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Introduction

In the fields of supramolecular chemistry and crystal engineering, the design and assembly of metal-organic coordination polymers become more and more popular because of an intriguing variety of architectures, topologies and potential applications in gas storage, ion-exchange, heterogeneous catalysis, magnetism, non-linear optics, molecular sensing, and electrical conductivity.¹⁻⁴ In recent years, researchers focus on designing and assembling the targeted structures of coordination polymers. In this respect, the rational and controllable preparation of metal-organic frameworks (MOFs) is one of the obvious challenges. MOFs are greatly affected by factors such as the organic ligands,⁵ the nature of metal ions,⁶ temperature,⁷ solvent,⁸ counterions,⁹ and so on. In order to build novel molecular architectures, the

Syntheses, characterizations and properties of five new metal–organic complexes based on flexible ligand 4,4'- (phenylazanediyl)dibenzoic acid†

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Five new metal–organic frameworks have been synthesized under hydrothermal conditions, in CH₃CN–H₂O, DMF–CH₃CH₂OH–H₂O and DMA–H₂O, namely, [ZnL(bimx)_{0.5}]_n (1), {[CoL(4,4'-bipy)]·DMF}_n (2), {[CdL(4,4'-bipy)]·DMF}_n (3), {[ZnL(bibp)]·DMA·(H₂O)₂]_n (4), {[CoL(bpyb)_{0.5}]·(H₂O)₂]_n (5) (bimx = 1,4-bis(imidazol-1-ylmethyl)benzene, 4,4'-biby = 4,4-pyridine, bibp = 4,4'-bis(imidazol-1-yl)biphenyl, bpyb = 1,4-bis(4-pyridyl)benzene, H₂L = 4,4'-(phenylazanediyl)dibenzoic acid. These complexes were characterized by elemental analysis, IR spectroscopy, TG and X-ray single-crystal diffraction. In compounds 1, 2 and 3, the bimx, 4,4'-bipy and L²⁻ anions act as bidentate ligands assembling with metal cations to form two-dimensional (2D) sheets. The sheets are stacked in ABAB fashion and accumulate into a 3D framework. Compound 4 possesses a 3D→3D 4-fold interpenetrating architecture with {6⁵·8} topological net, which is similar to the **cds** topology. Compound 5 also displays a 3D structure with {4⁴·6¹⁰·8} topology. The photochemical properties were investigated in the solid state at room temperature. The luminescent properties of compounds 1, 3 and 4 are discussed in detail. The UV-vis absorption spectra of compounds 2 and 5 are tested and discussed. In addition, the magnetic properties of compound 5 also are tested and simply analyzed.

geometries of the organic ligands have a great effect on the structural frameworks of coordination polymers; thus, much effort has been devoted to modifying the building blocks and to controlling the assembled motifs for required products via selecting different organic ligands.^{10,11} The reported research works show that multiple carboxylate ligands have been used as ideal organic linkers for building MOFs.¹² This is because their different coordination modes lead to diverse multidimensional architectures. As far as we know, elongated dicarboxylate ligands, tricarboxylate ligands and tetracarboxylate ligands have been employed by several groups to construct porous MOFs.¹³⁻¹⁵ Recently, non-rigid ligands have usually been the typical building elements in the multidimensional networks. The flexible ligands have variable coordination modes, and can adopt a variety of conformations according to the restrictions imposed by the coordination geometry of the metal ion, to meet the coordination requirements of the metal ions,16a which can result in more topological structures than a rigid ligand.^{16b} Therefore, we design and synthesize a "V-shaped" flexible ligand of 4,4'-(phenylazanediyl)dibenzoic acid. Auxiliary ligands are also a good choice for the construction of novel polymeric structures. A large number of metal-organic frameworks that are assembled by mixed-ligands and metal ions have been reported, showing that the combination of different ligands

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can result in greater tenability of structural frameworks than single ligands.^{17,18} The ligands containing imidazole or pyridine are regarded as important auxiliary ligands in the design and assembly of metal-organic coordination polymers. Hence, to obtain novel MOFs, we select 1,4-bis(imidazol-1ylmethyl)benzene (bimx) 4,4'-bipyridine (4,4'-bipy), 4,4'-bis(imidazol-1-yl)biphenyl (bibp) and 1,4-bis(4-pyridyl)benzene (bpyb) as the auxiliary ligands (Scheme 1). In the present work, we have synthesized five new coordination compounds with intriguing structures, namely, $[\text{ZnL}(\text{bimx})_{0.5}]_n$ (1), $\{ [CoL(4,4'-bipy)] \cdot DMF \}_n$ (2), $\{ [CdL(4,4'-bipy)] \cdot DMF \}_n$ (3), $\{[\text{ZnL}(\text{bibp})] \cdot \text{DMA} \cdot (\text{H}_2\text{O})_2\}_n$ (4), $\{[\text{CoL}(\text{bpyb})_{0.5}] \cdot (\text{H}_2\text{O})_2\}_n$ (5). All the compounds were characterized by elemental analysis, IR spectrum, X-ray crystallography and powder X-ray diffraction (PXRD). The details of their syntheses, structures and properties are reported below.

Experimental

Materials and methods

The H₂L was synthesized by 4-fluorobenzonitrile and phenylamine then hydrolyzing.¹⁹ Bibp, bimx and bpyb ligands were prepared by the literature methods. Reagents and solvents employed were commercially available and used as received. IR absorption spectra of the complexes were recorded in the range of 400–4000 cm⁻¹ on a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr). C, H and N analyses were carried out with a Perkin-Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu K α radiation (1.5418 Å), in which the X-ray tube was operated at 40 kV and 40 mA. The assynthesized samples were characterized by thermogravimetric analysis (TGA) on a Perkin-Elmer thermogravimetric analyzer Pyris 1 TGA up to 750 K using a heating rate of 10 K min⁻¹ under N_2 atmosphere. Temperature dependent magnetic susceptibility data for polycrystalline complex **5** were obtained on a SQUID magnetometer under an applied field of 2000 Oe over the temperature range of 1.8–300 K.

SYNTHESIS OF $[ZNL(BIMX)_{0.5}]_n$ (1). A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (29.7 mg, 0.1 mmol), H_2L (33.3 mg, 0.1 mmol) and bimx (23.8 mg, 0.1 mmol) was dissolved in mixed solvents (4 mL of distilled H_2O and 4 mL of CH_3CN). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 130 °C for three days. Large quantities of colorless-block crystals were obtained and the crystals were filtered off, washed with distilled water, and dried under ambient conditions. Yield of the reaction was *ca*. 63% based on the H_2L ligand. Anal. calcd for $C_{27}H_{20}N_3O_4Zn$: C, 62.86%, H, 3.91%, N, 8.15%; found: C, 62.55%, H, 3.96%, N, 8.34%. IR (KBr, cm⁻¹): 3454(w), 3130(w), 1592(s), 1548(m), 1526(m), 1491(s), 1406(s), 1370(s), 1309(m), 1267(s), 865(w), 785(w), 706(w), 695(w), 658(w), 558(w), 564(w).

SYNTHESIS OF {[CoL(4,4'-BIPY]]·DMF}_n (2). Co(NO₃)₂·6H₂O (29.1 mg, 0.1 mmol), H₂L (33.3 mg, 0.1 mmol) and 4,4'-bipy (15.6 mg, 0.1 mmol) were added to a mixed solvent of 2 mL of distilled H₂O, 2 mL of C₂H₅OH and 2 mL of DMF. The final mixture was sealed in a 15 mL Parr Teflon-lined stainless-steel under autogenous pressure and heated at 80 °C for three days. Large quantities of rose red-block crystals were obtained and the crystals were filtered off, washed with quantities of distilled water, and dried under ambient conditions. Yield of the reaction was *ca.* 65% based on the H₂L ligand. Anal. calcd for C₃₃H₂₈CoN₄O₅: C, 63.98%, H, 4.56%, N, 9.04%; found: C, 64.05%, H, 4.61%, N, 9.25%. IR (KBr, cm⁻¹): 3426(m), 2363(w), 1633(m), 1595(s), 1547(m), 1489(w), 1414(s), 1329(m), 1277(m), 1220(m), 1180(m), 1068(w), 851(w), 812(w), 781(w), 754 (w), 702(w), 630 (w), 573 (w), 532(w).

SYNTHESIS OF {[CDL(4,4'-BIPY)]·DMF}_n (3). Complex 3 was prepared in the same way as for 2 by using Cd(NO₃)₂·6H₂O (34.4 mg, 0.1 mmol) to replace Co(NO₃)₂·6H₂O. Large



1,4-bis(4-pyridyl)benzene (bpyb)

Scheme 1 Molecular structure of ligands.

quantities of light yellow-block crystals were obtained and the crystals were filtered off, washed with quantities of distilled water, and dried under ambient conditions. Yield of the reaction was *ca.* 54% based on the H₂L ligand. Anal. calcd for $C_{33}H_{28}CdN_4O_5$: C, 58.89%, H, 4.19%, N, 8.32%; found: C, 58.74%, H, 4.23%, N, 8.26%. IR (KBr, cm⁻¹): 3437(m), 2363(w), 1674(w), 1589(s), 1538(m), 1393(s), 1316(m), 1222(m), 1179(m), 1075(w), 1009(w), 851(w), 809(w), 779(w), 703(w), 672(w), 629(w), 525 (w).

SYNTHESIS OF {[ZNL(BIBP]]·DMA· $(H_2O)_2$ }_n (4). A mixture of Zn(NO₃)₂·6H₂O (29.7 mg, 0.1 mmol), H₂L (33.3 mg, 0.1 mmol) and bibp (28.6 mg, 0.1 mmol) was dissolved in 8 mL DMA-H₂O (1 : 1, v/v). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 100 °C for three days. Large quantities of colorless-block crystals were obtained and the crystals were filtered off, washed with distilled water, and dried under ambient conditions. Yield of the reaction was *ca*. 63% based on the H₂L ligand. Anal. calcd for C₄₂H₄₀ZnN₆O₇: C, 62.57%, H, 5.00%, N, 10.42%; found: C, 62.65%, H, 5.06%, N, 10.46%. IR (KBr, cm⁻¹): 3446(w), 3130(w), 2360(m), 1685(s), 1592(s), 1525(m), 1508(m), 1407(s), 1312(m), 1270(w), 1173(s), 1109(s), 1011(m), 952(m), 846(m), 786(m), 690(w), 557(w), 521(w), 463(w).

SYNTHESIS OF { $[CoL(BPYB)_{0.5}] \cdot (H_2O)_2 _n$ (5). Co(NO₃)₂·6H₂O (29.1 mg, 0.1 mmol), H₂L (33.3 mg, 0.1 mmol) and bpyb (23.2 mg, 0.1 mmol) were added to water (2 mL) and DMF (6 mL). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 100 °C for three days. Large quantities of black-block crystals were obtained and the crystals were filtered off, washed with distilled water, and dried under ambient conditions. Yield of the reaction was *ca*. 67% based on the H₂L ligand. Anal. calcd for C₂₈H₂₃CoN₂O₆: C, 62.00%, H, 4.27%, N, 5.16%; found: C, 62.03%, H, 4.35%, N, 5.21%. IR (KBr, cm⁻¹): 3442(m), 3072(w),

Table 1 Crystallographic data and structure refinement details for complexes 1-5

1650(m), 1593(s), 1553(m), 1488(m), 1394(s), 1310(s), 1221(m), 1139(m), 1014(m), 865(m), 845(w), 781(w), 694(w), 545(w), 447(w).

X-Ray crystallography

Single crystals of 1-5 were prepared in single crystal form. X-Ray crystallographic data of 1-5 were collected at room temperature using epoxy-coated crystals mounted on glass fiber. All measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). The structures of complexes **1–5** were solved by direct methods and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedures based on F^2 values.^{20a} The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The distribution of peaks in the channels of 3-5 were chemically featureless to refine using conventional discrete-atom models. To resolve these issues, the contribution of the electron density by the remaining water molecule was removed by the SQUEEZE routine in PLATON.^{20b} Relevant crystallographic data are presented in Table 1, while the selected bond lengths and angles are given in the ESI (Table S1, ESI[†]).

Results and discussion

Crystal structure of $\{\text{ZnL}(\text{bimx})_{0.5}\}_n$ (1)

The crystal structure determination reveals that compound **1** crystallizes in the triclinic crystal system of P_1 . The asymmetric unit contains one Zn(II) cation, half of the bimx ligand, one deprotonated L ligand (Fig. 1a). In an asymmetric unit, the two carboxylate groups of the L ligand take different coordination modes, one carboxylate group takes a bismonodentate

Compound	1	2	3	4	5
Formula	C ₂₇ H ₂₀ N ₃ O ₄ Zn	C33H28N4O5C0	C ₃₀ H ₂₁ N ₃ O ₄ Cd	C ₃₈ H ₂₇ N ₅ O ₄ Zn	$C_{28}H_{19}N_2O_4Cc$
Formula weight	515.83	619.52	599.92	683.04	506.38
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P_1	C2/c	C2/c	P2(1)/n	C2/c
ı/Å	9.6317(6)	28.3656(16)	28.676(4)	11.972(3)	25.0837(11)
b/Å	10.0666(6)	11.4712(6)	11.7344(15)	12.043(4)	8.7814(4)
c/Å	13.2230(8)	18.2929(10)	17.820(3)	27.792(8)	22.6654(10)
χ (°)	100.8150(10)	90.00	90.00	90.00	90.00
β (°)	108.2140(10)	102.8760(10)	101.202(2)	99.959(4)	91.8530(10))
γ (°)	102.0740(10)	90.00	90.00	90.00	90.00
Z	2	8	8	4	8
$V(Å^3)$	1145.87(12)	5802.6(5)	5882.1(15)	3947(2)	4989.9(4)
$D_{\rm c} (\rm g \ \rm cm^{-3})$	1.495	1.418	1.355	1.150	1.348
$\mu(Mo K\alpha) (mm^{-1})$	1.112	0.641	0.779	0.663	0.724
F(000)	530.0	2568	2416.0	1408.0	2080
Fotal, unique data	8428, 5687	18 291, 6652	17 472, 6802	26 485, 6922	13 679, 4399
R _{int}	0.0544	0.0968	0.0392	0.1043	0.1374
Observed data $[I > 2\sigma(I)]$	4617	5079	4540	5397	3601
$N_{\rm ref}, N_{\rm par}$	5687, 316	6652, 390	6578, 343	6922, 433	4399, 316
$R_1, WR_2 (I > 2\sigma(I))$ in-	0.0390/0.0894	0.0428/0.1180	0.0448/0.1301	0.0756/0.2145	0.0492/0.1376
S	0.948	1.005	1.020	1.084	1.073
Min. and max. residual density/e $Å^{-3}$	-0.618, 0.522	-0.448, 0.427	-0.843, 1.379	-1.213, 1.182	-0.558, 0.690



Fig. 1 (a) Coordination environment of the Zn(II) ions in **1**. The hydrogen atoms are omitted for clarity (30% ellipsoid probability). Symmetry codes: #1 = 1 - x, 2 - y, 1 - z; #2 = 1 + x, 1 + y, 1 + z; #3 = -x, 1 - y, -z; #4 = -x, 1 - y, 1 - z; #5 = -1 + x, -1 + y, -1 + z. (b) Views of the 1D beaded chain formed by the deprotonated L ligands and Cd cations. (c) A perspective view of the 2D framework. (d) The simplified ABAB fashion of compound **1**.

coordination mode to bridge two Zn centers while the other carboxylate group adopts a monodentate coordination mode (Scheme 2a). Zn(II) is four-coordinated, bound by three O atoms from three L ligands and one N atom from the bimx ligands to form a distorted tetrahedron geometry. Neighboring zinc atoms are also joined into a $[Zn_2(CO_2)_4]$ binuclear unit with a two-membered ring by the bridging carboxylates. The Zn–Zn distance across the binuclear unit is 3.347(4) Å. Two L ligands connect two $[Zn_2(CO_2)_4]$ units to form a M_2L_2 ring, and each $[Zn_2(CO_2)_4]$ unit binds to two adjacent units through the four L ligands to form a 1D beaded chain (Fig. 1b). Finally, the chains are connected by the bimx ligands to form a 2D sheet (Fig. 1c). The sheets are stacked in ABAB fashion (Fig. 1d). The Zn–O bond distances vary in the range of 1.9389(14)–1.9872(14) Å and the Zn–N bond distance is 2.0012(21) Å. All these distances fall in the normal range found in other Zn complexes.^{21,22}

Crystal structure of $\{[CoL(4,4'-bipy)] \cdot DMF\}_n$ (2)

The crystal structure determination reveals that compound **2** crystallizes in the monoclinic crystal system of C2/c. The



Scheme 2 Crystallographically established coordination modes of the carboxylic groups in compounds 1–5.

asymmetric unit contains one Co(II) cation, one 4,4'-bipy ligand, one deprotonated L ligand and one DMF molecule, which is omitted for clarity (Fig. 2a). In the asymmetric unit, the two carboxylate groups of the L ligand take different coordination modes, one carboxylate group takes a bismonodentate coordination mode to bridge two Co centers while the other carboxylate group adopts a chelating in bidentate mode (Scheme 2b). Co(II) is six-coordinate, bound by four O atoms from three L ligands and two N atoms from two 4,4'-bipy ligands. Neighboring cobalt atoms are also joined into a $[Co_2(CO_2)_4]$ binuclear unit. The Co-Co distance across the binuclear unit is 4.086 Å. Two L ligands connect two $[Co_2(CO_2)_4]$ units to form a M_2L_2 ring, and each $[Co_2(CO_2)_4]$ unit binds to two adjacent units through the four L ligands to form a 1D beaded chain. The chain can be simplified as the chain of a diagonal parallelogram (Fig. 2b). Finally, the chains are connected by the 4,4'-bipy ligands to form a 2D sheet (Fig. 2c). The sheets are stacked in ABAB fashion and form a 3D framework (Fig. 2d). The Co-O bond distances vary in the range of 2.0196(14)-2.2024(15) Å, and the Co-N bond distances vary in the range of 2.1760(18)-2.1805(18) Å. All these distances fall in the normal range found in reported Co complexes.

Crystal structure of ${[CdL(4,4'-bipy)] \cdot DMF}_n$ (3)

X-Ray analysis reveals that the asymmetric unit of compound 3 consists of one crystallographically independent cadmium(II) cation, one deprotonated L²⁻ ligand, one 4,4'-bipy ligand and one free DMF molecule. The DMF molecule was removed by the SQUEEZE routine in PLATON. As shown in Fig. 3a, the L ligand adopts the similar coordination mode (Scheme 2c), in which one carboxylate group takes a μ_3 -chelating-bridging tridentate mode while the other carboxylate group adopts a chelating bidentate mode. The Cd center is seven-coordinated by five oxygen atoms belonging to four separated L ligands as well as two nitrogen atoms from 4,4'-bipy ligands with the Cd-O distances ranging from 2.313(3) Å to 2.546(3) Å and Cd-N distances ranging from 2.330(3) Å to 2.341(4) Å, which can be compared with values reported previously.23 Two L ligands connect two $[Cd_2(CO_2)_4]$ units to form a M_2L_2 ring, and each $[Cd_2(CO_2)_4]$ unit binds to two adjacent units through the L to form a 1D beaded chain (Fig. 3b). The Cd-Cd distance across the binuclear unit measures 3.863 Å. Then, the 4,4'-bipy ligands join all infinite 1D chains into a 2D layer (Fig. 3c). The layers are stacked in ABAB fashion, which is similar to compound 2, and simplified as in the Fig. 3d. As we know, the transition metal centers are bridged by flexible dicarbox-



Fig. 2 (a) Coordination environment of the Co(II) ions in compound **2**. The hydrogen atoms and lattice DMF molecules are omitted for clarity (30% ellipsoid probability). Symmetry codes: #1 = 0.5 - x, 1.5 - y, 2 - z; #2 = -0.5 + x, 1.5 - y, -0.5 + z; #3 = 1 - x, y, 2.5 - z; #4 = x, -1 + y, z; #5 = 0.5 + x, 1.5 - y, 0.5 + z. (b) Views of the beaded 1D chain formed by the L ligands and Co cations. (c) A perspective view of the 2D framework. (d) The simplified 3D structure of compound **2**.

ylate ligands to generate 1D chains, and 2D layers, which are pillared by rigid ligands into higher dimensional frameworks. The pimelic acid generates 2D layers, and the L acid is inclined to generate 1D chains.^{24a} The result implies that the subtle difference in co-ligand has a great influence on the structure of the complexes.

Crystal structure of $\{[ZnL(bibp)] \cdot DMA \cdot (H_2O)_2\}_n$ (4)

Compound 4 crystallizes in a monoclinic space group P2(1)/n, as shown in Fig. 4a, the asymmetric unit contains one Zn(II) ion, one deprotonated L ligand, one 4,4'-bibp ligand. The Zn(II) ion is coordinated by two carboxylic O atoms from two L ligands and two nitrogen atoms from two bibp ligands to form a distorted tetrahedron geometry. In addition, there are one DMA and two H₂O molecules removed by the SQUEEZE routine in PLATON. In an asymmetric unit, the two carboxylate groups of the L ligands take the same coordination modes. They all take a monodentate coordination mode (Scheme 2d). The bond lengths of Zn1–N2 and Zn1–N5#2 are 2.048(4) and 2.012(4) Å, respectively, and the Zn1–O1 distance is 1.943(4) Å. They are reasonably compared with the values in previously reported work.²⁵ The L ligands connect Zn atoms to form a 1D chain, which is composed of "V-shapes" (Fig. 4b). Then the bibp ligands join all infinite 1D chains into a 3D framework (Fig. 4c). With the topological viewpoint, the Zn can be viewed as 4-connecting nodes and the L ligands as linkers, the framework adopts the **cds** topology, a 4-connected $\{6^5 \cdot 8\}$ net, as shown in Fig. 4d. According to Blatov's classification,²⁶ the interpenetration can be classified as type Class IIIa, $Z = 4[2 \times 2]$ (Zt = 2; Zn = 2).

Crystal structure of ${[CoL(bpyb)_{0.5}] \cdot (H_2O)_2}_n$ (5)

The crystal structure determination reveals that complex **5** crystallizes in the monoclinic crystal system of C2/c. In the asymmetric unit, it contains an independent Co(II) cation, an L ligand, a half of a bipb ligand and two H₂O molecules (Fig. 5a). The coordination geometry for each Co atom is a distorted octahedron with four O atoms from four different ligands forming the middle plane. One nitrogen atom and one Co atom are in the axial position of the distorted octahedron. In this compound, the H₂L ligand acts as a "V-shape" link and the carboxylate group adopts a bismonodentate coordination





Fig. 3 (a) Coordination environment of the Cd(II) ions in **3**. The hydrogen atoms are omitted for clarity (30% ellipsoid probability). Symmetry codes: #1 = x, -1 + y, -1 + z; #2 = x, -y, 1 - z; #3 = x, y, -1 + z; #4 = 0.5 + x, 0.5 - y, 0.5 + z; #5 = -x, y, 0.5 - z; #6 = 0.5 - x, 0.5 - y, 1 - z; #7 = 0.5 - x, -0.5 - y, 1 - z; #8 = x, -1 + y, z; #9 = -0.5 + x, 0.5 - y, -0.5 + z. (b) View of the 1D chain formed by the L ligands and Cd cations. (c) A perspective view of the 2D framework. (d) The simplified formation of ABAB fashion.

mode (Scheme 2e) to bridge two Co centers to form paddlewheel $[Co_2(CO_2)_4]$ clusters, the distance of Co–Co is 2.745(7) Å. The Co–O bond lengths are in the range of 2.017(2)–2.095(2) Å and the Co–N bond length is 2.062(2) Å, which are all similar to those values found in reported complexes.^{24b} Each L^{2–} ligand links two SBUs to form a 2D layered network (Fig. 5b). Then the bpyb ligands link the layers to further generate an infinite 3D framework (Fig. 5c). The dinuclear Co(II) SBUs can be regarded as 6-connected nodes with the L ligands acting as linkers. A topology analysis reveals that the structure can be represented as the Schlafli symbol {4⁴·6¹⁰·8}, as displayed in Fig. 5d.

PXRD and TG results

To confirm whether the crystal structures are truly representative of the bulk materials, PXRD experiments are carried out for compounds 1–5. The PXRD experimental and computersimulated patterns of the corresponding complexes are shown in the ESI[†] (Fig. S1–S5). They show that the synthesized bulk materials and the measured single crystals are the same.

To estimate the stability of the coordination architectures, the thermal behavior of complexes **1–5** were studied by TGA.

For compound 1, there is not any weight loss before 430 °C, because compound 1 has not free small molecules such as H_2O , DMF, DMA, CH_3CN and so on in its system. So, it possesses better thermal stability before 430 °C. Compounds 2 and 3 have similar structures so have similar thermal stability. A weight loss is observed from 100 to 189 °C, which is attributed to the loss of the free DMF molecules. Their structures decompose quickly after 400 °C. For complex 4, a weight loss of 15.37% (calcd 15.26%) is observed from 90 to 190 °C, which is attributed to the loss of the free DMA and H_2O molecules, and it decomposes quickly after 400 °C. For complex 5, there is a weight loss of 6.64% (calcd 6.97%) in the extent from 80 to 100 °C, which is ascribed to the loss of two H_2O molecules. The TGA of the complexes are shown in the ESI† (Fig. S6).

Photochemical properties

During the past few years, the coordination polymers with d¹⁰ metal centers have been investigated for fluorescence properties with potential applications in photochemistry, chemical sensors, and light-emitting diodes (LEDs).^{26b} Compounds **1**, **3** and **4** are insoluble in common organic solvents; therefore, the

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(c)



Fig. 4 (a) Coordination environment of the Zn(II) ions in compound **4**. The hydrogen atoms are omitted for clarity (30% ellipsoid probability). Symmetry codes: #1 = 0.5 + x, 1.5 - y, 0.5 + z; #2 = -1 + x, 1 + y, z; #3 = 1 + x, -1 + y, z; #4 = -0.5 + x, 1.5 - y, -0.5 + z. (b) View of the "V-shapes" 1D chain structure formed by the L ligands and Zn cations along the *b* axis. (c) View of the 3D framework. (d) Schematic representation of the {6⁵-8} topological net with 4-fold interpenetrating architecture.

luminescent properties of the free ligands L, 4,4'-bipy, bibp and bimx and complexes **1**, **3** and **4** are investigated in the solid state and at room temperature, as depicted in Fig. 6. The emission peaks of the L, 4,4'-bipy, bibp and bimx ligands were observed with wavelengths at 423 nm for L (λ_{ex} = 304 nm), 370 nm for 4,4'-bipy (λ_{ex} = 317 nm), 438 nm for bibp (λ_{ex} = 321 nm) and 420 nm for bimx ($\lambda_{ex} = 352$ nm), which could be attributed to the $\pi^*-\pi$ or π^*-n transitions of the ligands. The emission peaks were at 415 nm in compound **1** ($\lambda_{ex} = 298$ nm), 457 nm in compound **3** ($\lambda_{ex} = 306$ nm) and 412 nm in compound **4** ($\lambda_{ex} = 362$ nm). Compound **1** exhibits an intense emission with a maximum at 415 nm upon excitation at 298 nm. They are



Fig. 5 (a) Coordination environment of the Co(II) ions in compound 5. The hydrogen atoms omitted for clarity (30% ellipsoid probability). Symmetry codes: #1 = -x, -y, -z; #2 = x, 1 - y, -0.5 - z; #3 = -x, -1 + y, 0.5 - z; #4 = 0.5 - x, -1.5 - y, -z; #5 = -x, 1 + y, 0.5 - z; #6 = x, 1 - y, 0.5 + z. (b) Views of the 2D net structure and Co(II) ions along the *c* axis. (c) Views of the 3D framework along the *b* axis. (d) The {4⁴·6¹⁰·8} topology net.



Fig. 6 Solid-state photoluminescent spectra of 1, 3 and 4 and the corresponding ligands at room temperature.

similar to those of the free L ligand so can be ascribed to the $\pi^*-\pi$ or π^*-n transitions within the molecular orbital manifolds of the imidazolyl of bimx moieties and phenyl rings of L moieties. The emission bands of compound 3 are also similar to those of the free L ligand but show a red shift of 34 nm as compared with that of the L ligand, which may be assigned to ligand to metal change transfer (LMCT).²⁷ Compound 4 exhibits mission characteristics similar to those of the L ligand but shows an obvious blue shift of 26 nm as compared with that of the L ligand. The phenomenon is probably caused by a change in the HOMO and LUMO energy levels of the deprotonated L²⁻ anions and neutral ligands coordinating to the metal centers, a charge-transfer transition between ligands and metal centers, and a joint contribution of the intraligand transitions or charge-transfer transitions between the coordinated ligands and the metal centers.²⁸ In addition, the blue shift is also attributed to the non-coplanar ligands and the different distortion among the benzene rings, which prevent the efficient electron transfer in compound 4.

All UV-vis absorption spectra for the three free ligands and complexes **2** and **5** were recorded in reflectance mode in solid state at room temperature, as shown in ESI[†] (Fig. S7). The L,



100

4.0

3.5

3.0

2.5

2.0

1.5

1.0

0.5

0.0

 $\chi_{M}T$ / cm³ K mol⁻¹

ò

50

bibp and 4,4'-bipy ligands show intense absorption peaks at 240–400 nm, which can be ascribed to π - π * and n- π * transitions of the ligands. Energy bands of **2** and **5** from 500–600 nm, are assigned as d–d transitions of the corresponding metal ions, while higher energy bands from 300 to 500 nm are assigned as probably being metal-to-ligand charge-transfer (MLCT) transitions.²⁹ The lower energy bands of compounds **2** and **5** in the 600–900 nm range are owing to the electronic transitions from ${}^{4}T_{1g}(F)$ to ${}^{4}T_{2g}(F)$.³⁰

Magnetic properties

As observed in the crystal structure, the adjacent Co atoms in complex 5 are bridged by carboxylate groups to form paddlewheel $[Co_2(CO_2)_4]$ clusters, thus its magnetic property is interesting. Variable-temperature magnetic susceptibility measurements were performed on a crystalline sample of 5 in the temperature range of 1.8-300 K. The temperature dependence of magnetic susceptibility data for 5 is shown in Fig. 7 in the form of $\chi_{M}T$ and $\chi_{M} vs T$ plots (χ_{M} is the molar magnetic susceptibility for two Co(II) ions). At room temperature, $\chi_{M}T$ is 3.921 cm³ K mol⁻¹, which is slightly greater than the expected value of 3.75 cm^3 K mol⁻¹ for two isolated high-spin Co(II) ions (g = 2 and S = 3/2) per formula because of the prominent orbital contribution arising from the 4T11g ground state of Co(II). Upon cooling, the $\chi_M T$ rapidly decreases and practically vanishes at T < 50 K, indicating antiferromagnetic coupling between the Co ions.³¹ The χ_M value slowly increases from $0.01307 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K to $0.01349 \text{ cm}^3 \text{ K mol}^{-1}$ at 229 K, but decreases to 0.00734 cm^3 K mol⁻¹ at 40 K, which is attributed to the spin-orbit coupling. Then the χ_M value rapidly increases to 0.04302 cm³ K mol⁻¹ at 2 K, which implies that there is a small amount of impurities in compound 5. The magnetic susceptibility data were fitted assuming that the carboxylate bridges of the Co(II) ions form an isolated spindimer system.

Conclusions

0.05

0.04

0.03

0.02

0.01

0.00

300

250

200

150

T/K

K mol⁻

In summary, we have successfully synthesized and characterized five new compounds by the self-assembly of H₂L, 4,4'-bipy, bibp, bpyb, bimx ligands, and different bivalent metal salts under different solvothermal conditions. The research explains that changing the central metals and the solvents may play an important role to construct the structural diversities of coordination polymers. In addition, the research provides a new example of the H₂L ligand for the design of novel frameworks. The flexible H₂L ligand can provide more possibilities for the construction of unusual topology structures and microporous coordination polymers. Subsequent works will be focused on the structures and properties of a series of coordination compounds constructed by the H₂L ligand with other auxiliary ligands and metal ions to prevent interpenetrating architecture to get good properties and porous structures of coordination polymers.

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