Constructing channel structures based on the assembly of *p*-sulfonatocalix[4]arene nanocapsules and $[M(bpdo)_3]^{2+}$ (M = Cu, Zn)†

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Novel channel structures based on $[M(bpdo)_3]^{2+}$ and *p*-sulfonatocalix[4]arene nanocapsules have been established; these are sustained exclusively by charge-assisted $\pi\cdots\pi$ interactions and sorption experiments show the porous materials have selective guest sorption properties.

Calixarenes as building blocks have been widely used in the fields of coordination and supramolecular chemistry due to their novel structures and potential applications in materials science.[1] The self-assembly of calixarenes with metal ions and organic molecules can afford various, wonderful supramolecular structures, such as porous structures,[2] molecular capsules,[3] bilayers[4] and 2- and 3D coordination polymers.[5] Among these compounds, the self-assembly of calixarenes into porous structures is a significant challenge that has attracted attention in recent times. Choosing appropriate calixarenes as building units can lead to extended porous networks, with unusual pore architectures and functions, which are held together either by strong metal–ligand bonding or by weak bonding forces such as hydrogen-bonds and π–π interactions. Recently chemists have paid their attentions to constructing porous structures based on water-soluble sulfonated calixarenes due to their interesting biological behaviours and potential application in building new synthetic materials.[6] Nevertheless, the self-assembly of sulfonated calixarenes into porous materials has rarely been reported.[7]

In this *communication*, we report a channel structure **1**, based on the guest-induced *p*-sulfonatocalix[4]arene nanocapsule and $[Cu(bpdo)_3]^{2+}$ (2,2′-bipyridine-*N*,*N*′-dioxide, bpdo). The sulfonatocalix capsules can be induced by suitable guest molecules by a combination of supramolecular interactions, such as coordination, electrostatic, hydrogen-bonding, and van der Waals interactions. When suitable guests, such as crown ethers or related macrocycles, amino acids, phenanthroline, H_2SO_4 *etc.*, are employed in these systems, highly-charged anionic capsules, or superanions, may be formed by the head-to-head dimerisation of two such calixarenes.[6,7b,8] Raston and co-workers have made excellent progress in this field and afforded many molecular capsules and 'Russian doll' inclusion complexes, in which a guest molecule, mainly a crown ether or aza macrocycle, is sandwiched between two calixarenes.[3] Changing the included molecule from pyridine *N*-oxide to [18-crown-6], Atwood and co-workers reported sulfonatocalix capsules packed into an icosahedron or a cuboctahedron, which is a dramatically different spheroidal array.[9] Inspired by their work, we reasoned that by subtly altering guest molecules or other factors, new supramolecular sulfonatocalix capsules could be expected. In our compound, $[Cu(bpdo)_2{\cdot}2H_2O]^{2+}$ successfully acts as a guest molecule, inducing two *p*-sulfonatocalix[4]arenes to form a dimeric supramolecular capsule (Fig. 1). This further interacts with the $[Cu(bpdo)_3]^{2+}$ through charge-assisted π-stacking interactions, forming a channel structure, the precursor to a porous material once activated.

For this *communication*, we chose bpdo as the guest ligand based on the following considerations: (1) according to the literature, 2,2′-bipyridine is a good guest for *p*-sulfonatocalix[4]arenes, which suggests that bpdo may be a potential guest;[10] (2) unlike 2,2′-bipyridine, it is soluble in aqueous solution, which makes it easy to obtain single crystals suitable for X-ray diffraction from the water solution; (3) a survey of the Cambridge Structural Database shows that bpdo can form various complexes with metal ions under different conditions, making some metal bpdo complexes potential guest molecules for *p*-sulfonatocalix[4]arenes. The reaction of $CuCl_2$, Na_4[*p*-sulfonatocalix[4]arene] and bpdo in a 3 : 2 : 9 molar ratio (pH = 5) afforded deep green crystals which were characterised using single crystal X-ray diffraction, and shown to be a hydrated compound **1**.‡

The asymmetric unit of compound **1** consists of Na^+, two $[Cu(bpdo)_3]^{2+}$, $[Cu(bpdo)_2{\cdot}2H_2O]^{2+}$, two *p*-sulfonatocalix[4]arenes and water molecules (Fig. S1†). In this structure, there

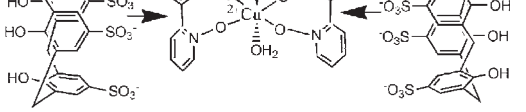

Fig. 1 Schematic diagram showing the interplay between *p*-sulfonatocalix[4]arenes and $[Cu(bpdo)_2{\cdot}2H_2O]^{2+}$.

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† Electronic supplementary information (ESI) available: Syntheses of compounds **1** and **2**, crystallographic information, supplementary figures, XRD and TGA of the compounds. CCDC reference numbers 686535 and 686536. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b807584k

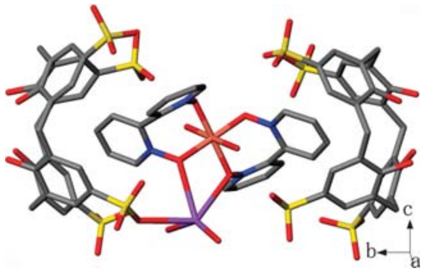

Fig. 2 Structure of the supramolecular nanocapsules based on the *p*-sulfonatocalix[4]arenes and $[Cu(bpdo)_2{\cdot}2H_2O]^{2+}$.

are three crystallographic positions for the copper ions and all the copper sites are six-old coordinated and have approximate octahedral geometry. In this work, the bpdo acts as ligand forming two different complexes with copper ions. Although we added excess bpdo for Cu ions (1 : 4) in a repeated experiment, $[Cu(bpdo)_2{\cdot}2H_2O]^{2+}$ as a guest still exists in this capsule. The two copper complexes carried out three functions: (1) balancing the negative charge; (2) the $[Cu(bpdo)_2{\cdot}2H_2O]^{2+}$ as a guest induces **1** into the dimeric capsule; (3) the $[Cu(bpdo)_3]^{2+}$ as building units are stacked with the supramolecular nanocapsule, forming a channel structure.

The nanocapsule is composed of two *p*-sulfonatocalix[4]-arenes, a sodium ion and $[Cu(bpdo)_2{\cdot}2H_2O]^{2+}$ (Fig. 2). Two *p*-sulfonatocalix[4]arenes take on an overall charge of −7, with one of the sulfonic groups being protonated. The $[Cu(bpdo)_2{\cdot}2H_2O]^{2+}$ bridges the two cones through charge-assisted π···π, C–H···π, and C–H···O interactions. The included two aryl rings of the bpdo ligands have weak π···π interactions to the phenyl rings of the host calixarenes with centroid···centroid distances of 3.816 and 3.923 Å. Two neighbouring aryl hydrogens from each of the two included bpdo ligands are directed towards the aromatic rings of the calixarenes with CH···π interactions (CH···centroid distances = 2.504, 2.641, 2.508 and 2.936 Å). Some aryl hydrogens of the included bpdo ligands interact through C–H···O hydrogen bonds to the neighbouring sulfonic groups of *p*-sulfonatocalix[4]arene, with distances from 3.218 to 4.036 Å. Although the hydrogen atoms of the two coordinated water molecules of $[Cu(bpdo)_2{\cdot}2H_2O]^{2+}$ were not located, hydrogen bonds with the neighbouring sulfonic groups of *p*-sulfonatocalix[4]arene are implied by short O···O contacts (O···O = 2.738 and 2.804 Å). In addition, the $[Cu(bpdo)_2{\cdot}2H_2O]^{2+}$ and one *p*-sulfonatocalix[4]arene are bridged by a sodium ion.

One $[Cu(bpdo)_3]^{2+}$ contains six aryl rings, which afford enough aryl rings and aryl hydrogens for charge-assisted π···π, CH···π, and C–H···O interactions with the neighbouring *p*-sulfonatocalix[4]arenes. The $[Cu(bpdo)_3]^{2+}$ and calixarenes form a layered structure in which the calixarenes are in a bilayer arrangement (Fig. 3). Two neighbouring calixarenes are held together through π···π interactions, with centroid···centroid distances of 3.500 Å, and further interact through charge-assisted π···π interactions and CH···π interactions with the neighbouring $[Cu(bpdo)_3]^{2+}$, forming the layer structure (Fig. 3 and Fig. S2†). The surfaces of the layers are full of cavities which are occupied by the aryl rings of $[Cu(bpdo)_2{\cdot}2H_2O]^{2+}$, that is to say the layers are separated by $[Cu(bpdo)_2{\cdot}2H_2O]^{2+}$ forming a tetragonal channel structure (Fig. 4).

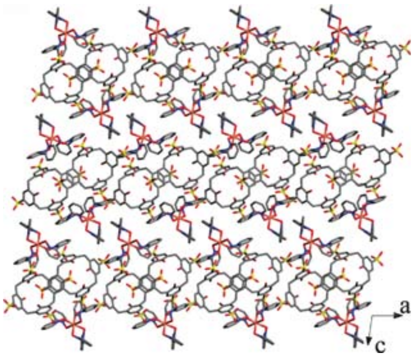

Fig. 3 A layered structure consisting of the *p*-sulfonatocalix[4]arenes and $[Cu(bpdo)_3]^{2+}$.

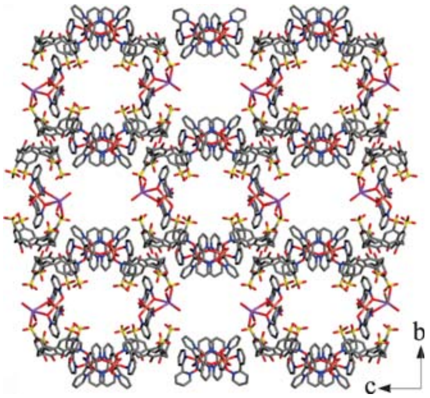

Fig. 4 The packing diagram shown down the *a* axis, showing the channel structure; the dissociative water molecules are omitted for clarity.

As shown in Fig. 4 and Fig. S3,† two capsules set up two sides of the tetragonal pore, while the $[Cu(bpdo)_3]^{2+}$ occupy the other two sides. The surfaces of the pores have many sulfonic groups, which may be the reason why the materials show such a high affinity for the polar solvents water and methanol. There are two kinds of large channels, *ca.* 1 nm in diameter, filled with molecular water. Different from traditional porous materials, this porous material is sustained exclusively by weak interactions, which determines that the porous material can be dissolved in hot water.

The supramolecular channel structure can also be formed under similar conditions with other divalent transition metal ions. In the presence of aqueous Zn^{2+} instead of Cu^{2+}, similar nanocapsule and channel structure **2** can also be obtained (Fig. S4–S6†).‡ The solvent-accessible volumes of the unit cells of **1** and **2** were estimated (PLATON program[11]) to be 8464.8 and 8065.1 $Å^3$, which are approximately 40.7 and 39.1% of the unit-cell volumes (20781 $Å^3$ and 20640.7 $Å^3$), respectively. After being evacuated at 150 °C for 5 h, powder XRD patterns of compounds **1** and **2** (Fig. S8 and S9†) are different from those simulated using the single-crystal data, which shows that the structures of these compounds change. The crystals of compounds **1** and **2** have weak diffraction quality. Meanwhile the colours of these crystals become deep. It also looks as if the crystals lose their crystallinity upon drying and the corresponding materials are therefore amorphous prior to

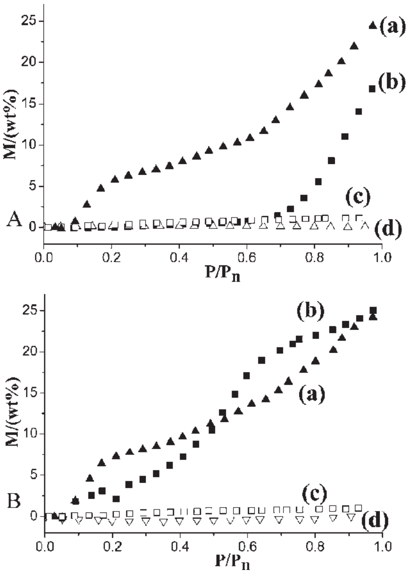

Fig. 5 Vapor adsorption isotherm curves of compound **1** (A) and **2** (B) at 298 K: (a) water, (b) methanol, (c) ethanol, (d) acetone.

adsorption measurements. To confirm the porosity of **1** and **2**, gas sorption experiments were carried out (Fig. 5). The adsorption isotherms of **1** and **2** for ethanol and acetone at 298 K reveal no obvious inclusion by the frameworks. For methanol and water, uptakes of 16.8, 24.4 and 25.1, 24.2 wt% are observed at $P/P_0 = 1$ in **1** and **2**, respectively; which shows that the compounds **1** and **2** have similar guest sorption properties. These compounds have selective guest sorption properties for water and methanol, which indicates that the channels of compounds **1** and **2** shrink and still possess pores after activation.

In summary, two novel channel structures based on $[M(bpdo)_3]^{2+}$ (M = Cu, Zn) and *p*-sulfonatocalix[4]arene nanocapsules have been established, which are sustained exclusively by charge-assisted $\pi\cdots\pi$ interactions. In addition, the ability to use $[M(bpdo)_2{\cdot}2H_2O]^{2+}$ as guest molecules to induce the *p*-sulfonatocalix[4]arenes to form supramolecular nanocapsules has been established. All the results suggest the porosity in **1** can also be obtained under similar conditions with different divalent metals and we have successfully done this. The structure affords us numerous possibilities for using $[M(bpdo)_a]^{b+}$ (a = 1–4, b = 1–4) as guests for *p*-sulfonatocalix[*n*]arenes (n = 4, 5, 6, 8) with a view to accessing more porous materials and other larger arrays such as spheres. This work is underway in our lab and will be reported in the future.

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Notes and references

‡ Crystal/refinement details for **1**: $C_{136}H_{165}Cu_3N_{16}NaO_{78.5}S_8$, M = 3749.93, space group $P2_1/c$, monoclinic, a = 15.6871(9) Å, b = 36.518(2) Å, c = 36.658(2) Å, V = 20781(2) Å^3, Z = 4, T = 193 K, λ = 0.71073 Å, R_{int} = 0.1147; a total of 102 971 reflections was collected in the range $1.25 < \theta < 25$, of which 355 565 were unique. GOF = 0.926, R_1 = 0.1187, wR_2 (all data) = 0.3386. Non-hydrogen atoms, except some dissociative water molecules (O23–O26, O68, O53, O81–O104), were refined anisotropically. Crystal/refinement details for **2**: $C_{136}H_{150}Zn_3N_{16}NaO_{71}S_8$, M = 3620.30, space group $C2/m$, monoclinic, a = 36.9777(18) Å, b = 36.6324(18) Å, c = 15.4075(8) Å, V = 20640.7(18) Å^3, Z = 4, T = 193 K, λ = 0.71073 Å, R_{int} = 0.0488; a total of 51 075 reflections was collected in the range $1.48 < \theta < 25$, of which 17 744 were unique. GOF = 1.087, R_1 = 0.1156, wR_2 (all data) = 0.3232. Non-hydrogen atoms, except some dissociative water molecules (C64–C68, O7–O16, O27–O51), were refined anisotropically. The waters of crystallisation have been modelled at partial occupancies varying from 0.2 to 0.8.
The high R_1 and wR_2 of compounds **1** and **2** are due to the weak crystal diffraction quality and the disorder of the molecular water.†

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