

# Head-to-tail self-assembly of a calix[4]arene inclusion polymer controlled by a pendant arm

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Received (in Columbia, MO, USA) 14th October 2004, Accepted 2nd March 2005

First published as an Advance Article on the web 30th March 2005

DOI: 10.1039/b416589f

A calix[4]arene functionalized at one phenolic group with a pendant ethoxy acetate group, forms an inclusion complex that is stable even in the presence of other potential guest molecules.

The construction of 1, 2 or 3-dimensional molecular networks sustained by strong hydrogen or dative bonding interactions has facilitated the generation of a wide range of mineralomimetic and novel network structures.<sup>1</sup> Such approaches to crystal engineering facilitate programming of physical properties in the solid-state since molecular components can be selected for their properties as well as their shape.<sup>2</sup> However, non-covalent interactions involved in inclusion complexes are relatively weak and this has limited our ability to design solid-state structures based upon host-guest chemistry. For example, although the conformations of calix[4]arenes, a ubiquitous class of inclusion compounds,<sup>3</sup> can be controlled *via* intramolecular hydrogen bonding, their packing motifs are diverse and unpredictable. Their packing motifs can be described as being one of, or a combination of, the following: guest mediated head-to-tail,<sup>4</sup> guest mediated face-to-face,<sup>5</sup> self-included<sup>6</sup> and, for the case of bulky substituents, discotic.<sup>7</sup> Notable exceptions in terms of crystal engineering are the one-dimensional inclusion polymers that have been constructed from calix[*n*]arenes by Hosseini.<sup>8</sup> These structures rely on guest mediated face-to-face interactions and are typically centrosymmetric. Therefore, a reliable strategy for generating head-to-tail non-centrosymmetric calix[4]arene networks remains to be developed. We report herein preliminary structural studies concerning a strategy which exploits the inclusion behaviour of a calix[4]arene that is functionalized at one phenolic moiety with a pendant moiety, 25-mono-(ethoxycarbonylmethoxy)-calix[4]arene, **1**.

**1** was synthesised by the literature method<sup>9</sup> and obtained in 20% yield after separation. Crystals of **1** were grown from acetone (solvent free, **1a**), chloroform (chloroform solvate, **1b**) and toluene (toluene solvate, **1c**) by slow evaporation. Crystals were also grown in chloroform in the presence of 5-fold excesses of naphthalene and *para*-dichlorobenzene, also affording **1b**. Fig. 1 reveals the molecular formula and structure of **1**.† All three crystal structures (**1a**, **1b**, and **1c**) reveal that the pendant ethoxy acetate group adopts an extended conformation (torsion angles are given in supplementary data†). The three non-substituted phenolic hydroxyl groups participate in the formation of an intramolecular ring of hydrogen bonds that sustains the cone conformation that is so common to calix[4]arenes.<sup>3</sup> The aromatic groups exhibit a dissymmetric flattened cone conformation, meaning that the

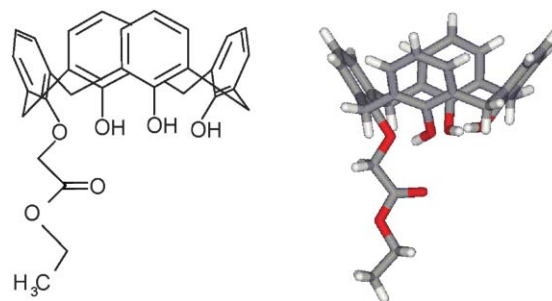


Fig. 1 Molecular formula and structure of **1**.

aromatic rings are not equivalent (tilt angles and distances are given in supplementary material†). There are no intramolecular interactions with the oxygen atoms of the ester group. An analysis of the three crystal structures reveals that crystal packing of the calixarenes is controlled by intermolecular inclusion of the pendant OCH<sub>2</sub>COOEt group with the calix moiety of **1** (Fig. 2). Intermolecular CH $\cdots$  $\pi$  contacts between the aromatic rings of **1** and the CH<sub>3</sub> atoms of the included pendant group are within the expected range for such interactions, 3.4–3.7 Å. This is in contrast to the equivalent tetra-substituted calix[4]arene, where a molecule of acetonitrile is included in the cavity and although a head-to-tail assembly is present, no aromatic $\cdots$ CH<sub>3</sub> contacts are present (the shortest distance being 6.75 Å).<sup>10</sup>

Three independent molecules of **1** are present in the unsolvated form of **1**, **1a**. The crystal packing of **1a** is illustrated in Fig. 3a, which reveals that the overall packing is anti-parallel, although adjacent chains can be either parallel or anti-parallel.

The repeat distances between calix are 10.43, 9.99 and 10.26 Å for **1a–c**, respectively compared to repeat distances of 12.98 Å and 5.66 Å seen in solvent mediated head-to-tail assemblies<sup>4</sup> and discotic assemblies,<sup>7</sup> respectively.

For the chloroform solvate **1b**, the inclusion polymers also form anti-parallel chains. The chloroform solvate molecules lie between these chains rather than in the cavity of the calix moiety. There are

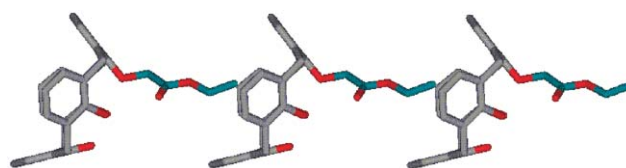
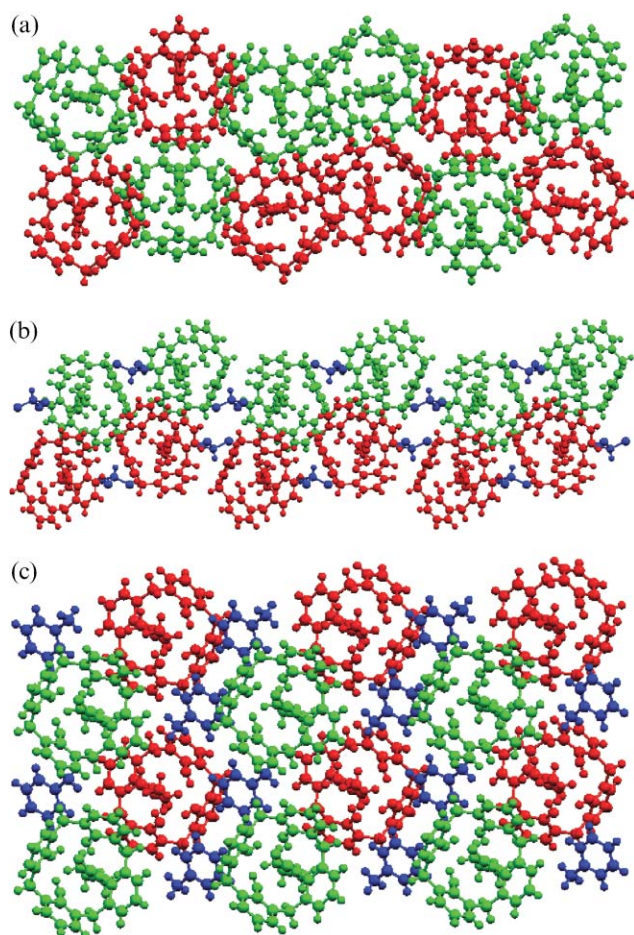


Fig. 2 The one dimensional inclusion polymer exhibited by **1**. Calix molecules repeat every 10.43, 9.99 and 10.26 Å for **1a–c**, respectively.

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**Fig. 3** a. The crystal packing of one unit cell of **1a** viewed in the *bc* plane. There are three molecules of **1** in the asymmetric unit. Head-to-tail chains of **1** lie parallel to the *a*-axis with 50% having their pendant arms oriented towards the viewer (green) and 50% oriented away (red). b. The crystal packing of three unit cells of **1b** viewed in the *bc* plane. Head-to-tail chains of **1** lie parallel to the *a*-axis with 50% having their pendant arms oriented towards the viewer (green) and 50% oriented away (red). c. The crystal packing of a  $3 \times 2$  grid of unit cells of **1c** viewed in the *bc* plane. There is one molecule of **1** and one solvent molecule in the asymmetric unit. Head-to-tail chains of **1** lie parallel to the *a*-axis with 50% having their pendant arms oriented towards the viewer (green) and 50% oriented away (red).

a plethora of weak interactions between chains (T-shape interactions of 3.7–4.0 Å, CH $\cdots\pi$  interactions of 3.7–3.9 Å). The hydrogen atoms of the chloroform molecules form weak hydrogen bonds (3.19 Å) with the OH phenolic moieties of **1**. The overall packing, illustrated in Fig. 3b, can be described as a corrugated sheet of anti-parallel inclusion polymers that is separated by included solvent molecules.

In the case of the toluene solvate **1c**, the one-dimensional inclusion polymer is once again present and the overall packing is similar to that of **1b** (Fig. 3c) except that the corrugation is more pronounced. The anti-parallel chains of **1** form  $\pi\cdots\pi$  interactions between adjacent calix moieties (3.51 Å) and T-shape interactions with the solvent (3.53 Å). In addition, weak CH $\cdots\pi$  interactions are noted between the anti-parallel bilayers (3.92 and 3.94 Å). In view of the well documented ability<sup>11</sup> of calix[4]arenes to form inclusion complexes with toluene, the presence of toluene

molecules between layers rather than in the cavities of the calix moieties is unexpected and underscores the robust nature of the interaction between the pendant arm and the calix which in turn supports the head-to-tail inclusion polymer motif. That crystals of **1** grown in the presence of other likely guests afforded only the chloroform solvate **1b** further suggests that the pendant arm motif described herein is robust enough to act as a general supramolecular synthon. This does not appear to be the case for the handful of calix[4]arenes that have been substituted at the rim rather than at the phenolic oxygen atoms.<sup>12</sup>

In conclusion, we have shown that **1** forms a one dimensional head-to-tail inclusion polymer motif that is stable even in the presence of molecules that are likely to form motif disrupting host–guest complexes. Work is currently underway to investigate if, as with equivalent cyclodextrin systems,<sup>12</sup> the inclusion polymers may be deposited as single chains onto surfaces from solution.

The authors wish to acknowledge the financial support of BioMerieux (SC), DeltaProteomics (5ANL) and CNRS; KS thanks the KBN Grant 4 T09A 068 25 for Polish support; MZ thanks the National Science Foundation, DMR 0101641.

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## Notes and references

† Crystallographic data: crystals were obtained by slow evaporation of calix[4]arene mono-*O*-ethoxycarbonylmethoxy from acetone, chloroform and toluene solutions. Crystal data for: (**1a**) C<sub>32</sub>H<sub>30</sub>O<sub>6</sub>, *M<sub>r</sub>* = 510.56, colorless, 0.20 × 0.25 × 0.30 mm, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 10.432(2), *b* = 16.514(3), *c* = 45.259(9) Å,  $\beta$  = 95.53(3)°, *V* = 7761(3) Å<sup>3</sup>, *Z* = 12,  $\rho_{\text{calc}}$  = 1.311 mg m<sup>-3</sup>,  $\theta_{\text{max}}$  = 25.01°,  $\mu(\text{MoK}\alpha)$  = 0.090 mm<sup>-1</sup>, 13676 independent reflections, 6098 [*I* > 2 $\sigma$ (*I*)], *R* = 0.168, *wR* = 0.189, GOF = 0.967 (all data), largest diff. peak and hole 0.65 and -0.43 e Å<sup>-3</sup>. (**1b**) C<sub>32</sub>H<sub>30</sub>O<sub>6</sub>·CHCl<sub>3</sub>, *M<sub>r</sub>* = 639.93, colorless, 0.35 × 0.25 × 0.13 mm, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 9.9991(3), *b* = 15.1151(4), *c* = 19.8410(6) Å,  $\beta$  = 99.564(2)°, *V* = 2957.0(2) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calc}}$  = 1.415 mg m<sup>-3</sup>,  $\theta_{\text{max}}$  = 24.71°,  $\mu(\text{MoK}\alpha)$  = 0.355 mm<sup>-1</sup>, 5008 independent reflections, 3937 [*I* > 2 $\sigma$ (*I*)], *R* = 0.064, *wR* = 0.088, GOF = 1.029 (all data), largest diff. peak and hole 0.243 and -0.260 e Å<sup>-3</sup>. (**1c**) C<sub>32</sub>H<sub>30</sub>O<sub>6</sub>·C<sub>7</sub>H<sub>8</sub>, *M<sub>r</sub>* = 602.69, colorless, 0.35 × 0.33 × 0.20 mm, triclinic, *P*1, *a* = 10.2613(3), *b* = 11.2683(3), *c* = 14.4682(3) Å,  $\alpha$  = 85.602(2),  $\beta$  = 71.504(2),  $\gamma$  = 80.313(1)°, *V* = 1563.29(7) Å<sup>3</sup>, *Z* = 2,  $\rho_{\text{calc}}$  = 1.280 mg m<sup>-3</sup>,  $\theta_{\text{max}}$  = 26.40°,  $\mu(\text{MoK}\alpha)$  = 0.085 mm<sup>-1</sup>, 6260 independent reflections, 4849 [*I* > 2 $\sigma$ (*I*)], *R* = 0.069, *wR* = 0.107, GOF = 1.017 (all data), Largest diff. peak and hole 0.226 and -0.196 e Å<sup>-3</sup>. Intensity data were collected at 200 K on a Bruker AXS diffractometer P4 (**1a**) and 100(2) K on a Nonius KappaCCD diffractometer (**1b** and **1c**) using MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Data corrected for Lorentz and polarisation effects but not for absorption. The structure was solved by direct methods and Fourier techniques (SHELXS-86<sup>13</sup>) and refined, on |*F*|<sup>2</sup> (SHELXL-97<sup>14</sup>). H-atoms were included in geometric positions and refined as ‘riding’ atoms (except those of hydroxyl groups which were located on Fourier difference maps with positional parameters refined) with isotropic thermal parameters based upon the corresponding bonding carbon atom (*U*<sub>iso</sub> = 1.2*U*<sub>eq</sub>, *U*<sub>iso</sub> = 1.5*U*<sub>eq</sub> for CH<sub>3</sub> and OH hydrogens). Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 252482–252484. See <http://www.rsc.org/suppdata/cc/b4/b416589/> for crystallographic data in .cif or other electronic format.

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