This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
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, a,b Liming Fan, a,b Weikuo Song, a Weiliu Fan, b Liming Sun, b Xian Zhao a,b

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-bib)] n (M = Cd (2), Mn (3), Fe(4)) (Hbcb = 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. Structural analysis revealed complex 1 exhibits an intriguing [Cd(COO) 3] n tube-like chain based 3D framework with unprecedented 6-connected (4 8 6) topology. Complexes 2–4 are isomorphism and show new 3D (3,5)-connected framework with the Point Schläfli symbol of (4 6 8)(4 6 8) 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 catalysis, and luminescence.  

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. Among these factors, tactical design or selection of the characteristic organic ligands according to their length, rigidity, and functional groups was proved to be one efficient route for achieving expected MOFs.

However, it is still a 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. 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.

Recent study on coordination assemblies using biphenyl-3,4,5-tricarboxylic acid (H 3 BPT) and bis(imidazole) linkers states a reliable strategy for obtaining new topological prototypes of coordination nets. 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 (Hbcb, Scheme 1). Compared with the rigid H 3 BPT, Hbcb 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 3 bcb and transitional metal ions and anticipated the rich structural features stored in H 3 bcb 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-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 3 bcb, compounds 1–4 exhibit 3D frameworks, built from the intriguing 1D metal-carboxyl chains, exhibiting undocumented topologies: 6-connected (4 8 6) for 1 and (3,5)-connected (4 6 8)(4 6 8) for 2–4.
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 diffraction 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 (H₂bcb) (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 H₂SO₄ in 500 mL ethanol was refluxed for 12 hours, and then poured into 500 mL H₂O. White solid was filtered and recrystallized from methanol with the yield of 85%. Anal. (%) calcld. for C₂₀H₁₂O₂: C, 59.34; H, 5.53. Found: C, 59.16; H, 5.40.

Synthesis of 4-(bromomethyl)benzonitrile (III). The mixture of 4-(bromomethyl)benzonitrile (0.1 mol, 19.6 g) and 10 mL concentrated H₂SO₄ in 500 mL ethanol was refluxed for 3 days, and then poured into 500 mL H₂O. Ethyl acetate was used to extract for three times. White solid was obtained after vacuum concentration with the yield of 56%. Anal. (%) calcld. for C₁₀H₁₂BrO₂: C, 49.41; H, 4.56. Found: C, 49.32; H, 4.43.

Synthesis of ethyl 3,5-bis(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 mol, 13.8 g) in 500 mL DMSO was refluxed at 120 °C for one week and then poured into 2000 mL H₂O. 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. (%) calcld. for C₂₉H₂₆O₅: C, 68.76; H, 5.97. Found: C, 68.58; H, 5.79.

Synthesis of 3,5-bis((4'-carboxylbenzyl)oxy)benzoic acid (H₂bcb) (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 H₂O (500 mL) was refluxed at 75 °C for one day and filtered. 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 C₂₉H₂₆O₅, 422.1). Anal. (%) calcld. for C₂₉H₂₆O₅: C, 65.40; H, 4.30. Found: C, 65.21; H, 4.13.

Synthesis of [Cd(Hbcb)]ₙ (1). A mixture of H₂bcb (0.20 mmol, 0.083 g), 3CdSO₄·8H₂O (0.13 mmol, 0.103 g), NaOH (0.10 mmol, 0.004 g) and 12 mL H₂O 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 °C/h) to room temperature. Light yellow block crystals of 1 were obtained. Yield of 37% (based on Cd). Anal. (%) calcld. for C₂₉H₂₆CdO₅·8H₂O: 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-bib)] (n) (2). A mixture of H₂bcb (0.20 mmol, 0.083 g), 1,4-bib (0.20 mmol, 0.042 g), 3CdSO₄·8H₂O (0.13 mmol, 0.103 g), NaOH (0.10 mmol, 0.004 g), and 12 mL H₂O 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 °C/h) to room temperature. Colourless block crystals of 2 were obtained. Yield of 57% (based on Cd). Anal. (%) calcld. for C₅₉H₄₅CdO₅·8H₂O: 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-bib)] (n) (3). The same synthetic procedure as for 2 was used except that 3CdSO₄·8H₂O was replaced by MnSO₄·H₂O (0.40 mmol, 0.068 g), giving colourless block crystals. Yield of 53% (based on Mn). Anal. (%) calcld. for C₅₉H₄₅MnO₅·8H₂O: 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 (s), 1106 (m), 1062 (s), 834 (m), 756 (m).

Synthesis of [Fe(Hbcb)(1,4-bib)] (n) (4). The same synthetic procedure as for 2 was used except that 3CdSO₄·8H₂O was replaced by FeSO₄·7H₂O (0.40 mmol, 0.112 g), giving orange block crystals. Yield of 62% (based on Fe). Anal. (%) calcld. for C₅₉H₄₅FeO₅·8H₂O: 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. 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...
Table 1 Crystal data for 1 – 4

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{12}H_{26}CdO_{8}</td>
<td>C_{12}H_{26}CdN_{4}O_{8}</td>
<td>C_{12}H_{26}MnN_{4}O_{8}</td>
<td>C_{12}H_{26}FeN_{4}O_{8}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>532.76</td>
<td>743.00</td>
<td>685.54</td>
<td>686.45</td>
</tr>
<tr>
<td>Space group</td>
<td>Pnma</td>
<td>Pnma</td>
<td>Pnma</td>
<td>Pnma</td>
</tr>
<tr>
<td>a (Å)</td>
<td>19.0064(19)</td>
<td>27.0432(17)</td>
<td>27.1949(17)</td>
<td>26.780(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>24.517(2)</td>
<td>8.0754(5)</td>
<td>8.1675(7)</td>
<td>8.1948(6)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>4.6956(5)</td>
<td>27.1949(17)</td>
<td>26.928(2)</td>
<td>26.8556(6)</td>
</tr>
<tr>
<td>σ (°)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>β (°)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
</tbody>
</table>

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

Complex 1

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(1)-O(5)</td>
<td>2.207(8)</td>
<td>Cd(1)-O(9)</td>
<td>2.257(6)</td>
</tr>
<tr>
<td>Cd(1)-O(7)</td>
<td>2.341(7)</td>
<td>Cd(1)-O(10)</td>
<td>2.275(6)</td>
</tr>
<tr>
<td>O(6)-Cd(1)-O(2)</td>
<td>90.26(2)</td>
<td>O(7)-Cd(1)-O(9)</td>
<td>95.83(3)</td>
</tr>
<tr>
<td>O(5)-Cd(1)-O(6)</td>
<td>81.23(3)</td>
<td>O(5)-Cd(1)-O(7)</td>
<td>144.9(3)</td>
</tr>
<tr>
<td>O(5)-Cd(1)-O(6)</td>
<td>84.6(3)</td>
<td>O(6)-Cd(1)-O(9)</td>
<td>86.9(3)</td>
</tr>
<tr>
<td>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.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Complex 3

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(1)-O(4)</td>
<td>2.609(3)</td>
<td>Mn(1)-O(8)</td>
<td>2.107(2)</td>
</tr>
<tr>
<td>Mn(1)-N(3)</td>
<td>2.403(4)</td>
<td>Mn(1)-N(7)</td>
<td>2.180(2)</td>
</tr>
<tr>
<td>O(4)-Mn(1)-N(1)</td>
<td>95.76(11)</td>
<td>O(4)-Mn(1)-O(7)</td>
<td>151.04(11)</td>
</tr>
<tr>
<td>O(8)-Mn(1)-N(1)</td>
<td>90.45(10)</td>
<td>O(4)-Mn(1)-N(3)</td>
<td>98.19(10)</td>
</tr>
<tr>
<td>Symmetry code: #3 x+1/2, y+1/2, z+1; #4 -x+1/2, y+1/2, z.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Complex 4

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(1)-O(9)</td>
<td>2.096(2)</td>
<td>Fe(1)-O(1)</td>
<td>2.0788(19)</td>
</tr>
<tr>
<td>Fe(1)-N(1)</td>
<td>2.199(2)</td>
<td>Fe(1)-N(2)</td>
<td>151.13(9)</td>
</tr>
<tr>
<td>O(8)-Fe(1)-N(3)</td>
<td>95.50(9)</td>
<td>O(8)-Fe(1)-N(3)</td>
<td>92.42(9)</td>
</tr>
<tr>
<td>O(2)-Fe(1)-N(1)</td>
<td>90.80(6)</td>
<td>O(2)-Fe(1)-N(3)</td>
<td>89.30(8)</td>
</tr>
<tr>
<td>Symmetry codes: #3 x+1/2, y+1/2, z+1; #4 -x+1/2, y+1/2, z.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Result and Discussion

Synthesis and Characterization. Complexes 1–4 were prepared from the solvothermal reaction of \( \text{H}_2\text{bcb} \) and related transitional metal salts in similar reaction conditions. Other transition metal salts also were used to react with \( \text{H}_2\text{bcb} \) 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-yl)benzene ligand, 1,4-bis(imidazol-1-yl)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 Hbcb. 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 \([\text{Cd}\text{bcb}]_n\) (1). Single-crystal X-ray diffraction analysis revealed that complex 1 crystallizes in the orthorhombic \(Pna_2_1\) space group. As shown in Fig. 1, the asymmetric unit of 1 contains one crystallographically independent \(\text{Cd}^{II}\) anion and one partly deprotonated Hbcb\(^{-}\) ligand. Each \(\text{Cd}^{II}\) ion is hexa-coordinated and surrounded by six carboxyl oxygen atoms from six individual Hbcb\(^{-}\) ligands, forming octahedral coordination geometry. The \(\text{Cd}−\text{O}\) bond distances around \(\text{Cd}^{II}\) are in the range of 2.199(6) to 2.371(3) Å, and the dihedral angles of \(\text{Cd}^{II}\) are 80.90(9)°, 82.5(3)°, respectively. And the one between two phenyl rings is 66.6(6)°. Those dihedral angles indicate that the Hbcbb 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 Hbcbb\(^{−}\) ligands and \(\text{Cd}^{II}\) act as 6-connected nodes, giving rise to an unprecedented 6-connected net with the Schl"afli symbol of \(\{4^6\}\), 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 \(\text{Cd}^{II}\) 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+\(y\), 0.5+\(z\)).

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\(^6\)) topology of 1.

Structural Description of \([\text{M}\text{bcb}(1,4-bib)]_n\) (M = \(\text{Cd}\) (2), \(\text{Mn}\) (3), \(\text{Fe}\) (4)). With the ancillary ligand of 1,4-bib being employed in the reaction, part of coordination 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*̅2*1*2*1*2 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 Hbcb2⁻ 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 \([\text{Cd}(1)–\text{N}(1) = 2.250(2), \text{Cd}(1)–\text{N}(3) = 2.305(2) \text{ Å}]\) and three oxygen atoms from three Hbcb2⁻ ligands \([\text{Cd}(1)–\text{O}(1) = 2.282(2), \text{Cd}(1)–\text{O}(2) = 2.323(2), \text{Cd}(1)–\text{O}(8) = 2.186(2) \text{ Å}]\), 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) 1−x, −y, −0.5+z; (C) 1−x, −1−y, 2−z; (D) 1.5−x, −0.5+y, z.)

Although the ligand of H3bcb is also partly deprotonated, Hbcb2⁻ in complex 2 act as one μ$_1$ node to coordinate with three Cd(II) ions, in which two deprotonated carboxyl groups adopt μ$_2$–η$_2$–η$_1$ coordination modes (Mode II), respectively, shown in Scheme 2. The dihedral angles between the two benzyl rings and central phenyl ring in Hbcb2⁻ are 62.6(5) and 89.9(3)°, respectively, and the one between two phenyl rings is 67.2(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)$_4$]$_{n}$ chain, with the Cd···Cd distance being 4.298 Å (Fig. S1). And then the Hbcb2⁻ anions act as bridging pillars, further expanded the 1D [Cd(COO)$_4$]$_{n}$ 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)$_4$]$_{n}$ chain along *c* direction. The linear [Cd(1,4-bib)$_4$]$_{n}$ 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 Schlӓfli symbol of (4·6·8)(4·6·8) by denoting Cd(II) and Hbcb2⁻ as five- and three-connected nodes, the bridging 1,4-bib ligands as linkers, respectively (Fig. 7).

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

**Figure 7.** Schematic view of the novel binodal (3,5)-connected (4·6·8)(4·6·8) topology of complex 2.

**Structural Comparisons.** As shown in the Scheme 2, the H3bcb exhibits two different coordination modes. Although both two coordination modes are partly deprotonated, the one in complex 1 adopts μ$_2$–η$_2$–η$_1$–η$_1$–η$_1$ coordination mode (Mode I), act as a trifunctional ligand, compared with bifunctional bridging Hbcb2⁻ linker with μ$_2$–η$_2$–η$_1$–η$_1$ coordination mode (Mode II).

The three carboxyl groups of trifunctional Hbcb2⁻ ligated with Cd(II) ions with monodentate μ$_1$–η$_1$, bridging μ$_2$–η$_1$, and bridging μ$_3$–η$_1$ carboxyl groups, obtained an interestingly 1D [Cd(COO)$_2$]$_{n}$ tube-like chain, which further expanded to the 6-connected (4·6·8) network. For complex 2, the coordination mode is simple, the bridging bifunctional Hbcb2⁻ 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)$_4$]$_{n}$ 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 to H3bcb and the packing structure due to that the stereospecific blockade of 1,4-bib make Hbcb2⁻ 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 H3bcb have different acidity.
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, indicative of pure products (Figure S4, Supporting Information). The thermogravimetric (TG) analyses on polycrystalline samples of complexes 1-4 were performed in N₂ 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 H₁bcb and complexes 1 and 2 have been investigated under 300 nm wavelength excitation at room temperature, and the normalised photoluminescent spectra were shown in Fig. 8. For the ligand H₁bcb, the main peak at 383 nm can be attributed to the π*→n or π*→π transitions. The emission spectra for 1 and 2 exhibit emission peaks of 334 and 361 nm, respectively, which may be assigned to the intraligand emission (π*→n or π*→π). These emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature since the Cd²⁺ ion is difficult to oxidize or reduce due to its d⁰ configuration. The blue-shifted results of the Cd²⁺-containing complexes can be attributed to the H₁bcb ligand conformational change after dehydrogenation, which make the conjugated system reduced. The difference of the emission behaviours for complexes 1 and 2 probably derive from the differences of solid-state crystal packing.

**Conclusions**

In summary, with the elaborately designed flexible and longer ligand of 3,5-bis(4'-carboxyphenyl)oxy)benzoic acid (H₁bcb), four new complexes with undocumented topologies were obtained. When the 1,4-bib ancillary linker was introduced into the reaction, a structural transformation from 6-connected (4⁵·6⁵) to 3,5-connected (4·6·8·4·6·8⁵) took place. The result demonstrated that the employment of the ancially, 1,4-bib linker in the assembly of metal-poly-carboxylates coordination polymers could lead to structural changes and unprecedented topologies since the stereospecific blockade of 1,4-bib make H₁bcb extremely unsymmetrical and distorted during the self-assembly process. This will be the subject of future studies in our lab.

**Acknowledgements.** The work was supported by financial support from the Natural Science Foundation of China (Grant Nos. 21101097, 91022034 and 51172127), the Excellent Youth Foundation of Shandong Scientific Committee (Grant JQ201015).

**Notes**

The authors declare no competing financial interest.

**References**


(15) (a) V. A. Blatov, A. P. Shevchenko and V. N. Serezhkin, J. Appl. Crystallogr., 2000, 33, 1193; (b) The network topology was evaluated by the program “TOPOS-4.0”, see: http://www.topos.ssu.samara.ru. (c) V. A. Blatov, M. O’Keeffe and D. M. Proserpio, CrystEngComm, 2010, 12, 44.


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$_3$bcbb) under hydrothermal conditions. With the modulation of ancillary ligand 1,4-bib, intriguing structural transformation from 6-connected ($4^8$) to (3,5)-connected (4·6·8)(4·6·8$^5$) took place.