

This paper is published as part of a *Dalton Transactions* theme issue on:

Nanomaterials for alternative energy sources

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Published in [issue 40, 2008](#) of *Dalton Transactions*

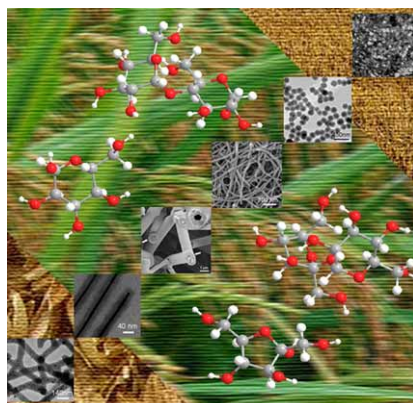


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Evidence of flexibility in the nanoporous iron(III) carboxylate MIL-89†

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Received 1st April 2008, Accepted 13th June 2008

First published as an Advance Article on the web 30th July 2008

DOI: 10.1039/b805408h

The very large expansion upon adsorption of liquids, up to 160% in cell volume, has been observed in the iron(III) *trans,trans* muconate MIL-89 [MIL = Material Institut Lavoisier]. The structure of lutidine-containing MIL-89 (lutidine = 2,6-dimethylpyridine) has been determined using X-ray powder diffraction and computer simulations. Finally, the consequences of adsorption of various polar and apolar liquids have been evaluated using *ex situ* synchrotron X-ray powder diffraction data and reveals that the swelling behavior of MIL-89 is selective but slightly different from the MIL-88 analogues.

Introduction

Metal–organic frameworks (MOFs) are a new and fascinating class of porous solids.¹ From small pore materials up to crystallised mesoporous solids, there is an increasing number of MOFs with different pore shapes, sizes and framework compositions that have been reported in the past decade.^{2–8} These solids might be used for many applications such as gas storage,^{9–12} separation,^{13,14} inclusion,^{15,16} thin films,^{17,18} delivery of nitric oxide,¹⁹ drug delivery²⁰ and so on. If most MOFs are rigid porous solids, there is a unique characteristic for a scarce number of MOFs, which consists in the flexibility of their framework.^{3,21,22} Kitagawa *et al.* have proposed that the pore opening that occurs upon external stimuli (gas, vapor, liquid) is governed by the host–guest interactions.³ The authors provided a classification of the different known behaviors of flexibility into six classes, according to the interactions and the dimensionality of the inorganic subnetwork. For instance, the nanoporous chromium or aluminum terephthalates, denoted MIL-53, decrease their cell volume by *ca.* 40% upon adsorption of carbon dioxide or water.⁹ Recently, our group also observed that the isorecticular class of MOFs MIL-88,^{23,24} which, at variance to MIL-53, swells upon adsorption of liquids with variations in cell volume from 85% up to 230% depending on the length of the organic spacer.^{25,26} The MIL-88 solids are highly selective adsorbents and, more generally, flexible MOFs could be of a great use for applications in adsorption,²⁷ separation,^{28,29} storage⁹ or drug delivery.³⁰

Recently, we have reported the synthesis and structure determination of the porous iron muconate or $\text{Fe}_3^{\text{III}}\text{O}(\text{CH}_3\text{OH})_3\text{Cl}[\text{O}_2\text{C}-\text{C}_4\text{H}_4-\text{CO}_2]_3\cdot\text{solv}$. (solv. = methanol, water), denoted MIL-89.²³ Its structure is similar to MIL-88, with trimers of iron(III) connected to dicarboxylate linkers. However, only the structure of the dried contracted form was previously solved from powder data. Its symmetry (*P6mm*) differs from that of hexagonal MIL-88 solids

($\overline{P6}2c$ or $P6_3/mmc$). This paper deals with the study of its flexible behavior when dispersed in various liquids, using high resolution synchrotron X-ray powder diffraction data and our computer simulation approach,²⁵ with particular emphasis on the lutidine containing MIL-89.

Results and discussion

The structure type of MIL-89 relates to that of MIL-88 (space group, $\overline{P6}2c$ or $P6_3/mmc$). However, in its dried form (MIL-89_{dry}) its symmetry is orthorhombic (space group, *Pbmn*). Topologically, both are built up from the connection of trimers of iron(III) octahedra that share a $\mu_3\text{-O}$ oxygen with the dicarboxylates (Fig. 1a) in such a way that two types of cavities exist: tunnels along [001], and bipyramidal cages with trimers at the vertices. Free chlorine atoms are the counter anions in MIL-89, whereas for the MIL-88 solids, free acetates or bound fluorine atoms act as the compensating anionic charges.

This difference could explain the change in symmetry between the two types. Anions are located at the center of the tunnels and interact with the hydrogen atoms of the linker (Fig. 1a). Additional structural information of the host–guest interactions is provided in the ESI.†

For studying the flexibility of MIL-89, X-ray powder patterns of MIL-89as (as = as-synthesised) dispersed in various polar or apolar structures were collected using the SNBL ESRF synchrotron facility. Most of the patterns are of medium quality but, in the case of lutidine (or 2,6-dimethylpyridine), a high-quality pattern could be obtained and indexed successfully in the hexagonal cell with $a = 16.42(1) \text{ \AA}$, $c = 16.18(1) \text{ \AA}$, $V = 3778(1) \text{ \AA}^3$ in the space group $P6_3/mmc$, confirming that both the filled forms of MIL-89 (MIL-89_{lut}) and MIL-88 solids are of the same structure type and that the decrease in symmetry occurs for MIL-89 upon pore contraction due to the departure of solvent. MIL-89 is highly flexible, with a large increase in cell volume upon adsorption of lutidine (Fig. 1b). In terms of swelling, this corresponds to a magnitude of 160% ($(V_{\text{lut}} - V_{\text{dry}}) / V_{\text{dry}}$) between its dry and open forms, when considering a pseudo hexagonal cell for MIL-89_{dry} ($a \sim 9.13 \text{ \AA}$, $c \sim 20.0 \text{ \AA}$, $V \sim 1470 \text{ \AA}^3$). A brief comparison with the isorecticular flexible MIL-88A, B, C and D solids²⁶ has been made and reveals (Fig. 2) that the swelling magnitude of MIL-89 (+160%) lies between those for MIL-88B (+125%) and

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† Electronic supplementary information (ESI) available: Synthesis and structural analysis parameters. See DOI: 10.1039/b805408h

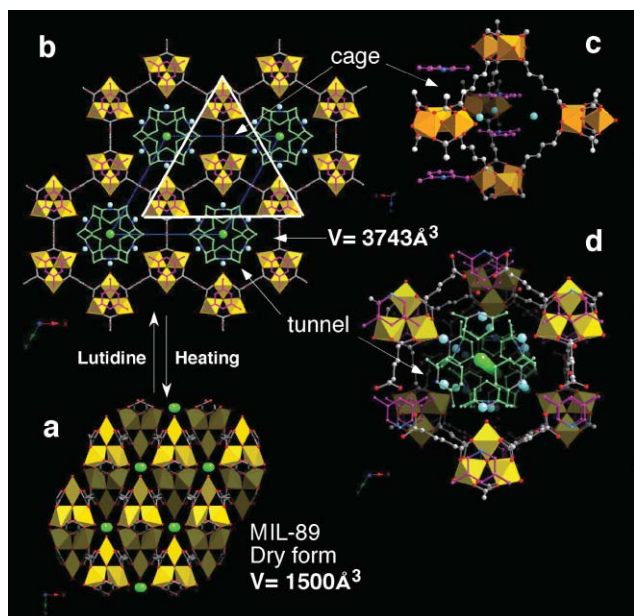


Fig. 1 The breathing phenomenon in MIL-89 from its dried to open form. (a) Dried form MIL-89ht, (b) open form in lutidine MIL-89_{lut}, (c) view of the lutidine molecules inside the cages and (d) view of the lutidine molecules inside the channels. The FeO₆ octahedra, the carbon atoms of the muconate and the oxygen atoms from methanol or water are in orange, white and cyan, respectively. For a better understanding, different colours represent the carbon and nitrogen atoms of lutidine: the C and N atoms from the lutidine from the cages are in purple and blue while the C and N atoms from the lutidine from the channels are in pale green and pale purple, respectively.

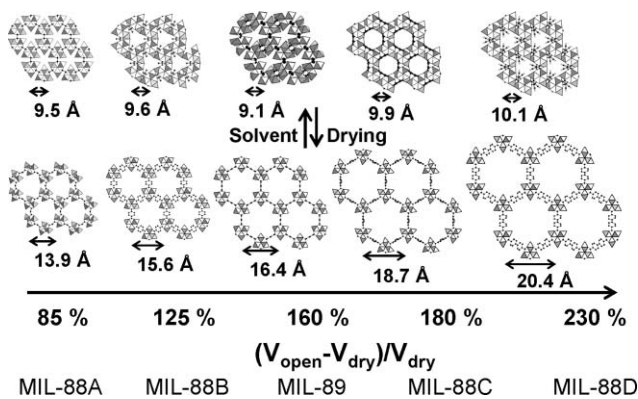


Fig. 2 Evolution of MIL-88A–D and MIL-89 solids in their dry and open states. The distances between the trimers in the (*ab*) plane is indicated for a better understanding. The corresponding increase in cell volume is represented at the bottom of the figure. Carbon atoms and iron octahedra are in black and grey, respectively.

MIL-88C (+180%), which is in agreement with the size of the organic spacer: 2,6-naphthalenedicarboxylate (88C) > *trans,trans* muconate (89) > terephthalate (88B). The free apertures of MIL-89_{op} are close to $9 \times 13 \text{ \AA}^2$ for the hexagonal tunnels and about $5 \times 11 \text{ \AA}^2$ for the windows of the cages.

The structure of MIL-89_{lut} was also solved using our previous computer simulation strategy.^{25,31} Starting from the structures of the *dried* form of MIL-89, the simulation provided the starting

atomic coordinates of the atoms of the hybrid framework for further Rietveld refinements.^{32,33} The lutidine molecules were localised using successive Fourier difference cycles.³⁴ Surprisingly, in contrast to MIL-88B, C and D solids where the solvent molecules were found to be highly disordered, the lutidine molecules exhibit a much lower degree of disorder. They occupy the two types of vacancies of the structure. Those located within the hexagonal channels (Fig. 1d), interact through hydrogen bondings *via* their nitrogen atoms (see X(1d)–O(3)) with the terminal water molecules and through van der Waals interactions *via* the methyl groups and the carbon atoms of the muconate. In the cages delimited by five trimers of octahedra, the lutidine molecules (Fig. 1c), interact through van der Waals bonds with the trimers and the muconate. In both cases, the organic molecules are partially disordered; in the tunnels, lutidine stays at two positions with a 50% occupancy. This might come from steric hindrance of the methyl groups that make it difficult for the formation of hydrogen bonds between the nitrogen group and the terminal water molecules of the trimer. Therefore, the lutidine molecules are oriented above or below the plane delimited by the trimers, which allows the nitrogen atoms to interact with the water molecules. The chlorine counter anions lie in the middle of the hexagonal channels and interact weakly with the hydrogen atoms of the free lutidine molecules. In the cages, the organic molecule exhibits a rotational disorder of its methyl groups, which are ascribed a corresponding 2/3 occupancy. Moreover, some residual free molecules of methanol and coordinated water molecules, which come from the as-synthesised solid (made in methanol from hydrated iron acetate) are also present, and interact with the oxygen atoms from the trimers.

Finally, the swelling of MIL-89 was studied by analysing the X-ray synchrotron radiation patterns for the as-synthesised powder dispersed (2 h at 298 K considered as sufficient to reach equilibrium) in a capillary filled with various polar or apolar liquids (Fig. 3).

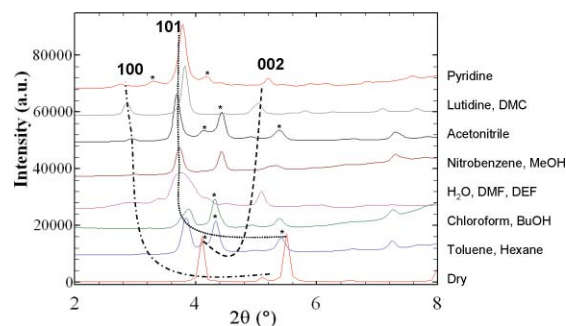


Fig. 3 X-Ray diffraction powder patterns for MIL-89 dispersed in various solvents at room temperature for two hours ($\lambda = 0.71118 \text{ \AA}$). (DMC = dimethylcarbonate, DMF = dimethylformamide, DEF = diethylformamide and BuOH = butanol). The lines reflect the evolution of the Bragg reflections (100), (101) and (002) upon adsorption of liquids. * = unassigned peaks, which are related to some intermediate state of the drying–swelling of MIL-89.

It seems that, on the whole, the hybrid solid MIL-89 adsorbs significant amounts of all kind of solvents as evidenced by a shift toward low angles of the main (100) and (101) Bragg peaks. Due to the poor quality of some of the patterns or to the presence

Table 1 Cell parameters of MIL-89 in various solvents

Liquid		Methanol	Ethanol	Lutidine	Pyridine
Open form	$a/\text{\AA}$	15.8	16.5	16.4	17.0
	$c/\text{\AA}$	16.75	15.9	16.1	15.7
	$V/\text{\AA}^3$	3615	3750	3750	3900
Cell expansion $\Delta V/V$ (%)		145	150	150	160

of mixtures of phases with different breathing amplitudes, it was not possible to index all the patterns. The presence of such mixtures could be due to either a distribution of particles and/or aggregate sizes that would change the diffusion of liquids within the pores, or to the presence of multiple domains with different breathing behaviors. However, for the same time of impregnation, the analysis of the cell volumes of some of the open forms indicate (Table 1) that the swelling amplitude, in the presence of polar liquids, varies between 130 and 160% with regards to the cell volume of the dried form (pseudo hexagonal cell: $a \sim 9.15 \text{ \AA}$, $c \sim 19.98 \text{ \AA}$, $V \sim 1470 \text{ \AA}^3$) and a classification for the affinity of the solvents towards MIL-89 as a function of its magnitude of swelling can be proposed as: pyridine > lutidine ~ dimethylcarbonate > acetonitrile > methanol ~ nitrobenzene > water ~ dimethylformamide (DMF) ~ diethylformamide (DEF) > chloroform ~ butanol > toluene ~ hexane. A comparison with the previous results obtained with the MIL-88A, B, C, D series built up from other spacers (fumarate, terephthalate, 2,6-naphthalenedicarboxylate, 4,4'-biphenyldicarboxylate) is proposed. This indicates that at first sight, the behavior of MIL-89 towards the adsorption of solvents is comparable to those of MIL-88B with an easier adsorption of polar solvents, except for water, but a partial swelling only in the presence of apolar liquids (toluene, hexane). Note, that as in the case of previous studies based on the MIL-88 solids, the starting MIL-89as compound used for this study was partially solvated with polar molecules (water, methanol), which might also explain the lower adsorption affinity for the apolar liquids.

Nevertheless, if it is not surprising that the aromatic polar liquids are easily incorporated in MIL-89, the lower adsorption of DMF and DEF however, is unexpected. In the case of MIL-88B and MIL-88C, they were easily adsorbed, more so than for lutidine, which is in contrast with MIL-89. A steric hindrance explanation cannot be argued. In MIL-89, this might come from the absence of aromatic rings and therefore less CH- π interactions that are supposed to play an active role in the adsorption of DMF or DEF in MIL-88C. The replacement of aromatic rings by an aliphatic chain in the MIL-88 or MIL-89 structure type has therefore the same effect as increasing or decreasing the spacer length and corresponds to a drastic modification of the swelling behavior. This confirms that the adsorption of organic molecules in MIL-88 and MIL-89 flexible solids strongly depends on the nature of the organic spacer with parameters such as its hydrophobicity, length as well as the presence of aromatic rings *versus* aliphatic chains. Another remark is noteworthy; in the case of water, toluene or hexane, mixtures of the dried starting phases and the open forms are observed by XRD, in agreement with very slow pore opening kinetics. This also highlights that each MIL-88 or MIL-89 flexible MOF exhibits unique sorption properties and that the

ongoing synthesis and structural determination of other analogues will contribute in providing new adsorbents for applications in adsorption, separation and drug delivery.

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