JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Microporous Polycarbazole with High Specific Surface Area for Gas Storage and Separation

Qi Chen,[†] Min Luo,[†,‡] Peter Hammershøj,[§] Ding Zhou,[†] Ying Han,[‡] Bo Wegge Laursen,[§]
Chao-Guo Yan,[‡] and Bao-Hang Han*[,†]

[†]National Center for Nanoscience and Technology, Beijing 100190, China
[‡]College of Chemistry & Chemical Engineering, Yangzhou University, Yangzhou 225002, China
[§]Nano-Science Center and Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen, Denmark

S Supporting Information

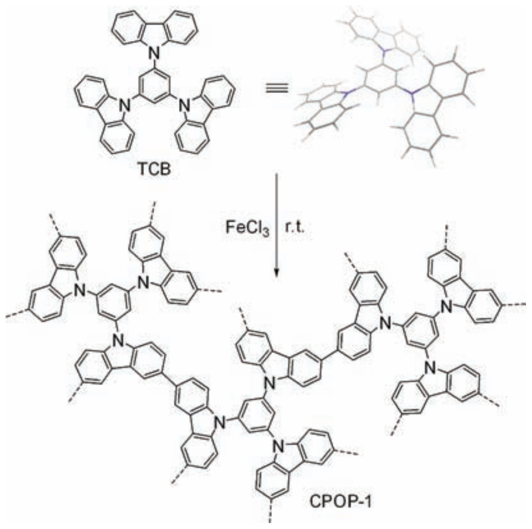
ABSTRACT: Microporous polycarbazole via straightforward carbazole-based oxidative coupling polymerization is reported. The synthesis route exhibits cost-effective advantages, which are essential for scale-up preparation. The Brunauer−Emmett−Teller specific surface area for obtained polymer is up to 2220 m^2 g^{-1}. Gas (H_2 and CO_2) adsorption isotherms show that its hydrogen storage can reach to 2.80 wt % (1.0 bar and 77 K) and the uptake capacity for carbon dioxide is up to 21.2 wt % (1.0 bar and 273 K), which show a promising potential for clean energy application and environmental field. Furthermore, the high selectivity toward CO_2 over N_2 and CH_4 makes the obtained polymer possess potential application in gas separation.

Increasing CO_2 concentration in the atmosphere mainly caused by the rapid consumption of fossil fuels has partly led to the global climate change and some environmental issues, which have drawn great attentions and concerns.[1] Therefore, CO_2 capture and utilizing clean energy source, such as hydrogen, are of interest to meet the energy and environmental demands. As a response, much effort has been devoted to explore suitable materials for CO_2 capture[2] or H_2 storage.[3] Microporous organic polymers with the intrinsic properties including large specific surface area, narrow pore size distribution, high chemical stability, and low skeleton density have exhibited potential applications in gas storage and separation.[4]

Versatile microporous organic polymers such as polyfluorene,[5] poly(phenylene−ethynylene),[6] polyphenylene,[7] polyimide,[8] polybenzimidazole,[9] polythiophene,[10] and the other hypercrosslinked polymers[11] were obtained smoothly through a template-free chemical process by selection of proper building blocks and polymerization reactions, which show efficient preparation and high flexibility in the molecular design. Since the capability of microporous organic polymers for the gas storage and separation is affected by multiple factors such as material nature, specific surface area, pore structure, and material morphology, it is still a challenge to develop microporous organic polymers with potential use and good performance for the gas storage and separation.

Polycarbazole with a good electroactivity and useful photophysical property[12] is a suitable candidate for exploration of porous organic polymers possessing special functions and properties. Rigid conjugated backbone of polycarbazole is beneficial for formation of a porous polymer with permanent porosity and high physicochemical stability. Nitrogen-containing conjugated structure makes the polymer electron-rich, which may enhance the interaction between specific sorbate molecule and adsorbent.[2c,5b] In this communication, preparation of microporous polycarbazole via carbazole-based oxidative coupling polymerization is reported (Scheme 1). The obtained carbazole-based porous organic polymer (CPOP) possesses a large specific surface area, a high gas uptake capacity, a good selectivity toward CO_2 over N_2 or CH_4, and an intrinsic photoluminescence property.

Scheme 1. Synthetic Route to Microporous Polycarbazole CPOP-1



Oxidative coupling polymerization of carbazole-based building block exhibits cost-effective advantages such as cheap catalyst, room temperature reaction, high yield and single monomer used in the polymerization, which are essential for

Received: January 14, 2012
Published: March 28, 2012

dx.doi.org/10.1021/ja300438w | *J. Am. Chem. Soc.* 2012, 134, 6084−6087

scale-up preparation of porous materials with potential application. Since the building blocks show a great influence on the porosity, specific surface area, and gas adsorption capacity of the porous organic polymers, design and/or selection of specific monomer is very important. We have reported that the monomers with propeller-like nonplanar conformation, such as tetraphenylethylene[13] and hexaphenylbenzene,[7b] are good building units to form microporous conjugated polymers. Therefore, a propeller-like building block containing three carbazole moieties, 1,3,5-tri(9-carbazolyl)-benzene (TCB), is selected as the monomer, which is commercially available or can be easily synthesized by copper-promoted N-arylation reaction between carbazole and 1,3,5-tribromobenzene. Oxidative coupling polymerization of TCB was promoted smoothly by anhydrous $FeCl_3$ in dry chloroform under nitrogen protection at room temperature. After polymerization, the desired polymer CPOP-1 was fully washed with methanol and concentrated HCl solution and was obtained in 95% yield followed by Soxhlet extraction with methanol and tetrahydrofuran. The polymer is chemically stable, even when exposed to dilute solutions of acid and base, such as HCl and NaOH. Thermal analysis (see Supporting Information, Figure S1) shows that the material is stable up to 400 °C under nitrogen and has no evidence for distinct glass transition for the polymer below the thermal decomposition temperature due to the nature of its cross-linking structures as shown in Figure S2 (see Supporting Information). The structure of CPOP-1 was clearly characterized at the molecular level by ^{13}C CP/MAS NMR spectrum. The ^{13}C NMR spectrum for the obtained polymer with assignment of the resonances is shown in Figure 1. The signal peak at 141.2 ppm corresponds to the substituted phenyl carbons binding with nitrogen atom. The high-intensity peak at 125.5 ppm is ascribed to the signal peak of other substituted phenyl carbons. The signal peak for unsubstituted phenyl carbons is located at 120.8 and 109.2 ppm, respectively.

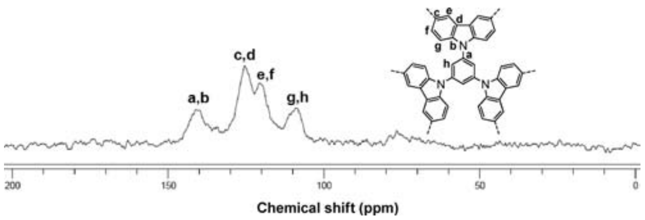


Figure 1. ^{13}C CP/MAS NMR spectrum of CPOP-1.

The porosity parameters of CPOP-1 were studied by sorption analysis using nitrogen as the sorbate molecule. Nitrogen adsorption−desorption isotherm of CPOP-1 measured at 77 K is shown in Figure 2, in which the fully reversible isotherm shows a rapid uptake at low pressure (0−0.1 bar) indicating a permanent microporous nature. The microporous polycarbazole exhibits a combination of type I and II nitrogen sorption isotherms according to the IUPAC classification.[14] The increase in the nitrogen sorption at a high relative pressure above 0.9 may arise in part from interparticulate porosity associated with the meso- and macrostructures of the samples and interparticular void.[15] The specific surface areas calculated in the relative pressure (P/P_0) range from 0.01 to 0.1 according to the previous reports[16] (see Supporting Information, Table S1 and Figure S3) show that the Brunauer−Emmett−Teller (BET) specific surface area of CPOP-1 is up to 2220 $m^2\ g^{-1}$.

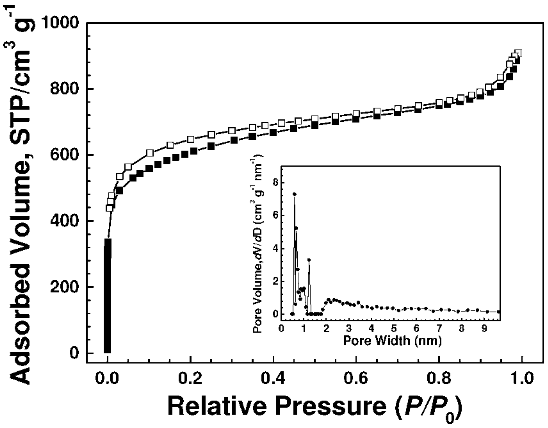


Figure 2. Nitrogen adsorption−desorption isotherms and the pore size distribution calculated by NLDFT (inset) of CPOP-1.

The pore size distribution (PSD) analysis based on the nonlocal density functional theory (NLDFT) approach has been used extensively to characterize a wide variety of porous materials although it does have limitations. PSD of the polymer calculated from the adsorption branch of the isotherms with the NLDFT approach indicates that CPOP-1 exhibits a dominant pore diameter centered at about 0.62 nm. Listed in Table S2 (see Supporting Information) are the key porosity parameters derived from the isotherm, such as the BET and Langmuir specific surface area, micropore surface area, and pore volume.

Microporous polycarbazole with a high specific surface area and a narrow pore distribution may interact attractively with small gas molecules through improved molecular interaction, which inspire us to investigate its gas (H_2 and CO_2) uptake capacities. On the basis of the hydrogen (77 K) and carbon dioxide (273 K) physisorption isotherms measured with a pressure up to 1.13 bar, CPOP-1 exhibits hydrogen storage of 2.80 wt % at 1.0 bar and carbon dioxide uptake of 21.2 wt % at 1.0 bar (Figure 3). Both hydrogen storage capacity and carbon dioxide uptake ability of CPOP-1 are exceptionally high. Actually, the adsorption capacities are among the best reported results for porous organic polymers under the same conditions. Moreover, they can be competitive with other kinds of porous materials such as activated carbons and metal−organic frameworks with even higher BET specific surface area.[2c,17] As far as we know, at 1.0 bar and 77 K, the hydrogen storage value of CPOP-1 is the highest one among the reported porous materials. Comparison of the high gas (H_2 and CO_2) uptake

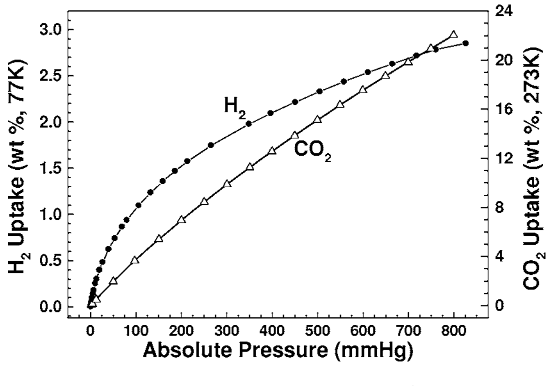


Figure 3. Gas adsorption isotherms of CPOP-1 (H_2 at 77 K; CO_2 at 273 K).

capacities of various porous materials with CPOP-1 at low pressure is listed in Tables S3 (see Supporting Information). These data prove that, besides the specific surface area, the molecular structure and chemical nature of the porous polymers also play crucial roles in the gas uptake capacity of microporous polymers. Therefore, selection of proper building blocks is an important premise for synthetic porous polymer designing.

In light of high CO_2 capture capacity, large surface area, and small pore size for CPOP-1, it is reasonable to study the selective uptake of CPOP-1 for small gases (CO_2, CH_4, and N_2) to evaluate its potential use in gas separation. In particular, the CO_2/CH_4 separation is one of very important processes in natural gas upgrading since the contamination of CH_4 with CO_2 will reduce the energy content of natural gas and cause equipment corrosion.[8b,18] The selectivity of CPOP-1 toward CO_2 over CH_4 and N_2 was investigated by collecting pure-component physisorption isotherms at 273 K (Figure 4). The CO_2 uptake shows a nearly linear increase with the pressure whereas that of CH_4 or N_2 has no apparent increase trend. At 273 K and 1.0 bar, the CO_2 uptake is up to 4.82 mmol g^{-1}. In comparison, the CH_4 and N_2 uptake of CPOP-1 under the same conditions is 0.13 and 0.19 mmol g^{-1}, respectively. The estimated ideal CO_2/CH_4 and CO_2/N_2 adsorption selectivity is 33 and 25, respectively. The isosteric heat of adsorption CO_2 is calculated based on adsorption isotherms of CO_2 at different temperatures (273 and 291 K) from 0 to 1.13 bar through the Clausius–Clapeyron equation[19] (see Supporting Information, Figures S4a–c). It can be observed that the isosteric heat of CPOP-1 is about 27 kJ mol^{-1} at zero coverage and drops to 23 kJ mol^{-1} as the uptake reaches 130 mg g^{-1}. The isosteric heat value is higher than HCP materials (20–24 kJ mol^{-1})[11c] or porous polybenzimidazole BILP-1 (19.7–26.5 kJ mol^{-1}),[9b] and can be comparable to some CMP materials (25–33 kJ mol^{-1}).[2c] The high selectivity toward CO_2 over N_2 or CH_4 can be ascribed to the electron-rich polycarbazole network and high charge density at the nitrogen sites of CPOP-1 might facilitate more favorably the interaction with the polarizable CO_2 molecules through local-dipole–quadrupole interactions.[2c,9b]

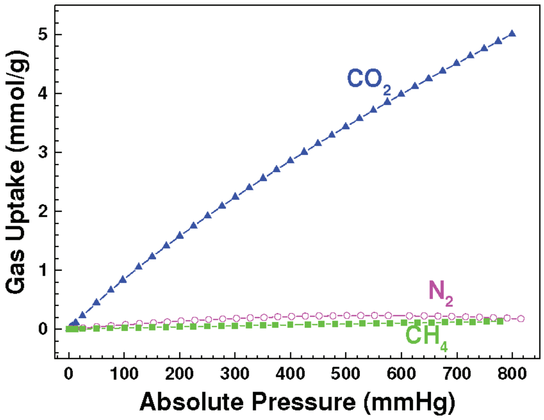


Figure 4. Gas adsorption isotherms (CO_2, triangle; N_2, circle; and CH_4, square) of CPOP-1 (273 K).

The microporous polycarbazole CPOP-1 exhibits strong photoluminescence properties and shows a green-yellow emission with a maximum wavelength at about 545 nm and a shoulder peak at 495 nm (see Supporting Information, Figure S5). As expected, CPOP-1 has a nonordered, amorphous structure proved by the X-ray diffraction (XRD) measurement (see Supporting Information, Figure S6). Figures S7 and S8 (Supporting Information) show scanning electron microscopy (SEM) image and high-resolution transmission electron microscopy (TEM) image of CPOP-1, respectively. The TEM image is indicative of porous structures of the materials, which is similar to some reported amorphous microporous organic polymers.[7b,13] SEM analysis of CPOP-1 displays that the polymer consists of aggregated particles with submicrometer sizes.

In conclusion, preparation of fluorescent microporous polycarbazole CPOP-1 via carbazole-based oxidative coupling polymerization is reported. The preparative strategy exhibits cost-effective advantages. The BET specific surface area for the obtained polymer is higher than 2000 m^2 g^{-1}. Gas (H_2 and CO_2) adsorption isotherms show that the hydrogen storage can reach to 2.80 wt % (1.0 bar and 77 K) and uptake capacity for carbon dioxide is up to 21.2 wt % (1.0 bar and 273 K), which can be competitive with the best reported results for porous organic polymers, activated carbons, and metal–organic frameworks under the same conditions. Furthermore, the good selectivity of the polymer toward CO_2 over N_2 and CH_4 makes it have a promising potential application in gas separation. Because of its good performance for the gas storage and separation, CPOP-1 with a large specific surface area exhibits potential use for clean energy applications and environmental field. Various microporous carbazole-based polymers have been prepared by this facile method and the related porosities and gas sorption analysis are under study.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of experimental materials and measurements; synthetic procedures for monomer TCB and polymer CPOP-1; thermal analysis and model structure of CPOP-1; BET specific surface area of CPOP-1 calculated over different pressure ranges; CO_2 adsorption isotherms of CPOP-1 at different temperatures and isosteric heat of CO_2 adsorption for CPOP-1; comparison of the gas (H_2 and CO_2) uptake capacities of various porous materials with CPOP-1 at low pressure; optical properties and XRD plot of CPOP-1; SEM and TEM images of CPOP-1; ^1H NMR, ^{13}C NMR, and MS of monomer TCB. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

hanbh@nanoctr.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The financial support of the Ministry of Science and Technology of China (Grant 2011CB932500), National Science Foundation of China (Grants 91023001, 60911130231, and 21002017), and the Chinese Academy of Science (Grant KJCX2-YW-H21) is acknowledged. The authors also acknowledge the financial support from the Danish-Chinese Center for Molecular Nanoelectronics funded by the Danish National Research Foundation and the Danish Agency for Science, Technology and Innovation.

■ REFERENCES

(1) Leaf, D.; Verolmec, H. J. H.; Hunt, W. F. Jr. *Environ. Int.* **2003**, *29* (2−3), 303−310.

(2) (a) D'Alessandro, D. M.; Smit, B.; Long, J. R. *Angew. Chem., Int. Ed.* **2010**, *49* (35), 6058−6082. (b) Ferey, G.; Serre, C.; Devic, T.; Maurin, G.; Jobic, H.; Llewellyn, P. L.; Weireld, G. D.; Vimont, A.; Daturi, M.; Chang, J.-S. *Chem. Soc. Rev.* **2011**, *40* (2), 550−562. (c) Dawson, R.; Stockel, E.; Holst, J. R.; Adams, D. J.; Cooper, A. I. *Energy Environ. Sci.* **2011**, *4* (10), 4239−4245.

(3) (a) Svec, F.; Germain, J.; Frechét, J. M. J. *Small* **2009**, *5* (10), 1098−1111. (b) Farha, O. K.; Yazaydın, A. Ö.; Eryazici, I.; Malliakas, C. D.; Hauser, B. G.; Kanatzidis, M. G.; Nguyen, S. T.; Snurr, R. Q.; Hupp, J. T. *Nat. Chem.* **2010**, *2* (11), 944−948. (c) Pumera, M. *Energy Environ. Sci.* **2011**, *4* (3), 668−674.

(4) (a) Cooper, A. I. *Adv. Mater.* **2009**, *21* (12), 1291−1295. (b) McKeown, N. B.; Budd, P. M. *Macromolecules* **2010**, *43* (12), 5163−5176. (c) Furukawa, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **2009**, *131* (25), 8875−8883. (d) Thomas, A.; Kuhn, P.; Weber, J.; Titirici, M.; Antonietti, M. *Macromol. Rapid Commun.* **2009**, *30* (4−5), 221−236.

(5) (a) Weber, J.; Thomas, A. *J. Am. Chem. Soc.* **2008**, *130* (20), 6334−6335. (b) Yuan, S.; Kirklin, S.; Dorney, B.; Liu, D.-J.; Yu, L. *Macromolecules* **2009**, *42* (5), 1554−1559.

(6) (a) 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), 8574−8578. (b) 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), 7710−7720.

(7) (a) Yuan, S.; Dorney, B.; White, D.; Kirklin, S.; Zapol, P.; Yu, L.; Liu, D.-J. *Chem. Commun.* **2010**, *46* (25), 4547−4549. (b) Chen, Q.; Luo, M.; Wang, T.; Wang, J.-X.; Zhou, D.; Han, Y.; Yan, C.-G.; Han, B.-H. *Macromolecules* **2011**, *44* (14), 5573−5577.

(8) (a) Ritter, N.; Antonietti, M.; Thomas, A.; Senkovska, I.; Kaskel, S.; Weber, J. *Macromolecules* **2009**, *42* (21), 8017−8020. (b) 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), 3033−3035. (c) Shultz, A. M.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. *Chem. Sci.* **2011**, *2* (4), 686−689.

(9) (a) Weber, J. *ChemSusChem* **2010**, *3* (2), 181−187. (b) Rabbani, M. G.; El-Kaderi, H. M. *Chem. Mater.* **2011**, *23* (7), 1650−1653.

(10) Schmidt, J.; Weber, J.; Epping, J. D.; Antonietti, M.; Thormas, A. *Adv. Mater.* **2009**, *21* (6), 702−705.

(11) (a) Davankov, V. A.; Ilyin, M. M.; Tsyurupa, M. P.; Timofeeva, G. I.; Dubrovina, L. V. *Macromolecules* **1996**, *29* (26), 8398−8403. (b) Tsyurupa, M. P.; Davankov, V. A. *React. Funct. Polym.* **2006**, *66* (7), 768−779. (c) Martín, C. F.; Stöckel, E.; Clowes, R.; Adams, D. J.; Cooper, A. I.; Pis, J. J.; Rubiera, F.; Pevida, C. *J. Mater. Chem.* **2011**, *21* (14), 5475−5483.

(12) (a) Morin, J. F.; Leclerc, M.; Ades, D.; Siove, A. *Macromol. Rapid Commun.* **2005**, *26* (10), 761−778. (b) Blouin, N.; Leclerc, M. *Acc. Chem. Res.* **2008**, *41* (9), 1110−1119.

(13) Chen, Q.; Wang, J.-X.; Yang, F.; Zhou, D.; Bian, N.; Zhang, X.-J.; Yan, C.-G.; Han, B.-H. *J. Mater. Chem.* **2011**, *21* (35), 13554−13560.

(14) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquérol, J.; Siemieniewska, T. *Pure Appl. Chem.* **1985**, *57* (4), 603−619.

(15) (a) Rose, M.; Klein, N.; Böhlmann, W.; Böhringer, B.; Fichtner, S.; Kaskel, S. *Soft Mater.* **2010**, *6* (16), 3918−3923. (b) Weber, J.; Schmidt, J.; Thomas, A.; Böhlmann, W. *Langmuir* **2010**, *26* (19), 15650−15656.

(16) Walton, K. S.; Snurr, R. Q. *J. Am. Chem. Soc.* **2007**, *129* (27), 8552−8556.

(17) (a) Ghanem, B. S.; Hashem, M.; Harris, K. D. M.; Msayib, K. J.; Xu, M.; Budd, P. M.; Chaukura, N.; Book, D.; Tedds, S.; Walton, A.; McKeown, N. B. *Macromolecules* **2010**, *43* (12), 5287−5294. (b) Chen, Q.; Wang, J.-X.; Wang, Q.; Bian, N.; Li, Z.-H.; Han, B.-H. *Macromolecules* **2011**, *44* (20), 7987−7993. (c) Choi, S.-H.; Drese, J. H.; Jones, C. W. *ChemSusChem* **2009**, *2* (9), 796−854.

(18) Lu, W.; Yuan, D.; Zhao, D.; Schilling, C. I.; Plietzsch, O.; Muller, T.; Bräse, S.; Guenther, J.; Blümel, J.; Krishna, R.; Li, Z.; Zhou., H.-C. *Chem. Mater.* **2010**, *22* (21), 5964−5972.

(19) Dunne, J. A.; Mariwala, R.; Rao, M.; Sircar, S.; Gorte, R. J.; Myers, A. L. *Langmuir* **1996**, *12* (24), 5888−5895.