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Three open-framework coordination polymers with new topological structures built on two tripod ligands

Jun Zhang [a,c], Yun-Shan Xue [a], Hong-Mei Wang [b], Min Fang [a,b], Hong-Bin Du [a,*], Yi-Zhi Li [a], Xiao-Zeng You [a]

[a] State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China
[b] Department of Chemistry, Nanjing Normal University, Nanjing 210097, China
[c] School of Materials and Chemical Engineering, Anhui University of Architecture, Hefei 230601, China

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ABSTRACT

By using flexible tricarboxylate 4,4′,4″-(((2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene))tris(oxy))tribenzoic acid (H_3L) and multiimidazole 1,3,5-tri(imidazo-1-ylmethyl)-2,4,6-trimethylbenzene (titb) ligands simultaneously, three novel coordination polymers $[M_3L_2(titb)_2]\cdot 2H_2O\cdot 2.5DMF$ (M = Co,**1**; Zn, **2**; Cd, **3**) were synthesized under solvothermal conditions and characterized by single-crystal X-ray diffraction, thermogravimetric and photoluminescent studies. The three compounds are isomorphous and possess a three-dimensional (3D) framework built from 2D sheets of L^{3-} ligands and M ions, and 1D chains of titb ligands and M ions. Topological analyses showed that they exhibit a novel (3,3,4,4) four-nodal 3D net constructed from two 4-connecting metal, and two 3-connecting L^{3-} and titb nodes. Compounds **2** and **3** are photoluminescent upon excitation at room temperature.

1. Introduction

Recently, coordination polymers have attracted interest because of their intriguing structural diversities and potential applications in the fields of gas adsorption, separation, catalysis, luminescence, etc. [1–3]. In the construction of these materials, the multidentate organic ligands play a vital role since the structural integrity of these ligands in most cases remains unaltered throughout the assembly process, which helps to realize predesigned structural topology of the final product. Therefore, considerable efforts in coordination polymers have been devoted to the design and synthesis of new ligands.

Among various ligands used for the construction of coordination polymers, the flexible tricarboxylates are often chosen because of their variable coordination modes to metal ions and abilities to form flexible frameworks [4,5]. We recently devised a flexible tripod tricarboxylate ligand 4,4′,4″-(((2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene))tris(oxy))tribenzoic acid (H_3L) and prepared several coordination polymers by using this ligand. Herein, we report their syntheses, structures, thermogravimetric and photoluminescent properties of three new coordination polymers, namely, $[M_3L_2(titb)_2]\cdot 2H_2O\cdot 2.5DMF$ (M = Co, **1**; Zn, **2**; Cd, **3**), built on tricarboxylate ligand H_3L and multiimidazole ligand 1,3,5-tri(imidazo-1-ylmethyl)-2,4,6-trimethylbenzene (titb) (Scheme 1). The introduction of the second titb ligand in the self-assembly process results in the formation of 3D frameworks with new topological structures.

2. Experimental

2.1. Materials

All commercially available chemicals are of reagent grade and were used as received without further purification. The synthesis of the ligand 4,4′,4″-(((2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene))tris(oxy))tribenzoic acid (H_3L) was given in the following section, and the ligand titb is prepared according to the reference [6].

2.2. Physical measurements

Elemental analyses of C, H, and N were performed on a Elementar Vario MICRO Elemental Analyzer at the Analysis Center of Nanjing University. Fourier transformed Infrared (FT-IR) spectra were obtained on a Bruker Vector 22 FT-IR spectrophotometer by using KBr pellets. Thermogravimetrical analyses (TGA) were performed in a N_2 atmosphere (a flow rate of 100 ml min^{-1}) on Diamond TG/DTA thermal analyzer from 30 to 800 °C, with a heating rate of 10 °C/min. X-ray powder diffraction (XRPD) data were collected on a Bruker D8 Advance instrument using a Cu Kα radiation (λ = 1.54056 Å) at room temperature. Solid state photoluminescence spectra were recorded using a SLM48000DSCF/AB2 spectrofluorometer.

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* Corresponding author.
E-mail address: hbdu@nju.edu.cn (H.-B. Du).

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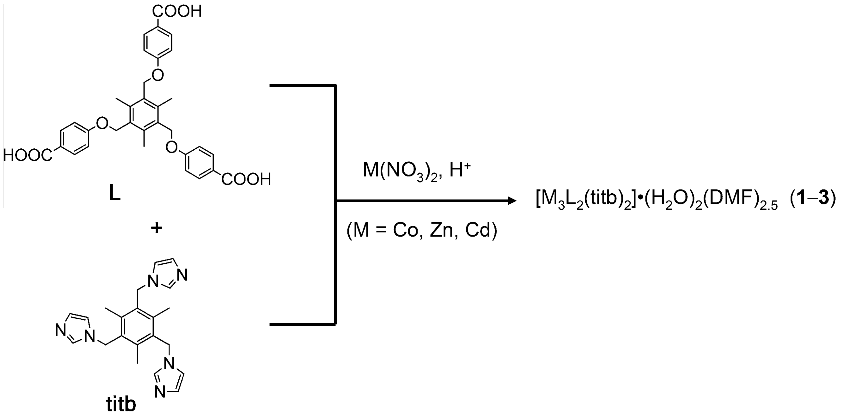

Scheme 1. Synthesis of **1**–**3**.

2.3. Synthesis

2.3.1. Preparation of H_3L

A mixture of methyl 4-hydroxybenzoate (2.28 g, 15.0 mmol), 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (1.95 g, 4.88 mmol), K_2CO_3 (3.32 g, 24.0 mmol) and 0.15 g 18-crown-6 in THF (50 ml) were stirred at 60 °C for about 24 h under a nitrogen atmosphere. The mixture was condensed to about 25 mL and then added 30 mL of aqueous Na_2CO_3 (1%) at 0 °C. The mixture was filtered after stirred for about 5 min and washed with water and ether, a white solid was obtained after drying in vacuum at 50 °C. The solid was added to the solution of KOH (0.60 g, 10.76 mmol) in 30 mL THF, 30 mL methanol and 30 ml water, and refluxed for about 48 h at 80 °C. The mixture was condensed to remove THF and methanol, then cooled to room temperature and filtered. The filtrate was acidified to pH ~1 with aqueous HCl (6 mol/L), and the prepecipitate was filtered, washed with water, and dried in vacuum to give a white solid H_3L (1.44 g). Yield: 51.8%. m.p.: 281–284 °C. *Anal.* Calc. for $C_{33}H_{30}O_9$: C, 69.46; H, 5.30. Found: C, 69.24; H, 5.57%. ^1H NMR (500 MHz, *d*-DMSO): δ: 12.59 (s), 7.92 (d, 6 H), 7.16 (d, 6 H), 5.21 (s, 6 H), 2.36 (s, 9 H). FT-IR (KBr, cm^{-1}): 2980 b, m, 2663 m, 2549 m, 1688 s, 1608 s, 1577 s, 1514 s, 1422 s, 1376 w, 1294 s, 1245 s, 1167 s, 1106 m, 1025 m, 983 s, 844 s, 770 s, 696 m, 664 m, 636 m, 600 m, 547 m, 505 m.

*2.3.2. $[Co_3L_2(titb)_2]\cdot 2H_2O\cdot 2.5DMF$ (**1**)*

To the solution of H_3L (0.030 g, 0.052 mmol) and titb (0.018 g, 0.050 mmol) in 4 mL of *N,N*-dimethylformamide (DMF) was added the solution of $Co(NO_3)_2\cdot 6H_2O$ (0.029 g, 0.10 mmol) in 2 mL of H_2O to give a turbid mixture. Two drops of aqueous HCl (1:1 volume) were added to the mixture and a clear solution with pH ≈5 was obtained. The solution was transferred into a vial, which was then sealed and heated at 100 °C for 3 days. The vial was then allowed to cool down to room temperature. Blue crystals (0.033 g) were obtained by filtration and washed with DMF and CH_2Cl_2 three times each, respectively. Yield: 58.9% (based on titb). *Anal.* Calc. for $C_{115.5}H_{123.5}Co_3N_{14.5}O_{22.5}$: C, 61.61; H, 5.53; N, 9.02. Found: C, 61.74; H, 5.47; N, 8.57%. FT-IR (KBr, cm^{-1}): 3394 m, b, 3119 m, 2925 m, 2353 m, 1668 s, 1598 s, 1552 s, 1505 s, 1362 s, 1296 s, 1229 s, 1163 s, 1097 s, 987 s, 854 s, 778 s, 691 m, 651 s, 611 m, 508 w, 422 w.

*2.3.3. $[Zn_3L_2(titb)_2]\cdot 2H_2O\cdot 2.5DMF$ (**2**)*

Colorless crystals (0.028 g) of **2** were obtained by following the same procedure as **1** with the replacement of $Co(NO_3)_2\cdot 6H_2O$ with $Zn(NO_3)_2\cdot 6H_2O$ and crystallization at 120 °C. Yield: 48.3% (based on titb). *Anal.* Calc. for $C_{115.5}H_{123.5}Zn_3N_{14.5}O_{22.5}$: C, 61.09; H, 5.48; N, 8.94. Found: C, 61.54; H, 5.43; N, 8.83%. FT-IR (KBr, cm^{-1}): 3636 w, 3397 m, b, 3116 m, 2917 m, 1667 s, 1601 s, 1562 s, 1360 s,

Table 1
Crystallographic data for **1**–**3**.

Compound reference	**1**	**2**	**3**
Chemical formula	$C_{115.5}H_{123.5}Co_3N_{14.5}O_{22.5}$	$C_{115.5}H_{123.5}Zn_3N_{14.5}O_{22.5}$	$C_{115.5}H_{123.5}Cd_3N_{14.5}O_{22.5}$
Formula mass	2251.60	2270.97	2412.03
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	23.5595(15)	23.4616(13)	24.100(3)
b (Å)	11.2040(7)	11.2113(6)	11.4627(14)
c (Å)	41.518(3)	41.580(2)	41.889(5)
β (°)	94.5160(10)	93.4720(10)	96.397(2)
Unit cell volume ($Å^3$)	10925.1(12)	10917.0(10)	11500(2)
T (K)	296(2)	296(2)	296(2)
No. of formula units per unit cell, *Z*	4	4	4
Absorption coefficient, μ (mm^{-1})	0.518	0.722	0.614
No. of reflections measured	27027	33427	28554
No. of independent reflections	9623	13105	10121
R_{int}	0.0433	0.0355	0.0607
Final R_1 values ($I > 2\sigma(I)$)[a]	0.0652	0.0498	0.0683
Final $wR(F^2)$ values ($I > 2\sigma(I)$)[a]	0.1698	0.1169	0.1576
Final R_1 values (all data)[a]	0.1037	0.0772	0.1158
Final $wR(F^2)$ values (all data)[a]	0.1846	0.1224	0.1698
Goodness of fit (GOF) on F^2	0.993	1.049	1.036
Largest difference in peak and hole (e $Å^{-3}$)	0.789/−1.162	1.273/−0.906	0.880/−0.895

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

Table 2
Selected interatomic distances (Å) and angles (°) for **1**–**3**.

1							
Co1–O5^{i}	1.959(4)	Co1–N1	1.997(4)	Co2–O1^{iii}	1.995(3)	Co2–N6	2.045(4)
Co1–O9	1.986(3)	Co1–N3^{ii}	2.001(4)				
O5^{i}–Co1–O9	106.3(2)	O5^{i}–Co1–N1	104.7(2)	O5^{i}–Co1–N3^{ii}	110.9(2)	O9–Co1–N1	113.1(2)
O9–Co1–N3^{ii}	108.0(2)	N1–Co1–N3^{ii}	113.7(2)	O1^{iii}–Co2–O1^{iv}	148.0(2)	O1^{iii}–Co2–N6^{v}	101.1(1)
O1^{iv}–Co2–N6^{v}	100.4(2)	N6^{v}–Co2–N6	94.4(2)				
2							
Zn1–O5^{iv}	1.964(2)	Zn1–N1	2.013(2)	Zn2–O1^{vi}	1.943(2)	Zn2–N6^{vii}	2.047(2)
Zn1–O9	1.978(2)	Zn1^{i}–N3	1.989(2)				
O5^{iv}–Zn1–O9	109.84(9)	O5^{iv}–Zn1–N1	103.06(9)	O5^{iv}–Zn1–N3^{v}	111.1(1)	O9–Zn1–N1	111.46(8)
O9–Zn1–N3^{v}	107.10(8)	N1–Zn1–N3^{v}	114.26(9)	O1^{vi}–Zn2–O1^{ii}	136.9(1)	O1^{ii}–Zn2–N6^{vii}	104.46(8)
O1^{vi}–Zn2–N6^{vii}	103.82(8)	N6^{vii}–Zn2–N6	96.6(1)				
3							
Cd1–O5^{ii}	2.179(9)	Cd1–N1	2.210(6)	Cd2–O1^{i}	2.293(5)	Cd2–N6	2.281(6)
Cd1–O9	2.208(5)	Cd1–N3^{iii}	2.204(7)				
O5^{ii}–Cd1–O9	106.5(3)	O5^{ii}–Cd1–N1	108.0(3)	O5^{ii}–Cd1–N3^{iii}	113.0(4)	O9–Cd1–N1	118.8(2)
O9–Cd1–N3^{iii}	99.9(2)	N1–Cd1–N3^{iii}	110.7(2)	O1^{v}–Cd2–O1^{i}	159.6(3)	O1^{v}–Cd2–N6	94.1(2)
O1^{i}–Cd2–N6	100.2(2)	N6^{iv}–Cd2–N6	91.1(3)				

Symmetry transformations: for **1**: (i) $-0.5+x, 1.5+y, z$; (ii) $x, -1+y, z$; (iii) $x, 1-y, -0.5+z$; (iv) $1-x, 1-y, 1-z$; (v) $1-x, y, 0.5-z$; (vi) $x, 1+y, z$; (vii) $0.5+x, -1.5+y, z$; for **2**: (i) $x, 1+y, z$; (ii) $-x, 1-y, -z$; (iii) $-0.5+x, -1.5+y, z$; (iv) $0.5+x, 1.5+y, z$; (v) $x, -1+y, z$; (vi) $x, 1-y, 0.5+z$; (vii) $-x, y, 0.5-z$; for **3**: (i) $1-x, 1-y, 1-z$; (ii) $-0.5+x, 1.5+y, z$; (iii) $x, -1+y, z$; (iv) $1-x, y, 0.5-z$; (v) $x, 1-y, -0.5+z$; (vi) $x, 1+y, z$; (vii) $0.5+x, -1.5+y, z$.

1294 m, 1235 s, 1168 s, 1099 s, 1026 m, 984 s, 942 m, 858 s, 785 s, 691 m, 653 s, 621 w, 604 w, 562 w, 503 w.

2.3.4. *[$Cd_3L_2(titb)_2$]·$2H_2O$·2.5DMF (3)*

To the solution of H_3L (0.029 g, 0.050 mmol) and titb (0.036 g, 0.10 mmol) in 4 mL of DMF was added the solution of $Cd(NO_3)_2·4H_2O$ (0.078 g, 0.25 mmol) in 2 mL of H_2O to give a turbid mixture. One drop of aqueous HCl (1:1 volume) was added to the mixture to obtain a clear solution with pH ≈5. The mixture was treated by following the same procedure as **1**. Colorless crystals (0.040 g) of **3** were obtained. Yield: 66.7% (based on H_3L). *Anal.* Calc. for $C_{115.5}H_{123.5}Cd_3N_{14.5}O_{22.5}$: C, 57.51; H, 5.16; N, 8.42. Found: C, 57.16; H, 5.09; N, 8.65%. FT-IR (KBr, cm^{-1}): 3401 m, b, 3124 m, 2922 m, 2361 m, 1667 s, 1596 s, 1515 s, 1388 s, 1298 s, 1227 s, 1168 s, 1097 s, 985 s, 855 s, 781 s, 688 m, 650 s, 616 m.

2.4. *X-ray crystal structure determination*

The data collections for single crystal X-ray diffraction for compounds **1**–**3** were carried out on a Bruker Smart APEX II CCD diffractometer at 291 K, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data reductions and absorption corrections were performed using the SAINT and SADABS programs [7], respectively. The structures were solved by direct methods using the SHELXS-97 program and refined with full-matrix least squares on F^2 using the SHELXL-97 program [8]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in geometrically calculated positions and refined using the riding model. The guest water and DMF molecules in the structures were highly disordered. The SQUEEZE subroutine of the PLATON [9] software suit was used to remove the scattering from the highly disordered guest molecules. The resulting new files were used to further refine the structures. The final densities were calculated from the SQUEEZE results, which is the density for the framework. Elemental and TG analyses reveal that the chemical formula of each compound contains two water and two and a half DMF molecules. Details of the crystal parameters, data collection and refinement results are summarized in the Table 1. Selected interatomic bond lengths and angles of **1**–**3** with their estimated standard deviations are given in the Table 2.

3. Results and discussion

3.1. *Synthesis*

Compounds **1**–**3** were prepared solvothermally using tricarboxylate acid (H_3L) and multiimidazole titb as co-ligands in acidic systems. It is necessary to use hydrochloric acid to adjust the pH value during the synthesis for growth of good quality of crystals. It is noted that compound **3** was synthesized under conditions slightly different with those of **1** and **2**, i.e. with different metal to ligand ratios. In addition, the presence of both ligands in the synthesis is vital to the formation of the title compounds. The phase purity for each product was confirmed by elemental analyses and X-ray powder diffraction (Fig. S1 in Supplementary data).

3.2. *Descriptions of X-ray crystal structures*

Single crystal X-ray diffraction studies revealed that **1**–**3** are isomorphous, and all crystallize in the centrosymmetric space

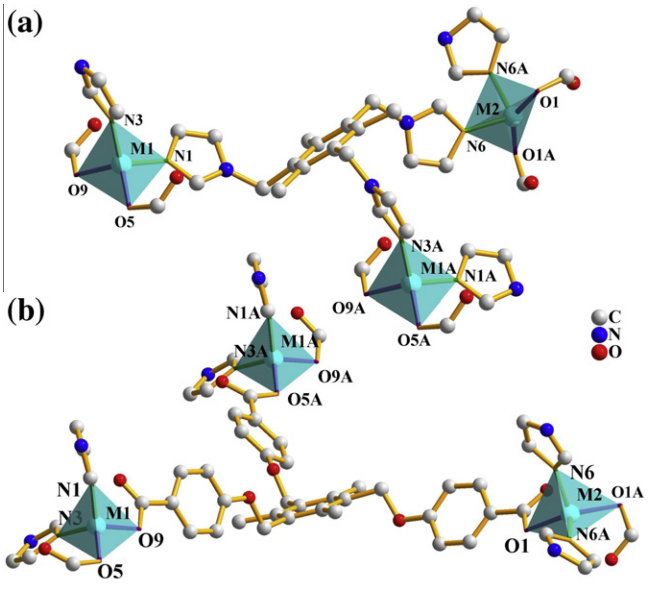

Fig. 1. Coordination environments of titb (a) and L^{3-} (b) for **1**–**3**. The H atoms are omitted for clarity.

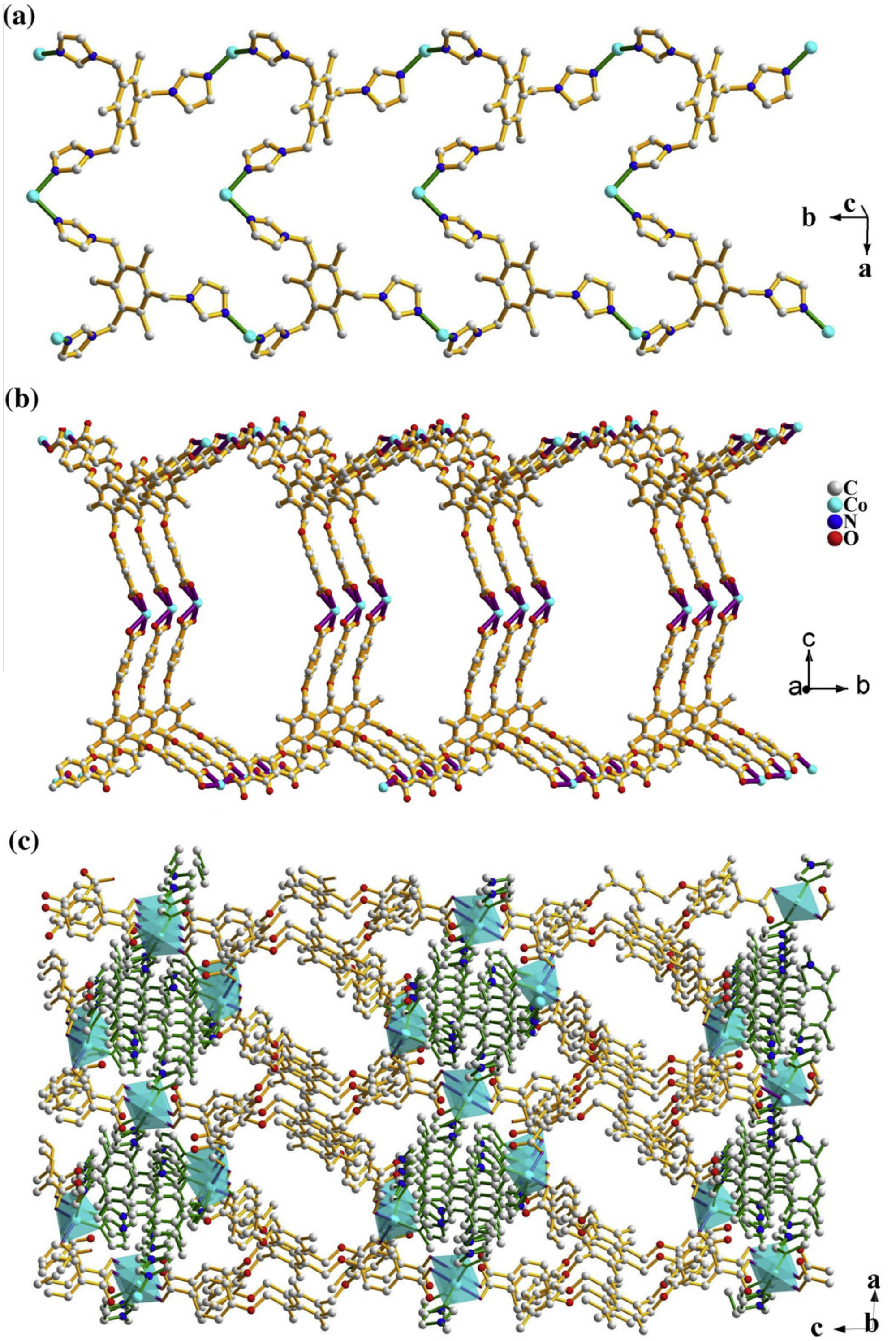

Fig. 2. Ball-and-stick representations of (a) a 1D chain made of titb and Co^{2+}, (b) a single 2D sheet made of L^{3-} and Co^{2+}, and (c) 3D framework of **1** built from 2D sheets interwoven by 1D chains (green colored). The H atoms are omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

group *C*2/*c*, which is associated with the point group C_{2h}. The compounds are built from metal ion, tricarboxylate acid (H_3L) and multiimidazole titb ligands. The asymmetric unit of each compound contains one and a half metal ions (Co(II) for **1**, Zn(II) for **2**, Cd(II) for **3**), one L^{3-}, one titb, one water, and one and one-forth DMF guest molecules (Fig. S2 in Supplementary data).

As shown in Fig. 1, both M1 and M2 (M = Co for **1**, Zn for **2**, Cd for **3**) centers adopt the highly distorted tetrahedral coordination geometries, coordinated by two O atoms from two different L^{3-}, and two N atoms from two different titb ligands. The M–O interatomic distances range 1.959(4)–1.995(3), 1.943(2)–1.978(2), 2.179(9)–2.293(5) Å for **1** (Co), **2** (Zn), and **3** (Cd), respec-

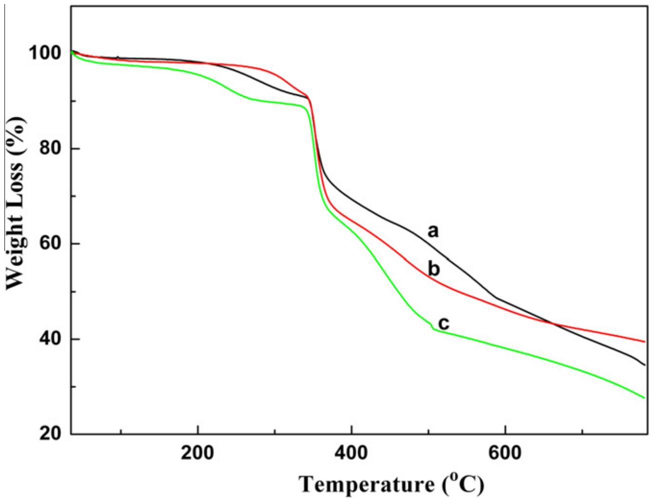

Fig. 3. TGA profiles under nitrogen for (a) **1**, (b) **2**, and (c) **3**.

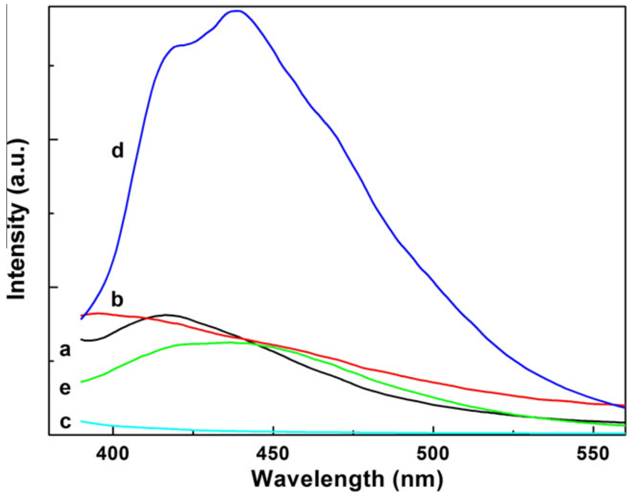

Fig. 4. Emission spectra (excited at 368 nm) of (a) H_3L, (b) titb, (c) **1**, (d) **2**, and (e) **3** at room temperature.

tively, consistent with those reported for other respective metal complexes [10–12]. The M–N bonds are within normal ranges [13–15], with interatomic distances ranging 1.997(4)–2.045(4), 1.989(2)–2.047(2), and 2.204(7)–2.281(6) Å for **1** (Co), **2** (Zn), **3** (Cd), respectively.

The L^{3-} ligand adopts a *cis*,*trans*,*trans*-conformation with its two benzoxylate rings on one side of the plane of the center benzene ring and the third on the other side (Fig. 1). Each L^{3-} ligand is in a slightly distorted trigonal coordination geometry, coordinating via its O-donor atoms to three metal ions in a monodentate mode. The angles between three arms of the L^{3-} ligand range 109.39(4)–127.24(5)° (**1**), 111.99(2)–124.94(3)° (**2**), 105.16(7)–130.6(1)° (**3**), respectively. Meanwhile, the titb ligand also adopts a *cis*,*trans*,*trans*-conformation, but in a highly distorted trigonal coordination geometry. The angles between three arms of the titb ligand range 109.39(4)–127.24(5)° (**1**), 111.99(2)–124.94(3)° (**2**), 105.16(7)–130.6(1)° (**3**), respectively. Each titb ligand coordinates to three metal ions by its N-donor atoms.

The three title compounds are 3D frameworks built from 2D sheets interwoven by 1D chains. As shown in Fig. 2a and Fig. S3 in Supplementary data, each 1D chain is made of 3-connecting titb ligands and 2-connecting M ions. It consists of two parallel 1D –titb–M–titb– single chains inter-connected by M ions to form an edge-sharing 4-membered ring chain with V-shaped cavities. Each 2D sheet, on the other hand, is made of 3-connecting L^{3-} ligands and 2-connecting M ions, as shown in Fig. 2b and Fig. S4 in Supplementary data. It consists of two sets of 1D –L–M–L– single chains, one of which includes parallel chains running along the (1 1 0) direction and the other contains parallel chains running along the (1 −1 0) direction. The two sets of single chains are linked by 2-connecting M ions to form a diamond-shaped 2D sheet in the *ab* plane. The 2D sheets are 3-fold interpenetrated to form a layer, which is then stacked along the *c*-axis and overlapped with each other to form a 3D van der Waals network. The 3D framework of the title compounds is then formed by connecting 2D sheets in the van der Waals network with 1D chains running along the *b*-axis via sharing M ions (Fig. 2c). This gives rise to an open framework with 1D elliptical channels running along the *b*-axis, inside which the disordered guest water and DMF molecules reside. PLATON [9] calculations show that the guest accessible volumes comprises 17.3%, 16.6%, and 19.4% of the unit cell volumes for compounds **1**–**3**, respectively. However, attempts to remove the guest molecules without destroying the framework have failed as indicated by PXRD studies, probably because the openings of the channels are too small (ca. 9.5 × 3.1 $Å^2$ in diameters).

From a topological point of view, the three compounds are four-nodal 3D frameworks constructed from two 4-connecting metal, and two 3-connecting L^{3-} and titb nodes, in which metal atoms and the centers of the ligands define the vertices and the ligand arms define the edges. The 4-connecting M nodes have a short point symbol of {8^5;10} and {8^3;10^2;12} for M1 and M2, respectively, while the 3-connecting ligand nodes have the same point symbol of {8^3} but with different extended point symbols of [8(2).8(2).8(2)] for L^{3-} and [8(2).8(3).8(3)] for titb ligand (Fig. S5 in Supplementary data). This gives rise to a 4-nodal (3,3,4,4) net with stoichiometry of $(3\text{-c})_4(4\text{-c})_3$, as calculated by TOPOS program [16].

3.3. Thermal studies

To study the framework stability of compounds **1**–**3**, thermogravimetric analyses (TGA) were carried out. As shown in Fig. 3, compounds **1**–**3** exhibited similar thermal decomposition behaviors. The losses of guest water molecules occurred before *ca.* 110 °C with the weight losses of 1.1%, 1.7%, and 2.4% (calculated 1.6%, 1.6%, 1.5%) for **1**–**3**, respectively. The guest DMF molecules started to vaporize between ca. 110 and ca. 340 °C with the weight losses of 7.9%, 8.1%, and 9.6% (calculated 8.0%, 8.0%, and 7.5%) for **1**–**3**, respectively. From ca. 340 to ca. 490 °C, compounds **1**–**3** lost its ligand titb as a result of thermal decomposition with a weight loss of 29.9%, 30.6%, and 29.0% (calculated 31.8%, 31.5%, and 29.7%), respectively. Above ca. 490 °C, the thermal decomposition of L began with the final residues unknown.

3.4. Photoluminescent properties

Considering d^{10} metal complexes usually exhibit excellent luminescent properties [17], the photoluminescent properties of the three compounds were investigated. The solid state UV absorption spectra of the compounds were recorded at room temperature (Fig. S6 in Supplementary data), which show all the three compounds exhibited absorption bands below 300 nm, likely due to the $\pi \cdots \pi^*$ transitions of the aromatic rings [18]. In addition, compound **1** showed absorption bands from 400 to 650 nm, owing to the open-shelled d^7 electron transitions of Co(II) ion. The room-temperature solid state photoluminescent spectra of the three compounds together with those of titb and H_3L ligands are shown in Fig. 4. Free ligand H_3L displayed weak, broad photoluminescence emissions with a center at ca. 420 nm upon excitation at 368 nm, while the titb ligand showed very weak emissions with a center at 400 nm. These emissions can be attributed to the $\pi\cdots\pi^*$ transitions of the aromatic rings. On the other hand, both compounds **2** and **3** with d^{10} metal centers exhibited fluorescence emissions upon excitation at $\lambda_{ex} = 368$ nm, while **1** with d^7 cobalt(II) has no photoluminescent emission. A strong, broad blue emission with the maximum at ca. 438 nm and a shoulder at ca. 420 nm were observed for **2,** and a weak, broad blue emission band with a center at ca. 436 nm and a shoulder at ca. 420 nm were observed for **3**. These emissions could be attributed to a ligand-centered excited state with involvement of metal-to-ligand charge transfers [17–19]. In comparison with the free ligands, the emissions in compounds **2** and **3** are red-shifted, which could be probably due to the decreased energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the ligands when coordinating to the metal ions. In addition, compound **2** showed much intense emissions compared with free ligands, which may be attributed to the chelation of the ligands to the metal centers. The chelation enhances the "rigidity" of the ligands and thus reduces the loss of energy through a radiationless pathway [17–19]. The weaker emissions in compound **3** in comparison with **2** could be attributed to the heavy atom effect of Cd.

4. Conclusions

By using flexible tripod multidentate 4,4′,4″-(((2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene))tris(oxy))tribenzoic acid (H_3L) and 1,3,5-tri(imidazo-1-ylmethyl)-2,4,6-trimethylbenzene (titb) ligands, we have successfully synthesized three new coordination polymers $[M_3L_2(\text{titb})_2]\cdot 2H_2O\cdot 2.5DMF$ (M = Co,**1**; Zn, **2**; Cd, **3**). The three compounds are isomorphous and possess a novel (3,3,4,4)-node open-framework structure. The use of a secondary ligand titb resulted in the formation of 3D frameworks with interesting structural topology. The syntheses of **1**–**3** suggest the possibilities to prepare more new coordination polymers by using two or more co-ligands.

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Appendix A. Supplementary material

CCDC 840932–840934 contains the supplementary crystallographic data for 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. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.06.034.

References

[1] (a) Z.-T. Yu, Z.-L. Liao, Y.-S. Jiang, G.-H. Li, G.-D. Li, J.-S. Chen, Chem. Commun. (2004) 1814;
(b) G.J. Hutchings, C.S. Heneghan, I.D. Hudson, S.H. Taylor, Nature 384 (1996) 341;
(c) S. Liu, C.E. Plecnik, E.A. Meyers, S.G. Shore, Inorg. Chem. 44 (2005) 282.

[2] (a) Y. Ke, D.J. Collins, D. Sun, H.-C. Zhou, Inorg. Chem. 45 (2006) 1897;
(b) J. Yao, Z.-D. Lu, Y.-Z. Li, J.-G. Lin, X.-Y. Duan, S. Gao, Q.-J. Meng, C.-S. Lu, CrystEngComm 10 (2008) 1379.

[3] (a) Z. Guo, H. Wu, G. Srinivas, Y. Zhou, S. Xiang, Z. Chen, Y. Yang, W. Zhou, M. O'Keeffe, B. Chen, Angew. Chem., Int. Ed. 50 (2011) 1;
(b) S. Thushari, J.A.K. Cha, H.H.-Y. Sung, S.S.-Y. Chui, A.L.-F. Leung, Y.-F. Yen, I.D. Williams, Chem. Commun. (2005) 5515.

[4] N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 38 (2005) 176.

[5] H. Wang, Y.-Y. Wang, G.-P. Yang, C.-J. Wang, G.-L. Wen, Q.-Z. Shi, S.R. Batten, CrystEngComm 10 (2008) 1583.

[6] H.K. Liu, W.Y. Sun, H.L. Zhu, K.B. Yu, W.X. Tang, Inorg. Chim. Acta 295 (1999) 129.

[7] SMART, and SADABS, Bruker AXS Inc., Madison, Wisconsin, USA.

[8] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.

[9] (a) A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7;
(b) A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, The Netherlands, 2006.

[10] (a) M. Menelaou, A. Konstantopai, N. Lalioti, C.P. Raptopoulou, V. Psycharis, A. Terzis, C. Mateescu, K. Tsarhopoulos, P. Rigas, A. Salifoglou, Inorg. Chem. 49 (2010) 11449;
(b) S. Su, Zh. Guo, G. Li, R. Deng, S. Song, C. Qin, C. Pan, H. Guo, F. Cao, S. Wang, H. Zhang, Dalton Trans. 39 (2010) 9123;
(c) Y. Gong, Y. Zhou, J. Li, R. Cao, J. Qin, J. Li, Dalton Trans. 39 (2010) 9923.

[11] (a) H.-Y. Liu, H. Wu, J.-F. Ma, Y.-Y. Liu, B. Liu, J. Yang, Cryst. Growth Des. 10 (2010) 4795;
(b) G.-Q. Kong, C.-D. Wu, Cryst. Growth Des. 10 (2010) 4590;
(c) X.-X. Zhou, H.-C. Fang, Y.-Y. Ge, Z.-Y. Zhou, Z.-G. Gu, X. Gong, G. Zhao, Q.-G. Zhan, R.-H. Zeng, Y.-P. Cai, Cryst. Growth Des. 10 (2010) 4014.

[12] (a) C. Ji, L. Huang, J. Li, H. Zheng, Y. Li, Z. Guo, Dalton Trans. 39 (2010) 8240;
(b) R. Ferreiros-Martinez, D. Esteban-Gomez, A. Blas, C. Platas-Iglesias, T. Rodriguez-Blas, Inorg. Chem. 48 (2009) 11821;
(c) L.-F. Ma, L.-Y. Wang, J.-L. Hu, Y.-Y. Wang, G.-P. Yang, Cryst. Growth Des. 9 (2009) 5334;
(d) L.-L. Liang, S.-B. Ren, J. Zhang, Y.-Z. Li, H.-B. Du, X.-Z. You, Dalton Trans. 39 (2010) 7723.

[13] (a) D. Lassig, J. Lincke, J. Griebel, R. Kirmse, H. Krautscheid, Inorg. Chem. 50 (2011) 213;
(b) Y. Ma, X.-B. Li, X.-C. Yi, Q.-X. Jia, E.-Q. Gao, C.-M. Liu, Inorg. Chem. 49 (2010) 8092;
(c) L.-F. Ma, Q.-L. Meng, L.-Y. Wang, B. Liu, F.-P. Liang, Dalton Trans. 39 (2010) 8210.

[14] (a) M.-L. Cao, J.-J. Wu, J.-J. Liang, B.-H. Ye, Cryst. Growth Des. 10 (2010) 4934;
(b) H.-B. Xu, Y.-T. Zhong, W.-X. Zhang, Z.-N. Chen, X.-M. Chen, Dalton Trans. 39 (2010) 5676;
(c) T.D. Keene, I. Zimmermann, A. Neels, O. Sereda, J. Hauser, M. Bonin, M.B. Hursthouse, D.J. Price, S. Decurtins, Dalton Trans. 39 (2010) 4937.

[15] (a) J.-S. Hu, Y.-J. Shang, X.-Q. Yao, L. Qin, Y.-Z. Li, Z.-J. Guo, H.-G. Zheng, Z.-L. Xue, Cryst. Growth Des. 10 (2010) 4135;
(b) S.-M. Fang, Q. Zhang, M. Hu, X.-G. Yang, L.-M. Zhou, M. Du, C.-S. Liu, Cryst. Growth Des. 10 (2010) 4773;
(c) S.-Q. Zang, R. Liang, Y.-J. Fan, H.-W. Hou, T.C.W. Mak, Dalton Trans. 39 (2010) 8022.

[16] (a) V.A. Blatov, A.P. Shevchenko, V.N. Serezhkin, J. Appl. Crystallogr. 33 (2000) 1193;
(b) V.A. Blatov, L. Carlucci, G. Ciani, D.M. Proserpio, CrystEngComm 6 (2004) 378.

[17] (a) V.W.W. Yam, K.K.W. Lo, Chem. Soc. Rev. 28 (1999) 323;
(b) L.-L. Liang, S.-B. Ren, J. Zhang, Y.-Z. Li, H.-B. Du, X.-Z. You, Cryst. Growth Des. 10 (2011) 1307;
(c) S.-B. Ren, L. Zhou, J. Zhang, Y.-Z. Li, H.-B. Du, X.-Z. You, CrystEngComm 11 (2009) 1834.

[18] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, third ed., Springer, Berlin, 2006.

[19] (a) S.L. Zheng, J.H. Yang, X.L. Yu, X.M. Chen, W.T. Wong, Inorg. Chem. 43 (2004) 830;
(b) M.D. Allendorf, C.A. Bauer, R.K. Bhakta, R.J.T. Houk, Chem. Soc. Rev. 38 (2009) 1330.