Gas Adsorption

DOI: 10.1002/anie.200900479

Amorphous Molecular Organic Solids for Gas Adsorption**

Jian Tian, Praveen K. Thallapally, Scott J. Dalgarno, Peter B. McGrail, and Jerry L. Atwood*

There has been intense interest in developing new porous materials for the storage and separation of important gases such as carbon dioxide and hydrogen. In this regard, crystalline materials such as zeolites,[1] metal–organic frameworks (MOFs) or coordination polymers (CPs),[2] and covalent organic frameworks[3] have been the subject of significant research. These classes of compounds generally possess nanochannel structures suitable for trapping guests and have concomitantly large surface areas. Amorphous materials such as activated carbon,[4] carbon nanotubes,[5] and cross-linked organic polymers[6] are also being investigated. Amorphous materials are typically difficult to characterize and display lower degrees of gas adsorption,[7] but their availability and scalability renders them industrially applicable. In the gas sorption arena, molecular organic solids have been largely neglected because of the close packing. Voids larger than 25 Å^3 are rarely seen in molecular organic crystals, but some exceptions have been reported.[8] One such example is the low-density phase of *p-tert*-butylcalix[4]arene (TBC4) that adopts a dimeric capsule-like arrangement.[8b] This phase is obtained by sublimation under reduced pressure, and the capsule exists with a slightly offset head-to-head arrangement of *t*Bu groups, and combination of the two cavities results in the generation of a void space of approximately 235 Å^3. Remarkably, it has been shown that various gases can penetrate crystalline low-density TBC4, coming to rest in the void space present within the capsule.[8d]

Selective gas storage within amorphous coordination polymer microparticles has recently been demonstrated by Mirkin and co-workers.[9] However, such a phenomenon has yet to be observed for amorphous molecular organic solids, which have generally been considered inactive for gas sorption and release.[7,10] Organic molecules typically pack so as to maximize attractive intermolecular interactions, and in doing so generally preclude the formation of large voids and channels.[11] Given this feature, the packing efficiency (PI) in organic crystals often falls between 0.59 to 0.69, and it is very difficult to calculate this value in the amorphous solid state owing to the general lack of structural characterization. We reasoned that molecules possessing large internal cavities in a rigid molecular structure should dramatically alter the close-packing and PI. Herein we show adsorption properties of amorphous molecular organic solids produced from noria (a waterwheel-like cyclic oligomer, **1**), a Boc-protected derivative (**2**),[12,13] and the related multivinylmonomer (**3**),[14] all of which are shown in Figure 1 A.

Molecule **1** was synthesized according to a one-pot procedure reported by Nishikubo and co-workers.[12,13] The molecular structure of noria **1** was not previously elucidated but was postulated from the structure of **2**.[12] In our hands, single platelike crystals of **1** were obtained by diffusion of methanol into a dimethylsulfoxide solution. Single crystal X-ray structural analysis showed that **1** is the expected double-cyclic ladder-type oligomer structure akin to **2**, possessing 24 hydroxy groups, six shallow cavities (around the periphery), and a large hydrophobic central cavity (Figure 1 A–C).[15,16] From examination of the crystal structure, the molecule has a flattened oval shape, with a central cavity and a portal diameter of approximately 7 and 5 Å, respectively. The internal volume of the cavity in **1** is calculated to be about 160 Å^3.[17]

Compound **1** was precipitated as a light yellow powder during synthesis.[13] Solvent-free **1** was isolated by drying under reduced pressure at 80 °C, as confirmed by thermogravimetric analysis (TGA, Figure S1 in the Supporting Information). X-ray powder diffraction (XRPD) and selected area electron diffraction (SAED) studies on dried samples of **1** showed the materials to be amorphous with minor crystallinity (Figure S2 in the Supporting Information). Grinding also affords totally amorphous **1** (Figure S2 in the Supporting Information). Unexpectedly, amorphous **1** rapidly gained weight upon cooling in air and when subsequently suspended in water produced copious air bubbles. This observation implied that the material contains significant porosity and readily adsorbs surrounding gases. Given this finding, we studied the porosity of the bulk sample of **1**.

The adsorption capacity of bulk **1** was measured volumetrically at room temperature for N_2, H_2, and CO_2 under isothermal conditions. The affinity of **1** for CO_2 is high and is significantly greater than for N_2 and H_2. The isotherm for CO_2 at room temperature exhibits a type I curve (Figure 1 D and Figure S4 in the Supporting Information), which is typically observed for microporous materials, and little hysteresis was observed within measurement accuracy. The rate of adsorption is rapid and equilibration was established within approximately 10 min. At the plateau region, approximately 4 mole

---

[*] J. Tian, Prof. J. L. Atwood
Department of Chemistry, University of Missouri-Columbia
Columbia, MO 65211 (USA)
E-mail: atwoodj@missouri.edu

Dr. P. K. Thallapally, Dr. P. B. McGrail
902 Battelle Blvd., Pacific Northwest National Laboratory
Richland, WA 99352 (USA)

Dr. S. J. Dalgarno
School of Engineering and Physical Sciences—Chemistry Heriot–Watt University, Riccarton, Edinburgh, EH14 4AS (UK)

[**] We acknowledge the NSF and DOE for financial support of this work. P.K.T. thanks the Office of Basic Energy Sciences (BES), U.S. Department of Energy (DOE) for work performed in the Environmental Sciences Laboratory. PNNL is a multi-program laboratory operated by Battelle Memorial Institute for the DOE under contract DE-AC05-76L01830.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200900479.

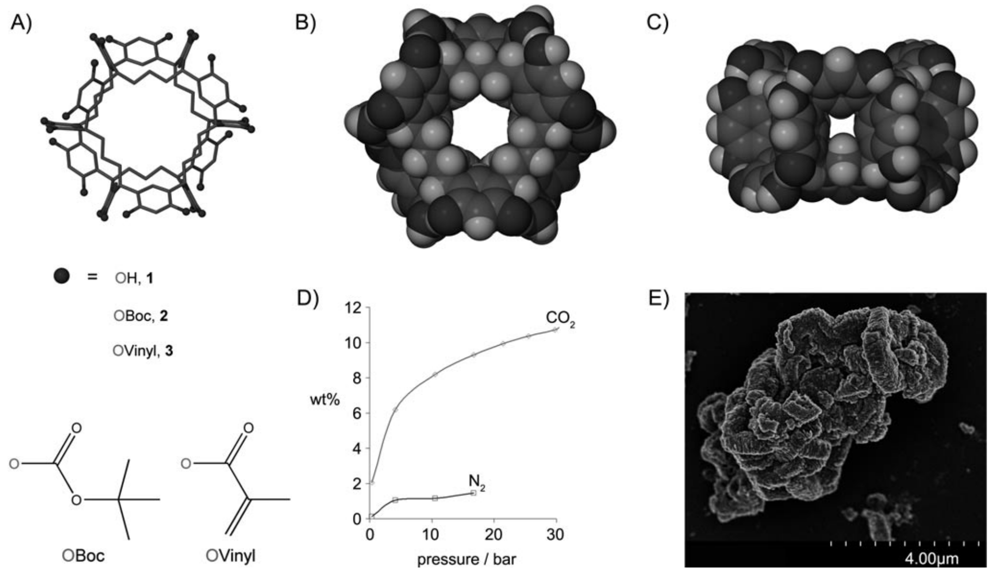

Figure 1. A) Schematic depiction of noria (**1**), Boc-protected derivative **2**, and multivinylmonomer **3**. B) Space-filling representation of the crystal structure of **1** showing the hydrophobic channel within the single molecule (solvent molecules omitted for clarity). C) Orthogonal view of (B) showing shallow cavities in **1**. D) Gravimetric CO_2 capacity for **1** at room temperature and pressure up to 30 bar. E) SEM image of particles of amorphous **1**.

CO_2 are absorbed per mole of host (**1**) at 30 bar and 298 K (equating to 11 wt% and 55 $cm^3 g^{-1}$ at STP). This value is much higher than that of the TBC4 organic capsules described above and matches that of the most useful molecular organic crystals described to date.[8a–e]

Absorption–desorption cycles can be repeated many times with no significant change of capacity within the porous material (as in conventional zeolites), as there is no change in the amorphous phase upon gas loading and release. The material is stable up to 320°C (Figure S1 in the Supporting Information), rendering **1** more thermally robust and chemically stable than many organic crystals and MOFs (or CPs).[3,8] It is noted that H_2 is not appreciably retained by the material at 77 K and 1 atm. The calculated BET surface area from N_2 sorption at 77 K is only 40 $m^2 g^{-1}$, suggesting very limited N_2 uptake at this temperature.[18] The BET surface area and pore volume of activated **1** were calculated using CO_2 as an adsorbate at three different temperatures. In all cases, sample **1** exhibits type I isotherms with surface areas ranging from 280 to 350 $m^2 g^{-1}$ and a pore volume of 0.13 $cm^3 g^{-1}$ (Figure S4 in the Supporting Information), which are relatively small compared to MOFs and organic polymers but significant for molecular organic solids. The pore size distribution shows a range of peaks from 3.6 to 8.0 Å, which is consistent with the microporous nature of the solid. Efforts to isolate the crystalline guest-free powders of **1** failed, as the starting phase rapidly loses single crystallinity upon removal from the mother liquor, thereby precluding structural analysis.

It remains to discuss the mechanism of gas diffusion within this new type of material. Scanning electron microscopy (SEM, Figure 1E) and transmission electron microscopy (TEM) analyses of powders of **1** revealed a complex morphology with no clear evidence of ordering.[18] Gas sorption isotherms, XRPD analysis, SAED, coupled with SEM and TEM analyses all support the conclusion that **1** is an amorphous molecular solid with intrinsic microporosity. Unlike crystalline microporous materials, organic molecules in an amorphous material generally pack in a disordered fashion, precluding the possibility for the existence of large channels and ordered interstitial voids. It is therefore possible that gases diffuse into the internal cavities of host molecules, as well as into disordered interstitial voids, by means of a temporary passage or window created by the thermal motion of or within these hosts. On the basis of the above calculated internal volume, it appears that the cavity in **1** may only accommodate two molecules of CO_2 based on 60% occupancy. Thus the remaining absorbed CO_2 molecules must reside in interstitial voids generated during the formation of the amorphous material. In guest-free organic solids, close packing is often achieved by insertion of part of one organic molecule into a cavity or void of a neighbor. This phenomenon is common for molecules with shallow cavities and/or small voids,[11] but it may not be the case for particular molecules possessing large "protected" internal cavities in an amorphous phase. The unique shape of the molecule may thus render the internal cavity relatively isolated and protected from 'blocking' by neighbors. However, it appears that in the case of amorphous **1**, shape also promotes the formation of interstitial voids, as evidenced by the quantity of additional CO_2 adsorbed relative to cavity volume.

To verify the assumption above, we synthesized the more bulky analogue **2** (Figures 1A and 2A) according to literature.[12] Twenty-four Boc groups are introduced as "arms" by protection of hydroxy groups. The overall cavity size of **2** is larger relative to **1** owing to the "Boc-assisted" extension of the tubular cavity in **1** (Figure 2A), resulting in a calculated internal volume of approximately 350 Å^3.[17] Removal of ethanol from a solution of **2** affords amorphous guest-free powders, as verified by XRPD, SAED, and TGA analysis (Figures S5 and S6 in the Supporting Information). Further analysis by SEM and TEM revealed spherical particles with diameters of approximately 200–500 nm (Figure 2D and Figure S7 in the Supporting Information). It is possible that the morphology and amorphous nature of the resulting particles are solvent-induced.

We believe that the cavity portals of **2** may be better protected from blocking from both ends by the bulky "arms"

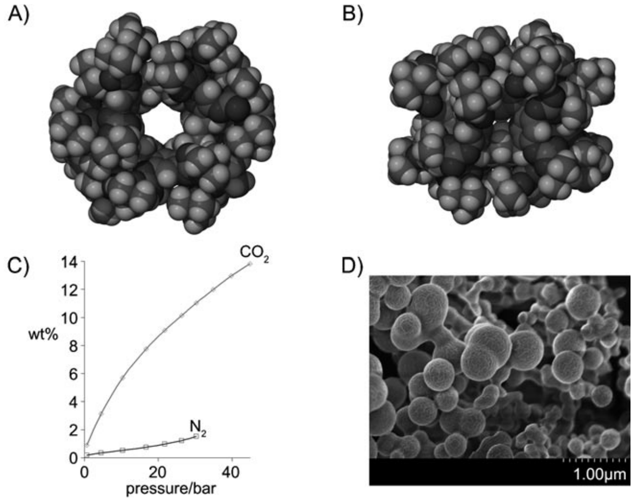

Figure 2. A) Space-filling representation of the crystal structure of **2** (solvent molecules omitted for clarity).[12] B) Orthogonal view of (A). C) Gravimetric CO$_2$ capacity for **2** determined at room temperature and pressure up to 45 bar. D) SEM image of particles of amorphous **2**.

of neighboring equivalents and that channels and interstitial voids are present, as evidenced by gas sorption studies (Figure 2C). Absorption capacities of powders of **2** were measured in an analogous fashion to those of **1**, showing high affinity for CO$_2$ over H$_2$ and N$_2$ with a typical type I sorption isotherm. In the low-pressure region, the study shows less sorption of CO$_2$ compared to **1**, which may be due to poorer fitting of CO$_2$ molecules in the larger void. However, in the plateau region, amorphous **2** shows higher sorption and reaches approximately 13 mole CO$_2$ absorbed per mole of host at 45 bar and 298 K (14.2 wt% and 71 cm^{3}g^{-1} at STP). As for **1**, sorption cycles with **2** can be repeated, and no appreciable sorption of N$_2$ and H$_2$ is observed at 298 K and 1 atm, even if the molecules enter the interior of the cavities.

On the basis of the above calculated internal volume, it appears that the cavity in **2** may only accommodate five molecules of CO$_2$, again based on 60% occupancy. The remaining eight adsorbed CO$_2$ molecules (per molecule of **2**) must reside in interstitial voids generated during amorphous material formation. Amorphous guest-free powders of **2** can also be isolated by different desolvation processes such as solvent removal from MeOH, CHCl$_3$, and ethyl acetate solutions. The resulting powders show very similar absorption capacities within measurement accuracy. This finding implies that the voids in the amorphous materials are inherent and are related to the molecular shape, showing little dependence on processing method (e.g. pressurization, desolvation, and regeneration).

TGA analysis shows that powders of **2** begin decomposition at around 150°C, presumably owing to loss of Boc groups (Figure S6 in the Supporting Information). Although displaying less thermal stability relative to **1**, and in line with literature, compound **2** shows enhanced film-forming ability.[19,20] Compound **1** was reported to be only soluble in dimethylsulfoxide, dimethylacteamide, dimethylformamide, toluene, and cyclohexane,[20] and the protecting groups present in **2** render the molecules more soluble. Self-standing films of **2** can be easily prepared using CHCl$_3$ solutions cast on glass plates (50 mg **2** in 1.0 mL CHCl$_3$) that are dried in vacuo at room temperature. Combination of our gas sorption findings and the propensity of **2** to form films suggests that this compound could potentially be used to form separation membranes. In this regard, absorption and desorption enthalpies of gas provide critical information about the nature of the adsorbents, which is obtained by calorimetric measurement. The enthalpies of CO$_2$ absorption in **1** and **2** were found to be 75 and 45 kJ mol^{-1}, respectively (Figure S9 in the Supporting Information), which is significantly less than the well-known methanolethanolamine (MEA) process for CO$_2$ removal and is comparable to zeolites (50–70 kJ mol^{-1})[21] and MOFs (20–90 kJ mol^{-1}).[22]

As expected, similar studies with multivinylmonomer derivative **3** (Figure 1A) showed an amorphous material that displays selective sorption of CO$_2$ over H$_2$ and N$_2$. The measured capacity is 12 wt% at 45 bar and 298 K (60 cm^{3}g^{-1} at STP),[18] corresponding to about 9 mole CO$_2$ per mole of host molecule. With a similar argument to that above, it is clear that the internal cavity of this molecule cannot contain this volume of gas, again suggesting the presence of interstitial voids in amorphous **3**. This material displays good film-forming ability in line with **2**,[19,20] and the similar sorption properties of **3** relative to **2** likely relate to structural similarity, which we believe governs the inherent porosity within the resulting amorphous phase.

To conclude, our studies show that molecular organic solids containing large accessible internal cavities are capable of forming amorphous phases that themselves contain interstitial voids. These materials can be easily synthesized, scaled, engineered, functionalized, and regenerated. They show selective uptake of CO$_2$ over H$_2$ and N$_2$, and they have good film-forming ability for potential separation applications. Additional preliminary studies show these kinds of material to have an affinity towards hydrocarbons, a feature we are further exploring. In light of current efforts to synthesize organic–inorganic hybrid molecules with large inner cavities (such as nanocages and molecular containers),[23,24] this new range of porous materials offers exciting opportunities for both fundamental study and potential industrial application.

Received: January 25, 2009
Revised: March 19, 2009

Keywords: adsorption · amorphous materials · molecular organic solids · solid-state structures

---

[1] a) D. W. Breck, *Zeolites Molecular Sieves, Chemistry and Use*, Wiley, New York, **1974**; b) *Introduction to Zeolite Science and Practice*, 3rd ed. (Eds.: J. Cejka, H. van Bekkum, A. Corma, F. Schüth), Elsevier, Amsterdam, **2007**.
[2] a) H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276; b) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705; c) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble, I.

Margiolaki, *Science* **2005**, *309*, 2040; d) S. R. Caskey, A. G. Wong-Foy, A. J. Matzger, *J. Am. Chem. Soc.* **2008**, *130*, 10870.

[3] a) A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger, O. M. Yaghi, *Science* **2005**, *310*, 1166; b) A. P. Côté, H. M. El-Kaderi, H. Furukawa, J. R. Hunt, O. M. Yaghi, *J. Am. Chem. Soc.* **2007**, *129*, 12914.

[4] V. C. Menon, S. Komarneni, *J. Porous Mater.* **1998**, *5*, 43.

[5] C. N. R. Rao, B. C. Satishkumar, A. Govindaraj, M. Nath, *ChemPhysChem* **2001**, *2*, 78.

[6] a) P. M. Budd, B. S. Ghanem, S. Makhseed, N. B. Mckewon, K. J. Msayib, C. E. Tattershall, *Chem. Commun.* **2004**, 230; b) N. B. McKeown, P. M. Budd, *Chem. Soc. Rev.* **2006**, *35*, 675; c) 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; *Angew. Chem. Int. Ed.* **2007**, *46*, 8574.

[7] R. E. Morris, P. S. Wheatley, *Angew. Chem.* **2008**, *120*, 5044; *Angew. Chem. Int. Ed.* **2008**, *47*, 4966.

[8] a) J. L. Atwood, L. J. Barbour, A. Jerga, *Science* **2002**, *296*, 2367; b) J. L. Atwood, L. J. Barbour, A. Jerga, *Angew. Chem.* **2004**, *116*, 3008; *Angew. Chem. Int. Ed.* **2004**, *43*, 2948; c) P. Sozzani, S. Bracco, A. Comotti, L. Ferretti, R. Simonutti, *Angew. Chem.* **2005**, *117*, 1850; *Angew. Chem. Int. Ed.* **2005**, *44*, 1816; d) P. K. Thallapally, L. Dobrzanacuteska, T. R. Gingrich, T. B. Wirsig, L. J. Barbour, J. L. Atwood, *Angew. Chem.* **2006**, *118*, 6656; *Angew. Chem. Int. Ed.* **2006**, *45*, 6506; e) G. S. Ananchenko, I. L. Moudrakovski, A. W. Coleman, J. A. Ripmeester, *Angew. Chem.* **2008**, *120*, 5698; *Angew. Chem. Int. Ed.* **2008**, *47*, 5616.

[9] Y.-M. Jeon, G. S. Armatas, J. Heo, M. G. Kanatzidis, C. A. Mirkin, *Adv. Mater.* **2008**, *20*, 2105.

[10] *Handbook of Porous Solids* (Eds.: F. Schüth), Wiley-VCH, Weinheim, **2002**.

[11] A. J. Kitaigorodsky, *Molecular Crystals and Molecules*, Academic Press, New York, **1973**.

[12] H. Kudo, R. Hayashi, K. Mitani, T. Yokozawa, N. C. Kasuga, T. Nishikubo, *Angew. Chem.* **2006**, *118*, 8116; *Angew. Chem. Int. Ed.* **2006**, *45*, 7948.

[13] The already high yield of the reaction can be further improved from 83% to 90% by scaling up the literature procedure by a factor of 20. In addition, while the authors of reference [12] stated that noria was precipitated as a white solid, using this method we consistently isolated a light yellow powder that, from analysis, was found to be pure **1**.

[14] Y. Saito, R. Saito, H. Kudo, T. Nishikubo, *Macromolecules* **2008**, *41*, 3755.

[15] Crystal data of noria **1:** $C_{63}H_{84}O_{18}S_6$, $M = 1321.66$, colorless prism, $0.25 \times 0.20 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$ (no. 2), $a = 15.169(5)$, $b = 15.637(5)$, $c = 18.838(6)$ Å, $\alpha = 99.509(5)$, $\beta = 111.210(6)$, $\gamma = 100.259(5)°$, $V = 3969(2)$ Å^3, $Z = 2$, Bruker SMART 1000 CCD diffractometer, $\mathrm{Mo}_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 173(2)$ K, $2\theta_{max} = 54.4°$, 27936 reflections collected, 17012 unique ($R_{int} = 0.0333$). Final GooF = 1.282, $R1 = 0.0955$, $wR2 = 0.2345$, R indices based on 9046 reflections with $I > 2\sigma(I)$ (refinement on F^2). The routine SQUEEZE was applied to the data to remove diffuse electron density associated with badly disordered solvent.[16] CCDC 717929 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34.

[17] For this approximate calculation, dummy atoms were placed at entrances to the molecular cavity prior to calculation of internal volume.

[18] See the Supporting Information.

[19] T. Nishikubo, H. Kudo, K. Mitani, US Patent 0123736A1, **2007**.

[20] H. Kudo, D. Watanabe, T. Nishikubo, K. Maruyama, D. Shimizu, T. Kai, T. Shimokawa, C. K. Ober, *J. Mater. Chem.* **2008**, *18*, 3588.

[21] J. A. Dunne, M. Rao, S. Sircar, R. J. Gorte, A. L. Myers, *Langmuir* **1996**, *12*, 5896.

[22] a) S. Bourrelly, P. L. Llewellyn, C. Serre, F. Millange, T. Loiseau, G. Férey, *J. Am. Chem. Soc.* **2005**, *127*, 13519; b) P. K. Thallapally, J. Tian, M. R. Kishan, C. A. Fernandez, S. J. Dalgarno, P. B. McGrail, J. E. Warren, J. L. Atwood, *J. Am. Chem. Soc.* **2008**, *130*, 16842.

[23] a) X. Liu, Y. Liu, G. Li, R. Warmuth, *Angew. Chem.* **2006**, *118*, 915; *Angew. Chem. Int. Ed.* **2006**, *45*, 901; b) M. Mastalerz, *Chem. Commun.* **2008**, 4756.

[24] a) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972; b) H. Northrop, H. Yang, P. J. Stang, *Chem. Commun.* **2008**, 5896.