DOI: 10.1002/anie.200704034

Metal–Organic Frameworks

Directing the Structure of Metal–Organic Frameworks by Oriented Surface Growth on an Organic Monolayer**

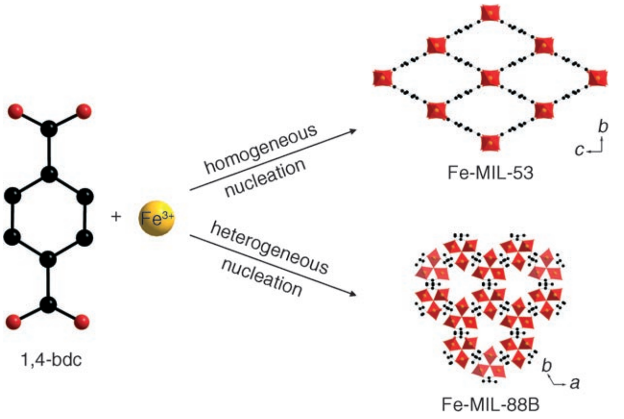
*Camilla Scherb, Alexander Schödel, and Thomas Bein**

The concept of biomineralization implies control of crystallization in terms of phase and orientation through interactions with organic macromolecules.[1] This is of particular interest for the synthesis of biomimetic materials.[2] If one strives to mimic the enormous structure-directing power of biomineralization in materials science, an artificial organic interface is needed. For example, functionalized self-assembled monolayers (SAMs)[3] have been shown to effect oriented growth and phase direction of dense-phase calcium carbonate.[4] The oriented growth of other dense materials such as lead sulfide[5] and zinc oxide,[6] and even the oriented growth of porous materials such as zeolites,[7] on SAMs has been reported. Studies on the growth of MOF-5 and HKUST-1 phases on organic monolayers were recently reported.[8] However, to our knowledge, so far it has not been possible to control the crystal structure of a porous material through interactions with molecular layers. This is expected to be particularly difficult due to the large, complex unit cells of these systems.

Herein we present a dramatic change in the crystallization of a porous metal–organic framework on moving from homogeneous nucleation to heterogeneous nucleation on an ordered SAM.

Due to their many potential applications such as gas sorption, molecular separation, storage, and catalysis, metal–organic frameworks (MOFs) have been intensively studied.[9] We have recently reported the tunable, oriented growth of the porous MOF HKUST-1 on different functionalized SAMs.[10] Herein we investigate the crystal growth of MOFs on mercaptohexadecanoic acid (MHDA) SAMs in the system Fe^{III}/bdc (bdc = 1,4-benzenedicarboxylic acid or terephthalic acid). In this system several open-framework structures are known, including MIL-53 and MIL-88. The structures of MIL-53 and MIL-88 are very flexible, and the cell constants of these materials are strongly dependent on pore content.[11] The framework flexibility of these materials enables their use for adsorption of different organic molecules and makes them interesting candidates for sensors.

In the monoclinic structure of $Fe(OH)(bdc)(py)_{0.85}$, the Fe^{III} analogue of MIL-53, chains of FeO_6 octahedra are connected by benzenedicarboxylate anions. Thus, rhomb-shaped one-dimensional (1D) channels are formed that run along the *a* axis of the structure.[12] The hexagonal 3D structure of MIL-88B is built up from trimers of FeO_6 octahedra linked to benzenedicarboxylate anions. Thus, the 3D pore system of MIL-88B consists of tunnels along the *c* axis connected by bipyramidal cages (Scheme 1).[13]



Scheme 1. In the system Fe^{III}/bdc we observe Fe-MIL-53 as the product of homogeneous nucleation and oriented Fe-MIL-88B as the product of heterogeneous nucleation on MHDA-functionalized gold surfaces.

Highly ordered thin films of MOF crystals were formed on the carboxylate-terminated SAMs. X-ray diffraction patterns of all synthesized thin films show two reflections at $2\theta = 9.2$ and 18.4° (Figure 1a). For further characterization the crystals were removed from the gold surface. The powder pattern of the removed crystals shows several additional reflections in comparison to the XRD patterns of the films (Figure 1b). The lack of these additional reflections in the XRD patterns of the film samples is proof of oriented assembly of the crystals on the functionalized gold surface.

We now turn our attention to the structural identity of the surface-grown MOF crystals. The reflections in the XRD pattern of the synthesized films fit both the (011) and (022) reflections of MIL-53 as well as the (002) and (004) reflections of MIL-88B (Figure 1).

The precipitate in the crystallization solution during film synthesis can be identified as the iron analogue of MIL-53 (Figure 1c). However, the powder pattern of the crystals removed from the surface does not fit the powder pattern of bulk MIL-53. An authentic sample of MIL-88B was prepared by bulk synthesis,[13,14] and the XRD pattern of this product (Figure 1d) agrees very well with that of the surface-removed

---

[*] C. Scherb, A. Schödel, Prof. T. Bein
Department Chemie und Biochemie
Ludwig-Maximilians-Universität
Butenandtstrasse 11 (E), 81377 München (Germany)
Fax: (+49) 89-2180-77622
E-mail: bein@lmu.de
Homepage: http://www.cup.uni-muenchen.de/pc/bein

[**] We would like to thank Sebastian Bauer (University of Kiel, Germany) for fruitful discussions.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

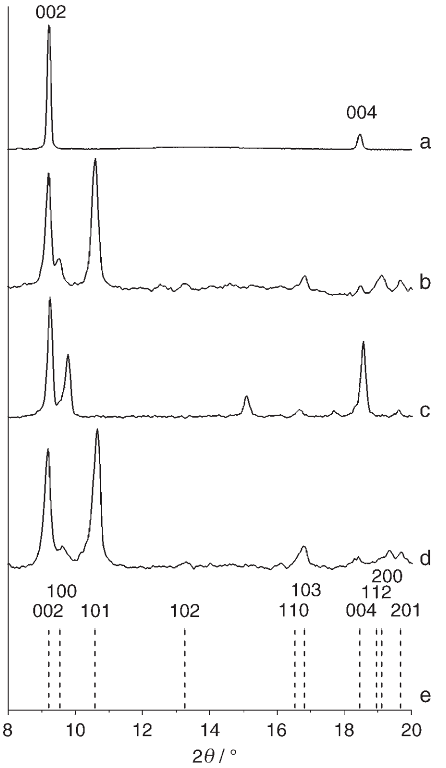


Figure 1. a) XRD pattern of the film on a gold substrate, b) powder pattern of the removed crystals, c) powder pattern of bulk Fe-MIL-53, d) powder pattern of bulk Fe-MIL-88B, and e) calculated reflection positions for Fe-MIL-88B. All patterns are normalized to the most intense reflection.

crystals. It is possible to index the reflections of the XRD pattern of the removed crystals in the space group of MIL-88B as $P\bar{6}2c$[15] (Figure 1e). The lattice constants were determined to be $a = 10.8$ and $c = 19.2$ Å.

As indicated in Scheme 1, Fe-MIL-53, the product of homogeneous nucleation from the crystallization solution, differs dramatically from Fe-MIL-88B, the product of heterogeneous nucleation on the functionalized gold surface. We attribute this dramatic effect to symmetry transfer, that is, the different symmetry relationships between the carboxylate-terminated SAMs and the two crystal systems. Carboxylate-terminated thiolates, as well as thiolates in general, are adsorbed on an Au(111) surface to form a $(\sqrt{3}\times\sqrt{3})$R30° overlayer.[16] The order of carboxylic acid SAMs responds sensitively to the deposition conditions.[17] The SAMs used in this study feature carboxylate termini and high crystallinity in the alkyl part of the film, as evidenced by the reflection/absorption infrared spectra presented in the Supporting Information. No crystal growth was observed with hydroxy- and alkyl-terminated SAMs or with untreated gold slides. Presented with a surface exposing (approximately) hexagonal symmetry, the reactants (Fe^{III} and bdc) clearly prefer to crystallize in the form of hexagonal MIL-88B instead of monoclinic MIL-53.

To investigate the morphology of the crystals grown on gold substrates, scanning electron micrographs of samples after different immersion times were taken. The scanning electron micrographs of three different samples are shown in Figure 2. After an immersion time of 24 h, small hexagonal pyramids with almost vertical orientation and a diameter of about 200 nm can be observed. Crystal intergrowth has already started after an immersion time of 24 h. After an immersion time of 3 d the gold surface is almost completely covered with pillarlike hexagonal crystals that are about 500 nm long. Samples with longer immersion times show cracked films in the SEM image. The cracking may be due to post-synthesis treatment of the samples (i.e., drying under nitrogen or evacuation during SEM).

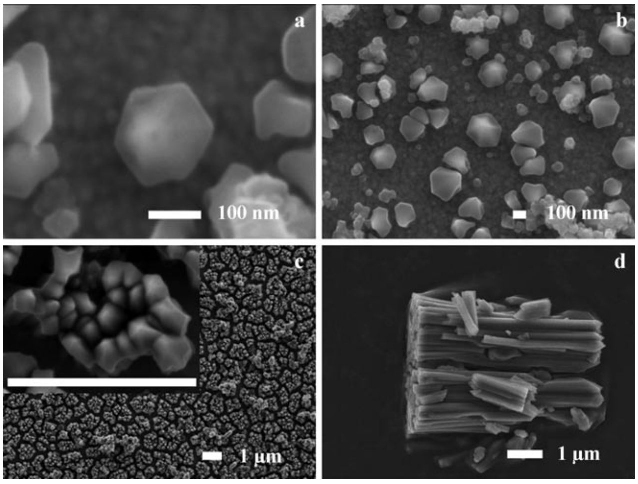


Figure 2. Scanning electron micrographs of samples after immersion times of a, b) 24 h and c) 3 days. d) A bundle of removed crystals after 9 days.

The morphology and symmetry of the crystals agree well with the structure of MIL-88B. The XRD pattern of the film shows exclusive orientation of the crystals in the [001] direction. This implies that the (001) plane of the crystals is parallel to the gold substrate. Figure 3 shows schematically the connection of MIL-88B to the carboxylate groups of the MHDA SAMs on the gold surface. The sixfold axis of the MIL-88B crystal lattice is aligned with the hexagonal symmetry of the SAM/liquid interface.

In addition, oriented crystal growth on the carboxylate-terminated SAMs can be explained by coordination of carboxylate at the metal atoms of the MOF. Since all terephthalic acid molecules are oriented along [001], substitution of the carboxylate groups of terephthalic acid by carboxylate moieties of the SAM will enable crystal growth only in the [001] direction (Figure 3).

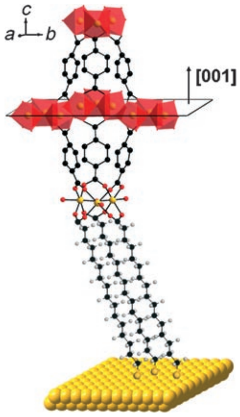


Figure 3. Oriented growth of MIL-88B crystals on MHDA SAMs on an Au(111) surface. Crystals grow in the [001] direction.

To investigate the properties of the grown crystals, particularly with regard to sorption behavior, samples were exposed to saturated DMF vapor for 24 h. Due to the framework flexibility of MIL-88B as a function of pore content, the DMF form of MIL-88B shows different reflection positions compared to the as-synthesized form.[15] Our results show clearly that the structure changed during uptake of DMF (Figure 4). The (002) reflection after DMF uptake lies at $2\theta = 10.02°$ (Figure 4b), a value fairly similar to that of $2\theta = 10.4°$ reported for bulk MIL-88B[15] (small differences are attributed to different partial pressures of DMF in these experiments and to surface attachment of the crystals). During desorption of DMF XRD measurements were performed every 30 min (Figure 4c–i). In the beginning desorption causes a continuous structural change, which after 24 h ends with the state shown in Figure 4j, which is similar to the initial state. The surface-bound MIL-88B crystals were synthesized in their expanded, DMF-loaded form, and shrinkage on drying provided space for expansion on renewed uptake of DMF. Obviously their elasticity can accommodate the shrinkage and expansion cycles demonstrated in the experiment.

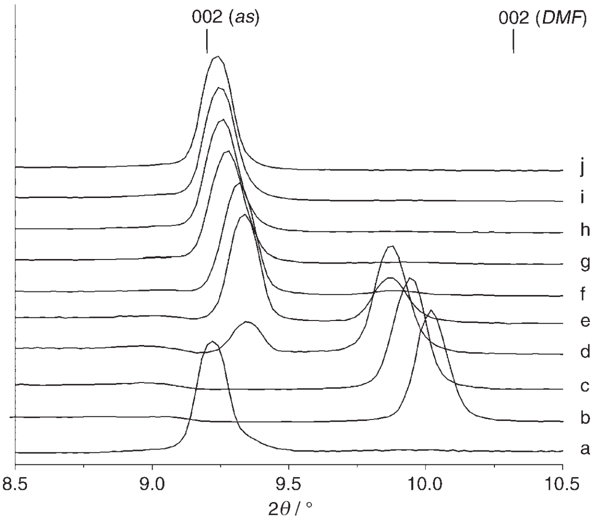


Figure 4. XRD patterns of MIL-88B films a) dried after synthesis, b) after exposure to DMF vapor for 24 h; c)–i) XRD measurements on sample (b) every 30 min during desorption in air, j) sample (b) after drying for 24 h.

In conclusion, we have shown striking structure-directed and oriented growth of MIL-88B on MHDA SAMs. Whereas MIL-53 is the product of homogeneous nucleation, oriented MIL-88B grows from the same crystallization solution on the functionalized gold surface. These remarkable results can be explained through favorable symmetry relationships between the hexagonally ordered SAMs and the hexagonal structure of MIL-88B. The carboxylate functionality of the MHDA SAMs can mimic the carboxylate groups of the bdc molecules and thus direct oriented growth on the surface. We could also show that the pores of MIL-88B crystals in the film are accessible to DMF molecules and that characteristic associated structural changes during the adsorption and desorption processes can be observed.

Future studies will show whether the concept of symmetry transfer between functional monolayers and complex crystalline materials can be adapted to other MOFs, and thus provide a powerful means to control structure and orientation in biomimetic materials systems.

Experimental Section

Prior to the growth of iron terephthalate crystals, gold substrates were treated with an ethanolic solution of MHDA by known procedures[18] to produce SAMs. The functionalized gold substrates were placed face-down in a crystallization solution obtained by solvothermal treatment of a synthesis mixture for MIL-53 at 150 °C for 2 days, filtration, and further treatment of the clear solution at 150 °C for 5 days.

Received: September 2, 2007
Revised: February 22, 2008

Keywords: crystal growth · iron · microporous materials · monolayers · surface chemistry

---

[1] a) H. A. Lowenstam, S. Weiner, *On Biomineralization*, Oxford University Press, New York, **1989**; b) L. Addadi, S. Weiner, *Angew. Chem.* **1992**, *104*, 159; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 153; c) S. Mann, *Nature* **1993**, *365*, 499.
[2] B. C. Bunker, P. C. Rieke, B. J. Tarasevich, A. A. Campbell, G. E. Fryxell, G. L. Graff, L. Song, J. Liu, J. W. Virden, G. L. McVay, *Science* **1994**, *264*, 48.
[3] J. Aizenberg, *Adv. Mater.* **2004**, *16*, 1295.
[4] a) J. Aizenberg, A. J. Black, G. M. Whitesides, *J. Am. Chem. Soc.* **1999**, *121*, 4500; b) L. Addadi, S. Raz, S. Weiner, *Adv. Mater.* **2003**, *15*, 959.
[5] F. C. Meldrum, J. Flath, W. Knoll, *Langmuir* **1997**, *13*, 2033.
[6] J. W. P. Hsu, Z. R. Tian, N. C. Simmons, C. M. Matzke, J. A. Voigt, J. Liu, *Nano Lett.* **2005**, *5*, 83.
[7] S. Feng, T. Bein, *Nature* **1994**, *368*, 834.
[8] S. Hermes, F. Schröder, R. Chelmowski, C. Wöll, R. A. Fischer, *J. Am. Chem. Soc.* **2005**, *127*, 13744; D. Zacher, A. Baunemann, S. Hermes, R. A. Fischer, *J. Mater. Chem.* **2007**, *17*, 2785.
[9] a) U. Müller, M. Schubert, F. Teich, H. Pütter, K. Schierle-Arndt, J. Pastré, *J. Mater. Chem.* **2006**, *16*, 626; b) N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176; c) A. K. Cheetham, C. N. R. Rao, R. K. Feller, *Chem. Commun.* **2006**, 4780.
[10] E. Biemmi, C. Scherb, T. Bein, *J. Am. Chem. Soc.* **2007**, *129*, 8054.
[11] a) T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Férey, *Chem. Eur. J.* **2004**, *10*, 1373; b) C. Mellot-Draznieks, C. Serre, S. Surblé, N. Audebrand, G. Férey, *J. Am. Chem. Soc.* **2005**, *127*, 16273.
[12] T. R. Whitfield, X. Wang, L. Liu, A. J. Jacobson, *Solid State Sci.* **2005**, *7*, 1096.
[13] S. Surblé, C. Serre, C. Mellot-Draznieks, F. Millange, G. Férey, *Chem. Commun.* **2006**, 284.
[14] C. Serre, F. Millange, S. Surblé, G. Férey, *Angew. Chem.* **2004**, *116*, 6445; *Angew. Chem. Int. Ed.* **2004**, *43*, 6285.
[15] C. Serre, C. Mellot-Draznieks, S. Surblé, N. Audebrand, Y. Filinchuk, G. Férey, *Science* **2007**, *315*, 1828.
[16] a) J. Li, K. S. Liang, G. Scoles, A. Ulman, *Langmuir* **1995**, *11*, 4418; b) L. H. Dubois, R. G. Nuzzo, *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.
[17] R. Arnold, W. Azzam, A. Terfort, C. Wöll, *Langmuir* **2002**, *18*, 3980.
[18] a) H. Wang, S. Chen, L. Li, S. Jiang, *Langmuir* **2005**, *21*, 2633; b) A. Ulman, *Chem. Rev.* **1996**, *96*, 1533; c) J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103.