

Synthesis, Properties, and Gas Separation Studies of a Robust Diimide-Based Microporous Organic Polymer

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Low-density microporous solids¹ have garnered considerable recent scientific and popular attention because of their many potential practical applications. Reflecting emerging energy challenges, catalysis,² hydrogen and methane storage,³ and chemical separations⁴ are among the most prolifically investigated applications. Yaghi and co-workers, in particular, have made pioneering contributions to the development of these materials with their work on metal-organic frameworks (MOFs)⁵ and, more

recently, two- or three-dimensional covalent organic frameworks (COFs).⁶ Both classes of materials are crystalline polymers and both are permanently microporous. In a recent work, Mirkin et al. have shown that by arresting the growth of a coordination polymer at early stages,⁷ one can create nano- or microparticles. These particles typically lack crystallinity, but nevertheless retain good permeability and porosity with respect to both ions and gases. From these studies, one can conclude that apparent crystallinity is not a requirement for permanent microporosity in coordination polymers and that perhaps this concept can also be applied to purely organic polymers. Indeed, several examples of noncrystalline “polymers of intrinsic microporosity” have already been reported, most notably by McKeown and co-workers.^{1d} Although the majority are one-dimensional, some are network polymers. Microporosity is achieved mainly by utilizing twisted (spiro type) monomers. Thomas and co-workers, for example, recently utilized spirobifluorene to produce porous polyimide and polyamide materials, suitable for hydrogen storage.^{1g}

Here we report the synthesis of a new porous organic polymer that features high surface area and pores of appropriate size and composition to capture CO₂ from mixtures with methane. Based on condensation of cheap and abundant amine- and anhydride-bearing monomers, **3** and **4**,⁸ the synthesis scheme produces a robust polyimide (**5**). Notably, the polymerization is achieved under mild conditions and without the use of expensive catalysts; see Scheme 1. The desired micro- and ultramicroporosity is engendered by using a tetrahedral building block (**3**) that is expected to produce a three-dimensional (locally diamondlike) network. Additionally facilitating porosity, by inhibiting efficient packing of any catenated regions, should be the large dihedral angle (nominally 90°) between the phenyl and diimide subunits of (**5**).

X-ray powder diffraction analysis of the as-synthesized solid polymer **5** revealed no diffraction, implying that **5** is amorphous (as expected from the irreversibility of the condensation reaction). SEM images of **5** and **6** (**5** heated under a vacuum at 160 °C for 24 h) revealed a series of agglomerates of imperfect, spherically shaped micro- and nanoparticles. To our surprise, thermal gravimetric analysis (TGA) of **5** and its activated analogue **6**, as well as resolvated **6**, showed stability up to 500 °C (see Figure 2a). The TGA results imply permanent porosity for **6**, because it takes up the same amount of solvent (~25 wt %) as originally contained in **5**. Solid-state ¹³C NMR showed

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- Representative reviews: (a) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191–214. (b) Tranchemontagne, D. J.; Mendoza-Cortés, J. L.; O’Keeffe, M.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1257–1283. (c) Spokoyny, A. M.; Sumrein, A.; Kim, D.; Mirkin, C. A. *Chem. Soc. Rev.* **2009**, *38*, 1218–1237. (d) McKeown, N. B.; Budd, P. M. *Chem. Soc. Rev.* **2009**, *38*, 675–683. (e) Cooper, A. I. *Adv. Mater.* **2009**, *21*, 1291–1295. (f) Maly, K. E. J. *Mater. Chem.* **2009**, *19*, 1781–1787. (g) Weber, J.; Antonietti, M.; Thomas, A. *Macromolecules* **2008**, *41*, 2880–2885.
- Lee, J.-Y.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450–1459.
- Murray, L. J.; Dinca, M.; Long, J. R. *Chem. Soc. Rev.* **2009**, *38*, 1294–1314.
- (a) Bae, Y. S.; Mulfort, K. L.; Frost, H.; Ryan, P.; Punathanam, S.; Broadbelt, L. J.; Hupp, J. T.; Snurr, R. Q. *Langmuir* **2008**, *24*, 8592–8598. (b) Bae, Y. S.; Farha, O. K.; Spokoyny, A. M.; Mirkin, C. A.; Hupp, J. T.; Snurr, R. Q. *Chem. Commun.* **2008**, 4135–4137. (c) Banerjee, R.; Furukawa, H.; Britt, D.; Knobler, C.; O’Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2009**, *131*, 3875–3877. (d) Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. *Chem. Soc. Rev.* **2009**, *38*, 1477–1504. (e) Kuhn, P.; Krüger, K.; Thomas, A.; Antonietti, M. *Chem. Commun.* **2008**, 5815–5817.
- Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O’Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469–72.
- (a) Cote, A. P.; Benin, A. I.; Ockwig, N. W.; O’Keeffe, M.; Matzger, A. J.; Yaghi, O. M. *Science* **2005**, *310*, 1166–1170. (b) El-Kaderi, H. M.; Hunt, J. R.; Mendoza-Cortés, J. L.; Cote, A. P.; Taylor, R. E.; O’Keeffe, M.; Yaghi, O. M. *Science* **2007**, *316*, 268–272. (c) Cote, A. P.; El-Kaderi, H. M.; Furukawa, H.; Hunt, J. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2007**, *129*, 12914–12915. (d) Uribe-Romo, F. J.; Hunt, J. R.; Furukawa, H.; Klöck, C.; O’Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2009**, *131*, 4570–4571. (e) Kuhn, P.; Antonietti, M.; Thomas, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 3450–3453. (f) Weber, J.; Thomas, A. *J. Am. Chem. Soc.* **2008**, *130*, 13333–13337. (g) Tilford, R. W.; Gemmill, W. R.; zur Loye, H. C.; Lavigne, J. J. *Chem. Mater.* **2006**, *18*, 5296–5301. (h) Tilford, R. W.; Mugavero, S. J. III; Pellechia, P. J.; Lavigne, J. J. *Adv. Mater.* **2008**, *20*, 2741–2746. (i) Wan, S.; Guo, J.; Kim, J.; Ihee, H.; Jiang, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 8826–8830. (j) Wan, S.; Guo, J.; Kim, J.; Ihee, H.; Jiang, D. *Angew. Chem., Int. Ed.* **2009**, DOI: 10.1002/anie.200900881.

(7) Oh, M.; Mirkin, C. A. *Nature* **2005**, *438*, 651–654.

(8) (a) Ganesan, P.; Yang, X.; Loos, J.; Savenije, T. J.; Abellon, R. D.; Zuilhof, H.; Sudholter, E. J. R. *J. Am. Chem. Soc.* **2005**, *127*, 14530–14531. (b) Treier, M.; Richardson, N. V.; Fasel, R. *J. Am. Chem. Soc.* **2008**, *130*, 14054–14055.

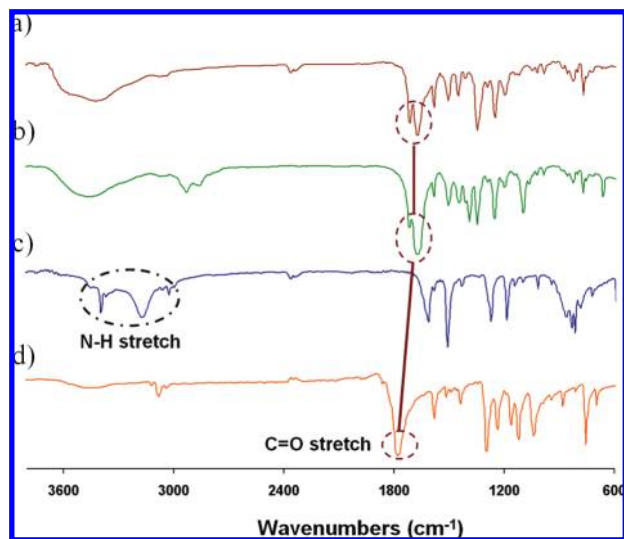
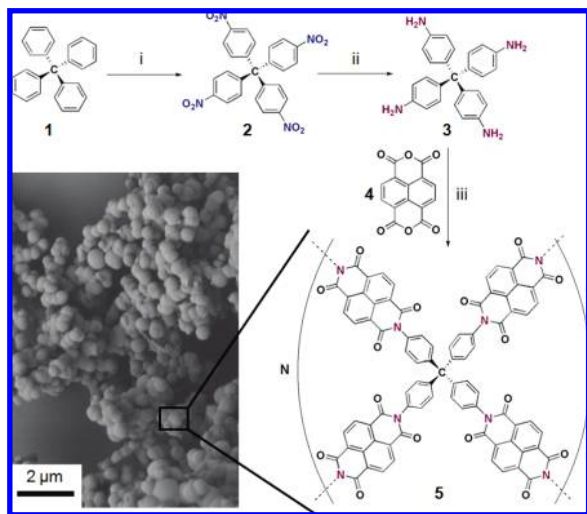


Figure 1. FT-IR spectra of (a) **6**, (b) **5**, (c) **3**, and (d) **4**. **5** and **6** contain O–H stretch bands due to the presence of water.

Scheme 1. ^a



^a (i) HNO_3 (fuming), $\text{Ac}_2\text{O}/\text{AcOH}$, rt, 50% (see the Supporting Information for safety note), (ii) Raney Ni/THF, reflux, 72%, (iii) DMF/proprionic acid.

the removal of solvent molecules, as evidenced by the almost complete disappearance of resonances at δ 35 and 30 attributed to DMF (see the Supporting Information, Figure SI-6). Polyimide connectivity and the presence of derivatives of both building blocks were confirmed by solid-state IR (Figure 1). In **5** and **6**, the carbonyl stretch is shifted toward lower energy by approximately 100 cm^{-1} relative to **4**, indicating amide bond formation. N–H stretches are diminished to undetected levels, suggesting essentially complete conversion of starting amine **3**. Control experiments with only one of the two reagents present produced no material under the conditions of Scheme 1, step iii.

The chemical stability of **5** was evaluated by soaking as-synthesized samples in pure water and in 0.1 M aq. HCl for 24 h. Remarkably, the material fully retained its porosity (see the Supporting Information, Table SI-1;

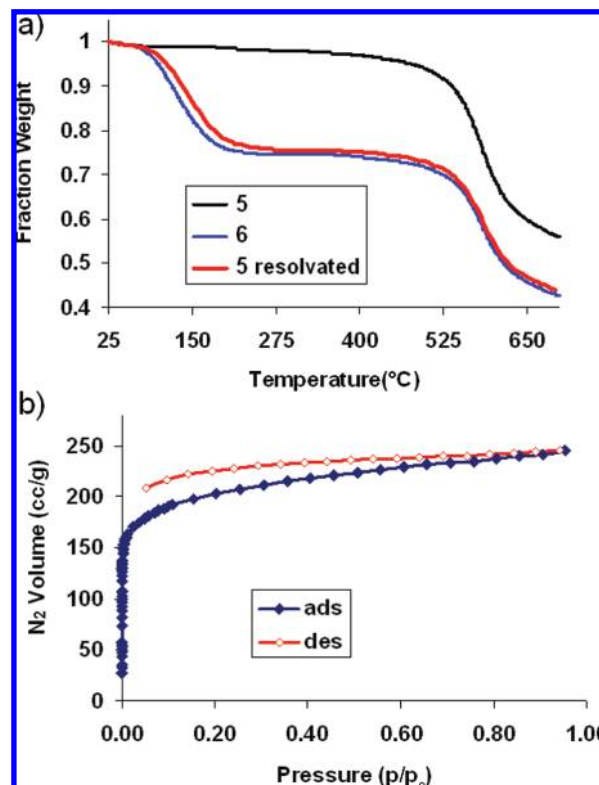


Figure 2. (a) TGA traces of **5** (bottom), **6** (top), and resolvated-**6** (middle); (b) nitrogen isotherm at 77 K.

successive processing of a single sample). The porosity of **6** was quantified via cryogenic adsorption of N_2 (see Figure 2b). The Brunauer–Emmet–Teller (BET) surface area, S.A., is $750 \pm 60\text{ m}^2/\text{g}$ (average of several samples). With CO_2 at 273 K, the measured nonlocal density functional theory (NLDFT) surface area is $\sim 900\text{ m}^2/\text{g}$. Pore size analysis (N_2 ; see the Supporting Information, Figure SI-1) yielded micro- and ultramicropores of diameter 3.5, 5.2, and 8.2 Å. A related, recently reported crystalline material, **COF-300** (constructed from **3** and terphthalaldehyde), shows a significantly higher surface area ($1360\text{ m}^2/\text{g}$) and pores of 7.2 Å diameter.^{6d} Also related is the spirobifluorene-based polyimide material, **PI1**, developed by Weber, Antonietti, and Thomas.^{1g} This amorphous material has an N_2 -accessible surface area of $\sim 1000\text{ m}^2/\text{g}$ and shows interesting pressure-dependent elastic deformation behavior.

In light of the relatively high surface area and small pores for **6**, we reasoned that it might be effective for small-molecule separations, including CO_2/CH_4 . In particular, we reasoned that the high charge density at the oxygen sites of **6** might facilitate local-dipole/quadrupole interactions with CO_2 that would be absent for CH_4 . The separation of carbon dioxide from methane is an important process in natural gas upgrading since CO_2 reduces the energy content of natural gas and facilitates pipeline corrosion.⁹ In this work, single-component adsorption isotherms for CO_2 and CH_4 were measured volumetrically^{4a} for **6** (see Figure 3a). From the measured

(9) Li, P. Y.; Tezel, F. H. *Micro. Meso. Mater.* **2007**, *98*, 94–101.

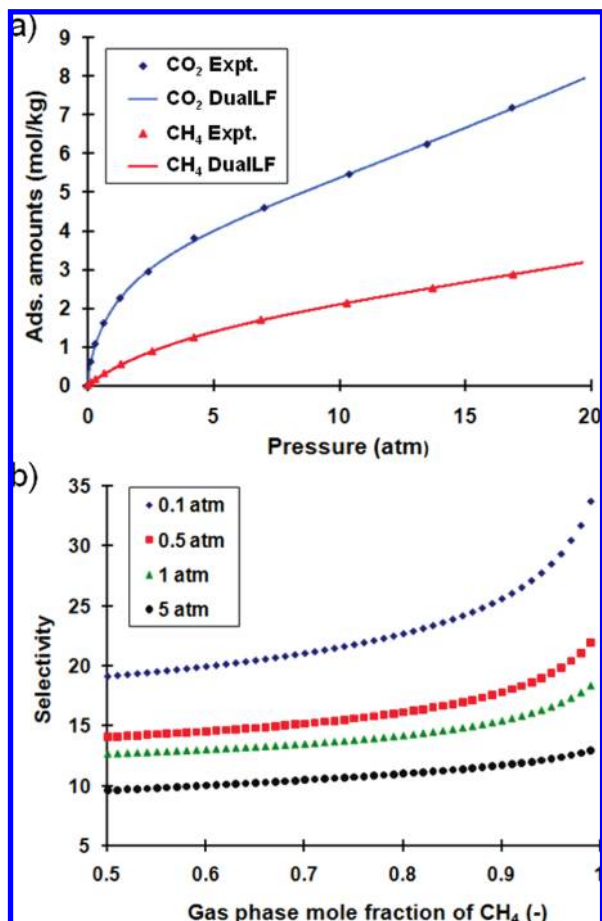


Figure 3. (a) CO₂ and CH₄ isotherms of **6** at 298 K and (b) selectivity of CO₂ over CH₄ at different pressures and mole fractions.

pure-component isotherms, the selectivities for CO₂/CH₄ mixtures were calculated using ideal adsorbed solution theory (IAST) (Figure 3b).¹⁰ Several studies have shown that IAST can be used to effectively predict gas mixture adsorption in zeolites,^{10b} and MOFs.^{10c} A dual-site Langmuir–Freundlich model was used to fit the pure isotherms, as shown in Figure 2b. The fitted isotherm parameters were used to predict the mixture adsorption in **6** by the IAST.

Compound **6** shows increasing CO₂/CH₄ selectivity with decreasing pressure and when the mole fraction of CH₄ (y_{CH_4}) approaches unity. In the case of $y_{\text{CH}_4} = 0.95$, which is a typical feed composition for natural gas purification, the selectivity is in the range of 12–28. Even at $y_{\text{CH}_4} = 0.5$, high selectivities (9–19) are obtained compared to MOFs (MOF results from GCMC simulations): Cu-BTC (6–10) and MOF-5 (2–3).¹¹ Experimental and calculated CO₂/CH₄ separations in the most recent study of ZIF materials showed selectivities of 5–10 at 298 K and 800 Torr.^{4c} Our results are similar to the CO₂/CH₄ selectivities reported for zeolites 13X (2–24).¹² However, compared to zeolites, **6** can be regenerated under milder conditions, thus requiring less expenditure of energy. These results indicate that **6** is a promising candidate for the separation and purification of CO₂ from various CO₂/CH₄ mixtures such as natural gas and landfill gas by adsorptive processes.

In summary, we have developed a new method for synthesizing high-area micro- and ultramicroporous organic polymers via amine/anhydride condensation. The first of these new materials, simply made from inexpensive precursors, shows outstanding thermal and chemical stability, and exceptional promise for CO₂/CH₄ separation. We are actively developing analogous materials with an eye toward catalysis and hydrogen-storage applications.

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Supporting Information Available: Experimental procedures for the synthesis of **2**, **3**, **5**, and **6**; SEM images and ¹³C CP-MAS NMR of **5** and **6**; elemental analysis data of **6** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(10) (a) Myers, A. L.; Prausnitz, J. M. *AIChE J.* **1965**, *11*, 121–127. (b) Babarao, R.; Hu, Z. Q.; Jiang, J. W.; Chempath, S.; Sandler, S. I. *Langmuir* **2007**, *23*, 659–666. (c) Yang, Q. Y.; Zhong, C. L. *J. Phys. Chem. B* **2006**, *110*, 17776–17783.

(11) Yang, Q. Y.; Zhong, C. L. *J. Phys. Chem. B* **2006**, *110*, 17776–17783.

(12) Cavenati, S.; Grande, C. A.; Rodrigues, A. E. *J. Chem. Eng. Data* **2004**, *49*, 1095–1101.