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Introduction

The design and construction of metal-organic coordination polymers (MOCPs) based on metal ions and multifunctional organic ligands have attracted great interest in the recent years, not only due to these solids' multifunctional applications in gas and selective molecule adsorption,¹ luminescence,² ion exchange,³ magnetism⁴ and catalysis,⁵ but also because of their complicated molecular architectures and topological features.⁶ In particular, the design and synthesis of high dimensional coordination polymers represents a quite active area. It is well known that the self-assembly process of MOCPs mainly depends on the combination of several factors, such as the nature of the organic ligands used, the versatility of the metal

Assembly of Zn/Cd coordination polymers containing helixes or polycatenane structures tuned by the tripyridyl–bis-amide ligands with different spacer: syntheses, structures, photoluminescent and photocatalytic properties[†]

Xiuli Wang,* Jingjing Huang, Lianli Liu, Guocheng Liu, Hongyan Lin, Juwen Zhang, Naili Chen and Yun Qu

Four new d¹⁰ metal–organic coordination polymers tuned by the "V"-shaped tri-pyridyl–bis-amide ligands with different spacers, namely, $[Zn(L_1)(BDC)] \cdot H_2O$ (1), $[Cd(L_1)(BDC)] \cdot H_2O$ (2), $[Zn(L_2)(BDC)]$ (3) and $[Cd(L_2)(BDC)]$ (4) (L₁ = N,N'-bis(pyridine-3-yl)pyridine-2,6-dicarboxamide, L₂ = N,N'-bis(pyridine-3-yl)pyridine-3,5-dicarboxamide, $H_2BDC = 1,4$ -benzenedicarboxylic acid) have been synthesized under hydrothermal conditions. In complexes 1 and 2, the metal ions are linked by L_1 to form left- and right-helical Zn/ Cd-L1 chains, which are further extended into two-dimensional (2D) wave-like layers by BDC anions. In 3, two L₂ ligands link two Zn^{II} ions forming the Zn₂(L₂)₂ loops, which are connected by BDC anions to form a (2.6^5) topological 2D network. In addition, the large $Zn_2(L_2)_2$ loops are threaded by the BDC rods from above and below 2D layers so as to form $2D \rightarrow 3D$ polyrotaxane and polycatenane structures. In **4**, the Cd^{II} ions are linked by L_2 ligands to generate 1D double chain ribbons with $Cd_2(L_2)_2$ loops, which are further connected by the BDC linkers to form a 3D framework. Two identical 3D frameworks interpenetrate each other in a twofold mode, giving rise to a polyrotaxane and polycatenane array, which is relative limited. The diverse structures of complexes 1-4 demonstrate that the tri-pyridyl-bis-amide ligands and the central metals have significant effect on the final structures. The thermal stability and fluorescent properties of complexes 1-4 have been investigated. In addition, the title complexes exhibit photocatalytic activity for dye methylene blue degradation under UV light.

coordination geometry and various experimental conditions.⁷ Currently, the increasing interest has been concentrated on the N-donor bridging ligands because it is the most important factor in the construction of high dimensional networks. Among various N-donor ligands, pyridyl–amide-based ligands are attracting more and more attention in the recent years. Chen *et al.* and our group have used some flexible bis-pyridyl–bis-amide ligands constructing many fascinating architectures and investigated these ligands' coordination behaviours.⁸ However, the semi-rigid tri-pyridyl–bis-amide ligands have been rarely reported to our knowledge.⁹

As an ongoing work in acylamide-based ligands,¹⁰ we try to explore the effect of the spacer and coordination sites of pyridyl–amide-based ligands on the assembly and structures of target complexes, thus in this work, two "V"-shaped tri-pyridyl– bis-amide ligands with different spacers, N,N'-bis(pyridine-3-yl) pyridine-2,6-dicarboxamide (L₁) and N,N'-bis(pyridine-3-yl) pyridine-3,5-dicarboxamide (L₂), were designed and employed to construct MOCPs. Comparing with the bis-pyridyl–bis-amide ligands, L₁ and L₂ ligands not only possess the semi-rigid spacer

Department of Chemistry, Bohai University, Liaoning Province Silicon Materials Engineering Technology Research Centre, Jinzhou, 121000, P. R. China. E-mail: wangxiuli@bhu.edu.cn

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to tune the flexibility of the whole ligands, but also have more N-donor coordination sites in the middle junction moieties to construct high-dimensional frameworks. On the other hand, acylamide groups of the ligands have the unique potential capability of providing two types of hydrogen bonding sites: the –NH moiety acting as an electron acceptor and the –C=O group as an electron donor.^{8a}

The aromatic dicarboxylates, as a kind of typical multidentate O-donor ligands, are proven to be good candidates for the self-assembly of coordination polymers because they can provide both structural scaffolding and necessary charge equalization.¹¹ Especially, the 1,4-benzenedicarboxylate (BDC) ligand has been proven useful in constructing high dimensional coordination polymer networks.¹² To the best of our knowledge, the tri-pyridyl-bis-amide ligands combining with aromatic dicarboxylates have not been reported in building MOCPs so far.

Considering the central metal's effect on the structures of MOCPs,¹³ here Zn^{II} and Cd^{II} ions were selected as central metal ions. On the basis of the aforementioned points, four coordination polymers have been synthesized by using BDC and L_1/L_2 mixed ligands under hydrothermal conditions, namely, $[Zn(L_1)(BDC)] \cdot H_2O$ (1), $[Cd(L_1)(BDC)] \cdot H_2O$ (2), $[Zn(L_2)(BDC)]$ (3) and $[Cd(L_2)(BDC)]$ (4). The effect of different N-donor ligands and the central metals on the ultimate frameworks have been represented and discussed. In addition, the thermal stability, photoluminescence properties along with photocatalytic properties of 1–4 have also been investigated in detail.

Experimental section

Materials and characterization

All chemicals were commercially available and used as purchased. Ligands L_1 and L_2 were prepared according to the literature.^{9f} FT-IR spectra were taken on a Varian FT-IR 640 spectrometer (KBr pellets). Elemental analyses (C, H, N) were carried out on a Perkin-Elmer 240C element analyzer. Thermogravimetric analyses (TGA) were recorded on a Pyris-Diamond TG instrument. The luminescence spectra were measured on a HITACHI F-4500 Fluorescence Spectrophotometer. UV-Vis absorption spectra were obtained using a SP-1900 UV-Vis spectrophotometer.

Preparation of the complexes 1-4

 $[\text{Zn}(\text{L}_1)(\text{BDC})]\cdot\text{H}_2\text{O}$ (1). A mixture containing of $\text{ZnSO}_4\cdot\text{7H}_2\text{O}$ (0.058 g, 0.2 mmol), L₁ (0.032 g, 0.1 mmol), 1,4-H₂BDC (0.025 g, 0.15 mmol) and water (8 mL) was placed in a 25 mL Teflon reactor and the pH value was adjusted around 7 by addition of 0.1 M NaOH solution. The mixture was heated at 120 °C for 6 days, and then the autoclave was gradually cooled to room temperature. Yellow block-shaped crystals of 1 were obtained in 54% yield (based on Zn). Elemental anal.(%) Anal. Calc. for C₂₅H₁₉N₅O₇Zn: C 52.97, H 3.38, N 12.36. Found: C 52.62, H 3.42, N 12.71. IR (KBr, cm⁻¹): 3238 m, 3057 w, 1689 s, 1604 s, 1544 m, 1494 m, 1350 s, 1288 w, 1207 w, 889 m, 821 w, 744 w, 657 m.

 $[Cd(L_1)(BDC)]$ ·H₂O (2). The same synthetic method as that for 1 was used except that $ZnSO_4$ ·7H₂O was replaced by $3CdSO_4$ ·8H₂O (0.052 g, 0.067 mmol). Yellow block-shaped crystals of 2 were obtained. Yield: 45% (based on Cd). Elemental anal.(%) Anal. Calc. for $C_{25}H_{19}N_5O_7Cd$: C 48.91, H 3.12, N 11.41. Found: C 49.34, H 3.07, N 11.12. IR (KBr, cm⁻¹): 3382 m, 3253 w, 1678 s, 1639 m, 1544 s, 1483 w, 1384 m, 1278 w, 1205 w, 889 m, 744 w, 657 m.

[Zn(L₂)(BDC)] (3). Complex 3 was prepared in the same way as 1 except that L₂ was used instead of L₁. Yellow block-shaped crystals of 3 were obtained. Yield: 55% (based on Zn). Elemental anal.(%) Anal. Calc. for $C_{25}H_{17}N_5O_6Zn$: C 54.71, H 3.12, N 12.76. Found: C 54.25, H 3.01, N 13.27. IR (KBr, cm⁻¹): 3419 w, 3184 w, 1681 s, 1587 s, 1544 m, 1377 s, 1299 w, 1205 w, 1091 w, 890 m, 719 w, 746 m, 657 m.

 $[Cd(L_2)(BDC)]$ (4). Complex 4 was obtained in the same way as that described for complex 3, except that $ZnSO_4 \cdot 7H_2O$ was replaced by $3CdSO_4 \cdot 8H_2O$. Yellow block-shaped crystals of 4 were obtained. Yield: 53% (based on Cd). Elemental anal.(%) Anal. Calc. for $C_{25}H_{17}N_5O_6Cd$: C 50.39, H 2.88, N 11.75. Found: C 49.93, H 2.76, N 12.08. IR (KBr, cm⁻¹): 3249 w, 3062 w, 1687 s, 1548 s, 1483 m, 1386 s, 1374 w, 1286 m, 1101 w, 1047 w, 891 m, 837 w, 742 m, 655 w.

X-ray crystallographic study

Crystallographic data for complexes 1–4 were collected on a Bruker Smart 1000 CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) by ω and θ scan mode at 293 K. The crystal structures were solved by direct methods using the SHELXS program of the SHELXTL crystallographic software package and refined by the full-matrix least-squares methods on F^2 using the SHELXTL.¹⁴ Non-hydrogen atoms were refined with anisotropic temperature parameters. The hydrogen atoms of organic ligands were generated geometrically and refined isotropically. The detailed crystal data and structures refinement for 1–4 are summarized in Table 1. Selected bond lengths and angles are given in Table S1, ESI.[†]

Results and discussion

Description of crystal structures

 $[Zn(L_1)(BDC)]\cdot H_2O$ (1). Single crystal X-ray crystallography reveals that complex 1 features a 2D wave-like layer structure. The asymmetric unit of 1 contains one crystallographically independent Zn^{II} ion, one L₁ ligand, one BDC anion, and one crystalline water molecule. As depicted in Fig. 1, the coordination environment around the Zn^{II} ion is composed of two nitrogen atoms (N1, N5#1) from two L₁ ligands and two oxygen atoms (O1, O2) from two BDC anions, exhibiting a distorted tetrahedral geometry. The Zn–O bond distances are 1.9462(18) [Zn(1)–O(1)] and 1.9606(17) Å [Zn(1)–O(2)], and the Zn–N bond distances are 2.084(2) [Zn(1)–N(1)] and 2.063(2) Å [Zn(1)–N(5)#1], which are comparable to those of the similar zinc complexes.^{8e} The BDC anion only adopts one type of bismonodentate coordination mode (Chart 1). Adjacent Zn^{II} ions

Complexes	1	2	3	4
Formula	C ₂₅ H ₁₉ N ₅ O ₇ Zn	C ₂₅ H ₁₉ N ₅ O ₇ Cd	C ₂₅ H ₁₇ N ₅ O ₆ Zn	C ₂₅ H ₁₇ N ₅ O ₆ Cd
Formula weight	566.84	613.86	548.83	595.84
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	8.8798(6)	9.064(3)	11.9526(9)	11.1167(6)
b/Å	9.2592(6)	9.558(3)	12.6037(9)	14.3657(7)
c/Å	15.0913(10)	13.644(4)	16.3810(12)	15.1482(8)
$\alpha/^{\circ}$	104.7570(10)	95.546(4)	90	90
$\beta/^{\circ}$	99.5260(10)	91.307(5)	102.0820(10)	93.2610(10)
γ/°	90.5160(10)	90.209(5)	90	90
$V/Å^3$	1181.63(14)	1176.2(6)	2413.1(3)	2415.2(2)
Ζ	2	2	4	4
$D/\mathrm{g}~\mathrm{cm}^{-3}$	1.593	1.733	1.511	1.639
μ/mm^{-1}	1.098	0.987	1.069	0.956
F(000)	580	616	1120	1192
Total reflections	6299	6242	12 710	15 306
Unique reflections	4164	4151	4373	5980
R _{int}	0.0120	0.0225	0.0398	0.0188
GOF	1.028	1.002	1.005	1.002
$R_1^a \left[I > 2\sigma(I) \right]$	0.0333	0.0271	0.0462	0.0260
wR_2^b (all data)	0.0937	0.0678	0.1424	0.0691
^{<i>a</i>} $R_1 = \Sigma F_0 - F_c / \Sigma F_0 .$	^b wR ₂ = $\Sigma [w(F_0^2 - F_c^2)^2] / \Sigma [w(F_$	$\binom{2}{2}^{2}^{2}^{2}^{1/2}.$		

are bridged by the BDC anions to form a 1D zigzag chain [Zn-BDC]_n (Fig. S1, ESI†).

An appealing structural feature in **1** is the presence of a biflexural helix, which is constructed by the L_1 ligands bridging the Zn^{II} ions (Fig. 2a). The pitch of the left- and right-handed helical chain is 8.880 Å. These helical chains are further linked by BDC anions from $[Zn-BDC]_n$ chains to furnish a 2D layer structure (Fig. 2b). In the 2D network, the Zn^{II} ion is linked by two L_1 ligands and two BDC anions, which can be considered as a 4-connected node. The BDC anion connects two Zn^{II} ions, which can be viewed as a linear linker. The L_1 ligand bridging two Zn^{II} ions acts as a 'V'-shape spacer. Thus, the structure can be classified as a 4-connected network with Schläfli symbol of $\{4^4 \cdot 6^2\}$ via the Topos40 program¹⁵ (Fig. 2c). Just as observed in Fig. S2, ESI,† the final 3D supramolecular framework of **1** is generated through the hydrogen bonding interactions between the carbon atoms [C(9)] of L₁ ligands and the oxygen atoms [O(3)] of carboxyl groups with the distance of 3.08 Å [C(9)– H(9A)···O(3)].

The similar left- and right-handed helical chains were obtained by Lu and co-workers,¹⁶ in which the chains were connected to each other by piperazine or pyrazine; while in complex **1**, the chains were further linked by BDC anions. In addition, both of them are extended into 2D layer structures.

 $[Cd(L_1)(BDC)]$ ·H₂O (2). When the Zn^{II} ion was replaced by Cd^{II} ion under the similar synthetic conditions, a structurally



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Fig. 1 The coordination environment of the Zn^{II} ion in **1** (at 30% probability level). The water molecules are omitted for clarity. Symmetry codes: #1 x - 1, y, z.

Chart 1 Coordination modes of metal Zn^{II} or Cd^{II} ions, the L_1 , L_2 ligands and dicarboxylate in complexes **1–4**.



Fig. 2 (a) The 1D Zn–L₁ left-hand helix and the right-hand helix. (b) The 2D coordination layer of complex 1. (c) Stick and simplified representations of the 2D structure for 1.

different complex 2 was obtained. It crystallizes in the triclinic space group $P\bar{1}$, and the asymmetric unit consists of one crystallographically independent Cd^{II} ion, one L₁ ligand, one BDC anion, and one lattice water molecule. Each Cd^{II} ion is seven-coordinated by five carboxyl oxygen atoms from three different BDC anions (O1, O2, O3, O4, O3#1) and two nitrogen atoms (N1, N5) from two L₁ ligands in a distorted pentagonal bipyramidal geometry (Fig. 3). The Cd–O bond distances are in the range of 2.2476(18)–2.614(2) Å and the Cd–N bond distances are 2.353(2) [Cd(1)–N(1)] and 2.431(2) [Cd(1)–N(5)] Å.

Interestingly, the L₁ ligands bridging adjacent Cd^{II} ions also afford left- and right-handed helical chains with the pitch of 9.558 Å (Fig. 4a). There are two types of BDC anions in complex 2, one adopts a μ_1 - η^1 : η^1 -bidentate chelating coordination mode with the two carboxyl groups and the other shows μ_2 - η^1 : η^2 coordination modes, respectively (Chart 1). Thus the Cd^{II}



Fig. 3 The coordination environment of the Cd^{II} ion in **2** (at 30% probability level). The water molecules are omitted for clarity. Symmetry codes: #1 -x + 2, -y, -z.

ions are linked by BDC anions to form a 2D layer structure (Fig. 4b).

From a topological viewpoint, the Cd^{II} ions are coordinated by two L₂ ligands and three BDC ligands, which can be viewed as a 5-connected node, the L₁ ligand is considered as a 'V'-shape spacer and the BDC anion is regarded as a linear linker. Then, the 2D corrugated structure can be classified as a 5-connected network with Schläfli symbol of $\{3^3 \cdot 4^4 \cdot 5^3\}$ (Fig. 4c). The extension of the 2D layer into a 3D supramolecular network is accomplished by two kinds of hydrogen bonding interactions (Fig. S3, ESI[†]). One is between the oxygen atoms [O(1W)] of lattice water molecules and the oxygen atoms [O(2)] of carboxyl groups with the distance of 2.88 Å [O(1W)– H(1WA)···O(2)]. The other is between the oxygen atoms [O(1W)] of lattice water molecules and the oxygen atoms [O(9)] of L₁ ligands with the distance of 2.93 Å [O(1W)–H(1WB)···O(9)].

In complex [Cd(BDC)(phen)]·H₂O (phen = 1,10-phenanthroline) obtained by Rao and co-workers,¹⁷ the coordination modes of BDC anions are the same as those of complex 2. However, the Cd^{II} ions are linked by BDC anions to form a different 2D layer due to the different angle between the BDC anions, and the phen ligands just chelate to the Cd^{II} ions as terminal group. While in complex 2, the L₁ ligands connect the Cd^{II} ions to form left- and right-handed helical chains subordinating to the 2D network.

[Zn(L₂)(BDC)] (3). When the L₂ ligand was used instead of L₁ ligand, a completely different framework of 3 was obtained. Single crystal X-ray diffraction analysis reveals that complex 3 is an interesting 2D → 3D polyrotaxane and polycatenane structure. The asymmetric unit consists of one crystallographically independent Zn^{II} ion, one L₂ ligand and one BDC anion. As shown in Fig. 5, each Zn^{II} ion adopts a distorted tetrahedron geometry, completed by two nitrogen atoms (N1, N5#1) from two L₂ ligands and two oxygen atoms (O1, O2) from two BDC anions. The Zn–O bond distances are 1.927(3) Å [Zn(1)–O(1)] and 1.969(3) Å [Zn(1)–O(2)], while the Zn–N bond distances are 2.057(3) Å [Zn(1)–N(1)] and 2.071(3) Å [Zn(1)–N(5)#1], respectively.



Fig. 4 (a) The L_1 ligands link the adjoining Cd^{II} ions into left- and right-helical chains. (b) The 2D coordination layer of complex **2**. (c) Stick and simplified representations of the 2D wave-like network of **2**.

In complex 3, the BDC anions take the μ_1 - η^1 : η^0 bismonodentate coordination mode bridging neighboring Zn^{II} ions to display a 1D zigzag chain (Fig. S4, ESI†). The two L_2





Fig. 5 The coordination environment (at 30% probability level) of the Zn^{II} ion in **3**. Symmetry codes: #1 -x, -y, -z.

ligands connect two Zn^{II} ions to form a 28-membered $Zn_2(L_2)_2$ loop with ca. 12 \times 12.59 Å² (Fig. S5a, ESI[†]), which may constitute a potential factor to generate polyrotaxane and polycatenane motifs. The adjacent loops are integrated by the 1D Zn-BDC chains to form a 2D network (Fig. 6a). The 2D sheet could be simplified to a 3-connected net with 6³-hcb topology if the loops are regarded as a linker. However, the description of the network cannot properly describe the topology of interpenetration¹⁸ as it would require linkers to pass through the $Zn_2(L)_2$ loops. If considering the Zn^{II} ion as a 4-connected node and the L₂ ligand as a 'V'-shape spacer, then a $(2 \cdot 6^5)$ topological net is created. Thus we obtain a network description that can be used to further describe the interpenetration. The most peculiar feature of 3 is the entangled fashion between the $Zn_2(L_2)_2$ loop and the BDC anion. The $Zn_2(L_2)_2$ loops within one sheet are large enough to be passed by the BDC rods from the above and below 2D layers, so as to form a 2D \rightarrow 3D polythreading structure, further giving rise to a 3D polyrotaxane and polycatenane array. The entangled fashion is shown in Fig. 6b and c: one $Zn_2(L_2)_2$ loop of the yellow layer is threaded by one pink BDC ion rod of the pink layer, and the loop of the pink layer is threaded by one light blue rod of the blue layer and so on. A closer inspection reveals that only two opposite rods perform such rotaxane-like behavior and the other two rods are free of such operation.

Sun and co-workers have obtained a similar 2D layer in $[Zn(bmimbp)(tbtpa)]_n$ (bmimbp = 4,4'-bis(2-methylimidazol-1ylmethyl)biphenyl, H₂tbtpa = tetrabromoterephthalic acid).¹⁹ The final structures were completely different, although they all contain flexible N-donors as loop linkers and aromatic dicarboxylate as rods. The 2D network was interlocked with each other in a 2D \rightarrow 2D parallel fashion, thus directly leading to the formation of a 2D polyrotaxane-like structure containing rotaxane-like motifs in $[Zn(bmimbp)(tbtpa)]_n$, while in complex 3 the 2D layer was interlocked with each other in a 2D \rightarrow 3D polyrotaxane and polycatenane array. The structure of complex 3 is similar to the complex $Zn(L)(BDC) \cdot (H_2O)_{0.5}$ (L = N_*N' -di(pyridin-3-yl)isophthalamide) reported by Luo and co-



Fig. 6 (a) The 2D layer and 4-connected ($2 \cdot 6^5$) topology matrix of **3**. (b) The representative description of $2D \rightarrow 3D$ polyrotaxane and polycatenane array in **3**. (c) Stick and simplified representations of $2D \rightarrow 3D$ framework in **3**.

workers.²⁰ In complex Zn(L)(BDC)·(H₂O)_{0.5}, a bis-pyridyl-bisamide ligand was used, while in complex **3**, we adopted a tripyridyl-bis-amide ligand with an extra N-donor coordination site in the middle junction moiety. Both the structures contain $Zn_2(L_2)_2$ loops with different dimensions. They are *ca.* 12 × 12.59 Å² in **3** and *ca.* 11.69 × 12.90 Å² in complex $Zn(L)(BDC)\cdot(H_2O)_{0.5}$. The twist degrees of the N-donor ligands shown by the dihedral angles between the terminal pyridyl rings and the central rings are 66.16° and 0° in complex $Zn(L)(BDC)\cdot(H_2O)_{0.5}$, while the dihedral angles are 63.30° and 10.23° in complex **3**.

[Cd(L₂)(BDC)] (4). Single crystal X-ray diffraction analysis reveals that complex 4 consists of two identical 3D frameworks that are interpenetrated in a parallel fashion, resulting in a twofold interpenetrating architecture showing both polyrotaxane and polycatenane characters. The asymmetric unit of 4 contains a Cd^{II} ion, one L₂ ligand and one BDC anion. The Cd^{II} anion is coordinated by four carboxyl oxygen atoms (O1, O2, O3, O4) from two BDC anions and three nitrogen atoms (N1, N5, N3#1) from three L₂ ligands showing distorted pentagonalbipyramid geometry in Fig. 7. The Cd–O bond distances are in



Fig. 7 The coordination environment (at 30% probability level) of the Cd^{II} ion in **4**. Symmetry codes: #1 - x + 1, -y + 1, -z + 1; #3 - x, 1 - y, 1 - z; #5 - 1 + x, y, z.

the range of 2.3021(16)-2.5283(17) Å, while the Cd-N bond distances are from 2.3350(19) to 2.6091(19) Å.

In complex 4, two carboxyl groups of the BDC anions take the same coordination mode of chelating μ_1 - η^1 : η^1 -bidentate to connect adjacent Cd^{II} ions forming a zigzag chain (Fig. 8a). The L_2 ligand adopts a μ_3 -bridging coordination mode (Chart 1), which is different from that in complex 3. The Cd^{II} ions are linked by L2 ligands to generate a 1D double chain ribbon with a 28-membered $Cd_2(L_2)_2$ loop. The dimension of the loop is *ca.* 12.37 \times 12.39 Å² (Fig. S5b, ESI[†]). The 1D double chains connect with the 1D Cd-BDC zigzag chains through sharing Cd^{II} ions to form a 3D architecture, as shown in Fig. 8a. Each Cd^{II} ion is connected to three L_2 ligands and two BDC anions and thus the Cd^{II} ion can be considered as a 5-connected node, whereas each L_2 ligand is bridged by three neighboring 5-connected Cd^{II} ions, and can be regarded as a 3-connected node. Topological analysis reveals that complex 4 forms a binodal 3,5-connected framework with the Schläfli symbol of $(4^2 \cdot 6^5 \cdot 8^3)(4^2 \cdot 6)^{21}$ Furthermore, two identical 3D frameworks interpenetrate each other in a twofold mode (Fig. 8c). On the other hand, if we regard the BDC anion as a single rod, the structure of 4 can be described as a 3D metalorganic polyrotaxane and polycatenane framework. The entangled fashion is shown in Fig. 8b: one loop of the blue 3D framework is threaded by one BDC anion rod of the pink 3D net and the loop of the pink 3D framework is threaded by one blue rod of the blue 3D net.

So far, although a number of interpenetrating networks have been reported,²² examples showing the polyrotaxane and polycatenane features have been rarely observed within coordination polymers.^{8a,19,23} Recently, Ma's group have reported a twofold interpenetrating 3D polyrotaxane framework [Cd_{1.5}(Tipa)(BDC)Cl]₂·4H₂O (Tipa = tri(4-imidazolylphenyl)amine.²⁴ However, the differences can be found by the insight into the complicated framework. The single 3D framework а polyrotaxane net in complex is $[Cd_{1.5}(Tipa)(BDC)Cl]_2 \cdot 4H_2O$, while in complex 4, the single 3D framework is just a 3,5-connected framework, which



Fig. 8 (a) Single 3D framework constructed by Zn^{II} –BDC chains and Zn^{II} –L₂ double chains in **4**. (b) The representative description of the entangled net in **4**. (c) Schematic representation of the twofold interpenetrated polyrotaxane and polycatenane framework of **4**.

interpenetrates each other in a twofold mode to obtain a polyrotaxane and polycatenane array.

Effects of the N-donor ligands and the central metals on the structures of the complexes

From the structure descriptions above, we can see that the N-donor ligands play important roles in the construction of the final structures. In this study, two kinds of tri-pyridyl-bis-

amide ligands were used to investigate the effect of nitrogen atoms' positions of the spacer groups on the structures. In complex 1 and 2, the L₁ ligands link metal ions forming leftand right-helixes, which are finally extended into 2D layers by BDC anions. However, the metal ions are connected by L₂ ligands to generate $M_2(L_2)_2$ loops, which are ultimately threaded by BDC anions into 3D polyrotaxane and polycatenane arrays in 3 and 4. All of these may be ascribed to the different positions of middle pyridyl-N atoms in L1 and L2 ligands. Moreover, the twist degrees of the L_1 and L_2 ligands can also influence the final structures of 1-4. The twist degrees of the N-donor ligands are shown by the dihedral angles between the three pyridyl rings: θ_1 represents the dihedral angle between the pyridyl group containing N1 atom and the central pyridyl ring; θ_2 is the dihedral angle between the pyridyl ring containing N5 atom and the central pyridyl group; θ_3 represents the dihedral angle between the pyridyl group containing N1 atom and the pyridyl ring containing N5 atom. As shown in Table S2, ESI[†], the difference in the θ angles between 1-4 is mainly attributed to the changes in the positions of the middle pyridyl-N atoms and the various conformations of ligands when they coordinate with the central metal atoms.

On the other hand, the central metals have significant effects on the resultant structures of the coordination polymers. The Zn^{II} ion displays four-coordinated distorted tetrahedral geometry in complexes 1 and 3. Whereas Cd^{II} ion adopts a seven-coordinated mode and can be regarded as distorted pentagonal-bipyramid geometry in complexes 2 and 4. Besides that, metal ions also influence the coordination modes of organic ligands. The carboxyl groups of BDC anions adopt a μ_1 - η^1 : η^0 -monodentate coordination mode in **1** and **3**, while carboxyl groups of BDC anions take μ_1 - η^1 : η^1 -bidentate or μ_2 - η^1 : η^2 coordination modes in 2 and 4. In 3, the L₂ ligands show µ2-bridging coordination modes to link Zn^{II} ions forming a $Zn_2(L_2)_2$ loop, however, in complex 4 the L_2 ligands displaying a µ3-bridging coordination mode connect adjacent Cd^{II} ions to form a 1D double chain containing a $Cd_2(L_2)_2$ loop. So, the difference in the coordination numbers of the central metals is also the key reason for the structural diversities.

Thermal stability analysis

Thermal gravimetric analyses (TGA) of complexes 1-4 were performed to investigate their thermal stabilities. The TG curves of complexes 1 and 2 exhibit two obvious weight loss steps (Fig. S6, ESI[†]). The first weight loss of 3.12% for 1 from 185 to 260 °C and 3.01% for 2 in the region of 185-245 °C is assigned to the elimination of the lattice water molecules (calcd: 3.18% for 1, 2.93% for 2). The second weight loss occurred at 356 °C for 1 and 330 °C for 2. The ZnO residue of 14.21% (calcd: 14.36%) is observed at 600 $\,^\circ \! C$ and the CdO residue of 21.06% (calcd: 20.92%) is occurred at 570 °C, which corresponds to the decomposition of organic components. Compared with complexes 1 and 2, the TG curves of 3 and 4 only show one step weight loss process, corresponding to the loss of BDC and L₂ ligands. The overall framework of 3 begins to collapse at 385 °C and ends at 530 °C with the ZnO residue of 14.67% (calcd: 14.83%). No obvious weight loss is observed



Fig. 9 Emission spectra of $L_1,\,L_2$ ligands and complexes 1--4 in the solid state at room temperature.

for complex 4 until the decomposition of the framework occurs at 370 $^{\circ}$ C, and the CdO residue of 21.79% (calcd: 21.55%) is obtained at 570 $^{\circ}$ C.

Fluorescence properties of complexes 1-4

MOFs with d¹⁰ metal atoms are promising candidates for photoactive materials with potential applications such as chemical sensors, photochemistry and electroluminescent displays.²⁵ The emission spectra of complexes 1-4 and free ligands have been investigated in the solid state at room temperature under the same experimental conditions. As illustrated in Fig. 9, L1 and L2 exhibit intense emission bands with a maximum at 431 nm upon excitation at 280 nm and a maximum at 432 nm upon excitation at 315 nm, respectively. The emission bands are probably attributable to the $\pi^*-\pi$ transitions. Intense emission peaks of complex 1 and complex 2 are found at 412 nm (λ_{ex} = 307 nm) and 408 nm (λ_{ex} = 307 nm), which are blue-shifted 19 nm and 23 nm as compared with those of the pure L_1 ligand. The fluorescent emission peaks can be observed at 414 nm (λ_{ex} = 325 nm) for 3, which is blue-shifted 18 nm compared with the free L₂ ligand. For complex 4, the emission band appears at 434 nm (λ_{ex} = 325 nm), which is similar to that of free L_2 ligand. It is well known that the Zn^{II} and Cd^{II} ions are difficult to oxidize or reduce because of the d¹⁰ configuration. Therefore, the emissions of these complexes can be attributed to intraligand transitions.²⁶ The different emission positions and intensities of 1-4 may be due to their different structures.

Photocatalytic properties

To study the photocatalytic activity of complexes 1–4, we selected methylene blue (MB) as a model dye contaminant to evaluate the photocatalytic activities in the purification of wastewater. The experiments were investigated through a typical process: 50 mg powder of the title complexes was dispersed in a 200 mL MB aqueous solution with the concentration of 10.0 mg L^{-1} , magnetically stirred in the dark



Fig. 10 (Top and middle) Absorption spectra of the MB solution during the decomposition reaction under UV irradiation with the presence of complex 1 and 2. (Bottom) Photocatalytic decomposition of MB solution under UV irradiation with the use of the title complexes and no catalyst under the same conditions.

for 0.5 h to ensure the equilibrium of the working solution. Then the solution was exposed to UV irradiation from a Hg lamp, kept continuously stirring. 5 mL of suspension was taken for centrifugal separation every 30 min. Then the transparent solution of the top layer was taken out for analysis. Under the same conditions, the simple photolysis comparative experiment was also completed without any catalyst. As illustrated in Fig. 10, Fig. S7 and S8, ESI[†], the absorption peaks of MB decreased obviously under the UV in the presence of 1 and 2, while the absorption peaks decreased much slowly in the presence of 3 and 4. Besides that, changes in the concentration of MB solution were plotted versus irradiation time. The calculation results show that the MB degrades approximately from 100% to 23% for complex 1, to 11% for complex 2, 54% for complex 3 and 74% for complex 4 after 180 min, respectively. It is obvious that the complexes 1 and 2 have higher photocatalytic activities for the degradation of MB than those of complexes 3 and 4. The possible reason maybe lies in the difference of components and structures.²⁷ After photocatalysis, the color, the morphology and the IR spectra of the complexes have not changed, which is illustrated by microscopy and FT-IR spectrometry (Fig. S9-S12, ESI[†]). The result indicates that the catalyst may be recycled after the catalytic experiments.

During the photocatalytic process, the central metal atoms and the coordinated ligands are involved. UV-Vis light induces N-donor ligands and BDC anions to produce O and/or N-metal charge transfer promoting electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Therefore, the HOMO strongly needs one electron to return to its stable state. Thus, one electron was captured from water molecules, which was oxygenated to generate the •OH radicals.²⁸ And then the •OH active species could decompose the dye effectively to complete the photocatalytic process.

Conclusion

The simultaneous use of the "V"-shaped tri-pyridyl-bis-amide ligands and 1,4-benzenedicarboxylate to react with d¹⁰ metals affords a series of interesting 2D or 3D networks. Both complexes 1 and 2 exhibit a 2D wave-like layer containing leftand right-helixes constructed by metal ions and tri-pyridyl-bisamide ligands. Based on $M_2(L_2)_2$ loops, complex 3 features a $2D \rightarrow 3D$ polyrotaxane and polycatenane structure and complex 4 displays a twofold interpenetrating 3D framework with polyrotaxane and polycatenane array. The changes in the positions of central pyridyl-N atoms and the twist degrees of the L_1 and L_2 ligands play an important role in constructing different high-dimensional structures. This result represents a rational synthesis strategy to modulate and control the formation of high-dimensional architectures, and further enriches crystal engineering. In addition, the photoluminescent properties of complexes 1-4 imply that these complexes may be good candidates for potential applications in optical materials. The photocatalytic behaviors of complexes 1 and 2 prove they may be good and stable photocatalysts for the photodegradation of MB. Currently, further studies are under investigation in our laboratory.

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