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A giant coordination cage based on sulfonylcalix[4]arenes†

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A strategy for building coordination cages by a [6 + 8] condensation of M^{II}_4-calix SBUs and rigid ancillary ligands was successfully applied to a cobalt–sulfonylcalix[4]arene system. A giant cage obtained with BTE ligands has an overall periphery diameter of 5.0 nm and an internal spherical cavity of 2.3 nm.

Coordination cages as a class of molecular containers have received considerable attention because of their intriguing structures and well-defined cavities.[1] Over the past few years, a number of elaborate coordination cages with various sizes and shapes have been reported.[2] However, it is still a challenge to design and prepare coordination cages using multimetal entities or metal clusters except with some paddle-wheel subunits as the vertexes.[3] A recently reported cubic cage with polyoxometalates as the vertexes gave some clues that the metals can be selectively coordinated and some active coordination sites can be left for constructing the coordination cage.[4] Square-planar M_4 secondary building units (SBUs) are a common kind of tectons chosen for the building of zeolite-like MOFs (ZMOFs).[5] They are bridged into the coordination cages by rigid tripodal ligands through a [6 + 8] condensation and also act as nodes to interconnect two adjacent cages to form the extended ZMOF. So it would be possible to build isolated coordination cages if the M_4 square is controlled to act as a terminal node by capping one side so that it just joins the building of one coordination cage.

Calixarenes have been documented to be a versatile ligand to construct polynuclear subunits.[6] It is found that a square-planar tetranuclear subunit capped by a calixarene molecule (like a shuttlecock) is a stable tecton, especially for thiacalixarene and its derivatives. Recently we successfully obtained a series of cobalt–*p*-*tert*-butylthiacalix[4]arene (H_4TC4A) complexes, which can be interconnected by metal cations or other ligands into high nuclearity clusters or chains.[7] It appears that the Co_4-TC4A shuttlecocks would be an ideal SBU for constructing coordination cages and we proposed a strategy to construct calixarene-based coordination cages by a [6 + 8] condensation using Co_4-TC4A shuttlecock SBUs as nodes and some rigid tripodal aromatic tricarboxylic acids as linkers.[8] We successfully obtained a series of nanocages of *p*-*tert*-butylthiacalix[4]arene or *p*-phenylthiacalix[4]arene by introducing 1,3,5-benzene-tricarboxylic acid (H_3BTC) and 4,4′,4″-benzene-1,3,5-triyltribenzoic acid (H_3BTB) into the cobalt-thiacalix[4]arene system. Dai and Wang also reported similar neutral cages with sulfonylcalixarene and H_3BTC.[9] Although various containers concerning calixarenes have been reported previously, most of them are constructed through hydrogen bonds or metal–calixarene coordination bonds.[10] The introduction of ancillary ligands would make the design and modification of coordination cages much easier. For instance, the cavity sizes and the portals of the cages can be tuned easily by applying different ancillary ligands.

To verify the universality of this strategy, we now extend the synthesis in the sulfonylcalixarene system. Here we present three anionic coordination cages from this new system, $\{[Co^{II}_4(SC4A\text{-}SO_2)(OH)]_6(TC)_8\}^{6-}$ ($H_4SC4A\text{-}SO_2$ = *p*-*tert*-butylsulfonylcalix[4]arene; **CIAC-105**: TC = BTC; **CIAC-106**: TC = BTB; **CIAC-107**: TC = 4,4′,4″-(benzene-1,3,5-triyltris-(ethyne-2,1-diyl)) tribenzoate (BTE)). Notably, **CIAC-107**, the largest one, has a giant molecular cage with periphery diameter of about 5.0 nm and inner diameter of the void of 2.3 nm (Fig. 1). To the best of our knowledge this is the largest coordination cage based on calixarenes.

All these three compounds were synthesized in an alkaline environment by the solvothermal method as our last report.[8] Although **CIAC-107** was obtained with H_3BTE, an analogue was not obtained with H_3BTE from the thiacalix[4]arene system. X-Ray structure determination‡ reveals that all the structures crystallize in the tetragonal system with space group *I*4/*m* and possess similar coordination cage structures which are also similar to those obtained with *p*-*tert*-butylthiacalix[4]arene.[8] All the cage structures possess crystallographically imposed C_{4h} symmetry, in which the C_4 axis passes through two opposite O2 sites bonding the $(Co4)_4$ clusters and is perpendicular to the $(O1)_4$ plane (with **CIAC-107** as an example). In **CIAC-107**, six tetranuclear Co_4-$(SC4A\text{-}SO_2)$ SBUs were connected by eight BTE ligands to form an octahedral cage (Fig. 1). Each Co_4-$(SC4A\text{-}SO_2)$ resides on the vertex, and acts as a four-connected node coordinated to four BTE molecules. A square-planar Co_4

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† Electronic supplementary information (ESI) available: Experimental section and crystallographic data, packing figures, TGA-DSC analyses, IR spectra, ESI spectrum, ^{1}H NMR spectra, gas sorption and I_2 adsorption of **CIAC-107**. CCDC 869988–869990. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc34265k

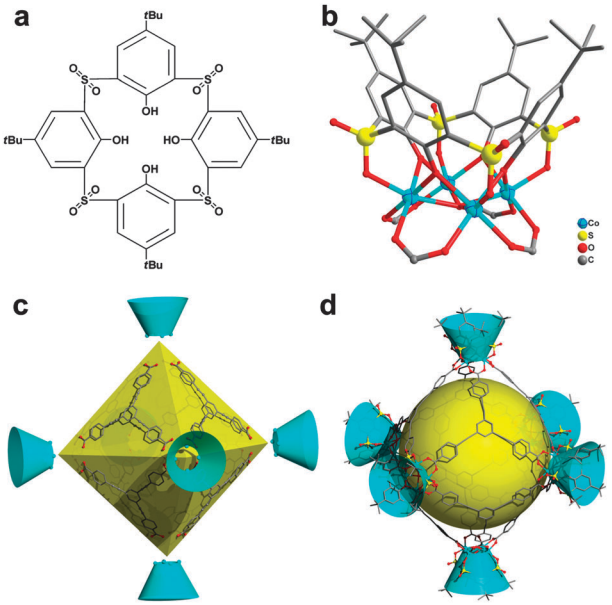

Fig. 1 A *p-tert*-butylsulfonylcalix[4]arene molecule (a), a shuttlecock-like Co^{II}_4-(SC4A-SO_2) unit (b), a scheme showing the cage construction by the shuttlecock-like SBUs and BTE ligand (c) and a discrete coordination cage of **CIAC-107** (d). The truncated cones denote the Co_4-(SC4A-SO_2) SBUs.

cluster core is capped by a conic SC4A-SO_2 ligand through four phenoxo oxygens and four axial sulfonyl oxygen atoms to form a shuttlecock-like unit. Each Co center adopts an octahedral geometry coordinated by one sulfonyl oxygen, two phenoxo oxygens, two carboxylate oxygen atoms from different BTE ligands and one μ_4-O atom. Bond valence sum calculations (BVS) suggested that all the cobalt ions are divalent. The μ_4-O atom exists as an anionic OH^-, which is confirmed by BVS and mass spectra. Four edge-sharing CoO_6 octahedra form a square-planar Co_4 cluster. Compared to our reported Co_4-TC4A SBUs in the nanocages,[8] the Co_4-(SC4A-SO_2) SBUs exhibit some change in the coordination environment. For two nanocages with the same tritopic linkers BTB (*i.e.*, **CIAC-103** and **CIAC-106**), the Co–Co distances are in the range of 3.226(4)–3.275(5) Å for the Co_4-TC4A SBUs while being 3.004(1)–3.023(1) Å for the Co_4-(SC4A-SO_2) SBUs. That is, the participation of the sulfonyl oxygens in the metal coordination leads to closer proximity in the Co_4-(SC4A-SO_2) SBU than in the Co_4-TC4A SBU, which might be related to the good crystallization of **CIAC-107** and the difficult synthesis of an analogue with *p-tert*-butylthiacalix[4]arene under the similar conditions.

Each BTE molecule acts as a face triangular linker bonding three Co_4-(SC4A-SO_2) SBUs. This connection mode generates a giant octahedral coordination cage by a [6 + 8] condensation. **CIAC-107** has an outer diameter of *ca.* 5.0 nm and an inner diameter of *ca.* 2.3 nm. Twelve shuttle-like apertures locate on the edges of the coordination octahedron with the portals being *ca.* 16.8 × 9.6 Å. The discrete octahedron cages adopt a pseudo-body-centered cubic (pseudo-bcc) packing mode to form a 3D open supramolecular structure. Calculation using the PLATON program gives a total potential solvent-accessible volume of *ca.* 78.6%. These volumes are presumably filled with counter-anions and disordered solvent molecules (*i.e.*, $(C_2H_5)_3NH^+$ and DMA), whose contribution was subtracted from the diffraction data by the SQUEEZE command in PLATON.[11] Nevertheless, on the basis of the SQUEEZE results and TGA measurement and elemental analysis, the suitable formula for **CIAC-107** would be $[(C_2H_5)_3NH]_6\{[Co_4(SC4A\text{-}SO_2)(OH)]_6(BTE)_8\}\cdot 128$ DMA. The TGA data indicate that the cage structure of **CIAC-107** is thermally stable and does not decompose until 430 °C (Fig. S1†).

Mass spectrometry (MS) is one of the most powerful techniques to confirm the structure and the stability of **CIAC-107** in solution. As shown in Fig. 2 and S7†, the ESI spectrum of the activated sample for gas sorption shows a very strong signal at m/z 1774.7 in the range of m/z = 1000–2500, which can be assigned to $\{[Co_4(SC4A\text{-}SO_2)(OH)]_6(BTE)_8\}^{6-}$. This signal confirms that the μ_4-O atoms bonding the Co_4 cluster are OH^- anions rather than the neutral H_2O solvent molecules, and also verifies that the cage structure is stable, remaining unchanged even after activation by supercritical carbon dioxide.

In order to evaluate the porosity of **CIAC-107**, gas sorption measurements were carried out on the sample activated with supercritical carbon dioxide (SCD). In fact, due to the weak interaction between the nanocages and their relative motion with respect to each other, samples of **CIAC-107** became fluffy amorphous fine powders upon activation. N_2 sorption (Fig. 3) exhibits a type-I adsorption isotherm, suggesting that the material possesses permanent porosity. The Langmuir surface area, BET surface area and pore volume were estimated to be 928 $m^2\ g^{-1}$, 770 $m^2\ g^{-1}$ and 0.75 $cm^3\ g^{-1}$, respectively. The rapid increase of nitrogen adsorption at a relatively high pressure (close to P/P_0 = 1) would be attributed to substantial interparticle sorption. The adsorption/desorption hysteresis in general might be attributed to the adsorption of the interstices between the nanocages packing in the solid state and the partially blocked apertures by the adjacent cages.[3a] H_2 sorption isotherms (Fig. S8†) also show adsorption/desorption hysteresis. The porosity of **CIAC-107** was also demonstrated by the adsorption of I_2 by sublimation.[12] As shown in Fig. S10†, the uptake of I_2 increases quickly in the first two days; uptake then slows down but is still linear and does not reach equilibration even after 15 days. After 366 h, the iodine uptake reaches 30.0 mg for 104.6 mg **CIAC-107** sample, corresponding to 28.6 wt% or 24.0 iodine atoms per cage molecule.

CIAC-105 and **CIAC-106** have similar cage structures as **CIAC-107** and the outer and inner diameters of both cages are

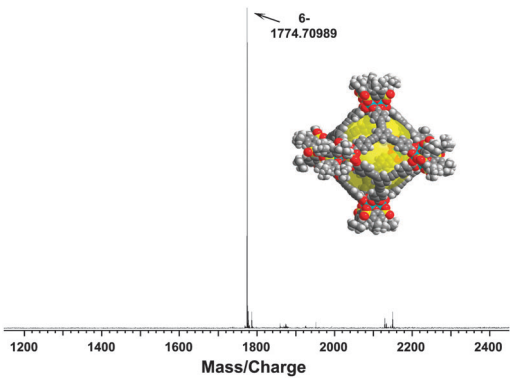

Fig. 2 ESI spectrum of **CIAC-107** in a DMF–methanol mixture.

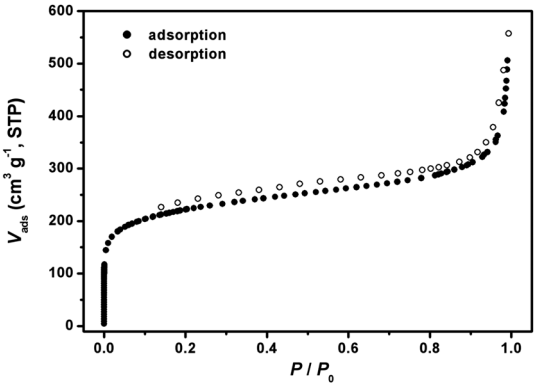

Fig. 3 Adsorption (●) and desorption (○) isotherms of N_2 on **CIAC-107**.

comparable with those of the corresponding cages obtained with *p-tert*-butylthiacalix[4]arene. It should be noted that although the cage structure of **CIAC-105** is very similar to **MOSC-1-Co**,[9] the μ_4-O atoms bonded to the M_4 clusters belong to different species, *i.e.*, neutral water molecules in **MOSC-1-Co** but anionic OH^- ions in **CIAC-105**. So **MOSC-1-Co** is a neutral cage while **CIAC-105** is an anionic one. An analogous **MOSC-4-Co** with BTB has also been mentioned though crystallographic information has not been provided.[9]

In summary, we successfully extended our strategy for building coordination cages with M_4-calix SBUs and rigid ancillary ligands into the cobalt–sulfonylcalix[4]arene system. Among three new coordination cages obtained, **CIAC-107** is the largest calixarene-based cage, which possesses an outer diameter of about 5.0 nm. This work indicates that some ultra big cages can be obtained if the linkers are big enough. However, upon close observation of the cage, it is observed the big BTE molecules are bent into an arc on the sideview. So what is the size utmost of the calixarene-based cage? Can some nanoparticles be inserted these cages for allosteric catalysis? Our efforts on these topics are ongoing.

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Notes and references

‡ *Crystal data*: **CIAC-105**: $C_{312}H_{294}Co_{24}O_{126}S_{24}$, M = 8243.23, tetragonal, space group $I4/m$, a = 26.3094(9), b = 26.3094(9), c = 44.152(3) Å, V = 30562(2) Å^3, T = 120(2) K, Z = 2, 220 985 reflections measured, 13 804 independent reflections (R_{int} = 0.0478); R_1 = 0.0847 ($I > 2\sigma(I)$), 0.0926 (all data); $wR(F^2)$ = 0.2322 ($I > 2\sigma(I)$), 0.2391 (all data). **CIAC-106**: $C_{456}H_{390}Co_{24}O_{126}S_{24}$, M = 10069.44, tetragonal, space group $I4/m$, a = 34.1605(10), b = 34.1605(10), c = 54.943(2) Å, V = 64116(4) Å^3, T = 293(2) K, Z = 2, 233 931 reflections measured, 12 876 independent reflections (R_{int} = 0.1454); R_1 = 0.0580 ($I > 2\sigma(I)$), 0.1137 (all data); $wR(F^2)$ = 0.1491 ($I > 2\sigma(I)$), 0.1682 (all data). **CIAC-107**: $C_{504}H_{390}Co_{24}O_{126}S_{24}$, M = 10645.92, tetragonal, space group $I4/m$, a = 37.232(13), b = 37.232(13), c = 60.29(3) Å, V = 83 575(59) Å^3, T = 120(2) K, Z = 2, 322 869 reflections measured, 10 252 independent reflections (R_{int} = 0.140); R_1 = 0.1084 ($I > 2\sigma(I)$), 0.1660 (all data); $wR(F^2)$ = 0.2273 ($I > 2\sigma(I)$), 0.2421 (all data). In the structures, disordered counter cations and solvents are subtracted by SQUEEZE; see ESI† for details).

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