

# Solid-state Supramolecular Architectures by *p*-Sulfonatocalix[4]arene with Bispyridinium Derivatives<sup>†</sup>

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Two supramolecular structures were obtained by inclusion complexation of *p*-sulfonatocalix[4]arene with 1,2-bis(pyridinium)ethane and 1,2-bis(4,4'-dipyridinium)ethane in single-crystal form, which have been examined from the aspects of binding mode, stoichiometry and extended structure. Effects of guest molecules, especially charges and terminal groups, on host conformation, binding and extended structures were carefully compared and summarized.

**Keywords** *p*-sulfonatocalix[4]arene, pyridinium compounds, crystal structure

## Introduction

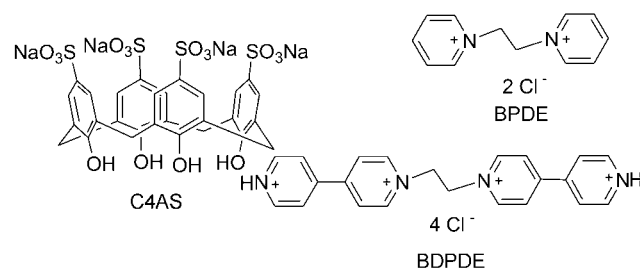
In the broad area of supramolecular chemistry and crystal engineering, *p*-sulfonatocalix[*n*]arenes (*C<sub>n</sub>AS*, *n* = 4, 5, 6, 8), with high water-solubility, multicharged rims, and flexible frameworks, are demonstrated to be a well-known kind of versatile building blocks.<sup>1</sup> Several kinds of spectacular architectures besides the conventional bilayer array<sup>2</sup> have been fabricated by *C<sub>n</sub>AS* upon complexation with various types of guest molecules and/or metal ions, such as molecular capsules,<sup>3</sup> the “ferris wheel”,<sup>4</sup> the “Russian doll”,<sup>5</sup> the helical array,<sup>6</sup> water-filled channels,<sup>7</sup> coordination and hydrogen-bonding polymers, honeycomb aggregates,<sup>8</sup> spheroidal<sup>9</sup> and tubular arrays,<sup>10</sup> and others.<sup>11</sup>

Among the family of these water-soluble calixarenes, *p*-sulfonatocalix[4]arene (C4AS), as the smallest conformation-constrained analogue, emerges to be the most popular subunit that is convenient for studying the influences of different guests upon the formation of supramolecular assemblies from host-guest complexes.<sup>1a,1b</sup> Up to now, our group has successfully constructed a series of the supramolecular architectures based on C4AS upon complexation with quinoline derivatives,<sup>12</sup> phenanthroline<sup>13</sup> and viologen derivatives.<sup>14</sup> C4AS forms a 2 : 2 “bis-molecular capsule” with phenanthroline, in which two guests are included into the cavity built-up by two face-to-face C4AS hosts.<sup>13</sup> Alternatively, C4AS forms the supramolecular architecture of spectacular polymeric capsules in the presence of benzyl viologen, whereas it forms a simple host-guest 2 : 1 complex with methyl viologen.<sup>14</sup>

In comparison with aforementioned guests,

dipyridinium compounds are also important supramolecular building blocks and may bring novel information about the structures of *C<sub>n</sub>AS* upon host-guest interaction for their flexible chains and high charge density.<sup>15</sup> In our previous work, supramolecular architectures formed by *p*-sulfonatocalix[5]arenes (C5AS) and dipyridinium compounds were reported that the conventional cone shape of C5AS is disrupted to assume a so-called partial-cone upon complexation with 1,2-bis(4,4'-dipyridinium)ethane (BDPDE) and the typical bilayer arrangements are destroyed upon complexation with 1,2-bis(pyridinium)ethane (BPDE).<sup>15a</sup> As a subsequent work of constructing supramolecular assemblies based on *C<sub>n</sub>AS*, in this study, we prepared two solid-state complexes of C4AS with BPDE (**1**) and BDPDE (**2**) in single-crystal form and wish to present a more in-depth and comprehensive investigation of the effects of guest molecules herein, especially focusing on how and to what extent the different terminal groups and charges of bispyridinium guests influence the structures of C4AS complexes. The structures of C4AS and bispyridinium guests are shown in Scheme 1.

**Scheme 1** Structures of employed host and guests



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## Experimental

### Materials

*p*-Sulfonatocalix[4]arene (C4AS) was synthesized and purified according to literature procedures.<sup>16</sup> Guest molecules 1,2-bis(pyridinium)ethane (BPDE) and 1,2-bis(4,4'-dipyridinium)ethane (BDPDE) were synthesized according to common preparation method for bispyridiniums.<sup>17</sup>

### Preparation of complexes

**Preparation of complex 1** C4AS (0.10 mmol) was dissolved in 1 mol/L HCl solution (20 mL), followed by adding 2 equiv. of BPDE. After stirring for a few minutes, filtrated, the filtrate was placed to evaporation for about three weeks. Then the colorless crystal formed was collected along with its mother liquor for the X-ray crystallographic analyses.

**Preparation of complex 2** C4AS (0.10 mmol) was dissolved in 1 mol/L HCl solution (30 mL), followed by adding 1 equiv. of BDPDE. After stirring for a few minutes, filtrated, the filtrate was placed to evaporation for about four weeks. Then the colorless crystal formed was collected along with its mother liquor for the X-ray crystallographic analyses.

**X-ray crystal structure analysis** The X-ray intensity data for **1** were collected on a standard Siemens SMART CCD Area Detector System equipped with a normal-focus molybdenum-target X-ray tube ( $\lambda = 0.71073 \text{ \AA}$ ) operated at 2.0 kW (50 kV, 40 mA) and a graphite monochromator at  $T = 293(2) \text{ K}$ . The X-ray intensity data for **2** were collected on a Rigaku MM-007 rotating anode diffractometer equipped with a Saturn CCD Area Detector System using monochromated Mo K $\alpha$  radiation at  $T = 113(2) \text{ K}$ . Data collection and reduction were performed by program of Crystalclear [Crystalstructure 3.7.0 and Crystalclear 1.36: Crystal Structure Analysis Package, Rigaku and Rigaku/MS (2000-2005), 9009 New Trails Dr. The Woodlands TX 77381, USA]. All the structures were solved by using direct method and refined, employing full-matrix least squares on  $F^2$  (Siemens, SHELXTL-97) [SHELX97: Sheldrick, G. M. (1997), University of Göttingen, Germany]. Table 1 lists the summaries of crystal data and refinements, which are the host-guest complexes of C4AS with BPDE (**1**) and BDPDE (**2**). CCDC-783846 (**1**), and 783847 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)). Some data are not good enough for the poor quality of the crystals obtained. In complex **2**, the S1, S2 and S3 sulfonate groups of C4AS are disordered and refined in two positions with equal occupancies. To satisfy charge balance, C4AS should possess 2 to 3 protonated sulfon-

ate groups, which are 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.<sup>18</sup>

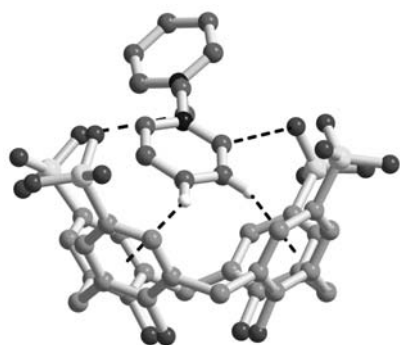
**Table 1** Crystal structure data and details of structure refinements for **1** and **2**

Complex	<b>1</b>	<b>2</b>
Formula	C <sub>40</sub> H <sub>54.5</sub> N <sub>2</sub> O <sub>25.25</sub> S <sub>4</sub>	C <sub>39</sub> H <sub>38</sub> N <sub>2</sub> O <sub>18.5</sub> S <sub>4</sub>
$F_w$ /(g·mol <sup>-1</sup> )	1095.60	958.95
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	11.540(2)	11.907(10)
<i>b</i> /Å	12.794(2)	12.445(10)
<i>c</i> /Å	18.316(3)	15.526(12)
$\alpha$ (°)	83.256(3)	83.75(2)
$\beta$ (°)	77.630(3)	79.618(18)
$\gamma$ (°)	69.731(3)	86.06(2)
$V/\text{\AA}^3$	2475.2(8)	2247(3)
<i>Z</i>	2	2
$D_c$ /(g·cm <sup>-3</sup> )	1.470	1.417
$\mu/\text{mm}^{-1}$	0.281	0.288
<i>F</i> (000)	1149	996
Crystal size/mm <sup>3</sup>	0.26 × 0.22 × 0.20	0.16 × 0.14 × 0.14
$\theta$ range/(°)	1.14–25.00	2.00–25.02
Reflections	12459/8605	13634/7826
collected/unique	[ <i>R</i> (int)=0.0170]	[ <i>R</i> (int)=0.0783]
GOF	1.052	0.963
Final <i>R</i> indices	$R_1 = 0.0674$	$R_1 = 0.1197$
[ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	$wR_2 = 0.2012$	$wR_2 = 0.3021$
<i>R</i> indices	$R_1 = 0.0798$ ,	$R_1 = 0.1775$
(all data)	$wR_2 = 0.2182$	$wR_2 = 0.3503$

## Results and discussion

### [BPDE<sup>2+</sup>][C4AS<sup>4-</sup> + 2H<sup>+</sup>]·9.25H<sub>2</sub>O (**1**)

In complex **1**, the BPDE guest is included slantways into the cavity of C4AS with one aromatic pyridinium ring immersed (Figure 1), and the long axis of BPDE forms an angle of 52.0° with the plane defined by four bridging methylenes. Different types of noncovalent interactions between the aromatic pyridinium ring and C4AS are observed, including two C—H... $\pi$  interactions [C(31)—H(31)...Ring of C(2)—C(7), 2.809 Å, 142.1° and C(32)—H(32)...Ring of C(9)—C(14), 2.926 Å, 144.0°] and one hydrogen bond [C(33)...O(10), 3.418 Å]. The other aromatic pyridinium ring of BPDE guest is fixed at the upper rim of C4AS. Furthermore, the 1 : 1 complex forms 2 : 2 dimer in virtue of the exerted pyridinium group (Figure 2a). The hydrogen bonds between the pyridinium group and sulfonate group of the opposite calixarene [C(38)...O(2), 3.442 Å; C(39)...O(3), 3.282 Å] contribute to the final formation of dimer in **1**. The ethyl spacer of BPDE also interacts with the sulfonate groups of the two C4AS via non-conventional hydrogen bond interactions (3.134 Å



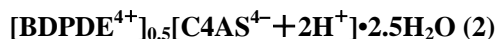
**Figure 1** Structural view of the host-guest 1 : 1 complex formed by C4AS and BPDE; the dashed lines represent the host-guest C—H $\cdots\pi$  and hydrogen bond interactions.

and 3.651 Å), respectively. Therefore, two C4AS and two BPDE give a 2 : 2 face-to-face dimer complex. Moreover, C4AS adopts a  $C_{4v}$  cone conformation (the S $\cdots$ S approaches of distal sulfonates, 11.035 and 10.361 Å) in complex **1**. According to the Ugozzoli-Andreotti convention,<sup>19</sup> the actual  $\varphi$  and  $\chi$  torsion angles values, which define the solid-state conformation of C4AS, are +87.6°, -93.1°; +96.8°, -91.8°; +88.9°, -91.5°; and +93.7°, -90.3°.

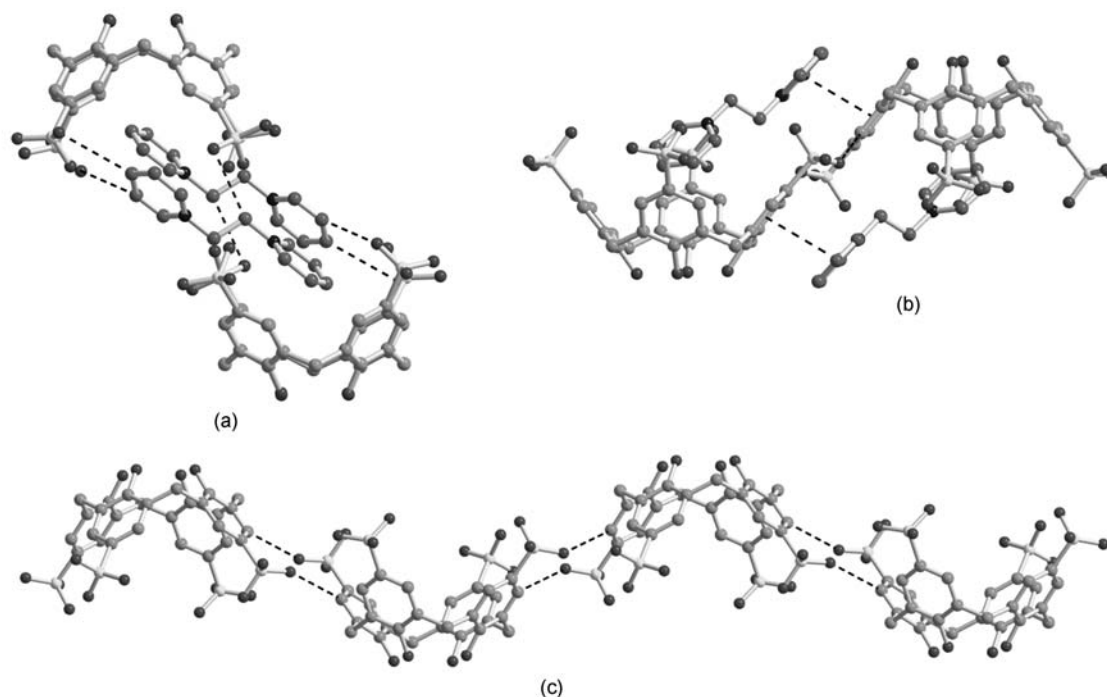
The extended structure of **1** exhibits the usual bilayer arrangement, which is maintained by complexation with BPDE (Figure 3). C4AS molecules arrange into regular up-down bilayers through intermolecular  $\pi\cdots\pi$  stacking [Ring of C(9)—C(14) $\cdots$ Ring of C(9)—C(14), 3.606 Å] and dual hydrogen bonding interactions [C(19) $\cdots$ O(12), 3.431 Å], as shown in Figure 2c. Interestingly, Figure 2b shows that the pyridinium group of BPDE has an unexpected  $\pi\cdots\pi$  stacking ( $\pi\cdots\pi$ : Ring of C(16) —

C(21) $\cdots$ Ring of N(2)—C(40), 3.618 Å) with a neighboring calixarene in one bilayer. That is, two calixarene hosts with two BPDE guests can form another type of 2 : 2 dimer, where two guest molecules arrange in a parallel manner. The hydrophilic layers in **1** are quite less extensive than the case in our previous report, for example, the C4AS complex with methyl viologen. This may be attributed to that one pyridinium group of BDPE inserts into the hydrophobic layer, drawing the calixarene layers more compact.

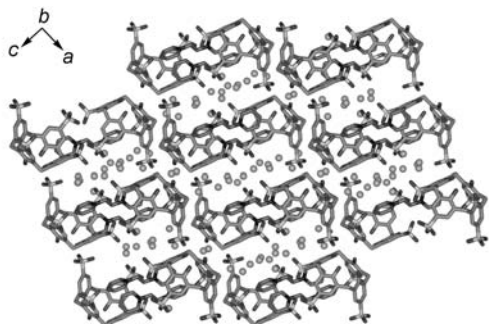
The most fascinating feature in complex **1** is that the hydrated channels are observed. By considering each 2 : 2 dimer as a repeating unit, it can be found that closed rectangular pores (17.7 Å $\times$ 8.6 Å) form among the spaces between them. Viewing from the crystallographic  $a\times c$  plane, **1** shows an assembling pattern of hydrated channels, where each pore runs an infinite extension along crystallographic  $b$  dimension (Figure 3). Such a well ordered channel topology is just the result of holding of BPDE as a pillar and the exactly regular packing of C4AS.



Unlike the 2 : 2 complex formed in **1**, the complexation of BDPDE with C4AS leads to a 2 : 1 complex. In **2**, two 4,4'-dipyridinium portions of each BDPDE guest are simultaneously included by two C4AS hosts, and the host-guest complexation is in a more slantwise manner such that the angle formed by the long axis of the corresponding 4,4'-dipyridinium portion and the plane of the bridged methylenes is 11.1°. As shown in Figure 4, the 4,4'-dipyridinium portions of BDPDE molecule are completely included by two



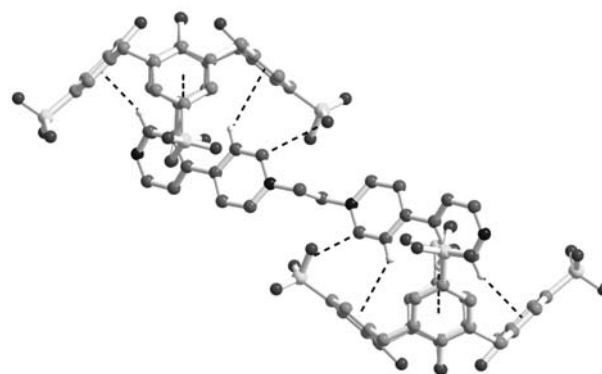
**Figure 2** View of the interactional mode of the C4AS with the BDPE counterions around (a and b), the chain in complex **1** formed by C4AS molecules (c).



**Figure 3** The extended structure of complex **1**.

C4AS hosts and each 4,4'-dipyridinium portion of BDPDE penetrates into one cavity of calixarene through one hydrogen bond [C(29)⋯O(13), 2.999 Å] and three C—H⋯ $\pi$  interactions [C(34)—H(34)⋯Ring of C(2)—C(7), 2.701 Å, 158.8°; C(35)—H(35)⋯Ring of C(23)—C(28), 3.173 Å, 151.3°; C(30)—H(30)⋯Ring of C(16)—C(21), 3.276 Å, 140.4°], respectively. To accommodate well the planer aromatic 4,4'-dipyridinium group of BDPDE, the conformation of C4AS with BDPDE guest in **2** adopts a pinched-cone conformation ( $C_{2v}$  symmetry), which is elucidated by the S⋯S distances between the opposite sulfonate groups [9.346 and 12.141 Å, respectively]. The actual  $\varphi$  and  $\chi$  torsion angles values, which define the solid-state conformation of C4AS, are +86.8°, -98.2°; +99.7°, -82.9°; +82.7°, -102.7°; and +103.7°, -86.1°. Furthermore, taking the relative position of the two face-to-face calixarenes into account, complex **2** can hardly be called as a molecular capsule or even a slipped capsule because the cavity of one C4AS resides over an edge of the other C4AS as a result of the slantwise orientation of the encapsulated BDPDE molecule.

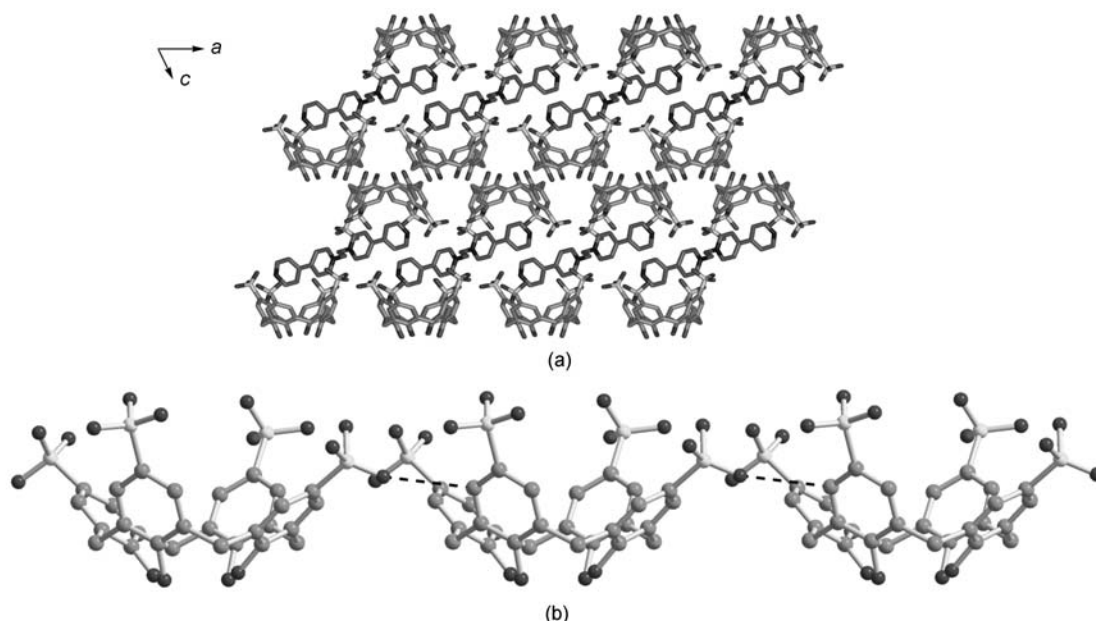
On close examination of complexes **1** and **2**, the 4,4'-dipyridinium portion of BDPDE is almost accum-



**Figure 4** Structural view of the host-guest 2 : 1 complex formed by C4AS and BDPDE; the dashed lines represent the host-guest C—H⋯ $\pi$  and hydrogen bond interactions.

bently included into the cavity of C4AS from the upper rim (11.1°), while the pyridinium group of BPDE is immersed into the hydrophobic cavity of C4AS in **1** (Figures 1 and 4). The structural difference between **1** and **2** should be predominantly caused by the different terminal groups owned by BDPDE and BPDE (Scheme 1). The terminals of BDPDE are more positively charged and rigid than BPDE, therefore, the conformation of C4AS in **2** is stretched along the axial orientation of 4,4'-dipyridinium to ensure there are as many host-guest interactions as possible ( $C_{2v}$  symmetry), whereas maintains the original cone conformation in **1**.

For the overall packing structures, **2** present the bi-layer arrangement through the hydrogen bond interactions among the calixarenes themselves [C(12)⋯O(5), 3.403 Å; C(26)⋯O(12), 3.205 Å], as shown in Figure 5b, and the one dimensional chain that linked the 2 : 1 complex together can be observed from crystallographic *a* dimension. In comparison to that of complexes **1** and **2**, an extension of calixarene layers can be observed in



**Figure 5** The extended structure (a) and the chain formed by C4AS molecules (b) in complex **2**.

complex **2**, where the classical  $\pi\cdots\pi$  stacking interactions between calixarenes are overwhelmed (Figure 5a). Moreover, no hydrated channels are observed in complex **2**.

## Conclusion

In summary, two supramolecular architectures formed by C4AS and 1,2-bispyridinium compounds (BPDE and BDPDE) have been carefully studied from viewpoints of both complexation mode and extended structure. BPDE forms 2 : 2 dimer with C4AS (**1**), while more positively charged and rigid BDPDE leads to a simple 2 : 1 complex **2**. Most interestingly, the extended structure of complex **1** shows infinitely extended hydrated channels, whereas complex **2** does not. Hence, our present work provides valuable information for selection of suitable manipulation factors in the pursuit of constructing functional solid-state materials in supramolecular chemistry and crystal engineering.

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