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## Diffusion of vaporous guests into a seemingly non-porous organic crystal†

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**The tetragonal apohost phase of *p*-tert-butyltetramethoxythiacalix[4]arene absorbs hydrochloric acid and iodine. These guest molecules occupy different sites in the solid-state structure – either within the small intrinsic voids of the macrocycle or within the interstitial spaces between the host molecules. This study illustrates the dynamic deformation of the host, providing strong mechanistic insight into the diffusion of guests into this seemingly non-porous material.**

In recent years much attention has been devoted to unravelling the mechanisms governing diffusion of guest molecules into crystalline materials. These studies have also raised questions about the fundamental nature of porosity, especially with regard to transient pores.<sup>1</sup> The effective design of new porous materials for practical applications relies on our understanding of the factors that underpin the creation of molecular space, as well as mechanics of diffusion processes.

A range of different design strategies have been used to create porous crystalline materials. The major classes of these materials include metal–organic frameworks (MOFs),<sup>2,3</sup> covalent organic frameworks (COFs),<sup>4</sup> and molecular crystals<sup>4–6</sup> where the “awkward” shapes of the molecules overcome their close packing tendencies.<sup>6–10</sup> Although significant efforts are being made to design materials with ever increasing accessible void space,<sup>11,12</sup> there is also great interest in materials that appear not to possess conventional channels or even pores, but are nevertheless permeable to guests. Indeed, transient porosity has been observed in

MOFs,<sup>13,14</sup> organic salts<sup>15</sup> and in low molecular weight purely organic materials.<sup>16–18</sup>

The incorporation of volatile mineral acids (hydrochloric or hydrobromic) into crystalline materials has thus far been limited to metal–organic materials, accompanied by a concomitant acid–base gas–solid reaction.<sup>19–26</sup> The reaction in these reports involves either protonation of a pyridyl metal-coordinated group,<sup>19–23</sup> or protonation of a zwitterionic system.<sup>24–26</sup> Perhaps as might be anticipated, significant structural strain is associated with these transformations, leading to characterization of the products by means of powder X-ray diffraction<sup>19–25</sup> or atomic force microscopy<sup>26</sup> rather than by single-crystal diffraction. Interestingly, all of these reports are associated with seemingly non-porous materials, implying that the acid–base reaction provides a strong incentive for the guest uptake. We have previously reported the diffusion of water into a seemingly non-porous hydrophobic crystal composed of a particular apohost phase of *p*-tert-butyltetramethoxythiacalix[4]arene (**1**, Fig. 1).<sup>27</sup> As a continuation of this work we were interested in determining if incorporation of HCl by **1** would also be possible, and if inclusion of the acid could be achieved without utilizing a formal acid–base reaction.

Crystal growth by means of sublimation produced a mixture of phases comprising a monoclinic form **1a** (space group *C2/c*) and the desired “porous” tetragonal form **1b** (space group *P4<sub>2</sub>m*). In both of these forms the calixarene assumes the 1,3-alternate

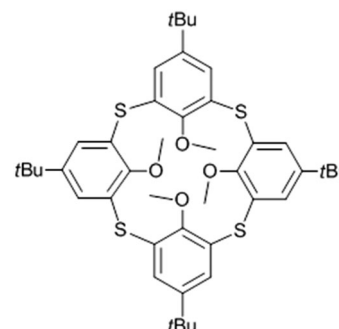


Fig. 1 *p*-tert-Butyltetramethoxythiacalix[4]arene **1**.

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† Electronic supplementary information (ESI) available: Details of the synthesis of **1**, along with general experimental protocols and detailed descriptions of the crystallographic procedures and structures. CCDC 973280 (**1**<sub>HCl</sub>), 973281 (**1**<sub>HCl·H<sub>2</sub>O</sub>), 973282 (**1**<sub>I<sub>2</sub></sub>) and 973283 (**1**<sub>I<sub>2</sub>·H<sub>2</sub>O</sub>). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc07366e

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conformation and both structures therefore possess small vacant pockets within the protective shell of the macrocycle (*endo*- or intrinsic<sup>28</sup> pores). However, the parallel pillars of calixarenes in phase **1b** also form isolated hydrophobic pockets in the interstitial spaces between the columns (*i.e.* extrinsic pores<sup>28</sup>). Such additional voids are not present in the more efficiently packed phase **1a**.

Two subtly different (*i.e.* symmetry-independent) calixarene molecules (**1b<sub>1</sub>** and **1b<sub>2</sub>**, see Fig. 2) are present in **1b**. In the case of **1b<sub>1</sub>** the molecule possesses  $\bar{4}$  symmetry and the two *endo* voids are thus identical. The second molecule (**1b<sub>2</sub>**) possesses *2mm* symmetry, which does not require identical geometries for the two voids – two distal aromatic rings are tilted at a slightly greater angle relative to each other than their corresponding neighbors. This asymmetry of the two molecular extremities creates two *endo* voids that differ slightly in volume. Potential guest molecules are therefore presented with a choice of three distinct voids to occupy in phase **1b**.

Exposure of **1b** to dry HCl vapor for one week yielded **1b<sub>HCl</sub>**, which was characterized by single crystal X-ray diffraction (space group *P4<sub>2</sub>1m*). The structure possesses significant electron density associated with the incorporation of HCl into the *endo*

cavities. Energy-dispersive X-ray (EDX) spectroscopic analysis of **1b<sub>HCl</sub>** confirmed the incorporation of chloride into **1b** while similar analysis of **1a** (which was also present during exposure to HCl vapor) failed to produce any peaks associated with chloride (ESI†).

Similar to the inclusion of H<sub>2</sub>O into **1b**, HCl ultimately occupies two of the three unique *endo* pores, and could be modelled at 18% site occupancy in the two symmetry-related pockets of **1b<sub>1</sub>** and also exclusively in the larger pocket of **1b<sub>2</sub>** with 50% site occupancy. In **1b<sub>1</sub>** the closest Cl⋯O distance to a methoxy oxygen atom is 3.277(11) Å, and the corresponding value in **1b<sub>2</sub>** is 3.041(6) Å. These distances are in good agreement with literature values for Cl⋯O<sub>ether</sub> interactions (3.23(6) Å), in contrast to the shorter distance expected for an O<sub>water</sub>⋯O<sub>ether</sub> interaction (2.93(8) Å).<sup>29</sup>

In order to probe the effect of water on the diffusion of HCl into **1b**, a crystal was placed in a sealed container containing wet HCl vapor for one week to yield **1b<sub>HCl·H<sub>2</sub>O</sub>**. Single crystal X-ray diffraction analysis indicates selective occupancy of the distinct *endo* voids: the two symmetry-related cavities **1b<sub>1</sub>** each contain H<sub>2</sub>O molecules with a site occupancy of 22%, whereas cavity **1b<sub>2</sub>** appears to be occupied by HCl (20% occupancy). The identities of the guests were inferred from their different distances to the methoxy oxygen atoms (2.947(18) and 3.138(12) Å, respectively).

Although both **1b<sub>HCl</sub>** and **1b<sub>HCl·H<sub>2</sub>O</sub>** display non-stoichiometric guest occupancy, efforts to increase the occupancy by extended exposure resulted in significant degradation of single-crystal quality without any increase in occupancy being observed. Owing to phase impurity of the apohost resulting from sublimation growth, it is difficult to monitor the change in guest occupancy with time using techniques such as powder X-ray diffraction or gravimetric analysis.

We have already speculated<sup>27</sup> that rotation of the *tert*-butyl groups guarding the interstitial pockets facilitates the movement of the guests through the lattice. In order to probe this conjecture further, crystals of **1b** were exposed to vapors consisting of larger guest molecules; is it possible that a hydrophobic guest might occupy the interstitial voids, thereby confirming at least the notion that these can constitute a pathway for diffusion?

Iodine is a relatively large, linear and non-polar compound with a sufficiently high vapor pressure to make it suitable for diffusion experiments. Exposure of **1a** and **1b** to anhydrous iodine vapor rapidly yields visual confirmation that **1b** is capable of iodine uptake (see ESI† for video file). Single crystal X-ray diffraction analysis of **1b<sub>2</sub>** (*P4<sub>2</sub>1m*) shows significant electron density in the interstitial pockets (Fig. 3). The peaks could be modelled as iodine (20% site occupancy) with an I–I bond length of 2.682(3) Å. As observed for HCl, prolonged exposure of **1b** to iodine vapor failed to increase the guest occupancy.

The influence of water on iodine uptake was also explored to determine whether the inclusion of iodine would also be suppressed by competition with H<sub>2</sub>O. Crystals of **1b** were placed in a vial containing both water and iodine vapors for 10 days. The resulting crystal structure **1b<sub>2</sub>·H<sub>2</sub>O** (*P4<sub>2</sub>1m*) was compared to that of **1b<sub>2</sub>**; both structures yielded site occupancy factors of 20% for iodine, but **1b<sub>2</sub>·H<sub>2</sub>O** shows additional incorporation of water into both *endo* pockets **1b<sub>1</sub>** (2 × 25%) and **1b<sub>2</sub>** (25%). It therefore appears that the *exo* and *endo* voids possess different

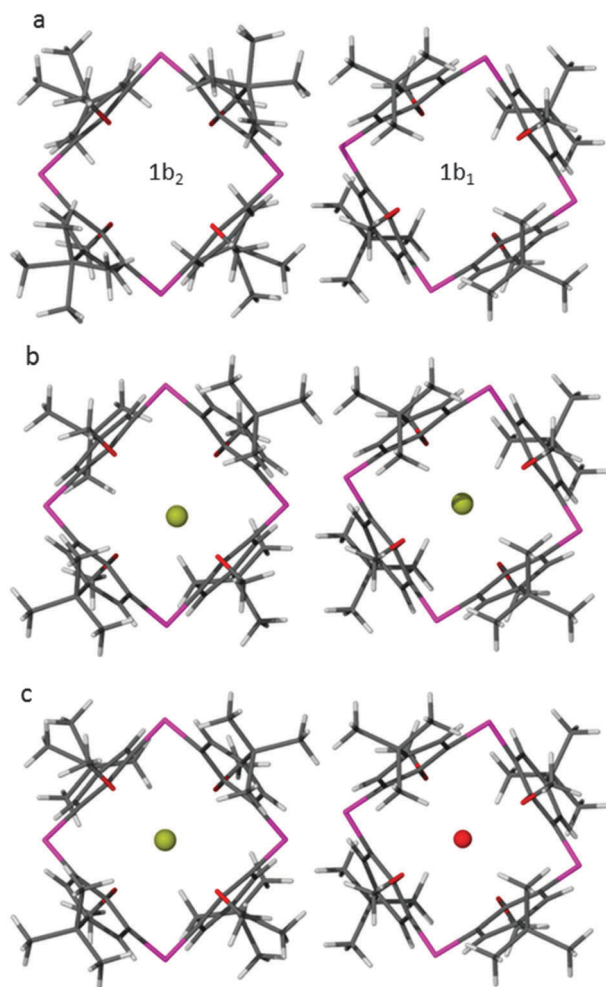


Fig. 2 Calixarene molecules in the structures of (a) **1b**, (b) **1b<sub>HCl</sub>** and (c) **1b<sub>HCl·H<sub>2</sub>O</sub>** viewed along [001]. Symmetry-imposed disorder has been suppressed.



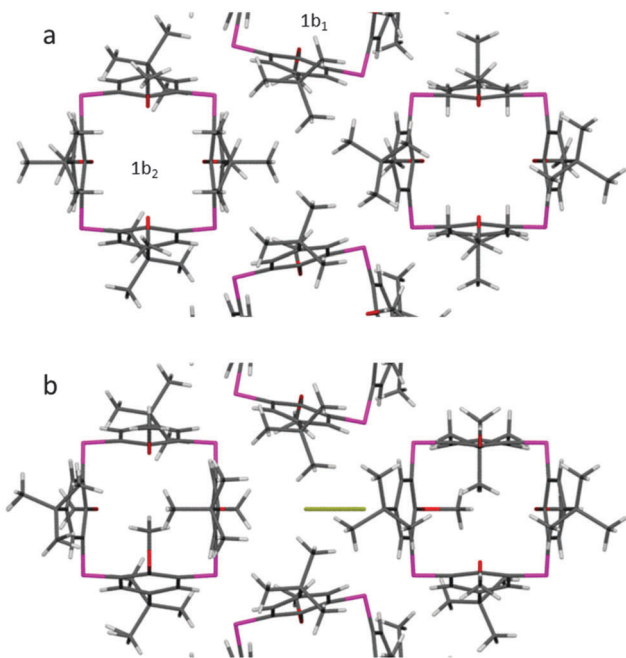


Fig. 3 Corresponding structures of (a) **1b** and (b) **1b<sub>2</sub>** viewed along [001]. Symmetry-imposed disorder has been suppressed for clarity.

enough environments that both the polar H<sub>2</sub>O and the non-polar iodine can diffuse through the lattice simultaneously, each ultimately being unaffected by the other's presence.

Although guest uptake by **1b** does not alter the space group, it is interesting to compare the structure of **1b<sub>2</sub>** with that of **1b<sub>HCl</sub>**. In the former, one of the methoxy methyl groups of **1b<sub>1</sub>** rotates upon guest uptake to occupy a second position that projects into the calixarene cavity. This is most likely a steric requirement to accommodate the iodine molecule within the *exo* cavity, and it allows a linear head-on arrangement of iodine relative to the oxygen atom of the inwardly oriented methoxy group (see Fig. S3, ESI<sup>†</sup>). Similar arrangements have been observed in other structures (CSD average I...O<sub>ether</sub> = 2.84(8) Å), as compared to 2.911(4) observed in **1b<sub>2</sub>**. This orientation is probably due to electronic stabilization between I<sub>2</sub> molecules interacting with the lone pairs of the oxygen atom.<sup>30</sup> A second large scale distortion of the geometry of **1** in **1b<sub>2</sub>** relative to that in **1b** is that two of the symmetry related distal aromatic rings in **1b<sub>1</sub>** assume more "upright" positions in the former, *i.e.* they are pushed inwards by the interstitial guest.

The competition experiments between H<sub>2</sub>O and HCl or I<sub>2</sub> raises some interesting questions: how are guest molecules able to sense the most suitable position to occupy and then how are they able to organize themselves optimally? The mixed occupancy that results when H<sub>2</sub>O and HCl are in competition implies similar affinities for these two guests by the host sites. Preferential occupancy of **1b<sub>2</sub>** by HCl seems to stem from size selectivity, which also suggests the ability of the guest to move between *endo* cavities. The interplay between H<sub>2</sub>O and I<sub>2</sub> is apparently different since no reduction in the occupancy of iodine occurs in the presence of water. This implies that the water molecules must spend most of their time in the *endo* pores, perhaps rapidly traversing from one pore to the next, whereas iodine only associates with the intermolecular pores.

Since sorption occurs under relatively mild conditions, the drive for **1b** to fill its voids with suitable guests must be an energetically favorable process. The different environments offered by the *endo* and *exo* pockets must facilitate favorable interactions that allow the guests to enter and traverse the material. Mechanistically, the clathrate **1b<sub>2</sub>** illustrates the inherent flexibility incorporated into the structure of **1b**. A map of the guest-accessible space associated with the alternative conformation of **1** adopted by **1b<sub>2</sub>** in order to incorporate the guest provides an impression of the size and shape that the cavities in **1b** can assume when host flexibility is taken into account (Fig. 4). While no permanent channels are apparent in either **1b** or **1b<sub>2</sub>** (even when using a probe radius of 1.2 Å), the rocking motion of the aryl rings of **1b<sub>1</sub>** would most likely result in the formation of transient channels that allow guest transport. Although the interstitial pocket of **1b** is also hydrophobic in nature, the inversion of the methoxy group provides a temporary polar site that may help to facilitate the diffusion of polar guests through the structure.

The fact that the occupancy of the guests reaches a non-stoichiometric limit, even after prolonged exposure to the guest vapors, may be due to a self-terminating process or insufficient partial pressure of the guest. It is evident that guest diffusion

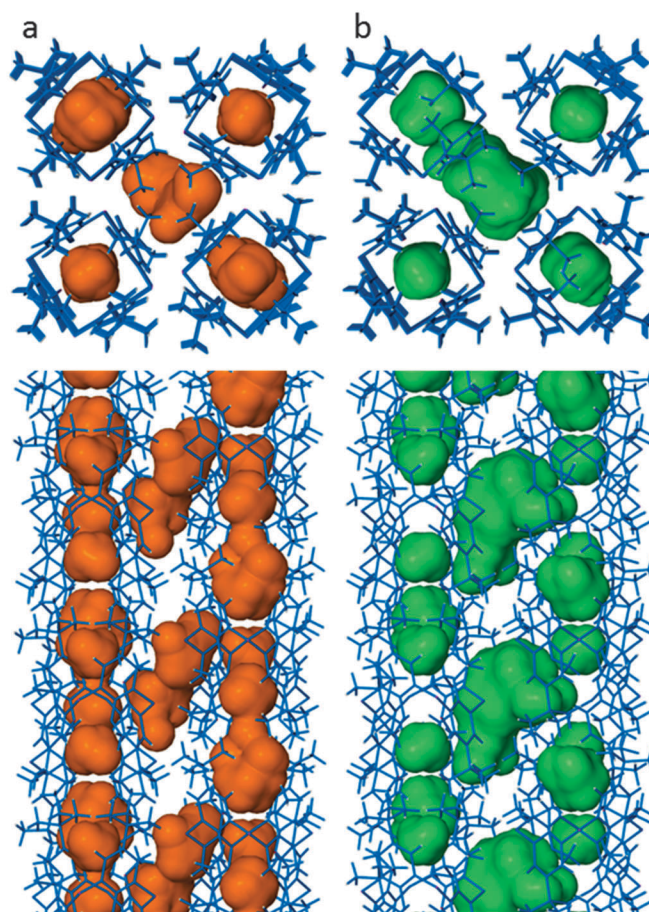


Fig. 4 Connolly surfaces of *endo* and intermolecular pores of calixarenes (a) **1b** and (b) **1b<sub>2</sub>** viewed along to [001] (top) and [110] (bottom). Symmetry-related disorder and the I<sub>2</sub> guest have been suppressed for clarity. Connolly surfaces have been generated using a probe radius of 1.2 Å.



requires deformation of the host structure, but for this to occur there must be some free space. Guest uptake reduces the amount of available space, thus inhibiting the ability of the host to deform – hence guest occupancy may reach a critical limit beyond which further uptake is precluded.

In summary, we have demonstrated two contrasting examples of guest sorption by a seemingly non-porous and purely organic structure; void occupancy is based on size, polarity and inter-guest competition. Deformation of the host structure to incorporate iodine provides insight into a possible “breathing” mechanism that allows guest transport through the crystal. Although we have not focused on the release of HCl from **1b**<sub>HCl</sub>, we show that it is possible to trap the guest without the requirement for an acid–base reaction. Indeed, the use of HCl in synthetic laboratories and industrial applications is widespread, with estimates of global production exceeding 20 million tonnes annually. However, its use as an anhydrous reagent is often complicated by its highly hygroscopic and volatile nature. It is likely that certain reactions and applications would greatly benefit from an easily handled solid material capable of controllably releasing HCl in an anhydrous fashion, specifically where catalytic quantities are required. As a proof of concept, this study represents a possible stepping stone towards creating a smart material capable of slowly/controllably releasing HCl (or other guests) as a reagent.

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