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Metal–Organic Frameworks

Improving the Hydrogen-Adsorption Properties of a Hydroxy-Modified MIL-53(Al) Structural Analogue by Lithium Doping**

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To realize an energy-efficient and sustainable transportation system, hydrogen as a fuel in combination with fuel cell electric vehicles (FCEV) is one of the most promising energy carriers.[1a] Using solid-state materials as hydrogen carriers could provide a higher hydrogen density than the current state-of-the art automotive systems employing compressed hydrogen at 70 MPa.[1] Within this field of research, porous metal–organic frameworks (MOFs) have been shown to be very suitable candidates for future applications in hydrogen-storage technology.[2] Recently, a number of theoretical works dealing with this topic proposed that doping MOFs with lithium significantly enhances the hydrogen-adsorption properties of a given material.[3] However, in the majority of the calculations, doping with lithium atoms or cations which are situated above the usually planar core of the linker is investigated.[3b–h] This situation is hard to realize experimentally because there is no a clear relation, in terms of molecular fragments, to the chemical structure of the linker. Therefore, it is not surprising that only a few examples can be found for the reactivity of MOFs with elemental lithium.[4] An experimentally more feasible suggestion was made by Klontzas et al. who proposed to establish lithium-doping of MOFs via addition of lithium alkoxide groups to the organic linker.[3a] Since lithium alkoxide groups are well-known functional groups in organic chemistry, this particular modification appears to be the most practicable from our point of view.

Our approach to establish lithium-doping in the above mentioned manner involves the treatment of a MOF which incorporates pendant hydroxy groups (that is, hydroxy groups which are not coordinating), and exhibits permanent porosity with a suitable lithium base. But among the MOFs that fulfill the first requirement,[5] there are only two examples for materials that were sufficiently characterized to be named a microporous coordination polymer.[5a–c] However, they were not suitable for our purpose.[6] Therefore, our first task was the synthesis of a MOF which fulfils the above-mentioned requirements. It should be noted that it is not straightforward to synthesize a hydroxy-modified MOF by using a hydroxy-modified linker because the hydroxy groups are often found to be coordinated to metal centers after synthesis because of their nucleophilic properties.[7,5d–g] Recently, Bauer et al. showed that it is possible to synthesize isoreticular forms of MIL-53(Fe), MIL-88B(Fe), and MIL-101(Fe) carrying a free amino group at the linker 2-aminoterephthalic acid. The synthesis conditions were determined by high-throughput methods.[8–11] Since an amino group has nucleophilic properties similar to those of the hydroxy group, we assumed that the synthesis of a hydroxy-modified MIL-53(Al) analogue is feasible by employing 2-hydroxyterephthalic acid as the linker.

Typically, MIL-53(Al) is synthesized under hydrothermal conditions by treating terephthalic acid with aluminum nitrate at 220 °C for 72 h in an autoclave. Our first attempt to synthesize the hydroxy-functionalized MIL-53(Al) was to simply substitute terephthalic acid by 2-hydroxyterephthalic acid (H_2BDC-OH) in the standard synthesis procedure.[8a] But unfortunately we were not able to find suitable hydrothermal conditions for this case (Figure S1, see supporting information for details). Thus, we developed a novel synthesis route to hydroxy-modified MIL-53(Al) based on the ambient pressure route for $Cu_3(BTC)_2$ (BTC = 1,3,5-benzenetricarboxylate) from our previous work.[12] Owing to the very low solubility of H_2BDC-OH in pure water even under reflux, a 1:1 mixture of *N*,*N*′-dimethylformamide (DMF) and water was used. Pure DMF is not suitable because the MIL-53(Al) network incorporates bridging hydroxy ions that link the AlO_6 octahedra into infinite chains. Thus, water must be present in the synthesis mixture to provide the hydroxy ions for the formation of the MIL-53 framework. This approach resulted in compound **1**, exhibiting almost the same powder X-ray diffraction (XRD) pattern as the DMF form of MIL-53 discussed in ref. [8b] (Figure S2, Supporting Information) showing that **1** has a framework analogous to the MIL-53 structure. To remove impurities and to exchange the DMF guests for a solvent which is easier to remove (Figure S3, Supporting Information) a soxhlet extraction with ethanol was performed. The resulting compound, **2** (MIL-53(Al)-OH), shows exactly the same powder XRD pattern as the low-temperature form (lt form) of MIL-53(Al) (Figure 1; after degassing and rehydration).

Compound **2** shows significant microporosity as evident from the nitrogen-adsorption isotherm (Figure 2) yielding specific surface areas of 1566 $m^2\,g^{-1}$ and 1631 $m^2\,g^{-1}$ according to the BET- and Langmuir model, respectively. Thus, a

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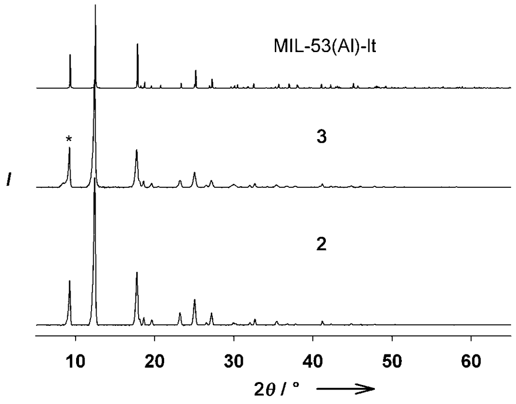

Figure 1. Powder XRD pattern of **2** (bottom) and **3** (middle) after heating to 120 °C for 24 h under vaccum and subsequent rehydration. Calculated pattern for MIL-53(Al)-lt with structure data from ref. [8a] (top). The hydroxy groups seem to be disordered since no symmetry reduction occurs. This was also found for the amino functionalized MIL-53.[11] See Supporting Information (Figure S4) for the XRD pattern of the degassed material.

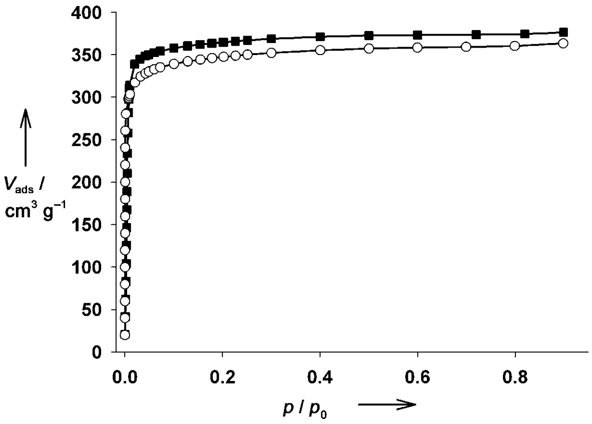

Figure 2. Comparison of the nitrogen adsorption isotherms of **2** (■) and **3** (○) at 77 K after activation under vacuum at 120 °C for 24 h.

compound with a structure similar to MIL-53(Al) was prepared under ambient pressure. To demonstrate the presence of pendant hydroxy groups in the network and to rule out any transformation of the hydroxy functionality during synthesis, the IR spectrum of **2** was recorded (Figure 3). The region relevant for OH-stretching modes of hydroxy groups shows two signals. The narrow signal at 3680 cm^{-1} is assigned to the μ_2-OH bridges connecting the AlO_6 octahedra.[8a] The broad band at 3265 cm^{-1} indicates the presence of an additional hydroxy group in the framework which is attributed to the one connected to the 2-hydroxyterephthalate linker. The relatively broad appearance of the signal shows that hydrogen bonding is involved. An intramolecular bridging mode similar to that in salicylic acid is most likely since 2-hydroxyterephthalic acid, like salicylic acid, has a hydroxy group in *ortho* position to a carboxylate group.[13] Compound **2** can be considered as a MIL-53(Al) structural analogue carrying a pendant hydroxy group and, based on chemical analysis (see Supporting Information), can be formulated as [Al(OH)(BDC-OH)].

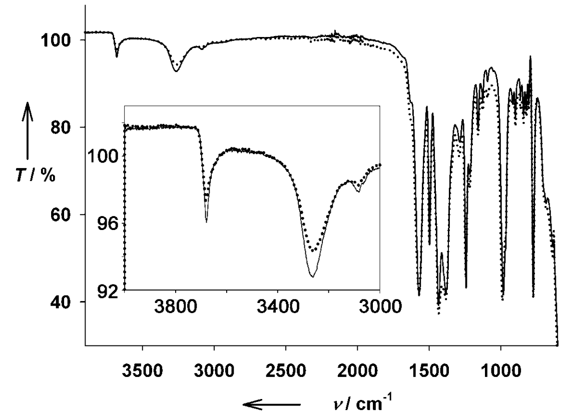

Figure 3. ATR-IR spectra of **2** (——) and **3** (•••••). The materials were dried under vacuum at 120 °C for 24 h prior to the measurements. Inset enlargement of the 3000–4000 cm^{-1} range. (The IR spectrum of MIL-53 is in the Supporting Information; Figure S6.)

To prepare a lithium alkoxide modified MOF as proposed by Klontzas et al.,[3a] the hydroxy group of **2** has to be treated with a lithium-containing base in a heterogeneous reaction. Subsequent deprotonation of the hydroxy group would give the lithium alkoxide species. The choice of the base is very crucial because the generally strong nucleophilicity of common bases (such as LiOH and *n*BuLi) means most of them are capable of substituting carboxylate moieties from the metal center resulting in a collapse of the framework. Thus, we decided that a sterically hindered base, such as lithium diisopropylamide (LDA), would be most suitable for our purpose. Furthermore LDA is small enough to diffuse into the channels of MIL-53 (see Supporting Information, Figure S5). The reaction of LDA with **2** in THF at −78 °C followed by soxhlet extraction with diethyl ether led to a yellowish solid, **3**.

To check whether the textural properties of the framework are unchanged in the conversion from **2** into **3**, compound **3** was investigated by nitrogen adsorption and powder X-ray diffraction. The nitrogen-adsorption isotherm of **3** shows a slight decrease of the adsorbed gas volume compared to **2** (Figure 2). The apparent Langmuir and BET surface areas for **3** are 1450 m^2g^{-1} and 1384 m^2g^{-1}, respectively. This corresponds to a loss of approximately 180 m^2g^{-1} both in Langmuir and BET surface area, indicating that essentially no framework damage has taken place during the LDA treatment. The same conclusion can be drawn from the powder XRD pattern of **3** (Figure 1). After degassing and rehydration, almost the same diffraction pattern is obtained for **2** and **3**, that is, the MIL-53(Al)-lt structure (Figure 1). The only difference is a small shoulder appearing at the left side of the first reflection in **3**. This feature may be due to some structure domains which do not adopt the MIL-53(Al)-lt structure upon rehydration but retain the MIL-53(Al)-ht structure (see below for a possible explanation of this behavior; ht = high temperature).

The ^{7}Li magic angle spinning (MAS) NMR spectrum of **3** exhibits one single resonance at a chemical shift of δ = 0.40 ppm (Supporting Information, Figure S7). The chemical shift for solid LDA ranges from δ = 2.9 to 0.7 ppm depending on its chemical environment.[14] Since the chemical shift of **3** does not fall into this region, we assume that the resonance is not caused by residual LDA remaining in the porous network. Furthermore, the chemical shift of a lithium phenolate (lithium(2,6-di-*tert*-butyl-4-methylphenolate) which is comparable to **3** is $\delta = 0.39$ ppm.[15] Thus the ^{7}Li signal for **3** originates from a lithium phenolate type species, that is involving lithium cations having an oxygen contact.

Further information on the status of the lithium atoms in the framework is obtained by comparing the IR spectra of **2** and **3** (Figure 3). Three main conclusions can be drawn:

1) The IR spectra of **2** and **3** look basically the same confirming that the framework structure was preserved/no major damage occurred during the LDA treatment. This was also evident from nitrogen adsorption isotherms (Figure 2) and powder XRD patterns (Figure 1).
2) No LDA impurities are present, these would cause additional IR absorptions in the aliphatic C–H-stretching region which are not observed. Thus the resonance in the ^{7}Li NMR spectrum (Supporting Information, Figure S7) is solely caused by lithium ions being transferred from LDA to the framework.
3) Both OH species of the framework, that is, the bridging OH groups and the pendant OH groups of the hydroxyterephthalate linker are involved because both IR signals lose intensity (Note: this is not resolved in the ^{7}Li NMR spectrum and only a single resonance is observed). Thus, as expected, LDA did not attack one type of OH groups selectively. This may also provide an explanation for the observed shoulder in the XRD pattern of **3** (Figure 1). The ht–lt phase transformation in MIL-53 was proposed to be mediated through hydrogen bonds between the μ_2-hydroxy groups and water guest molecules.[8a] Since some of the protons of the μ_2-hydroxy groups are exchanged by lithium cations, the ht–lt transformation may be hindered, thus, leading to an additional reflection at a position indicative for the ht-variant of MIL-53(Al).

Furthermore it is evident from the IR spectra that the exchange of protons by lithium is far from complete for both OH species in the framework, otherwise the respective IR absorptions would have vanished entirely. The chemical analysis for **3** (see Supporting Information) confirms that 15% of the acidic framework protons are exchanged by lithium. Thus, **3** can be described as a MIL-53(Al) analogue doped with lithium alkoxide groups at the organic linker and with some of the μ_2-OH protons exchanged by lithium cations.

Figure 4 shows the low-pressure hydrogen adsorption isotherms of **2** and **3** at 77 K. The adsorbed amount of hydrogen corresponds to 0.50 and 1.7 wt% at 1 bar for **2** and **3**, respectively. While the result for **2** is within the range previously observed for MIL-53(Al),[16] the hydrogen uptake of **3** is significantly larger by approximately 1.2 wt%. For both materials, the hydrogen sorption is fully reversible as evident from the adsorption and desorption isotherms (Figure 4).

Note, however, that the observed increase of the weight-based hydrogen-storage capacity is not caused exclusively by the lithium doping. Liu et al. reported that MIL-53(Al) undergoes a temperature-induced, transformation from the ht phase to the lt phase (this phase has a significantly decreased pore volume). The transformation occurs slowly upon cooling. At the low temperatures typically required in hydrogen-adsorption experiments, this transformation means that the hydrogen adsorption isotherms can depend on the length of the cryogenic pretreatment,[17] that is, the values for hydrogen uptake at a certain pressure depend on how far the ht–lt phase transition has proceeded which in turn depends on the time the sample was exposed to cryogenic temperatures. Compounds **2** and **3** may have different behaviors with respect to the ht–lt phase transition and this will interfere with the effect of the lithium-doping on hydrogen adsorption.

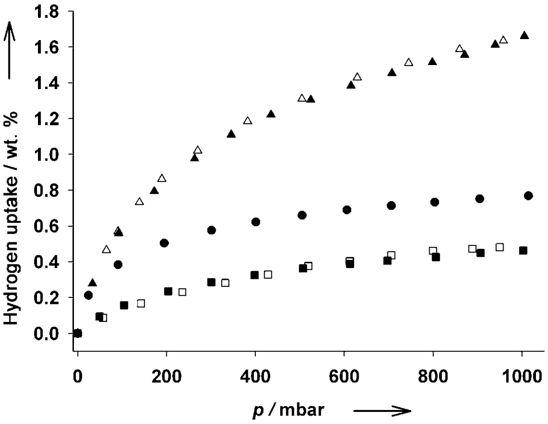

Figure 4. Low-pressure hydrogen sorption isotherms of **2** (■/□) and **3** (▲/△) (The samples were cooled to 77 K for 15 min prior to the measurements) and of **3** after cooling the sample for 3 h to 77 K prior to the measurement (●). Closed symbols: Adsorption; open symbols: Desorption.

In an effort to separate these effects, the hydrogen adsorption isotherm for **3** was recorded after the sample had been cooled to 77 K for 3 h prior to the measurement; a decreased capacity of only 0.8 wt% was found (Figure 4). However, a detailed analysis of these effects to separate the pure effect of lithium-doping from the effect of the ht–lt phase transition will require further studies involving structural investigations under a controlled hydrogen atmosphere.

The analysis of the isosteric heat of adsorption (q_{st}, Figure 5) clearly shows the impact of Li$^+$ ion doping on hydrogen sorption. While q_{st} ranges from 5.8 to 4.4 kJ mol^{-1} for **2** in agreement with reported data,[18] the values for **3** range from 11.6 to 6.4 kJ mol^{-1}. We assume that initially hydrogen adsorbs at high-affinity adsorption sites at or near the lithium cations, subsequent adsorption is at less-favored sites which still show somewhat higher q_{st} values than **2**. The initial value of 11.6 kJ mol^{-1} for **3** is in close agreement with the theoretical predicted maximum value of approximately 13 kJ mol^{-1}.[3a]

The experimental evidence confirms that lithium doping carried out in the described fashion has a significant impact on the hydrogen-adsorption properties of MIL-53. The results are very promising and further support the usefulness of lithium doping, proposed by Mulfort et al.[4] Furthermore, our experimental procedure is more facile than the one reported in ref. [4] and should be applicable in a more general fashion.

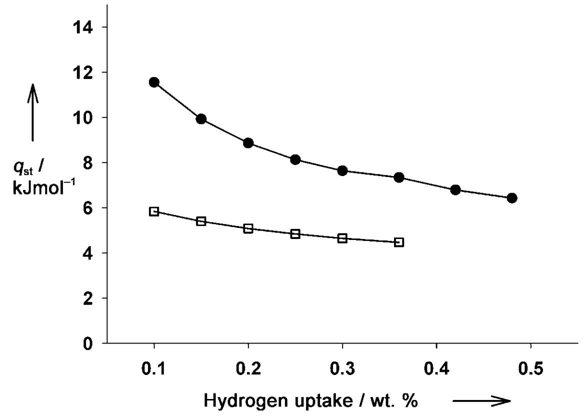

Figure 5. Plots of the isosteric heat of adsorption for **2** (□) and **3** (●) versus loading. (See Supporting Information for details of the measurements.)

In summary, we have presented the synthesis and characterization of a MIL-53(Al) structural analogue which incorporates pendant hydroxy groups and was prepared in an ambient pressure synthesis instead of the usually applied hydrothermal reaction. The pendant hydroxy groups can be converted into lithium alkoxide groups by treatment with LDA without significantly changing the MOF structure. This route opens up the possibility of synthesizing lithium alkoxide modified MOFs and studying their hydrogen-adsorption properties. Although the exchange of acidic protons by lithium cations was not complete, it still gave a material with an increased weight-based hydrogen adsorption capacity and the predicted increase in isosteric heat of adsorption compared to the undoped material. Future work is aimed at achieving a complete exchange of acidic framework protons by lithium cations.

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[1] a) R. von Helmolt, U. Eberle, *J. Power Sources* **2007**, *165*, 833–843; b) M. Felderhoff, C. Weidenthaler, R. von Helmolt, U. Eberle, *Phys. Chem. Chem. Phys.* **2007**, *9*, 2643–2653.

[2] a) D. Zhao, D. Yuan, H.-C. Zhou, *Energy Environ. Sci.* **2008**, *1*, 222–235; b) D. J. Collins, H.-C. Zhou, *J. Mater. Chem.* **2007**, *17*, 3154–3160.

[3] a) E. Klontzas, A. Mavrandonakis, E. Tylianakis, G. E. Froudakis, *Nano Lett.* **2008**, *8*, 1572–1576; b) A. Blomqvist, C. M. Araújo, P. Srepusharawoot, R. Ahuja, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 20173–20176; c) S. S. Han, W. A. Goddard III, *J. Am. Chem. Soc.* **2007**, *129*, 8422–8423; d) A. Mavrandonakis, W. Klopper, *J. Phys. Chem. C* **2008**, *112*, 11580–11585; e) P. Dalach, H. Frost, R. Q. Snurr, D. E. Ellis, *J. Phys. Chem. C* **2008**, *112*, 9278–9284; f) A. Mavrandonakis, E. Tylianakis, A. K. Stubos, G. E. Froudakis, *J. Phys. Chem. C* **2008**, *112*, 7290–7294; g) B. Huang, H. Lee, W. Duan, J. Ihm, *Appl. Phys. Lett.* **2008**, *93*, 063107; h) Y. J. Choi, J. W. Lee, J. H. Choi, J. K. Kang, *Appl. Phys. Lett.* **2008**, *92*, 173102; i) S. J. Kolmann, B. Chan, M. J. T. Jordan, *Chem. Phys. Lett.* **2008**, *467*, 126–130.

[4] a) K. L. Mulfort, J. T. Hupp, *Inorg. Chem.* **2008**, *47*, 7936–7938; b) K. L. Mulfort, J. T. Hupp, *J. Am. Chem. Soc.* **2007**, *129*, 9604–9605; c) K. L. Mulfort, T. M. Wilson, M. R. Wasielewski, J. T. Hupp, *Langmuir* **2009**, *25*, 503–508; d) F. Millange, G. Férey, M. Morcrette, C. Serre, M.-L. Doublet, J.-M. Grenèche, J.-M. Tarascon, *Stud. Surf. Sci. Catal.* **2007**, *170B*, 2037–2041.

[5] a) C.-D. Wu, A. Hu, L. Zhang, W. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 8940–8941; b) C.-D. Wu, W. Lin, *Angew. Chem.* **2007**, *119*, 1093–1096; *Angew. Chem. Int. Ed.* **2007**, *46*, 1075–1078; c) W. Morris, C. J. Doonan, H. Furukawa, R. Banerjee, O. M. Yaghi, *J. Am. Chem. Soc.* **2008**, *130*, 12626–12627; d) X. Li, R. Cao, W. Bi, Y. Wang, X. Li, Z. Guo, *Cryst. Growth Des.* **2005**, *5*, 1651–1656; e) A. Roth, A. Buchholz, W. Plass, *Z. Anorg. Allg. Chem.* **2007**, *633*, 383–392; f) S.-R. Fan, L.-G. Zhu, *Inorg. Chem.* **2006**, *45*, 7935–7942; g) H.-L. Gao, L. Yi, B. Zhao, X.-Q. Zhao, P. Cheng, D.-Z. Liao, S.-P. Yan, *Inorg. Chem.* **2006**, *45*, 5980–5988; h) P. D. C. Dietzel, R. Blom, H. Fjellvåg, *Eur. J. Inorg. Chem.* **2008**, 3624–3632; i) A. Zingiryan, J. Zhang, X. Bu, *Inorg. Chem.* **2008**, *47*, 8607–8609; j) C. D. Ene, F. Tuna, O. Fabelo, C. Ruiz-Pérez, A. M. Madalan, H. W. Roesky, M. Andruh, *Polyhedron* **2008**, *27*, 574–582; k) P. D. C. Dietzel, R. Blom, H. Fjellvåg, *Dalton Trans.* **2006**, 2055–2057; l) Y. Huang, B. Yan, M. Shao, *J. Solid State Chem.* **2008**, *181*, 2935–2940; m) X.-J Li, X.-Y. Wang, S. Gao, R. Cao, *Inorg. Chem.* **2006**, *45*, 1508–1516.

[6] One of the compounds exhibits a rather complicated homochiral structure[5a,b] which we regarded to be not suitable for introducing lithium alkoxide groups into a MOF under facile experimental conditions. The other[5c] was published after our work was completed (December 2008).

[7] a) P. D. C. Dietzel, B. Panella, M. Hirscher, R. Blom. H. Fjellvåg, *Chemm. Commun.* **2006**, 959–961; b) N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 1504–1518; c) N. Xu, W. Shi, D.-Z. Liao, S.-P. Yan, P. Chen, *Inorg. Chem.* **2008**, *47*, 8748–8756; d) P. Thuéy, *CrystEngComm* **2008**, *10*, 79–85.

[8] a) T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Férey, *Chem. Eur. J.* **2004**, *10*, 1373–1382; b) C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër, G. Feréy, *J. Am. Chem. Soc.* **2002**, *124*, 13519–13526.

[9] C. Mellot-Draznieks, C. Serre, S. Surblé, N. Audebrand, G. Férey, *J. Am. Chem. Soc.* **2005**, *127*, 16273–16278.

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

[11] S. Bauer, C. Serre, Th. Devic, P. Horcajada, J. Marrot, G. Férey, N. Stock, *Inorg. Chem.* **2008**, *47*, 7568–7576.

[12] M. Hartmann, S. Kunz, D. Himsl, O. Tangermann, S. Ernst, A. Wagener, *Langmuir* **2008**, *24*, 8634–8642.

[13] a) W. Cochran, *Acta. Crystallogr.* **1953**, *6*, 260–268; b) M. Sundaralingam, L. H. Jensen, *Acta Crystallogr.* **1965**, *18*, 1053–1058; c) G. E. Bacon, R. J. Jude, *Z. Kristallogr.* **1973**, *138*, 19–40.

[14] M. Hartung, H. Günther, J.-P. Amoureux, C. Fernandéz, *Magn. Reson. Chem.* **1998**, *36*, S61–S70.

[15] A. Pepels, PhD thesis, University of Siegen (Germany), **2001**.

[16] G. Férey, M. Latroche, C. Serre, F. Millange, T. Loiseau, A. Percheron-Guégan, *Chem. Commun.* **2003**, 2976–2977.

[17] Y. Liu, J.-H. Her, A. Dailly, A. J. Ramirez-Cuesta, D. A. Neumann, C. Brown, *J. Am. Chem. Soc.* **2008**, *130*, 11813–11818.

[18] B. Schmitz, U. Müller, N. Trukhan, M. Schubert, G. Férey, M. Hirscher, *ChemPhysChem* **2008**, *9*, 2181–2184.