Supplementary Material (ESI) for Chemical Communications

An isoreticular class of Metal-Organic-Frameworks based on the MIL-88 topology

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Supporting information

Quantitative analysis.

MIL-88B: C: 38.6 % N: 1.64 % F: 1.96 % Cr: 16.86 %

MIL-88C: C: 43.4 % Fe: 17.54 % Cl: traces

MIL-88D: C: 54.75 % N: 3.0 % F: 1.29 % Cr: 13.35 %

Phase / Atomic ratio	F/M	C/M	N/M
MIL-88B: Obs	0.32	9.92	0.36
MIL-88B: Calc.	0.33	9.67	0.333
MIL-88C: Obs	----------	12.1	----------
MIL-88C: Calc.		11.55	
MIL-88D: Obs	0.26	17.7	0.82
MIL-88D: Calc.	0.33	17	----------

M=Cr (MIL-88B and D); M=Fe (MIL-88C).

N.B. : as in the chromium carboxylate MIL-100, a partial substitution of the fluorine counter anions by hydroxyl groups is probably occuring in MIL-88B and MIL-88D. This would explain the lower fluorine experimental content observed in both cases.

Table S1 : Crystal data and structure refinement parameters for **MIL-88B**, **MIL-88C** and **MIL-88D** or $Cr_3^{III}OX.\{O_2C\text{-}C_6H_4\text{-}CO_2\}_3.8H_2O.C_5H_6N$, $Fe_3^{III}O.\{O_2C\text{-}C_{10}H_6\text{-}CO_2\}_3.[CH_3CO_2].H_2O.nCH_3OH$ and $Cr_3^{III}OX\{O_2C\text{-}C_{12}H_8\text{-}CO_2\}_3.xH_2O.yC_5H_6N$ *(X=F, OH; n~6.6, x~23.75, y~2.46))*

Formula	**MIL88B**	**MIL-88C**	**MIL-88D**
Chemical formula	$Cr_6F_2O_{42}C_{58}N_2H_{68}$	$Fe_6O_{45.2}C_{89.2}H_{88.8}$	$Cr_6F_2O_{71.5}N_{4.92}C_{108.6}H_{124.5}$
Molar weight ($g.mol^{-1}$)	1812	2218.4	2995.4
Calculated density ($g.cm^{-3}$)	1.51	1.74	1.43
Crystal system	Hexagonal	Hexagonal	Hexagonal
Space group	*P -6 2 c* (n°190)	*P -6 2 c* (n°190)	*P -6 2 c* (n°190)
a (Å)	11.028 (1)	10.175(1)	12.165(1)
c (Å)	18.972(1)	23.772(2)	27.191(1)
V ($Å^3$)	1998.2(3)	2115.2(3)	3485.4(2)
Z	1	1	1
Figures of merit	M_{19}/F_{19}=21/25	M_{14}/F_{14}=23/43	M_{20}/F_{20}=20/35
Radiation λ (Cu K_α)	1.54059, 1.54439	1.54059, 1.54439	1.54059, 1.54439
$\chi=K_{\alpha2}/K_{\alpha1}$	0.5	0.5	0.5
Temperature (K)	296	296	296
2θ range (°)	5-60	6-60	5-60
N. reflections	122	153	209
N. independent atoms	15	18	22
N. intensity parameters	37	46	58
N. profile parameters	15	12	16
N. soft distance constraints	36	43	20
R_P	12.0	9.7	10.3
R_{WP}	14.8	13.1	13.8
R_{Bragg}	8.7	10.4	8.3
Isotropic thermal factor	2.0(2)	3.0(2)	3.0(2)
Profile function	Pseudo-Voigt	Pseudo-Voigt	Pseudo-Voigt
Background	Polynomial (6 parameters)	Polynomial (5 parameters)	Polynomial (6 parameters)
N. of asymmetry parameters	2	2	2
N. of strain parameters	6	4	6
Preferred orientation vector	0 0 1	0 0 1	0 0 1
Preferred orientation coefficient	0.20	0.02	0.10

Figures

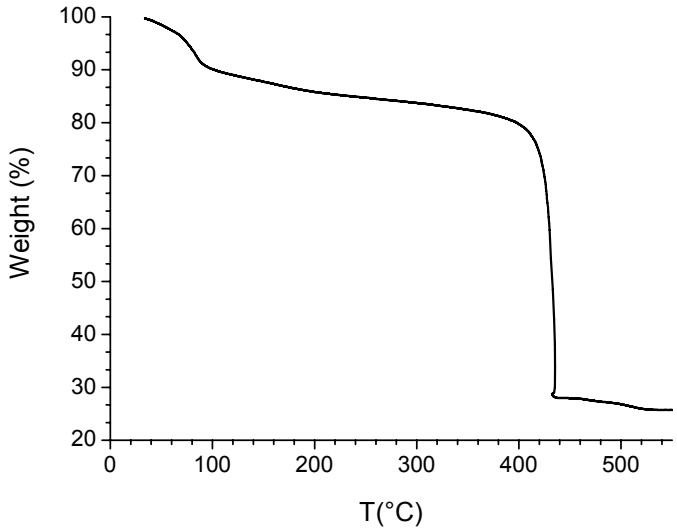

Figure S1a: TGA of MIL-88B under O_2 atmosphere.

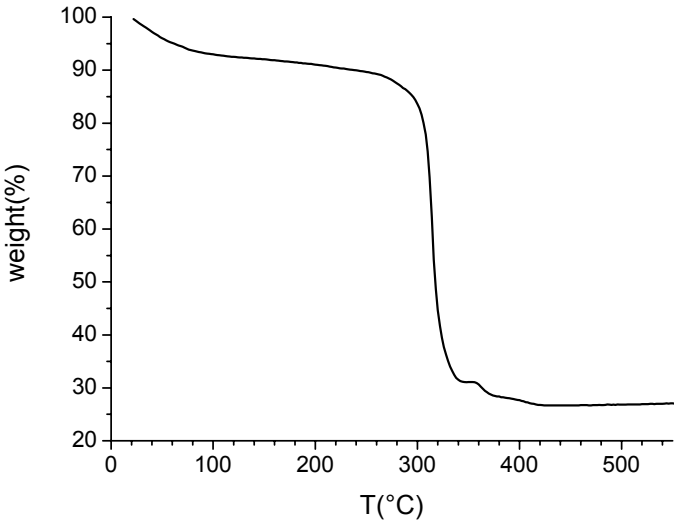

Figure S1b: TGA of MIL-88C under O_2 atmosphere.

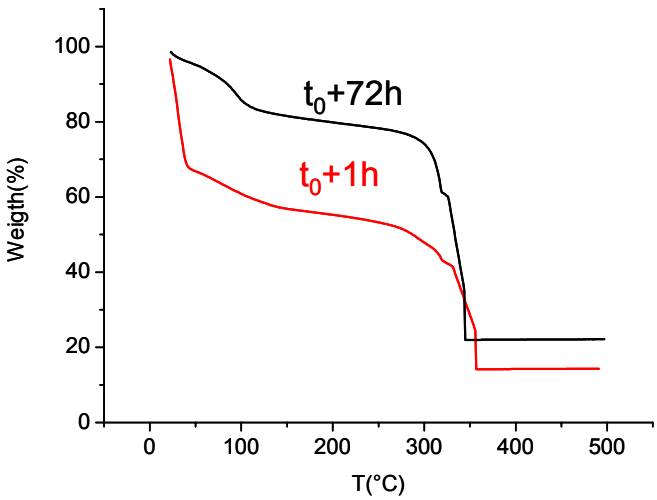

Figure S1c: TGA of MIL-88D performed under O_2 atmosphere dried a few hours at room temperature. Bottom (red): after one hour; Top (black): after 3 days.

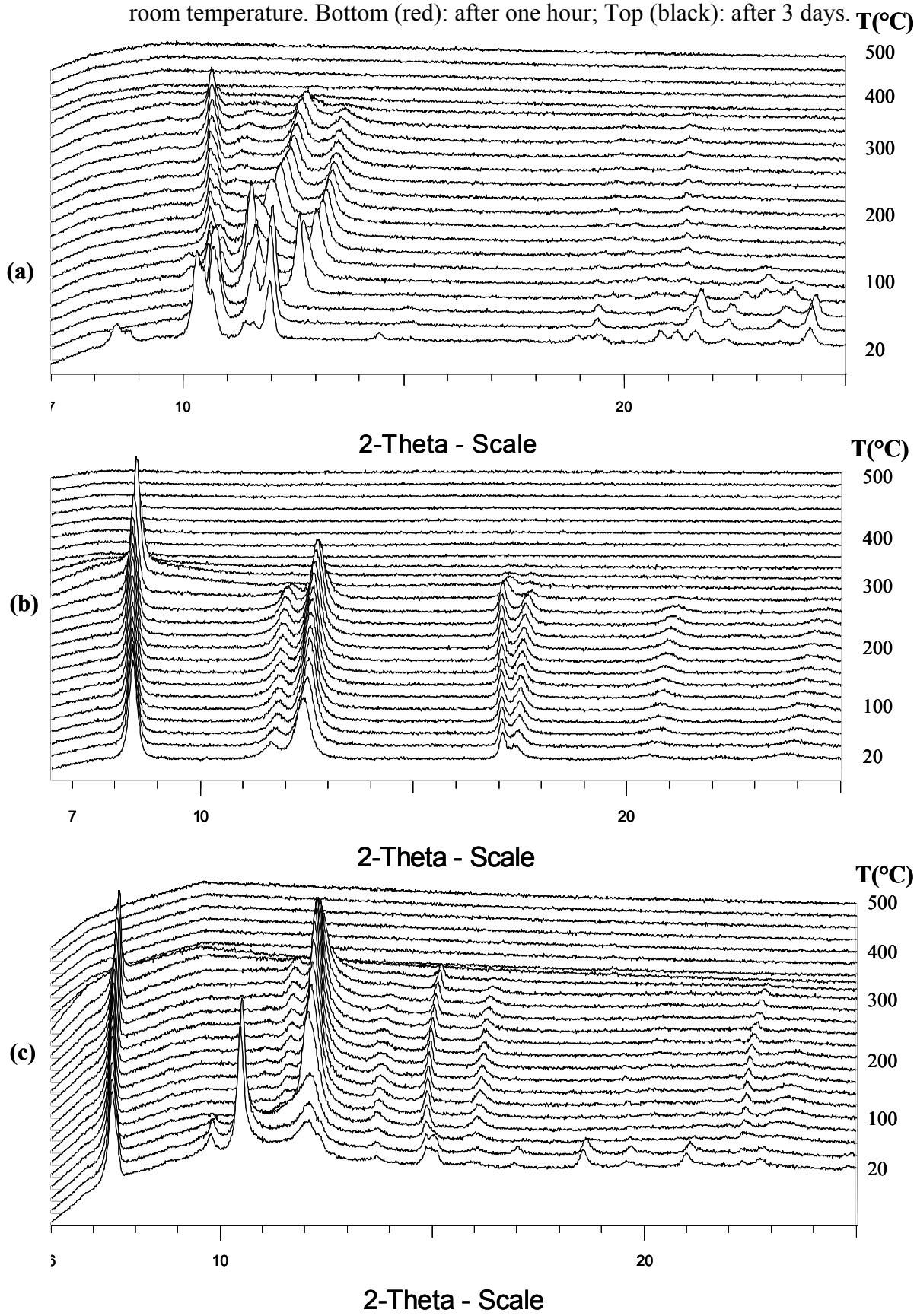

Figure S2: X-Ray thermodiffractometry of MIL-88B, C, D under air atmosphere. *Experiments were performed in the furnace of a Siemens D-5000 diffractometer in*

the θ-θ mode (λ_{Co}). (range: 6-25° (2θ); 3s/step = 1.30 h per pattern). Heating rate was of 5°C/min.

Comparison of TGA results and expected losses.

Phase / Loss	Solvant loss*	Departure of bound solvant + carboxylate + strongly interacting pyridine** + anion (acetate or HX***)
MIL-88B: Obs	14 %	59 %
MIL-88B: Calc.	15 %	60 %
MIL-88C: Obs	10.0 %	63 %
MIL-88C: Calc.	11.7	66.65 %
MIL-88D: Obs (to+1h)	44.8 %	41.5 %
MIL-88D: Calc.	40.55 %	44.67 %

(*): The threshold temperature used for the observed free solvent loss depends on the nature of the solvant: methanol: 100°C (MIL-88C) , H_2O+pyridine: 200°C (MIL-88B and D).
(**): pyridine in MIL-88B present in the cages is assumed to leave the solid at higher temperature (after 200°C)
(***): X=F, OH

N.B.: The higher discrepency observed for TGA results from MIL-88D comes probably from the rapid departure of the free solvant under air atmosphere. In fact, the X-Ray diffraction pattern was collected six hours after washing the sample in pyridine. Two TGA were performed on MIL-88D after drying one hour at room temperature (TGA n°1) or 72 hours (TGA n°2) show the rapid decrease in solvant weight loss with time. As a consequence, the amount of free solvant deduced from the structure determination is intermediate between the values observed for TGA n°1 and TGA n°2.
A similar behavior for MIL-88B and C is also expected but at a lower scale.

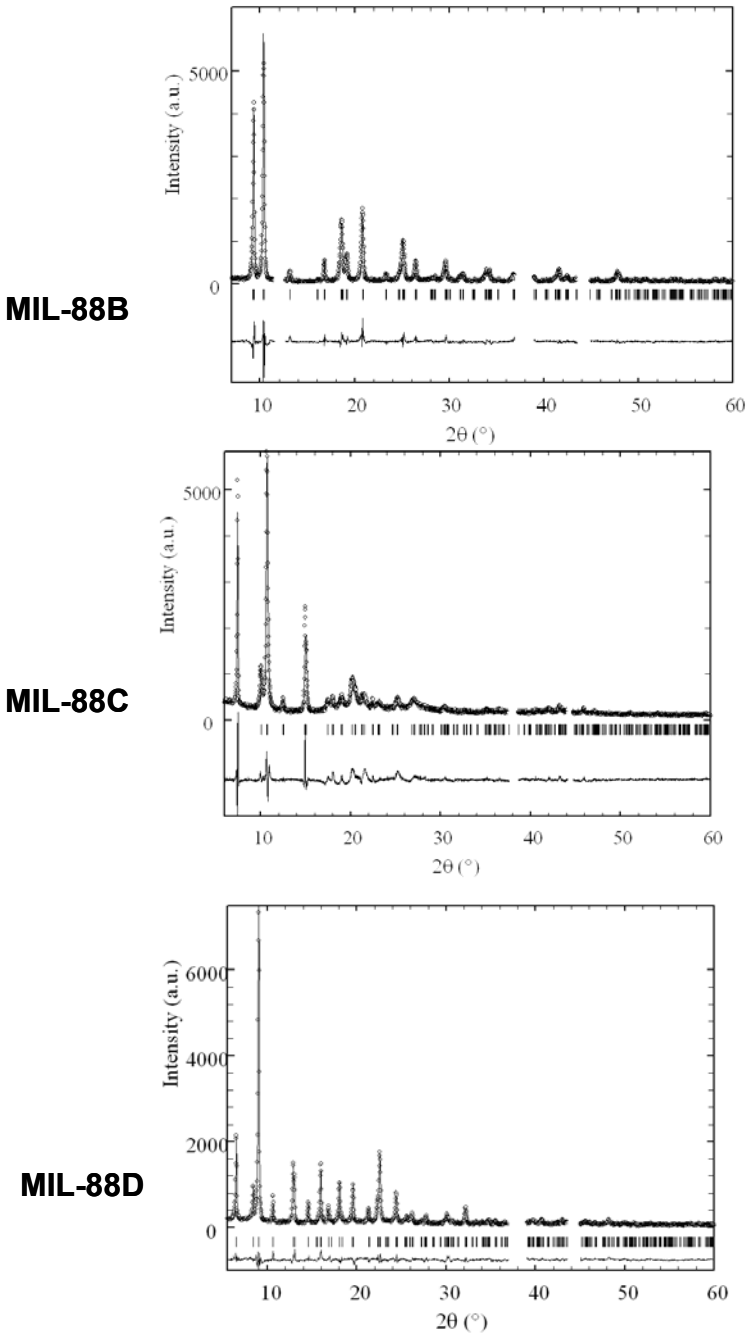

Figure S3 : Final Rietveld plots of MIL-88B, MIL-88C and MIL-88D.