

# **Self-catenated Coordination Polymers Involving Bis-pyridyl-bis-amide**

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**ABSTRACT:** The synthesis, structures and properties of five new coordination polymers containing bis-pyridyl-bis-amide and polycarboxylate ligands,  $\{[\text{Cd}(1,2\text{-bdc})(\mathbf{L}^1)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$  [1,2-H<sub>2</sub>bdc = benzene-1,2-dicarboxylic acid;  $\mathbf{L}^1 = N,N'$ -di(3-pyridyl)suberoamide], **1**,  $\{[\text{Cd}_2(1,3\text{-bdc})_2(\mathbf{L}^1)_3]\cdot 8\text{H}_2\text{O}\}_n$  (1,3-H<sub>2</sub>bdc = benzene-1,3-dicarboxylic acid), **2**,  $[\text{Cd}(1,4\text{-bdc})(\mathbf{L}^1)(\text{H}_2\text{O})_2]_n$  (1,4-H<sub>2</sub>bdc = benzene-1,4-dicarboxylic Acid), **3**,  $\{[\text{Cd}_2(1,2,3\text{-Hbtc})_2(\mathbf{L}^1)_3]\cdot 4\text{H}_2\text{O}\}_n$  (1,2,3-H<sub>3</sub>btc = 1,2,3-benzene-tricarboxylic acid), **4**, and  $[\text{Cd}(1,4\text{-pda})(\mathbf{L}^2)]_n$  [ $\mathbf{L}^2 = N,N'$ -di(3-pyridyl)adipoamide; 1,4-H<sub>2</sub>pda = 1,4-phenylenediacetic acid], **5**, are reported, which have been characterized by single crystal X-ray diffraction. Complex **1** forms a loop-like 1D chain, whereas **2** and **4** show 3D frameworks with a new self-catenated net with point symbol (6<sup>5</sup>·8). Complex **3** displays a 2D layer with the **sql** topology and **5** displays a rare 8T17 self-catenated net. The dimensionality and structural types of **1** - **3** can be adjusted by varying the ligand isomerism of the dicarboxylate ligands.

## INTRODUCTION

The design and synthesis of new coordination polymers with controlled dimensionality have become the center of interests in the chemical and material communities.<sup>1-8</sup> These complexes thus prepared have attracted a great attention not only due to their intriguing topological features but also their potential applications in the areas such as gas storage, separation, catalysis, ion exchange and magnetism.<sup>9-14</sup> Judicial choice of spacer ligand with diverse functionalities and metal-ion template may lead to well-defined coordination polymers. Although enormous examples of interesting coordination polymers<sup>15</sup> have been reported, the control of structural diversity remains a challenge in the field of crystal engineering and the influential factors are less ascertained. Self-catenated nets are single nets that exhibit the peculiar feature of containing shortest rings through which pass other components of the same network.<sup>16,17</sup> Catenation can be identified by the presence of edge(s) that thread a ring, in other words, they share at least one point with a disc-like film bounded by the ring.<sup>16,17</sup>

The mixed-ligand assembly system is an important strategy for the generation of new coordination polymers.<sup>18-25</sup> We have reported a series of coordination polymers based on the isomeric *N,N'*-di(2-pyridyl)adipoamide, *N,N'*-di(3-pyridyl)adipoamide and *N,N'*-di(4-pyridyl)adipoamide, and benzenedicarboxylate ligands.<sup>22</sup> The structural diversity of these Zn(II) and Cd(II) coordination polymers are subject to the changes of the donor atom positions of the spacer ligands, leading to the formation of a series of coordination polymers involving a 3D self-catenated net of  $\{4^{24}.5.6^3\}$ -**ilc** topology.<sup>22</sup> Recently, we have also reported that reactions of the flexible *N,N'*-di(3-pyridyl)suberoamide (**L**<sup>1</sup>) with Cu(II) salts in the presence of the isomeric phenylenediacetic acids

under hydrothermal conditions afforded  $\{[\text{Cu}(\mathbf{L}^1)(1,2\text{-pda})]\cdot\text{H}_2\text{O}\}_n$  (1,2-H<sub>2</sub>pda = 1,2-phenylenediacetic acid),  $\{[\text{Cu}(\mathbf{L}^1)(1,3\text{-pda})]\cdot 2\text{H}_2\text{O}\}_n$  (1,3-H<sub>2</sub>pda = 1,3-phenylenediacetic acid), and  $\{[\text{Cu}(\mathbf{L}^1)(1,4\text{-pda})]\cdot 2\text{H}_2\text{O}\}_n$ , which form a single 3,5-coordinated 3D net with the  $(4^2.6^5.8^3)(4^2.6)\text{-}3,5\text{T1}$  topology, a 5-fold interpenetrated 3D structure with the  $(6^5.8)\text{-cdfs}$  topology and the first 1D self-catenated coordination polymer, respectively.<sup>25</sup> The ligand-isomerism of the phenylenediacetate ligands was found important in determining the structural types. Obviously, by manipulating the isomeric effect from bis-pyridyl-bis-amide or dicarboxylate ligand, self-catenated coordination polymers can be achieved.

As our continuing efforts to investigate the correlation between the mixed-ligand system and the structural diversity of novel coordination polymers, we sought to investigate the structure-directing roles of the spacer ligands on the construction of bis-pyridyl-bis-amide-based Cd(II) coordination polymers by changing their donor atom positions and flexibility. The syntheses, crystal structures, and thermal and luminescent properties of  $\{[\text{Cd}(1,2\text{-bdc})(\mathbf{L}^1)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$  [1,2-H<sub>2</sub>bdc = benzene-1,2-dicarboxylic Acid;  $\mathbf{L}^1 = N,N'$ -di(3-pyridyl)suberoamide], **1**,  $\{[\text{Cd}_2(1,3\text{-bdc})_2(\mathbf{L}^1)_3]\cdot 8\text{H}_2\text{O}\}_n$  (1,3-H<sub>2</sub>bdc = benzene-1,3-dicarboxylic Acid), **2**,  $[\text{Cd}(1,4\text{-bdc})(\mathbf{L}^1)(\text{H}_2\text{O})_2]_n$  (1,4-H<sub>2</sub>bdc = benzene-1,4-dicarboxylic Acid), **3**,  $\{[\text{Cd}_2(1,2,3\text{-Hbtc})_2(\mathbf{L}^1)_3]\cdot 4\text{H}_2\text{O}\}_n$  (1,2,3-H<sub>3</sub>btc = 1,2,3-benzene-tricarboxylic acid), **4**, and  $[\text{Cd}(1,4\text{-pda})(\mathbf{L}^2)]_n$  [ $\mathbf{L}^2 = N,N'$ -di(3-pyridyl)adipoamide], **5**, form the subject of this report.

## EXPERIMENTAL SECTION

**General Procedures.** Elemental analyses were performed on a PE

2400 series II CHNS/O or an Elementar Vario EL cube analyzer. IR spectra (KBr disk) were obtained from a JASCO FT/IR-460 plus spectrometer. Thermal gravimetric analyses (TGA) measurements were carried out on a TG/DTA 6200 analyzer. Emission spectra were performed on a Hitachi F-4500 spectrometer. Powder X-ray diffraction was carried out using a Bruker D2 PHASER diffractometer with  $\text{CuK}\alpha$  ( $\lambda_\alpha = 1.54 \text{ \AA}$ ) radiation.

**Materials.** The reagents  $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ , 1,2-benzenedicarboxylic acid (1,2- $\text{H}_2\text{bdc}$ ), 1,3-benzenedicarboxylic acid (1,3- $\text{H}_2\text{bdc}$ ), 1,4-benzenedicarboxylic acid (1,4- $\text{H}_2\text{bdc}$ ) and benzene-1,2,3-tricarboxylic acid (1,2,3- $\text{H}_3\text{btc}$ ) were purchased from Aldrich Chemical Co.,  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  from Alfa Aesar and 1,4-phenylenediacetic acids from ACROS Co.. The ligands *N,N'*-di(3-pyridyl)suberoamide ( $\text{L}^1$ ) and *N,N'*-di(3-pyridyl)adipoamide ( $\text{L}^2$ ) were prepared according to published procedures.<sup>26-29</sup>

**Preparation of  $\{[\text{Cd}(\mathbf{1,2\text{-bdc}})(\text{L}^1)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ , **1**.** A mixture of  $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$  (0.034 g, 0.10 mmol), 1,2- $\text{H}_2\text{bdc}$  (0.017 g, 0.10 mmol) and  $\text{L}^1$  (0.033 g, 0.10 mmol) in 5 mL  $\text{H}_2\text{O}$  and 5 mL MeOH was sealed in a 23mL Teflon-lined stainless steel autoclave, which was then heated under autogenous pressure to 120 °C for two days. Slow cooling of the reaction system afforded colorless crystals suitable for single crystal X-ray diffraction. Yield: 0.034 g (52 %). Anal Calcd for  $\text{C}_{26}\text{H}_{32}\text{CdN}_4\text{O}_9$  (MW = 656.96, **1** +  $\text{H}_2\text{O}$ ): C, 47.53; H, 4.91; N, 8.53 %. Found: C, 47.91; H, 5.61; N, 9.11 %. IR ( $\text{cm}^{-1}$ ): 3742(w), 3291(m), 3063(m), 2936(m), 2858(w), 2362(w), 1694(w), 1665(w), 1550(s), 1482(m), 1406(s), 1331(w), 1285(m), 1222(w), 1119(m), 1035(w), 975(w), 853(m), 808(m), 740(w),

704(m), 645(w), 563(w), 443(w).

**Preparation of  $\{[\text{Cd}_2(\mathbf{1,3\text{-bdc}})_2(\mathbf{L}^1)_3]\cdot 8\text{H}_2\text{O}\}_n$ , **2**.** Prepared as described for **1**, except that  $\text{CdBr}_2\cdot 4\text{H}_2\text{O}$  (0.068 g, 0.20 mmol), 1,3- $\text{H}_2\text{bdc}$  (0.034 g, 0.20 mmol) and  $\mathbf{L}^1$  (0.098 g, 0.30 mmol) were used. Yield: 0.063 g (37 %). Anal Calcd for  $\text{C}_{70}\text{H}_{90}\text{Cd}_2\text{N}_{12}\text{O}_{22}$  (MW = 1676.35): C, 50.15; H, 5.41; N, 10.03 %. Found : C, 50.00; H, 5.11; N, 8.72 %. IR ( $\text{cm}^{-1}$ ): 3861(w), 3742(w), 3336(w), 2935(m), 2361(s), 1692(s), 1605(s), 1547(s), 1478(s), 1385(s), 1332(w), 1283(w), 1223(w), 1169(w), 917(s), 729(s), 418(w).

**Preparation of  $[\text{Cd}(\mathbf{1,4\text{-bdc}})(\mathbf{L}^1)(\text{H}_2\text{O})_2]_n$ , **3**.** Prepared as described for **1**, except that 1,4- $\text{H}_2\text{bdc}$  (0.017 g, 0.10 mmol) was used. Yield: 0.023 g (37 %). Anal Calcd for  $\text{C}_{26}\text{H}_{30}\text{CdN}_4\text{O}_8$  (MW = 638.94): C, 48.87; H, 4.73; N, 8.77 %. Found: C, 48.78; H, 5.27; N, 8.62 %. IR ( $\text{cm}^{-1}$ ): 3742(w), 3436(m), 1687(m), 1548(s), 1425(m), 1375(m), 1271(w), 754(w), 526(w).

**Preparation of  $\{[\text{Cd}_2(\mathbf{1,2,3\text{-Hbtc}})_2(\mathbf{L}^1)_3]\cdot 4\text{H}_2\text{O}\}_n$ , **4**.** Prepared as described for **1**, except that  $\text{Cd}(\text{CH}_3\text{CO}_2)_2\cdot 2\text{H}_2\text{O}$  (0.027g, 0.10 mmol), 1,2,3- $\text{H}_3\text{btc}$  (0.021 g, 0.10 mmol) and  $\mathbf{L}^1$  (0.033 g, 0.10 mmol) were used. Yield: 0.034 g (40 %). Anal Calcd for  $\text{C}_{72}\text{H}_{82}\text{Cd}_2\text{N}_{12}\text{O}_{22}$  (MW = 1692.30): C, 50.92; H, 4.88; N, 9.92 %. Found: C, 51.03; H, 4.64; N, 9.82 %. IR ( $\text{cm}^{-1}$ ): 3445(s), 2928(m), 2359(m), 1675(m), 1604(m), 1584(m), 1550(s), 1485(s), 1458(m), 1429(m), 1415(m), 1382(s), 1335(m), 1195(m) , 1165(m), 1107(w), 1055(w), 934(w), 805(m), 778(w), 727(m), 705(m), 638(w), 556(w) 475(w), 445(w), 417(m) 407(m).

**Preparation of  $[\text{Cd}(\mathbf{1,4\text{-pda}})(\mathbf{L}^2)]_n$ , **5**.** Prepared as described for **1**,

except that  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (0.053 g, 0.20 mmol),  $\mathbf{L}^2$  (0.054 g, 0.20 mmol) and 1,4- $\text{H}_2\text{pda}$  (0.038 g, 0.20 mmol) were used. Yield: 0.042 g (33 %). Anal calcd for  $\text{C}_{26}\text{H}_{26}\text{CdN}_4\text{O}_6$  (MW = 602.91): C, 51.79; N, 9.29; H, 4.35 %. Found: C, 51.26; N, 9.07; H, 4.42 %. IR ( $\text{cm}^{-1}$ ): 3267.79(m), 3062.41(s), 2916.81(m), 1662.34(m), 1553.39(s), 1478.17(w), 1425.14(m), 1284.36(m), 1126.22(w), 1050.05(w), 937.23(m), 808.99(m) 721.27(w) 594.92(w), 414.62(w).

**X-ray crystallography.** The diffraction data for complexes **1** – **5** were collected on a Bruker AXS SMART APEX II diffractometer at 22 °C, which was equipped with a graphite-monochromated  $\text{MoK}_\alpha$  ( $\lambda_\alpha = 0.71073$  Å) radiation. Data reduction was carried out by standard methods with use of well-established computational procedures.<sup>30</sup> The structure factors were obtained after Lorentz and polarization correction. An empirical absorption correction based on “multi-scan” was applied to the data for these complexes. The positions of some of the heavier atoms were located by the direct or Patterson method. The remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements.<sup>31</sup> All the hydrogen atoms complexes **1** – **5** were added by using the HADD command in SHELXTL 5.10. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1. Specified hydrogen bonds (with esds except fixed and riding H) for **1** - **5** are listed in Tables S1 – S5, respectively.

## RESULTS AND DISCUSSION

**Structure of 1.** Figure 1(a) shows the coordination environment of Cd(II) ion, which is coordinated by two pyridyl nitrogen atoms from two  $\mathbf{L}^1$  ligands [ $\text{Cd-N} = 2.293(2)$  and  $2.337(3)$  Å], four carboxylate oxygen

atoms from two 1,2-bdc<sup>2-</sup> ligands [Cd-O = 2.335(2) - 2.644(2) Å] and one oxygen atom of a water molecule [Cd-O = 2.359(2) Å], resulting in a distorted pentagonal bipyramidal geometry. Figure 1(b) shows that the Cd(II) ions are bridged by the 1,2-bdc<sup>2-</sup> ligands to form dinuclear units, which are linked by the L<sup>1</sup> ligands to form 1D looped chains, as shown in Figure 1(c). The Cd---Cd distances that are bridged by 1,2-bdc<sup>2-</sup> and L<sup>1</sup> are 5.11 and 18.46 Å, respectively. The 1D looped chains are interlinked through the N-H---O [H---O = 1.97 Å; ∠N-H---O = 171.5°] hydrogen bonds to the carboxylate oxygen atoms to form a 2D supramolecular layer. Noticeably, the larger rings of the looped chain are supported by the N-H---O [H---O = 2.17 Å; ∠N-H---O = 159.4°] hydrogen bonds to the carbonyl oxygen atoms while the smaller rings are supported by the O-H---O [H---O = 1.90 and 2.31 Å; ∠O-H---O = 162.2 and 145.3°] hydrogen bonds from the coordinated water molecules to the carboxylate oxygen atoms, Figure S1.

**Structures of 2 and 4.** The coordination environments about the Cd(II) ions are shown in Figure 2(a) and Figure 2(b) for **2** and **4**, respectively. The metal ions exhibit distorted pentagonal bipyramidal geometry with two nitrogen atoms apical and one equatorial and the left four equatorial positions are occupied by two chelating carboxylates. This same local metal coordination results in the same underlying net even if the two structures are not isomorphous but have similar cell axis and angles (total cell volume differs by 1% only) The extra carboxylic acid group in the ligands (1,2,3-Hbtc<sup>2-</sup> vs 1,3bdc<sup>2-</sup>) remains uncoordinated. In details the Cd(II) metal centers of **2** are coordinated by three pyridyl nitrogen atoms from three L<sup>1</sup> ligands [Cd(1)-N = 2.341(3) – 2.435(3) Å; Cd(2)-N = 2.365(3) – 2.384(3) Å] and four carboxylate oxygen atoms from two 1,3-bdc<sup>2-</sup> ligands [Cd(1)-O = 2.310(2) – 2.522(2) Å; Cd(2)-O = 2.293(2) –



2.403(2) Å]. Similarly each of the Cd(II) ions of **4** is coordinated by three pyridyl nitrogen atoms from three **L**<sup>1</sup> ligands [Cd-N = 2.376(4) – 2.439(4) Å] and four carboxylate oxygen atoms from two 1,2,3-Hbtc<sup>2-</sup> ligands [Cd-O = 2.353(3) – 2.516(4) Å], resulting also in a distorted pentagonal bipyramidal geometry. The Cd(II) ions in **2** and **4** are also singly and doubly bridged by the **L**<sup>1</sup> ligands in an alternate fashion and singly bridged by the 1,3-bdc<sup>2-</sup> and 1,2,3-Hbtc<sup>2-</sup> ligands, respectively, resulting in isorecticular 3D coordination networks. The Cd---Cd distances that are bridged by 1,3-bdc<sup>2-</sup> and **L**<sup>1</sup> are 10.05 – 10.08 Å and 19.67 – 22.01 Å, respectively, and those that are bridged by 1,2,3-Hbtc<sup>2-</sup> and **L**<sup>1</sup> ligands are 9.59 and 19.63 – 21.40 Å, respectively.

The 3D framework of **2** is supported by the N-H---O hydrogen bonds to the water oxygen atoms [H---O = 1.92 – 2.38 Å; ∠N-H---O = 117.1 – 169.0°] and carbonyl oxygen atoms [H---O = 2.20 Å; ∠N-H---O = 173.1°], while O-H---O hydrogen bonds from water molecules to water molecules [H---O = 1.86 – 2.18 Å; ∠O-H---O = 122.7 – 175.4°], carboxylate oxygen atoms [H---O = 1.85 – 1.93 Å; ∠O-H---O = 162.7 – 175.3°] and carbonyl oxygen atoms [H---O = 1.88 – 2.18 Å; ∠O-H---O = 135.5 – 172.2°] are also observed, Figure S2. Similarly, the 3D framework of **4** is supported by the N-H---O hydrogen bonds to the water oxygen atoms [H---O = 1.97 and 2.08 Å; ∠N-H---O = 169.8 and 151.6°] and O-H---O hydrogen bonds from water molecules to carboxylate oxygen atoms [H---O = 2.04 – 2.33 Å; ∠O-H---O = 120.9 – 174.4°], Figure S3. Moreover, O-H---O hydrogen bonds from the uncoordinated carboxylic groups of **4** to the carbonyl oxygen atoms [H---O = 2.28 Å; ∠O-H---O = 124.6°] and carboxylate oxygen atoms [H---O = 2.29 Å; ∠O-H---O = 112.7°] are also observed.

If the Cd(II) ions of **2** and **4** are regarded as 4-connected nodes and the two-connected  $\mathbf{L}^1$ , 1,3-bdc<sup>2-</sup> and 1,2,3-Hbtc<sup>2-</sup> ligands are simplified as linkers, the two structures are isorecticular and they have the same underlying net: a new uninodal 4-connected self-catenated 3D nets with the (6<sup>5</sup>·8) topology, Figure 2(c), with the vertex symbol [6.6.6.6.6<sub>2</sub>.10<sub>12</sub>], determined using ToposPro.<sup>32</sup> A careful analysis of the net shows that can be formed by cross-linking sets of parallel stacking of 5-fold interpenetrated **hcb** layers (see Figure S4). The layers stack AAA... normal to the longest axes (> 22 Å, [001] for **2** and [100] for **4**) and are pillared by  $\mathbf{L}^1$  ligands. Self-catenated nets that arise from subset of interpenetrated nets are known,<sup>33</sup> while the net observed here is the first example from crosslink of interpenetrated 2D nets. As highlighted in Figure 2(d), each shortest six-membered ring is catenated by four rods of the same network. The result indicates that the uncoordinated carboxylic acid group of 1,2,3-Hbtc<sup>2-</sup> ligand between **2** and **4** has no effect on the overall topology.

**Structure of 3.** Figure 3(a) shows the coordination environment of the Cd(II) ion, which is coordinated by two pyridyl nitrogen atoms from two  $\mathbf{L}^1$  ligands [Cd-N = 2.351(2) Å], four oxygen atoms from two 1,4-bdc<sup>2-</sup> ligands [Cd-O = 2.280(1) Å] and two water molecules [Cd-O = 2.331(1) Å] to form a distorted octahedral geometry. Figure 3(b) shows that the Cd(II) ions are bridged by the  $\mathbf{L}^1$  and 1,4-bdc<sup>2-</sup> ligands to form 2D layers and Figure 3(c) depicts its schematic drawing with the **sql** topology. The Cd---Cd distances that are bridged by 1,4-bdc<sup>2-</sup> and  $\mathbf{L}^1$  are 11.76 and 19.99 Å, respectively. The 2D layers are interlinked through the N-H---O [H---O = 2.17 Å; ∠N-H---O = 153.7°] hydrogen bonds to the carboxylate oxygen atoms and O-H---O hydrogen bonds from water molecules to the carboxylate oxygen atoms [H---O = 1.93 Å; ∠O-H---O = 148.1°] and

carbonyl oxygen atoms [H---O = 1.98 Å; ∠O-H---O = 151.7°] to form a 3D supramolecular structure, Figure S5.

**Structure of 5.** Crystals of **5** conform to the triclinic space group  $P\bar{1}$  with one Cd(II) cation, two halves of two  $L^2$  ligands lying about inversion centers and two halves of two 1,4-pda<sup>2-</sup> anions that are also lying about inversion centers in the asymmetric unit. Figure 4(a) shows the coordination environments of the dinuclear Cd(II) metal centers. Each of the Cd(II) ion is seven-coordinated by two pyridyl nitrogen atoms from two  $L^2$  ligands [Cd-N = 2.293(2) and 2.375(1) Å] and five oxygen atoms from three 1,4-pda<sup>2-</sup> ligands [Cd-O = 2.252(1) – 2.560 (1) Å], resulting in a distorted pentagonal-bipyramidal geometry. The Cd(II) ions are linked together by the 1,4-pda<sup>2-</sup> ligands that adopt the  $\mu_2$ - $\kappa^1, \kappa^1, \kappa^1, \kappa^1$  coordination mode to form 2D layers, Figure 4(b), which are further connected by the 1,4-pda<sup>2-</sup> ligands that adopt the  $\mu_4$ - $\kappa^2, \kappa^1, \kappa^2, \kappa^1$  coordination mode and the  $L^2$  ligands to afford a 3D structure. The 3D framework is supported by the N-H---O hydrogen bonds to the carbonyl oxygen atoms [H---O = 1.98 Å; ∠N-H---O = 169.3°] and carboxylate oxygen atoms [H---O = 1.94 Å; ∠N-H---O = 171.3°], Figure S6.

If the Cd<sub>2</sub>(μ-COO)<sub>2</sub> dimeric units are taken as structural building units SBU and defined as nodes, the structure of **5** can be simplified as a 8-coordinated net with a rare self-catenated (4<sup>24</sup>.6<sup>4</sup>)-8T17 topology, Figure 4(c). The self-catenation could be seen as cross-linking of the 2D 4<sup>4</sup>-**sql** nets pillared by rods. As highlighted in Figure 4(d), each shortest four-membered ring is catenated by two rods of the same network. Notwithstanding the self-catenation of strong 4-rings, the net 8T17 has a tiling: the essential rings are not catenated, a phenomena already known for example<sup>33</sup> for the 5-c net **fnu**, see Figure S7. The 8T17 net has been

observed in two coordination networks containing similar long and short ligands and dimeric ( $\text{Cd}_2$ ) or trimeric ( $\text{Zn}_3$ ) SBUs, as shown in  $\{\text{Cd}(1,4\text{-bdc})[1,4\text{-bis}(1,2,4\text{-triazol-1-ylmethyl)benzene}]\cdot n\text{H}_2\text{O}\}_n$ ,<sup>34,35</sup> and  $[\text{Zn}_3(1,4\text{-bdc})_3(1,4\text{-bis}(\text{pyridin-4-ylmethoxy)benzene})]_n$ ,<sup>36</sup> respectively.

**Self-catenation involving bis-pyridyl-bis-amide ligands.** Although the self-catenated coordination polymers have been the subject of studies during recent years,<sup>37</sup> those that involve bis-pyridyl-bis-amide ligands remain scarcely reported. While  $\{[\text{Cu}(\text{L}^1)(1,4\text{-pda})]\cdot 2\text{H}_2\text{O}\}_n$  (1,4- $\text{H}_2\text{pda}$  = 1,4-phenylenediacetic acid) is the first 1D self-catenated coordination polymer,<sup>25</sup> the complex  $[\text{Co}_3(1,4\text{-bdc})_3(\text{L}^3)]_n$  ( $\text{L}^3$  = *N,N'*-bis(3-pyridinyl)-1,4-benzenedicarboxamide) forms a unique self-catenated 3D net with the  $(3^6.4^{10}.5^{11}.6)$ -8T53 topology<sup>38</sup> (with catenation of 6-rings) and  $\{[\text{Cd}_2(1,4\text{-bdc})_2(\text{L}^2)]\cdot 3\text{H}_2\text{O}_3\}_n$  exhibits self-catenated 3D net of  $\{4^{24}.5.6^3\}$ -**ilc** topology<sup>22</sup> (with self-catenation of 4-rings with four other 4-rings).

**Conformations and bonding modes of the ligands.** The  $\text{L}^1$  and  $\text{L}^2$  can be arranged in A and G conformations, which are given when the C-C-C-C torsion angle ( $\theta$ ) is  $180^\circ \geq \theta > 90^\circ$  and  $0^\circ \leq \theta \leq 90^\circ$ , respectively, and based on the relative orientation of the C=O (or N-H) groups, each conformation can adopt *cis* or *trans* arrangement.<sup>7</sup> Due to the difference in the orientations of the pyridyl nitrogen atom positions, three more orientations, *anti-anti*, *syn-anti* and *syn-syn*, are possible for the ligand. Based on this descriptor, the ligand conformations of complexes **1** – **5** are assigned and listed in Table 2. Noticeably, to show the unique self-catenation mode of  $(6^5.8)$  topology, the  $\text{L}^1$  ligands in **2** and **4** adopt three and two different ligand conformations, respectively, which are rarely observed for the bis-pyridyl-bis-amide ligands.<sup>7</sup> Moreover, all

the skeleton carbon atoms of the  $L^1$  ligands of **2** and **4** adopt the AAAAA conformation. The various ligand conformations indicate that  $L^1$  and  $L^2$  ligands are sufficiently flexible to adjust to the stereochemical requirements for the formation of the complexes **1** - **5**, which adopts the conformation that maximize their intra- and intermolecular forces.

Various bonding modes are observed for the polycarboxylate ligands in **1** - **5**, Table 2. Both of the 1,2-bdc<sup>2-</sup> and 1,3-bdc<sup>2-</sup> ligands in **1** and **2** chelate the metal centers through all the four carboxylate oxygen atoms, adopting the  $\mu_2-\kappa^1, \kappa^1, \kappa^1, \kappa^1$  mode. While the 1,4-bdc<sup>2-</sup> ligand **3** bridges two metal centers through one of the oxygen atoms of each carboxylate group that display the  $\mu_2-\kappa^1, \kappa^0, \kappa^1, \kappa^0$  mode, the 1,2,3-Hbtc<sup>2-</sup> ligands of **4** adopt the  $\mu_2-\kappa^1, \kappa^1, \kappa^0, \kappa^0, \kappa^1, \kappa^1$  bonding mode. Noticeably, the 1,4-pda<sup>2-</sup> ligands of **5** show two types of bonding modes of  $\mu_2-\kappa^1, \kappa^1, \kappa^1, \kappa^1$  and  $\mu_4-\kappa^2, \kappa^1, \kappa^2, \kappa^1$ , resulting in a rare self-catenated (4<sup>24</sup>.6<sup>4</sup>)-8T17 topology.

**Thermal gravimetric analyses.** Thermal gravimetric analyses (TGA) were carried out to examine the thermal decomposition of **1** - **5**. The samples were heated up in nitrogen gas at a pressure of 1 atm with a heating rate of 10 °C min<sup>-1</sup> and finished at 900 °C, Figure S8 – Figure S12 and Table 3. The TGA curve of **1** shows that a total weight loss of 4.65 % occurred between 30 and 180 °C, presumably due to the removal of the cocrystallized H<sub>2</sub>O (calcd 5.64 %). The weight loss of 75.97 % in 240 – 560 °C can be ascribed to the decomposition of the  $L^1$  and 1,2-bdc<sup>2-</sup> ligands (calcd 74.26 %). For complex **2**, a total weight loss of 8.39 % occurred between 30 and 200 °C, presumably due to the removal of the cocrystallized H<sub>2</sub>O (calcd 9.11 %). The weight loss of 76.55 % occurred between 280 and 800 °C can be ascribed to the decomposition of the  $L^1$  and 1,3-bdc<sup>2-</sup> ligands (calcd 74.64 %). For complex **3**, a total weight loss

of 6.32 % occurred between 30 and 220 °C, presumably due to the removal of the coordinated H<sub>2</sub>O (calcd 5.64 %). The weight loss of 73.42 % in 280 – 600 °C can be ascribed to the decomposition of the L<sup>1</sup> and 1,4-bdc<sup>2-</sup> ligands (calcd 74.26 %). The TGA curve of **4** shows that a total weight loss of 4.76 % occurred between 30 and 200 °C, presumably due to the removal of the cocrystallized H<sub>2</sub>O (calcd 4.25 %). The weight loss of 83.58 % in 200 – 900 °C can be ascribed to the decomposition of the L<sup>1</sup> and 1,2,3-Hbtc<sup>2-</sup> ligands (calcd 82.61 %). For complex **5**, the TGA curve shows the gradual weight loss of 79.07 % in 290 - 800 °C, which is due to the decomposition of the L<sup>2</sup> and 1,4-pda<sup>2-</sup> ligands (calculated 78.70 %).

The TGA results show that the weight losses that are due to the removal of cocrystallized and the bonded water molecules occurred in 30 – 220 °C, and the organic ligands decomposed at temperatures above 200 °C. Noticeably, there is an 80 °C difference in decomposing the organic ligands between **2** and **4** that adopt the same self-catenation mode, which may be due to the different polycarboxylate ligands that result in different supramolecular interactions.

**Luminescent properties.** The emission spectra of the free organic ligands and complexes **1** – **5** were measured in the solid at room temperature, Figure S13 – S24 and Table 4. The L<sup>1</sup>, L<sup>2</sup> and polycarboxylic acids show the emissions in the range 315 - 450 nm, which may be tentatively ascribed to the intraligand (IL)  $n \rightarrow \pi^*$  or  $\pi \rightarrow \pi^*$  transitions. The red and blue shifts with respect to the organic ligands observed for complexes **1** - **5** are most probably due to the different ligand conformations and coordination modes adopted by the organic ligands and the formation of different structural types. Noticeably, the red-shift of the emission wavelength of **4** with respect to the corresponding

polycarboxylic acid is significantly larger than that of **2**, indicating that the uncoordinated carboxylic groups that result in multiple O-H...O hydrogen bonds may play important role in determining the luminescent properties. It has been shown that hydrogen bonding changes the electron density distributions of the complex and thus the luminescent properties could be controlled by tuning hydrogen bonding.<sup>39</sup> Since the Cd(II) ions are hardly oxidized or reduced, it is not probable to assume that the emissions of **1** - **5** are due to ligand-to-metal charge transfer (LMCT) or metal-to-ligand charge transfer (MLCT). These emissions can most probably be attributed to intraligand and/or ligand-to-ligand charge transfer (LLCT).<sup>40,41</sup>

## CONCLUSIONS

Five new Cd(II) coordination polymers have been synthesized under hydrothermal conditions, which show 1D, 2D and 3D structures. The structures of complexes **1** - **3** are directed by the isomeric 1,2-, 1,3- and 1,4-bdc<sup>2-</sup> ligands, forming a loop-like 1D chain, a novel 3D self-catenated coordination network with the (6<sup>5</sup>·8) topology and a 2D layer with the **sql** topology, respectively. While complex **4** is isorecticular to **2**, complex **5** displays a rare 8T17 self-catenated net. We have shown that the uncoordinated carboxylic acid group of 1,2,3-Hbtc<sup>2-</sup> ligand has no effect on the structural diversity of **2** and **4**, but it plays important roles in determining the thermal and luminescent properties. We have also further verified that by manipulating the isomeric effect of the dicarboxylate ligands, self-catenated coordination polymers incorporating the flexible bis-pyridyl-bis-amide ligands can be expected.

## ASSOCIATED CONTENT

### Supporting information

Hydrogen bondings (Figure S1 – Figure S3, Figure 5 – Figure 6). The self catenated ( $6^5 \cdot 8$ ) net observed in **2** and **4** as composed by 5-fold interpenetrated **hcb** pillared by long edges (Figure S4). The coordinates for the net 8T17 observed in **5** and his tiling (Figure S6). TGA curves (Figure S8 – Fig S12). Emission/excitation spectra (Figure S13 – Figure 24). PXRD patterns (Figure S25 – Figure S29). H-bonding distances and angles (Table S1 – Table S5). The supporting information is available free of charge on the ACS Publications website at DOI: xxxx. CCDC no. 1513966 - 1513969 and 1427438 contain the supplementary crystallographic data for this paper. 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](mailto:deposit@ccdc.cam.ac.uk) or www: <http://www.ccdc.cam.ac.uk>.

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**Table 1.** Crystal data for complexes **1** – **5**.

compound	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
formula	C <sub>26</sub> H <sub>30</sub> N <sub>4</sub> O <sub>8</sub> Cd	C <sub>70</sub> H <sub>90</sub> N <sub>12</sub> O <sub>22</sub> Cd <sub>2</sub>	C <sub>26</sub> H <sub>30</sub> N <sub>4</sub> O <sub>8</sub> Cd	C <sub>72</sub> H <sub>82</sub> N <sub>12</sub> O <sub>22</sub> Cd <sub>2</sub>	C <sub>26</sub> H <sub>26</sub> N <sub>4</sub> O <sub>6</sub> Cd
fw	638.94	1676.33	638.94	1692.29	602.91
crystal system	Triclinic	Triclinic	Triclinic	monoclinic	Triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
a, Å	10.9835(5)	8.9238(2)	7.5603(1)	22.9306(3)	10.8380(2)
b, Å	11.2125(5)	18.3006(5)	9.1784(1)	8.5814(1)	11.8382(2)
c, Å	11.4719(5)	22.3464(6)	11.0848(2)	18.6084(2)	11.9775(2)
$\alpha$ , °	77.499(2)	95.791(2)	99.108(1)	90	96.794(1)
$\beta$ , °	88.485(2)	96.459(2)	104.424(1)	96.646(1)	112.865(1)
$\gamma$ , °	75.493(2)	91.696(2)	113.295(1)	90	110.682(1)
V, Å <sup>3</sup>	1334.75(10)	3604.64(16)	655.08(2)	3637.09(8)	1265.20(4)
Z	2	2	1	2	2
D <sub>calc</sub> , g/cm <sup>3</sup>	1.590	1.544	1.620	1.545	1.583
F(000)	652	1732	326	1740	612
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	0.874	0.675	0.891	0.670	0.912
range(2 $\theta$ ) for data collection, deg	3.64 $\leq$ 2 $\theta$ $\leq$ 56.74	2.74 $\leq$ 2 $\theta$ $\leq$ 56.70	3.96 $\leq$ 2 $\theta$ $\leq$ 56.58	3.58 $\leq$ 2 $\theta$ $\leq$ 56.58	3.85 $\leq$ 2 $\theta$ $\leq$ 56.65
independent reflections	6605	17917	3246	9033	6283
data / restraints / parameters	[R(int) = 0.0388]	[R(int) = 0.0430]	[R(int) = 0.0250]	[R(int) = 0.0370]	[R(int) = 0.0278]
quality-of-fit indicator <sup>c</sup>	6605 / 0 / 347	17917 / 7 / 938	3246 / 0 / 178	9033 / 1 / 514	6283 / 0 / 334
final R indices	1.034	1.056	1.046	1.039	1.029
[I > 2 $\sigma$ (I)] <sup>a,b</sup>	R1 = 0.0413, wR2 = 0.0924	R1 = 0.0463, wR2 = 0.1044	R1 = 0.0247, wR2 = 0.0613	R1 = 0.0592, wR2 = 0.1599	R1 = 0.0243, wR2 = 0.0528
R indices (all data)	R1 = 0.0606, wR2 = 0.0994	R1 = 0.0736, wR2 = 0.1170	R1 = 0.0259, wR2 = 0.0623	R1 = 0.0881, wR2 = 0.1820	R1 = 0.0297, wR2 = 0.0556

<sup>a</sup>R<sub>1</sub> =  $\Sigma||F_o| - |F_c|| / \Sigma|F_o|$ . <sup>b</sup>wR<sub>2</sub> =  $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ . w = 1 / [ $\sigma^2(F_o^2) + (ap)^2 + (bp)$ ].

p =  $[\max(F_o^2 \text{ or } 0) + 2(F_c^2)] / 3$ . **1**: a = 0.0504, b = 0.2157; **2**: a = 0.0475, b = 4.7674; **3**: a = 0.0862, b = 6.5480; **4**: a = 0.0246, b = 0.3513; **5**:

<sup>c</sup>quality-of-fit =  $[\Sigma w(|F_o^2| - |F_c^2|)^2 / (N_{\text{observed}} - N_{\text{parameters}})]^{1/2}$ .

**Table 2.** Ligand conformation of bis-pyridyl-bis-amide and bonding mode of polycarboxylate in **1 – 5**.

Complex	ligand conformation	bonding mode
<b>1</b>	GAGAA- <i>trans syn-syn</i>	$\mu_2-\kappa^1, \kappa^1, \kappa^1, \kappa^1$
<b>2</b>	AAAAA- <i>trans syn-anti</i>	$\mu_2-\kappa^1, \kappa^1, \kappa^1, \kappa^1$
	AAAAA- <i>trans syn-syn</i>	
	AAAAA- <i>trans anti-anti</i>	
<b>3</b>	AAAAA- <i>trans syn-syn</i>	$\mu_2-\kappa^1, \kappa^0, \kappa^1, \kappa^0$
<b>4</b>	AAAAA- <i>cis anti-syn</i>	$\mu_2-\kappa^1, \kappa^1, \kappa^0, \kappa^0, \kappa^1, \kappa^1$
	AAAAA- <i>trans anti-anti</i>	
<b>5</b>	GAG- <i>trans syn-syn</i>	$\mu_2-\kappa^1, \kappa^1, \kappa^1, \kappa^1$
	AAA- <i>trans syn-syn</i>	$\mu_4-\kappa^2, \kappa^1, \kappa^2, \kappa^1$

**Table 3.** Thermal properties of **1 – 5**.

Complex	Weight loss of H <sub>2</sub> O, T, °C (found / calc), %	Weight loss of ligand, T, °C (found / calc), %
<b>1</b>	30-180 (4.65/5.64)	240-560 (75.97/74.26)
<b>2</b>	30-200 (8.39/9.11)	280-800 (76.55/74.64)
<b>3</b>	30-220 (6.32/5.64)	280-600 (73.42/74.26)
<b>4</b>	30-200 (4.76/4.25)	200-900 (83.58/82.61)
<b>5</b>		290-800 (79.07/78.70)

**Table 4.** Luminescent properties of **L<sup>1</sup>**, **L<sup>2</sup>**, dicarboxylic acids and **1 - 5** in the solid state.

Compound	$\lambda_{\text{ex}}/\lambda_{\text{em}}$ (nm)	Compound	$\lambda_{\text{ex}}/\lambda_{\text{em}}$ (nm)
<b>L<sup>1</sup></b>	320/435	1,2,3-H <sub>3</sub> btc	289/315
<b>L<sup>2</sup></b>	368/418	<b>1</b>	379/445
1,2-H <sub>2</sub> bdc	337/433	<b>2</b>	372/444
1,3-H <sub>2</sub> bdc	353/430	<b>3</b>	372/441
1,4-H <sub>2</sub> bdc	333/430	<b>4</b>	320/419
1,4-H <sub>2</sub> pda	376/450	<b>5</b>	368/440

## Captions

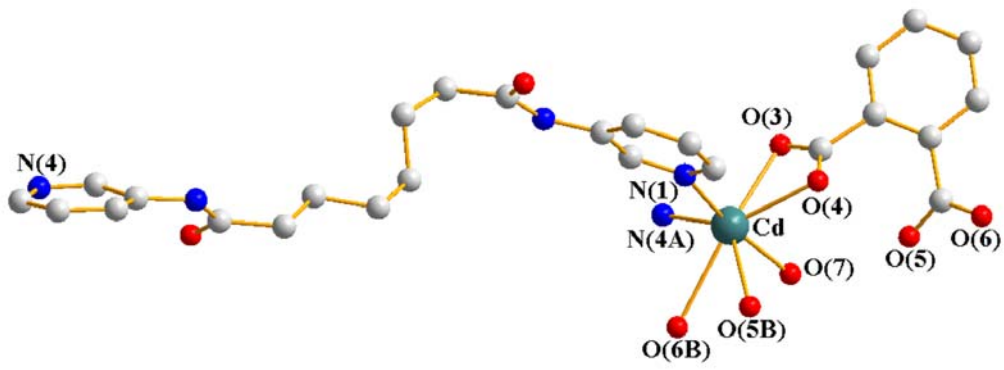
**Figure 1.** (a) Coordination environment about the Cd(II) ion for **1**. Symmetry transformations used to generate equivalent atoms: (A)  $-x + 1, -y + 2, -z$ ; (B)  $-x + 2, -y, -z + 1$ . (b) 1D looped-chain for **1**. (c) Simplified 1D looped-chain structure for **1**.

**Figure 2.** (a) Coordination environment about the Cd(II) ion for **2**. Symmetry transformations used to generate equivalent atoms: (A)  $-x + 1, -y + 1, -z + 1$ . (b) Coordination environment about the Cd(II) ion for **4**. Symmetry transformations used to generate equivalent atoms: (A)  $x, -y + 1/2, z + 1/2$ ; (B)  $-x + 1, -y + 1, -z + 2$ . (c) A drawing showing the 3D structures of **2** and **4** with the  $(6^5.8)$  topology. (d) Each shortest six-membered ring is catenated by four rods of the same network.

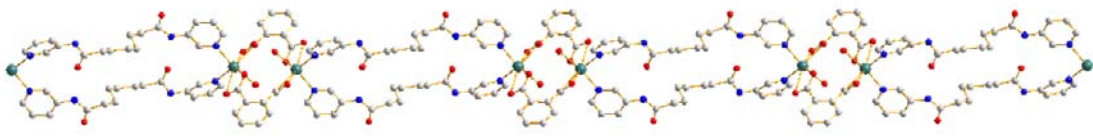
**Figure 3.** (a) Coordination environment about the Cd(II) ion for **3**. Symmetry transformations used to generate equivalent atoms: (A)  $-x, -y, -z$ ; (B)  $-x + 3, -y + 1, -z + 1$ ; (C)  $-x + 1, -y, -z + 1$ . (b) The 2D structure of **3**. (c) A simplified drawing showing the **sql** topology.

**Figure 4.** (a) Coordination environment about the Cd(II) cation in **5**. Symmetry transformations used to generate equivalent atoms: (A)  $-x + 1, -y + 1, -z + 1$ . (b) A drawing showing the 2D layer formed by the Cd(II) ions and 1,4-pda<sup>2-</sup> ligands. (c) A drawing showing the 8-coordinated net with the  $(4^{24}, 6^4)$ -8T17 topology. (d) Each shortest four-membered ring is catenated by two rods of the same network.





(a)

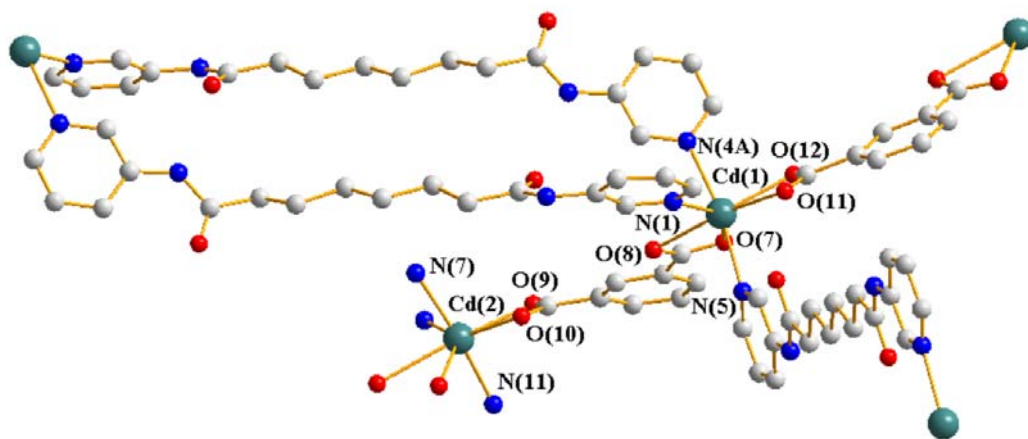


(b)

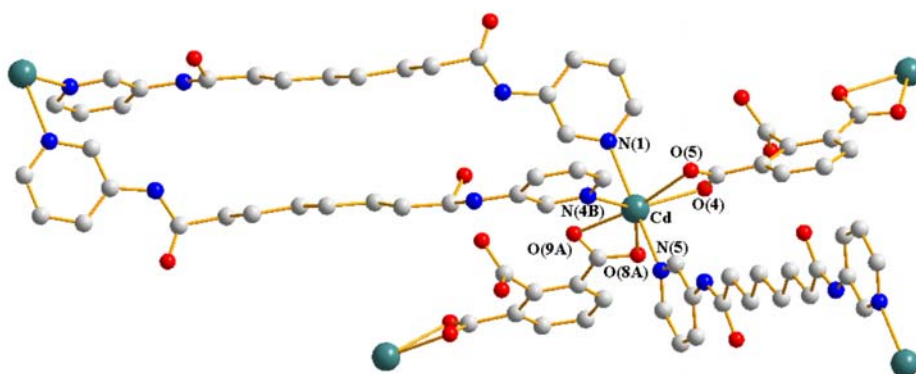


(c)

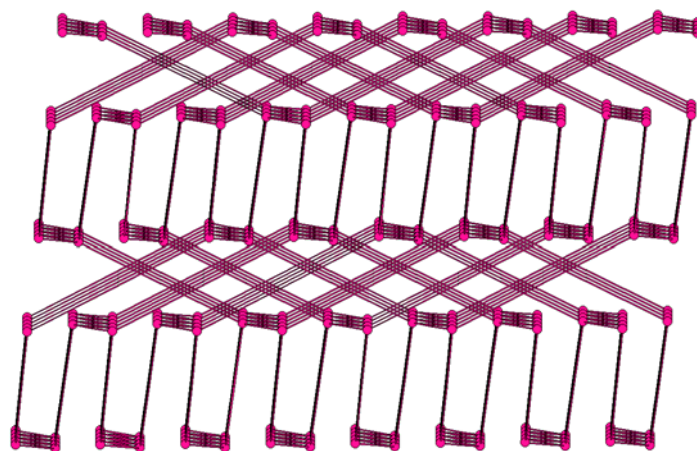
**Figure 1**



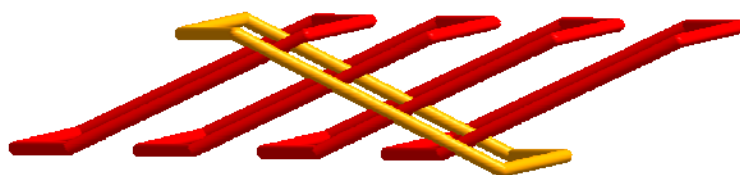
(a)



(b)

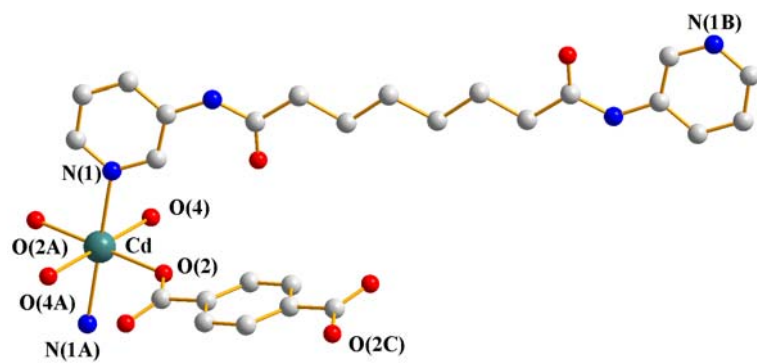


(c)

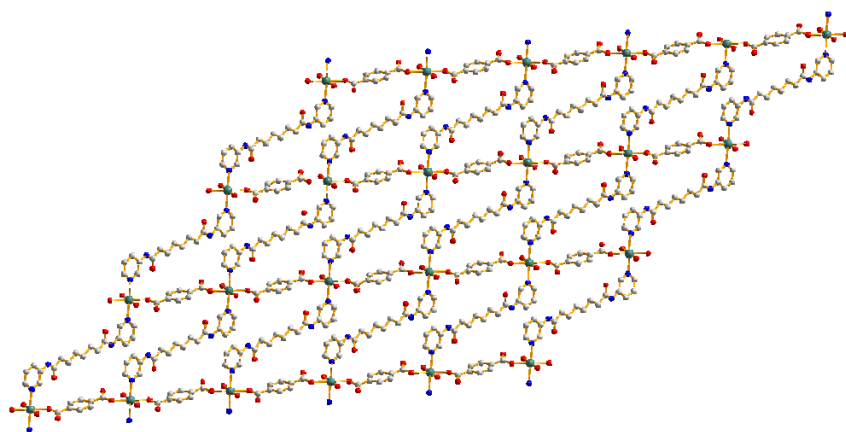


(d)

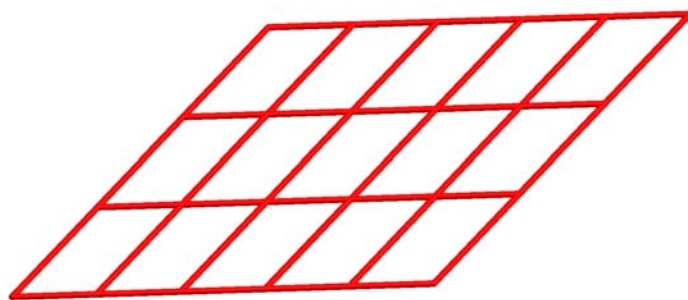
Figure 2



(a)

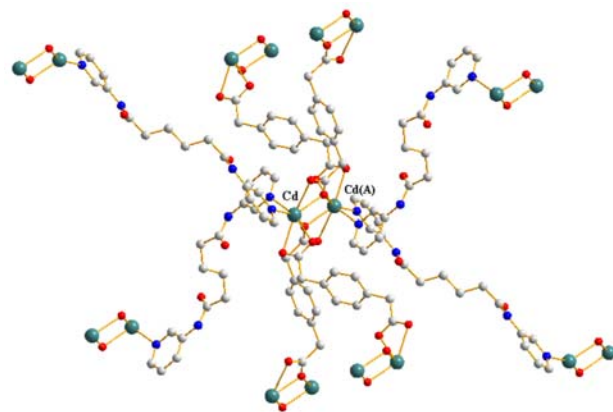


(b)

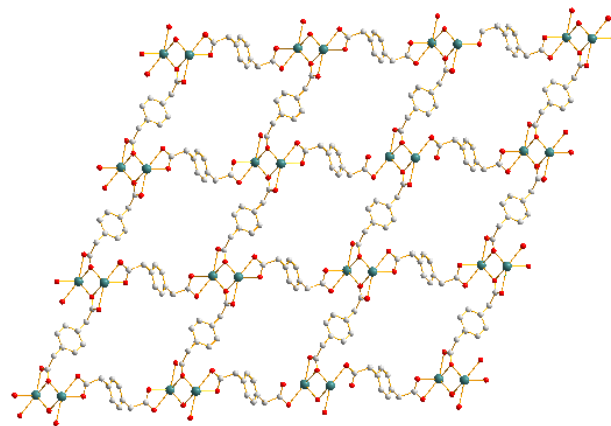


(c)

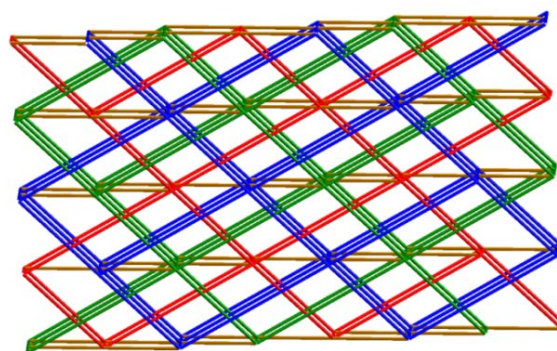
**Figure 3**



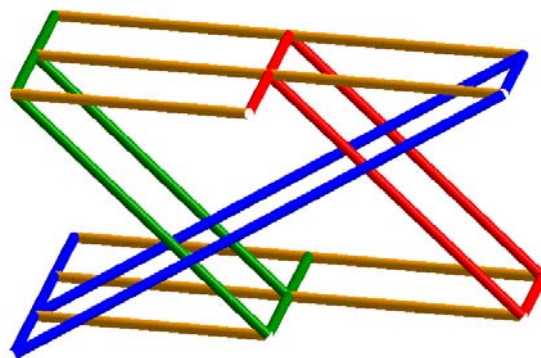
(a)



(b)



(c)



(d)

**Figure 4**

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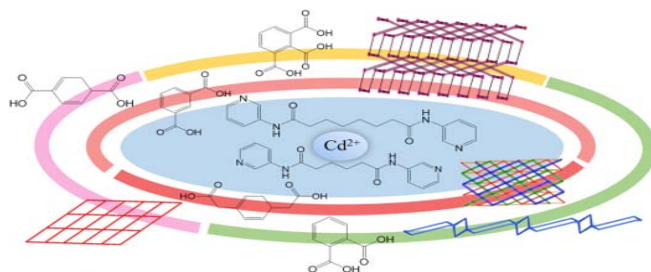
## Self-catenated Coordination Polymers Involving Bis-pyridyl-bis-amide

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By manipulating the isomeric effect of the dicarboxylate ligands, self-catenated coordination polymers incorporating the flexible bis-pyridyl-bis-amide ligands can be expected.