Postsynthetic modification of an imine-based microporous organic network

Phillip A. Kerneghan, Shira D. Halperin, David L. Bryce, and Kenneth E. Maly

Abstract: A highly cross-linked microporous organic network with imine linkers was prepared by condensation of tetrakis(4-aminophenyl)methane with terephthaldehyde. Gas adsorption studies indicate that the material exhibits permanent microporosity, and guest exchange experiments demonstrate that small molecules can diffuse into the network. Postsynthetic modification of this microporous network was achieved by treatment with borane in THF, which reduced the imine groups to the corresponding amines as shown by IR and ^{13}C CP-MAS solid-state NMR spectroscopy. The resulting material showed enhanced resistance to acidic hydrolysis compared with the imine precursor, and retained its ability to absorb guest molecules. The amine network was amenable to further postsynthetic modifications. Specifically, acetylation of this network using acetic anhydride was demonstrated.

Key words: imines, synthesis, microporous polymers, postsynthetic modification.

Résumé : On a préparé un réseau organique microporeux très réticulé à l'aide de coupleurs imines par condensation du tétrakis(4-aminophényl)méthane avec du téréphtaldéhyde. Des études d'adsorption de gaz indiquent que le matériau comporte une microporosité permanente alors que des expériences d'échange de molécule invitée démontrent que les petites molécules peuvent diffuser dans le réseau. On a réalisé des modifications postsynthétiques de ce réseau microporeux par un traitement avec du borane dans le THF qui a permis de réduire les groupes imines en amines correspondantes, tel que démontré par la spectroscopie infrarouge et la RMN du ^{13}C à l'état solide dans le mode de la rotation à l'angle magique avec polarisation croisée (RAM-PC). Le matériau qui en résulte présente une résistance accrue à l'hydrolyse acide par comparaison avec le précurseur imine et il conserve sa facilité à absorber des molécules invitées. Le réseau amine peut être amené à d'autres modifications postsynthétiques. On a démontré, en particulier, la possibilité d'acyler ce réseau à l'aide d'anhydride acétique.

Mots-clés : imines, synthèse, polymères microporeux, modification postsynthétique.

[Traduit par la Rédaction]

Introduction

Microporous solids are an important class of materials because their small pore sizes and high surface area make them potentially useful for chemical separation, catalysis, or gas storage.[1] Metal–organic frameworks (MOFs), which are crystalline three-dimensional coordination polymers, have been extensively studied, and show large surface areas and well-defined channels and pores.[2] In addition to coordination polymers, recent studies have focused on covalently linked microporous solids derived entirely from organic building blocks.[3] These materials, which include highly cross-linked polymers,[4] polymers of intrinsic microporosity (PIMs),[5] other amorphous polymers,[6] and covalent organic frameworks (COFs),[7] also exhibit large surface areas that make them potentially suitable for applications.

An important challenge in the field of microporous solids is the control of the properties of these materials, and, in particular, the incorporation of specific functional groups into the materials. The incorporation of any desired functionality into microporous solids often requires that desired groups be attached to the molecular building blocks prior to network formation and that these groups be compatible with the reaction conditions for network formation. An alternative strategy for incorporating desired functional groups involves covalent "postsynthetic" modification of the microporous material. Covalent postsynthetic modification of a porous coordination polymer was first reported by Seo et al.,[8] who showed that a network bearing uncoordinated and exposed pyridine groups could be methylated using iodomethane. More recently, Cohen and co-workers[9,10] demonstrated that covalent postsynthetic modification of MOFs can be used effectively to incorporate functionality into these microporous solids while maintaining a desired network topology. Similarly, postsynthetic modification of a permeable organic hydrogen-bonded network by reaction of thiols with exposed allyl groups has also been demonstrated.[11] Although postsynthetic modification of polymers such as polyolefins is well-established,[12] comparable postsynthetic transformations of organic microporous materials has not been reported, in part because many microporous polymers do not have the requisite functional groups for further reactions. In other cases, microporous

Received 15 November 2010. Accepted 21 January 2011. Published at www.nrcresearchpress.com/cjc on 26 April 2011.

P.A. Kerneghan, S.D. Halperin, and K.E. Maly. Wilfrid Laurier University, 75 University Ave. W, Waterloo, ON N2L 3C5, Canada.
D.L. Bryce. Department of Chemistry and Centre for Catalysis Research and Innovation, University of Ottawa, 10 Marie Curie Pvt, Ottawa, ON K1N 6N5, Canada.

Corresponding author: K.E. Maly (e-mail: kmaly@wlu.ca).

doi:10.1139/V11-014

Scheme 1.

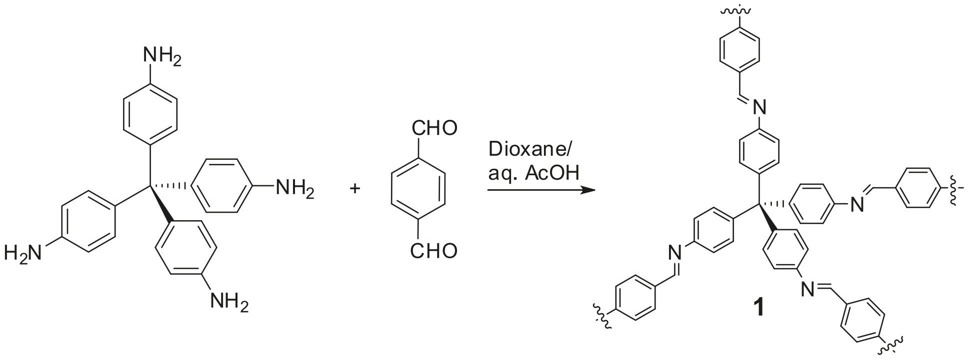
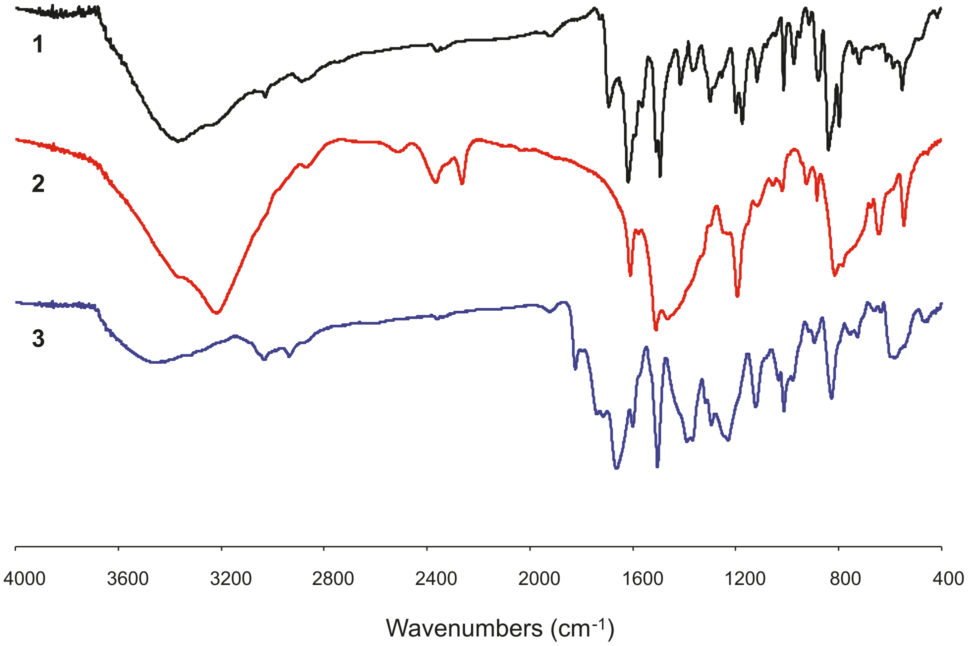


Fig. 1. Infrared spectra of imine network **1**, amine network **2**, and acetylated network **3**.



organic solids such as COFs are linked by readily hydrolyzed groups such as boroxines or boronates that make them sensitive to further synthetic transformations. Postsynthetic modification of microporous organic materials therefore requires networks that are robust enough to withstand further reaction conditions, as well as functional groups that are accessible to reagents that can diffuse into the porous network.

Recently, Yaghi and co-workers[7d] introduced a new class of COFs based on imine linking groups. Schwab et al.[13] also used Schiff base formation for the preparation of microporous polymer networks. The presence of imine groups as linkers for organic microporous materials presents a unique opportunity for postsynthetic modification of the organic framework by reduction of these imines to the corresponding amines. Although imines are susceptible to hydrolysis, the corresponding amine networks are expected to display increased chemical stability. Moreover, the amine groups provide a functional handle for further synthetic transformations. Such an approach could provide access to new microporous organic solids with diverse functionality and controllable properties. Herein we report the postsynthetic modification of an imine-based microporous network by reduction and show that it can produce a network with enhanced resistance to hydrolysis. We also demonstrate that the reduced network can undergo further synthetic transformations, such as acetylation of the amino groups.

Results and discussion

Imine network **1** was prepared as outlined in Scheme 1 using terephthaldehyde and tetrakis(4-aminophenyl)methane[14] under solvothermal conditions in a mixture of dioxane and aqueous acetic acid, as described by Yaghi and co-workers.[7d]

The formation of the imine network was confirmed by IR spectroscopy (Fig. 1) and ^{13}C CP-MAS solid-state NMR spectroscopy (Fig. 2); the results are consistent with the previously reported data[7d] as well as the spectroscopic data from model compounds (See Supplementary data). Further investigation by powder X-ray diffraction showed that in contrast to Yaghi's[7d] crystalline and multiply interpenetrated COF, network **1** diffracted very weakly, showing broad reflections consistent with largely amorphous material (see Supplementary data). Despite the amorphous nature of **1**, nitrogen adsorption studies showed a sharp uptake at low pressure, indicating that the material was indeed microporous (Fig. 3).

Fig. 2. ^{13}C CP-MAS spectra of imine network **1**, reduced network **2**, and acetylated network **3**. Signals marked with * indicate spinning side bands, and the two signals marked with # for the spectrum of **2** correspond to included THF.

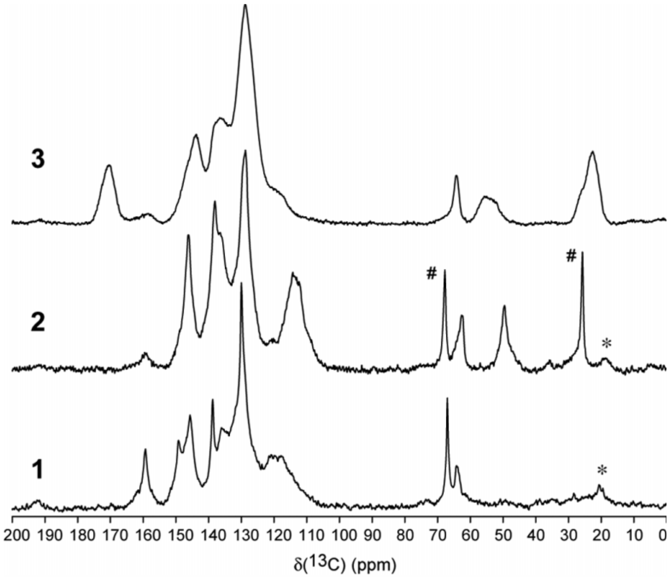


Fig. 3. Nitrogen adsorption isotherm for **1** measured at 77 K.

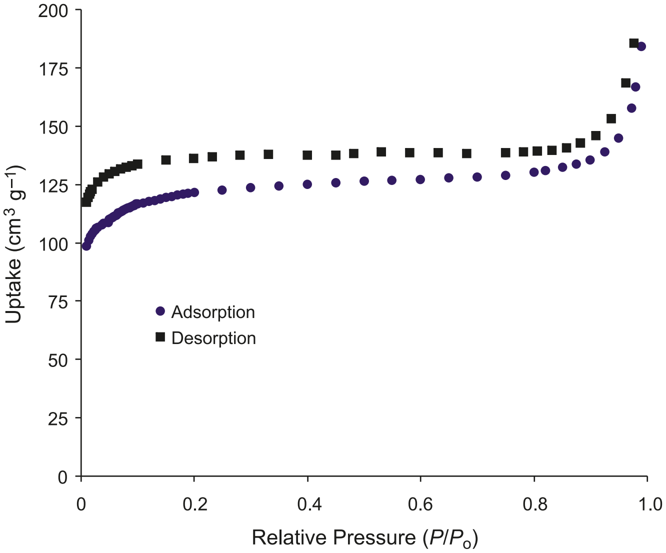
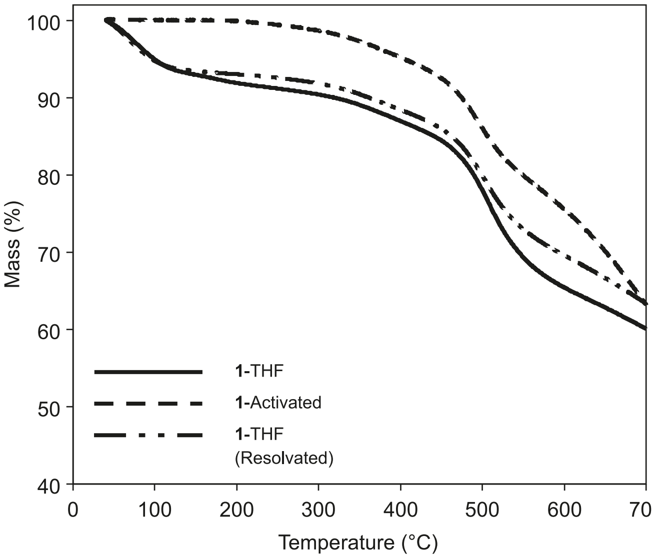


Fig. 4. Thermogravimetric analysis traces of **1** with THF, activated, and resolvated with THF.



From the adsorption data, the Brunauer–Emmett–Teller (BET) surface area was determined to be 416 m^2/g. This value is significantly lower than that reported by Yaghi and co-workers (1360 m^2/g)[7d], but is comparable to some other microporous networks. We attribute these differences in the properties of our material compared with Yaghi's to the sensitivity of COF network formation to slight variations in the reaction conditions. It is noteworthy that some hysteresis is observed in comparing the adsorption and desorption isotherms. This observation is consistent with the results of Yaghi and co-workers[7d] and indicates some flexibility of the framework. Thermogravimetric analysis of **1** solvated with THF showed ~7% mass loss below 100 °C, corresponding to the loss of the solvent (Fig. 4), with substantial mass loss above 450 °C, corresponding to decomposition of the network. Subsequent activation by heating at 100 °C under vacuum overnight, followed by resolvation with THF showed a similar uptake compared with the original solvated network, providing further support for the porosity of the material and evidence that it can take up small molecules. Further solvent-exchange experiments and subsequent analysis by TGA showed that the guest molecules can be exchanged (see Supplementary data). These thermal analysis experiments demonstrate that **1** is permeable to guest molecules, and therefore may be suitable for postsynthetic modification by allowing reactants to diffuse into the porous network.

Network **1** was suspended in anhydrous THF and treated with an excess of borane–THF (Scheme 2). After standing for 24 h, the solid was collected and washed with water, followed by THF. The IR spectrum of **2** showed a substantial attenuation of the C=N stretching band at 1615 cm^{-1} and a concomitant increase in the N–H stretching band at ~3200 cm^{-1} (Fig. 1). These results are consistent with the reduction of the imine linkages of **1** to the corresponding amines. Further confirmation of the reduction was provided by ^{13}C CP-MAS spectroscopy, which showed a disappearance of the signal at 159 ppm and the appearance of a signal at 50 ppm, corresponding to the benzylic carbon of the reduced product (Fig. 2). Based on integration of the aromatic region and comparison with the remaining imine signal, the conversion is estimated to be ~83%. These chemical shifts are consistent with those of *N*-benzylideneaniline and the corresponding *N*-benzylaniline model compounds (see Supplementary data). These results, which show reduction of the imines, indicate that the reducing agent is able to penetrate the porous network and react with interior imine sites.

Nitrogen adsorption measurements on **2** show showed negligible uptake and gave a BET surface area of 10 m^2/g, indicating that the material no longer exhibited microporosity (see Supplementary data). We attribute this observation to the increased flexibility of the network upon reduction, allowing it to collapse upon evacuation. Thermogravimetric analysis showed that reduced network **2** shows comparable thermal stability to **1** with substantial decomposition at

Scheme 2.

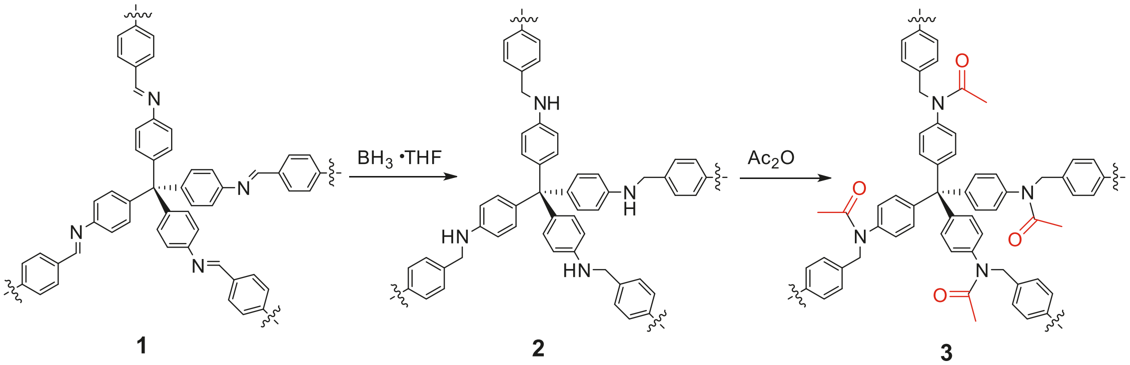
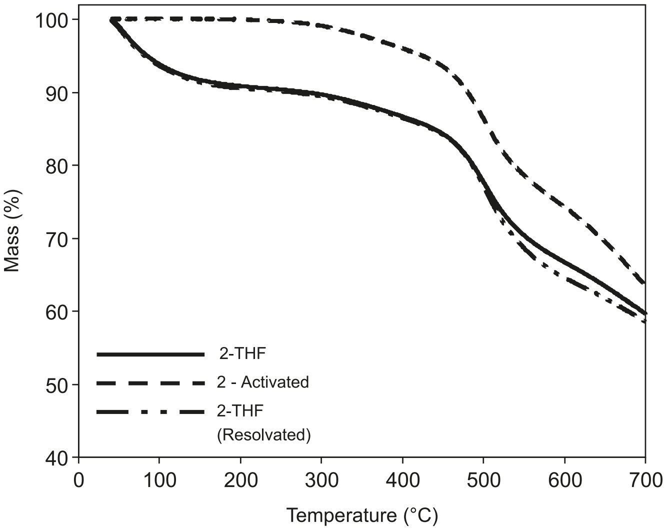


Fig. 5. Thermogravimetric analysis traces of **2** with THF, activated, and resolvated with THF.



temperatures >400 °C. Activation resulted in complete loss of solvent, as demonstrated by TGA, and subsequent resolvation showed solvent uptake very similar to the original solvated material, suggesting that although **2** does not exhibit permanent microporosity, it retains its ability to uptake guest molecules (Fig. 5). The stability of networks **1** and **2** to acidic hydrolysis was evaluated by heating at reflux in 2 mol/L HCl. Imine network **1** is readily hydrolyzed to its corresponding starting materials, as shown by dissolution of the material after only a few minutes of gentle heating. In contrast, network **2** remained insoluble after heating at reflux for 3 h.

The IR spectrum of the material recovered after acid digestion of **2** shows a very broad N–H stretching band that is characteristic of ammonium salts (see Supplementary data), suggesting that **2** has been protonated and that these materials may ultimately be used to prepare novel permeable ionic networks.

The amine groups present in **2** not only increase the chemical stability of the network, but also provide an opportunity for further synthetic transformations. To demonstrate that subsequent postsynthetic transformations are possible, we decided to explore acetylation using acetic anhydride. Network **2** was immersed in acetic anhydride, and allowed to stand at room temperature overnight to ensure complete exchange of the solvent for acetic anhydride. The reaction mixture was subsequently heated at 100 °C in a sealed tube for 24 h. After cooling to room temperature, the solid was collected by filtration and washed thoroughly with THF to yield acetylated network **3**. Evidence for acetylation was provided by IR spectroscopy, which showed a substantial decrease in the intensity of the N–H stretching band and the appearance of a band at 1658 cm^{-1}, which is consistent with the amide C=O stretching. It is noteworthy that the observed C=O stretching is not consistent with the absorbance bands of either acetic acid (1714 cm^{-1}) or remaining acetic anhydride (1755 cm^{-1}), providing evidence for amide formation. The ^{13}C CP-MAS NMR spectrum of **3** shows a change in the aromatic region of the spectrum, as well as the diagnostic appearance of two new signals at 22 and 170 ppm, which are consistent with the incorporation of acetamide methyl and carbonyl carbons, respectively, into the structure. Indeed, these signals are consistent with the solution ^{13}C NMR spectrum of model compound *N*-benzyl-*N*-phenylacetamide (see Supplementary data.)

In summary, we have demonstrated postsynthetic modification of a microporous organic network for the first time. Network **2**, prepared by reduction of imine **1**, loses its permanent microporosity, presumably because the framework is more flexible and collapses upon removal of guests. However, **2** retains high thermal stability and the ability to uptake guest molecules, and also shows enhanced resistance to acid hydrolysis, suggesting that this may ultimately provide a route to more chemically robust microporous organic solids. In addition, we have shown that further synthetic transformations are possible, which may offer an approach for preparing new microporous organic solids with controlled properties for potential applications in gas storage, molecular separations, and heterogeneous catalysis.

Experimental

General

All starting materials and solvents were obtained from commercial sources and used without purification, unless otherwise specified. Anhydrous and oxygen-free THF was dispensed from a custom-built solvent purifier that used purification columns packed with activated alumina and supported copper catalyst (Glasscontour, Irvine, California). Tetrakis(4-aminophenyl)methane was prepared according to published procedures and recrystallized from DMSO–H_2O prior to use,[14] and terephthaldehyde (99%) was purchased from Sigma-Aldrich and recrystallized from water prior to use. IR spectra were recorded as KBr disks using a PerkinElmer Spectrum BX FT-IR spectrometer.

Samples for ^{13}C CP-MAS NMR spectroscopy were ground into fine powders and packed into 4 mm o.d. zirconia rotors. NMR spectra were acquired with high-power proton decoupling at 9.4 T ($\nu_0(^{13}C)$ = 100.6 MHz) using a Bruker Avance III console and a 4 mm triple-resonance Bruker MAS NMR probe. The magic angle was set by maximizing the number of rotational echoes in a ^{79}Br MAS NMR experiment on powdered KBr. Carbon-13 CP-MAS NMR pulse calibrations and chemical shift referencing were performed using adamantane (δ = 38.55 ppm for the high-frequency peak, relative to the primary standard TMS). Ninety degree ^{1}H pulse widths were 3.45 μs, contact pulses were 1.5 or 2.0 ms, acquisition times were 40–50 ms, and recycle delays were 20–50 s. Approximately 1000 to 2000 scans were averaged for each of the COF samples. MAS rates were chosen to eliminate the overlap of spinning sidebands with resonances of interest, and ranged from 11 111 to 13 600 Hz. FIDs were processed with zero-filling, 15–20 Hz exponential apodization, and Fourier transformation.

Gas adsorption isotherms were measured volumetrically using a Micromeritics ASAP 2010 automated adsorption analyzer. Samples were degassed at room temperature for 7 h prior to measurement. A liquid nitrogen bath (77 K) was used for the N_2 isotherms. The N_2 gas used was UHP grade. Brunauer–Emmett–Teller (BET) method was used to determine the specific surface areas (ABET, $m^2\ g^{-1}$) using the adsorption data over 0.05–0.20 relative pressure (P/P_0).

Synthesis of network 1[7d]

A pyrex glass tube with a 6 mm i.d. and an 8 mm o.d. was charged with tetrakis(4-aminophenyl)methane (20 mg, 0.052 mmol), terephthaldehyde (12 mg, 0.089 mmol), and a mixture of dioxane (0.8 mL) and 2 mol/L AcOH (0.2 mL). The tube was flash-frozen in liquid nitrogen, evacuated to a pressure of 150 mTorr (1 Torr = 133.322 Pa), and flame-sealed at a length of 12 cm. The contents of the tube were allowed to warm to room temperature and then heated at 100 °C for 72 h. The yellow solid formed was collected via filtration and washed repeatedly with THF. The yellow precipitate was collected and dried under vacuum at 100 °C for 24 h to evacuate the pores of all solvent guest molecules. Yield: 48 mg.

Synthesis of network 2

An oven-dried flask was charged with **1** (104 mg) and purged with $N_2(g)$ for 15 min. Borane–THF (15 mL, 1 mol/L) was then added to the flask and the mixture was allowed to stir for 24 h at room temperature. The solid was collected by filtration and washed with THF to yield 97 mg of **2** as a beige solid.

Synthesis of network 3

Network **2** (96 mg) was submerged in Ac_2O for 18 h to allow Ac_2O to exchange into the pores of the network. This mixture was then placed into a sealed glass tube, heated to 100 °C, and stirred for 24 h. The solid was collected via filtration, washed with THF, and submerged in THF for 24 h to remove any remaining Ac_2O. The solid was collected via filtration and washed with THF to give **3** (109 mg) as a beige solid.

Supplementary data

Supplementary data (synthesis and characterization, details of spectroscopic characterization, powder X-ray diffraction studies, characterization of model compounds, and representative thermogravimetric analysis) are available with the article through the journal Web site (www.nrcresearchpress.com/cjc).

Acknowledgments

We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canada Foundation for Innovation, the Ontario Research Fund, and Wilfrid Laurier University, Waterloo, Ontario, for financial support. We are also grateful to Dr. T. Maris for powder X-ray diffraction studies and to Drs. S. Lang and J. Ripmeester for assistance with the gas adsorption studies.

References

(1) (a) Davis, M. E. *Nature* **2002** *417* (6891), 813. doi:10.1038/nature00785; (b) Morris, R. E.; Wheatley, P. S. *Angew. Chem. Int. Ed.* **2008** *47* (27), 4966. doi:10.1002/anie.200703934.

(2) For a recent review, see Long, J. R.; Yaghi, O. M. *Chem. Soc. Rev.* **2009** *38* (5), 1213. doi:10.1039/b903811f.

(3) For a recent review, see Maly, K. E. J. *Mater. Chem.* **2009** *19* (13), 1781. doi:10.1039/b816089a.

(4) (a) Germain, J.; Hradil, J.; Fréchet, J. M. J.; Svec, F. *Chem. Mater.* **2006** *18* (18), 4430. doi:10.1021/cm061186p; (b) Germain, J.; Fréchet, J. M. J.; Svec, F. *J. Mater. Chem.* **2007** *17* (47), 4989. doi:10.1039/b711509a.

(5) (a) McKeown, N. B.; Budd, P. M. *Chem. Soc. Rev.* **2006** *35* (8), 675. doi:10.1039/b600349d; (b) Budd, P. M.; Butler, A.; Selbie, J.; Mahmood, K.; McKeown, N. B.; Ghanem, B.; Msayib, K.; Book, D.; Walton, A. *Phys. Chem. Chem. Phys.* **2007** *9* (15), 1802. doi:10.1039/b618053a; (c) Ghanem, B. S.; Msayib, K. J.; McKeown, N. B.; Harris, K. D. M.; Pan, Z.; Budd, P. M.; Butler, A.; Selbie, J.; Book, D.; Walton, A. *Chem. Commun. (Camb.)* **2007** (1): 67. doi:10.1039/b614214a; (d) Ghanem, B. S.; McKeown, N. B.; Budd, P. M.; Fritsch, D. *Macromolecules* **2008** *41* (5), 1640. doi:10.1021/ma071846r.

(6) (a) Weber, J.; Antonietti, M.; Thomas, A. *Macromolecules* **2007** *40* (4), 1299. doi:10.1021/ma062598m; (b) Thomas, A.; Goettmann, F.; Antonietti, M. *Chem. Mater.* **2008** *20* (3), 738. doi:10.1021/cm702126j; (c) Weber, J.; Antonietti, M.; Thomas, A. *Macromolecules* **2008** *41* (8), 2880. doi:10.1021/ma702495r; (d) Jiang, J. X.; Su, F.; Trewin, A.; Wood, C. D.; Campbell, N. L.; Niu, H.; Dickinson, C.; Ganin, A. Y.; Rosseinsky, M. J.; Khimyak, Y. Z.; Cooper, A. I. *Angew. Chem. Int. Ed.* **2007** *46* (45), 8574. doi:10.1002/anie.200701595; (e) Jiang, J.-X.; Su, F.; Trewin, A.; Wood, C. D.; Niu, H.; Jones, J. T. A.; Khimyak, Y. Z.; Cooper, A. I. *J. Am. Chem. Soc.* **2008** *130* (24), 7710. doi:10.1021/ja8010176; (f) Farha, O. K.; Spokoyny, A. M.; Hauser, B. G.; Bae, Y.-S.; Brown, S. E.; Snurr, R. Q.; Mirkin, C. A.; Hupp, J. T. *Chem. Mater.* **2009** *21* (14), 3033. doi:10.1021/cm901280w.

(7) (a) Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. *Science* **2005** *310* (5751), 1166. doi:10.1126/science.1120411; (b) Côté, A. P.; El-Kaderi, H. M.; Furukawa, H.; Hunt, J. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2007** *129* (43), 12914. doi:10.1021/ja0751781; (c) El-Kaderi,

H. M.; Hunt, J. R.; Mendoza-Cortes, J. L.; Côté, A. P.; Taylor, R. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2007** *316* (5822), 268. doi:10.1126/science.1139915; (d) Uribe-Romo, F. J.; Hunt, J. R.; Furukawa, H.; Klock, C.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2009** *131* (13), 4570. doi:10.1021/ja8096256; (e) Tilford, R. W.; Gemmill, W. R.; zur Loye, H. C.; Lavigne, J. J. *Chem. Mater.* **2006** *18* (22), 5296. doi:10.1021/cm061177g; (f) Tilford, R. W.; Mugavero, S. J.; Pellechia, P. J.; Lavigne, J. J. *Adv. Mater. (Deerfield Beach Fla.)* **2008** *20*, 2741. doi:10.1022/adma.200800030.

(8) Kim, K.; Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J. *Nature* **2000** *404* (6781), 982. doi:10.1038/35010088.

(9) For a recent review, see Wang, Z. Q.; Cohen, S. M. *Chem. Soc. Rev.* **2009** *38* (5), 1315. doi:10.1039/b802258p.

(10) (a) Wang, Z. Q.; Cohen, S. M. *J. Am. Chem. Soc.* **2007** *129* (41), 12368. doi:10.1021/ja074366o; (b) Tanabe, K. K.; Wang, Z. Q.; Cohen, S. M. *J. Am. Chem. Soc.* **2008** *130* (26), 8508. doi:10.1021/ja801848j; (c) Wang, Z. Q.; Cohen, S. M. *Angew. Chem. Int. Ed.* **2008** *47* (25), 4699. doi:10.1002/anie.200800686; (d) Jones, S. C.; Bauer, C. A. *J. Am. Chem. Soc.* **2009** *131* (35), 12516. doi:10.1021/ja900893p.

(11) Brunet, P.; Demers, E.; Maris, T.; Enright, G. D.; Wuest, J. D. *Angew. Chem. Int. Ed.* **2003** *42* (43), 5303. doi:10.1002/anie.200352252.

(12) Boaen, N. K.; Hillmyer, M. A. *Chem. Soc. Rev.* **2005** *34* (3), 267. doi:10.1039/b311405h.

(13) Schwab, M. G.; Fassbender, B.; Spiess, H. W.; Thomas, A.; Feng, X. L.; Müllen, K. *J. Am. Chem. Soc.* **2009** *131* (21), 7216. doi:10.1021/ja902116f.

(14) Ganesan, P.; Yang, X. N.; Loos, J.; Savenije, T. J.; Abellon, R. D.; Zuilhof, H.; Sudholter, E. J. R. *J. Am. Chem. Soc.* **2005** *127* (42), 14530. doi:10.1021/ja053689m.