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ARTICLE

Syntheses, Structures, and Luminescence Properties of Four Metal-Organic Polymers With Undocumented Topologies Constructed From 3,5-Bis((4'-carboxylbenzyl)oxy)benzoate Ligand

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ABSTRACT: Solvothermal reactions of one semirigid tricarboxylic acid and transitional metal cations in the absence or presence of 1,4-bis(1H-imidazol-4-yl)benzene (1,4-bib) afford four coordination polymers, namely, $[Cd(Hbcb)]_n$ (**1**), and $[M(Hbcb)(1,4\text{-bib})]_n$ (M = Cd (**2**), Mn (**3**), Fe(**4**)) (H_3bcb = 3,5-bis((4'-carboxylbenzyl)oxy)benzoic acid). Their structures have been determined by single-crystal X-ray diffraction analyses and further characterized by elemental analyses, IR spectra, powder X-ray diffraction (PXRD), and thermogravimetric (TG) analyses. Strucural analysis revealed complex **1** exhibits an intriguing $[Cd(COO)_2]_n$ tube-like chain based 3D framework with unprecedented 6-connected $(4^8{\cdot}6^7)$ topology. Complexes **2–4** are isomorphism and show new 3D (3,5)-connected framework with the Point Schläfli symbol of $(4{\cdot}6{\cdot}8)(4{\cdot}6^4{\cdot}8^5)$ based on the $[M(COO)]_n$ chain. Moreover, photoluminescent properties of **1** and **2** have been investigated in the solid state at room temperature.

Introduction

The rational design and construction of functional materials based on organic ligands has been a subject of growing interest in the past two decades due to their exceptionally artistic topologies and tremendous potential applications, such as gas adsorption and separation, ion exchange, nonlinear optics, heterogeneous catalysis, and luminescence.[1–4] These intriguing properties and excellent applications are mostly attributed to the distinct architecture and composition of the metal-organic polymers.[5] It is well-known that the experimental conditions during the self-assembly process play a vital role on the growth of the single crystals, such as temperature, metal ions, template, pH value, counteranion, reaction period, concentrations of the raw materials, and so on.[6,7] Among these factors, tactical design or selection of the characteristic organic ligands according to their length, rigidly, and functional groups was proved to be one efficient route for achieving expected MOFs.[8,9]

However, it is still one tremendous challenge to design and synthesize such crystal materials for coordination chemistry researchers, although considerable progress in the practical and theoretic approaches have been achieved.[10,11] The most common strategy is one-pot reaction of metal ions and selected organic ligands by serendipitous self-assembly although it is impossible to predict the final crystal structure. This strategy has been proved effective and were widely applied in many systems.[12,13]

Recent study on coordination assemblies using biphenyl-3,4',5-tricarboxylic acid (H_3BPT) and bis(imidazole) linkers states a reliable strategy for obtaining new topological prototypes of coordination nets.[13c] Also, a minor change of the carboxylate building blocks may be applied to realize good structural control of the resulting coordination polymers. Thus, these considerations inspired us to explore novel metal-organic coordination architectures with the designed semirigid 3,5-bis((4'-arboxylbenzyl)oxy)benzoic acid (H_3bcb, Scheme 1). Compared with the rigid H_3BPT, H_3bcb is a more flexible and longer ligand, which owns the followed intriguing characters: (i) three carboxyl groups may be partially or completely deprotonated, resulting in rich coordination modes and interesting topologies with higher dimensionalities, (ii) three benzoate groups separated could form different dihedral angles through the rotation of –O–C– groups, thus it may coordinate metal centers in different orientations. These characters may lead to helical structures, cavities, interpenetration, and other novel motifs with extraordinary topologies. Taking account of the above viewpoints, recently we began to assemble polymeric complexes with H_3bcb and transitional metal ions and anticipated the rich structural features stored in H_3bcb will induce new metal-organic structures.

In this paper, four new complexes with interestingly topologies have been synthesized, namely, $[Cd(Hbcb)]_n$ (**1**), and $[M(Hbcb)(1,4\text{-bib})]_n$ (M = Cd (**2**), Mn (**3**), Fe(**4**)). Their structures and properties were measured and identified by physical methods. Due to the excellent coordination abilities of H_3bcb, compounds **1–4** exhibit 3D frameworks, built from the intriguing 1D metal-carboxyl chains, exhibiting undocumented topologies: 6-connected $(4^8{\cdot}6^7)$ for **1** and (3,5)-connected $(4{\cdot}6{\cdot}8)(4{\cdot}6^4{\cdot}8^5)$ for **2–4**.

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† Electronic Supplementary Information (ESI) available: Additional Figures, powder X-ray diffraction (PXRD) patterns, thermogravimetric analysis (TGA) and IR spectra for **1–4**. X-ray crystallographic data, CCDC 986465–986468 for **1–4**. See DOI:10.1039/c4ra00000x.

Experimental Section

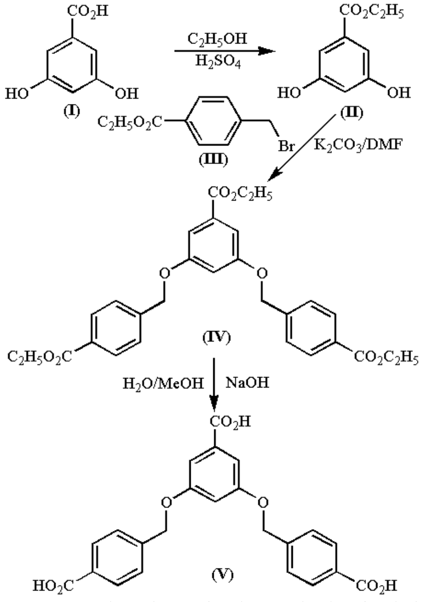
Materials and Physical Measurements. All chemicals were purchased from Jinan Henghua Sci. & Tec. Co. Ltd. without further purification. IR spectra were measured on a NEXUS 670 FTIR spectrometer at the range of 600-4000 cm^{-1}. Elemental analyses were carried out on a CE instruments EA 1110 elemental analyzer. X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with Cu-Kα radiation. Thermogravimetric analyses (TGA) were performed under air condition from room temperature to 800 °C with a heating rate of 10 °C min^{-1} on Perkin-Elmer TGA-7 thermogravimetric analyzer. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

Synthesis of 3,5-bis((4′-carboxylbenzyl)oxy)benzoic acid (H_3bcb) (Scheme 1).

Synthesis of ethyl 3,5-dihydroxybenzoate (II). The mixture of 3,5-dihydroxybenzoic acid (0.1 mol, 15.4 g) and 10 mL concentrated H_2SO_4 in 500 mL ethanol was refluxed for 12 hours, and then poured into 500 mL H_2O. White solid was filtrated and recrystallized from methanol with the yield of 85%. Anal. (%) calcd. for $C_9H_{10}O_4$: C, 59.34; H, 5.53. Found: C, 59.16; H, 5.40.

Synthesis of ethyl 4-bromomethylbenzoate (III). The mixture of 4-(bromomethyl)benzonitrile (0.1 mol, 19.6 g) and 10 mL concentrated H_2SO_4 in 500 mL ethanol was refluxed for 3 days, and then poured into 500 mL H_2O. Ethyl acetate was used to extract for three times. White solid was obtained after vacuum concentration with the yield of 56%. Anal. (%) calcd. for $C_{10}H_{11}BrO_2$: C, 49.41; H, 4.56. Found: C, 49.32; H, 4.43.

Synthesis of ethyl 3,5-bi(4-cyanophenoxy)benzoate (IV). The mixture of **II** (0.05 mol, 9.1 g), **III** (0.10 mol, 24.2 g), and potassium carbonate (0.1 mmol, 13.8 g) in 500 mL DMSO was refluxed at 120 ˚C for one week and then poured into 2000 mL H_2O. The obtained solid was recrystallized from methanol and purified by Silica gel chromatography with a eluting mixture of chloroform and acetone (2:1, v/v), with 36% yield. Anal. (%) calcd. for $C_{29}H_{30}O_8$: C, 68.76; H, 5.97. Found: C, 68.58; H**,** 5.79.



Scheme 1. The scheme for the synthesis of H_3bcb.

Synthesis of 3,5-bis((4′-carboxylbenzyl)oxy)benzoic acid (H_3bcb) (V). The mixture of IV (0.05 mol, 25.3 g) and NaOH (0.2 mol, 8.0 g) in the mixed solvent of EtOH (500 mL) and H_2O (500 mL) was refluxed at 75 ˚C for one day and filtrated. The filtrated solution was adjusted to pH = 3 to result in white solid. Recrystallization was applied in DMSO with the yield of 72%. EI-MS: m/z $[M-H]^-$, 421.1 (calcd for $C_{23}H_{18}O_8$, 422.1). Anal. (%) calcd. for $C_{23}H_{18}O_8$: C, 65.40; H, 4.30. Found: C, 65.21; H, 4.13.

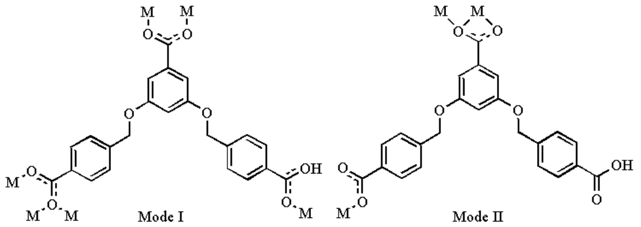
Synthesis of $[Cd(Hbcb)]_n$ (1). A mixture of H_3bcb (0.20 mmol, 0.083 g), $3CdSO_4{\cdot}8H_2O$ (0.13 mmol, 0.103 g), NaOH (0.10 mmol, 0.004 g) and 12 mL H_2O was placed in a Teflon-lined stainless steel vessel, heated to 170 °C for 3 days, followed by slow cooling (a descent rate of 10 ^oC/h) to room temperature. Light yellow block crystals of **1** were obtained. Yield of 37% (based on Cd). Anal. (%) calcd. for $C_{23}H_{16}CdO_8$: C, 51.85; H, 3.03. Found: C, 52.17; H, 3.12. IR (KBr pellet, cm^{-1}): 3039 (m), 2642 (w), 1683 (s), 1592 (vs), 1549 (vs), 1360 (vs), 1247 (s), 1060 (m), 824 (m), 770 (m), 720 (w).

Synthesis of $[Cd(Hbcb)(1,4\text{-}bib)]_n$ (2). A mixture of H_3bcb (0.2 mmol, 0.083 g), 1,4-bib (0.20 mmol, 0.042 g), $3CdSO_4{\cdot}8H_2O$ (0.13 mmol, 0.103 g), NaOH (0.10 mmol, 0.004 g), and 12 mL H_2O was placed in a Teflon-lined stainless steel vessel, heated to 170 °C for 3 days, followed by slow cooling (a descent rate of 10 ^oC/h) to room temperature. Colourless block crystals of **2** were obtained. Yield of 57% (based on Cd). Anal. (%) calcd. for $C_{35}H_{26}CdN_4O_8$: C, 56.59; H, 3.53; N, 7.54. Found: C, 56.30; H, 3.69; N, 7.82. IR (KBr pellet, cm^{-1}): 3134 (m), 2596 (m), 1692 (s), 1593 (vs), 1527 (vs), 1371 (s), 1154 (s), 1049 (m), 834 (m), 753 (m).

Synthesis of $[Mn(Hbcb)(1,4\text{-}bib)]_n$ (3). The same synthetic procedure as for **2** was used except that $3CdSO_4{\cdot}8H_2O$ was replaced by $MnSO_4{\cdot}H_2O$ (0.40 mmol, 0.068 g), giving colourless block crystals. Yield of 53% (based on Mn). Anal. (%) calcd. for $C_{35}H_{26}MnN_4O_8$: C, 61.32; H, 3.82; N, 8.17. Found: C, 61.30; H, 4.03; N, 8.02. IR (KBr pellet, cm^{-1}): 3125 (m), 2876 (w), 1691 (s), 1595 (vs), 1442 (vs), 1371 (vs), 1237 (m), 1062 (s), 834 (m), 756 (m).

Synthesis of $[Fe(Hbcb)(1,4\text{-}bib)]_n$ (4). The same synthetic procedure as for **2** was used except that $3CdSO_4{\cdot}8H_2O$ was replaced by $FeSO_4{\cdot}7H_2O$ (0.40 mmol, 0.112 g), giving orange block crystals. Yield of 62% (based on Fe). Anal. (%) calcd. for $C_{35}H_{26}FeN_4O_8$: C, 61.24; H, 3.82; N, 8.16. Found: C, 61.37; H, 3.96; N, 8.45. IR (KBr pellet, cm^{-1}): 3145 (m), 2877 (m), 1692 (s), 1595 (vs), 1406 (vs), 1371 (vs), 1248 (s), 1050 (s), 835 (m), 754 (m).

X-ray Crystallography. Intensity data collection was carried out on a Siemens SMART diffractometer equipped with a CCD detector using Mo-*Kα* monochromatized radiation (λ = 0.71073 Å). The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program based on the method of Blessing. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXTL package.[14] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically with fixed isotropic thermal parameters. Crystallographic data for complexes **1**–**4** are given in Table 1. Selected bond lengths and angles for **1**–**4** are listed in Table 2. For complexes of **1**–**4**, further details on the crystal structure investigations may be obtained from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, CAMBRIDGE CB2 1EZ, UK, [Telephone:+44-(0)1223-762-910, Fax: +44-(0)1223-336-033; Email: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk/ deposit], on quoting the depository number CCDC-986465 for **1**, 986466 for **2**, 986467 for **3**, and 986468 for **4**. Topological analysis of the coordination networks of **1**–**4** was performed with the program package TOPOS.[15]



Scheme 2. The coordinaion modes of H_3bcb in complexes **1**–**4**.

Table 1 Crystal data for **1 – 4**

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{23}H_{16}CdO_8$	$C_{35}H_{26}CdN_4O_8$	$C_{35}H_{26}MnN_4O_8$	$C_{35}H_{26}FeN_4O_8$
Formula weight	532.76	743.00	685.54	686.45
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*P*na2$_1$	*P*bcn	*P*bcn	*P*bcn
a (Å)	19.0064(19)	27.0432(17)	26.780(2)	26.4977(19)
b (Å)	24.517(2)	8.0754(5)	8.1675(7)	8.1948(6)
c (Å)	4.6956(5)	27.1949(17)	26.928(2)	26.8556(6)
α (°)	90.00	90.00	90.00	90.00
β (°)	90.00	90.00	90.00	90.00
γ (°)	90.00	90.00	90.00	90.00
V(Å^3)	2188.0(4)	5938.9(6)	5889.9(9)	5831.5(6)
Z	4	8	8	8
D_{calcd} (Mg/m^3)	1.617	1.662	1.546	1.564
μ(mm^{-1})	1.045	0.800	0.513	0.583
θ range	1.36–25.00	1.68–25.00	1.69–25.00	1.70–25.10
Reflections collected	11049	29097	28793	28865
Data/Parameters	3730/290	5239/434	5188/434	5139/434
F(000)	1064	3008	2824	2832
T(K)	293(2)	296(2)	293(2)	296(2)
R_{int}	0.0364	0.0573	0.1282	0.0668
R_1 (wR_2) [$I > 2\sigma(I)$]	$R_1 = 0.0680$	$R_1 = 0.0309$	$R_1 = 0.0488$	$R_1 = 0.0406$
	$wR_2 = 0.2271$	$wR_2 = 0.0538$	$wR_2 = 0.0987$	$wR_2 = 0.0905$
R_1 (wR_2) (all data)	$R_1 = 0.0778$	$R_1 = 0.0507$	$R_1 = 0.0972$	$R_1 = 0.0731$
	$wR_2 = 0.2400$	$wR_2 = 0.0577$	$wR_2 = 0.1088$	$wR_2 = 0.0984$
Gof	1.002	1.001	1.007	1.007

$R_1 = \Sigma|\,|F_o|-|F_c|\,|/\,\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2]/\,\Sigma w(F_o^2)^2]^{1/2}$

Table 2 Selected bond lengths (Å) and angles (º) for **1 – 4**.

Complex **1**							
Cd(1)-O(5)$^{\#1}$	2.207(8)	Cd(1)-O(6)$^{\#2}$	2.257(6)	Cd(1)-O(2)	2.28(2)	Cd(1)-O(1)$^{\#3}$	2.305(7)
Cd(1)-O(7)$^{\#4}$	2.341(7)	Cd(1)-O(6)$^{\#5}$	2.375(8)	O(5)$^{\#1}$-Cd(1)-O(6)$^{\#2}$	103.1(3)	O(5)$^{\#1}$-Cd(1)-O(2)	165.8(5)
O(6)$^{\#2}$-Cd(1)-O(2)	90.2(6)	O(5)$^{\#1}$-Cd(1)-O(1)$^{\#3}$	95.8(3)	O(6)$^{\#2}$-Cd(1)-O(1)$^{\#3}$	98.8(3)	O(2)-Cd(1)-O(1)$^{\#3}$	86.9(5)
O(5)$^{\#1}$-Cd(1)-O(7)$^{\#4}$	81.2(3)	O(6)$^{\#2}$-Cd(1)-O(7)$^{\#4}$	174.9(3)	O(2)-Cd(1)-O(7)$^{\#4}$	85.3(6)	O(1)$^{\#3}$-Cd(1)-O(7)$^{\#4}$	83.3(3)
O(5)$^{\#1}$-Cd(1)-O(6)$^{\#5}$	87.4(3)	O(6)$^{\#2}$-Cd(1)-O(6)$^{\#5}$	92.92(18)	O(2)-Cd(1)-O(6)$^{\#5}$	86.9(5)	O(1)$^{\#3}$-Cd(1)-O(6)$^{\#5}$	166.8(3)
O(7)$^{\#4}$-Cd(1)-O(6)$^{\#5}$	84.6(2)						
Symmetry code: #1 -*x*+1/2, *y*-1/2, *z*+3/2; #2 *x*+1/2, -*y*+3/2, *z*+1; #3 *x*, *y*, *z*+1; #4 *x*-1/2, -*y*+3/2, *z*-1; #5 -*x*+1/2, *y*-1/2, *z*+1/2.							
Complex **2**							
Cd(1)-O(8)$^{\#3}$	2.186(2)	Cd(1)-N(1)	2.250(2)	Cd(1)-O(1)	2.282(2)	Cd(1)-N(3)	2.305(2)
Cd(1)-O(2)$^{\#4}$	2.323(2)	O(8)$^{\#3}$-Cd(1)-N(1)	98.11(9)	O(8)$^{\#3}$-Cd(1)-O(1)	108.76(8)	N(1)-Cd(1)-O(1)	94.34(8)
O(8)$^{\#3}$-Cd(1)-N(3)	88.68(9)	N(1)-Cd(1)-N(3)	171.49(9)	O(1)-Cd(1)-N(3)	88.26(8)	O(8)$^{\#3}$-Cd(1)-O(2)$^{\#4}$	154.40(8)
N(1)-Cd(1)-O(2)$^{\#4}$	93.59(9)	O(1)-Cd(1)-O(2)$^{\#4}$	92.87(7)	N(3)-Cd(1)-O(2)$^{\#4}$	78.17(8)		
Symmetry code: #3 -*x*+1, -*y*-1, -*z*+2; #4 -*x*+3/2, *y*-1/2, *z*.							
Complex **3**							
Mn(1)-O(4)$^{\#3}$	2.069(3)	Mn(1)-O(8)$^{\#4}$	2.107(2)	Mn(1)-O(7)	2.180(2)	Mn(1)-N(1)	2.193(3)
Mn(1)-N(3)	2.237(3)	O(4)$^{\#3}$-Mn(1)-O(8)$^{\#4}$	108.68(11)	O(4)$^{\#3}$-Mn(1)-O(7)	151.04(11)	O(8)$^{\#4}$-Mn(1)-O(7)	98.19(10)
O(4)$^{\#3}$-Mn(1)-N(1)	95.76(11)	O(8)$^{\#4}$-Mn(1)-N(1)	95.68(11)	O(7)-Mn(1)-N(1)	92.04(11)	O(4)$^{\#3}$-Mn(1)-N(3)	89.13(11)
O(8)$^{\#4}$-Mn(1)-N(3)	90.45(10)	O(7)-Mn(1)-N(3)	79.86(10)	N(1)-Mn(1)-N(3)	170.49(12)		
Symmetry codes: #3 *x*+1/2, -*y*+1/2, -*z*+1; #4 -*x*+1/2, *y*+1/2, *z*.							
Complex **4**							
Fe(1)-O(8)$^{\#3}$	1.996(2)	Fe(1)-O(2)	2.0788(19)	Fe(1)-O(1)$^{\#4}$	2.095(2)	Fe(1)-N(3)	2.153(2)
Fe(1)-N(1)	2.199(2)	O(8)$^{\#3}$-Fe(1)-O(2)	151.13(9)	O(8)$^{\#3}$-Fe(1)-O(1)$^{\#4}$	109.85(9)	O(2)-Fe(1)-O(1)$^{\#4}$	97.44(8)
O(8)$^{\#3}$-Fe(1)-N(3)	95.50(9)	O(2)-Fe(1)-N(3)	92.38(9)	O(1)$^{\#4}$-Fe(1)-N(3)	92.68(9)	O(8)$^{\#3}$-Fe(1)-N(1)	89.94(9)
O(2)-Fe(1)-N(1)	80.90(8)	O(1)$^{\#4}$-Fe(1)-N(1)	89.30(8)	N(3)-Fe(1)-N(1)	173.19(9)		
Symmetry codes: #3 *x*+1/2, -*y*+3/2, -*z*+2; #4 -*x*+1/2, *y*-1/2, *z*.							

Result and Discussion

Synthesis and Characterization. Complexes **1–4** were prepared from the solvothermal reaction of H_3bcb and related transitional metal salts in similar reaction conditions. Other transition metal salts also were used to react with H_3bcb under similar reaction condition of complex **1**, unfortunately we just obtained some unknown powder substance in the end. The ancillary co-ligands were introduced to adjust the final structure with mixed ligands strategy. The linear 1,4-bib (1,4-bis(1H-imidazol-4-yl)benzene) as well as some other bridging imidazole linkers (V-shaped 1,3-bis(1H-imidazol-4-yl)benzene ligand, the flexible 1,3-bis(imidazol-1-ylmethyl)benzene ligand, 1,4-bis(imidazol-1-ylmethyl)benzene ligand, and longer 4,4'-bis(imidazol-1-yl)biphenyl ligand) have been selected as co-ligands to modify the network, but only three 1,4-bib based complexes were constructed, which might attribute to the coordination preference of H_3bcb. Besides, the 1,4-bib ligand can separated the neighbouring cations with a proper distance. The solid state of **1–4** are stable upon exposure to air.

Structural Description of [Cd(Hbcb)]$_n$ (1). Single-crystal X-ray diffraction analysis revealed that complex **1** crystallizes in the orthorhombic *P*na2_1 space group. As shown in Fig. 1, the asymmetric unit of **1** contains one crystallographically independent Cd^{II} anion and one partly depronated Hbcb^{2-} ligand. Each Cd^{II} ion is hexa-coordinated and surrounded by six carboxyl oxygen atoms from six individual Hbcb^{2-} ligands, forming octahedral coordination geometry. The Cd−O bond distances range from 2.199(6) to 2.371(3) Å, and the dihedral angles around Cd^{II} are in the range of 80.90(9)−174.85(9)°.

The ligand of Hbcb^{2-} acts as one μ_6 node to coordinate with six Cd^{II} ions, in which the protonated carboxyl group adopts monodentate μ_1-η^1:η^0 coordination mode and the two deprotonated carboxyl groups adopt bridging μ_2-η^1:η^1 and μ_3-η^2:η^1 modes, respectively (Mode I, Scheme 2). It is noteworthy that the Cd^{II} ions are linked by the carboxyl groups to form an unprecedented 1D tube-like [Cd(COO)$_2$]$_n$ chain, with the diameter being *ca*. 2.04 Å. The nearest Cd···Cd distances are 3.824 and 4.696 Å, respectively (Fig. 2). Furthermore, three parallel [Cd(COO)$_2$]$_n$ chains are connected by three carboxyl groups of one Hbcbb^{2-} linker, leaving one 3D [Cd(Hbcb)]$_n$ framework (Fig. 3). The dihedral angles between two phenyl rings and central phenyl ring in one Hbcb^{2-} are 27.5(3), and 82.5(3)°, respectively. And the one between two phenyl rings is 66.6(6)°. Those dihedral angles indicate that the Hbcbb^{2-} is extremely unsymmetrical and distorted during the self-assembly process. Besides, the void volume in **1** is 14.7% of the crystal volume (321.3 out of the 2188.1 Å^3 unit cell volume), calculated by PLATON.[16]

To better understand the structure of **1**, the topological analysis approach is employed. From the topological point of view, both Hbcb^{2-} ligands and Cd^{II} act as 6-connected nodes, giving rise to an unprecedented 6-connected net with the Schläfli symbol of $(4^8 \cdot 6^7)$, shown in Fig. 4. To our knowledge, this topology has never been reported before.

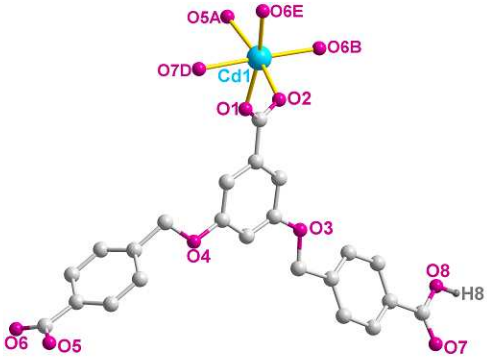


Figure 1. ORTEP representation of **1** showing the local coordination environment around Cd^{II} center. (Symmetry codes: (A) 0.5−*x*, −0.5+*y*, 1.5+*z*; (B) 0.5+*x*, 1.5−*y*, 1+*z*; (D) −0.5+*x*, 1.5−*y*, −1+*z*; (E) 0.5−*x*, −0.5+*y*, 1.5+*z*.).

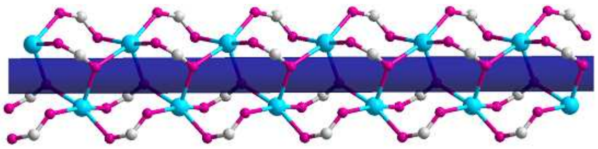


Figure 2. The intriguing 1D [Cd(COO)$_2$]$_n$ tube-like chain in complex **1**.

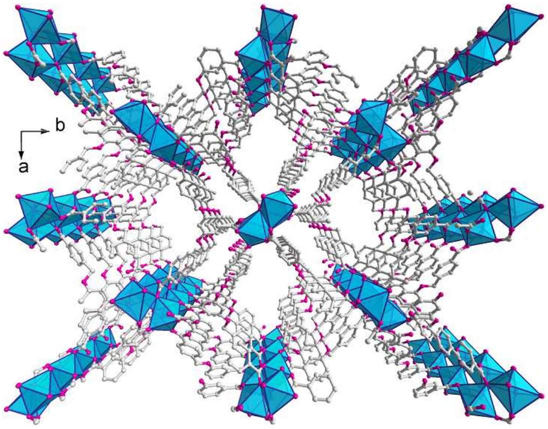


Figure 3. The 3D frameworks view along *c* axis in complex **1**.

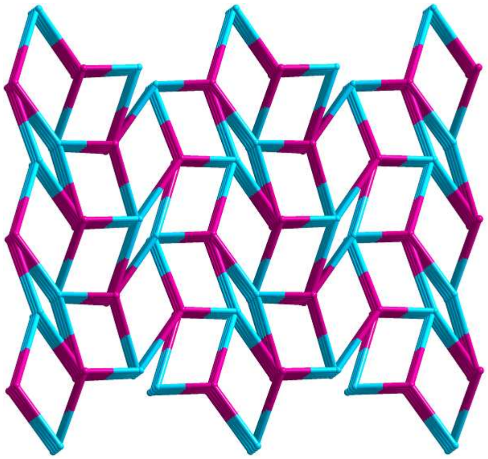


Figure 4. Schematic view of the novel 6-connected $(4^8 \cdot 6^7)$ topology of **1**.

Structural Description of [M(Hbcb)(1,4-bib)]$_n$ (M = Cd (2), Mn (3), Fe(4)). With the ancially ligand of 1,4-bib being employed in the reaction, part of coordiantion geometry around metal center were occupied by nitrogen atoms from imidazole rings in 1,4-bib ligand. The stereospecific blockade of 1,4-bib resulted in distorted trigonal bipyramidal coordination geometries around metal cations in **2-4**.

The single-crystal X-ray diffraction analyses reveal that complexes **2**–**4** are isomorphous and crystallize in the orthorhombic *P*bcn space group, herein only the structure of **2** will be discussed as a representation. As shown in Fig. 5, there are one crystallographically independent Cd^{II} ion, one Hbcb^{2-} ligand, and one 1,4-bib ligand in the asymmetric unit. Each Cd^{II} center is penta-coordinated by two nitrogen atoms from two 1,4-bib ligands [Cd(1)–N(1) = 2.250(2), and Cd(1)–N(3) = 2.305(2) Å] and three oxygen atoms from three Hbcb^{2-} ligands [Cd(1)–O(1) = 2.282(2), Cd(1)–O(2) = 2.323(2), and Cd(1)–O(8) = 2.186(2) Å], forming a distorted trigonal bipyramidal coordination geometry.

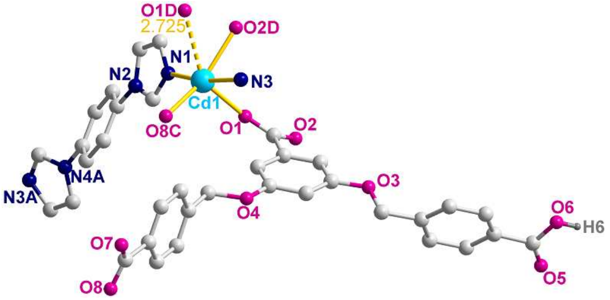


Figure 5. ORTEP representation of **2** showing the local coordination environment around Cd^{II} center. (Symmetry codes: (A) *x*, −*y*, −0.5+ *z*; (C) 1−*x*, −1−*y*, 2−*z*; (D) 1.5−*x*, −0.5+*y*, *z*.).

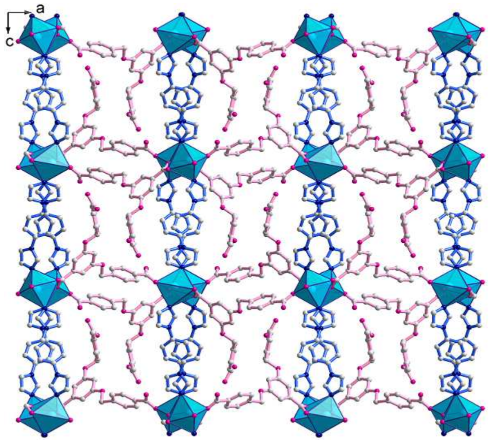


Figure 6. View of the 3D frameworks in complex **2**.

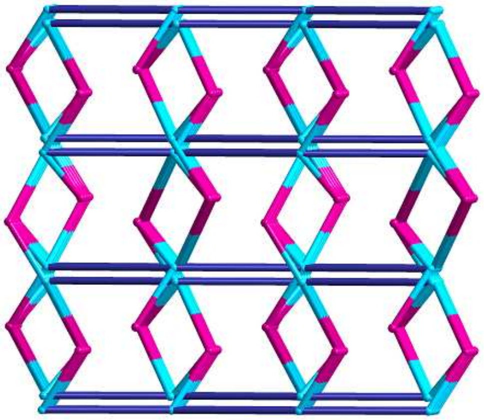


Figure 7. Schematic view of the novel binodal (3,5)-connected $(4\cdot6\cdot8)(4\cdot6^4\cdot8^5)$ topology of complex **2**.

Although the ligand of H$_3$bcb is also partly deprotonated, Hbcb^{2-} in complex **2** act as one μ_3 node to coordinate with three Cd^{II} ions, in which two deprotonated carboxyl groups adopt μ_2-η^2:η^1 and μ_1-η^1:η^0 coordination modes (Mode II), respectively, shown in Scheme 2. The dihedral angles between the two benzyl rings and central phenyl ring in Hbcbb^{2-} are 62.6(5) and 89.9(3)°, respectively, and the one between two phenyl rings is 62.7(8)°. The dihedral angles are slightly different for compounds **2-4**: 63.2(6), 88.5(9), and 63.2(2)° for complex **3**; and 64.3(7), 87.1(9), and 63.3(6)° for complex **4**.

Each Cd^{II} ions are linked by μ_2-η^2:η^1 carboxyl groups to form a 1D [Cd(COO)]$_n$ chain, with the Cd···Cd distance being 4.298 Å (Fig. S1). And then the Hbcbb^{2-} anions act as bridging pillars, further expanded the 1D [Cd(COO)]$_n$ chains to a 2D [Cd(Hbcb)]$_n$ sheet along the *ab* plane (Fig. S2). Besides, the ancillary 1,4-bib as bridging linkers connected with the metal centres, successfully constructed a linear [Cd(1,4-bib)]$_n$ chain along *c* direaction. The linear [Cd(1,4-bib)]$_n$ chains pulling the neighbouring 2D [Cd(Hbcb)]$_n$ sheets together, finally generated a 3D framework (Fig. 6).

From the viewpoint of structural topology, the overall frameworks of complex **2** can be defined as a new binodal (3,5)-connected nets with the Schläfli symbol of $(4\cdot6\cdot8)(4\cdot6^4\cdot8^5)$ by denoting Cd^{II} and Hbcb^{2-} as five- and three-connected nodes, the bridging 1,4-bib ligands as linkers, respectively (Fig. 7).

Structural Comparisons. As shown in the Scheme 2, the H$_3$bcb exhibits two different coordination modes. Although both two coordination modes are partly deprotonated, the one in complex **1** adopts μ_6-η^1:η^0-η^1:η^1-η^1:η^2 coordintion mode (Mode I), act as a trifunctional ligand, compared with bifunctional bridging Hbcb^{2-} linker with μ_3-η^1:η^2-η^0:η^1 coordintion mode (Mode II). The three carboxyl groups of trifunctional Hbcb^{2-} ligated with Cd^{II} ions with monodentate μ_1-η^1:η^0, bridging μ_2-η^1:η^1, and bridging μ_3-η^1:η^2 carboxyl groups, obtained an interestingly 1D [Cd(COO)$_2$]$_n$ tube-like chain, which further expanded to the 6-connected $(4^8\cdot6^7)$ network. For complex **2**, the coordination mode is simple, the bridging bifunctional Hbcb^{2-} interact with Cd^{II} ions fromed a 2D [Cd(Hbcb)]$_n$ layer, and the neighbouring 2D layers are further interact with each other though the hydrogen bonds between protonated carboxyl groups and the deprotonated ones of different sheets. Then, the 2D [Cd(Hbcb)]$_n$ layers are further expanded along the 1D [Cd(1,4-bib)]$_n$ chains direction, given a 3D (3,5)-connected framework finally. The 1,4-bib ligand in complex **2** was thought act as a pillar to support adjacent [Cd(Hbcb)]$_n$ layers. The structural differences indicated the co-ligand of 1,4-bib has great influences on the coordination modes of H$_3$bcb and the packing structure due to that the stereospecific blockade of 1,4-bib make Hbcbb^{2-} extremely unsymmetrical and distorted during the self-assembly process. Thence, when the 1,4-bib ancillary ligand were added in construction of CPs, the polycarboxylates tend to connect with fewer metal ions (the change of coordination modes), and adjust themselves to satisfy the needs of lowest system energy by twisting, rotating, and folding, further effect the final structure. It is also noteworthy that the protonated carboxyl group on the benzyl ring in complexes **1**–**4** shows that three carboxyl groups in H$_3$bcb have different acidity.

X-ray Podwer Diffraction Analyses and Thermal Analyses.

Powder X-ray diffraction (XRD) has been used to check the phase purity of the bulky samples in the solid state. For complexes **1**–**4**, the measured XRD patterns are closely identical to the simulated patterns generated from the results of single-crystal diffraction data by Mercury program,[17] indicative of pure products (Figure S4, Supporting Information). The thermogravimetric (TG) analyses on polycrystalline samples of complexes **1**–**4** were performed in N_2 atmosphere and the TG curves are shown in Figure S5. For complex **1**, the whole structure is stable below 425 °C, and then the framework collapses with a result of thermal decomposition. For complexes **2**–**4**, the water-free networks are stable below 350°C, 370°C, and 340°C, respectively.

Photoluminescent Investigation. The photoluminescent properties of H_3bcb and complexes **1** and **2** have been investigated under 300 nm wavelength excitation at room temperature, and the normalised photoluminescent spectres were shown in Fig. 8. For the ligand H_3bcb, the main peak at 383 nm can be attributed to the $\pi^*\rightarrow n$ or $\pi^*\rightarrow\pi$ transitions. The emission spectra for **1** and **2** exhibit emission peaks of 334 and 361 nm, respectively, which may be assigned to the intraligandemission ($\pi^*\rightarrow n$ or $\pi^*\rightarrow\pi$). These emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature since the Cd^{II} ion is difficult to oxidize or reduce due to its d^{10} configuration.[18] The blue-shifted results of the Cd^{II}-containing complexes can be attributed to the H_3bcb ligand conformational change after dehydrogenation, which make the conjugated system reduced.[19] The difference of the emission behaviours for complexes **1** and **2** probably derive from the differences of solid-state crystal packing.

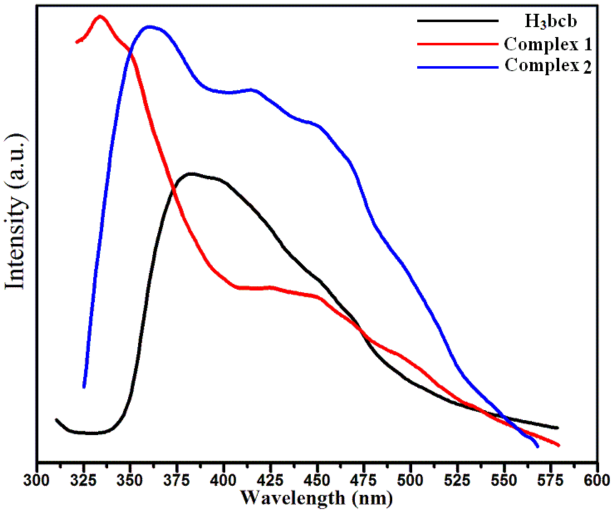


Figure 8. Solid-state emission spectra of H_3bcb ligand and the complexes **1** and **2** at room temperature.

Conclusions

In summary, with the elaboratly designed flexible and longer ligand of 3,5-bis((4'-carboxylbenzyl)oxy)benzoic acid (H_3bcb), four new complexes with undocumented topologies were obtained. When the 1,4-bib ancillary ligand was introduced into the reaction, a structural transformation from 6-conncected ($4^8\cdot6^7$) to (3,5)-connected ($4\cdot6\cdot8$)($4\cdot6^4\cdot8^5$) took place. The result demonstrated that the employment of the anciallry 1,4-bib linker in the assembly of metal–polycarboxylates coordination polymers could lead to structural changes and unprecedented topologies since the stereospecific blockade of 1,4-bib make $Hbcbb^{2-}$ extremely unsymmetrical and distorted during the self-assembly process. This will be the subject of future studies in our lab.

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Notes
The authors declare no competing financial interest.

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Table of Contents Graphic and Synopsis

Syntheses, Structures, and Luminescence Properties of Four Metal-Organic Polymers With Undocumented Topologies Constructed From 3,5-Bis((4'-carboxylbenzyl)oxy)benzoate Ligand

Xiutang Zhang, Liming Fan, Weikuo Song, Weiliu Fan, Liming Sun, Xian Zhao

Four 3D coordination architectures were obtained based on a new flexible ligand of 3,5-bis((4'-carboxylbenzyl)oxy)benzoic acid (H_3bcb) under hydrothermal conditions. With the modulation of ancillary ligand 1,4-bib, intriguing structural transformation from 6-conncected ($4^8 \cdot 6^7$) to (3,5)-connected ($4 \cdot 6 \cdot 8$)($4 \cdot 6^4 \cdot 8^5$) took place.