Electronic Supplementary Information for Dalton Transactions


# *Evidence of flexibility in the nanoporous iron(III) carboxylate MIL-89*

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## Materials and methods :

*Preparation of the samples.* MIL-89 was prepared as reported before.[1] MIL-89 was then dispersed by stirring (10 mg of solid for 1 ml of liquid) in methanol, pyridine and lutidine (2,6-dimethylpyridine) for one hour at room temperature Glass capillaries were then filled with slurries and sealed to prevent evaporation of the solvant.

*X-Ray diffraction data.* The *in situ* synchrotron powder diffraction experiments have been carried out at the Swiss-Norwegian Beamlines at the European Synchrotron Radiation Facility. The data were collected on the 1.0 mm quartz capillaries filled with the sample and a solvent, using MAR345 imaging plate at a sample-to-detector distance of 340 mm, $\lambda$ = 0.71118 Å. The data were integrated using Fit2D program (Dr. A. Hammersley, ESRF) and a calibration measurement of a NIST $LaB_6$ standard sample.

*Computer simulation.* Modelling was used in order to yield a structural model for the framework of the MIL-89 compound in its solvated forms (open pores), and possibly initiate Rietveld refinement of the structure. The starting structural model was obtained previously from the MIL-88B crystal structure, using our computational "ligand-replacement" strategy, used previously to predict the closed and open forms of the MIL-88 series of isoreticular solids.[2] By substituting in the original open form of the MIL-88B topology the terephthalate by the trans, trans muconic acid, the framework model

of MIL-89 in its open form was generated. The solvated (open pores) form was simulated using the cell parameters obtained by indexing the observed diffraction pattern that correspond to their observed cell parameters from MIL-89 dispersed in 2,6 dimethylpyridine or Lutidine. The simulation was performed on framework exclusively – i.e. in the absence of solvent molecules – in order to yield starting framework models for further Rietveld refinement where solvent molecules could be located from difference Fourier maps.

*Structure refinement.* The framework of MIL-$89_{Lut}$ was obtained starting from the atomic coordinates from the computer simulation and the program Fullprof2k and its graphical interface Winplotr. [3,4] Successive Fourier differences were performed using Shelxtl to locate the position of the guest species.[5] Please note that we propose here only an approached structure of these latter solids filled with solvent. It is obvious that using powder data, the position of the free solvent molecules, sometimes disordered at room temperature, is rather approximative.

**References.**

(1) C. Serre, F. Millange, S. Surblé, and G. Férey, *Angew. Chem. Int. Ed*, 2004, 43, 2

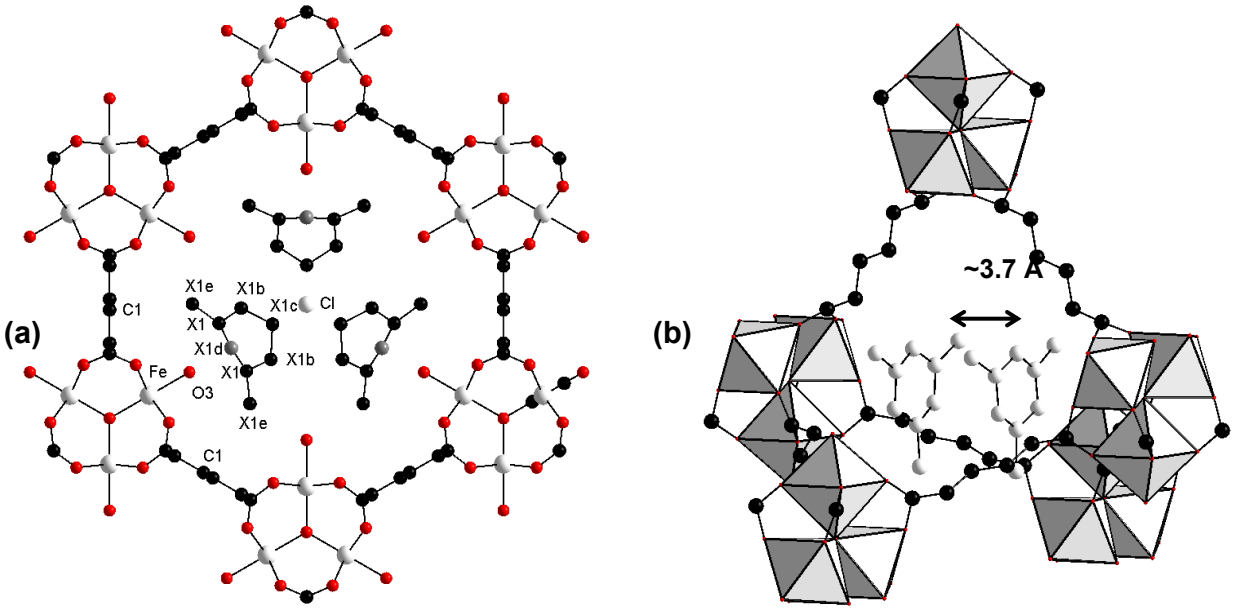
(2) (a) C. Mellot-Draznieks, C. Serre, S. Surblé, N. Audebrand, and G. Férey, *J. Am. Chem. Soc.*, 2005, **127**, 16273; (b) S. Surblé, C. Serre, C. Mellot-draznieks, F. Millange, and G. Férey, *Chem. Comm.*, 2006, 284; (c) C. Mellot-draznieks, *J. Mater. Chem.*, 2007, **17**, 4348

(3) J. Rodriguez-Carvajal, In "Collected Abstracts of Powder Diffraction Meeting", Toulouse, France, 1990, 127.

(4) T. Roisnel and J. Rodriguez-Carvajal, In "Abstracts of the 7th European Powder Diffraction Conference", Barcelona, Spain, 2000, 71.

(5) 'SHELXL97', University of Göttingen, Germany, 1997.

## Structural analysis of the host-guest interactions




Figures S1: (a) : view of the lutidine-MI-L89 interactions along the tunnes (c axis). (b) : view of the lutidine-MIL-89 interactions within the cages (long a and b axis). For the right figure : Iron, chlorine, oxygen, nitrogen and carbon atoms are in grey, white, red, dark grey and black, respectively. For the left figure : iron octahedra, carbon atoms from the framework are in grey and black while nitrogen and carbon atoms from Lutidine are in white.

**Table S1 :** Atomic coordinates for the energy-minimized frameworks **MIL-89** in its simulated open form.

a=b=16.400 Å and c=16.100 Å, Space group $P6_3/mmc$

| Atom | $x_{sim}$ | $y_{sim}$ | $z_{sim}$ |
|---|---|---|---|
| Fe | 0.46500 | -0.26760 | 1/4 |
| O(1) | 1/3 | 2/3 | 1/4 |
| O(2) | 0.81120 | 0.47220 | -0.33640 |
| O(3) | 0.20400 | -0.20400 | 1/4 |
| C(1) | 0.48900 | 0.51100 | 0.04260 |
| C(2) | 0.58200 | 0.41800 | -0.13260 |
| C(3) | 0.55700 | 0.44300 | -0.05070 |
| H(1) | 0.58000 | 0.42000 | 0.0005 |
| H(2) | 0.49000 | 0.51000 | -0.09900 |

**Table S2 :** Experimental atomic coordinates for **MIL-89** in Lutidine.

a=b=16.418 Å and c=16.183 Å, Space group $P6_3/mmc$

| Atom | x | y | z | Site occupancy |
|---|---|---|---|---|
| Fe | 0.465(1) | -0.267(1) | 1/4 | |
| Cl | 0 | 0 | 0.131(7) | 50 % |
| O(1) | 1/3 | 2/3 | 1/4 | |
| O(2) | 0.823(1) | 0.478(1) | -0.337(1) | |
| O(3) | 0.203(1) | -0.203(1) | 1/4 | |
| C(1) | 0.492(1) | 0.508(1) | 0.041(1) | |
| C(2) | 0.573(1) | 0.427(1) | -0.135(2) | |
| C(3) | 0.555(1) | 0.445(1) | -0.055(1) | |
| Om | 0.501(1) | 0.499(1) | 1/4 | 50 % |
| Cm | 0.546(1) | 0.454(1) | 1/4 | 50 % |
| C(1a) | 0.055(1) | -0.195(1) | 0.201(2) | 50 % |
| C(1b) | 0.009(1) | -0.159(1) | 1/4 | |
| N(1c) | 0.057(1) | -0.057(1) | 1/4 | |
| C(1d) | 0.131(1) | -0.131(1) | 0.145(1) | 50 % |
| C(1e) | 0.020(3) | -0.297(1) | 0.193(2) | 50 % |
| C(2a) | 0.771(1) | 0.542(1) | 0.080(9) | 66.67 % |
| X(2b) | 0.716(1) | 0.431(1) | 0.084(4) | |
| X(2c) | 0.618(1) | 0.236(1) | 0.099(2) | |

m for methanol; X=N or C

***Table S2 :*** *Crystal data and structure refinement parameters for the open forms of* ***MIL-89*** *or* $Fe_6^{III}O_2Cl_2.\{O_2C\text{-}C_4H_4\text{-}CO_2\}_6.\ 10C_7H_{10}N.\ 6CH_3OH$

| Formula | **MIL89_Lutidine** |
|---|---|
| Chemical formula | $Fe_6Cl_2O_{32}C_{100}N_{10}H_{148}$ |
| Solvant | Lutidine |
| Molar weight ($g.mol^{-1}$) | 2790 |
| Calculated density ($g.cm^{-3}$) | 1.24 |
| Crystal system | Hexagonal |
| Space group | *P 6₃/mmc* (n°194) |
| *a* (Å) | 16.418 (1) |
| *c* (Å) | 16.183(1) |
| *V* ($Å^3$) | 3777.9(2) |
| *Z* | 1 |
| Figures of merit (à définir) | $M_{15}/F_{15}$=20/50 |
| Radiation λ(Å) | 0.71118 |
| Temperature (K) | 296 |
| $2\theta$ range (°) | 1.9-26.6 |
| N. reflections | 202 |
| N. independent atoms | 19 |
| N. structural parameters | 34 |
| N. profile parameters | 9 |
| N. soft distance and angles (?) constraints | 47 |
| $R_P$ | 6.3 |
| $R_{Bragg}$ | 18.7 |
| Isotropic overall atomic displacement parameter | 5.2(2) |
| Profile function | Pearson VII |
| Background | Experimental |
| N. of asymmetry parameters | 2 |

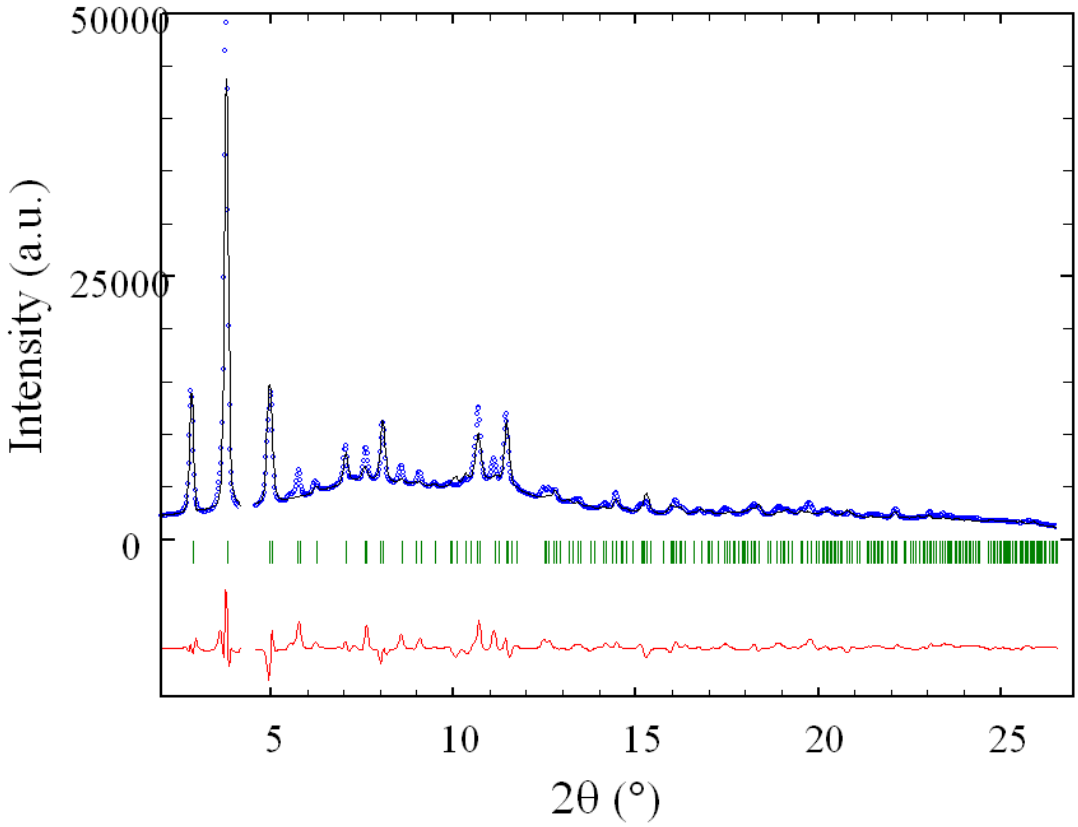



**Figure S1** : Rietveld pattern of MIL-89 in Lutidine (λ=0.71113 Å).

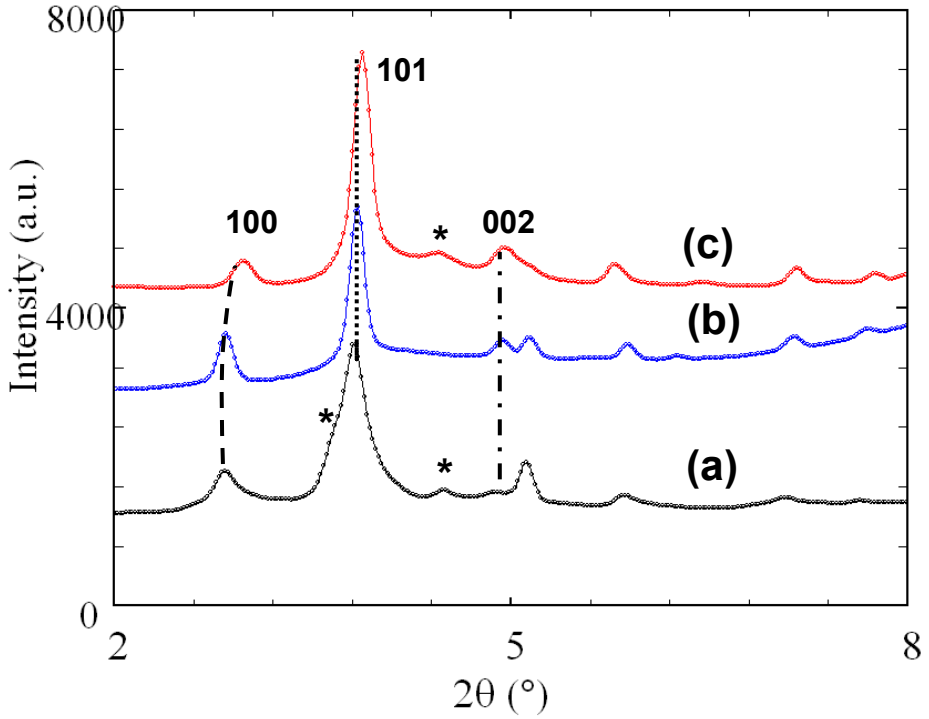



**Figure S2 :** X-ray diffraction patterns of (a) : MIL-89 dispersed in ethanol for 2 hours; (b) MIL-89 dispersed in ethanol for 5 days; (c) : MIL-89 made in ethanol and dried a few hours at room temperature. The (100), (101) and (002) Bragg reflections are represented for a better understanding. (*) correspond to peaks non indexed in the hexagonal cell (Space group $P6_3/mmc$) and are attributed to partially dried and contracted MIL-89 crystallites.