempt mainly yielded MIL-53 with a minor MIL-68 side phase, which can be clearly identified by the reflection at 4.88 ° (Figure 3 of the main text). Since we did not further remove the DMF from the sample pores, Figure 3 of the main text depicts MIL-53 with DMF inside of the pores, denoted as MIL-53DMF.

Measurement of PXRD patterns and indexing of the MIL-53(AI)DMF pattern

All PXRD patterns were collected on a PANalytical EMPYREAN diffractometer in Bragg-Brentano geometry (θ - θ) equipped with a pixcel^{3D} line detector. The X-ray source was operated at 40 kV and 40 mA providing Cu K α_1 radiation ($\lambda = 1.5406$ Å).

The PXRD pattern of MIL-53(AI)*DMF* was indexed using the Pawley method within the software HighScore Plus. As a starting point, we assumed the monoclinic space group C2/c (no. 15) and unit cell parameters previously reported for MIL-53(Fe)*DMF*⁴. The peak shape and background fitting was carried out by a Pseudo Voigt function. Table S1 summarizes the obtained unit cell parameters for MIL-53(AI)*DMF* in comparison to the reported unit cell parameters for MIL-53(Fe)*DMF*⁴, MIL-53(AI)*It* and MIL-53(AI)ht^{1, 5}.

	Space group	a / Å	b / Å	c / Å	β/°	Ref.
MIL-53(AI) <i>DMF</i>	C2/c	18.875	11.591	6.621	111.804	This work
MIL-53(Fe)DMF	C2/c	19.068	11.2869	6.8685	108.925	4
MIL-53(Al) <i>lt</i>	Сс	19.513	7.612	6.576	104.24	1
MIL-53(Al) <i>lt*</i>	C2/c	19.633	7.160	6.559	104.29	5
MIL-53ht	Imma	6.6085	16.675	12.813	90	1
MIL-53 <i>ht</i>	Imma	6.6295	16.7322	12.8357	90	5

Table S1 Unit cell parameters of MIL-53(AI)DMF, MIL-53(Fe)DMF, MIL-53(AI)/t and MIL-53(AI)ht.

* phase transition induced by mechanical pressure

Figure S1 depicts the Pawley-fit as well as the Bragg positions. The obtained hkl planes are summarized in Table S2.



Fig. S1 Pawley-fit of the MIL-53*DMF* PXRD pattern. Measured pattern (black), calculated pattern (red) and difference curve (blue). Allowed Bragg positions are marked by vertical black bars.

h	k	Ι	20 / °	d-spacing / Å	h	k	Ι	20/°	d-spacing / Å
1	1	0	9.116	9.693	3	3	0	27.635	3.225
2	0	0	10.063	8.783	3	1	-2	28.348	3.146
0	2	0	15.252	5.805	3	3	-1	28.469	3.133
1	1	-1	15.378	5.757	1	1	-2	28.566	3.122
3	1	0	16.959	5.224	4	0	-2	28.570	3.122
3	1	-1	18.256	4.856	1	3	1	28.687	3.109
2	2	0	18.315	4.840	0	0	2	29.002	3.076
1	1	1	18.585	4.770	6	0	0	30.559	2.923
4	0	0	20.229	4.386	0	4	0	30.808	2.900
2	2	-1	20.880	4.251	2	2	-2	31.068	2.876
0	2	-1	21.026	4.222	5	1	-2	31.678	2.822
0	2	1	21.026	4.222	1	1	2	32.268	2.772
1	3	0	23.536	3.777	6	2	-1	32.490	2.754
4	2	-1	25.264	3.522	2	4	0	32.494	2.753
5	1	-1	25.277	3.521	4	2	-2	32.549	2.749
4	2	0	25.442	3.498	0	2	-2	32.934	2.717
2	2	1	25.627	3.473	0	2	2	32.934	2.717
3	1	1	25.760	3.456	4	2	1	32.972	2.714
5	1	0	26.524	3.358	6	0	-2	33.518	2.671
1	3	-1	26.669	3.340	5	3	-1	33.525	2.671
2	0	-2	26.892	3.313	3	3	1	33.900	2.642

Table S2 hkl planes, Bragg positions and d-spacings obtained from the Pawley-fit

Table S2 (continued)

h	k	Ι	2θ / °	d-spacing / Å	h	k	Ι	2θ / °	d-spacing / Å
2	4	-1	34.063	2.630	7	3	0	42.992	2.102
7	1	-1	34.112	2.626	1	1	-3	43.153	2.095
0	4	-1	34.156	2.623	8	2	-2	43.699	2.070
0	4	1	34.156	2.623	9	1	-1	43.887	2.061
2	0	2	34.265	2.615	7	3	-2	43.911	2.060
6	2	0	34.331	2.610	6	4	0	43.957	2.058
5	3	0	34.499	2.598	4	2	-3	44.051	2.054
5	1	1	34.665	2.586	8	2	0	44.138	2.050
3	3	-2	35.956	2.496	2	2	-3	44.275	2.044
1	3	-2	36.133	2.484	7	1	1	44.484	2.035
7	1	0	36.671	2.449	4	2	2	44.596	2.030
4	4	-1	37.019	2.426	3	3	2	44.657	2.028
6	2	-2	37.022	2.426	9	1	-2	45.560	1.989
4	4	0	37.145	2.418	6	4	-2	46.174	1.964
2	4	1	37.278	2.410	5	5	-1	46.180	1.964
2	2	2	37.708	2.384	7	1	-3	46.262	1.961
7	1	-2	37.717	2.383	6	2	-3	46.326	1.958
3	1	2	38.560	2.333	3	5	1	46.468	1.953
5	3	-2	38.703	2.325	5	1	2	46.572	1.949
1	5	0	39.142	2.300	2	4	2	46.749	1.942
1	3	2	39.201	2.296	5	5	0	46.930	1.934
8	0	-2	40.686	2.216	0	2	-3	46.971	1.933
7	3	-1	40.772	2.211	0	2	3	46.971	1.933
8	0	0	41.151	2.192	0	6	0	46.974	1.933
1	5	-1	41.203	2.189	1	1	3	47.121	1.927
5	3	1	41.248	2.187	9	1	0	47.275	1.921
8	2	-1	41.262	2.186	3	3	-3	47.384	1.917
2	4	-2	41.355	2.181	3	5	-2	48.071	1.891
3	1	-3	41.608	2.169	2	6	0	48.173	1.887
4	0	2	41.635	2.167	1	5	-2	48.210	1.886
6	2	1	41.811	2.159	5	3	-3	48.367	1.880
3	5	0	41.868	2.156	1	3	-3	48.784	1.865
3	5	-1	42.452	2.128	10	0	-2	49.310	1.847
6	4	-1	42.477	2.126	2	6	-1	49.319	1.846
4	4	-2	42.524	2.124	0	6	-1	49.387	1.844
1	5	1	42.607	2.120	0	6	1	49.387	1.844
5	1	-3	42.694	2.116	9	3	-1	49.452	1.842
0	4	-2	42.831	2.110	8	4	-1	49.777	1.830
0	4	2	42.831	2.110	7	3	1	49.998	1.823
4	4	1	42.861	2.108					

Calculation of the MIL-53DMF pore geometry

A lozenge-shaped geometry model previously described in literature^{4, 6} was assumed to describe the pore geometry of MIL-53. The most prominent reflection in the MIL-53*DMF* pattern at 9.116 ° (Figure S1) corresponds to the (110) plane (space group *C2/c* for MIL-53*DMF*⁴). This plane describes the edges of the lozenge. By using the Bragg equation, the distance $d_{(110)}$ between two parallel edges can be calculated. For MIL-53*DMF*, the diffraction angle at 9.116 ° corresponds to a d-spacing of 9.693 Å. The parameter $L_{Lozenge} = 10.606$ Å was adopted from literature⁶. The angle α_L can now be calculated:

$$\alpha_{L} = \arcsin^{[ii]} \left(\frac{d_{(110)}}{L_{Lozenge}} \right)$$

The diagonals of the lozenge W and H can be calculated by the following two equations:

$$W = 2L_{Lozenge} \cdot cos\left(\frac{\alpha_L}{2}\right)$$
$$H = 2L_{Lozenge} \cdot sin\left(\frac{\alpha_L}{2}\right)$$

Table S3 depicts the calculated values and those reported in literature for the adsorption of DMF in MIL-53.

Table S3 Calculated angles and diagonals for MIL-53(AI) DMF and MIL-53(Fe)DMF⁴.

Reference	α, / °	β <i>ι</i> / °	W / Å	H / Å	H/W
This work	66.05	113.95	17.785	11.561	0.650
Ref. 4	64.08	115,92	-	-	0.626



Fig. S3 Illustration of the MIL-53 pore geometry as lozenge-shaped geometric model as proposed by Millange et al.⁴.

Infrared spectra of MIL-53DMF and MIL-53lt



Fig. S3 Infrared spectra of the MIL-53*lt* and MIL-53*DMF* (a) from 1800 to 400 cm⁻¹ and (b) magnification showing the range from 1700 to 1350 cm⁻¹.

The infrared spectrum of MIL-53*DMF* (Figure S3) exhibits an additional band at 1672 cm⁻¹ which is assigned to the C=O stretching mode of adsorbed DMF². Furthermore the $\delta(\mu$ -OH) bending is disturbed in the presence of DMF. Figure S3 (b) shows the shift of the BDC carboxylate vibrational bands^{1, 7}. Both asymmetric stretching bands are shifted to higher energies whereas only one of the two symmetric vibrational bands is influenced when DMF is adsorbed in the pores. Table S4 summarizes the band positions of the four carboxylate stretching vibrations.

Table S4 Vibrational modes and band positions of the four carboxylate stretching vibrations of the terephthalate linker in MIL-53.

	MIL-53 <i>lt</i> (narrow pore)	MIL-53 <i>DMF</i>
Vibrational mode	band position / cm ⁻¹	band position / cm ⁻¹
v _{as} (COO)	1573	1601
v _{as} (COO)	1504	1508
v _s (COO)	1406	1412
v _s (COO)	1443	1443



Fig. S4 Thermogravimetric curves (solid lines) and derivatives (dashed lines) of MIL-53*lt* and MIL-53*DMF*. 5 K min⁻¹ heating rate in air.

Figure S4 shows the TG curves of MIL-53*lt* and MIL-53*DMF*. The weight loss below 75 °C for MIL-53*lt* corresponds to the desorption of water adsorbed from the atmosphere. MIL-53*DMF* reveals a weight loss of approximately 26 wt.-% up to 200 °C which is related to the desorption of DMF from the pores. Both samples thermally decompose at temperatures above 550 °C.

SEM Images of MIL-53 prior and after immersion in DMF



Fig. S5 SEM images of activated MIL-53 (a-b) and after immersion for 3 d in DMF at 130 °C (c-d).

Some crystals of hydrothermally synthesized and activated MIL-53 (Fig. S5 (a-b)) reveal a certain elongated shape which is characteristic for preferred orientation. After stirring the particles in DMF for three days (Fig. S5 (c-d)), they were ground by mechanical forces. Consequently, the morphology changed from rod-shaped to rather cubic crystals.

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