Solid-state supramolecular architectures by *p*-sulfonatocalix[5]arene with bispyridinium derivatives: factors of spacers and terminal groups†

Xin Su, Dong-Sheng Guo and Yu Liu*

Received 29th May 2009, Accepted 24th October 2009
First published as an Advance Article on the web 24th November 2009
DOI: 10.1039/b910623e

Three solid-state supramolecular structures were obtained by inclusion complexation of *p*-sulfonatocalix[5]arene with 1,2-bis(4,4′-methylpyridinium)ethane, 1,2-bis(4,4′-aminopyridinium)ethane and 1,4-bis(pyridinium)butane. All three complexes have been thoroughly examined from the aspects of binding mode, stoichiometry and extended structure. Effects of guest molecules, especially spacers and terminal groups, on host conformation, binding and extended structures were carefully compared and summarized.

Introduction

Among various types of supramolecular host compounds used to construct solid-state supramolecular architectures, *p*-sulfonatocalix[*n*]arenes (**C*n*AS**, $n = 4, 5, 6, 8$) have been receiving extensive attention for years.[1] Due to their prominent features, such as very high water-solubility, multi-charged rims and flexible frameworks, various supramolecular assemblies have been fabricated by complexing with a wide range of guest molecules and/or metal ions. Typical architectures include "molecular capsules",[2] "Ferris wheels",[3] "Russian dolls",[4] helical arrays,[5] water-filled channels,[6] coordination and hydrogen-bonding polymers,[7] honeycomb aggregates,[8] spheroidal and tubular arrays,[9] *etc.*, in addition to the traditional bilayer motif first reported by Atwood *et al.*[10] It is not difficult to find that different conformations of **C*n*AS** and extended structures of complexes should be attributed to the inducement of guest molecules and ions. Therefore, the manipulation of guests plays a significant role in understanding the formation of those spectacular architectures and, further, designing functional supramolecular assemblies in a reasonable way.

Until now, *p*-sulfonatocalix[4]arene (**C4AS**), the smallest and simplest analogue, is the most widely studied member in this family.[1a,1b] For instance, capsules are a typical form in **C4AS**-based supramolecular assemblies.[2] Raston *et al.* have reported molecular capsules generating from interactions with crown ethers,[1a,1b,2a] amino acids,[11] nucleic acid bases and derivatives[12] by **C4AS**, in which hydrogen bonds, π···π stacking, and hydrophobic effects all contribute to the formation and stabilization of the capsules. Recent reports have also focused on polymeric capsules[2f] and capsules containing metal complexes.[13] Coleman *et al.* have studied complexation of **C4AS** with nitrogen containing compounds for developing potential drug delivery systems[14] and generic co-crystal formers.[15]

In comparison to **C4AS**, the investigation into **C5AS** remains still immature. It is estimated that only 10 structures involving **C5AS** have been reported in the Cambridge Structural Database according to statistic by Makha *et al.*[16] and later reports.[17] Besides the difficulty in material preparation, it is also pointed out that the process of crystallization of **C5AS** is a choke point as well because of its pseudo 5-fold local symmetry.[16] In most structures reported, **C5AS** generally shows similar conformation and packing pattern to **C4AS**, that is, **C5AS** adopts a bowl-shaped form and aggregates in an up-down bilayer manner. Noticeably, Raston *et al.*[2b] reported that **C5AS** can form "bis-molecular capsule" with two 1,4-diazabicyclo[2.2.2]octane molecules encapsulated in the pseudo- double cone cavity. The novel partial-cone conformation of **C5AS** induced by 1,2-bis(4,4′-dipyridinium)ethane (**BDPDE**) has been reported in our previous work.[18] We also found that **C5AS** can form more compact bis-molecular capsules with phenanthroline than **C4AS**, benefiting from its larger bowl cavity.[2e] In a more recent work, Makha *et al.* described the unusual dense bilayer packing of **C5AS** induced by ytterbium(III) in the presence of tetraphenylphosphonium.[16] Besides the above, **C5AS** has also been employed to construct molecular capsules with charged aza-crown ethers[19] and multicomponent bilayers.[17]

As a subsequent work of constructing supramolecular assemblies by **C5AS** with bispyridinium compounds, we 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 spacers and terminal groups of bispyridinium guests influence the structures of **C5AS** complexes. All bispyridinium guests are shown in Scheme 1.

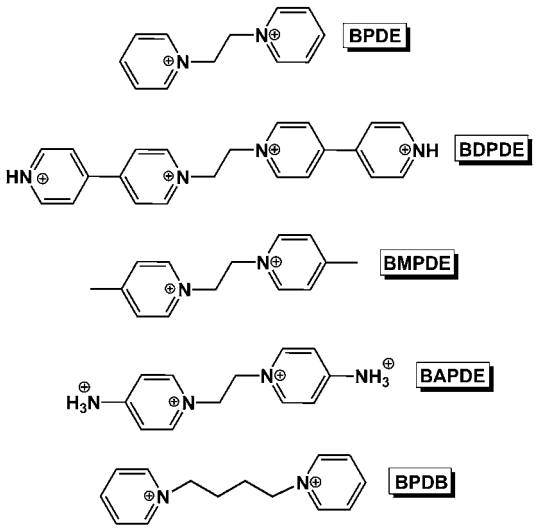
Results and discussions

$[C5AS^{5-} + 4H^+][BMPDE^{2+}]_{0.5}\cdot 3H_2O$ (3)

In complex **3**, one **BMPDE** molecule is corresponding to two **C5AS** hosts that have crystallographically imposed twofold symmetry, as shown in Fig. 1. Each methylpyridyl group of **BMPDE** resides in one cavity of **C5AS** in a slantwise manner *via* two unconventional hydrogen bonds (C36–H36···ring of C2–C7,

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, P. R. China. E-mail: yuliu@nankai.edu.cn; Fax: +86-22-23503625; Tel: +86-22-23503625

† Electronic supplementary information (ESI) available: Crystal data and structure refinements. CCDC reference numbers 728423, 728424 and 728425. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b910623e



Scheme 1 Structural illustration of bispyridinium compounds.

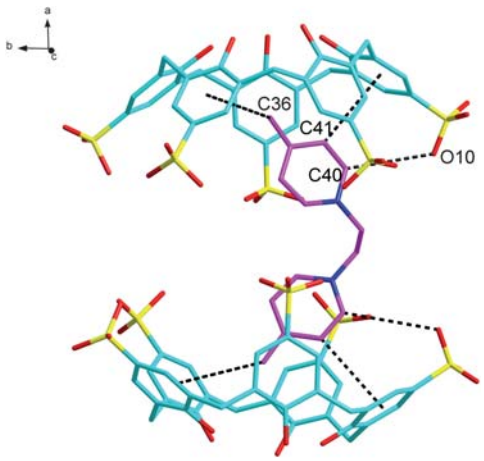


Fig. 1 2 : 1 dimer complex in **3**.

3.385 Å, 144.5° and C41–H41···ring of C16–C21, 2.744 Å, 150.5°), resulting in the 2 : 1 *face-to-face* dimer complex.

Compared with **BPDE**, **BMPDE** possesses two additional methyl groups at terminal positions, which causes great diversity in structures between complexes **1** and **3**. From the aspect of inclusion stoichiometry, two **C5AS** hosts form a 2 : 2 dimer with two **BPDE** guests in **1**, where two **BPDE** molecules arrange closely in a parallel manner, while in **3**, only one **BMPDE** molecule is encapsulated by two **C5AS** hosts to form 2 : 1 dimer. Such distinction should be attributed to the effect of methyl groups in **BMPDE**, that is, the methyl groups are unfavourable for **BMPDE** molecules to approach each other by π···π stacking, and thus, the *face-to-face* two C5AS hosts can only accommodate one **BMPDE** molecule inside.

Conformations of **C5AS** are different in **1** and **3** as well that **C5AS** in **1** is somewhat disturbed by longitudinal insertion of **BPDE** dimer, **C5AS** in **3** almost maintains its intrinsic form with the actual φ and χ torsion angle values of 99.532°, −82.696°; 51.216°, −84.890°; 110.542°, −70.213°; 53.755°, −103.269°; 91.138°, −78.049°, which defines the solid-state conformation of calixarene based on the Ugozzoli–Andreetti convention.[20] In **1**, one **C5AS** cavity is filled by two pyridinium groups, while in **3**, one **C5AS** cavity is just filled with one methyl pyridinium group. There are fewer and weaker host–guest interactions between **BMPDE** and **C5AS** than **BPDE**. Both factors provide an explanation to why the cone conformation of **C5AS** in **3** is maintained.

The extended structure of **3** exhibits the usual bilayer arrangement, which is maintained by complexation with **BMPDE**. **C5AS** molecules arrange into regular up-down bilayers through intermolecular π···π stacking (π···π: ring of C16–C21···ring of C30–C35, 3.871 Å; C–H···π: C15–H15···ring of C9–C14, 3.613 Å, 159.5° and C17–H17···ring of C9–C14, 3.601 Å, 153.4°) and hydrogen bonding interactions (O12···O13, 2.809 Å), as shown in Fig. 2. By considering each 2 : 1 dimer as a repeating unit, it can be found that closed cyclic pores (10.6 × 10.6 Å^2) form among the spaces between them. Viewing from the crystallographic $a \times b$ plane, complex **3** shows a assembling pattern of hydrated channels, where each pore runs an infinite extension along crystallographic c dimension. Such a well-ordered channel topology is just the result of holding of **BMPDE** as a pillar and the exactly regular packing of **C5AS**. Moreover, it can also be noticed that **BMPDE** guest assumes a distorted conformation to fulfil the highly ordered bilayer arrangement of **C5AS**.

[C5AS^{5-} + H$^+$][BAPDE^{4+}]·6H$_2$O (4)

Among the five guest molecules employed, **BAPDE** and **BMPDE** are of nearly identical length and molecular structure, but their complexes with **C5AS** are of obvious difference. Unlike the 2 : 1 dimer formed in **3**, the complexation of **BAPDE** with **C5AS** leads to a 2 : 2 dimer. More interestingly, the dimer in **4** is much different from that in **1**. For the dimer in **1**, two pyridinium portions of each **BPDE** guest are simultaneously included by both **C5AS** hosts, and the dimerization orientation of **BPDE** molecules is almost perpendicular to the axis of the dimer unit. In **4**, the whole **BAPDE** molecule is completely included by one **C5AS**. As shown in Fig. 3a, one aminopyridinium group is immersed into the cavity of **C5AS** and held by six independent

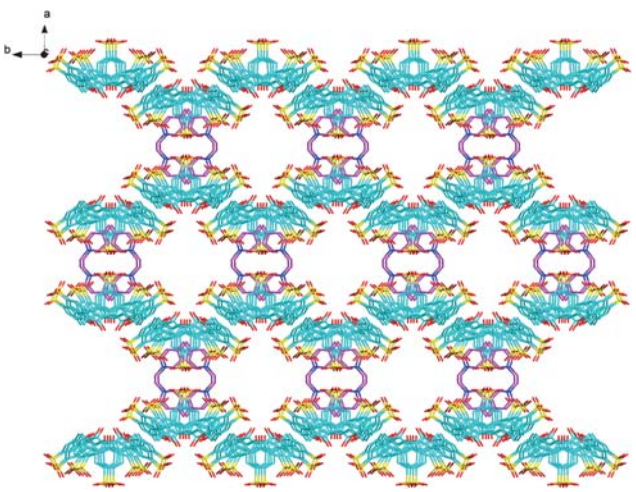


Fig. 2 The extended structure of complex **3**.

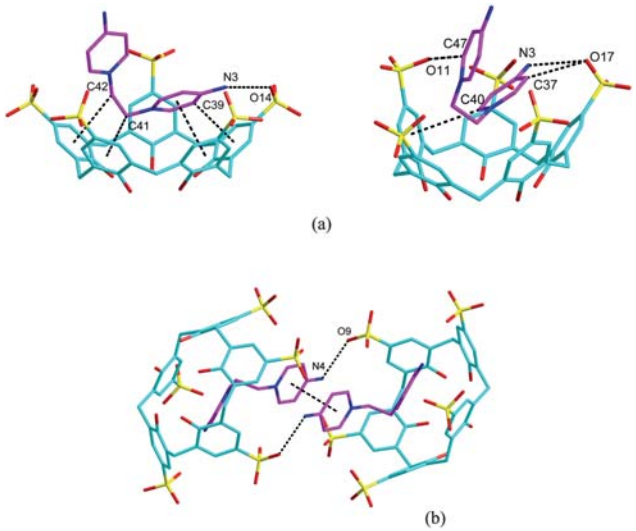
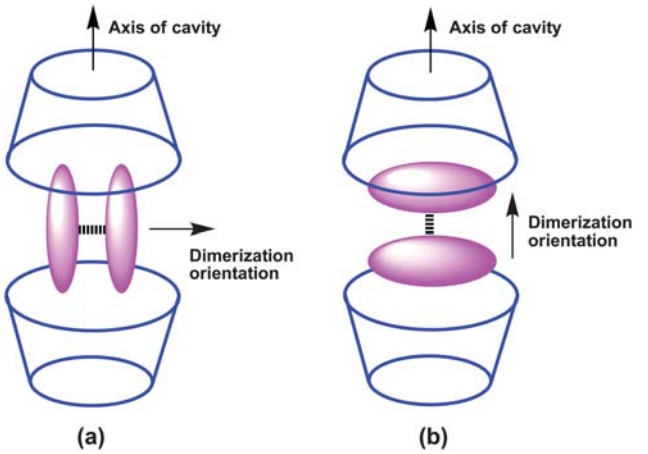


Fig. 3 (a) View of the 1 : 1 inclusion structure between **C5AS** and **BAPDE** in **4**; (b) view of the further 2 : 2 dimer in **4**.

host–guest interactions, which are three hydrogen bonds (N3···O14, 3.043 Å; N3···O17, 3.028 Å; C37···O17, 3.204 Å) and three π–stacking interactions (C–H···π: C39–H39···ring of C15–C20, 3.388 Å, 130°; C40–H40···ring of C8–C13, 3.550 Å, 159°; π···π: ring of C22–C27···ring of N1–C40, 3.846 Å), respectively. The ethyl spacer of **BAPDE** is also immersed into the cavity of **C5AS** *via* two C–H···π interactions (C41–H41···ring of C29–C34, 3.516 Å, 147°; C42–H42···ring of C1–C6, 3.515 Å, 139°), which is different from all the other complexes reported here. The other aminopyridinium group is fixed at the upper rim of **C5AS**, captured by one sulfonate group through one unconventional hydrogen bond (C47···O11, 3.161 Å). Furthermore, the 1 : 1 complex forms 2 : 2 dimer in virtue of the exerted amniopyridinium group (Fig. 3b). Two kinds of non-covalent interactions from the exerted amniopyridinium groups contribute to the final formation of dimer in **4**, one is the π···π stacking between two amniopyridinium groups (ring of N2–C472···ring of N2–C47, 3.771 Å), the other is the dual hydrogen bonds between the amino group and sulfonate group of the opposite calixarene (N4···O9, 2.953 Å). As a result, the dimerization orientation of **BAPDE** molecules prefers to be parallel to the axis of the dimer unit. The cartoon in Scheme 2 illustrates the mode of assembly difference between the structures **1** and **4**.

The structural difference between **3** and **4** should be predominantly caused by the different terminal groups owned by **BMPDE** and **BAPDE**. The methyl group in **BMPDE** is more likely to enter into the hydrophobic cavity of **C5AS**, stabilized by C–H···π interactions, whereas the protonated amino group prefers to locate at the upper rim of **C5AS**, forming electrostatic and hydrogen bonding interactions with sulfonate groups. Consequently, the conformation of **BAPDE** is more distorted than **BMPDE** to ensure there are as many host–guest interactions as possible. On the other hand, in comparison with **2**, although both **BDPDE** and **BAPDE** have positively charged terminals, **BDPDE** is longer in length and is more rigid than **BAPDE**. It is therefore able to dramatically disrupt the original cone conformation of **C5AS** to the partial-cone form. However,



Scheme 2 The cartoon illustration for comparing the dimers in **1** (a) and **4** (b). The axis of the dimmer unit has been defined as the line that passes through the center points of the two opposite calixarene molecules.

BAPDE can not induce the change of **C5AS** conformation, but only adjusts its own conformation to fit the cavity of **C5AS** well.

In the overall structure, **C5AS** molecules in **4** also show bilayer arrangement, aggregating through π···π stacking interactions (ring of C1–C6···ring of C15–C20, 3.602 Å) and C–H···π (C28–H28···ring of C8–C13, 3.906 Å, 168°), as shown in Fig. 4a. The one dimensional chain that linked the 2 : 2 dimers together can be observed from crystallographic *b* dimension (Fig. 4b), where

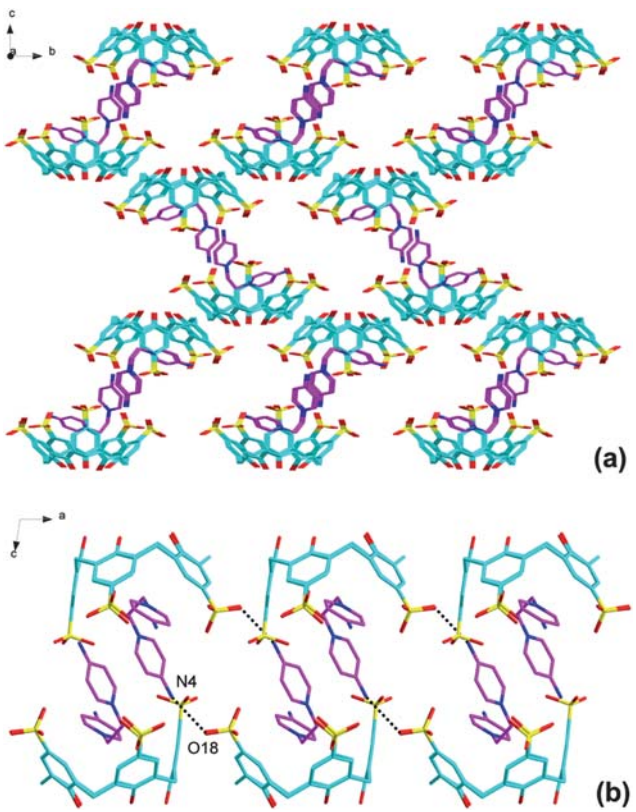


Fig. 4 (a) The extended structure of **4**; (b) One-dimensional chain linked by hydrogen bond in **4**.

the amino group of **BAPDE** in a 2 : 2 dimer unit form hydrogen bond (N4···O18, 2.988 Å) with the sulfonate group belonging to the neighbouring dimer unit. Therefore, the subtle amino terminal exerts extraordinary influence over not only the inclusion structure but also the overall structure of **4**.

Moreover, hydrated channels are also found in **4** viewing from the crystallographic $b \times c$ plane, extending infinitely along crystallographic a dimension, with the size of 7.8 × 15.6 Å^2. Careful examination of the assembling patterns in **3** and **4** reveals evident difference between them. On one hand, the hydrated channels in **4** have lower symmetry than those in **3** since two **C5AS** molecules in each 2 : 2 **C5AS/BAPDE** dimeric unit are slipped to some extent. On the other hand, compared with **3** (6.404 Å), the thickness of hydration layers in **4** has been increased to 7.273 Å, mainly due to the supporting of hydrophilic aromatic rings of **BAPDE** guests, while, as a sharp contrast, the thickness of calixarene layers (7.140 Å) decreases greatly compared with that in **3** (8.286 Å), which is probably caused by the relatively declining orientation of the host molecules.

$[C5AS^{5-} + 4H^+][BPDB^{2+}]_{0.5}\cdot 3H_2O$ (5)

In the aforementioned complexes of **C5AS** with bispyridinium compounds, we mainly discuss the effect of terminal groups to the supramolecular architectures constructed by **C5AS**. To clarify the influence of bridged spacers, **BPDB** is further employed as a comparative guest with a longer spacer of two carbon atoms. As compared with **BPDE**, **BPDB** possesses more molecular flexibility. Interestingly, the complexation of **C5AS** with **BPDB** exhibits better symmetry than the other four cases. In each asymmetric unit of **5**, there are only half **C5AS** and a quarter **BPDB** observed. That is, the calixarene lies about a mirror plane and the **BPDB** moiety has 2/m symmetry with some disorder. The symmetric plane is perpendicular to the aromatic ring of C16–C19 (C16–C17–C18–C17–C16–C19) and passes through C18 and C19 atoms (Fig. 5). By growing the asymmetric unit, it is found that **C5AS** forms a 2 : 1 inclusion complex with **BPDB**, which is also reflected from the host–guest molar ratio in the asymmetric unit. Two kinds of host–guest interactions (π···π: ring of C2–C7···ring of N1–C22B, 4.112 Å; Unconventional hydrogen bonds: C22···O2, 3.369 Å or C23···O2, 3.363 Å) are observed to stabilize the intermolecular inclusion, in which the former one is dual owing to the complex symmetry. As a result, each **C5AS** cavity donates a total of three noncovalent interactions to capture the **BPDB** guest. It is easily acceptable for **C4AS** to form inclusion complexes with symmetric plane as its intrinsic C_{4v}/C_{2v} conformation, and a number of cases have been reported so far.[2f] However, for **C5AS** with lower symmetry, it is still somewhat interesting to obtain the highly symmetric complex.

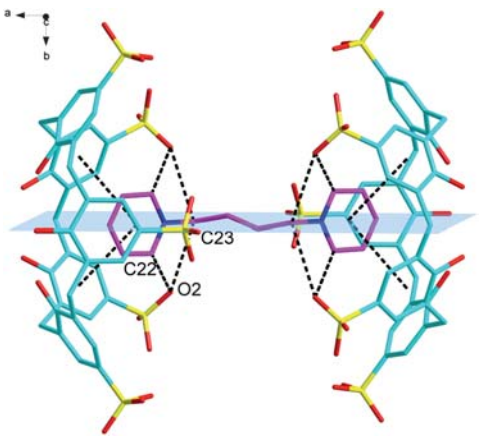


Fig. 5 2 : 1 complex with inner symmetric plane formed by **C5AS** and **BPDB** in **5**.

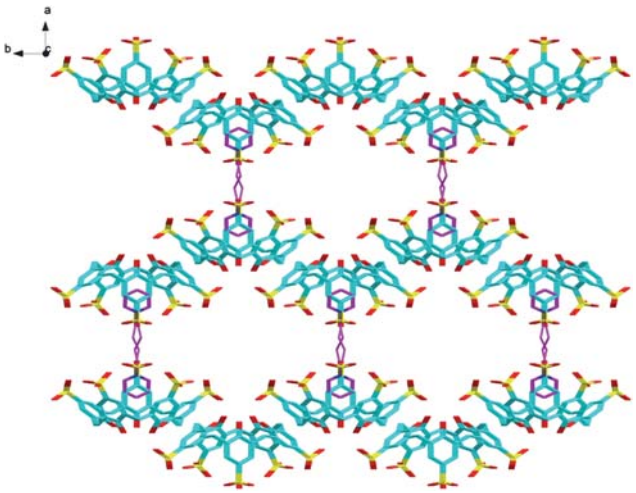


Fig. 6 The extended structure of complex **5**.

Table 1 Thickness of hydration layers and calixarene layers and sizes of hydrated channels formed in **3–5**

	3	**4**	**5**
Thickness of hydration layer/Å	6.404	7.273	7.351
Thickness of calixarene layer/Å	8.286	7.140	8.382
Size of hydrated channels/Å^{-2}	10.6 × 10.6	7.8 × 15.6	15.6 × 15.6

Aggregating in virtue of hydrogen bond (O9···O7, 2.919 Å) and π···π stacking (ring of C9–C14···ring of C9–C14, 3.687 Å), **C5AS** molecules form bilayer arrangement all the same (Fig. 6). Resembling the cases of **3** and **4**, nano hydrated channels are also observed in **5** viewing from the crystallographic $a \times b$ plane, extending along c dimension. The size of pore in **5** (15.6 × 15.6 Å^2) is much larger than those of the former two, resulting from the longer spacer of **BPDB**. **BPDB** can hold the calixarene layers further apart from each other than the ethyl-bridged bispyridinium compounds, which allows the formation of larger nano channels in **5**. The corresponding data of comparable thicknesses of hydration/calixarene layers and sizes of hydrated channels in **3–5** are listed in Table 1.

Conclusions

In summary, three supramolecular architectures formed by **C5AS** and 1,2-bispyridinium compounds have been carefully studied from viewpoints of both complexation mode and extended structure. Both **BMPDE** and **BPDE** form 2 : 1 complexes with **C5AS**, while more positively charged **BAPDE**

leads to 2 : 2 dimer, and all the extended structures of three complexes show infinitely extended hydrated channels. By comparing with two others that have been reported, the effects of guest molecules, especially their terminal groups and spacers, on the structure of the assemblies are thoroughly investigated. While terminal groups should always influence the binding modes in complexes by altering the skeleton of guest molecules, spacers tend to directly decide the size of hydrated channels by controlling the thickness of hydration layers. Such findings should be of particular importance not only in the mechanism of solid-state binding behaviour between **C5AS** and model guests, but also in designing and constructing various functional assemblies based on **C5AS** by introducing suitable molecules.

Experimental

Materials

Pentasodium *p*-sulfonatocalix[5]arene (**C5AS**)[21] was synthesized and purified according to literature procedures. Guest molecules 1,2-bis(4,4′-methylpyridinium)ethane (**BMPDE**), 1,2-bis(4,4′-aminopyridinium)ethane (**BAPDE**) and 1,4-bis(pyridinium)butane (**BPDB**) were synthesized according to common preparation method for bispyridiniums.[22]

Preparation of complexes

Preparation of 3. C5AS (0.10 mmol) was dissolved in 1 M HCl solution (20 mL), followed by adding 2 equiv. of **BMPDE**. After stirring for a few minutes, the solution was filtrated and the filtrate was placed to evaporation for about 3 weeks. Then the colourless crystal formed was collected along with its mother liquor for the X-ray crystallographic analysis. Yield: 23% (25.9 mg).

Preparation of 4. C5AS (0.10 mmol) was dissolved in 1 M HCl solution (20 mL), followed by adding 1 equiv. of **BAPDE**. After stirring for a few minutes, the solution was filtrated and the filtrate was placed to evaporation for about 4 weeks. Then the colourless crystal formed was collected along with its mother liquor for the X-ray crystallographic analysis. Yield: 31% (43.2 mg).

Preparation of 5. C5AS (0.10 mmol) was dissolved in 1 M HCl solution (20 mL), followed by adding 1 equiv. of **BPDB**. After stirring for a few minutes, the solution was filtrated and the filtrate was placed to evaporation for about 4 weeks. Then the colourless crystal formed was collected along with its mother liquor for the X-ray crystallographic analysis. Yield: 28% (31.0 mg).

Single-crystal X-ray diffraction

The X-ray intensity data for **3** and **5** were collected on a standard Bruker SMART-1000 CCD Area Detector System equipped with a normal-focus molybdenum-target X-ray tube (λ = 0.71073 Å) operated at 2.0 kW and a graphite monochromator at T = 294(2) K. All the structures were solved by using direct method and refined, employing full-matrix least squares on F^2 (CrystalStructure, SHELX97).[23] The X-ray intensity data for **4** were collected on a Rigaku MM-007 rotating anode diffractometer equipped with a Saturn CCD Area Detector System using monochromated Mo Kα (λ = 0.71070 Å) radiation at T = 113(2) K. Data collection and reduction were performed using the program Crystalclear.[24] A summary of crystal data and structure refinements is given in the ESI, Table S1.†

To satisfy the charge balance, **C5AS** in **3** and **5** should possess four protonated sulfonate groups, while **C5AS** in **4** 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.[19]

Acknowledgements

This work was supported by 973 Program (2006CB932900), NNSFC (no. 20721062 and 20703025) and 111 Project (B06005), which are gratefully acknowledged. Also, we would like to express our gratitude to Miss Rebecca L. Wise from University of Maryland, College Park, for her assistance in the preparation of this manuscript.

References

1 J. L. Atwood, L. J. Barbour, M. J. Hardie and C. L. Raston, *Coord. Chem. Rev.*, 2001, **222**, 3; S. J. Dalgarno, J. L. Atwood and C. L. Raston, *Chem. Commun.*, 2006, 4567; F. Perret, A. N. Lazar and A. W. Coleman, *Chem. Commun.*, 2006, 2425.
2 M. J. Hardie, J. A. Johnson, C. L. Raston and H. R. Webb, *Chem. Commun.*, 2000, 849; S. J. Dalgarno, M. J. Hardie and C. L. Raston, *Chem. Commun.*, 2004, 2802; D.-Q. Yuan, M.-Y. Wu, B.-L. Wu, Y.-Q. Xu, F.-L. Jiang and M.-C. Hong, *Cryst. Growth Des.*, 2006, **6**, 514; C. B. Smith, M. Makha, C. L. Raston and A. N. Sobolev, *New J. Chem.*, 2007, **31**, 535; Y. Liu, H.-Y. Zhang, F. Ding, K. Chen and H.-B. Song, *Chem.–Eur. J.*, 2007, **13**, 466; D.-S. Guo, X. Su and Y. Liu, *Cryst. Growth Des.*, 2008, **8**, 3514.
3 A. Drljaca, M. J. Hardie, J. A. Johnson, C. L. Raston and H. R. Webb, *Chem. Commun.*, 1999, 1135.
4 M. J. Hardie and C. L. Raston, *J. Chem. Soc., Dalton Trans.*, 2000, 2483; A. Drljaca, M. J. Hardie, C. L. Raston and L. Spiccia, *Chem.–Eur. J.*, 1999, **5**, 2295; A. Drljaca, M. J. Hardie and C. L. Raston, *J. Chem. Soc., Dalton Trans.*, 1999, 3639; S. Airey, A. Drljaca, M. J. Hardie and C. L. Raston, *Chem. Commun.*, 1999, 1137.
5 C. B. Smith, L. J. Barbour, M. Makha, C. L. Raston and A. N. Sobolev, *Chem. Commun.*, 2006, 950.
6 A. Lazar, E. D. Silva, A. Navaza, C. Barbey and A. W. Coleman, *Chem. Commun.*, 2004, 2162; Y. Liu, D.-S. Guo, H.-Y. Zhang, S. Kang and H.-B. Song, *Cryst. Growth Des.*, 2006, **6**, 1399; C. Liu, F. Luo, W. Liao, D. Li, X. Wang and R. Dronskowski, *Cryst. Growth Des.*, 2007, **7**, 2282.
7 H. R. Webb, M. J. Hardie and C. L. Raston, *Chem.–Eur. J.*, 2001, **7**, 3616; S. J. Dalgarno and C. L. Raston, *Chem. Commun.*, 2002, 2216; J. L. Atwood, S. J. Dalgarno, M. J. Hardie and C. L. Raston, *New J. Chem.*, 2004, **28**, 326; J. L. Atwood, L. J. Barbour, S. J. Dalgarno, C. L. Raston and H. R. Webber, *J. Chem. Soc., Dalton Trans.*, 2002, 4351.
8 Y. Liu, Q. Li, D.-S. Guo and K. Chen, *Cryst. Growth Des.*, 2007, **7**, 1672.
9 G. W. Orr, L. J. Barbour and J. L. Atwood, *Science*, 1999, **285**, 1049; J. L. Atwood, L. J. Barbour, S. J. Dalgarno, M. J. Hardie, C. L. Raston and H. R. Webb, *J. Am. Chem. Soc.*, 2004, **126**, 13170.
10 A. W. Coleman, S. G. Bott, S. D. Morley, C. M. Means, K. D. Robinson, H.-M. Zhang and J. L. Atwood, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1361.
11 J. L. Atwood, T. Ness, P. J. Nichols and C. L. Raston, *Cryst. Growth Des.*, 2002, **2**, 171; P. J. Nichols and C. L. Raston, *J. Chem. Soc., Dalton Trans.*, 2003, 2923.

12 P. J. Nichols, M. Makha and C. L. Raston, *Cryst. Growth Des.*, 2006, **6**, 1161.
13 Y.-F. Bi, W.-P. Liao and H.-J. Zhang, *Cryst. Growth Des.*, 2008, **8**, 3630; W.-P. Liao, Y.-F. Bi, S. Gao, D.-Q. Li, H.-J. Zhang and R. Dronskowski, *Eur. J. Inorg. Chem.*, 2008, 2959.
14 A. W. Coleman, A. N. Lazar and J.-Y. Renault, French Patent, 2006, FR 2904782; O. Shkurenko, K. Suwinska and A. W. Coleman, *CrystEngComm*, 2008, **10**, 821.
15 A. W. Coleman, A. N. Lazar, K. Suwinska and O. Danyluk, French Patent, 2006, FR 2899814; N. Dupont, A. N. Lazar, F. Perret, O. Danylyuk, K. Suwinska, A. Navazaa and A. W. Coleman, *CrystEngComm*, 2008, **10**, 975.
16 M. Makha and A. N. Sobolev, *Cryst. Growth Des.*, 2007, **7**, 1441.
17 S. J. Dalgarno, J. E. Warren, J. L. Atwood and C. L. Raston, *New J. Chem.*, 2008, **32**, 2100.
18 D.-S. Guo, H.-Y. Zhang, C.-J. Li and Y. Liu, *Chem. Commun.*, 2006, 2592.
19 S. J. Dalgarno, J. L. Atwood and C. L. Raston, *Cryst. Growth Des.*, 2006, **6**, 174.
20 F. Ugozzoli and G. D. Andreetti, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1992, **13**, 337.
21 J. W. Steed, C. P. Johnson, C. L. Barnes, R. K. Juneja, J. L. Atwood, S. Reilly, R. L. Hollis, P. H. Smith and D. L. Clark, *J. Am. Chem. Soc.*, 1995, **117**, 11426.
22 M. I. Attalla, N. S. McAlpine and L. A. Summers, *Z. Naturforsch., Teil B*, 1984, **39**, 74.
23 G. M. Sheldrick, *SHELX97*: University of Gottingen, Germany, 1997.
24 *CrystalStructure 3.7.0 and Crystalclear 1.36: Crystal Structure Analysis Package*, Rigaku and Rigaku/MSC, 2000–2005, The Woodlands, TX.

