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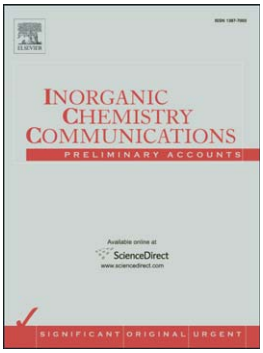

Three Cd(II) coordination polymers assembled by flexible 2,2'-azodibenzoic acid and N-donor auxiliary ligand: Structural diversities and luminescent properties

Lei-Lei Liu, Cai-Xia Yu, Yan Zhou, Juan Sun, Pan-Pan Meng, Dong Liu, Rong-Jian Sa

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Three Cd(II) coordination polymers assembled by flexible 2,2'-azodibenzoic acid and N-donor auxiliary ligand: Structural diversities and luminescent properties

Lei-Lei Liu[a,*], Cai-Xia Yu[a], Yan Zhou[a], Juan Sun[a], Pan-Pan Meng[a], Dong Liu[b,*], Rong-Jian Sa[c]

[a] *College of Chemistry and Chemical Engineering, Anyang Normal University, Anyang 455000, Henan, P. R. China*

[b] *College of Chemistry and Materials Science, Huaibei Normal University, Huaibei 235000, Anhui, P. R. China*

[c] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P. R. China*

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*Corresponding author. Tel: + 86 372 2900040; Fax: + 86 372 2900040.

*Correspondence to: L. L. Liu, College of Chemistry and Chemical Engineering, Anyang Normal University, Anyang 455000, Henan, P. R. China.

E-mail address: liuleileimail@163.com (L.-L. Liu), dongliu@chnu.edu.cn (D. Liu).

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Abstract

Hydrothermal reactions of $Cd(OAc)_2 \cdot 2H_2O$ with 2,2'-azodibenzoic acid (H_2L) and three N-donor ancillary ligands in MeOH/H_2O at 120°C gave rise to three cadmium(II) coordination polymers $[CdL(bpy)]_n$ (**1**), $\{[Cd_4L_4(bpe)(H_2O)_2] \cdot 2H_2O\}_n$ (**2**) and $[CdL(bpp)]_n$ (**3**) [bpy = 4,4'-bipyridine, bpe = 1,2-bis(4-pyridyl)ethylene, bpp = 1,3-bis(4-pyridyl)propane]. Structural analysis reveals that compound **1** possesses a novel three-fold interpenetrating diamondoid framework constructed by linking Cd centers with L and pillared bpy ligands. Compound **2** comprises a 3D network with a rare Schläfli symbol of $(4^4 6^5 8^1)(4^4 6^2)$, the 3D structure is built from 2D $[CdL_2]_n$ nets and pillared bpe ligands. Compound **3** exhibis the same 6^6 topology with that of **1**. Such a 3D architecture contains 1D helical $[Cd(bpp)]_n$ chains and $[CdL]_n$ chains along the *a* axis and *b* axis, respectively. The structural differences among **1**−**3** indicate that the N-donor ancillary ligands have significant effects on the formation of the final architectures. Photoluminescent properties of **1**−**3** in solid state were also investigated.

Keywords: N-donor ancillary ligands; 2,2'-azodibenzoic acid; Cd(II) coordination polymers; Structural diversities; Photoluminescent properties

The synthesis and design of novel coordination polymers has attracted a considerable amount of attention due to their intriguing architectures as well as their potential applications in luminescence, adsorption and catalysis [1−3]. The ultimate aim of coordination chemistry is to

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control the structures of target products and investigate the relationships between structures and properties. Although crystal engineering affords us a powerful tool for the design and construction of expected coordination frameworks [4], the rational design and synthesis of coordination polymers with desired structures and properties is still a long-term challenge. The structural diversity of such materials is usually influenced by many factors, such as metal ions, metal/ligand ratios, the nature of organic ligands, pH value and counter anion [5, 6]. Without a doubt, among these factors, the selection of appropriate ligands is a very important one in the formation of desired products. The length, rigidity, coordination modes, functional groups, or substituents of organic ligands have critical effects on the final structures of coordination polymers [7]. In recent years, the N-donor spacer ligands are extensively employed as ancillary ligands to construct unique structures with beautiful aesthetics and various functions due to their bent backbones, rigidity/flexibility and versatile bridging fashions [8].

On the other hand, it is well known that a mixed-ligands system [9] consisting of two or more types of ligands provides more possibilities to construct coordination polymers with fantastic topologies. One of the most fruitful aspects is the combination of various carboxylic acids and neutral pyridine-containing [10] auxiliary ligands, where the carboxylic acid ligands balance the positive charge of the metal centers and form secondary building units, while the auxiliary ligands mediate and satisfy the coordination environments metal centers. As a result, many functional coordination polymers with intriguing structure motifs have been reported. Recently, we have successfully synthesized a series of 2D and 3D Cd(II) coordination polymers based on the 3,3'-azodibenzoic acid through regulating the reaction solvents or temperatures [11]. 2,2'-Azodibenzoic acid is less flexible than 3,3'-azodibenzoic acid due to the steric ground. To

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further probe the influence of systematic variations of ligand structures on the overall molecular architectures, we extend the building blocks from 3,3'-azodibenzoic acid to its isomer 2,2'-azodibenzoic acid to explore the isomeric effect on network assembly. In addition, to our knowledge, studies engaged in the coordination chemistry of 2,2'-azodibenzoic acid has been less explored. Taking account of these, we employed auxiliary rigid 4,4′-bipyridine (bpy), semi-rigid 1,2-bis(4-pyridyl)ethylene (bpe), and flexible 1,3-bis(4-pyridyl)propane (bpp) N-donor ligands, the investigation on the Cd^{II}-H_2L system was carried out to explore the effects of co-ligands incorporate into coordination architectures. Herein, we reported the syntheses and characterizations of three new coordination polymers: $[CdL(bpy)]_n$ (**1**), $\{[Cd_4L_4(bpe)(H_2O)_2]\cdot 2H_2O\}_n$ (**2**) and $[CdL(bpp)]_n$ (**3**). The results indicated that the ancillary ligands could affect the formation of these cadmium(II) coordination polymers significantly. The crystal structures, topological analyses and fluorescence properties of these complexes are discussed in detail.

In all hydrothermal reactions reported here, the pH value was kept at *ca.* 9.0. Reactions of $Cd(OAc)_2\cdot 2H_2O$ with H_2L and bpy/bpe/bpp in H_2O for four days at 120 °C and cooled to ambient temperature at a rate of 5 °C h^{-1} produced orange crystals of **1** (52% yield), yellow crystals of **2**−**3** (45% and 62% yields) [12, 13]. The IR spectra of **1**−**3** showed peaks in the range of 1604−1615 cm^{-1} and 1375−1410 cm^{-1}, which is indicative of the existence of coordinated carboxylic groups [11]. The strong peaks at 826–865 cm^{-1}, and middle peaks in the range of 624–662 cm^{-1} mean the existence of pyridyl groups in the complexes of **1**−**3** [7e]. The identities of **1**−**3** were further confirmed by single-crystal diffraction analysis. The PXRD patterns of **1**−**3** were matched with the simulated patterns generated from their single crystals data (Fig. S1).

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Compound **1** crystallizes in the monoclinic space group *C*2/*c*, and its asymmetric unit contains half of an independent [CdL(bpy)] molecule. As shown in Fig. 1a, each Cd atom adopts a disordered octahedral coordination geometry, being coordinated by four O (O1, O2, O1C, O2C) atoms of chelating carboxylate groups from two L ligands and two N (N1, N1C) atoms from two bpy ligands. Each Cd^{II} ion is interlinked by bridging L ligands to form a 1D $[CdL]_n$ chain extending along the *ac* plane (Fig. S2). Each monodentate bpy ligand coordinated with one Cd center in the $[CdL]_n$ chain, thereby forming a rare 1D comb-like $[CdL(bpy)]_n$ chain. Each chain is connected to its adjacent ones *via* bpy ligands (pink) to form a wrinkled 2D (4,4) layer with parallelogrammic meshes (10.69 × 11.67 $Å^2$) (Fig. 1b). Furthermore, the bpy ligands are employed as pillars to link the 2D layer to afford a 3D network with 1D rhombic channels along the [100] direction (Fig. 1c). These channels are filled by mutual interpenetration of three independent equivalent frameworks, generating a 3-fold interpenetrating 3D architecture. From a topological point of view [14], such a 3D net can be simplified as a 6^6 diamondoid network through treating Cd atoms as nodes while L and bpy ligands as linkers (Fig. 1d).

(**Figure 1** here)

Compound **2** crystallizes in the triclinic space group $P\bar{1}$, and its asymmetric unit contains one half of $[Cd_4L_4(bpe)(H_2O)_2]$ unit, two halves of H_2O solvent molecules. The coordination environment of Cd^{2+} in **2** is similar with that of in **1**. Cd1 atom is coordinated by four O (O1, O4, O5, O7) atoms of four bridging carboxylate groups from three different L ligands, one N (N5) atom from one bpe ligand and one (O1W) atom from H_2O molecule to furnish a octahedral coordination geometry (Fig. 2a). Cd2 atom is also octahedrally coordinated by four O (O1, O2, O5, O6) atoms of two chelating carboxylate groups from two different L ligands and two O (O3, O8)

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atoms of two bridging carboxylate groups from two L ligands (Fig. 2b). Cd2 and [Cd(H_2O)] subunit are bridged by one carboxylate group and one L ligand to generate a dinuclear [$Cd_2L(CO_2)(H_2O)$] unit. The [$Cd_2L(CO_2)(H_2O)$] units are bridged by another carboxylate groups from the second L ligands to form a 1D chain (Fig. S3). And the 1D chains are interlinked by L ligands to produce a 1D ladder-like structure extending along the *a* axis (Fig. S4). Each 1D ladder-like structure is further interconnected with neighbouring ones *via* the third L ligands to form a 2D network extending along the *a* axis (Fig. 2c). Furthermore, similar to that of **1**, the bpe ligands are also employed as pillars to support the 2D networks to form a 3D structure (Fig. 2d). Topologically, if the Cd(II) centres are considered as nodes, the L and bpe ligands are considered as linkers, the structure of **2** can be specified as a (3,4)-connected framework with a Schläfli symbol of ($4^4 6^5 8^1$)($4^4 6^2$) (Fig. 2e).

(**Figure 2** here)

Compound **3** crystallizes in the orthorhombic space group $P2_12_12_1$, and its asymmetric unit contains one half of [CdL(bpp)] unit. Each Cd atom in **3** is six-coordinated by four O (O1, O2, O3A, O4A) atoms of chelating carboxylate groups from two L ligands, and two N (N1, N4B) atoms from two bpp ligands. (Fig. 3a). As shown in Fig. 3b, Cd(II) ions are linked by two carboxylate groups of L ligands, giving rise to an infinite helical $[CdL]_n$ chain (the right-handed helix) along the *b* axis. Notably, Cd(II) ions are bridged by bpp ligands also generating a 1D helical $[Cd(bpp)]_n$ chain along the *c* axis (Fig. 3c). The neighbouring chains exhibit two kinds of helix (the left-handed helix and the right-handed helix, respectively) (Fig. S5). It is interesting that such 1D helical $[CdL]_n$ and $[Cd(bpp)]_n$ chains are braided together to form a 2D network extending along *ab* plane (Fig. S5). Such 2D networks are further connected by the 1D helical

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$[CdL]_n$ chains from the adjacent 2D networks to produce a 3D architecture (Fig. 3d). And the left-handed and right-handed $[Cd(bpp)]_n$ chains are arranged in an alternative way (Fig. 3d). If the Cd(II) ions are regarded as 4-connected nodes, and L ligands and bpp are considered as linkers, the 3D framework can be simplified as a 6^6 diamondoid network (Fig. 3e).

(**Figure 3** here)

The formation of different structures of **1**−**3** with different N-donor ligands deserves comments. Firstly, the carboxylate groups of L ligands in **1**−**3** show different coordination modes. For **1** and **3**, two carboxylate groups of L ligand both adopt μ_1-η^1:η^1 chelating mode. And the L ligands further bridged the Cd(II) ions, leading to the formation of the 1D $[CdL]_n$ chain. For **2**, there are three distinct L ligands. The carboxylate groups of L ligands adopt μ_2-η^1:η^1 and μ_2-η^2:η^1 bridging modes, respectively. The Cd atoms and L ligands resulted in the generation of the 2D $[CdL_2]_n$ network. Secondly, the 1D $[CdL]_n$ chains of **1** and 2D $[CdL_2]_n$ networks of **2** are pillared by bpy (**1**) and bpe (**2**) ligands generating the 3D structures. However, in **3**, because of the employment of flexible bpp ligand, left- and right-handed helical motifs constructed by Cd(II) ions and bpp appear, which are further linked by L ligands to form the final 3D structure. The difference between **1**, **2** and **3** indicated that N-donor ligands play important roles in the construction of polymers **1**−**3**. Thirdly, compound **1** possesses a three-fold interpenetrating 3D structure while **2** and **3** hold non-interpenetrating 3D structures. From the above-mentioned comparison, it is noted that the ancillary ligands greatly affected the coordination geometry of Cd atoms, coordination modes of carboxylate groups as well as the whole structures of these compounds.

The photoluminescent properties of **1**−**3** in the solid state at room temperature were investigated (Fig. S6). The maximal emission peaks of complexes **1**−**3** appear at 468 nm (λ = 353 nm) for **1**,

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468 nm (λ = 353 nm) for **2**, and 467 nm (λ = 353 nm) for **3**. In addition, the maximal emission was observed at 427 nm (λ = 365 nm) for the free bpy, 371 nm (λ = 345 nm) for the free bpe and 436 nm (λ = 354 nm) for the free bpp, while no clear luminescence was detected for H_2L ligands, as reported previously [11]. In comparison with that of bpy, bpe and bpp, the emission bands of **1**−**3** are 41, 97 and 32 nm red-shifted, respectively. Such broad emission bands may be assigned to ligand-to-metal charge transfer (LMCT) [15], the difference for the emissions of **1**−**3** may be a result of the effect of organic ligand coordination to the metal centers and interchromophore coupling [16]. In addition, comparing with free bpp ligand, the photoluminescent intensity of **3** has an obvious enhancement, which may be ascribed to ligand chelation to the metal center, which effectively increases the rigidity and reduces the loss of energy by radiationless decay [17]. Furthermore, in **1** and **3**, the photoluminescent intensity of **1** is higher than that of **3**, which may be attributed to the existing of rigid bpy ligand in **1** while the flexible bpp ligand in **3**. These results were consistent with the previous studies [8a] and further showed compounds **1**−**3** may be candidates for potential photoactive materials.

In summary, we have successfully isolated three new coordination polymers resulting from one flexible dicarboxylate ligand and three N-donor ligands with $Cd(OAc)_2{\cdot}2H_2O$. Compound **1** has an unusual three-fold 3D interpenetrating 6^6 diamondoid framework constructed by the 1D $[CdL]_n$ chains and the pillars bpy ligands. Compound **2** holds a 3D structure built from the 2D $[CdL_2]_n$ networks and the pillars bpe ligands that exhibits a rare $(4^4 6^5 8^1)(4^4 6^2)$ topological structure. Compound **3** possesses a novel 3D architecture constructed by the 1D helical $[CdL]_n$ and $[Cd(bpp)]_n$ chains *via* sharing the Cd atoms and also displays a 6^6 topology. Compared related complexes, the N-donor ligands have an effect on final structures.

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Appendix A. Supplementary data

CCDC 965283-965285 contains the supplementary crystallographic data for compounds **1–3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at …..

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[12] Synthesis: A mixture of $Cd(OAc)_2 \cdot 2H_2O$ (13 mg, 0.05 mmol), H_2L ligand (7 mg, 0.025 mmol), bpy (4 mg, 0.025 mmol), 0.020 M NaOH (0.3 mL) and H_2O (4 mL) was sealed in a 10 mL Pyrex glass tube and heated at 120 °C for 4 days, then cooled to room temperature at a rate of 5 °C h^{-1}. The orange prisms of **1** were collected and washed thoroughly with H_2O and dried in air. Yield: 7 mg (52%, based on H_2L). Anal. Calcd. for $C_{24}H_{16}N_4CdO_4$: C, 53.70; H, 3.00; N, 10.44. Found: C, 53.50; H, 3.38; N, 10.01. IR (KBr disc): 3059 (m), 1604 (s), 1591 (s), 1549 (m), 1375 (m), 1221 (m), 1159 (w), 1070 (m), 1006 (m), 865 (m), 814 (m), 768 (m), 715 (m), 660 (m), 628 (w), 559 (w), 477 (w), 414 (w) cm^{-1}. Compound **2** was prepared as yellow blocks in a similar manner to that used for the preparation of **1** by using bpe (5 mg, 0.025 mmol) instead of bpy. Yield: 5 mg (45%, based on H_2L). Anal. Calcd. for $C_{68}H_{50}N_{10}Cd_4O_{20}$: C, 45.97; H, 2.84; N, 7.88. Found: C, 45.70; H, 2.69; N, 8.07. IR (KBr disc): 3386 (m), 3300 (m), 3059 (w), 2932 (w), 1607 (s), 1592 (s), 1381 (s), 1254 (w), 1135 (w), 1098 (m), 1014 (w), 965 (m), 826 (m), 778 (m), 770 (m), 661 (m), 586 (m), 479 (w), 416 (w) cm^{-1}. Compound **3** was prepared as yellow blocks in a similar manner to that used for the preparation of **1** by using bpp (5 mg, 0.025 mmol) instead of bpy. Yield: 9 mg (62%, based on H_2L). Anal. Calcd. for $C_{27}H_{22}N_4CdO_4$: C, 56.02; H, 3.83; N, 9.68. Found: C, 56.15; H, 3.88; N, 9.39. IR (KBr disc): 3446 (m), 3065 (w), 2941 (w), 1615 (s), 1547 (s), 1410 (m), 1401 (s), 1226 (m), 1144 (w), 1069 (w), 1018 (m), 956 (w), 857 (m), 804 (m), 781 (m), 662 (w), 611 (w), 522 (w), 443 (w) cm^{-1}.

[13] Crystal data for **1**: $C_{24}H_{16}CdN_4O_4$, M_r = 536.82, monoclinic, space group *C*2/*c*, a = 20.666(4) Å, b = 7.1240(14) Å, c = 15.446(3) Å, β = 110.53(3)°, V = 2129.6(8) $Å^3$, Z = 4, D_c = 1.674 g cm^{-3}, F(000) = 1072.0 and μ = 1.066 mm^{-1}, 10744 reflections measured, 1874 unique

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reflections (R_{int} = 0.0225). R_1 = 0.0278, wR_2 = 0.0696 and *GOF* = 1.064 based on 1761 observed reflections with $I > 2\sigma(I)$. For **2**: $C_{34}H_{25}Cd_2N_5O_{10}$, M_r = 888.41, triclinic, space group $P\bar{1}$, a = 7.5764(15) Å, b = 14.120(3) Å, c = 15.795(3) Å, α = 71.81(3)°, β = 87.78(3)°, γ = 79.38(3)°, V = 1577.5(6) Å^3, Z = 2, D_c = 1.870 g cm^{-3}, F(000) = 880.0 and μ = 1.419 mm^{-1}, 10497 reflections measured, 5531 unique reflections (R_{int} = 0.0877). R_1 = 0.0490, wR_2 = 0.1304 and *GOF* = 0.996 based on 3099 observed reflections with $I > 2\sigma(I)$. For **3**: $C_{27}H_{22}CdN_4O_4$, M_r = 578.90, orthorhombic, space group $P2_12_12_1$, a = 11.624(2) Å, b = 13.338(3) Å, c = 16.603(3) Å, V = 2574.1(9) Å^3, Z = 4, D_c = 1.494 g cm^{-3}, F(000) = 1168.0 and μ = 0.888 mm^{-1}, 27451 reflections measured, 4525 unique reflections (R_{int} = 0.0444). R_1 = 0.0261, wR_2 = 0.0482 and *GOF* = 1.033 based on 4102 observed reflections with $I > 2\sigma(I)$. Structural data for the three compounds were collected on a Bruker Smart Apex-II CCD area detector by using graphite monochromated Mo Kα (λ = 0.071073 nm) at 296(2) K. The crystal structures of **1**–**3** were solved by direct method refined on F^2 by full-matrix least-squares techniques with the SHELXTL-97 program [18].

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Captions for Figures

Fig. 1. (a) View of the coordination environments of Cd center in **1** with labeling schemes. Symmetry codes: (A) − *x* − 1/2, − *y* + 1/2, − *z* − 1; (B) − *x*, − 1 − *y*, − *z*; (C) − *x*, *y*, − *z* − 1/2; (D) *x*, − *y* − 1, *z* − 1/2; (E) *x* + 1/2, − *y* + 1/2, *z* + 1/2. (b) View of a 2D (4,4) layer in **1** extending along the *ac* plane. (c) View of a 3D framework in **1** looking down the *a* axis. (d) View of the three-fold interpenetration model in **1**. Each single net represents a topology with a Schläfli symbol 6^6. Atom color codes: Cd, cyan; O, red; N, blue; and C, green and pink. All H atoms are omitted for clarity.

Fig. 2. (a)−(b) View of the coordination environments of Cd1 and Cd2 centers in **2** with labeling schemes. Symmetry codes: (A) – *x* + 2, – *y*, − *z* + 2; (B) – *x* + 3, − *y*, − *z* + 1; (C) – *x* + 1, − *y* + 1, − *z* + 2; (D) – *x* + 1, − *y*, − *z* + 1. (c) View of a 2D network in **2** extending along the *ac* plane. (d) View of a 3D structure in **2** looking down the *a* axis. (e) Schematic view of a $(4^4 6^5 8^1)(4^4 6^2)$ topological net of **2**. Green lines represent the bpe ligands. Atom color codes: Cd, cyan; O, red; N, blue; and C, green and pink. All H atoms are omitted for clarity.

Fig. 3. (a) View of the coordination environments of Cd center in **3** with labeling schemes. Symmetry codes: (A) – *x* + 2, *y* − 1/2, − *z* + 1/2; (B) *x* + 1/2, − *y* − 1/2, − *z* + 1. (b) View of a 1D helical $[CdL]_n$ chain in **3** extending along the *b* axis. (c) View of a 1D helical $[Cd(bpp)]_n$ chain in **3** extending along the *a* axis. (d) View of a 3D structure in **3** looking along the *a* axis. (e) Schematic view of a 6^6 topological net of **3**. Atom color codes: Cd, cyan; O, red; N, blue; and C, green and pink. All H atoms are omitted for clarity.

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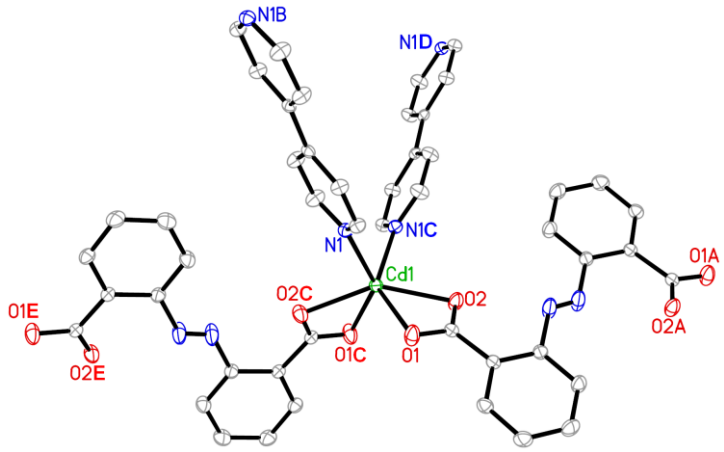

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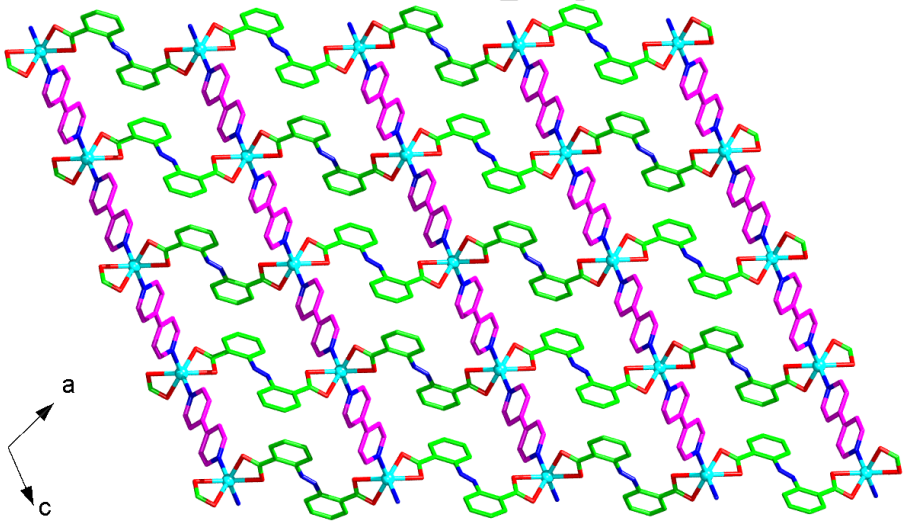

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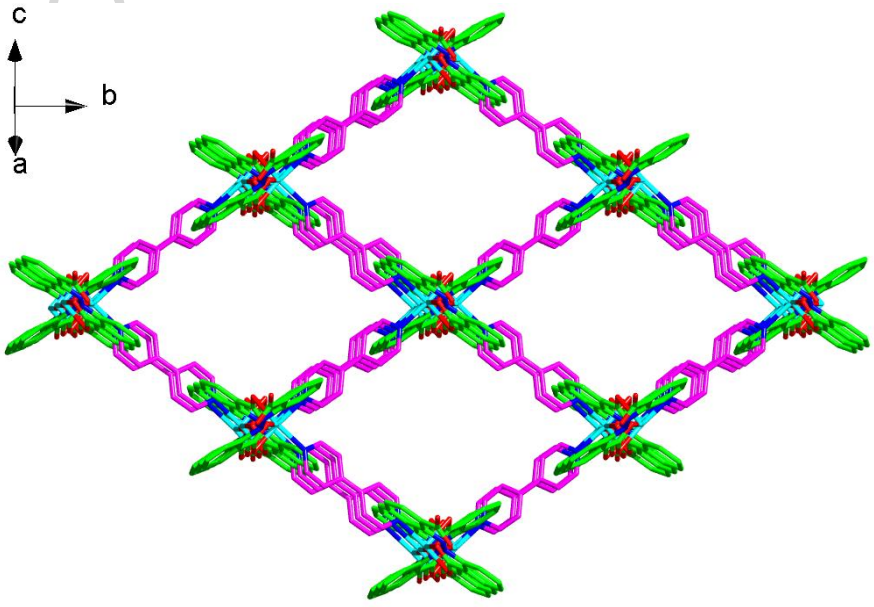

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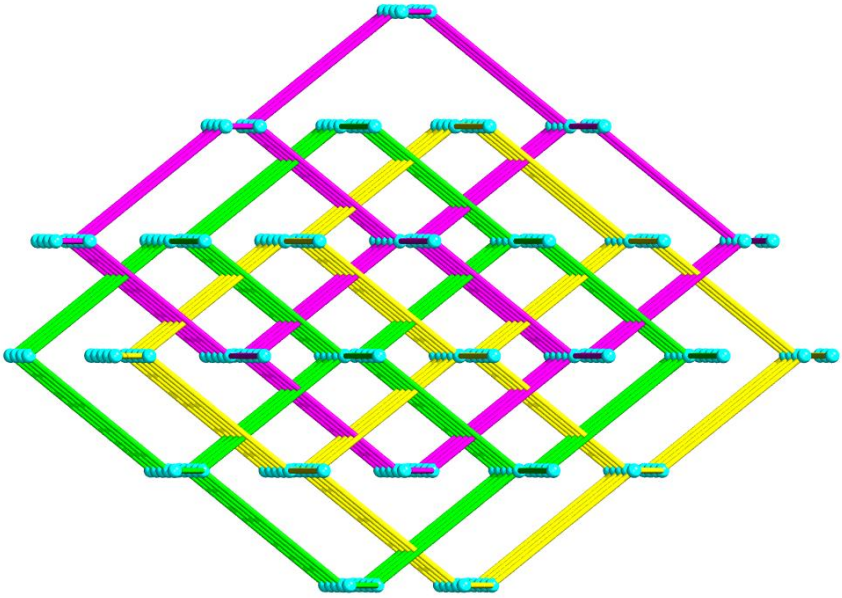

(d)

Fig. 1

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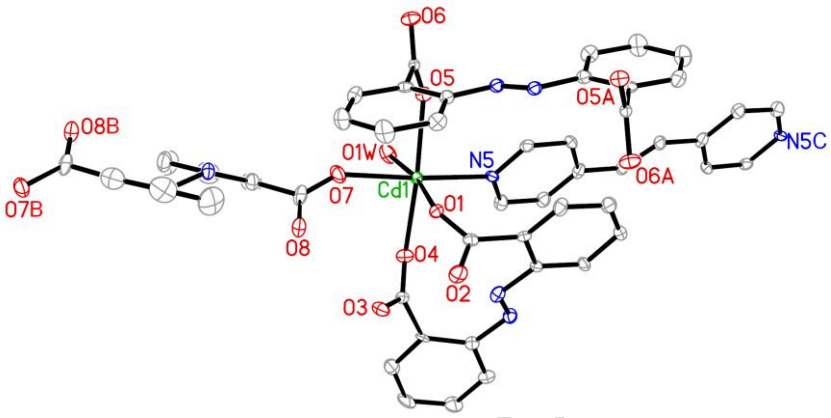

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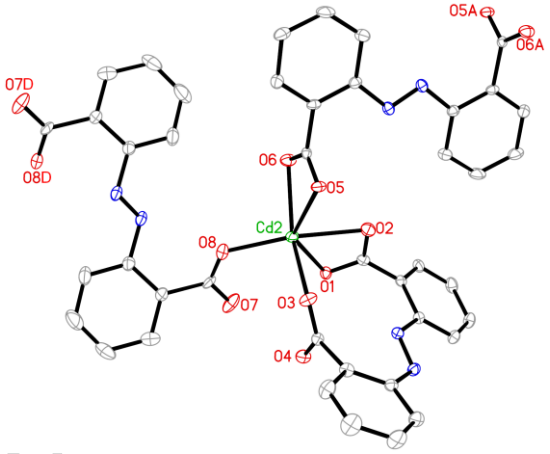

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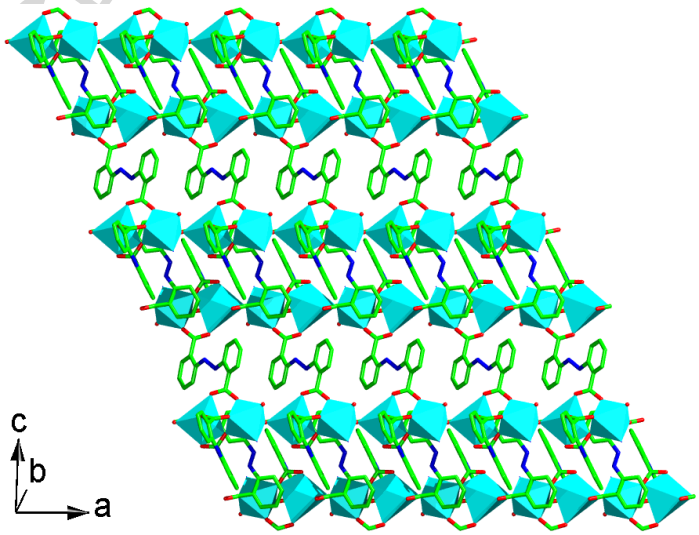

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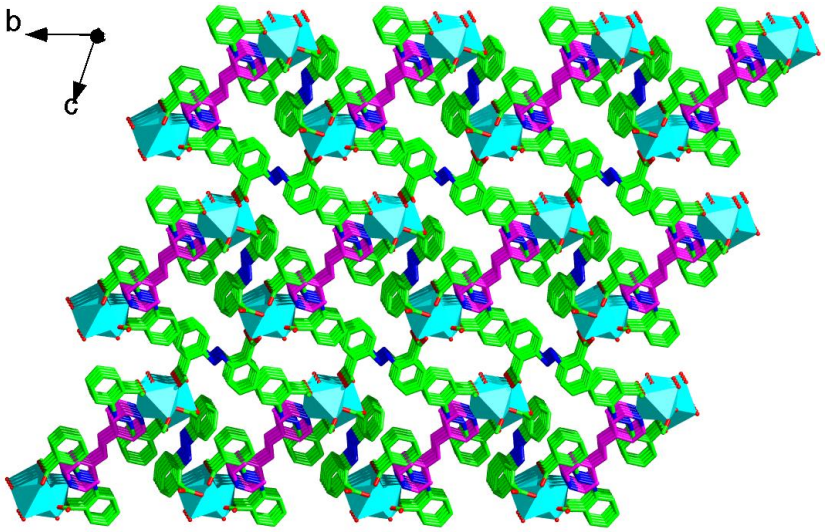

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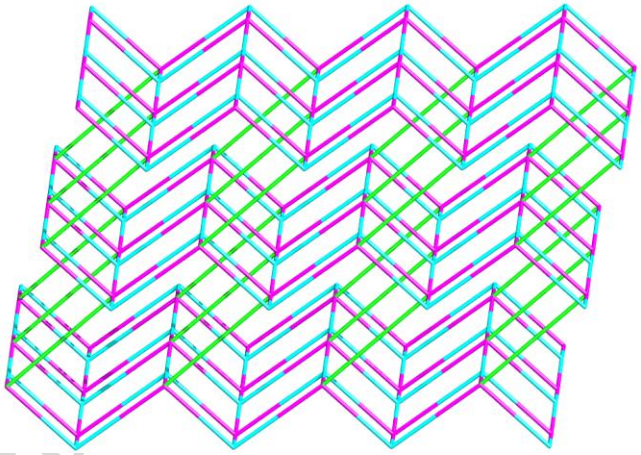

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Fig. 2

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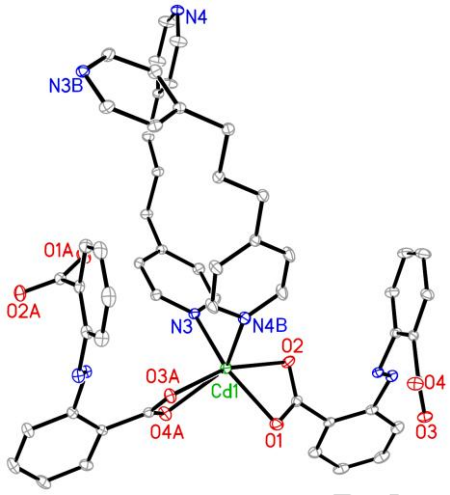

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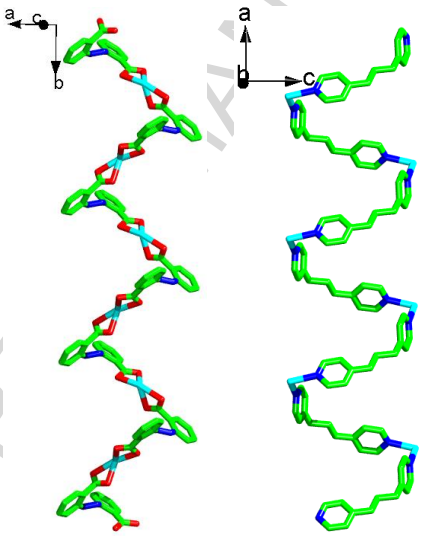
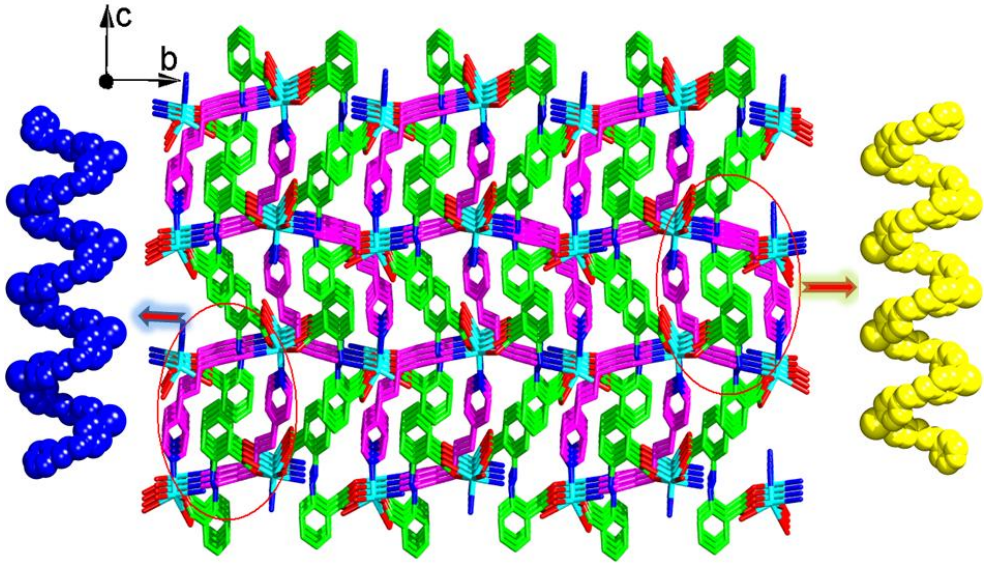


(b) **(c)**



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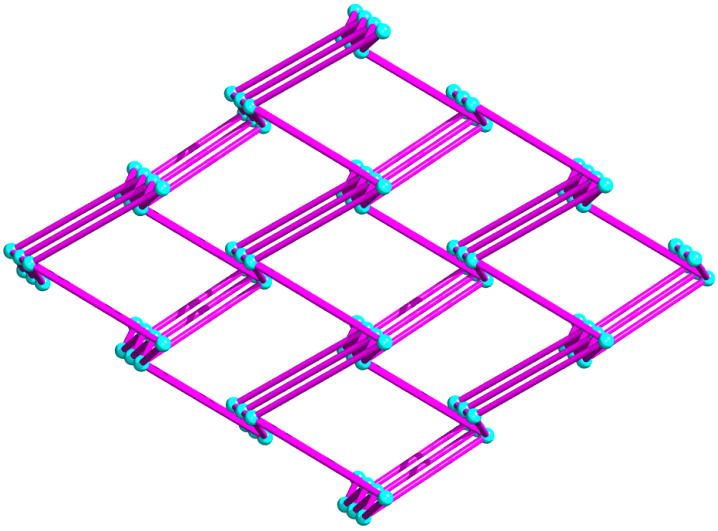

(e)

Fig. 3

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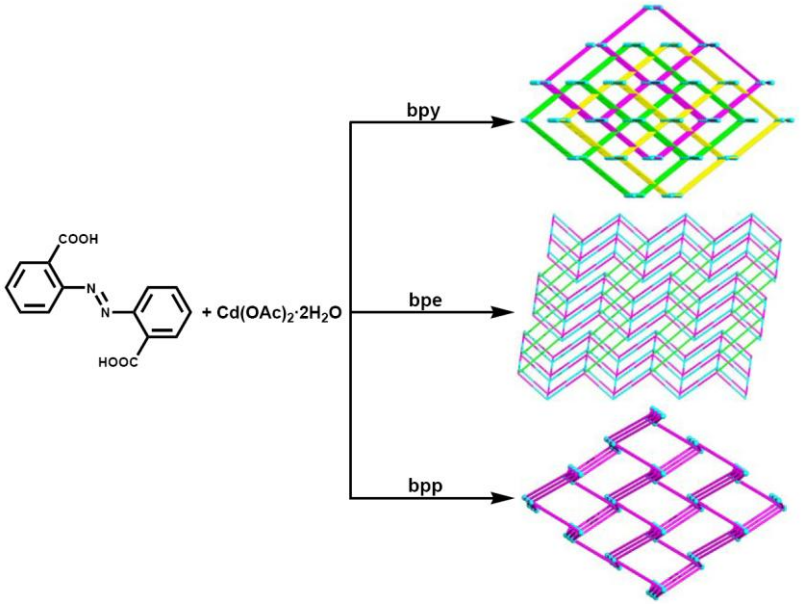
Graphical Abstract



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Graphical Abstract

Three Cd(II) coordination polymers assembled by flexible 2,2'-azodibenzoic acid and N-donor auxiliary ligand: Structural diversities and luminescent properties

Lei-Lei Liu[a,*], Cai-Xia Yu[a], Yan Zhou[a], Juan Sun[a], Pan-Pan Meng[a], Dong Liu[b,*], Rong-Jian Sa[c]

Three new cadmium(II) coordination polymers with novel 3D structures have been successfully synthesized by assembly of flexible 2,2'-azodibenzoic acid (H_2L) with three N-donor auxiliary ligands (bpy, bpe, bpp). The effects of auxiliary ligand have been discussed and the spectroscopic properties of these complexes were also studied.

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Research Highlights

►Reactions of $Cd(OAc)_2$, 2,2'-azodibenzoic acid and bpy/bpe/bpp produce coordination polymers **1-3**. ►The formation of the coordination polymers depends on N-donor auxiliary ligand. ► Compounds **1-3** have 3D novel structures with 6^6, $(4^4 6^5 8^1)(4^4 6^2)$ and 6^6 topology motifs.

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