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Construction of a unique 3D coordination polymer from assembly of $Cd(NO_3)_2$ with a new tetrakis(*m*-carboxyphenyl)azo calix[4]arene ligand

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ABSTRACT

Reactions of 25,26,27,28-tetrahydroxy-calix[4]arene (1) with 4 equiv. of *m*-carboxybenzenediazonium chloride in the presence of NaOAc·3H₂O in DMF produced a new azo calix[4]arene [H₄L] (2) (H₄L = 5,11,17,23-tetrakis[(*m*-carboxyphenyl)azo]-25,26,27,28-tetrahydroxycalix[4]arene) in 96% yield. Hydrothermal reactions of Cd(NO₃)₂·4H₂O with H₄L at 90 °C under pH = 5.0–6.0 gave rise to a coordination polymer {[H₃O]₂ [Cd₇L₄(DMF)₄(EtOH)₂(H₂O)₂]·5DMF·11.5EtOH·H₂O]_n (3). Compound **3** was characterized by elemental analysis, IR, powder X-ray diffraction, and single-crystal X-ray diffraction. Compound **3** consists of a 3D framework with an unprecedented $(3^{3}4^{6}5^{2}6^{3}7^{1})(3^{6}4^{13}5^{8}6^{1})$ topology. The thermal properties of **2** and **3** were also investigated.

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The fascinating area of self-assembly presently attracts the attention of many scientists [1]. Starting with a number of selected building blocks, it offers almost unlimited possibilities for the construction of various intriguing architectures [1,2]. In recent years, water-soluble calix[4]arenes as the building blocks in selfassembly processes have been investigated as the presence of native cavity-like structures showing interesting inclusion properties and a wide range of metal coordination complexes both in solution and in the solid state [3]. Some calix[4]arene complexes could be arranged into so-called molecular capsules. "Ferris wheels" and "Russian dolls". etc. through coordination bond and/or weak interactions such as hydrogen bonding, $\pi \cdots \pi$ stacking, electrostatic and van der Waals interactions and so on [3a,b,e,h,4]. In addition, a number of supramolecular compounds via self-assembly of main group, transition metal or lanthanide species, and additional organic molecules with water-soluble p-sulfonatocalix[4]arenes (C4AS) have been reported [3b,d,4d,e,5]. To our knowledge, studies engaged in coordination polymers via self-assembly of azo calix[4]arenes with transition metals have not been reported yet. In this work, we used 25,26,27,28tetrahydroxy-calix[4]arene (1) [6] as a starting material to successfully prepare a new water-soluble azo calix[4]arene with four carboxylic groups, 5,11,17,23-tetrakis[(m-carboxyphenyl)azo]-25,26,27,28-tetrahydroxycalix[4]arene (2, H₄L). This compound is anticipated to have the following two interesting features. One is that it contains four carboxylic groups, which may adopt a lot of bridging modes when it binds to metal centers. The other is that it is four long and flexible carboxylic groups, which may have more chances to create various coordination environments for metals, thereby forming various intriguing supramolecular architectures. With these ideas in mind, we carried out the solvothermal reactions of Cd(NO₃)₂·4H₂O with H₄L and isolated a unique 3D coordination polymer {[H₃O]₂ [Cd₇L₄(DMF)₄(EtOH)₂(H₂O)₂]·5DMF·11.5EtOH·H₂O]_n (**3**). Herein we report its synthesis, crystal structure, and thermal property.

Compound 1 was employed to react with 4 equiv. of *m*carboxybenzenediazonium chloride and NaOAc·3H₂O in DMF affording an azo calix[4]arene product 2 in 96% yield (Scheme 1) [7]. Treatment of **2** with 2 equiv. of $Cd(NO_3)_2 \cdot 4H_2O$ in DMF/EtOH at pH = 5.0-6.0 followed by a hydrothermal treatment at 90 °C for one day produced orange block crystals of 3 in 62% yield [8]. It was worth noting that when the reaction temperature was raised up to 140 °C with the variable pH values from 2.0 to 6.0, only 3 was generated with a lower yield. In all of the cases, if the pH values and reaction temperatures were fixed, changes of Cd(NO₃)₂·4H₂O/H₄L molar ratios from 1:1 to 1:2 to 2:1 always generated the same product 3. Compounds 2 and 3 were stable towards oxygen and moisture, and 2 was soluble in DMF and DMSO, but 3 was almost insoluble in common organic solvents. We investigated the exchange properties of 3 to other solvents. When the crystals of 3 were immersed into the normal solvents such as CH₂Cl₂, CHCl₃, MeCN, and MeOH, its powder X-ray diffraction patterns showed that solvent exchange did not take place. We also attempted the so-called single-crystal-to-single-crystal

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Scheme 1. Synthetic route of new azo calix[4]arene ligand 2.

conversion of **3** by placing its single crystal in the atmosphere of MeOH, MeCN or pyridine vapor but all failed. The elemental analyses of **2** and **3** were consistent with their chemical formula. The ¹H NMR spectrum of **2** in DMSO- d_6 exhibited two singlets, one doublet–doublet and one triplet for the phenyl groups at 8.27 ppm, 7.85 ppm, 7.96–8.03 ppm, 7.59–7.63 ppm, and the bridging methylene groups at

4.17–4.56 ppm. And the signal for the bridging methylene groups appear at $\delta = 31.44$ ppm in its ¹³C NMR spectrum, suggesting existence of a cone conformation of the tetra-substituted calix[4] arene in solution at room temperature [9]. The IR spectra of **2** showed an C=O and C-O stretching vibrations at 1715 and 1470 cm⁻¹, which downshifted to 1658 and 1385 cm⁻¹ of **3**, indicating existence of



Fig. 1. (a) – (d) View of the coordination environments of Cd centers in **3** with labeling schemes. Symmetry codes: (A) -x+2, -y, z; (B) -x+2, -y-1, -z; (C) -x+2, -y, -z; (D) x+1, y, z; (E) -x+2, -y, -z-1. All hydrogen atoms are omitted for clarity.

coordinated carboxylic groups [10]. The middle peaks at in the range of 1593–1596 cm⁻¹ were assigned to the asymmetric N=N vibration of complexes **2** and **3** [9]. Compound **3** was finally confirmed by X-ray crystallography [11]. The X-ray powder pattern of **3** was matched with the simulated patterns generated from their single crystals data (Fig. S1).

Compound 3 crystallizes in the triclinic space group Pi, and its asymmetric unit contains half a $[Cd_7L_4(DMF)_4(EtOH)_2(H_2O)_2]^{2-1}$ dianion, a protonated H₃O⁺ cation, one guarter of EtOH, five halves of EtOH, three EtOH, one DMF, three halves of DMF, and half a H₂O solvent molecules. As shown in Fig. 1, the Cd atoms in 3 adopt two different coordination geometries. Cd1 is seven-coordinated by six O atoms of three chelating carboxylate groups from three different H₄L ligands and one O atom from one EtOH molecule (Fig. 1a). Cd2 is octahedrally coordinated by four O atoms of four carboxylate groups from four different H₄L ligands, two O atoms from one DMF and one H₂O molecule (Fig. 1b). Cd3 adopts the same coordination geometry as Cd1, coordinated by four O atoms of four carboxylic groups from four different H₄L ligands, two O atoms of one chelating carboxylate groups from H₄L ligand and O atom from one DMF molecule (Fig. 1c). Cd4 is also octahedrally coordinated by four O atoms of two chelating carboxylate groups from two different H₄L ligands, two O atoms of two carboxylate groups from two different H₄L ligands (Fig. 1d). Besides, it is noted that there existed two weak interactions (2.878 Å) between Cd4 and O21 and between Cd4 and O21A. The carboxylate groups in **3** also show three different coordination modes: chelating, bridging, chelating-bridging. For the seven-coordinated Cd, the mean Cd–O bond length (2.437(5) Å) of **3** (Table S1) is longer than that of the corresponding one in [Cd₂(BTC)₂(H₂O)₂]·2HCHA·2EtOH·2H₂O (2.380(2) Å, BTC = 1,3,5-benzenetricarboxylate, CHA = cyclohexylamine) [13a]. For the six-coordinated Cd, the mean Cd–O bond length (2.138(6) Å) of **3** is shorter than that of the corresponding one in [Cd $(PDC)(4-nitrobenzoate)_2(H_2O)]$ (2.312(5) Å, HPDC = 4-piperidinecarboxylic acid) [13b].

Interestingly, Cd3, Cd3A, Cd3B, Cd3C, Cd4 and Cd4A are linked by two L ligands to form a hexanuclear $[Cd_6L_2]$ cage-like unit with an approximate dimension of 2.98 Å (between O13 and O14) × 8.07 Å (between C65 and C109)×17.43 Å (between C84 and C112) Å (Fig. 2a). Each Cd atom in such a unit interconnects its equivalent ones *via* L ligands to form a 1D chain extending along the *a* axis (Fig. S2). Besides, Cd1, Cd1A, Cd1B, Cd1C, Cd2 and Cd2A atoms and two other L ligands to produce another [Cd₆L₂] cage-like unit with a rough size of 2.50 Å (between O1 and O4) \times 9.02 Å (between C39 and C51) \times 18.94 Å (between C14 and C42) Å. Such a unit also creates a 1D chain extending along the *c* axis. These two 1D chains are interconnected together by two chelating and/or bridging carboxylates, affording a 2D network extending with ac plane (Fig. S3). Each 2D network is further connected by Cd2 atoms to form an unprecedented 3D framework (Fig. 2b), which is calculated by the Platon program [14] showing that the effective solvent accessible volume of 3396.8 Å³ per unit cell (41.7% of the total cell volume) is filled with DMF, EtOH and H₂O solvent molecules. The calix[4]arene parts between two layers in the 3D structure not only exhibited a vertical up-down fashion but also a slipped up-down fashion (Fig. S4). Topologically, compound 3 consists of a 3D (6,8)-connected framework with one L ligand as a 6-connecting node and one L as a 8-connecting node (Fig. 2c). According to Wells [15], such a net can be further specified by an new Schläfli symbol of $(3^34^65^26^37^1)(3^64^{13}5^86^1).$

Thermogravimetric (TGA) and differential thermal analysis (DTA) experiments were carried out to study the thermal stability of azo groups in **2** and **3**. The DTA curves (Fig. S5) exhibited the onset at 283 °C (**2**) and 285 °C (**3**) and the maximum at 290 °C (**2**) and 295 °C (**3**) with the exothermic energy of 324 J/g for **2** and 373 J/g for **3**, respectively, which were ascribed to the decomposition of azo groups [16]. As shown in the TGA curve of **3** (Fig. S6), the weight loss (observed 21.27%) in the range of 20–231 °C corresponded to the





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Fig. 2. (a) View of one hexanuclear [Cd₆L₂] cage-like unit of **3**. Symmetry codes: A: -x+1, -y, -z-1; B: -x+2, -y, -z-1; C: x-1, y, z. (b) View of a 3D framework in **3** looking along the *b* axis. The yellow and purple spheres represent the two kinds of cavities in **3**. (c) Schematic view of a ($3^{3}4^{6}5^{2}6^{3}7^{1}$)($3^{6}4^{13}5^{8}6^{1}$) topological net of **3**. The sky blue and yellow balls represent 6- and 8-connected nodes, respectively. Atom color codes: Cd, green; O, red; N, blue; and C, gray. All hydrogen atoms are omitted for clarity.

removal of all the coordinated and uncoordinated EtOH, H_2O and DMF molecules (calculated 21.47%). As shown in the TGA curve of **2** (Fig. S6), the weight loss (observed 10.57%) in the range of 235–364 °C was ascribed to the removal of four azo groups (calculated 11.02%). For **3**, the removal of four azo groups started at 248 °C for **3**, which is consistent with that of **2**.

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Appendix A. Supplementary data

CCDC no. 810114 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge via http://www. ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2011.03.077.

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- [7] A solution of m-carboxybenzenediazonium chloride prepared from m-aminobenzoic acid (2.74 g, 20 mmol), sodium nitrite (1.38 g, 20 mmol) and concd. HCl (7.5 mL) in 35 mL of water was slowly added into a cold (0-5 °C) solution containing 1 (2.0 g, 4.72 mmol) and sodium acetate trihydrate (8.16 g, 60 mmol) in 50 mL of DMF. After being stirred for 4 h, the red suspension was adjusted to be acidic with 300 mL of aqueous HCl (0.25%). The mixture was warmed at 60 °C for 30 min to produce 2 as a reddish solid, which was filtered and thoroughly washed with water and MeOH, and dried in vacuo. Yield: 4.61 g (96%). Anal. Calcd. for C₅₆H₄₀N₈O₁₂: C, 66.14; H, 3.96; N, 11.02. Found: C, 66.02; H, 3.83; N, 11.33. IR (KBr disc): 3407 (m), 2948 (w), 1715 (s), 1699 (m), 1593 (m), 1532 (w), 1470 (m), 1450 (m), 1332 (w), 1268 (s), 1189 (w), 1119 (w), 899 (w), 810 (w), 761 (m), 684 (w), 502 (w) cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.27 (s, 4 H, ArH), 7.96-8.03 (dd, 8 H, J = 8 Hz, ArH), 7.85 (s, 8 H, ArH), 7.59-7.63 (t, 4 H, J = 8 Hz, ArH), 4.17 and 4.56 (br, d, 8 H, ArCH₂Ar). ¹³C NMR (400 MHz, DMSO-*d*₆): δ 167.00, 158.24, 151.82, 145.00, 132.06, 130.67, 130.20, 129.81, 126.96, 124.74, 121.88, 31.44
- [8] To a 10 mL Pyrex glass tube was loaded $Cd(NO_3)_2 \cdot 4H_2O$ (8 mg, 0.025 mmol), H_4L (13 mg, 0.0125 mmol), 1.5 mL of DMF and 1.5 mL of EtOH, forming a red clear solution. After the pH value was adjusted to 5.0-6.0 by addition of 0.5 M HClO₄, the tube was sealed and heated in an oven to 90 °C for one day, and then cooled to ambient temperature at the rate of 5 °C h⁻¹ to form red blocks of 3, which were collected and washed with EtOH and dried in air. Yield: 14 mg (62%, based on Cd). Anal. Calcd. for C₂₇₈H₂₃₁Cd₇N₄₁O_{75.5}: C, 53.75; H, 4.90; N, 9.24. Found: C, 53.99; H, 4.63; N, 9.65. IR (KBr disc): 3428 (m), 2927 (w), 1659 (s), 1596 (m), 1548 (s), 1470 (s), 1385 (s), 1267 (m), 1116 (m), 1020 (w), 913 (w), 771 (w), 688 (m), 666 (w), 505 (w) cm⁻¹
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- [11] Crystal data for 3: C₂₇₈H₂₃₁Cd₇N₄₁O_{75.5}, M_r=6140.92, triclinic, space group Pi, $a = 18.7929(5), b = 19.0242(4), c = 26.2547(11) \text{ Å}, \alpha = 74.825(6)^{\circ}, \beta = 78.090$ (6)°, $\gamma = 64.843(5)°$, V = 8151.2(6) Å³, Z = 1, $D_c = 1.251$ g cm⁻³, $\mu = 0.526$ mm⁻¹, 64479 reflections measured, 28444 unique reflections (Rint=0.0495), 21941 observed reflections ($I > 2\sigma(I)$), 1808 parameters, $R_1 = 0.0843$, $wR_2 = 0.2277$, S = 1.106. X-ray single-crystal diffraction data for **3** was collected on a Rigaku Mercury CCD diffractometer by using graphite monochromated Mo-K α $(\lambda = 0.71073 \text{ Å})$. Cell parameters were refined by using the program CrystalClear (Rigaku and MSC, version 1.3, 2001). The crystal structures of 3 was solved by direct methods and refined on F^2 by full-matrix least-squares methods with the SHELXL-97 program [12]. In 3, two EtOH solvent molecules were found to be disordered over two positions with an occupancy factor of 0.737/0.263 for O30, C128-C129/O30A, C128A-C129A, and 0.462/0.538 for O35, C139-C140/O35A, C139A-C140A. All non-hydrogen atoms except for those of DMF (027-029, N19-N21, C119-C127 and O32, N22, C132-C134), EtOH (O31, C130-C131 and O35-O40, C139-C150) and H₂O (O2W and O3W) solvent molecules were refined anisotropically. The H atom of the protonated water molecule (O2W) was located from Fourier maps. Except those of CO₂H groups and the water solvent molecules of 3, all other H atoms were introduced at the calculated positions and included in the structure-factor calculations.
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