



## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application**:

*<http://193.49.43.2:8080/smis/servlet/UserUtils?start>*

### ***Reports supporting requests for additional beam time***

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: <i>Structural study of the giant breathing of the flexible nanoporous metalocarboxylates MIL-88</i>	<b>Experiment number:</b> CH-1999
<b>Beamline:</b> BM01-A	<b>Date of experiment:</b> from: 25.04.2006 to: 28.04.2006	<b>Date of report:</b> 16.08.2006
<b>Shifts:</b> 9	<b>Local contact(s):</b> Yaroslav Filinchuk	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): C. Serre,* Institut Lavoisier, UMR CNRS 8180, Versailles, France F. Millange,* Institut Lavoisier, UMR CNRS 8180, Versailles, France S. Surblé,* Institut Lavoisier, UMR CNRS 8180, Versailles, France		

## Report:

### Introduction.

A new class of porous solids has emerged recently,<sup>1</sup> the so-called “metal-organic frameworks (MOF)”, which are very efficient adsorbents with high capacity for gas storage.<sup>2,3</sup> We also focused our attention to the synthesis and structural characterization of new porous MOF materials.<sup>4-6</sup> For instance, the MIL88(A, B, C, D)<sup>6</sup> are a new isoreticular series of a nanoporous solid based on Chromium or Iron(III) trimeric building units and dicarboxylate ligands (fumarate, terephthalate, naphthalene, 4,4' biphenyl). Preliminary sorption laboratory tests for MIL-88 solids showed that they exhibit a giant breathing capacity when loaded with various solvents (water, alcohols). The purpose of this proposal was first to collect high resolution powder diffraction data of their open forms when immersed in various solvents in order to determine both the structures of their open forms as well as some first results concerning their selective adsorption of solvents.

### Experimental section


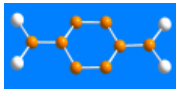
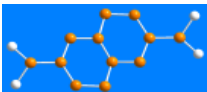
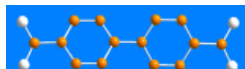
The MIL-88A, B, C, D solids were prepared as described previously.<sup>4,7</sup> The solids were first dried at 120°C under air to remove the free solvent molecules. Then, a few mg of each solid was dispersed in one ml of various solvents (water, alcohols, DMF, DEF, acetone, acetonitrile, hexane, toluene, pyridine, lutidine...) and dispersed using magnetic stirring from one hour (MIL88A, B) up to one night (MIL-88C, D). Then, the resulting slurries were introduced in 1 mm glass capillaries. Dozen of high resolution X-Ray powder patterns, of each solid dispersed in a large range of solvent, were then collected at the BM01-A beamline at  $\lambda \cong 0.71 \text{ \AA}$  using the MAR-345 image plate detector.

## Results and Discussion

For each solid, it was possible to find an adequate solvent that provokes both a high pore opening while giving rise to a high quality X-Ray powder pattern. The corresponding cell parameters have been determined using DicovlGV and the winplotr interface of Fullprof. Besides, back to our laboratory, we were able to estimate the cell parameters of the dried and contracted forms of each solid using X-Ray thermodiffraction.

Finally, the structural parameters of the MIL-88A, B, C and D solids at the different stages of pore opening are summarised in the following table:

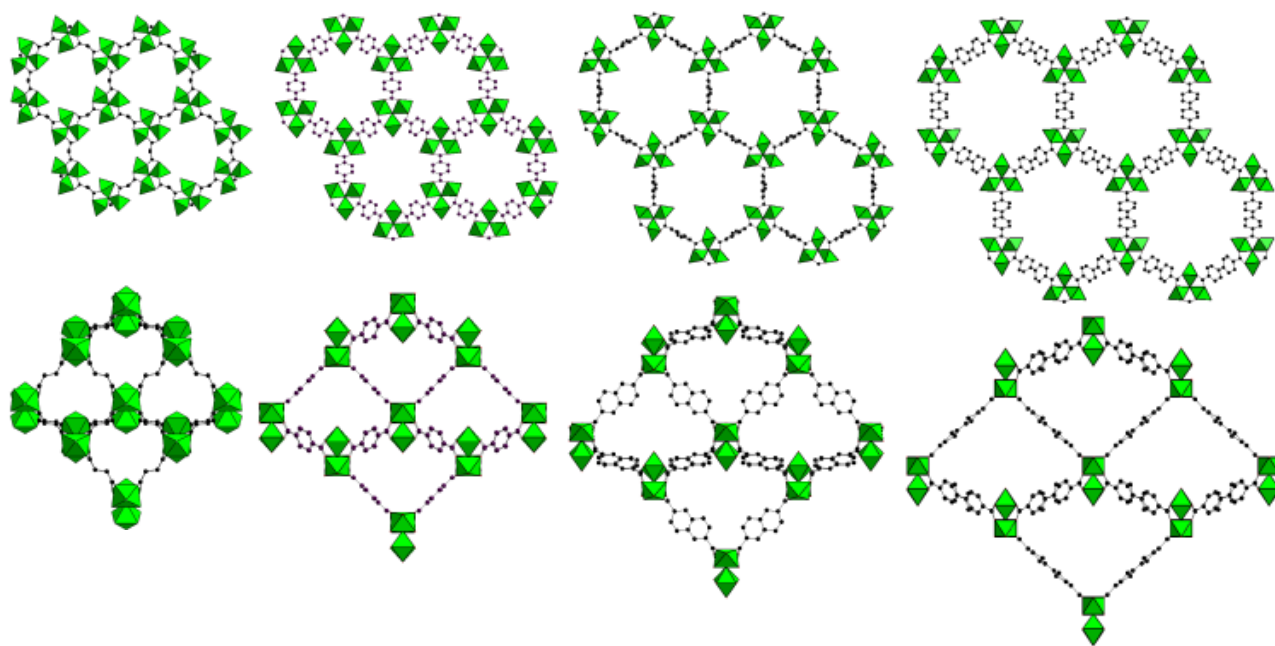
**Table 1:** Structural parameters of the MIL-88 series (dried, as-synthesised, open forms). S.G. P-62C (n°190)

Solid	Carboxylic acid	a(Å)	c(Å)	V(Å <sup>3</sup> )	Cell expansion	Estimated. Pore size	Solvent
MIL-88A	<b>Fumaric</b> 	9.6 11.1 13.9	14.8 14.5 12.6	1180 1480 2120	> 85 %	~5-7 Å	Water
MIL-88B	<b>Terephthalic</b> 	9.6 11.0 15.7	19.1 19.0 16.1	1500 2000 3400	> 120 %	~7-10 Å	Ethanol
MIL-88C	<b>2,6 Naphtalene</b> 	9.9 10.2 18.7	23.8 23.6 18.8	2020 2100 5600	> 170 %	~10-15 Å	Pyridine
MIL-88D	<b>4,4' biphenyl</b> 	10.1 12.1 20.5	27.8 27.5 22.4	2480 3500 8100	> 220 %	~12-16 Å	Ethanol

It appears that the breathing amplitude is an increasing function of the size of the linker, from 85 % with the short fumarate carboxylate up to 220 % with the longer biphenyl linker. Such breathing amplitudes have never been reached to date in porous solids. In addition, the crystal structures of the open forms have been successfully refined, starting from crystallographic atomic positions determined from computer simulation, despite the very large number of free solvent molecules entrapped in the pores of these solids (see figure 1). The pore sizes along the c axis vary from 6-7Å for MIL-88A up to 15-16 Å for MIL-88D. Along the a and b axis, some corrugated pores are also present with pore sizes going from 5-7 Å up to 10-12 Å. The corresponding accessible volumes are huge, and reaches almost 80 % in the case of MIL-88D !!! Its apparent volumic density (i.e. without the solvent molecules) is close to 0.37 g.cm<sup>3</sup>, indicating that this solid possesses more accessible volume for organic molecules than the highly porous MOFs MOF-177 or MIL-101 !!

In a second step, we have estimated the cell parameters and the pore opening as a function of the nature of the solvent for each solid of the MIL-88 series. It indicated that these solids are selective sorbants with a selectivity governed by a competition between the polar trimer of iron or chromium octahedra and the

organic linker. For instance, with the naphthalene form MIL-88C, short polar solvents (water, ethanol) or apolar liquids (hexane, toluene) are incorporated only in small amounts, provoqing only a 7-8 % cell expansion; increasing the number of CH<sub>2</sub> or CH<sub>3</sub> groups in polar molecules (Butanol, Dimethylcarbonate, Dimethylformamide) leads to a gradual increase of the pore opening (from 15 up to 60 %) while diethylformamide opens totally the pores (165 % of increase in cell volume). This is probably due to the increasing number of interactions between the CH bonds and the aromatic rings of the naphthalene linker that provoques the pore opening. Finally, aromatic and polar liquids such as pyridine open the pores (+170 %) but surprinsingly, dimethylpyridine almost does not opens the pores of MIL-88C !! These first sorption tests reveal that these highly flexible solids are also highly selective sorbants.



**Figure 1:** crystal structures of the open-forms of the MIL-88A, B, C, D solids; top view: along the c axis; down: along the a axis. Solvent molecules have been omitted for a better understanding.

## Conclusion

The study of the breathing phenomenon upon adsorption of solvents was performed on a series of porous hybrid metalcarboxylates of the MIL-88 structure type, using the SNBL BM01-A line. It allowed the determination of the structures of their open forms, involving unprecedented breathing capacities from 85 % up to 220% in cell volume, as well as first results concerning their selective sorption behavior.<sup>8</sup>

## References

- <sup>1</sup> M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **295** 469 (2002)
- <sup>2</sup> G. Férey, M. Latroche, C. Serre, F. Millange, T. Loiseau, A. Percheron-Guégan, *Chem. Commun.* 2276 (2003).
- <sup>3</sup> S. Bourrelly, P. Llewellyn, C. Serre, F. Millange, T. Loiseau, G. Férey *J. Am. Chem. Soc.* 2005, *127*(39), 13519
- <sup>4</sup> G. Férey, C. Serre, C. Mellot-Draznieks, F. Millange, S. Surblé, J. Dutour, I. Margiolaki, *Angew. Chem. Int. Ed.* **43** 6296 (2004).
- <sup>5</sup> G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* 2005, *309*, 2040
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<sup>7</sup> S. Surblé, C. Serre, C. Mellot-Draznieks, F. Millange, G. Férey, *Chem. Comm.* 2006, 284

<sup>8</sup> C. Serre, C. Mellot-Draznieks, S. Surblé, N. Audebrand, Y. Filinchuk, G. Férey, *Submitted* 2006