Host–Guest Systems

A New Type of Material for the Recovery of Hydrogen from Gas Mixtures**

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Sustained global dependence on fossil fuels as a primary source of energy is beset by several intractable problems which include dwindling reserves, increasingly unacceptable levels of pollution, and relatively low conversion efficiency.[1] Of several proposed alternative technologies, hydrogen-based fuel cells have emerged as being particularly attractive, especially for mobile applications.[2] The smooth transition to hydrogen as a viable and sustainable source of energy is, however, not without its own set of challenges. Much needs to be accomplished to realize the necessary infrastructure and technological advances that will ultimately lead to the production, purification, transport, storage, and conversion of hydrogen as an everyday consumer commodity.[3]

In the short term, escalated production of hydrogen will most likely continue to rely on conventional technologies such as steam reforming of natural gas:followed by the water-gas shift reaction:The final step in the production process involves the purification of H_2 by the removal of impurities such as CH_4, CO, H_2O, and, primarily, CO_2.[4]

$$CH_4+H_2O \rightleftharpoons CO+3\,H_2$$

$$CO+H_2O \rightleftharpoons CO_2+H_2$$

Separation technology is critical to the deployment of hydrogen as a source of energy since the purity of hydrogen supplied to fuel cells affects their performance and longevity, and therefore their economic viability. Compact, durable, and inexpensive purification devices will be required if hydrogen is to fulfill its promise. New hydrogen plants are generally based on the use of pressure-swing adsorption (PSA) for the final purification of hydrogen. This technique utilizes the difference in adsorption properties of various molecules:[5] components of a gas mixture are selectively adsorbed onto a solid matrix at high pressure, and subsequently desorbed by lowering the pressure.[6] In recent years, both the design and operation of PSA processes have developed to the extent that any notable further improvement in gas separation necessitates the discovery of a new adsorbent material.[7] Although zeolites and activated carbon materials are currently employed to good economic effect, there is a continued demand for new designer materials that can be utilized for gas storage and separation.[8] Although carbon nanotubes and metal-organic frameworks have undergone substantial scrutiny in this regard,[9] molecular crystals have received little consideration since their constituent molecules generally pack with an efficiency deemed to preclude porosity.[10] We now show that a nonporous organic molecular crystal can indeed be exploited for the purification of hydrogen gas.

We recently reported that a crystalline polymorph of pure *p-tert*-butylcalix[4]arene (TBC4), prepared by sublimation, forms a bilayer-type structure which contains large lattice voids of approximately 235 Å^3 (Figure 1).[11] Immersing these crystals in liquid vinyl bromide for a period of 15 minutes results in a single-crystal-to-single-crystal phase transition during which the vinyl bromide diffuses through the lattice to fill the vacancies. The phase transition is characterized by a lateral shift of the bilayers (by approximately 6 Å) relative to one another to allow guest diffusion, and to achieve a well-packed final structure that incorporates one molecule of vinyl bromide per TBC4 cavity. In our continued efforts directed at understanding the dynamics of guest transport through the TBC4 lattice, we noted that addition of sublimed TBC4 to liquid nitrobenzene caused numerous bubbles to emanate from the crystals (Figure 2). This chance observation implies that the crystals initially contain highly volatile molecules which are forced out of the lattice by incoming nitrobenzene. Since the pure host phase is crystallized under vacuum at 230 °C, the possibility of having formed the lattice around small gas molecules can be ruled out.[12] The most plausible explanation is that, upon removal from the sublimation

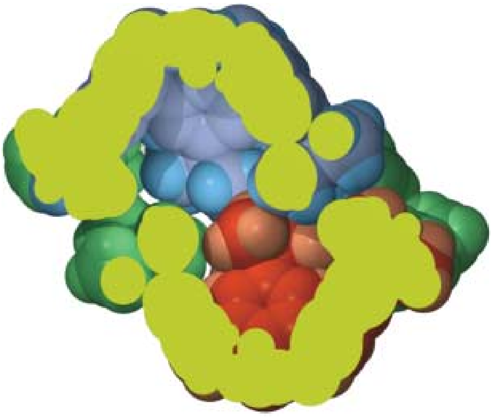

Figure 1. A section (yellow) through the TBC4 dimer (red and blue molecules) formed upon sublimation. The two empty calixarene cavities face one another in an offset arrangement, which yields a relatively large hourglass-shaped void with an estimated free volume of 235 Å^3. Gaps between the *tert*-butyl groups at the equator of the dimer are blocked by *tert*-butyl groups (green) of neighboring calixarenes and there are thus no channels leading to the voids.

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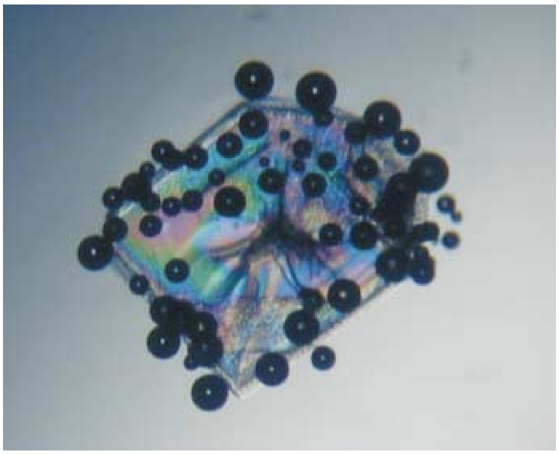

Figure 2. Photograph showing air escaping from platelike crystals of TBC4. After exposure of sublimed single crystals to the atmosphere for two days they were immersed in nitrobenzene. Air bubbles immediately began to emanate from the sides of the crystals as nitrobenzene enters the lattice, expelling the gas.

apparatus, the crystals absorb air while left exposed to the atmosphere prior to further handling.

The X-ray structure of a sublimed crystal was elucidated after its exposure to the atmosphere for two days. The host lattice is identical to that of the pure phase (that is, no lateral shift of the bilayers is apparent). Once the atomic parameters of the host molecule had been resolved, a significant level of residual electron density was located within the calixarene cavity. In contrast, structural analysis of a freshly sublimed crystal did not reveal any appreciable residual electron density at this site. Although a presumed combination of thermal motion, partial occupancy, and disorder precluded modeling the residual electron density as either O_2 or N_2, it is reasonable to infer that this electron density within the calixarene cavity arises from the absorption of air from the atmosphere. This result raises the intriguing question of how a seemingly nonporous material might have the ability to absorb gas into its lattice under ambient conditions.[13]

Sorption isotherms for air, N_2, O_2, and CO_2 were each recorded at 23 °C on freshly sublimed crystals (Figure 3 a). In all cases, the initial pressure was approximately 700 torr (93.3 kPa) and the gas was absorbed, over a period of about 24 h or longer, until equilibrium was reached. Under the above conditions, it appears that the crystals are able to discriminate between the various gases in both their rate of uptake and amount absorbed. Indeed, since the composition of air is on the order of 78 % N_2 and 21 % O_2,[14] the sorption rates for air, N_2, and O_2 are approximately self-consistent. Of the three pure gases tested, CO_2 is absorbed far more rapidly and to a significantly greater extent than either N_2 or O_2. Correspondingly, it is known that the rate of gas adsorption on activated carbon can be correlated with the condensability of the gas under consideration.

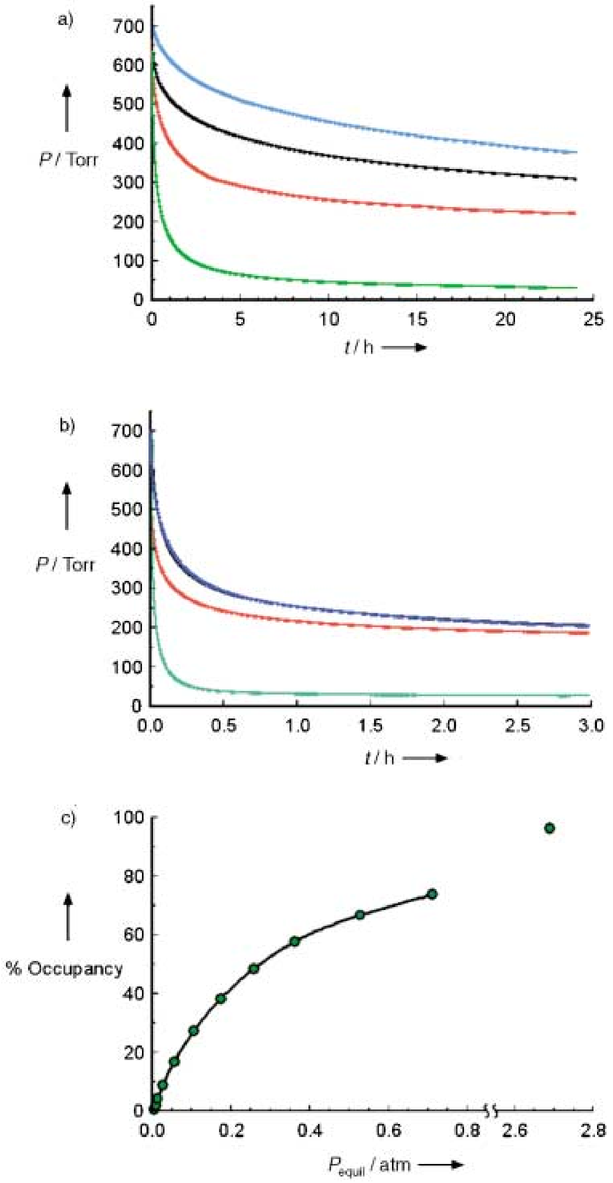

Figure 3. Gas sorption isotherms recorded at 23 °C. a) Isotherms for TBC4 sample (5.714 g; blue: N_2, black: air, red: O_2, and green: CO_2). The chamber was evacuated for at least 1 h between experiments to remove the absorbed gas from the sample. b) Crushing the crystals resulted in the rate of gas absorption increasing markedly while the equilibrium pressures were unchanged (note that the isotherms for N_2 and air are overlapped). c) Occupancy of the lattice voids by CO_2 (assuming a 2:1 molar ratio of TBC4:CO_2) versus equilibrium pressure. Full occupancy is obtained as the pressure approaches 3 atm.

As anticipated, equilibrium was reached far more rapidly when the sorption experiments (Figure 3 b) were repeated after the host crystals had been crushed by means of a mortar and pestle. However, the amount of gas absorbed appears to be unaffected by grinding, which further supports our claim that the gas is assimilated into the lattice rather than adsorbed onto the surface of the particles. It is interesting to note that the selectivity between O_2 and N_2 is diminished markedly when the particle size is reduced. Figure 3 c reveals a type I relationship[15] between the equilibrium pressure and the percentage of calixarene cavities occupied by CO_2. Since two calixarene molecules are required to form one discrete lattice void it appears that, on average, each lattice void can be almost fully occupied by one gas molecule at approximately three atmospheres of CO_2 pressure. Indeed, the occupancy is almost 80 % even at one atmosphere of pressure.

Unexpectedly, exposure of the material to hydrogen at pressures of up to 7 atm did not result in any discernable absorption of this gas. As a result of the large disparity between the affinity of the TBC4 substrate for CO_2 and H_2, coupled with the acute current commercial interest in separating these gases, we exposed the material to a 3:1 mixture of CO_2:H_2 at an initial pressure of 1 atm for 19 h. The composition of the gas mixture, both before and after exposure to TBC4, was determined by gas chromatography (Figure 4). This experiment illustrates rather dramatically that the substrate selectively sequesters CO_2 from the mixture, even at moderately low pressures, thus leaving the supernatant gas rich in H_2.

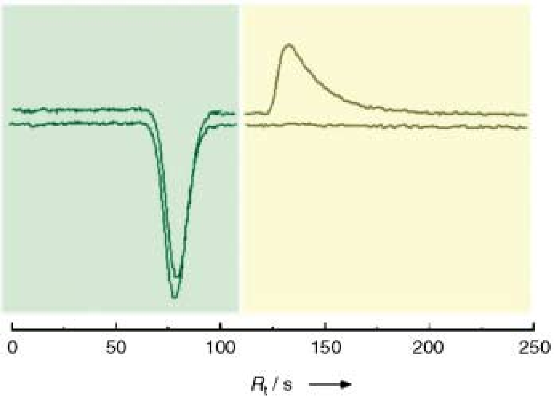

Figure 4. Gas chromatogram showing the composition of the supernatant CO_2/H_2 mixture prior and subsequent to the gas sample being subjected to TBC4. The intensity of the hydrogen peak (green box) does not change during the absorption experiment, while the carbon dioxide peak (yellow box) was entirely diminished, thus indicating that the solid selectively absorbs CO_2. Thermal conductivity detection of the gas mixture necessitated the use of nitrogen carrier gas to quantify the amount of hydrogen and, in a successive run, helium carrier gas to analyze the carbon dioxide content. ($T_{column} = -70\,°C$; flow rate: 60 ml min^{-1} nitrogen or helium; column: 120×0.5 cm; stationary phase: 20 % DC200 Chromosorb PAWDMCS80/100 mesh).

Guest species that normally exist as liquids or vapors are capable of appreciable intermolecular interactions that can provide the impetus for rearranging host molecules as part of a dynamic inclusion process. In contrast, volatile gases such as O_2, N_2, and CO_2 possess characteristically weak interactive capabilities, yet are still able to find and occupy the lattice voids without discernable disruption of the host lattice, or even the need for suitably sized pores. Thus, "soft" layered structures may employ as-yet unknown mechanisms that can allow the passive influx of gas molecules at rates comparable to those observed for porous materials. Moreover, the fate of the volatile hydrogen is clear: it is not absorbed. The hydrogen molecules may well visit the interior of the crystal, but if they do so, they are not retained. However, the classical riddle of how the ship gets into the bottle remains, at least for now, a subject for speculation.

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