DOI: 10.1002/anie.201006664

Nanoporous Organics Enter the Cage Age**

*Andrew I. Cooper**

cages · gas separation · microporous materials

Nanoporous materials are important in applications such as molecular separations and catalysis. In recent years, research in this area has been dominated by nanoporous networks, in particular metal–organic frameworks (MOFs),[1] covalent organic frameworks (COFs),[2] and nanoporous polymers.[3] In principle, there are advantages in nanoporous materials comprised of single molecules, rather than extended networks. The vision is as follows: researchers develop a modular set of porous molecular building units, analogous to Lego blocks, which can then be assembled to order. Pore "modules" might incorporate reactive chemical functionality, either by chemical derivatization or by molecular encapsulation,[4] and these reactive modules can then be combined in a "mix-and-match" fashion. However, while porous molecular solids are known,[5] there are several obstacles to achieving this modular assembly scheme. For example, molecular solids lack the extended directional coordination or covalent bonding found in MOFs,[1] and COFs,[2] and polymers,[3] and hence it is quite challenging to "design" their assembly. Most materials so far are single-component crystals with limited chemical functionality.[5,6] The lack of extended covalent or coordination bonding in molecular crystals also means that incipient porosity is often lost upon desolvation[5a,l] Moreover, when porosity is retained, the permanent surface areas in molecular solids (Brunauer–Emmett–Teller surfaces areas, SA_{BET}, up to around 1000 $m^2 g^{-1}$)[5g,l,6] are much lower than in state-of-the-art MOFs,[1d,e] COFs,[2] and polymer networks[3b] (SA_{BET} = 5500–6200 $m^2 g^{-1}$).[7]

Mastalerz and co-workers have just made an important step forward in developing porous organic molecules which could ultimately compete with networks for particular applications.[8] Building on their earlier synthesis of an *endo*-functionalized adamantoid cage compound **3** (Figure 1 a),[9] they have produced a molecular organic crystal with an unprecedented surface area of $SA_{BET} = 1375\ m^2 g^{-1}$,[8] surpassing other molecular crystalline solids such as metal–organic polyhedra,[5g] phthalocyanine nanoporous crystals,[5l] and the smaller imine-linked cages described by our group last year.[6] Crystallographic structure analysis for **3** reveals a molecular solid with a remarkably low density of 0.51 $g\,cm^{-3}$ and interconnected pores (Figure 1 b).

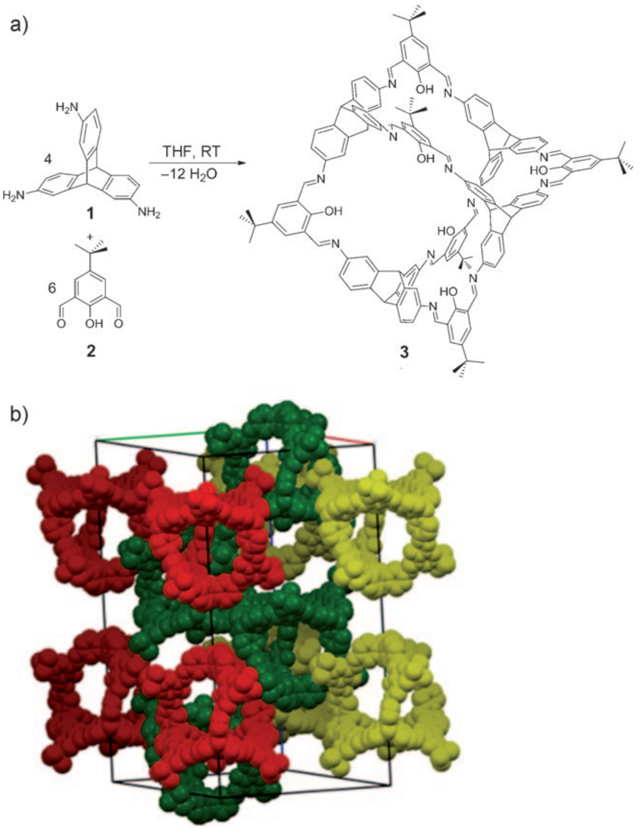

Figure 1. a) Synthesis of the *endo*-functionalized adamantoid cage compound **3** through a [4+6] cycloimination reaction. b) Packing of the molecules in the unit cell is mediated by π–π stacking interactions which leads to a low-density highly porous organic solid.

Not only is this material highly porous, but it also defies many of the potential disadvantages of molecular crystals. The nanoporosity is retained when the material is desolvated, despite the large solvated cavity volume (ca. 678 $Å^3$). Although the macroscopic crystal morphology is lost rapidly upon desolvation, the resulting microcrystalline powder retains the same crystallographic packing and pore structure. In this respect, **3** can be compared with COFs,[2] for example, where microcrystalline powders are typically obtained. The material also has good physical stability: the solid is desolvated by heating to 200 °C and shows no weight loss until 450 °C when analyzed by thermogravimetric analysis. As such, with the notable exception of its molecular solubility,

---

[*] Prof. A. I. Cooper
Department of Chemistry and Centre for Materials Discovery
University of Liverpool, Crown Street, Liverpool, L69 7ZD (UK)
Fax: (+44) 151-794-2316
E-mail: aicooper@liverpool.ac.uk

[**] A.I.C. is a Royal Society Wolfson Research Merit Award holder. We acknowledge EPSRC (EP/H000925/1) for financial support.

the physicochemical properties of molecular crystal **3** are not unlike many MOF[1] and COF[2] materials.

What gives this molecular material such high levels of porosity? The answer lies in the large, covalently prefabricated pore volume. The enhancement in pore volume for **3** with respect to an earlier [6+4] tetrahedral imine cage, **CC3**,[6] can be gauged from the space filling models given in Figure 2.

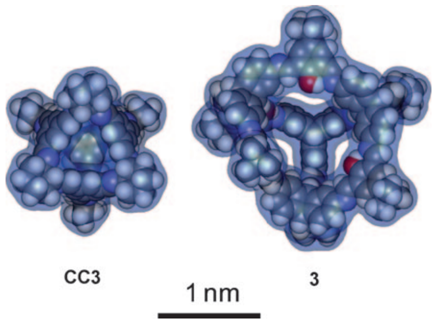

Figure 2. Bigger is better. Comparison of molecular structure for two [6+4] imine cages, **CC3**[6] ($SA_{BET} = 624\ m^2 g^{-1}$) and the new cage **3** ($SA_{BET} = 1375\ m^2 g^{-1}$).[8] The solvent-accessible surface (probe radius 1.42 Å) is shown in blue.

This pore volume translates to a substantial increase in nitrogen uptake and surface area for **3** with respect to **CC3**. Interestingly, CO_2, CH_4, and H_2 uptakes were slightly lower for **3** at 1 bar than observed for **CC3**,[6] most likely because of its larger average pore size: one would expect **3** to absorb more of these gases than **CC3** at higher pressures, closer to saturation. It is noteworthy that molecules **3** and **CC3** consist exclusively of light elements: this gives advantages in terms of specific surface area for a given cavity volume over materials such as metal–organic polyhedra.[5g] The porous crystal of **3** also shows good selectivity for CO_2 over CH_4, possibly as a result of the polar hydroxy groups in the cage cavities. The authors also suggest that the sorption properties might be varied in the future by functionalization of these hydroxy groups.[8]

The properties of **3** highlight the advantages of synthetic strategies which involve covalent prefabrication of internal molecular void volume.[10] From the isolated molecular structures illustrated in Figure 2, one might anticipate that the porosity in **3** would exceed that of **CC3**, provided that the pores interconnect. This suggests a degree of “designability” in intrinsically porous molecules that might be harder to achieve in extrinsically porous molecular crystals: that is, those where porosity arises from inefficient packing between molecules.[5c] Indeed, we highlighted **3** as a potential “undiscovered” nanoporous material in a Perspective article[5c] that was submitted just prior to this new study,[8] based solely on the molecular model presented for **3** in Mastalerz’s earlier synthesis paper.[9] It did not remain undiscovered for long! The structure of **3** also underlines the challenge that exists in terms of structural prediction for such molecular crystals. The crystal packing of **3** is dominated by π–π interactions,[8] while the related series of arene-linked cages, **CC1–CC3**,[6] do not exhibit π–π stacks at all. As such, there is no simple “rule of thumb” to anticipate how such cage molecules will assemble in the solid state. There is also a suggestion of polymorphism for **3**.[8] This may in principle be useful—for example, in preparing materials with switchable porosity[11]—but it also further complicates attempts to rationalize and predict structure.

To summarize, this porous molecular solid is an important milestone. Mastalerz and co-workers have almost matched the porosity obtained in the first generation of COFs reported by Yaghi et al. in 2005.[2a] Of course, surface area and pore volume are not everything—indeed, these metrics are perhaps sometimes the subject of too much focus.[7] The curious chemist will ask, however, whether we can design molecular solids which reach the surface areas exhibited by the second generation of 3-dimensional COFs[2b] ($SA_{BET} > 4000\ m^2 g^{-1}$). This is a stern test for the crystal engineering community and may require molecular solids with densities lower than $0.25\ g\,cm^{-3}$. For now, Mastalerz and colleagues lead the pack.

Received: October 23, 2010

---

[1] a) M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, S. Kitagawa, *Angew. Chem.* **1997**, *109*, 1844; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1725; b) X. B. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *Science* **2004**, *306*, 1012; c) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble, I. Margiolaki, *Science* **2005**, *309*, 2040; d) H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. O. Yazaydin, R. Q. Snurr, M. O’Keeffe, J. Kim, O. M. Yaghi, *Science* **2010**, *329*, 424; e) O. K. Farha, A. Ö. Yazaydın, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr, J. T. Hupp, *Nat. Chem.* **2010**, *2*, 944.

[2] a) A. P. Côté, A. I. Benin, N. W. Ockwig, M. O’Keeffe, A. J. Matzger, O. M. Yaghi, *Science* **2005**, *310*, 1166; b) H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortes, A. P. Côté, R. E. Taylor, M. O’Keeffe, O. M. Yaghi, *Science* **2007**, *316*, 268.

[3] a) N. B. McKeown, P. M. Budd, *Macromolecules* **2010**, *43*, 5163; b) T. Ben, H. Ren, S. Q. Ma, D. P. Cao, J. H. Lan, X. F. Jing, W. C. Wang, J. Xu, F. Deng, J. M. Simmons, S. L. Qiu, G. S. Zhu, *Angew. Chem.* **2009**, *121*, 9621; *Angew. Chem. Int. Ed.* **2009**, *48*, 9457.

[4] F. Hof, S. L. Craig, C. Nuckolls, J. Rebek, Jr., *Angew. Chem.* **2002**, *114*, 1556; *Angew. Chem. Int. Ed.* **2002**, *41*, 1488.

[5] a) L. J. Barbour, *Chem. Commun.* **2006**, 1163; b) N. B. McKeown, *J. Mater. Chem.* **2010**, DOI: 10.1039/C0JM01867H; c) J. R. Holst, A. Trewin, A. I. Cooper, *Nat. Chem.* **2010**, *2*, 915; d) R. M. Barrer, V. H. Shanson, *J. Chem. Soc. Chem. Commun.* **1976**, 333; e) J. L. Atwood, L. J. Barbour, A. Jerga, *Science* **2002**, *296*, 2367; f) P. Sozzani, S. Bracco, A. Comotti, L. Ferretti, R. Simonutti, *Angew. Chem.* **2005**, *117*, 1850; *Angew. Chem. Int. Ed.* **2005**, *44*, 1816; g) D. J. L. Tranchemontagne, Z. Ni, M. O’Keeffe, O. M. Yaghi, *Angew. Chem.* **2008**, *120*, 5214; *Angew. Chem. Int. Ed.* **2008**, *47*, 5136; h) A. Comotti, S. Bracco, G. Distefano, P. Sozzani, *Chem. Commun.* **2009**, 284; i) J. H. Chong, S. J. Ardakani, K. J. Smith, M. J. MacLachlan, *Chem. Eur. J.* **2009**, *15*, 11824; j) J. Tian, P. K. Thallapally, S. J. Dalgarno, P. B. McGrail, J. L. Atwood, *Angew. Chem.* **2009**, *121*, 5600; *Angew. Chem. Int. Ed.* **2009**, *48*, 5492; k) K. J. Msayib, D. Book, P. M. Budd, N. Chaukura, K. D. M. Harris, M. Helliwell, S. Tedds, A. Walton, J. E. Warren, M. Xu, N. B. McKeown, *Angew. Chem.* **2009**, *121*, 3323; *Angew. Chem. Int. Ed.* **2009**, *48*, 3273; l) C. G.

Bezzu, M. Helliwell, J. E. Warren, D. R. Allan, N. B. McKeown, *Science* **2010**, *327*, 1627.

[6] T. Tozawa, J. T. A. Jones, S. I. Swamy, S. Jiang, D. J. Adams, S. Shakespeare, R. Clowes, D. Bradshaw, T. Hasell, S. Y. Chong, C. Tang, S. Thompson, J. Parker, A. Trewin, J. Bacsa, A. M. Z. Slawin, A. Steiner, A. I. Cooper, *Nat. Mater.* **2009**, *8*, 973.

[7] J. R. Holst, A. I. Cooper, *Adv. Mater.* **2010**, DOI: 10.1002/adma.201002440.

[8] M. Mastalerz, M. W. Schneider, I. M. Oppel, O. Presly, *Angew. Chem.* **2011**, *123*, 1078; *Angew. Chem. Int. Ed.* **2011**, *50*, 1046.

[9] M. Mastalerz, *Chem. Commun.* **2008**, 4756.

[10] M. Mastalerz, *Angew. Chem.* **2010**, *122*, 5164; *Angew. Chem. Int. Ed.* **2010**, *49*, 5042.

[11] J. T. A. Jones, D. Holden, T. Mitra, T. Hasell, D. J. Adams, K. E. Jelfs, A. Trewin, D. J. Willock, G. M. Day, J. Bacsa, A. Steiner, A. I. Cooper, *Angew. Chem.* **2011**, *123*, 775; *Angew. Chem. Int. Ed.* **2011**, *50*, 749.