Hydrogen Storage

DOI: 10.1002/anie.200906936

Lithium-Doped Conjugated Microporous Polymers for Reversible Hydrogen Storage**

*An Li, Rui-Feng Lu, Yi Wang, Xin Wang, Ke-Li Han, and Wei-Qiao Deng**

Hydrogen storage is of great interest as environmentally clean and efficient fuels are required for future energy applications.[1] Several pioneering strategies have been developed and significant performances have been achieved for hydrogen storage, including chemisorption of dihydrogen in the form of light metal hydrides,[2] metal nitrides and imides,[3] physisorption of dihydrogen onto carbon,[4] clathrate hydrates,[5] and porous network materials such as carbon nanotubes (CNTs),[6] zeolites,[7] and metal–organic framework (MOF) materials.[8] However, hydrogen storage in these systems requires either high pressure or very low temperature, or both, thus severely limiting the applicability for mobile applications, which require working conditions of 1–20 bar and ambient temperature. The synthesis of functional materials with high hydrogen uptake and delivery under safe and ambient conditions remains a key challenge for establishing hydrogen economy.

It has been reported that atomically dispersed alkali-metal ions (e.g., Li^+ and Na^+) are capable of clustering several H_2 molecules bound through electrostatic charge–quadrupole and charge-induced dipole interactions.[9] Thus ab initio simulations showed that Li-doped pillared graphene can bind reversibly up to 6.5 mass% of H_2 at 20 bar at room temperature.[9a] In addition, ab initio simulations showed that doping of MOFs with atomically dispersed alkali-metal cations can reversibly achieve up to 5.5 mass% of H_2 at 100 bar at room temperature.[10] These results suggest that the high electron affinity of the sp^2 carbon framework can essentially separate the charge from the Li center, thus providing strong stabilization of the molecular H_2 and dramatically improving the hydrogen uptake value compared to that of undoped systems. Recently, experimental investigations also showed that H_2 uptake of the MOFs can be remarkably improved by introduction of Li^+ ions into MOF systems. For instance, an Li-doped MOF, which was prepared by reaction of lithium diisopropylamide (LDA) with the MOF MIL-53(Al), was reported to exhibit nearly double the hydrogen uptake compared with an undoped MOF.[11] The doping of Li into the MOF has also been reported to remarkably enhance the isosteric heats of H_2 adsorption compared to those of the undoped MOF.[12] To date, no material that consists of an active Li dopant and has ultrahigh hydrogen storage capacity has been reported. The difficulty in demonstrating this concept relates to whether agglomeration of the Li atoms occurs during synthesis.

Recently, conjugated microporous polymers (CMPs) have received considerable research interest for hydrogen storage because of their finely tunable microporosity, large surface areas, and high stability.[13] Herein, we report the first experimental evidence that Li^+ ion dopants dramatically enhance hydrogen storage in a CMP matrix. The hydrogen storage amount can reach up to 6.1 wt% at 1 bar and 77 K, which is among the best reported to date for physisorption hydrogen storage materials including MOFs and CNTs.

The CMP we selected was produced from 1,3,5-triethynylbenzene, which has active sites ($C\equiv C$ bonds) for binding of metallic ions, large BET surface areas with microporous character, and good chemical (totally insoluble in all organic solvents), and thermal stability (thermogravimetric analysis (TGA) shows that the thermal decomposition temperature of the CMP is greater than 300 °C).[13b] These physicochemical properties suggest that the selected CMP is appropriate as a host for Li doping. Also, this material contains only three kinds of light elements (C, H, and Li), which is a great advantage for gravimetric adsorption.

We synthesized the CMP by Pd^{II}/Cu^{I}-catalyzed homocoupling polymerization.[13b] To dope the CMP with Li, we immersed the CMP in a solution of the naphthalene anion radical salt ($Li^+C_{10}H_8^{\bullet-}$) in THF.[14,15] The mixture was stirred for several hours under an inert atmosphere to allow thorough penetration of Li^+ ions into the CMP network. The mixture was filtered and the solid product was washed with dry THF several times followed by removal of the solvent at room temperature and subsequent removal of the naphthalene under vacuum at 120 °C. The field emission scanning electron microscopy (FE-SEM) images (Figure 1 a,b) show that the CMP and Li-CMP consist of agglomerated microgel particles and have porous features. TGA shows that the CMP have good thermal stability (Figure 1 c, thermal decomposition temperature > 300 °C). In the case of the CMP treated with $Li^+C_{10}H_8^{\bullet-}$ (0.5 wt% Li), an obvious weight loss (ca. 10%) was observed in the temperature range 100–150 °C. This feature suggests the removal of the residual naphthalene absorbed in the CMP matrix, and is consistent with a previous report.[16] Figure 1 d shows the high-resolution

---

[*] K.-L. Han, Prof. W.-Q. Deng
State Key Lab of Molecular Reaction Dynamics
Dalian Institute of Chemical Physics, Chinese Academy of Sciences
Dalian 116023 (China)
E-mail: dengwq@dicp.ac.cn
Homepage: http://www.nmce.dicp.ac.cn/
Dr. A. Li, Dr. R. F. Lu, Dr. Y. Wang, Prof. X. Wang
Nanyang Technological University, CBC and CBE
50 Nanyang Drive, Singapore 639798 (Singapore)

[**] We are grateful to Prof. W. A. Goddard for helpful discussions. This research was supported by the "100-Talent Program" of the Chinese Academy of Sciences, NSFC grant nos. 20833008 and Ministry of Education in Singapore (ARC24/07, no. T206B1218RS).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200906936.

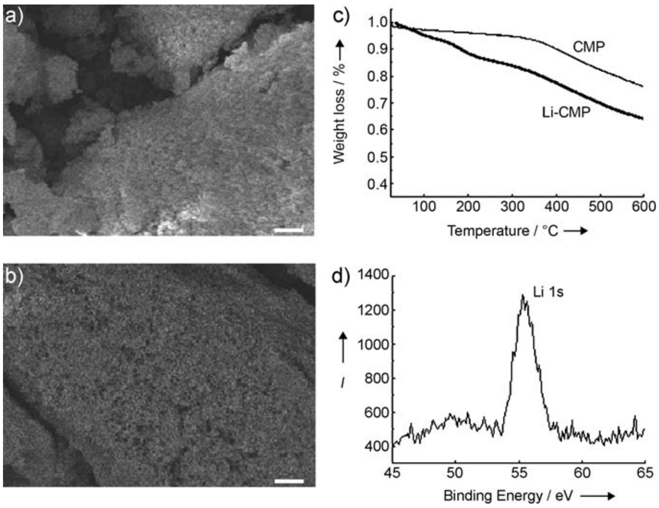

Figure 1. FE-SEM images of a) CMP and b) Li-CMP (0.5 wt% Li); scale bars: 1 μm; c) TGA curves of CMP and Li-CMP (0.5 wt% Li); d) Li 1s XPS spectra of the Li-CMP. (Li 1s around 55.4 eV, suggesting that the doped Li into CMP matrix is in an ionic state with one negative charge per Li atom, the spectrum was calibrated to the binding energy of the adventitious C 1s peak at 285.0 eV.)

X-ray photoelectron spectra (XPS) of Li 1s and C 1s regions for Li-CMP. The Li 1s peak at 55 eV is assigned to an ionic state with one negative charge per Li atom.

Figure 2 a shows the hydrogen adsorption and desorption isotherms of the CMP and Li-CMP with various Li contents at 77 K. All the samples show reversible hydrogen uptake, with nearly no hysteresis between the absorption and desorption isotherms, thus indicating that hydrogen is reversibly physisorbed.[17] The CMP exhibits a relative small hydrogen uptake value of 1.6 wt% at 1 bar. The Li-CMP with 0.5 wt% Li exhibits a significant maximum volume of 6.1 wt%, which is nearly four times that of the CMP, when the pressure was increased to 1 bar. This volume is the one of largest hydrogen uptakes observed at ambient pressure at 77 K. We carried out several hydrogen sorption experiments using the Li-CMP with various Li contents. When the Li content is higher than 0.5 wt%, the hydrogen uptake sharply decreased compared to that of the Li-CMP with optimal Li content (0.5 wt%). For example, the maximum hydrogen uptake volume was found to be 2.6 wt% for the Li-CMP with 1.43 wt% Li and 1.1 wt% for the Li-CMP with 7.21 wt% Li. This result suggests that agglomeration of Li may take place at high Li content, which in turn causes a decrease in hydrogen uptake.

Figure 2 b shows that the isotherm for the CMP exhibits a small initial slope ($P < 0.01$ MPa) and then reaches its saturation state quickly as the pressure is further increased. This result implies a weak interaction between the gas and the host material. However, the isotherm for the Li-CMP exhibits a large initial slope with nearly linear increases in hydrogen uptake in the pressure range $0.02\,\text{MPa} < P < 0.1$ MPa (Figure 2 c). This uptake value suggests the presence of a strong interaction between hydrogen and the Li-CMP, even at high hydrogen coverage. We determined the isosteric heat of sorption for hydrogen on the CMP and the Li-CMP (Figure 2 d) as a function of hydrogen uptake by comparison of the adsorption isotherms at 77 K and 87 K (Figure 2 b, c). The data were fitted by using a virial-type expression (Equation S1 in the Supporting Information[18]), and the heat of adsorption (Q_{st}) was then calculated from the fitting parameters (Equation S2 in the Supporting Information), which were commonly employed to evaluate and compare the isosteric heats of different MOFs.[17]

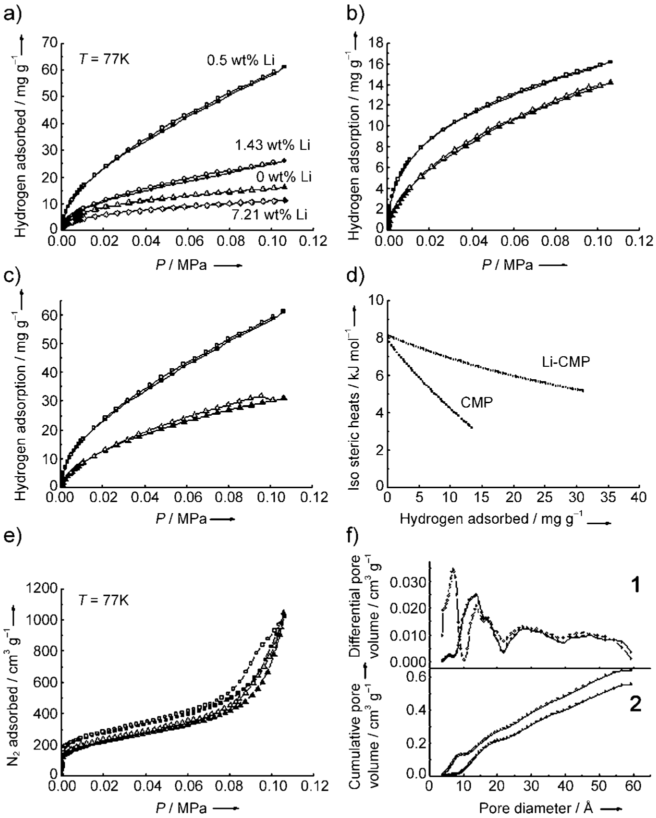

Figure 2. a) Hydrogen adsorption (filled symbols) and desorption (empty symbols) isotherms of the Li-CMPs with various Li contents at 77 K. b) Hydrogen adsorption and desorption isotherms of the CMP at 77 K (■/□) and 87 K (▲/△). c) Hydrogen adsorption and desorption isotherms of the Li-CMP (0.5 wt% Li) at 77 K (■/□) and 87 K (▲/△). d) Isosteric heats of hydrogen adsorption of CMP and Li-CMP (0.5 wt% Li). e) Nitrogen adsorption (filled sybols) and desorption (empty symbols) isotherms measured for CMP (■/□) and Li-CMP (0.5 wt% Li, ▲/△) at 77 K. f) Pore-size distribution (1) and cumulative pore volume (2) curves of CMP (○) and Li-CMP (0.5 wt%, ●).

As shown in Figure 2 d, at low hydrogen coverage, the adsorption enthalpies for the CMP and Li-CMP were 7.7 kJ mol^{-1} and 8.1 kJ mol^{-1}, respectively. With increasing hydrogen coverage, the adsorption enthalpies of the CMP dropped sharply to 3.2 kJ mol^{-1} while the adsorption enthalpies for the Li-CMP decreased smoothly to 5.1 kJ mol^{-1} at high loading. For the entire loading range, the enthalpies of the Li-CMP were higher than those of the CMP. These results thus provide direct evidence for the existence of a strong interaction between hydrogen molecules and the Li-CMP.

The hydrogen sorption of the Li-CMP with optimal Li content (0.5 wt%) at 273 K and 0.1 MPa was also carried out (Figure S3 in the Supporting information). The isotherm for the Li-CMP is quite different from that observed at 77 K, as the hydrogen uptake increased almost linearly as the pressure increased. The maximum amount of hydrogen adsorbed at this temperature reached approximately 0.1 wt %, which is far less than that obtained at 77 K. It should be noted that the isotherm is not saturated and higher hydrogen uptake would be expected at higher pressures.

We also investigated the changes in porous properties before and after Li doping on the gas sorption performance of the CMP since the porous feature of the CMP-based materials plays an important role in their gas sorption ability.[19] Figure 2 e shows nitrogen isotherms of the CMP and Li-CMP (0.5 wt% Li) at 77 K. Both the CMP and Li-CMP display type I adsorption isotherms and the materials consist of micropores and mesopores. The BET surface areas, which were calculated by fitting to the BET equation ($0.002\,\text{MPa} < P < 0.032\,\text{MPa}$), were found to be $955\,\text{m}^2\text{g}^{-1}$ for the CMP and $795\,\text{m}^2\text{g}^{-1}$ for the Li-CMP. Analysis of the CMP porous properties showed that the total pore volume (calculated at $P = 0.106\,\text{MPa}$) of the CMP is $1.58\,\text{cm}^3\text{g}^{-1}$, which is close to that of the Li-CMP ($1.61\,\text{cm}^3\text{g}^{-1}$). However, the Li-CMP exhibits a micropore volume of $0.21\,\text{cm}^3\text{g}^{-1}$, which is less than that of the CMP ($0.26\,\text{cm}^3\text{g}^{-1}$). Moreover, it is clear from pore-size distribution curves (Figure 2 f) that the differential micropore volume is obviously greater for the CMP than the Li-CMP at a pore size of approximately 0.8 nm. It is well known that large BET surface areas, small pore sizes, and large pore volumes facilitate hydrogen sorption. Consequently, it can be confirmed that the enhancement in hydrogen uptake of the Li-CMP is caused by doping Li into the CMP network rather than changes in porous properties of material. We also investigated the porous properties of Li-CMP samples with different Li contents; indeed both the BET surface areas and pore volumes decrease with further increase in Li content above 0.5 wt %. Accordingly, it can be concluded that the hydrogen adsorption performance can be greatly improved by doping Li into the CMP network, however, a relatively high BET surface area as well as a large pore volume is a prerequisite.

To further understand the effect of Li doping on hydrogen sorption performance of the Li-CMP, we used the Polymer Builder[20] to computationally generate a five-generation dendrimer that consists of three triple bonds and one aromatic ring, and has similar seed and repeat units (Figure 3). The dendrimer was built into an amorphous unit cell to describe a condensed polymer system. We then carried out grand canonical ensemble Monte Carlo (GCMC) simulations[20] to estimate the hydrogen sorption behavior of the CMP and Li-CMP networks. To model the Li-CMP, 26 lithium atoms were doped into our model structure to mimic the experimental conditions (see the Supporting Information for the ab initio force field (FF) parameters and more calculation details). From the hydrogen molecule density plots for Li-CMP (Figure 3), the adsorbed hydrogen molecules are mostly clustered around the Li atoms; adsorption does not obviously appear to occur adjacent to the C≡C triple bonds and aromatic rings in the CMP framework. At 77 K and at an ambient pressure of 0.1 MPa, this clustering should lead to a significant adsorption enhancement for Li-doped CMP compared to CMP.

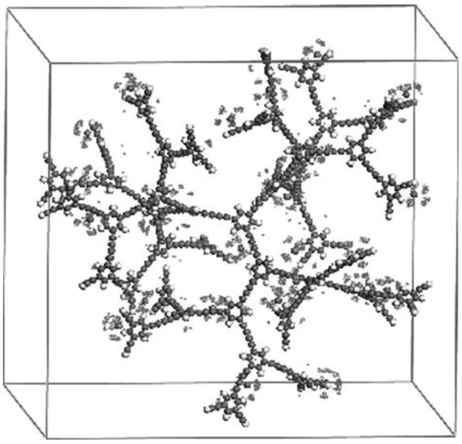

Figure 3. Snapshots of adsorbed hydrogen molecule density from GCMC simulations for Li-CMP at 77 K and 1 atm. C gray, Li pink, H atoms of CMP white, density of adsorbed H_2 red).

In summary, we have demonstrated a strategy to enhance the hydrogen storage capacity of CMP by doping with Li^+ ions. We found that the capacity of these Li-CMP structures for hydrogen at 1 bar and 77 K, 6.1 wt %, is one of the highest capacity reported to date for physisorption materials such as MOFs carbon nanotubes under the same conditions. We anticipate that further increases in performance can be expected by controlling the amounts of Li dopant in the conjugated microporous polymers.

Experimental Section

Details of experimental procedures and calculation results are given in the Supporting Information.

Synthesis of Li-CMP: The CMP was synthesized according to a published procedure[13b] (see the Supporting Information). Synthesis of Li-CMP was carried out under an argon atmosphere in a glove box. THF was dried over sodium wire. A small piece of clean lithium wire (diameter = 3.2 mm; Aldrich) was immersed in dry THF to remove excess mineral oil. Then the lithium (ca. 2.0 mg) was placed in a solution of naphthalene in THF (200 mL, 0.1M) and the mixture was stirred vigorously. The solution turned from colorless to light green after about 1 h, then to dark green after prolonged stirring. 25 mL of the resulting solution was transferred by syringe to a known mass of CMP. The mixture was stirred for several hours to allow the complete penetration of lithium ions into the CMP network, then the mixture was filtered through a glass frit and the solid product was washed several times with dry THF. Residual solvent was removed under vacuum at room temperature. The removal of naphthalene was performed by degassing the sample at 120 °C under vacuum until the pressure was below 1×10^{-5} torr; the sample was then maintained at this pressure and temperature for several hours.

Adsorption measurements: Samples of a known weight (20–40 mg) were loaded into a preweighed sample tube under an argon atmosphere and the tube was then sealed to prevent exposure to oxygen and atmospheric moisture during transfer and weighing. The samples were evacuated at 120 °C under a dynamic vacuum below 10^{-5} torr for 24 h on an Autosorb-1 from Quantachrome Instruments prior to gas adsorption measurements. After evacuation, the tube containing degassed samples were precisely weighed again to obtain the mass of evacuated samples. Ultrahigh purity He, H_2, and N_2 were used for all adsorption measurements. The data were converted to gravimetric units using the conversion factor 2.0 mg hydrogen per

22.4 cm^3 at STP. It should be noted that the excess and total adsorptions were not measured in this work. H_2 and N_2 isotherms at 77 K were measured in a liquid nitrogen bath using a 77 K sensor, H_2 isotherms at 87 K were measured in liquid argon bath using a 87 K sensor, H_2 isotherms at 273 K were measured in an ice–water mixture bath using a 273 K sensor.

Received: December 9, 2009
Revised: March 2, 2010

Keywords: doping · hydrogen storage · lithium · microporous materials · polymers

---

[1] a) U. Eberle, M. Felderhoff, F. Schüth, *Angew. Chem.* **2009**, *121*, 6732 – 6757; *Angew. Chem. Int. Ed.* **2009**, *48*, 6608 – 6630; b) V. V. Struzhkin, B. Militzer, W. L. Mao, H. Mao, R. J. Hemley, *Chem. Rev.* **2007**, *107*, 4133 – 4151.
[2] L. Schlapbach, A. Züttel, *Nature* **2001**, *414*, 353 – 358.
[3] P. Chen, Z. Xiong, J. Luo, J. Lin, K. L. Tan, *Nature* **2002**, *420*, 302 – 304.
[4] G. Yushin, R. Dash, J. Jagiello, J. E. Fischer, Y. Gogotsi, *Adv. Funct. Mater.* **2006**, *16*, 2288 – 2293.
[5] a) W. L. Mao, H. K. Mao, A. F. Goncharov, V. V. Struzhkin, Q. Guo, J. Hu, J. Shu, R. J. Hemley, M. Somayazulu, Y. Zhao, *Science* **2002**, *297*, 2247 – 2249; b) W. L. Mao, H. K. Mao, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 708 – 710.
[6] a) A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, M. J. Heben, *Nature* **1997**, *386*, 377 – 379; b) C. Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Cheng, M. S. Dresselhaus, *Science* **1999**, *286*, 1127 – 1129.
[7] A. Zecchina, S. Bordiga, J. G. Vitillo, G. Ricchiardi, C. Lamberti, G. Spoto, M. Bjorgen, K. P. Lillerud, *J. Am. Chem. Soc.* **2005**, *127*, 6361 – 6366.
[8] a) N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, *Science* **2003**, *300*, 1127 – 1129; b) J. L. C. Rowsell, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4748 – 4758; *Angew. Chem. Int. Ed.* **2005**, *44*, 4670 – 4679; c) X. B. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *Science* **2004**, *306*, 1012 – 1015.
[9] a) W. Q. Deng, X. Xu, W. A. Goddard, *Phys. Rev. Lett.* **2004**, *92*, 166103; b) A. Blomqvist, C. Moysés Araújo, P. Srepusharawoot, R. Ahuja, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 20173 – 20176.
[10] S. S. Han, W. A. Goddard, *J. Am. Chem. Soc.* **2007**, *129*, 8422 – 8423.
[11] K. L. Mulfort, J. T. Hupp, *J. Am. Chem. Soc.* **2007**, *129*, 9604 – 9605.
[12] D. Himsl, D. Wallacher, Martin Hartmann, *Angew. Chem.* **2009**, *121*, 4710 – 4714; *Angew. Chem. Int. Ed.* **2009**, *48*, 4639 – 4642.
[13] a) J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak, A. I. Cooper, *Angew. Chem.* **2007**, *119*, 8728 – 8732; *Angew. Chem. Int. Ed.* **2007**, *46*, 8574 – 8578; b) J. X. Jiang, F. Su, H. Niu, C. D. Wood, N. L. Campbell, Y. Z. Khimyak, A. I. Cooper, *Chem. Commun.* **2008**, 486 – 488; c) E. Stöckel, X. Wu, A. Trewin, C. D. Wood, R. Clowes, N. L. Campbell, J. T. A. Jones, Y. Z. Khimyak, D. J. Adams, A. I. Cooper, *Chem. Commun.* **2009**, 212 – 214; d) J.-X. Jiang, A. Trewin, F. Su, C. D. Wood, H. Niu, J. T. A. Jones, Y. Z. Khimyak, A. I. Cooper, *Macromolecules* **2009**, *42*, 2658 – 2666; e) R. Dawson, A. Laybourn, R. Clowes, Y. Z. Khimyak, D. J. Adams, A. I. Cooper, *Macromolecules* **2009**, *42*, 8809 – 8816.
[14] M. Inagaki, O. Tanaike, *Synth. Met.* **1995**, *73*, 77 – 81.
[15] C. D. Stevenson, C. V. Rice, P. M. Garland, B. K. Clark, *J. Org. Chem.* **1997**, *62*, 2193 – 2197.
[16] M. Ichikawa, M. Soma, T. Onishi, K. Tamaru, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3672 – 3679.
[17] L. C. Jesse, J. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc.* **2007**, *128*, 1304 – 1315.
[18] L. Czepirski, J. Jagiello, *Chem. Eng. Sci.* **1989**, *44*, 797 – 801.
[19] J. X. Jiang, F. Su, A. Trewin, C. D. Wood, H. Niu, J. T. A. Jones, Y. Z. Khimyak, A. I. Cooper, *J. Am. Chem. Soc.* **2008**, *130*, 7710 – 7720.
[20] Polymer Builder module of the Material Studio program. The GCMC calculations were carried out using the sorption module of the Materials Studio program (Accelrys, San Diego) with the FF described in the Supporting Information.