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Conformational isomerism leads to supramolecular isomerism and nanoscale inclusion in 2D extended framework solids based on *C*-methylcalix[4]resorcinarene

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Co-crystallization of *C*-methylcalix[4]resorcinarene 1 with 4,4′-bipyridine 2 in the presence of *m*-xylene results in the formation of a 2D brick framework, 3c·2(*m*-xylene), that possesses nanoscale cavities that host four aromatics as guests in which 1 adopts a ‘T-shaped’ conformation.

With the recognition that strategies for the deliberate design[1] of molecular crystalline solids[2] can lead to new materials with predictable properties realized (*e*.g. inclusion),[3–6] increased efforts have been placed upon understanding and controlling those factors that govern the assembly of molecules and/or ions in the solid state. For the design of extended solids with cavities that accommodate molecules as guests,[7] relatively strong, directional forces (*e.g.* hydrogen bonds) have attracted much attention in this regard owing to the structure-directing abilities of such interactions to be predicted with a reasonable degree of accuracy. Despite successes in exploiting such forces, however, it is, perhaps, surprising to note that nanoscale processes of molecular inclusion,[8] where, for example, multiple copies of a guest occupy a closed cavity in a solid, remain rare. Indeed, the successful engineering of cavities able to accommodate multiple guests can, in principle, provide a route to solids with guests that undergo reaction in the solid state[9] and bear relevance to problems of separations of large molecules.[10]

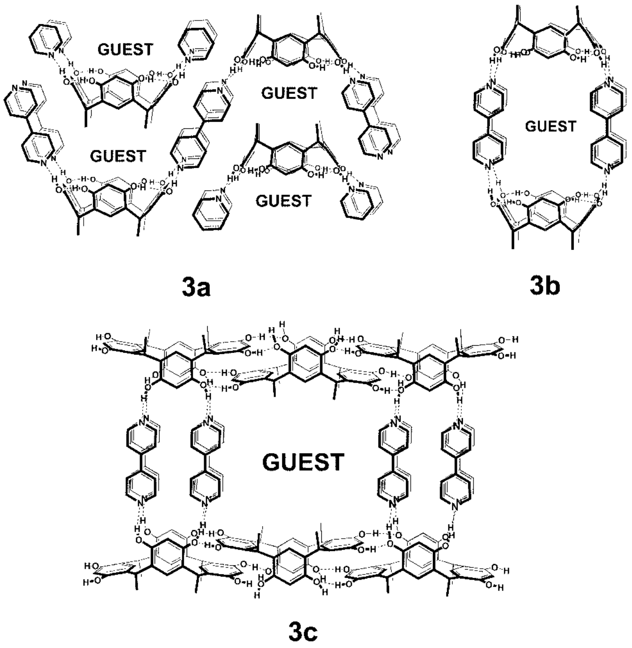
With this in mind, using a template-based method to molecular self-assembly we report the ability of the components of two supramolecular isomers **3** of composition **1**·2(**2**) (where **1** = *C*-methylcalix[4]resorcinarene, **2** = 4,4′-bipyridine),[11] that define a hydrogen-bonded, wave-like network **3a**[12] and carcer-and-like capsule **3b**,[13] to undergo a structural reorganization in the presence of a suitable aromatic guest to form a two-dimensional (2D) isomer **3c** of the parent components (Scheme 1). The network **3c**·2(*m*-xylene) defines a 2D symmetrical brick framework[14–16] that exhibits closed multi-molecular cavities of nanoscale dimensions, that, owing to the ability of **1** to adopt a ‘T-shaped’ conformation,[17] accommodate four identical aromatics as guests. Whereas supramolecular isomerism involving ligand conformational isomerism has been observed in inclusion compounds based on coordination polymers,[18] **3c**·2(*m*-xylene) represents, to our knowledge, a novel example of an organic inclusion compound that exhibits supramolecular isomerism involving conformational isomerism by a molecular receptor.†

When **1** (0.020 g) was co-crystallized with 2 equiv. of **2** (0.011 g) from a boiling aliquot of EtOH in the presence of 10 equiv. of *m*-xylene according to eqn. (1), single crystals of

$$\mathbf{1} + 2(\mathbf{2}) + 10(m\text{-xylene}) + \text{EtOH (excess)} \rightarrow \mathbf{3c}\cdot 2(m\text{-xylene}) \quad (1)$$

3c·2(*m*-xylene) suitable for X-ray analysis grew within a period of approximately 4 days. The formulation of **3c**·2(*m*-xylene) was determined by single-crystal X-ray diffraction‡ and ^{1}H NMR spectroscopy.

A space-filling view of the X-ray crystal structure of **3c** is shown in Fig. 1. As in the case of the wave-like framework **3a**·guest (guest = ferrocene, toluene, MeCN)[11,12] and carcer-and-like capsule **3b**·guest (guest = nitrobenzene),[13] four molecules of **2**, each of which serves as a bifunctional hydrogen



Scheme 1

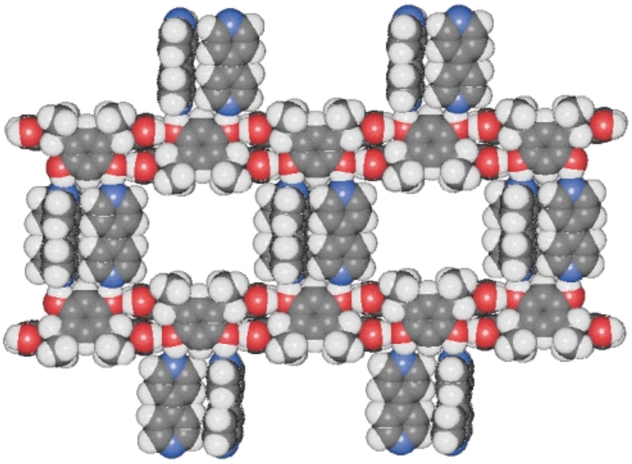


Fig. 1 Space-filling view of the X-ray crystal structure of **3c** (guests have been omitted for clarity). Color scheme: grey = carbon; white = hydrogen; blue = nitrogen; red = oxygen.

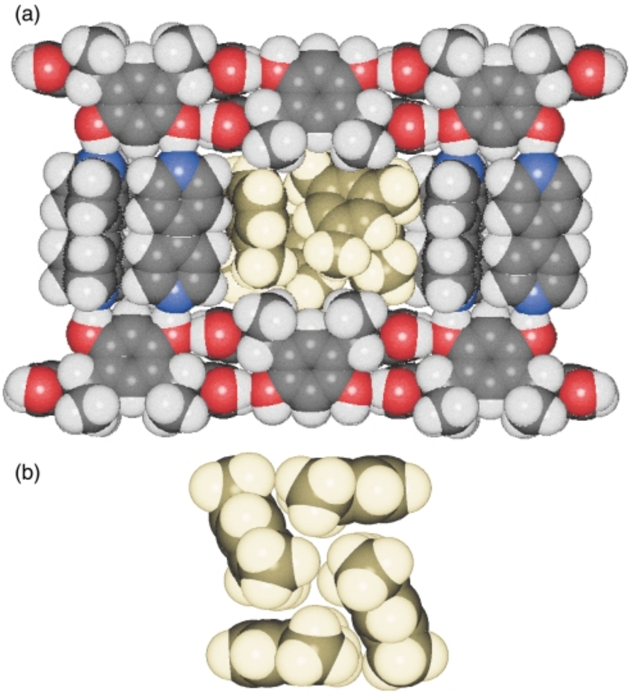


Fig. 2 Space-filling view of the guests of **3c**: (a) a view showing the guests within the brick framework, and (b) a view showing the edge-to-face π–π interactions of the guests. Color scheme: grey–yellow = guest atoms (Note: two *m*-xylene guests lie disordered, each across three sites).

bond acceptor, have assembled with **1** such that the bipyridines participate in four O–H···N hydrogen bonds with two opposite resorcinol units of the macrocycle [O···N separations (Å): O(1)···N(1) 2.770(4), O(2)···N(3) 2.727(4), O(5)···N(4) 2.774(4), O(6)···N(2) 2.725(4)]. Unlike **3a** and **3b**, however, the pyridine units of **3c** interact with **1** such that they participate in edge-to-face, rather than face-to-face, π–π interactions[24] along the upper rim of **1** and the cavity of **1** is closed. The remaining resorcinol units, which are co-planar and lie approximately perpendicular to the resorcinol moieties involved in the O–H···N forces, form four intermolecular O–H···O hydrogen bonds with two neighbouring molecules of **1**, making **1**, in the form of a 'T-shaped' building block,[17] an eight-fold hydrogen bond donor [O···O separations (Å): O(1)···O(4) 2.749(4), O(2)···O(7) 2.754(4), O(3)···O(5) 2.768(4), O(6)···O(8) 2.735(3)]. As a consequence of the assembly process, a 2D layered symmetrical brick framework **3c**, with large, closed rectangular cavities (cavity dimensions *ca.* 14 × 11 × 6 Å) of idealized D_{2h} symmetry, has formed.§

A view depicting the guests of **3c**·2(*m*-xylene) is shown in Fig. 2. Four molecules of *m*-xylene, which lie around a crystallographic center of inversion, are located within each cavity [Fig. 2(*a*)] such that the aromatics assemble by way of edge-to-face π–π interactions [Fig. 2(*b*)].[24] In this arrangement, two guests, which are related by symmetry, are positioned within the cavity such that the aromatic rings of the guests interact with **2** by way of edge-to-face π–π interactions,[23] while the remaining guests, each of which lies equally disordered across three sites, fill the host, in contrast to the ordered guests, such that the aromatics lie approximately parallel to the face of the cavity. Thus, the cavities of **3c**·2(*m*-xylene) have formed by way of template effects involving multiple guests in which the size, shape and electronic properties of an individual guest, presumably, do not favour an assembly process that leads to **3a** or **3b**.[15] Here, the conformational flexibility of **1** has provided access to a cavity, in the form of **3c**, that accommodates four molecules of *m*-xylene in which the O–H···N interactions between **1** and **2** are maintained[11–13] and **1** self-assembles by way of O–H···O forces.[17]

We have revealed the ability of **1**, in a 'T-shaped' conformation,[17] to assemble with **2** in the presence of a suitable guest to form a 2D symmetrical brick framework **3c** that possesses cavities of nanoscale dimensions which host four identical aromatics as guests. With such observations realized, we are currently investigating whether **3c** may be used as a host for multiple guests able to undergo reaction in the solid state.[9] We are also exploring whether molecules may be selected, *a priori*,[15] to induce formation of additional supramolecular isomers, able to accommodate single or multiple guests, based on **3**.¶ These observations should also bear relevance to materials in which derivatives of **1** and **2** are employed for the assembly process.

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Notes and references

† Molecular receptors typically adopt a number of conformations which make such molecules attractive building blocks for assembly processes leading to supramolecular isomerism by extended frameworks.[19] For an earlier account of **3c** see ref. 20.

‡ *Crystal data* for **3**·2(*m*-xylene): triclinic, space group $P\bar{1}$, a = 12.908(1), b = 13.791(1), c = 16.649(1) Å, α = 93.770(1), β = 102.761(1), γ = 91.189(2)°, U = 2882.3(3) Å^3, D_c = 1.27 g cm^{-3}, Mo-Kα radiation (λ = 0.71070 Å) for Z = 2. Least squares refinement based on 4226 reflections with $I_{net} > 2.0\sigma(I_{net})$ (out of 7512 unique reflections) led to a final value of R = 0.059. Aromatic and hydroxy hydrogen atoms were placed by modelling the moieties as rigid groups with idealised geometry, maximising the sum of the electron density at the calculated hydrogen positions. Structure solution was accomplished using SHELXS-86[21] and refinement was conducted using SHELXL93[22] locally implemented on a pentium-based IBM-compatible computer. Structure refinements and production of the figures were accomplished with the aid of RES2INS.[23]

CCDC 162090. See http://www.rsc.org/suppdata/cc/b1/b102856c/ for crystallographic data in .cif or other electronic format.

§ Adjacent layers lie staggered such that the cavities are closed.

¶ Molecules of similar shape to *m*-xylene may be used to induce formation of **3c** (unpublished results).

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