
Yu Liu,* Kun Chen, Dong-Sheng Guo, Qiang Li, and Hai-Bin Song

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China

Received July 2, 2007; Revised Manuscript Received September 7, 2007


Introduction

Water-soluble sulfonatocalixarenes, as a significant branch of calixarene chemistry, have attracted considerable interest of chemists due to their unique structures and properties.¹ As one class of versatile supramolecular hosts, sulfonatocalixarenes can effectively include various kinds of guest molecules with different sizes/shapes in aqueous solution, such as amino acids and polypeptides,² organic and inorganic cations,³ neutral organic molecules,⁴ bovine serum albumin,⁵ cholinergic ligands,⁶ and so on, which gives them potential applications in the fields of analytical chemistry and biochemistry. Moreover, they are well-known supramolecular building blocks in crystal engineering that are suitable for constructing splendid supramolecular architectures in the solid state.¹⁶,⁷ In this context, the smallest analogue, p-sulfonatocalix[4]arene, has been investigated more widely than others owing to its steady cone conformation, easy synthesis, and crystallization. Commonly, p-sulfonatocalix[4]arene adopts a cone conformation and displays an interlocked layered arrangement in an up-and-down fashion through multiple interactions including π-stacking interactions and hydrogen bonds.¹⁶,⁸ However, these antiparallel assembly structures are not invariable. p-Sulfonatocalix[4]arene can assemble themselves into structures such as molecular capsules,⁹ Russian dolls,¹⁰ ferris wheels,¹¹ coordination polymers,¹² two-dimensional (2D) hydrogen polymers,¹³ etc. in the presence of amino acids, nucleic acid–bases, polynuclear metal aqua cations, lanthanide cations, and so on. In particular, as reported by Atwood and co-workers, p-sulfonatocalix[4]arene assemble themselves into the spectacular structures of spheroids and tubules¹⁴ induced by lanthanide cations and pyridine N-oxide. Coleman and co-workers reported that the typical bilayer was replaced by a zigzag bilayer arrangement in the presence of arginine.¹⁵ More recently, Raston and co-workers reported that the complex of p-sulfonatocalix[4]arene and Co(III) sepulchrate cation assumes a helical strand in the presence of lanthanide.¹⁶

Thiacalixarenes possess some intrinsic characteristics (larger cavity, low electron-density, more flexibility, and additional sites) that conventional calixarenes lack, which result from the bridging methylene being replaced by sulfur atoms.¹⁷ As a result, the chemistry of thiacalixarenes is much different from that of conventional calixarenes.¹⁸ The water-soluble p-sulfonatothiacalix[4]arene also displays distinguishable inclusion/complexation properties to diverse guests in aqueous solution in comparison with p-sulfonatocalix[4]arene.¹⁹ Up to now, the solid-state supramolecular architectures based on p-sulfonatocalix[4]arene have gained some attention.²⁰ In most cases, p-sulfonatothiacalix[4]arene presents a bilayer array similar to p-sulfonatocalix[4]arene.²¹ However, once a suitable guest molecule is introduced, it presents obvious structural differences between p-sulfonatocalix[4]arene and p-sulfonatothiacalix[4]arene. For example, p-sulfonatocalix[4]arene assumes the 1,3-alternate conformation upon complexation with 4,4′-dipyridinium,²² while p-sulfonatothiacalix[4]arene assumes the 1,2-alternate conformation.²³ More recently, we also found that the Cu-imidazole complex can induce p-sulfonatothiacalix[4]arene to adopt the 1,2-alternate conformation owing to the unique bis-tridentate coordination of bridged S atoms and phenolic hydroxyls.²⁴ Furthermore, during the course of self-aggregation, the S···S interactions between bridged S atoms can contribute to the construction of the supramolecular assembly of p-sulfonatothiacalix[4]arene, which cannot be obtained by p-sulfonatocalix[4]arene.²³b,c It can be seen that p-sulfonatothiacalix[4]arene should be a novel supramolecular building block, possibly with more potential, but not a simple derivative of p-sulfonatocalix[4]arene. Therefore, the close comparison of the solid-state architectures between p-sulfonatocalix[4]arene and p-sulfonatothiacalix[4]arene appears to be a topic of interest, which has been paid less attention up to now. In previous work, we primarily compared the solid-state structures between p-sulfonatocalix[4]arene and p-sulfonatothiacalix[4]arene upon complexation with 2,2′-dipyridinium and 4,4′-dipyridinium.²³a In this paper, we further compare the solid-state inclusion behaviors and the aggregation-structures of p-sulfonatocalix[4]arene and p-sulfonatothiacalix[4]arene upon complexation with quinoline derivatives. A total of four crystal complexes 1–4 were obtained, in which not only the structural differences between
Experimental Section

8-Aminoquinoline (AQ) and 8-hydroxyquinoline (HQ) are commercially available and were used without further purification. p-Sulphonatocalix[4]arene tetrasodium (Na₄(p-sulphonatocalix[4]arene⁴⁺)) and its Na⁺(p-sulphonatocalix[4]arene⁴⁺) were prepared according to literature methods. In pH ≈ 1 or 1 N HCl solution, both AQ and HQ exist in the protonated forms (AQ⁺ and HQ⁺). Elemental analyses were performed on a Perkin-Elmer 2400C instrument.

Synthesis of [HQ⁺]₄(dp-sulphonatocalix[4]arene⁴⁺)·13.5H₂O (1): HQ (36.1 mg, 0.249 mmol) and Na₄(dp-sulphonatocalix[4]arene⁴⁺) (50.0 mg, 0.06 mmol) were dissolved in distilled water (10 mL). Then the solution was adjusted to pH ≈ 1 by HCl and stirred for 10 h. After filtration, the filtrate was allowed to evaporate slowly at room temperature, yielding the crystals suitable for X-ray analysis after 10 days. Anal. calcld for C₄₇H₄₁N₄O₂₉S₄ (M = 1319.36): C, 42.33; H, 3.74; N, 2.65; S, 19.98; found: C, 42.33; H, 3.74; N, 2.65; S, 19.98.

Synthesis of [HQ⁺]₄(dp-sulphonatocalix[4]arene⁴⁺)·7.75H₂O (3): HQ (33.1 mg, 0.228 mmol) and Na₄(dp-sulphonatocalix[4]arene⁴⁺) (50.0 mg, 0.055 mmol) were dissolved in 1 N HCl. Heated until clear, the solution was stirred for 10 h at room temperature and filtered. Then the filtrate was allowed to evaporate slowly at room temperature, yielding crystals suitable for X-ray analysis after nine days. Anal. calcld for C₄₇H₄₁N₄O₂₉S₄ (M = 1319.36): C, 42.33; H, 3.74; N, 2.65; S, 19.98; found: C, 42.33; H, 3.74; N, 2.65; S, 19.98.

Synthesis of [AQ⁺]₄(dp-p-sulphonatocalix[4]arene⁴⁺)·2.5H₂O (4): AQ (35.9 mg, 0.249 mmol) and Na₄(dp-p-sulphonatocalix[4]arene⁴⁺) (50.0 mg, 0.06 mmol) were dissolved in 1 N HCl (10 mL), and the solution was stirred for 10 h. After being filtered, the filtrate was allowed to evaporate slowly at room temperature, yielding the crystals suitable for X-ray analysis after 14 days. Anal. calcld for C₆₀H₆₁N₄O₂₆.75S₈ (M = 1562.14): C, 47.31; H, 4.07; N, 3.08; S, 16.84; found: C, 48.10; H, 4.01; N, 3.72; S, 17.16.

Synthesis of [AQ⁺]₄(dp-p-sulphonatocalix[4]arene⁴⁺)·1.25H₂O (2): AQ (36.1 mg, 0.228 mmol) and Na₄(dp-p-sulphonatocalix[4]arene⁴⁺) (50.0 mg, 0.055 mmol) were dissolved in distilled water (10 mL). Then the solution was adjusted to pH ≈ 1 by HCl and heated until clear. After that, the solution was stirred for 10 h at room temperature and filtered. Then the filtrate was allowed to evaporate slowly at room temperature, yielding the crystals suitable for X-ray analysis after seven days. Anal. calcld for C₆₀H₆₁N₄O₂₆.75S₈ (M = 1562.14): C, 47.31; H, 4.07; N, 3.08; S, 16.84; found: C, 48.10; H, 4.01; N, 3.72; S, 17.16.

Experimental Section

8-Aminoquinoline (AQ) and 8-hydroxyquinoline (HQ) are commercially available and were used without further purification. p-Sulphonatocalix[4]arene tetrasodium (Na₄(p-sulphonatocalix[4]arene⁴⁺)) and p-sulphonatocalix[4]arene tetrasodium (Na₄(p-sulphonatocalix[4]arene⁴⁺)) were prepared according to literature methods. In pH ≈ 1 or 1 N HCl solution, both AQ and HQ exist in the protonated forms (AQ⁺ and HQ⁺). Elemental analyses were performed on a Perkin-Elmer 2400C instrument.

Synthesis of [HQ⁺]₄(dp-sulphonatocalix[4]arene⁴⁺)·13.5H₂O (1): HQ (36.1 mg, 0.249 mmol) and Na₄(dp-sulphonatocalix[4]arene⁴⁺) (50.0 mg, 0.06 mmol) were dissolved in distilled water (10 mL). Then the solution was adjusted to pH ≈ 1 by HCl and stirred for 10 h. After filtration, the filtrate was allowed to evaporate slowly at room temperature, yielding the crystals suitable for X-ray analysis after 10 days. Anal. calcld for C₄₇H₄₁N₄O₂₉S₄ (M = 1319.36): C, 42.33; H, 3.74; N, 2.65; S, 19.98; found: C, 42.33; H, 3.74; N, 2.65; S, 19.98.

Synthesis of [AQ⁺]₄(dp-p-sulphonatocalix[4]arene⁴⁺)·2.5H₂O (4): AQ (35.9 mg, 0.249 mmol) and Na₄(dp-p-sulphonatocalix[4]arene⁴⁺) (50.0 mg, 0.06 mmol) were dissolved in 1 N HCl (10 mL), and the solution was stirred for 10 h. After being filtered, the filtrate was allowed to evaporate slowly at room temperature, yielding the crystals suitable for X-ray analysis after 14 days. Anal. calcld for C₆₀H₆₁N₄O₂₆.75S₈ (M = 1562.14): C, 47.31; H, 4.07; N, 3.08; S, 16.84; found: C, 48.10; H, 4.01; N, 3.72; S, 17.16.

Synthesis of [AQ⁺]₄(dp-p-sulphonatocalix[4]arene⁴⁺)·1.25H₂O (2): AQ (36.1 mg, 0.228 mmol) and Na₄(dp-p-sulphonatocalix[4]arene⁴⁺) (50.0 mg, 0.055 mmol) were dissolved in distilled water (10 mL). Then the solution was adjusted to pH ≈ 1 by HCl and heated until clear. After that, the solution was stirred for 10 h at room temperature and filtered. Then the filtrate was allowed to evaporate slowly at room temperature, yielding the crystals suitable for X-ray analysis after seven days. Anal. calcld for C₆₀H₆₁N₄O₂₆.75S₈ (M = 1562.14): C, 47.31; H, 4.07; N, 3.08; S, 16.84; found: C, 48.10; H, 4.01; N, 3.72; S, 17.16.
ac.uk/data_request/cif. Some sulfonate groups of the p-sulfonatocalix[4]arene in 1, 4 and guest molecules in 1–4, are disordered and refined in two or more positions, respectively. To satisfy the charge balance, the host calixarene in 1, 3, and 4 should, respectively, possess 0.5, 1.5, 2.75 protonated sulfonate 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.

### Result and Discussion

All the complexes 1–4 obtained crystallize in the same triclinic system, and their structural solutions were performed in the same space group P1. The asymmetric units contain following: 1 crystallographically distinct p-sulfonatocalix[4]arene, 3.5 HQ+, and 13.5 water molecules for 1; 1 p-sulfonatocalix[4]arene, 4 HQ+, and 6.75 water molecules for 2; 1 p-sulfonatocalix[4]arene, 2.5 HQ+, and 7.75 water molecules for 3; 1 p-sulfonatocalix[4]arene, 1.25 AQ−, and 9 water molecules for 4. Viewing in the mass, calixarenes all maintain the bowl shape to accommodate the guest molecules, and the up–down antiparallel manner of aggregation is not thoroughly overcome yet. However, on close examination of these four complexes, their precise structures are distinct from each other, including the conformations of calixarenes, including modes, and the extended arrays. The results will now be discussed in detail.

**Structure of [HQ+]x·[p-sulfonatocalix[4]arene]4−·0.5H+·13.5H2O (1)**. Among the 3.5 HQ+, one is included into the cavity of p-sulfonatocalix[4]arene to form the cavitate, and the others are restricted in the crystal lattice as counterions to form the clathrate. As shown in Figure 1a, the HQ+ is slantways included into the cavity of p-sulfonatocalix[4]arene with the portion of pyridine ring immersed, forming a total of four host–guest interactions between aromatic rings of calixarene and pyridine of HQ+ (three C−H···π interactions: C31−H31···ring of C22 to C27, 2.620 Å and 176.8°, C29−H29···ring of C8 to C13, 3.079 Å and 132.7°, C30−H30···ring of C15 to C20, 2.860 Å and 116.4°; a relative weak π···π interaction: the pyridine ring···the ring of C1 to C6, 4.151 Å). The 1La axis of quinoline forms an angle of 42.5° with the plane defined by four bridging methylenes.30 To accommodate well the planar aromatic HQ+ guest, p-sulfonatocalix[4]arene adopts the pinched-cone conformation (C2s symmetry), which is elucidated by S···S distances between the opposite sulfonate groups (8.342 and 11.782 Å, respectively). The dihedral angles formed by the planes of two splaying aromatic rings and the plane defined by four phenolic oxygen atoms are 130.2° and 141.7°, and those formed by the two pinched rings are 106.2° and 114.5°.

For the extended structure of complex 1, p-sulfonatocalix[4]arenes assemble into a common bilayer arrangement (Figure 1b) with the thicknesses of hydrophobic and hydrophilic layers of 8.3 and 8.6 Å. (The thickness of the hydrophilic layer is defined as the perpendicular distance between the planes comprising the sulfur-bonded aromatic carbon atoms.33) Thus, the whole distance of one bilayer unit is 16.9 Å, which is wider than the bilayer thickness of 13.7 Å formed by sole p-sulfonatocalix[4]arenes with a smaller hydrophilic layer of 5.4 Å and a similar hydrophilic layer of 8.3 Å. The extension of the hydrophobic layer may be attributed to the unconventional manner of constructing the calixarene layer in complex 1. In general, each p-sulfonatocalix[4]arene is surrounded by other four antidirection ones, forming four independent π-stacking (π···π or C−H···π) interactions, and then construct the bilayer structure by interlocking calixarenes in an up–down fashion.

However, in complex 1, three of the four walls of calixarene are surrounded by calixarene themselves, while the fourth one is adjacent to the HQ+ counterion, as shown in Figure 1c. In other words, one type of HQ+ counterion intercalates into the calixarene layers but does not reside in the hydrophilic region, which makes the hydrophilic layers looser. As a result, there are three independent π···π interactions (4.338 Å, ring of C1 to C6···ring of C1 to C6; 3.718 Å, ring of C8 to C13···ring of C8 to C13; 4.019 Å, ring of C15 to C20···ring of C15 to C20) between calixarene themselves. Moreover, the intercalated HQ+ is parallel to the fourth wall of the calixarene, and π···π stacks respectively with aromatic rings of two calixarenes (3.533–3.943 Å), forming an exo sandwich complex. Therefore, the immersion of the HQ+ counterion contributes to the formation of calixarene layers to some extent.

![Figure 1](image-url) Views of complex 1 (a) inclusion structure, (b) packing structure, (c) host molecule environment in a hydrophobic layer. The broken lines represent the intermolecular hydrogen bonds or π-stacking interactions between host and guest.
Structure of \([\text{HQ}^+]_4[p\text{-sulfonatocalix}[4]\text{arene}]_4\cdot 6.75\text{H}_2\text{O} \) (2). In complex 2, HQ\(^+\) is included in the cavity of \(p\)-sulfonatocalix[4]arene in a more horizontal manner than that in complex 1 (the \(\text{L}a\) axis of quinoline forms an angle of 13.5° with the plane defined by four bridging sulfurs). This is mainly owing to the larger cavity size of \(p\)-sulfonatocalix[4]arene as compared to \(p\)-sulfonatothiacalix[4]arene, which can simultaneously accommodate the portions of the pyridine ring and phenol ring. As shown in Figure 2a, not only the pyridine but also the phenol form the host–guest C–H\(\cdots\)π interactions with the aromatic cavity of \(p\)-sulfonatothiacalix[4]arene. In addition, there is an unconventional hydrogen bond formed to stabilize the complex (C49\(\cdots\)O5, 3.293 Å and 138.8°).

Figure 2. Views of complex 2 (a) inclusion structure, (b) dimer structure, (c) host molecule environment in the hydrophobic layer (d) extended structure. The broken lines represent the hydrogen bonds or π-stacking interactions between host and guest.

The same as \(p\)-sulfonatocalix[4]arene in complex 1, \(p\)-sulfonatocalix[4]arene in 2 also assumes the pinched-cone conformation with trans S\(\cdots\)S approaches of 8.394 and 12.094 Å as a result of guest inducing. The dihedral angles formed by the planes of two splaying aromatic rings and the plane defined by four phenolic oxygen atoms are 131.5°, 140.9° and those formed by two pinched rings are 108.7° and 108.0°.

In the further structure of 2, the included HQ\(^+\) guest interacts with another adjacent \(p\)-sulfonatothiacalix[4]arene by two strong hydrogen bonds (N3\(\cdots\)O8, 2.740 Å and 149.4°; O19\(\cdots\)O7, 1.888 Å and 175.5°). Consequently, a face-to-face dimer (host–guest 2:2) is formed as shown in Figure 2b. In addition, the dimer is “sealed” by two identical HQ\(^+\) counterions through two sets of hydrogen bonds. Each HQ\(^+\) counterion donates not only its NH group to an N–H\(\cdots\)O hydrogen bond (N1\(\cdots\)O16, 2.775 Å and 164.6°) to a sulfonate group of one \(p\)-sulfonatothiacalix[4]arene but also its OH group to an O–H\(\cdots\)O hydrogen bond.
(O17−O9, 2.625 Å and 171.2°) to a sulfonate group of the other p-sulfonatocalix[4]arene.

Differing much from the bilayer array in 1, complex 2 presents a relatively complicated extended structure. There are none of the π-stacking interactions between calixarenes detected. p-Sulfonatocalix[4]arenes just arrange themselves into a simple dimer in an up-down fashion via the diplex S···O van der Waals interactions (S2···O12, 3.275 Å) between bridging sulfur atoms and sulfonate oxygen atoms. Besides this, the other three aromatic walls of p-sulfonatocalix[4]arenes are surrounded by HQ⁺ cations as shown in Figure 2c. Therefore, when all the HQ⁺ cations are taken into account within the extended structure, the overall structure of complex 2 shows the corrugated bilayer arrangement (Figure 2d). There is no obvious ambit of hydrophobic and hydrophilic layers observed because the penetration of HQ⁺ cations into the calixarene layers destroys the regular array of p-sulfonatocalix[4]arenes to a great extent. HQ⁺ cations not only form π···π interactions (3.577−4.226 Å) with the exo aromatic rings of p-sulfonatocalix[4]arenes but also donate several hydrogen bonds (N2−O9, 2.911 Å and 117.04°; O20···O15, 2.697 Å and 174.2°; O21···O13, 2.854 Å and 160.9°) to sulfonate groups of p-sulfonatocalix[4]arenes to contribute to the formation of aggregation.

Structure of [HQ⁺]₂·[p-sulfonatocalix[4]arene]⁴⁺·1.5H₂O (3). Upon increasing the acidity of the mother liquor from pH ≈ 1 to 1 M HCl, the binding manner of p-sulfonatocalix[4]arene with HQ⁺ guest changes concomitantly. As shown in Figure 3a, HQ⁺ is included into the cavity of p-sulfonatocalix[4]arene with the portion of the phenol ring immersed in complex 3. Besides three C−H···π(C31−H31···ring of C7 to C12, 2.788 Å and 143.1°; C32−H32···ring of C13 to C18, 2.828 Å and 132.7°; C33−H33···ring of C19 to C24, 2.589 Å and 166.9°) and one weak π···π (ring of C1 to C6···ring of C28 to C33, 4.111 Å) interactions between phenol ring of HQ⁺ and aromatic rings of calixarene, there are additional two host−guest hydrogen bonds donated by sulfonate groups (conventional: O17···O8, 2.609 Å and 168.8°; nonconventional: C27···O14, 2.433 Å and 160.4°). As comparison with the binding geometry in complex 2, the HQ⁺ guest rotates an angle of 57.8° to enter into the cavity of calixarene in complex 3. The angle of binding manner from complexes 2 to 3 is just like our previous results of complexation of p-sulfonatocalix[4]arenes with 1,10-phenanthroline. Moreover, it also can be seen that the conformation of p-sulfonatocalix[4]arene is somewhat distorted. This may mainly be attributed to the strong hydrogen bond between the phenolic hydroxyl of HQ⁺ and the sulfonate oxygen atom (O17···O8) that draws the 4-hydroxybenzenesulfonate unit more vertical to the plane of bridging S atoms.

Somewhat similar to that in complex 2, the included complex of p-sulfonatocalix[4]arene with the HQ⁺ guest in 3 also forms a face-to-face dimer as shown in Figure 3b. The included HQ⁺ guest interacts with the sulfonate groups of the opposite p-sulfonatocalix[4]arene, forming two hydrogen bonds
can also be said that there is a "bis-molecular" capsule formed in complex \( \text{3} \). In the dimer of complex \( \text{3} \), it cannot be called a molecular capsule or even a slipped capsule. Over an edge of the other complex is a distinguishable difference between them. In the dimer of \( \text{3} \), the cavity of one \( \text{p-sulfonatothiacalix[4]arene} \) resides over an edge of the other \( \text{p-sulfonatothiacalix[4]arene} \), and so it cannot be called a molecular capsule or even a slipped capsule. In the dimer of complex \( \text{3} \), the two cavities of \( \text{p-sulfonatothiacalix[4]arene} \) face well each other, and then it can also be said that there is a “bis-molecular” capsule formed in complex \( \text{3} \), whose height is 15.4 Å (the length defined as the perpendicular distance between the top plane and the bottom plane of the four phenol oxygen atoms of one calixarene). This result further demonstrates that the pH value is a crucial factor for control and design of molecular capsules based on \( \text{p-sulfonatocalix[4]arenes} \). Differing from complex \( \text{2} \), complex \( \text{3} \) presents a regular bilayer extended structure with the thicknesses of hydrophobic and hydrophilic layers of 7.8 and 5.8 Å. Thus, the whole distance of one bilayer unit is 13.6 Å, which is a little narrower than the thickness of 14.0 Å formed by sole \( \text{p-sulfonatothiacalix[4]arene} \). However, the hydrophobic layer in complex \( \text{3} \) is wider than that in sole \( \text{p-sulfonatothiacalix[4]arene} \) (7.2 Å). Similar to that in complex \( \text{1} \), the extension of the hydrophobic layer may be attributed to the unconventional manner of constructing the calixarene layer. Three walls of every \( \text{p-sulfonatothiacalix[4]arene} \) abut three unidirectional host molecules and the fourth parallels one \( \text{HQ}^+ \) counterion, as shown in Figure 3c. Consequently, there are two \( \pi \cdots \pi \) interactions (ring of C1 to C6 \cdots ring of C1 to C6, 3.742 Å; ring of C19 to C24 \cdots ring of C19 to C24, 3.462 Å), one particular \( \text{S} \cdots \text{S} \) interactions (S1 \cdots S4, 3.568 Å) and one hydrogen bond (O3 \cdots O16, 2.987 Å and 132.28°) among calixarene themselves. Besides these, the HQ\(^+\) guests within the hydrophobic layers form \( \pi \cdots \pi \) interactions (3.578–3.932 Å) with aromatic rings of two alternative \( \text{p-sulfonatothiacalix[4]arenes} \). On the other hand, in despite of the large size of cation guests of HQ\(^+\), the thickness of the hydrophilic layer in complex \( \text{3} \) is narrower than that formed by sole \( \text{p-sulfonatothiacalix[4]arene} \). It can be said that the formation of a “bis-molecular” capsule enhances the compactness of the hydrophilic layers in complex \( \text{3} \).

**Structure of [AQ\(^+\)]\_1.25[p-sulfonatocalix[4]arene\(^4\)-+2.75H\(^-\)]·9H\(_2\)O (4).** Replacing the hydroxyquinoline by aminoquinoline as a guest, \( \text{p-sulfonatocalix[4]arene} \) displays a similar binding manner with it. As shown in Figure 4a, the AQ\(^+\) is slantways included in the cavity of \( \text{p-sulfonatocalix[4]arene} \) with a portion of pyridine ring immersed, forming a total of five host–guest interactions between aromatic rings of calixarene and pyridine of HQ\(^+\) (three C–H \cdots \pi \) interactions: C29–H29 \cdots ring of C1 to C6, 2.684 Å and 157.5°; C30–H30 \cdots ring of C13 to C18, 2.658 Å and 131.7°; C31–H31 \cdots ring of C15 to C20, 2.685 Å and 139.7°; one unconventional hydrogen bond: C33–O10, 3.343 Å and 155.2°; one \( \pi \cdots \pi \) interaction: the pyridine ring of the guest \cdots the ring of C22 to C27, 3.785 Å). The \( \text{La} \) axis of quinoline forms an angle of 45° with the plane defined by four bridging methylenes. As a result of being induced by the AQ\(^+\) guest, \( \text{p-sulfonatocalix[4]arene} \) adopts a pinched-cone conformation of \( C_{2v} \) symmetry with the characteristics of trans S \cdots S approaches of 11.862 and 8.860 Å and the dihedral angles between the planes of two splaying aromatic rings and the plane defined by four phenolic oxygen atoms are 132.8°, 139.6° and the two pinched rings are 109.2° and 117.1°, which is similar to those in complex \( \text{1} \).

On close examination of the further structure, there is one \( \pi \cdots \pi \) interaction (3.806 Å) between AQ\(^+\) included in the cavity of \( \text{p-sulfonatocalix[4]arene} \), which means a face-to-face dimer formed. Except that, however, there is no any other interaction or link between these two \( \text{p-sulfonatocalix[4]arene} \) molecules comprising the dimer, and they are apart from each other a little far (16.6 Å, the length defined as the perpendicular distance between the planes comprising the four phenol oxygen atoms of one calixarene). So it is not suitable to call the dimer a capsule. Upon crystal packing, complex \( \text{4} \) displays a typical bilayer structure with the thicknesses of hydrophobic and hydrophilic layers of 5.5 and 10.1 Å, respectively (Figure 4b). The thickness of hydrophilic layers is wider than that of single \( \text{p-sulfonatocalix[4]arene} \) (8.3 Å), which may be attributed to the \( \pi \)-stacking AQ\(^+\) cations included in the dimer. This pair of \( \pi \)-stacking AQ\(^+\) cations acts as a pillar that hold the \( \text{p-sulfonatocalix[4]arene} \) molecules further apart. On the other hand, the thickness of hydrophobic layer is similar to that of sole \( \text{p-sulfonatocalix[4]arene} \) (5.4 Å) and much thinner than those in complexes \( \text{1} \) and \( \text{3} \). Unlike the fact that each calix[4]arene is surrounded by three antiparallel ones and one HQ\(^+\) counterion in \( \text{1} \) and \( \text{3} \), each \( \text{p-sulfonatocalix[4]arene} \) is surrounded by other four antidirection ones with four indepen-
dent C–H⋯π interactions (2.991–3.608 Å), forming the most typical bilayer array.

Conclusion

In summary, complexes 1–4 obtained are closely discussed and compared to each other on both the manner of the host–guest binding and the extended structure. It is found that (1) p-sulfonatocalix[4]arene can accommodate an HQ+ guest with a more horizontal orientation than p-sulfonatocalix[4]arene owing to its wider cavity size; (2) p-sulfonatocalix[4]arenes form the dimerization of the “bis-molecular” capsule in complex 3, whereas they form only the slipped face-to-face dimer in complex 2; (3) AQ+ guest with the amino group replacement of the hydroxyl group is included in the cavity of p-sulfonatocalix[4]arene with a geometry similar to the HQ+ guest; (4) complexes 1, 3, and 4 all present the packing structure of a bilayer array with distinguishable hydrophobic and hydrophilic regions; however, their corresponding thicknesses are different on account of the different driving forces of aggregation; (5) complex 2 presents a more complicated extended structure than the others as a result of the penetration of three HQ+ counterions into calixarene layers. The observations demonstrate that by replacement of methylene bridges by sulfur atoms, p-sulfonatocalix[4]arene can form very distinguishable supramolecular architectures from p-sulfonatocalix[4]arene even though the same guests are employed, and further the pH value is also an important factor for the manipulation and design of supramolecular architectures based on sulfonatocalixarenes.

Acknowledgment. This work was supported by 973 Program (2006CB932900), NNSFC (20673061) and the Science and Technology Innovation Foundation of Nankai University, which are gratefully acknowledged.

Supporting Information Available: X-ray crystallographic data as CIF files. These materials are available free of charge via the Internet at http://pubs.acs.org.

References


Supporting Information Available: X-ray crystallographic data as CIF files. These materials are available free of charge via the Internet at http://pubs.acs.org.


(29) *SHELX97*; Sheldrick, G. M. University of Göttingen, Germany, 1997.


CG070607S