A Novel Supramolecular Assembly Constructed by Cu/imidazole Complex with 1,2-Alternate *p*-Sulfonatothiacalix[4]arene
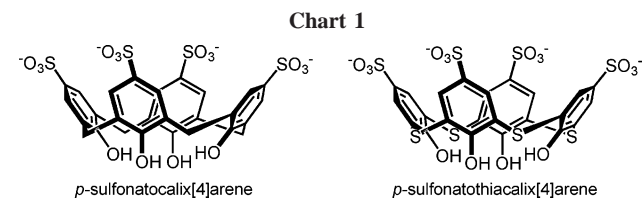
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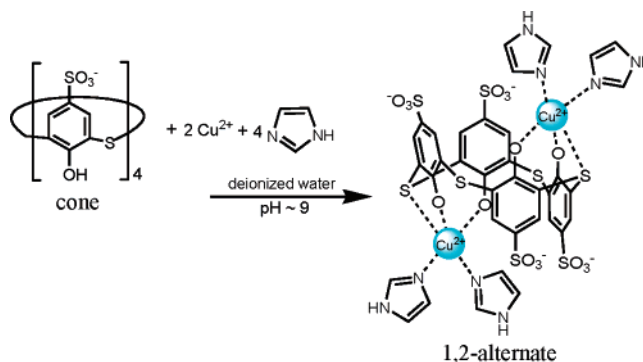
ABSTRACT: A novel supramolecular assembly has been prepared by *p*-sulfonatothiacalix[4]arene/copper(II)/imidazole through the conjoined hydrogen bonds, showing that *p*-sulfonatothiacalix[4]arene with 1,2-alternate conformation can bind copper(II) with a bis-tridentate coordination manner, and further displays charge-transfer behavior.

Thiacalixarenes,[1] as a new family of calixarenes, represent very fascinating synthesis receptors with many potential applications in supramolecular chemistry in recent years.[2] Possessing four sulfur atoms instead of the methylene bridges, thiacalixarenes possess a lot of intrinsic features differing from the methylene-bridged calixarenes, such as enlargement of the calix skeleton to provide larger cavity and more flexibility, ready oxidizability to sulfoxide and sulfone for providing new members of S bridged calixarenes, additional coordination sites to specific metal controlled by oxidation state of S, and so on.[3] Because of these distinct characteristics, thiacalixarenes are regarded as a unique molecular scaffold rather than a simple substitute of the "classical" calixarenes. However, as well as calixarenes, thiacalixarenes also possess poor water solubility, which confined their uses in organic solvent. Therefore, to further explore the various properties of thiacalixarenes in aqueous solution, *p*-sulfonatothiacalix[4]arene (STC4A), a new analogue of water-soluble calixarenes, was prepared by Miyano et al.[4] As anticipated, STC4A exhibits several extraordinary complex behaviors with not only organic molecules[5] but also metal ions[6] in aqueous solution, which cannot be obtained by *p*-sulfonatocalixarenes.

Chart 1

p-sulfonatocalix[4]arene   *p*-sulfonatothiacalix[4]arene

On the other hand, the solid-state supramolecular chemistry of the "classical" *p*-sulfonatocalixarenes have been well-studied by Atwood and Raston et al.,[7] who demonstrated that the compounds can form various molecular assemblies in the presence of suitable guests. In this field, STC4A has also gained some investigations on the construction of solid-state supramolecular architectures.[5b,8–10] The seminal report by Zhu et al.[8a] reveals that STC4A usually prefers the cone conformation in the solid state and arranges itself 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. Furthermore, it has been validated that not only the cone conformation of STC4A can be disrupted to assume infrequent 1,2-alternate[5b,9d] or partial cone conformer[9b] but also the extended structures of STC4A can be induced to present various splendid aggregations rather than a traditional bilayer array in the presence of suitable guests (either organic molecules or metal ions). For example, the supramolecular assemblies of molecular capsules[8d,8e,10a], water-filled channels,[9b] and hydrogen-bonded polymers[8d] based on STC4A have been one after the other reported by our group and others. However, among all

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Scheme 1

1,2-alternate

these STC4A complexes reported before, the unique coordination ability of bridged S atoms is employed less frequently to construct the highly complex assemblies.[8f,10b] In fact, the coordination of bridged S atoms should be one of the most important factors to control both STC4A's conformation and its assembled structures, which can be reflected from the relative studies of thiacalix[4]arene material.[11] Therefore, exploration of the effects of the lower-rim coordination of STC4A attracts more and more attention. In the present communication, we wish to report our investigation on a dinucleating copper complex of STC4A together with imidazole ligands, in which STC4A act as a bis-tridentate chelating ligand with its 1,2-alternate conformation.

On treatment of an aqueous solution of STC4A with a 4-fold excess of Cu(ClO$_4$)$_2$ and a 20-fold excess of imidazole, brown crystals of [Cu$_4$(STC4A)(imidazole)$_{12}$(H$_2$O)$_{11}$] (**1**) were obtained after the solution stood for several hours, Scheme 1.[12] Compound **1** crystallizes in a triclinic system and the structural solution was performed in the space group $P\bar{1}$.[13] It should be noted that compound **1** has one crystallographic inversion center at its midpoint, and only half of each molecule is crystallographically independent. Therefore, in each asymmetric unit, there are half of a STC4A^{8-}, one [Cu(imidazole)$_2$]$^{2+}$, two half molecules of [Cu(imidazole)$_4$]$^{2+}$ as counterions, and a total of 5.5 water molecules of crystallization that are disordered over 10 positions.

The most fascinating feature in **1** is that STC4A adopts the 1,2-alternate conformation rather than its traditional cone shape as shown in Figure 1a. According to the Ugozzoli−Andreetti convention,[14] the actual ϕ and χ torsion angles values, which define the solid-state conformation of STC4A, are +79.8, −82.5; +142.5, +135.8; −79.8, +82.5; and −142.5, −135.8°. In fact, the solid-state 1,2-alternate conformation of STC4A has already been obtained by our group and others.[5b,9c,15] However, the present 1,2-alternate conformation of STC4A differs to some extent from the previous results. As comparison with complex of STC4A with 4,4-dipyridinium (STC4A-4-DPD),[9c] not only the actual ϕ and χ torsion angles values of STC4A (in STC4A-4-DPD: +79.0, −85.8; +145.7, +130.2; −79.0, +85.8; and −145.7, −130.2°) but also
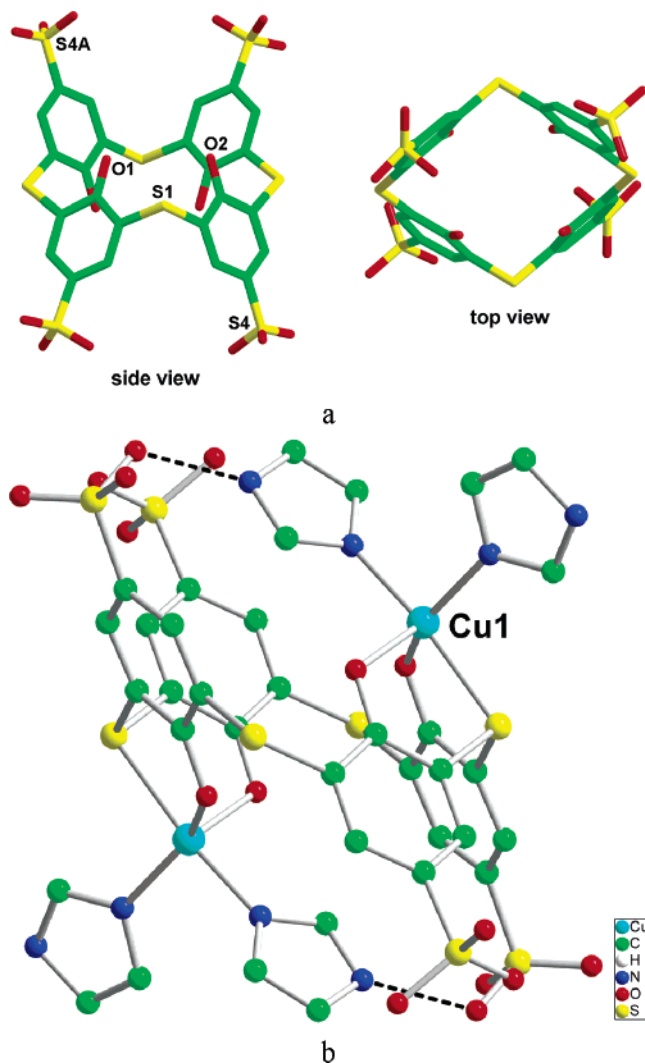
Figure 1. X-ray structure of complex **1**: (a) view showing the 1,2-alternate conformation of STC4A; (b) view showing the bis-tridentate coordination mode of STC4A with [Cu(imidazole)$_2$]$^{2+}$ cations. Selected bond distances (Å) and angles (deg): Cu1−N1 2.039(5), Cu1−N3 1.961(5), Cu1−O1 2.167(4), Cu1−O2 1.956(4), Cu1−S1 2.362(2), C1−O1 1.303(6), C7−O2 1.316(6), C2−S1, 1.777(5), C12−S1 1.779(5), C8−S2 1.768(5), C13−N1 1.338(8), C14−N1 1.376(8), C16−N3 1.310(8), C17−N3 1.365(8), N1−Cu1−S1 93.46(16), N1−Cu1−O1 101.59(18), N1−Cu1−O2 144.59(19), N3−Cu1−S1 172.35(15), N3−Cu1−O1 94.30(17), N3−Cu1−O2 88.57-(18), C1−O1−Cu1 116.5(3), C7−O2−Cu1 119.4(3), C2−S1−Cu1 97.30-(17), C12−S1−Cu1 95.21(18), C2−S1−C12 103.3(2), C13−N1−Cu1 126.9(5), C14−N1−Cu1 126.2(5), C16−N3−Cu1 125.6(5), C17−N3−Cu1 129.0(5), C8−S2−C6$^{\#3}$ 107.3(3). The broken lines represent the intermolecular hydrogen bonds between donor and acceptor.

the S···S approach of distal sulfonates (in **1**: S4−S4A, 12.561 Å; STC4A-4-DPD, 13.859 Å) are different. That is to say, the framework of STC4A in **1** is shrunken to be shorter than that in STC4A-4-DPD. It is attributed to the factors of inducing STC4A to the 1,2-alternate form being different between **1** and the STC4A-4-DPD complex. STC4A in STC4A-4-DPD assumes the 1,2-alternate form because the cone shape of STC4A cannot suitably accommodate the 4-DPD guest in its cavity. However, in **1**, STC4A assumes the 1,2-alternate form, which is induced by the cooperative bis-tridentate coordination of copper cations with one bridged S atom and two lower-rim phenolic hydroxy groups. To achieve better coordination behavior, the bridged S atom needs to be more approximate to phenolic oxygen atoms (S1−O1, 3.026 Å; S1−O2, 2.944 Å), and then STC4A in **1** appears to have a more compact 1,2-alternate conformation than the others. As a result, the overturned 1,2-alternate conformation in **1** does not lead to
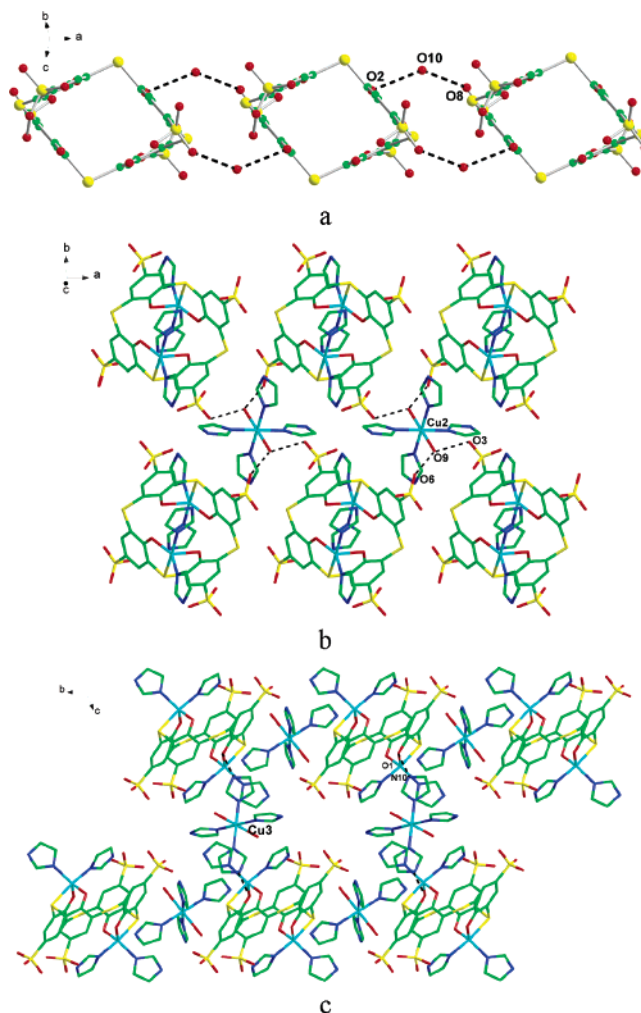

Figure 2. Views of the extended structure of complex **1**: (a) 1D chain formed by STC4A themselves and solvent water molecules; (b) 2D layer structure linked by Cu2 counterions; (c) overall 3D packing structure of **1**, in which Cu3 counterions reside between the layers and join them together.

elongated bridged S−C bonds (see Figure 1) relative to those in the cone conformation,^{8a} which is also different from the STC4A-4-DPD case in which the conformational change made all the bridged S−C bonds elongated about 0.1 Å.

In addition, another interest should be concerned with the coordination behavior of STC4A with [Cu(imidazole)$_2$]$^{2+}$ (Cu1). As mentioned above, the multinuclear Cu(II) complexes of *p-tert*-butylthiacalix[4]arene have been reported previously.^{11a,11e} Although it also provides the bis-tridentate coordination mode to Cu(II), the cone conformation of thiacalix[4]arene is retained. Simultaneously, Zhu et al. also reported the 2D coordination polymer based on the Cu(II) tetramer with STC4A,^{8f} in which STC4A acts as a multi-tridentate ligand with the conventional cone conformation. However, much differently in the present complex **1**, STC4A prefers to adopt the 1,2-alternate conformation as a bis-tridentate dinucleating ligand with two Cu(II) at the anti position (Figure 1b). Herein, the additional imidazole ligands play the crucial role in manipulating the conformation of STC4A. Each Cu(II) cation is five-coordinated by a total of one S atom and two O atoms in STC4A and two N atoms in imidazoles. Therefore, the space hindrance between STC4A and imidazole ligands compels STC4A to present the uncommon 1,2-alternate conformation, which is an accessible conformation depending on the choice of metal and coligands. Moreover, the hydrogen-bonding interactions (N4A···O7, 2.901 Å, 141.0°) between sulfonate groups and NH groups of imidazoles help reinforce the stability of 1,2-alternate thiacalixarene. Upon coordination with Cu1, the bridged S−C bonds are affected slightly,
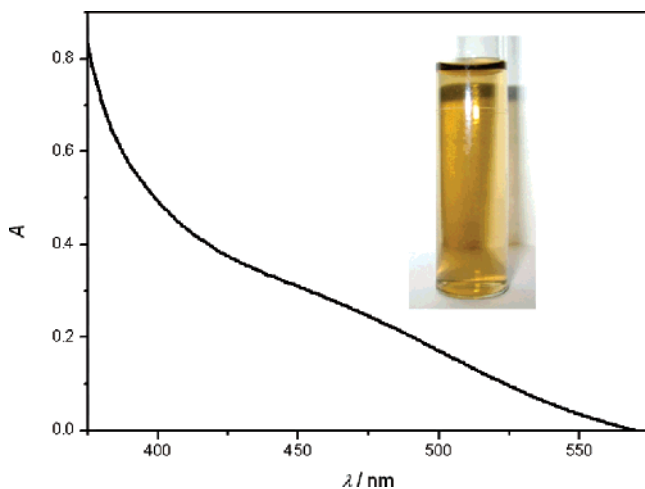
Figure 3. UV−vis spectrum of complex of STC4A−Cu(II) ([STC4A] = 2.0×10^{-3} mol L^{-1}, [STC4A]:[Cu(II)] = 1:2). Inset: visible color change of Cu(II) solution upon coordination by STC4A.

which can be seen from the almost equivalent lengths between S1−C2 (participate in coordination) and S2−C8 (do not participate in coordination) bonds. However, it is interesing that all the phenolic C−O bonds in **1** are shortened, although it is well-known that the coordination of O atoms may elongate the covalent bonds to some extent. This should be attributed to the deprotonation of the phenolic hydroxyls.

As investigated by Iki and co-workers,[16] the pK_{a1-4} values of four phenolic hydroxyls in STC4A are 2.18, 8.45, 11.99, and 11.62, respectively. So STC4A can be utilized as divergent −4, −5, −6, −7, and −8 charged tectons upon adjusting different pH values. But the STC4A^{7-} and STC4A^{8-} hosts are relatively difficult because they need stronger basic conditions. For complex **1**, the pH value of its mother liquid is at about 9. It is worth mentioning that STC4A unexpectedly presents the negative eight charge. In other words, all of the phenolic hydroxyls in STC4A are deprotonated. The deprotonations of hydroxyls may mainly be attributed to the basicity of imidazole. However, according to the pH value of the mother liquid and the pK_a value of imidazole (pK_{a1}, 6.993-(+1); pK_{a2}, 10.58(0)),[17] the lower-rim phenolic hydroxyls of STC4A cannot be fully deprotonated in the present case. So it should be helped by the coordination of Cu(II) ions. In the present case, the H proton and Cu(II) ion compete for binding to the phenolic O atom and Cu(II) showed preferential binding because of its help in coordinating to other O and bridged S atoms. Also, it is possible their complexation can increase the thermodynamic acidities of phenolic hydroxyls by polarization effects.

To satisfy the charged balance of STC4A^{8-}, we need additional positively charged cations besides the two Cu1 cations coordinated by STC4A. In complex **1**, there are two [Cu(imidazole)$_4$(H$_2$O)$_2$]$^{2+}$ cations (Cu2 and Cu3) restricted in the crystal lattice as counterions. Unlike Cu1 with coordination number five, Cu2 and Cu3 counterions are six-coordinated by four imidazole ligands and two additional water molecules. For the further extended structure of **1**, because of the conventional cone shape of STC4A disrupted, its typical bilayer array is no long maintained. The noncovalent interactions (π-stacking and hydrogen bonding) between calixarenes do not appear any more. The STC4A molecules are held apart from each other by either counterions or water molecules. Primarily, the 1,2-alternate STC4As are linked together to be a monodimensional chain structure by solvent water molecules (O10···O2, 2.833 Å; O10···O8, 2.844 Å), as shown in Figure 2a. Moreover, the chains extend along the crystallographic *b* direction through the joining of Cu2 counterions (O9···O3, 2.853 Å; O9···O6, 2.716 Å) to present the bidimensional layer array at the *a*×*b* plane (Figure 2b). By viewing from the crystallographic *a* direction, the complexed layer structures are separated by Cu3 counterions (Figure 2c). In

addition, the hydrogen bonds (N10···O1, 2.795 Å) between imidazole and STC4A linkage them together to form the tridimensional hydrogen-bonded polymers. Therefore, when all these Cu-(II) ions and water molecules are taken into account within the extended strucutre, the overall structure of **1** also retains some layered structure character. However, one cannot observe any hydrophobic layers in complex **1**, and hence, there are certainly no alternations between hydrophobic layers and hydrophilic layers.

In solution, although the conformation behavior of STC4A upon complexation with Cu(II)/Imidazole cannot be validated (^{1}H NMR spectrum cannot be well-preformed because of the paramagnetism of Cu(II)), the coordination of bridge S atoms in STC4A with Cu-(II) can be observed from the color change of the mother liquid. When *p*-sulfonatocalix[4]arene is added into the Cu(II) solution, there is no obvious color change and the mother liqiud maintains its original blue color. However, adding STC4A into the Cu(II) solution, the color of solution changes to light brown (Figure 3 inset), and the complex displays the new UV−vis absorbance around 475 nm, as shown in Figure 3. This can be attributed to the characteristic absorption peak of ligand-to-metal charge transfer (LMCT) from S atom to Cu(II). The further addition of imidazole ligand makes the brown color darker, indicating that imidazole as an alkali enhances the tridentate coordination ability of STC4A besides as coligand.

In summary, a novel 1,2-alternate conformation of STC4A induced by bis-tridentate coordination of copper ions has been observed, and complex **1** then presents the overall packing structure of hydrogen-bonded polymers. The present results inspired us to prepare the lower-rim coordinated complexes of calixarenes with metal ions through the cooperative coordination of suitable ligands, which can also achieve the research goal of building spectacular supramolecular architectures. Differently from most previous reports that mainly concern the contributions of upper-rim sulfonate groups and cavities of calixarenes upon complexation with guests, this research provides a new project to not only manipulate the conformation of sulfonatocalixes but also further overcome their bilayer arrays.

Supporting Information Available: X-ray crystallographic data as a CIF file (CCDC reference 631451). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) To a solution of *p*-sulfonatothiacalix[4]arene (90.4mg, 0.1mmol) in 10 mL of deionized water was added Cu(ClO$_4$)$_2$·6H$_2$O (148.2 mg, 0.4 mmol) and then imidazole (136.2 mg, 2.0 mmol). After being heated for a moment, the brown solution was allowed to stand for several hours. The crystalline compound suitable for X-ray structural analysis was then obtained as brown blocks with a yield of 72.8 mg (35%).

(13) The X-ray intensity data for compound **1** were collected on a standard Siemens SMART CCD area detector system equipped with a normal-focus molybdenum-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2.0 kW (50 kV, 40 mA) and a graphite monochromator at $T = 293$-(2) K. The structure was solved by using direct methods and refined employing full-matrix least squares on F^2 (Siemens, SHELXTL-97). Crystal data for **1**: C$_{60}$H$_{78}$Cu$_4$N$_{24}$O$_{27}$S$_8$, $M_r = 2078.10$, triclinic, space group $P\bar{1}$, $a = 11.426(4)$ Å, $b = 13.704(4)$ Å, $c = 14.625(5)$ Å, $\alpha = 110.958(5)°$, $\beta = 94.824(5)°$, $\gamma = 93.252(6)°$, $Z = 1$, $V = 2121.6$-(11) Å^3, $D_c = 1.626$ g/cm^3, $\mu = 1.276$ mm^{-1}, $\theta_{max} = 26.44°$, $F(000) = 1066$, crystal dimensions $0.30 \times 0.25 \times 0.20$ mm^3, reflections collected/unique, 12187/8576 ($R_{int} = 0.0402$), final R indices [$I > 2\sigma(I)$] $R_1 = 0.0633$, $wR_2 = 0.1403$, R indices (all data) $R_1 = 0.1348$, $wR_2 = 0.1741$, goodness-of-fit on $F^2 = 1.000$. Some oxygen atoms of the sulfonate groups (O3, O4, O5, O8) were disordered and refined in two positions with equal occupancies. Anal. Calcd. for **1**: C, 34.68; H, 3.78; N, 16.18; S, 12.34. Found: C, 35.21; H, 3.64; N, 16.47; S, 12.55.

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