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### Metal(II) coordination polymers based on a flexible *N*,*N*',*N*''-tris(3-pyridyl)-1,3,5-benzenetricarboxamide ligand and organic polycarboxylate ligands: Syntheses, structures, and luminescence

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#### ABSTRACT

Four metal(II) coordination polymers based on a flexible ligand N,N',N''-tris(3-pyridyl)-1,3,5-benzenetricarboxamide (L), namely,  $[Co(L^1)(L)]_n$  (1),  $\{[Cd(L^1)(L)] \cdot 0.5H_2O\}_n$  (2),  $\{[Zn_{1.5}(L^2)(L)(H_2O)_2] \cdot 1.5H_2O\}_n$  (3) and  $\{[Co_{1,5}(L^2)(L)(H_2O)_2]$ .1.5H<sub>2</sub>O}<sub>n</sub> (**4**), where H<sub>2</sub>L<sup>1</sup> = 1,4-benzenedicarboxylic acid and H<sub>3</sub>L<sup>2</sup> = 1,3,5-benzenetricarboxylic acid, have been synthesized under hydrothermal conditions. The structure analyses reveal that compounds 1 and 2 are isomorphic three-dimensional networks and posses (3,5)-connected nets with  $(4^2 \cdot 6)_2(4^2 \cdot 6^4 \cdot 8^{10} \cdot 10)$  topology. Both **3** and **4** are isomorphic layered structures, which can be simplified as  $2D \rightarrow 2D$  interpenetrating undulated  $6^3$ -hcb nets. The structural differences indicate that the effect of polycarboxylate ligands play an important role in the resulting structures of these networks. Moreover, thermal properties and luminescent properties were also investigated for the compounds. © 2012 Elsevier Ltd. All rights reserved.

#### 1. Introduction

The design and syntheses of porous coordination polymers (PCPs), also called metal-organic frameworks (MOFs) are of great current interest due to their potential applications in storage, recognition, adsorption, magnetism, and catalysis as well as their intriguing variety of architectures and fascinating new topologies [1]. The most common approach to build coordination frame works (MOFs) is rational combination of suitable organic ligand and metal salt with specific coordination geometry [2]. The organic ligand is important because changing the structure of the ligand can lead to various interesting porous MOFs. Accordingly, a careful choice or design of ligands with suitable groups is the key for the construction of functional coordination compounds with desired structural features and physical-chemical properties [3].

In recent years, there has been much attention in the use of threeconnected centers as basic structural units for the construction of framework materials. Especially flexible tripodal ligands such as 1,3,5-tris(imidazol-1-ylmethyl)benzene, 1,3,5-tris(imidazol-1ylmethyl)-2,4,6-trimethylbenzene, 1,3,5-tris(4-pyridylmethyl)benzene, 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene, etc. [4], have been widely used in the construction of MOFs. Compared with the rigid tripodal ligands, the flexible tripodal ligand N,N',N"-tris(3pyridyl)-1,3,5-benzenetricarboxamide ligand (L, Scheme 1), has excellent coordinating ability, and many conformations can be induced by metal salts due to their flexibility and low symmetry [5]. Besides, it may show much more possible coordination modes because the existence of three carbonyl oxygen atoms and three pyridine nitrogen atoms.

On the other hand, polycarboxylate organic ligands are extremely important in the synthesis of MOFs because of the diversity of the coordination modes with the metal ions, high structural stability and sensitivity to pH values of the carboxylate groups [6]. A large number of metal-carboxylate frameworks have been reported so far, and some groups altered carboxylate ligands in a two-ligand system in order to obtain different dimensional architectures ranged from one to three dimensional [7]. However, because of the complexity and difficult prediction of the resulting composition or structure, the influential principles in a two-ligand system are less ascertained and not conclusive [8].

On the basis of the above considerations, in this paper, we focused our attention on two-ligand assembly reactions of the flexible tripodal ligands *N*,*N'*,*N''*-tris(3-pyridyl)-1,3,5-benzenetricarboxamide ligand (L), together with different carboxylate ligands and different metal salts. Five novel metal-organic frameworks,  $[Co(L^1)(L)]_n$ (**1**), {[Cd(L<sup>1</sup>)(L)] $\cdot 0.5H_2O_n$  (**2**), {[Zn<sub>1.5</sub>(L<sup>2</sup>)(L)(H<sub>2</sub>O)<sub>2</sub>] $\cdot 1.5H_2O_n$  (**3**) and { $[Co_{1.5}(L^2)(L)(H_2O)_2] \cdot 1.5H_2O$ }<sub>n</sub>(**4**), where  $H_2L^1 = 1,4$ -benzenedicarboxylic acid and  $H_3L^2 = 1,3,5$ -benzenetricarboxylic acid (Scheme 2), have been obtained under hydrothermal conditions. Their single-crystal structures, thermal stability and luminescent properties are systematically investigated.

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#### 2. Experimental

#### 2.1. Materials and physical measurements

The L ligand was prepared according to the literature method [9]. All other chemicals purchased were of reagent grade or better and were used without further purification. Elemental analyses were performed with a Perkin-Elmer 240C element analyzer. IR spectra were recorded as KBr pellets in the range 4000–400 cm<sup>-1</sup> on Perkin-Elmer spectrometer. Thermogravimetric analysis (TGA) was performed on a NETZCH STA 449C with a heating rate of 10 min<sup>-1</sup> under in an air atmosphere. The Excitation and emission spectra of the ligands and compounds in the solid state were measured on a Perkin-Elmer LS 55 luminescence spectrometer. The decay lifetimes and the quantum yields of these compounds were measured on a Perkin-Elmer FLS-920 spectrometer. The excitation wavelengths in photoluminescence quantum yield measurement were set as 330 nm, and the scan range of emission spectra were 350–650 nm with a scan step of 1 nm.

#### 2.2. Syntheses of the metal compounds

#### 2.2.1. Synthesis of $[Co(L^1)(L)]_n$ (**1**)

A mixture of CoCO<sub>3</sub> (0.1 mmol, 0.0119 g),  $H_2L^1$  (0.1 mmol, 0.0166 g), L (0.05 mmol, 0.0219 g), and water (10 mL) was adjusted and then heated at 120 °C in a Teflon-lined autoclave for 3 days, followed by slow cooling to room temperature. The resulting purple prismatic crystals were collected. Elemental *Anal.* Calc. for C<sub>32</sub>-H<sub>22</sub>CoN<sub>6</sub>O<sub>7</sub>: C, 58.10; H, 3.35; N, 12.70. Found: C, 58.25; H, 3.24; N, 12.81%. IR (cm<sup>-1</sup>): 3280(w), 1684(s), 1644(m), 1583(m), 1540(s), 1481(s), 1424(w), 1391(w), 1294(s), 1239(m), 1127(w), 1047(m), 801(s), 754(s), 700(s), 642(m), 588(m).

#### 2.2.2. Synthesis of $\{[Cd(L^1)(L)] \cdot 0.5H_2O\}_n$ (2)

The synthesis of compound **2** was carried out as described above for compound **1** except that CdCO<sub>3</sub> were used instead of CoCO<sub>3</sub>. The resulting colorless prismatic crystals were collected. Elemental *Anal.* Calc. for  $C_{32}H_{23}CdN_6O_{7.5}$ : C, 53.09; H, 3.20; N,



**Scheme 1.** Structure of the N,N',N''-tris(3-pyridyl)-1,3,5-benzenetricarboxamide (L) ligand.



Scheme 2. Structures of the carboxylic acids used in this work.

11.61. Found: C, 53.25; H, 3.10; N, 11.81%. IR  $(cm^{-1})$ : 3455(w), 3240(w), 1678 (s), 1654(m), 1543(s), 1540(s), 1482(s), 1427(w), 1382(w), 1297(m), 1232(m), 1131(w), 1046(m), 841(s), 746(s), 695(m), 635(s), 520(s).

#### 2.2.3. Synthesis of $\{[Zn_{1.5}(L^2)(L)(H_2O)_2] \cdot 1.5(H_2O)\}_n$ (**3**)

A mixture of ZnCO<sub>3</sub> (0.075 mmol, 0.0125 g),  $H_3L^2$  (0.05 mmol, 0.0105 g), L (0.05 mmol, 0.0219 g), and water (10 mL) was adjusted and then heated at 120 °C in a Teflon-lined autoclave for 3 days, followed by slow cooling to room temperature. The resulting colorless prismatic crystals were collected. Elemental *Anal.* Calc. for C<sub>66-</sub> $H_{56}Zn_3N_{12}O_{25}$ : C, 49.13; H, 3.50; N, 10.42. Found: C, 49.26; H, 3.68; N, 10.65%. IR (cm<sup>-1</sup>): 3426(m), 3086(w), 1683(s), 1627(s), 1542(s), 1486(s), 1411(s), 1311(m), 1298(m), 1232(s), 1191(m), 1068(w), 917(m), 884(w), 805(s), 720(m), 649(m), 569(m).

#### 2.2.4. Synthesis of { $[Co_{1.5}(L^2)(L)(H_2O)_2] \cdot 1.5(H_2O)$ }<sub>n</sub> (4)

The synthesis of compound **4** was carried out as described above for compound **3** except that CoCO<sub>3</sub> and heated at 120 °C were used instead of ZnCO<sub>3</sub> and heated at 150 °C, respectively. The resulting purple prismatic crystals were collected (yield, ca. 30% based on Co). The yield of the colorless prismatic crystals is ca. 30% based on Zn. Elemental *Anal.* Calc. for C<sub>66</sub>H<sub>56</sub>Co<sub>3</sub>N<sub>12</sub>O<sub>25</sub>: C, 49.73; H, 3.54; N, 10.54. Found: C, 49.57; H, 3.72; N, 10.61%. IR (cm<sup>-1</sup>): 3452(m), 2979(w), 2926(w), 1681 (s), 1619(s), 1558(s), 1479(s), 1417(s), 1356(m), 1330(m), 1295(s), 1233(m), 1128(w), 1058(w), 917(w), 803(m), 724(m), 575 (m).

#### 2.3. Crystal structure determination

Single-crystal X-ray diffraction data of the four compounds were recorded on an Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromated Mo K $\alpha$  radiation  $(\lambda = 0.71073 \text{ Å})$  at 293 K. Absorption corrections were applied using multi-scan technique. All the structures were solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program [10]. Non-hydrogen atoms of the compounds were refined with anisotropic temperature parameters except the disordered atoms. N6 and C29 to C33 in compounds **3** and **4** are disordered and were split over two sites with a total occupancy of 1. The hydrogen atoms of the disordered atoms were not included in the model. The hydrogen atoms attached to carbon atoms were generated geometrically and refined using a riding model with d(C-H) = 0.93 Å,  $U_{iso} = 1.2 U_{eq}(C)$  for aromatic atoms. The hydrogen atoms attached to oxygen and nitrogen atoms were located from difference Fourier map. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restrains. However, some water H atoms of compounds 2, 3, and 4 were not included in the model. The detailed crystallographic data and structure refinement parameters for these compounds are summarized in Table 1. Selected bond distances and angles and hydrogen bonds for them are listed in S1a-S4b (Supporting Information).

#### 3. Results and discussion

#### 3.1. Syntheses of the compounds

The hydrothermal method has been proved to be an effective way to synthesize compound crystals. Under hydrothermal conditions, the properties of the reactants are quite different from those under conventional conditions. So some fantastic structures and novel topologies may be produced under hydrothermal reactions. Compounds **1–4** were prepared by reactions of polycarboxylic

| Table 1          |               |              |                |
|------------------|---------------|--------------|----------------|
| Crystal data and | structure rei | finement for | compounds 1-4. |

| Compound                                 | 1                      | 2   | 3                              | 4               |
|--|------------------------|---|--------------------------------|-----------------|
| Formula                                  | $C_{32}H_{22}CoN_6O_7$ | C <sub>32</sub> H <sub>23</sub> CdN <sub>6</sub> O <sub>7.5</sub> | $C_{66}H_{56}Zn_3N_{12}O_{25}$ | C66H56C03N12O25 |
| Formula weight                           | 661.49                 | 723.96  | 1613.34                        | 1594.02         |
| Crystal system                           | triclinic              | triclinic   | triclinic                      | triclinic       |
| Space group                              | ΡĪ                     | ΡĪ  | ΡĪ                             | ΡĪ              |
| a (Å)                                    | 8.7692(18)             | 8.6957(17)  | 10.282(2)                      | 10.228(2)       |
| b (Å)                                    | 11.736(2)              | 11.849(2)   | 11.063(2)                      | 11.060(2)       |
| <i>c</i> (Å)                             | 15.474(3)              | 16.089(3)   | 14.673(3)                      | 14.757(3)       |
| α (°)                                    | 105.41(3)              | 97.21(3)  | 99.64(3)                       | 100.10(3)       |
| β (°)                                    | 105.41(3)              | 104.71(3)   | 91.00(3)                       | 90.91(3)        |
| γ (°)                                    | 106.62(3)              | 108.56(3)   | 100.59(3)                      | 100.58(3)       |
| V (Å <sup>3</sup> )                      | 1443.6(5)              | 1481.1(5)   | 1615.4(6)                      | 1613.5(6)       |
| Ζ  | 2                      | 2   | 1                              | 1               |
| $D_{\text{calcd}}$ (g cm <sup>-3</sup> ) | 1.522                  | 1.623   | 1.658                          | 1.640           |
| F(000)                                   | 678                    | 730   | 826                            | 817             |
| GOF on F <sup>2</sup>                    | 1.050                  | 1.058   | 1.032                          | 1.038           |
| $R_1^{a}[I > 2\sigma(I)]$                | 0.0406                 | 0.0261  | 0.0438                         | 0.0424          |
| $wR_2^{b}[I > 2\sigma(I)]$               | 0.0877                 | 0.0559  | 0.1077                         | 0.1090          |



**Fig. 1.** (a) Coordination environment around the Co(II) centers in **1**. Hydrogen atoms are omitted for clarity. Symmetry code: #1 x, y - 1, z; #2 -x + 2, -y + 1, -z + 1; #3 -x + 1, -y, -z + 2; #4 -x + 1, -y + 1, -z + 1. (b) The chain constructed by Co(II) atoms and L<sup>1</sup> ligands. (c) The ladder-like chain constructed by Co(II) atoms and L ligands. (d) The 3D structure of compound **1**. (e) The (3,5)-connected net with  $(4^2.6)_2(4^2.6^4.8^{10}.10)$  topology of compound **1**.

acids  $(H_2L^1 \text{ and } H_3L^2)$ , metal carbonates  $(CoCO_3, CdCO_3 \text{ and } ZnCO_3)$ , and L ligand under hydrothermal condition.

#### 3.2. Description of crystal structures

#### 3.2.1. Crystal structure of $[Co(L^1)(L)]_n$ (1)

Compound **1** crystallizes in the monoclinic space group  $P\bar{1}$ . The results of crystallographic analysis reveal that the asymmetric unit of compound **1** consists of one Co(II) atom, two half of L<sup>1</sup>, and one L ligand. As shown in Fig. 1a, each Co(II) atom is six-coordinated by three O atoms of two carboxylate groups from two L<sup>1</sup> and two N atoms and one O atom from three L ligands in octahedral coordination geometry. The Co–N bond distances are 2.159(2) and 2.180(2) Å and the Co–O bond lengths are in the range of 2.0537(17)–2.1902(19) Å (Table S1a).

The carboxylate groups of one kind of  $L^1$  connect the Co(II) in monodentate mode, while those of the other kind of  $L^1$  adopt a chelating coordination mode. The two kinds of  $L^1$  ligands link the Co(II) atoms alternately, forming a chain (Fig. 1b). In addition, each ligand L coordinates to three Co(II) atoms through one Co–O bond and two Co–N bonds in mode I as a tridentate ligand (Scheme 3), forming a ladder-like chain along *b* axis (Fig. 1c). The two kinds of chains are further connected by the sharing Co(II) centers, resulting in a 3D network of compound **1** (Fig. 1d).

From the topological view, the L ligands can be viewed as 3connected nodes, while the Co(II) centers can be considered as 5connected nodes. Thus, the whole 3D framework of compound **1** can be simplified as a (3,5)-connected net with  $(4^2 \cdot 6)_2(4^2 \cdot 6^4 \cdot 8^{10} \cdot 10)$  topology (Fig. 1e).



Mode I

Scheme 3. The coordination modes of the L ligand.

Mode II

In addition, hydrogen bonding interactions  $(N1\cdots O2#6 = 3.042 \text{ Å}, N2\cdots N4#1 = 2.947 \text{ Å} and N3\cdots O2#6 = 2.895 \text{ Å})$  (symmetry code: #1 *x*, *y* – 1, *z*; #6 *x* + 1, *y* + 1, *z*) contained in this structure presumably help to further reinforce the 3D framework (Table S1b).

#### 3.2.2. Crystal Structure of $\{[Cd(L^1)(L)] \cdot 0.5H_2O\}_n$ (2)

 $CdCO_3$  was selected to react with  $L^1$  and L under similar synthetic conditions, and a new compound **2** was obtained. Compound **2** is isomorphous with **1**. Nevertheless, some differences exist between the two compounds.

Firstly, as shown in Fig. 2a, compound **2** contains one Cd(II) atom, two halves of L<sup>1</sup>, one L ligand, and two quarters of uncoordinated solvent molecule. While compound **1** does not contain any free water molecules. Secondly, Co(II) atom in compound **1** is six-coordinated displaying distorted octahedral coordination geometry. Whereas Cd(II) atom in compound **2** is seven-coordinated by four O atoms from two carboxylate groups of two independent L<sup>1</sup> ligands and two N atoms and one O from three independent L ligands in a pentagonal bipyramid environment (Fig. 2a). The Cd–N bond distances are 2.3044(16) and 2.343(2) Å, respectively and the Cd–O bond lengths are 2.3046(19)–2.5174(18) Å (Table S2a). Moreover, both of the two kinds of L<sup>1</sup> in compound **1** bridge two Cd(II) atoms in a chelating coordination mode to generate a chain (Cd–L<sup>1</sup> chain) (Fig. 2b), whereas the two kinds of L<sup>1</sup> in compound **1** adopt different coordination modes.

In addition, the structural stability of compound **2** is also stabilized by hydrogen bonding interactions between the N atom of the L ligand and O atoms of the L<sup>1</sup> (N4···O4#6 = 2.946 Å and N6#6···O4 = 3.245 Å) and between the N atom of the two L (N5···N1#5 = 2.925 Å) (symmetry codes: #5 x, y - 1, z; #6 x + 1, y, z) (Table S2b).

# 3.2.3. Crystal structures of $\{[Zn_{1.5}(L^2)(L)(H_2O)_2] \cdot 1.5H_2O\}_n$ (**3**) and $\{[Co_{1.5}(L^2)(L)(H_2O)_2] \cdot 1.5H_2O\}_n$ (**4**)

In order to explore the influence of organic polycarboxylate ligands on the structures of the resultant compounds, carboxylate ligands  $H_3L^2$  were introduced to react with MCO<sub>3</sub> and the L ligand under similar reaction conditions, and two new isomorphic compounds  $\{[Zn_{1.5}(L^2)(L)(H_2O)_2]\cdot 1.5H_2O\}_n$  (**3**) and  $\{[Co_{1.5}(L^2)(L)(H_2O)_2]\cdot 1.5H_2O\}_n$  (**4**) were obtained. Here we just take compound **3** for example and discuss its structure in detail.

The X-ray crystallographic study shows that there are two crystallographically independent Zn(II) centers with different coordination environments, one crystallographically independent ligands L, one L<sup>2</sup> ligand, two coordinated water molecules, and



**Fig. 2**. (a) ORTEP view of **2** showing the local coordination environment of Cd(II) atom with hydrogen atoms omitted for clarity. Symmetry code: #1 x, y + 1, z; #2 - x + 1, -y, -z; #3 - x, -y + 1, -z; #4 - x, -y, -z + 1. (b) The Cd–L<sup>1</sup> chain in compound **2**.



**Fig. 3.** (a) ORTEP view of **3** showing the local coordination environment of Zn(II) atom with hydrogen atoms omitted for clarity. N6 and C29–C33 are statistically disordered over two sites, and here only one disorder position is shown for clarity. Symmetry code: #1 -x, -y - 2, -z + 2; #2 x + 1, y, z; #3 -x + 2, -y, -z + 2. (b) The one-dimensional structure of Zn–L<sup>2</sup>. (c) The four-membered ring of (Zn2)<sub>2</sub>L<sub>2</sub>. (d) The layer of compound **3**. (e) The 6<sup>3</sup>-hcb net of compound **3**. (f) A view of the 2D  $\rightarrow$  2D interpenetrating undulated 6<sup>3</sup>-hcb net.

one and a half of lattice water molecules in the asymmetric unit of compound **3** (Fig. 3a). N6 and C29–C33 of one pyridyl ring in L ligand are disordered over two sites. The Zn1 is six-coordinated by four water molecules in the equatorial positions and two O atoms from carboxylate groups of two L<sup>2</sup> in the apical positions showing octahedral coordination geometry with the Zn–O bond distances in the range of 2.051(2)-2.175(3) Å. The Zn2 is four-coordinated by two N atoms from two independent L ligands and two O atoms from carboxylate groups of two L<sup>2</sup> showing an slightly distorted tetrahedral geometry with the Zn–N bond distances of 2.034(3) and 2.038(3) Å and the Zn–O bond lengths of 1.983(2) and 1.989(2) Å respectively.

Each  $L^2$  ligand connects two Zn2(II) atoms and one Zn1(II) atoms to form a ladder-like chain with the Zn1 on the rungs (Zn1...Zn1 10.282 Å) and the Zn2 on the siderails (Zn2...Zn2

10.282 Å) (Fig. 3b). Each L ligand coordinates to two Zn2(II) atoms as a bidentate ligand in mode II (Scheme 3) through two Zn–N bonds, forming a four-membered ring  $(Zn2)_2L_2$  (Fig. 3c). Further, the  $(Zn2)_2L_2$  rings are bridged by the neighboring ladder-like chains to construct a layer of compound **3** (Fig. 3d).

Topologically, the layer of compound **3** can be simplified as an undulated honeycomb net ( $6^3$ -**hcb**) (Fig. 3d), if the Zn2 and  $L^2$  are considered as 3-connected nodes and the Zn1 and L are viewed as linkers. Furthermore, the a more impressive structural characteristic of compound **3** is that there are two identical 2D undulated single nets interpenetrating in a 2D  $\rightarrow$  2D parallel fashion, as shown in (Fig. 3f).

Besides, the crystal structure of compound **3** is further strengthened through hydrogen bonding interactions between the uncoordinated water molecules and the ligands (Table S3b).



Fig. 4. Solid-state photoluminescent spectra of L and compounds 2 and 3 at room temperature.

#### 3.3. Discussion

#### 3.3.1. Coordination modes of L ligand

From the structure description above, we can see that the *N*,*N*',*N*''-tris(3-pyridyl)-1,3,5-benzenetricarboxamide (L) ligand can bend and rotate freely when coordinating to the central metals due to the flexible nature of the ligand. Moreover, L have six potential coordination nodes (three carbonyl oxygen atoms and three pyridine nitrogen atoms), which can participate in coordination and greatly beautify and enrich the MOFs' structures. Thus, the L ligand can show many possible coordination modes. In compounds **1–4** the L ligand show two different coordination modes (Scheme 3). In **1** and **2**, L links the metal centers through one Co-O bond and two Co–N bonds in mode I as a tridentate ligand. Nevertheless, in compounds **3** and **4**, the L ligands act as bidentate ligands bridging two metal ions through pyridyl nitrogen atoms in mode II.

# 3.3.2. Influence of the auxiliary ligand on the structures of compounds We have selected two polycarboxylate ligands (H<sub>2</sub>L<sup>1</sup> to H<sub>3</sub>L<sup>2</sup>) as auxiliary ligands. Though different metal carbonates are used, but the structures of compounds 1 and 2 are the same, as well as 3 and 4. Thus, the metal centers do not show influence in the resultant

structures of the compounds in this experimental system. Nevertheless, the structural differences between compounds **1** and **4** clearly illustrate that the carboxylate anions play an important roles in structures. In this work, compounds **1** and **4** were synthesized under similar reaction conditions, except using different auxiliary ligands ( $H_2L^1$  for **1**;  $H_3L^2$  for **4**), which result in two distinctive structures, Compound **1** shows a 3D structure and **4** possesses a layer structure. Obviously, the distinctive structures are attributed to the difference of carboxylate groups' numbers of the carboxylate ligands.

#### 3.4. Thermal analyses

To examine the thermal stability of these compounds, thermogravimetric analysis (TGA) were carried out. As shown in Fig. S1, the TGA curves of compounds **1** and **2** are similar, as well as **3** and **4** due to their similar structures. For compound **1**, the decomposition of the compound occurs at 346 °C, indicating high thermal stability of the frameworks. For compound **2**, the decomposition of the framework occurs from 372 °C. The loss of lattice water molecules of **2** was not observed. It is probably that the lattice water molecules lost in the air. For **3** and **4**, the gradual weight loss between about 87 and 154 °C can be attributed to the release of water molecules (obsd 5.8%; calcd 7.81% for **3**, and obsd 5.4%; calcd 7.90% for **4**). Then no obvious weight loss is observed until the decomposition of the frameworks occurs at 340 °C.

#### 3.5. Luminescent properties

Coordination compounds with d<sup>10</sup> metal centers and conjugated organic linkers are promising candidates for photoactive materials with potential applications in chemical sensors, photochemistry and electroluminescent display [11]. Hence, the solidstate photoluminescence properties of ligand L, together with and compounds **2** and **3** were investigated at room temperature (Fig. 4). The main emission peak of L is at 441 nm ( $\lambda_{ex} = 335$  nm), which is ascribed to the  $\pi^* \rightarrow n$  or  $\pi^* \rightarrow \pi$  electronic transition [12]. Compared with the luminescence of free ligand, the emissions of **2** ( $\lambda_{em} = 401$  nm,  $\lambda_{ex} = 326$  nm), and **3** ( $\lambda_{em} = 410$  nm,  $\lambda_{ex} = 332$  nm) undergo some blue-shifts. Because the Zn(II) and Cd(II) ions are difficult to oxidize or to reduce, the emissions of compounds **2** and **3** is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature, which can be assigned to the intraligand transitions of the L ligands. The blue



Fig. 5. The decay lifetime curves of 2 and 3 in the solid state. The black circles represent experimental data, and the solid red lines represent fitting results). (Color online.)

shifts may be attributed to the coordination effects of the L ligands to metal cations, which increases the ligand conformational rigidity and reduces the non-radiative decay of the intraligand [13].

The fluorescence lifetimes of **2** and **3**,  $\tau$ , are investigated in the solid state at room temperature, and the curves of the fluorescence decay of them are illustrated in Fig. 5. The decay curves of them are well fitted into a single-exponential function as  $I = A\exp(-t/\tau) + y_0$  with luminescence lifetimes  $\tau 2 = 1.53$  ns and  $\tau 3 = 1.80$  ns, respectively. The luminescent lifetimes of these compounds are much shorter than the lifetime of the emission resulting from a triplet state (>10<sup>-3</sup> s), indicating the emissions should arise from the singlet state [14]. The nanosecond range of the lifetimes in the solid state at room temperature reveals that their emissions are fluorescent in nature.

Quantum yield,  $\Phi$ , is a measure of the emission efficiency of a fluorochrome and is defined as the number of photons emitted divided by the number of photons absorbed. The emission quantum yields ( $\Phi$ ) have also been measured for L, **2** and **3** single crystals. The quantum yields of L is 0.04, while those of compounds **2** and **3** in the solid state are 0.07 and 0.14, respectively, which similar to that reported for some MOFs [15,16]. Quantum yields show that in, the metal complexes are more fluorescent compared to the ligand L, and this is supposedly due to the greater rigidity of the ligand system attained upon complexation, which reduces the loss of energy through non-radiative channels of the intraligand emission excited state [17].

#### 4. Conclusions

In summary, four novel metal—organic frameworks with N,N',N''-tris(3-pyridyl)-1,3,5-benzenetricarboxamide flexible tripodal ligand (L) have been synthesized and characterized. The different polycarboxylate ligands influence the coordination mode of the L ligands and thus result in two kinds of distinct networks. The results demonstrate the L is an excellent flexible polydentate ligand for construction of coordination polymers with diverse structures. Photoluminescent spectra show that compounds **2** and **3** they may be good candidates for luminescent materials. Further investigations of this system about functional coordination polymers are still in progress.

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#### Appendix A. Supplementary data

CCDC 886475–886478 contains the supplementary crystallographic data for **1–4**. 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 http://dx.doi.org/ 10.1016/j.poly.2012.10.047.

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