Three 2 D copper(II)/cadmium(II) coordination polymers based on semi-rigid/flexible bis-pyridyl-bis-amide ligands and 5-aminoisophthalate: Syntheses, structures and properties

HONGYAN LIN^a, HUIZHE LU^b, MAO LE^a, JIAN LUAN^a, XIULI WANG^{a,*} and GUOCHENG LIU^a

^aDepartment of Chemistry, Bohai University, Jinzhou 121000, P. R. China

^bDepartment of Applied Chemistry, China Agricultural University, Beijing, 100193, P. R. China
e-mail: wangxiuli@bhu.edu.cn

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Abstract. Three new transition metal coordination polymers [Cu(3-bpcb)_{0.5}(5-AIP)]·2H₂O (**1**), [Cd(3-bpc b)_{0.5}(5-AIP)(H₂O)]·H₂O (**2**) and [Cd(3-bpsa)_{0.5}(5-AIP)(H₂O)]·2H₂O (**3**) have been hydrothermally synthesized by self-assembly of 5-aminoisophthalic acid (5-H₂AIP), semi-rigid or flexible bis-pyridyl-bis-amide ligands [3-bpcb = N,N'-bis(3-pyridinecarboxamide)-1,4-benzene, 3-bpsa = N,N'-bis(3-pyridyl)succinamide], and copper chloride or cadmium nitrate. X-ray diffraction analysis reveals that compounds **1** and **2** possess similar 2 D double-layered structures with (3,4)-connected (6³)(6⁵·8) topology, while compound **3** displays a 2 D layer with {6².10}{6} topology. The adjacent layers of **1–3** are finally extended into 3 D supramolecular frameworks by hydrogen bonding interactions. The bis-pyridyl-bis-amide ligands with different flexibilities play an important role in the construction of final topological structures for the title compounds. Further, the electrochemical behavior of the compound **1** and the fluorescent and photocatalytic properties of compounds **1–3** have been investigated.

Keywords. Bis-pyridyl-bis-amide ligand; coordination polymer; crystal structure; fluorescent property; photocatalytic property.

1. Introduction

Coordination polymers have attracted intensive attention during the past decades, not only for their diverse topological structures but also for their potential applications in catalysis, gas storage, luminescence and magnetism.^{1–3} Till now, a great number of these compounds with intriguing structures and desired properties have been successfully prepared by hydrothermal method.^{4–6} Although many factors can affect the ultimate structures of coordination compounds, the selection of suitable organic ligands plays a crucial role.^{7–9} Among the diverse organic ligands, the analogs of dipyridyl-based N-heterocyclic ligands has been widely utilized to bridge metal ions, and a large number of coordination compounds with intriguing architectures and interesting properties have been constructed with these organic ligands.^{10–13}

Recently, semi-rigid/flexible bis-pyridyl-bis-amide ligands as one of the dipyridyl-based ligands have proven to be excellent bridging ligands for building up metal-organic coordination frameworks and

supramolecular networks,^{14–18} because it can satisfy the coordination requirements of metal ions by its backbone bending for appropriate twist angle and interact with each other by hydrogen bonds among the amide groups. For example, Cao's group and Chen's group have reported a series of transition metal (Zn, Cd, Hg) coordination compounds based on the flexible bis-pyridyl-bis-amide ligands containing different -(CH₂)_n- (n = 0, 4, 10) backbones and aromatic polycarboxylates.^{19–21} Utilizing the mixed ligands of semi-rigid/flexible bis-pyridyl-bis-amide ligands with various bridging backbones [benzene, cyclohexane, -(CH₂)_n- (n = 1–6, 8)] and polycarboxylates, our group has prepared a series of Co(II)/Cu(II) coordination compounds showing remarkable photocatalytic activities for the degradation of organic dyes.^{22–25} However, so far, the related reports about Cd(II) coordination compounds based on semi-rigid/flexible bis-pyridyl-bis-amide ligands are limited,^{22,24} which prompted us to initiate this study.

In this paper, we select the N, N'-bis(3-pyridinecarboxamide)-1,4-benzene (3-bpcb) and N,N'-bis(3-pyridyl)succinamide (3-bpsa) as neutral N-heterocyclic ligands (scheme 1) and 5-aminoisophthalic acid (5-H₂AIP) as

*For correspondence

Scheme 1. The ligands 3-bpcb and 3-bpsa used in this work.

the auxiliary ligand, three new 3 D supramolecular structural compounds based on 2 D layered polymeric networks, $[\text{Cu}(3\text{-bpcb})_{0.5}(5\text{-AIP})]\cdot 2\text{H}_2\text{O}$ (**1**), $[\text{Cd}(3\text{-bpcb})_{0.5}(5\text{-AIP})(\text{H}_2\text{O})]\cdot \text{H}_2\text{O}$ (**2**) and $[\text{Cd}(3\text{-bpsa})_{0.5}(5\text{-AIP})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ (**3**) have been successfully prepared under hydrothermal conditions. The influence of bis-pyridyl-bis-amide ligands with different flexibilities on the structures of coordination compounds has been discussed. Moreover, the thermal stability, electrochemical behavior of compound **1** bulk-modified carbon paste electrode (**1**-CPE), fluorescent and photocatalytic properties of the title compounds have been studied.

2. Experimental

2.1 Materials and methods

Ligands 3-bpcb and 3-bpsa were synthesized by the methods of the literature.^{26,27} Other chemical reagents were commercially obtained and used without further purification. FT-IR spectra (KBr pellets) were measured on a Varian FT-IR 640 spectrometer with KBr pellet in the $500\text{--}4000\text{ cm}^{-1}$ region. Thermogravimetric analyses (TGA) were carried out with a Pyris Diamond TG-DTA instrument. The fluorescence spectra were taken on a HITACHI F-4500 Fluorescence Spectrophotometer. Electrochemical experiments were performed with a CHI 440 Electrochemical workstation. A conventional three-electrode cell was used at room temperature. The carbon paste electrode bulk-modified with compound **1** (**1**-CPE) was used as working electrode.¹⁴ An SCE and a platinum wire were used as reference and auxiliary electrodes, respectively.

2.2 Preparation of the complexes

2.2a Synthesis of $[\text{Cu}(3\text{-bpcb})_{0.5}(5\text{-AIP})]\cdot 2\text{H}_2\text{O}$ (1**):** A mixture of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.034 g, 0.20 mmol), 5- H_2AIP (0.036 g, 0.20 mmol), 3-bpcb (0.032 g,

0.10 mmol), H_2O (12 mL) and NaOH (0.014 g, 0.35 mmol) was stirred for 20 min, then transferred and sealed in a 25 mL Teflon reactor, which was heated at 120°C for 4 days leading to the formation of blue block crystals **1**. Yield: $\sim 33\%$ (based on Cu). Anal. Calc. for $\text{C}_{17}\text{H}_{16}\text{CuN}_3\text{O}_7$ (437.88): C 46.63, H 3.68, N 9.60. Found: C 46.51, H 3.52, N 9.82%. IR (KBr, cm^{-1}): $\nu = 3560\text{ m}, 3478\text{ m}, 3415\text{ s}, 3231\text{ w}, 2362\text{ m}, 1645\text{ m}, 1613\text{ s}, 1550\text{ s}, 1511\text{ m}, 1480\text{ w}, 1391\text{ s}, 1296\text{ m}, 1251\text{ w}, 1176\text{ w}, 1081\text{ w}, 916\text{ w}, 834\text{ m}, 751\text{ w}, 618\text{ s}, 527\text{ w}$.

2.2b Synthesis of $[\text{Cd}(3\text{-bpcb})_{0.5}(5\text{-AIP})(\text{H}_2\text{O})]\cdot \text{H}_2\text{O}$ (2**):** The synthesis method of **2** is similar to that for **1** except for $\text{Cd}(\text{NO}_3)_2\cdot 2\text{H}_2\text{O}$ (0.063 g, 0.23 mmol) as the substitute of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.034 g, 0.20 mmol), and the different amount of NaOH (0.018 g, 0.45 mmol) was added to adjust pH value. Yield: $\sim 39\%$ (based on Cd). Anal. Calc. for $\text{C}_{17}\text{H}_{16}\text{CdN}_3\text{O}_7$ (486.73): C 41.95, H 3.31, N 8.63. Found: C 41.71, H 3.22, N 8.80%. IR (KBr, cm^{-1}): $\nu = 3490\text{ m}, 3392\text{ m}, 3210\text{ s}, 3042\text{ w}, 2364\text{ m}, 1619\text{ s}, 1561\text{ s}, 1480\text{ w}, 1436\text{ w}, 1366\text{ s}, 1265\text{ s}, 1163\text{ m}, 1112\text{ w}, 1068\text{ w}, 1011\text{ m}, 929\text{ w}, 827\text{ s}, 745\text{ s}, 643\text{ w}, 592\text{ w}, 535\text{ w}$.

2.2c Synthesis of $[\text{Cd}(3\text{-bpsa})_{0.5}(5\text{-AIP})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ (3**):** The synthesis method of **3** is similar to that for **2** except for 3-bpsa (0.027 g, 0.10 mmol) was used instead of 3-bpcb (0.032 g, 0.10 mmol), and different amount of NaOH (0.016 g, 0.40 mmol) was added to adjust the pH value. Yield: $\sim 43\%$ (based on Cd). Anal. Calc. for $\text{C}_{15}\text{H}_{18}\text{CdN}_3\text{O}_8$ (480.72): C 37.48, H 3.77, N 8.74. Found: C 37.61, H 3.62, N 8.91%. IR (KBr, cm^{-1}): $\nu = 3420\text{ w}, 3368\text{ s}, 3080\text{ w}, 2928\text{ s}, 2865\text{ w}, 1675\text{ s}, 1470\text{ s}, 1420\text{ w}, 1370\text{ s}, 1321\text{ s}, 1280\text{ s}, 1198\text{ w}, 1127\text{ s}, 1047\text{ w}, 1007\text{ m}, 809\text{ w}, 770\text{ s}, 716\text{ w}, 614\text{ w}, 530\text{ w}$.

2.3 X-ray crystallography

Crystallographic data for the title compounds were collected using a Bruker Smart Apex II diffractometer (Mo-K α radiation, graphite monochromator, $\lambda = 0.71073\text{ \AA}$ for **1** and **3**, $\lambda = 0.71069\text{ \AA}$ for **2**) by ω scan mode in the range of $1.50^\circ \leq \theta \leq 25.00^\circ$ for **1** $144^\circ \leq \theta \leq 25.00^\circ$ for **2** and $1.90^\circ \leq \theta \leq 24.99^\circ$ for **3**. Structure solution and refinement based on observed reflections gave the final $R_1(wR_2) = 0.0398$ (0.1241) for **1**, $R_1(wR_2) = 0.0284$ (0.0662) for **2** and $R_1(wR_2) = 0.0475$ (0.1213) for **3**. All of the structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXS program of the SHELXTL package.^{28,29} Metal atoms in the compounds were located from the E -maps, and all

non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the organic ligands were placed in geometrically idealized positions and refined isotropically. The hydrogen atoms of lattice water and coordinated water molecules in compounds **1–3** were added by difference Fourier maps. But the hydrogen atoms of nitrogen atom (N1) from the 5-AIP ligand could not be found from the residual peaks and were directly included in the final molecular formula for compound **2**. A summary of crystal data and structure refinements for the title compounds are provided in table 1. The coordination modes of metal ions and organic ligands in compounds **1–3** are listed in table 2. The data of selective bond distances and angles are listed in table S1. The related hydrogen bonding geometries of **1–3** are given in table S2.

3. Results and Discussion

3.1 Synthesis

Some factors may affect crystallization and structural formation of the coordination polymers in the hydrothermal reactions, such as initial reactants, reactant ratio, temperature and systematic pH, etc.^{30,31} In order to investigate the influence of different factors on the assembly of coordination polymers, we tried to synthesize the title compounds by selecting copper(II)/cadmium ions, two semi-rigid/flexible bis-pyridyl-bis-amide ligands, as well as adjusting the

reactants ratio and pH. Although we have successfully prepared compounds **1–3**, the yields for the title compounds are low (<50% in all case). There are amounts of byproducts during the hydrothermal synthesis, which may be the unreacted organic ligands or non-crystalline target/desired complexes. The experimental results indicate that syntheses of the compounds are affected not only by the stoichiometries of the reactants but also by the types of co-ligands in the reaction medium.³²

The dicarboxylate ligands are extremely suitable to participate in the construction of coordination architectures with transitional metal ions, wherein the former can adopt various coordination geometries by utilizing their carboxyl groups in completely or partially deprotonated state. So, the introduction of bridging dicarboxylates is beneficial towards the formation of intricate coordination polymers.^{19,33} In addition, the differences of substituent groups have influence on the final architectures of the coordination polymers. In this work, the dicarboxylic acid 5-H₂AIP with the electron-donating amino group is selected due to the following advantages: (i) serving as a naturally bent ligand, it possesses the dissymmetric unit with high rigidity, which tends to yield metal-organic compounds without interpenetrating structures;³⁴ (ii) it is closely similar to the tripus-type 1,3,5-benzenetricarboxylic acid (1,3,5-H₃BTC) ligand, and its one amino group and two carboxyl groups may provide potential coordination sites leading to generation of high dimensional compounds.³⁵ In compounds **1–3**, 5-AIP anions

Table 1. Crystal data and structure refinement for compounds **1–3**.

Empirical formula	C ₁₇ H ₁₆ CuN ₃ O ₇	C ₁₇ H ₁₆ CdN ₃ O ₇	C ₁₅ H ₁₈ CdN ₃ O ₈
Formula weight	437.88	486.73	480.72
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P21/c	P -1	P -1
<i>a</i> , Å	15.1463(13)	7.9088(8)	8.540(3)
<i>b</i> , Å	7.6805(7)	8.1050(8)	10.039(3)
<i>c</i> , Å	15.6641(13)	14.6760(15)	11.214(4)
α , °	90	89.140(2)	92.837(6)
β , °	116.4100(10)	75.2470(10)	105.408(7)
γ , °	90	80.092(2)	102.628(6)
<i>V</i> , Å ³	1632.1(2)	895.75(16)	898.5(5)
<i>Z</i>	4	2	2
<i>D</i> _{calc} , g·cm ^{−3}	1.782	1.805	1.777
μ , mm ^{−1}	1.390	1.266	1.265
<i>F</i> (000)	896	486	244
Total reflections	8315	4628	5077
Unique reflections	2872	3139	3158
<i>R</i> _{int}	0.0293	0.0160	0.0330
GOOF	1.082	1.041	1.033
<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0398	0.0284	0.0475
<i>wR</i> ₂ ^b (all data)	0.1241	0.0662	0.1213

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

Table 2. The coordination numbers and modes of metal ions, 5-H₂AIP, 3-bpcb and 3-bpsa ligands in compounds 1–3.

	Metal ions	Ligand 5-H ₂ AIP	Ligand 3-bpcb/3-bpsa
1			Cu1...Cu1 distance: 17.99 Å
2			Cd1...Cd1 distance: 15.58 Å
3			Cd1...Cd1 distance: 15.36 Å

adopted two different coordination modes (table 2), which bridge the metal ions to build 2 D layers (for compounds 1–2) or 1 D ribbon-like chain for compound 3.

3.2 Description of crystal structures of [Cu(3-bpcb)_{0.5}(5-AIP)]·2H₂O (**1**) and [Cd(3-bpcb)_{0.5}(5-AIP)(H₂O)]·H₂O (**2**)

Single crystal X-ray diffraction analyses reveal that compounds 1–2 crystallize in the monoclinic space group P2₁/c and possess similar 2 D double-layered structures, so we will discuss in detail the structure of compound 1 as an example. The asymmetric unit of compound 1 contains one crystallographically independent Cu(II) ion, a half of 3-bpcb ligand, one 5-AIP anion and two lattice water molecules. As shown in figure 1a, the Cu(II) ion is penta-coordinated by one pyridyl nitrogen atom from a 3-bpcb ligand with Cu1–N2 distance of 1.995(3) Å, an amino nitrogen atom of a 5-AIP anion with Cu1–N1#2 distance of 2.270(3) Å and three carboxyl oxygen atoms of two separated 5-AIP anions [the distances: Cu1–O2#1, 1.910(3) Å; Cu1–O3, 2.075(2) Å; Cu1–O4, 2.033(3) Å], completing a distorted tetragonal pyramid geometry. The bond angles

around the Cu(II) ion are 99.71(11)° for N2–Cu–N1#1, 63.58(10)°–93.19(10)° for O–Cu–O, and 89.88(11)°–153.54(12)° for O–Cu–N.

In compound 1, each 5-AIP anion adopts a monodentate-monodentate-chelating coordination mode (table 2): one carboxyl group coordinates to one Cu(II) ion with a monodentate mode, the other group coordinates to another Cu(II) ion exhibiting a chelating mode, and the amino group also coordinates to one Cu(II) ion showing a monodentate mode. The adjacent Cu(II) ions are bridged by the 5-AIP anions to form a 2 D [Cu(5-AIP)]_n layer (figure 1b). Without considering the connection of 3-bpcb ligand, the 5-AIP anion serves as a μ₃-bridging ligand and connects Cu(II) ions to build a 2 D (6,3) hexagonal grid polymeric network (figure S1). Then two neighbouring layers are interlinked by 3-bpcb ligands with a bidentate bridging mode (via ligation of pyridyl nitrogen atoms, table 2) to produce a honeycomb-like double-layer structure (figure 1c), in which the 3-bpcb ligand bridges two Cu(II) ions from two adjacent layers with the Cu...Cu non-bonding distance of 17.99 Å. The dihedral angle between two pyridyl rings of 3-bpcb ligand is 0°.

In the 2 D network of 1, each Cu(II) ion is surrounded by three 5-AIP anions and one 3-bpcb ligands, which can be regarded as a 4-connected node.

Figure 1. (a) The coordination environment for Cu(II) ion in compound **1** (at 50% probability level); (b) The 2D [Cu(5-AIP)]_n layer formed by 5-AIP ligand in **1**; (c) The 2D double layer of **1** formed by [Cu(5-AIP)]_n layer and 3-bpcb ligands; (d) The scheme of 2D double layer in **1**; (e) The 3D supramolecular framework of compound **1** formed by hydrogen bonding interactions [hydrogen bond: blue dot line, N1...O4; pink dot line, N1...O1].

Figure 2. (a) The coordination environment for Cd(II) ion in compound **2** (at 50% probability level); (b) The 3D supramolecular framework of **1** formed by hydrogen bonding interactions [hydrogen bond: blue dot line, N1...O2; pink dot line, N1...O3].

Each 5-AIP anion bridges three Cu(II) ions, which is defined as a 3-connected node. Each 3-bpcb ligand with bidentate bridging mode is regarded as a simple linear linker. Thus, the 2D structure of **1** can be classified as a (3,4)-connected binodal topology, and its Schläfli symbol is {6³}{6⁶} (figure 1d). The neighboring 2D double-layer networks are further extended into a 3D supramolecular network by hydrogen bonding interactions between the nitrogen atom (N1) and oxygen atoms (O1 or O4) of 5-AIP ligands [N1–H1A...O1 = 3.163(4) Å, N1–H1B...O4 = 2.989(5) Å] (figure 1e).

For compounds **1–2**, based on the same mixed-ligands system of the semi-rigid 3-bpcb and 5-AIP, we obtained two similar 2D polymeric networks. However, there are some intrinsic differences among them. In **2**, the Cd(II) ion adopts a six-coordinated distorted octahedral geometry (figure 2a and table 2), which is significantly different from five-coordinated Cu(II) ion in **1**. For Cu(II) and Cd(II) ions, the difference of the coordination modes may be due to their different atomic radius. In **2**, the coordination mode of 5-AIP ligand is the same as that in **1**, and the 3-bpcb also adopts the similar bidentate bridging mode (table 2). But slight differences of conformations for

ligand 3-bpcb can be observed. In compound **1**, the 3-bpcb bridges two Cu(II) ions with the non-bonding Cu1...Cu1 distances of 17.99 Å; while in **2**, the 3-bpcb links two Cd(II) ions and the non-bonding Cd1...Cd1 distance is 15.58 Å. Due to the differences on coordination numbers of metal ions and coordination modes of organic ligand 3-bpcb in compounds **1** and **2**, the final 3 D supramolecular networks are slightly different (figure 2b).

In our previous studies, by utilizing the same 3-bpcb ligand, three Cu(II) compounds derived from three different polycarboxylates (1,2-H₂BDC 1,2-benzenedicarboxylate; H₂SIP, 5-sulfoisophthalic acid; H₄btec, 1,2,4,5-benzene tetracarboxylic acid) have been obtained,^{36,37} [Cu₃(3-bpcb)(1,2-BDC)₂(μ₂-OH)₂], [Cu₂(3-bpcb)_{1.5}(SIP)(μ₃-OH)]·H₂O and [Cu₃(3bpcb)₃(btec)_{1.5}], which represent three different 3 D coordination networks: a 4-nodal mixed (3,4,4,5)-connected 3D structure with the (3·4·5)₂(3·4²·5·8⁶)₂(3²·8·9²·10)(4²·8²·10²) Schläfli symbol, a novel 3-nodal (5,6,6)-connected (3³·4³·5³·6³·7²·8)(3³·4³·5³·6)(3³·4⁶·5⁴·6²) topology and a unique trinodal 4-connected (6⁴·8²)₃ topology. In this study, we have obtained compound **1** with a 2 D layered structure by selecting the dicarboxylate 5-AIP. The results reveal that different polycarboxylates play an important role in the formation of different coordination frameworks. Moreover, we have also prepared four Co(II) compounds based on the 3-bpcb ligand and four different aromatic dicarboxylates with various substituent groups (3-nitrophthalic acid, 5-nitroisophthalic acid, 1,3-benzenedicarboxylate and 5-H₂AIP),^{15,38} showing three diverse 2 D polymeric layers and one 1 D chain-like structure, which indicates that the substituent groups of dicarboxylates play an important role in the assembly of metal-organic compounds. Although, several related Co(II) and Cu(II) compounds based on the 3-bpcb ligand have been obtained, the Cd(II) compound containing the 3-bpcb ligand has not been synthesized so far. Compound **2** represents the first Cd(II) compound derived from the semi-rigid bis-pyridyl-bis-amide ligand 3-bpcb.

3.3 Description of crystal structures of [Cd(3-bpsa)_{0.5}(5-AIP)(H₂O)]·2H₂O (**3**)

Different from compounds **1–2**, selection of a flexible bis-pyridyl-bis-amide ligand 3-bpsa results in compound **3**. X-ray diffraction analysis shows that the asymmetric unit of compound **3** consists of one independent Cd(II) ion, a half of 3-bpsa ligand, one 5-AIP ligand, one coordinated water molecule and two lattice water molecules. The coordination environment

of Cd(II) ion is shown in figure 3a. The Cd1 ion is seven-coordinated by four carboxyl oxygen atoms from

Figure 3. (a) The coordination environment for Cd(II) ion in compound **3** (at 50% probability level); (b) The 2 D polymer layer formed by {Cd₂(5-AIP)₂}_n chains and 3-bpsa ligands; (c) The scheme of polymeric layer for **3**; (d) The 3 D supramolecular framework of **3** formed by hydrogen bonding interactions [hydrogen bond: blue dot line, N2...O2W; black dot line, O1...O2W, O1W...O2W, O1W...O2].

two 5-AIP ligands with Cd–O distances of 2.310(4)–2.503(4) Å, one nitrogen atom from the amino group of 5-AIP [Cd1–N3 = 2.426(4) Å], one nitrogen atom from a 3-bpsa ligand with Cd–N1 distance of 2.322(4) Å, and one oxygen atom of a coordinated water molecule [Cd–O1W = 2.321(4) Å], showing a distorted decahedral geometry. In compound **3**, the 5-AIP ligand adopts a monodentate-chelating-chelating coordination mode to bridge three Cd(II) ions with its two carboxyl groups and one amino group (table 2), which is different from that in compounds **1** and **2**. For ligand 5-AIP in the three title compounds, the diversities of the coordination modes may be assigned to the different mixed ligands systems and different systematic pH. Each 5-AIP bridging ligand links three adjacent Cd(II) ions to construct a 1 D neutral $\{\text{Cd}_2(5\text{-AIP})_2\}_n$ ribbon-like chain for **3** (figure S2). The 3-bpsa ligand displays a bidentate bridging coordination mode (via ligation of pyridyl nitrogen atoms), and its two pyridyl rings are parallel. The adjacent 1 D $\{\text{Cd}_2(5\text{-AIP})_2\}_n$ ribbon-like chains are linked by the 3-bpsa to give a 2 D polymeric layer of **3** (figure 3b).

Topologically, each Cd(II) ion is surrounded by one 3-bpsa ligand and three 5-AIP ligands, which can be defined as a 4-connected node. Each 5-AIP links three metal Cd(II) ions, regarded as a 3-connected node. The 3-bpsa ligating with two 4-connected Cd(II) ions serves as a simple linear linker. Thus the 2 D layer of **3** is best described as a (3,4)-connected framework with $\{6^2.10\}\{6\}$ topology, as shown in figure 3c. Moreover, the 2 D layers of **3** are extended into 3 D supramolecular networks by two types of hydrogen bonding interactions [N–H...O hydrogen bond: N2...O2W = 3.010(6) Å; and O–H...O hydrogen bond: O2W...O1 = 2.945(6), O2W...O1W = 2.768(6), O1W...O2 = 2.697(5) Å], as shown in figure 3d.

3.4 Effect of semi-rigid/flexible bis-pyridyl-bis-amide ligands and 5-aminoisophthalate on the structures of three copper(II)/cadmium(II) coordination polymers

In this paper, we chose two bis-pyridyl-bis-amide ligands: the semi-rigid 3-bpcb and the flexible 3-bpsa, to assemble with Cu(II)/Cd(II) ions and dicarboxylic acid (5-H₂AIP), aiming to study their influences on the architectures of the coordination polymers. As shown above, when semi-rigid 3-bpcb is selected as neutral N-heterocyclic ligand to be introduced into the Cu-5-H₂AIP or Cd-5-H₂AIP systems, two similar 2 D double-layered architectures **1–2** are constructed. In these two compounds, the ligand 5-AIP adopts the same bridging coordination modes (monodentate-monodentate-chelating mode), which link the adjacent

metal ions to form the similar 2 D $[\text{M}(5\text{-AIP})]_n$ (M = Cu(II) or Cd(II)) layers. Although 3-bpcb ligands display the same bidentate bridging modes, there are slight differences of conformations (table 2). For compounds **1–2**, the similar 2 D double-layered structures with (3,4)-connected $(6^3)(6^5 \cdot 8)$ topologies are generated, but their final 3 D supramolecular networks are slightly different due to the different coordination numbers of metal ions and organic ligand 3-bpcb.

For compounds **2** and **3**, based on the same transitional metal Cd(II) ions and 5-AIP anions, when the flexible ligand 3-bpsa was used, the compound **3** with a 2 D sheet structure was obtained. In compounds **2** and **3**, the Cd(II) ions and 5-AIP ligands respectively exhibit different coordinated modes (table 2): Cd(II) ions, a six-coordinated distorted octahedral geometry (in **2**) and a seven-coordinated distorted decahedral geometry (in **3**); 5-AIP anions, a monodentate-monodentate-chelating mode (in **2**) and a monodentate-chelating-chelating mode (in **3**). The Cd(II) ions are bridged by 5-AIP with different coordination modes to construct a 2 D $[\text{Cd}(5\text{-AIP})]_n$ layer (for **2**) or a 1 D neutral $\{\text{Cd}_2(5\text{-AIP})_2\}_n$ ribbon-like chain (for **3**). Then ligands 3-bpcb or 3-bpsa showing μ_2 -bridging coordinated modes connect the adjacent 2 D layers of **2** or 1 D ribbon-like chains of **3**. Consequently, the architecture of **3** is a 2 D polymeric network with the $\{6^2.10\}\{6\}$ topology, which is completely different from that of **2**. Notably, compounds **1–3** are 2 D layered polymers derived from transitional metal Cu(II)/Cd(II) ions bridged by the same dicarboxylate 5-AIP and ligands 3-bpcb or 3-bpsa, but they possess different structural features. Although many factors are involved, the differences of metal ions, bis-pyridyl-bis-amide ligands and their unique combination around metal ions, as depicted above, presumably play the key role in determining the final framework structures. These observations indicate the suitable combination of the semi-rigid/flexible bis-pyridyl-bis-amide ligands, dicarboxylates ligands and various transitional metal ions may lead to forming different architectures.

3.5 Thermal stability analyses of compounds **1–3**

To study their thermal stabilities, thermal gravimetric (TG) analyses of compounds **1–3** were performed under a flow of nitrogen with a heating rate of 10°C min^{−1} (figure 4). All of the TG curves exhibit two obvious weight loss steps in the region of 25–600°C. For **1**, the first weight loss indicates removal of the lattice water molecules (obsd.: 7.89%, calcd.: 8.22%) from 168°C to 225°C. The second weight loss in the range of 290–500°C was assigned to the collapse of polymeric

Figure 4. Thermal gravimetric curves of compounds **1–3**.

framework. The remaining weight (18.45%) corresponds to the percentage (18.27%) of Cu and O components, indicating that the final product is CuO. For compounds **2** and **3**, the first weight loss of 7.75% in the range of 120–255°C for **2** and 10.83% in the range of 139–212°C for **3** are equivalent to the elimination of the coordinated water and lattice water molecules (calcd.: 7.40% for **2**, 11.23% for **3**). The second weight loss was observed in the range of 260–450°C for **2** and 220–360°C for **3**, corresponding to the decomposition of organic ligands. The remaining residue corresponds to the formation of CdO (obsd.: 22.85%, calcd.: 23.09% for **2**; obsd.: 27.19%, calcd.: 26.71% for **3**).

3.6 Electrochemical behavior of **1**-CPE

Recently, the redox properties of the copper(II) coordination compounds are found to be attractive for the application in electrochemical materials.^{24,39} The insolubility of the copper(II) compound **1** in water and common solvents illustrates that the bulk-modified carbon paste electrode (CPE) is the optimal selection for studying its electrochemical property. Compared with other modified film electrodes, the three-dimensional bulk-modified CPE shows high stability. This electrode can be renewed by squeezing a little carbon paste out glass tube and a fresh surface is exposed whenever needed, which is especially useful in practical applications. The electrochemical behavior of **1** bulk-modified carbon paste electrode (**1**-CPE) was studied in 0.1 M H₂SO₄ + 0.05 M Na₂SO₄ aqueous solution. Figure 5 shows the cyclic voltammograms of the **1**-CPE at different scan rates. It can be seen that there is a reversible redox peak at the **1**-CPE in the potential range of 500

Figure 5. Cyclic voltammograms of **1**-CPE in 0.1 M H₂SO₄ + 0.05 M Na₂SO₄ aqueous solution at different scan rates (from inner to outer) of 20, 50, 80, 100, 120, 140, 160, and 180 mVs⁻¹. The inset shows the plots of the anodic and the cathodic peak currents vs. scan rates.

to -45 mV and its mean peak potential $E_{1/2} = (E_{pa} + E_{pc})/2$ was -20 mV (scan rate: 100 mV s⁻¹), which should be attributed to the redox of Cu(II)/Cu(I).^{40,41} The effect of scan rates on the electrochemical behavior of the **1**-CPE can be observed in figure 5. When the scan rates vary from 20 to 180 mVs⁻¹, the peak potentials change gradually: the cathodic peak potentials shifted to negative direction and the corresponding anodic peak potentials shifted to positive direction with increasing scan rate. As shown in inset of figure 5 the anodic and the cathodic peak currents were proportional to the scan rates, indicating that the redox process for **1**-CPE was a surface-controlled process. The electrochemical behavior of **1**-CPE is similar to those of other Cu(II) compounds bulk-modified CPEs.^{42,43} The differences of peak potential for these Cu(II) compounds based-CPEs may be attributed to the different coordination environments of copper(II) ions, various organic ligands and diverse coordination frameworks of copper compounds.²⁴

3.7 Fluorescent properties of compounds **1–3**

In order to study the fluorescent properties and potential applications of the title complexes, we have measured the emission spectra of compounds **1–3** and the free ligands 3-bpcb and 3-bpsa in the solid state at room temperature. As shown in the insert of figure 6, the free 3-bpcb and 3-bpsa ligands display emission at 446 nm and 400 nm ($\lambda_{ex} = 300$ nm), respectively, which may be attributed to the π - π^* transitions.^{44,45} For compounds

Figure 6. (a) The fluorescent emission spectra of compounds **1–2** (The inset shows the fluorescent spectra of the free ligand 3-bpcb); (b) The fluorescent emission spectrum of compound **3** (The inset is the fluorescent emission of the free ligand 3-bpsa).

1 and **2**, the intense fluorescent emissions are observed at 439 nm for **1** and 449 nm for **2** (figure 6a), respectively. Compared with the 3-bpcb, compound **1** is blue-shifted with 7 nm, while the compound **2** is red shifted by 3 nm. For **3**, the emission peak can be seen at 386 nm (figure 6b). Compared to the free ligand 3-bpsa, compound **3** is blue-shifted by 14 nm. The blue-shift (for **1** and **3**) or red-shift (for **2**) phenomena in the emission spectra may be attributed to ligand-centered electronic transition or metal-to-ligand charge transfer transition, which is similar to the reported d^{10} metal complexes

Figure 7. Absorption spectra of the MB solution during the decomposition reaction under UV irradiation with the presence of compounds **1–3**.

with N-donor ligands.^{46–48} The differences in fluorescence behaviors for compounds **1–3** are probably caused by the various N-donor ligands, different metal ions

and their coordination environments as well as the final coordination frameworks.

3.8 Photocatalytic properties of compounds 1–3

Recently, coordination polymers as photocatalysts have attracted much attention due to their potential applications in purifying waste streams under UV irradiation by decomposing organic dyes.^{49–51} In this work, methylene blue (MB) is selected as a model pollutant in aqueous media to evaluate the photocatalytic effectiveness of the compounds 1–3. The photodecomposition experiments of MB have been investigated through a typical process: 60 mg powder of compounds 1–3 was mixed with 90 mL MB aqueous solution (10.0 mg L⁻¹), and stirred for 30 min in the dark. Then the solution was exposed to UV irradiation and kept stirring. Each sample (5.0 mL) was taken out for analysis every 30 min. It can be found that the absorption peaks of MB decrease gradually as time goes by (figure 7). Additionally, the concentration of MB solution vs reaction time (*t*) of compounds 1–3 was plotted. As depicted in figure S3, it can be observed that the photocatalytic activities increased from 9% (without any catalyst) to about 87% for 1, 67% for 2 and 45% for 3 after UV irradiation for a duration of 210 min. These experimental results indicate that compounds 1–3 possess good photocatalytic activities for the degradation of MB under UV irradiation, which may be used as potential candidates as photocatalysts for the reduction of some organic dyes.

4. Conclusions

In summary, three new metalorganic coordination compounds derived from the semi-rigid/flexible bis-pyridyl-bis-amide ligands (3-bpcb and 3-bpsa) and the aromatic dicarboxylate 5-H₂ AIP have been hydrothermally synthesized. Three compounds show diverse layer structures with two kinds of topologies: (6³)(6⁵·8) topology for 1 and 2, {6².10{6} topology for 3. The bis-pyridyl-bis-amide ligands with different flexibility show great effect on the structures of title compounds. Moreover, the electrochemical behavior of compound 1 and fluorescent properties of the title compounds may make them potential candidates as electrochemical and fluorescent materials. Further studies on synthesis of other metal-organic complexes with this semi-rigid/flexible bis-pyridyl-bis-amide ligand and its analogues are underway in our laboratory.

Supplementary Information

Crystallographic data for the structures reported in the paper have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers CCDC 949958 for 1, 949959 for 2 and 1024049 for 3. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The tables of selected bond lengths and angles, the related hydrogen bonding geometries of compounds 1–3, as well as additional figures are available at www.ias.ac.in/chemsci.

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