Metal–Organic Frameworks

DOI: 10.1002/anie.201104597

Metal–Organic Frameworks with a Three-Dimensional Ordered Macroporous Structure: Dynamic Photonic Materials**

Yi-nan Wu, Fengting Li, Wei Zhu, Jiecheng Cui, Cheng-an Tao, Changxu Lin, Phillip M. Hannam, and Guangtao Li**

Metal–organic frameworks (MOFs) are a fascinating class of hybrid porous crystalline materials with distinct features including high porosity, high specific surface area, tremendous structural diversity, and chemical tailorability. These features make them very attractive for numerous applications.[1] In particular, their extremely rich host–guest chemistry and flexible or dynamic porous frameworks responsive to external stimuli have drawn considerable attention for the development of chemical or biological sensors.[2] Although this sensing application is often stated as a paradigm, only limited reports have been published that demonstrate or explore this advanced application based on MOF materials.[3] In this context, the design and development of a general and appropriate signal transducer is critical. The main problem is the fact that because the cavities of MOFs are generally small, their modification with reporter molecules, which can readily signal analyte-binding events by means of changes in color, redox potential, or other properties, is difficult.[3] Up to now, a handful of MOF-based sensors have been described, in which the framework luminescence was used for signal transduction.[4] Recently, microcantilever, Fabry-Pérot interference, quartz crystal microbalance, and localized surface plasmon resonance (LSPR) have also been used in the fabrication of MOF-based sensors.[3,5] Nevertheless, the development of a more general and effective transduction scheme still remains one of the principal challenges in this field.[3]

Herein we report a new transduction scheme through the fabrication of MOF-based films (MOFFs) with ordered macroporous structure. We show that the integration of a porous photonic structure into MOFs can endow these materials with optical elements, by which the molecular recognition events of MOFs can be efficiently converted to a readable optical signal without the need of molecular reporters and sophisticated technical equipments. A three-dimensional (3D) ordered macroporous structure, also called an inverse-opal structure, gives rise to bright colors through the diffraction of light. Its unique optical properties are described by the Bragg equation and are extremely sensitive to the changes in refractive index and lattice parameters [$\lambda = 2D(n^2_{\text{eff}} - \cos^2\theta)^{1/2}$], where D is the distance between 111 lattice planes, n_{eff} is the volume-weighted average refractive index of the network [$n_{\text{eff}} = 0.74\, n_{\text{macropore}} + 0.26\, n_{\text{MOF}}$], and θ is the Bragg angle of the incident light.[6] Obviously, the incorporation of this porous photonic structure into MOF materials will provide a general signal transduction scheme for the development of MOF-based sensors and afford a novel class of hierarchically structured materials consisting of 3D highly ordered and interconnected macropores array with a thin MOF skeleton (Figure 1). The ordered macropores

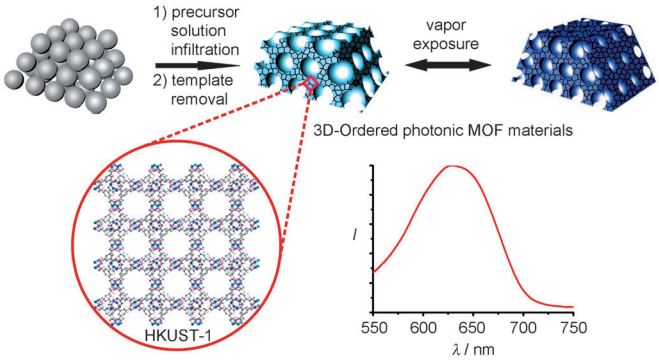

Figure 1. Schematic illustration of the preparation of metal-organic frameworks with three-dimensional ordered macroporous structure, which can be served as dynamic photonic materials.

array within the MOF provides an optical signal. The resulting hierarchical porous structure is especially beneficial in sensor applications that require high specific surface area, more interaction sites, efficient mass transport, and easier accessibility to the active sites through the interconnected macropore system. More importantly, the uptake and release of guest species by the microporous MOF skeleton as well as its structural response triggered by external stimuli can directly produce a readable optical signal through a change of the diffraction properties of the ordered macropores array, which is usually easily visible with the naked eye. As a proof of concept, the most studied $Cu_3(BTC)_2$ (BTC = benzenetricarboxylate) MOF,[7] HKUST-1, was chosen in this work, and a MOF-based self-reporting sensor was constructed based on our strategy. Such a sensor can rapidly, selectively, and optically detect organic vapors, and it also exhibits excellent stability and reversibility.

[*] Y. Wu, Prof. Dr. F. Li, P. M. Hannam
College of Environmental Science and Engineering
State Key Laboratory of Pollution Control and Resource Reuse
Tongji University, 200092 Shanghai (China)
E-mail: fengting@tongji.edu.cn

Y. Wu, W. Zhu, J. Cui, C. Tao, C. Lin, Prof. Dr. G. Li
Key Lab of Organic Optoelectronic and Molecular Engineering
Department of Chemistry, Tsinghua University, 100084 Beijing (China)
E-mail: lgt@mail.tsinghua.edu.cn

[**] We gratefully acknowledge financial support from the Sino-America Cooperation Program (2009DFA90740), the NSFC (20533050, 50873051, and 50673048), MOST (2007AA03Z07), and the Trans-regional Project (TRR61).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201104597.

A colloidal crystal templating method was used to prepare HKUST-1 films with 3D-ordered macroporous structure (Figure 1). We employed a three-step approach: fabrication of a polystyrene (PS) opaline template; infiltration of the colloidal crystal template with a clear MOF precursor solution followed by solvent evaporation for crystallization of MOF; and selective dissolution of the PS template to afford 3D-ordered macroporous structure (inverse opal). Uniform PS particles with a diameter of about 330 nm were used in this work, and for improving the film formability of HKUST-1, polystyrene latex with a carboxylic acid terminated surface was utilized in our case.[8] Applying clear MOF precursor solutions for controlled MOF growth is the key point in our nanofabrication. Very recently, De Vos and co-workers developed a general concept for MOF processing that is based on the use of a stable precursor solution of MOF primary building blocks.[9] They found that through the control of MOF crystallization kinetics in the clear precursor solution, spatial and temporal control of MOF formation, particularly in confined spaces, is possible. This is the prerequisite for the successful fabrication of metal–organic frameworks with three-dimensional ordered macroporous structure described here.

A PS colloidal template with a face-centered-cubic (fcc) structure was prepared, as shown in Figure 2a,b. This template film has a thickness of about 30 μm and exhibits a three-dimensional ordered structure. After infiltration of the template with clear solution of Cu^{2+}/H_3BTC in DMSO, the evaporation of DMSO at 90 °C resulted in the formation of well-defined HKUST-1 crystals in the confined spaces of the template. The template was removed by treatment with tetrahydrofuran (THF). The purity/identity of the prepared HKUST-1 photonic film was confirmed by FTIR spectroscopy (Figure S1 in the Supporting Information). In contrast to the crystallization of purely inorganic materials,[10] we found that the crystallization of MOFs[11] can easily adapt to the imposed physical boundaries. Three-dimensional ordered and interconnected macropores within the HKUST-1 film have the same diameter as the PS template particles (Figure 2c,d), indicative of the successful replication of the template structure. A SEM cross-section of the HKUST-1 thin film is displayed in Figure S2 in the Supporting Information. The thickness of the film is about 20 μm. It should be noted that with this colloidal crystal templating method, the fabrication of large-area inverse-opal HKUST-1 films is possible (Figure 2f). The structure of the prepared HKUST-1 film was confirmed by powder X-ray diffraction (XRD), which shows XRD patterns similar to those of the conventional bulk HKUST-1 powders as well as the simulated one (Figure 3a). The HKUST-1 crystal is a copper-based porous coordination

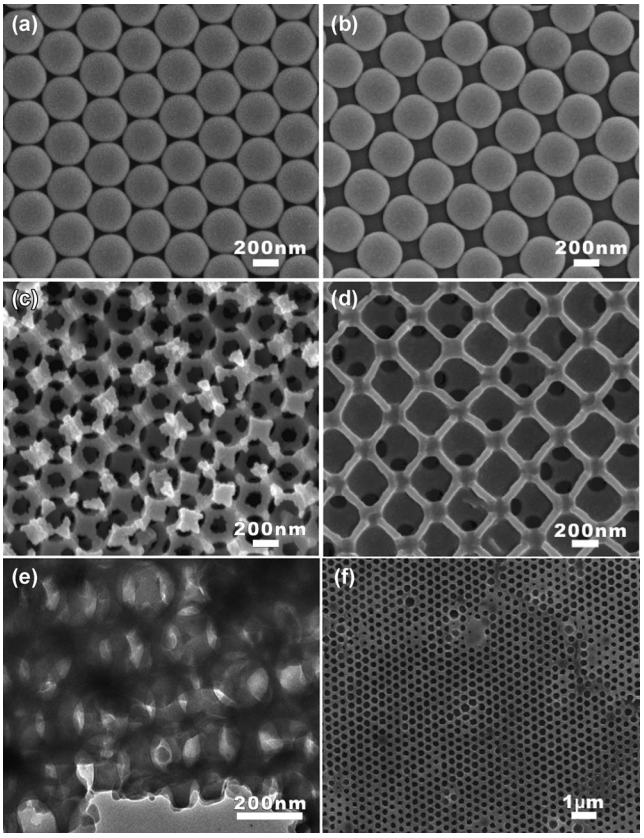

Figure 2. SEM images of the PS colloidal crystal templates with a a) 111 crystal plane and a b) 100 crystal plane, and the corresponding inverse-opal HKUST-1 films (c,d); TEM image (e) and large-scale SEM image (f) of an inverse-opal HKUST-1 film.

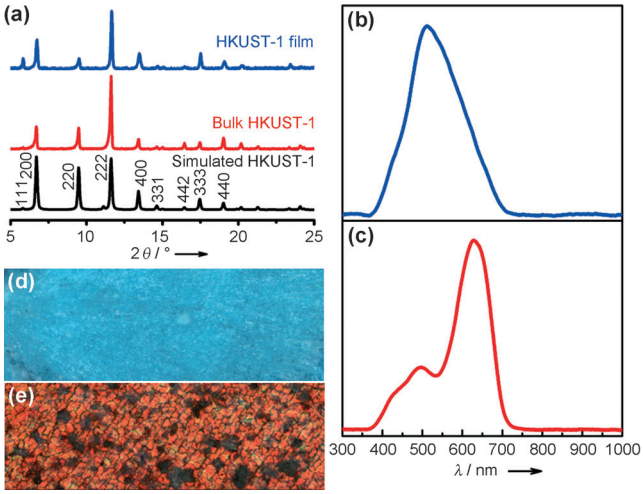

Figure 3. a) Comparison of XRD patterns of the prepared materials with the simulated XRD pattern. b,c) UV/Vis reflectance spectra of bulk HKUST-1 crystals produced by solvothermal approach (b) and the prepared photonic HKUST-1 film (c). d,e) Optical images of bulk HKUST-1 crystals (d) and the prepared photonic HKUST-1 film (e).

polymer, and exhibits absorption at 550 nm and a blue color (Figure 3b,d). However, the introduction of the ordered macroporous structure gives the HKUST-1 film a beautiful bright-red color through Bragg diffraction with visible light (Figure 3c,e). Consistent with this observation, we found that the inherent absorption of HKUST-1 at 550 nm is suppressed, and a strong diffraction peak at 629 nm dominates in UV/Vis spectrum (Figure 3c). Clearly, the simple introduction of an ordered macroporous structure imparts the MOF materials with new optical properties, and we could fabricate novel photonic materials based on MOFs. We show herein that this

optical element produced only from the structurization of MOF materials can be used as a facile signal transducer to self-report the adsorbate-induced structural flexibility of MOFs.

The photonic HKUST-1 film prepared here was first dried at 120 °C under vacuum to remove the absorbed water from its micropores. N_2-adsorption studies on the activated photonic film (Figure S3 in the Supporting Information) reveal that the prepared HKUST-1 film has a surface area of 1075 $m^2 g^{-1}$ and a pore volume of 0.44 $cm^3 g^{-1}$. It is expected that upon the exposure to environmental vapor, the capture of guest molecules and their interaction with the microporous framework of the HKUST-1 skeleton will cause a change in the MOF refraction index (n) or/and the MOF structure and thereby the induced distortions of the ordered macropores array in the HKUST-1 film will show a specific optical response, according to Bragg equation. Figure 4a shows the reflection spectra of the photonic HKUST-1 film and its

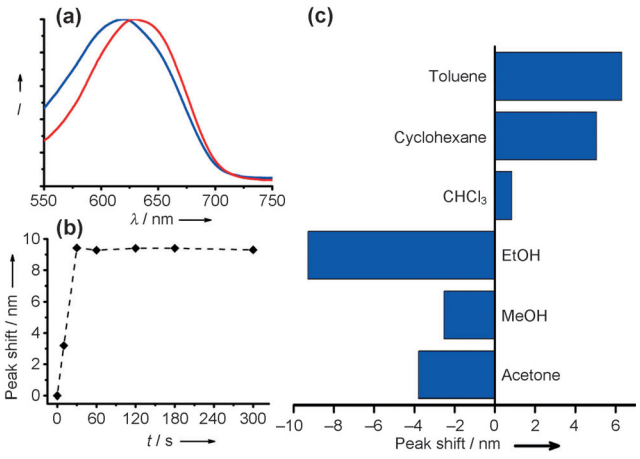

Figure 4. a) UV/Vis spectra of the photonic HKUST-1 film before (red) and after (blue) exposure to ethanol vapor. b) Kinetic response upon exposure to ethanol vapor. c) Schematic representation of changes in diffraction peak shifts in response to different organic vapors.

response upon exposure to ethanol vapor. A blue shift of about 9 nm from 629 nm to 620 nm is observed. Owing to its highly ordered and hierarchical porous structure, the photonic MOF film is indeed very sensitive and the response time is only 30 s (Figure 4b). Additionally, different from dye molecule, the optical properties used in our MOF systems originate from the periodical pore structure (the inverse-opal photonic structure). Thus, these optical properties are very stable (no quenching and no bleaching), and the background signal is very low. In our case, the signal-to-noise ratio is about 50, and the sensitivity of the HKUST-1 based sensor to organic vapors reaches 10 ppm. In response to a series of organic vapors, the photonic HKUST-1 film displays apparent selectivity, and not only red-shifted but also blue-shifted Bragg reflections were recorded (Figure 4c). This result indicates that the interaction between the guest and MOF host depends strongly on the physicochemical properties of guest molecules.[12] According to the Bragg equation, the location of reflectance peak (λ) of the photonic crystal is determined by the lattice parameter (D) and the effective refractive index (n_{eff}) when the incident angle (θ) is given. Any change of the lattice parameters and/or the effective refractive index can induce a shift in the reflectance peak of the photonic crystal. In this work, a sample of bulk HKUST-1 was also prepared as a reference material, and the effect of differently loaded gases on its structural parameters was investigated using XRD. Probably as a result of the rigid framework structure, we found that the loading of different gases has little influence on the structural parameters and thus the lattice parameter of the inverse-opal structure (Figure S4 in the Supporting Information). Thus, it seems that the change of the effective refractive index after the loading of the gas molecules may be the main reason for the observed shifts of the photonic absorption. It should be noted that the adsorbed vapors could be completely removed; the photonic MOF film can be easily recovered by simply heating or under vacuum.

The preliminary results described above are encouraging. The introduced optical element through simple structurization of MOF materials can sensitively "self-feel" or self-report the subtle change of MOFs either by a change in the refraction index or in the structure. The highly ordered and hierarchical pore structure (interconnected macrospore array and microporous MOF) is especially favorable to sensing efficiency. Although this new transduction scheme was tested in HKUST-1, in principle, it can be used as a general and effective transduction approach for creating various MOF-based sensors. The shift of the reflectance peak of HKUST-based sensor upon exposure to organic vapors is not remarkable compared to other types of photonic sensing devices (e.g. polymer-based). To further demonstrate the unique advantages of this new transduction scheme, more flexible ZIF-8 was used for the fabrication of MOF-based sensor (Figure 5a). As expected, upon exposure to organic vapors, the ZIF-8 based sensor exhibits a distinct shift ($\approx$75 nm) of the diffraction peak accompanying a distinct color change, which can be detected by the naked eye

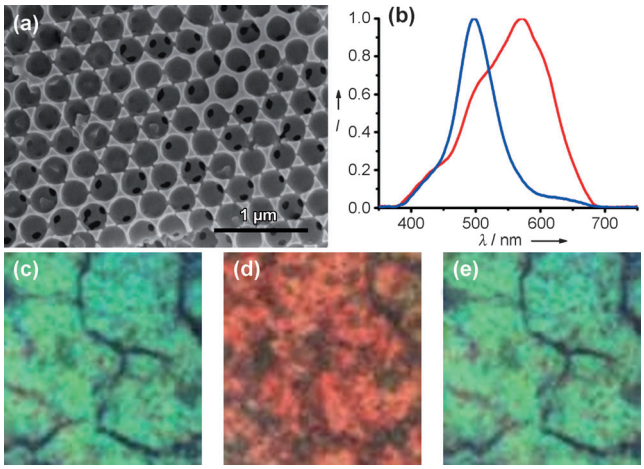

Figure 5. a) SEM image of the photonic ZIF-8 film. b) UV/Vis spectra of the photonic ZIF-8 film before (blue) and after (red) exposure to methanol vapor. c–e) Optical images of the photonic ZIF-8 film before (c) and after (d) exposure to methanol vapor, and after subsequent removal of methanol under vacuum (e).

(Figure 5c–e). These results clearly show that the simple integration of 3D-ordered macroporous structure into MOF materials indeed can be used as a general approach for fabricating label-free MOF-based sensors. These results also indicate that after the optimization of the preparation conditions, in particular, the choice of MOF, it is possible to produce more practical and inexpensive MOF-based sensors like "pH paper" without the use of any sophisticated technical equipment. In addition, since the interconnected macropore structure provides high specific surface area and efficient mass transport, the inverse-opal structure should be very beneficial to the construction of high-performance photonic sensors.

Kitagawa et al. and Férey et al. have recently developed more flexible MOFs; in some cases the volume change of the MOF reached more than 200% upon application of external stimuli.[13,14] It can be anticipated that the integration of 3D-ordered macroporous structure with such MOFs could afford more attractive dynamic photonic materials. Actually, the formed photonic MOFs can be served as a useful platform for conveniently studying the host–guest chemistry of MOFs.

In summary, we report the first example of a metal–organic framework with a 3D-ordered macroporous structure. We showed that the integration of this macroporous array into MOFs endows the resulting materials with an additional optical element, which can be facilely used as a general and effective signal transducer together with the formed hierarchical pore structure. In view of the virtually unlimited tunability of MOFs, it is expected that the association of MOFs, especial the target-selectivity of functional "breathing" MOFs,[13,14] with the accessible macroporous photonic structure can significantly extend the function and potential of MOFs and afford a new type of dynamic photonic materials. Thus, we believe our work may open up a new route to generate multifunctional MOFs with a wide range of potential applications.

Experimental Section

Synthesis of polystyrene colloidal crystal templates: Non-cross-linked, monodisperse polystyrene spheres with carboxylic acid terminated surfaces were synthesized using an emulsifier-free emulsion polymerization technique. In a typical synthesis, a three-necked, 200 mL round-bottomed flask was filled with water (80 mL) and heated to 75 °C before styrene (7.0 g) and methacrylic acid (0.35 g) were added under intensive stirring. Pure nitrogen was bubbled to deaerate the mixture for 30 min. In a separate 25 mL polyethylene bottle, sodium hydroxide (0.024 g) and sodium carbonate (0.024 g) was dissolved in water (5 mL), and the solution was added to the former solution which was reheated to 75 °C. Potassium persulfate initiator (0.03 g) was added to water (5 mL) and the solution was deaerated for 10 min. After the initiator was added to the total solution, nitrogen was passed through the flask for 10 min. The temperature was kept at 75 °C for 12 h. After alternating centrifugation and dispersion using water several times to expunge residues, monodisperse COOH-terminated polystyrene particles (330 nm) were obtained and fully dispersed in water with a weight concentration of about 0.1%; these were transferred into clean 7 mL vials for the formation of colloidal crystal templates. A clean glass slide was put into each vial vertically for colloidal crystal growth.[15] After complete volatilization of water, COOH-terminated polystyrene colloidal crystal templates remained on both sides of each glass slide, and their stability was enhanced by sintering at 90 °C for 2 h.

Preparation of HKUST-1 film with 3D-ordered macroporous structure: Clear HKUST-1 precursor solutions were prepared according to the literature.[9] In a typical preparation, $Cu(NO_3)_2{\cdot}3H_2O$ (1.22 g) and 1,3,5-benzenetricarboxylate (H_3BTC; 0.58 g) were dissolved in DMSO (5.0 mL). The clear precursor solution was heated to 90 °C and then was infiltrated into the COOH-terminated polystyrene colloidal crystals templates under vacuum. After evaporation of the solvent at 90 °C for 24 h, the templates were removed by immersion in THF solution. This treatment was repeated several times, and the resulting samples were dried at 120 °C under vacuum overnight.

Characterization: XRD measurements were performed on a Bruker D8 Advance X-Ray powder diffractometer. TEM images were obtained using a JEM 2010 high-resolution transmission electronic microscope at an acceleration voltage of 120 kV. SEM images were obtained using a field emission scanning electron microscopy (ESSEM) on a JEOL JSM-5400 system at an accelerating voltage of 8 kV. Optical spectra and photos of the HKUST-1 films were acquired with an Ocean Optics USB2000 fiber optic spectrophotometer coupled to an optical microscope. N_2 adsorption–desorption isotherm measurements were carried out on a QuadraSorb SI instrument at 77 K. Prior to the measurement, the sample was degassed at 100 °C for 6 h in the vacuum line. The FTIR spectra were measured on a Spectrum One FTIR spectrometer (Perkin–Elmer) by the KBr pellet method.

Received: July 4, 2011
Published online: October 17, 2011

Keywords: hierarchical structures · metal–organic frameworks · photonic materials · sensors

[1] a) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705; b) S. T. Meek, J. A. Greathous, M. D. Allendorf, *Adv. Mater.* **2011**, *23*, 249; c) D. Zacher, R. Schmid, C. Wöll, R. A. Fischer, *Angew. Chem.* **2011**, *123*, 184; *Angew. Chem. Int. Ed.* **2011**, *50*, 176; d) R. E. Morris, P. S. Wheatley, *Angew. Chem.* **2008**, *120*, 5044; *Angew. Chem. Int. Ed.* **2008**, *47*, 4966; e) A comprehensive introduction into the MOF field is given in the thematic issue "Metal-Organic Frameworks" (Eds.: J. Long, O. M. Yaghi), *Chem. Soc. Rev.* **2009**, *38*, 1201.

[2] O. Shekhah, J. Liu, R. A. Fischer, C. Wöll, *Chem. Soc. Rev.* **2011**, *40*, 1081.

[3] G. Lu, J. T. Hupp, *J. Am. Chem. Soc.* **2010**, *132*, 7832.

[4] a) M. D. Allendorf, C. A. Bauer, R. K. Bhakta, R. J. T. Houk, *Chem. Soc. Rev.* **2009**, *38*, 1330; b) A. Lan, K. Li, H. Wu, D. H. Olson, T. J. Emge, W. Ki, M. Hong, J. Li, *Angew. Chem.* **2009**, *121*, 2370; *Angew. Chem. Int. Ed.* **2009**, *48*, 2334; c) K. C. Stylianou, R. Heck, S. Y. Chong, J. Bacsa, J. T. A. Jones, Y. Z. Khimyak, D. Bradshaw, M. J. Rosseinsky, *J. Am. Chem. Soc.* **2010**, *132*, 4119.

[5] a) E. Biemmi, A. Darga, N. Stock, T. Bein, *Microporous Mesoporous Mater.* **2008**, *114*, 380; b) M. D. Allendorf, R. J. T. Houk, L. Andruszkiewicz, A. A. Talin, J. Pikarsky, A. Choudhury, K. A. Gall, P. J. Hesketh, *J. Am. Chem. Soc.* **2008**, *130*, 14404; c) L. E. Kreno, J. T. Hupp, R. P. Van Duyne, *Anal. Chem.* **2010**, *82*, 8042.

[6] a) A. Stein, F. Li, N. R. Denny, *Chem. Mater.* **2008**, *20*, 649; b) D. P. Puzzo, A. C. Arsenault, I. Manners, G. A. Ozin, *Angew. Chem.* **2009**, *121*, 961; *Angew. Chem. Int. Ed.* **2009**, *48*, 943.

[7] A. Schoedel, C. Scherb, T. Bein, *Angew. Chem.* **2010**, *122*, 7383; *Angew. Chem. Int. Ed.* **2010**, *49*, 7225.

[8] a) S. Hermes, F. Schroder, R. Chelmowski, C. Wöll, R. A. Fischer, *J. Am. Chem. Soc.* **2005**, *127*, 13744; b) D. Zacher, A.

Baunemann, S. Hermes, R. A. Fischer, *J. Mater. Chem.* **2007**, *17*, 2785; c) D. Zacher, J. N. Liu, K. Huber, R. A. Fischer, *Chem. Commun.* **2009**, 1031.
[9] R. Ameloot, E. Gobechiya, H. Uji-i, J. A. Martens, J. Hofkens, L. Alaerts, B. F. Sels, D. E. De Vos, *Adv. Mater.* **2010**, *22*, 2685.
[10] W. C. Yoo, S. Kumar, R. L. Penn, M. Tsapatsis, A. Stein, *J. Am. Chem. Soc.* **2009**, *131*, 12377.
[11] a) S. Diring, S. Furukawa, Y. Takashima, T. Tsuruoka, S. Kitagawa, *Chem. Mater.* **2010**, *22*, 4531; b) T. Tsuruoka, S. Furukawa, Y. Takashima, K. Yoshida, S. Isoda, S. Kitagawa, *Angew. Chem.* **2009**, *121*, 4833; *Angew. Chem. Int. Ed.* **2009**, *48*, 4739; c) S. Hermes, T. Witte, T. Hikov, D. Zacher, S. Bahnmuller, G. Langstein, K. Huber, R. A. Fischer, *J. Am. Chem. Soc.* **2007**, *129*, 5324; d) H. Bux, F. Y. Liang, Y. S. Li, J. Cravillon, M. Wiebcke, J. Caro, *J. Am. Chem. Soc.* **2009**, *131*, 16000.
[12] S. Kitagawa, K. Uemura, *Chem. Soc. Rev.* **2005**, *34*, 109.
[13] S. Horike, S. Shimomura, S. Kitagawa, *Nat. Chem.* **2009**, *1*, 695.
[14] a) C. Serre, C. Mellot-Draznieks, S. Surble, N. Audebrand, Y. Filinchuk, G. Férey, *Science* **2007**, *315*, 1828; b) F. Millange, C. Serre, N. Guillou, G. Férey, R. I. Walton, *Angew. Chem.* **2008**, *120*, 4168; *Angew. Chem. Int. Ed.* **2008**, *47*, 4100; c) G. Férey, C. Serre, *Chem. Soc. Rev.* **2009**, *38*, 1380; d) G. Férey, *Chem. Soc. Rev.* **2008**, *37*, 191.
[15] J. Huang, C. A. Tao, Q. An, W. X. Zhang, Y. G. Wu, X. S. Li, D. Z. Shen, G. T. Li, *Chem. Commun.* **2010**, *46*, 967.

