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Syntheses, structures and photoluminescent properties of Zn(II)/Co(II) coordination polymers based on flexible tetracarboxylate ligand of 5,5'-(butane-1,4-diyl)-bis(oxy)-di isophthalic acid



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ABSTRACT

Three new mixed-ligand metal-organic frameworks based on 5,5'-(butane-1,4- diyl)-bis(oxy)-diisophthalic acid and transitional metal cations with the help of two ancillary bridging N-donor pyridyl and imidazole linkers, $[Zn(L)_{0.5}(4,4'-bpy)] \cdot 2(H_2O)$ (1), $[M(L)_{0.5}(bib)] \cdot 4(H_2O)$ (M = Zn (2), Co (3)), (4,4'bpy=4,4'-bipyridine, bib=1,4-bis (1H-imidazol-1-yl)-butane), have been synthesized under solvothermal conditions. Their structures and properties were determined by single-crystal and powder X-ray diffraction analyses, IR spectra, elemental analyses and thermogravimetric analyses (TGA). Compounds 1–3 display a 3D 3-fold interpenetrated frameworks linked by the L⁴⁻ ligands, ancillary N-donor linkers and the free water molecules in the crystal lattice. Topological analysis reveals that 1–3 are a (4,4)connected **bbf** topology net with the (6⁴ · 8²)(6⁶) topology. The effects of the L⁴⁻ anions, the N-donor ligands, and the metal ions on the structures of the coordination polymers have been discussed. Furthermore, luminescence properties and thermogravimetric properties of these compounds were investigated.

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1. Introduction

In recent years, the metal-organic frameworks (MOFs) has attracted considerable attention not only for their intriguing architectures [1,2] and bewitching topological nets [3,4], but also for their potential applications in gas storage substances [5,6], luminescent materials [7–9], magnetism substances [10–12], catalysis [13,14], nonlinear optics [15–17] and so on. The current research in the fields of MOFs has promoted the design of a target structure with specific properties and functions [18,19]. Therefore, the investigation of the relationship between the topological structure and the conformation of ligands is a challenging task for chemists working on creating fascinating inorganic function compounds, and it is necessary to research some properties of the resulting coordination polymers.

Recently, flexible multi-carboxylate ligands with two or more aromatic rings were used to build interesting coordination frameworks [20–23], especially some flexible frameworks with

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http://dx.doi.org/10.1016/j.jssc.2016.05.023 0022-4596/© 2016 Elsevier Inc. All rights reserved. functional organic groups [24–26]. The flexibility of the organic flexible multicarboxylate ligands provide the constructed functional MOFs tunable structures, which further have affected the properties [27–30]. Moreover, when the ancillary ligands are introduced to build the frameworks, the final structures have greater tunability [31-33]. The ancillary bridging imidazole or pyridine linkers holding different lengths and flexibilities have great effects on the final architectures and topology as well as coordination modes and molecular conformations of multicarboxylate acids [34–36]. Therefore, preparing novel functional MOFs using such kinds of flexible multicarboxylate and ancillary bridging imidazole or pyridine linkers should be attempted. In this article, we have chosen the flexible multicarboxylic acid, namely, 5,5'-(butane-1,4diyl)-bis(oxy)-diisophthalic acid (H₄L), and two ancillary bridging imidazole or pyridine linkers, namely, 4,4-bipyridine (4,4'-bpy) [37–40] and 1,4-bis (1H-imidazol-1-yl)-butane (bib) [41–43]. Herein, three 3D 3-fold interpenetrated frameworks were obtained through a mix ligand strategy under similar solvothermal reactions, $[Zn(L)_{0.5}(4,4'-bpy)] \cdot 2(H_2O)$ (1), $[M (L)_{0.5}(bib)] \cdot 4(H_2O)$ (M = Zn (2), Co (3)) (Fig. S1, S2). Moreover, the syntheses, crystal structures, topologies, thermal stabilities and photoluminescent properties are reported in this paper.

2. Experimental section

2.1. Materials and general methods

The ligands H₄L and bib were prepared according to the literature [44-47]. Other chemicals were obtained from commercial sources and used without further purification, such as K₂CO₃ (A.R., $\geq 99\%$), $Zn(NO_3)_2 \cdot 6H_2O$ (A.R., $\geq 99\%$) $Co(NO_3)_2 \cdot 6H_2O$ (A. R., \geq 99%) NaOH (A.R., \geq 99%), 4,4'-bpy (A.R., \geq 99%), CH₃OH (A.R., \geq 99%), 5-hydroxy-isophthalic acid diethyl ester (A.R., \geq 98%), 1,4dichlorobutane (A.R., \geq 98%), and so on. Fourier Transform Infrared Spectra (FT-IR) were measured on Nexus-670FT spectrum instrument at the range of $4000-400 \text{ cm}^{-1}$ using KBr pellets. Compounds 1-3 were examined by and TEM (FEI Tecnai G2 F20 200 kV) (Fig. S6), and compounds 1 and 2 were examined by SEM (Hitachi S4800 SEM and Bruker QUANTAX 200 EDX) at accelerating voltage up to 10 KV (Fig. S7). The Elemental analyses of C, H, and N were carried out on a Perkin-Elmer 2400 CHNS elemental analyzer. Thermogravimetric analyses were performed on a STA409pc thermogravimetric analyzer from 30 to 700 °C at a heating rate 10 °C min⁻¹ under air atmosphere. Powder X-ray diffractometer (PXRD) was performed on a X'Pert PRO (PW3071/ xx Bracket) diffractometer with Cu K α radiation (λ =1.5406 Å). UV-vis spectra were measured on a TU-1901 UV-vis spectrophotometer in the solid state at room temperature. Solid-state photoluminescent spectra were measured on an Edinburgh FLS920 fluorescence spectrometer at room temperature Scheme 1.

2.2. Synthesis

2.2.1. Synthesis of 5,5'-(butane-1,4-diyl)-bis(oxy)-diisophthalic acid (H₄L)

5-hydroxy-isophthalic acid diethyl ester (2.38 g, 10 mmol) and anhydrous K₂CO₃ (3 g, 22 mmol) were put in a 50 mL round bottom flask under nitrogen atmosphere and treated with 20 mL of dry DMF. The reaction mixture was stirred for 1 h at 70 °C followed by addition of 1,4-dichlorobutane (0.64 g, 5 mmol), and the resulting mixture was stirred for 20 h in an oil-bath at 80 °C. At the end of the period, the solution was allowed to cool to room temperature and then poured into ice-water (100 mL) with vigorous stirring that afforded a white precipitated (tetraethyl 5,5'-(butane-1,4-diyl)-bis(oxy)-diisophthalate) which was collected by filtration, washed with water three times, and dried in air. Then the tetraethyl 5,5'-(butane-1,4-diyl)-bis(oxy) diisophthalate (2.65 g, 5 mmol) was hydrolyzed by refluxing it with 95% ethanol solution for 1 h followed by addition of NaOH (0.8 g, 20 mmol) and the reaction mixture was refluxed for 15 h in an oil-bath. Finally, the resulting solution was poured into ice-water (100 mL) with vigorous stirring and was acidified carefully with 4 M HCl to obtain a white precipitate. After keeping it overnight in the freezer, the white solid was collected by filtration and dried at air. Yield: 2.02 g (96%). FT-IR (KBr, cm⁻¹): 3096.35(s), 2961(s), 1697(s), 1597(m), 1462(m), 1402(m), 1273(m), 1126(w), 1051(m), 909(w), 759(w), 668(w), 530(w), 479(w).

2.2.2. Synthesis of $[Zn(L)_{0.5}(4,4'-bpy)] \cdot 2(H_2O)$ (1)

A solution of Zn(NO₃)₂• (H₂O)₆ (0.0145 g, 0.05 mmol) in CH₃OH (0.5 mL) and a solution of 4,4'-bpy (0.0096 g, 0.05 mmol) in CH₃OH (0.5 mL)were added with stirring to a solution of H₄L (0.0104 g, 0.025 mmol) in DMF (1 mL), then 2 mL H₂O was added to this mixture solution. After the mixture solution was stirred for 20 min, 2 drops of 1 mol/L HNO₃ solution was added to this reaction solution, and then the reaction mixture solution were stirred for another 20 min. The colorless solution had been obtained and then sealed in a 5 mL sealing glass vessel. The vessel was heated to 80 °C and held at that temperature for 48 h, then slowly cooling to room temperature, block crystals of 1 for single crystal X-ray diffraction were obtained by filtration and dried at air. yield:80%. Anal. Caled.(%): C 52.09, H 4.08, N 6.02. Found (%): C 52.62, H 4.17, N 5.94. EDX El. AN. (wt%): Zn 11.41, O 26.07, C 54.95, N 7.57. (at%): Zn 2.52, O 23.55, C 66.12, N 7.81. FT-IR (KBr, cm⁻¹): 3455(s), 3101(w), 2951(w), 2907(w), 2870(w), 1615(s), 1570(s), 1491(m), 1453(m), 1411(s), 1377(s), 1351(s), 1317(m), 1259(m), 1221 (m), 1121(m), 1070(m), 1048(s), 923(w), 874(w), 816(s), 777(s), 731 (s), 638(m), 543(w), 469(w).

2.2.3. Synthesis of $[M(L)_{0.5}(bib)] \cdot 4(H_2O)$ (M = Zn(2), Co(3))

The synthesis of compound 2 and 3 was similar to that of compound 1 except that 4,4'-bpy (0.0096 g, 0.05 mmol) was replaced by bib (0.0095 g, 0.05 mmol) for **2** and **3**, and $Zn(NO_3)_2$. $(H_2O)_6$ (0.0145 g, 0.05 mmol) was replaced by $Co(NO_3)_2 \cdot (H_2O)_6$ (0.0145 g, 0.05 mmol) for 3. For compound 2, Anal. Caled. (%): C: 47.23, H: 5.25, N:11.01. Found(%): C: 47.42, H: 5.12, N: 11.08. EDX El. AN. (wt%): Zn 9.59, O 23.89, C 52.56, N 13.96. (at%): Zn 2.09, O 21.29, C 62.40, N 14.21. FT-IR (KBr, cm⁻¹): 3469(s), 3131(m), 2949 (m), 2872 (m), 1667(m), 1621(s), 1575(s), 1529(m), 1451(m), 1404 (s), 1375(s), 1346(s), 1261(m), 1237(m), 1098(s), 1052(s), 952(m), 923(w), 843(w),803(m), 729(m), 657(m), 627(w), 551(w), 426(w). For compound 3, Anal. Caled. (%): C: 47.11, H: 5.32, N:11.11. Found (%): C: 47.40, H: 5.06, N: 11.09. FT-IR (KBr, cm⁻¹): 3428(s), 3130 (m), 2949(m), 2872 (w), 1667(w), 1617(m), 1560(s), 1453(m), 1408 (m), 1376(s), 1351(s), 1262(m), 1235(m), 1097(s), 1052(s), 950(m), 923(w), 840(w), 806(m), 781(m), 730(m), 659(m), 627(w), 543(w).

3. X-ray crystallography

Single-crystal X-ray data for compound **1–3** were collected on an Bruker Smart Apex II CCD diffractometer using graphite monochromated Mo K α radiation (λ =1.71073 Å) at room temperature. Empirical absorption correction was applied. The structures were solved by direct methods and refined by the full-matrix least-squares methods on F^2 using the SHELXTL-97 software [48]. All non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were placed in the calculated positions. Pertinent crystallographic data collection and parameters are collated in Table 1. Selected bond lengths and angles are collated in Table S1. Topological analyses of the compounds were performed by using the TOPOS software [49]. CCDC-1444200, CCDC-1471013 and CCDC-1444201 contain the supplementary crystallographic data for compound **1**, **2** and **3**, respectively. These data can be obtained free of charge from the Cambridge crystallographic data centre via



Scheme 1. Synthesis of 5,5'-(butane-1,4-diyl)-bis(oxy)diisophthalic acid (H₄L).

Table 1							
Crvstal d	data	and	structure	refinement	for	compound	1-3.

Compound	1	2	3
Empirical formula Formula weight T (K) Crystal system space group $a (\hat{A})$ $b (\hat{A})$ $c (\hat{A})$ $a (^{\circ})$ $\beta (^{\circ})$ $\gamma (^{\circ})$ $V (\hat{A}^{3})$ Z Calculated density (Mg/m ³) $M (mm^{-1})$ F(000) θ range for data collection($^{\circ}$) Reflections collected / unique R(int)	$\begin{array}{c} {\bf 1} \\ \hline \\ C_{20}H_{15}N_2O_7Zn \\ 460.71 \\ 293(2) \\ \\ Monoclinic \\ P2_1/c \\ 7.4085(10) \\ 15.002(2) \\ 17.9311(19) \\ 90 \\ 107.583(5) \\ 90 \\ 107.583(5) \\ 90 \\ 1899.8(4) \\ 4 \\ 1.611 \\ 1.340 \\ 940 \\ 1.81-28.39 \\ 13765/4737 \\ 0.0302 \\ \end{array}$	2 $C_{20}H_{21}N_4O_9Zn$ 526.78 293(2) Monoclinic $P_{2_1/c}$ 8.045(4) 17.549(8) 18.014(7) 90 108.093(18) 90 2417.5(19) 4 1.447 1.071 1084 1.66–27.64 15532/5567 0.0611	$\begin{array}{c} 3 \\ \hline \\ \mathbf{C}_{20}\mathbf{H}_{21}\mathbf{CoN_4O_9} \\ 520.34 \\ 293(2) \\ \mathbf{Monoclinic} \\ P2_1/c \\ 8.0319(8) \\ 17.9407(19) \\ 17.9407(19) \\ 17.9318(17) \\ 90 \\ 108.644(4) \\ 90 \\ 2448.3(4) \\ 4 \\ 1.412 \\ 0.755 \\ 1072 \\ 3.18-28.42 \\ 64579/6081 \\ 0.0358 \\ \end{array}$
Data / restraints / parameters Goodness-of-fit on F^2 $R_1, wR_2 [I > 2\sigma(I)]^a$ $R_i wR_2$ (all data)	4737/0/261 1.046 0.0715, 0.2147 0.0910, 0.2298	5567/0/307 1.045 0.0820, 0.2289 0.1035, 0.2466	6081/4/307 1.067 0.0903, 0.2549 0.1077, 0.2806

^a $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|, \ w R_2 = \Sigma [w (F_0^2 - F_c^2)^2] / \Sigma [w (F_0^2)^2]^{1/2}.$

www.ccdc.cam.ac.uk/data_request/cif.

4. Result and discussion

4.1. Synthesis and general characterization

All crystallization of compounds **1–3** were synthesized under similar reaction conditions by solvothermal methods, by changing metal ions and solvent, the single crystals suitable for the singlecrystal X-ray diffraction analysis were finally obtained. For compounds **1–3**, the measured PXRD patterns closely match the simulated patterns generated from the results of Single-Crystal Diffraction data, indicating pure phases of 1–3 products (Figs. 5–7). The IR spectra of H₄L and compound **1–3** also show characteristic the asymmetric and symmetric stretching vibrations of the carboxylate groups are observed in the ranges of 1597–1621 and 1346–1402 cm⁻¹, respectively [50,51] (Fig. S3).

4.2. Structure descriptions

4.2.1. Description of crystal structure of compound 1

Single-crystal X-ray structure determination of compound **1** reveals a 3-fold interpenetrated three-dimensional (3D) framework that crystallizes in the monoclinic space group *P21/c*. The relevant asymmetric unit consists of one crystallographically independent Zn(II) ion in a distorted tetrahedral geometry, a half of coordinated L^{4-} ligand, one coordinated 4,4'-bpy and two lattice water molecules. The coordination geometry around the Zn(II) metal ion is found to be distorted tetrahedral.

The tetrahedral [ZnN₂O₂] geometry around the Zn(II) metal ion is comprised of two oxygen atoms from two different L^{4-} ligand units, and two nitrogen atoms from two different 4,4'-bpy ligands (Fig. 1(a)). The bond distances of Zn-O and Zn-N are in the range 1.952–2.079 Å and the bond angles around the Zn (II) centre are in the range 95.38– 132.51°. In the compound 1, on the one hand the 4,4'-bpy ligand connects two tetrahedral [ZnN₂O₂] centres in the 1D metal-pyridyl chains through the N atoms of the pyridyl rings with a separation of 10.9588 Å resulting in the formation of a V-shaped chain as shown in Fig. 1(b). In the 1D metal-pyridyl chain, the dihedral angle between two pyridyl rings is 13.022°. Therefore, two pyridyl rings of 4,4'-bpy are not coplanar. On the other hand each L^{4-} ligand connects to four $[ZnN_2O_2]$ tetrahedrons at four orientational positions by a μ_1 - η^1 : η^0 monodentate modes forming a 2D network, characterized by the C_{phenyl} -O...O- C_{phenyl} torsion angle of 180° in the central part of the L^{4-} ligand, and the torsion angle of C_{phenyl} -O...CH₂-CH₂, $O-CH_2...CH_2-CH_2, \quad CH_2-CH_2...CH_2-CH_2, \quad CH_2-CH_2...CH_2-O, \quad \text{and} \quad$ CH₂-CH₂... O-C_{phenyl} is 178°, 179°, 180°, 179°, and 178° in the L⁴⁻ ligand, and the dihedral angle between two phenyl rings of L^{4-} is 0° , hence all oxygen and carbon atoms of the L⁴⁻are mainly coplanar (Fig. 1(c)). Finally, the 2D network structures formed by \tilde{L}^{4-} ligand and [ZnN₂O₂] tetrahedra were interconnected by the 1D metal-pyridyl chains to form a 3D framework with channels $(15.0977 \text{ Å} \times 22.2255 \text{ Å})$ (Fig. 2(a)). The 3D grid allows each frameworks to be penetrated by two other independent frameworks to form the interesting 3-fold interpenetrating 3D frameworks, with isolated water molecules occupying the neutral channels (Fig. 2(b)).

A better insight into the nature of compound **1** can be provided by a topology analysis. The extension of the structure of **1** into a (4,4)-connected **bbf** topology net [52–54] is accomplished by binding two L^{4–} ligands and two bib ligands to the four-connected Zn (II) nodes. The L^{4–} ligands can be simplified as a four-connected node, the bib ligands are taken as linkers, and the 3D structure can be simplified as a 4-connected net with the Schläfli symbol of (6⁴ · 8²)(6⁶) (Fig. 2(c)). The topological analysis of **1** reveals that the individual 3D framework has spacious space, it allows another two identical 3D frameworks to interpenetrate it in a normal mode giving a 3-fold interpenetrated 3D to 3D frameworks (Fig. 2(d)).

4.3. Description of crystal structure of compound 2 and 3

When the auxiliary ligand was changed from rigid 4,4'-bpy to flexible bib used in the preparation for **2** and **3**. The results of Single-crystal X-ray structure determination show that the structure of compound **2** are similar to that of compound **3**, so we describe the structure of the compound **3** as an example, compound **3** with a 3D framework crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit contains one independent Co(II) ion, a half of coordinated L^{4–} ligand, one coordinated bib and four lattice water molecules. As shown in Fig. **3**(a), the Co (II) metal ion



Fig. 1. (a) Molecular diagram representing the coordination environment around the Zn(II) metal ions in **1**. (b) 1D V-shaped metal-pyridyl chain formed by tetrahedral $[ZnN_2O_2]$ geometry and 4,4'-bpy in **1**. (c) The 2D network structure formed by L^{4-} ligands and $[ZnN_2O_2]$ tetrahedra.

is four-coordinated by two oxygen atoms from two different L^{4-} ligand units, and two nitrogen atoms from two bib ligands respectively. The bond distances of Co-O and Co-N are in the range 1.963–2.024 Å and the bond angles around the Co (II) centre are in the range 97.56–124.01°. In the compound **3**, the N-donor imidazolyl ligand bib occurs in one kind of coordination mode.

The bib ligand connects two tetrahedral $[CoN_2O_2]$ centres in the 1D metal-imidazolyl chains through the N atoms of the imidazolyl rings, creating a separation of 13.61 Å to form a V-shaped chain as shown in Fig. 3(b). In the 1D structure, the flexible bib exhibits *anti-gauche-anti* conformation and the dihedral angle between two imidazolyl rings is 62.015°. In compound **3**, each L^{4–} ligand connects to

four Co atoms at four angles in a μ_1 - η^1 : η^0 monodentate modes and connects the [CoN₂O₂] tetrahedra in a 2D network conformation, characterized by the C_{phenyl}-O...O-C_{phenyl} torsion angle of 180° in the central part of the L⁴⁻ ligand and the dihedral angle between two phenyl rings is 0°, but the torsion angle of C_{phenyl}-O...CH₂-CH₂. O-CH₂...CH₂-CH₂. CH₂-CH₂...CH₂-CH₂. CH₂-CH₂...CH₂-O, and CH₂-CH₂...O-C_{phenyl} is 157.94°, 83.55°, 180°, 83.55°, and 157.94°, respectively. The two phenyl rings of L⁴⁻ is coplanar, but a great changes have taken place in the -(CH₂)₄- of L⁴⁻ ligand (Fig. 3(c)). In this compound, the 2D network structure formed by L⁴⁻ ligand and [CoN₂O₂] tetrahedra was linked by the 1D metal-imidazolyl chains to form a 3D framework with channels (18.1567 Å × 24.0957 Å) (Fig. 4



Fig. 2. (a) 3D frameworks of **1** formed by L⁴- ligand, [ZnN₂O₂] tetrahedra and 4,4'-bpy. (b) 3-fold interpenetrating 3D frameworks of **1**. (c) the individual 3D topos structure of **1** with the Schläfli symbol of (6⁴ · 8²)(6⁶). (d) the 3D 3-fold interpenetrated topos structure for **1**.

(a)). Longer length of co-ligand (bib) in compound **2** and **3** than that of co-ligand (bpy) in compound **1** resulted in that compound **2** and **3** exhibit larger channels of individual 3D frameworks in size (18.1567 Å × 24.0957 Å) than those (15.0977 Å × 22.2255 Å) of compound **1**. Correspondingly, compound **2** and **3** with larger channels size accommodate more H₂O molecules than compound **1**. The 3D grid allows each frameworks to be penetrated by two other independent frameworks to form the interesting 3D 3-fold interpenetrating frameworks with isolated water molecules occupying the neutral channels (Fig. 4(b), S5).

From the view of topology, by treating the Co (II) atoms and the L^{4-} ligands as a four-connected node, the bib ligands are taken as linkers, the 3D single framework can be simplified as a (4,4)-connected **bbf** topology net, like compound **1**, with the Schläfli symbol of $(6^4 \cdot 8^2)(6^6)$ (Fig. 4(c)). The topological analysis of **3** reveals that the 3D individual framework have spacious space, it allows another two identical 3D single frameworks to interpenetrate it in a normal mode giving a 3-fold interpenetrated 3D to 3D framework (Fig. 4(d)).

4.4. PXRD studies and thermogravimetric analyses

The simulated of single X-ray diffraction data and experimental PXRD patterns of compounds 1–3 obtained at room temperature are shown in (Figs. 5–7). Rietveld full-profile fitting results based on the structural parameters of compounds 1–3 indicate the positions of the major diffraction peaks are in agreement with those calculated single crystal data (Figs. S9–S11). The difference intensities between simulated and experimental patterns may be due to the variation in preferred orientation of crystalline powder samples during collection of the experimental XRD data.

Thermogravimetric analyses (TGA) and Differential thermal

gravity (DTG) for the H₄L and the crystalline samples of compounds 1-3 were recorded under air atmosphere in the temperature range of 30–700 °C (Fig. 8, S8). The TGA curves of all three compounds have released the lattice water before 350 °C, reflecting the fact that the lattice water in the framework is unstable and easy to separate from framework at low temperatures. The first weight losses corresponding to the release of water molecules are observed before 365 °C for compound 1 (observed 9.12%, calculated 7.83%), 323 °C for compound 2 (observed 11.36%, calculated 13.69%), 325 °C for compound 3 (observed 16.34%, calculated 13.84%). The anhydrous compositions begin to decompose at 365 °C and ending above 490 °C for 1, at 323 °C and ending above 497 °C for **2**, and at 325 °C and ending above 417 °C for **3**, due to the decomposition of the organic part of the framework. The remaining weight may correspond to the formation of ZnO for compound 1 (observed 18.14%, calculated 17.72%) and compound 2 (observed 20.12%, calculated 15.39%), CoO for compound 3 (observed 15.63%, calculated 14.42%).

4.5. UV-vis absorption spectra of compound 1-3

The UV–vis spectra of compound **1–3** together with the free H₄L ligand in the solid state at room temperature were measured. The Kubelka-Munk functions [55–57] converted from the diffuse reflectance data were plotted in Fig. 9. The H₄L exhibits strong absorption with a maximum at 316 nm in the range of 280–352 nm, which probably corresponds to the π - π * and n- π * transitions centered on the benzene ring. The absorption of 4,4'-bpy is strong in a similar range with one peak at 290 nm [58,59]. Compared to the free H₄L ligand, compound **1–3** exhibit absorption with maxima at 307 nm, 308 nm, 305 nm, respectively, and the absorption peaks of compounds **1, 2,** and



Fig. 3. (a) Molecular diagram representing the coordination environment around the Co (II) metal ions in **3.** (b) 1D V-shaped metal-imidazoly chain formed by tetrahedral $[CoN_2O_2]$ geometry and bib in **3.** (c) The 2D network structure formed by L⁴⁻ ligand and $[CoN_2O_2]$ tetrahedra.

3 have slightly blue-shifted in the same range. In compound **1**, the absorption peak is more stronger than other compound at 280 nm, which may be attributed to the effect of 4,4'-bpy. In compound **3**, the characteristic absorption bands of UV–vis spectra around 580 nm are correlated with the d-d transitions of tetrahedral coordinated Co^{2+} [60–63].

4.6. Photoluminescence properties

The metal-organic frameworks are promising candidates for applicable photoluminescent materials such as chemical sensors, light emitting diodes, electro-chemical sensors and so on. Although a lot of transition metal ions and rare-earth ions have been used to construct MOFs, the Zn-based MOFs are the most interested transition metal based luminescent MOFs. The d¹⁰ metal ions not only have various coordination numbers and geometries, but also display luminescent properties with functional ligands [64,65]. The photoluminescence properties of compound **1** and **2** together with the free H₄L ligand, were investigated in the solid state at room temperature (Table 2) and depicted in Fig. 10, S4. The photoluminescent spectra of the free ligands show the main peak at 412 nm (λ_{ex} =339) for H₄L, 466 nm (λ_{ex} =390 nm) for 4,4'-bpy [66], 436 nm (λ_{ex} =380 nm) for bib [67–69], respectively, which may be caused by the π^* - π and π^* -n transition. The emission spectra for bands were observed at 452 nm (λ_{ex} =337 nm) for **1**, 401 and 418 nm (λ_{ex} =348 nm) for **2**. As the literature reported, the d¹⁰ configured Zn(II) cations are electrochemically inert, therefore, when coordinated by ligands, they cannot take an electron from the ligand with their 3d-orbitals, nor donate an electron to the ligand [36].



Fig. 4. (a) 3D framework of **3** formed by L^{4-} ligand, $[CON_2O_2]$ tetrahedra and bib. (b) 3-fold interpenetrating 3D framework for **3**. (c) the 3D single topos structure of **3** with the Schläfli symbol of $(6^4 \cdot 8^2)(6^6)$. (d) the 3D 3-fold interpenetrated topos structure for **3**.



Fig. 5. As-synthesized and simulated X-ray diffraction patterns of compound 1.

In comparison to the free ligands, the emission maxima of **1** is redshifted by 40 nm as compared to free H₄L ligand, and close to the free 4,4'-bpy ligand, inferring their emission bands may be assigned to the intra-ligand charge transfer (ILCT), neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) happened. The emission peaks of **2** are close to free H₄L ligand, so the emission bands of **2** can probably be attributed to the intra-ligand charge transfer



Fig. 6. As-synthesized and simulated X-ray diffraction patterns of compound 2.

(ILCT). Experimental results show that compound **3** is non-emissive under similar conditions, indicating the emissions of organic ligands may be quenched completely in the compound, which may be due to the emission quencher of Co (II) in the structure. In term of the structures and emission spectra of compound **1** and **2**, it is inferred that different ligands co-ligands may be an important factor on influencing different luminescent properties of compounds [36].



Fig. 7. As-synthesized and simulated X-ray diffraction patterns of compound 3.



Fig. 8. Thermogravimetric curves of the H₄L and the compounds 1-3.



Fig. 9. UV-vis spectrogram of compounds 1, 2, 3, and free H_4L ligand in the solid state.

5. Conclusions

In summary, we successfully designed and synthesized three coordination polymers based on flexible multicarboxylic acid 5,5'-(butane-1,4-diyl)-bis(oxy)-diisophthalic acid (H₄L), and one rigid ancillary bridging pyridine linkers 4,4' -bipyridine (4,4'-bpy) for **1**, one flexible

Table 2

wavelengths of the emission maxima and excitation (nm) of **1**, **2**, and organic ligands at room temperature.

Ligand /compound	λ_{ex}/nm	$\lambda_{\rm em}/{\rm nm}$
H ₄ L 4.4'-bpv	339 390	412 466
bib	380	436
1	337	452
2	348	418, 401



Fig. 10. Solid-state emission spectra at room temperature for the free H_4L and 1, 2 (slit width = 0.5 nm).

ancillary imidazole linkers 1,4-bis (1H-imidazol-1-yl)-butane (bib) for 2 and 3. These compounds display interesting and versatile coordination features from 3D to 3D parallel entangled frameworks. Topological analysis reveals that 1-3 are 3D (4,4)-connected bbf topology net with the $(6^4 \cdot 8^2)(6^6)$ topology. The adjustable channels size of individual 3D framework is realized by using different lengths of co-ligands from byp to bib with keeping similar architectures of compounds 1-3. In compound 3, the assignment of characteristic absorption bands of UV-vis spectra at 580 nm correlated with the d-d transitions of Co²⁺ ions in field of tetrahedral coordination is confirmed by the result of the single-crystal X-ray structure analysis. The solid-state photoluminescent properties of 1 and 2 were investigated, and the emission bands were assigned to the intra-ligand charge transfer (ILCT), and the different emission wavelength due to the effect of co-ligands. The solid-state thermal stabilities were investigated. The frameworks of 1, 2 and 3 are stable under 350 °C.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2016.05.023.

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