Metal–Organic Frameworks

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Functionalized Coordination Space in Metal–Organic Frameworks

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fluorinated ligands · host–guest systems · organic–inorganic hybrid composites · porous materials

The minimalist approach to control and functionalize space developed by the German architect Ludwig Mies van der Rohe (1886–1969) belongs to the foundations of modern architecture. In his "skin and bones" approach, space was structured using industrial steel frameworks and plate glass. His slogan "less is more" could also be the motto for an exciting class of compounds: As in the famous buildings designed by Mies van der Rohe, in metal–organic frameworks (MOFs), very open structures are created by using recently developed design principles. Donor–acceptor metal–ligand bonds are used to define a characteristically structured coordination space. Whereas in traditional coordination chemistry the structure and reactivity situation at a given metal center are usually emphasized, in this new context the emphasis is on the engineering of the size, shape, and the arrangement of the space left between and confined by the ligands.

The surfaces of these voids, cavities, trenches, and channels in these extended, often rather complicated periodic frameworks define the properties of these materials. Porous (crystalline) coordination polymers (PCPs), or synonymously metal–organic open frameworks (MOFs), are an emerging class of hybrid soft inorganic–organic solid state materials which offer virtually unlimited options for the tailoring of their properties.[1] These compounds have an infinite network with backbones constructed by metal ions as connectors and organic ligands as linkers.

Unlike in a zeolite, there are no inner atoms, and every constituent is exposed and is part of the inner surface. The properties of this surface enveloping the space left between and confined by the constituents of the framework can be precisely tuned by attaching functional groups to the ligands. Originally, MOFs were introduced because of their stunning capacity for gas storage, but recently many other applications, including separation, cleaning, and optoelectronics have emerged.

Yaghi, O'Keeffe and co-workers coined the term reticular synthesis in connection with MOFs to point out the possibility of designing such networks using a modular approach.[2] The prerequisite of such a deliberate synthesis using inorganic and organic molecular building blocks is the maintained structural integrity of the modules through the assembly and crystallization process under the reaction conditions. This integrity, however, is not found in many cases. The MOFs named Matériaux de l'Institut Lavoisier (MILs) developed by the Ferey group appear to fulfill this criterion to some extent, with the chromium terephtalate based MIL-101 holding the current world record in porosity.[3] High designability and perfect regularity are key aspects of the chemistry of the MOF coordination space. Another highly important feature resulting from the hybrid organic–inorganic character are the dynamic structural properties, as Kitagawa and co-workers have demonstrated.[4]

The flexible switching between open and closed states of certain MOFs affects the pores, or more generally the coordination space, and is a function of the adsorbed guest molecules. Together with external stimuli, such as pressure and temperature, this property allows the development of advanced functional materials much beyond the capability of more rigid porous materials, such as zeolites. The challenge is to achieve cooperative properties, for example, by a proper functionalization of the organic ligands, in which the embedding of guest molecules leads to a specific response of the framework.

The rapid increase in the number of articles dealing with MOFs and related materials over the last 10 years has without doubt been triggered and continuously fuelled by the prospect of using MOFs as novel materials for hydrogen storage technology.[5] Other no less interesting applications are emerging as well, including separation,[6] catalysis,[7] ion exchange,[8] sensors,[9] optoelectronics or photovoltaics,[10] and drug release.[11] However, quite many of the fascinating ideas associated with these applications demand the selective functionalization of the organic linkers at will and without changing the overall structural properties of the framework; this is not an easy task.[12,13] The chemistry of MOF network formation is highly sensitive to the conditions of the reaction, which includes the functional groups attached at the organic linkers. In particular, non-innocent groups, such as -OH,

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-NH_2, or -COOH can obviously interfere with the coordination chemistry associated with the assembly of the building units under solvothermal conditions, and may direct nucleation and crystal growth, leading to unpredictable results. Alternatively, functionalization of the linkers after the formation of the network has been demonstrated, but this method cannot be regarded as a widely applicable concept; its success depends critically on the given MOF.[14]

Herein, we highlight two recent reports on functionalized MOFs that each represent a significant advancement in the field. Omary and co-workers described perfluorous MOFs with superior volumetric gas uptake and a hysteretic sorption of dihydrogen, which indicates the possibility of loading at high pressures but effective hydrogen storing at low pressures.[12] Fujita et al. developed a modular synthesis of functional MOFs with a two-component framework. Whereas one component is an integral part of the framework, the other is more loosely bound, and can be exchanged even after the buildup of the porous, crystalline matrix.[13]

In the latter communication, Fujita et al. discovered a biporous MOF consisting of two interpenetrating networks based on aromatic building units (Figure 1).[15] The units used

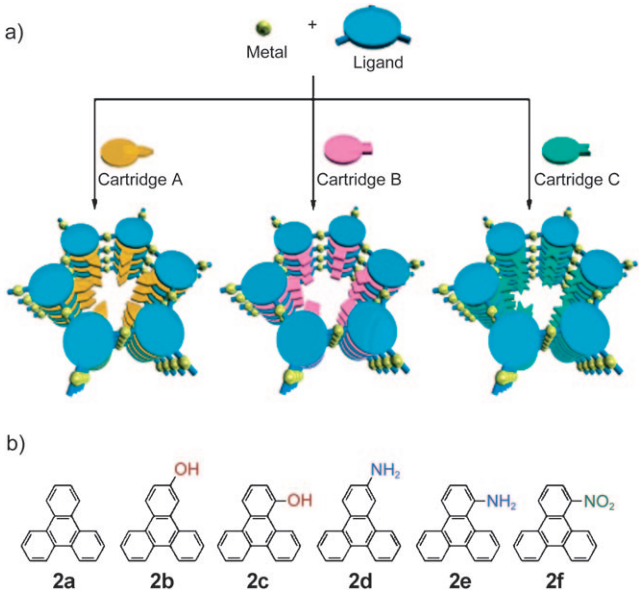
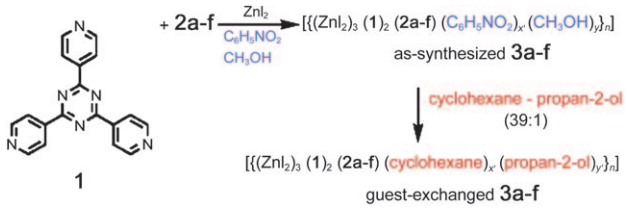


Figure 1. a) Modular synthesis of three-dimensional porous $[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2}n)]$ (**3***n*; ***n*** = **a**–**f**). b) The library of (substituted) triphenylene cartridges **2a**–**f**. Reproduced from Ref. [13]

are 2,4,6-tris(4-pyridyl)-1,3,5-triazine (**1**) and triphenylene (**2a**). Whereas **1** forms an infinite three-dimensional network by coordination to ZnI_2, the second aromatic unit **2a** intercalates between the units of **1**, which lie parallel to one another. The formation is driven by strong π–π stacking interactions, resulting in a composite having the formula $[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2a})]$ (**3a**; Scheme 1). The structure of **3a** contains two different types of channels (A and B). The cylindrically shaped channel A is lined with the hydrogen atoms of the π-stacked units **1** and **2a**. Channel B is trigonal prismatic in



Scheme 1. Preparation and guest exchange of **3a**–**f**. Reproduced from Ref. [13].

shape, and two of the three walls are the π faces of **1**, with the remaining wall composed of the edges of **1** and **2a**.

It should be noted that triphenylene **2a**, although not covalently bound to the framework, cannot be replaced by common aromatic compounds, and thus acts as a part of the framework under guest-exchange conditions.[15] However, during the synthesis of the framework, the authors observed that the triphenylene unit **2a** can easily be replaced by the functionalized triphenylenes **2b**–**2f** (called "cartridges" by the authors) with full retention of the overall structural properties of the framework. Thus a homologous group of MOFs **3b**–**3f** is established that differs only by the functional substituents at the triphenylene unit which protrude from the walls into the open space of the network (Scheme 1). For example, the acidic hydroxy groups of **3b** are mainly directed towards pore A (68% occupancy according to X-ray diffraction and refinement), whereas the remaining groups are located in the region between pores A and B.

Using **2c** instead of **2b**, the hydroxy groups of the resulting network **3c** were directed into the pore A with 100% occupancy. The biporous structural type outlined above results in two strikingly different chemical environments in the two channels. The pores A become hydrophilic, and pores B remain hydrophobic, as in the parent framework **3a**. This property allows spectacular tuning of the guest exchange reaction. For example, when **3c** was immersed into a mixture of propan-2-ol and cyclohexane (1:39), the initial guest molecules nitrobenzene and methanol, which were present from the synthesis of **3c**, were completely exchanged: propan-2-ol taken up with perfect selectivity by pores A, and cyclohexane exclusively by pores B (Scheme 1). The recognition of propan-2-ol was driven by hydrogen bonding to the surface hydroxy groups at the pore walls, as shown by X-ray diffraction studies. The authors suggest that MOFs with properly modified pores will be candidates for smart membrane materials for alcohol separation on a large scale, and possibly make them useful for biofuel production in industry.

Equally ambitious and visionary are the claims of Omary et al. when introducing their Communication on the first perfluoro MOFs (FMOFs): "*Compared to their nonfluorous counterparts, FMOFs with fluoro-lined or fluoro-coated channels or cavities are expected to possess enhanced thermal stability and catalytic activity, higher gas affinity and selectivity, and higher stability to oxygen and light.*"[12] Following their previous work on the optoelectronic properties of coinage-metal triazolates,[16] the authors then employed the sodium salt of 3,5-bis(trifluoromethyl)-1,2-4-triazolate (NaTz) and combined it with silver nitrate in methanol solution. The X-

ray diffraction analysis of the colorless crystals that were obtained revealed a neutral open framework consisting of sixfold connected tetranuclear [Ag_4Tz_6] units with tetracoordinate silver(I) ions linked together by individual three-coordinate silver(I) centers (FMOF-1; Figure 2). All the nitrogen atoms of the triazolate ligands are engaged in

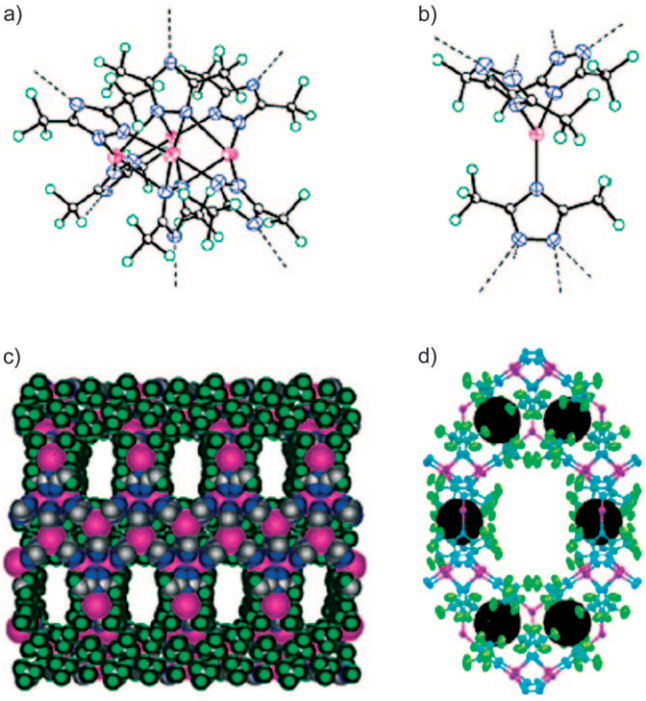


Figure 2. Structure of FMOF-1. a) Tetranuclear [Ag_4Tz_6] cluster, b) three-coordinate silver(I) centers, c) space-filling representation of the large fluoro-lined channels, and d) a perspective view of the small cavities, denoted by black spheres, surrounding the large channels. C gray, N blue, F green, Ag pink. Reproduced from Ref. [12]

binding to the two different types of silver(I) atoms. The key feature is the presence of channels (12.2 Å × 7.3 Å, semi-rectangular cross-section) with highly hydrophobic walls, as the trifluoromethyl groups of the Tz ligands point towards the axis of the channels. A closer examination of the channel walls reveals the presence of diamond-shaped small cavities inside the walls (ca. 6.4 Å × 4.9 Å in dimension) decorated by two pairs of trifluoromethyl substituents which allow the communication between the cavities and the adjacent channels (Figure 2d).

The adsorption isotherms (77 K) of O_2 and N_2 were measured and, as expected, revealed two distinct of pore-filling steps related to the two types of pores (Figure 3). An apparent specific surface area of 810.5 $m^2 g^{-1}$ and a total pore volume of 0.324 $cm^3 g^{-1}$ were extracted from the fitting of the BET equation to the N_2 isotherm. The volumetric hydrogen storage capacity for FMOF-1 at 77 K and 64 bar was determined to be 41 $kg m^{-3}$. This value almost reaches the target of 45 $kg m^{-3}$ defined by the US Department of Energy (DOE) for the year 2010 in connection with the development of gas-storage tanks for hydrogen-fueled vehicles, and is among the best values for hydrogen storage in MOFs

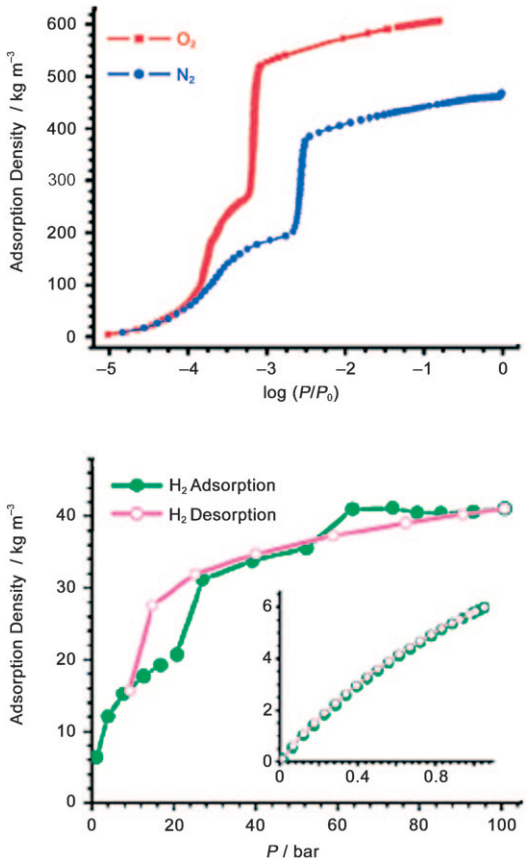


Figure 3. Volumetric uptake of N_2 and O_2 gases (top), and H_2 gas (bottom) in FMOF-1 at 77 K. Inset: isotherms of a low-pressure run of the H_2 adsorption/desorption cycle. Reproduced from Ref. [12]

reported to date. Nevertheless, attention must be drawn to the fact that the cited DOE target is the volumetric dihydrogen uptake capacity at practical temperatures (−20 °C to + 50 °C) for fuelling typical vehicles. If the authors measured the dihydrogen uptake under those conditions rather than at liquid nitrogen temperature (−196 °C, 77 K), the capacity must be much lower than the present value. Furthermore, the gravimetric storage capacity of O_2 at 77 K and 0.03 bar is 33.7 wt. % and the H_2 uptake at the same conditions is 2.3 wt. %; these data are not better than those of other, non-fluorinated MOFs, which is a consequence of the comparably high density of FMOF-1 (1.790 $g cm^{-3}$).

Even more interesting, however, is the documented hysteretic dihydrogen adsorption/desorption behavior. The desorption isotherm (Figure 3, bottom) does not retrace the adsorption curve, but rather exhibits a remarkable drop at about 14 bar. The authors point out that this drop is not an artifact, but they do not provide a specific explanation for the observation; rather, they cite a quite detailed discussion of the effect by Thomas et al. on similar hysteretic adsorption and desorption of hydrogen at nanoporous frameworks of the general type [$\{Ni_2(bipy)_3(NO_3)_4\}_\infty$] (bipy = 4,4-bipyridyl).[17] The key factors appear to be the comparatively small pore windows with sizes close to the kinetic diameter of the hydrogen molecule, the large specific pore volume, and some flexibility of the framework to allow the communication

between the pores and channels; that is, opening and closing the sashes of the windows. In FMOF-1, the trifluoromethyl substituents at the triazolate linkers may play the role of such gates to the cavities (Figure 2). Although a detailed explanation is lacking to date, the findings of Omary and co-workers warrant an in-depth study, including a theoretical modeling of the effect, and may trigger a more systematic search for MOF materials with such hysteretic loading properties.

FMOF-1 also shows the highest volumetric uptake of dioxygen reported to date for a porous solid-state adsorbent, with an adsorption density of 592 $kg\,m^{-3}$ even at a low pressure of 0.03 bar. Thus, the storage properties of the perfluoro-functionalized MOF relates well to the well-known property of perfluorocarbons as excellent solvents for oxygen, with a capacity over ten times larger than that observed in the parent hydrocarbons or in water.

The common motive of the two significant advances in creating the porous crystalline coordination matrices highlighted herein is the deliberate fine-tuning of the ligands or linkers of the MOFs. As all parts of a ligand are part of an inner wall in these open structures, such small changes in the ligand immediately modify the chemical and physical properties. Consequently, the functionality of the remaining coordination space, and thus the effective adsorption and even recognition of guest molecules, can be optimized.

The demonstration by Omary and co-workers that a trifluoromethyl-substituted triazolate linker renders interesting properties to MOFs is rather convincing, but the generalization of the concept has to be proved. The transfer to many other MOFs with interesting structures and dynamic properties is not straightforward, and regarding gravimetric storage capacity, the increased density of those materials may be a problem. The same holds to some extent for the modular synthesis based on the special π-stacked frameworks developed by Fujita and co-workers. However, demonstrating the tailoring of the adsorption properties of these particular biporous metal–organic frameworks is most remarkable, and will certainly stimulate much further research on functionalized MOFs. The modular synthesis concept of the triazine/triphenylene type π-stacked MOFs should, for example, allow the design of partly fluorinated walls by trifluoromethyl substitution at the triphenylene "cartridges" instead of the polar hydroxy groups of **2b**.

In the rapidly developing field of porous (crystalline) coordination polymers, the two reports highlighted herein emphasize only a few aspects. In a recent review,[1b] Kitagawa and Matsuda address five major areas of further development in the field of functional MOFs:

1) Unprecedented cooperative properties between guest molecules and the framework are expected in restricted micropores if a suitable combination of structure and functional groups present at the coordination space.[18]
2) Fabrication of homogenous thin layers is important in various applications, such as sensors, membranes, and (opto)electronic devices.[19]
3) An ultimate goal is the control of the arrangement of the channels at the mesoscale. Methods need to be developed for the fabrication of size- and shape-selected small MOF nanocrystals.[20]
4) A particular challenge is the introduction of anisotropy by chiral frameworks, with applications in enantioselective sorption or recognition and asymmetric catalysis.[7f, g]
5) The design of redox-active and more generally switchable frameworks by electric and magnetic fields or by light will be a hot topic in the future.[21]

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[1] a) G. Férey, *Chem. Soc. Rev.* **2008**, *37*, 191 – 214; b) D. Tanaka, S. Kitagawa, *Chem. Mater.* **2008**, *20*, 922 – 931; c) S. Kitagawa, R. Matsuda, *Coord. Chem. Rev.* **2007**, *251*, 2490 – 2509; d) K. Uermura, S. Kitagawa, *Chem. Soc. Rev.* **2005**, *34*, 109 – 119.

[2] a) O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Phys. Chem. Chem. Phys.* **2007**, *9*, 1035 – 1043; b) N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176 – 182; c) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705 – 714; d) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319 – 330.

[3] G. Ferey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble, I. Margiolaki, *Science* **2005**, *309*, 2040 – 2042.

[4] S. Kitagawa, R. Kitaura, S.-I. Noro, *Angew. Chem.* **2004**, *116*, 2388 – 2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334 – 2375.

[5] a) H. Frost, R. Q. Snurr, *J. Phys. Chem. A* **2007**, *111*, 18794 – 18803; b) T. B. Lee, D. Kim, D. H. Jung, S. B. Choi, J. H. Yoon, J. Kim, K. Choi, S. H. Choi, *Catal. Today* **2007**, *120*, 330 – 335; c) J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. Howard, O. M. Yaghi, *Science* **2005**, *309*, 1350 – 1354; d) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469 – 472; e) M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, S. Kitagawa, *Angew. Chem.* **1997**, *109*, 1844 – 1846; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1725 – 1727; f) M. Dincă, J. R. Long, *Angew. Chem.* **2008**, DOI: 10.1002/ange.200801163; *Angew. Chem. Int. Ed.* **2008**, DOI: 10.1002/anie.200801163.

[6] a) U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastre, *J. Mater. Chem.* **2006**, *16*, 626 – 636; b) R. Q. Snurr, J. T. Hupp, S. T. Nguyen, *AIChE J.* **2004**, *50*, 1090 – 1095; c) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, *Nature* **2005**, *436*, 238 – 241.

[7] a) F. X. Llabres i Xamena, A. Abad, A. Corma, H. Garcia, *J. Catal.* **2007**, *250*, 294 – 298; b) M. Sabo, A. Henschel, H. Froede, E. Klemm, S. Kaskel, *J. Mater. Chem.* **2007**, *17*, 3827 – 3832; c) R. Zou, H. Sakurai, Q. Xu, *Angew. Chem.* **2006**, *118*, 2604 – 2608; *Angew. Chem. Int. Ed.* **2006**, *45*, 2542 – 2546; d) S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp, T. E. Albrecht-Schmitt, *Chem. Commun.* **2006**, 2563 – 2565; e) S. Hermes, M.-K. Schröter, R. Schmid, L. Khodeir, M. Muhler, A. Tissler, R. W. Fischer, R. A. Fischer, *Angew. Chem.* **2005**, *117*, 6394 – 6397; *Angew. Chem. Int. Ed.* **2005**, *44*, 6237 – 6241; f) C.-D. Wu, A. Hu, L. Zhang, W. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 8940 – 8941; g) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, J. Young, K. Kim, *Nature* **2000**, *404*, 982 – 986.

[8] T. Y. Shvareva, S. Skanthakumar, L. Soderholm, A. Clearfield, T. E. Albrecht-Schmitt, *Chem. Mater.* **2007**, *19*, 132 – 134.

[9] a) C. A. Bauer, T. V. Timofeeva, T. B. Settersten, B. D. Patterson, V. H. Liu, B. A. Simmons, M. D. Allendorf, *J. Am. Chem. Soc.* **2007**, *129*, 7136 – 7144; b) B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian, E. B. Lobkovsky, *Adv. Mater.* **2007**, *19*, 1693 – 1696; c) B. V. Harbuzaru, A. Corma, F. Rey, P. Atienzar, J. L. Jorda, H. Garcia, L. D. Carlos, J. Rocha, *Angew. Chem.* **2008**, *120*, 1096 – 1099; *Angew. Chem. Int. Ed.* **2008**, *47*, 1080 – 1083.

[10] a) G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray, J. D. Cashion, *Science* **2002**, *298*, 1762 – 1765; b) F. X. Llabres i Xa-

mena, A. Corma, H. Garcia, *J. Phys. Chem. C* **2007**, *111*, 80 – 85; c) M. Alvaro, E. Carbonell, B. Ferrer, F. X. Llabres i Xamena, H. Garcia, *Chem. Eur. J.* **2007**, *13*, 5106 – 5112.

[11] P. Horcajada, C. Serre, M. Vallet-Regi, M. Sebban, F. Taulelle, G. Férey, *Angew. Chem.* **2006**, *118*, 6120 – 6124; *Angew. Chem. Int. Ed.* **2006**, *45*, 5974 – 5978.

[12] C. Yang, X. Wang, M. A. Omary, *J. Am. Chem. Soc.* **2007**, *129*, 15454 – 15455.

[13] M. Kawano, T. Kawamichi, T. Haneda, T. Kojima, M. Fujita, *J. Am. Chem. Soc.* **2007**, *129*, 15418 – 15419.

[14] a) Z. Q. Wang, S. M. Cohen, *J. Am. Chem. Soc.* **2007**, *129*, 12368 – 12369; b) S. S. Kaye, J. R. Long, *J. Am. Chem. Soc.* **2008**, *130*, 806 – 807.

[15] O. Ohmori, K. Kawano, M. Fujita, *Angew. Chem.* **2005**, *117*, 1998 – 2000; *Angew. Chem. Int. Ed.* **2005**, *44*, 1962 – 1964.

[16] C. Yang, M. Messerschmidt, P. Coppens, M. A. Omary, *Inorg. Chem.* **2006**, *45*, 6592 – 6594.

[17] X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *Science* **2004**, *306*, 1012 – 1015.

[18] a) T. Uemura, Y. Ono, K. Kitagawa, S. Kitagawa, *Macromolecules* **2008**, *41*, 87 – 94; b) K. Uemura, S. Kitagawa, K. Fukui, K. Saito, *J. Am. Chem. Soc.* **2004**, *126*, 3817 – 3828; c) S. Kitagawa, M. Kondo, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739 – 1753.

[19] a) O. Shekhah, H. Wang, S. Kowarik, F. Schreiber, M. Paulus, M. Tolan, C. Sternemann, F. Evers, D. Zacher, R. A. Fischer, C. Wöll, *J. Am. Chem. Soc.* **2007**, *129*, 15118 – 15119; b) E. Biemmi, C. Scherb, T. Bein, *J. Am. Chem. Soc.* **2007**, *129*, 8054 – 8055; c) S. Hermes, F. Schröder, R. Chelmowski, C. Wöll, R. A. Fischer, *J. Am. Chem. Soc.* **2005**, *127*, 13744 – 13745.

[20] a) S. Hermes, T. Witte, T. Hikov, D. Zacher, S. Bahnmuller, G. Langstein, K. Huber, R. A. Fischer, *J. Am. Chem. Soc.* **2007**, *129*, 5324 – 5325; b) S. Masaoka, D. Tanaka, H. Kitahata, S. Araki, R. Matsuda, K. Yoshikawa, K. Kato, M. Takata, S. Kitagawa, *J. Am. Chem. Soc.* **2006**, *128*, 15799 – 15808; c) T. Uemura, Y. Hoshino, S. Kitagawa, K. Yoshida, S. Isoda, *Chem. Mater.* **2006**, *18*, 992 – 995; d) T. Uemura, S. Kitagawa, *Chem. Lett.* **2005**, *34*, 132 – 137.

[21] a) J. Milon, M. C. Daniel, A. Kaiba, P. Guionneau, S. Brandes, J. P. Sutter, *J. Am. Chem. Soc.* **2007**, *129*, 13872 – 13878; b) L. H. Xie, S. X. Liu, C. Y. Gao, R. G. Cao, J. F. Cao, C. Y. Sun, Z. M. Su, *Inorg. Chem.* **2007**, *46*, 7782 – 7788; c) M. P. Suh, H. R. Moon, E. Y. Lee, S. Y. Jang, *J. Am. Chem. Soc.* **2006**, *128*, 4710 – 4718; d) H. R. Moon, J. H. Kim, M. P. Suh, *Angew. Chem.* **2005**, *117*, 1287 – 1291; *Angew. Chem. Int. Ed.* **2005**, *44*, 1261 – 1265; e) Z. Wang, Y. J. Zhang, T. Liu, M. Kurmoo, S. Gao, *Adv. Funct. Mater.* **2007**, *17*, 1523 – 1536.

