

Unique conformation and packing structure of *p*-sulfonatocalix[5]arene induced by 1,2-bis(pyridinium)ethane compounds

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In the presence of 1,2-bis(4,4'-dipyridinium)ethane, *p*-sulfonatocalix[5]arene (C5AS) adopts an unseen partial-cone conformation to form back-to-back dimers, whereas C5AS crystallizes in face-to-face dimers to form a wavy layer, rather than the expected bilayer, arrangement upon complexation with 1,2-bis(pyridinium)ethane.

The construction of nanometre-sized supramolecular architectures has recently attracted much attention in the broad area of supramolecular chemistry and crystal engineering.¹ In this field, the water-soluble sulfonatocalix[*n*]arenes (*n* = 4, 5, 6, 8) (CAS) are a well-known family of building synthons, which can be assigned to design various extended structures,^{2,3} and have even demonstrated a strong potential in bio-applications.⁴ In general, CAS arrange themselves in an up-down antiparallel fashion to form clay-type bilayer arrangements.⁵ However, it has been well-documented to date that this traditional bilayer structure can be perturbed to present versatile host-guest assemblies, such as 'molecular capsules',⁶ 'ferris wheels',⁷ 'Russian dolls',⁸ 2-D coordination polymers,⁹ hydrogen-bonded polymers¹⁰ and even helical arrays.¹¹ In particular, Atwood *et al.* have shown that C4AS form large molecular assemblies of spectacular nanometre-scale spheroids or helical tubules, in which the bilayer arrays are thoroughly overcome.¹² On the other hand, it has also been documented that the bilayer arrangements of calixarenes are destroyed without exception once their cone conformations are disturbed by guests.^{13,14}

Among these calix[*n*]arenes, the investigation of calix[5]arenes is relatively infrequent due to the difficulty of material preparation. Likewise, the solid-state supramolecular chemistry of water-soluble calix[5]arene (C5AS) is poorly developed and remains in its infancy.¹⁵ C5AS commonly adopts a splayed bowl form in the solid state and assembles into up-down bilayer arrangements, similar to those of C4AS. Interestingly, a recent report by Raston *et al.* shows that the novel 'pseudo-double cone' conformation of C5AS was established with two calixarenes organized in a 'bis-molecular capsule', shrouding two guests and two water molecules within.^{15c} Obviously, C5AS possesses the characteristics of both a wider cavity than C4AS and more conformational constraints than C6AS and C8AS, and thus could potentially be used to build significant complex architectures. This is implied to some extent by solution studies which showed that C5AS included some special guests in a different manner compared with C4AS, due to its larger

cavity.^{16,17} Therefore, construction of supramolecular aggregations on C5AS with various guests attracts chemists' interest more and more.

In the present communication, two solid-state complexes (**1** and **2**) of C5AS with 1,2-bis(4,4'-dipyridinium)ethane (BDPDE) and 1,2-bis(pyridinium)ethane (BPDE) were respectively prepared in single-crystal form.† The BDPDE and BPDE guests are also important supramolecular building blocks and may bring novel information about the structures of C5AS upon host-guest interaction. The structures obtained show that the conventional cone shape of C5AS is disrupted to assume a so-called partial-cone upon complexation with BDPDE in complex **1**, and the typical bilayer arrangements are destroyed upon complexation with BPDE in complex **2**.

The crystals of **1** and **2** are triclinic with the space group $P\bar{1}$, and their asymmetric units both comprise one C5AS host. However, there are one BDPDE molecule and a total of 12.25 water molecules disordered over 17 positions in **1**, and two BPDE and 5.5 water molecules disordered over 9 positions in **2**. In the structure of **1** (Fig. 1a), BDPDE inserts into the cavity of C5AS in

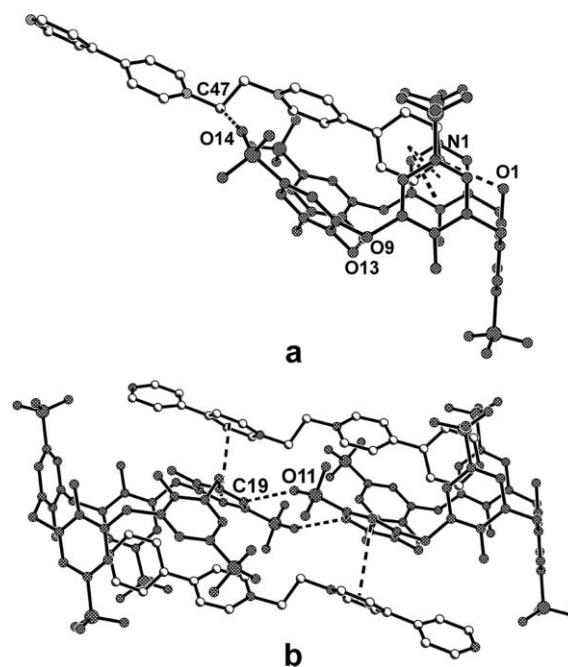


Fig. 1 (a) View of the asymmetric unit of complex **1**, showing the novel partial-cone conformation of C5AS. (b) View of the host-guest back-to-back dimer. Solvent molecules and hydrogen atoms have been omitted for clarity. The dashed lines represent the intermolecular hydrogen bonds or $\pi\cdots\pi$ interactions.

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a latitudinal orientation, and is confined by two hydrogen bonds ($N1 \cdots O1$, 2.725(7) Å; $C47 \cdots O14$, 3.157(9) Å) and two $\pi \cdots \pi$ interactions (ring of $C_{36-40}, N1 \cdots$ ring of C_{9-14} , 3.798 Å; ring of $C_{36-40}, N1 \cdots$ ring of C_{30-35} , 3.798 Å). It is noted that one of the SO_3^- groups turns down in the opposite direction, and then C5AS presents the hitherto unseen solid-state conformation, *i.e.*, partial-cone. The actual ϕ and χ torsion angles values, which define the solid state conformation of C5AS according to the Uguzzoli-Andreotti convention,¹⁸ are 49.4(6), -100.0(5); 96.0(5), -88.7(5); 92.6(5), -55.5(6); 115.3(5), 108.3(5); -106.0(5), -114.7(5)°. As a result, the cyclic hydrogen-bond network between the phenolic oxygen atoms at the lower rim of C5AS is destroyed. Only one hydrogen bond ($O9 \cdots O13$, 2.730(6) Å) remains to contribute to the conformational stability. Another exceptional feature in **1** should be mentioned that a novel back-to-back dimer is afforded *via* twofold host-guest $\pi \cdots \pi$ interactions (ring of $C_{48-52}, N_3 \cdots$ ring of C_{16-21} , 3.516 Å) and host-host hydrogen bonds donated by an aromatic hydrogen atom to a sulfonate oxygen atom ($C19 \cdots O11$, 3.259(6) Å), as illustrated in Fig. 1b.

The extended structure of **1** reveals that the partial-cone C5AS are also packed in a bilayer arrangement (Fig. 2), in which each calixarene layer is constructed through a total of seven crystallographically unique interactions. They are three π -stacking interactions ($\pi \cdots \pi$ centroid distances of 3.669, 3.659 and 3.857 Å), three hydrogen bonds between phenoxy groups of C5AS and sulfonate groups of adjacent C5AS ($O13 \cdots O15$, 2.702(5) Å; $O17 \cdots O12$, 2.788(5) Å; $O5 \cdots O6$, 2.723(6) Å), and a non-conventional hydrogen bond between a methylene bridge and a sulfonate group ($C29 \cdots O15$, 3.496(8) Å). To the best of our knowledge, this structure is the first example of the bilayer arrangement of water-soluble calixarenes with a non-cone conformation.

In the structure of **2** (Fig. 3), one BPDE guest penetrates into the cavity of C5AS in a longitudinal orientation, which is distinctly different from the binding manner in complex **1**. The other BPDE guests reside in the crystal lattice as counterions, in which one of them lies about an inversion centre while another is disordered (with half-occupancy) about another inversion centre. There are four host-guest interactions in **2**, including three hydrogen bonds ($C36 \cdots O14$, 3.13(1) Å; $C40 \cdots O18$, 3.24(1) Å; $C42 \cdots O18$, 3.28(1) Å) and one C-H $\cdots\pi$ interaction ($C39$ -H39 \cdots ring $_{C1-C6}$, 3.13 Å, 152.3°). Furthermore, the included BPDE guest interacts with an adjacent C5AS host by an additional three hydrogen bonds ($C41A \cdots O14$,

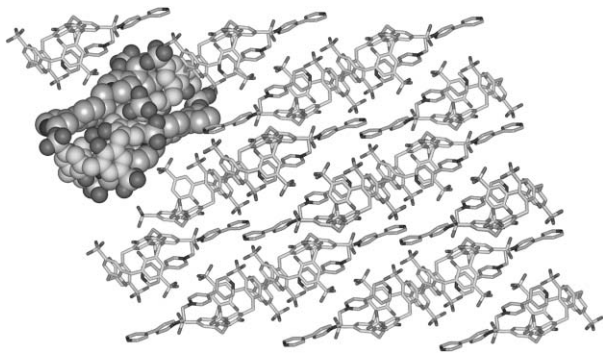


Fig. 2 Stick diagram for complex **1** showing the bilayer extended structure with C5AS in the partial-cone shape. One dimer is in space-filling mode. Water molecules and hydrogen atoms are omitted for clarity.

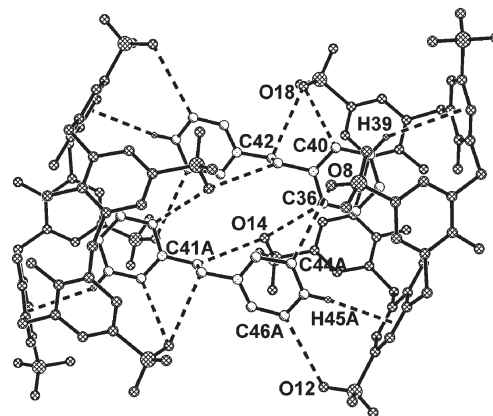


Fig. 3 View showing the face-to-face dimer of complex **2**. The host-guest interactions are joined with dashed lines. Only asymmetric four hydrogen bonds and two C-H $\cdots\pi$ interactions are labeled.

3.20(1) Å; $C44A \cdots O8$, 3.52(2) Å; $C46A \cdots O12$, 3.50(2) Å) and one C-H $\cdots\pi$ interaction ($C45A$ -H45A \cdots ring $_{C15-C20}$, 3.20 Å, 141.9°). Consequently, a face-to-face dimer (or a 'bis-molecular capsule' as mentioned by Raston^{15c}) is presented. Although the cone shape of C5AS is not destroyed in **2** as in **1**, its conformation distorts to a large extent as a result of immersion of the BPDE guest. The torsion angles are 94.0(7), -38.7(8); 80.8(9), -139.3(7); 99.8(7), -50.9(8); 91.3(7), -94.6(6); 76.5(7), -101.1(7)°. The cyclic hydrogen-bonded network at the lower rim is partially disturbed to present only three hydrogen-bonds ($O1 \cdots O17$, 2.849(7) Å; $O9 \cdots O5$, 2.884(9) Å; $O17 \cdots O13$, 2.723(6) Å), and a non-conventional intramolecular hydrogen bond ($C28 \cdots O13$, 2.809(7) Å) due to the conformational perturbation.

Close examination of the crystal packing of **2** reveals that the C5AS do not assemble into a typical bilayer array, but arrange themselves into hydrophobic bis-chains along the crystallographical *a* direction *via* only two intermolecular π -stacking interactions (edge to face: $C7$ -H7 \cdots ring $_{C8-C13}$, 2.74 Å, 135.1°; face to face: ring $_{C1-C6} \cdots$ ring $_{C1-C6}$, 3.720 Å), as shown in Fig. 4a. These calixarene chains further extend to the wavy layer structure (*a* \times *b* plane) through host-guest interactions, and then form a 3-D structure *via* peripheral $\pi \cdots \pi$ interactions of BPDE located between the layers with C5AS (ring $_{C48-C52} \cdots$ ring $_{C22-C27}$, 3.723 Å; ring $_{C54-C58, N4} \cdots$ ring $_{C15-C20}$, 3.616 Å) (Fig. 4b). At first glance, the packing structure of **2** seems to retain bilayer arrangements. However, one cannot observe any hydrophobic layers in the crystal, and hence there are certainly no alternations between hydrophobic layers and hydrophilic layers. That is to say, the classical bilayer of C5AS does not exist in **2** as the calixarene layers are thoroughly spaced by hydrophilic guest molecules.

In conclusion, two inclusion complexes of C5AS with BDPDE and BPDE were respectively prepared and their structures were determined by X-ray crystallographic analysis. The structures obtained demonstrate that pyridiniums are considered to be active guests to either induce the conformation of C5AS to form a partial-cone or to destroy its classical bilayer. Endeavours to investigate the inclusion complexation of CAS with various pyridiniums are going on.

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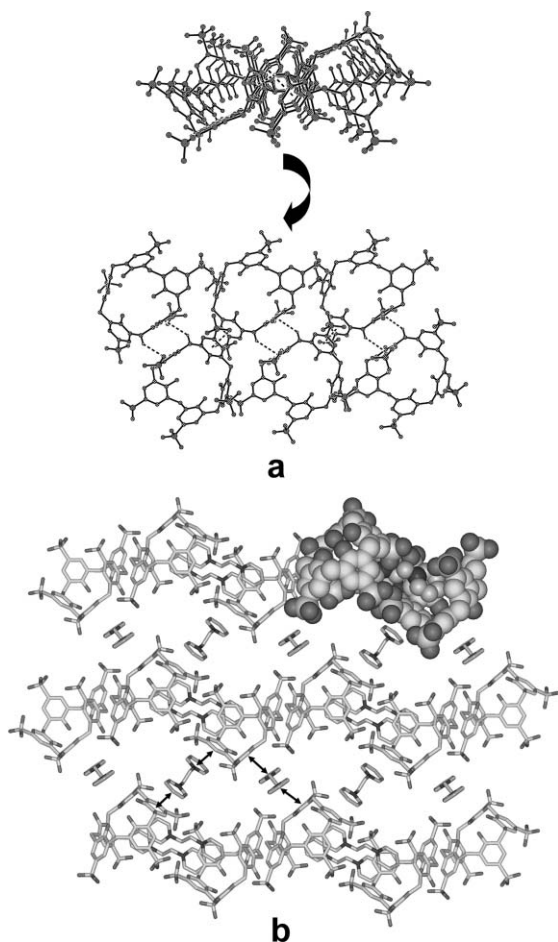


Fig. 4 (a) The bis-chains fabricated by C5AS molecules; (b) the overall structure of complex **2** viewed from the crystallographical *a* direction (the wavy layer running perpendicular to the plane of the page). One dimer unit is in space-filling mode.

Notes and references

† Preparation of **1**. To a 1 M HCl solution of C5AS (0.10 mmol, 40 mL), 2 equiv. of 1,2-bis(4,4'-dipyridinium)ethane bromic salt (BDPDE) was added. After stirring for a few minutes the mixture was filtered and the filtrate was allowed to evaporate for about two days. Then the yellow crystal formed was collected along with its mother liquor for X-ray crystallographic analysis. Crystal data for **1**: $C_{57}H_{72.5}N_4O_{32.25}S_5$, *M* 1489.99, triclinic, space group $P\bar{1}$, $a = 13.4122(13)$, $b = 15.3616(15)$, $c = 19.3740(18)$ Å, $\alpha = 68.031(2)$, $\beta = 82.944(2)$, $\gamma = 65.8540(10)^\circ$, $V = 3361.9(6)$ Å³, $Z = 2$, $D_c = 1.472$ g cm⁻³, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $T = 293(2)$ K, $F(000) = 1561$, crystal dimensions $0.28 \times 0.22 \times 0.18$ mm, reflections collected/unique, 17187/11749 ($R_{\text{int}} = 0.0215$), final *R* indices [$I > 2\sigma(I)$] $R_1 = 0.0738$, $wR_2 = 0.2122$, *R* indices (all data) $R_1 = 0.1090$, $wR_2 = 0.2545$, goodness of fit on $F^2 = 1.030$.

Preparation of **2**. To a 1 M HCl solution of C5AS (0.10 mmol, 20 mL), 4 equiv. of 1,2-bis(pyridinium)ethane bromic salt (BPDE) was added. After stirring for a few minutes the mixture was filtered and the filtrate was allowed to evaporate for about ten days. Then the colorless crystal formed was collected along with its mother liquor for X-ray crystallographic analysis. Crystal data for **2**: $C_{59}H_{65}N_4O_{25.5}S_5$, *M* 1398.45, triclinic, space group $P\bar{1}$, $a = 11.9113(14)$, $b = 16.1145(19)$, $c = 19.514(2)$ Å, $\alpha = 94.990(2)$,

$\beta = 91.308(2)$, $\gamma = 105.576(2)^\circ$, $V = 3590.2(7)$ Å³, $Z = 2$, $D_c = 1.294$ g cm⁻³, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $T = 293(2)$ K, $F(000) = 1462$, crystal dimensions $0.32 \times 0.26 \times 0.20$ mm, reflections collected/unique, 18253/12521 ($R_{\text{int}} = 0.0303$), final *R* indices [$I > 2\sigma(I)$] $R_1 = 0.1180$, $wR_2 = 0.3117$, *R* indices (all data) $R_1 = 0.1872$, $wR_2 = 0.3824$, goodness of fit on $F^2 = 1.265$.

To satisfy charge balance, C5AS in both complexes should possess one protonated sulfonate group, which is acceptable given the pH of the reaction solution. Unfortunately, it was not possible to locate all hydrogen atoms from the Fourier difference map for this to be clarified.^{14f}

CCDC 600932 for **1** and 600933 for **2**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603569h

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