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Self-Assembly from Two-Dimensional Layered Networks to Tetranuclear Structures: Syntheses, Structures, and Properties of Four Copper–Thiacalix[4]arene Compounds

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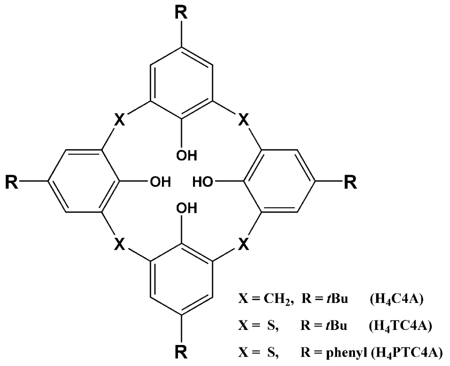
Two new copper–thiacalix[4]arene compounds, $[Cu^I_2Cl_2(H_4TC4A)](CH_3OH)$ (**1**) and $[Cu^I_2Cl_2(H_4PTC4A)](CH_3OH)(CHCl_3)_{0.5}$ (**2**) (where H_4TC4A = *p*-*tert*-butylthiacalix[4]arene and H_4PTC4A = *p*-phenylthiacalix[4]arene), were synthesized by the solvothermal method in the mixed $CH_3OH/CHCl_3$ (1:1) solvent and reassembled in air at room temperature to two other structures, $[Cu^{II}_4Cl_3(HCO_2)(TC4A)(CH_3OH)_2(H_2O)](CHCl_3)(CH_3OH)_{2.7}$ (**3**) and $[Cu^{II}_4Cl_4(PTC4A)(CH_3OH)_4]$ (**4**), respectively. All these four compounds were characterized by TG analyses, FTIR spectroscopy, and single-crystal X-ray diffraction analyses. Compounds **1** and **2** feature two-dimensional layered networks, while compounds **3** and **4** are assembled by some tetranuclear units. The luminescence of compounds **1** and **2** in the solid state and magnetic properties of compound **3** were studied.

Introduction

Thiacalix[*n*]arenes (*n* = 4–8), possessing several phenolic groups and bridging sulfur atoms ready for various coordination modes and conformational transformations, have been successfully synthesized and widely investigated in recent years in the field of both coordination chemistry and cluster chemistry.[1–5] Especially *p*-*tert*-butylthiacalix[4]arene (H_4TC4A), one of the most important derivatives of calix[4]arene, which has inclusion behavior different from that of the typical *p*-*tert*-butylcalix[4]arene (H_4C4A, Scheme 1), has attracted increasing attention.[6] A series of H_4TC4A compounds incorporating alkali metal,[7] transition metal,[8] and/or lanthanide species[9,10] have been synthesized and structurally characterized. In these complexes, not only the phenolic oxygen atoms but also the bridging sulfur atoms bond the metals, and the featuring M_x cores (x = 1–4) are either bonded to the lower rim of the calixarene or sandwiched between two calixarenes.[4] However, in spite of the increasing amount of studies on H_4TC4A, the solid-state supramolecular chemistry of another thiacalix[4]arene derivative, deep-cavity *p*-phenylthiacalix[4]arene (H_4PTC4A), remains unexplored since its first synthesis by Lhoták et al. about six years ago.[11]



Scheme 1.

Here we present the syntheses of two 2D thiacalix[4]arene compounds, $[Cu^I_2Cl_2(H_4TC4A)](CH_3OH)$ (**1**) and $[Cu^I_2Cl_2(H_4PTC4A)](CH_3OH)(CHCl_3)_{0.5}$ (**2**), and two other tetranuclear compounds reassembled from these 2D networks, $[Cu^{II}_4Cl_3(HCO_2)(TC4A)(CH_3OH)_2(H_2O)](CHCl_3)(CH_3OH)_{2.7}$ (**3**) and $[Cu^{II}_4Cl_4(PTC4A)(CH_3OH)_4]$ (**4**). Single-crystal X-ray diffraction analyses revealed that compounds **1** and **2** present the first two 2D complexes of thiacalix[4]arenes in which the calixarenes are arranged in an "up-down" fashion and bonded to the metal ions through the bridging sulfur atoms. However, the 2D networks were destroyed in the reassembly, and the reassembled structures (**3** and **4**) are constructed by the iso-

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lated tetranuclear units through the supramolecular stacking interactions. The syntheses, crystal structures, and properties of these four compounds will be described.

Results and Discussion

Syntheses

As the mixed Mn-Gd compound in our previous work,[10] compounds **1** and **2** were obtained by solvothermal methods[12] from the mixed $CH_3OH/CHCl_3$ solution. It is found that the kind of solvents and the solvothermal method play a crucial role in the formation of the target products. If the syntheses were performed in pure CH_3OH or $CHCl_3$ solvent, no target products were obtained but only a white precipitate. Otherwise, only black precipitates formed if the reaction proceeded at ambient conditions. Compounds **3** and **4** were reassembled from compounds **1** and **2**, respectively. However, the reassembly did not take place under the same conditions. That is, compound **3** formed easily by just keeping the crystals of **1** in the mother liquid at ambient conditions, but compound **4** did not form unless the crystals of **2** were picked out from the mother liquid and put into methanol. The transformation of Cu^{I} to Cu^{II} is surely due to oxidation by O_2 in air. The formation of formate anions in **3** can be explained as the oxidation of methanol by the oxygen in air catalyzed by the Cu^{I}–H_4TC4A compound of **1**.[13] A further study revealed that the deliberate addition of a small amount of water does result in a good yield of the target compounds, which might be attributed to the fact that the water molecules are not only involved in the crystal structures but are also helpful in the transformation of Cu^{I} to Cu^{II} and the formation of the formate anions. Possible reaction equations in the reassembly processes can be summarized as shown in Scheme 2.

$$4Cu^{+} + O_2 + 2H_2O = 4Cu^{2+} + 4OH^{-}$$

$$CH_3OH + O_2 + OH^{-} \xrightarrow{Cu^{I}\text{-}H_4C4AS} HCOO^{-} + 2H_2O$$

$$H_4TC4A + 4OH^{-} \leftrightarrow TC4A^{4-} + 4H_2O$$

$$H_4PTC4A + 4OH^{-} \leftrightarrow PTC4A^{4-} + 4H_2O$$

Scheme 2.

Structures of the Complexes

Single-crystal X-ray diffraction structure analyses reveal that compounds **1** and **2** feature similar layered networks as shown in Figure 1. To the best of our knowledge, these are the first two examples of thiacalix[4]arenes with 2D layer structures. Compounds **1** and **2** crystallize in a monoclinic system with space group *C2/m*, and both compounds show similar metal–calixarene connections (Table S1). As shown in Figures 2a and 2c, in both compounds, all the copper centers [Cu1] are coordinated by two Cl anions [with the distances Cu1–Cl 1 2.32 Å, Cu1–Cl1a 2.37 Å in **1** and Cu1–Cl1 2.31 Å, Cu1–Cl1a 2.38 Å in **2**] and two sulfur atoms from two thiacalix[4]arene ligands [Cu1–S1 2.31 Å, Cu1–S2 2.30 Å for **1** and Cu1–S1 2.30 Å, Cu1–S2 2.29 Å for **2**]. The nearest Cu···Cu distances are 2.66 Å in **1**, while they are 2.87 Å in **2**. The longer Cu···Cu distance in **2** can be attributed to the larger spatial steric hindrance of the larger H_4PTC4A ligands. The shorter intermetallic distance in **1**, less than twice the van der Waals radius of Cu^{I} (1.4 Å), indicates a strong Cu···Cu interaction. Each of the thiacalix[4]arene ligands bonds four double-edge-sharing-tetrahedron units, and each of the double-tetrahedron units is connected to four thiacalix[4]arene ligands in both cases (Figure 2). Notably, in these two compounds, the calixarene molecules are coordinated to the metals just by the bridging sulfur atoms, which is by far different from those coordinating through both the bridging sulfur atoms and the phenolic oxygen atoms.[4,7–10] Similar connections are only observed in a silver compound reported recently.[14] The reasonable explanation might be that this kind of connection is governed by the coordination of Cu^{I} and the affinity of sulfur atoms to the copper atoms.

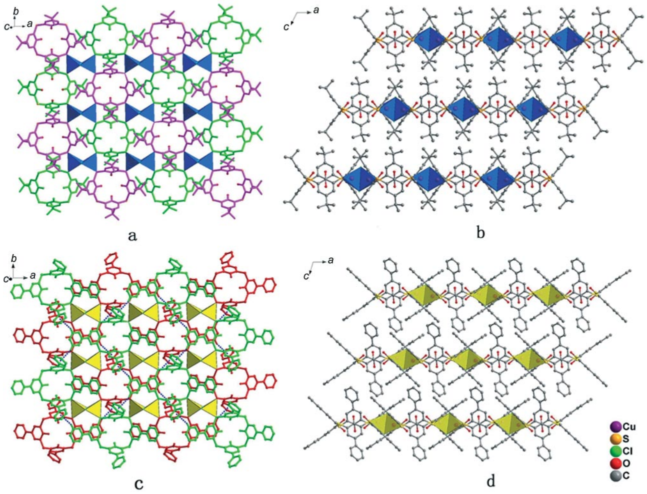

Figure 1. 2D layered networks of **1** (a) and **2** (c) and their stacking in **1** (b) and **2**(d). The "up-down" fashion of thiacalix[4]arene ligands are highlighted in different colors. The double-edge-sharing-tetrahedron units are presented in blue (**1**) and yellow (**2**). The blue doted lines in **2** (c) stand for the C–H···π interactions.

Both H_4TC4A and H_4PTC4A ligands adopting the cone conformation are arranged in an "up-down" fashion and linked by the double-tetrahedron units to form a 2D 4^4 topology. With a close examination of the layered structures, intralayer C–H···π interactions (ca. 3.01 Å) can be found between the H atoms and aromatic rings of the phenyl group of H_4PTC4A ligands in **2**, while such interactions are not found for **1** with H_4TC4A ligand. Such intralayer supramolecular interactions play an important role in stabilizing compound **2**, so that **2** is more stable in the mixed $CH_3OH/CHCl_3$ solvent than **1** as mentioned in the synthesis section. The extended structures of **1** and **2** are stacked by the layered motifs through supramolecular stacking interactions (e.g. van der Waals forces). The interstices are filled by isolated solvent molecules (Figure 1b and Figure 1d).

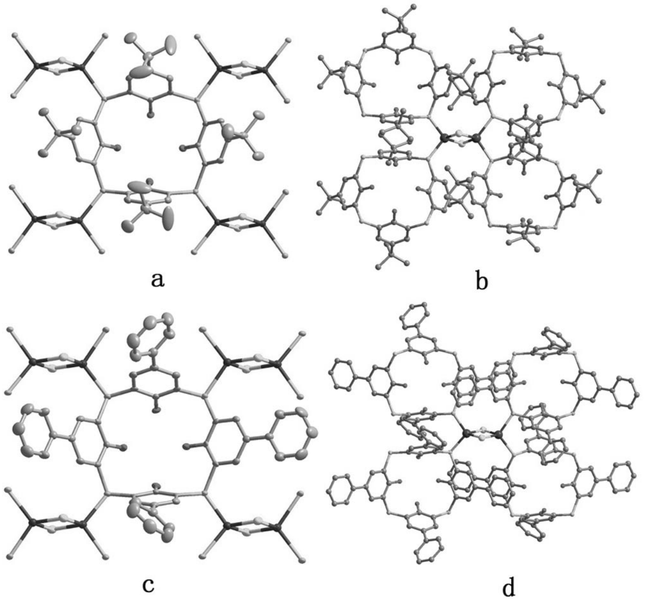

Figure 2. Coordination environment in **1** and **2** showing the 4-connected mode of thiacalix[4]arene ligands (a, c) and double-edge-sharing-tetrahedron units (b, d). The hydrogen atoms and solvent molecules are omitted for clarity (hereafter the same).

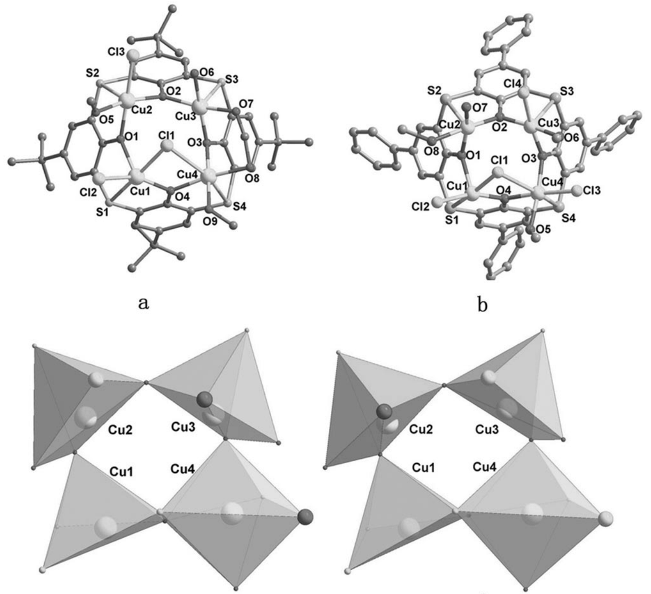

Figure 3. Coordination environment (a, b) and polyhedral representation (c, d) of the of Cu^{II} atoms in **3** (a, c) and **4** (b, d).

Both compounds **3** and **4** feature tetranuclear units with similar geometric parameters (Table S1). All the shuttlecock-like tetranuclear units can be thought of as a metal square bonding to the lower rim of the calixarene, but their arrangements are quite different in these two compounds. Compound **3** crystallizes in a monoclinic system with space group *C*/2*c* while **4** crystallizes in a triclinic system with space group $P\bar{1}$. There are four independent crystallographic copper sites in an asymmetric unit, three five-coordinate centers [Cu1, Cu2, and Cu3] and one six-coordinate center [Cu4]. As shown in Figures 3c and 3d, Cu1, Cu2, and Cu3 have a pyramidal coordination, while Cu4 has a distorted octahedral coordination geometry. All these four copper sites are bonded by two phenolic oxygen atoms and one sulfur atom, and their other coordination sites are occupied by Cl and/or O atoms (Figure 3). The bond valence calculation indicated that all the four copper sites are occupied by Cu^{II} atoms. The phenolic oxygen atoms of a calixarene bridge adjacent Cu^{II} atoms into a square, and then a shuttlecock-like tetranuclear unit forms. These tetranuclear units differ much from those reported for the Cu_4^{II}-$(TC4A)_2$ compound in which four six-coordinate Cu^{II} centers are sandwiched between two fully deprotonated calixarenes.[8a] Furthermore, it should be noted that the formate anion formed in the reassembly process from **1** to **3**, which is confirmed by charge balance considerations and IR spectra of **3** (Figure S1). Moreover, compound **4** is the first metal–organic compound of *p*-phenylthiacalix[4]arene.

The stacking of the tetranuclear units differs much in compound **3** from that in **4** due to the different supramolecular interactions. In compound **3**, the shuttlecock-like units are arranged in the "up-down" mode, the nearest Cu···Cu distance between two adjacent units being approximately 9.09 Å, and are interconnected by the C–H···S hydrogen bonds (ca. 3.86 Å) (Figure 4). However, in compound **4**, one phenyl group penetrates into the cavity of an opposite calixarene to form a C–H···π interaction (ca. 3.50 Å), and two shuttlecock-like units form a "hand-shake" motif. The arrangement of the PTC4A ligand is similar to that of *p*-

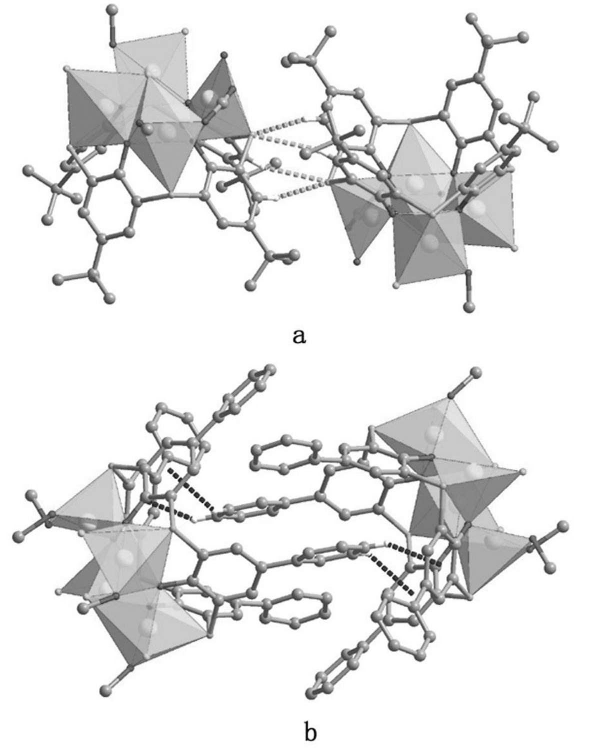

Figure 4. View of the tetranuclear units linked by supramolecular interactions showing the "up-down" fashion (a, in **3**) and "hand-shake" mode (b, in **4**) of thiacalix[4]arenes.

phenylcalix[4]arene reported by C. L. Raston.[15] The nearest inter-unit Cu···Cu separation is approximately 13.52 Å, which is rather longer than that in **3**. The distinct difference between the inter-unit Cu···Cu distances in these two compounds leads to obviously different extended structures, as shown in Figure S3. That is, the substitution of the *t*Bu group by *p*-phenyl group at the upper rim of thiacalix[4]arene affects the packing of the as-synthesized compounds a lot. In view of the attracting progresses achieved with TC4A and its derivatives,[4,7–10] especially in cluster chemistry, the PTC4A ligand would be another promising multidentate candidate for constructing polynuclear complexes.

Photoluminescence of Compounds 1 and 2

The d^{10} metal compounds are known to exhibit interesting photoluminescence properties.[16] In the present work, the photoluminescence of two Cu^I compounds (**1** and **2**) was examined in the solid state at room temperature, and the results are shown in Figure 5. For comparison, the photoluminescence of the free ligands was also studied. It is found that, in the solid state, both H_4TC4A and H_4PTC4A exhibit an emission upon excitation at 350 nm with maxima at 367 and 383 nm, respectively, which might be attributed to the intra-ligand $\pi^*\rightarrow\pi$ transition of the calixarene ligands. Compounds **1** and **2** both exhibit blue photoluminescence with emission peaks at approximately 410 and 470 nm for **1** and 403 and 467 nm for **2** upon excitation at 230 nm. The emission peaks at 410 and 403 nm should be assigned to the emission of the ligands. The redshifted peaks at 470 and 467 nm are in accordance with the photoluminescence properties of cuprous halide clusters, and the emissions may be attributed to a mixture of chlorine-to-copper charge transfer and d–s transitions due to Cu···Cu interactions within the Cu_2 cluster.[16,17]

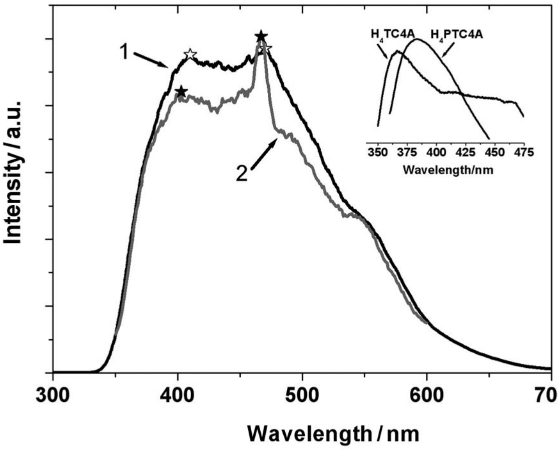

Figure 5. Emission spectra of compounds **1** and **2** in the solid state at room temperature (the inset shows emission spectra of H_4TC4A and H_4PTC4A in the solid state).

Magnetic Properties

To investigate interactions between the Cu^{II} ions in the similar tetranuclear units of **3** and **4**, the magnetic properties of compound **3** were studied. The temperature-dependent magnetic susceptibility of **3** was measured at 2–300 K with an applied field of 1000 Oe (Figure 6). The $\chi_M T$ value of **3** at 300 K is 1.49 $cm^3 mol^{-1} K$, which is consistent with that for four magnetically isolated Cu^{II} ions (1.50 $cm^3 mol^{-1} K$ with $S = 1/2$ and $g = 2$). Upon cooling, the $\chi_M T$ value decreases continuously to 0.42 $cm^3 mol^{-1} K$ at 50 K, and then keeps decreasing gradually to 0.19 $cm^3 mol^{-1} K$ at 2 K. The reciprocal susceptibility data of **3** above 150 K obeys the Curie–Weiss law with the Curie constant $C = +2.19\ cm^3 K mol^{-1}$ and the Weiss constant $\theta = -139.42$ K, which indicates dominant antiferromagnetic interactions between the metals. As reported, μ-phenoxido-bridged Cu^{II} cores with $Cu–O_{phenoxido}–Cu$ angles greater than 99° exhibit strong antiferromagnetic interactions with *J* values of several hundred wavenumbers.[18] Here the $Cu–O_{phenoxido}–Cu$ angles are in the range 109.0–118.5°, and our result obeys the normal trend for Cu^{II} cores bridged by μ-phenoxido ligands. Further interpretation of the magnetic properties cannot be carried out, because there are too many *J* volumes to be considered on the basis of the structural analysis.

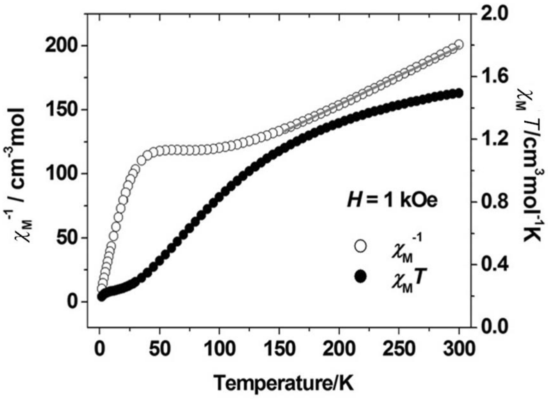

Figure 6. Plots of $\chi_M T$ and $1/\chi_M$ vs. *T* for **3** in a 1 kOe field (the solid line represents the Curie–Weiss fitting).

Conclusions

Two two-dimensional (2D) Cu^I–thiacalix[4]arene compounds **1** and **2** were solvothermally assembled and reassembled into two tetranuclear compounds of Cu^{II}, **3** and **4**, under ambient conditions. Compounds **1** and **2** present the first two examples with 2D layered structures for the thiacalixarene ligands, and their reassembled structures show two similar shuttlecock-like Cu^{II}_4-thiacalix[4]arene units that are arranged in different "up-down" and "handshake" modes due to different supramolecular interactions between calixarenes. This work provides some examples for the design of network/polynuclear materials using thiacalix[4]arene, especially the deep-cavity phenylthiacalix[4]-

arene, which might lead to some novel multifunctional materials. Our efforts to prepare similar compounds with other transition metal or lanthanide elements are ongoing.

Experimental Section

Materials and Measurements: *p-tert*-Butylthiacalix[4]arene and *p*-phenylthiacalix[4]arene were synthesized by literature methods,[19,11] and the other reagents were purchased from commercial sources and used as received. IR spectra (KBr pellets) were obtained with a Bruker Vertex 70 spectrometer. The TGA measurement was performed with a PYRIS DIAMOND instrument in the flow of N_2 with a heating rate of 10 °C min^{-1}. The photoluminescence spectra were recorded with a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer. The magnetic susceptibility measurement for **3** was performed with a Quantum Design MPMS XL-5 SQUID system in the range 2–300 K. Diamagnetic corrections for the sample and sample holder were applied to the data.

[$Cu^I_2Cl_2(H_4TC4A)](CH_3OH)$ (1): Colorless crystals of **1** were obtained from the reaction of the mixture of *p-tert*-butylthiacalix[4]-arene (0.1 g, 0.14 mmol), CuCl (0.06 g, 0.6 mmol), $CHCl_3$ (5 mL), CH_3OH (5 mL), and several drops of water in a 20 mL Teflon-lined autoclave, which was kept at 130 °C for 3 d and then slowly cooled to 20 °C at about 4 °C h^{-1}. The crystals of **1** were carefully picked out and washed with $CHCl_3$ for the measurements. Yield ≈ 70% with respect to calixarene. The result of the elemental analysis for this compound deviated much from the calculated values and is meaningless, because the solvent molecules involved in the lattices can be lost easily. The similar results were obtained for the other three compounds.

[$Cu^I_2Cl_2(H_4PTC4A)](CH_3OH)(CHCl_3)_{0.5}$ (2): The synthesis of **2** follows procedures similar to those for **1**; *p-tert*-butylthiacalix[4]-arene is replaced by *p*-phenyltetrathiacalix[4]arene (0.1 g, 0.125 mmol). Colorless crystals of **2** were carefully separated and collected for single-crystal X-ray diffraction and other measurements as well as the reassembly experiments. Yield ≈ 65% with respect to calixarene.

[$Cu^{II}_4Cl_3(HCO_2)(TC4A)(CH_3OH)_2(H_2O)](CHCl_3)(CH_3OH)_{2.7}$ (3): Upon being kept in the mother liquid at ambient conditions, colorless crystals of **1** gradually disappeared, and the colorless solution became dark. Black crystals of **3** appeared in several days, and the solutions became colorless again. The crystals were isolated by filtration and then washed with methanol/chloroform (1:1). Yield ≈ 45% with respect to calixarene.

[$Cu^{II}_4Cl_4(PTC4A)(CH_3OH)_4$] (4): When the colorless crystals of **2** (0.2 g, ca 0.05 mmol) were kept in CH_3OH (10 mL) under ambient conditions for several days, the colorless solution became dark, and then black crystals of **4** appeared. Yield ≈ 15% with respect to **2**.

X-ray Crystallography: The intensity data were recorded with a Bruker APEX-II CCD system with Mo-K_α radiation (λ = 0.71073 Å). The crystal structures were solved by means of direct methods and refined by employing full-matrix least-squares on F^2 (SHELXTL-97).[20] All non-hydrogen atoms were refined anisotropically except some solvent molecules, and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. Hydrogen atoms on solvent molecules could not be generated and were included in the molecular formula directly. In addition, the high R_1 and wR_2 factors for compounds **1**–**4** might be due to the weak high-angle diffractions and the disorders. All the crystal data and structure refinement details for these four compounds are given in Table 1. CCDC-735303, -735304, -735305, -735306 (for compounds **1**–**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): IR spectra, TG curves, extended structures of **3** and **4**, and table of selected bonds and angles for **1**, **2**, **3**, and **4**.

Table 1. Crystallographic data for compounds **1**–**4**.

	1	**2**	**3**	**4**
Formula	$C_{41}H_{52}Cl_2Cu_2O_5S_4$	$C_{49.5}H_{36.5}Cl_{3.5}Cu_2O_5S_4$	$C_{46.74}H_{66.96}Cl_6Cu_4O_{11.74}S_4$	$C_{52}H_{44}Cl_4Cu_4O_8S_4$
Formula wt.	951.05	1090.68	1411.71	1321.07
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	*C*2/*m*	*C*2/*m*	*C*2/*c*	$P\bar{1}$
a /Å	21.5395(10)	21.9382(13)	21.1690(5)	11.8305(9)
b /Å	18.3510(8)	18.2436(10)	22.4319(5)	11.9127(9)
c /Å	12.1941(6)	11.7748(7)	27.7993(6)	19.3412(14)
α /°	90	90	90	98.7220(10)
β /°	116.4550(10)	106.8100(10)	107.7130(10)	96.8670(10)
γ /°	90	90	90	101.1220(10)
V /Å^3	4315.3(3)	4511.3(5)	12575.0(5)	2612.4(3)
Z	4	4	8	2
T /K	187(2)	187(2)	150(2)	187(2)
D_c /g cm^{-3}	1.464	1.606	1.491	1.679
μ /mm^{-1}	1.345	1.385	1.773	2.025
F(000)	1976	2220	5786	1336
Total data	12038	12561	68549	15534
Unique data	3929	4112	11070	9094
R_{int}	0.0404	0.0578	0.0300	0.0434
GOF	1.057	1.102	1.134	0.981
$R1$[a] $[I>2\sigma(I)]$	0.0397	0.0611	0.0913	0.0553
$wR2$[b](all data)	0.1061	0.1962	0.2973	0.1578

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Acknowledgments

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