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Synthesis, Crystal Structure and Photoluminescent Property of Metal-Organic Frameworks with Mixed Carboxylate and Imidazole-Containing Ligands[†]

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Three new metal-organic frameworks (MOFs), namely [Zn(tib)(PDC)] (**1**), $[Zn_3(tib)_2(CHDC)_3]\cdot 8H_2O$ (**2**) and $[Zn_3(tib)_2(BTC)_2]\cdot 4.95H_2O$ (**3**) were synthesized by hydrothermal reactions of $ZnCl_2$ with 1,3,5-tris(1-imidazolyl)-benzene (tib) and different carboxylate ligands of 2,6-pyridinedicarboxylic acid (H_2PDC), 1,4-cyclohexanedicarboxylic acid (H_2CHDC) and 1,3,5-benzenetriacetic acid (H_3BTC), respectively. The complexes were characterized by IR, thermogravimetric analysis, single crystal and powder X-ray diffractions. Complex **1** has a binuclear structure, in which one imidazole group of tib is free of coordination, while **2** has three-dimensional (3D) framework with the CHDC-Zn microcycles filled into the tib-Zn 3D net, and **3** is a 2-fold interpenetrating 3D framework with the interconnection of two one-dimensional (1D) chains formed by BTC-Zn and tib-Zn, respectively. The different structures of **1**—**3** are resulted from the distinct carboxylate ligands. In addition, complexes **1**—**3** show obvious emissions at room temperature in the solid state.

Keywords zinc(II) complex, metal-organic framework, crystal structure, photoluminescence

Introduction

Metal-organic frameworks (MOFs) have attracted great attention of chemists in the past decades, not only because of their intriguing structures and topologies, but also due to their potential applications in many fields, such as catalysis, carbon dioxide capture, hydrogen storage, non-linear optics, chemical sensor and so on.[1-3] Meanwhile, the structure of MOFs can be affected by many factors, thus the control synthesis of MOFs with desired structures and properties is always a great challenge for crystal engineering.[4,5] We focus on the design and synthesis of MOFs with imidazole-containing ligands.[6-8] According to the previously reported works, the MOFs based on mixed carboxylate and imidazole-containing ligands usually have fantastic structural characters, since the carboxylate groups are versatile and can have different coordination modes to satisfy the coordination requirements of metal centers.[9,10] At the same time, it also added difficulty to predict the final structure of the MOFs. Thus, further studies are needed to understand the formation and structure of MOFs.

In our previous study, two unprecedented homochiral enantiomers $[Cd(tib)(1,4\text{-}BDC)]\cdot 2H_2O$ (*L* and *R*) and one achiral complex $[Cd_2(tib)(1,4\text{-}BDC)_2(H_2O)]\cdot 2H_2O$ were obtained from one pot reaction with achiral mixed rigid ligands 1,3,5-tris(1-imidazolyl)benzene (tib) and 1,4-benzenedicarboxylic acid (1,4-H_2BDC).[9b] The enantiomers show interesting ferroelectric property and are the first example of helical chain based chiral 3D complex constructed by two rigid ligands *via* huge distortion.[9b] Encouraged by this fantastic result, we chose some other carboxylic acids together with tib ligand to react with Zn(II) salt to construct new MOFs.

In this study, we present three new MOFs, namely [Zn(tib)(PDC)] (**1**), $[Zn_3(tib)_2(CHDC)_3]\cdot 8H_2O$ (**2**) and $[Zn_3(tib)_2(BTC)_2]\cdot 4.95H_2O$ (**3**) with tib and different carboxylic acids of 2,6-pyridinedicarboxylic acid (H_2PDC), 1,4-cyclohexanedicarboxylic acid (H_2CHDC) and 1,3,5-benzenetriacetic acid (H_3BTC), respectively. The complexes are well characterized, and show obvious photoluminescence property at room temperature in

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the solid state.

Experimental

Materials and general methods

All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. The ligand tib was synthesized according to the method reported previously.[8b] FT-IR spectra were recorded in the range of 400—4000 cm^{-1} on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. Thermogravimetric analyses (TGA) were carried out on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of 10 ℃ min^{-1}. Powder X-ray diffraction (PXRD) patterns were obtained on a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα (λ=0.15418 nm) radiation at room temperature. The luminescence spectra for the powdered solid samples were measured at room temperature on an Aminco Bowman Series2 spectrofluorometer with a xenon arc lamp as light source. In the measurements of emission and excitation spectra the pass width is 5 nm. All the measurements were carried out under the same experimental conditions.

Preparation of [Zn(tib)(PDC)] (1)

A mixture of tib (27.6 mg, 0.1 mmol), H_2PDC (16.7 mg, 0.1 mmol), $ZnCl_2$ (27.3 mg, 0.2 mmol) and NaOH (8.0 mg, 0.2 mmol) in H_2O (10 mL) was sealed in a 16 mL Teflon lined stainless steel container and heated at 180 ℃ for 3 d. After cooling to the room temperature, colorless platelet crystals were collected by filtration and washed by water and ethanol several times. Yield: *ca*. 49%. IR (KBr pellet) v: 3348 (m), 1618 (s), 1578 (m), 1396 (m), 1274 (m), 1190 (m), 1018 (m), 785 (m), 741 (m), 696 (w) cm^{-1}. Anal. calcd for $C_{44}H_{30}N_{14}O_8Zn_2$: C 52.14, H 2.98, N 19.35; found C 52.14, H 3.06, N 19.97.

Preparation of $[Zn_3(tib)_2(CHDC)_3]\bullet 8H_2O$ (2)

The complex was obtained by the same procedure used for preparation of **1**, except that H_2CHDC (17.2 mg, 0.1 mmol), instead of H_2PDC, was used as the starting material. Colorless column crystals were collected by filtration with a yield 46% based on Zn(II) after washing by water and ethanol several times. IR (KBr pellet) v: 3398 (m, br), 1621 (s), 1585 (s), 1512 (s), 1409 (m), 1245 (m), 1111 (w), 1074 (m), 1026 (m), 953 (m), 860 (w), 758 (w), 655 (w) cm^{-1}. Anal. calcd for $C_{54}H_{70}N_{12}O_{20}Zn_3$: C 46.22, H 5.03, N 11.98; found C 45.79, H 3.89, N 12.24.

Preparation of $[Zn_3(tib)_2(BTC)_2]\bullet 4.95H_2O$ (3)

A mixture of tib (27.6 mg, 0.1 mmol), H_3BTC (25.2 mg, 0.1 mmol), $ZnCl_2$ (27.3 mg, 0.2 mmol) and NaOH (12.0 mg, 0.3 mmol) in H_2O (10 ml) was sealed in a 16 mL Teflon lined stainless steel container and heated at 180 ℃ for 3 d. After cooling to the room temperature, light-brown block crystals were collected by filtration and washed by water and ethanol several times. Yield: *ca*. 38% based on the Zn(II). IR (KBr pellet) v: 3434 (s, br), 1617 (s), 1514 (s), 1379 (s), 1295 (m), 1257 (m), 1115 (m), 1074 (m), 1005 (m), 941 (m), 857 (m), 754 (m), 645 (m), 580 (w) cm^{-1}. Anal. calcd for $C_{54}H_{51.9}N_{12}O_{16.95}Zn_3$: C 48.53, H 3.91, N 12.58; found C 49.04, H 3.76, N 11.97.

X-ray crystallography

The crystallographic data for **1** and **2** were collected on a Bruker Smart Apex CCD area-detector diffractometer with graphite-monochromated Mo Kα radiation (λ=0.071073 nm) at 20(2) ℃ using the ω-scan technique. The diffraction data was integrated by using the *SAINT* program,[11] which was also used for the intensity corrections for the Lorentz and polarization effects. Semi-empirical absorption correction was applied using the *SADABS* program.[12] The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the *SHELXL-97* crystallographic software package.[13] Hydrogen atoms of the ligands in the structures were generated geometrically. In **2**, the water molecules of O7W and O8W disordered into two positions with site occupancy factors of 0.66(2), 0.34(2) and 0.659(8), 0.341(8), respectively. The data collection for **3** was carried out on a Rigaku RAXIS-RAPID imaging plate diffractometer at −73 ℃, with graphite-monochromated Mo Kα radiation (λ=0.071075 nm). The structure was solved by direct methods with SIR92[14] and expanded using Fourier techniques.[15] All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method on F^2. Hydrogen atoms of the ligands in the structure were generated geometrically. The imidazole ring atoms (C31, C32, C33 and N32), carboxylate oxygen atoms (O3 and O4), and free water molecule (O8) disordered into two positions with site occupancy factors of 0.525(8) and 0.475(8), respectively. The atoms O6, C151 (C153), C152 (C154) and free water molecule (O7) disordered into two positions with site occupancy factors of 0.623(16), 0.377(16) and 0.60(5), 0.40(5), respectively. The free water molecule O9 occupied with a factor of 0.475(8). All calculations were carried out on SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation.[16] Detail of the crystal parameters, data collection and refinements for **1**—**3** are summarized in Table 1. Selected bond lengths and angles for **1**—**3** are listed in Table 2. Hydrogen bonding distances and angles for **1** are listed in Table S1. Further details are provided in the Supporting Information.

Results and Discussion

Crystal structure of [Zn(tib)(PDC)] (1)

The asymmetric unit of **1** contains one Zn(II), one tib and one PDC^{2-} ligand (Figure 1a). The central Zn(II) with distorted trigonal bipyramid coordination geometry is five-coordinated by two oxygen and one nitrogen atoms from one PDC^{2-} and the other two nitrogen atoms from two different tib ligands. The equatorial plane is formed by three nitrogen atoms (N1, N3A and N7), while the apical positions are occupied by the two oxygen atoms (O1 and O3). The Zn—O/Zn—N bond lengths range from 0.1983(2) to 0.2169(2) nm, and the bond angles around the Zn(II) are in the range of 76.79(8)°—152.55(7)° (Table 2). It is interesting to note that one imidazole group with N5 of tib ligand does not participate in the coordination, and thus each tib ligand links two, rather than three, Zn(II) atoms. Meanwhile, the PDC^{2-} acts as a terminal chelating ligand, meaning both carboxylate groups adopting μ_1-η^1:η^0-monodentate coordination mode (Scheme S1a). Two PDC^{2-}, two tib and two Zn(II) form a binuclear unit with a Zn-Zn distance of 1.0 nm (Figure 1b). Furthermore, the benzene ring and the adjacent imidazole ring planes of tib are nearly parallel with a dihedral angle of 7.19° and a centroid-centroid distance of 0.376 nm, indicating the existence of π-π interactions, which further link the binuclear units to give a two-dimensional (2D) network (Figure S1).[17] In addition, the C—H···O and C—H···N hydrogen bonds further link the 2D network to three-dimensional (3D) framework (Figure 1c and Table S1).

Crystal structure of $[Zn_3(tib)_2(CHDC)_3]\cdot 8H_2O$ (2)

When the auxiliary acid changed from H_2PDC to H_2CHDC, complex **2** was obtained. X-ray crystallographic analysis revealed that complex **2** crystallized in monoclinic $P2_1/c$ space group (Table 1). In the asymmetric unit, there are three independent Zn(II) atoms (Zn1, Zn2 and Zn3), two tib, three $CHDC^{2-}$ ligands (Figure 2a) and eight free water molecules. Both Zn1 and Zn3 atoms are four-coordinated with distorted tetrahedral coordination geometry by two nitrogen atom from two different tib and two oxygen atoms from two distinct $CHDC^{2-}$ ligands. Each Zn2 atom with distorted trigonal bipyramid coordination geometry is five-coordinated by two nitrogen atoms (N3, N5G) from two different tib and three oxygen atoms (O8E, O11F and O12F) from two distinct $CHDC^{2-}$ ligands. The Zn—N and Zn—O bond lengths and the bond angles around Zn(II) atoms in **2** are comparable with other Zn(II) coordination polymers.

Each tib ligand in **2** coordinates with three Zn(II) atoms using its three imidazole groups to form a 3D tib-Zn framework (Figure S2), rather than the tib-Zn binuclear unit in **1**. The carboxylate groups of $CHDC^{2-}$ adopt two different coordination modes in complex **2**: μ_1-η^1:η^1 chelate and μ_1-η^1:η^0 monodentate, which makes each $CHDC^{2-}$ ligand link two Zn(II) atoms (Scheme S1b and S1c). It is noteworthy that H_2CHDC with a mixture of *cis*- and *trans*-isomers was used, however, only *cis*-$CHDC^{2-}$ was found in the complex, since the complexes with *cis*- or *trans*-isomer may show different property.[18] Six $CHDC^{2-}$ ligands and six Zn(II) atoms form a 54-membered ring (Figure S3), which fills into the void of the 3D tib-Zn framework to result in the final structure of complex **2** (Figure 2b). From the topological

Table 1 Crystallographic data for complexes **1**—**3**

	1	2	3
Formula	$C_{44}H_{30}N_{14}O_8Zn_2$	$C_{54}H_{70}N_{12}O_{20}Zn_3$	$C_{54}H_{51.9}N_{12}O_{16.95}Zn_3$
M_w	1013.56	1403.33	1336.31
Temp./K	293(2)	293(2)	200
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
a/nm	1.20405(14)	2.4972(2)	1.9460(9)
b/nm	1.9514(2)	1.36883(11)	1.6088(8)
c/nm	0.83621(9)	1.82727(14)	1.7973(7)
β/(°)	90.909(2)	101.097(1)	107.741(19)
V/nm^3	1.9645(4)	6.1293(8)	5.3593(40)
Z	2	4	4
D/(g•cm^{-3})	1.714	1.503	1.656
F(000)	1032	2848	2742
θ range/(°)	1.7—25.3	1.7—25.0	3.17—25.0
Reflections collected	9821	29795	19919
Independent reflections	3548	10775	4703
GOF on F^2	0.95	0.96	1.05
$R\ [I>2\sigma(I)]^a$	0.0404	0.0587	0.0799
$wR_2\ [I>2\sigma(I)]^b$	0.0854	0.1312	0.1869

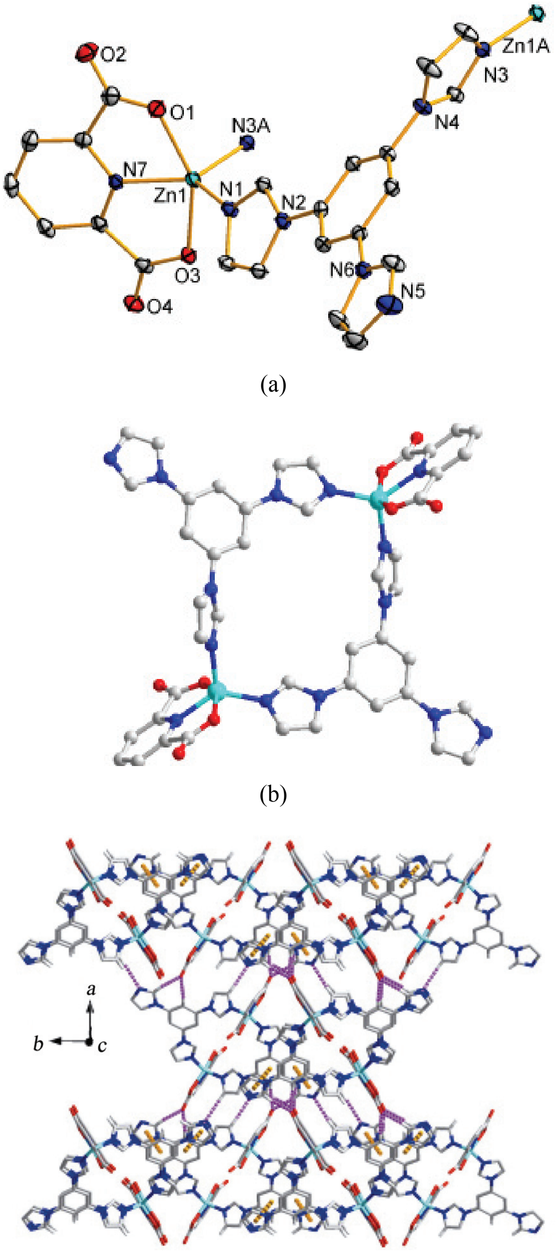
^{a} $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; ^{b} $wR_2=|\Sigma w(|F_o|^2-|F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$. $P=(F_o^2+2F_c^2)/3$.

Table 2 Selected bond lengths (nm) and bond angles (°) for complexes **1**—**3**[a]

	1		
Zn1—O1	0.2169(2)	Zn1—O3	0.2129(2)
Zn1—N1	0.2001(2)	Zn1—N7	0.2002(3)
Zn1—N3#1	0.1983(2)		
O1-Zn1-O3	152.55(7)	O1-Zn1-N1	96.57(9)
O1-Zn1-N7	76.79(8)	O1-Zn1-N3#1	100.96(9)
O3-Zn1-N1	95.19(9)	O3-Zn1-N7	76.90(8)
O3-Zn1-N3#1	98.30(9)	N1-Zn1-N7	131.97(10)
N1-Zn1-N3#1	109.59(10)	N3#1-Zn1-N7	118.41(10)
	2		
Zn1—O1	0.1969(4)	Zn1—N7	0.2026(4)
Zn1—O5	0.1964(3)	Zn1—N1	0.2037(4)
Zn2—N3	0.2058(4)	Zn2—O12#2	0.2184(4)
Zn2—O8#3	0.2000(4)	Zn2—N5#4	0.2076(4)
Zn2—O11#2	0.2207(5)	Zn3—O9	0.1934(4)
Zn3—O3	0.1968(4)	Zn3—N11	0.2001(4)
Zn3—N9#5	0.2012(4)		
O1-Zn1-O5	113.66(19)	O1-Zn1-N1	98.18(17)
O1-Zn1-N7	107.03(18)	O5-Zn1-N1	107.21(15)
O5-Zn1-N7	122.03(16)	N1-Zn1-N7	105.79(15)
O11#2-Zn2-N3	147.31(16)	O11#2-Zn2-O12#2	57.29(15)
O12#2-Zn2-N3	90.02(15)	O12#2-Zn2-N5#4	110.69(15)
O8#3-Zn2-N3	103.18(15)	N3-Zn-N5#4	97.79(15)
O8#3-Zn2-N5#4	99.00(16)	O8#3-Zn2-O11#2	104.55(16)
O8#3-Zn2-O12#2	145.56(16)	O11#2-Zn2-N5#4	94.64(1)
O3-Zn3-O9	95.10(15)	O3-Zn3-N9#5	117.19(16)
O3-Zn3-N11	111.44(15)	O9-Zn3-N11	117.02(17)
O9-Zn3-N9#5	104.39(16)	N9#5-Zn3-N11	110.92(15)
	3		
Zn1—O1	0.1969(5)	Zn1—N12	0.2014(5)
Zn2—N32#9	0.2043(17)	Zn2—O5#6	0.1906(6)
Zn2—O3	0.1997(13)	Zn2—N52#7	0.2021(7)
O1-Zn1-O1#8	113.5(3)	O1-Zn1-N12#8	122.1(2)
N12-Zn1-N12#8	103.2(3)	O1-Zn1-N12	98.6(2)
O5#6-Zn2-O3	109.4(4)	O5#6-Zn2-N52#7	100.2(2)
O3-Zn2-N52#7	129.5(4)	O5#6-Zn2-N32#9	119.2(6)
N52#7-Zn2-N32#9	89.1(5)	O3-Zn2-N32#9	109.4(7)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $1-z$; #2 $1+x$, $3/2-y$, $-1/2+z$; #3 $-x$, $1/2+y$, $1/2-z$; #4 x, $5/2-y$, $-1/2+z$; #5 $-1-x$, $1/2+y$, $3/2-z$; #6 x, $-y+1$, $z+1/2$; #7 z, $-y$, $z+1/2$; #8 $-x+1$, y, $-z+1/2$; #9 $-x$, y, $-z+1/2$.

view of this complicated 3D framework,[19] the Zn(II) atom, tib and $CHDC^{2-}$ ligands can be simplified as four-, three- and two-(bridging) connectors, respectively. Thus, complex **2** can be simplified as a (3,4)-connected net with Point (Schläfli) symbol of $(3{\bullet}6{\bullet}7^2{\bullet}8{\bullet}9)(3{\bullet}6^2{\bullet}7{\bullet}9{\bullet}10)(3{\bullet}7{\bullet}8)(6{\bullet}7{\bullet}9)(6^2{\bullet}7{\bullet}9{\bullet}10^2)$ (Figure 2c).



(a)

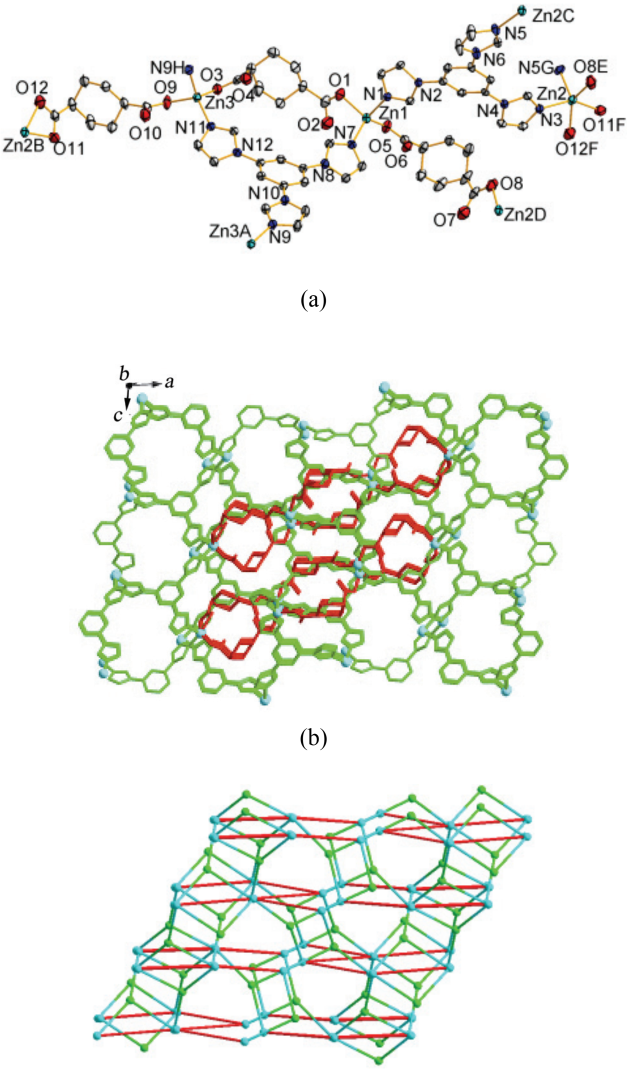
(b)

(c)

Figure 1 (a) The ORTEP drawing of **1** with thermal ellipsoids set to 30% probability level. All H atoms are omitted for clarity. (b) The binuclear structure of complex **1**. (c) The 3D structure of complex **1** (π-π interactions: yellow dotted lines; hydrogen bonds: pink dotted lines).

Crystal structure of $[Zn_3(tib)_2(BTC)_2]{\bullet}4.95H_2O$ (3)

To further investigate the effect of the auxiliary carboxylic acid on the structure of coordination polymer, H_3BTC was used to react with $ZnCl_2$ and tib. Complex **3** was obtained under the same conditions for preparations of **1** and **2**. X-ray crystallographic analysis revealed that complex **3** crystallizes in monoclinic *C*2/*c* space group (Table 1). In the asymmetric unit, there are two crystallographic different Zn(II) atoms: Zn1 and Zn2. Each Zn1 atom, sitting on a special position with half occupancy, is four-coordinated with a distorted



(a)

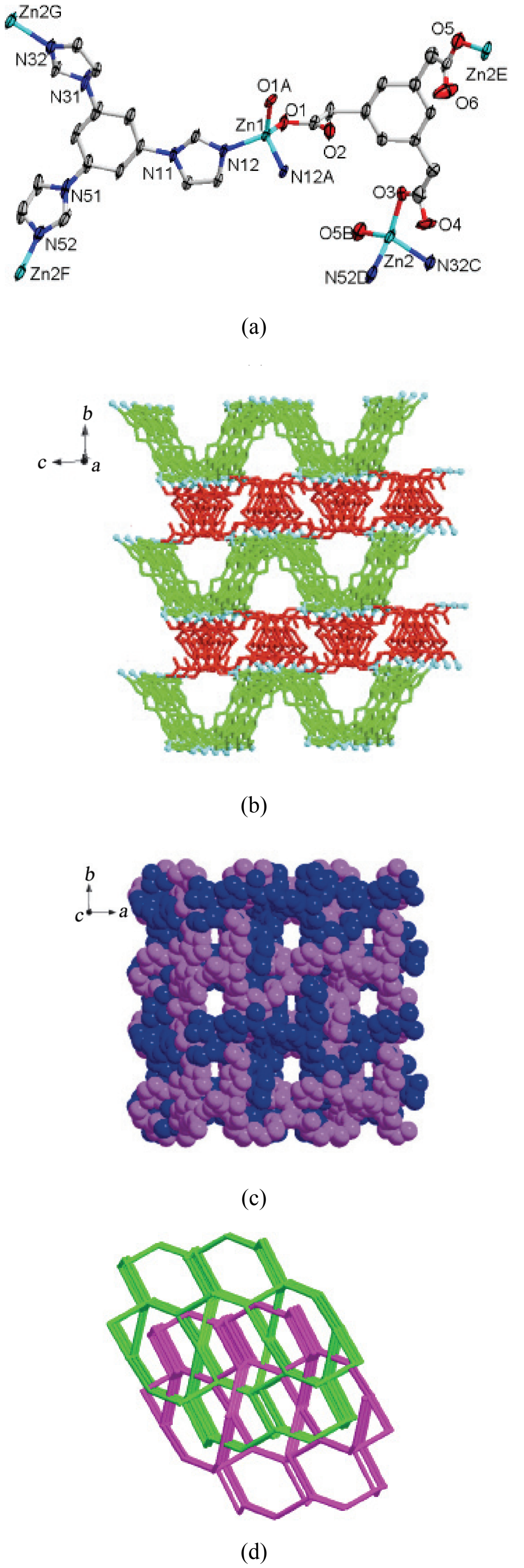
(b)

(c)

Figure 2 (a) The ORTEP drawing of **2** with thermal ellipsoids set to 30% probability level. All H atoms and free water molecules are omitted for clarity. (b) The 3D structure of complex **2**, where the green and red represented tib ligands and $CHDC^{2-}$ ligands, respectively. (c) The topological view of 3D framework of complex **2** (green balls for tib ligands, turquoise balls for the Zn(II), red lines for $CHDC^{2-}$ ligands).

tetrahedral coordination geometry by two nitrogen atoms (N12 and N12A) from two different tib and two oxygen atoms (O1 and O1A) from two distinct BTC^{3-} ligands (Figure 3a). Each Zn2 atom with distorted tetrahedral coordination geometry is four-coordinated by two oxygen atoms (O3 and O5B) from two different BTC^{3-} and two nitrogen atoms (N32C and N52D) from two distinct tib ligands.

Each tib ligand in **3** connects three Zn(II) atoms (one Zn1 and two Zn2) to form a one-dimensional (1D) chain (Figure S4). Meanwhile, each BTC^{3-} ligand adopts *cis*,*cis*,*trans*-conformation and links three Zn(II) to form a 1D infinite ladder-like chain, in which each carboxylate group adopts μ_1-η^1:η^0 monodentate coordination mode (Scheme S1d and Figure S5). The two different



(a)

(b)

(c)

(d)

Figure 3 (a) The ORTEP drawing of **3** with thermal ellipsoids set to 30% probability level. All H atoms and free water molecules are omitted for clarity. (b) The 3D structure of complex **3**, where the green and red represented tib ligands and BTC^{3-} ligands, respectively. (c) and (d) Space-filling and topological views of 2-fold interpenetrating 3D framework of complex **3**.

kinds of 1D chains interconnected to form the final 3D framework of **3** (Figure 3b). It is noteworthy that there are open channels with size of 1.73 nm×0.73 nm in the single 3D net of **3** along the *c* direction, which allows another identical net to penetrate, namely, the entire structure of **3** is a 2-fold interpenetrated 3D framework (Figure 3c). Using the same topological analysis method for complex **3**, the Zn(II), tib and BTC^{3-} ligands can be viewed as four-, three- and three-connector, respectively. Thus, complex **3** can be simplified as (3,4)-connected net with Point (Schläfli) symbol of $(4•8^2)_2(4•8^5)_2$-$(8^2•10)_2(8^6)$ (Figures 3d and S6).

Effect of the auxiliary carboxylate ligands

The structural differences between complexes **1**—**3** are mainly ascribed to the effect of the auxiliary carbxylate ligands. As it is known, the coordination abilities/modes and the flexibilities of the auxiliary carboxylate ligands are the most important factors to affect the MOFs' structures.[20] For example, the previously reported complexes $[Zn(tib)(1,3\text{-}BDC)]•H_2O$ (**4**) and $[Zn_2(tib)(1,4\text{-}BDC)Cl_2]•2H_2O$ (**5**) were synthesized under the same reaction conditions except that 1,3-H_2BDC (1,3-benzenedicarboxylic acid) and 1,4-H_2BDC were used, instead of the auxiliary carboxylate ligands of H_2PDC, H_2CHDC and H_3BTC used in this work.[21] Complex **4** is a 2D (4,4) network, where the 1,3-BDC^{2-} works as simple bridging ligand, while **5** is a different 2D network constructed by $Zn_4(tib)_2$ and $Zn_4(1,4\text{-}BDC)_2$ subunits. Comparing complexes **1** and **4**, it is clear that the PDC^{2-} ligand is much easier to chelate one metal ion as the terminal ligand due to the existence of the center nitrogen atom, which blocks the extension of the unit to higher dimensional framework, and leads to the formation of zero-dimensional (0D) binuclear structure of **1**. By comparing the flexible cyclohexane skeleton in **2** and the rigid benzene one in **5**, it is obvious that the flexible $CHDC^{2-}$ is much easier to satisfy the coordination requirement of the metal ion to form high-dimensional framework. As far as the BTC^{3-}, it has three flexible carboxylate groups which can satisfy the requirement of metal center to form complicated 3D frameworks.[22] The results of present study further confirm that the auxiliary carboxylate ligands are versatile and important in construction of MOFs.

TGA and PXRD

Thermogravimetric analyses (TGA) were carried out for the synthesized complexes, and the results are shown in Figure S7. No obvious weight loss was found for complex **1** until the decomposition of the framework occurred at *ca*. 420 ℃. For **2**, the weight loss of 9.74% was observed before 180 ℃ corresponding to the release of free water molecules (calcd. 10.26%), and further decomposition occurred at 350 ℃. Complex **3** shows a weight loss of 6.05% before 160 ℃ corresponding to the departure of free water molecules (calcd. 6.60%); further weight loss was observed at about 410 ℃.

Furthermore, the phase purity of the complexes was confirmed by the powder X-ray diffraction (PXRD) measurements and the results are given in Figure S8, where the as-synthesized pattern is consistent with the simulated one from the corresponding complex.

Photoluminescence properties of the complexes 1—3

Inorganic-organic hybrid coordination polymers, especially those with d^{10} metal centers, have been investigated for photoluminescent properties, because of their potential applications as fluorescence-emitting materials.[23] In the present work, the emission spectra of Zn(II) complexes **1**—**3** together with tib, H_2PDC, H_2CHDC and H_3BTC ligands, were measured in the solid state at room temperature, and all the measurement were excited at a wavelength of 360 nm. Intense emission bands were observed at 405 nm for the free tib ligand, which are same as those reported previously,[24] and no obvious emission band was detected for free H_2PDC, H_2CHDC and H_3BTC ligands. As shown in Figure 4, intense emissions were observed at 396, 400 and 407 nm for complexes **1**—**3**, respectively. The emissions of complexes **1**—**3** are tentatively ascribed to the intraligand transition of tib due to their similarity. And the observed red or blue shift of the emission maximum between the complexes and the ligand is considered to mainly originate from the influence of the coordination of the ligand to the metal atom. In addition, it is noteworthy that complexes **2** and **3** showed intense emission compared with free tib ligand and **1** at room temperature, which may be attributed to the different rigidity of the crystal packing in the solid state.

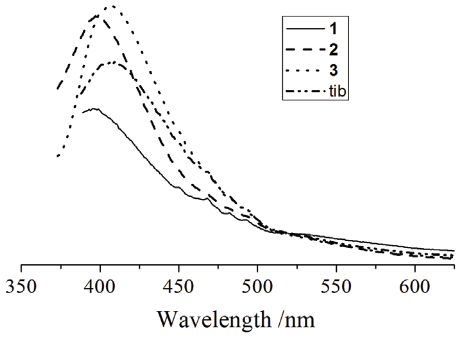


Figure 4 Emission spectra of **1**—**3** and tib ligand in the solid state at room temperature.

Conclusions

Three new coordination polymers have been successfully synthesized under hydrothermal conditions by reactions of tib ligand together with auxiliary carboxylate ligands and $ZnCl_2$. The structural differences between complexes **1**—**3** and previously reported **4** and **5** are mainly ascribed to the different auxiliary carboxylate ligands. Meanwhile, the synthesized complexes have high stabilities and show obvious photoluminescent emissions at room temperature in the solid state.

Supplementary Material

CCDC 891618—891620 contain the supplementary crystallographic data for **1**—**3**. The data can be obtained free of charge via the Internet at http://www.ccdc.ca-m.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Email: deposit@ccdc.cam.ac.uk.

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