Guest capture, storage and removal in the TATM host framework: a single-crystal study†‡

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The organic host molecule, tris(5-acetyl-3-thienyl)methane (TATM) is known to form a variety of van der Waals inclusion compounds. Surprisingly, this host framework has been shown to be stable despite near-complete guest loss. In the present study we examine the degree to which guests can be removed from the host cavities without framework collapse, as well as the ability of the depleted host framework to re-adsorb guest molecules, including adsorption of a two-component mixture of guests, all in a host system that has no channels for transport. The response of the host framework to changes in guest content is reported as well.

Introduction

There is great interest in the design and synthesis of robust, organic or metal–organic inclusion frameworks that incorporate guest molecules and have potential for applications such as storage, recognition, separation or delivery. To be truly functional as storage or separation media, reactions involving inclusion frameworks must be easily reversible. One way that this may occur is for the framework to be stable and remain intact upon guest removal and subsequent guest adsorption. Some metal–organic frameworks meet this requirement,[1–9] however, with a few notable exceptions,[10–16] the cavities in most organic inclusion compounds collapse when the guest molecules are removed and the material is of no further use.

In order to gain further insight, beside structure, the thermodynamics and kinetics of inclusion in compounds with void space should also be considered. van der Waals and Platteeuw produced their elegant statistical mechanical theory of clathrate stability in 1959[17] and this has remained a valuable approach to understanding materials such as the gas hydrates. One of the premises of the theory was that inclusion compounds existed in dense and open crystal forms, the latter being only stable thermodynamically in the presence of a minimum number of guests in the cages. Except for a few examples, this has been difficult to verify, one reason being that often the open phases persist while metastable—thus kinetics plays an important but often unknown role. Another was that the clathrate structure should not depend on the nature of the guest, and this is observed in some cases where there are just one or a few families of structures with interchangeable guests. Usually these have frameworks with directional bonding and considerable strength, such as the clathrate hydrates and β-quinol clathrate. It has been far more difficult to describe frameworks in terms of a thermodynamic model where the host lattice is held together by non-directional, van der Waals interactions. Yet, for the purposes of materials design, it is of some interest to try and learn about the role of residual guests in propping open or pillaring a framework close to collapse. Whereas the calixarenes have proved to be a fertile ground for the discovery of stable or metastable open frameworks[18,19] the large number of possible structures and complex phase relationships[20,21] make this a less attractive area for detailed investigation. The well-known organic host molecule, tris(5-acetyl-3-thienyl)methane, or TATM, is a more tractable subject for investigation, as, so far, only a single dense phase has been found[22] and no guest-free open phases are known. Here, we investigate the structure and stability of TATM inclusions with respect to guest removal and re-adsorption.

TATM is a tripodal host molecule that forms van der Waals inclusion compounds with many small organic guest molecules.[23–33] These inclusion compounds exist in a variety of stoichiometries and structural motifs, however, compounds with a 2 : 1 host–guest ratio appear to be most common for small guests.[22–25,27,30–33] In a typical 2 : 1 inclusion, two acetyl thienyl groups of each TATM molecule form the host cavity (Fig. 1, left) while the third acetyl thienyl group pi-stacks with an acetyl thienyl group of another cavity to form 1-D ribbons. Adjacent ribbons interdigitate and interact through weak C–H···O hydrogen bonding to form a layered motif (Fig. 1, right).

Guest-free TATM was known only in an amorphous state until it was shown recently that crystalline guest-free TATM could be obtained by layering crystals of a TATM/guest inclusion compound with distilled water and heating (~70 °C) for several weeks.[22] During that time, the solvent

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† Dedicated to Professor Jerry Atwood on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Tables of unit cell and conformational parameters as a function of guest occupancy for TATM/acetone and TATM/DCE (ESI Table 1) and crystal data, data collection and final refinement parameters for **1aA**, **1bB**, **3** (ESI Table 2) and for the TATM/DCE/acetone mixed guest system (ESI Table 3). CCDC reference numbers 677778–677797. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718592h

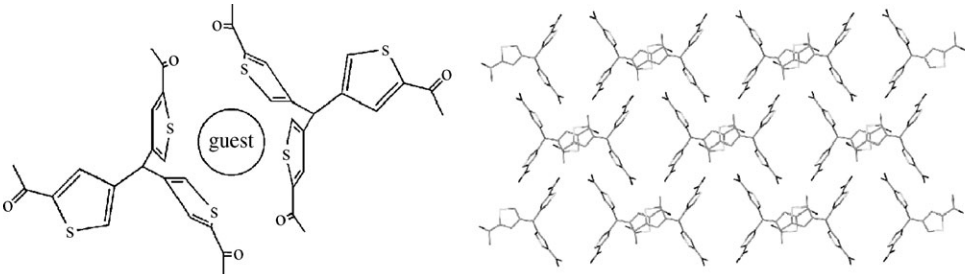

Fig. 1 Left: representation of a typical 2 : 1 TATM host : guest compound. Right: view of the layered TATM framework (guest molecules omitted).

guest is slowly leached out and rearrangement of the TATM molecules occurs to give a densely packed structure with little void space (Fig. 2).

While the discovery of this 'guest-free' form of TATM may suggest that the TATM host framework is not stable with respect to guest loss, it was also noted that during structural analysis a 'substantially guest-free' crystal was found in which 90% of the guest molecules were removed but the TATM host framework with empty cavities had remained intact.[22] The observance of this partially empty TATM host suggests that the crystal framework may be stable up to some minimal guest occupancy and that collapse of the TATM host framework begins only after complete (or near complete) guest loss has occurred. To study the stability of the TATM framework, we examined the degree to which guests can be removed from the host cavities without framework collapse, as well as the ability of the depleted host framework to re-adsorb guest molecules, including adsorption of a two-component mixture of guests. We also studied the structural effects of guest desorption and adsorption by measuring changes in the unit cell parameters and molecular conformation of the host as guest is removed or inserted, and as the percentage of each component in the two-component guest mixture is varied.

Experimental

TATM was prepared according to literature methods[34] from commercially available reagents (Aldrich). Crystals of the TATM/guest inclusions were grown by slow evaporation of a concentrated solution of TATM in the appropriate guest solvent. The guest solvent was partially removed from the TATM inclusions by adding water to the TATM/guest crystals and heating the sample in the oven at 70–80 °C for several weeks. Crystals of the TATM/DCE/acetone mixed guest systems were grown by heating TATM in capped vials containing a mixture of the two solvent guests and then letting the vials cool slowly.

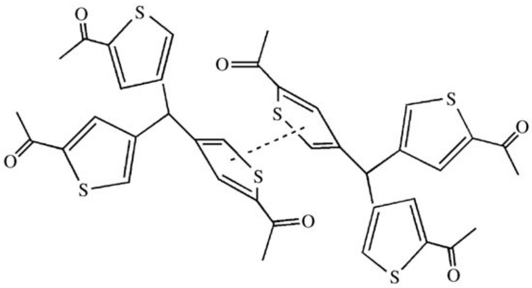

Fig. 2 Representation of the asymmetric unit of guest-free TATM. The dotted line indicates π–π stacking between thienyl rings.

Single-crystal X-ray diffraction data were measured on a Bruker-Nonius Smart CCD diffractometer at either 125 K or 100 K (for mixed-guest systems), using graphite-momochromatized Mo-Kα radiation (λ = 0.71073 Å) in the ω scan mode. The data reduction included a correction for Lorentz and polarization effects. The crystal structures were solved by direct methods, and the structure was refined by full-matrix least-squares routines using the SHELXTL program suite. A multi-scan absorption correction was made with SADABS software. Direct methods yielded all non-hydrogen host atoms in the unit cell. The hydrogen atoms of the host thienyl rings were located in the difference Fourier map, while the hydrogen atom of the central methine carbon of the host, the methyl hydrogen atoms of the host and all guest hydrogen atoms were placed in calculated positions with a riding temperature factor and bond length constraints. All non-hydrogen atoms of the host and guest atoms of sufficient occupancy were refined anisotropically. For the guest removal studies, a single crystal was mounted on a loop in oil and the X-ray diffraction data were measured. For the guest capture studies, a single crystal was glued to a glass fiber and a preliminary data set was collected to determine the initial guest occupancy of the crystal. The mounted crystal was then placed in a small vial situated within a larger vial containing the guest solvent, and sealed. After one day of exposure to the guest solvent vapor the X-ray data were recollected for the crystal and the new guest occupancy was determined. The crystal data, data collection, and refinement parameters for the crystals studied are summarized in Tables 1 and 2.

Results and discussion

We chose to study guest removal and reabsorption into 2 : 1 host–guest TATM inclusion compounds that crystallize in the triclinic $P\bar{1}$ space group and have unit cell parameters of approximately a = 8 Å, b = 10.5 Å, c = 12 Å, α = 95°, β = 107°, γ = 96°. Such TATM/guest compounds are obtained with guest molecules such as acetone, ethanol, methanol, 1,2-dichloroethane (DCE), cyclohexane and difluoropropane. For this study, acetone and DCE were chosen as appropriate guest molecules and crystals of TATM/acetone and TATM/DCE were grown by slow evaporation of

Table 1 Crystal data, data collection and final refinement parameters for six crystals of TATM/acetone. All data sets are collected at 125 K and analyzed in space group $P\bar{1}$

Crystal Empirical formula	**1** $2(C_{19}H_{16}O_3S_3)\cdot$ 1(acetone)	**1a** $2(C_{19}H_{16}O_3S_3)\cdot$ 0.84(acetone)	**1b** $2(C_{19}H_{16}O_3S_3)\cdot$ 0.80(acetone)	**1c** $2(C_{19}H_{16}O_3S_3)\cdot$ 0.60(acetone)	**1d** $2(C_{19}H_{16}O_3S_3\cdot$ 0.40(acetone)	**1e** $2(C_{19}H_{16}O_3S_3)\cdot$ 0.24(acetone)
a (Å)	8.1097(8)	8.0970(12)	8.0791(10)	8.032(4)	7.990(3)	7.9572(17)
b (Å)	10.5562(10)	10.5845(15)	10.6375(13)	10.645(5)	10.661(4)	10.694(2)
c (Å)	12.3382(12)	12.3055(18)	12.2329(15)	12.144(6)	12.050(4)	11.958(3)
α (°)	94.864(2)	95.020(3)	95.240(2)	95.345(6)	95.542(5)	95.691(3)
β (°)	107.949(2)	107.818(2)	107.497(2)	107.251(6)	106.816(4)	106.430(3)
γ (°)	95.909(2)	95.907(2)	95.945(3)	95.810(6)	95.760(5)	95.669(3)
V (Å^3)	991.89(17)	990.8(2)	991.4(2)	978.2(8)	969.0(6)	962.6(4)
Crystal size	0.30 × 0.16 × 0.05	0.32 × 0.32 × 0.26	0.32 × 0.32 × 0.10	0.24 × 0.16 × 0.12	0.32 × 0.16 × 0.08	0.14 × 0.14 × 0.08
# Reflections	12 473	11 973	5002	10 967	9744	6589
# Unique	5501	5448	3352	3978	3417	2018
R(int)	0.0233	0.0270	0.0156	0.0428	0.0609	0.0472
R indices ($>2\sigma$)	$R_1 = 0.0370$	$R_1 = 0.0529$	$R_1 = 0.0370$	$R_1 = 0.0594$	$R_1 = 0.0590$	$R_1 = 0.0354$
(all data)	$wR_2 = 0.0996$	$wR_2 = 0.1506$	$wR_2 = 0.1003$	$wR_2 = 0.1267$	$wR_2 = 0.1310$	$wR_2 = 0.0803$

concentrated solutions of TATM in the appropriate guest solvent. The crystal structures of both the acetone[33] and DCE[32] inclusion compounds were determined previously at 125 and 173 K, respectively, however, the single-crystal XRD data were recollected for both inclusions at 125 K (Tables 1 and 2). The crystal structures of both TATM/acetone (**1**) (Table 1) and TATM/DCE (**2**) (Table 2) are isostructural (TATM/DCE shown in Fig. 3) with one TATM molecule and one half of a guest molecule in the asymmetric unit. In both compounds the guests are disordered across an inversion center and the DCE guest is further disordered over two positions (77 : 23).

Guest removal in single crystals

To assess the stability of the TATM host framework upon guest removal the conversion from 'guest-filled' to 'partially occupied' to 'guest-free' TATM crystals was first studied by heating (80 °C) a small sample of TATM/acetone crystals in distilled water and monitoring the changes in crystal appearance over time. As shown in Fig. 4, the conversion can be thought of as occurring in three phases. In phase I the crystals are clear, pale yellow prisms and are fully occupied with the guest species (Fig. 4, left). In phase II solvent loss is occurring *via* a single-crystal-to-single-crystal transformation; the crystals are opaque and their quality has diminished slightly (Fig. 4, middle) but the host lattice remains intact. It is at this point in the conversion that the effects of solvent removal on the host framework can be suitably determined. Finally, in Phase III all crystal quality has been lost, the crystals redissolve and recrystallize, and clear colorless prisms emerge as indicated by the arrow in Fig. 4, right. In this final stage of conversion, 100% of the solvent guest has been removed from the cavities and the TATM molecules have rearranged to form the dense, completely guest-free form of TATM.

To determine how much guest can be removed from the TATM inclusions in Phase II without framework collapse, larger samples of TATM/acetone and TATM/DCE crystals were heated in an oven (80 °C) with water, as above, for a period of approximately three weeks, at which time the majority of crystals had an opaque appearance characteristic of Phase II. We note that crystals in all three phases were present in the sample and thus the rate of guest loss was not uniform throughout the sample. Presumably the rate varies with the size of the individual crystals. X-Ray diffraction data were collected at 125 K for five phase II crystals of TATM/acetone (**1a–1e**) and TATM/DCE (**2a–2e**). All ten crystals were isostructural (space group $P\bar{1}$) to the fully occupied TATM/acetone or TATM/DCE inclusions but the solvent guest occupancies were reduced to 84% (**1a**), 80% (**1b**), 60%

Table 2 Crystal data, data collection and final refinement parameters for six crystals of TATM/DCE. All data sets are collected at 125 K and analyzed in space group $P\bar{1}$

Crystal Empirical formula	**2** $2(C_{19}H_{16}O_3S_3\cdot$ 1(DCE)	**2a** $2(C_{19}H_{16}O_3S_3)\cdot$ 0.26(DCE)	**2b** $2(C_{19}H_{16}O_3S_3)\cdot$ 0.24(DCE)	**2c** $2(C_{19}H_{16}O_3S_3)\cdot$ 0.24(DCE)	**2d** $2(C_{19}H_{16}O_3S_3)\cdot$ 0.21(DCE)	**2e** $2(C_{19}H_{16}O_3S_3)\cdot$ 0.06(DCE)
a (Å)	7.9859(8)	7.9255(34)	7.944(4)	7.931(2)	7.964(4)	7.9498(16)
b (Å)	10.9220(11)	10.8054(46)	10.813(6)	10.798(3)	10.792(5)	10.739(2)
c (Å)	12.2218(13)	11.9461(51)	11.977(6)	11.948(3)	12.002(6)	11.936(2)
α (°)	97.398(2)	96.507(60)	96.448(7)	96.264(4)	96.368(6)	95.861(3)
β (°)	106.184(2)	105.889(6)	105.998(7)	105.987(3)	106.028(6)	106.164(2)
γ (°)	96.687(2)	96.037(6)	95.975(7)	95.939(3)	95.933(6)	95.609(3)
V (Å^3)	1002.17(18)	967.6(7)	972.9(9)	968.2(4)	975.6(8)	965.09
Crystal size	0.40 × 0.24 × 0.10	0.32 × 0.16 × 0.08	0.24 × 0.24 × 0.08	0.32 × 0.32 × 0.08	0.30 × 0.16 × 0.05	0.16 × 0.16 × 0.05
# Reflections	12 146	8231	9319	10 217	10 240	10 955
# Unique	5512	2769	3310	3926	3934	3928
R(int)	0.0198	0.0731	0.0619	0.0382	0.0587	0.0412
R indices ($>2\sigma$)	$R_1 = 0.0334$	$R_1 = 0.0872$	$R_1 = 0.0725$	$R_1 = 0.0626$	$R_1 = 0.0903$	$R_1 = 0.0440$
(all data)	$wR_2 = 0.0931$	$wR_2 = 0.2183$	$wR_2 = 0.1966$	$wR_2 = 0.1511$	$wR_2 = 0.2275$	$wR_2 = 0.1137$

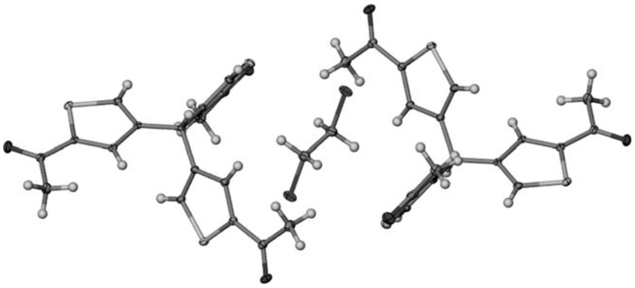

Fig. 3 The 2 : 1 TATM/DCE inclusion compound (**2**). Only the major position of the guest DCE molecule is shown.

(**1c**), 40% (**1d**) and 24% (**1e**), for the five TATM/acetone crystals (Table 1) and 26% (**2a**), 24% (**2b**), 24% (**2c**), 21% (**2d**) and 6% (**2e**) for the five TATM/DCE crystals (Table 2). The broad range of guest occupancies, although more limited in the TATM/DCE crystals (6–26%) than the TATM/acetone crystals (24–80%), confirms that the rate of guest loss is not the same in each crystal, but varies with crystal size (see Tables 1 and 2) and is clearly faster in smaller crystals. Furthermore, the data shows that the TATM host–guest framework is stable to guest loss. Up to 94% of the guest molecules were removed from the inclusion compounds with no indication of framework collapse in any of the crystals as each of the TATM host molecules continue to appear to be well-ordered. The degree to which guest desorption can occur without framework collapse is remarkable; examples of organic frameworks that are stable upon partial guest loss typically report depleted guest occupancies that are much higher than reported here.[14,16] Although no such crystals were found, it is plausible that with careful control even more of the guest solvent may be removed from the TATM host framework without rearrangement of the lattice framework or destruction of the crystal.

Changes in unit cell parameters and conformation of TATM upon guest removal

Although framework collapse does not occur upon guest loss small changes are observed in the unit cell parameters and conformation of the TATM molecules as the solvent occupancy decreases in the TATM/acetone and TATM/DCE inclusions. Specifically, for TATM/acetone, unit cell axes *a* and *c* clearly decrease in length with decreasing guest occupancy while the *b* axis increases (Fig. 5). In addition, the β and γ angles increase while α decreases upon decreased guest occupancy (Fig. 5). In the TATM framework, the host–guest inclusions are stacked vertically along the *a* axis with the central carbon atoms of the two TATM molecules aligned approximately along the *c* axis. As the guest molecules are removed the distance between vertically stacked inclusions as well as TATM molecules within an inclusion are reduced and so both the *a* and *c* axes decrease in length. The increase in the *b* axis is presumably to compensate for the contraction of the *a* and *c* axes. As can be seen from Table 2, the trends in unit cell parameters are not as clear for the TATM/DCE inclusion crystals as they are for TATM/acetone and the ambiguity may be due in part to the reduced distribution of guest occupancies in the TATM/DCE crystals. For instance, all of the TATM/DCE crystals that were screened have guest occupancies below 26% and four of five guest occupancies are within 5% of each other. In addition, the partially occupied TATM/DCE crystals were found to be of slightly poorer quality than the TATM/acetone crystals and so the unit cell parameters in general may not be as well determined for TATM/DCE.

Three distinct conformations of the acetyl thienyl rings have been reported in TATM inclusion compounds (Table 3) and are typically described by three torsion angles (τ_1, τ_2, τ_3) about the central methine C–H bond and whether the S atom and C=O group are *syn* (S) or *anti* (A) to one another.[35] The TATM molecules of the TATM/acetone and /TATM/DCE inclusions adopt conformation I. An alternative method for describing the conformation of TATM molecules is to measure the angle between two planes; The first plane is defined by the central methine carbon atom and the three thienyl carbon atoms bonded to it and the second plane is the plane of a thienyl ring, as defined by the central methine carbon atom, a sulfur atom and the two intervening carbon atoms of the thienyl ring.

Angles between planes ($\angle_1$, $\angle_2$, $\angle_3$) and torsion angles (τ_1, τ_2, τ_3) for TATM/acetone and TATM/DCE are listed in ESI Table 1 and plots of the changes in these angles as a function of guest occupancy for TATM/acetone are shown in Fig. 6. Angles τ_1, τ_3 and $\angle_1$, $\angle_3$ describe the two acetyl thienyl moieties of each TATM molecule (Fig. 1) that form the host cavity and angles τ_2 and $\angle_2$ correspond to the third acetyl thienyl group. For TATM/acetone torsion angle τ_1 increases with decreasing guest occupancy while τ_3 decreases and angles $\angle_1$ and $\angle_3$ decrease with decreasing guest while $\angle_2$ increases. The trend for τ_2 is less obviously but generally seems to increase.

The changes in torsion angles and angles between planes occur because as the guest molecules are removed the acetyl thienyl groups of TATM appear to shift in such a way as to reduce the distance between the two thienyl rings surrounding the guest while concomitantly increasing the distance between

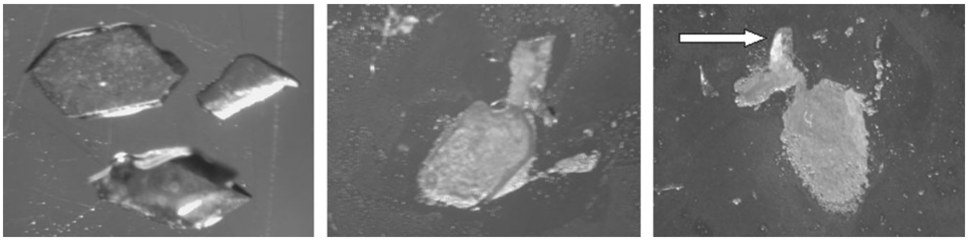

Fig. 4 Three phases of guest removal in TATM/acetone crystals: (left) phase I, crystal prior to guest loss; (middle) phase II, partial guest loss with framework intact; (right) phase III, recrystallization to give dense guest-free form of TATM.

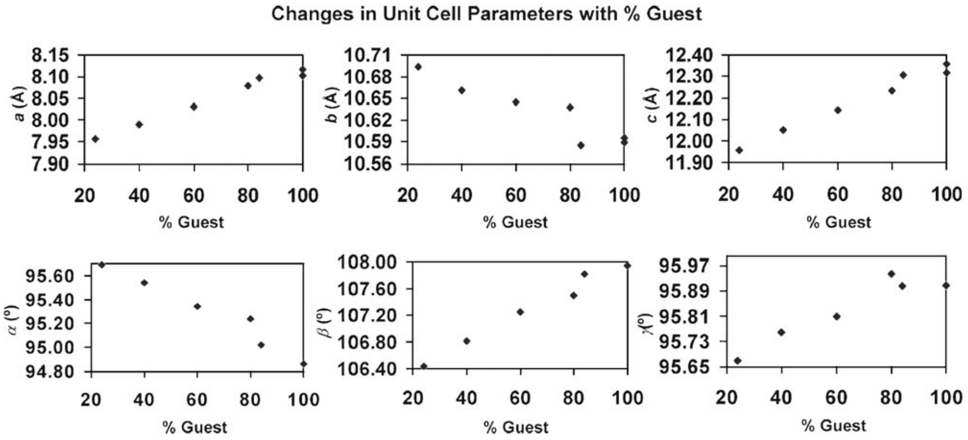

Fig. 5 Plots showing the changes in unit cell parameters as a function of % guest occupancy for crystals of TATM/acetone.

methyl groups. We note that values of τ_2 and $\angle_2$ vary the least over the range of guest occupancies since the associated acetyl thienyl moiety is not involved in the host–guest interaction. Similar trends in conformation of the TATM molecule are observed for crystals of TATM/DCE (ESI, Table 1‡) but the poorer crystal quality and narrow distribution of guest occupancies does not allow for a more rigorous treatment of the data.

Guest adsorption in single crystals

It is also possible for the partially empty TATM host cavities to absorb guest molecules. Two of the partially depleted TATM/acetone crystals, with 84% (**1a**) and 80% (**1b**) solvent occupancy, were exposed to acetone vapor overnight. Upon re-collection of the X-ray diffraction data the guest occupancies had increased to 100% (**1aA**) and 96% (**1bB**) (ESI Table 2‡), respectively. Subsequent exposure of the 96% occupied TATM/acetone crystal (**1bB**) to acetone vapor gave a fully occupied inclusion. Refilling the depleted cavities with acetone guest leads to further loss of crystal quality and less reliable unit cell parameters, however, the changes in unit cell parameters and torsion angles that occurred during guest removal are effectively reversed upon guest insertion.[36]

New guests can also be adsorbed by the partially depleted cavities. A crystal of TATM/DCE with partial guest occupancy of (39%) was exposed to acetone vapor overnight. Upon re-collection of the X-ray diffraction data both DCE (39%) and acetone (50%) were present in the host–guest framework. Fig. 7 shows the mixed guest inclusion. The DCE and acetone guest molecules occupy the same positions in the mixed guest inclusion as they do in the normal TATM/acetone and TATM/DCE inclusions. We note that the unit cell parameters and conformational angles for the mixed guest TATM/DCE/acetone inclusion crystal (**3**) (ESI Table 2‡) were intermediate to those of the fully occupied TATM/acetone (**1**) and TATM/DCE (**2**) crystals.[37]

Table 3 The three general conformations of TATM in its inclusion compounds as described by a combination of torsion angles and sulfur-carbonyl positions

Conformation	τ_1 (°)	τ_2 (°)	τ_3 (°)	Orientation of C=O (wrt S)
I	~0	~105	~160	SSS
II	~0	~130	~150	SSA
III	~0	~100	~15	SSS

Adsorption of mixed guests in single crystals

The inclusion of both acetone and DCE in the TATM crystal prompted us to further explore TATM's affinity for the mixed guest system and the effect different ratios of guest would have on the crystallographic and conformational parameters. Crystals of TATM were grown from a 1 : 1 equimolar mixture of acetone and DCE. The crystals were found to contain 64% DCE and 36% acetone by ^{1}H NMR. This was confirmed by single-crystal X-ray diffraction; full data sets were collected for several crystals and the guest occupancies were consistent (64% DCE, 36% acetone) for each crystal studied. To obtain crystals with different guest ratios the crystallizations were repeated using varying ratios of the two guests (*i.e.* 2 : 1 DCE : acetone 1 : 2 DCE : acetone) and crystals with DCE : acetone occupancies of 76 : 24 and 40 : 60% were obtained.[38] Plots of the unit cell parameters and conformation angles for the mixed TATM/DCE/acetone crystals as well as the fully occupied TATM/DCE and TATM/acetone (in terms of %DCE are shown in Fig. 8 and 9.

As can be seen from Fig. 8 and 9 unit cell parameters *a* and β and conformational parameters $\angle_2$, $\angle_3$, τ_2 and τ_3 all increase as the percentage of DCE decreases (acetone increases), while unit cell and conformational parameters *b*, α, γ and τ_1 decrease. The trends for cell axis *c* and angle $\angle_1$ are less clear but overall seem to increase as the amount of DCE in the mixed inclusion decreases. The trends for the mixed guest TATM/DCE/acetone system are as expected since values of *a*, *c*, β, $\angle_1$, $\angle_2$, $\angle_3$, τ_2 and τ_3 are typically smaller for the TATM/DCE inclusion than for TATM/acetone, while *b*, α, γ and τ_1 are larger. One observation worth noting is that for each TATM/DCE/acetone crystal the unit cell and conformational parameters are more similar to those of the fully occupied TATM/DCE inclusion than the TATM/acetone inclusion even when percentage of acetone in the inclusion is greater (*i.e.* 40% DCE : 60% acetone). This suggests that the

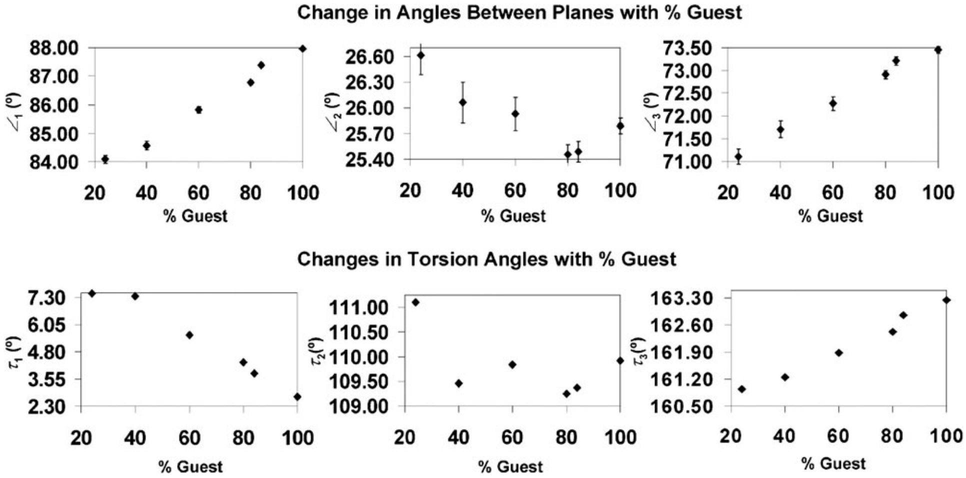

Fig. 6 Plots showing the changes in angles between planes as a function of % guest occupancy for crystals of TATM/acetone.

TATM/DCE inclusion is more favorable than the TATM/acetone inclusion, which is supported by the fact that TATM includes more DCE than acetone from a mixture of the two guests even though equimolar amounts of the two solvents are used.[39–43]

Comparison with other organic hosts

The TATM host framework has been shown to be stable to near complete guest loss. Several other examples of organic molecules surviving complete or partial guest desorption without undergoing a phase change are known and include classic examples such as Gossypol[10] and Dianin's compound.[15] More recently, crystals of a diaminotriazine derivative that incorporate dioxane were shown to remain stable upon removal of up to 63% of the dioxane guest molecules under vacuum.[14] Similar to the present study, the crystals showed a systematic contraction of the unit cell parameters as the guest was removed. A benzene adduct of an acridinylresorcinol host was found to readily lose one of two molecules of guest benzene and then adsorb one molecule to regenerate the full adduct without loss of the framework integrity.[16] A series of dipeptides, labeled the AV class after one of its members L-alanyl-L-valine (AV), forms hexagonal channels that are stable with or without included guest molecules (typically water).[12,44] Furthermore, crystals of the AV dipeptide with small guest molecules such as acetonitrile or methanol were found to remain intact upon heating and guest removal. The guest-free crystals could then be soaked in a new solvent to obtain a new inclusion, however, larger solvents such as 2-propanol could not be removed once incorporated.[12]

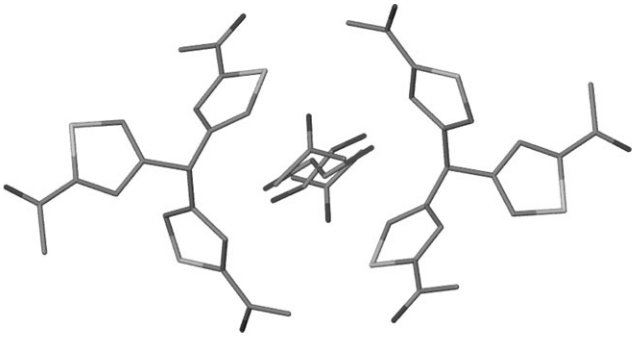

Fig. 7 Crystal structure of the TATM/39% DCE/50% acetone mixed-guest inclusion compound (**3**). All positions of the guest molecules are shown.

With the exception of the AV work, the ability of organic frameworks to withstand (partial) guest desorption has been demonstrated mainly by powder X-ray diffraction (PXRD) studies in which there is essentially no change in the powder pattern of the host material once the guest has been removed.[14–16] While PXRD data is important and useful, the advantage to being able to measure single-crystal X-ray diffraction data after each stage of guest loss is that we are able to directly observe the small changes that occur in the conformation of the host framework (in addition to unit cell changes) as the guest is being desorbed or adsorbed. The systematic changes in unit cell and conformational parameters, along with the absence of host molecule disorder in the partially depleted crystals after each stage of guest release, suggests that guest loss is uniform throughout the sample and negates the possibility that the crystals contain some domains of normal guest composition and host conformation and other disordered domains with reduced guest and altered host conformation.[14]

The stability of the TATM host framework with respect to guest desorption and adsorption is quite remarkable. Though other organic frameworks have shown similar robustness, their stability is, at least in part, governed by the fact that the host frameworks are often two and three-dimensional networks formed through extensive H-bonding interactions (and often π–π stacking as well) that give the framework a high degree of rigidity and stability.[12–16] In contrast, the TATM framework is unique in that there are no strong H-bond interactions between host molecules; instead, the network is supported by occasional π–π stacking of thienyl rings, very weak C–H···O H-bonds and general van der Waals interactions between the layers.

It is likely that the TATM system and others like it will not fit into a class of materials that will be easily described by the van der Waals and Platteuw approach. Even though there is a single dense form, polymorphism is common for TATM

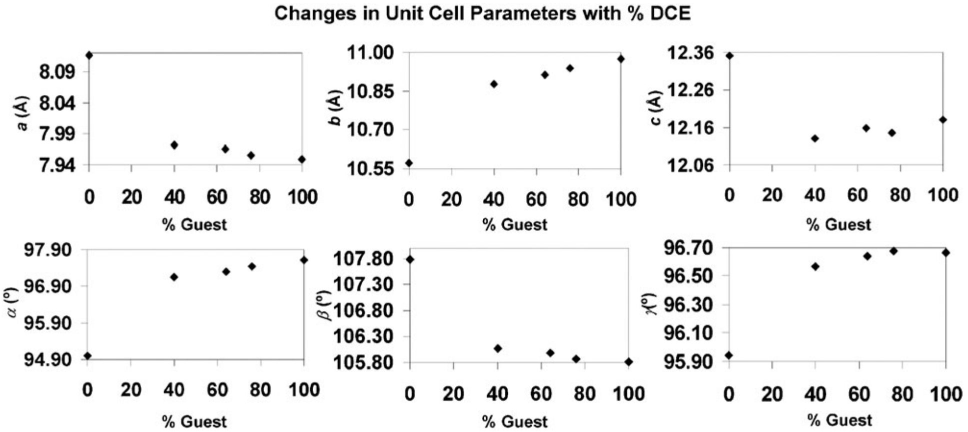

Fig. 8 Plots showing the changes in unit cell parameters as a function of %DCE for crystals of the mixed guest system TATM/DCE/acetone (%DCE: 76, 64, 40). Data are compared to data for TATM/DCE (%DCE: 100) and TATM/acetone (%DCE: 0).[38]

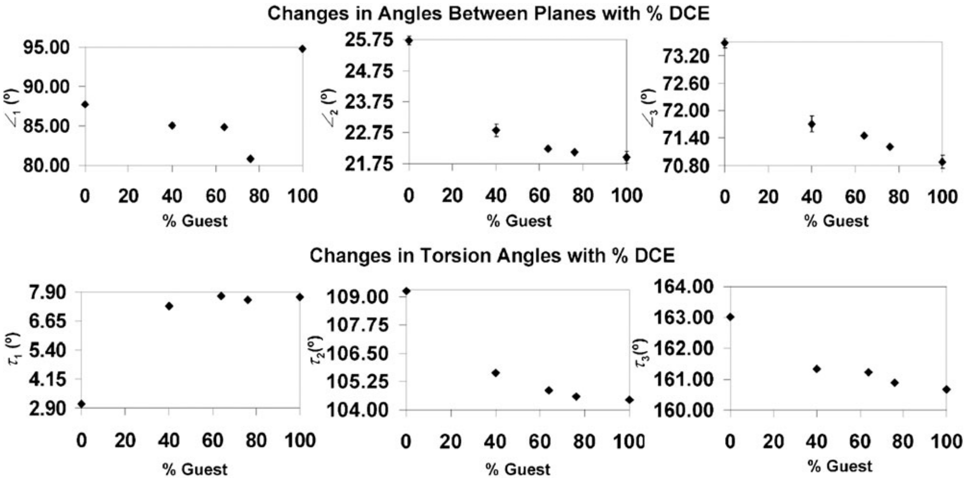

Fig. 9 Plots showing the changes in conformational parameters as a function of %DCE for crystals of the mixed guest system TATM/DCE/acetone. (%DCE: 76, 64, 40). Data are compared to data for TATM/DCE (%DCE: 100) and TATM/acetone (%DCE: 0).[38]

compounds (the five forms of the 1 : 1 dichloropropane–TATM compound[33]), indicating that a large number of guest–host configurations of nearly the same free energy is possible. Other factors are that the unit cell structures and volumes are quite sensitive to the cage occupancy and also to the presence of mixed guest species—both counter the assumptions inherent in the vdW–P approach.

Conclusions

In the present study we have examined the structural changes that occur within a 2 : 1 TATM host : guest framework as the included guest species is depleted. Remarkably single crystals remain stable despite loss of up to 95% of the included guest molecules. The depleted framework will readily absorb guest molecules to reform the fully-occupied 2 : 1 complex. The response of the host structure to both variable guest occupancy and the presence of mixed guests has been inferred from a series of single-crystal X-ray diffraction experiments. The depleted framework appears to be stabilized by a combination of π–πstacking, weak C–H···O, and van der Waals interactions. Guest molecules are readily transported into and out of the framework despite an apparent lack of channels, suggesting that cooperative dynamics may play a role, as in the low density phase of *p*-*tert*-butylcalix[4]arene.[45,46]

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36 Unit cell parameters and conformational angles (τ, $\angle$) for **1aA** and **1bB**. **1aA** (100% acetone): a = 8.1018(6), b = 10.5888(8), c = 12.3159(9) Å, α = 94.999(1), β = 107.765(1), γ = 95.960(1)°, τ_1 = 3.80, τ_2 = 109.37, τ_3 = 162.85°, $\angle_1$ = 87.39(8), $\angle_2$ = 25.49(12), $\angle_3$ = 73.21(9)°. **1bB** (96% acetone): a = 8.1349(6), b = 10.5100(8), c = 12.3775(9) Å, α = 94.624(1), β = 108.274(1), γ = 95.778(1)°, τ_1 = 2.01, τ_2 = 110.38, τ_3 = 163.19°, $\angle_1$ = 81.97(5), $\angle_2$ = 27.84(9), $\angle_3$ = 78.89(2)°.

37 Unit cell parameters and conformational angles (τ, $\angle$) for **3**: (50% acetone, 39% DCE): a = 8.0358(32), b = 10.8004(44), c = 12.2348(49) Å, α = 96.582(5), β = 106.786(5), γ = 96.366(5)°, τ_1 = 5.00, τ_2 = 106.52, τ_3 = 161.43°, $\angle_1$ = 86.28(21), $\angle_2$ = 23.91(35), $\angle_3$ = 23.91(35)°.

38 Single-crystal X-ray diffraction data were collected at 100 K for the mixed guest TATM/DCE/acetone inclusions. Therefore X-ray diffraction data for TATM/DCE and TATM/acetone were recollected at 100 K for comparison.

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