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Four cadmium(II) coordination polymers with an N- and O-donor ligand: Structural characterization, in situ reaction and fluorescent property

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ABSTRACT

Cadmium nitrate tetrahydrate reacts with 5-(1H-benzotriazol-1-ylmethyl)isophthalic acid (H₂L) under hydrothermal conditions to yield four complexes, [Cd(L¹)(py)₂(H₂O)] (**1**), [Cd(L)(DMF)(H₂O)] (**2**), [Cd(L)] (**3**) and [Cd(L)] (**4**) [L¹ = in situ generated 5-(2H-benzotriazol-2-ylmethyl)isophthalate, py = pyridine, DMF = *N*,*N*-dimethylformamide], which have been characterized by single crystal and powder X-ray diffraction, IR, elemental and thermogravimetric analyses. Complexes **1–4** exhibit structural diversity, which is dependent upon different experimental conditions. As a result, complex **1** has a chain structure, which can be further linked by hydrogen bonding and C-H···*π* interactions to form a 2D network structure; **2** displays a double-stranded chain structure and a 3D supramolecular framework can be built *via* hydrogen bonding and π -*π* stacking interactions; **3** and **4** are a pair of isomers: **3** is a binodal (3,6)-connected 2D kgd network with (4³)₂(4⁶·6⁶·8³) topology, while **4** displays a binodal (3,6)-connected 3D **rtl** (4·6²)₂(4²·6¹⁰·8³) framework architecture. Significantly, an in situ rearrangement reaction of H₂L to H₂L¹ occurs during the synthesis of **1**. The influential factors of the synthetic strategies on the coordination modes of the ligand and the structures of resultant complexes are discussed. Furthermore, the fluorescent properties of **1–4** were preliminarily investigated.

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1. Introduction

In recent years, coordination supramolecular chemistry has mainly been concerned with the design and assembly of crystalline materials based on metal centers and bridging ligands, and consequently, exploration of such hybrid materials with interesting properties and potential applications has been becoming the main aim of crystal engineering of coordination chemistry [1]. It is known that the functional properties of complexes are largely dependent on the nature of the metal centers and bridging ligands, and their architectures. For example, complexes with porous framework architectures may show sorption or catalytic properties [2]; metal ions possessing unpaired electrons, such as Mn(II), Co(II), Ni(II) and Cu(II) etc., could be bridged by ligands to form polynuclear subunits which may mediate magnetic interactions [3]; moreover, complexes containing metal centers with a d^{10} electron configuration, such as Zn(II) and Cd(II), may exhibit luminescent properties [4]. Therefore, it may be significant to pursue structural diversity by attempting to use different experimental conditions, though it is still a great challenge to assemble complexes with target structures because of complicated factors influencing the assembly process [5]. However, the complexity of self-assembly may also give access to composite polymers with novel functional properties as there is a vast domain of potentially multifunctional materials [6]. Among many influential factors, the intrinsic nature of the organic ligands has been proven to play a decisive role in the formation of complexes [7].

In previous research, rigid carboxylate ligands, such as isophthalate, terephthalate and 1.3.5-benzetricarboxylate, have been well studied in the syntheses of complexes due to their fine coordinating capacities and appropriate connectivity [8]. Meanwhile, benzotriazole and its benzene ring-substituted derivatives may induce new coordination insight for structural evolution in crystal engineering based on their steric hindrance and more potential coordination sites [9]. However, the combination of both benzotriazolyl and carboxylate functional groups in a single organic ligand remains less investigated. Recently, we have been focusing our attention on the coordination reactions of metal salts with an N- and O-donor ligand: 5-(1H-benzotriazol-1-ylmethyl)isophthalic acid (H₂L). Our main goals are to synthesize complexes with fascinating structures and interesting properties and to seek for further comprehension of the relationship between the experimental conditions and the structures of the resultant complexes. The H₂L ligand has an advantage over other N- or O-donor ligands since it possesses two functional groups, namely carboxylate and flexible benzotriazol-1-ylmethyl groups. Due to the relative orientation of the two carboxylate groups and their potential mutable coordination patterns, such as $\mu_1 - \eta^1$: η^0 -monodentate, $\mu_1 - \eta^1$: η^1 -chelating and $\mu_2 - \eta^1$: η^1 -bridging modes, H₂L can act as a





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multi-connector in the assembly of complexes [10]. Furthermore, the flexible benzotriazol-1-ylmethyl arm in H₂L has more spatial freedom to adopt different orientations [11], which originates from its axial rotation to a different angle to satisfy coordinating requirements. The potential variable coordination modes and conformations of H₂L provide the feasibility to assemble complexes with various structures by regulating the experimental conditions. We report herein the syntheses and characterization of four new coordination polymers, $[Cd(L^1)(py)_2(H_2O)]$ (1), $[Cd(L)(DMF)(H_2O)]$ (2), [Cd(L)] (3) and [Cd(L)] (4) [py = pyridine, DMF = *N*,*N*-dimethyl-formamide]. The fluorescence of 1–4 was also examined.

2. Experimental

2.1. Materials and measurements

All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. According to the reported literature [12], a similar experimental procedure was used to synthesize the H₂L ligand. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C elemental analyzer. Thermogravimetric analyses (TGA) were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of 10 °C min⁻¹. FT-IR spectra were recorded in the range 400-4000 cm⁻¹ on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. Powder X-ray diffraction (PXRD) patterns were obtained on a Shimadzu XRD-6000 X-ray diffractometer with Cu K α (λ = 1.5418 Å) radiation at room temperature. The luminescence spectra for the powdered solid samples were measured on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width was 5 nm, and all the measurements were carried out under the same experimental conditions.

2.2. Synthesis of $[Cd(L^1)(py)_2(H_2O)]$ (1)

A solution of $Cd(NO_3)_2$ ·4H₂O (61.8 mg, 0.2 mmol) and H₂L (29.7 mg, 0.1 mmol) in pyridine/H₂O (2:8, 10 mL) was stirred for 30 min. Then reaction mixture was placed in a 16 mL Teflon-lined

Table 1

Crystal data and structure refinements for complexes 1-4.

stainless steel container and heated at 210 °C for 72 h. The oven was then turned off and cooled down naturally to ambient temperature. After cooling to room temperature, colorless slender crystals of **1** were obtained in an approximate yield of 20% based on H₂L. *Anal.* Calc. for $C_{25}H_{21}N_5O_5Cd$: C, 51.43; H, 3.63; N, 11.99. Found: C, 51.16; H, 3.42; N, 11.79%. IR (KBr pellet, cm⁻¹): 3422 (br, m), 1615 (s), 1603 (s), 1568 (s), 1552 (s), 1447 (s), 1376 (s), 1302 (w), 1275 (w), 1243 (m), 1220 (m), 1098 (m), 1071 (w), 1036 (w), 778 (m), 751 (s), 727 (s), 700 (s).

2.3. Synthesis of $[Cd(L)(DMF)(H_2O)]$ (2)

The reaction mixture of Cd(NO₃)₂·4H₂O (61.8 mg, 0.2 mmol), H₂L (29.7 mg, 0.1 mmol) and 5 mL DMF in 5 mL H₂O was sealed in a 16 mL Teflon-lined stainless steel container and heated at 100 °C for 48 h. The oven was then cooled down at a rate of 10 °C/h. After cooling to room temperature, colorless plate crystals of **2** were obtained in an approximate yield of 25% based on H₂L. *Anal.* Calc. for C₁₈H₁₈N₄O₆Cd: C, 43.35; H, 3.64; N, 11.23. Found: C, 43.56; H, 3.52; N, 11.49%. IR (KBr pellet, cm⁻¹): 3332 (br, m), 1646 (m), 1615 (m), 1556 (s), 1497 (m), 1454 (s), 1438 (s), 1372 (s), 1242 (m), 1219 (m), 1113 (m), 930 (w), 789 (m), 773 (s), 757 (s), 722 (s), 676 (m).

2.4. Synthesis of [Cd(L)] (3)

The reaction mixture of Cd(NO₃)₂·4H₂O (61.8 mg, 0.2 mmol), H₂L (29.7 mg, 0.1 mmol) and KOH (11.2 mg, 0.2 mmol) in 10 mL H₂O was sealed in a 16 mL Teflon-lined stainless steel container and heated at 180 °C for 72 h. The oven was then turned off and cooled down naturally to ambient temperature. After cooling to room temperature, colorless needle crystals of **3** were obtained in an approximate yield of 20% based on H₂L. *Anal.* Calc. for C₁₅H₉₋ N₃O₄Cd: C, 44.19; H, 2.23; N, 10.31. Found: C, 44.46; H, 2.44; N, 10.52%. IR (KBr pellet, cm⁻¹): 1616 (s), 1561 (s), 1457 (s), 1386 (s), 1314 (w), 1290 (w), 1243 (w), 1227 (m), 1171 (w), 808 (w), 783 (m), 768 (s), 744 (s), 728 (s), 593 (w).

Compound	1	2	3	4
Empirical formula	C ₂₅ H ₂₁ N ₅ O ₅ Cd	C ₁₈ H ₁₈ N ₄ O ₆ Cd	$C_{15}H_9N_3O_4Cd$	$C_{15}H_9N_3O_4Cd$
Formula weight	583.87	498.76	407.65	407.65
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	ΡĪ	$P2_1/c$	$P2_1/c$
a (Å)	15.5435(10)	9.7945(3)	8.439(5)	11.3010(6)
b (Å)	10.3174(7)	10.4765(3)	11.404(5)	9.1272(5)
c (Å)	17.9635(9)	11.3523(4)	17.255(5)	16.8393(7)
α (°)	90.00	73.84	90.00	90.00
β(°)	119.374(4)	65.96	119.279(17)	127.069(3)
γ (°)	90.00	64.10	90.00	90.00
T (K)	293(2)	293(2)	293(2)	293(2)
V (Å ³)	2510.4(3)	949.82(5)	1448.4(11)	1385.90(12)
Ζ	4	2	4	4
$D_{\text{calc}} (\text{g cm}^{-3})$	1.545	1.744	1.869	1.954
$\mu (\mathrm{mm}^{-1})$	0.915	1.194	1.532	1.601
F(000)	1176	500	800	800
θ (°)	1.50-28.32	2.18-28.24	2.24-28.35	2.26-28.33
Reflections collected	17748	6794	10220	9683
Unique reflections	6243	4606	3608	3452
Goodness-of-fit (GOF) F ²	1.025	1.090	1.006	1.062
R_1^{a} , wR_2^{b} [$I > 2\sigma(I)$]	0.0541, 0.1351	0.0187, 0.0499	0.0273, 0.0688	0.0386, 0.1047
R_1 , w R_2 (all data)	0.0688, 0.1368	0.0193, 0.0502	0.0322, 0.0709	0.0436, 0.1083

^a $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$.

^b $wR_2 = |\Sigma w(|F_0|^2 - |F_c|^2)|/\Sigma |w(F_0)^2|^{1/2}$, where $w = 1/[2(F_0^2) + (aP)^2 + bP]$. $P = (F_0^2 + 2F_c^2)/3$.



Scheme 1. Schematic representation of the hydrothermal syntheses of complexes **1–4**.



Scheme 2. Coordination modes of the ligands in complexes 1-4.

2.5. Synthesis of [Cd(L)] (4)

Complex **4** was synthesized by the same hydrothermal procedure as that used for the preparation of **3**, except raising the reaction temperature to 210 °C. Colorless block crystals of **4** were obtained in an approximate yield of 20% based on H₂L. *Anal.* Calc. for C₁₅H₉N₃O₄Cd: C, 44.19; H, 2.23; N, 10.31. Found: C, 44.36; H, 2.07; N, 11.12%. IR (KBr pellet, cm⁻¹): 1618 (s), 1552 (s), 1497 (m), 1455 (s), 1430 (w), 1380 (s), 1356 (m), 1282 (m), 1250 (w), 1219 (m), 1170 (m), 804 (m), 780 (m), 765 (s), 740 (s), 722 (s), 596 (m).

2.6. X-ray crystallography

The crystallographic data collections for complexes **1–4** were carried out on a Bruker Smart Apex CCD area-detector diffractometer using graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 293(2) K. The diffraction data were integrated by using the sAINT program [13], which was also used for the intensity corrections for the Lorentz and polarization effects. A semi-empirical absorption correction was applied using the sADABS program [14]. The



Scheme 3. The proposed mechanism of the rearrangement reaction of the $(L^1)^{2-}$ ligand in complex **1**.

structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix leastsquares technique using the SHELXL-97 crystallographic software package [15]. In **1–4**, all hydrogen atoms bonded to C were generated geometrically; hydrogen atoms in the water molecules in **1** and **2** were found at reasonable positions in the difference Fourier maps and located there. The details of crystal parameters, data collection and refinements for the complexes are summarized in Table 1; selected bond lengths and angles are listed in Table S1; hydrogen bonds in **1** and **2** are listed in Table S2.

3. Results and discussion

3.1. Preparation

As is shown in Scheme 1, the hydrothermal reactions of a stoichiometric amount of cadmium nitrate tetrahydrate with H_2L under different experimental conditions provided single crystalline materials of **1–4**, which are stable in air. The ligand H_2L/H_2L^1 exhibits varied coordination modes as observed in complexes **1–4** (Scheme 2). The crystal structures of **1–4** are discussed in detail in the following sections.

3.2. Crystal structural description of $[Cd(L^1)(py)_2(H_2O)]$ (1)

It is noteworthy that the rearrangement of H_2L to H_2L^1 (vide supra) occurred in the formation of **1**. As shown in Scheme 3, the rearrangement reaction takes places under alkaline conditions, as reported previously [16]. Considering the synthetic conditions of complexes **1–4**, a high concentration of hydroxyl may be crucial for the occurrence of the rearrangement. The complete deprotonation of the in situ generate H_2L^1 ligand could be further confirmed by IR spectroscopy because of no characteristic vibration band in the range 1680–1760 cm⁻¹ was observed.

Crystallographic analysis reveals that complex **1** exhibits a chain structure with the asymmetric unit containing one Cd(II) center, one $(L^1)^{2-}$ ligand, two coordinated pyridine molecules and one coordinated water molecule. As shown in Fig. 1a, each Cd(II) center is seven-coordinated with a distorted pentagonal bipyramidal geometry by two N atoms (N21, N31) from two coordinated pyridine molecules, with Cd–N bond distances of 2.352(4) and 2.323(4) Å, and five O atoms from two carboxylate groups and one coordinated water molecule, with Cd–O bond lengths in the range 2.314(3) to 2.566(3) Å. The Cd–O and Cd–N bond distances are comparable to previously reported values for Cd(II) complexes. The coordinating bond angles around Cd(II) vary from 51.91(10)° to 176.13(12)° (Table S1). Both carboxylate groups in the



Fig. 1. (a) The coordination environment of the Cd(II) ions in **1** with the ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity. (b) The 1D structure of **1**. (c) The double-chain structure in **1** extended by hydrogen bonding interactions. (d) The 2D network of **1** extended by hydrogen bonding and C-H \cdots π stacking interactions.

 $(L^{1})^{2-}$ ligand adopt $\mu_{1-}\eta^{1}$: η^{1} -chelating coordination modes (Scheme 2A), exhibiting almost identical C-O bond lengths, consistent with electron delocalization, and with the angles subtended at cadmium being 51.91(10)° and 53.61(10)°, respectively. The in situ generated benzotriazol-2-ylmethyl group is free of coordination. Therefore, each $(L^{1})^{2-}$ ligand acts as a μ_{2} -bridge to link two Cd(II) atoms; meanwhile each metal atom is surrounded by two different $(L^{1})^{2-}$ ligands. This interconnection repeats infinitely to give rise to a chain structure along the [100] direction

(Fig. 1b). Moreover, hydrogen bonding and C–H··· π interactions are available in **1** to arrange the molecular building blocks, which are very important for the construction and stabilization of the resultant molecular structure: (1) O(5)–H(20)···O(3)#1 [#1: 1 – *x*, 1–*y*, 2 – *z*; O(5)···O(3)#1 = 2.731(5) Å; \angle O(5)–H(20)–O(3)#1 = 139°], hydrogen bonding interactions between H atoms in water molecules and carboxylate O atoms from adjacent chains (Table S2). The hydrogen bonding interactions link the adjacent chains to form a double-chain structure (Fig. 1c). (2) Stacking



Fig. 2. (a) The coordination environment of the Cd(II) ions in **2** with the ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity. (b) The neutral double-stranded chain of **2**. (c) Schematic view of the right- and left-handed helical chains in **2**. (d) The 2D network of **2** extended by hydrogen bonding interactions. (e) The 3D framework of **2** constructed through hydrogen bonding and π - π stacking interactions.

interactions between C24–H12 and the central benzene ring (symmetry code: -x, -1/2 + y, 3/2-z; the distance between H12 and the centroid of the central benzene ring plane is 2.643 Å), and then adjacent double-stranded chains can be further linked to yield a 2D supramolecular network by taking the C–H··· π stacking interactions into account (Fig. 1d).

3.3. Crystal structural description of [Cd(L)(DMF)(H₂O)] (2)

Complex **2** exhibits a double-stranded chain structure. There are one Cd(II), one L^{2-} ligand, one coordinated DMF and one coordinated water molecule in the asymmetric unit of **2**. As shown in Fig. 2a, each Cd(II) center is six-coordinated by one benzotriazolyl nitrogen atom, one coordinated DMF, one coordinated water oxygen atom and three carboxylate oxygen atoms from two different

 L^{2-} ligands to furnish a distorted octahedral coordination geometry. The DMF oxygen atom and the benzotriazolyl nitrogen atom occupy the apices and the other four oxygen atoms are located in the equatorial plane. The coordinating bond lengths vary from 2.2148(11) to 2.3921(13) Å and the coordinating bond angles are in the range 56.37(4)° to 172.13(5)°. One of carboxylate groups in the L^{2-} ligand exhibits the $\mu_1-\eta^1$: η^0 -monodentate coordination mode, and the other is a $\mu_2-\eta^1$: η^1 -chelating one (Scheme 2B). As depicted in Fig. 2b, each L^{2-} ligand bridges three Cd(II) centers to construct a double-stranded chain structure with a nearest intrachain Cd…Cd distance of 9.543 Å. Interestingly, because of the flexibility of the L^{2-} ligand, the double-chain extends along the [100] direction in a spiral way. If some organic moieties are ignored, a pair of right- and left-handed helical chains could be isolated from the neutral double-stranded chain (Fig. 2c). Each



Fig. 3. (a) The coordination environment of the Cd(II) ions in **3** with the ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity. (b) View of secondary building unit SBU $[Cd_2(COO)_2]$ in **3**. (c) View of the 2D network of **3**. (d) View of nodes representing the SBU and the L²⁻ ligand in **3**. (e) View of the binodal (3,6)-connected 2D kgd network of **3**.

chain is interlinked to form a supramolecular layer motif *via* hydrogen-bonding interactions between water molecules and carboxylate oxygen atoms (Fig. 2d, Table S2). Another structural feature in **2** is that the adjacent layers recognize each other through strong offset π - π stacking interactions, ultimately leading to a 3D supramolecular framework (Fig. 2e). The centroid–centroid distance between the central benzene rings is 3.643 Å.

3.4. Crystal structural description of [Cd(L)] (3)

Complex **3** shows a 2D network structure based on Cd(II) and the L^{2–} ligand. The asymmetrical unit is composed of one Cd(II) ion and one L^{2–} ligand. In complex **3**, each Cd(II) center is tetracoordinated by one benzotriazolyl N atom and four carboxylate O atoms from three different L^{2–} ligands to furnish a distorted tetragonal pyramid coordination geometry (Fig. 3a). The best equatorial plane is defined by the O1, O2, O3 and O4 atoms from three L^{2–} ligands, and the metal is deviated by 0.497 Å toward N13 from the mean plane. The axial positions are occupied by one benzotriazolyl nitrogen atom (N13) from another L^{2–} ligand. The coordinating bond lengths vary from 2.1747(17) to 2.3273(18) Å; the coordinating bond angles are in the range $56.24(7)^{\circ}$ to $157.02(7)^{\circ}$. The carboxylate groups in L^{2-} adopt $\mu_1-\eta^1$: η^0 -monodentate and $\mu_2-\eta^1$: η^1 -bridging coordination modes, resulting in the formation of the carboxylate-bridged binuclear secondary building unit (SBU) [Cd₂(COO)₂] with a Cd···Cd distance of 3.84 Å (Fig. 1a), which is shorter than the sum of two van der Waals radii (4.60 Å) [17]. In **3**, each L^{2-} ligand links three SBUs; each SBU is surrounded by six L^{2-} ligands. This kind of connection proceeds infinitely to generate a 2D network structure (Fig. 3c). If using topology to analyze the structure, each SBU could be regarded as a 6-connector node and the L^{2-} ligand as a 3-connector node (Fig. 3d), and thus the resultant structure of **3** could be simplified as a binodal (3,6)-connected 2D **kgd** network with $(4^3)_2(4^{6.6} \cdot 8^3)$ topology (Fig. 3e) [18].

3.5. Crystal structure description of [Cd(L)] (4)

Complexes **3** and **4** are a pair of isomers. The asymmetric unit of **4** is also composed of one Cd(II) and one L^{2-} ligand. As shown in Fig. 4a, each metal atom is coordinated by one benzotriazolyl nitrogen atom and five carboxylate oxygen atoms from three



Fig. 4. (a) The coordination environment of the Cd(II) ions in **4** with the ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity. (b) View of SBU $[Cd_2(COO)_2]$ in **4**. (c) View of the 2D network in **4**. (d) View of the 3D framework of **4**. (e) View of nodes representing the SBU and the L²⁻ ligand in **4**. (f) View of the binodal (3,6)-connected 3D **rtl** framework architecture of **4**.

 L^{2-} ligands, with a Cd–N bond length of 2.275(4) Å and an average Cd–O distance of 2.342 Å. The bond angles around the Cd(II) atom are in the range 54.97(9)° to 150.68(10)°, and thus the Cd(II) atom displays a distorted octahedral coordination geometry with the $[NO_5]$ donors set. The coordination mode of the L^{2-} ligand in 4 can be described as follows: one carboxylate adopts a $\mu_2 - \eta^2$: η^1 -chelating/bridging coordination mode, resulting in the formation of the carboxylate-bridged binuclear secondary building unit (SBU) $[Cd_2(COO)_2]$, with a Cd···Cd distance of 3.84 Å (Fig. 4b); the other carboxylate shows the $\mu_1 - \eta^1 : \eta^1$ -chelating mode; each benzotriazolyl group is bound to a Cd(II) ion. So the L^{2-} ligand displays a $\mu_4 - \eta^2$: $\eta^1 - \eta^1$: $\eta^1 - \eta^1$ mode to bridge four different metal atoms. Each Cd(II) center is also surrounded by four different L^{2–} ligands. The interconnections of metals and ligands repeat infinitely to yield a 3D framework architecture (Fig. 4d), within which 2D networks can be isolated with the free-of-coordination benzotriazolyl groups (Fig. 4c). Topological analysis can be used for a better comprehension of the structural features. Each SBU can be viewed as a 6-connected node and each L^{2-} ligand can be considered as a 3-connector bridge (Fig. 4e). According to the rules of simplification, the 3D architecture of **4** can be simplified as a binodal (3,6)-connected **rtl** framework with $(4.6^2)_2(4^2.6^{10}.8^3)$ topology (Fig. 4f).

3.6. Coordination modes of the H_2L ligand and structural comparisons of 1-4

All the carboxylate groups of $L^{2-}/(L^{1})^{2-}$ in the four complexes are found to be completely deprotonated and involved in coordination. The carboxylate coordination modes of the ligands in complexes **1–4** are different from each other, that is $\mu_2 - \eta^{1:} \eta$

(Scheme 2). As for the flexible benzotriazolylmethyl group, it undergoes an in situ rearrangement reaction in 1, emerging as the 2H-benzotriazol-2-ylmethyl group and being free of coordination. In 2-4, the bidentate N-donor group just coordinates to a single metal atom. The $L^{2-}/(L^{1})^{2-}$ ligands exhibit a variety of coordination modes in 1-4, which demonstrates influential factors of the synthetic strategies on the coordination modes of the ligands. The Cd(II) centers in 1-4 are seven-, six-, five- and five-coordinated, respectively. As a result, complexes **1–4** exhibit different structures: **1** and **2** are 1D structures; **3** displays a 2D network structure; 4 shows a 3D framework architecture. The results show that the synthetic strategies can efficiently influence the coordination modes of the ligand and the structures of the resultant complexes. Certainly, the potential variable coordination modes and conformations of H₂L provide the feasibility to assemble complexes with various structures by adjusting the experimental conditions.

3.7. Thermal stabilities and PXRD of complexes 1-4

The phase purity of **1–4** could be proved by powder X-ray diffraction (PXRD) analyses. As shown in Fig. S1, each pattern of the bulk sample was in agreement with the simulated pattern from the corresponding single crystal data.

Thermogravimetric analyses (TGA) were carried out for complexes **1–4**, and the results are shown in Fig. S2. Complex **1** shows a weight loss of 3.26% from 96 to 120 °C, corresponding to the release of coordinated water molecules (calcd 3.08%), and a continuous weight loss starting at 167 °C could be assigned to the liberation of pyridine molecules, accompanied by the subsequent decomposition of the framework. For **2**, a weight loss of 3.33% was found between 92 and 140 °C due to the release of water molecules (calcd 3.61%), and a weight loss of 14.36% in the temperature range 210–273 °C corresponds to the liberation of coordinated DMF molecules (calcd 14.65%). The decomposition temperature of **2** is 363 °C. As for **3** and **4**, no obvious weight loss can be observed before the decomposition of the frameworks occurred at 406 °C for **3** and 455 °C for **4**.

3.8. Fluorescent properties of complexes 1-4

The luminescent properties of complexes with d^{10} metal centers, such as Cd(II), are of interest for their potential application as photoactive materials [19]. Therefore, the luminescent properties of **1–4**, as well as the free H₂L ligand, were investigated in the solid state at room temperature. As shown in Fig. S3, intense bands were observed at 422 nm (λ_{ex} = 325 nm) for **1**, 410 nm $(\lambda_{ex} = 344 \text{ nm})$ for **2**, 418 nm $(\lambda_{ex} = 337 \text{ nm})$ for **3**, 415 nm (λ_{ex} = 326 nm) for **4** and 418 nm (λ_{ex} = 336 nm) for the H₂L ligand. As for the origin of the fluorescence of the complexes, it may be assigned to an intra-ligand transition of the coordinated L^{2-} ligands, since Cd(II) is difficult to be oxidized or reduced due to its d^{10} configuration, and additionally a similar emission can be observed for the free H₂L ligand [20]. Meanwhile, the observed red shift (for complex 1) and blue shift (for 2 and 4) of the emission maxima for the complexes compared to the H₂L ligand may originate from the coordination interactions between the metal atom and the ligand [21]. As for the luminescent intensities, it is very difficult to analyze them quantitatively because they relate not only to the structures of the complexes but also to the amount of sample used in the measurements. Therefore, although the complexes have potential application as photoactive materials due to their intense fluorescent emissions, it is still significant and urgent to pay more attention to their spectroscopic studies for a better comprehension of the luminescent mechanism.

4. Conclusion

A carboxylate and benzotriazolyl-containing ligand, 5-(1H-benzotriazol-1-ylmethyl)isophthalic acid (H₂L), was selected as an organic block which can display potential variable coordination modes. Hydrothermal reactions of the H₂L ligand with a Cd(II) salt under different experimental conditions provide four complexes with different structures, varying from 1D to 3D, whilst the L²⁻ ligand in the complexes is found to show a variety of coordination modes. Moreover, an in situ rearrangement reaction of H₂L to H₂L¹ occurs during the synthesis of complex **1**. The results might illustrate the aesthetic diversity of coordinative supramolecular chemistry, although more investigations are needed to understand the essential reasons for this difference. As expected, these cadmium polymers exhibit strong luminescent emissions.

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Appendix A. Supplementary material

CCDC 910152–910154 and 893793 contains the supplementary crystallographic data for **1–4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.poly.2013.01.038.

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