SUPPORTING INFORMATION

Rapid and Reversible Formation of a Crystalline Hydrate of a Metal-Organic Framework Containing a Tube of Hydrogen-Bonded Water

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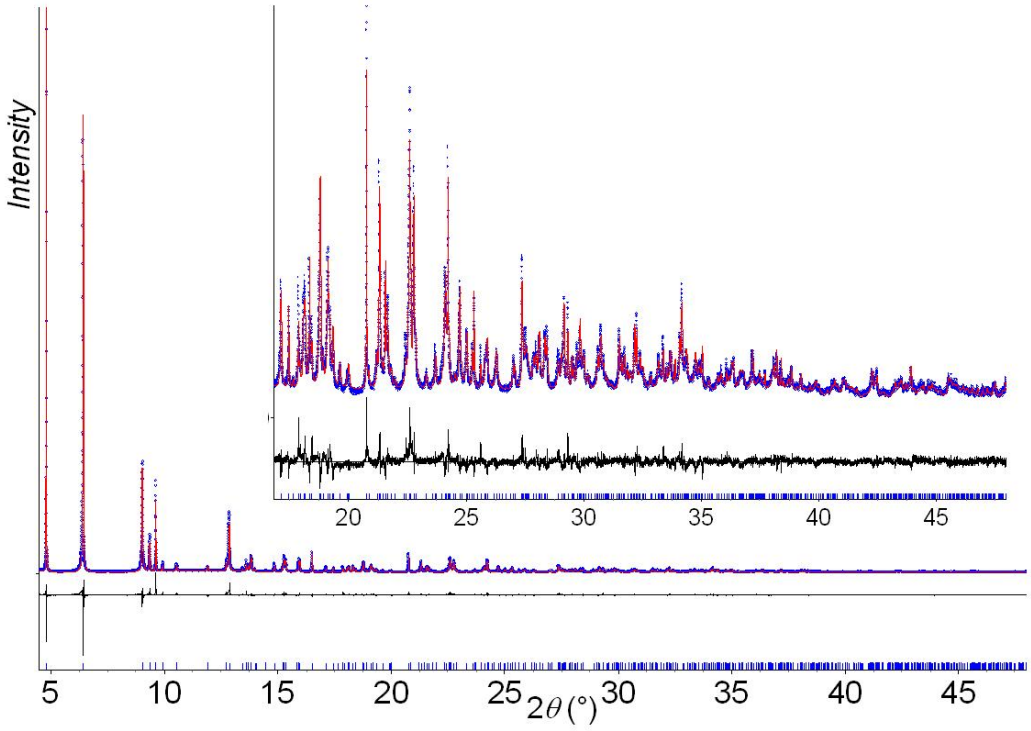
S1: Structure Solution

Crystallographic data for the two MIL-53 (Cr) materials studied, resulting from Rietveld refinements

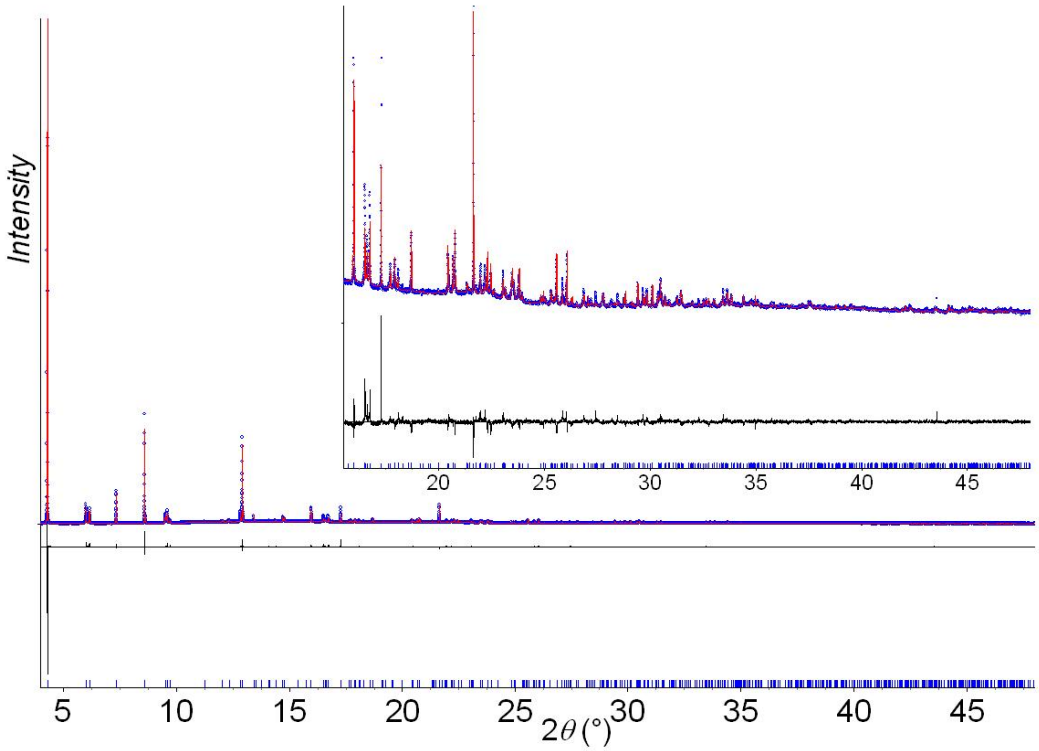
	MIL-53(Cr)(H_2O)	MIL-53(Cr)(6.2H_2O)
a / Å	20.9168(2)	14.8731(3)
b / Å	7.7005(1)	15.2449(3)
c / Å	6.7780(2)	6.83653(6)
β / °	114.3624(9)	-
V/ Å^3	994.51(3)	1550.11(5)
S. G.	*C* 2/*c*	*I m c m*
M_{20}	155	275
R_B	0.050	0.076
R_P, R_{WP}	0.0718, 0.090	0.059, 0.077

Indexing, Rietveld refinements and difference Fourier calculations were performed using the TOPAS software.[1] Unit cells and space groups were found unambiguously with satisfactory figures of merit. For MIL-53(Cr)(H_2O), the already published[2] atomic coordinates of its skeleton were used as starting model in the Rietveld refinement, whereas those of the anhydrous MIL-53(Cr) compound where used for the superhydrated MIL-53(Cr)(6.2H_2O). In both cases, the independent terephthalate ion was treated as rigid body, and the anisotropic line broadening effect was corrected by using spherical harmonics series. Successive difference Fourier calculations allowed to localize the water molecules trapped inside the channel for the two compounds.

At the final stage, Rietveld refinement of MIL-53(Cr)(H_2O) involved the following structural parameters : 4 atomic coordinates (Cr and Ow) , 3 translation parameters of terephthalate ion, 3 distances and 1 torsion angle for the organic moiety , 4 thermal factors and 1 scale factor. The Rietveld refinement of MIL-53(Cr)(6.2H_2O) involved 7 atomic coordinates (O_1, Ow_1,Ow_2, Ow_3 and Ow_4) , 2 translation parameters of terephthalate ion , 3 distances for the organic moiety, 3 thermal factors, 1 parameter for the occupancy of Ow_4 and 1 scale factor. The final Rietveld plots correspond to satisfactory crystal structure model indicators and profile factors. In both cases, soft restrains were applied on the Ow--Ow distances.



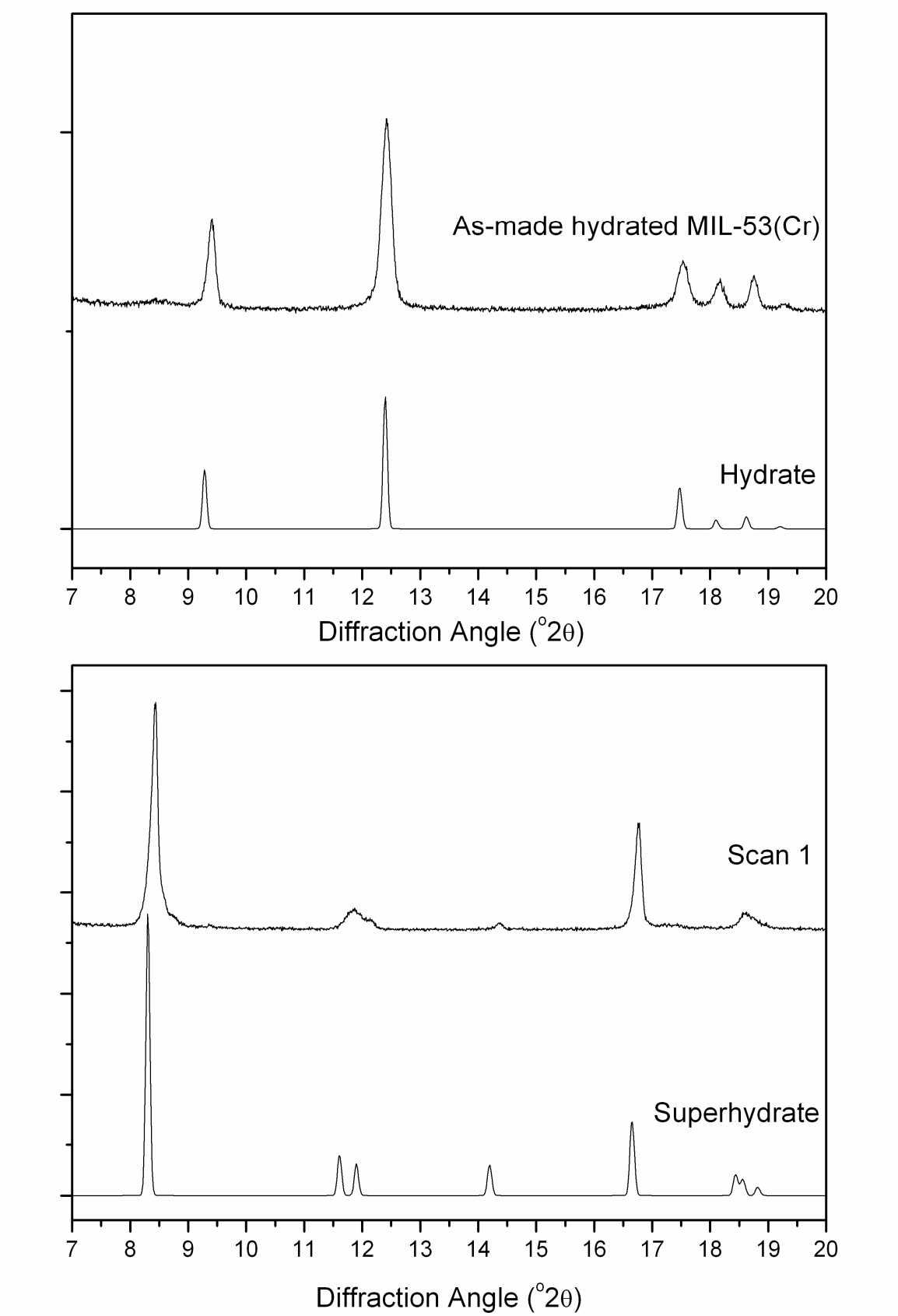
Final Rietveld plot of MIL-53(Cr)(H_2O)

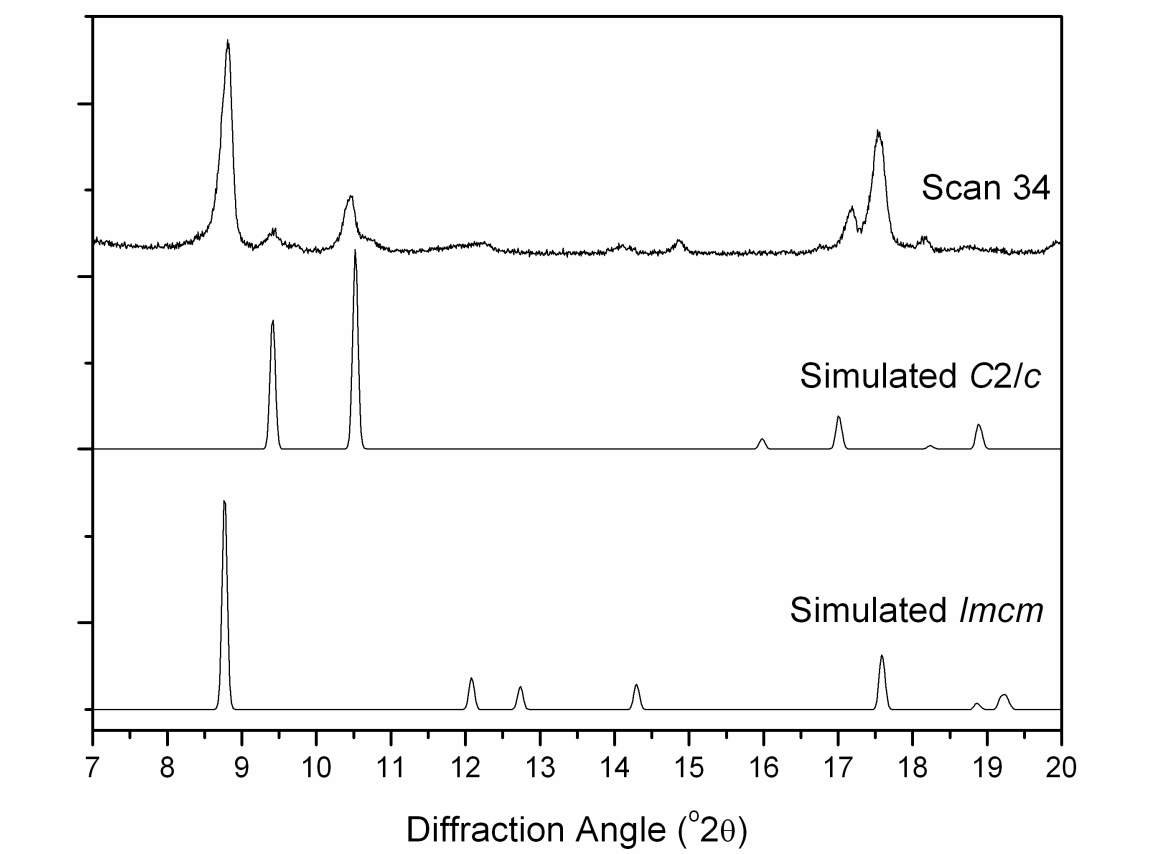


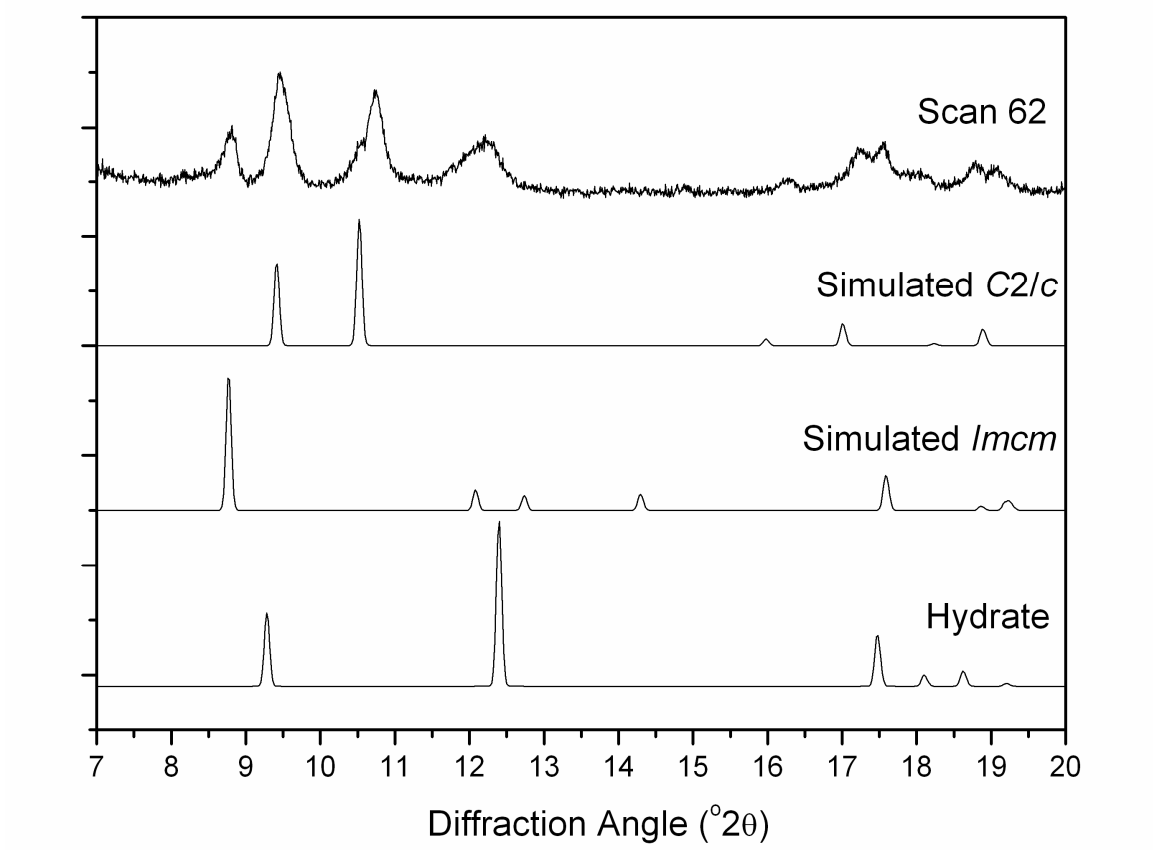
Final Rietveld plot of MIL-53(Cr)(6.2H_2O)

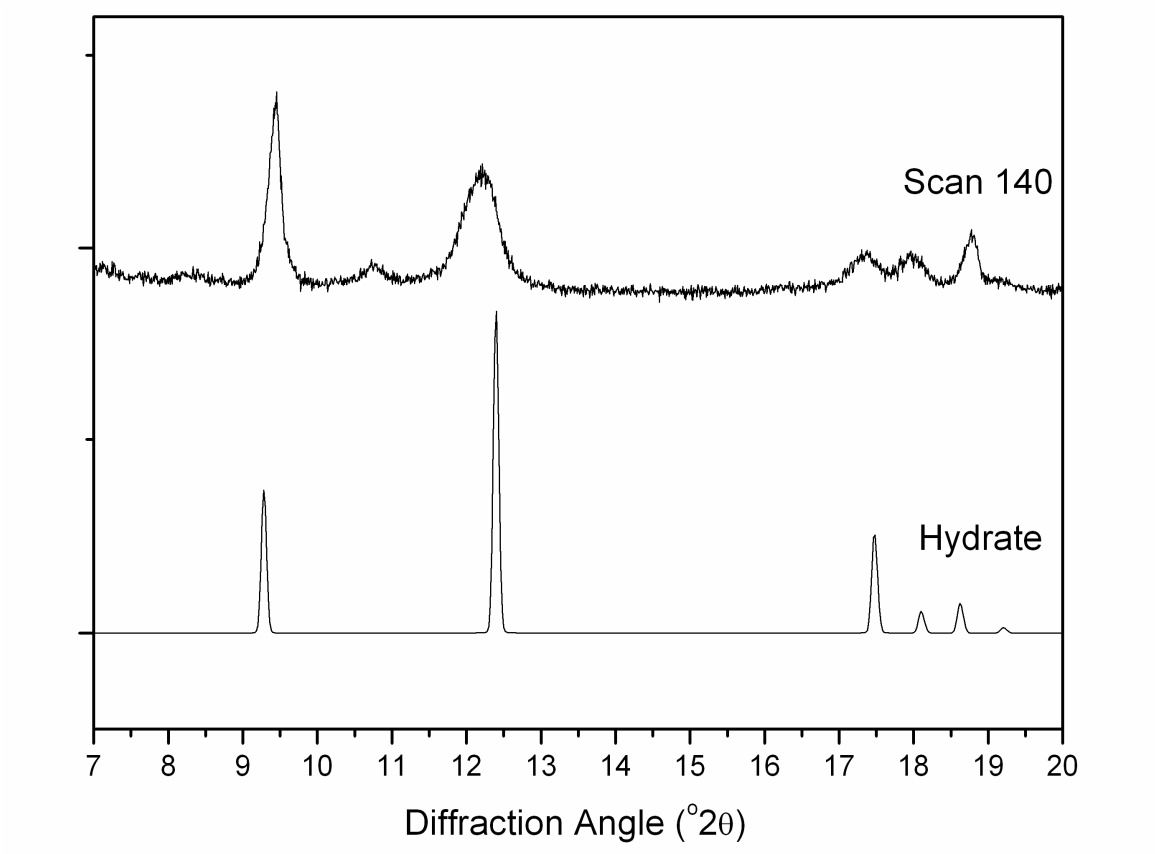
S2: *In situ* powder XRD

Intermediate hydrated states were identified by reference to solvent swollen versions of MIL-53(Fe).[3-4] Two partially hydrated forms can be identified: one with monoclinic *C*2/*c* symmetry ($a \sim 19.70$ Å, $b \sim 9.40$ Å, $c \sim 6.88$ Å, $\beta \sim 107.5^{\circ}$, $V \sim 1215$ Å^3; similar to MIL-53(Fe)[0.5 lutidine]), and one with orthorhombic *Imcm* symmetry ($a \sim 13.90$ Å, $b \sim 14.65$ Å, $c \sim 6.83$ Å $V \sim 1391$ Å^3; smaller in volume than the superhydrated phase).




Scan 34
Simulated C2/c
Simulated Imcm
7 8 9 10 11 12 13 14 15 16 17 18 19 20
Diffraction Angle (°2θ)


Scan 62
Simulated C2/c
Simulated Imcm
Hydrate
7 8 9 10 11 12 13 14 15 16 17 18 19 20
Diffraction Angle (°2θ)



1 Topas V4.2: General Profile and Structure Analysis Software for Powder Diffraction Data Bruker AXS Ltd, 2004.
2. F. Millange, C. Serre, G. Férey, *Chem*. *Comm*., 642 (2002)
3. F. Millange, N. Guillou, R. I. Walton, J-M. Grenèche, I. Margiolaki, G. Férey, *Chem*. *Comm*., 4732 (2008)
4 F. Millange, N. Guillou, M. E. Medina, G. Férey, A. Carlin-Sinclair, K. M. Golden, R. I. Walton, *Chem*. *Mater*., 22, 4237 (2010)