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Bridging different Co₄-calix[4]arene building blocks into grids, cages and 2D polymers with chiral camphoric acid†

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The employment of three different kinds of Co₄-calix[4]arene molecular building blocks (MBBs) generated *in situ* with (1*R*,3*S*)-(+)-camphoric acid has resulted in different architectures ranging from a grid, to a chiral cage, to a 2D polymer. The sorption behaviors and magnetic properties of these have been investigated.

Thiacalixarenes, a kind of multidentate ligands with sulfur-bridging phenolic groups, have been documented to be good candidates for the synthesis of polynuclear coordination compounds.¹ It is found that one thiacalix[4]arene molecule or one molecule of its oxidized derivative sulfonylcalix[4]arene (Fig. 1a) prefers to coordinate to four divalent transition metal (TM) ions by its four lower-rim phenolic oxygen atoms and four bridging sulfur/sulfonyl oxygen atoms. By bridging with a μ₃/μ₄-X it forms shuttlecock-like cationic [TM₄(calix[4]arene)-(μ₃/μ₄-X)]^{Y+} molecular building blocks (MBBs).^{1*d,2*} These hold suitable curvature to be further linked into polynuclear coordination compounds with well-defined shapes and sizes or extended into 1D/2D structures, especially with the inclusion of anionic species (including anionic clusters, carboxylates, tetrazoles, carbonates and phosphates/phosphonates) for charge balance.³ For instance, they can be bridged into discrete Co₃₂ nanospheres with Co^{III}O₆ clusters,⁴ octahedral M₂₄ (M = Mg, Co and Ni) coordination cages with di/tri-carboxylates,⁵ high-nuclearity M_{4*n*} (M = Co or Ni, *n* = 2–6) nanocages with phosphate/phosphonate ligands, tetragonal-

prismatic Co₃₂ cages by *in situ* generated bitetrazoles⁶ and two-dimensional metal-calixarene polymers comprising pre-designed M₁₂ (M = Fe, Co) cages bridged with isonicotinate.⁷

In spite of the fact that it is facile to construct polymeric complexes with different linkers from TM₄-calix[4]arene MBBs, there is no report on calixarene-based coordination complexes linked by chiral ligands, even though these are extensively used in the synthesis of homochiral metal-organic polymeric assemblies and frameworks with potential applications including heterogeneous asymmetric catalysis or enantioselective recognition/separation. Among these chiral ligands, the readily available (1*R*,3*S*)-(+)-camphoric acid (abbreviated as H₂CAM, Fig. 1a) is particularly appealing, since it possesses two carboxylic acid groups located in a suitable geometry to act as an excellent bent, divergent linker between metal cations. With a detailed search of the literature, there is a plethora of camphorate-based coordination complexes with intriguing structures and various nuclearities.⁸ However, coordination complexes based on MBBs and chiral ligands have rarely been described. In this work, we present three novel calix[4]arene-based coordination complexes utilizing (1*R*,3*S*)-(+)-camphoric acid (H₂CAM) as the linker, formed under solvothermal conditions. The molecular formulas for these three complexes are as follows: [Co₈(BSC4A)₂(CAM)₂(μ₄-H₂O)₂Cl₄]·9CH₃OH (1), [Co₈(BTC4A)₂(CAM)₃(μ₄-Cl)₂(CH₃OH)₂(dma)₂]·0.5DMA·3CH₃OH (2), [Co₄(PTC4A)(CAM)(μ-HCOO)(μ₄-Cl)(H₂O)(CH₃OH)_{1.7}(DMF)_{1.3}]_{*n*} (3) (H₄BSC4A = *p*-*tert*-butylsulfonylcalix[4]arene; H₄BTC4A = *p*-*tert*-butylthiacalix[4]arene; H₄PTC4A = *p*-phenylthiacalix[4]arene; DMA = *N,N'*-dimethylacetamide; DMF = *N,N'*-dimethylformamide; dma = dimethylamine). Complex 1 features a window frame-like rhombus grid, and 2 presents the first chiral calixarene coordination nanocage, while 3 features a 2D polymer structure, novel in a metal-calixarene system. To the best of our knowledge, these coordination complexes give the first examples of complexes based on Co₄-calix[4]arene and chiral ligands. Herein, the preparations, crystal structures, magnetic properties and

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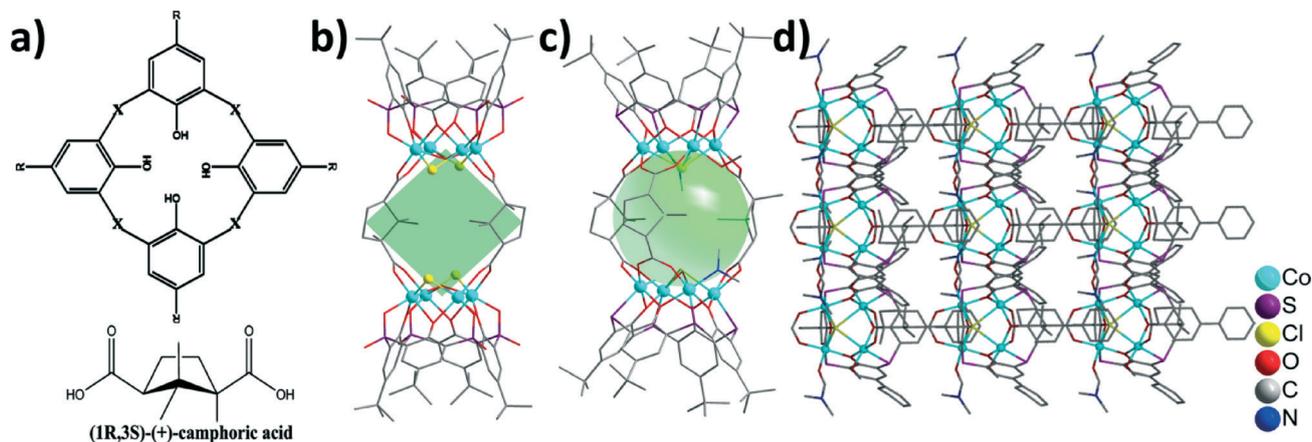


Fig. 1 (a) The structures of ligands used in this paper. For H₄BTC4A, R = tBu, X = S; for H₄PTC4A, R = phenyl, X = S; for H₄BSC4A, R = tBu, X = SO₂. View of the molecular structures of complexes **1** (b) and **2** (c). (d) The extended structure of complex **3**. The hydrogen atoms are omitted for clarity.

sorption behaviours of complexes **1–3** are presented and discussed.

Red block crystals of **1** were synthesized from a mixture of CoCl₂·6H₂O, H₄BSC4A and H₂CAM in CH₃OH solvent at 160 °C. Crystallographic analysis revealed that **1** crystallizes in the triclinic system and the structure solution was performed in the space group *P* $\bar{1}$. The structure features a window frame-like rhombus grid (Fig. 1b). Its asymmetric unit contains one Co₄-BSC4A MBB, one CAM²⁻ ligand and two bridged Cl⁻ anions. In this case, all four cobalt sites are bonded to the lower rim of a fully-deprotonated BSC4A⁴⁻ ligand in a cone conformation to form a Co₄-BSC4A shuttlecock-like MBB. All cobalt sites are six-coordinated in a distorted octahedron and coordinated by two phenolic O atoms and one S atom from one BSC4A⁴⁻ ligand, one carboxylic O atom from one CAM²⁻ ligand, one μ_4 -O from a water molecule and one μ_2 -Cl. We noted that C43, C45 and C48 in the CAM²⁻ ligand showed disorder with their symmetrical equivalent positions with occupancies of 0.5 (see CIF file for details). \ddagger Two Co₄-BSC4A MBBs are bridged by two inversion-related CAM²⁻ ligands into a window frame-like rhombus grid, which is quite different from the reported Co₁₆ squares constructed by four Co₄-BSC4A MBBs with eight rigid 1,3-benzenedicarboxylates.⁹

The reaction of H₄BTC4A and H₂CAM with CoCl₂·6H₂O in an acidic DMA-CH₃OH mixed solution resulted in the isolation of a chiral Co₈ coordination nanocage (**2**). Complex **2** is the only one in this series with a chiral space group *I*2 and a Flack parameter of 0.06(2), suggesting each single crystal is homochiral. Structural study revealed that it contains a Co₈ core, which is built by two Co₄-BTC4A MBBs as vertices and three CAM²⁻ ligands as linkers (Fig. 1c). Complex **2** has a crystallographic two-fold axis, so its asymmetric unit contains one BTC4A⁴⁻ ligand, one and a half CAM²⁻ ligands, one Cl⁻ anion, one *in situ* generated dma molecule, one CH₃OH molecule and four crystallographically unique Co(II) ions. All Co(II) sites are six-coordinated in a distorted octahedral environment and coordinated by two phenoxy O atoms, one S

atom, one μ_2 -Cl, one carboxylic O atom and one other component (a carboxylic O atom for Co1 and Co2, a CH₃OH for Co3 and a dma molecule for Co4). It should be noted that one CAM²⁻ ligand is in a general position, while the other one lies with some minor disorder about a twofold axis in this structure. Moreover, the CAM²⁻ ligands adopt two different kinds of coordination modes (Fig. S1 \dagger). Different from the reported Co₂₄ coordination nanocage with di/tri-carboxylates,^{5,10} this coordination nanocage contains a small inner cavity and has rather small ports, which hinder us from further studying its chiral encapsulation and recognition behavior.

Replacing the H₄PTC4A ligand with the H₄BTC4A ligand in a similar reaction to that for the preparation of **2** affords red block crystals of **3**. Complex **3** crystallizes in an orthorhombic system with the space group *Cmca* and shows a novel calixarene-based 2D polymer structure (Fig. 1d). This reveals that the substituent of the upper-rim groups of the thiocalix[4]arene has an important influence on the resulting structure of the coordination complexes. Within the structure of **3**, there are two crystallographically different cobalt sites, and both are six-coordinated and distorted octahedral in geometry. Except for two phenoxy O atoms, two carboxyl O atoms, one S atom and one μ_4 -Cl, the Co1 site is still bound by one O from the formate ligand, which originates from the *in situ* decarbonylation of the DMF solvent, while the Co2 site is still coordinated by a disordered combination of DMF and CH₃OH, refined in a ratio of 65 : 35 (Fig. S2 \dagger). Co1, Co2, Co1A and Co2A (generated by the mirror symmetry operation through the (010) plane) are capped by a PTC4A⁴⁻ ligand adopting a cone conformation to form a shuttlecock-like Co₄-PTC4A MBB. Then each MBB is connected by two CAM²⁻ ligands with some minor disorder and two HCOO⁻ anions, to form a calixarene-based 2D motif (Fig. S3 \dagger). The Co₄-PTC4A MBBs can be thought as four-connected nodes while the bridging CAM²⁻ and HCOO⁻ ligands act as two-connected linkers. Moreover, these HCOO⁻ anions are generated from the decarbonylation of DMF in a solvothermal environment

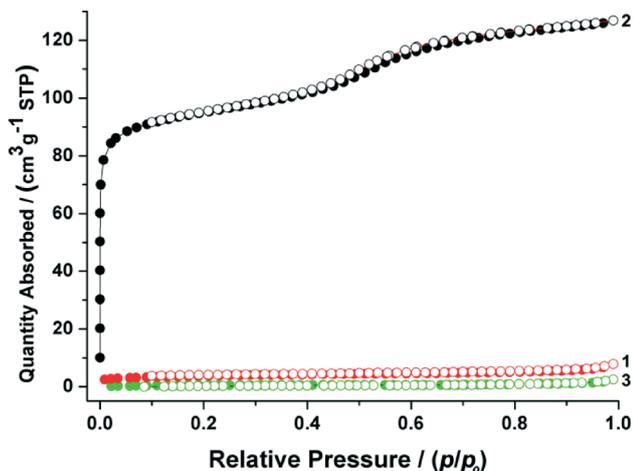


Fig. 2 Nitrogen gas sorption isotherms of activated complexes 1–3. Solid and open circles represent adsorption and desorption data, respectively.

according to the literature.^{3h} Although Liao and coworkers have presented two novel 2D metal-calixarene polymers that were designed and assembled by M_4 -BTC4A MBBs and $\{MCl_2\}$ ($M = Co, Fe$) units and isonicotinates in very recent years,⁷ there is no example of a 2D network constructed from the deep-cavity Co_4 -PTC4A MBBs.

In order to confirm the porosity of these supramolecular stacking structures, the N_2 adsorption properties of complexes 1–3 were measured at 77 K for the activated samples. As can be seen from Fig. 2, the N_2 sorption isotherm of 2 exhibits a pseudo-type I isotherm with a saturated uptake of $127 \text{ cm}^3 \text{ g}^{-1}$ at 77 K and 1.0 bar, characteristic of materials with permanent microporosity. The corresponding Langmuir and Brunauer–Emmett–Teller (BET) surface areas are $455 \text{ m}^2 \text{ g}^{-1}$ and $317 \text{ m}^2 \text{ g}^{-1}$, respectively. However, the experimental N_2 sorption values obtained for 1 and 3 are essentially negligible, suggesting their structural collapse and concomitant loss of porosity upon solvent removal. Moreover, the H_2 , CO_2 and

CH_4 adsorption for 2 were also examined and these are shown in Fig. S4.†

The variable-temperature magnetic measurements of complexes 1–3 were investigated on the polycrystalline samples in the temperature range of 2–300 K at an applied direct current magnetic field of 1 kOe (Fig. 3). At 300 K, the $\chi_m T$ values for complexes 1–3 are significantly higher than the expected values: observed 22.09 , 21.68 and $11.88 \text{ cm}^3 \text{ K mol}^{-1}$ for 1–3, respectively (calculated values of 15 , 15 and $7.5 \text{ cm}^3 \text{ K mol}^{-1}$ for 8, 8 and 4 uncoupled $Co(II)$ ions, respectively). This can be attributed to the orbital moment as a consequence of spin–orbital coupling of the $Co(II)$ ions, which is known to be significant in an octahedral field.¹¹ Upon cooling, the $\chi_m T$ products for all three complexes continuously decrease to 0.31 , 0.44 and $0.51 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K, respectively, characteristic of intramolecular antiferromagnetic interactions. The magnetic behaviors of complexes 1–3 are similar to those reported for calix[4]arene-based cobalt complexes.^{3a–g,4} Moreover, the magnetic data of complex 1 above 100 K obey the Curie–Weiss law ($1/\chi_m = T/C - \theta/C$), giving a Curie constant $C = 28.01 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and a Weiss constant $\theta = -95.24 \text{ K}$, and fitting those of 2 and 3 above 50 K give $C = 24.10$ and $13.29 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and $\theta = -32.92$ and -36.41 K for 2 and 3 (Fig. S5–S7†), respectively. The negative Weiss constants also indicate the presence of antiferromagnetic behavior between the spin carriers, and/or the spin–orbit coupling effect of $Co(II)$ ions.

In summary, by employing three different kinds of Co_4 -calix[4]arene MBBs with chiral H_2CAM ligands, we have obtained grids, chiral cages and 2D polymer structures. Complex 1 features a window frame-like rhombus and 2 presents the first chiral calixarene coordination nanocage, while 3 features a 2D polymer structure, novel in a metal-calixarene system. It is obvious that the introduction of chiral dicarboxylic acids leads to the formation of these fascinating structures. Moreover this work also presents a possible way to build metal-calixarene assemblies with chiral ligands, and efforts with other chiral ligands are also ongoing.

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Notes and references

† Crystal data for complex 1: $C_{109}H_{156}O_{43}Cl_4S_8Co_8$, $M_r = 3024.21$, triclinic, space group $P\bar{1}$, $a = 12.6110(3)$, $b = 13.0901(6)$, $c = 23.1334(11) \text{ \AA}$, $\alpha = 86.751(4)$, $\beta = 89.566(3)$, $\gamma = 66.489(4)$, $V = 3495.7(2) \text{ \AA}^3$, $Z = 1$, $F(000) = 1566$, $\lambda = 1.54184 \text{ \AA}$, $T = 100(2) \text{ K}$, $2\theta_{\max} = 135.0$, reflections collected/unique $26\,472/12\,438$ ($R_{\text{int}} = 0.0592$), final $R_1 = 0.0629$, $wR_2 = 0.1564$, $\text{GoF} = 0.978$. Crystal data for complex 2: $C_{121}H_{168.5}N_{2.5}O_{25.5}Cl_2S_8Co_8$, $M_r = 2865.06$, monoclinic, space group $I2$, $a = 11.7307(6)$, $b = 21.7103(11)$, $c = 27.7720(13) \text{ \AA}$, $\alpha = 90$, $\beta = 89.317(5)$, $\gamma = 90$, $V = 7072.4(6) \text{ \AA}^3$, $Z = 2$, $F(000) = 2988$, $\lambda = 1.54184 \text{ \AA}$, $T = 100(2) \text{ K}$, $2\theta_{\max} = 140.0$, reflections collected/unique $14\,926/10\,287$ ($R_{\text{int}} = 0.0645$), final $R_1 = 0.0771$, $wR_2 =$

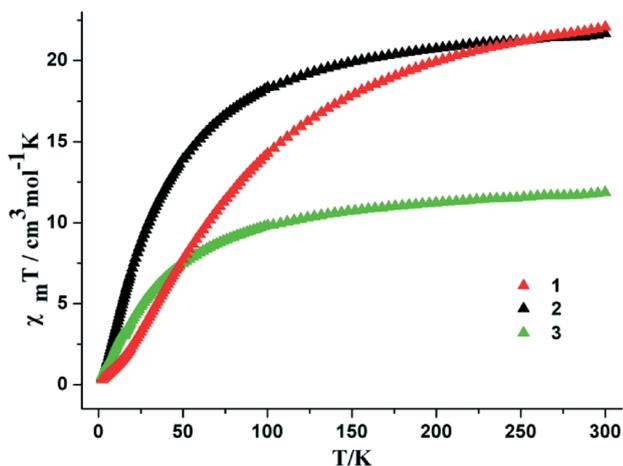


Fig. 3 The temperature dependence of the magnetic susceptibilities of complexes 1–3 in a 1 kOe field.

0.2223, GooF = 1.095. Crystal data for complex 3: $C_{62.6}H_{69.9}N_{1.3}O_{12}ClS_4Co_4$, $M_r = 1431.89$, orthorhombic, space group *Cmca*, $a = 20.4878(9)$, $b = 15.1811(6)$, $c = 39.3306(11)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90$, $V = 12\,232.9(8)$ Å³, $Z = 8$, $F(000) = 5702$, $\lambda = 1.54184$ Å, $T = 100(2)$ K, $2\theta_{max} = 140.0$, reflections collected/unique 15 591/6003 ($R_{int} = 0.0327$), final $R_1 = 0.0869$, $wR_2 = 0.2359$, GooF = 1.071. The diffraction data of 1 and 2 were treated by the "SQUEEZE" method routine in PLATON to subtract diffuse electron density. This had the effect of dramatically improving the agreement indices.

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