Engineering void space in organic van der Waals crystals: calixarenes lead the way

Scott J. Dalgarno,[a] Praveen K. Thallapally,[b] Leonard J. Barbour*[c] and Jerry L. Atwood*[a]

Received 12th October 2006
First published as an Advance Article on the web 2nd January 2007
DOI: 10.1039/b606047c

Seemingly non-porous organic solids have the ability for guest transport and have also been shown to absorb gases, including hydrogen, methane and acetylene, to varied extents. These materials also show potential for gas separation technology, display remarkable water transport through hydrophobic crystals, and clearly show that molecules within crystals are capable of cooperating with guests as they move through non-porous environments. This work is presented within a broader topic which also encompasses crystal engineering and (microporous) metal-organic frameworks (MOF's).

The impending energy crisis and related global pollution issues have inspired the investment of much effort towards the discovery of new materials for gas storage and sequestration. In this regard, many researchers are focusing their efforts on the design and construction of novel porous materials with large void spaces that can accommodate volatile molecular species (*e.g.* energy carriers such as hydrogen gas). A significant target is the 6.0 weight percentage (wt%) storage of H_2, set out by the U.S. Department of Energy (DOE) for the development of H_2 fuelled transportation by 2010, although these targets are set somewhat higher for the future.[1] Thus the development of a material that would store this amount of hydrogen at room temperature would no doubt generate enormous commercial and industrial interest.

The primary purpose of this tutorial review is to describe our own recent work in the area of guest transport and storage using porous organic solids. The remarkable phenomenon of crystal porosity is attracting increasing attention, and we aim to describe this work in the context of other materials that are used for guest storage. We begin by describing some of the tremendous recent advances in the area of crystal engineering, with particular reference to the development of microporous coordination networks (or metal-organic frameworks, commonly referred to as MOF's). These topics are too expansive to cover comprehensively in this tutorial review and we have therefore selected a limited number of key references that outline recent progress in the field. Typically these are themselves reviews that cover vast contributions by individual research groups involved in these areas of research (and that cite all the relevant literature from other research groups). We then describe our own work with calixarenes in the context of

Scott J. Dalgarno

Scott J. Dalgarno was born in Aberdeen, Scotland in 1978. He obtained his MChem and PhD at The University of Leeds, working with Colin Raston and Michaele Hardie, on molecular capsules and coordination networks based on the self-assembly of the p-sulfonatocalix[4,5,6,8]arenes. He graduated in 2004 and till present has been a postdoctoral research fellow in the Atwood research group at the University of Missouri-Columbia, working on the self-assembly of pyrogallol[4]arenes and the inclusion and characterisation of other molecules within these very large capsular assemblies.

Praveen K. Thallapally

Praveen K. Thallapally was born in Khajipally, Medak, India in 1973. He obtained his PhD in 2003 from the University of Hyderabad working with Gautam R. Desiraju on crystal engineering and polymorphism of C_3 symmetrical molecules. After graduation he moved to the Atwood research group at the University of Missouri-Columbia (UMC) as a postdoctoral research associate where he investigated gas storage and separation using porous and nonporous calixarene derivatives, self assembled pyrogallol[4]arenes using hydrogen and metal coordination bonds. In 2006 he moved to Pacific Northwest National Laboratory (PNNL) as a Sr. Research Scientist. His research interests include gas storage and separation, gas hydrates, and solid-state chemistry.

---

[a] Department of Chemistry, University of Missouri-Columbia, 601 S. College Ave., Columbia, MO 65211, USA. E-mail: AtwoodJ@missouri.edu
[b] Pacific Northwest National Laboratory, MS K6-81, 902 Batelle Blvd., Richland, WA 99352, USA
[c] Department of Chemistry, University of Stellenbosch, Matieland 7602, South Africa

crystal engineering of porosity and highlight the recent literature and developments.

Crystal engineering

Crystal engineering has come to the fore in recent years with several journals now being devoted to the subject. The concept has been known for some time, and the use of the theory in important areas such as novel pharmaceutical discovery/development is attracting increasing attention.[2] For a recent, concise, and general review of crystal engineering, the reader is directed to a Focus article by Braga.[3] In this report, the author addresses the question, "Crystal engineering, Where from? Where to?" In terms of the "where from?", some work dating back to the 1990's is cited, but the concept is also proposed to have existed from around 1955—rather than the more commonly referenced year of 1971—and the author also describes other important works through the 70's and 80's. By far the most important aspect of this article, in the context of the current review, is the focus it places on the significance of the supramolecular perception as a paradigm shift for crystal engineering. What about the 'where to?' While crystal engineering has its roots primarily in organic chemistry (see below for an example) the article by Braga shows how this field has developed into periodical coordination chemistry and the discovery of whole new classes of materials.

One of the most promising areas of research in this field has been the formation and structual identification of MOF's. These materials are rigid, offer structural and thermal stability, and are ideal for solvent removal to generate void space that is suitable for guest storage. The importance of this field is demonstrated by the fact that the reader can typically find a new MOF report on a near daily basis in journals commonly subscribed to by the majority of academic institutions. The predicted construction or synthesis of MOF's lies well within the realms of crystal engineering, and single crystal X-ray diffraction is invaluable in elucidating the salient structural features of the materials and characterising void spaces.

Microporous coordination networks: MOF's through crystal engineering

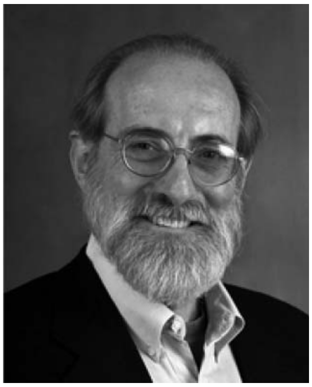
As is the case for crystal engineering with organic molecules (only), searches for articles in the areas of microporous coordination networks and MOF's will return equally as many diverse reports from the literature if not more. Therefore, we will focus again on select articles, but will examine these areas further as they have gained much interest at the highest levels in recent times.

As suggested in the previous paragraph, the formation of coordination polymers (or networks) is an expansive topic that encompasses the formation of porous materials, highly connected materials and interpenetrated nets, or networks with unusual topologies. To demonstrate the versatility associated with this area of chemistry, we have selected an Account of high connectivity materials by Schröder, Hubberstey, Champness and co-workers,[4] and a review of functional porous coordination polymers by Kitagawa and co-workers.[5] Both articles discuss how the majority of coordination polymers reported to date are formed by building-block methodology through designed motifs. This typically involves the combination of metal centres with bridging organic ligands that results in the formation of networks that can have anions (and or solvent molecules) residing in interstitial space, although anions can also be coordinating. Metal centre geometry therefore plays a large part in determining the topology of the resultant networks, although bridging ligand shape is also very important.

In the Account, the authors cover many other important works, and their own extends into high connectivity materials by combining lanthanide(III) metal centres (that have high coordination numbers) with 4,4′-bipyridine-*N,N*′-dioxide.[4] This ligand forms different types of coordination with lanthanide(III) centres (Fig. 1), and these materials are placed amongst a number of other coordination polymers in order to describe these collective examples in terms of 4^4- and 6^3-subnet tectons (topological classifications based on the angles present at each node in a specific network). The authors' extensive

Leonard J. Barbour

Len Barbour was born in Pretoria, South Africa in 1965. In 1994 he obtained his PhD under the supervision of Luigi Nassimbeni at the University of Cape Town where he investigated thermodynamic and structural aspects of solvate formation and decomposition. He then undertook a postdoctoral fellowship with Jerry Atwood at the University of Missouri-Columbia (UMC) where he continued to pursue his interest in supramolecular chemistry. In 1997 he was appointed as Research Assistant Professor at UMC but in 2003 he moved back to South Africa as an Associate Professor at the University of Stellenbosch. He was promoted to Professor of Chemistry in 2005 and his research interests include the study of solid-state phenomena with particular emphasis on the design and characterisation of porous materials for gas sorption.



Jerry L. Atwood

Jerry L. Atwood was born in Missouri, where he received a BS in 1964. After receiving his PhD from the University of Illinois, in 1968, while working in the lab of Galen D. Stucky, he accepted a position as Assistant Professor at the University of Alabama, where he rose to the position of University Research Professor in 1987. He then moved to the University of Missouri-Columbia in 1994, where he is currently a Curators' Professor and Chair of Chemistry. His research interests include molecular capsules and aspects of porosity in the solid state.

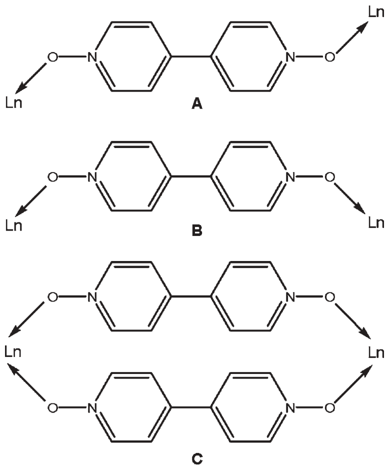


Fig. 1 Different coordination modes formed by 4,4′-bipyridine-*N,N′*-dioxide. The ligand can form anti (A), syn (B), and double bridged (C) arrangements that result in the formation of highly connected coordination networks. (Reproduced with permission from ref. 4. Copyright 2005 the American Chemical Society.)

works with this system serve as a good example of how particular reaction conditions can dramatically affect the resulting coordination network. More importantly however, the Account presents a simpler approach to the description and visualisation of complex coordination networks, and gives the reader a noteworthy introduction to network topologies.

Although the review by Kitagawa covers some areas concerning coordination polymers that are also elaborated here in association with other research groups, the article also covers topics such as 'connectors and linkers', 'design and motifs', 'porous structures' and 'functions of coordination polymers'.[5] With respect to 'connectors and motifs', Kitagawa has used the 'pillared layer' to form coordination polymers that 'expand and shrink', and that also show selective guest sorption.[6] Similar studies by Kim and co-workers have employed 'paddle wheels' (zinc carboxylate clusters) with 1,4-diazabicyclo[2.2.2]octane (DABCO) linkers to construct pillared square grid nets.[7,8] These materials show unusual dynamic behaviour depending on guest molecules,[8] and have implications for hydrogen storage, although the H_2 uptake is only ~2 wt% at 78 K.

Recent developments in metal-organic framework chemistry have proven to be particularly important in the use of robust materials for guest storage. Of the many research groups involved in this field, Yaghi and co-workers have arguably been one of the most prolific, and instead of focusing on the synthesis of coordination networks with metal cations and organic ligands such as 4,4′-bipyridine, they employed multidentate ligands such as carboxylates to consistently arrive at more rigid networks. This strategy results in *neutral* frameworks owing to the metal cations and the anionic nature of the ligands and their extensive studies are comprehensively reviewed in an Account on Modular Chemistry with Secondary Building Units (SBU's), as well as a Mini review on strategies for hydrogen storage in MOF's.[9,10]

SBU's—metal carboxylate clusters—can be used to design highly porous and robust MOF's. Simply, SBU's are modelled on the basic copper acetate and zinc acetate motifs (for example) that have D_{4h} and T_d symmetry respectively.[9] These clusters can then readily be linked in any number of ways by varying the organic ligand possessing the carboxylate functionality used in the MOF synthesis (Fig. 2). This modular approach has allowed the authors to synthesise and characterise many tailored MOF's by employing these fundamental shapes in the prediction of topology prior to ligand selection. Additional merits of these materials lie in the typically high percentage yields found during synthesis, and the fact that solvent molecules can easily be removed to afford porosity. The degree of porosity is controllable through catenation (which is also dependent on the modular approach), and this can have implications in guest selection for particular pore sizes.[9] With respect to H_2 storage with MOF's, the authors summarise a number of materials that were studied under various conditions to give the reader an overview of work performed in this area thus far.[10] They also stress that only a fraction of the known 2-D and 3-D MOF's have been examined for properties such as H_2 storage media. Schröder, Champness, Hubberstey and co-workers are also active in this area and have recently reported new MOF's that store 6 wt% H_2 at 78 K and pressures below 80 bar.[11]

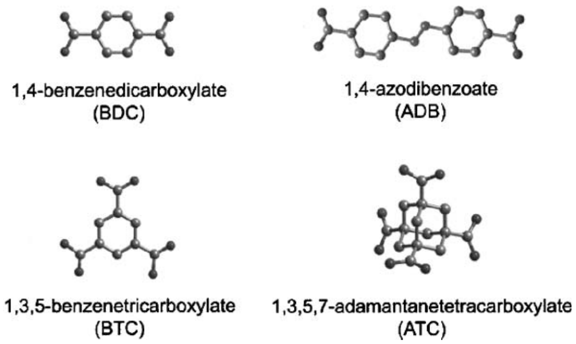


Fig. 2 Examples of polytopic ligands that can be used to taylor MOF construction. (Reproduced with permission from ref. 9. Copyright 2001 the American Chemical Society.)

More recent developments in the synthetic aspect of this area also include the formation of zeolite-like metal-organic frameworks (ZMOF's) that are built from tetrahedral building units (TBU's).[12] Eddaoudi and co-workers show how these materials have extra-large cavities (significantly larger than MOF's), and that these voids may be used as (host–guest)–guest sensors, for example (Fig. 3). Porous crystalline covalent organic frameworks (COF's) have also recently been synthesised by Yaghi and co-workers. These materials have large pore volumes, can display high thermal stability, and have high surface areas.[13]

Porosity

Before proceeding with a discussion of porosity in van der Waals crystals, it is important to briefly discuss the term and its proper use. Here the reader is directed to a recent Focus Article by Barbour, in which three different kinds of porosity are described: conventional porosity, porosity "without pores" and virtual porosity.[14] Conventional porosity applies to

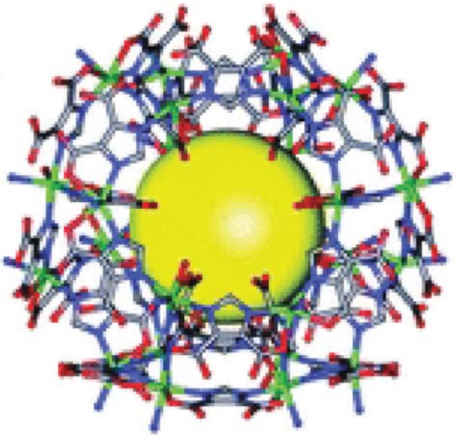
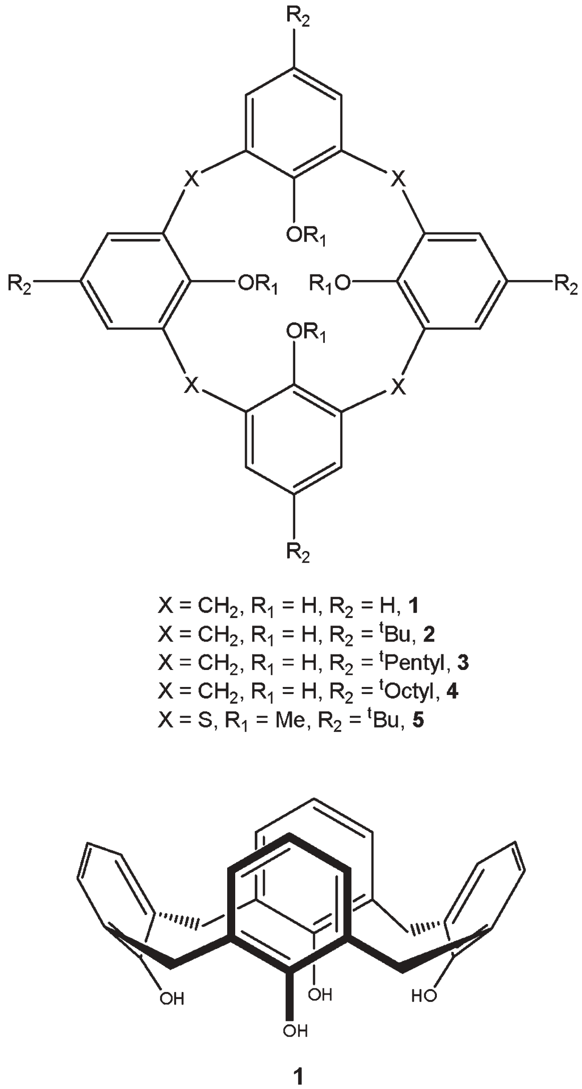


Fig. 3 The *sod*-ZMOF that is constructed from tetrahedral building units (TBU's). The large volume of the structure is represented by the yellow spheroid. (Reproduced with permission from ref. 12. Copyright 2006 the Royal Society of Chemistry.)

materials such as zeolites or MOF's which retain structural rigidity upon guest removal. Hence, permeability is retained and it is easy to rationalise from the atomic coordinates of the host framework why the material is porous. Porosity "without pores" relates to seemingly non-porous materials that possess void spaces accessible to guest molecules as evidenced by guest uptake experiments; this topic is specifically addressed in the present article in the context of calixarenes that exhibit this remarkable behaviour. The term "virtual porosity" refers to the unfortunate tendency of misrepresenting crystal structures as being porous either by deleting guest molecules from lists of atomic coordinates, or by visualising packing diagrams in the stick or ball-and-stick metaphor. In many of these cases no supporting evidence is presented to demonstrate that the material in question is indeed permeable. Here we wish to re-emphasise that the term should be used in the proper context so as not to detract from the true importance of an apparently extraordinary phenomenon.

Calix[*n*]arenes

One of our main research thrusts involves crystal engineering with calix[*n*]arenes, macrocyclic molecules that are easily functionalised at either the upper or lower rim of the molecular skeleton.[15] Depending on this functionalisation, conformational control over the skeleton can be achieved although the cone conformation is common when the lower rim comprises hydroxyl functionality (Fig. 4). While we use these molecules in many different ways (when functionalised appropriately), we have found the simple calix[4]arenes to display the most remarkable properties in van der Waals crystals. We will therefore limit much of our discussion to five such molecules: calix[4]arene (or *p*-H-calix[4]arene),[16] *p*-*tert*-butylcalix[4]arene (TBC4),[17–22] *p*-*tert*-pentylcalix[4]arene,[21] *p*-*tert*-octylcalix[4]arene,[21] and 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetramethoxy-2,8,14, 20-tetrathiacalix[4]arene[23] (**1–5** respectively, Fig. 4). More recent results by Ananchenko and co-workers,[24–26] that have also focused on this phenomenon (albeit with different calix[4]arenes), will also be discussed in the context of our studies, as will a recent article by Sozzani and co-workers,[27] on methane and carbon dioxide storage in a porous van der Waals crystal.



$X = CH_2, R_1 = H, R_2 = H$, **1**
$X = CH_2, R_1 = H, R_2 = {}^tBu$, **2**
$X = CH_2, R_1 = H, R_2 = {}^tPentyl$, **3**
$X = CH_2, R_1 = H, R_2 = {}^tOctyl$, **4**
$X = S, R_1 = Me, R_2 = {}^tBu$, **5**

Fig. 4 Schematic diagrams of calix[4]arenes **1–5**. The typical cone conformation adopted by calix[4]arenes with 'lower rim' OH functionality is also shown for **1**.

Interstitial voids: calix[4]arene (1)

Molecules in the organic solid state are usually closely packed[28] and crystals possessing interstitial lattice voids greater than ~25 Å^3 are generally considered to be rare. Our current interest in crystals that do not always obey the tenets of close-packing originated with a study of simple calix[4]arene solvates.[16] A CSD search reveals that two acetone solvates of **1** are known.[29] One of these solvates (**1a**) is composed of a 1 : 1 host : guest adduct in which the acetone molecule inserts one of its methyl groups into the relatively small calixarene cavity. The packing arrangement is dense but otherwise unremarkable. The second solvate consists of a trigonal 3 : 1 host : guest adduct (**1b**) in which three host molecules form a mutually self-included van der Waals trimer

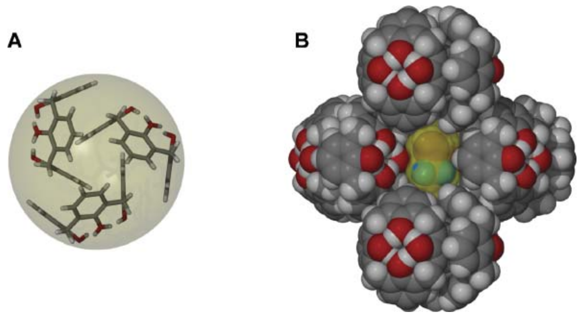


Fig. 5 Two views of the near-spheroidal trimeric arrangement formed by **1** in the solid state ($\mathbf{1_3}$).[16] A) The stick representation shows the self-inclusion of each molecule of **1** within each neighbouring cavity in $\mathbf{1_3}$. B) Space filling representation of the occupation of an interstitial void in the host lattice by CF_3Br. The void (yellow semitransparent surface) is generated by the packing of neighbouring $\mathbf{1_3}$ assemblies and only van der Waals contacts are observable between the host trimers and guest atoms. Colours: gray, C; white, H; red, O; blue, F; brown, Br. (Reproduced with permission from ref. 16. Copyright 2002 AAAS.)

with near-spherical shape (Fig. 5a). Indeed, these trimers pack as a hexagonal close-packed (hcp) arrangement of spheres even though small deviations from perfect spherical geometry exist in the form of protrusions and indentations. Consider the hcp arrangement of only five spheres situated at the vertices of a regular triginal bipyramid: in a lattice composed of perfect spheres this arrangement would form two tetrahedral holes linked by a relatively narrow channel. However, in **1b** the geometrical irregularities of the calixarene trimer result in significant widening of this channel such that the two tetrahedral holes merge to form a single lattice void of approximately 153 Å^3. In **1b** the void is occupied by a disordered acetone molecule and a further search of the CSD reveals that the identical host packing mode is adopted by several other simple solvates.

Thermogravimetric analysis (TGA) of **1a** (Fig. 6) shows that two thirds of the acetone molecules can be removed with an onset temperature of *ca.* 70 °C, and that the remaining acetone can only be removed at the surprisingly high temperature of *ca.* 225 °C to give the pure apohost phase **1c**. X-ray powder diffraction confirms that loss of two thirds of the acetone from **1a** results in rearrangement of the structure to form **1b**, and that the structure of **1c** is almost identical to that of **1b**. Retention of acetone guest molecules to a temperature of 225 °C implies remarkable stability of the inclusion compound **1b** and similar results were obtained for other solvates with the same host packing mode. We noted from the TGA results that the pure host compound sublimes at *ca.* 270 °C. Since the structure of **1c** had not as yet been determined, we grew crystals of the apohost phase by sublimation of **1** at 270 °C under vacuum. Single-crystal diffraction studies revealed that the structure of **1c** is indeed the same as that of the host lattice of **1b**. Since the crystals were grown under vacuum conditions, the interstitial lattice voids are empty.

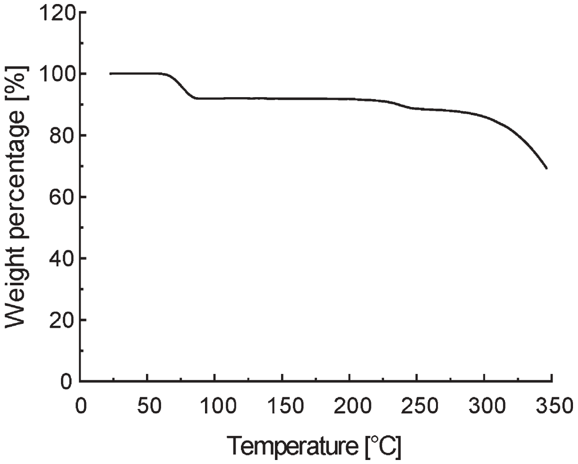


Fig. 6 Thermogram of the acetone solvates of **1** showing loss of two thirds of the acetone guest molecules at *ca.* 70 °C and the remaining third at *ca.* 225 °C.

The remarkable thermal stability of **1b** and analogous solvates is most likely due to the fact that the host packing arrangement after guest-loss is the same as before. Thus there appears to be no energetic advantage in giving up the guest molecules. We therefore reasoned that, in its trigonal form, **1** should be capable of retaining even highly volatile gas molecules. Although **1** has low solubility in condensed volatile freons and halons, we noted that **1c** could be crystallised from a solution of **1** in toluene (the latter is too large to be accommodated in the lattice void). Consequently, it was possible to incorporate guests such as CF_3Br, C_2F_6 and CF_4 by co-dissolving these gases with **1** in toluene. The presence of freons and halons was observable by single crystal X-ray diffraction studies (*e.g.* Fig. 5b), ^{19}F NMR spectroscopy, and TGA.

It was also possible to effect a solid–solid phase-transformation from the non-hcp acetone solvate to the hcp gas-included phase. This was achieved by heating crushed crystals of the acetone solvate at 50 °C in a steel pressure vessel in the presence of gas. Analysis of the resulting crystalline material confirmed the successful phase transformation and near-stoichiometric incorporation of the freon within the hcp lattice. This method was also used to entrap methane within the lattice voids and thermogravimetric analysis shows stabilisation of this gas in the solid to a temperature of 320 °C above its normal boiling point. Close inspection of the host packing arrangement shows that no pores are present and it is thus easy to rationalise why the guest molecules cannot escape without disassembly of the host lattice, which only occurs at relatively high temperature.

Guest transport in a seemingly nonporous organic solid; *p-tert*-butylcalix[4]arene (TBC4, 2)

TBC4 is well known in supramolecular chemistry not just as a useful host, but also as a key synthetic platform for the synthesis of numerous other functionalised calix[4]arenes.[15] Well over 800 research articles have been reported on **2** and yet it continues to display new, interesting and unique phenomena in the organic solid state. Pure TBC4 forms quite distinct polymorphs, depending on crystallisation conditions.[18,30,31] A high-density polymorph **2a** was grown from a solution of **2** in tetradecane which had been heated for seven hours. The structure of **2a** consists of an efficiently packed (packing

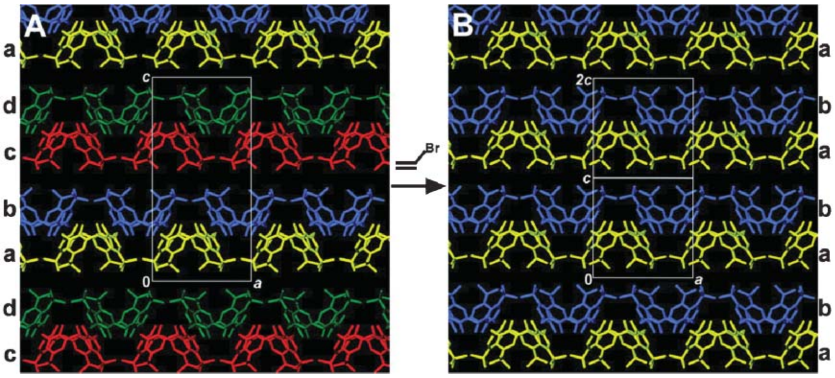


Fig. 7 The single-crystal-to-single-crystal phase transformation observed in a sublimed crystal of **2** after submersion in vinyl bromide.[17] The two forms of the bi-layer arrangement have similar unit cell axes, and the phase transformation results in a change from **ab/cd** to **ab/ab** packing in adjacent bi-layers. (Reproduced with permission from ref. 17. Copyright 2002 AAAS.)

efficiency = 0.67) arrangement of calixarene dimers in which each calixarene inserts one of its *tert*-butyl groups into the cavity of its counterpart.[30]

Sublimation of **2** under vacuum at 280 °C results in the growth of single crystals of a low density polymorph **2b** in which the molecules are arranged to form bi-layers. In this arrangement, the empty cavities belonging to two calixarenes embedded in neighbouring bi-layers overlap partially to form a "skewed capsule" (Fig. 7A)[17] with an approximate free volume of 235 Å^3. This results in a relatively low packing efficiency of 0.59 for the material. Although the two calixarene molecules that primarily form the capsule are not perfectly eclipsed, potential channels leading to the void space are blocked by *tert*-butyl groups of neighbouring molecules. After soaking a single crystal of **2b** in vinyl bromide at −5 °C for 15 minutes, further X-ray diffraction studies show that the material has undergone a single-crystal to single-crystal phase transformation from an **ab/cd** type to **ab/ab** type bi-layer arrangement (Fig. 7B).[17] A remarkable feature of this transformation is that even though neither phase is porous, the cavity of each TBC4 in the **ab/ab** type bi-layer is occupied by a molecule of vinyl bromide, with resulting packing efficiency of 0.64. From this evidence it is clear that cooperative effects between neighbouring TBC4 molecules *must* occur to allow the vinyl bromide to permeate through the seemingly nonporous material, thereby causing adjacent bi-layers to shift by approximately 5.9 Å whilst retaining monocrystallinity. Notably, both phases have closely related unit cell dimensions and it was also shown that both phases can co-exist in the same crystal by halting the diffusion process after approximately 5 minutes. Examination of a 1 : 1 **2** : toluene adduct under controlled heating showed a more remarkable single-crystal to single-crystal phase transformation in which TBC4 layers slide along one another by approximately 9 Å with calixarene molecules rotating by 38° relative to neighbouring bi-layers.

Gas separation and storage with calix[4]arenes: TBC4, 2

In order to probe the energetics of guest uptake by **2b**, nitrobenzene was added to both the sample and reference pans of a differential scanning calorimeter (DSC). After allowing the temperature of the sample chamber to equilibrate, crystals of **2b** were dropped into the sample pan and the heat-flow profile recorded (Fig. 8). The guest-uptake process was expected to yield a large exothermic response in the thermogram. Indeed, the initial trend was exothermic but the exotherm was almost immediately swamped by a large endothermic peak. Although counter-intuitive, these results can now be explained owing to our current understanding of the processes involved.

Upon immersion of the crystals in nitrobenzene, the immediate appearance of bubbles indicated the presence of volatile species (Fig. 9). A single crystal of **2b** was left exposed to the atmosphere for two days, after which X-ray diffraction studies showed significant residual electron density in the TBC4 cavity and that the packing arrangement of the calixarene molecules is no different from that of the freshly sublimed material.[19] Given that the crystals were prepared *in vacuo*, this implies that the material absorbs air into the 235 Å^3 cavities despite the seemingly nonporous nature of the structure. A manometric system was constructed in order to measure sorption isotherms for a range of gases. A systematic study of the sorption of N_2, O_2, and CO_2 introduced to **2b** at an approximate initial pressure of 700 Torr shows that the gases are absorbed to varied extents (Fig. 10A). The sorption

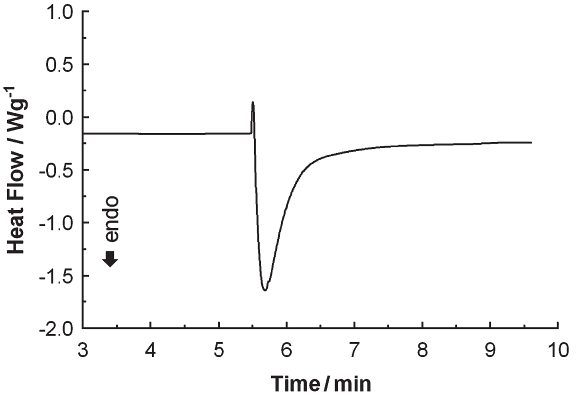


Fig. 8 Isothermal DSC trace for the inclusion of nitrobenzene into the TBC4 lattice. Solutions (30 μl) of nitrobenzene saturated with TBC4 (to minimize contributions from evaporation) were added to both the sample and reference pans and allowed to equilibrate at 23 °C for about 5.5 minutes. Crystals of TBC4 (2.34 mg), also equilibrated at 23 °C, were then added to the sample pan.

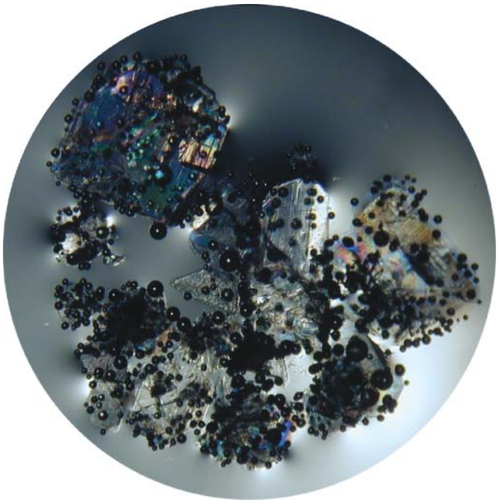


Fig. 9 Crystals of sublimed TBC4 are immersed in nitrobenzene. Air bubbles immediately begin to emanate from the crystals as nitrobenzene enters the lattice, expelling the gas.

of CO_2 is more rapid than that of N_2 and O_2, and the CO_2 occupancy in the cavities was found to be 80% at just one atmosphere (atm) of pressure, although this can be increased to 100% at just 3 atm. Disappointingly, no measurable sorption of H_2 gas at pressures reaching 7 atm was observed. However, we noted that the currently employed production process of 95% of the world's H_2 is hampered by impurities such as CH_4, CO, H_2O and, particularly, CO_2. We exposed crystals of **2b** to a 3 : 1 CO_2 :H_2 gas mixture and, using gas chromatography (Fig. 10B), showed that CO_2 can be efficiently removed from such a mixture to afford a hydrogen-rich supernatant gas.

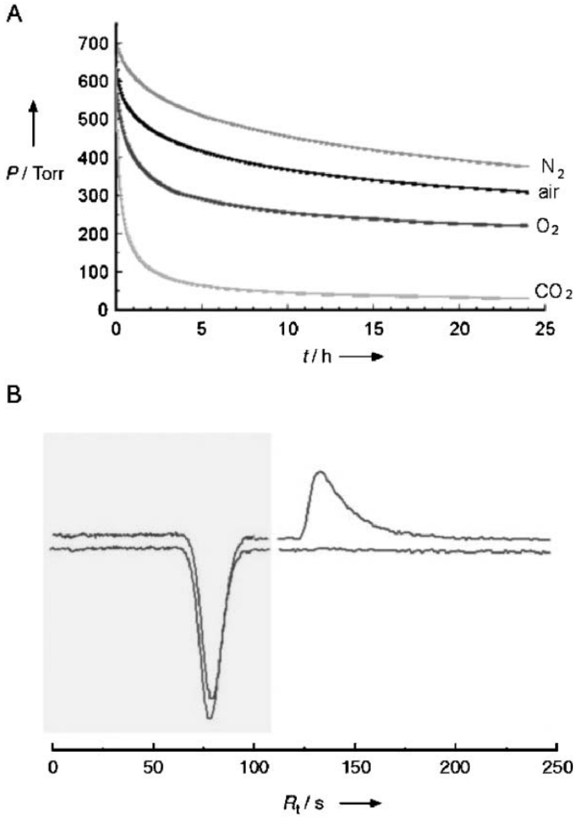


Fig. 10 Diagrams of A) gas sorption isotherms for sublimed **2**, and B) a gas chromatogram showing the purification of a CO_2/H_2 gas mixture using sublimed **2**. In B), the hydrogen peak (in shaded area) is unchanged, whilst the CO_2 peak is completely diminished, thereby demonstrating that sublimed **2** can be used in the purification of H_2 gas mixtures. (Reproduced with permission from ref. 19. Copyright 2004 Wiley.)

The successful sorption of the above mentioned gases (in sublimed **2**) prompted further examination of such capabilities of the material towards other gases that include methane, hydrogen (at higher pressure) and acetylene.[19–22] It was assumed that, given the 100% occupancy of CO_2 within the TBC4 void, and the approximate dimensions of the gas (5.2 Å long, and 3.4 Å in diameter), such a void space could accommodate at least two molecules of methane based on its near isotropic shape and average diameter of 3.8 Å (Fig. 11). At a similar pressure of ~750 Torr, and at ambient temperature, **2b** was found to absorb methane gas such that 14% of the voids or capsules are occupied by two molecules of methane at 0.54 atm pressure.

Further study of H_2 sorption by sublimed **2** at higher pressure (34.5 atm) showed that under such conditions, the material *was* active and that hydrogen occupancy was

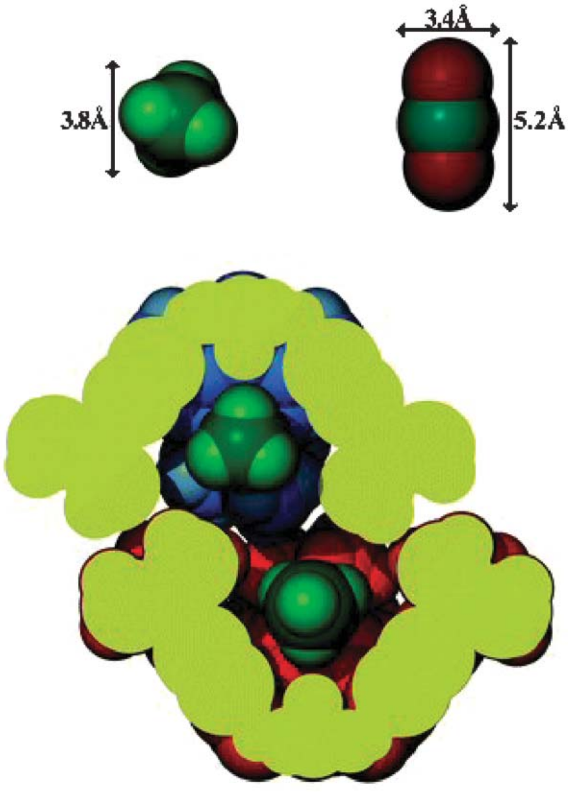


Fig. 11 Figure showing the approximate dimensions of methane (3.8 Å) and carbon dioxide (3.4 × 5.2 Å). A cross-sectioned capsule of sublimed **2** is shown, with two molecules of methane placed in the void space to convey the suitability of the environment for the gas. (Reproduced with permission from ref. 20. Copyright 2005 the Royal Society of Chemistry.)

0.2 wt%.[21] Although this is slightly disappointing in terms of generating a potential hydrogen storage material based on organic crystals, it does nevertheless demonstrate the principle and encourages future studies in this area.

The absorption of acetylene at an initial pressure ~800 Torr reached equilibrium after 3 h, and an occupancy study (% occupancy *vs* equilibrium pressure) revealed that the uptake of acetylene at STP is ~2% by weight.[22] This value corresponds to the complete filling of the void space in sublimed **2** at ~1 atm pressure, whereas 3 atm are required for the same phenomenon in the case of CO_2. Absorption and desorption isotherms for both CO_2 and acetylene show that at 100% occupancy (at 1 atm for acetylene and 3 atm for CO_2), the process of uptake and release is fast for CO_2 (Fig. 12). For acetylene, a hysteresis loop is observed for this process, indicating that the gas is stabilised in the void space generated in sublimed **2**.

Although it was not possible to observe the acetylene in X-ray diffraction studies, the stabilisation was confirmed when the material (previously subjected to an atmosphere of the gas) was studied using ^{13}C MAS NMR, which showed a characteristic peak for stored acetylene. Most importantly, in the context of guest storage, the calculated density of the stored gas at STP is approximately 0.18 g cm^{-3} which corresponds to stabilising acetylene at 18 MPa (90 times the compression limit for safe storage).

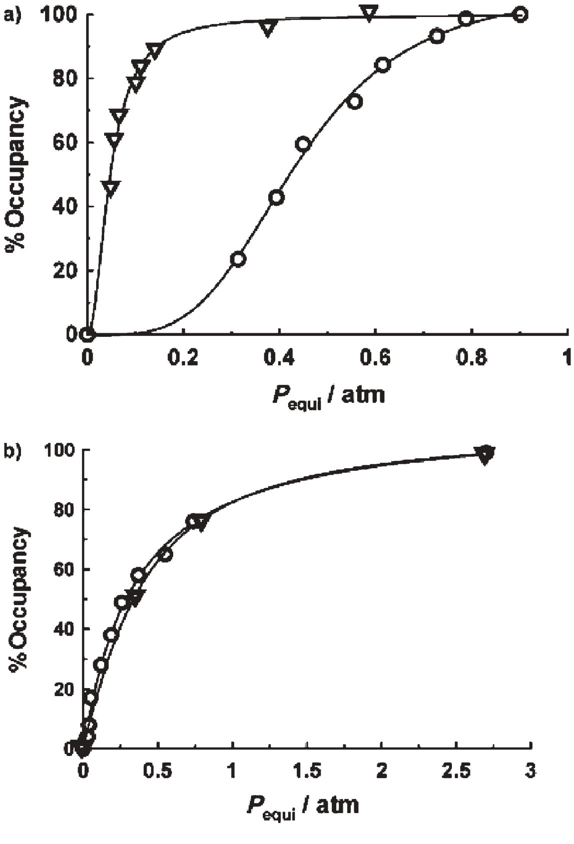


Fig. 12 Adsorption (circles) and desorption (triangles) isotherms of a) acetylene, and b) carbon dioxide. The 100% void occupancy by CO_2 was achieved at 3 atm pressure. (Reproduced with permission from ref. 22. Copyright 2006 Wiley.)

Gas storage by other calix[4]arenes; *p-tert*-pentylcalix[4]arene (3) and *p-tert*-octylcalix[4]arene (4)

Whilst studying the higher pressure absorption of H_2 by **2b**, sublimed samples of **3** and **4** were also examined for similar behaviour.[21] Sublimed crystals of **3** and **4** were studied using single crystal X-ray diffraction, which revealed structures very different to the low density polymorph found for **2**. Although the calixarene molecules **3** and **4** were not found to form guest-free capsules with a large internal void space, the molecular cavities and lattice structures were found to contain discrete void space volumes of ~110 and ~82.5 Å^3 respectively (Fig. 13). For **3**, the molecular cavity and interstitial lattice void spaces are connected, while for **4** the "free volume" is composed of two separate void spaces (~23.5 Å^3 from the molecular cavity and 59 Å^3 from the interstitial lattice void). These structures share a similarity with that of **2b** in that they are seemingly nonporous, but permeable.

The hydrogen storage capacity observed for these materials was similar to that of **2** (~0.2 wt%), but also hints at the potential for the use of organic materials for hydrogen sorption.

Water transport through a nonporous hydrophobic crystal: 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetramethoxy-2,8,14,20-tetrathiacalix[4]arene, 5

In keeping with our interest in the transport of guest molecules in single crystals, we extended our studies to the diffusion of water in seemingly nonporous hydrophobic single crystals.[23] Sublimation of **5** results in the formation of two types of single crystal, both of which were studied using X-ray diffraction,

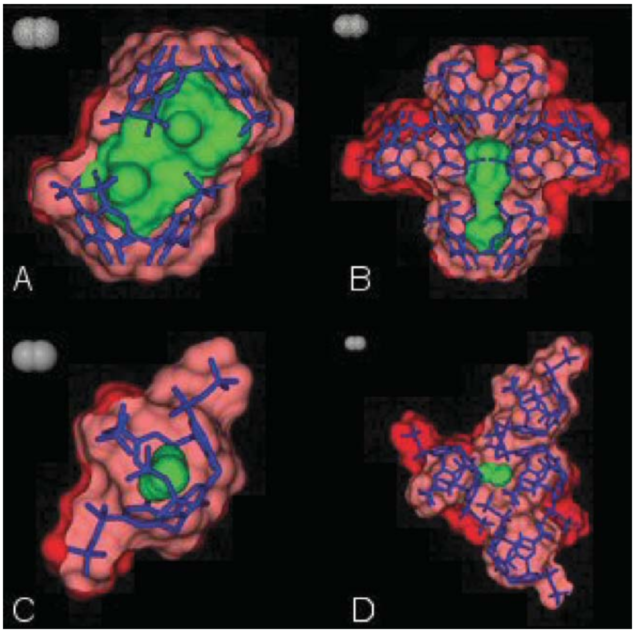


Fig. 13 Visualisations of the free void space present in the crystal structures of sublimed, **2** (A), **3** (B), and **4** (C and D). In order to give an idea of scale relative to each figure, a hypothetical H_2 molecule has been placed in the upper left hand corner of each. (Reproduced with permission from ref. 21. Copyright 2005 the Royal Society of Chemistry.)

and were found to be polymorphs of one another (type I and II), only one of which is of interest in the context of this section (type II). The type II polymorph contains two crystallographically unique molecules of **5** (**5a** and **5b**) which are in the 1,3-alternate conformation owing to the lower rim O–Me substitution (that disrupts the typical cone stabilising hydrogen-bonding motif found in lower rim hydroxyl analogues such as **1–4**). The result of this conformational distortion is that each calixarene possesses two small clefts, each bounded by two distal *tert*-butyl groups and two distal methoxy groups. Owing to crystallographic symmetry, **5a** has two unique clefts, one of which is significantly larger than the other. On the other hand, **5b** has two crystallographically equivalent clefts of equal size. Further expansion of the structure reveals that **5a** and **5b** stack in columns such that the clefts are entirely isolated

Upon immersing a previously studied type II crystal of **5** in water for 8 h, re-collection of X-ray diffraction data and subsequent structural solution reveals residual electron density in the larger of the two clefts of **5a**, and in both clefts of **5b**. The former was modelled with a site occupancy of one while the latter were modelled as being 50 : 50 disordered over the two equivalent sites. The presence of H_2O (in a 1 : 1 H_2O : **5** ratio) was confirmed by IR and TGA analysis.

An interesting point to note is that even though the structure does not appear to be porous, water molecules travel through the crystal and become lodged in the molecular clefts generated by the conformational distortion of **5**. Although it is difficult to arrive at a clear conclusion as to how the water molecules travel through the crystal, it seems plausible that the *p-tert*-butyl groups of **5** may rotate cooperatively to allow the guest transport to occur. This result suggests that classical views of water diffusion processes—through channels large enough to accommodate a water molecule (based on van der Waals diameter)—may be unsuitable at this scale, that crystals are not as impervious and rigid as expected, or that van der Waals forces can act more as accommodating factors rather than rigid barriers.

Guest transport and gas storage in other calix[4]arenes and molecular crystals (respectively)

Ananchenko and co-workers have recently focused their attention on the preparation of a new type of van der Waals dimeric capsule based on functionalised 'upper rim' calix[4]-arenes.[24–26] In their studies, the molecules in the capsule arrangement bear resemblance to the skewed capsule formed by sublimation of **2**, and solvent loss from the interior of the capsules within single crystals is observed (with preservation of monocrystallinity). From this observation, crystals of the capsules placed in a hot (70 °C) solution of dibenzyl ketone (DBK) underwent exchange of DBK for chloroform molecules on the interior of the capsules within single crystals, as monitored by X-ray diffraction and other techniques (Fig. 14).[24] These van der Waals capsules can be used for the phototransformation of stilbene and can be assembled with different alkanoyl functionality at the upper rim.[25–26]

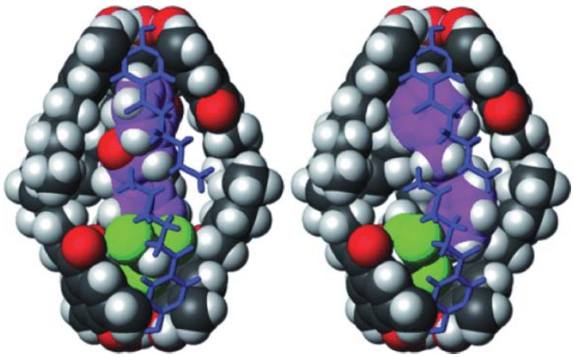


Fig. 14 Illustrations of van der Waals dimeric capsules formed from *p*-hexanoylcalix[4]arene. These views show capsules in which chloroform molecules have left the interior of the assembly, and have been replaced by dibenzylketone. (Reproduced with permission from ref. 24. Copyright 2006 Wiley.)

It should be noted that Sozzani and co-workers reported methane and carbon dioxide storage in a conventionally porous van der Waals crystal.[27] The authors show by single-crystal X-ray diffraction single crystals that molecular crystals of tris-*o*-phenylenedioxycyclotriphosphazene (TPP) contain empty hexagonal pores. The structure possesses significant free void space in the form of nanochannels (with a minimum diameter of 4.6 Å) which are suitable for gas sorption studies. The uptake of Ar, N_2, O_2, H_2, CH_4, and CO_2 was investigated, and the material was found to selectively absorb methane or carbon dioxide. Methane storage was reached up to 0.7 mol of methane per mol of TPP. Indeed, at 195 K and STP, methane uptake was 2.4 and 0.6 wt% respectively. Carbon dioxide uptake was found to be much higher (12 wt% at STP), and ^{13}C MAS NMR of the material exposed to either gas showed characteristic signals for each when stored in the sample. Examination of the NMR signal shifts was indicative of the environment experienced by the absorbed gas and allowed the authors to precisely define the interactions between the guest and the inner surface of the host.

Conclusions

Significant advances have been made towards developing materials that can store or transport guests to varied extents. In the combined areas of crystal engineering and MOF development, this has been realised predominantly by Yaghi and co-workers, but more recently by Schröder and co-workers in their recent work where they show a ~6 wt% H_2 storage at low temperature (77 K).[9–11] Eddaoudi and co-workers are taking the dimensions of these materials to new limits to afford materials with concomitant potential.[12] Although this storage limit is reaching the current target outlined by the DOE (at low temperature and pressures below 80 bar), the temperature issue remains a problem, and one that must be solved with these storage materials to render them suitable candidates for use in the transport industry.

With regard to calix[*n*]arenes, these simple materials show remarkable properties in their ability to cooperate within a single crystal to facilitate guest transport.[17] One of the most surprising examples of this is the notable transport of water molecules through a hydrophobic crystal.[23] Conventional wisdom dictates that this would not be plausible, yet the process is relatively rapid and must therefore be cooperative.

Recent work by ourselves[32,33] and others[24] in this field further demonstrates the concept, and our work on the storage of gases within cavities in seemingly non-porous TBC4 crystals provide further and continuing evidence for the phenomenon.

Acknowledgements

Owing to space restrictions we have not mentioned many contributions that are related to the topic of this tutorial review. These omissions do not serve as criticism of the work of others. Rather, we have attempted to provide pertinent and concise examples from our own work and these are placed in context by referring the reader to a small selection of reviews that highlight certain features of this fascinating area of research. We would like to thank our colleagues (past and present) for their contributions to this work, with particular thanks to Dr Agoston Jerga.

References

1 *Hydrogen, Fuel Cells & Infrastructure Technologies Program: Multi-Year Research, Development and Demonstration Plan*, U.S. Department of Energy, 2005, http://www.eere.energy.goc/hydrogenandfuelcells/mypp/.

2 P. Vishweshwar, J. A. McMahon, J. A. Bis and M. J. Zaworotko, *J. Pharm. Sci.*, 2006, **95**, 499.

3 D. Braga, *Chem. Commun.*, 2003, 2751 and references therein.

4 R. J. Hill, D.-L. Long, N. R. Champness, P. Hubberstey and M. Schröder, *Acc. Chem. Res.*, 2005, **38**, 337 and references therein.

5 S. Kitagawa, R. Kitaura and S.-I. Noro, *Angew. Chem., Int. Ed.*, 2005, **43**, 2334 and references therein.

6 T. K. Maji, K. Uemura, H.-C. Chang, R. Matsuda and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 3269.

7 D. N. Dybstev, H. Chun and K. Kim, *Angew. Chem., Int. Ed.*, 2004, **43**, 5033.

8 H. Chun, D. N. Dybstev, H. Kim and K. Kim, *Chem.–Eur. J.*, 2005, **11**, 3521.

9 M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keefe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319 and references therein.

10 J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4670 and references therein.

11 X. Lin, J. Jia, X. Zhao, K. M. Thomas, A. J. Blake, G. S. Walker, N. R. Champness, P. Hubberstey and M. Schröder, *Angew. Chem., Int. Ed.*, 2006, DOI: 10.1002/anie.200601991 and references therein.

12 Y. Liu, V. C. Kravtsov, R. Larsen and M. Eddaoudi, *Chem. Commun.*, 2006, 1488.

13 A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166.

14 L. J. Barbour, *Chem. Commun.*, 2006, 1163.

15 Z. Asfar and V. Bohmer, *Calixarenes 2001*, Kluwer Academic Publications, Dordrecht, 2001.

16 J. L. Atwood, L. J. Barbour and A. Jerga, *Science*, 2002, **296**, 2367.

17 J. L. Atwood, L. J. Barbour, A. Jerga and B. L. Schottel, *Science*, 2002, **298**, 1000.

18 J. L. Atwood, L. J. Barbour and A. Jerga, *Chem. Commun.*, 2002, 2952.

19 J. L. Atwood, L. J. Barbour and A. Jerga, *Angew. Chem., Int. Ed.*, 2004, **44**, 2948.

20 J. L. Atwood, L. J. Barbour, P. K. Thallapally and T. B. Wirsig, *Chem. Commun.*, 2005, 51.

21 P. K. Thallapally, G. O. Lloyd, T. B. Wirsig, M. W. Bredenkamp, J. L. Atwood and L. J. Barbour, *Chem. Commun.*, 2005, 5272.

22 P. K. Thallapally, L. Dobrańska, T. R. Gingrich, T. B. Wirsig, L. J. Barbour and J. L. Atwood, *Angew. Chem., Int. Ed.*, 2006, **45**, 6506 and references therein.

23 P. K. Thallapally, G. O. Lloyd, J. L. Atwood and L. J. Barbour, *Angew. Chem., Int. Ed.*, 2005, **44**, 3848.

24 G. S. Ananchenko, K. A. Udachin, A. Dubes, J. A. Ripmeester, T. Perrier and A. W. Coleman, *Angew. Chem., Int. Ed.*, 2006, **45**, 1585.

25 G. S. Ananchenko, K. A. Udachin, J. A. Ripmeester, T. Perrier and A. W. Coleman, *Chem.–Eur. J.*, 2006, **12**, 2441.

26 G. S. Ananchenko, K. A. Udachin, M. Pojarova, A. Dubes, J. A. Ripmeester, S. Jebors and A. W. Coleman, *Cryst. Growth Des.*, 2006, **6**, 2141.

27 P. Sozzani, S. Bracco, A. Comotti, L. Ferretti and R. Simunoti, *Angew. Chem., Int. Ed.*, 2005, **44**, 1816.

28 A. J. Kitaigorodsky, *Molecular Crystals and Molecules*, Academic Press, New York, 1973.

29 R. Ungaro, A. Pochini, G. D. Andreetti and V. Sangermano, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1979.

30 E. B. Brouwer, K. A. Udachin, G. D. Enright, J. A. Ripmeester, K. J. Ooms and P. A. Halchuk, *Chem. Commun.*, 2001, 565.

31 E. B. Brouwer, G. D. Enright, K. A. Udachin, S. Lang, K. J. Ooms, P. A. Halchuk and J. A. Ripmeester, *Chem. Commun.*, 2003, 1416.

32 L. Dobrzańska, G. O. Lloyd, H. G. Raubenheimer and L. J. Barbour, *J. Am. Chem. Soc.*, 2006, **128**, 698.

33 L. Dobrzańska, G. O. Lloyd, C. Esterhuysen and L. J. Barbour, *Angew. Chem., Int. Ed.*, 2006, **45**, 5856.