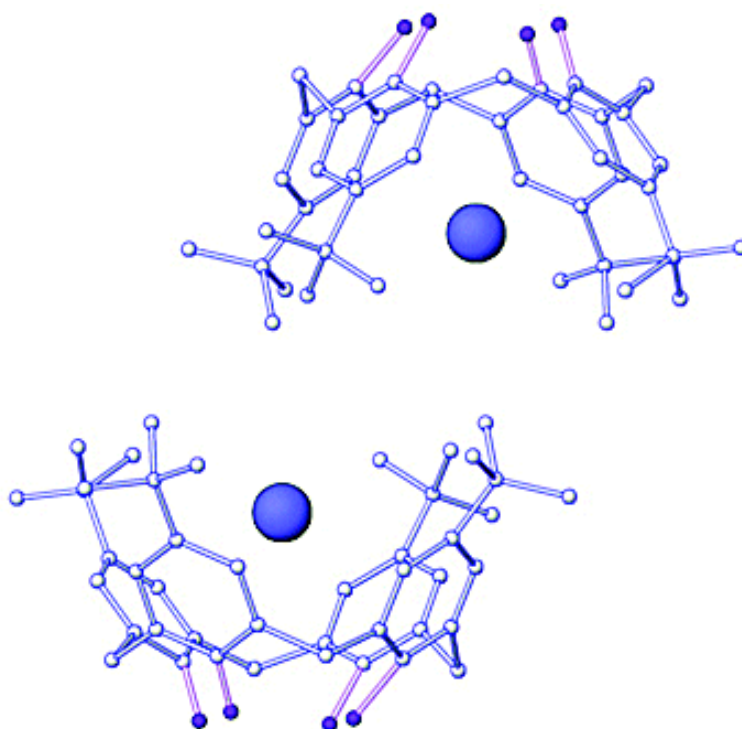Communication

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Thermally Programmable Gas Storage and Release in Single Crystals of an Organic van der Waals Host

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The synthesis of frameworks for storage, processing, and controlled release of molecular species is a much-researched topic today. Many such frameworks have been assembled via directional bonds of various strengths, for example, covalent, H-bonding, and metal-coordination, yielding frameworks of varying degree of robustness.[1−3] As well, recently there has been a keen interest in frameworks that transform under some sort of external stimuli to take on different functions, these sometimes being referred to as smart, responsive, or third generation materials.[4,5] Few simple van der Waals solids have shown a propensity for this kind of application,[6] although such solids often are flexible, suggesting that there should be a dimension of response possible.[4,5,7] Crystalline van der Waals solids that can change function cyclically via a relatively low energy pathway clearly have the potential for applications. Herein, we report examples of process control in *p-tert*-butylcalix[4]arene (tBC) where guests can be loaded into or released from single crystals by controlling guest concentration and temperature.

p-tert-Butylcalix[4]arene (tBC) is an extremely versatile inclusion host, with several guest-directed structural motifs.[8] By far, the most common are the 1:1 (*P4/n*) and 2:1 (*P4/nnc*) tetragonal crystal forms, obtained by recrystallization of the host material from solvents consisting of small guests (benzene, toluene, pentane) in the first instance, and from somewhat larger guests (hexane, *p*-xylene) in the second. Guest-free forms are obtained by heating inclusion compounds above ∼150 °C, yielding either a dense, self-included form or a low-density *P2₁/n* form (**1**), depending on the conditions.[7,9] The low-density form in fact can be converted to the *P4/n* 1:1 compound by exposing the material to guest liquid.[7]

Single crystals of guest-free **1** can also be converted into a new family of 1:1 guest−host materials where the host lattice does not change; that is it remains *P2₁/n*. When a single crystal of **1** is heated at temperatures between room temperature and 140 °C in a sealed tube under ∼20 atm of xenon, the Xe guest filled at least half of the cavities, the single crystal remaining intact and the crystal structure of the product (**2**) remaining the same (Figure 1) as that for the empty form. These crystals were stable at room temperature for a period of at least days. Structural information for **1** and **2** is given in the Supporting Information.

The accessibility of crystal form **1** with respect to the loading and release of small guest molecules was tested for NO, air, SO₂, and Xe by sealing the gas and host material into a Pyrex tube to achieve pressures of 10−20 atm. Release of the gases as a function of temperature from the products was checked with TGA (Figure 2a) for Xe also under isothermal conditions at 100 °C (Figure 2b), the weight losses varying between 4% and 10%. The larger guests are retained quite tenaciously considering that the bulk guest materials are well above their boiling points. The isothermal plot for Xe shows that the rate of guest release becomes slower with increasing length of time, suggesting that the process is thermally
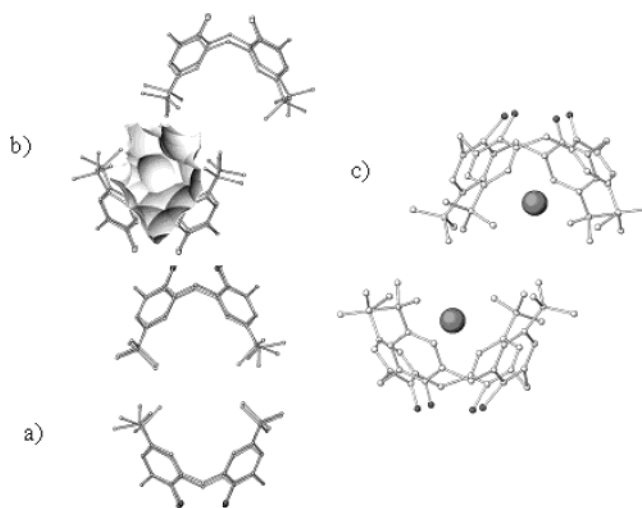

Figure 1. Crystal structure of the empty host (**1**) and the inclusion compound with xenon (**2**); (a) empty calixarenes (**1**), view along *a* axis; (b) empty calixarenes (**1**), view along *c* axis; the shading shows the van der Waals surface inside the cavity; (c) compound with Xe (**2**), view along *a* axis.
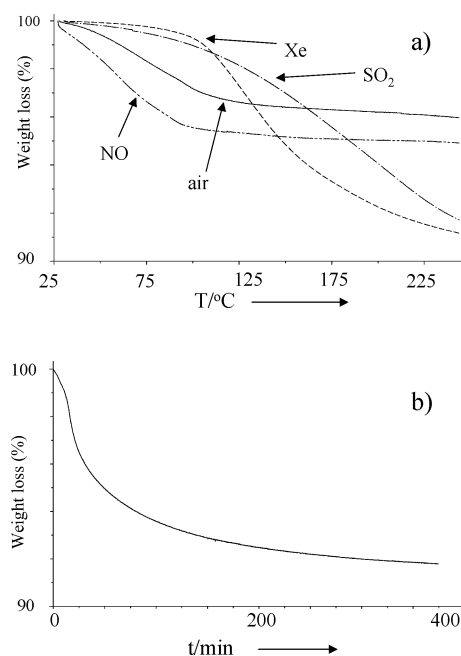

Figure 2. Thermogravimetric analysis of *p-tert*-butylcalix[4]arene guest host compounds; (a) temperature scans for Air, NO, Xe, SO₂; (b) isothermal run at 100 °C for the Xe compound.

activated with the interior guests traveling a longer diffusional path length than those near the surface of the particles. Xe NMR
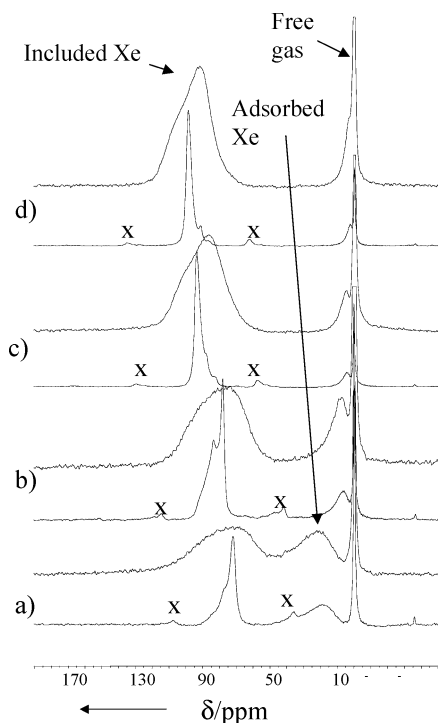
Figure 3. [129]Xe NMR spectra recorded under continuous flow conditions with hyperpolarized xenon at different temperatures: (a) 25 °C, (b) 60 °C, (c) 80 °C, (d) 100 °C. Both static-sample spectra as well as those obtained under magic angle spinning conditions are shown. Effective Xe gas pressure is 7 Torr; X marks spinning sidebands.

spectroscopy, using hyperpolarized xenon produced in a continuous flow system system,[10] lends itself well as an in-situ probe of the temperature-dependent access to the guest sites in **1**.[11] Figure 3 shows a set of [129]Xe spectra for **1** in contact with a flowing gas mixture (98% He, 1% N$_2$, 1% Xe) containing HP Xe (partial pressure 7 Torr) as a function of temperature under both static and spinning conditions.

The room-temperature spectrum shows resonances at 0, ~20, and 75 ppm which can be assigned to free xenon gas, Xe interacting with the outside surface, and xenon interacting with host cavities, respectively. The width and shape of the 20 ppm line suggest that considerable exchange occurs. As the temperature increases, the latter line shifts toward that of the free gas, as the rate of exchange with xenon in the free gas also increases. The isotropic low field line always shows some fine structure. We attribute this to the presence of a phase change that takes place for the empty lattice at ~90 °C.[9b]

Loading of the host will change the transition temperature, and nonuniform loading will give a range of such transition temperatures. The largest change in the spectrum comes between 60 and 80 °C, where the strongest isotropic component shifts from the high field to the low field side of the complex peak, so it is likely that the bulk of the sample transforms in this temperature range. At the highest temperature, the Xe powder pattern has an isotropic chemical shift of ~105 ppm which corresponds to Xe inside the calixarene cavities. So, as the temperature is increased from room temperature to 100 °C, the Xe atom locations change from a good fraction being external to the host cavities to being almost

completely included. The spectra confirm that passage in and out of the crystal by flowing xenon gas is rather difficult at room temperature and much easier at 100 °C. We also note that the Xe powder pattern is quite different from that obtained previously for the mixed Xe/nitrobenzene calix compound, the larger chemical shift confirming that the cavity is much smaller in **2** than in the known versions of the 1:1 compound.[12] The observation of reversible functional behavior involving the release or adsorption of guest species makes the material suitable for applications such as the release of packaged reagents (SO$_2$, HCl) or the controlled release of biologically active species (NO). Storage of guest molecules, including low-boiling gases, can be accomplished by loading at about room temperature under a high guest pressure, followed by storing at a suitable temperature. Controlled release can then be accomplished by thermal programming. Another application is molecular sieving, as it was noted that even at room temperature compound **1** takes up components from air. Studies of selective adsorption for possible gas separations are currently in progress. It is clear that the collective weak forces in van der Waals hosts are remarkably strong in retaining highly volatile guests;[6,13] yet they can be responsive to external conditions so that cavity hosts should be considered for possible applications, a role primarily considered for the many novel open channel systems recently reported.[1−3]

Supporting Information Available: Crystallographic data of **1**, **2**, and further experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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