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Diverse Conformation and Extended Structure of *p*-Sulfonatothiacalix[4]arene Manipulated by Guest Molecules

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ABSTRACT: Three crystalline complexes were prepared by the inclusion complexation of *p*-sulfonatothiacalix[4]arene with [Cu(2-DPD)$_2^{2+}$] (**2**; 2-DPD represents 2,2′-dipyridine), [Cu(Phen)$_2^{2+}$] (**4**; Phen represents 1,10-phenanthroline), and [Co(Phen)$_3^{2+}$] (**5**), respectively. These crystal structures are comparable to those reported *p*-sulfonatothiacalix[4]arene complexes with 2-DPD (**1**), [Ni(2-DPD)$_3^{2+}$] (**3**), and 4,4′-dipyridine (4-DPD) (**6**), indicating that *p*-sulfonatothiacalix[4]arene in **2**, **4**, and **5** is cleft to a pinched cone (C_{2v}) to different extents upon cocomplexation with metal 2-DPD (or Phen) complexes, while *p*-sulfonatothiacalix[4]arene in **1** maintains the conventional cone shape of C_{4v} symmetry with shallow inclusion of 2-DPD. Particularly, *p*-sulfonatothiacalix[4]-arene assumes the partial-cone conformation in **3** and the 1,2-alternate conformer in **6**, respectively. Furthermore, the assembly behavior of *p*-sulfonatothiacalix[4]arene is influenced dramatically by the presence of various guests, such as bilayer arrangements for **1** and **2**, corrugated bilayers for **4** and **5**, and even water-filled channels for **3** and hydrogen-bonded polymers for **6**.

Introduction

Calixarenes have received considerable attention since the report of tractable synthetic routes to the parent macrocycles[1] and have been applied in diverse areas such as catalysis, enzyme mimics, host−guest chemistry, selective ion transport, and sensors due to their complex abilities, conformational flexibility, and reactivity.[2] In this field, the supramolecular chemistry of water-soluble calixarenes has been, and continues to be, widely investigated because of the diversity of such molecules in forming inclusion or coordination complexes in both solution and the solid state.[3]

Thiacalix[4]arene tetrasulfonates,[4] a new family of water-soluble calixarenes, possess characteristics of shape and structure apparently homologous with those of *p*-sulfonatocalix[4]arene. However, many studies have revealed that thiacalix[4]arenes should be regarded as a unique molecular framework for the second-generation calixarene chemistry, rather than a simple substitute for conventional calixarenes, because replacement of the methylene linkages of calix[4]arenes by sulfide provides various intrinsic characteristics of thiacalix[4]arenes, which cannot be obtained by calix[4]arenes.[5,6] Therefore, *p*-sulfonatothiacalix[4]arene shows much different inclusion behavior toward some organic molecules and metal ions in solution as compared with *p*-sulfonatocalix[4]arene.[7,8] Inspired by such inherent characteristics (wider cavity, lower electron density, more flexibility, and so on), *p*-sulfonatothiacalix[4]arene can be assumed to be a potential supramolecular building block in addition to *p*-sulfonatocalix[4]arene species to construct significantly supramolecular assemblies in the presence of suitable guest molecules.

On the other hand, calixarenes and their derivatives are conformationally mobile molecules. Their conformations depend on hydrogen bonding, steric and electrostatic forces, guest complexation, and a lesser degree of solvent effects.[9,10] In the same way, *p*-sulfonatothiacalix[4]arene can adjust its own cavity to a different extent to accommodate guest molecules according to their various size/shape, and *p*-sulfonatothiacalix[4]arene may present a spectacular extended structure of complexes. It also can be said that the guest-induced conformation of calixarene should be proposed as one of the crucial factors in constructing the highly complex supramolecular architectures. In this area, Atwood et al. have paid much attention to the *p*-sulfonatocalix-[4]arene series.[11] We are more interested in *p*-sulfonatothiacalix-[4]arene's flexible framework as compared with that of *p*-sulfonatocalix[4]arene. *p*-Sulfonatothiacalix[4]arene possesses theoretically four classical conformations designated as the cone, partial cone, 1,3-alternate, and 1,2-alternate. In general, *p*-sulfonatothiacalix[4]arene prefers a cone conformation in the solid state stabilized by a circular array of hydrogen bonds between the OH groups and is arranged in an up−down fashion to form a claylike bilayer with the hydrophobic midsections of adjacent molecules mutually aligned and engaged in intermolecular π-stacking interactions[12] resembling the analogue of well-known *p*-sulfonatocalix[4]arene, except for the unique case of *p*-sulfonatothiacalix[4]arene in the 1,2-alternate conformation stabilized by 1,4-dioxane.[7c] Just recently, Hong et al. reported guest-induced molecular capsules based on cone-shaped *p*-sulfonatothiacalix[4]arene, which likewise has a traditional extended structure of a bilayer array.[13] Despite the scattered reports of the individual complexation of *p*-sulfonatothiacalix-[4]arene with guests (both organic molecules and metal ions),[12,13] including those from our groups,[8b,14,15] a systematic investigation of the binding manner, conformation, and aggregation of *p*-sulfonatothiacalix[4]arene with appropriate guests has not previously been undertaken. Therefore, to obtain a novel solid-state conformation of *p*-sulfonatothiacalix[4]arene and further construct a spectacular supramolecular assembly, most of our endeavors have been directed at choosing different guest molecules that can be suitably complexed with *p*-sulfonato-thiacalix[4]arene. It is our particular interest to investigate how and to what extent the gradual difference between guest structures affects the inclusion modes, conformation features, and assembly behavior of *p*-sulfonatothiacalix[4]arene complexes in the solid state.

In the present study, we prepared three supramolecular complexes of *p*-sulfonatothiacalix[4]arene with [Cu(2-DPD)$_2^{2+}$] (**2**; 2-DPD represents 2,2′-dipyridine), [Cu(Phen)$_2^{2+}$] (**4**; Phen represents 1,10-phenanthroline), and [Co(Phen)$_3^{2+}$] (**5**) by

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Table 1. Crystal Structure Data and Details of Structure Refinements for 2, 4, and 5

	2	4	5
CCDC deposit no.	CCDC-294215	CCDC-294216	CCDC-294217
formula	$C_{64}H_{59}Cu_2N_8O_{23.50}S_8$	$C_{72}H_{58}Cu_2N_8O_{23}S_8$	$C_{60}H_{52}CoN_6O_{23}S_8$
fw	1699.75	1786.81	1540.51
cryst syst	monoclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	*Pbca*
a, Å	16.464(7)	14.435(6)	19.576(5)
b, Å	14.907(6)	14.994(6)	21.306(5)
c, Å	31.124(1)	18.939(8)	29.998(7)
α, deg	90	100.004(8)	90
β, deg	105.050(9)	94.554(7)	90
γ, deg	90	108.504(7)	90
V, Å^3	7377(5)	3788(3)	12 512(5)
Z	4	2	8
D_c, g/cm^3	1.530	1.559	1.633
μ, mm^{-1}	0.884	0.864	0.630
F(000)	3492	1832	6328
cryst size, mm^3	0.30 × 0.28 × 0.20	0.24 × 0.18 × 0.16	0.35 × 0.30 × 0.25
θ range, deg	1.87−25.09	1.10−25.01	1.36−25.01
no. of collected/unique rflns	44 406/12 997 (R(int) = 0.0271)	19 683/13 281 (R(int) = 0.0391)	61 964/11 026 (R(int) = 0.0741)
GOF	1.087	1.107	1.136
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0758, wR2 = 0.2164	R1 = 0.0784, wR2 = 0.2013	R1 = 0.0658, wR2 = 0.1533
R indices (all data)	R1 = 0.0852, wR2 = 0.2262	R1 = 0.1692, wR2 = 0.2550	R1 = 0.1307, wR2 = 0.2156

hydrothermal synthesis. Comparison of the crystal structures of these supramolecular complexes with those reported for the *p*-sulfonatothiacalix[4]arene complexes with 2-DPD (**1**),[8b] [Ni(2-DPD)$_3^{2+}$] (**3**),[15] and 4,4′-dipyridine (4-DPD) (**6**)[8b] will serve to establish the cross-link between the structure of supramolecular aggregation and the size/shape of guests and may further contribute to the prediction of supramolecular structures of a wide variety of *p*-sulfonatothiacalix[4]arene complexes.

Experimental Section

2,2′-Dipyridine (2-DPD) and 1,10-phenanthroline (Phen) are commercially available and were used without further purification. Metal perchlorate salts ($Cu(ClO_4)_2\cdot 6H_2O$, $Ni(ClO_4)_2\cdot 6H_2O$, $Co(ClO_4)_2\cdot 6H_2O$) were prepared utilizing their oxides or carbonic salts with perchlorate acid. *p*-Sulfonatothiacalix[4]arene tetrasodium (Na^+_4(*p*-sulfonatothiacalix[4]arene^{4-}))[4] was prepared according to the procedures described previously. Elemental analyses were performed on a Perkin-Elmer 2400C instrument.

The synthesis of [2-DPD$^+$]$_2$[2-DPD^{2+}]$_{0.5}$[*p*-sulfonatothiacalix[4]arene^{4-}+H$^+$]·4.5H$_2$O (**1**), [Ni(2-DPD)$_3^{2+}$]$_3$[*p*-sulfonatothiacalix[4]arene^{4-}][Cl$^-$]$_2$·5.5H$_2$O (**3**), and [4-DPD^{2+}]$_2$[*p*-sulfonatothiacalix[4]arene^{4-}]·2H$_2$O (**6**) have been reported in our previous work.[8b,15] Crystals of [Cu(2-DPD)$_2^{2+}$·H$_2$O][Cu(2-DPD)$_2^{2+}$][*p*-sulfonatothiacalix[4]arene^{4-}]·6.5H$_2$O (**2**), [Cu(Phen)$_2^{2+}$][Cu(Phen)$_2^{2+}$·H$_2$O][*p*-sulfonatothiacalix[4]arene^{4-}]·5.5H$_2$O (**4**), and [Co(Phen)$_3^{2+}$][*p*-sulfonatothiacalix[4]arene^{4-}+2H$^+$]·7H$_2$O (**5**) were synthesized by hydrothermal synthesis. The mixture was suspended in a Teflon-lined stainless steel bomb. After the bomb was sealed, the system was heated at 120 °C under hydrothermal conditions for 2 days and then cooled gradually to room temperature at a rate of 2 °C/h. Crystalline solids suitable for X-ray crystallography were obtained.

Preparation of 2 (Blue). $Cu(ClO_4)_2\cdot 6H_2O$ (40.5 mg, 0.11 mmol), 2-DPD (51.5 mg, 0.33 mmol), and *p*-sulfonatothiacalix[4]arene (50.0 mg, 0.055 mmol) were suspended in 6 mL of water (pH ∼1 adjusted by HCl). Anal. Calcd for $C_{64}H_{59}Cu_2N_8O_{23.50}S_8$ (M_r = 1699.8): C, 45.22; H, 3.50; N, 6.59; S, 15.09. Found: C, 45.49; H, 3.42; N, 6.63; S, 15.28.

Preparation of 4 (Blue). $Cu(ClO_4)_2\cdot 6H_2O$ (40.8 mg, 0.11 mmol), Phen (65.3 mg, 0.33 mmol), and *p*-sulfonatothiacalix[4]arene (50.0 mg, 0.055 mmol) were suspended in 8 mL of water (pH ∼1 adjusted by HCl). Anal. Calcd for $C_{72}H_{58}Cu_2N_8O_{23}S_8$ (M = 1786.8): C, 48.40; H, 3.27; N, 6.27; S, 14.35. Found: C, 48.92; H, 3.14; N, 6.42; S, 14.51.

Preparation of 5 (Orange). $Co(ClO_4)_2\cdot 6H_2O$ (40.3 mg, 0.11 mmol), Phen (65.3 mg, 0.33 mmol), and *p*-sulfonatothiacalix[4]arene (100.0 mg, 0.11 mmol) were suspended in 1 M HCl (10 mL). Anal. Calcd for $C_{60}H_{52}CoN_6O_{23}S_8$ (M_r = 1540.5): C, 46.78; H, 3.40; N, 5.46; S, 16.65. Found: C, 47.07; H, 3.25; N, 5.54; S, 16.86.

X-ray Crystal Structure Analysis. The X-ray intensity data for **2**, **4**, and **5** were collected on a standard Siemens SMART CCD area detector system equipped with a normal-focus molybdenum-target X-ray tube (λ = 0.710 73 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 F^2 (Siemens, SHELXTL-97). Summaries of crystal data and refinements are given in Table 1. CCDC-294215 (**2**), 294216 (**4**), and 294217 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax (+44) 1223-336-033 or email deposit@ccdc.cam.uk). Some data are not good, due to the poor quality of the crystals obtained. One sulfonate group of *p*-sulfonatothiacalix[4]arene in **2** is disordered and refined in two positions with equal occupancies. To satisfy the charge balance, *p*-sulfonatothiacalix[4]arene in **5** should possess two 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.[16]

Results and Discussion

During our ongoing investigation of the inclusion phenomena and assembly behavior of *p*-sulfonatothiacalix[4]arene, six complexes were prepared in their monocrystalline forms via the method of hydrothermal synthesis or solvent volatilization. Complex **1** was prepared by slow volatilization of the solvent, and the other five complexes were prepared by hydrothermal synthesis for their poor water solubility. Their molecular structures have been determined by single-crystal X-ray diffraction analysis. Complexes **1**−**6** crystalline in the triclinic space group $P\bar{1}$, monoclinic space group $P\bar{1}$, triclinic space group $P\bar{1}$, triclinic space group $P\bar{1}$, orthorhombic space group *Pbca*, and triclinic space group $P\bar{1}$, respectively. The asymmetric units contain the following: 1 crystallographically distinct *p*-sulfonatothiacalix[4]arene, 2.5 2-DPD, and 4.5 water molecules for **1**; 1 *p*-sulfonatothiacalix[4]arene, 2 [Cu(2-DPD)$_2^{2+}$], and 7.5 water molecules for **2**; 1 *p*-sulfonatothiacalix[4]arene, 3 [Ni(2-DPD)$_3^{2+}$], 2 Cl$^-$, and 5.5 water molecules for **3**; 1 *p*-sulfonatothiacalix[4]arene, 2 [Cu(Phen)$_2^{2+}$], and 6.5 water molecules for **4**; 1 *p*-sulfonatothiacalix[4]arene (two of its sulfonate groups should be protonated), 1 [Co(Phen)$_3^{2+}$], and 7 water molecules for **5**; 1 *p*-sulfonatothiacalix[4]arene, 2 4-DPD, and 2 water molecules for **6**. Among these crystals, some sulfonate groups of *p*-sulfonatothiacalix[4]arene and several water molecules are disordered at two or more positions. On close examination of these six complexes, three of the four

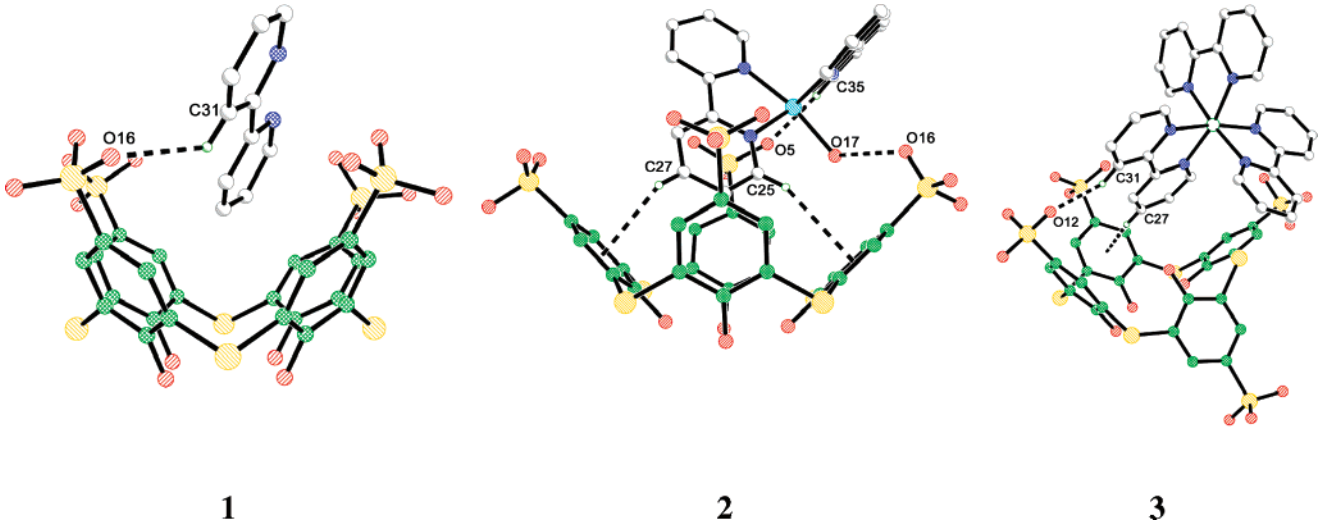

Figure 1. View of complexes **1**−**3**. The other guests, water molecules, and hydrogen atoms are omitted for clarity. The broken lines represent the intermolecular hydrogen bonds or the C−H···π interactions between host and guest.

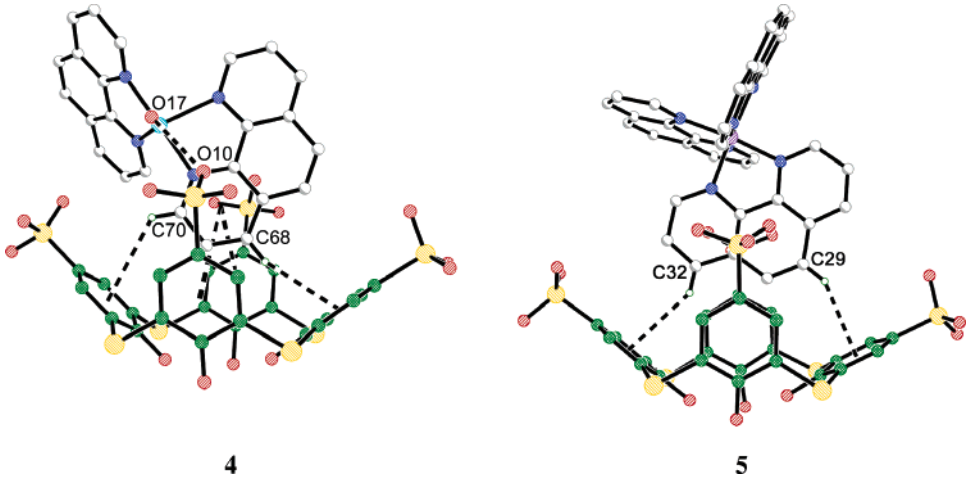

Figure 2. View of complexes **4** and **5**. The other guests, water molecules, and hydrogen atoms are omitted for clarity. The broken lines represent the intermolecular hydrogen bonds or the C−H···π interactions between host and guest.

classic conformers of *p*-sulfonatothiacalix[4]arene, cone (both C_{4v} and C_{2v} symmetry), partial cone, and 1,2-alternate, were presented by adjusting the different size/shape of guests, respectively. Furthermore, the extended structures of *p*-sulfonatothiacalix[4]arene complexes were also distorted to different extents. The results will now be discussed in detail.

Conformation of *p*-Sulfonatothiacalix[4]arene. The complex structures of 2-DPD guest species (**1**−**3**) are shown in Figure 1. For each unit, only one guest molecule is embraced into the cavity of *p*-sulfonatothiacalix[4]arene and the other guests are restricted in the crystal lattice as counterions, which are not shown for clarity. As can be seen from Figure 1, 2-DPD in **1** penetrates slantwise into the cavity of the host, and *p*-sulfonatothiacalix[4]arene maintains the original form of C_{4v} symmetry with hardly any disturbance (the S···S approaches of trans sulfonate groups are nearly equidistant, 10.726 and 11.152 Å).[8b] Further, the inclusion complexation of *p*-sulfonatothiacalix[4]arene with metal 2-DPD coordinates was performed, since the particular three-dimensional complex structure may provide unanticipated cocomplexes with *p*-sulfonatothiacalix[4]arene as compared with the planar 2-DPD ligand. The resultant cocomplex **2** of *p*-sulfonatothiacalix[4]-arene with a 1:2 ratio of Cu to 2-DPD cation shows that there are two environments for $[Cu(2\text{-}DPD)_2^{2+}]$ cations: one is located in the cavity of *p*-sulfonatothiacalix[4]arene through second-sphere coordination,[17] while the other is complexed in the outer sphere by one SO_3^- of *p*-sulfonatothiacalix[4]arene. Figure 1 shows the inner binding manner of $[Cu(2\text{-}DPD)_2^{2+}]$ with *p*-sulfonatothiacalix[4]arene. Different types of noncovalent interactions between $[Cu(2\text{-}DPD)_2^{2+}]$ and *p*-sulfonatothiacalix-[4]arene are observed, including two C−H···π interactions (C25−H25···ring of C19−C24, 3.153 Å and 149.9°; C27−H27···ring of C7−C12, 2.788 Å and 131.8°), one hydrogen bond (O17−O16, 2.730 Å), and one nonconventional hydrogen bond (C35−O5, 3.179 Å), which indicates the rather strong complex stability. As a result, *p*-sulfonatothiacalix[4]arene in **2** is pinched to a cleft-shaped C_{2v} form in order to accommodate compatibly the $[Cu(2\text{-}DPD)_2^{2+}]$ guest. The S···S distances (8.915 and 11.983 Å, respectively) show clearly the C_{2v} conformation. Interestingly, the typical cone shape of *p*-sulfonatothiacalix[4]-arene is disrupted to assume the unique partial-cone conformation in the cocomplex **3** of *p*-sulfonatothiacalix[4]arene with a 1:3 Ni-2-DPD coordinate.[15] In other words, during the course of inclusion complexation, *p*-sulfonatothiacalix[4]arene adjusts its own cone form to partial cone so that the large $[Ni(2\text{-}DPD)_3^{2+}]$ cation can be immersed into the "cavity" more deeply.

With these three complex structures, we can primarily conclude that the configuration of the guest molecule does exert

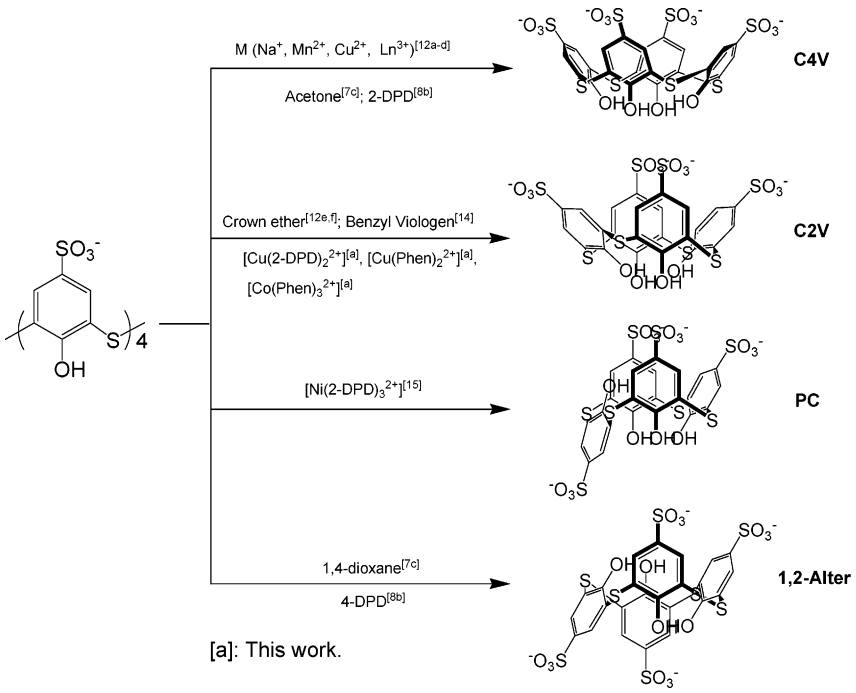

Figure 3. Illustration of the conformational interconversion of *p*-sulfonatothiacalix[4]arene induced by guest molecules: view of complexes **4** and **5**.

an extraordinary influence over the the conformation of the *p*-sulfonatothiacalix[4]arene host. Moreover, to further investigate the effect of the guest on controlling the *p*-sulfonatothiacalix[4]arene conformation and present more valuable data, we enlarged the guest size/shape from 2-DPD to a Phen ligand. Thus, two cocomplexes of *p*-sulfonatothiacalix[4]arene with $[Cu(Phen)_2^{2+}]$ (**4**) and $[Co(Phen)_3^{2+}]$ (**5**) were successfully prepared (Figure 2).

Complex **4** also possesses two $[Cu(Phen)_2^{2+}]$ cations in the cell to match one *p*-sulfonatothiacalix[4]arene^{4-} anion, the same as the case in **2**. One is again coordinated by a dissociative water molecule and penetrated into the cavity of *p*-sulfonatothiacalix[4]arene with one ligand ring, and the other is present in the void of the crystal lattice (exo-calix complex). As shown in Figure 2, one Phen of the included $[Cu(Phen)_2^{2+}]$ cation penetrates almost vertically into the calixarene cavity, which is stabilized by not only two edge-to-face π-stacking interactions (C68−H68···ring of C7−C12, 2.889 Å and 159.5°; C70−H70···ring of C19−C24, 3.129 Å and 128.5°) and one hydrogen bond (O17−O10, 2.667 Å) but also two relatively weak $\pi\cdots\pi$ interactions (4.243 and 4.309 Å). The trans S···S approaches of *p*-sulfonatothiacalix[4]arene in **4** are 12.654 and 8.795 Å, and the dihedral angles among the opposite aromatic rings are 99.8 and 43.1°. From the S···S approaches and the *p*-benzene angles, we can see that the *p*-sulfonatothiacalix[4]arene in **4** is pinched to a greater extent than in **2** due to the enlargement of guest molecules.

In complex **5**, *p*-sulfonatothiacalix[4]arene may be diprotonated (sulfonate groups) because of the strong acidity and, therefore, there is only one $[Co(Phen)_3^{2+}]$ needed corresponding to one *p*-sulfonatothiacalix[4]arene unit. From Figure 2, we can see that one Phen of $[Co(Phen)_3^{2+}]$ inserts into the cavity of *p*-sulfonatothiacalix[4]arene with the more aclinic orientation than that in **4**, which is only stabilized by two C−H···π interactions (C29−H29···ring of C13−C18, 2.792 Å and 151.3°; C32−H32···ring of C1−C6, 2.916 Å and 143.5°). The host−guest $\pi\cdots\pi$ interactions in **5** (4.796 and 4.558 Å) are weaker than those in **4**, which can be ignored. The different binding manners of the Phen ligand between **4** and **5** may arise from differences in acidity of the mother liquids or the guest structures. Comparing carefully the complex structures of **2**, **4**, and **5**, we find that *p*-sulfonatothiacalix[4]arene in **5** presents the most obvious characteristics of C_{2v} among these complexes, with trans S···S approaches of 13.266 and 7.683 Å and the of the para aromatic rings of 112.9 and 28.1°, despite the penetration depth of Phen in **5** (4.884 Å) being shallower than that in **4** (4.299 Å).[18]

When we replaced the guest 2-DPD with its isomeric compound 4-DPD, the very unusual host−guest complex of *p*-sulfonatothiacalix[4]arene with 4-DPD (**6**)[8b] was obtained. Although there the only difference between both DPD guests was the nitrogen position, both the conformational features of *p*-sulfonatothiacalix[4]arene in **6** and the physical properties of the two complexes are distinctly different, in which *p*-sulfonatothiacalix[4]arene adopts the 1,2-alternate conformation with the 4-DPD guest lies at the upper rim, as illustrated in Figure 6. Furthermore, complex **6** is yellow and hardly water-soluble, while complex **1** is colorless and water-soluble. These phenomena greatly resemble those in the case of *p*-sulfonatocalix[4]arene with 4-DPD.[11a] Therefore, 4-DPD can be assumed to be an active guest molecule to perturb the conformation of sulfonato calix species, and endeavors to investigate the inclusion complexation of other sulfonato calix compounds (such as C5AS and C6AS) with 4-DPD are ongoing.

Reviewing the 2-DPD series (2-DPD, $[Cu(2\text{-}DPD)_2^{2+}]$, $[Ni(2\text{-}DPD)_3^{2+}]$), we find that the larger the guest molecules, the more ($C_{4v} \rightarrow C_{2v} \rightarrow$ partial cone) the conformation of *p*-sulfonatothiacalix[4]arene distorts to accommodate the guest molecules. However, the conformational conversion of *p*-sulfonatothiacalix[4]arene does not conform to the above "rule" for the Phen series ($[Cu(Phen)_2^{2+}]$ (**4**) and $[Co(Phen)_3^{2+}]$ (**5**)); that is, the larger $[Co(Phen)_3^{2+}]$ does not result in the conformation of *p*-sulfonatothiacalix[4]arene becoming another novel form. In fact, *p*-sulfonatothiacalix[4]arenes in **4** and **5** assume analogous cone shapes of C_{2v} symmetry, which are consistent with that of *p*-sulfonatocalix[4]arene upon complexation with

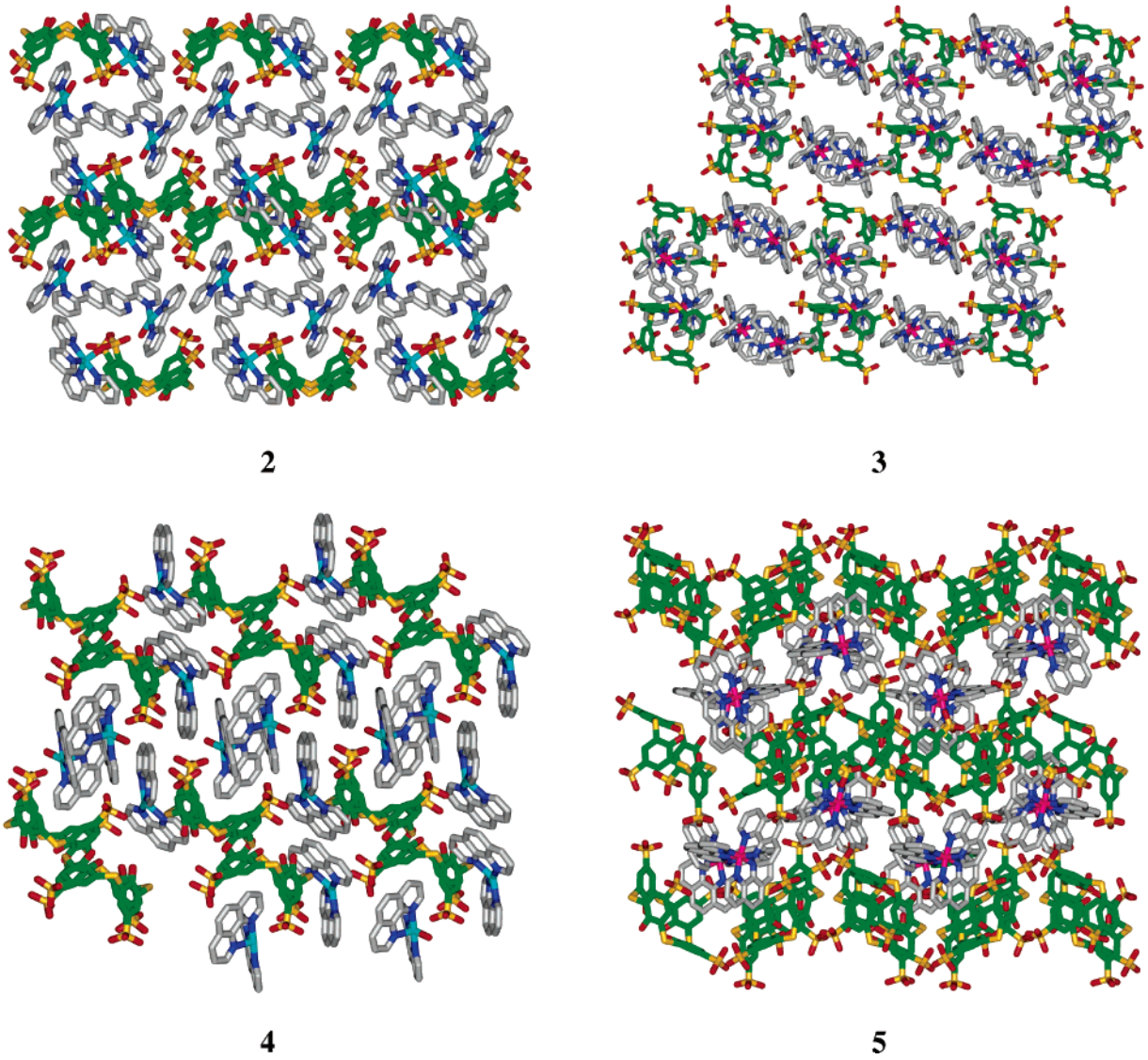

Figure 4. Packing structures of complex **2** (viewed from the *c* direction), **3** (viewed from the *a* direction), **4** (viewed from the *b* direction), and **5** (viewed from the *b* direction). The hydrogen atoms and solvent water molecules are deleted for clarity.

the cation $[Ni(Phen)_3^{2+}]$.[19] With a little hindsight, the C_{2v} conformation is particularly suited to the inclusion of such large planner guest species. A survey of the inclusion complex structures of *p*-sulfonatothiacalix[4]arene with guests is shown in Figure 3, revealing that (a) *p*-sulfonatothiacalix[4]arene maintains the original cone shape of C_{4v} symmetry upon complexation with metal ions and some small organic guest molecules; (b) *p*-sulfonatothiacalix[4]arene is pinched to the C_{2v} form to accommodate large planar or cyclic guests; (c) *p*-sulfonatothiacalix[4]arene is destroyed to assume the novel partial-cone conformation during the course of second-sphere coordination with the $[Ni(2\text{-}DPD)_3^{2+}]$ guest due to the guest penetrating into the cavity of *p*-sulfonatothiacalix[4]arene to the deepest degree;[15] (d) *p*-sulfonatothiacalix[4]arene adopts the so-called 1,2-alternate conformation upon complexation with 1,4-dioxane and 4-DPD guests, where the two guests possess similar shapes of symmetry. Thus, we might conclude reasonably that the size/shape of guests is crucial in controlling the host conformation, but the large guests will not do well.

Extended Structure of *p*-Sulfonatothiacalix[4]arene. Many studies have demonstrated a remarkable ability to control the assembly behavior of *p*-sulfonatocalix[4]arene into bilayers, capsules, nanoscale spheres, tubular arrays, and beyond in the presence of different guests.[3e,f,20] In the present system of *p*-sulfonatothiacalix[4]arene, the conformations of the calixarene host are disrupted to different extents upon complexation with various guest molecules, and the corresponding classic bilayer aggregation of *p*-sulfonatothiacalix[4]arene is also seen to be further perturbed, depending on the appropriate guests. Among these six complexes, *p*-sulfonatothiacalix[4]arenes in the cone shape (complexes **1**, **2**, **4**, and **5**) assemble themselves into a bilayer arrangement accompanied by some assistant distortion, while the other two complexes (**3** and **6**) show unusual extended structures. *p*-Sulfonatothiacalix[4]arene in **3** fabricates infrequently water-filled channels through complicated hydrogen-bonded interactions with guests, and the hydrogen-bonded polymers are taken on in **6**.

Upon crystal packing, the extended structure of **2** reveals a bilayer arrangement, with *p*-sulfonatothiacalix[4]arene packing in a similar manner through a total of three crystallographically unique interactions (Figure 4). There are one $\pi\cdots\pi$ (between ring C19−C24 and ring C19−C24, 3.737 Å) and two particular S1···S2 (which is impossible in *p*-sulfonatocalix[4]arene chemistry) interactions (3.555 Å). The bilayer structure gives thicknesses of the hydrophobic and hydrophilic layers of 5.42 and 9.58 Å (The thickness of the hydrophilic layer is defined as the

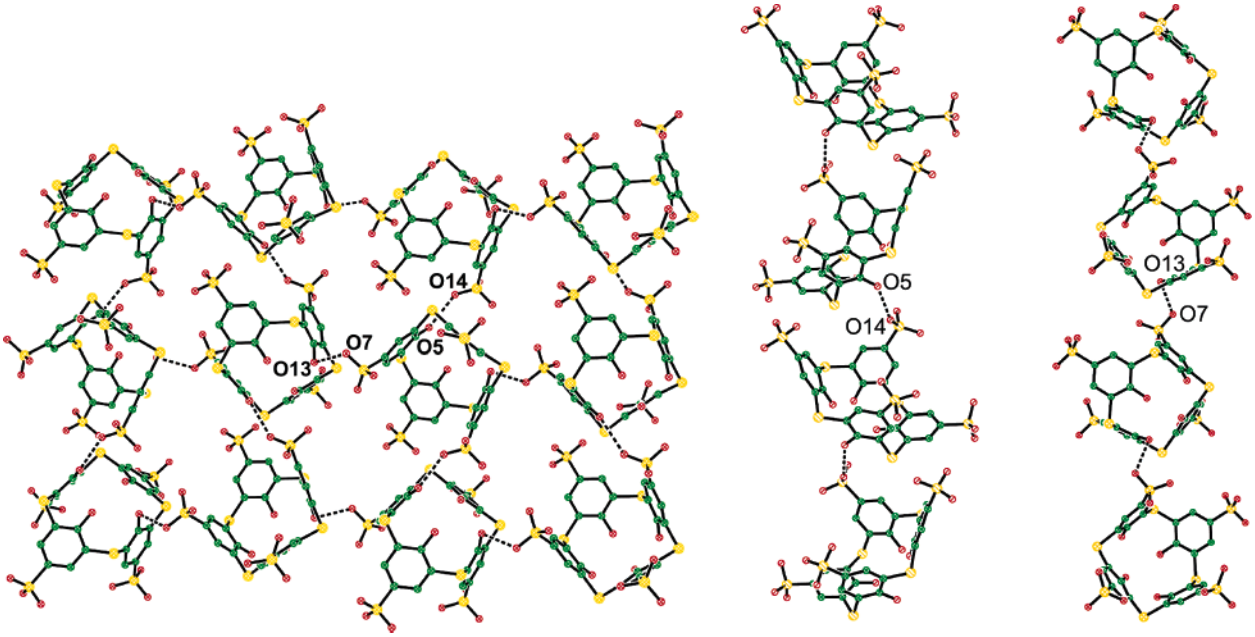

Figure 5. Views showing the intermolecular hydrogen-bonded network of *p*-sulfonatothiacalix[4]arene itself in **5**. Hydrogen atoms are omitted for clarity, and H-bonds are drawn between the donor and acceptor atoms.

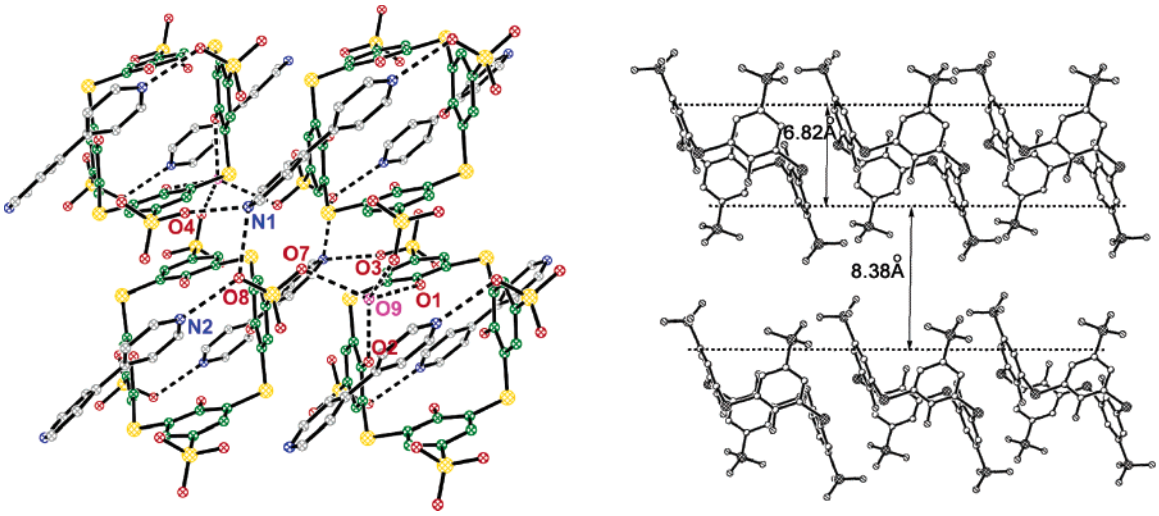

Figure 6. Extended structure of complex **6**: (left) the complicated hydrogen-bonded network on the $a \times b$ plane (only unrepeatable hydrogen bonds are labeled); (right) the further layer array.

perpendicular distance between the planes comprising the sulfur-bonded aromatic carbon atoms.[21]) Thus, the whole distance of one bilayer unit is 15.00 Å, which is wider than the thickness of 14.03 Å formed by a single *p*-sulfonatothiacalix[4]arene host with a larger hydrophobic layer of 7.21 Å and a smaller hydrophilic layer of 6.82 Å.[12a] In addition, these distances are also much different from those of complex **1**. The hydrophobic and hydrophilic layers of **1** are approximately in the region of 5.05 and 8.90 Å, resulting in a repeat distance sum of 13.95 Å. For these differences, one reasonable explanation is that the unique S···S interactions between the bridge S atoms shorten the width of the hydrophobic layer. On the other hand, the large guests of copper complexes appear as pillars that hold the hydrophilic layers more apart.

The packing structures of the Phen series **4** and **5** also both present bilayer arrangements, but the layers are impacted to become corrugated, as shown in Figure 4. This should be attributed to the fact that the array of bulky guests destroys the regular aggregation of *p*-sulfonatothiacalix[4]arene to some extent. In the extended structure of **4**, there is only one $\pi\cdots\pi$ interaction of *p*-sulfonatothiacalix[4]arene itself (between ring C7−C12 and ring C7−C12, 3.418 Å) reinforced additionally by one hydrogen bond (O5···O8, 3.132 Å). As a portion of one $[Cu(Phen)_2^{2+}]$ is located in the hydrophobic region, one Phen ligand participates in constructing the calixarene layer with a total of three noncovalent interactions, including two $\pi\cdots\pi$ interactions (between ring C19−C24 and ring C40−C43, C47, C48, 3.568 Å; between ring C37−C40, C48, N3 and ring C40−C43, C47, C48, 3.664 Å) and one Cu1···O16 coordinate interaction (3.038 Å). In complex **5**, the corrugated shape of the bilayer array is rare, except for a sample reported in the *p*-sulfonatocalix[6]arene system,[22] and even the dominating forces in the calixarene layer are unique. Most commonly, sulfonatocalixarenes assemble themselves into bilayer structures mainly through intermolecular π-stacking interactions ($\pi\cdots\pi$ or C−H···π[23]), which might be reinforced by some hydrogen-bond or S···S interactions. However, complex **5** shows a novel bilayer arrangement that is built up entirely by hydrogen bonds,

and no π-stacking interaction is detected. If the hydrophobic layer from the crystallographic *c* direction is overlooked, each calixarene unit donates two oxygen atoms of the sulfonates to form intermolecular hydrogen bonds with adjacent calixarenes to fabricate an interlocked netlike layer structure of calixarenes (Figure 5). In the crystallographic *a* direction, *p*-sulfonatothiacalix[4]arene interconnects through the O5···O14 (2.663 Å) H bond, aligned along the screw axis to form *head-to-tail* helical superstructures with a 2-fold axis. In the same way, the similar helical superstructure along the *b* direction is linked by the other O13···O7 (2.678 Å) H bond. In addition, there are also several H bonds involved in the contribution of some solvent water molecules to the construction of the hydrophobic layer. To the best of our knowledge, such a bilayer arrangement based on individual hydrogen bonds with no π-stacking interactions has not been observed.

In complex **6**, the bowl shape of *p*-sulfonatothiacalix[4]arene constructing classic bilayer arrays is disrupted to a 1,2-alternate conformation, and then a novel arrangement of a hydrogen-bonded polymer is formed (Figure 6). There are four crystallographically distinct hydrogen bonds contributed by crystalline water molecules (O1−O9, 2.872 Å; O2−O9, 2.960 Å; O9−O3, 2.959 Å; O9−O7, 2.955 Å) in addition to three host−guest hydrogen bonds (N1−O4, 2.979 Å; N1−O8, 3.096 Å; N2−O8, 2.862 Å), which participate in building a hydrogen-bonded network. Further examination of the crystal packing reveals that complex **6** also presents a layer structure with a hydrophobic region of 6.82 Å and a hydrophilic region of 8.38 Å.

Conclusion

Combining the present results and those reported before, it can be concluded that the molecular conformations of *p*-sulfonatothiacalix[4]arene can be manipulated by changing guest molecules, such as the size, shape, and even heteroatom position. *p*-Sulfonatothiacalix[4]arene maintains the original cone shape of C_{4v} symmetry upon complexation with metal ions and some small organic guest molecules, and it is pinched to the C_{2v} form to accommodate large planar or cyclic guests. Interestingly, the traditional cone shape of *p*-sulfonatothiacalix[4]arene is destroyed to assume a novel partial-cone conformation during the course of second-sphere coordination with a $[Ni(2\text{-}DPD)_3^{2+}]$ guest. In addition, *p*-sulfonatothiacalix[4]arene adopts the so-called 1,2-alternate conformation upon complexation with 1,4-dioxane and 4-DPD guests, where the two guests possess similar shapes of symmetry. On careful examination of the crystal packings of complexes **1**−**6**, it is also noticeable that the extended structures of *p*-sulfonatothiacalix[4]arene complexes are further affected by guest molecules. *p*-Sulfonatothiacalix[4]arene in **1** and **2** arrange themselves into classical bilayer arrays through respective noncovalent interactions including π···π, S···S, H-bond interactions, and so on. The extended structures of corrugated bilayers are displayed in complexes **4** and **5** due to the intervention of Phen guest species. Remarkably, water-filled channels and hydrogen-bonded polymers are formed in **3** and **6**, respectively, as a result of the conformational conversion of *p*-sulfonatothiacalix[4]arene. This in turn implies that the supramolecular architecture of *p*-sulfonatothiacalix[4]arene is designable through the subtle selection of guest molecules. Our further goal is to keep on designing and constructing significant molecular assemblies based on the potential building block *p*-sulfonatothiacalix[4]arene in the presence of suitable guest molecules.

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Supporting Information Available: X-ray crystallographic data as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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