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# Three new two-dimensional metal-organic coordination polymers derived from bis(pyridinecarboxamide)-1,4-benzene ligands and 1,3-benzenedicarboxylate: Syntheses and electrochemical property

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#### ABSTRACT

Three new metal-organic coordination polymers,  $[Co(3-bpcb)(1,3-BDC)] \cdot H_2O$  (1),  $[Co(4-bpcb)(1,3-BDC)] \cdot H_2O$  (2) and  $[Cu(4-bpcb)(1,3-BDC)]_2 \cdot 0.5(4-bpcb)$  (3), have been hydrothermally synthesized using *N*,*N'*-bis(3-pyridinecarboxamide)-1,4-benzene (3-bpcb) or *N*,*N'*-bis(4-pyridinecarboxamide)-1,4-benzene (4-bpcb) and 1,3-benzenedicarboxylate (1,3-H\_2BDC) mixed ligands and characterized by elemental analyses, IR, TG, XRPD and single-crystal X-ray diffraction. Complexes 1–2 exhibit the similar two-dimensional (2D) network with different undulation degrees and dimensions, owing to different N positions from the 3-bpcb and 4-bpcb ligands. 1,3-BDC ligand in complexes 1 and 2 shows two coordination modes. The adjacent 2D layers for 1–2 are further linked by hydrogen bonding interactions to form a three-dimensional (3D) supramolecular network. Complex 3 possesses infinite 3-fold interpenetrating 2D network composed of three kinds of Cu-4-bpcb one-dimensional (1D) chains and 1,3-BDC ligands, in which 1,3-BDC only shows one coordination mode. The 2D network is further extended into 3D supramolecular framework by hydrogen bonding interactions. The non-coordinated 4-bpcb ligands existing in the 2D network connect with adjacent 2D layers through the hydrogen bonding interactions. In addition, the electrochemical behaviors and the fluorescence property of complexes 1–3 have been reported.

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#### 1. Introduction

Remarkable progress has been achieved in the research of metal-organic coordination polymers in recent years, not only because of their fascinating structural diversities and framework topologies, but also due to their potential applications in the fields of catalysis, luminescence, gas adsorption, nonlinear optics (NLO) and magnetic materials [1–4]. The rational design and construction of these metal-organic coordination polymers mainly depend on proper choice of the transition metal ions and the judicious selection of the multifunctional ligands [5]. It is known that aromatic polycarboxylate ligands as a kind of multifunctional ligands have attracted extensive attention, owing to their versatile coordination modes and structural features [6,7]. In particular, 1,3-benzenedicarboxylate (1,3-H<sub>2</sub>BDC) is one of the most successful polycarboxylate ligands with the characteristic of their angular bifunctionality [8] and appropriate connectivity [9–11] of two

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carboxyl groups. To the best of our knowledge, numerous excellent metal-organic coordination polymers based on  $1,3-H_2BDC$  ligand have been reported [12-14].

On the other hand, the organic N-containing ligands, particularly long multipyridyl organic bridging ligands, play an important role in the formation of high-dimensional metal-organic coordination polymers [15,16]. As reported previously, the long and symmetrical bipyridyl organic ligands N,N'-bis(4-pyridinecarboxamide)-1,4-benzene (4-bpcb) and N,N'-bis(3-pyridinecarboxamide)-1,4-benzene (3-bpcb) are efficient and versatile organic ligands for the construction of abundant and novel polymer architectures, and the structure with undulated layers have been obtained [17,18]. The ligands 4-bpcb and 3-bpcb are chosen to construct novel metal-organic coordination polymers in view of their following characteristics: first, as the bifunctional ligands, the antioxidation (stability) of 4-bpcb and 3-bpcb are improved; second, the larger conjugated systems can be obtained through the coordination of the lone pair from the bipyridyl N atoms with metal atoms, which may increase flexibility of the electron cloud [19]; third, **4-bpcb** and **3-bpcb** with the excellent coordination ability and their long spacers may tend to form high-dimensional

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framework. However, the examples that employ the **4-bpcb** or **3-bpcb** ligand and aromatic polycarboxylate ligands with rigid backbones to generate high-dimensional framework are limited [20]. Therefore, it is well worth studying the metal-organic coordination polymers based on **4-bpcb** or **3-bpcb** and aromatic polycarboxylate ligands.

On the basis of the aforementioned points, we choose the long and symmetrical bipyridyl organic ligands **4-bpcb** and **3-bpcb** (Scheme 1), 1,3-H<sub>2</sub>BDC and metal salts (Co<sup>II</sup> and Cu<sup>II</sup>) as reactants, and fortunately obtain three new two-dimensional (2D) metalorganic coordination polymers, namely [Co(3-bpcb)(1,3-BDC)]. H<sub>2</sub>O (**1**),  $[Co(4-bpcb)(1,3-BDC)] \cdot 2H_2O$  (**2**) and  $[Cu(4-bpcb)(1,3-BDC)]_2 \cdot 0.5(4-bpcb)$  (**3**). Moreover, the electrochemical behaviors and the fluorescence property of the three complexes are investigated.

#### 2. Results and discussion

#### 2.1. Description of crystal structures

X-ray diffraction analysis reveals that complex **1** is an undulated 2D layer coordination polymer constructed from **3-bpcb** and 1,3-BDC ligands. The coordination environment of Co<sup>II</sup> atom is shown in Fig. 1. The Co<sup>II</sup> atom is six-coordinated by two nitrogen atoms belonging to two **3-bpcb** ligands [the distances: Co(1)–N(1) 2.1459 (17) Å, Co(1)–N(2) 2.1548(17) Å], four oxygen atoms from three 1,3-BDC anions [the distances: Co(1)–O(1) 2.0370(15) Å, Co(1)–O (2) 2.0479(17) Å, Co(1)–O(3) 2.1522(16) Å, Co(1)–O(14) 2.2831 (17) Å], showing a distorted octahedron geometry. The **3-bpcb** ligand assumes one coordination mode (Scheme 1a), namely, bridging bidentate mode. The dihedral angle between the two pyridyl rings of **3-bpcb** ligands connect the adjacent Co<sup>II</sup> atoms to build one-dimensional (1D) zigzag chain (Fig. S1). Two



Scheme 1. Coordination modes of **3-bpcb**, **4-bpcb** and 1,3-BDC ligands in complexes 1–3.



Fig. 1. The coordination environment of Co<sup>II</sup> in complex 1.

carboxyls of 1,3-BDC anion show two different coordination modes: one is bidentate bridging coordination, the other is chelating coordination (Scheme 1d). The 1,3-BDC ligands link Co<sup>II</sup> atoms by two coordination modes to form another 1D ladder-like chain, as shown in Fig. S2. The alternate connection of the two types of 1D chain constructs a 2D sheet, as shown in Fig. 2 and Fig. S3. Each metal Co<sup>II</sup> atom links two **3-bpcb** and three 1,3-BDC ligands, which can be defined as a 5-connected node. Each 1,3-BDC links three metal Co<sup>II</sup> atoms, which suggest a 3-connected node. The **3-bpcb** ligating with two 5-connected Co<sup>II</sup> atoms serves as a bridging ligand. Thus the 2D structure is best described as a (3, 5)-connected network, as shown in Fig. 2.

These 2D sheets are further extended to a three-dimensional (3D) supramolecular network by hydrogen bonding interactions. Some C-H···O hydrogen bonding interactions are observed in Fig. 3. The intermolecular C-H···O hydrogen bonds are formed by the carbon atoms C(3), C(16) and the oxygen atoms O(5), O(6) of **3-bpcb** ligands, the carbon atom C(5) of **3-bpcb** and the oxygen atom O(14) of 1,3-BDC ligand. The observed distances are 3.120 (3) Å, 3.149(3) Å and 3.177(3) Å for C(3)-H(3A)···O(5), C(16)-H (16A)···O(6) and C(5)-H(5A)···O(14), respectively.

Single crystal X-ray diffraction reveals that the structure of 2 is also a 2D layer network, which is similar to that of complex 1 except for small undulation. The building unit of complex 2 contains one Co<sup>ll</sup> atom, one organic ligand **4-bpcb**, one 1,3-BDC ligand and two lattice water molecules. As shown in Fig. 4. each center Co<sup>II</sup> atom shows hex-coordination environment containing two nitrogen atoms from two 4-bpcb ligands and four oxygen atoms from three 1,3-BDC ligands with Co(1)-N(3), Co(1)-N(4), Co(1)-O(1), Co(1)-O(2) and Co(1)–O(3), Co(1)–O(4) bond distances of 2.1618(19) Å, 2.1664(19) Å, 2.0018(16) Å, 2.0256(15) Å, 2.1117(16) Å and 2.3006 (17) Å, respectively. The **4-bpcb** ligand in complex **2** displays bidentate coordination mode (Scheme 1b). Two nitrogen atoms of **4-bpcb** bridge two Co<sup>II</sup> atoms to form a 1D chain (Fig. S4). The two pyridyl rings of **4-bpcb** ligand in complex **2** are not coplanar with the dihedral angle of 16.73°. Two carboxyls of 1,3-BDC exhibit different coordination modes which are similar to those in complex **1** (Scheme 1d). One carboxyl bridges Co<sup>II</sup> atoms (Co1 and Co1A), the other carboxyl chelates Co<sup>II</sup> atoms, forming double track 1D ladderlike chains, which is similar to complex 1. The 2D layer network is constructed by the 4-bpcb and 1,3-BDC ligands (Fig. 5). The 2D structure in complex 2 is also a (3, 5)-connected network due to the same connected nodes of each metal Co<sup>II</sup> atom and each 1,3-BDC ligand. Compared with complex 1, the 2D layer structure of



Fig. 2. Stick and simplified representations of 2D coordination layer in complex 1.



Fig. 3. The 3D supramolecular network by hydrogen bonding interactions in complex 1.

complex **2** is almost flat without undulation, which is mainly due to the difference of coordination sites between **4-bpcb** and **3-bpcb** ligands.

Just as observed in Fig. 6, these neighboring layers are further extended into a 3D supramolecular network through hydrogen bonds among the lattice water molecules, **4-bpcb** ligands, and 1,3-

BDC anions. That is, lattice water molecules O(1W) serve as Hdonor and interact with the oxygen atoms O(5), O(6) of **4-bpcb** ligands via hydrogen bonds  $[O(1W)-H(1W)\cdots O(5) 2.829(4) Å$ ,  $O(1W)-H(2W)\cdots O(6) 2.979(5) Å]$ . The N(1), N(2), C(12) from **4-bpcb** ligands and oxygen atoms O(1W), O(4) from lattice water molecules and 1,3-BDC are involved in the formation of N–H···O and C–H···O hydrogen bonds. The distances of N(1)–H(1)···O(1W), N (2)–H(2)···O(4), and C(12)–H(12)···O(4) are 2.886(5) Å, 2.952(3) Å, and 3.178(4) Å, respectively.

X-ray crystallography shows that complex **3** is 3-fold interpenetrating 2D layer coordination polymer constructed from Cu<sup>II</sup> atoms, **4-bpcb** and 1,3-BDC ligands, and further extended into a 3D supramolecular framework by hydrogen bonding interactions. Meanwhile, the non-coordinated **4-bpcb** ligands also exist in the 3D supramolecular framework. The coordination environment of Cu<sup>II</sup> atom is shown in Fig. 7, three crystallographically independent Cu<sup>II</sup> atoms [Cu(1), Cu(2) and Cu(3)] are all bridged by two nitrogen atoms from two **4-bpcb** ligands [Cu(1)–N(3) 2.007(3) Å, Cu(1)–N (4) 2.015(3) Å, Cu(2)–N(7) 2.012(3) Å, Cu(2)–N(7A) 2.012(3) Å, Cu (3)–N(1) 2.023(3) Å, Cu(3)–N(1A) 2.023(3) Å], chelated by four oxygen atoms from two 1,3-BDC ligands, showing an octahedron geometry.

In complex **3**, three different 1D chains are built from three crystallographically independent Cu<sup>II</sup> atoms and **4-bpcb** ligands. These three kinds of 1D chains are of alternating emergence (-Cu1-**4-bpcb**-, -Cu2-**4-bpcb**-, -Cu1-**4-bpcb**-, -Cu3-**4-bpcb**-) (Fig. 8a). Although the ligand **4-bpcb** shows only one coordination



Fig. 4. The coordination environment of Co<sup>II</sup> in complex 2.



Fig. 5. Stick and simplified representations of the 2D structure in complex 2.



Fig. 6. The 3D supramolecular network by hydrogen bonding interactions in complex 2.



Fig. 7. The coordination environment of  $Cu^{II}$  in complex 3.



Fig. 8. (a) The 1D chain structure based on Cu<sup>II</sup> and 4-bpcb ligand in complex 3. (b) The 1D chain structure based on Cu<sup>II</sup> and 1,3-BDC ligand in complex 3.

mode: bidentate (Scheme 1c), the dihedral angles of the two pyridyl rings of **4-bpcb** belonging to different 1D chain are distinct. In the two chains of -Cu2-**4-bpcb**- and -Cu3-**4-bpcb**-, the two pyridyl rings of **4-bpcb** ligands are coplanar, whereas the two pyridyl rings of **4-bpcb** ligand in the -Cu1-**4-bpcb**- chain are not coplanar with the dihedral angle of 4.40°. In addition, the -Cu2-4**bpcb**– and –Cu3–**4-bpcb**– chains are parallel. Compared with complexes 1 and 2, 1,3-BDC in complex 3 only shows one coordination mode, and two carboxyl groups of 1,3-BDC chelate two Cu<sup>ll</sup> atoms, respectively (Scheme 1e). The 1,3-BDC ligands link Cu<sup>ll</sup> atoms to form a 1D zigzag chain with Cu1…Cu2, Cu1…Cu3 distance of 9.281 Å, 9.235 Å, respectively (Fig. 8b). Two types of 1D chains comprised of Cu<sup>II</sup> atoms and different ligands (**4-bpcb** or 1,3-BDC) are linked by each other to form an undulated 2D layer network (Fig. 9 and Fig. S5). Each metal Cu<sup>II</sup> atom linked by two **4-bpcb** ligands and two 1,3-BDC ligands can imply a 4-connected node. The **4-bpcb** ligating with two 4-connected Cu<sup>II</sup> atoms serves as a bridging ligand. Complex **3** adopts 3-fold interpenetrating 4-connected  $4^{4}6^{2}$  topology (Fig. 10).

Fig. 11 shows that a 3D supramolecular framework is generated via interlayer hydrogen bonding interactions. Non-coordinated ligands **4-bpcb** connect adjacent layers through the hydrogen bonding interactions with N(9)–H(9A)···O(11) distance of 3.035 (6) Å. The nitrogen atoms N(2), N(5), N(6), and N(10) from **4-bpcb** ligands link the oxygen atoms O(8), O(5), O(2), and O(4) from 1,3-BDC anions by way of N–H···O hydrogen bond, respectively. The separations of N(2)–H(2A)···O(4) are 3.179(5) Å, 2.870(5) Å, 2.981(5) Å, and 2.980(5) Å, respectively. In addition, the oxygen atoms O(2), O(5), and O(8) from 1,3-BDC ligands and carbon atoms C(30), C(40), and C(23) from the **4-bpcb** ligands are involved in the formation of C–H···O hydrogen bonds [distance: C(30)–H(23)···O(2) 3.235(6) Å, C(40)–H(40)···O(5) 3.172(5) Å, C(23)–H(23)···O(8) 3.313(6) Å].



Fig. 9. Stick and simplified representations of the 2D structure in complex 3.



Fig. 10. Schematic perspective of  $4^{4}6^{2}$  3-fold interpenetrating network of complex 3.

Both complexes **1** and **2** are based on metal cobalt atoms, 1,3-BDC anion and isomeric *N,N'*-bis(pyridinecarboxamide)-1,4benzene ligands with different N positions of the two pyridyl rings (position 3 for **1** and 4 for **2**), which result in not only the change of the undulation degree of 2D layer network, but also the distinction of dimensions of the 2D grids (16.201 × 7.560 Å for **1** and 19.997 × 4.195 Å for **2**). For **2** and **3**, Co<sup>II</sup> and Cu<sup>II</sup> complexes based on the same **4-bpcb** and 1,3-BDC ligands show distinct 2D crystal structures, which can be attributed to different valence shell electron configurations of different metal atoms [21]. Complex **2** shows a 2D layer network comprised of a kind of Co–**4-bpcb** 1D chain and 1,3-BDC ligand with two coordinate modes, however, complex **3** exhibits 3-fold interpenetrating 2D network comprised of three kinds of Cu–**4-bpcb** 1D chains and 1,3-BDC ligands with only one coordinate mode.

#### 2.2. IR spectra of complexes 1-3

The main features of IR spectra for complexes **1–3** concern the carboxylate groups of 1,3-BDC and the **3-bpcb** or **4-bpcb** ligand (Figs. S6–8). No strong absorption peaks around 1700 cm<sup>-1</sup> for –COOH are observed, which implies that carboxyl groups of organic moieties in the title complexes are completely deprotonated [22,23]. The strong peaks at 1677, 1617, and 1384 cm<sup>-1</sup> for **1**, 1646, 1613, and 1393 cm<sup>-1</sup> for **2**, and 1665, 1614, and 1368 cm<sup>-1</sup> for **3** may be attributed to the asymmetric and symmetric vibrations of carboxylate groups. The presence of the expected characteristic bands at 1564, 1504, 1105, and 712 cm<sup>-1</sup> for **1**, 1567, 1496, 1093, and 735 cm<sup>-1</sup> for **2**, and 1561, 1515, 1063, and 732 cm<sup>-1</sup> for **3**, suggest the  $\nu_{C-N}$  stretching of the pyridyl ring of the **3-bpcb** or **4-bpcb** ligand.

## 2.3. X-ray powder diffraction and thermogravimetric analyses of title complexes

The X-ray powder diffraction (XRPD) patterns for complexes **1–3** are presented in Figs. S9–11, respectively. The as-synthesized

patterns are in good agreement with the corresponding simulated ones, indicating the phase purities of the samples.

Thermogravimetric (TG) analyses are performed to estimate the thermal stability of complexes 1–3 as shown in Figs. S12–14. The TG curves of complexes 1-2 show two weight loss steps in the temperature range of 30–750 °C, while the TG curve of complex **3** exhibits only one weight loss stage between 20 °C and 750 °C. For complexes 1-2, the first weight loss stages start at 80 °C up to 120 °C for 1, 75 °C up to 145 °C for 2, giving the weight loss of about 3.34% for 1, 6.43% for 2, corresponding to the loss of the lattice water molecules (calcd. 3.22% for 1, 6.23% for 2). The second weight loss occurring from 320 °C to 485 °C for 1, from 270 °C to 470 °C for 2, may suggest the decomposition of 3-bpcb or 4-bpcb and 1,3-BDC molecules. The weight losses are about 83.32% for 1. 80.71% for 2. in correspondence with the calculated value of 83.38% for **1**, 80.79% for **2**. The remaining weights (13.34% for **1**, 12.86% for **2**) correspond to the percentage (13.40% for 1, 12.98% for 2) of Co and O components in CoO. In comparison with 1 and 2, the weight loss of complex 3 begins at 275 °C and completes by 450 °C with only one weight loss of 87.13% (calcd. 87.21%), indicating complete decomposition of 4-bpcb and 1,3-BDC molecules to form CuO as a final product. The percent of the residue is about 12.87%, which is in accordance with the expected value 12.79%.

#### 2.4. Fluorescence property of complexes 1-3

The fluorescence property of complexes **1–3** and the free ligands (**3-bpcb** and **4-bpcb**) have been studied at room temperature in the solid state (Figs. S15 and S16). The free ligand **3-bpcb** exhibits the emission peak at 450 nm with the excitation at 310 nm. For **1**, upon excitation at 320 nm, it shows strong peak with the emission at 436 nm, which is blue-shifted relative to that of the free ligand **3-bpcb**. The emission spectrum for the free **4-bpcb** ligand reveals a main peak at 470 nm with  $\lambda_{ex} = 310$  nm. The fluorescence peaks at about 452 nm and 469 nm are found in the emission spectra of **2** and **3** when they are excited at 310 nm and 300 nm,



Fig. 11. The 3D supramolecular framework by hydrogen bonding interactions in complex 3.



Fig. 12. Cyclic voltammograms of 1-CPE (+700 to +350 mV), 2-CPE (+800 to 0 mV), 3-CPE (+800 to 0 mV) in 1 M H<sub>2</sub>SO<sub>4</sub> solution for complexes 1–3. Scan rate: 100 mVs<sup>-1</sup>.

respectively. The blue-shifted emission occurs in the complex **2** while complex **3** has no significant change. It may be attributed to the coordination environments of different metal atoms.

## 2.5. Electrochemical behaviors of complexes **1–3** modified carbon paste electrode (1-CPE, 2-CPE, and 3-CPE)

Complexes **1**–**3** are all insoluble in water and common organic solvents. Thus, the complexes **1**–**3** bulk-modified carbon paste electrodes (**1**-CPE, **2**-CPE, **3**-CPE) are fabricated as the working electrodes [24,25], which become the optimal choice to study the electrochemical property of these complexes [26]. The cyclic voltammograms of the **1**-CPE to **3**-CPE in 1 M H<sub>2</sub>SO<sub>4</sub> solution are recorded in Fig. 12. It can be seen clearly that in the potential range of +700 to

+350 mV and +800 to 0 mV, a reversible redox peak is observed at the **1**-CPE and **2**-CPE, respectively, which could be attributed to the redox of Co<sup>II</sup>/Co<sup>I</sup> [27]. The mean peak potentials  $E_{1/2} = (E_{pa} + E_{pc})/2$  are +509 mV (100 mVs<sup>-1</sup>) for **1**-CPE and +510 mV (100 mVs<sup>-1</sup>) for **2**-CPE. In the potential range of +800 to 0 mV, a reversible redox peak attributed to the redox of Cu<sup>II</sup>/Cu<sup>I</sup> is observed at the **3**-CPE [28–30], the mean peak potential  $E_{1/2} = (E_{pa} + E_{pc})/2$  are +494 mV (100 mVs<sup>-1</sup>) for **3**-CPE.

Scan rates effect on the electrochemical behavior of the **3**-CPE is investigated in the potential range of +800 to 0 mV in 1 M  $H_2SO_4$  solution. As shown in Fig. 13, with the scan rates increasing from 40 to 300 mVs<sup>-1</sup>, the peak potentials changed gradually: the cathodic peak potentials gradually shift to the negative direction and the corresponding anodic peak potentials shifted to the positive direction. The inset of Fig. 13 shows that the peak currents are



**Fig. 13.** Cyclic voltammograms of the **3**-CPE in 1 M  $H_2SO_4$  solution at different scan rates (from inner to outer: 40, 60, 80, 100, 120, 140, 160, 180, 200, 250, 300 mVs<sup>-1</sup>). The inset shows the plots of the anodic and cathodic peak currents against scan rates.



Fig. 14. Cyclic voltammograms of the bare CPE in 1 M H<sub>2</sub>SO<sub>4</sub> solution containing 1.0 mmol/L KNO<sub>2</sub> (a), 3-CPE in 1 M H<sub>2</sub>SO<sub>4</sub> solution containing (b~d): 0.0, 2.0 and 4.0 mmol/L KNO<sub>2</sub>. Scan rate: 120 mVs<sup>-1</sup>.

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Crystal data and structure refinements for complexes 1-3.

	1	2	3
Empirical formula	C26H20C0N4O7	C26H22C0N4O8	C <sub>61</sub> H <sub>43</sub> Cu <sub>2</sub> N <sub>10</sub> O <sub>13</sub>
Formula weight	559.36	577.39	1251.15
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P1	P1	P1
<i>a</i> (Å)	8.601(5)	10.067(1)	12.400(2)
b(Å)	10.064(5)	10.4787(11)	13.722(2)
<i>c</i> (Å)	13.771(5)	14.271(2)	17.556(3)
$\alpha(^{\circ})$	98.444(5)	106.793(2)	77.925(2)
β(°)	98.080(5)	104.070(2)	80.552(2)
$\gamma(^{\circ})$	99.451(5)	104.935(1)	73.759(2)
<i>V</i> (Å <sup>3</sup> )	1146.4(10)	1307.9(3)	2786.7(8)
Ζ	2	2	2
$D_{\text{calc}}(\text{g cm}^{-3})$	1.609	1.461	1.491
$\mu(mm^{-1})$	0.807	0.713	0.840
F(000)	566	590	1282
Minimum/maximum trans	0.856/0.886	0.814/0.892	0.777/0.860
Total reflections	9077	6637	28,420
Unique reflections	4018	4521	13,544
R <sub>int</sub>	0.0126	0.0164	0.0944
GOF	1.049	0.994	0.974
$R_1(I > 2\sigma(I))$	0.0286	0.0370	0.0660
$wR_2(I > 2\sigma(I))$	0.0805	0.1157	0.0714
$\Delta \rho_{\rm max}({\rm e~\AA^{-3}})$	0.701	0.470	0.580
$\Delta \rho_{\min}(e \ \text{\AA}^{-3})$	-0.357	-0.398	-0.489

 $R_1 = \sum |F_0| - |F_c| / \sum |F_0|, wR_2 = \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]^{1/2}.$ 

proportional to the scan rates up to 300 mVs<sup>-1</sup>, suggesting that the redox process for **3**-CPE is surface-controlled.

Fig. 14 shows cyclic voltammograms for the electrocatalytic reduction of nitrite at a bare CPE and the **3**-CPE in 1 M  $H_2SO_4$  solution. There is no redox peak at the bare CPE at the presence of nitrite in the potential range of +800 to 0 mV. With the addition of nitrite, the reduction peak currents increase markedly while the corresponding oxidation peak currents decrease markedly at the **3**-CPE. The results indicate that **3**-CPE possesses good electrocatalytic activity toward the reduction of nitrite.

#### 3. Conclusions

In summary, we have successfully synthesized three new metalorganic coordination polymers, [Co(**3-bpcb**)(1,3-BDC)]·H<sub>2</sub>O (**1**), [Co  $(4-bpcb)(1,3-BDC)] \cdot 2H_2O$  (2) and  $[Cu(4-bpcb)(1,3-BDC)]_2 \cdot 0.5(4-bpcb)(1,3-BDC)]_2 \cdot 0.5(4$ bpcb) (3), which based on mixed 3-bpcb or 4-bpcb and 1,3-BDC ligands. Complexes 1–3 all exhibit 2D layer structures and are ultimately extended into 3D supramolecular framework by hydrogen bonding interactions. The different N positions of the two pyridyl rings have influence on dimensions and undulation degree of 2D networks for complexes 1–2. The selection of different metal atoms plays an important in changing the structures of complexes 2–3. Complex 2 contains a kind of Co-4-bpcb 1D chain and 1,3-BDC ligand, while complex 3 with 3-fold interpenetrating network consists of three kinds of Cu-4-bpcb 1D chains and 1,3-BDC ligands. In addition, the non-coordinated 4-bpcb ligands in complex 3 consolidate the 3D supramolecular framework by hydrogen bonding interactions. Electrochemical and fluorescent properties of complexes 1–3 reveal that the three complexes may possess potential applications in the field of electrochemistry and fluorescence.

#### 4. Experimental

#### 4.1. Materials and measurements

All chemicals were purchased from commercial sources and used without further purification. The ligands **4-bpcb** and **3-bpcb** were synthesized by the literature methods [31]. Elemental

analyses (C, H, N) were performed on a Perkin–Elmer 240C element analyzer. FT-IR spectra (KBr pellets) were obtained on a Magna FT-IR 560 spectrometer. Thermogravimetric data for the complexes **1–3** were carried out on a Pyris Diamond thermal analyzer. Fluorescence spectra were recorded at room temperature on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer. X-ray powder diffraction investigations were carried out on a Bruker AXS D8-Advanced diffractometer with Cu-K $\alpha$  ( $\lambda$  = 1.5406 Å) radiation in the 2 $\theta$  range of 5–50°. A CHI 440 electrochemical workstation connected to a Digital-586 personal computer was used for control of the electrochemical measurements and for data collection. A conventional three-electrode system was used with an SCE as reference electrode, a platinum wire as auxiliary electrode and the modified electrode as the working electrode, respectively.

#### 4.2. Preparation

#### 4.2.1. Synthesis of [Co(3-bpcb)(1,3-BDC)] · H<sub>2</sub>O (**1**)

A mixture of CoCl<sub>2</sub>·2H<sub>2</sub>O (0.035 g, 0.20 mmol), **3-bpcb** (0.032 g, 0.10 mmol), 1,3-H<sub>2</sub>BDC (0.033 g, 0.20 mmol), H<sub>2</sub>O (12 mL) and NaOH (0.017 g, 0.43 mmol) was stirred for 30 min at room temperature and then transferred to a 25 mL Teflon-lined autoclave and kept at 120 °C for 4 days. After slow cooling to room temperature, orange red block crystals of **1** were obtained (yield: ca. 34% based on Co). *Anal.* Calc. for C<sub>26</sub>H<sub>20</sub>CoN<sub>4</sub>O<sub>7</sub>: C 55.78, H 3.58, N 10.01. Found: C 55.81, H 3.54, N 10.03%. IR (KBr, cm<sup>-1</sup>): 3407(w), 3261(w), 3148(w), 3081(w), 2342(m), 1677(s), 1617(s), 1564(s), 1504(s), 1471 (s), 1384(s), 1311(m), 1278(w), 1218(m), 1105(m), 1051(w), 1019(w), 972(w), 912(w), 872(w), 826(m), 712(s), 633(m), 565(w).

#### 4.2.2. Synthesis of [Co(4-bpcb)(1,3-BDC)]·2H<sub>2</sub>O (2)

The synthesis method of **2** is similar to that of **1** except for ligand **4-bpcb** as the substitute of **3-bpcb**, and the different amount of NaOH (0.019 g, 0.47 mmol) was added to adjust the systematic pH (yield: ca. 31% based on Co). *Anal.* Calc. for  $C_{26}H_{22}CoN_4O_8$ : C 54.04, H 3.81, N 9.70. Found: C 54.08, H 3.77, N 9.67%. IR (KBr, cm<sup>-1</sup>): 3446 (w), 3316(w), 3063(w), 2347(w), 2316(w), 1646(s), 1613(s), 1567(s), 1496(s), 1451(m), 1393(s), 1314(s), 1276(m), 1217(m), 1171(w), 1093 (m), 1054(m), 1003(m), 917(w), 904(w), 840(s), 735(s), 671(s), 618 (w).

#### 4.2.3. Synthesis of [Cu(4-bpcb)(1,3-BDC)]<sub>2</sub>.0.5(4-bpcb) (**3**)

A mixture of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.045 g, 0.26 mmol), **4-bpcb** (0.060 g, 0.19 mmol), 1,3-H<sub>2</sub>BDC (0.033 g, 0.20 mmol), H<sub>2</sub>O (12 mL) and NaOH (0.018 g, 0.45 mmol) was stirred for 30 min at room temperature and then transferred to a 25 mL Teflon-lined autoclave and kept at 120 °C for 4 days. After slow cooling to room temperature, purple block crystals of **3** were obtained (yield: ca. 27% based on Cu). *Anal.* Calc. for C<sub>61</sub>H<sub>43</sub>Cu<sub>2</sub>N<sub>10</sub>O<sub>13</sub>: C 58.51, H 3.44, N 11.19. Found: C 58.47, H 3.46, N 11.22%. IR (KBr, cm<sup>-1</sup>): 3506(w), 3377(w), 3313(w), 3145(w), 2372(w), 1665(s), 1614(s), 1561(s), 1515(s), 1484 (w), 1400(s), 1368(s), 1315(s), 1271(m), 1225(m), 1172(w), 1114(w), 1063(m), 953(w), 913(m), 836(m), 732(m), 674(m).

## 4.2.4. Preparation of complexes 1–3 bulk-modified carbon paste electrode

The **1**-CPE was fabricated as follows: 0.5 g graphite powder and 0.035 g complex **1** were mixed and ground together by agate mortar and pestle for about half an hour, and then 0.21 mL paraffin oil was added and stirred with a glass rod. The homogenized mixture was used to pack 3 mm inner diameter glass tubes to a length of 0.8 cm. The electrical contact was established with the copper stick, and the surface of the **1**-CPE was polished by weighing paper. In a similar manner, **2**-, and **3**-CPEs were made with complexes **2**–**3**.

#### 4.3. X-ray crystallography study

X-ray diffraction analyses data for complexes **1**–**3** were collected with a Bruker APEX diffractometer with Mo K $\alpha$  (graphite monochromator,  $\lambda = 0.71073$  Å). The structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [32,33]. For the complexes, all nonhydrogen atoms except the oxygen atom (O2W) of water molecule in complex **2** were refined anisotropically, the hydrogen atoms of the ligands **3-bpcb** and **4-bpcb** were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The crystal parameters, data collection, and refinement results for complexes **1**–**3** are summarized in Table 1. Selected bond distances and bond angles are listed in Table S1. Hydrogen bonding geometries are summarized in Table S2.

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#### Appendix A. Supplementary data

CCDC 787707, 786146 and 786147 contain the supplementary crystallographic data for the compounds **1–3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

#### Appendix. Supplementary data

Crystallographic data in CIF, IR spectra, TG curves and the tables with the selected bond lengths and bond angles can be found, in the online version at doi:10.1016/j.jorganchem.2010.12.009.

#### References

- [1] V.V. Adrabinska, Coord. Chem. Rev. 251 (2007) 1987-2016.
- [2] S.L. James, Chem. Soc. Rev. 32 (2003) 276–288.

- [3] J.A. Rood, W.C. Boggess, B.C. Noll, K.W. Henderson, J. Am. Chem. Soc. 129 (2007) 13675–13682.
- [4] C.Y. Li, C.S. Liu, J.R. Li, X.H. Bu, Cryst. Growth Des. 7 (2007) 286–295.
- [5] X.Q. Liang, X.H. Zhou, C. Chen, H.P. Xiao, Y.Z. Li, J.L. Zuo, X.Z. You, Cryst. Growth Des 9 (2009) 1041–1053.
- [6] R. Sun, Y.Z. Li, J.F. Bai, Y. Pan, Cryst. Growth Des 7 (2007) 890-894.
- [7] S. Wang, J.F. Bai, H. Xing, Y.Z. Li, Y. Song, Y. Pan, M.F. Scheer, X.Z. You, Cryst. Growth Des 7 (2007) 747–754.
- [8] J.J. Perry, G.J. McManus, M.J. Zaworotko, Chem. Commun. (2004) 2534-2535.
- [9] S.Y. Yang, L.S. Long, R.B. Huang, L.S. Zheng, Chem. Commun. (2002) 472–473.
  [10] B. Moulton, H. Abourahma, M.W. Bradner, J. Lu, G.J. McManus, M.J. Zaworotko, Chem. Commun. (2003) 1342–1343.
- [11] H. Abourahma, G.J. McManus, B. Moulton, R.D.B. Walsh, M.J. Zaworotko, Macromol. Symp. 196 (2003) 213–227.
- [12] Y.F. Zhou, Y.J. Zhao, D.F. Sun, J.B. Weng, R. Cao, M.C. Hong, Polyhedron 22 (2003) 1231–1235.
- [13] Y.F. Zhou, F.L. Jiang, D.Q. Yuan, B.L. Wu, R.H. Wang, Z.Z. Lin, M.C. Hong, Angew. Chem. Int. Ed. 43 (2004) 5665–5668.
- [14] Y.F. Zhou, D.Q. Yuan, F.L. Jiang, Y.Q. Xu, M.C. Hong, J. Mol. Struct. 796 (2006) 203–209.
- [15] L.K. Sposato, R.L. LaDuca, Polyhedron 29 (2010) 2239–2249.
- [16] D.P. Martin, R.M. Supkowski, R.L. LaDuca, Cryst. Growth Des 8 (2008) 3518-3520.
- [17] J. Pansanel, A. Jouaiti, S. Ferlay, M.W. Hosseini, J.M. Planeix, N. Kyritsakas, New J. Chem. 30 (2006) 71–76.
- [18] J. Pansanel, A. Jouaiti, S. Ferlay, M.W. Hosseini, J.M. Planeix, N. Kyritsakas, New J. Chem. 30 (2006) 683–688.
- [19] Y.Y. Niu, Y.L. Song, J. Wu, H.W. Hou, Y. Zhu, X. Wang, Inorg. Chem. Commun. 7 (2004) 471–474.
- [20] X.L. Wang, H.Y. Lin, B. Mu, A.X. Tian, G.C. Liu, Dalton Trans. 39 (2010) 6187–6189.
- [21] L. Carlucci, G. Ciani, D.M. Proserpio, S. Rizzato, CrystEngComm 5 (2003) 190-199.
- [22] X.J. Gu, D.F. Xue, Cryst. Growth Des 6 (2006) 2551–2557.
- [23] LJ. Bellamy, The Infrared Spectra of Complex Molecules. Wiley, New York, 1958.
- [24] T. Kuwana, W.G. French, Anal. Chem. 36 (1964) 241–242.
- [25] F.A. Schultz, T. Kuwana, J. Electroanal. Chem. 10 (1965) 95–103.
- [26] A.X. Tian, J. Ying, J. Peng, J.Q. Sha, H.J. Pang, P.P. Zhang, Y. Chen, M. Zhu, Z.M. Su, Cryst. Growth Des 8 (2008) 3717–3724.
- [27] T.V. Mitkina, N.F. Zakharchuk, D.Y. Naumov, O.A. Gerasko, D. Fenske, V.P. Fedin, Inorg. Chem. 47 (2008) 6748–6755.
- [28] G.G. Gao, L. Xu, W.J. Wang, W.J. An, Y.F. Qiu, Z.Q. Wang, E.B. Wang, J. Phys. Chem. B. 109 (2005) 8948–8953.
- [29] A. Salimi, V. Alizadeh, H. Hadadzadeh, Electroanalysis 16 (2004) 1984–1991.
  [30] B.K. Santra, P.A.N. Reddy, G. Neelakanta, S. Mahadevan, M. Nethajia,
- A.R. Chakravartya, J. Inorg. Biochem. 89 (2002) 191–196.
- [31] M. Sarkar, K. Biradha, Cryst. Growth Des 6 (2006) 202-208.
  [32] G.M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structure.
- University of Göttingen, Göttingen, Germany, 1997.[33] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structure. University of Göttingen, Göttingen, Germany, 1997.