Polymeric Capsules and Honeycomb Aggregates Formed by p-Sulfonatoicalix[6]arene with Phenanthrolinium Compounds

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ABSTRACT: Two crystalline complexes were prepared by the inclusion complexation of p-sulfonatoicalix[6]arene (C6AS) with 1,10-phenanthroline (Phen+) (1) and 6,7-dihydro-5H-[1,4]diazepino[1,2,3,4-lmn]-[1,10]phenanthroline-4,8-diium (PPQ2+) (2). p-Sulfonatoicalix[6]arene, in complex 1, maintains the conventional centrosymmetric “up-down” double partial cone conformation, whereas it assumes a novel unsymmetric up-down double partial cone conformation induced by PPQ2+ guest in complex 2. Furthermore, p-sulfonatoicalix[6]arene aggregates to the overall structure of multipillars in the presence of Phen+ guest and presents the honeycomb-type packing structure upon complexation with PPQ2+.

As a versatile building block capable of binding various guest molecules, the water-soluble p-sulfonatoicalix[n]arenes (CnAS, n = 4, 5, 6, 8) have attracted considerable attention in the broad area of supramolecular chemistry, crystal engineering, and even biochemistry.1 In the presence of suitable guest molecules, they can be assigned to design several kinds of supramolecular architectures besides the conventional bilayer array,2 including molecule capsules,3,4 ferris wheel,5 Russian doll,6 helical arrays,6 water channel,7 and particularly, spheres and tubular arrays8 once the bilayer array is thoroughly overcome. Among them, the smallest conformation-constrained analogue, C4AS, has been much more widely studied than the others.9a However, for the larger analogue, C6AS, it is somewhat difficult to construct supramolecular architectures because of its high charge, flexible conformation,9d and disadvantages of material refinement and complex crystallization1b relative to C4AS. So far, several research achievements on C6AS have been gained in the endeavors of some researchers such as Atwood and Raston et al.9 On their own, C6AS also arrange themselves in an up-down antiparallel fashion to form a clay-type bilayer arrangement.9b Furthermore, C6AS can form a corrugated bilayer arrangement,9c hydrogen-bond arrays,9d molecular capsule,9e and ferris wheel10 when some specific guest molecules are employed, such as crown ether, pyridine N-oxide, 4,4′-dipyridine-N,N′-dioxide, lanthanide cations, and tetraphenylphosphonium. As can be seen from the aforementioned complexes, C6AS acts as a divergent receptor with two possible conformations: up-down double partial cone conformation or up-up double cone conformation. Furthermore, C6AS possesses a higher charge and more flexible framework than C4AS. All these intrinsical characteristics promise C6AS as a much better potential subunit to construct novel supramolecular architectures that cannot be obtained by C4AS, which has recently attracted more and more interests, although it is a relatively formidable challenge.9d

In our previous work,10 it was found that the C4AS and C5AS can form bis-molecular capsules induced by the 1,10-phenanthroline (Phen+) guest. Herein, we further investigated the complex behavior of C6AS11 with Phen+ (see Chart 1). Moreover, bis-(quaternary salt), 6,7-dihydro-5H-[1,4]diazepino[1,2,3,4-lmn]-[1,10]phenanthroline-4,8-diium (PPQ2+),12 is also employed. As comparison with Phen+, PPQ2+ possesses one more positive charge and is not yet a coplanar structure, which may result in its forming a distinct aggregate with C6AS. Two solid-state complexes are successfully prepared in single-crystal form,13 and their precise structures are identified by X-ray diffraction as [C6AS]+–[2H]+–[Phen+]–[2H2O] (1) and [C6AS]+–[PPQ2+]+–[31H2O] (2).14

In complex 1, C6AS adopts the centrosymmetric up-down double partial cone conformation and provides two identical binding sites for Phen+ guests. Differing hence from C4AS and C5AS, the complexation of C6AS with Phen+ leads to a 1:2 host–guest inclusion stoichiometry. As shown in Figure 1a, two Phen+ guests are simultaneously immersed into the up cavity and down cavity of C6AS by two independent C−H···π interactions. Further, each

Figure 1. (a) 1:2 complex formed by C6AS with Phen+, the dashed lines represent the host–guest C−H···π interactions (C−H···centroid of aromatic ring = 3.133(5) Å, 156.58(2)°, 2.916(2) Å, 145.77(2)°); (b) view of Phen+ dimer, the three dashed lines represent the triplex π···π interactions (centroid of aromatic ring···centroid of aromatic ring = 3.569(5), 3.901(3), 3.569(5) Å); (c) view showing the structure of polymeric capsules in complex 1; (d) view of space-filling mode of polymeric capsules.
included Phen$^+$ guest interacts with another in the adjacent unit through $\pi\cdots\pi$ interactions to form a face-to-face Phen dimer (Figure 1b). Therefore, with the cooperation of these intermolecular C–H···$\pi$ and $\pi\cdots\pi$ interactions, the spectacular structure of so-called polymeric capsules is presented in 1 (Figure 1c). Each capsule unit is composed of two face-to-face half-C6AS units containing a Phen dimer with height of 11.862 Å and then extends infinitely to form polymers through the linkage of the covalent bonds between the up cavity and the down cavity of C6AS. That is, the up–down double partial cone conformation of C6AS enables the opportunity to construct extensive polymeric capsules rather than the simple molecular capsules of C4AS and C5AS. Previously, there have been reported several polymeric capsules based on CnAS held together by metal complexation as well as $\pi$-stacking and other weak interactions along the equatorial orientation. However, the present result still represents the first example of polymeric capsules based on C6AS along the axial orientation. In addition, the capsule unit in 1 is much more compact than those corresponding capsules of C4AS and C5AS, which can be attributed to Phen$^+$ included into the C6AS cavity in a more slantwise manner and the triplex $\pi\cdots\pi$ interactions resulting in the smaller volume of the Phen dimer.

The overall structure of complex 1 reveals that the C6AS molecules are not packed in the traditional bilayer arrangement. Viewing from the crystallographical $a$ direction, it presents a novel multipillar aggregate (Figure 2), in which each pillar represents a suit of polymeric capsules. Moreover, there are two kinds of almost isostructural pillars, which are shown in different colors. Each kind of pillar is surrounded by four other kind of pillars, and the other Phen$^+$ guests as counterions and water molecules fill the interspace among the pillars. On the other hand, the packing structure of 1 seems to display some layered character when being viewed from other directions. However, none of the interactions between C6AS to form a bilayer array can be found, and there are not clear hydrophobic and hydrophilic layers in 1.

In complex 2, C6AS also exists in up–down form with two PPQ$^{2+}$ guest molecules included into its cavities. However, close examinations of the bond lengths and angles of methylene bridges reveal that C6AS in 2 assumes a particular up–down double partial cone conformation, which differs much from that in 1 and those reported before. The classical up–down conformation of C6AS is centrosymmetric, and two axes of the up cavity

![Figure 2](image1.png)

**Figure 2.** Overall packing diagram showing the multipillar aggregate of complex 1, in which each pillar represents a suit of polymeric capsules (pillars extending perpendicular to the plane of the page). The solvent molecules and all hydrogen atoms have been omitted for clarity.

![Chart 1](image2.png)

**Chart 1**

![Figure 3a](image3a.png)

(a) View of the novel unsymmetric “up–down” double partial cone conformation of C6AS in complex 2. The PPQ$^{2+}$ molecules insert into the cavities of C6AS in two different manners, one into (b) its distal cavity A in the longitudinal orientation and the other into (c) its proximate cavity B in the latitudinal orientation.

![Figure 3b](image3b.png)

![Figure 3c](image3c.png)
and down cavity are parallel to each other. In 2, on the other hand, it is obvious that the two axes of the up and down cavities form an angle of 54.12° instead of the parallel manner. In addition, the S...S approaches of trans sulfonates between up and down cavities are distinct from each other (S...S = 12.388(18), 7.958(10) Å). Therefore, the two cavities of C6AS in 2, which can be named cavity A and cavity B, are not equal to each other entirely. The trans sulfonate groups of A are in proximate position, whereas those of B are in proximate position. To the best of our knowledge, such an unsymmetric conformation of C6AS has never been reported before, which maybe result from the guest inducing. For the exceptional conformation of C6AS, it can also be reflected from the inclusion geometries of PPQ2+ guests. The binding manners of the two included PPQ2+ into the cavities of C6AS are different from each other. One PPQ2+ guest inserts into distal cavity A of C6AS in longitudinal orientation (Figure 3b) through two C–H...π interactions (C–H... centroid of aromatic ring = 2.656(7) Å, 152.00(3)°; 2.530(6) Å, 153.13(3)°; one π...π interaction (centroid of aromatic ring...centroid of aromatic ring = 3.802(16) Å) and two nonconventional hydrogen bonds (donor...acceptor = 3.892(7), 3.377(6) Å). Although the other inserts into proximate cavity B of C6AS in latitudinal orientation (Figure 3c) through two π...π interactions (centroid of aromatic ring...centroid of aromatic ring = 4.186(8), 4.044(19) Å); one C–H...π interaction (C–H... centroid of aromatic ring: 2.636(3), 176.09(3)°) and three nonconventional hydrogen bonds (donor...acceptor = 3.642(9), 3.329(19), 3.354(6) Å).

In the extended structure of 2, the common centrosymmetric up–down conformation of C6AS is distorted to be a unsymmetric form, and thereby, the classical packing structure of bialayer array is thoroughly disturbed. As shown in Figure 4, C6AS arrange themselves to be the nanoporous honeycomb-type structure. Every six C6AS molecules compose a nanoscopic hexagon through intermolecular multiple hydrogen bonds (donor...acceptor = 2.775(6), 2.792(5) Å) and multiple π...π interactions (centroid of aromatic ring...centroid of aromatic ring = 3.899(14), 3.514(4), 3.727(13) Å), which act as the unrepeatable unit of honeycomb. In addition, each C6AS contributes to form the other two hexagons, therefore making sure all the hexagons are closely conjoined together and thus present the honeycomb-type structure extending infinitely on the crystallographical a–b plane. In other words, each C6AS molecule participates in construction of three hexagonal frameworks, so every hexagon possesses two crystallographically independent C6AS molecules. In the inner interspace of every hexagon, two PPQ2+ counterions are filled, π-stack exo to the cavities of C6AS through two C–H...π interactions (C–H... centroid of aromatic ring = 2.648(4) Å, 157.04(3)°; 3.093(6) Å, 120.85(3)°) and one π...π interaction (centroid of aromatic ring...centroid of aromatic ring = 4.120(13) Å).

In summary, two complexes 1 and 2 of C6AS with Phen+ and PPQ2+ were prepared, respectively, and their structures were determined by X-ray crystallographic analysis. In the presence of Phen+ guest, C6AS exists in the common centrosymmetric up–down double partial cone conformation and further assembles into polymeric capsules. In the presence of PPQ2+, C6AS is induced to adopt the unseen unsymmetric up–down double partial cone conformation and further forms the novel honeycomb-type aggregates. These results obtained demonstrate that both Phen+ and PPQ2+ are effective guests to manipulate the aggregate structure of C6AS exceeding the regular bilayer array. Furthermore, the simple modification from Phen+ to PPQ2+ leads to distinct structures between 1 and 2. Endeavors to investigate the supramolecular architectures of CnAS with other Phen derivatives are going on.

Acknowledgment. This work was supported by the 973 Program (2006CB932900), NNSFC (90306009 and 20073061) and the Science and Technology Innovation Foundation of Nankai University, which are gratefully acknowledged.

Supporting Information Available: X-ray crystallographic data in CIF format (CCDC reference numbers 626913 for 1 and 630297 for 2) and PXRD data (PDF). These materials are available free of charge via the Internet at http://pubs.acs.org.

References


(14) The X-ray intensity data for 1 and 2 were collected on a Rigaku MM-007 rotating anode diffractometer equipped with a Saturn CCD Area Detector System using monochromated Mo-Kα radiation at T = 113(2) K. Data collection and reduction were performed by program of CrystalClear. The structures were solved by using the direct method and refined employing full-matrix least squares on F² (CrystalStructure, SHELXTL-97). (a) Crystal data for 1: C₃₀H₁₀₈N₈O₁₃S₃, M = 2395.77, triclinic, space group P1, a = 18.256(3) Å, b = 18.995(3) Å, c = 19.708(4) Å, α = 104.437(3)°, β = 107.218(6)°, γ = 109.746(8)°, V = 5948.7(17) Å³, Z = 2, Dc = 1.484 g cm⁻³, λ(Mo-Kα) = 0.7107 Å, T = 113(2) K, F(000) = 2320, μ = 0.239 mm⁻¹, approximate crystal dimensions 0.14 × 0.08 × 0.06 mm³, θ range = 1.34–25.00°, reflections collected/unique, 36 120/17 370 (I(-background) > 2σ(I)), final R indices [I > 2σ(I)] R₁ = 0.0726, wR₂ = 0.1764, R indices (all data): R₁ = 0.1088, wR₂ = 0.1986, goodness of fit on F² = 1.072. To satisfy charge balance, C₆AS in 1 should possess two protonated sulfonate groups, which are acceptable given the pH of the reaction solution. The oxygen atoms of the sulfonate group (S₅) are disordered over two positions. In addition, the hydrogen atoms from the Fourier difference map for this to be clarified. In addition, the oxygen atoms of some sulfonate groups (S₂ and S₆) are disordered P in 1, approximate crystal dimensions 0.14 × 0.08 × 0.06 mm³, θ range = 1.34–25.00°, reflections collected/unique, 36 120/17 370 (I(-background) > 2σ(I)), final R indices [I > 2σ(I)] R₁ = 0.0726, wR₂ = 0.1764, R indices (all data): R₁ = 0.1088, wR₂ = 0.1986, goodness of fit on F² = 1.072. To satisfy charge balance, C₆AS in 1 should possess two protonated sulfonate groups, which are acceptable given the pH of the reaction solution. The oxygen atoms of the sulfonate group (S₅) are disordered over two positions. In addition, the hydrogen atoms from the Fourier difference map for this to be

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