Organic crystals absorb hydrogen gas under mild conditions†

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We have studied the hydrogen sorption on three well-known organic hosts that possess vacant lattice voids large enough to accommodate H_2 molecules.

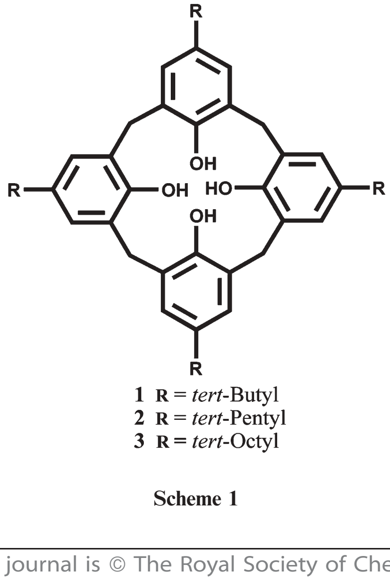
Hydrogen storage has been identified as one of the principal enabling technologies for the future widespread use of hydrogen fuel cells in stationary, portable and mobile applications.[1] Many different solutions to this problem, based on either chemical or physical sequestration, have been proposed. Each method has its own set of seemingly insurmountable technical challenges and no ideal solution has emerged thus far. Studies of physical adsorption onto nanoporous substrates initially yielded spectacular claims of hydrogen sorption capacities: 5 to 10 percent by weight (wt%) at room temperature and "moderate pressure" for single-walled carbon nanotubes (SWNTs)[2] and 4.5 wt% at 78 K and 20 atm for metal–organic frameworks (MOFs).[3] However, these claims were based on certain assumptions and have subsequently been adjusted to far more modest values.[4]

Much effort has been devoted to designing MOFs[5] but crystals composed of purely organic compounds have largely been ignored as gas sorption substrates since such molecules usually pack with efficiencies in the narrow range of 60 to 67%. However, a few exceptions to this phenomenon are known to exist. For example, an apohost phase of calix[4]arene, grown by sublimation at 300 °C under vacuum contains void space of ~ 153 Å^3 and it is possible to entrap and stabilize volatile gases such as freons, halons and methane in these interstices at temperatures well above their normal boiling points.[6]

Similarly, low-density apohost phases of sublimed *p-tert*-butylcalix[4]arene, **1** and *p-tert*-pentylcalix[4]arene, **2** (Scheme 1) possess lattice voids of ~ 235 and 110 Å^3, respectively.[7] Despite an apparent lack of porosity, these crystals readily and reversibly absorb volatile gases such as N_2, O_2, CO_2 and CH_4 at room temperature and pressures below three atmospheres.[8] Since no uptake of hydrogen gas was observed under these conditions, it was demonstrated that this material can be utilized to separate H_2 and CO_2 from a mixture of the gases.[8a] We now report the effect of increased pressure on the ability of these crystals to absorb hydrogen gas. Furthermore, we have investigated the hydrogen sorption properties of another related calix[4]arene compound, *viz.* *p-tert*-octylcalix[4]arene, **3**.

In order to record absorption isotherms, we constructed a device which has been described elsewhere.[8b] Crystals of **1** were grown by sublimation at 280 °C under vacuum and crushed. A sample of **1** (1.50 g) was sealed in the sample chamber (10.1 cm^3) which was then evacuated for 2 h at room temperature in order to remove any residual gas. Hydrogen gas was introduced into the sample chamber at an initial pressure of 34.5 atm and the pressure was recorded continuously. Fig. 1a shows a plot of pressure change with time as the hydrogen gas was absorbed by the sample. After approximately 25 min, equilibrium was reached at close to 31.0 atm. The net pressure change corresponds to a hydrogen occupancy of 0.2 wt% at equilibrium. Similar experiments were conducted using sublimed and crushed samples of **2** (1.37 g) and **3** (1.55 g) and the resulting isotherms are shown in Fig. 1b and 1c, respectively. At room temperature and equilibrium pressures of approximately 30.6 (after 40 min) and 33.1 atm, respectively, compounds **2** and **3** absorb hydrogen to give occupancies of 0.2 and 0.1 wt%, respectively.

The structures of **1** and **2** have already been described in some detail.[9] The calixarene molecules in **1** pack in one of the bilayer modes characteristic to these compounds.[10] Each cup-shaped host molecule faces a host molecule in an adjacent layer to form a lattice of offset face-to-face calixarene dimers. The cavities of the two molecules comprising each dimer combine to form a relatively large void of 270 Å^3 as shown in Fig. 2a.[11] Similarly, the molecules in **2** are also arranged to form bilayers, but in a mode quite dissimilar from that of **1**. The calixarene molecules are stacked in columns along [001] and each column consists of molecules facing



1 R = *tert*-Butyl
2 R = *tert*-Pentyl
3 R = *tert*-Octyl

Scheme 1

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† Electronic supplementary information (ESI) available: Crystal structure solution and refinement of **3**. See http://dx.doi.org/10.1039/b511341e

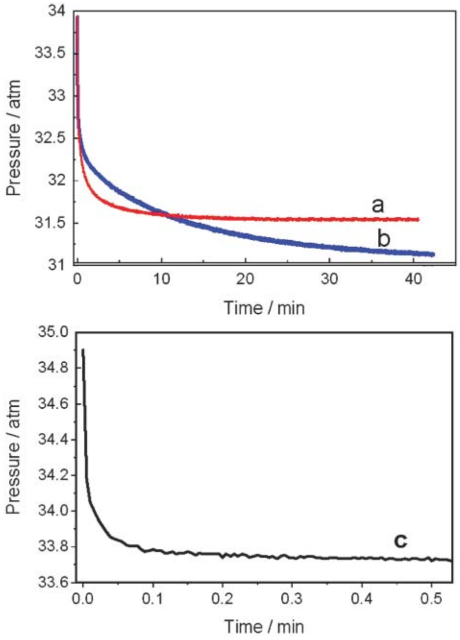

Fig. 1 Sorption isotherms for hydrogen uptake by compounds (a) **1**, (b) **2** and (c) **3**.

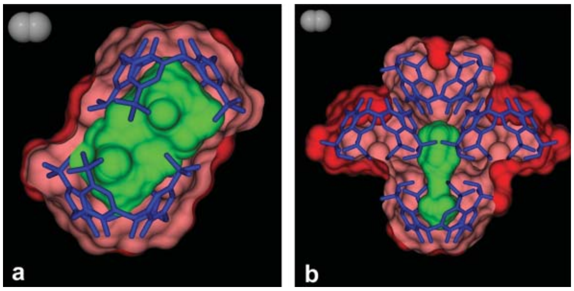

Fig. 2 (a) The dimeric capsule formed by two facing, but slightly offset molecules of **1**. (b) Columns of **2** stack adjacent to one another and form a void space between successive host molecules. The void space extends into the cavity of the lower host molecule. In (a) and (b) the host molecules are shown in capped-stick representation with hydrogen atoms omitted. The red/pink: surface represents the exterior shell of the host assemblies and the green regions represent the guest-accessible voids. Surfaces were generated using a probe radius of 1.17 Å. In order to illustrate the scale, hypothetical hydrogen molecules are shown in the top left-hand corners of (a) and (b). The volume of H_2 is approximately 12 Å^3 assuming a bond distance of 1 Å and a van der Waals radius of 1.17 Å.

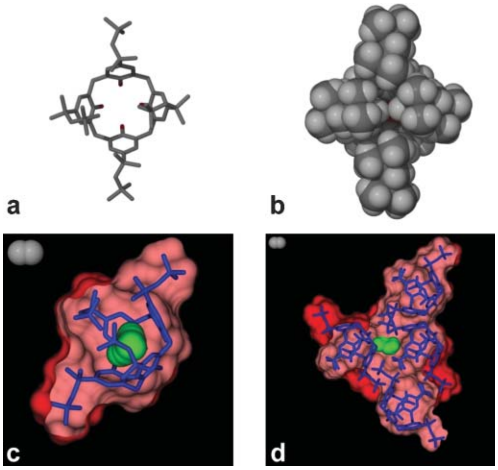

Fig. 3 Capped stick (a) and space filling (b) representations of **3** showing the orientations of the *tert*-octyl moieties. (c) The molecular cavity encloses a small void of *ca.* 23.5 Å^3 and (d) an additional interstitial void of *ca.* 59 Å^3 is present in the lattice.

the same direction, and with a repeat distance of 13.46 Å. Each column is surrounded by four nearest-neighbor columns running in the opposite direction. The upper rim of each calixarene molecule is situated between the upper rims of four opposing molecules. Fig. 2b shows that an elongated void of ∼110 Å^3 is formed between two successive calixarene molecules within the column. This void is bounded laterally by four molecules in the neighboring and opposing columns. The molecular cleft of the host molecule is guarded by the *p-tert*-pentyl groups which are positioned symmetrically about the upper rim such that their ethyl moieties extend across the opening of the cavity. The entrance to the cavity thus consists of a small pore approximately 1.22 Å in radius and, using a probe radius of 1.17 Å to define the void volume, the molecular cleft forms part of a cavity that extends into the column interstice. The overall structure is nonporous: the cavity shown in Fig. 2b is the only unique cavity in the structure. Based on our previous studies, it is reasonable to infer that the hydrogen molecules diffuse through the apparently nonporous lattice and become embedded in these voids. It has already been established that, under dynamic situations, the van der Waals boundaries of molecules in crystals do not necessarily behave as might be expected for classical macroscopic surfaces.

The sublimed phase of **3** were studied by means of single crystal X-ray diffraction.[12]‡ The solid state structure of **3** reveals that two *tert*-butyl moieties of distal *p-tert*-octyl groups are directed away from the molecular cleft, while the remaining two *tert*-butyl moieties reach into the cleft (Fig. 3a and 3b). Thus a relatively small intramolecular cavity of only ∼23.5 Å^3 is formed (Fig. 3c) and is completely isolated from the exterior of the calixarene molecule. An additional void of 59 Å^3 is formed interstitially between six molecules of **3** (Fig. 3d).

Although compounds **1–3** are closely related to one another in terms of their chemical structures, their solid state structures are quite different. In all three cases the molecular cavities define void spaces that are large enough to accommodate hydrogen molecules. Although the hydrogen sorption capacities of **1–3** are relatively low compared to many MOFs reported thus far, we have now shown that it is possible to use organic materials for hydrogen sorption. This is a new concept in the field of hydrogen storage despite falling short of the technologically relevant goal of 6 wt%. While preliminary results indicate that the capacities of **1–3** can be improved (up to 0.6 wt%) by lowering the experimental temperature to 200 K, we have decided to focus our attention on room temperature studies.

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Notes and references

‡ **Crystal data for 3**: $C_{60}H_{88}O_4$, M = 873.30, colorless prism, 0.25 × 0.25 × 0.20 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 11.3633(17), b = 38.624(6), c = 12.6614(19) Å, β = 101.881(2)°, V = 5438.0(14) Å^3,

$Z = 4$, $D_c = 1.067$ g cm^{-3}, $F_{000} = 1920$, Mo-Kα radiation, $\lambda = 0.71073$ Å, $T = 173(2)$K, $2\theta_{max} = 54.3°$, 47813 reflections collected, 12034 unique ($R_{int} = 0.0919$). The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997), respectively. Final $GooF = 1.057$, $R_1 = 0.0786$, $wR_2 = 0.1791$, R indices based on 6101 reflections with $I > 2\sigma(I)$ (refinement on F^2), 738 parameters, 30 restraints. Lp and absorption corrections applied, $\mu = 0.064$ mm^{-1}. CCDC 280984. See http://dx.doi.org/10.1039/b511341e for crystallographic data in CIF or other electronic format.

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