Gas-induced transformation and expansion of a non-porous organic solid

PRAVEEN K. THALLAPALLY[1]*, B. PETER McGRAIL[1], SCOTT J. DALGARNO[2†], HERBERT T. SCHAEF[1], JIAN TIAN[2] AND JERRY L. ATWOOD[2]*

[1]902 Battelle Blvd., Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, Washington 99352, USA
[2]Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211, USA
[†]Current address: School of Engineering and Physical Sciences - Chemistry, Heriot-Watt University, Edinburgh, EH14 4AS, UK
*e-mail: Praveen.Thallapally@pnl.gov; atwoodj@missouri.edu

Published online: 13 January 2008; doi:10.1038/nmat2097

Organic solids composed by weak van der Waals forces are attracting considerable attention owing to their potential applications in gas storage, separation and sensor applications[1]. Herein we report a gas-induced transformation that remarkably converts the high-density guest-free form of a well-known organic host (*p-tert*-butylcalix[4]arene) to a low-density form and vice versa[1], a process that would be expected to involve surmounting a considerable energy barrier[2]. This transformation occurs despite the fact that the high-density form is devoid of channels or pores[3]. Gas molecules seem to diffuse through the non-porous solid into small lattice voids, and initiate the transition to the low-density kinetic form with ∼10% expansion of the crystalline organic lattice, which corresponds to absorption of CO_2 and N_2O (refs 4,5). This suggests the possibility of a more general phenomenon that can be exploited to find more porous materials from non-porous organic and metal–organic frameworks that possess void space large enough to accommodate the gas molecules[6–13].

There are only a few documented examples[1] of single-crystal-to-single-crystal phase transformations because single crystals tend to lose their structural integrity on such transformation. However, when structural integrity is preserved, it provides valuable insight into the dynamic processes that occur during such a transformation[1]. In the present context metal–organic frameworks containing flexible ligands are known to undergo various kinds of transformation[8]. Few transformations are irreversible, and the original network can be re-obtained only by returning to the original temperature[9]. In a number of other cases, an increase in temperature leads to the reversible removal of guest solvent molecules, with concomitant rearrangement of the host lattice[8,9]. As a consequence of this the original network is not retained, and is re-obtained only by the re-absorption of the same (or in some cases different) solvent molecules[4,5,8]. To our knowledge, there are no reports of 'gas-driven' phase transformations involving thermodynamically stable phases converting to kinetic phases in either organic materials or metal–organic frameworks[5,6].

Herein we report the first instance of a 'gas-induced transformation', which remarkably converts the high-density 'guest-free' (and thermodynamic) form of *p-tert*-butylcalix[4]arene (**1**) to the low-density (and kinetic) form, a process that would be expected to involve surmounting a considerable energy barrier. Surprisingly, this process is temperature dependent (remarkably with the transformation being favoured at lower temperature) and involves a significant expansion of the crystal lattice with concomitant molecular reorientation from the former to the latter.

Calixarenes are cyclic polyphenolic compounds that have been studied extensively as host materials[1]. Within this large family of molecules, *p-tert*-butylcalix[4]arene (**1**) has shown promise in the area of gas storage at standard temperature and pressure[3,10]. Within the literature on the basis of this well studied host, it is known that kinetic (**1a**) and thermodynamic (**1b**) guest-free forms of **1** can be respectively obtained by sublimation under reduced pressure[1] or by crystallization from tetradecane over three days at 70 °C (ref. 11). It is also well known that **1** can form a range of inclusion compounds, 1:1, 1:2, with various guest molecules (see Supplementary Information, Fig. S1)[10].

Single-crystal analysis of **1a** shows molecules of **1** to be slightly offset as dimeric capsules that pack in a bilayer fashion. The dimeric capsules have an empty cavity (Fig. 1a) that has an estimated free volume of approximately 235 Å^3 and results in the material having a relatively low packing efficiency of 0.59 (see Supplementary Information, Fig. S2). Similar analysis of the polymorphic high-density form **1b** shows a well-packed arrangement of calixarene 'self-included' dimers (Fig. 1b) in which a *tert*-butyl group from each of molecule of **1** inserts deep into the neighbouring cavity. This arrangement consequently affords a higher packing efficiency of 0.69 (see Supplementary Information, Fig. S3), and even though the dimers are fairly well-packed we have further examined the crystal structure and that observed interstitial lattice voids of about 40 Å^3 exist within the crystal structure (Fig. 2). These voids are isolated and access to them seems to be guarded by the *tert*-butyl groups in molecules of **1** (Fig. 2).

Phase **1a** has been shown to undergo a single-crystal-to-single-crystal transformation on immersing crystals in vinyl bromide for ∼15 min (ref. 1). During this process, vinyl bromide permeates the seemingly non-porous lattice, resulting in the formation of the more stable 1:1 host:guest phase, **1c** (Fig. 1c), which has a packing efficiency of 0.67 (see Supplementary Information, Figs S4,S5). However, a similar phase transformation has not been reported in an organic material when the permeating species is a gas. Examination of the differential scanning calorimetry profile of **1a** under vacuum shows an exotherm at ∼190 °C, which is attributed to the phase transformation that takes place

© 2008 Nature Publishing Group

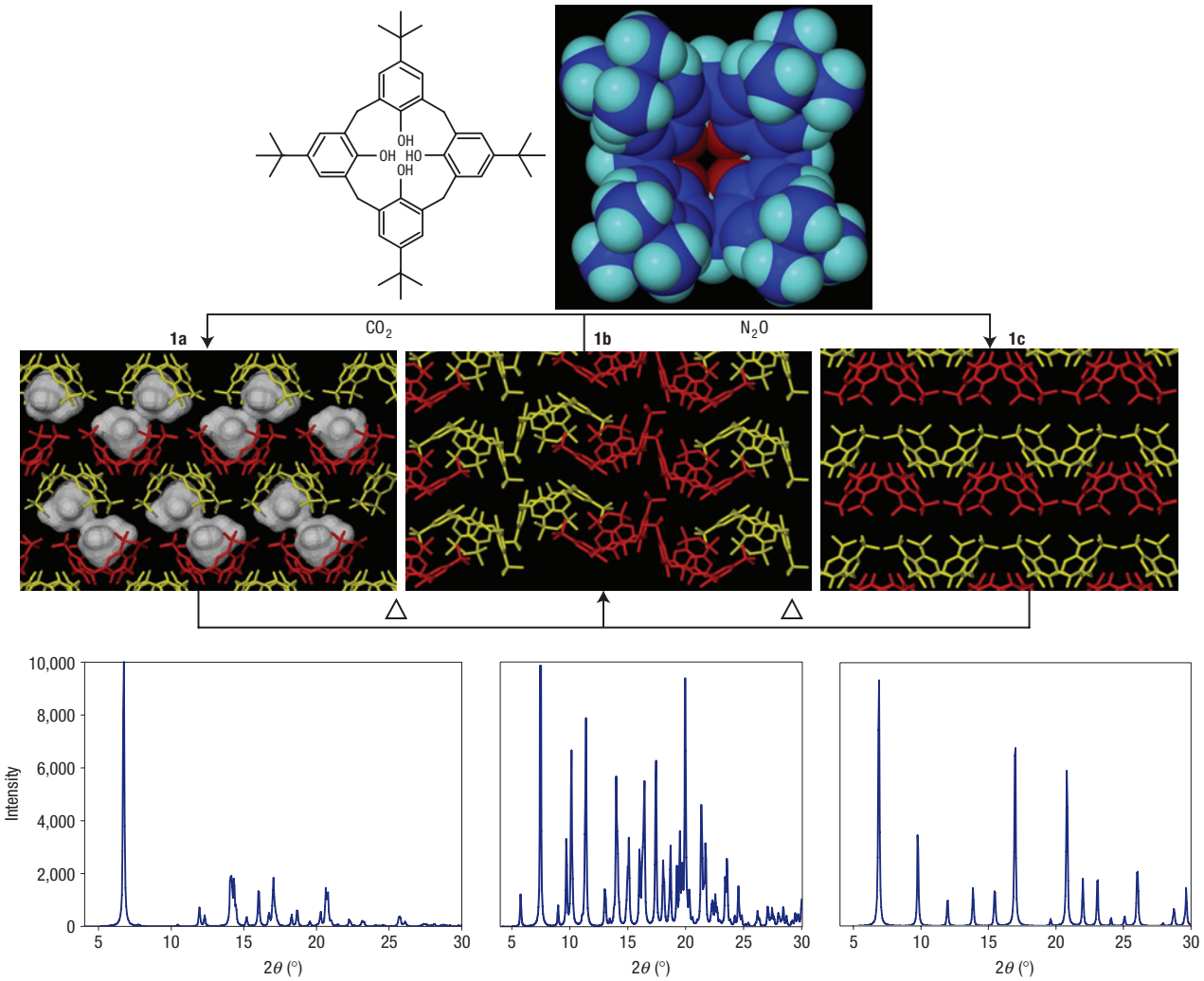

Figure 1 Guest-free and 1:1 host:guest complex of 1. 1a, The bilayer packing mode of **1a**, with the unoccupied void shown in grey. **1b**, The close packed arrangement of calixarenes in thermodynamic form **1b**, showing a lack of large voids in the crystal. **1c**, 1:1 host:guest complex, **1c**, with guest molecules removed. Simulated powder patterns of corresponding phases are shown below. Compare with the experimental powder patterns in Figs 3 and 4.

from **1a** to **1b** (see Supplementary Information, Fig. S6). This is supported by collecting variable-temperature X-ray powder diffraction (XRPD) data on freshly sublimed material under vacuum (see Supplementary Information, Fig. S7). The powder patterns of **1a** at variable temperatures indicate considerable phase-change onset at ∼140 °C, and this transformation continues until it reaches the more stable form. The experimental powder pattern of **1a** at 200 °C is identical to the simulated powder pattern obtained from structure **1b** (see Supplementary Information, Figs S8,S9); the bilayer arrangement of dimeric capsules collapses into the close-packed self-included form with increasing temperature. At ∼200 °C, and in line with the literature, high temperature induces a more rapid conversion from **1a** to **1b**, in ∼30 min. It is most important to note that, after transforming to the more stable form **1b**, the original phase **1a** cannot be regenerated by simply returning to the original temperature (see Supplementary Information, Fig. S10), as is the case for some materials[11]. This therefore demonstrates the truly significant thermodynamic stability of **1b** over **1a**. To transform the bilayer packing mode in **1a** to the self-included dimers of **1b**, each calixarene rotates through 24° around the crystallographic axis followed by a 3.9 Å translation moving towards the facing layer, thus leaving no pores in the resulting structure (**1b**) for gas sorption. Similarly, the structural transformation of various forms of **1** to **1b** has been shown[10,12] using various spectroscopic techniques (see Supplementary Information, Fig. S1)[13–18]; however, there are no reports on the effect of various gases on the high-density form of **1b** (ref. 11).

We have now directly examined the effects of various gas (CO_2, N_2O, CH_4, H_2 and He) pressures on low- and high-density polymorphic forms of **1** using single-crystal X-ray and *in situ* high-pressure powder diffraction experiments. The XRPD patterns of **1a** with various gas pressures confirm no structural change, suggesting that **1a** is the more stable phase with trapped guest gas molecules in the crystal lattice (see Supplementary Information, Figs S11,S12)[5,10,13–18]. When similar studies were undertaken on **1b**, some gases induced a phase transformation to the kinetic phase **1a**. This process must involve a considerable energy barrier, as molecules of **1** in each self-included dimer are 'pushed apart' to form bilayer dimeric capsules with simultaneous gas inclusion in the resulting cavity. *In situ* XRPD of **1b**, exposed to a high pressure of either hydrogen or helium (3 MPa) over a period of

© 2008 Nature Publishing Group

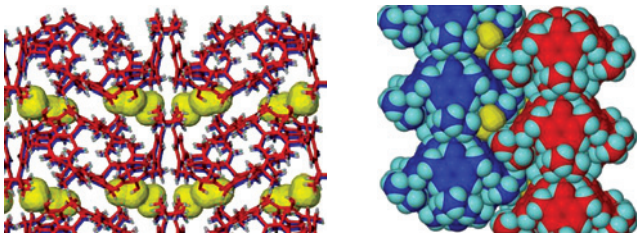

Figure 2 Two layers of self-included dimers in 1b with 40 Å^3 void spaces shown in yellow between the layers. The lattice voids are guarded by *tert*-butyl groups of the host.

24 h, showed no change in the powder pattern of the material (see Supplementary Information, Fig. S13). However, when exposed to 3.5 MPa (500 psi) of CO_2 at room temperature, **1b** was found to transform to **1a** in ~2 h (Fig. 3a). As a result, the entire solid expands by 33% along the [100] direction and shrinks by 17 and 7% along the [010] and [001] directions. Comparison of the unit-cell dimensions of **1a** and **1b** shows a crystal volume increase, which is initially dependent on CO_2, of 10.2% (Fig. 3c; Supplementary Information, Fig. S14). The same transformation took place at even lower pressures (0.70 MPa, 100 psi) of CO_2 and N_2O, but over a longer time period (one month). The kinetic phase is stable on release of gas pressure and does not revert to the starting phase **1b** unless heated to high temperature. The stability of the kinetic phase on release of gas and phase transformation was further supported by the solid-state nuclear magnetic resonance technique (see Supplementary Information, Fig. S15).

In contrast, exposure of **1b** to higher pressures (3.5 MPa, 500 psi) of N_2O results in the transformation to **1a** in just ~10 min (Fig. 4a), but simulated and experimental powder patterns show that **1a** is further transformed to the yet more stable 1:1 phase, **1c** (see Supplementary Information, Fig. S16). As a result, the crystal volume further increases by 13% going from **1b** to **1c** and it is therefore possible to selectively transform **1b** to the desired form with ease simply through a judicious choice of gas (see Supplementary Information, Fig. S1).

To understand the phase transformation, single-crystal X-ray diffraction studies were conducted on a crystal of **1b** after sequential exposure to CO_2 at 3.5 MPa (500 psi). After ~30 min exposure, a single crystal was found to retain its original form, but a further 30 min exposure afforded a diffuse powder pattern, indicating that the crystal is not surviving the CO_2-induced transformation to **1a** (see Supplementary Information, Figs S17–S19). However, XRPD shows the presence of low- and high-density phases after 60 min exposure of CO_2, with complete conversion taking approximately 2 h (Fig. 3a).

Unlike conventional porous materials reported for adsorption and desorption of gases, or the expansion of metal–organic frameworks by formation of gas hydrates[19] or flexible metal–organic frameworks where windows can control sorption behaviour[20], no pores are found in the crystal lattice of **1b**. However, it seems plausible that gas molecules diffuse through **1b**, presumably into the 40 Å^3 voids (Fig. 2) that are guarded by the *tert*-butyl groups until all the voids are filled. Such a process would require cooperative movement within the crystal lattice to provide the temporary passage for gas molecules, which can be thought to 'hop' between adjacent voids. Single-crystal X-ray analysis of **1b** at −100 and 25 °C suggests that at low temperature three out of four *tert*-butyl groups are disordered over two positions, whereas all are disordered at room temperature. Therefore, we speculate that limited rotation of *tert*-butyl groups in **1b** would enable the

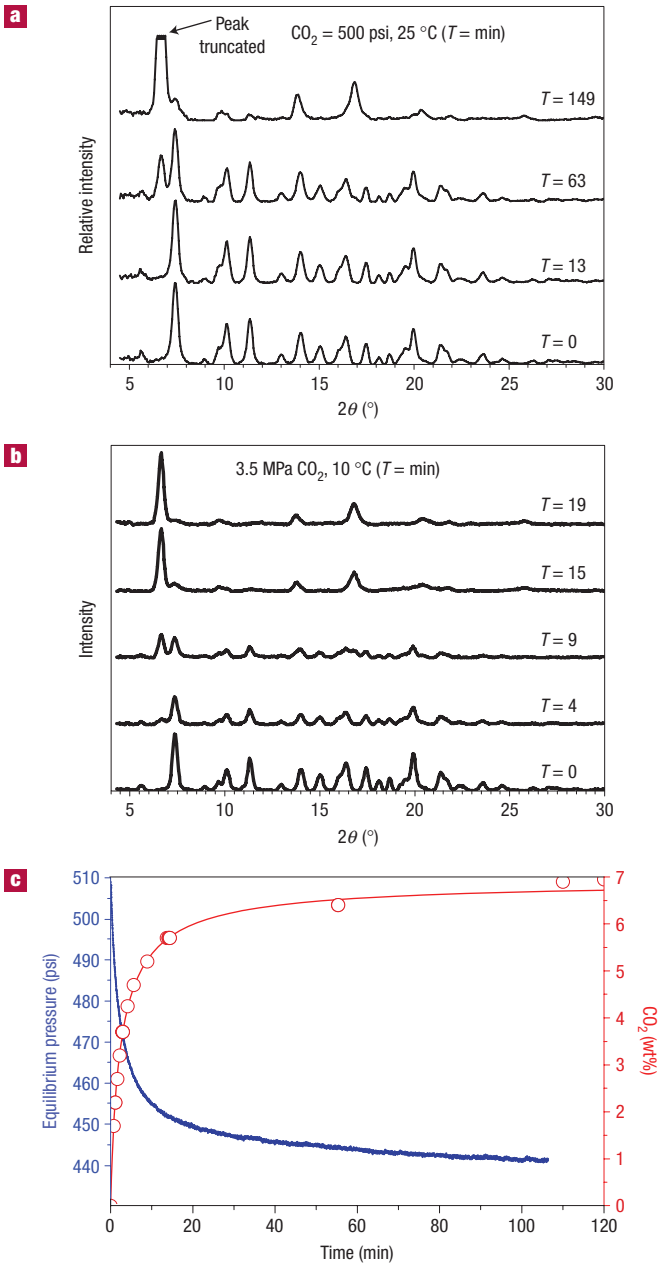

Figure 3 Gas-induced transformation and expansion of 1b to 1a at 3.5 MPa of CO_2. a, At room temperature; **b**, at 10 °C. The transformation is much faster at 10 °C compared with room temperature; prolonged exposure to CO_2 may result in phase **1c** via **1a**. Notice that the presence of the low- and high-density phases is clear at both temperatures. **c**, Uptake of CO_2 by **1b** that transforms to **1a** as a function of time. The rate of uptake is the same before and after conversion.

gas molecules to diffuse through the solid, and simultaneously that the energy released after the gas is trapped in the crystal is enough to transform **1b** to the more stable form **1a** with included gas molecules.

The temperature dependence of the rate of the phase transition on sorption of CO_2 and N_2O into the 40 Å^3 cavities in **1b** can be correlated principally with the rotational behaviour of the *tert*-butyl groups lining (and blocking) the cavities. The rate of translation of a polyatomic gas varies with temperature as $T^{3/2}$ (ref. 21), whereas the rate of rotation of *tert*-butyl groups varies

© 2008 Nature Publishing Group

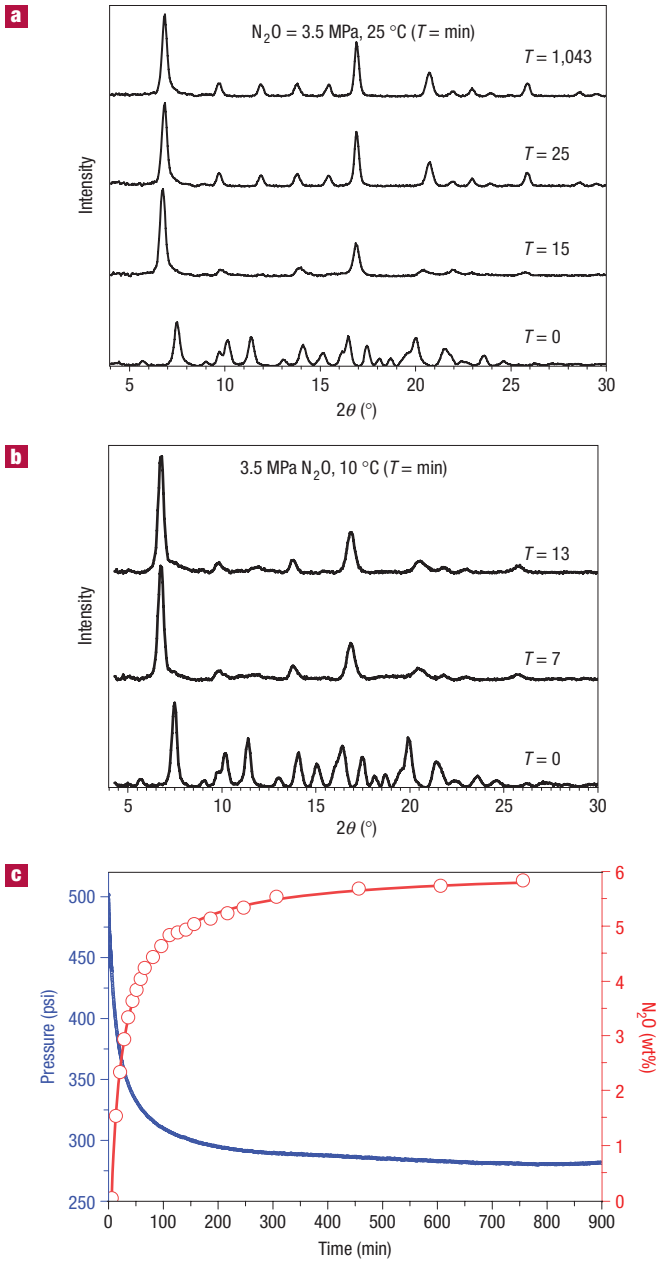

Figure 4 Nitrous-oxide-induced transformation of 1b to 1a and to 1c at 3.5 MPa. a, At room temperature; **b**, at 10 °C. Transformation from **1b** to **1c** taking place through the low-density phase **1a**. **c**, Uptake of N_2O at high pressure in **1b**, which spontaneously converts to **1c**.

according to a higher-order exponential function, increasing by almost three orders of magnitude from $T = -80\,°C$ to $T = 35\,°C$ in butylated hydroxytoluene[21]. Translational diffusion rates for CO_2 would only double over this same temperature range. Consequently, the rotational frequency of the *tert*-butyl groups in **1b** increases with temperature much faster than the collision frequency of the CO_2 molecules impinging on the cavities. Hence, from a statistical mechanics perspective, higher temperatures would result in increasing interference of the *tert*-butyl groups with the translational motion of gas molecules trying to enter the cavities of **1b.** This is shown by the fact that exposure of **1b** to 3.5 MPa (500 psi) of CO_2 at 10 °C (Fig. 3b) results in a very rapid conversion to **1a** in ~10 min (<5 min with N_2O under the same conditions, Fig. 4b), whereas at 50 °C, no conversion of phase **1b** was detected even after remaining at 3.5 MPa pressure of CO_2 for two weeks (see Supplementary Information, Fig. S20). Hence, there seems to be a finite temperature range for sorption of the gases into the cavities of **1b**, with subsequent phase transformation.

The phase changes occurring in **1b** involve substantial rearrangement of the self-included dimers within any particular crystallite. The heavy energetic load involved in expanding the crystal lattice by 10% seems to be borne by the pressure of gas molecules in most or all of the cavities. These selective gas effects suggest not only that the gas molecules must be of a particular size to be efficiently sorbed into **1b**, but also that the energy of the van der Waals interactions between the gases and the 40 Å^3 cavity walls is an important consideration.

With regard to phase transformations, it has been pointed out in reference to metals and alloys that 'Vacant lattice sites, interstitial atoms, dislocations, stacking faults, and grain boundaries are comparatively unimportant in a description of the equilibrium state, but their presence may be fundamental to the process of transformation'[22]. The proposed mechanism of phase transformation for the high-density, thermodynamic phase, **1b**, to the low-density, kinetic phase, **1a**, is based on the presence of the 40 Å^3 cavities. In support of this mechanism we examined the self-included form of *p-tert*-butylthiacalix[4]arene[23], **2**, that posses cavities of 25 Å^3 guarded by *tert*-butyl groups and does not undergo phase transformation at high pressures (see Supplementary Information, Figs S21,S22). Because the two compounds are isostructural, in our view this emphasizes the importance of the absorption of the gas into the 40 Å^3 cavities as the first step in the mechanism.

The discovery of a reversible phase transition on inclusion of selected gaseous molecules in *p-tert*-butylcalix[4]arene at high pressure and temperature points to a unexpectedly facile concerted mobility of molecules in the organic solid state. The demonstrated ability to alter the phase state of **1b** at will suggests the possibility of exploiting this remarkable behaviour in other non-porous organic and metal–organic frameworks for carbon-capture and hydrogen-storage applications. The capture of CO_2 from large, industrial, power or synfuel plants will require materials that are simultaneously an order of magnitude larger and an order of magnitude cheaper ($5/ton of captured CO_2). Hence, there is a critical need for alternative materials for CO_2 capture that have high adsorption capacity, selectivity and rates of regenerability at an economically viable cost. If successful, some of these materials (organic and metal coordination solids) could be used for carbon capture and sequestration applications[24]. It is reasonable to expect that this control of structure will lead to a control of function, and function is key to applications of organic solids.

Received 19 April 2007; accepted 14 November 2007; published 13 January 2008.

References

1. Atwood, J. L. *et al.* Guest transport in a nonporous organic solid *via* dynamic van der Waals cooperativity. *Science* **298**, 1000–1002 (2002).
2. Santoro, M. *et al.* Amorphous silica-like carbon dioxide. *Nature* **441**, 857–860 (2006).
3. Dalgarno, S. J. *et al.* Engineering void space in organic van der Waals crystals: Calixarenes lead the way. *Chem. Soc. Rev.* **36**, 236–245 (2007).
4. Mellot-Draznieks, C. *et al.* Very large swelling in hybrid frameworks: A combined computational and powder diffraction study. *J. Am. Chem. Soc.* **127**, 16273–16278 (2007).
5. Serre, *et al.* Role of solvent–host interactions that lead to very large swelling of hybrid frameworks. *Science* **315**, 1828–1830 (2007).
6. Yaghi, O. M. *et al.* Reticular synthesis and the design of new materials. *Nature* **423**, 705–714 (2003).
7. Zhao, X. *et al.* Hysteretic adsorption and desorption of hydrogen by nanoporous metal–organic frameworks. *Science* **306**, 1012–1015 (2004).
8. Kitagawa, S., Kitaura, R. & Noro, S. Functional porous coordination polymers. *Angew. Chem. Int. Edn* **43**, 2334–2375 (2004).
9. Zhang, J. P. *et al.* Temperature or guest induced drastic single-crystal-to-single-crystal transformations of a nanoporous coordination polymer. *J. Am. Chem. Soc.* **127**, 14162–14163 (2005).
10. Ripmeester, J. A. *et al.* What we have learned from the study of solid *p-tert*-butylcalix[4]arene. *Chem. Commun.* 4986–4996 (2006).

© 2008 Nature Publishing Group

11. Brouwer, E. B. *et al*. The complex relationship between guest-free polymorphic products and desolvation of *p-tert*-butylcalix[4]arene inclusion compounds. *Chem. Commun.* 1416–1417 (2003).
12. Udachin, K. A. *et al*. Pseudopolymorphism in the *p-tert*-butylcalix[4]arene–*n*-butylamine system: Directing the structural motif. *Chem. Commun.* 2162–2163 (2002).
13. Thallapally, P. K. *et al*. Acetylene absorption and binding in a nonporous crystal lattice. *Angew. Chem. Int. Edn* **45**, 6506–6510 (2006).
14. Thallapally, P. K. *et al*. Organic crystals absorb hydrogen gas under mild conditions. *Chem. Commun.* 5272–5273 (2005).
15. Thallapally, P. K. *et al*. Crystal engineering of nonporous organic solids for methane sorption. *Chem. Commun.* 4420–4421 (2005).
16. Thallapally, P. K., McGrail, P. B. & Atwood, J. L. Sorption of nitrogen oxides in a nonporous crystal. *Chem. Commun.* 1521–1523 (2007).
17. Enright, G. D. *et al*. Thermally programmable gas storage and release in single crystals of an organic van der Waals host. *J. Am. Chem. Soc.* **125**, 9896–9897 (2003).
18. Brouwer, E. B. *et al*. Solid-state NMR and diffraction studies of *p-tert*-butylcalix[4]arene.nitrobenzene.xenon. *Chem. Commun.* 939–940 (1997).
19. Kondo, A. *et al*. Novel expansion/shrinkage modulation of 2D layered MOF triggered by clathrate formation with CO_2 molecules. *Nano Lett.* **6**, 2581–2583 (2006).
20. Bradshaw, D., Warren, J. E. & Rosseinsky, M. J. Reversible concerted ligand substitution at alternating metal sites in an extended solid. *Science* **315**, 977–980 (2007).
21. Polson, J. M., Fyfe, J. D. D. & Jeffrey, K. R. The reorientation of t-butyl groups in butylated hydroxytoluene: A deuterium nuclear magnetic resonance spectral and relaxation time study. *J. Chem. Phys.* **94**, 3381–3384 (1991).
22. Christian, J. W. *The Theory of Transformations in Metals and Alloys* (Pergamon, Oxford, 1981).
23. Kumagai, H. *et al*. Facile synthesis of *p-tert*-butylthiacalix[4]arene by the reaction of *p-tert*-butylphenol with elementary sulfur in the presence of a base. *Tet. Lett.* **38**, 3971–3972 (1997).
24. Department of Energy. *A Research Needs Assessment for the Capture, Utilization and Disposal of Carbon Dioxide From Fossil Fuel-Fired Power Plants* 61–80, DOE/ER-30194 (Massachusetts Institute of Technology, Cambridge, 1993).

Acknowledgements

This work was supported in part by Laboratory Directed Research and Development funding. In addition, portions of the work were supported by the US Department of Energy, Office of Energy Efficiency and Office of Fossil Energy. The Pacific Northwest National Laboratory is operated by Battelle for the US Department of Energy under Contract DE-AC05-76RL01830. We thank P. F. Martin and S. D. Barton for gas sorption and solid-state nuclear magnetic resonance measurements. We also thank of one of the referees for thoughts about the mechanism.
Correspondence and requests for materials should be addressed to P.K.T. or J.L.A.
Supplementary Information accompanies this paper on www.nature.com/naturematerials.

Author contributions

P.K.T. and J.L.A. analysed and interpreted the data from H.T.S. and J.T. H.T.S. and J.T. carried out powder diffraction and single-crystal diffraction experiments. P.K.T., B.P.M., S.J.D. and J.L.A. wrote the paper.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

© 2008 Nature Publishing Group