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Porous Networks Assembled from Octaphenylsilsesquioxane Building Blocks

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ABSTRACT: Octaphenylsilsesquioxane (OPS) derivatives represent a class of high functionality building blocks with perfect three-dimensional symmetry for the construction of rigid and highly porous polymers. Copper-mediated in-situ homocoupling of an OPS derivative with eight para-disposed triple bonds yields a porous network with surface areas up to 1000 m^2/g. Introducing a monoalkyne capping agent to lower cross-linking density led to a ~200 m^2/g increase in surface area. Exceptional thermal robustness of the silsesquioxane cage and strong covalent bonds resulting from the cross-linking process render the resulting porous networks stable to heat and water.

Introduction

Driven by potential applications such as hydrogen storage, efficient separations, and catalysis, the field of porous material is undergoing a renaissance. Much of this activity has advanced through demonstrations of coordination polymers that, with judicious choice of linkage chemistry and synthetic conditions, can display unprecedented levels of surface area. Such microporous coordination polymers rely on reversible chemistry to allow defect correction during assembly. This often leads to single crystals with sufficient size and quality to enable study by X-ray methods.[1] At the same time, there is a recognition that employing reversible coordination chemistry and heavy metals places limitations on certain applications and ultimate performance. As a result, porous polymers prepared by irreversible covalent bond formation chemistry are of immense current interest because of several characteristic advantages: a broad variety of organic reactions can be employed for synthesis leading to diverse functionalities, metal-free materials can be obtained, and air stability is readily achieved.[2] These advantages have led some to reexamine irreversible covalent bond forming reactions capable of yielding porous polymers.[3]

There are two primary synthetic strategies employed to generate porous polymers by irreversible chemistry: (1) templation by porogens and (2) reaction of rigid moieties that result in nonplanarity or three-dimensional structures in the product. The porogen method of porosity induction can be further classified according to the strength of structure: flexible polymer resins and rigid hyper-cross-linked polymers. Flexible polymer resins have the characteristic of permanent porosity even in the dry state and are normally synthesized by the suspension polymerization method.[4] Low Brunauer−Emmett−Teller (BET) surface areas of ca. 500 m^2/g are typical.[5] Hyper-cross-linked polymers can be obtained by, for example, copolymerization of styrene and divinylbenzene or by cross-linking of linear polystyrene chains using the Friedel−Crafts reaction.[6,7] Such copolymers have been obtained with BET surface areas up to ~2000 m^2/g.[8]

The second method of porosity induction is employing monomer geometry in concert with kinetically controlled polymerization. Significant examples include the so-called polymers of intrinsic microporosity (PIMs), where the proportion of free volume is increased to the extent that monomers are effectively interconnected to yield porosity in the product, and conjugated microporous polymers (CMPs), where the considerable torsional flexibility of the reacting units is locked in during synthesis. For example, phthalocyanine-based polymers were built by polycondensation of linear monomers, but they were found to be nonporous presumably due to a densely packed structure;[9] however, by introducing three-dimensional and rigid linking units to the networks that intentionally contort geometry and promote inefficient packing, PIMs with BET surface areas in the range of 500−1000 m^2/g were obtained.[10,11] CMPs are rigid hyper-cross-linked poly(aryleneethynylene) polymers that, like PIMs, are amorphous but have demonstrated synthetic control over pore size distribution by introducing a broad variety of monomer geometries.[12] CMPs, synthesized by a Sonogashira−Hagihara cross-coupling reaction, have BET surface areas in the range of 500−1200 m^2/g.[13−15] Additionally, Yuan et al. synthesized highly conjugated porous polymer networks using stereocontorted cores such as spirobifluorene and tetraphenylmethane with BET surface areas up to 1000 m^2/g.[16] Very recently, Ben et al. reported an exceptionally high BET surface area 5600 m^2/g of locally diamond-like structured porous aromatic framework using tetrakis(4-bromophenyl)methane with strong covalent bonds.[17] This is an incredible finding that, if found to be applicable to other structural classes and generalizable to less expensive reaction chemistries, could change the face of porous materials.

Absent from these previous studies are examples of highly functionalized building blocks, e.g., molecules containing many equivalent functional groups on the monomer. From a classical polymer standpoint, having a high degree of functionality should lead to a rapid network formation under the Flory−Stockmayer model[18,19] or percolation theory,[20,21] although perfection of that network is not predicted. It therefore seemed an intriguing scientific question to determine if highly functional monomers bearing rigid linkages would give rise to porous polymers.

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Cubic silsesquioxane derivatives are particularly attractive in this regard because these are octafunctional and exceptionally robust with respect to heat and in water.[22,23] Additionally, the most intriguing aspect of octaphenylsilsesquioxane (OPS, $(C_6H_5SiO_{1.5})_8$) is that the structure of the monomer is three-dimensional with functional groups extending equally into each octant of Cartesian space. Three-dimensional building blocks may afford higher surface areas than two-dimensional building blocks because they tend to resist sheetlike packing which leads to blocked adsorption sites; this has been well illustrated by covalent organic frameworks built from reversible boronic acid condensation.[24−26]

Furthermore, no highly porous networks derived from building blocks of cubic shape have been reported to date, and only limited experimental attempts have been made. For example, Zhang et al. reported BET specific surface areas of 380−530 m^2/g for flexible porous structures produced from a hydrosilylative copolymerization with aliphatic linkages which bridge silsesquioxane cages.[27] A potential problem inherent to the hydrosilylation strategy is that aliphatic moieties formed during polymerization reduce rigidity and compromise thermal stability and mechanical strength. Tamaki et al., therefore, introduced the rigid linking unit pyromellitic acid dianhydride to bridge amino-functionalized silisesquioxane (octaaminophenylsilsesquioxane, OAPS), but the resultant material was nonporous perhaps because half of the eight amine groups on the aromatic rings of OAPS were meta-disposed, resulting in an unsymmetrical cubic monomer that limits the potential to yield even locally periodic structure.[28] Very recently, some progress has been made in this area with the report of Sonogashira coupling of diynes and triynes with silsesquioxanes bearing eight *p*-bromostyryl groups.[29] These materials display surface areas of up to ~1000 m^2/g and, perhaps due to their many degrees of torsional freedom, or cage rearrangement during synthesis, possess rather broad multimodal pore size distributions.

Recent work by Asuncion et al. succeeded in synthesizing octaalkynylated silsesquioxanes (octaalkyneSQs), including *p*-$(TMSC{\equiv}C)_8$OPS, from *para*-octaiodophenylsilsesquioxane, *p*-I_8OPS,[31] by a Sonogashira coupling reaction in which the functionalities are rigid and para-disposed.[30] This molecule offers excellent potential as a building block to make a rigid and highly porous network.

Experimental Section

Characterization. *FTIR Analyses*. Infrared absorption spectra were collected on a Nicolet AVATAR 360 FTIR instrument. The samples were ground with KBr to make 1 wt % mixtures and pelleted. Nitrogen was purged through the instrument for 10 min before data collection. Scans (32) were collected for each sample at a resolution of 4 cm^{-1}.

Raman Spectroscopy. Raman spectra were collected using a Renishaw inVia Raman microscope equipped with a Leica microscope, RenCam CCD detector, 633 nm He−Ne laser, 1200 lines/nm grating, and 50 μm slit. Spectra were collected in extended scan mode in the range 3500−100 cm^{-1} and analyzed using the Wire 3.1 software package. Calibration was performed using a silicon standard. After collecting spectra, a polynomial smoothing filter based on the Savitsky−Golay algorithm, as implemented in version 12.01 of the ACD/SpecManager package, was applied to reduce noise.

Surface Area. Nitrogen sorption isotherms were measured volumetrically at 77 K in the range $5.00 \times 10^{-2} \le P/P_0 \le 1.00$ with a NOVA 4200e by Quantachrome Instruments (Boynton Beach, FL). Ultrahigh purity N_2 (99.999%) was purchased from Cryogenic Gasses used as received.

Pore Size Distribution. Argon sorption experiments were performed at 87 K in the range $1.00 \times 10^{-5} \le P/P_0 \le 1.00$ with an Autosorb-1C by Quantachrome Instruments. Ultrahigh purity Ar (99.999%) was purchased from Cryogenic Gasses and used as received. Pore size distributions were calculated using the Nonlinear Density Functional Theory (NLDFT) kernel as implemented in version 1.2 of the ASWin software package.

Thermal Behavior. Samples were held in a platinum pan under a nitrogen atmosphere and analyzed on a TA Q50 apparatus. A temperature ramp was conducted from 25 to 500 °C at 3 °C/min with a balance flow rate of 40 mL/min and sample flow rate of 60 mL/min.

Materials. *p*-$(TMSC{\equiv}C)_8$OPS was synthesized according to a slightly modified literature procedure[31] (see Supporting Information), and characterization was consistent with the previous report. Trimethyl(phenylethynyl)silane was synthesized by the literature procedure.[32] *N,N*-Dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), *N,N*-dibutylformamide (DBF), and CuCl were used as received. *N,N*-Diethylformamide (DEF) was decolorized with activated carbon and passed through a silica column prior to use.

Synthetic Procedure. *General Synthetic Procedure for Cross-Linked OPS*. To a dry 25 mL Schlenk flask containing the solvent (5 mL) under nitrogen and equipped with a magnetic stir bar was added *p*-$(TMSC{\equiv}C)_8$OPS (30.0 mg, 0.0166 mmol) and CuCl (16.4 mg, 0.166 mmol). The mixture was heated to reflux for 24 h followed by cooling to room temperature and filtration. The solid was washed with CH_2Cl_2 (3 × 10 mL). Immersion in acetone (10 mL) for 1 day, during which time the acetone was replaced three times, was followed by washing with water (3 × 10 mL). The resultant light brown solid was immersed in 10 mL of CH_2Cl_2 for 24 h. The solvent was removed under vacuum at room temperature, yielding the product in > 90% yield (composition assumed based on the model in Figure 1).

Synthetic Procedure for Cross-Linked OPS Derivatives with Monoalkyne Capping Agent. To a dry 25 mL Schlenk flask containing DEF (5 mL) under nitrogen and equipped with a magnetic stir bar was added *p*-$(TMSC{\equiv}C)_8$OPS (30.0 mg, 0.0166 mmol), trimethyl(phenylethynyl)silane (as specified), and CuCl (16.4 mg, 0.166 mmol). The mixture was heated to reflux for 24 h followed by cooling to room temperature and filtration. The solid was washed with CH_2Cl_2 (3 × 10 mL). Immersion in acetone (10 mL) for 1 day, during which time the acetone was replaced three times, was followed by washing with water (3 × 10 mL). The resultant light brown solid was immersed in 10 mL of CH_2Cl_2 for 24 h. The solvent was removed under vacuum at room temperature, yielding the product in > 90% yield (composition assumed based on the model in Figure 1).

Results and Discussion

A wide variety of synthetic parameters and material activation conditions must be explored to find the optimal porosity for a network derived from a given building block. In order to set an expectation for the maximum accessible surface area achievable for OPS-derived networks, an ideal assembly model was created and optimized using the Forcite module in Material Studio (Figure 1). The topology of bcu[33] was introduced to offer a rational basis for designed construction of an ideal assembly derived from eight coordinated units. In this ideal model, diaryl butadiynes play a role as linkers that bridge silsesquioxane cores.

After making an ideal model, the accessible surface area was calculated by the method of Snurr.[34] According to the calculation, the ideal model based on the bcu net turned out to be the most auspicious net structure possible for OPS derivatives with eight para-disposed functionalities. The pore diameter is 21.3 Å, and an accessible surface area of 6440 m^2/g is computed. This exceptionally high accessible surface area of an ideal model is due to the perfect periodic assembly of three-dimensional monomer components and is unlikely to be reached in practice unless

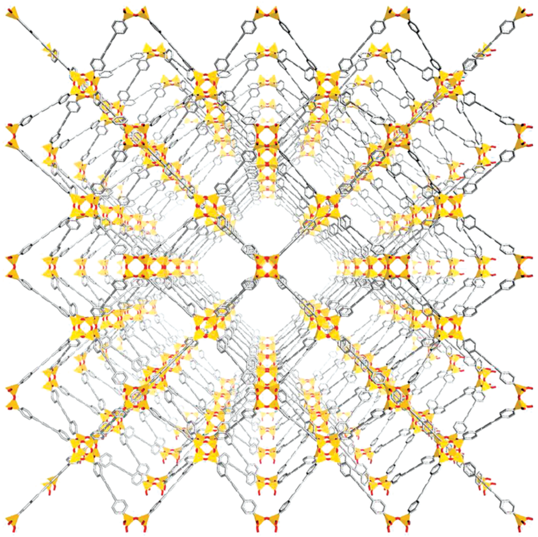


Figure 1. Ideal model of the porous network derived from oxidative coupling of p-(HC≡C)$_8$OPS.

reversibility in the bond-forming reactions takes place. Unfortunately, perfect periodicity by in-situ homocoupling is unlikely because the product is synthesized under kinetic control. Furthermore, a high degree of functionality of monomers is predicted to result in rapid network formation and amorphous structure under classical polymer theories.[35]

In-Situ Homocoupling. Because of the sensitivity of OPS derivatives to basic conditions and fluoride, an in-situ homocoupling reaction was carried based on the molecular precedents from Nishihara et al.[36] The reaction involves transmetalation from silicon to copper followed by oxidative dimerization to form butadiynes. Applying this condition, boiling with a copper(I) salt, to p-(TMSC≡C)$_8$OPS led to a porous network with surface area up to 1000 m^2/g.

Comparisons of the vibrational spectra of p-(TMSC≡C)$_8$OPS to the porous network by FTIR and Raman spectroscopy suggest that the C−C bond forming in-situ homocoupling reaction proceeds as desired (Figure 2). FTIR indicates that the porous network does not have peaks at 850−810 (cm^{-1}) corresponding to ν-Si−CH$_3$, and Raman spectroscopy also shows that the network does not have peaks at 2980−2800 cm^{-1} (ν-CH$_3$). Absence of acetylenic C−H stretches in IR and Raman spectra[37] suggests that deprotected ethynyl units are linked together to form butadiyne linkages (Figures S1 and S2).

Solvents for Cross-Linking Reaction. Changing solvent can have a profound effect on polymer porosity; the range of conditions that can be employed in the case of p-(TMSC≡C)$_8$OPS is somewhat limited by the need for a polar solvent to allow the Si−Cu transmetalation to proceed efficiently. Therefore, the four pure solvents DMF, DMA, DEF, and DBF were introduced. These solvents vary in bulkiness considerably and therefore might be expected to alter porosity if there is a role for solvent acting as a template (Scheme 1).[38] Prior to surface area measurements, porous networks synthesized by the procedure were activated under vacuum for 3 h at 300 °C; this temperature was chosen because TGA experiments reveal less than 10% weight loss below this temperature (Figure S6). Experimentally, the bulkiness of the solvent and surface area of the porous network are uncorrelated (Figure 3). All nitrogen sorption isotherms for the porous networks assembled from various solvents are very similar, implying that the porosity and the patterns of pore size distribution of these porous networks do not substantially differ (Figure 4). Porous networks synthesized from DEF as solvent resulted in the highest surface area; therefore, DEF was selected for further study of the influence of additional reaction conditions.

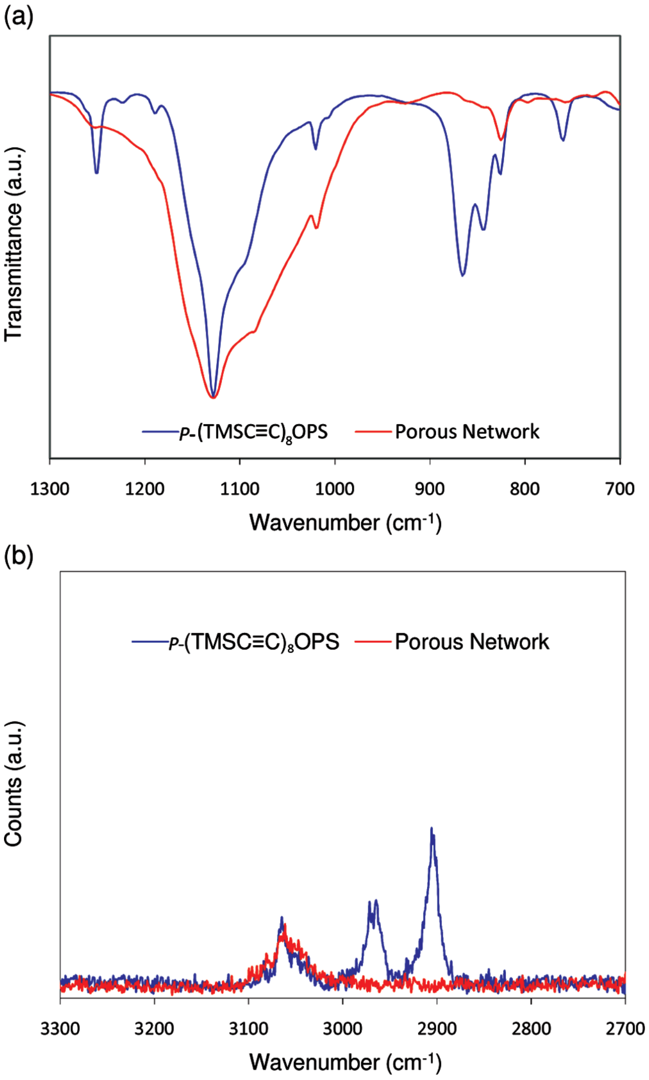
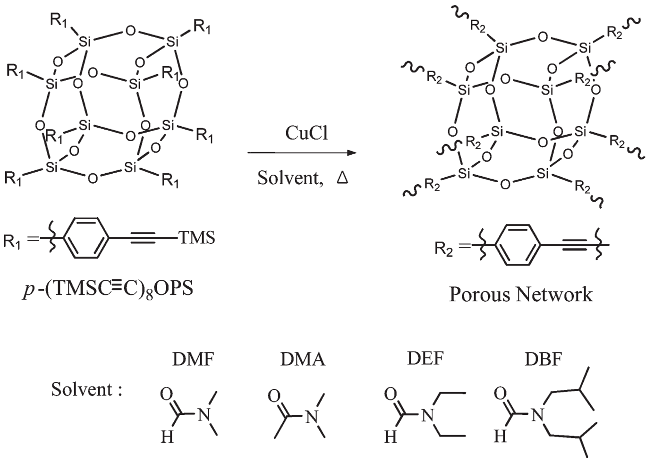


Figure 2. (a) FTIR and (b) Raman spectra of p-(TMSC≡C)$_8$OPS and the porous network assembled in DEF.

Scheme 1. Synthetic Process for the in-Situ Homocoupling Reaction



Influence of Cross-Linking Density on Surface Area. In considering how to maximize the surface area of OPS-based

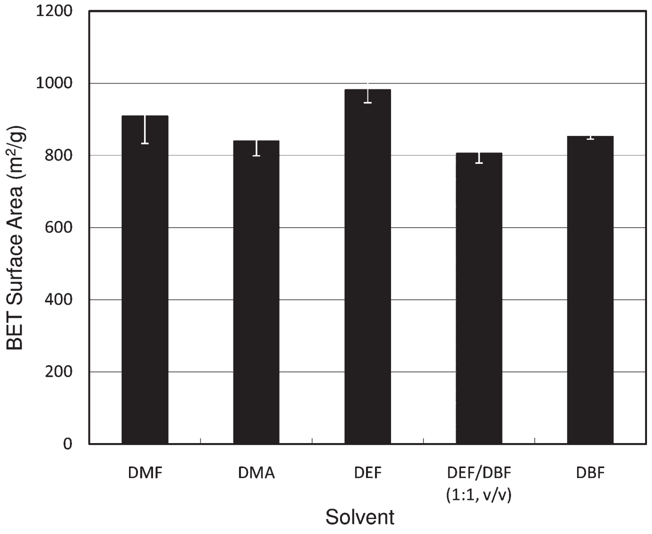


Figure 3. Surface areas of porous networks assembled in various solvents. Reported surface areas are the average of determinations for two separate synthetic preparations for each material.

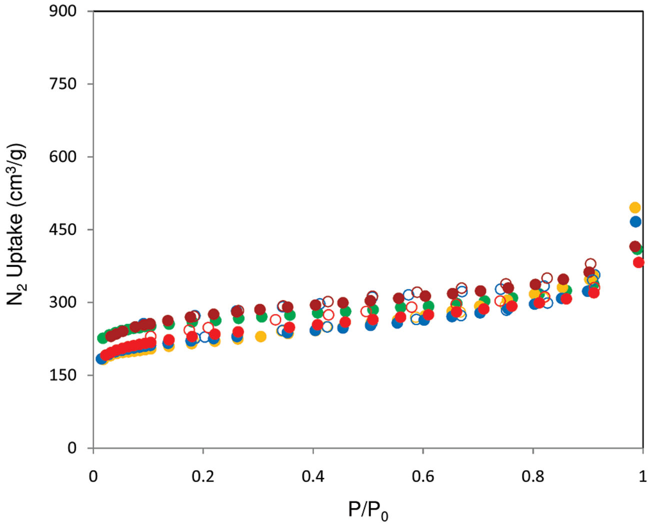
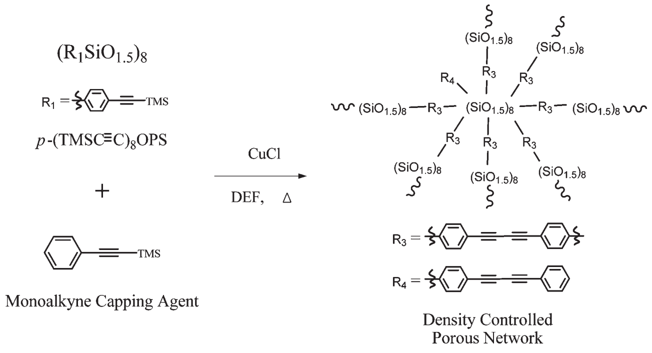


Figure 4. Nitrogen sorption isotherms at 77 K of porous networks assembled in DMF (green), DMA (yellow), DEF (brown), DEF/DBF (1:1, v/v) (blue), and DBF (red). Filled markers represent adsorption points, and open markers represent desorption points.

Scheme 2. Synthetic Process for the in-Situ Homocoupling Reaction in the Presence of Monoalkyne Capping Agent



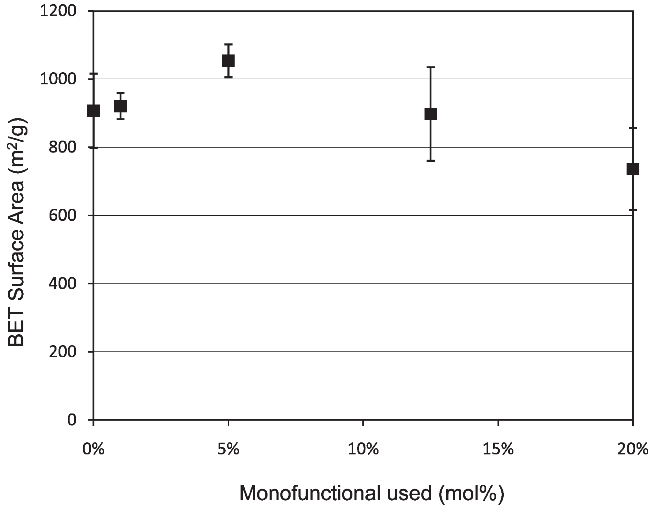


Figure 5. Surface areas for porous networks assembled with specific mol % of monoalkyne capping agent. Reported surface areas are the average of determinations for three separate synthetic preparations for each material. Error bars indicate one standard deviation of uncertainty.

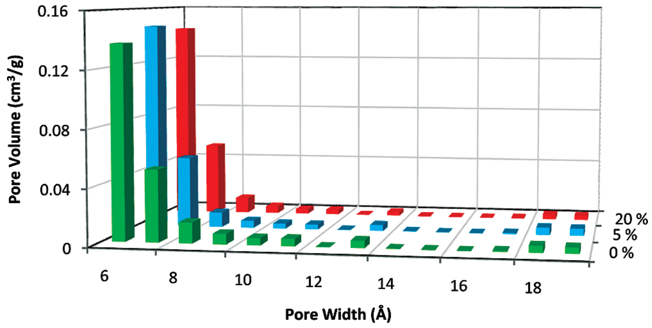


Figure 6. Pore size distribution data of porous networks assembled with monoalkyne capping agent. Monoalkyne capping agent used (mol %) on the *y*-axis.

polymers, the effect of cross-linking density was next considered. With such a high degree of functionality in the monomer, the possibility exists that the network is too dense to allow guest diffusion throughout, and therefore having a somewhat lower extent of cross-linking density would be desirable. This was achieved by adding substoichiometric amounts of the monoalkyne capping agent trimethyl(phenylethynyl)silane; this species can also form butadiyne linkages in the cross-linked material through an in-situ terminal alkyne coupling reaction (Scheme 2). The capping agent effectively suppresses cross-linking reactions because it has a functionality of one. This decreases cross-linking density, leading to more open pores. A significant increase of surface area was obtained as a result of the addition of the monoalkyne to the reaction mixture (Figure 5). Moreover, it was observed that surface area increases until 5 mol %, i.e., 0.625 mol % on a functionality basis, at which point adding more monoalkyne capping agent decreases surface area perhaps due to structural collapse.

The permanent porosity of the networks was confirmed by measurement of a pore size distribution from argon sorption data (Figure 6). As deduced from the nitrogen sorption isotherms (Figure 7), the pore size distribution data for porous networks with 0, 5, and 20 mol % of the monoalkyne are very similar, and the majority of the pore sizes fall below 12 Å. Pore volumes calculated at the saturation point from nitrogen sorption data at which micropore filling is completed and macropore filling is about to begin[39] are 0.437, 0.501, and 0.383 cm^3/g for porous networks with 0, 5, and 20 mol % of monoalkyne capping agent, respectively (Figure 7).

Stability to Heat and in Water. Thermogravimetric analyses confirm that all porous networks dealt with in this study

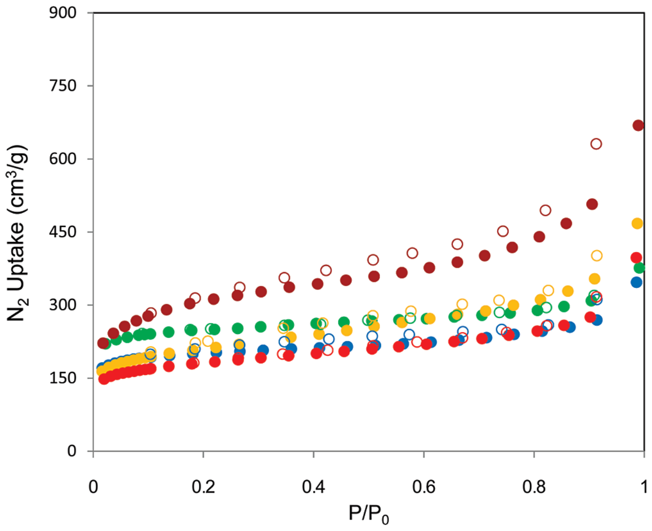


Figure 7. Nitrogen sorption isotherms at 77 K of porous networks assembled with 0 (blue), 1 (green), 5 (brown), 12.5 (yellow), and 20 mol % (red) of monoalkyne capping agent. Filled markers represent adsorption points, and open markers represent desorption points.

had insubstantial weight loss in nitrogen to 500 °C (Figures S6 and S7). Stability to heat of porous networks assembled with monoalkyne capping agent might be expected to be lower than that of the network without the capping agent because the cross-linking density of the network is reduced. Experimental data, however, showed that even though addition of the capping agent resulted in notable changes to the surface area and pore volume of the networks, it did not affect the thermal behavior. Porous networks assembled from various solvents also showed comparable behavior in thermal decomposition as the networks with the capping agent.

Another attractive feature of networks built from covalent bonding is the potential for greater chemical stability than porous materials based on metal coordination chemistry; in particular, instability to moisture limits potential applications for some porous coordination polymers.[40] Therefore, making a porous and water-stable material is one key challenge to be met. For determining the stability of the OPS-based networks under humid conditions, the cross-linked networks were exposed to air at room temperature for more than 1 month, and surface areas before and after the exposure were measured. No notable changes of surface areas were observed. Furthermore, immersion of the network synthesized in DEF without monoalkyne capping agent in water at room temperature for at least 3 days led to retention of surface area of the porous network (Figure S8). These results confirm the stability of the networks toward water.

Conclusions

The current work suggests that perfectly symmetric cubic silsesquioxane offers considerable potential to build porous and stable sorbents. Network solids derived from p-(TMSC≡C)$_8$OPS are readily synthesized by an in-situ homocoupling reaction, and permanent porosity with surface areas greater than 1000 m^2/g was achieved. Decreasing cross-linking density by introduction of a monofunctional capping agent to the network effectively improves surface area, a feature requiring validation in other classes of irreversibly assembled networks. Highly porous and stable cross-linked networks have vast potential as advanced materials for various applications in sorption and catalysis, and studies exploiting these new functional networks are currently underway.

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Supporting Information Available: Synthetic procedures, infrared and Raman spectroscopic data, gas sorption isotherms, and thermogravimetric analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Rowsell, J. L. C.; Yaghi, O. M. *Microporous Mesoporous Mater.* **2004**, *73*, 3–14.
(2) Germain, J.; Fréchet, J. M. J.; Svec, F. *Small* **2009**, *5*, 1098–1111.
(3) McKeown, N. B.; Budd, P. M. *Macromolecules* **2010**, *43*, 5163–5176.
(4) Sherrington, D. C. *Chem. Commun.* **1998**, 2275–2286.
(5) Rohr, T.; Knaus, S.; Gruber, H.; Sherrington, D. C. *Macromolecules* **2002**, *35*, 97–105.
(6) Davankov, V. A.; Ilyin, M. M.; Tsyurupa, M. P.; Timofeeva, G. I.; Dubrovina, L. V. *Macromolecules* **1996**, *29*, 8398–8403.
(7) Tsyurupa, M. P.; Davankov, V. A. *React. Funct. Polym.* **2002**, *53*, 193–203.
(8) Germain, J.; Hradil, J.; Fréchet, J. M. J.; Svec, F. *Chem. Mater.* **2006**, *18*, 4430–4435.
(9) McKeown, N. B. *J. Mater. Chem.* **2000**, *10*, 1979–1995.
(10) Budd, P. M.; McKeown, N. B.; Fritsch, D. *J. Mater. Chem.* **2005**, *15*, 1977–1986.
(11) McKeown, N. B.; Budd, P. M. *Chem. Soc. Rev.* **2006**, *35*, 675–683.
(12) Jiang, J.; 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*, 8574–8578.
(13) Jiang, J.; Su, F.; Trewin, A.; Wood, C. D.; Campbell, N. L.; Niu, H.; Jones, J. T. A.; Khimyak, Y. Z.; Cooper, A. I. *J. Am. Chem. Soc.* **2008**, *130*, 7710–7720.
(14) Weber, J.; Thomas, A. *J. Am. Chem. Soc.* **2008**, *130*, 6334–6335.
(15) Stöckel, E.; Wu, X.; Trewin, A.; Wood, C. D.; Clowes, R.; Campbell, N. L.; Jones, J. T. A.; Khimyak, Y. Z.; Adams, D. J.; Cooper, A. I. *Chem. Commun.* **2009**, 212–214.
(16) Yuan, S.; Kirklin, S.; Dorney, B.; Liu, D.; Yu, L. *Macromolecules* **2009**, *42*, 1554–1559.
(17) Ben, T.; Ren, H.; Ma, S.; Cao, D.; Lan, J.; Jing, X.; Wang, W.; Xu, J.; Deng, F.; Simmons, J. M.; Qiu, S.; Zhu, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 9457–9460.
(18) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083.
(19) Stockmayer, W. H. I. *Chem. Phys.* **1944**, *12*, 125.
(20) Den Nijs, M. P. M. *J. Phys. A: Math. Gen.* **1979**, *12*, 1857.
(21) Nienhuis, B.; Riedel, E. K.; Schick, M. *J. Phys. A: Math. Gen.* **1979**, *13*, L189.
(22) Zhang, C.; Babonneau, F.; Bonhomme, C.; Laine, R. M.; Soles, C. L.; Hristov, H. A.; Yee, A. F. *J. Am. Chem. Soc.* **1998**, *120*, 8380–8391.
(23) Cordes, D. B.; Lickiss, P. D.; Rataboul, F. *Chem. Rev.* **2010**, *110*, 2081–2173.
(24) Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. *Science* **2005**, *310*, 1166–1170.
(25) Côté, A. P.; El-Kaderi, H. M.; Furukawa, H.; Hunt, J. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2007**, *129*, 12914–12915.
(26) El-Kaderi, H. M.; Hunt, J. R.; Mendoza-Cortés, J. L.; Côté, A. P.; Taylor, R. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **316**, *13*, 268–272.
(27) Zhang, C.; Babonneau, F.; Bonhomme, C.; Laine, R. M.; Soles, C. L.; Hristov, H. A.; Yee, A. F. *J. Am. Chem. Soc.* **1998**, *120*, 8380–8391.
(28) Tamaki, R.; Choi, J.; Laine, R. M. *Chem. Mater.* **2003**, *15*, 793–797.
(29) Chaikittisilp, W.; Sugawara, A.; Shimojima, A.; Okubo, T. *Chem.—Eur. J.* **2010**, DOI: 10.1002/chem.201000249.
(30) Asuncion, M. Z.; Roll, M. F.; Laine, R. M. *Macromolecules* **2008**, *41*, 8047–8052.
(31) Roll, M. F.; Asuncion, M. Z.; Kampf, J.; Laine, R. M. *ACS Nano* **2008**, *2*, 320–326.
(32) Benkeser, R. A.; Hickner, R. A. *J. Am. Chem. Soc.* **1958**, *80*, 5298–5300.
(33) Wells, A. F. *Three-Dimensional Nets and Polyhedra*; Wiley: New York, 1977.
(34) Düren, T.; Millange, F.; Férey, G.; Walton, K. S.; Snurr, R. Q. *J. Phys. Chem. C* **2007**, *111*, 15350–15356.

(35) Odian, G. *Principles of Polymerization*; John Wiley & Sons, Inc.: Hoboken, NJ, 2004.
(36) Nishihara, Y.; Ikegashira, K.; Hirabayashi, K.; Ando, J.; Mori, A.; Hiyama, T. *J. Org. Chem.* **2000**, *65*, 1780–1787.
(37) Lambert, J. B.; Shurvell, H. F.; Lightner, D. A.; Cooks, R. G. *Organic Structural Spectroscopy*; Prentice Hall: Upper Saddle River, NJ, 1998.
(38) Okay, O. *Prog. Polym. Sci.* **2000**, *25*, 71–779.
(39) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, T. *Pure Appl. Chem.* **1985**, *57*, 603–619.
(40) Greathouse, J. A.; Allendorf, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 10678–10679.