



## Guests inducing *p*-sulfonatocalix[4]arenes into nanocapsule and layer structure

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### ABSTRACT

Reaction of sodium *p*-sulfonatocalix[4]arene and TbCl<sub>3</sub> in the presence of 2,2'-bipyridine-*N,N'*-dioxide (bpdo) gives the 2:1 supramolecular nanocapsule  $[[\text{Tb}(\text{bpdo})_2 \cdots 4\text{H}_2\text{O}]^{3+} \cap \{p\text{-sulfonatocalix[4]arene}^{4-}\}_2]$ , which further interacts with the  $[\text{Tb}(\text{bpdo})_4]^{3+}$  through charge-assisted  $\pi$ -stacking interactions forming a channel structure **1**. In further investigation, we tried to use the terpyridine-1,1',1'-trioxide (tpto) instead of bpdo. Although we failed to isolate a supramolecular capsules based on the tpto, lanthanide and *p*-sulfonatocalix[4]arene, a layer structure derived from *p*-sulfonatocalix[4]arene with an unusual  $[\text{Cu}(\text{tpto})_2]^{2+}$  incorporation into the cavity of the calixarene and an outside  $[\text{Cu}(\text{tpto})_2]^{2+}$  balancing the charge, has been obtained. Fluorescence spectra show clearly that compound **1** possesses the luminescence characteristics of Tb<sup>3+</sup> and the ligand bpdo can sensitize Tb<sup>3+</sup> ion. Gas sorption experiment shows the channel structure **1** has highly selective gas sorption properties for water and methanol.

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### 1. Introduction

Water soluble sulfonated calix[*n*]arenes (*n*=4–8) as host molecules and building units have been attracting attention in the broad area of supramolecular chemistry and crystal engineering, showing potential applications in material science and biological science [1]. Among these calixarenes, *p*-sulfonatocalix[4]arene has been mostly investigated due to its ability to retain a cone conformation in both solution and the solid state and its ease of synthesis. *p*-Sulfonatocalix[*n*]arenes possessing the cavities show the inclusion properties for various guests such as organic molecules or metal complexes, and coordination abilities to metal ions; which make these hosts as versatile synthons for constructing supramolecular assemblies. The self-assembly sulfonated calix[*n*]arenes can afford various wonderful structures such as nanometer scale spheroidal, nanotube [2], stranded helices [3], bilayer [4], porous material [5], capsules [6], etc., which depend on the guest molecules and metal ions. Among these, the self-assembly sulfonated calix[*n*]arenes into multi-component capsule is a significant challenge that has been attracting attention in recent times. Most capsules focus on the use of the sulfonated calix[4,5]arenes to construct novel nanostructures by combining the supramolecular interactions

such as coordination, electrostatic, hydrogen-bonding, and van der Waals interactions. When suitable guests are employed in these systems, highly charge anionic capsules, or superanions, may be formed by the head to head dimerization of two such calixarenes. The sulfonated calix[4,5]arene capsules that are capable of encapsulating various guest molecules such as crown ethers or related macrocycles [6a,6b], amino acids [1c], phenanthroline [6c], H<sub>2</sub>SO<sub>4</sub> [7] and so forth have been established. Raston and co-workers [6] have made excellent work in these fields. Many of their work focus on the formation of 'Russian doll' inclusion complexes in which a guest molecule, mainly a crown ether or aza macrocycle, is sandwiched between two calixarenes. With torus shaped [18-crown-6], Atwood et al. [8] reported a spheroidal array of 12 calixarenes either in the form of an icosahedron or a cuboctahedron. When suitable guests and metal ions are employed in these systems, novel supramolecular capsules based on the sulfonated calix[4,5]arenes can be expected.

In our previous work, we used  $[\text{Cu}(\text{bpdo})_2 \cdot 2\text{H}_2\text{O}]^{2+}$  as a guest molecule inducing two *p*-sulfonatocalix[4]arenes into dimeric supramolecular capsule, which further interacted with  $[\text{Cu}(\text{bpdo})_3]^{2+}$  through charge-assisted  $\pi$ -stacking interaction forming a nanochannel structure [9,10]. In extending our investigation, we reason that the new supramolecular assemblies could be obtained through the use of the lanthanide ions (Ln<sup>3+</sup>) instead of transition metal M<sup>2+</sup> ions. According to the Cambridge Structural Database, different from the M<sup>2+</sup> ions, the Ln<sup>3+</sup> ions have larger coordination number. With the bpdo, it can form  $[\text{M}(\text{bpdo})_4]^{2+}$ . We also note that the conformation of  $[\text{M}(\text{bpdo})_2 \cdot 2\text{H}_2\text{O}]$  is different from the  $[\text{Ln}(\text{bpdo})_2 \cdot 4\text{H}_2\text{O}]^{3+}$ , which

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makes it uncertain whether the  $[\text{Ln}(\text{bpdo})_2 \cdot 4\text{H}_2\text{O}]^{3+}$  is an effective guest for the formation of similar supramolecular capsule. In this paper, we successfully used  $[\text{Tb}(\text{bpdo})_2 \cdot 4\text{H}_2\text{O}]^{3+}$  as a guest molecule inducing two *p*-sulfonatocalix[4]arenes into dimeric supramolecular capsule, which further interacts with the  $[\text{Tb}(\text{bpdo})_4]^{3+}$  through charge-assisted  $\pi$ -stacking interactions forming a nanoporous structure. In further investigation, we tried to use the tpto instead of bpdo. Although we failed to isolate a supramolecular capsule based on the tpto, lanthanide and *p*-sulfonatocalix[4]arene, a layer structure derived from *p*-sulfonatocalix[4]arene with an unusual  $[\text{Cu}(\text{tpto})_2]^{2+}$  incorporation into the cavity of the calixarene and an outside  $[\text{Cu}(\text{tpto})_2]^{2+}$  balancing the charges, has been prepared.

## 2. Results and discussion

The reaction of *p*-sulfonatocalix[4]arene sodium salt and bpdo in the presence of  $\text{TbCl}_3$  afforded suitable crystals for single-crystal X-ray diffraction and showed to be a hydrated complex. The reproducibility of the formation of the complex **1** was checked by repeated cell dimension determinations on different samples that appeared to be uniform morphology. Compound **1** crystallizes in triclinic space group *P*-1. The basic structural motif consists of  $\text{Na}^+$ ,  $[\text{Tb}(\text{bpdo})_4]^{3+}$ ,  $0.33[\text{Tb}(\text{bpdo})]^{3+}$ , and a supramolecular *p*-sulfonatocalix[4]arene nanocapsule in which the  $[\text{Tb}(\text{bpdo})_2 \cdot 4\text{H}_2\text{O}]^{3+}$  as guest is trapped (Fig. S1). The Tb centers of  $[\text{Tb}(\text{bpdo})_4]^{3+}$  and  $[\text{Tb}(\text{bpdo})_2 \cdot 4\text{H}_2\text{O}]^{3+}$  are octacoordinate and have approximate square anti-prismatic geometry. The  $[\text{Tb}(\text{bpdo})]^{3+}$  in the structure has a low distribution level (0.33 per asymmetric unit), which is essential in balancing the negative charge. Although we added enough bpdo for Tb ions (1:4) in this system,  $[\text{Tb}(\text{bpdo})_2 \cdot 4\text{H}_2\text{O}]^{3+}$  and  $[\text{Tb}(\text{bpdo})]^{3+}$  still exist in this system.

As shown in Figs. 1 and 2, the nanocapsule is composed of two *p*-sulfonatocalix[4]arenes and  $[\text{Tb}(\text{bpdo})_2 \cdot 4\text{H}_2\text{O}]^{3+}$ . Each calix[4]arene adopts the cone conformation with the cavity of each occupied by an aryl ring of the bpdo ligand. The cavity of *p*-sulfonatocalix[4]arene is the smallest in calixarene. This result indicates that new supramolecular assemblies can be expected when larger *p*-sulfonatocalix[5,6,8]arenes replace the *p*-sulfonatocalix[4]arene. For  $[\text{Tb}(\text{bpdo})_2 \cdot 4\text{H}_2\text{O}]^{3+}$ , the Tb(III) ion is coordinated four oxygen atoms from two bpdo ligands with the average distance 2.351 Å. In addition, the neighboring aryl rings of

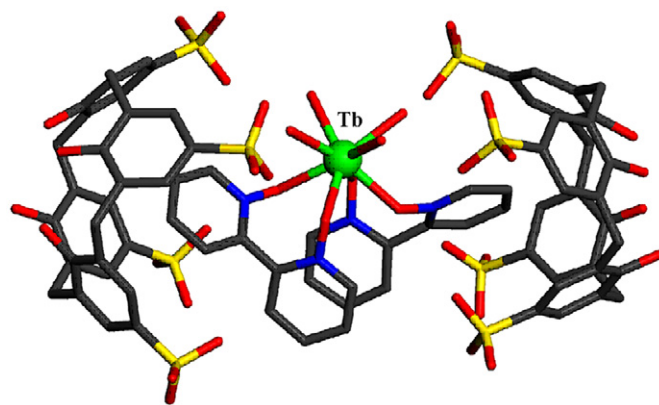


Fig. 2. Structure of the supramolecular nanocapsules based on the *p*-sulfonatocalix[4]arenes and  $[\text{Tb}(\text{bpdo})_2 \cdot 4\text{H}_2\text{O}]^{3+}$ .

the bpdo ligands have the obvious  $\pi \cdots \pi$  interactions with the centroid $\cdots$ centroid distance of 3.751 Å.

The two cones are bridged by  $[\text{Tb}(\text{bpdo})_2 \cdot 4\text{H}_2\text{O}]^{3+}$  through the charge-assisted  $\pi \cdots \pi$ , C–H $\cdots$  $\pi$ , and C–H $\cdots$ O interactions. The size of the capsule is about 19 Å. The included two aryl rings of the bpdo ligands have the charge-assisted  $\pi \cdots \pi$  interactions to the phenyl rings of the host calixarenes with the centroid $\cdots$ centroid distances of 4.098, 4.497, 4.474, and 4.280 Å. Two neighboring aryl hydrogens from each of two included aryl rings are directed towards the aromatic rings of the calixarenes with CH $\cdots$  $\pi$  interactions (CH $\cdots$ centroid distances = 2.614, 2.680, 2.680, and 2.657 Å). Some aryl hydrogens of the included bpdo ligands interact through C–H $\cdots$ O hydrogen bonds to the neighboring sulfonic groups of *p*-sulfonatocalix[4]arene with the distances from 3.227 to 3.567 Å. Although hydrogen atoms of four coordinated water of  $[\text{Tb}(\text{bpdo})_2 \cdot 4\text{H}_2\text{O}]^{3+}$  are not located, hydrogen bonds with the neighboring sulfonic groups of *p*-sulfonatocalix[4]arenes are implied by short O $\cdots$ O contacts (O $\cdots$ O distances = 2.724, 2.787, 2.770, and 2.799 Å).

One  $[\text{Tb}(\text{bpdo})_4]^{3+}$  owns eight aryl rings, which affords enough aryl rings and aryl hydrogens through  $\pi \cdots \pi$ , CH $\cdots$  $\pi$ , and C–H $\cdots$ O interactions with the six neighboring *p*-sulfonatocalix[4]arenes. The  $[\text{Tb}(\text{bpdo})_4]^{3+}$  interacts through four  $\pi \cdots \pi$  interactions to the four neighboring calixarenes with the centroid $\cdots$ centroid distances of 3.585, 3.568, 3.677, and 3.783 Å, and two CH $\cdots$  $\pi$  interactions to another two calixarenes with CH $\cdots$ centroid distances 2.711 and 2.910 Å (Fig. S2). In addition, the  $[\text{Tb}(\text{bpdo})_4]^{3+}$  is involved in lots of C–H $\cdots$ O interactions with the phenol and sulfonic groups of neighboring calixarenes.

The  $[\text{Tb}(\text{bpdo})_4]^{3+}$  and calixarenes form a layered structure where the calixarenes are in bilayer arrangement. Two neighboring calixarenes interact with each other through the  $\pi \cdots \pi$  interactions with the centroid $\cdots$ centroid distance of 3.587 Å, which further interact through charge-assisted  $\pi \cdots \pi$  interactions and CH $\cdots$  $\pi$  interactions to the four neighboring  $[\text{Tb}(\text{bpdo})_4]^{3+}$  forming a layer structure (Fig. 3). The surface of the layer is full of cavities, which are occupied by the aryl rings of  $[\text{Tb}(\text{bpdo})_2 \cdot 4\text{H}_2\text{O}]^{3+}$ . As shown in Fig. 4, the supramolecular layers are separated by the  $[\text{Tb}(\text{bpdo})_2 \cdot 4\text{H}_2\text{O}]^{3+}$  forming tetragonal channel structure. There are two kinds of large channels, ca. 1 nm, in diameters filled with water molecules. From Fig. 4, we can also say that two capsules set up two sides of the tetragonal pore, while two  $[\text{Tb}(\text{bpdo})_4]^{3+}$  occupy the other two sides. The surface of the pores has many sulfonic groups and this porous material can be dissolved in hot water.

It is interesting to contrast the structure of **1** with the aforementioned 'Russian doll' inclusion complexes. The common

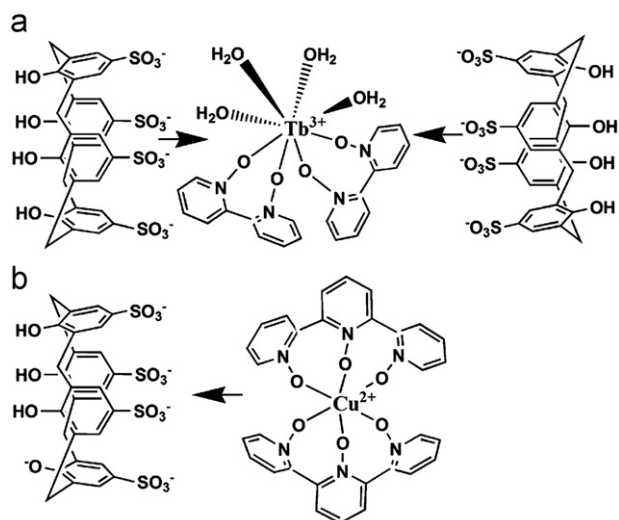


Fig. 1. (a) Schematic diagram showing the interplay of *p*-sulfonatocalix[4]arenes with  $[\text{Tb}(\text{bpdo})_2 \cdot 4\text{H}_2\text{O}]^{3+}$ . (b) Schematic diagram showing the interplay of *p*-sulfonatocalix[4]arene with  $[\text{Cu}(\text{tpto})_2]^{2+}$ .

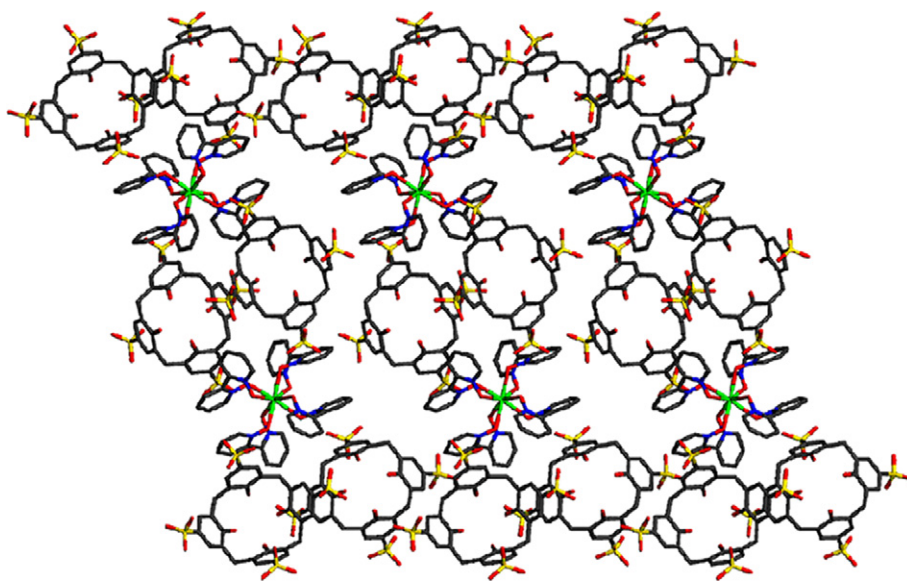


Fig. 3. A layered structure consist of the *p*-sulfonatocalix[4]arene and the  $[\text{Tb}(\text{bpdo})_4]^{3+}$ .

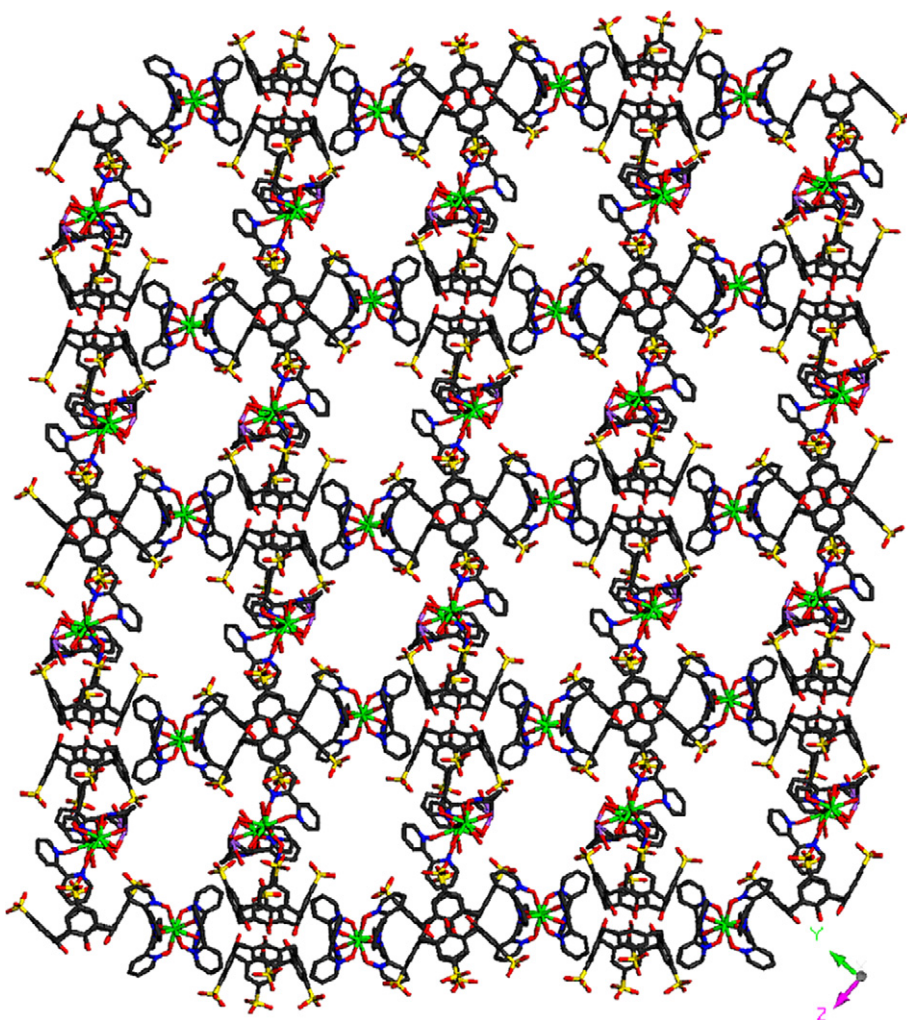


Fig. 4. The packing diagram down the *a*-axis showing the porous structure, the dissociative water molecules are omitted for clarity.

structural characteristic in both cases is that all these capsules are formed by the head to head dimerization of two such calixarenes, and the guests shroud the two calixarenes through

supramolecular interactions. In this case, the capsules are separated by the  $[\text{Tb}(\text{bpdo})_4]^{3+}$ , resulting in the formation of channels down the *a*-axis within the structure.

In our extending investigation, we reason that the new supramolecular assemblies could be obtained through the use of the terpyridine-1,1',1'-trioxide (tpto) instead of bpdo. As we all know, tpto has larger size than tpto, which has different supramolecular and coordinated behavior with bpdo. Meanwhile, the cavity of *p*-sulfonatocalix[4]arene is easy to embrace phenyl rings, which indicates tpto may be a suitable guest for calixarene. However we only isolated the crystals of compound **2**.

Complex **2** belongs to the triclinic crystal system, crystallizing in the space group *P*–1. Fig. 5 shows the basic unit of **2**, which indicates the supramolecular interactions between the *p*-sulfonatocalix[4]arene and  $[\text{Cu}(\text{tpto})_2]^{2+}$ . The basic structural motif consists of  $\text{Na}^+$ , two  $[\text{Cu}(\text{tpto})_2]^{2+}$ , *p*-sulfonatocalix[4]arenes<sup>5-</sup> and water molecules. In this structure, there are two crystallographic positions for the copper ions and both the copper sites are six-fold coordinated by the six oxygen atoms of tpto ( $\text{Cu}-\text{O}=1.937(3)-2.333(3)\text{\AA}$ ) and have approximate octahedral geometry. There are two kinds of  $[\text{Cu}(\text{tpto})_2]^{2+}$ , one trapped inside the cavity of calixarene, and the other outside  $[\text{Cu}(\text{tpto})_2]^{2+}$  balancing the negative charges. In  $[\text{Cu}(\text{tpto})_2]^{2+}$ , two aryl rings of tpto orthogonal to the aryl rings of the other tpto have involved in  $\text{CH}\cdots\pi$  interactions, with  $\text{CH}\cdots$ centroid distances of 3.013, 3.191, 3.196, and 3.310 Å, and angles of 143.36°, 144.90°, 143.02°, and 141.59°, respectively (Fig. S3). *p*-Sulfonatocalix[4]arene takes on an overall charge of –5, with one of the hydroxy groups being deprotonated.

The inside  $[\text{Cu}(\text{tpto})_2]^{2+}$  interacts with host calixarene through charge-assisted  $\text{CH}\cdots\pi$  and  $\text{C}-\text{H}\cdots\text{O}$  interactions. The included aryl ring of the tpto ligand has two charge-assisted  $\text{CH}\cdots\pi$  interactions to the phenyl rings of the host calixarene ( $\text{CH}\cdots$ centroid distances=2.794 and 2.818 Å;  $\text{CH}\cdots$ centroid angles=126.54° and 135.13°). The inside  $[\text{Cu}(\text{tpto})_2]^{2+}$  is also involved in lots of  $\text{C}-\text{H}\cdots\text{O}$  interactions with the sulfonic groups of host calixarene ( $\text{CH}\cdots\text{O}$  distances=3.403, 3.234, 3.257, and 3.322 Å;  $\text{C}-\text{H}\cdots\text{O}$  angles=148.22°, 120.90°, 133.46°, and 115.14°). Although hydrogen atoms of the coordinated water molecules of  $\text{Na}^+$  were not located, hydrogen bonds with the neighboring sulfonic groups of host calix[4]arene and the oxygen atoms of tpto are implied by short  $\text{O}\cdots\text{O}$  contacts ( $\text{O}\cdots\text{O}=2.721, 2.884, 2.871, \text{ and } 2.897\text{\AA}$ ). The included  $[\text{Cu}(\text{tpto})_2]^{2+}$  has obvious charge-assisted  $\pi\cdots\pi$  interactions with the neighboring calixarenes with the centroid $\cdots$ centroid distances of 3.819 Å. As shown in Fig. 6, the included  $[\text{Cu}(\text{tpto})_2]^{2+}$  bridges the calixarenes forming a columnar array.

As shown in Figs. 7 and S4, these columnar arrays are linked by sodium ions forming a layer structure ( $\text{Na}-\text{O}$  distance=2.672(6) and 2.716(5) Å). The neighboring calixarenes, which are bridged by the sodium ions have no  $\pi\cdots\pi$  stacking interactions. A striking feature of the structure is the intercalation of outside  $[\text{Cu}(\text{tpto})_2]^{2+}$  between the neighboring calixarenes through charge-assisted  $\pi$ -stacking

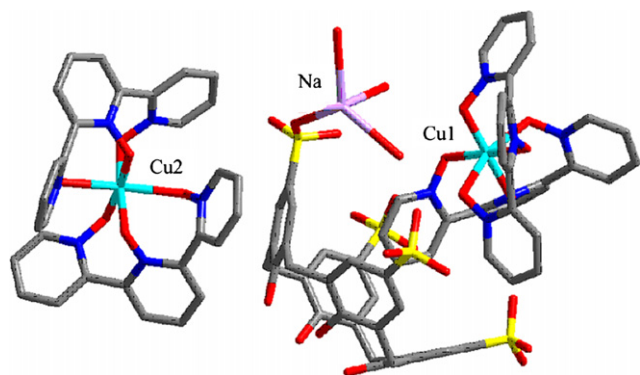


Fig. 5. The asymmetric unit of compound **2**.

interactions with the centroid $\cdots$ centroid distances of 3.690 and 3.773 Å (Fig. 8). Meanwhile, the  $[\text{Cu}(\text{tpto})_2]^{2+}$  is involved in  $\text{C}-\text{H}\cdots\text{O}$  interactions with the phenol of calixarene ( $\text{CH}\cdots\text{O}$  distances=3.260 and 3.403 Å;  $\text{C}-\text{H}\cdots\text{O}$  angles=159.22° and 152.69°). In addition,  $[\text{Cu}(\text{tpto})_2]^{2+}$  is also involved in  $\text{C}-\text{H}\cdots\text{O}$  interactions with the sulfonic groups of calixarene of neighboring polymer ( $\text{CH}\cdots\text{O}$  distances=3.581 and 3.819 Å;  $\text{C}-\text{H}\cdots\text{O}$  angles=148.22° and 157.03°).

The packing diagram for structure **2** shows that the neighboring layers in which the calixarenes oriented in opposite directions are stacking together forming a double-layer structure (Fig. 9). The included  $[\text{Cu}(\text{tpto})_2]^{2+}$  has obvious charge-assisted  $\text{C}-\text{H}\cdots\text{O}$  interactions with the calixarenes of the neighboring layers ( $\text{CH}\cdots\text{O}$  distance=3.146 Å,  $\text{C}-\text{H}\cdots\text{O}$  angle=128.77°). The common structural characteristic in compounds **1** and **2** is that both the cavities of host calixarenes include an aryl of guest through  $\text{CH}\cdots\pi$  interactions. However, in the compound **2**, the guest  $[\text{Cu}(\text{tpto})_2]^{2+}$  has larger size, which leads to the failure of  $[\text{Cu}(\text{tpto})_2]^{2+}$  to form supramolecular capsule.

The excitation spectra of compound **1** by monitoring the  $\text{Tb}^{3+}$  emission at 543 nm are shown in Fig. 10. The excitation spectrum shows a maximum peak at 296 nm with two shoulders at 368 and 377 nm. The former is due to the absorption of the ligand, and the latter (two shoulders) is due to the *f-f* electrons transitions of  $\text{Tb}^{3+}$ . Fig. 10 shows the photoluminescence spectra of the compound **1** excited by the maximum excitation wavelength at 296 nm. The emission spectra consist of the characteristic emission lines of the  $\text{Tb}^{3+}$ , i.e.,  ${}^5\text{D}_4\rightarrow{}^7\text{F}_6$  (489 nm),  ${}^5\text{D}_4\rightarrow{}^7\text{F}_5$  (543 nm),  ${}^5\text{D}_4\rightarrow{}^7\text{F}_4$  (split at 582 and 590 nm),  ${}^5\text{D}_4\rightarrow{}^7\text{F}_3$  (621 nm). The luminescence of the complex is from all  $\text{Tb}(\text{III})$  species. Due to the effect of the coordinated water, the energy transfer from ligand to metal in the  $[\text{Tb}(\text{bpdo})_4]^{3+}$  is better than that in the  $[\text{Tb}(\text{bpdo})_2\cdot 4(\text{H}_2\text{O})]^{3+}$ . So the former contributes more to the luminescence of the complex. The decay curves of  $\text{Tb}^{3+}$  ions are shown in Fig. S5. It can be fitted by double-exponential functions, showing that the  $\text{Tb}^{3+}$  ions lie in the different chemical environment. The lifetimes of  ${}^5\text{D}_4\rightarrow{}^7\text{F}_5$  transition of compound **1** are 0.31 ms (75.6%) and 0.08 ms (24.4%).

The solvent-accessible volume of the unit cell of **1** was estimated, (PLATON program) to be 3460.8 Å<sup>3</sup>, which is approximately 35.5% of the unit-cell volume (9751.6 Å<sup>3</sup>). The powder XRD pattern of compound **1** at room temperature is not fitted well with the simulated from the single-crystal data due to the weak diffraction quality of compound **1** (Fig. S9). After evacuated at 150 °C for 5 h, powder XRD patterns of compound **1** was different from the simulated from the single-crystal data, which showed that the compound changed structure. It also looks like the crystals lost their crystallinity upon drying and the corresponding materials were therefore amorphous prior to adsorption measurements. To confirm the porosity of **1**, gas sorption experiments were carried out (Fig. 11). The adsorption isotherms **1** for ethanol and acetone at 298 K revealed no obvious inclusion by the framework. For methanol and water, uptakes of 19.0 and 16.5 wt% were observed at  $P/P_0=1$  in **1**, respectively, which shows the compound **1** has the selective guest sorption properties for water and methanol. Meanwhile the result indicates the channels of compound **1** shrink and still possess the pores after activated.

### 3. Conclusion

In summary, a novel porous material based on the  $[\text{Tb}(\text{bpdo})_4]^{3+}$  and *p*-sulfonatocalix[4]arene nanocapsule has been established and its structure was determined by X-ray crystallographic analysis. Gas sorption experiments showed the porous materials have selective gas sorption properties. In further investigation, a novel layer material based on the  $[\text{Cu}(\text{tpto})_2]^{2+}$  and *p*-sulfonatocalix[4]arenes has also been established. In

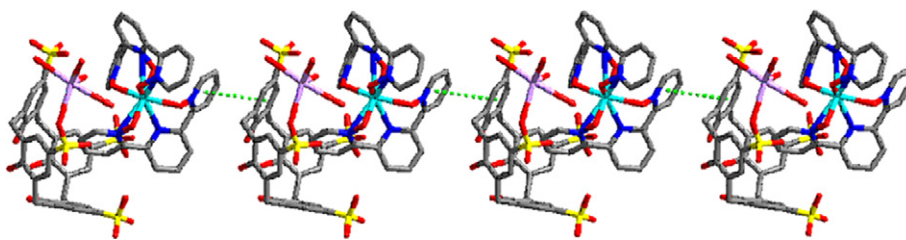


Fig. 6. The include  $[\text{Cu}(\text{tpdo})_2]^{2+}$  bridge the calixarenes forming a columnar arrays.

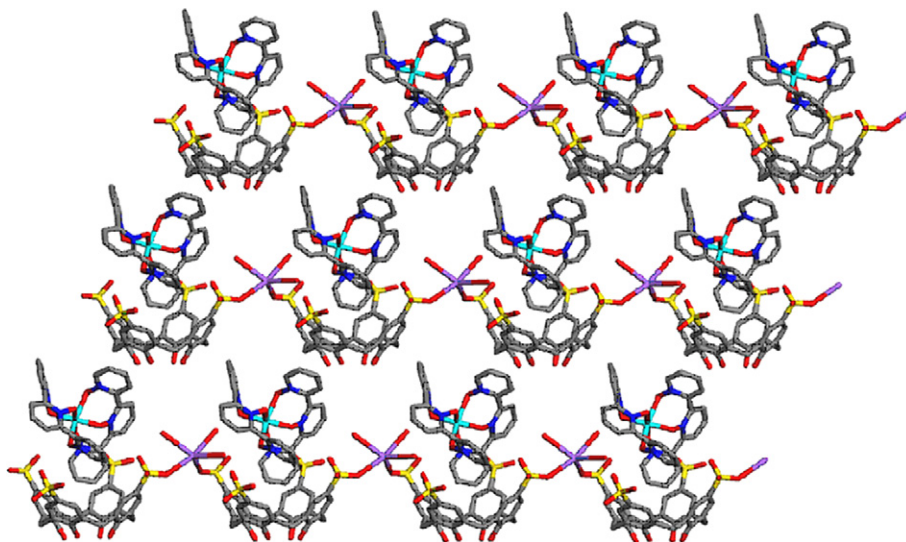


Fig. 7. The columnar arrays are linked by sodium ion forming a layer structure.

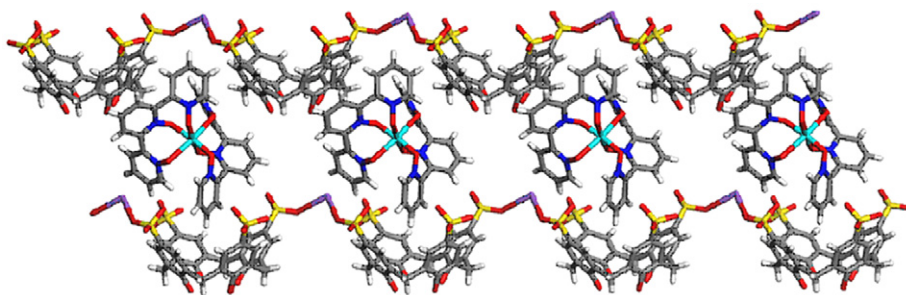


Fig. 8. The intercalation between the calixarene and outside  $[\text{Cu}(\text{tpdo})_2]^{2+}$ .

addition, the structures demonstrated that  $[\text{Tb}(\text{bpdo})_2 \cdot 4\text{H}_2\text{O}]^{3+}$  can be as effective guest to induce the *p*-sulfonatocalix[4]arenes into supramolecular nanocapsule. All these results suggest rich supramolecular/crystal engineering possibilities for materials built up from  $[\text{M}(\text{L})_a]^{b+}$  ( $M$ =transition metal or lanthanide metal;  $a=2$ ;  $b=2$  or 3;  $L$ =bpdo or tpdo) and *p*-sulfonatocalix[5,6,8]arenes, and this is likely to lead into larger arrays such as nanocapsules, nanospheres, and nanorods. Meanwhile, endeavors to investigate the inclusion complexation of calix[5,6, and 8]arenes with above guests are going on.

## 4. Experimental section

### 4.1. Characterization

The powder X-ray diffraction (XRD) of the compounds **1** and **2** were examined on a Rigaku-Dmax 2500 diffractometer using  $\text{Cu } K\alpha$  radiation ( $\lambda=0.15405 \text{ nm}$ ). The vapor-phase adsorption

measurements of organic molecules on the products were performed at  $25^\circ\text{C}$  on a VTI MB-300G Gravimetric Sorption Analyzer. Fourier transform infrared (FTIR) spectra were measured within the  $4000\text{--}400 \text{ cm}^{-1}$  wavenumber range using a Perkin-Elmer model 580B IR spectrophotometer with the KBr pellet technique. Thermogravimetric analysis (TGA) was performed on a SDT2960 analyzer (Shimadzu, Japan) up to  $700^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  under  $\text{N}_2$ . The luminescence photoluminescence spectra were obtained with a Fluorolog spectrophotometer equipped with a 450 W xenon lamp as the excitation source. The luminescence decay curve of the emitting levels of compound **1** was recorded under excitation at 296 nm with the third harmonic of a Spectra-physics Nd:YAG laser (using a 5 ns pulse width and 5 mJ of energy per pulse) as the excitation source. The luminescence lifetimes were calculated by Origin 7.0 software package.

Bpdo, tpdo [11], and *p*-sulfonatocalix[4]arene [12] were prepared by literature methods, whilst other reagents were purchased without further purification.

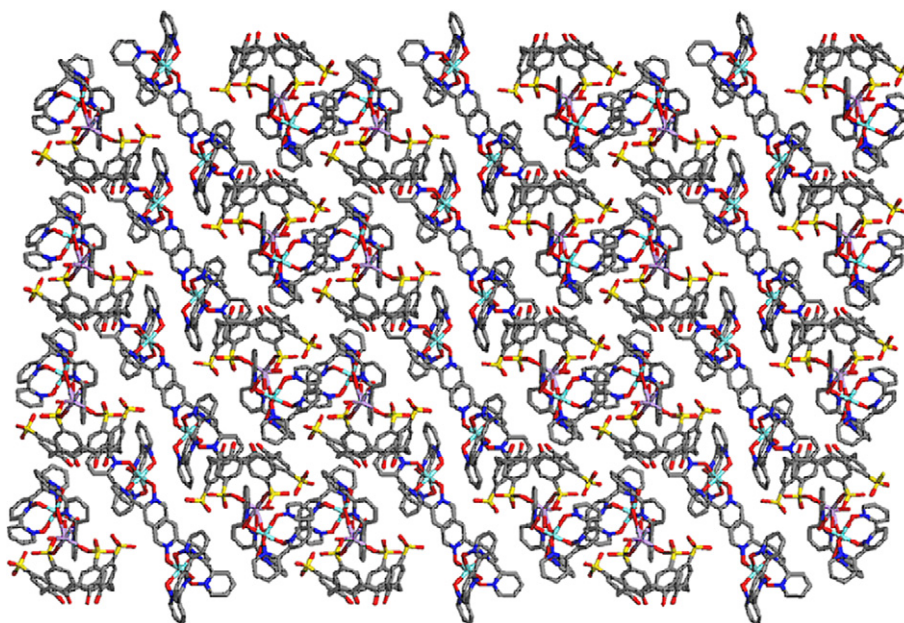


Fig. 9. The calixarenes are orient in opposite direction forming a double-layer structure.

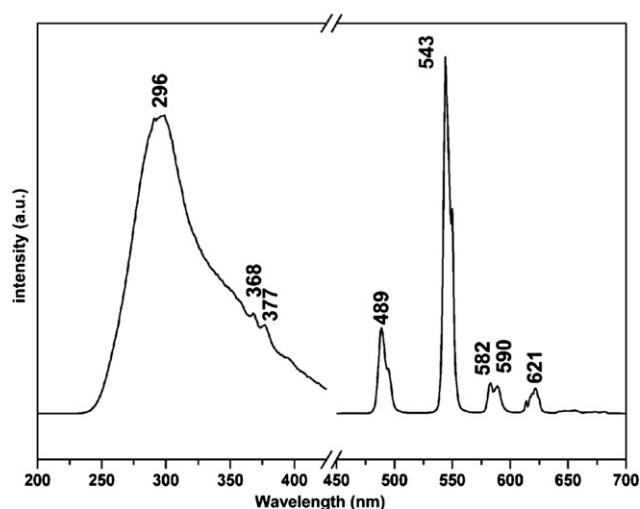


Fig. 10. The excitation and emission spectra of compound **1** in the solid state.

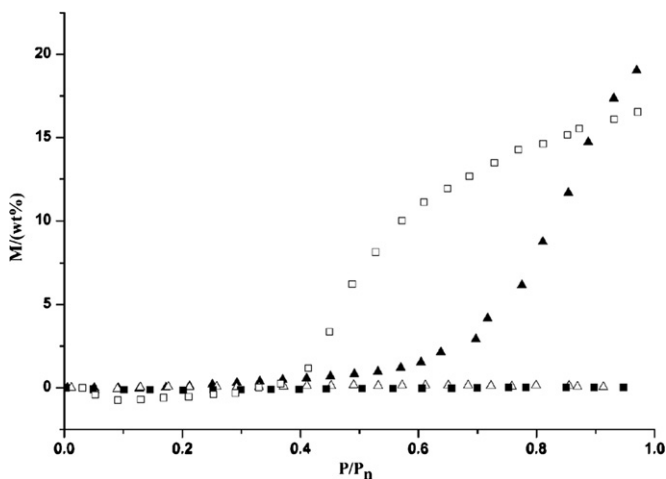


Fig. 11. Vapor-adsorption isotherm curves of compound **1** at 298 K: water ( $\square$ ), methanol ( $\blacktriangle$ ), ethanol ( $\triangle$ ), acetone ( $\blacksquare$ ).

**Synthesis of compound 1:** Mixture of  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  (0.285 g, 0.75 mmol),  $\text{Na}_4[\text{p-sulfonato-calix[4]arene}]$  (0.416 g, 0.5 mmol), and bpdo (0.423 g, 2.25 mmol) was dissolved in hot water (3:2:9, pH=3). Colorless crystals of the title compound **1** were obtained after volatilizing at room temperature (0.396 g, the yield was not calculated because the disordered water molecules have been subtracted from the structure). IR: sulfonate absorption: 1039s, 1117m, 1155s, 1213s, 1262m  $\text{cm}^{-1}$ .

**Synthesis of compound 2:** Mixture of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.085 g, 0.5 mmol)  $\text{Na}_5[\text{p-sulfonato-calix[4]arene}]$  (0.215 g, 0.25 mmol) and tpto (0.281 g, 1 mmol) (pH=5) was dissolved in hot water (2:1:4). After several days, deep green crystals of the title compound **2** were obtained after volatilizing at room temperature (0.325 g, yield 53%). IR: sulfonate absorption: 1041s, 1117m, 1194s, 1213s, 1272m  $\text{cm}^{-1}$ . Microanalysis (CHN) was not feasible due to the highly hydrated nature of the compounds.

#### 4.2. Crystal structure determinations

Data were collected on a Bruker SMART 1000 CCD diffractometer with  $\text{MoK}\alpha$  radiation using the  $\omega$ -scan mode ( $\lambda=0.71069 \text{ \AA}$ ). Data were corrected for absorption using the SADABS program. The structures were solved by direct methods using SHELXS-97 and refined by means of full-matrix least-squares techniques using the SHELXL-97 program as implemented in WINGX. The positions of hydrogen atoms attached to carbon were generated geometrically.

**Crystal/refinement details for 1:**  $\text{C}_{119.33}\text{H}_{99.33}\text{N}_{12.67}\text{NaO}_{54.17}\text{S}_8\text{Tb}_{2.33}$ ,  $M=3227.73$ . The compound **1** crystallized in the space group  $P-1$ , triclinic,  $a=16.9184(8) \text{ \AA}$ ,  $b=24.1640(11) \text{ \AA}$ ,  $c=25.8181(12) \text{ \AA}$ ,  $\alpha=97.3160(10)^\circ$ ,  $\beta=106.2180(10)^\circ$ ,  $\gamma=101.2820(10)^\circ$ ,  $V=9751.6(8) \text{ \AA}^3$ ,  $Z=2$ ,  $T=193 \text{ K}$ ,  $\lambda=0.71073 \text{ \AA}$ ,  $R_{\text{int}}=0.0370$ ; A total of 50,679 reflections were collected in the range  $1.65 < \theta < 25.00$ , of which 33,806 were unique.  $\text{GOF}=0.989$ ,  $R_1=0.1071$ ,  $wR_2$  (all data)=0.2080. Non-hydrogen atoms except some water molecules (O52–O59) were refined anisotropically. The disordered solvent to the diffraction pattern of compound **1** was subtracted from the observed data by the “SQUEEZE” method as implemented in PLATON (P. van der Sluis, A.L. Spek, Acta Crystallogr., Sect. A 1990, 46, 194).

**Crystal/refinement details for 2:**  $C_{88}H_{110}Cu_2N_{12}NaO_{51}S_4$ ,  $M=2430.19$ . The complex crystallized in the space group  $P-1$ , triclinic,  $a=14.2392(12)\text{Å}$ ,  $b=14.2756(12)\text{Å}$ ,  $c=27.679(2)\text{Å}$ ,  $\alpha=93.3830(10)^\circ$ ,  $\beta=91.6800(10)^\circ$ ,  $\gamma=112.2900(10)^\circ$ ,  $V=5188.8(8)\text{Å}^3$ ,  $Z=2$ ,  $T=193\text{K}$ ,  $\lambda=0.71073\text{Å}$ ,  $R_{\text{int}}=0.0265$ . A total of 29,074 reflections were collected in the range  $1.48 < \theta < 26.09$ , of which 19,997 were unique.  $GOF=1.041$ ,  $R_1$  (all data)=0.0959,  $wR_2$  (all data)=0.2209. Non-hydrogen atoms were refined anisotropically. CCDC-688431, 698352 contains 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](http://www.ccdc.cam.ac.uk/data_request/cif).

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2010.04.025](https://doi.org/10.1016/j.jssc.2010.04.025).

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