CRYSTAL GROWTH & DESIGN
2007
VOL. 7, NO. 12
2601–2608

Comparable Inclusion and Aggregation Structures of *p*-Sulfonatothiacalix[4]arene and *p*-Sulfonatocalix[4]arene upon Complexation with Quinoline Guests

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

ABSTRACT: Four supramolecular complexes of *p*-sulfonatocalix[4]arene and *p*-sulfonatothiacalix[4]arene with 8-hydroxyquinolinium (HQ^+) and 8-aminoquinolinium (AQ^+) guests were prepared, and their structures were determined by single-crystal X-ray diffraction as $[HQ^+]_{3.5}[p\text{-sulfonatocalix[4]arene}^{4-} + 0.5H^+]\cdot 13.5H_2O$ (**1**), $[HQ^+]_4[p\text{-sulfonatothiacalix[4]arene}^{4-}]\cdot 6.75H_2O$ (**2**), $[HQ^+]_{2.5}[p\text{-sulfonatothiacalix[4]arene}^{4-} + 1.5H^+]\cdot 7.75H_2O$ (**3**), and $[AQ^+]_{1.25}[p\text{-sulfonatocalix[4]arene}^{4-} + 2.75H^+]\cdot 9H_2O$ (**4**), respectively. The results obtained show that *p*-sulfonatothiacalix[4]arene can offer different inclusion structures with a HQ^+ guest from *p*-sulfonatocalix[4]arene, and the formation of a molecular capsule based on *p*-sulfonatothiacalix[4]arene and HQ^+ is pH-dependent. Furthermore, the aggregation structures of complexes **1**−**4** are comparatively discussed from the viewpoint of the manner of aggregation and driving forces.

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.[1c,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.[1a,8] However, these antiparallel assembly structures are not invariable. *p*-Sulfonatocalix[4]arenes 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 animo 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]arenes assemble themselves into the spectacular structures of spheroids and tubules[14] 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 arranges in 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 methylenes 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*-sulfonatothiacalix[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,25] 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

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10.1021/cg070607s CCC: $37.00
Published on Web 11/15/2007

Chart 1. Structure of Host Calixarene and the Axes of Quinoline Derivatives

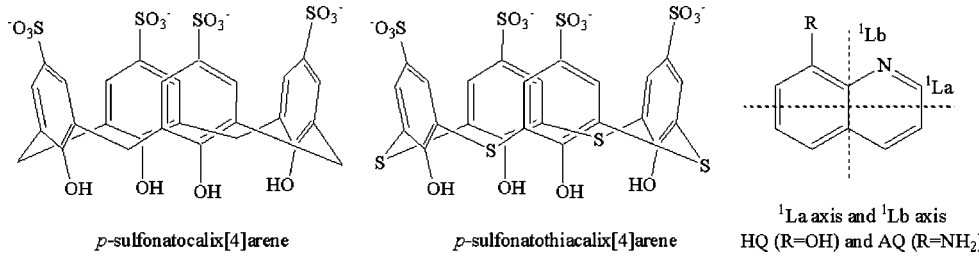

Table 1. Crystal Structure Data and Details of Structure Refinements for 1–4

	1	2	3	4
CCDC deposit no.	652296	652297	652298	652299
formula	$C_{59.5}H_{75.5}N_{3.5}O_{33}S_4$	$C_{60}H_{61.5}N_4O_{26.75}S_8$	$C_{46.5}H_{49}\ N_{2.5}O_{26.25}S_8$	$C_{40}H_{54}N_{2.5}O_{25}S_4$
fw	1495.97	1523.14	1319.36	1098.10
cryst syst	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	13.717(2)	14.1505(15)	13.946(2)	12.3509(18)
b, Å	14.226(2)	14.4629(18)	14.5569(18)	13.869(2)
c, Å	17.487(3)	19.925(3)	16.7522(13)	16.973(3)
α, deg	74.664(4)	78.034(9)	61.272(8)	69.059(2)
β, deg	89.778(5)	75.103(9)	72.327(11)	76.398(2)
γ, deg	84.475(5)	62.032(6)	83.847(12)	82.312(2)
V, Å^3	3274.7(9)	3462. 5(8)	2838.4(6)	2635.4(7)
Z	2	2	2	2
D_c, g/cm^3	1.517	1.464	1.544	1.384
μ, mm^{-1}	0.244	0.342	0.403	0.264
F(000)	1570	1583	1367	1151
cryst size, mm^3	0.12 × 0.16 × 0.24	0.32 × 0.38 × 0.40	0.30 × 32 × 0.36	0.20 × 0.24 × 0.30
θ range, deg	1.21−25.68	1.6−27.9	1.5−27.9	1.57−25.01
no. of collected /unique rflns	25073/12337 (R(int) = 0.0320)	26915/12162 (R(int) = 0.0410)	26689/13301 (R(int) = 0.0312)	12967/9071 (R(int) = 0.0281)
GOF	1.087	1.057	1.062	1.050
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0656 wR2 = 0.1844	R1 = 0.0894 wR2 = 0.2488	R1 = 0.0634 wR2 = 0.1895	R1 = 0.0913 wR2 = 0.2548
R1 = R indices (all data)	R1 = 0.0808 wR2 = 0.1986	R1 = 0.1103, wR2 = 0.2705	R1 = 0.0790 wR2 = 0.2044	R1 = 0.1506 wR2 = 0.3142

p-sulfonatocalix[4]arene and *p*-sulfonatothiacalix[4]arene but also the influences of substituent groups (OH and NH_2) of quinoline guests and acidities of mother solutions are compared and discussed.

Experimental Section

8-Aminoquinoline (AQ) and 8-hydroxyquinoline (HQ) are commercially available and were used without further purification. *p*-Sulfonatothiacalix[4]arene tetrasodium (Na^+_4(*p*-sulfonatothiacalix[4]arene^{4-})) and *p*-sulfonatocalix[4]arene tetrasodium (Na^+_4(*p*-sulfonatocalix[4]arene^{4-})) were prepared according to literature methods.[26] In pH ≈ 1 or 1 N HCl solution, both AQ and HQ exist in the protonated forms (AQ^+ and HQ^+).[27] Elemental analyses were performed on a Perkin-Elmer 2400C instrument.

Synthesis of $[HQ^+]_{3.5}$[*p*-sulfonatocalix[4]arene^{4-} + 0.5H$^+$]·13.5H$_2$O (1). HQ (36.1 mg, 0.249 mmol) and Na^+_4(*p*-sulfonatocalix[4]arene^{4-}) (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. calcd for $C_{59.5}H_{75.5}N_{3.5}O_{33}S_4$ (M_r = 1495.97): C, 47.77; H, 5.09; N, 3.28; S, 8.57; found: C, 48.55; H, 5.02; N, 3.31; S, 8.62.

Synthesis of $[HQ^+]_4$[*p*-sulfonatothiacalix[4]arene^{4-}]·6.75H$_2$O (2). HQ (33.1 mg, 0.228 mmol) and Na_4^+(*p*-sulfonatothiacalix[4]arene^{4-}) (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. calcd for $C_{60}H_{61.5}N_4O_{26.75}S_8$ (M_r = 1523.14): C, 47.31; H, 4.07; N, 3.68; S, 16.84; found: C, 48.10; H, 4.01; N, 3.72; S, 17.16.

Synthesis of $[HQ^+]_{2.5}$[*p*-sulfonatothiacalix[4]arene^{4-} + 1.5H$^+$]·7.75H$_2$O (3). HQ (33.1 mg, 0.228 mmol) and Na^+_4(*p*-sulfonatothiacalix[4]arene^{4-}) (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. calcd for $C_{46.5}H_{49}N_{2.5}O_{26.25}S_8$ (M_r = 1319.36): C, 42.33; H, 3.74; N, 2.65; S, 19.44; found: C, 43.22; H, 3.34; N, 2.80; S, 19.98.

Synthesis of $[AQ^+]_{1.25}$bp[*p*-sulfonatocalix[4]arene^{4-} + 2.75H$^+$]·9H$_2$O (4). AQ (35.9 mg, 0.249 mmol) and Na^+_4(*p*-sulfonatocalix[4]arene^{4-}) (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 suited for X-ray analysis after 14 days. Anal. Calcd for $C_{40}H_{54}N_{2.5}O_{25}S_4$ (M_r = 1098.10): C, 43.75; H, 4.96; N, 3.19; S, 11.68; found: C, 44.58; H, 4.80; N, 3.26; S, 11.90.

X-ray Crystal Structure Analysis. The X-ray intensity data for **1**−**3** 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 the Crystalclear program.[28] The X-ray intensity data for **4** were collected on a standard Siemens SMART CCD area detector system equipped with a normal-focus molybdenum-target X-ray tube (λ = 0.71073 Å) operated at 2.0 kW (50 kV, 40 mA) and a graphite monochromator at T = 293(2) K. The structures were solved by using direct methods and refined, employing full-matrix least-squares on F2 (Siemens, SHELXTL-97).[29] In view of the poor quality of the crystals obtained, some data are not good. Summaries of crystal data and structure refinements are given in Table 1. CCDC-652296, 652297, 652298, and 652299 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.

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 $P\bar{1}$. The asymmetric units contain following: 1 crystallographically distinct *p*-sulfonatocalix[4]arene, 3.5 HQ^+, and 13.5 water molecules for **1**; 1 *p*-sulfonatothiacalix[4]arene, 4 HQ^+, and 6.75 water molecules for **2**; 1 *p*-sulfonatothiacalix[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 $[HQ^+]_{3.5}$[*p*-sulfonatocalix[4]arene^{4-} + 0.5H^+]·13.5H_2O (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 ^{1}La 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 (C_{2v} 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.[31]) 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 hydrophobic 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.

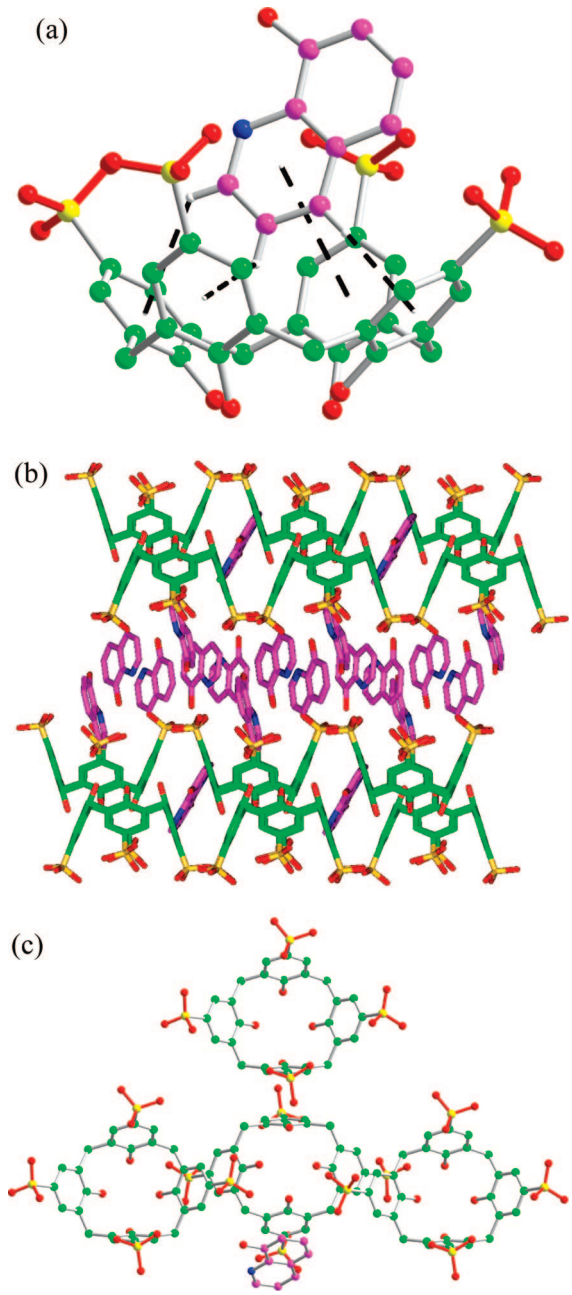

Figure 1. Views of complex **1** (a) inclusion structure, (b) packing structure, (c) host molecule environment in a hydrophobic layer. The broken lines represent the intermolecular hydrogen bonds or π-stacking interactions between host and guest.

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 hydrophobic 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.

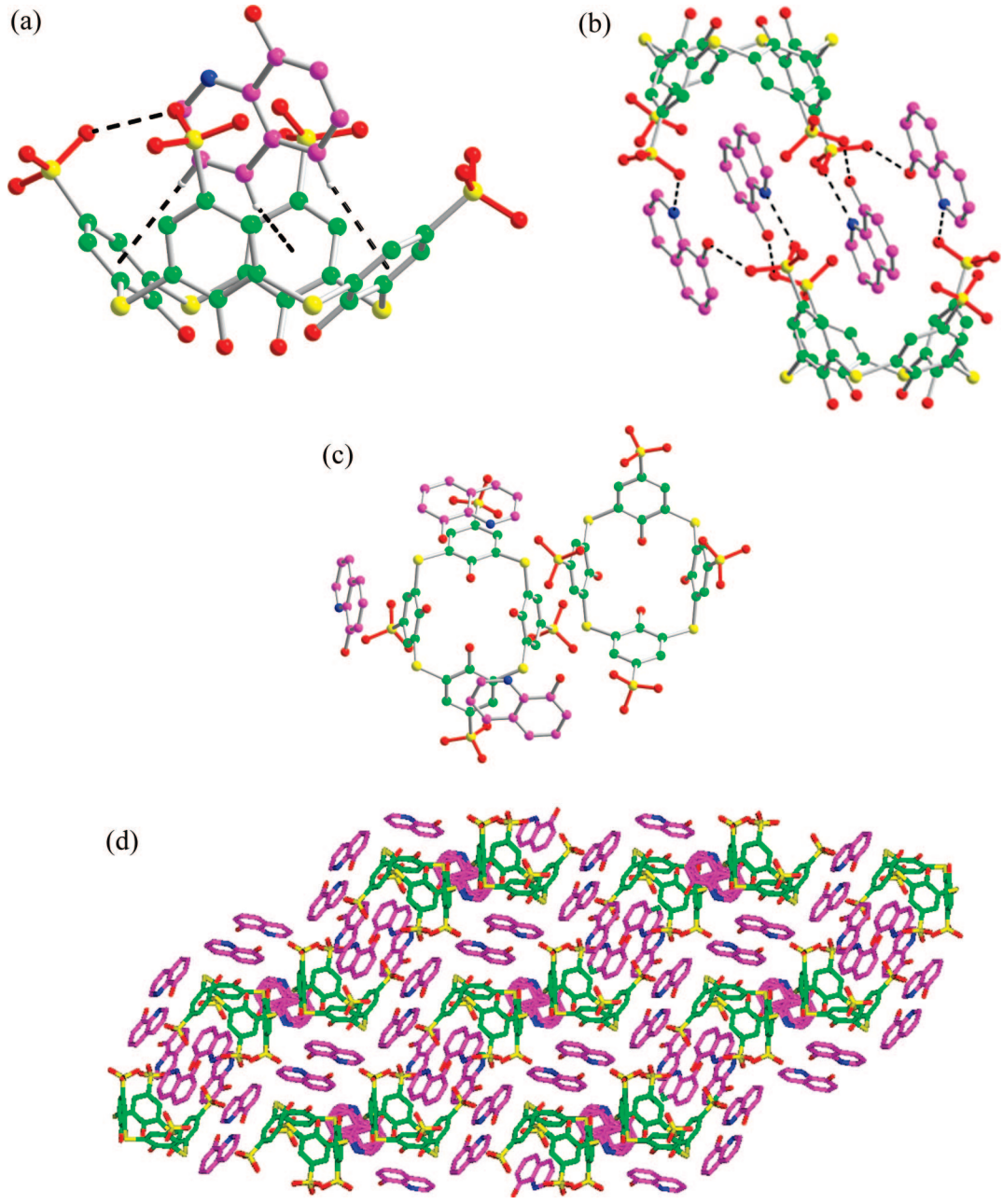

Figure 2. Views of complex **2** (a) inclusion structure, (b) dimer structure, (c) host molecule environment in the hydrophobic layer (d) extended structure. The broken lines represent the hydrogen bonds or π-stacking interactions between host and guest.

Structure of $[HQ^+]_4$[*p*-sulfonatothiacalix[4]arene^{4-}]·6.75H_2O (2). In complex **2**, HQ^+ is included in the cavity of *p*-sulfonatothiacalix[4]arene in a more horizontal manner than that in complex **1** (the ^{1}La 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*-sulfonatothiacalix[4]arene as compared to *p*-sulfonatocalix[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···π interactions with the aromatic cavity of *p*-sulfonatothiacalix[4]arene (C50−H50···ring of C1 to C6, 2.687 Å and 149.9°; C46−H46···ring of C13 to C18, 2.696 Å and 162.3°; C51−H51···ring of C19 to C24, 2.996 Å and 127.7°). In addition, there is an unconventional hydrogen bond formed to stabilize the complex (C49···O5, 3.293 Å and 138.8°). The same as *p*-sulfonatocalix[4]arene in complex **1**, *p*-sulfonatothiacalix[4]arene in **2** also assumes the pinched-cone conformation with trans S···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−O8, 2.740 Å and 149.4°; O19−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···O hydrogen bond (N1−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···O hydrogen bond

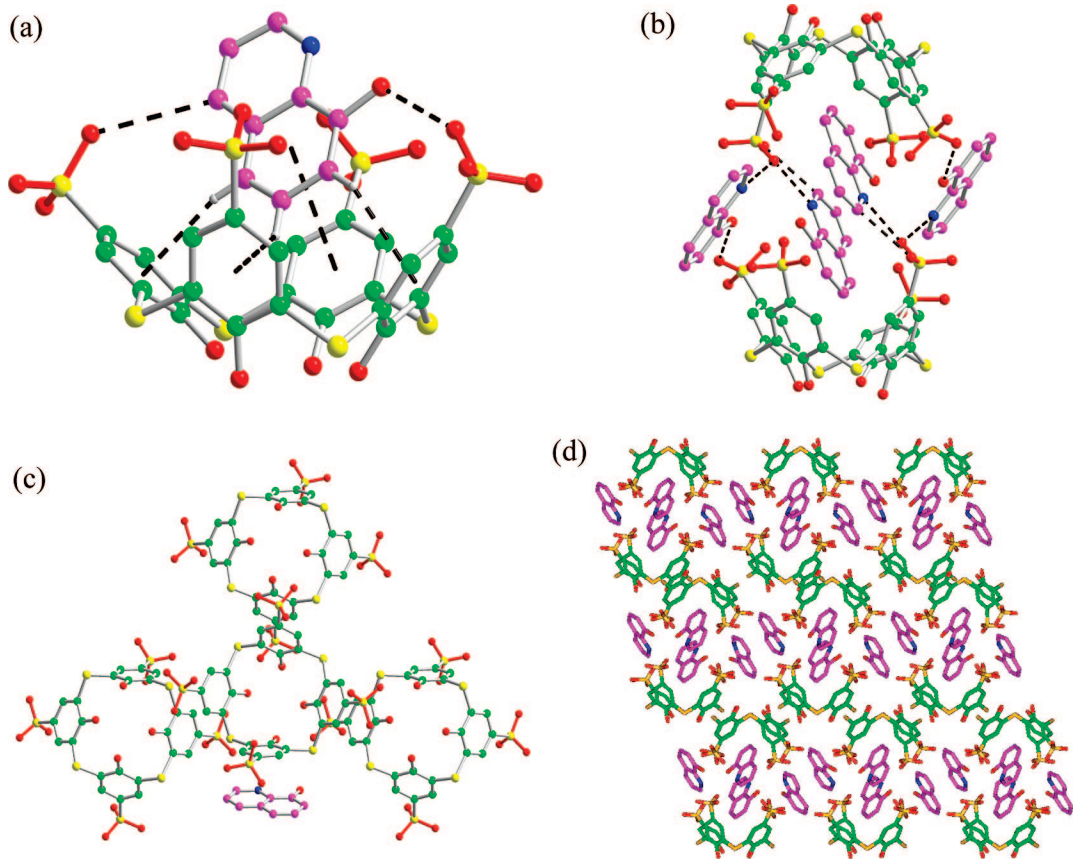

Figure 3. Views of complex **3** (a) inclusion structure, (b) capsule structure, (c) host molecule environment in the hydrophobic layer (d) arrangement of the capsules. The broken lines represent the hydrogen bonds or π-stacking interactions between host and guest.

(O17−O9, 2.625 Å and 171.2°) to a sulfonate group of the other *p*-sulfonatothiacalix[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*-Sulfonatothiacalix[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*-sulfonatothiacalix[4]arene are surrounded by HQ^+ counterions as shown in Figure 2c. Therefore, when all the HQ^+ counterions 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^+ counterions into the calixarene layers destroys the regular array of *p*-sulfonatothiacalix[4]arenes to a great extent. HQ^+ counterions not only form $\pi\cdots\pi$ interactions (3.577−4.226 Å) with the exo aromatic rings of *p*-sulfonatothiacalix[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*-sulfonatothiacalix[4]arenes to contribute to the formation of aggregation.

Structure of $[HQ^+]_{2.5}$[*p*-sulfonatothiacalix[4]arene^{4-}+ 1.5H$^+$]·7.75H$_2$O (3). Upon increasing the acidity of the mother liquor from pH ≈ 1 to 1 M HCl, the binding manner of *p*-sulfonatothiacalix[4]arene with HQ^+ guest changes concomitantly. As shown in Figure 3a, HQ^+ is included into the cavity of *p*-sulfonatothiacalix[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, 2.828Å and 132.7°; C33−H33···ring of C19 to C24, 2.589 Å and 166.9°) and one weak $\pi\cdots\pi$ (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 change of binding manner from complexes **2** to **3** is just like our previous results of complexation of *p*-sulfonatocalixarenes with 1,10-phenanthroline.[32] Moreover, it also can be seen that the conformation of *p*-sulfonatothiacalix[4]arene is distorted to a more asymmetric fashion by complexation with an HQ^+ guest under 1 M HCl conditions. The dihedral angles formed by the two pinched aromatic rings and the plane defined by four phenolic oxygen atoms are 126.5°, 105.5°, while those formed by two splaying aromatic rings are 145.3°, 119.5°, and the trans S···S approaches are 11.666 and 9.615 Å. In comparison with the conformation of *p*-sulfonatothiacalix[4]arene in **2**, the S···S approach between the splaying rings in **3** is somewhat shorter. 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*-sulfonatothiacalix[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*-sulfonatothiacalix[4]arene, forming two hydrogen bonds

(N1···O11, 2.818 Å and 162.1°; C25···O12, 3.118 Å and 134.9°). As a result, the host–guest 2:2 dimer is presented, which is further "sealed" by two identical HQ^+ counterions through two sets of hydrogen bonds. The sulfonate groups of two opposite calixarenes are linked together by two HQ^+ counterions, in which each HQ^+ counterion donates not only its NH group to N−H···O hydrogen bond (N2···O11, 2.748 and 159.1 Å) to the sulfonate group of one *p*-sulfonatothiacalix[4]arene but also its OH group to the O−H···O hydrogen bond (O18···O7, 2.612 Å and 178.1°) to the sulfonate group of the other *p*-sulfonatothiacalix[4]arene. However, examining closely the two dimers in complexes **2** and **3**, it can be found that there is a distinguishable difference between them. In the dimer of complex **2**, the cavity of one *p*-sulfonatothiacalix[4]arene resides over an edge of the other *p*-sulfonatothiacalix[4]arene, and so it cannot be called a molecular capsule or even a slipped capsule. In the dimer of complex **3**, the two cavities of *p*-sulfonatothiacalix[4]arenes face well each other, and then it can also be said that there is a "bis-molecular" capsule formed in complex **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 *p*-sulfonatocalixarenes.[12c] Differing from complex **2**, complex **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 *p*-sulfonatothiacalix[4]arenes.[21] However, the hydrophobic layer in complex **3** is wider than that in sole *p*-sulfonatothiacalix[4]arenes (7.2 Å). Similar to that in complex **1**, the extension of the hydrophobic layer may be attributed to the unconventional manner of constructing the calixarene layer. Three walls of every *p*-sulfonatothiacalix[4]arene abut three antidirectional host molecules and the fourth parallels one HQ^+ counterion, as shown in Figure 3c. Consequently, there are two $\pi\cdots\pi$ interactions (ring of C1 to C6···ring of C1 to C6, 3.742 Å; ring of C19 to C24···ring of C19 to C24, 3.462 Å), one particular S···S interactions (S1···S4, 3.568 Å) and one hydrogen bond (O3···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 *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 **3** is narrower than that formed by sole *p*-sulfonatothiacalix[4]arenes. It can be said that the formation of a "bis-molecular" capsule enhances the compactness of the hydrophilic layers in complex **3**.

Structureof$[AQ^+]_{1.25}$[*p*-sulfonatocalix[4]arene^{4-}+2.75H^+]·9H_2O (4). Replacing the hydroxylquinoline by aminoquinoline as a guest, *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 *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···π interactions: C29−H29··· ring of C1 to C6, 2.684 Å and 157.5°; C30−H30···ring of C13 to C18, 2.658Å and 131.7°; C31−H31···ring of C15 to C20, 2.683 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···the ring of C22 to C27, 3.785 Å). The ^{1}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, *p*-sulfonatocalix[4]arene adopts a pinched-cone conformation of C_{2v} symmetry with the characteristics of trans S···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 **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 *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 *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 **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 *p*-sulfonatocalix[4]arene (8.3 Å), which may be attributed to the π-stacking AQ^+ cations included in the dimer. This pair of π-stacking AQ^+ cations acts as a pillar that hold the *p*-sulfonatocalix[4]arene molecules further apart. On the other hand, the thickness of hydrophobic layer is similar to that of sole *p*-sulfonatocalix[4]arenes (5.4 Å) and much thinner than those in complexes **1** and **3**. Unlike the fact that each calix[4]arene is surrounded by three antiparallel ones and one HQ^+ counterion in **1** and **3**, each *p*-sulfonatocalix[4]arene is surrounded by other four antidirection ones with four indepen-

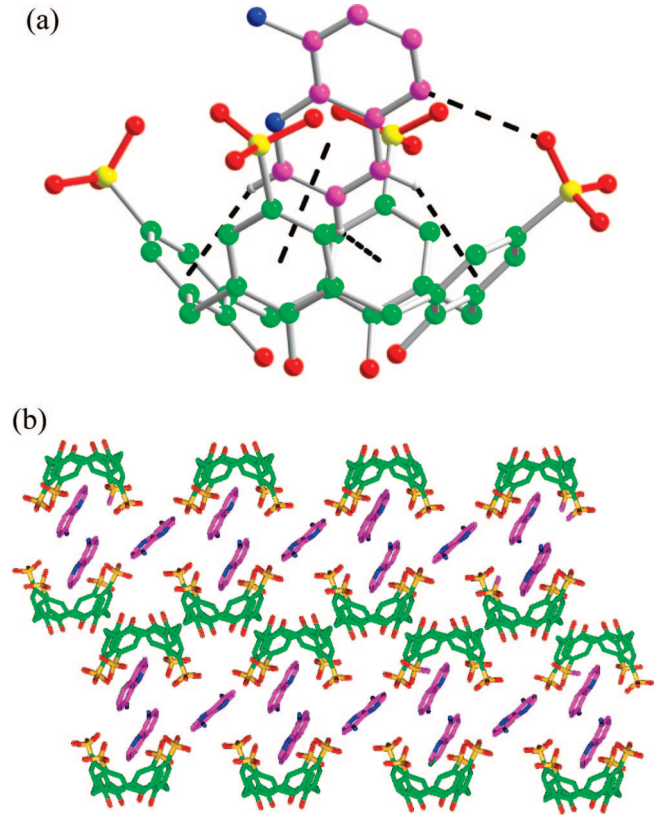

Figure 4. Views of complex **4** (a) inclusion structure, (b) bilayer structure arrangement. The broken lines represent the hydrogen bonds or π-stacking interactions between host and guest.

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*-sulfonatothiacalix[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*-sulfonatothiacalix[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*-sulfonatothiacalix[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.

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CG070607S