

Two 2D metal–calixarene aggregates incorporating pre-designed coordination nanocages†

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Two 2D metal–calixarene aggregates were designed and assembled by M_4 -TC₄A (M = Fe, Co; TC₄A = *p*-tert-butylthiacalix[4]arene) SBUs and $\{MCl_2\}$ units with isonicotinic acid molecules, which presents a possible way to build the extended metal–calixarene assemblies incorporating pre-designed nanocages using multifunctional linkers.

Coordination cages have received considerable attention because of their intriguing structures and well-defined cavities^{1–3} that can act (1) as a host to incorporate various guests;⁴ (2) as a molecular sieve used for gas separation and storage;⁵ and (3) as a micro-reactor to construct nano-materials or a microreactor with catalytic properties.⁶ Over the past few years, a number of elaborate coordination cages with various sizes and shapes have been reported.⁷ However, the reasonable design and synthesis of novel coordination cages is still one of the most challenging issues in synthetic and coordination chemistry. Especially, the extended networks such as the layers or MOFs with the pre-designed coordination cages remain challenging.⁸

Calixarenes (including resorcinarenes and pyrogallolarenes) have been documented to be a versatile candidate to construct coordination cages,^{9,10} most of which are constructed by bonding the metals with the upper rim of calixarenes. However, the coordination cages involving the lower rim of calixarenes are relatively less. The M_4 -calix[4] (M = Co^{II}, Mn^{II}, Fe^{II}; calix[4] = *p*-tert-butylthiacalix[4]arene (H_4 TC₄A) or *p*-tert-butylsulfonylcalix[4]arene (H_4 SC₄A-SO₂)) subunit, a shuttlecock-like motif with a tetranuclear square capped by a calixarene molecule through its lower rim, was reported to be an excellent secondary building unit

(SBU) for the cluster construction.¹¹ According to the results obtained by Kajiura,¹² this entity can maintain the cone conformation even in a highly dilute solution, and some carboxylate chelates can bond it through the left coordination sites of the metal square. Based on this view, we successfully obtained a series of coordination nanocages of H_4 TC₄A or H_4 SC₄A-SO₂ by introducing planar ternary aromatic carboxylic acids into the cobalt-calix[4]arene system.¹³ Hong and Wang also reported similar cages using di- or ternary carboxylic acids.¹⁴ All these studies further indicate that the shuttlecock-like M_4 -calix[4] entity holds the desired curvature necessary for the construction of coordination cages and would also be an excellent SBU in this field.

As mentioned above, the M_4 -calix[4] SBUs can be bridged by di- or ternary carboxylic acids into some nanocages through a [6+8] or [6+12] condensation.^{13,14} It would be possible to obtain different cages if carboxylic acid is substituted by other ligands having different functional groups and the M_4 -calix[4] SBUs are bridged by the metal cations. Furthermore, these cages can be interconnected into some extended aggregates such as a layer or MOF by occupying the vacant coordination sites of metal bridges. To prove this hypothesis, isonicotinic acid (INA), a linear ligand, having both a carboxylate group and an N donor atom at two ends, was chosen as a bridge. It was designed that the INA ligands would bond the M_4 -calix[4] SBUs through their carboxylate groups and additional metal bridges through their N donors to form some nanocages which are further connected into a layer by using the vacant coordination sites of the metal bridges. Fortunately, this hypothesis was found to be true with two novel isostructural 2D nanocage-based aggregates $\{[M^II_4Cl(TC_4A)(INA)_4](M^II Cl_2)_n\}^{n-}$ (**CIAC-109**: M = Fe; **CIAC-110**: M = Co; TC₄A = *p*-tert-butylthiacalix[4]arene, INA = isonicotinic acid). As we know, these coordination layers give the first examples for the extended networks with the pre-designed calixarene-based nanocages.

Compounds **CIAC-109** and **-110** are isostructural and both crystallize in the tetragonal system with the space group $I4/m.\ddagger$ Compound **CIAC-109** is described in detail as an example hereafter. In **CIAC-109**, the shuttlecock-like Fe_4 -TC₄A SBUs were connected by isonicotinic acid and $\{FeCl_2\}$ units to form a novel nanocage-based 2D motif. The shuttlecock-like Fe_4 -TC₄A SBU is

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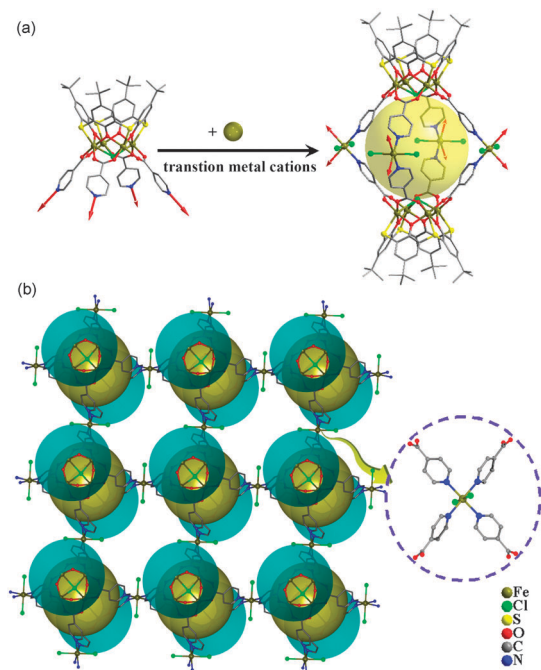


Fig. 1 Scheme of a dumbbell-like entity with M_4 -TC₄A SBU and the formation of a coordination cage (a) and the 2D aggregate incorporating the nanocages (b). The coordination of metal bridges is shown in the dashed circle. The cyan cone represents the calixarene molecule.

similar to those reported.^{11,13,14} Each Fe center of the Fe₄ square adopts a distorted octahedral geometry coordinated by two phenoxy oxygens, one sulfur atom from one fully deprotonated TC₄A ligand, one μ_4 -chloride anion, and two carboxylate oxygen atoms from different INA molecules. Four edge-sharing Fe(O₄SCl) octahedra form a square-planar Fe₄ cluster with the Fe...Fe edges being about 3.29 Å and Fe-Fe-Fe angles being 90°. A TC₄A ligand adopting a cone conformation caps on the tetranuclear Fe₄ square by four phenoxy oxygens and four S bridges to form a shuttlecock-like subunit. Each Fe₄-TC₄A SBU acts as a four-connected node and is bonded by four INA molecules through their carboxylate groups to form a dumbbell-like motif (Fig. 1). The N rims of two tail-to-tail motifs are coordinated by four similar $\{FeCl_2\}$ units, that is, these two motifs are bridged by four $\{FeCl_2\}$ bridges into a cage structure. Due to the six-coordination nature of iron in $\{FeCl_2\}$ units, there are two vacant coordination sites for each $\{FeCl_2\}$ bridge, which can be occupied by two INA N atoms from an adjacent cage. So one cage is interconnected with four adjacent cages through its four $\{FeCl_2\}$ bridges and then a layer with interconnecting nanocages forms (Fig. 1 and Fig. S1, ESI[†]). As we know, this is the first example for the 2D assemblies with calixarene-based coordination cages as the building blocks. The layer can also be thought as a grid with some highly ordered pores of 10.6×10.6 Å² if the nanocages and $\{FeCl_2\}$ units are thought as the four-connected nodes and the linkers, respectively.

As shown in Fig. S2 (ESI[†]), the layers are staggered in the *ab* plane and stacked alternately along the *c* axis by hydrogen bonds and electrostatic interactions with the counterions into a

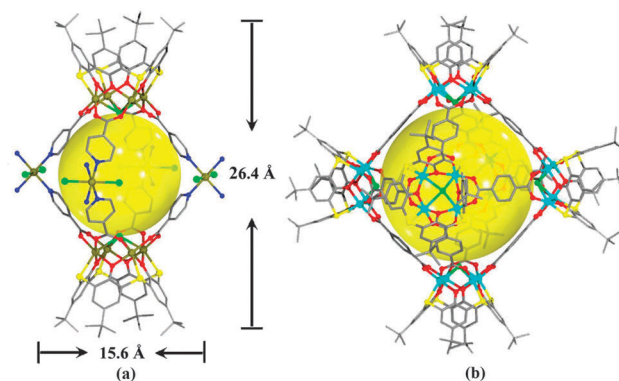


Fig. 2 A $\{[Fe^{II}_4Cl(TC_4A)]_2(Fe^{II}_2Cl_2)_4(INA)_8\}$ nanocage (a) compared with the $\{[Co^{II}_4Cl(TC_4A)]_6(BDC)_{12}\}$ cage (b, ref. 14a).

3D supramolecular structure. A series of axiolytic supramolecular voids form in the stacked layer, which penetrate the grid of a middle layer and interconnect with the cavities of two opposite TC₄A molecules from the upper and bottom layers (Fig. S3, ESI[†]). The dimensions are approximately 10.6×24.9 Å². Some triethylamine counterions and lattice solvent molecules might occupy these cavities.

It should be noted that the coordination cages in these two compounds present a new kind of calixarene-based cages with large fusiform apertures across two opposite M_4 -calix[4] SBUs. Different from the reported $\{Co^{II}_{24}\}$ cage with the linear binary acid linker 1,4-benzenedicarboxylic acid,^{14a} these cage structures look like some cylinders with a size of $\phi 15.6 \times 26.4$ Å³ (Fig. 2), which have a spherical cavity with a dimension of 10.6 Å. It is found that the linkers on the equatorial edges disappear due to the substitution of the M_4 -TC₄A SBUs with the monometallic $\{FeCl_2\}$ units and four larger fusiform apertures across the opposite M_4 -TC₄A SBUs are formed, which are different from those across two adjacent SBUs found in the nanocages with planar ternary acids.^{13,14b} The sizes of all the fusiform apertures are about 7.5×13.2 Å².

To confirm the architectural rigidity and porosity of these structures, the gas sorption properties of the activated samples of compound **CIAC-109** were measured. As shown in Fig. 3, the N₂ adsorption isotherm at 77 K exhibits a type I behavior in the range $P/P_0 = 0-0.8$, indicative of the presence of permanent microporosity.

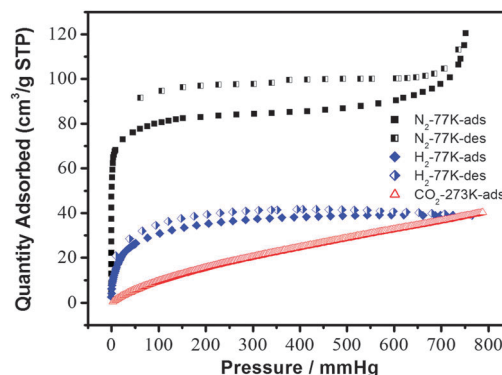


Fig. 3 Gas sorption isotherms on **CIAC-109** ('ads' and 'des' represent adsorption and desorption, respectively).

The second augments in the range $P/P_0 > 0.8$ and can be attributed to the adsorption on the external crystallite surface.¹⁵ From the N₂ adsorption branch, the Langmuir and BET surface areas were calculated to be 360 and 251 m² g⁻¹, respectively. Both N₂ and H₂ sorption isotherms show adsorption-desorption hysteresis, which might be attributed to the adsorption of the interstices between the layers and the aforementioned partially blocked apertures by the adjacent layers. CO₂ adsorption was also examined.

Due to their well-ordered crystalline structure, high surface area and porosity, metal organic frameworks were proved to be excellent precursors for preparing porous metal oxide materials by thermolysis.¹⁶ The title compounds possess a well-defined 2D metal-organic structure and porosity so that they might also act as good precursors for the corresponding metal oxide materials. Here **CIAC-109** was chosen as an example. First, the thermal properties of **CIAC-109** were studied. As shown in Fig. S6 (ESI[†]), the first weight loss (18.53%) takes place between 30 and 250 °C, corresponding to the removal of the lattice DMF molecules and the (C₂H₅)₃NH⁺ cation (19.84%). The subsequent heating results in the decomposition of the metal-organic framework at a temperature above 350 °C with a cliffy weight loss in the TG curve. When temperature is higher than 550 °C, the curve became steady. The powder XRD pattern of the obtained reddish brown powder (Fig. S11, ESI[†]) indicated that a pure α -Fe₂O₃ phase (JCPDS card no. 33-0664) with high crystallinity was produced after calcination. Energy dispersive X-ray spectroscopy (EDS) analysis reveals that the Fe:O ratio is 41.25:58.75, which also suggests the final product to be α -Fe₂O₃. Little sulfur detected can be assigned to the residue of TC₄A thermolysis. SEM observation gave more morphological details. As shown in Fig. S11 (ESI[†]), an agglomerated block of the α -Fe₂O₃ product is comprised of the nanoparticles of about 30–40 nm.

In summary, two 2D aggregates based on coordination cages have been synthesized and characterized. In these structures, the shuttlecock-like M₄-TC₄A (M = Fe, Co) SBU is bonded by four isonicotinic acid molecules to form a dumbbell-like entity. Two tail-to-tail dumbbells are bridged by four monometallic {MCl₂} units through the M–N bonds into a novel coordination cage. And then these cages are interconnected with each other by sharing the {MCl₂} bridges to form some novel nanocage-based layers. The gas sorption isotherms reveal that the structures possess permanent microporosity. This work presents not only the first example for the layer structures with pre-designed calixarene-based nanocages but also a possible way to build the extended metal-calixarene assemblies with such designed cavities.

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Notes and references

[†] Crystal data: **CIAC-109**: C₆₄H₆₀Cl₃Fe₅N₄O₁₂S₄, $M = 1591.00$, tetragonal, space group $I4/m$, $a = 15.561(2)$, $b = 15.561(2)$, $c = 40.195(8)$, $V = 9733(3)$ Å³, $T = 185(2)$ K, $Z = 4$, 48 586 reflections measured, 6087 independent reflections ($R_{\text{int}} = 0.0393$; $R_1 = 0.0691$ ($I > 2\sigma(I)$), 0.0787 (all data);

$wR(F^2) = 0.2163$ ($I > 2\sigma(I)$), 0.2226 (all data)); **CIAC-110**: C₆₄H₆₀Cl₃Co₅N₄O₁₂S₄, $M = 1606.40$, tetragonal, space group $I4/m$, $a = 15.6006(3)$, $b = 15.6006(3)$, $c = 38.9682(19)$, $V = 9484.0(5)$ Å³, $T = 150(2)$ K, $Z = 4$, 46 394 reflections measured, 4334 independent reflections ($R_{\text{int}} = 0.0820$; $R_1 = 0.0510$ ($I > 2\sigma(I)$), 0.0705 (all data); $wR(F^2) = 0.1336$ ($I > 2\sigma(I)$), 0.1438 (all data). The contribution of disordered counter cations and solvents was subtracted from the diffraction data by SQUEEZE; see ESI[†] for details).

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