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How Linker's Modification Controls Swelling Properties of Highly Flexible Iron(III) Dicarboxylates MIL-88

Patricia Horcajada,*,† Fabrice Salles,‡ Stefan Wuttke,†,§ Thomas Devic,† Daniela Heurtaux,† Guillaume Maurin,‡ Alexandre Vimont,§ Marco Daturi,§ Olivier David,† Emmanuel Magnier,† Norbert Stock,∥ Yaroslav Filinchuk,⊥,# Dmitry Popov,∞ Christian Riekel,● Gérard Férey,† and Christian Serre*,†

†Institut Lavoisier, (UMR CNRS 8180), Université de Versailles, 45, Avenue des Etats-Unis, 78035, Versailles Cedex, France

‡Institut C. Gerhardt Montpellier, UMR CNRS 5253, UM2, ENSCM, Place E. Bataillon, 34095 Montpellier Cedex 05, France

§Laboratoire Catalyse et Spectrochimie LCS, UMR CNRS 6506, ENSICAEN, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex 4, France

∥Institute of Inorganic Chemistry, Christian-Albrechts-Universität, Otto-Hahn-Platz 6/7, 24118 Kiel, Germany

⊥SNBL at ESRF, Rue Jules Horowitz, 38043 Grenoble, France

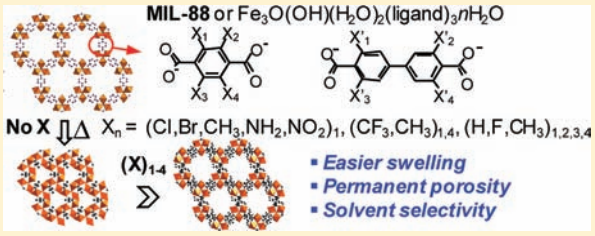
#Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Place L. Pasteur 1, B-1348 Louvain-la-Neuve, Belgium

∞HPCAT, Geophysical Laboratory, Carnegie Institution of Washington, 9700 South Cass Avenue, Building 434E, Argonne, Illinois 60439, United States

●ESRF, 6 Rue Jules Horowitz, B.P.220, 38043 Grenoble, France

S *Supporting Information*

ABSTRACT: A series of organically modified iron(III) terephthalate MIL-88B and iron(III) 4,4′-biphenyl dicarboxylate MIL-88D flexible solids have been synthesized and characterized through a combination of X-ray diffraction, IR spectroscopy, and thermal analysis (MIL stands for Material from Institut Lavoisier). The swelling amplitude of the highly flexible MOFs tuned by introducing functional groups onto the phenyl rings shows a clear dependence on the steric hindrance and on the number of groups per aromatic ring. For instance, while the introduction of four methyl groups per spacer in dried MIL-88B results in a large permanent porosity, introducing two or four methyl groups in MIL-88D allows an easier pore opening in the presence of liquids without drastically decreasing the swelling magnitude. The influence of the degree of saturation of the metal center and the nature of the solvent on the swelling is also discussed. Finally, a computationally assisted structure determination has led to a proposal of plausible structures for the closed (dried) and open forms of modified MIL-88B and MIL-88D and to evaluation of their framework energies subject to the nature of the functional groups.



INTRODUCTION

Metal−organic frameworks (MOFs) are a fascinating class of porous solids. From materials with micropores to crystallized 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.[1−10] These porous solids might be used for several applications such as gas storage[11−14] and separation,[15−17] insertion of metal nanoparticles,[18,19] delivery of nitric oxide,[20,21] drug delivery,[21−23] etc. If most MOFs are rigid, there is a unique characteristic for a scarce number of MOFs that consists of the flexibility of their framework.[3,4] Kitagawa et al.[3] have proposed that the pore opening that occurs upon internal stimuli (gas, vapor, liquid) is governed by the host−guest interactions with a classification of the different types of flexibility into six categories depending on the strength of the interactions and the dimensionality of the inorganic subnetwork: (i) 1D frameworks by ion exchange,[24] (ii) 2D networks by the layer shift,[25] (iii) 2D solids by elongation/shortening of interdigitated layers,[26−28] (iv) 3D pillared layers,[29] (v) expansion and shrinking of 3-D frameworks,[11] and (vi) 3D interpenetrated grids.[30] This leads to original sorption behaviors and thus potential applications in separation,[31,32] storage,[11] drug delivery,[21,22] and sensors as thin films.[33−35] For instance, MIL-53 solids, which are 3D metal(III) terephthalates presenting 1D pore channels, exhibit unusual stepwise adsorption isotherms for a large variety

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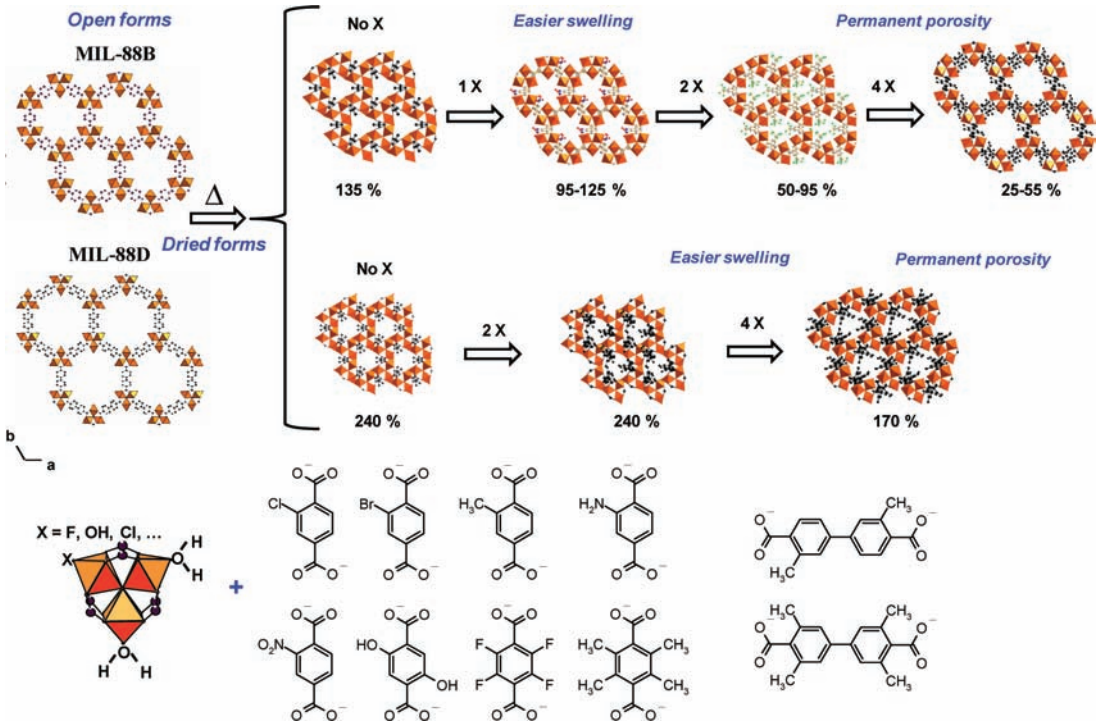

Figure 1. Schematic view along the *c* axis of the structure and the flexibility of the MIL-88B and D modified solids as a function of the number of functional groups (X) per spacer (on the top). Amplitudes of swelling, corresponding to the structural switching from the open to the closed forms, are given in % (=100 × $(V_{op} - V_{dry})/V_{dry}$) below each crystal structure. μ_3-Oxo-centered trimer of iron(III) octahedra is also shown (left bottom). Functionalizing organic linkers are shown in the right bottom. Metal polyhedra, carbon, oxygen, and fluorine are in orange, black, red, and green, respectively. Hydrogen atoms have been removed for sake of clarity.

of adsorbates, associated with a structural transition involving large changes of the unit cell volume.[11] Recently, some of us have also reported an isoreticular class of MOFs, labeled as MIL-88 and formulated as $M_3O(L)_3(H_2O)_2(X)$, with M = Fe, Cr, L = linear dicarboxylate, X = anion,[36,37] that could swell upon immersion in liquids with variations in unit cell volume from 85% to 230% depending on the nature/length of the organic spacer.[38,39] Besides that, the functionalization of organic linkers has already been proposed for the usual rigid MOFs, sometimes affecting gas sorption properties.[40] Nevertheless, only a few studies have been reported so far on the outcome of such an approach for flexible MOFs.[41−45] In this case, the functionalization leads not only to the modification of the physicochemical properties of the framework (polarity, acidity−basicity, potential host−guest interactions, ...) but also to important changes in the pore opening (flexibility) and in the selective adsorption of guests. Indeed, for the flexible iron terephthalate MIL-53, we have recently shown that the presence of functional groups affects strongly the initial pore opening (size and shape) and the selective adsorption of liquid guests through the existence of specific guest−framework interactions.[45] In spite of the exceptional highly flexible behavior of the porous MIL-88 family, studies reported on these solids are scarce, probably because of the high structural complexity of the frameworks. Thus, only a few papers have reported on structure and flexibility of MIL-88 nets.[36−39,46] In addition, some of the nonfunctionalized MIL-88 solids have been evaluated as drug nanocarriers, and first in vivo (rats) toxicity tests have revealed no sign of toxicity, emphasizing the potential interest of this material for medical applications.[21] The consequences of the ligand functionalization on the encapsulation of the model drug caffeine have also been assessed and further rationalized by means of a quantitative structure−activity relationship approach (QSAR).[47] Consequently, beyond the curiosity, the modulation of the breathing phenomenon of the MIL-88 family using functionalized linkers is an interesting but still unexplored topic that might find applications in separation, catalysis, or drug delivery. For extracting the trends of swelling versus the nature of the substituents and of the solvents, we report here the synthesis and characterization of an unprecedentedly large series of MIL-88 solids built from different modified terephthalates and 4,4′-biphenyldicarboxylates complemented by a detailed analysis of their swelling properties in different solvents using a joint experimental/modeling approach.

RESULTS AND DISCUSSION

MIL-88B solids with modified terephthalic acids of the formula $C_6H_{4-x}R_x(CO_2H)_2$ (R = CH_3, CF_3, NH_2, F, Cl, Br, OH, NO_2; see Figure 1) as well as two MIL-88D compounds, built up from 2,2′-dimethyl or 2,2′,6,6′-tetramethyl-4,4′-biphenyldicarboxylic acids, have been synthesized using either hydro or solvothermal conditions (Figure 1) (see Supporting Information for details). X-ray powder diffraction (XRPD), thermal analysis [thermogravimetric analysis (TGA) and X-ray powder thermodiffraction (XRPTD)], elemental analysis, and infrared spectroscopy (IR) have confirmed that all the resulting solids belong to the MIL-88 structure type (see Supporting Information). Moreover, in the cases of MIL-88B(2OH) and MIL-88B($4CH_3$), the crystal structures were solved using the microdiffraction setup available at the synchrotron beamline

ID13 (ESRF; Grenoble, France). It confirmed once again that the solids are isostructural to MIL-88B, i.e., built up from μ_3-oxo-centered corner-sharing trimers of iron(III) octahedra connected through the dicarboxylate linkers (Figure 1) in such a way that two types of cavities exist: tunnels along [001] and bipyramidal cages with trimers at the vertices. Taking into account the symmetry, the organic substituents are disordered on the phenyl rings, as confirmed by the crystal structure analysis of MIL-88B(2OH). Each trimer possesses two terminal water molecules and one counterion to compensate the cationic framework, which could be either bound directly onto the metal centres (X = F, OH) or rest free within the pores (X = Cl, acetate, ...) (see Figure 1).

Swelling as a Function of the Organic Linker. Ex situ synchrotron X-ray powder diffraction tests have been performed at the synchrotron beamline BM1A (ESRF; Grenoble, France) by using glass capillaries filled with the title powders dispersed at room temperature in polar liquids (alcohols and pyridine). It is clearly indicated that all the modified solids swell in appropriate polar solvents. All powder patterns of the investigated materials have been successfully indexed in the $P\bar{6}2c$ (No. 190) or $P6_3/mmc$ (No. 194) space group, both space groups being characteristic of the MIL-88 type frameworks (see Supporting Information Table S15 and Figure S45). Therefore, the modified MIL-88 materials show, on the whole, similar cell parameters as the nonmodified MIL-88B and D solids in their open forms (except MIL-88B(2OH); see below). However, slight changes in the unit cell volumes are present in the open modified MIL-88 solids with a unit cell volume increase by a few dozen to 100 Å^3 compared to the nonmodified solid (Table S15). This might be due to the presence of bulky functional groups that require the framework to swell to a larger extent in order to be able to accommodate the guest molecules. This phenomenon was previously observed with the flexible functionalized MIL-53(Fe) solids.[45] One could also point out that the MIL-88B(2OH) solid presents an intermediate unit cell volume of 2800 Å^3 in ethanol vs 3200−3500 Å^3 for the other analogues, probably because of the existence of strong hydrogen bonding between the OH groups of the linker and of the alcohol molecules that stabilize a partial pore opening during adsorption. However, differences in cell volumes between each form are much higher in the dried state, as deduced from X-ray laboratory thermodiffractometry experiments (Table 1, Figure 2, and Figure S46).

A clear dependence of the unit cell volume of the modified MIL-88B and MIL-88D solids on both the number and the size[48] of the functional group is observed (see below for more details). For instance, the ratio of the unit cell volume of the dried form to that of the open version varies for the modified MIL-88B as indicated in Table 1. In the case of MIL-88D, almost no change in the unit cell volume is observed for the dimethyl form while the tetramethyl analogue exhibits a smaller breathing amplitude of ∼105% in comparison to 240% for the original MIL-88D(Cr) solid.

The crystal structures of the modified MIL-88B and MIL-88D solids in both dried and open states have been determined using a computational assisted structure determination strategy based on energy minimization procedures and classical force fields for representing the interactions within the framework. Indeed, all the functionalized structures were first built from the initial atomic coordinates of the nonmodified MIL-88B and MIL-88D frameworks and further geometry optimized by imposing the experimental unit cell parameters obtained from the X-ray diffraction refinement (see Supporting Information). One should keep in mind that the so-proposed structure models were obtained without considering the interactions with the solvent molecules, even for the open forms. This procedure has already been validated to propose plausible closed (dried) and open structures for the MIL-53(Fe) series and for the different forms of the flexible Co(BDP) solid that exist upon N_2 adsorption.[45,49]

On the basis of these simulated structures, the origin of the decrease in the swelling magnitude can be explained in terms of

Table 1. Unit Cell Volumes and Amplitudes of Swelling of the Dried Forms of Modified MIL-88B and MIL-88D as a Function of the Nature of the Functional Groups[a]

	MIL-88B		MIL-88D	
	closed form		closed form	
functional group	a (Å) c (Å) V (Å^3)	swelling amplitude[b] (%)	a (Å) c (Å) V (Å^3)	swelling amplitude[b] (%)
4H	9.5 19.0 1485	136	10.2 27.6 2490	237
NH_2	9.7 18.5 1510	132		
Cl	9.9 19.0 1610	117		
CH_3	10.35 19.2 1780	97		
Br	10.5 18.9 1805	94		
$2CH_3$	10.4 19.1 1790	96	10.3 27.8 2560	228
2OH	10.6 18.7 1820	92		
NO_2	11.5 18.8 2150	63		
4F	11.8 18.8 2270	54		
$2CF_3$	12.1 18.5 2350	49		
$4CH_3$	13.9 16.8 2810	25	13.7 25.6 4100	105

[a] Unit cell volumes of open forms of MIL-88B and MIL-88D have been taken as 3500 and 8400 Å^3, respectively.[39] [b] Swelling amplitude is defined as $(V_{op} - V_{dry})/V_{dry}$ in %. V_{op}(MIL-88B) = 3500 Å^3 (MIL-88B(2CF$_3$) in MeOH). V_{op}(MIL-88D) = 8400 Å^3 (MIL-88D(4CH$_3$) in EtOH). Estimation of cell parameters have been deduced from the XRPTD experiments using the Powdercell software.

steric hindrance (Figure 3). In their dried forms, the MIL-88 structures contract along the *a* and *b* directions while expanding along the *c* axis, resulting in an overall decrease of the unit cell volume (Figure 3). The opening of the structures can be estimated from the angle (θ) formed between the linker and the bipyramid height (see insert Figure 3). One can deduce a rather good relation between this angle and the effective steric parameter of the functional groups,[48] which is a nondimensional parameter that takes into account not only the van der Waals volume but also the geometry (for more details see ref 41, Figure 3).

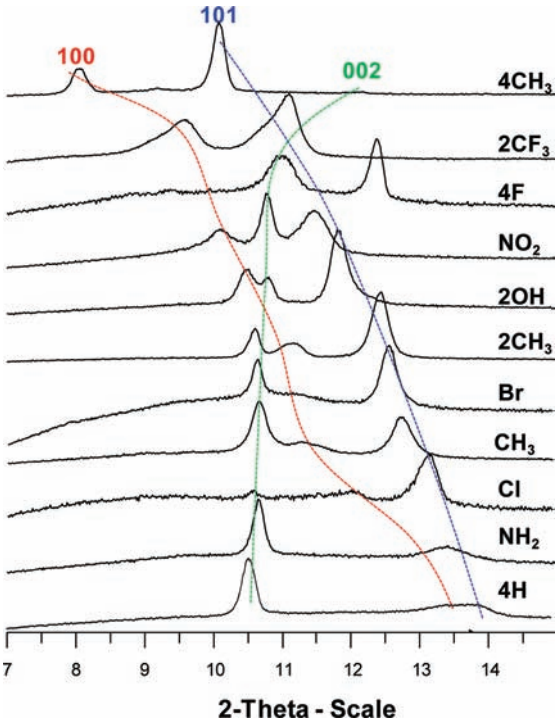

Figure 2. XRPD ($\lambda_{Co} \approx 1.79$ Å) of the dried forms of the various functionalized MIL-88B samples. Dotted lines for the three first Miller indices have been added for easier tracking.

In the case of the dried MIL-88B structure, the phenyl rings, located either above or below the trimers (in regards to the *c* axis), are almost packed along the *c* axis and thus may interact through $\pi-\pi$ interactions (see C−C distances within the 3.5−4 Å range), which stabilizes the structure in its closed form. In the case of the modified solids, as illustrated in Figure 4 for the methyl substituted MIL-88B or MIL-88D structures, the substitution of one or several aromatic protons by functional groups results in an increase of the minimum distances between the phenyl rings due to steric and intramolecular interactions effects. This makes it more difficult to observe a contraction of the structure along the *a* and *b* axes and therefore reduces the breathing capability of these solids. Interestingly, the trimers do not seem to be twisted anymore within the *ab* plane when methyl groups are present. Note that the changes in magnitudes of swelling ($(V_{op} - V_{dry})/V_{dry}$ in %) and the unit cell parameters fully agree with the trend for the effective steric effect of the substitution (Figure 3 and Table 1). At first glance, the smaller change in cell contraction between the tetramethyl MIL-88D solid in comparison with the tetramethyl MIL-88B compound seems obscure (Figure 4). However, one should remember that the methyl groups are located on the same phenyl ring in MIL-88B while they occupy two different aromatic rings that can rotate independently in MIL-88D (see Figure 1), this effect being even more pronounced in the dried forms. This leads to larger minimum distances (>5 Å) between the rings in the dried MIL-88B form and to a much smaller pore contraction.

The consequences of the steric effect in terms of permanent porosity have been first evaluated using nitrogen adsorption experiments at 77K (see Supporting Information). While the MIL-88B(H, Cl, Br, NH_2, NO_2, 2OH) solids do not exhibit any significant surface area ($S_{BET} < 30\ m^2 \cdot g^{-1}$), the 4F, CH_3, $2CH_3$, $4CH_3$, and $2CF_3$ MIL-88B forms show a permanent porosity with type I isotherms, indicating a rigid behavior toward adsorption of nitrogen with BET surface area of approximately 30, 80, 60, 1220, and 330 $m^2 \cdot g^{-1}$, respectively. The hindrance of the

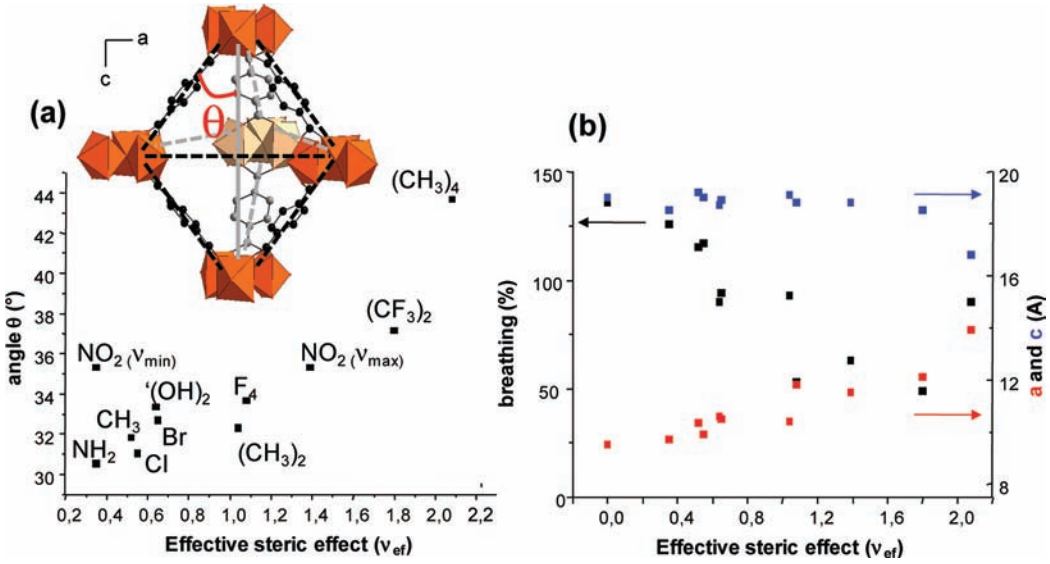

Figure 3. Variation of (a) the θ angle of the bipyramid characteristic of the MIL-88 structure in the dried form and (b) the swelling amplitude and the unit cell parameters *a*, *c* versus the effective steric parameter of the functional group. Insert (top left): definition of the angle θ (hydrogen atoms are omitted for clarity; metal polyhedral and carbons are in orange and black, respectively).

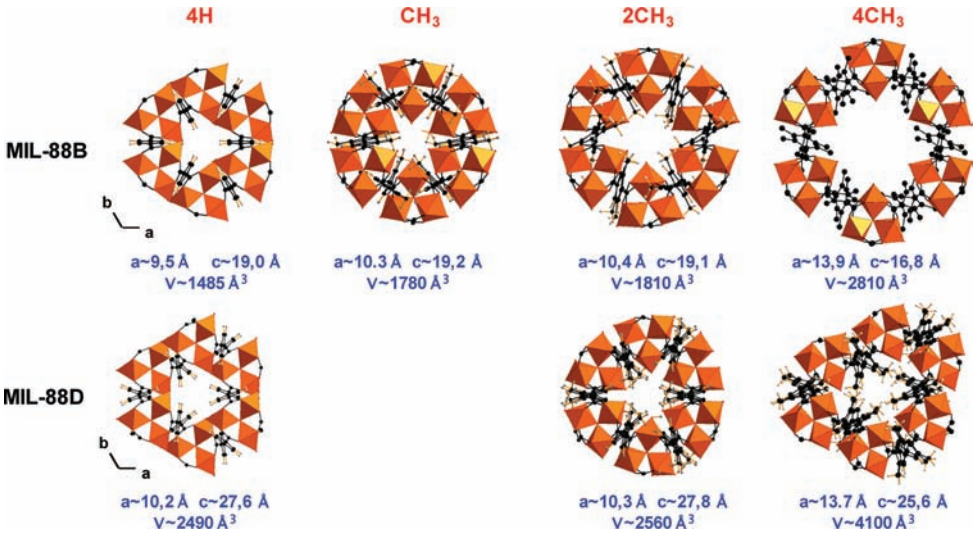

Figure 4. View along the *c* axis of one pore of the dried MIL-88B, MIL-88(CH_3), MIL-88B($2CH_3$) and MIL-88B($4CH_3$), MIL-88D, MIL-88D($2CH_3$), and MIL-88D($4CH_3$) solids. Metal polyhedra, carbon atoms, and hydrogen atoms are in orange, black, and gray, respectively. The corresponding cell parameters are provided for a better understanding.

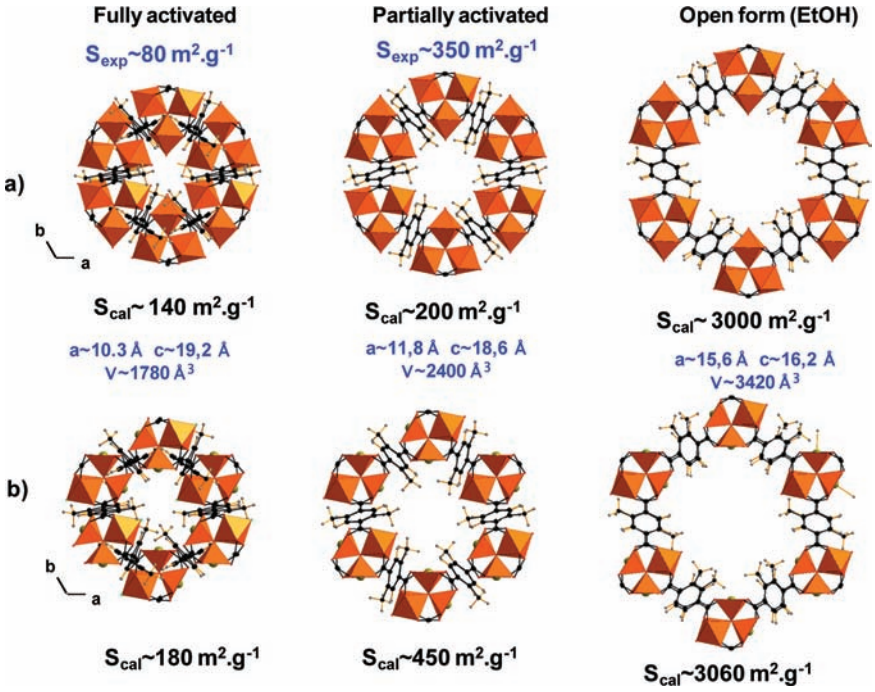

Figure 5. View along the *c* axis of the structure of MIL-88B(CH_3) as a function of the quality of the activation (left, properly activated; center, badly activated; right, fully open). Metal polyhedra, carbon atoms, and hydrogen atoms are in orange, black, and gray, respectively. Top (a): hexacoordinated Fe atoms only. Bottom (b): two pentacoordinated and one hexacoordinated Fe atom per trimer. The corresponding surface areas and cell parameters are given for a better understanding.

monosubstituted MIL-88B is generally not enough to maintain a sufficient pore opening for gases. MIL-88B(2OH) shows no significant porosity, since its lower thermal stability rules out its proper activation before its framework alteration. Noteworthy, the presence of residual molecules in the pores, associated with a partial activation, leads to a permanent porosity. For instance, after washing MIL-88B(CH_3) with DMF and a calcination in air at 200 °C, a higher surface area (S_{BET} = 350 $m^2 \cdot g^{-1}$) is observed compared to the properly purified solid (washed with DMF, followed by an exchange with EtOH and then heated at 150 °C; S_{BET} = 80 $m^2 \cdot g^{-1}$) (see Figures 5 and S21). This is likely to be due to the presence of remaining DMF still trapped in specific pockets that blocks partially the pore contraction and thus leads to a higher pore opening. This is supported by XRPD analysis of the poorly activated sample for which the unit cell parameters are $a \approx 11.8$ Å, $c \approx 18.6$ Å, and $V \approx 2400$ Å^3 (see Figure S21) vs $a \approx 9.3$ Å, $c \approx 19.1$ Å, and $V \approx 1630$ Å^3 for the properly activated sample. The theoretical surface area for the well activated sample

is equal to 180 $m^2 \cdot g^{-1}$, while the one of the partially activated sample, not taking into account the presence of residual guest species, varies between 200 and 450 $m^2 \cdot g^{-1}$ depending on the presence or not of the coordinated water molecules on the trimers upon activation (see below for further information about coordinated water and the Supporting Information for more details about the calculations). Likely, the observed experimental BET surface area corresponds to a partial removal of the coordinated water. Similarly, the same feature might occur in the case of other MIL-88 structures reported previously. One could cite the iron(III) tetrafluoroterephthalate $[Fe_3O(F_4BDC)_3(H_2O)_3(DMF)_{3.5}]$ or MIL-88B-4F[50] or the scandium terephthalate $[Sc_3O(BDC)_3(H_2O)_3 \cdot Cl_{0.5}(OH)_{0.5}(DMF)_4(H_2O)_3]$ or MIL-88B(Sc).[51] Both exhibit a significant nitrogen accessible porosity with surface areas of 635 ($S_{Langmuir}$) and 634 $m^2 \cdot g^{-1}$ (S_{BET}), respectively, while very low surface areas are obtained for the properly activated MIL-88B-4F and MIL-88B samples.

The theoretical accessible surface areas estimated from the simulated structure models for the dried state (see Table S16) confirm that only some modified MIL-88B structures possess a permanent porosity including the CH_3, $2CH_3$, $4CH_3$, and $2CF_3$ functionalized solids while others do not show significant accessibility for a N_2 sized probe molecule.

For the $4CH_3$ analogue, the experimental BET surface area of the fully activated sample reaches 1216 $m^2 \cdot g^{-1}$, which is close to the theoretical surface areas ranging from 1096 to 1208 $m^2 \cdot g^{-1}$, considering either only hexacoordinated or a 2:1 ratio of hexacoordinated and pentacoordinated iron metal sites, as detailed below.

These conclusions are consistent with the experimental observation stated above. However, although a significant surface area was predicted for MIL-88B(4F) and MIL-88B(NO_2), the experimental N_2 adsorption measurement did not show any accessible surface to the nitrogen molecules. This later observation could be justified through the estimation of the free aperture in the simulated structures, taking into account the van der Waals radii. One should bear in mind that this geometric parameter can only be approximately determined because of the complex shape of the pores and the dynamic effects (possibility to freely rotate the spacer/functional groups and/or partial breathing during the adsorption processes), as well as the possible presence of residual coordinated water molecules. Indeed, the pore sizes for the dried forms of MIL-88B(4F) and MIL-88B(NO_2) are similar to the nitrogen dimensions (~3.8 Å), probably preventing the penetration of the gas inside the cavity. The free apertures for the other solids range from 3 to 5.5 Å following the sequence MIL-88(Br) < MIL-88B(Cl) ~ MIL-88B(2OH) ~ MIL-88B(NH_2) ~ MIL-88B(NO_2) ~ MIL-88B(4F) ≪ MIL-88B(CH_3) < MIL-88B($2CH_3$) < MIL-88B($2CF_3$) < MIL-88B($4CH_3$). In addition, one should be aware that the unit cell parameters used for simulating the structure models have been obtained from experimental X-ray thermodiffraction data collected at high temperatures (T > 100 °C), whereas N_2 adsorption measurements were obtained at low temperature (77 K). Thermal contraction/expansion effect cannot be excluded. This fact, together with the nitrogen molecule size at 77 K (~3.8 Å), could explain the very small adsorbed amount of N_2 in MIL-88B(4F) with a free aperture of <4 Å. In the case of the modified tetramethyl MIL-88D solids, a low permanent porosity for nitrogen ($S_{BET} \approx 210$ $m^2 \cdot g^{-1}$) has been observed.

Thermal Characterization. The thermal behavior of the samples was investigated by X-ray thermodiffraction, TG analysis, and in situ IR analysis (see Supporting Information). All analyses led to consistent results regarding the solvent desorption behavior of the samples. The free and/or coordinated solvent/water departure occurs under high vacuum (used in the in situ IR studies) at rather low temperature (T < 100 °C), whereas under gas atmospheres (O_2 or air/Ar/CH_4 employed in the TGA and XR thermodiffraction analysis) it occurs at higher temperature (up to 200 °C). The departure of the water coordinated to the iron metal (two irons per trimer; see Figure 1) leads theoretically to the formation of pentacoordinated iron sites, such as those observed previously with the iron trimer based MIL-100(Fe) MOF.[52] Unsaturated pentacoordinated iron(III) sites were observed with a Lewis acid character that can strongly interact with unsaturated probe molecules, such as NO[53] or propylene.[54] Moreover, the partial reduction of one iron per trimer as a consequence of the counterion departure is likely to occur, as recently reported for the iron trimer MIL-100(Fe) (iron trimesate).[50] In addition to the potential presence of Lewis acid sites in the MIL-88 modified samples, structural transitions have been observed upon activation for some of these solids depending on the conditions (heating under air or vacuum). High quality XRPD has been collected at 150 °C under air on the MIL-88B($4CH_3$) sample, i.e., at conditions where the pores are not fully contracted and the removal of the coordinated water is not maximal. This reveals a monoclinic, pseudohexagonal unit cell with a = 16.31(1) Å, b = 17.43(1) Å, c = 12.83(1) Å, β = 121.07(3)°, V = 3123(1) $Å^3$, space group $P2_1/n$ (No. 13) (see Figure S48). However, full analysis of all structural changes associated with the complete desorption of guest molecules coordinated on the metal sites is very complex because of the moderate thermal stability (see below) and the strong decrease in crystallinity of MIL-88 samples.

Under vacuum, the thermal stability, evaluated using IR spectroscopy, is close to 200 °C for all the MIL-88B solids except for MIL-88B(Cl) and MIL-88B(2OH) that show a stability up to 250 and 25 °C, respectively. The MIL-88B(Cl) solid seems to be slightly more thermally stable than the other functionalized MIL-88. By contrast, the very low thermal stability of the MIL-88B(2OH) can come from the redox reactivity of the ligand (BDC-2OH).[55] Such a low stability for a MOF based on BDC-2OH linker has already been observed in the series of the functionalized iron terephthalate MIL-53(Fe) samples.[45] In addition, the MIL-88D samples are stable up to 200−250 °C. Furthermore, under air, X-ray thermodiffraction experiments reveal a thermal stability around 250 and 200 °C for all the functionalized MIL-88B and MIL-88D solids, respectively (except for MIL-88B(2OH)), which remains slightly lower than for the nonmodified MIL-88 (300 °C). Therefore, one can argue that the introduction of functional groups does not generally lead to a drastic change of the thermal stability.

Swelling as a Function of the Solvent Properties. The influence of the functionalization on the swelling properties of MIL-88D has been investigated (Figure 6). It was shown previously that the longer the organic spacer in MIL-88, the harder is the pore opening in the liquid state.[39] For instance, the dried MIL-88D required the use of hot pyridine to reopen its pores whereas the partially opened MIL-88D in its as-synthesized form can be fully reopened in some selected liquids. This can be explained by a lighter π-stacking effect in the partially open MIL-88D structures, due to the possible rotation of the two phenyl rings, as it can be deduced from the simulated structures. This feature is also in agreement with the easier accessibility of the porosity, starting from a partial pore opening, as observed above

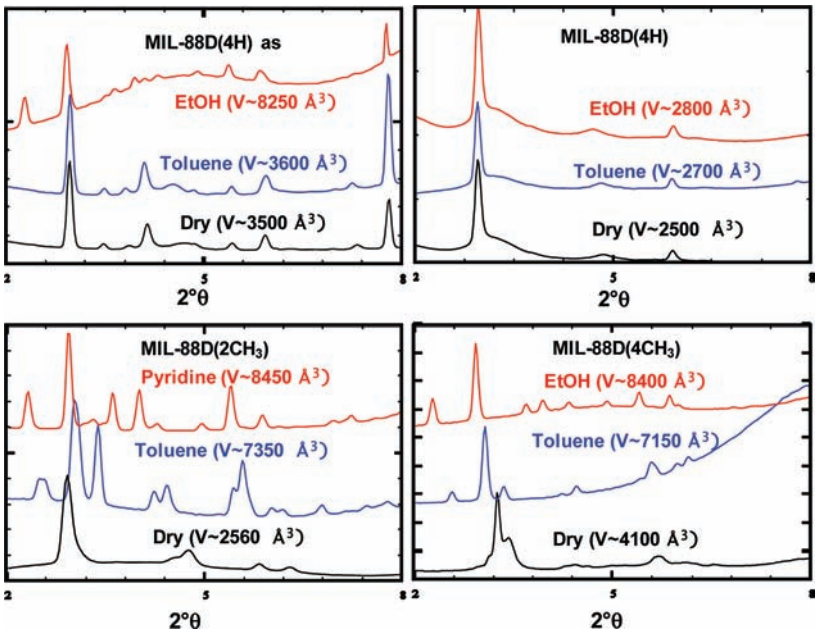

Figure 6. X-ray diffraction patterns ($\lambda \approx 0.7$ Å) and corresponding approximate unit cell volume of different MIL-88D samples immersed in various solvents.

Table 2. Cell Parameters of Various MIL-88D, MIL-88D-($2CH_3$), and MIL-88D ($4CH_3$) in a Few Selected Solvents

MIL-88D/liquid	dry *a* (Å) *c* (Å) *V* (Å^3)	ethanol *a* (Å) *c* (Å) *V* (Å^3)	toluene *a* (Å) *c* (Å) *V* (Å^3)	pyridine *a* (Å) *c* (Å) *V* (Å^3)
4H	10.2	10.3	10.1	11.2
	27.6	27.8	27.8	27.3
	2490	2800	2700	2990
4H_as	12.0	20.5	12.6	20.7
	22.0	22.7	27.8	22.2
	3500	8250	3620	8240
$2CH_3$	10.3		18.9	20.4
	27.8		24.3	22.7
	2560		7500	8250
$4CH_3$	13.7	20.5	18.4	
	25.6	22.7	24.4	
	4100	8250	7200	

for the N_2 adsorption on partially activated MIL-88 samples.[50,51] Ex situ swelling tests of modified di- or tetramethyl MIL-88D solids dispersed in toluene, ethanol, or pyridine were realized (Table 2 and Figure 6). Nonpolar liquids did not lead, however, to any pore opening whatever the initial contraction state of MIL-88D. On the contrary, the polar aliphatic ethanol or polar aromatic nitrobenzene allowed the pore opening but only when starting from the as-synthesized solid (i.e., partially open). It appears that polar liquids almost completely open the pores of the MIL-88D($4CH_3$) solid with resulting unit cell volumes within the 7200−8300 Å^3 range. This was expected because of the slight increase of the initial accessible pore size, considering the unit cell volume of the MIL-88D($4CH_3$) sample (4100 Å^3) which is slightly larger than those of the as-synthesized nonmodified MIL-88D (~3500 Å^3). While MIL-88D did not show any pore opening in toluene (see Table 2 and Figure 6), this nonpolar solvent surprisingly leads to a large pore opening of MIL-88D-($4CH_3$) ($V \approx 7200$ Å^3). Another unexpected behavior is obtained for the fully contracted MIL-88D($2CH_3$) dry analogue, which possesses in its dry state a unit cell volume ($V \approx 2560$ Å^3) similar to that of the nonmodified dried form of MIL-88D ($V \approx 2500$ Å^3). The dried form of MIL-88D($2CH_3$) reopens to a large extent not only in the polar liquids (pyridine; $V \approx 8250$ Å^3) but also in toluene, with a unit cell volume close to 7500 Å^3. Indeed, this observation confirms that the initial pore opening is not the only key parameter that will govern the adsorption of liquids within the MIL-88 solids. Other factors such as the presence of additional groups (methyl) that can either decrease the intra-framework interactions ($\pi-\pi$) through steric effects or increase the interframework van der Waals or $-CH-\pi$ interactions with the adsorbate molecules (toluene) are crucial.

Indeed, the adsorption of liquids in the highly flexible MIL-88 solids is driven by the minimal accessible pore size and the host−guest interactions, as it was demonstrated previously for other flexible solids.[45,56] Another explanation could come from the energetics of the breathing. The introduction of two methyl groups in MIL-88D does not reduce the swelling ability but most likely reduces the $\pi-\pi$ interactions within the dried form and, therefore, should reduce the energy required to reopen the pores.

Energetics of the Different Forms. As a further step, the energy corresponding to the geometry-optimized structures for all functionalized MIL-88B in their dried and open forms has been computed. Note that these calculations were performed considering the structures in both states with hexacoordinated iron metal centers. The energy required for the pore opening can thus be estimated in a first approximation from the framework energy difference between the energies of the open and the closed structures. The resulting energy values are negative in the cases of the MIL-88B, MIL-88B(Br), MIL-88B(4F), MIL-88B($2CH_3$), and MIL-88B($4CH_3$), emphasizing that the structure is expected

to evolve toward the open form upon solvent immersion without the need to employ drastic conditions such as highly polar solvents or high temperature. The situation differs for the other functionalized solids for which the energy difference is positive with the following sequence: MIL-88B($2CF_3$) > MIL-88B-(2OH) > MIL-88B(NO_2) > MIL-88B(NH_2) > MIL-88B(Cl). Here, it means that the higher this energy difference is, the larger is the additional energy that needs to be supplied from "outside" for initiating the swelling of these MIL-88B structures.

This result clearly establishes that the energetic cost for opening the MIL-88B strongly depends on the nature of the functionalized groups. This is often compensated (or even over-compensated) by external stimuli including additional host−guest interactions or thermal effect.[57] Therefore, modification of flexible MOFs can significantly change their ability of swelling in the presence of liquids. This will have strong consequences in the selectivity of the pore opening, since the energetic benefits from host−guest interactions have to exceed those of intraframework interactions in order to allow the structure to swell.

Thus, an appropriate choice of the functional group will allow us to (re)orientate the selectivity of the adsorption in the MIL-88 structures. Further liquid phase adsorption tests are currently in progress to analyze, in detail, the consequences of functionalization in these highly flexible hybrid solids.

CONCLUSION

We report here the synthesis, characterization, and structural analysis of a large series of functionalized highly flexible nontoxic iron(III) dicarboxylates MOFs with the MIL-88 topology. It appears that the swelling behavior of these MOFs is drastically affected by functionalization following two main directions. First, a decrease in the breathing amplitude is proportional to the size of the functional group and the number of such groups per spacer, leading in some cases to a permanent porosity for nitrogen after complete activation of the samples. Second, introducing functional groups, by modifying the energetics of the host−guest/intraframework interactions and/or by lowering the initial diffusion barrier of the guest, strongly facilitates the swelling behavior in liquid phase, including an unexpected breathing in nonpolar solvents. This paves the way for the use of these functionalized flexible solids for adsorption, separation, catalysis, and/or biomedical applications.

ASSOCIATED CONTENT

Supporting Information. Synthesis details, characterization, XRD data, TGA, elemental analysis results, N_2 adsorption porosimetry, structural description, simulation methodology, and zipped files containg crystallographic information in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
horcajada@chimie.uvsq.fr; serre@chimie.uvsq.fr

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