

Benzyl Effects of Supramolecular Architectures Constructed by *p*-Sulfonatocalix[4]arene and Viologen Guests: from Simple 2:1 Complex to Polymeric Capsules

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ABSTRACT: Two novel supramolecular assemblies have been constructed by *p*-sulfonatocalix[4]arene (**C4AS**) and viologen guests, showing that **C4AS** presents 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.

As a significant and interesting topic of crystal engineering, the construction of supramolecular assemblies has attracted more and more attention in recent years. *p*-Sulfonatocalix[*n*]arenes (**C_nAS**, *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.¹ Up to now, several kinds of spectacular architectures besides the conventional bilayer array² have been fabricated by **C_nAS** upon complexation with various types of guest molecules and/or metal ions, such as molecular capsules,³ the “ferris wheel”,⁴ the “Russian doll”,⁵ the helical array,⁶ water-filled channels,⁷ coordination and hydrogen-bonding polymers,⁸ honeycomb aggregates,⁹ spheroidal and tubular arrays,¹⁰ etc.¹¹ 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.^{1a,b} Possessing an intrinsic bowl shape, **C4AS** can form molecular capsules in the presence of diverse guest molecules, such as crown ethers,^{1a,b,3a} amino acids,¹² nucleic acid bases and derivatives,¹³ etc., which have been carefully investigated by Raston and co-workers, revealing that the encapsulated guests show noncovalent interactions like hydrogen bonding, π -stacking, and hydrophobic effects, with the “cap” molecules, which contribute much to the formation and stabilization of the capsules. Our recent work also reported that **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.^{3e}

Viologens, one class of dicationic redox couples,¹⁴ have been widely applied as herbicides,¹⁵ probes to study DNA and zeolites,¹⁶ and important subunits in constructing functional molecular assemblies/machines and electrochromic display devices.¹⁷ In a previous study, we have investigated the binding behaviors of **C_nAS** (*n* = 4, 5) with methyl viologen (**MV**) in aqueous solution, showing that they can form stable complexes with complex stability constants greater than $1 \times 10^4 \text{ M}^{-1}$.¹⁸ From the perspective of crystal design, it is also fascinating to employ viologens as guests to further pursue supramolecular architectures based on **C_nAS** and gain deeper insights into the manipulation of guests. The symmetrical viologen molecules possess two identical binding sites to be included into the calixarene cavity, which provide excellent preorganized structures to form molecular capsules. Herein, we prepared two solid-state complexes of **C4AS** with **MV** and benzyl viologen (**BV**) in single-crystal form,¹⁹ and their structures were identified by X-ray diffraction as $\text{C}_{40}\text{H}_{50}\text{N}_2\text{O}_{23}\text{S}_4$ (**1**) and $\text{C}_{40}\text{H}_{54.5}\text{N}_1\text{O}_{26.25}\text{S}_4$ (**2**),²⁰ respectively. The two viologens share the same skeleton, but have

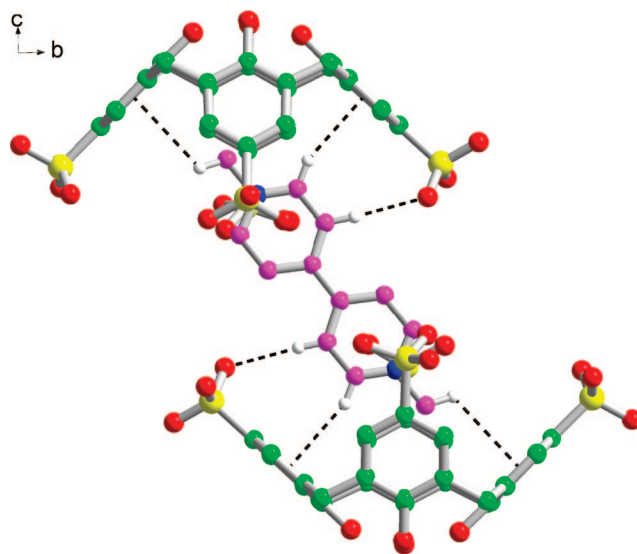


Figure 1. Structural view of the host–guest 2:1 complex formed by **C4AS** and **MV**; the dashed lines represent the host–guest C–H \cdots π and hydrogen-bonding interactions.

different substituents, and induce diverse inclusion/aggregation structures of **C4AS**.

Complexes **1** and **2** crystallize in the monoclinic space group *C2/c* and in the triclinic space group *P* $\bar{1}$, respectively. In the asymmetric unit, there are one crystallographically distinct **C4AS**, two half **MV**, and 3 water molecules for **1**; one **C4AS**, one-half **BV**, and 10.25 water molecules for **2**. Among these two crystals, some sulfonate groups of **C4AS** and several water molecules disordered at two or more positions. To satisfy the charge balance, **C4AS** in both complexes should possess two or three protonated sulfonate groups, 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.²¹

In complex **1**, **C4AS** includes both the methyl group and the aromatic pyridinium ring of **MV** into its cavity with one hydrogen bond ($\text{C}_{30}\cdots\text{O}_{14}$, 3.351 Å) and two C–H \cdots π interactions ($\text{C}_{34}\text{–H}_{34}\cdots\text{Ring of C}_{9\text{–}14}$, 3.252 Å, 102.0°; $\text{C}_{29}\text{–H}_{29}\cdots\text{Ring of C}_{23\text{–}28}$, 2.691 Å, 159.1°), as shown in Figure 1. The host–guest complexation is in a slantwise manner such that the angle formed by the long axis of **MV** and the plane of the bridged methylenes is 39.3°. As anticipated, two methylic pyridinium portions of one **MV** are simultaneously included by two **C4AS** hosts. That is, two calixarene hosts share one **MV** guest to form a 2:1 complex. Furthermore, taking the relative position of the two face-to-face

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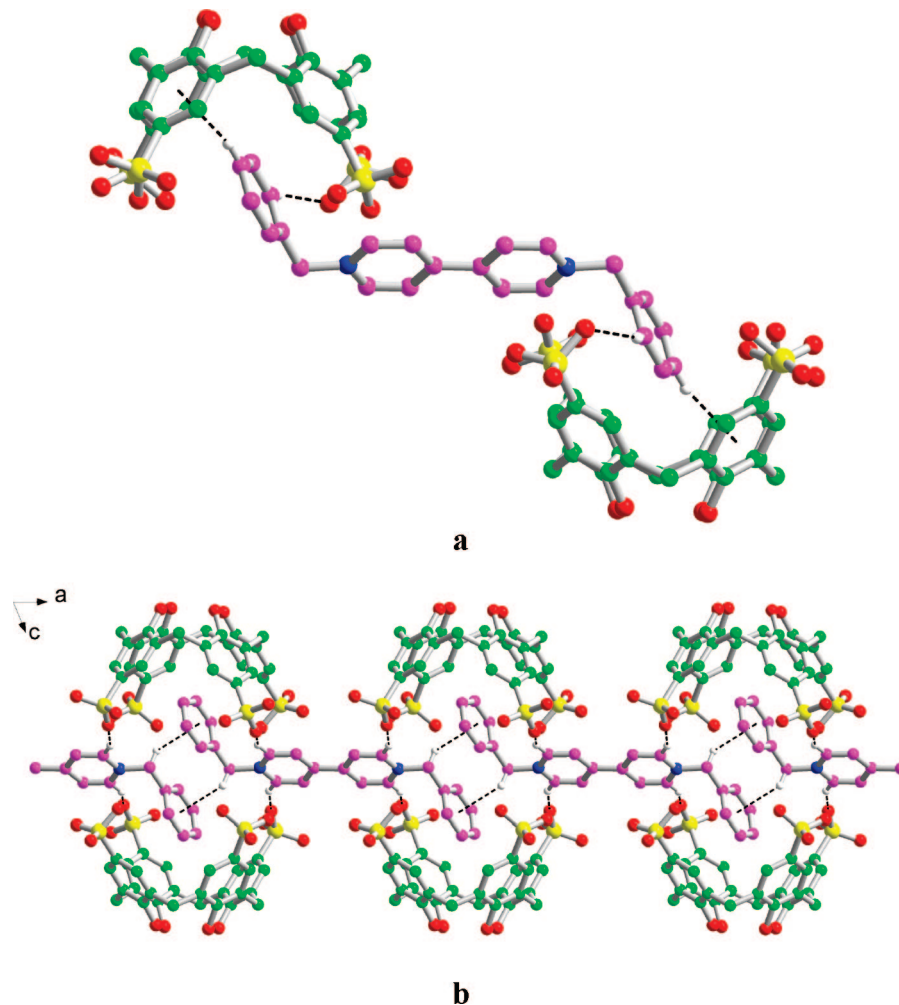


Figure 2. (a) 2:1 complex formed by C4AS with BV; (b) view showing the structure of polymeric capsules observed in **2**. The dashed lines represent the host-guest C–H $\cdots\pi$ and hydrogen-bonding interactions.

calixarenes into account, complex **1** 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 MV molecule. In addition, it should be mentioned that the present 2:1 stoichiometry in the solid state is speciously inconsistent with the previous 1:1 stoichiometry in solution. The same phenomenon is also observed for the host-guest complexation of C4AS with crown ethers in a previous report by Raston and co-workers.²² In fact, it is reasonably acceptable that the 1:1 solution complexes act as precursors to solid-state complexes (or capsules).^{3e}

Differently from **1**, C4AS in **2** only accommodates the benzyl group of BV into its cavity without further inclusion of the pyridinium portion. As shown in Figure 2a, each benzyl group of BV penetrates into one cavity of calixarene through one hydrogen bond (C₃₃⋯O₄, 3.412 Å) and one C–H⋯ π interaction (C₃₁–H₃₁⋯Ring of C_{16–21}, 2.726 Å, 167.6°), leading to the 2:1 host-guest stoichiometry with the 4,4'-dipyridinium portion holding the two C4AS far apart from each other. The conformational distortions of C4AS are also different upon complexation with MV and BV guests. C4AS is induced to the pinched-cone conformation of C_{2v} symmetry by MV in **1** (the S⋯S approaches of distal sulfonates, 8.211 Å and 11.823 Å), whereas it maintains the original C_{4v} cone conformation in **2** (the S⋯S approaches of distal sulfonates, 10.792 and 10.191 Å).

The most fascinating feature in **2** is that a calixarene from one bilayer lines up with a calixarene of another bilayer to give the appearance of capsule. Furthermore, based on the linking of the

4,4'-dipyridinium portion, the morphology that can be called as the polymeric capsules are observed in the further aggregation structure as shown in Figure 2b. Two benzyl groups in neighboring BV guests are immersed into the cage of two face-to-face C4AS hosts to constitute the asymmetric unit of the capsule, mainly originating from the dimerization of benzyl groups (C–H⋯ π interaction: C₃₅–H₃₅⋯Ring of C_{29–34}, 3.130 Å, 129.5°). Moreover, two hydrogen bonds between the 4,4'-dipyridinium portion and sulfonate groups (C₃₆⋯O₁₆, 3.094; C₄₀⋯O₁₀, 3.298 Å) make an additional contribution to jointing two calixarene caps together and sealing the capsule unit. Besides acting as the constituent of sealing, the 4,4'-dipyridinium portion also plays a great role as a linker that holds the capsule units together along the equatorial orientation, leading to the one-dimensional polymerization of capsules. Although there have been several reports of polymeric capsules based on CnAS held together by metal complexation, π -stacking, and other noncovalent interactions,^{1a,8a,13,23} the linking pattern of the polymeric capsules in **2** is still particular in that the third component is not needed to achieve the polymerization of capsules. Most of the reported polymeric capsules based on CnAS are triad complexes in which another subunit besides host and guest (such as metal ions) contributes to hold the capsule units together. Recently, we also reported the polymeric capsules based on C6AS dyad that extend infinitely along the axial orientation though the linkage of the covalent bonds between the up cavity and the down cavity of C6AS.⁹ Therefore, the present structure in **2** represents a typical example that the BV guest dramatically acts as not only the subunit

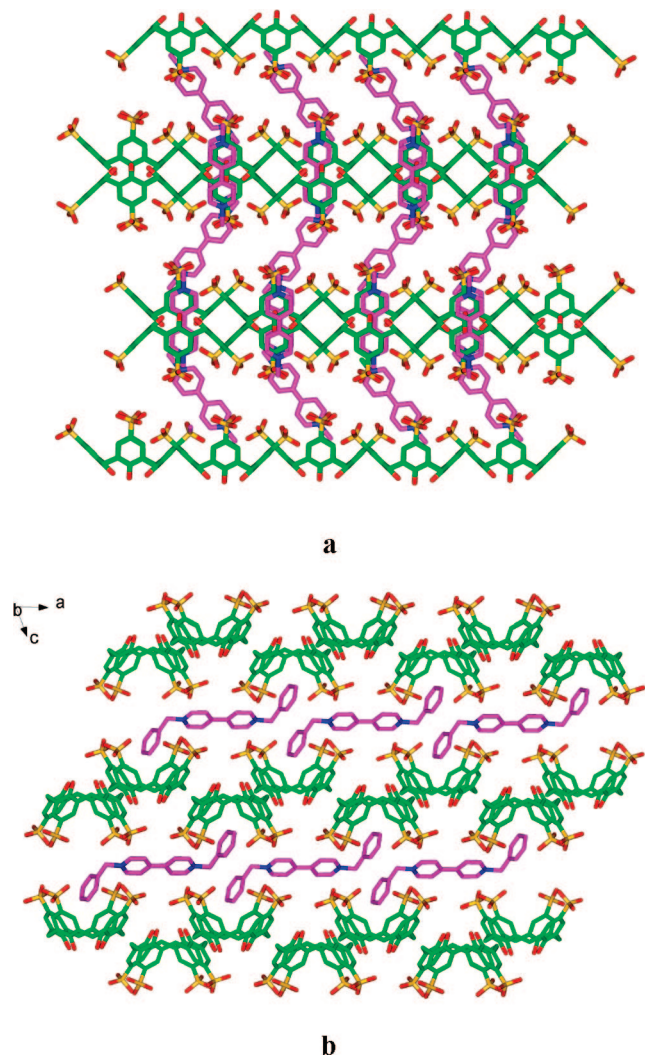


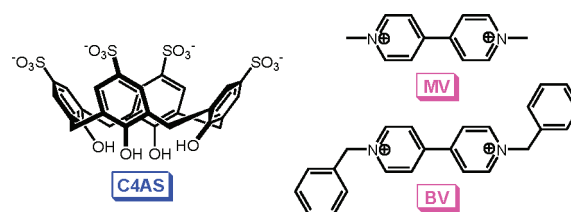
Figure 3. View of the overall extended structures of (a) **1** and (b) **2** in a bilayer array.

to induce the formation of the capsule unit but also the self-linker to hold the capsules equatorially together.

For the overall packing structures, both **1** and **2** present the bilayer arrangement through the π -stacking interactions among the calixarenes themselves (for **1**, Ring of C_{23–28}···Ring of C_{9–14}, 3.967 Å; Ring of C_{2–7}···Ring of C_{2–7}, 4.257 Å; for **2**, Ring of C_{9–14}···Ring of C_{9–14}, 3.750 Å; Ring of C_{2–7}···Ring of C_{2–7}, 3.668 Å; C₂₂–H₂₂···Ring C_{16–21}, 3.124 Å, 111.1°) as shown in Figure 3. In addition, the MV counterions in **1** penetrate vertically through the hydrophobic layers, and also make significant contributions to the formation of regularly arranged calixarene layers via π ··· π interactions (Ring of C_{16–21}···Ring of C_{35–39}, N₂, 3.857 Å). On the other hand, a more significant extension of the hydrophilic layers can be observed in complexes **1** and **2** in comparison to that of C4AS itself (thicknesses: C4AS, 8.3 Å; **1**, 9.1 Å; **2**, 8.9 Å). This means that the viologen guests appear as pillars to hold the calixarene layers more apart. Moreover, although the molecular length of MV is less than that of BV, MV induces more extensive structure of hydrophilic layers because of the spatial orientation of MV guests that are more vertical to the calixarene layers.

In summary, we have demonstrated the construction of diverse supramolecular architectures based on C4AS in the presence of viologen guests. In virtue of the two binding sites owned by viologens, C4AS forms host–guest 2:1 complexes with both MV (**1**) and BV (**2**) guests. Most interestingly, complex **2** further presents the spectacular aggregation of polymeric capsules, whereas complex **1** does not, and even cannot be called a slipped capsule.

Chart 1. Schematic Structures of Employed Host and Guests, C4AS, MV, and BV



Finally, the conventional bilayer arrangement is observed in the overall packing structures of both **1** and **2**. Successfully realizing the design of advanced molecular assemblies manipulated by guests, 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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Supporting Information Available: X-ray crystallographic data of complexes **1** and **2** as CIF files (also available as CCDC reference numbers 626914 and 626915). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (19) *p*-sulfonatocalix[4]arene (**C4AS**, 0.10 mmol) was dissolved in 1 M HCl solution (20 mL), followed by the addition of 2 equiv. of methyl viologen (**MV**) or benzyl viologen (**BV**). After the solution was stirred for a few minutes, and filtrated, the filtrate was placed to evaporate for about 3–4 weeks. The yellow (**1**) and colorless (**2**) crystals formed were collected along with their mother liquors for the X-ray crystallographic analyses.
- (20) The X-ray intensity data for **1** and **2** were collected on a standard Bruker SMART-1000 CCD area detector system equipped with a normal-focus molybdenum-target X-ray tube ($\lambda = 0.71073 \text{ \AA}$) operated at 2.0 kW and a graphite monochromator at $T = 293(2) \text{ K}$. All the structures were solved by using the direct method and refined, employing full-matrix least squares on F^2 (CrystalStructure, SHELX97). Crystal data for **1**: $\text{C}_{40}\text{H}_{50}\text{N}_5\text{O}_{23}\text{S}_4$, $M_r = 1055.06$, monoclinic, space group $C2/c$, $a = 20.890(9) \text{ \AA}$, $b = 18.703(8) \text{ \AA}$, $c = 29.646(13) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 99.368(8)^\circ$, $\gamma = 90^\circ$, $V = 11429(9) \text{ \AA}^3$, $F(000) = 4416$, $Z = 8$, $\rho_{\text{calcd}} = 1.226 \text{ g/cm}^3$, $\mu = 0.238 \text{ mm}^{-1}$, approximate crystal dimensions $0.32 \times 0.28 \times 0.20 \text{ mm}^3$, θ range = $1.47\text{--}25.02^\circ$, 25352 measured reflections, of which 9902 ($R_{\text{int}} = 0.1397$) were unique, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.1454$, $wR_2 = 0.3566$, R indices (all data): $R_1 = 0.2543$, $wR_2 = 0.4313$, GOF = 1.135. Crystal data for **2**: $\text{C}_{40}\text{H}_{54.5}\text{N}_1\text{O}_{26.25}\text{S}_4$, $M_r = 1097.59$, triclinic, space group $P\bar{1}$, $a = 14.074(4) \text{ \AA}$, $b = 14.475(4) \text{ \AA}$, $c = 15.773(4) \text{ \AA}$, $\alpha = 72.909(4)^\circ$, $\beta = 65.995(4)^\circ$, $\gamma = 79.968(4)^\circ$, $V = 2800.3(12) \text{ \AA}^3$, $F(000) = 1151$, $Z = 2$, $\rho_{\text{calcd}} = 1.302 \text{ g/cm}^3$, $\mu = 0.250 \text{ mm}^{-1}$, approximate crystal dimensions $0.32 \times 0.28 \times 0.22 \text{ mm}^3$, θ range = $1.46\text{--}25.01^\circ$, 13 833 measured reflections, of which 9694 ($R_{\text{int}} = 0.0394$) were unique, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.1293$, $wR_2 = 0.3732$, R indices (all data): $R_1 = 0.1666$, $wR_2 = 0.4055$, GOF = 1.456.
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