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Synthesis and characterization of four coordination polymers constructed with d¹⁰ metals and mixed flexible ligands under solvothermal conditions

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ABSTRACT

Solvothermal reactions of flexible 1,2-phenylenedioxydiacetic acid (H₂PDA) or hydroquinone-0,0'-diacetic acid (H₂QDA) with zinc nitrate or cadmium nitrate in the presence of auxiliary 1,1'-(1,4-but-anediyl)bis(imidazole) (BBI) ligand gave rise to four coordination polymers, namely, {[Zn(PDA)(B-BI)]·3H₂O}_n (**1**), {[Zn(PDA)(BBI)]·DMF}_n (**2**), {[Cd₂(QDA)(BBI)]·4H₂O}_n (**3**), [Cd(QDA)(BBI)]_n (**4**). All the compounds were characterized by elemental analysis, IR and single-crystal X-ray diffraction methods. Compound **1** exhibits a puckered (2D) (4, 4) grid net with a Schlafli symbol of 4⁴ 6². Compound **2** has the dinuclear Zn₂(PDA)₂ "loops" which are further connected by BBI ligands into 2D sheet along (01 – 1) plane with a Schlafli symbol of 2.6⁵. Interestingly, the Zn₂(PDA)₂ "loops" are penetrated by BBI ligands of the other equivalent net. Thus an unusual 2D polyrotaxane-like structure is formed containing rotaxane-like motifs. Compound **3** possesses a three-dimensional (3D) diamond-type network with a Schlafli symbol of 6⁶. Compound **4** has the dinuclear cadmium core as the node and shows a 3D threefold interpenetrating 8-connected uninodal network with a Schlafli symbol of 3⁶4¹⁸5³6. The structural differences of these complexes give some insights into the effect of solvent on the construction of coordination polymers with the same components under solvothermal conditions. In addition, the fluorescent properties of **1–4** were also investigated.

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1. Introduction

Investigation on novel coordination polymers constructed with transition metals and organic ligands has attracted much attention due to their intriguing architectures and potential applications as functional materials [1–12]. During the past decades, a large number of coordination polymers have been successively designed and synthesized through rational combination of the organic ligands and metal ions. In particularly, many researchers paid much attention on the exploitation of rigid pyridine- or imidazole-based and multicarboxylates ligands such as 1,3-benzenedicarboxylate, 1,3,5-benzenetricarboxylate and 4,4'-biphenyldicarboxylate [13–17]. Compared with the rigid ligands with single conformation, flexible ligands may adopt several kinds of conformations when coordinate to metal ions, which make it more difficult to predict and control the final coordination networks. So the use of flexible ligands in the formation of coordination polymers may generate novel complexes with interesting topologies and attractive properties [18-21]. In this respect, Our research are mainly focused on the exploitation of flexible ligands in the hope of getting novel metal-organic coordination polymers.

In this paper, 1,2-phenylenedioxydiacetic acid (H₂PDA), hydroquinone-0,0'-diacetic acid (H₂QDA) and 1,1'-(1,4-butanediyl) bis(imidazole) (BBI) were selected as the mixed ligands based on the following considerations: (1) both H₂PDA and H₂QDA possess flexibility owing to the presence of -O-CH₂- group between the phenyl ring and carboxyl moiety, the flexible and multifunctional coordination sites provide a high likelihood for generation of structures with high dimensions; (2) the flexible nature of $-CH_2$ - spacers in BBI ligand allows the ligand to bend and rotate freely when coordinating to metal centers so as to conform to the coordination geometries of metal ions. The solvothermal reactions of these mixed flexible ligands with d¹⁰ metals (Zn and Cd) in different solvents, such as water or N,N-dimethyl formamide (DMF), gave rise to four coordination polymers, $\{[Zn(PDA)(BBI)], 3H_2O\}_n$ (1), which forms a puckered 2D layer, $\{[Zn(PDA)(BBI)], DMF\}_n$ (2), which forms an intriguing $2D \rightarrow 2D$ self-catenated net, {[Cd(QDA)(BBI)]·3H₂O}_n(**3**), which forms an uninterpenetrated diamond-like 3D net, $[Cd(QDA)(BBI)]_n$ (4), which forms a threefold interpenetrated 3D net. The different outcomes could be definitely ascribed to the different solvent system. We herein report on their reactions, crystal structures and photoluminescent properties.





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2. Experimental

2.1. Materials and physical measurements

The ligand BBI was synthesized as previous literature [22]. Other chemicals and reagents were obtained from commercial sources and used as received. All Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Dmax2500 diffractometer with Cu K α radiation (λ = 1.5406 Å) with a step size of 0.02°. The experimental PXRD patterns are in good agreement with the corresponding simulated ones (Fig. A.10, Supplementary data). The elemental analyses for C, H and N were performed on an Elementar Vario Micro Cube analyzer. The IR spectra were recorded on a Thermo Nicolet IR200 FT-IR spectrometer as KBr pellets (4000-400 cm⁻¹). Thermal analysis was performed with a Shimadzu DTG-60 thermogravimetric analyzer at a heating rate of 5 °C/min and a flow rate of $100 \text{ cm}^3/\text{min}$ (N₂). The fluorescent spectra were obtained on a Hitachi F-4600 spectrofluorometer.

2.2. Synthesis of complexes

2.2.1. Synthesis of $\{[Zn(PDA)(BBI)], 3H_2O\}_n$ (1)

A mixture of H₂PDA (0.023 g, 0.1 mmol), BBI (0.021 g, 0.1 mmol) and Zn(NO₃)₂·6H₂O (0.030 g, 0.1 mmol) in H₂O (7.0 mL) was placed in a 16 mL Teflon-lined stainless steel vessel and heated to 160 °C for 72 h to give rise to colorless block crystals of 1, which were collected by filtration. The colorless crystals obtained were washed with water and dried in air. Yield: 0.038 g (70% based on Zn). Anal. Calc. for C₂₀H₂₈N₄O₉Zn: C, 45.00; H, 5.29; N, 10.50. Found: C, 44.74; H, 5.02; N, 10.36%. IR (KBr pellet, cm⁻¹): 3426 w, 3138 w, 2902 w, 1662 m, 1605 s, 1585 s, 1509 s, 1426 s, 1341 m, 1320 w, 1231 s, 1112 m, 1070 m, 944 w, 828 m, 807 m, 702 m, 657 w.

2.2.2. Synthesis of $\{[Zn(PDA)(BBI)], DMF\}_n$ (2)

Compound 2 was prepared in a manner similar to that described for 1, using the same components in the same molar ratio except that DMF was used as solvent instead of H₂O. Colorless

Table 1	l
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Summary o	f crysta	llographic	data	for 1	-4
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Table 2

Selected bond lengths (Å) and angles (°) for 1-4.

Compound 1			
Zn(1)-N(2)	1.994(3)	Zn(1)-N(3)	1.999(3)
Zn(1)-O(1)#1	2.069(3)	Zn(1)-O(6)	1.970(2)
O(1)-Zn(1)#2	2.069(3)		
O(6)-Zn(1)-N(2)	107.11(12)	O(6)-Zn(1)-N(3)	116.49(12)
N(2)-Zn(1)-N(3)	106.72(12)	O(6)-Zn(1)-O(1)#1	98.19(12)
N(2)-Zn(1)-O(1)#1	130.65(14)	N(3)-Zn(1)-O(1)#1	98.28(13)
Compound 2			
Zn(1) - N(2)	2.009(2)	Zn(1) - N(3)	1.994(2)
Zn(1) - O(2)#3	1.976(2)	Zn(1) - O(5)	1.966(2)
O(2) - Zn(1) #3	1.976(2)		
O(5) - Zn(1) - O(2) #3	106.56(9)	O(5) - Zn(1) - N(3)	113.84(10)
O(2)#3-Zn(1)-N(3)	111.57(10)	O(5) - Zn(1) - N(2)	104.90(9)
O(2)#3-Zn(1)-N(2)	108.42(9)	N(3)-Zn(1)-N(2)	111.16(10)
Commoned 3			
Compound 3	2 105(2)	C-1(1) N(1)#4	2 105(2)
Cd(1) = N(1) Cd(1) = O(2)	2.195(2)	Cd(1) = N(1) # 4 Cd(1) = O(2) # 4	2.195(2)
U(1) = U(2) V(1) = Cd(1) = V(1) # d	2.2100(10)	U(1) = U(2) # 4 V(1) = Cd(1) = O(2)	2.2100(10)
N(1) = Cu(1) = N(1) = 4 N(1) = 4	115.00(11)	N(1) - Cd(1) - O(2) N(1) - Cd(1) - O(2) + 4	121.36(7)
N(1)#4-Cd(1)-O(2) N(1)#4-Cd(1)-O(2)#4	105.75(7) 121.29(7)	N(1) - Cu(1) - O(2) + 4 O(2) Cd(1) O(2) + 4	105.75(7)
N(1)#4-Cu(1)=O(2)#4	121.36(7)	0(2) - Cu(1) - 0(2) + 4	80.90(9)
Compound 4			
Cd(1)-N(1)	2.364(5)	Cd(1) - N(3)	2.233(4)
Cd(1)-O(2)	2.475(3)	Cd(1)-O(3)	2.331(4)
Cd(1) - O(5)	2.306(3)	Cd(1) - O(6)	2.622(4)
Cd(1)-O(5)#5	2.506(3)	O(5)-Cd(1)#5	2.506(3)
N(3)-Cd(1)-O(5)	103.45(14)	N(3)-Cd(1)-O(3)	158.04(14)
O(5)-Cd(1)-O(3)	96.21(13)	N(3)-Cd(1)-N(1)	87.91(16)
O(5)-Cd(1)-N(1)	127.27(16)	O(3)-Cd(1)-N(1)	87.90(17)
N(3)-Cd(1)-O(2)	103.73(13)	O(5)-Cd(1)-O(2)	140.07(13)
O(3)-Cd(1)-O(2)	54.34(12)	N(1)-Cd(1)-O(2)	82.38(17)
N(3)-Cd(1)-O(5)#5	85.75(13)	O(5)-Cd(1)-O(5)#5	68.97(12)
O(3)-Cd(1)-O(5)#5	92.36(13)	N(1)-Cd(1)-O(5)#5	163.65(16)
O(2)-Cd(1)-O(5)#5	84.50(12)	N(3)-Cd(1)-O(6)	95.98(15)
O(5)-Cd(1)-O(6)	51.73(11)	O(3)-Cd(1)-O(6)	103.92(15)
N(1)-Cd(1)-O(6)	76.18(16)	O(2)-Cd(1)-O(6)	150.22(14)
O(5)#5-Cd(1)-O(6)	119.46(11)		

Symmetry codes: #1: x + 1, y, z; #2: x - 1, y, z; #3: -x + 1, -y, -z + 1; #4: -x, y, -z + 3/2; #5: -x + 1, -y, -z + 1.

Compounds	1	2	3	4
Chemical formula	C ₂₀ H ₂₈ N ₄ O ₉ Zn	C ₂₃ H ₂₈ N ₅ O ₇ Zn	$C_{20}H_{28}N_4O_9Cd$	C ₂₀ H ₂₂ N ₄ O ₆ Cd
Formula Mass	533.83	551.87	580.86	526.82
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/n$	ΡĪ	C2/c	ΡĪ
a (Å)	11.037(1)	9.367(1)	10.296(1)	9.663(1)
b (Å)	16.559(1)	10.250(1)	15.522(1)	9.762(1)
c (Å)	13.018(1)	13.849(2)	15.603(1)	12.051(1)
α (°)	90	78.883(1)	90	100.725(1)
β (°)	95.524(5)	86.361(2)	96.021(1)	94.975(1)
γ (°)	90	80.004(2)	90	106.713(1)
V (Å ³)	2368.1(3)	1284.3(1)	2479.8(3)	1057.8(2)
T (K)	296(2)	296(2)	296(2)	296(2)
Ζ	4	2	4	2
D_{calc} (g cm ⁻³	1.497	1.427	1.556	1.654
$\mu (\mathrm{mm}^{-1})$	1.094	1.007	0.935	1.077
F(000)	1112	574	1184	532
No. of reflections measured	11954	7994	6254	5499
No. of independent reflections	4167	5671	2179	3692
No. of parameters	307	325	155	280
R _{int}	0.0214	0.0137	0.0157	0.0133
Final R_1^a values $(I > 2\sigma(I))$	0.0431	0.0427	0.0233	0.0373
Final wR_2^{b} values $(I > 2\sigma(I))$	0.0999	0.1273	0.0659	0.1064
Final R_1 values (all data)	0.0539	0.0499	0.0240	0.0396
Final wR_2 values (all data)	0.1044	0.1331	0.0664	0.1080
Goodness of fit (GOF) on F^2	1.057	1.077	1.063	1.009
Largest difference in peak and hole (e $Å^{-3}$)	1.068 and -0.709	0.993 and -0.626	0.899 and -0.282	0.982 and -1.103

^a $R = \sum (||F_0| - F_c||) / \sum |F_0|.$ ^b $wR_2 = [\sum w(|F_0|^2 - |F_c|^2)^2 / \sum w(|F_0|^2)]^{1/2}.$



Fig. 1. (a) View of the coordination environment of Zn1 in 1. The solvent water molecules and hydrogen atoms are omitted for clarity. Symmetry codes: (A) 1 + x, y, z; (B) 2 - x, 1 - y, 2 - z; (C) 1 - x, 1 - y, 1 - z. (b) View of a section of the 1D chain extending along the *a* axis. (c) View of the 2D layer of **1** extending along the (010) plane. (d) Schematic representation the (4, 4) net of **1**.



Scheme 1. Coordination modes of PDA²⁻ and QDA²⁻ ligands in complexes 1-4.

block crystals of **2** were collected by filtration, washed with water and dried in air. Yield: 0.036 g (66% based on Zn). *Anal.* Calc. for $C_{23}H_{28}N_5O_7Zn$: C, 50.02; H, 5.11; N, 12.69. Found: C, 49.54; H, 5.06; N, 12.51%. IR (KBr pellet, cm⁻¹): 3422 w, 3123 w, 2936 w, 1637 s, 1524 w, 1504 s, 1409 s, 1310 w, 1290 w, 1252 s, 1207 m, 1129 s, 1106 m, 1046 m, 954 w, 839 w, 755 m, 656 m.

2.2.3. Synthesis of $\{[Cd_2(QDA)(BBI)] \cdot 4H_2O\}_n$ (3)

A mixture of H_2 QDA (0.023 g, 0.1 mmol), BBI (0.021 g, 0.1 mmol) and Cd(NO₃)₂·4H₂O (0.038 g, 0.1 mmol) in H₂O (7.0 mL) was placed in a 16 mL Teflon-lined stainless steel vessel

and heated to 160 °C for 72 h to give rise to colorless block crystals of **3**, which were collected by filtration. The colorless crystals obtained were washed with water and dried in air. Yield: 0.037 g (63% based on Cd). *Anal.* Calc. for $C_{20}H_{28}N_4O_9Cd$: C, 41.36; H, 4.86; N, 9.65. Found: C, 41.17; H, 4.62; N, 9.36%. IR (KBr pellet, cm⁻¹): 3431 w, 3121 w, 2936 w, 1605 s, 1506 s, 1416 s, 1329 w, 1293 w, 1237 m, 1202 s, 1093 m, 948 w, 829 m, 723 m, 658 m.

2.2.4. Synthesis of $[Cd(QDA)(BBI)]_n$ (4)

Compound **4** was prepared in a manner similar to that described for **3**, using the same components in the same molar ratio



Fig. 2. (a) View of the coordination environment of Zn1 in **2**. The solvent DMF molecules and hydrogen atoms are omitted for clarity. Symmetry codes: (A) -1 - x, -y, 1 - z; (B) -x, 1 - y, 2 - z; (C) 1 - x, -y, 1 - z. (b) View of a dinuclear [Zn₂(PDA)₂] unit in **2**. (c) View of one 2D layer extending along (01–1) plane. (d) The 4-connected (2.6⁵) topology of **2**. (e) The two fold interpenetrating layer of **2**. (f) The 3D packing of **2** viewed along the approximate *a* axis.

except that DMF was used as solvent instead of H_2O . Colorless block crystals of **4** were collected by filtration, washed with water and dried in air. Yield: 0.048 g (75% based on Cd). *Anal.* Calc. for $C_{20}H_{22}N_4O_6Cd$: C, 45.60; H, 4.21; N, 10.64. Found: C, 45.23; H, 4.16; N, 10.28%. IR (KBr pellet, cm⁻¹): 3426 w, 3138 w, 2902 w, 1662 s, 1585 s, 1509 s, 1426 s, 1341 m, 1283 w, 1112 m, 1070 s, 944 m, 828 m, 807 m, 767 w, 702 m, 657 m.

2.3. Crystal structure determination

Single crystals of **1–4** suitable for X-ray analysis were selected directly from the above preparations. These crystals were mounted on glass fibers and then the crystallographic data collections were carried out on a Bruker Smart ApexII CCD area-detector diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 23 °C using ω - and φ -scan technique. The diffraction data was integrated by using the SAINT program [23], which was also used for the

intensity corrections for the Lorentz and Polarization effects. Semiempirical absorption correction was applied using the sadabs program [24]. The crystal structures of 1-4 were solved by direct method using sir97 program [25] and refined anisotropically for all non-hydrogen atoms by full-matrix least squares on all F^2 data using SHELXL97 [26], The single suite WINGX was used as an integrated system for all the crystallographic programs [27]. The hydrogen atoms of the water solvent molecules in 1 and 3 were located from the Fourier map with the O-H distances being fixed at 0.85 Å and allowed to ride on their parent oxygen atoms before the final cycle refinement, the $U_{iso}(H) = 1.2 U_{eq}(O)$. All other hydrogen atoms were added according to theoretical models, assigned isotropic displacement parameters and allowed to ride on their respective parent atoms, the $U_{iso}(H) = 1.2 U_{eq}(C)$ or $1.5U_{eq}(C)$. Crystal data and a structure determination summary for 1-4 are listed in Table 1. The selected bond lengths and angles for 1-4 are listed in Table 2. The hydrogen bonds are listed in Table A1 (Supplementary data).



Fig. 3. (a) View of the coordination environment of Cd1 in 3. The solvent water molecules and hydrogen atoms are omitted for clarity. Symmetry codes: (A) 1 - x, 2 - y, 2 - z; (B) -0.5 - x, 1.5 - y, 1 - z; (C) -x, y, 1.5 - z. (b) A diamond-type network in **3**. (c) View of the double left- and right-handed helical chain. (d) 3D net work of **3** constructed by the double helical chains and QDA anions.

3. Results and discussions

3.1. Crystal structures of complexes 1-4

3.1.1. $\{[Zn(PDA)(BBI)] \cdot 3H_2O\}_n$ (**1**)

Compound **1** crystallizes in the monoclinic space group P2(1)/n, and the asymmetric unit contains one PDA anion, one BBI molecule, one Zn cation and three water solvent molecules. In the crystal structure, there is only one crystallographically unique Zn(II) atom. Each Zn(II) center is tetrahedrally coordinated by two N atoms from two BBI ligands(Zn1-N2 = 1.994(3) Å, Zn1-N3 = 1.999(3) Å), two O atoms from two PDA ligands(Zn1-O6 = 1.970(2) Å, Zn1–O1A = 2.069(3) Å) (Fig. 1a). Each PDA anion bridges two Zn(II) cations to yield a wave like chain through bismonodentate coordination mode (Scheme 1a) along a axis (Fig. 1b). The two kinds of BBI ligands (Fig. A.1, Supplementary data), exhibiting trans-conformation, act as bidentate bridging ligands. All the two kinds of BBI ligands have a dihedral angle of 0° between two imidazole rings, which indicate that the two imidazole rings are absolutely parallel. The Zn-PDA chain and its symmetry-related ones are connected by the two kinds of BBI ligands alternatively to form puckered 2D sheet extending along the (010) plane (Fig. 1c). From the topological point of view, the 2D plane of **1** can be reduced to a (4, 4) grid net with a Schlafli symbol of $4^4 6^2$ (Fig. 1d). There are two kinds of the smallest four-membered circuits in the network (Fig. A.2, Supplementary data). Each circuit consists of four Zn(II) cations at the corners connected by two BBI molecules and two PDA anions, which make up four edges. In both of the two circuits, the Zn(II) ions are bridged by BBI and PDA alternatively. In circuits I and II, the length of PDA edge is 11.037(5) Å, while the length of the BBI edge is different, in I the length of the BBI edge is 12.007(3) Å. The adjacent 2D layers are further connected via hydrogen bonds between PDA and solvent water molecules to form the resultant supramolecular architectures (Fig. A.3, Table A1, Supplementary data).

3.1.2. $\{[Zn(PDA)(BBI)] \cdot DMF\}_n$ (2)

Compound **2** crystallizes in triclinic space group $P\bar{1}$ and the asymmetric unit contains one PDA anion, one BBI ligand, one Zn(II) cation and one DMF solvent molecule. As shown in Fig. 2a, the crystallographically unique Zn(II) is four-coordinated by two oxygen atoms from two PDA anions (Zn1–O5 = 1.966(2) Å, Zn1–O2C = 1.976(2) Å) and two nitrogen atoms from two BBI ligands



Fig. 4. (a) View of the coordination environment of Cd1 in **4**. The hydrogen atoms are omitted for clarity. Symmetry codes: (A) 1 - x, 1 - y, -z; (B) 2 - x, 1 - y, 2 - z; (C) 1 - x, -y, 1 - z; (D) 2 - x, -y, -z; (E) 2 - x, -1 - y, 1 - z. (b) View of a dinuclear [Cd₂(QDA)₄(BBI)₄] unit in **4**. (c) View of the 2D (4, 4) layer extending along (2 - 1 - 1) plane. (d) 3D net work of **4** constructed by the double helical chains and 2D step-shaped layers. (e) Schematic representation of a $3^{6}4^{18}5^{3}6$ topological net of **4**, the ball represents the dinuclear Cd(II) unit.

(Zn1-N2 = 2.009(2)Å, Zn1-N3 = 1.994(2)Å), showing a tetrahedral coordination geometry (ZnO_2N_2) . Two PDA anions act as bis-monodentate coordination mode (Scheme 1a) to link adjacent Zn(II) atoms to yield $Zn_2(PDA)_2$ "loops" (Fig. 2b). The BBI ligands with the same conformation as in **1** then further connect the "loops" into 2D sheet along (01-1) plane (Fig. 2c). Two identical 2D single nets are interpenetrated with each other and form an interesting twofold parallel interpenetrated 2D \rightarrow 2D architecture (Fig. A.4, Supplementary data). The $Zn_2(PDA)_2$ "loops" are penetrated by BBI ligands of the other net and if the loops are considered as single links, the whole structure of **2** can be described as a (6, 3) networks which can not properly describe the topology of interpenetration as it would require the links to pass through the middle of other links. The PDA anions of the $Zn_2(PDA)_2$ "loops" must be viewed as 2-connected nodes instead of single links, which results in a 4-connected (2.6^5) topology (Fig. 2d) [28]. Thus an unusual 2D polyrotaxane-like structure is formed containing rotaxane-like motifs. Although the single net of **2** has large channels, they are mainly filled by the other equivalent net, leaving only small voids to host the guest DMF molecules (Fig. 2e). The interpenetrated 2D sheets are further connected with their symmetry-related ones via weak interlayer C-H···O hydrogen bonds forming the resultant 3D supramolecular architecture (Fig. 2f and Table A1, Supplementary data).

3.1.3. {[Cd₂(QDA)(BBI)]·4H₂O}_n (**3**)

Single crystal X-ray diffraction reveals that compound **3** crystallizes in monoclinic space group C2/c and has a 3D porous architecture based on 1D Cd–BBI chains. The asymmetric unit of **3** consists of half of the QDA anion, half of the BBI ligand, one Cd(II) cation and two solvent water molecules. Fig. 3a shows the coordination environment of the Cd(II) cation in **3**. Each Cd(II) adopts a tetrahedral geometry and is coordinated by two O atoms each from two different QDA anions (Cd1–O2 = 2.217(2) Å, Cd1–O2C = 2.217(2) Å) two N atoms each from two different BBI ligands(Cd1–N1 = 2.195(2) Å, Cd1–N1C = 2.195 Å).

From the topological point of view, each Cd(II) ion can be considered as a single node and the QDA anions and the BBI ligands as linear bridging linkers, and then the structure possesses a diamond-type network with a Schlafli symbol of 6^6 , as shown in Fig. 3b.

Unlike that found in compounds **1** and **2** in which the BBI ligand adopts two different *trans*-conformation, the BBI ligand in **3** adopts only one trans-conformation (Fig. A.3, Supplementary data). The Cd(II) ions are connected by BBI ligands to form the alternate leftand right-handed helical chains along [101] direction with the pitches of 17.769(4) Å(Fig. 3c), these double chains are further interlinked by QDA anions through monodentate carboxylate groups with a trans-conformation (Scheme 1b) to form 3D network (Fig. 3d). It is worth noting that there are alternate left- and righthanded helices in the double chains, so the whole framework does not show chirality. To the best our knowledge, the connection of metal ions by a bridging BBI ligand in the S-shaped conformation normally generates one single left- or right-handed helices [29,30]. The 1D alternate left- and right-handed helices chains as found in 3 are heretofore unreported in the study of BBI ligand and its derivatives.

3.1.4. [Cd(QDA)(BBI)]_n (**4**)

Single crystal X-ray diffraction reveals that Compound **4** crystallizes in triclinic space group $P\bar{1}$ and the asymmetric unit contains one QDA anion, one BBI ligand and one Cd(II) cation. The coordination environment around the Cd(II) can be described as a distorted pentagonal bipyramid (Fig. 4a). Cd(II) ion is seven-coordinated by four carboxylic oxygen atoms (O2, O5, O5C, O6) and one nitrogen atom (N1) from BBI ligand at the equatorial plane, and one other carboxylic oxygen atom (O3) and one other nitrogen atom (N3) at the axial positions. The Cd–O (carboxylate) bond lengths are in the range of 2.306(3)–2.622(4) Å and Cd–N (BBI)-bond lengths are 2.233(4), 2.364(5) Å, respectively.

The QDA ligands display two coordination modes (Scheme 1c and d) and the BBI ligands show two different conformation modes (Fig. A.6, Supplementary data). Cd1 and its symmetry-related Cd1A are bridged by two QDA ligands to generate a dinuclear $[Cd_2(QDA)_4(BBI)_4]$ unit (Fig. 4b). Each pair of Cd(II) atoms in this



Fig. 5. The fluorescent emission spectra of 1-4 in solid state at room temperature.

dinuclear unit interconnects its equivalent ones via QDA bridges to form a step-shaped 2D (4, 4) layer (Fig. A.7a, Supplementary data) with parallelogram grids $(14.685 \times 16.861 \text{ Å}^2)$ extending along the (2-1-1) plane (Fig. 4c). As in compound **3**, the BBI ligands in 4 bridge the Cd(II) ions to form alternate left- and righthanded helical double chains with a pitch of 16.861(5)Å (Fig. A.7b, Supplementary data), but it is different that BBI ligands display only one conformation in 3 while two different conformations in 4. The aforementioned 2D layer is connected to its neighboring ones by such helical chains to form a 3D net (Fig. 4d). If the dinuclear Cd(II) unit is considered as 8-connecting nodes, the QDA anion and BBI ligand as connector, the whole structure of **4** can be described as a 8-connected uninodal net with a Schlafli symbol of $3^{6}4^{18}5^{3}6$ (Fig. 4e). Although the single net of **4** has large channels, they are mainly penetrated by the other two equivalent nets, leaving only 19 $Å^3$ cavities per unit cell (1.8% of the total cell volume calculated by the PLATON program) (Fig. A.7c. Supplementary data). The cavities are too small to host the solvent DMF molecules.

3.2. Effect of solvents on the structures of 1-4

It is well known that the solvent can have a significant structure directing effect on the formation of the final structures [31]. The same reaction in different solvents may result in different structural topologies [32-34]. The ratio of reagents, the reaction temperature and time are the same for the syntheses of complexes 1 and 2, as well as 3 and 4, only differing in solvents used. But the resultant structures are quite different for 1 and 2, as well as 3 and **4**: complex **1** is a 2D wave like uninterpenetrating layer, while complex **2** is a $2D \rightarrow 2D$ interpenetrating layer; complex **3** is an uninterpenetrating diamond like 3D framework, while complex 4 is a threefold interpenetrating 3D framework. The structural differences between them results from the different solvents used in the synthesis. 1 and 3 were synthesized using H₂O as solvent, while 2 and 4 were obtained using DMF as solvent. Because the polarity of H₂O is bigger than that of DMF, the conformation of the flexible ligands BBI, PDA²⁻ and QDA²⁻ are induced differently by solvents, which resulted in the different adaptive packing patterns.

3.3. Thermal stability

Thermogravimetric analysis (TGA) experiments were conducted to determine the thermal stability of 1-4. The experiments were performed on samples consisting of numerous single crystals under N₂ atmosphere with a heating rate of 5 °C min⁻¹, as shown in Fig. A.8 in Supplementary data. For compound **1**, the weight losses of guest water molecules were observed in the temperature ranges of 37–75 °C, and then until 270 °C large amounts of weight losses were observed. For 2, the TGA curve showed the weight losses of DMF molecules occurred in the temperature ranges of 25-80 °C, and then until 270 °C large amounts of weight losses were observed. In the case of **3**, the consecutive weight loss of the guest water molecules occurred during 25-280 °C, and then large amounts of weight losses were observed. For 4, there was no weight loss until 220 °C at which point large amounts of weight losses occurred because it did not include solvent molecules. The weight loss of 4 corresponded well to the expected from compositional formula, however, due to the volatility of the guest molecules included in 1-3, the experimental weight losses for solvent molecules from TGA measurements did not coincide with the calculated from the formula.

3.4. Fluorescent properties

Coordination polymers constructed with d¹⁰ metal centers and conjugated organic ligands have been investigated for fluorescence properties because of their various applications in chemical sensors, photochemistry and structure electroluminescence (EL) displays and light-emitting diodes (LEDs) [35-38]. Thus, the solid state emission spectra of all the resulting compounds 1-4, together with those of the free BBI, H₂PDA and H₂QDA ligands were measured at room temperature. All measurements of emission spectra were excited at a wavelength of 284 nm. Emission was observed at 566, 568 and 566 nm for BBI, H₂PDA and H₂QDA free ligands (Fig. A.9, Supplementary data), respectively. The photoluminescence spectra of compounds 1-4 are shown in Fig. 5. It is clear that there are intense emission bands at 573 nm for 1, 568 nm for 2, 568 nm for **3** and 567 nm for **4**, respectively. These emissions are neither metal to ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature since the Zn²⁺ or Cd²⁺ ions are difficult to oxidize or reduce due to their d¹⁰ configuration. Therefore, they can probably be assigned to intraligand $(\pi - \pi^*)$ fluorescent emission due to their almost similar resemblance of the emission bands with those of the free ligands [39-42].

4. Conclusions

In this paper, we have successfully synthesized four coordination polymers with different topological structures under solvothermal conditions. With the same reactant components, the assembly of compounds **1–4** in different solvents give rise to different frameworks. The results demonstrate that the solvents have important influence on the final topological structures of the resultant complexes. In addition, these compounds also exhibit emissions in the solid-state at room temperature.

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Appendix A. Supplementary material

CCDC 800454, 800455, 800456 and 800457 contain the supplementary crystallographic data for complexes **1–4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.04.044.

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