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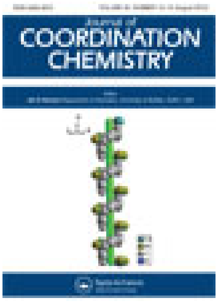

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Syntheses, structures, and photoluminescence of three cadmium(II) coordination polymers with flexible bis(benzimidazole) ligands

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Syntheses, structures, and photoluminescence of three cadmium(II) coordination polymers with flexible bis(benzimidazole) ligands

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Three cadmium(II) coordination polymers, $[CdBr_2(L_1)]_n$ (**1**), $[CdI_2(L_2)]_n$ (**2**), and $Cd_2Br_4(L_3)_2$ (**3**), where $L_1 = 1,3$-bis(5,6-dimethylbenzimidazole)propane, $L_2 = 1,4$-bis(5,6-dimethylbenzimidazole)butane, and $L_3 = 1,6$-bis(5,6-dimethylbenzimidazole)hexane, have been synthesized by hydrothermal methods and characterized by elemental analyses, IR spectra, TGA, PXRD, and X-ray crystallographic diffraction. Complex **1** contains a 1-D helical chain in which $CdBr_2$ units are linked by L_1. For **2**, each CdI_2 is connected by two different conformations of L_2 to form a 1-D zigzag chain. For **3**, each $CdBr_2$ is linked by L_3 bridges to afford a binuclear structure. These results indicate that the spacer length of the ligands play important roles in assembly of Cd(II) coordination polymers. Thermogravimetric analyses and solid-state luminescent properties of the complexes have also been investigated.

Keywords: Cadmium(II) coordination polymers; Crystal structure; Flexible bis(benzimidazole); Luminescent properties

1. Introduction

Coordination polymers based on self-assembly of metal centers and organic ligands have interesting architectures [1] and potential applications in adsorption, separation, magnetism, luminescence, catalysis, etc. [2–5]. Temperature, pH, solvent, metals, ligands, cations and/or anions, supramolecular interaction (π–π stacking and hydrogen-bond interactions), etc. can be key parameters for the formation of these compounds [6–9]. Flexible bridging ligands bearing alkyl spacers are good choices of N-donor ligand; flexible spacers allow the ligands to bend and rotate when coordinating, allowing structural diversity. A number of coordination polymers based on flexible bis(benzimidazoles) have been constructed [10]. For example, reactions of CuSCN with a set of benzimidazolyl-based linkers with different spacer lengths gave coordination polymers with different structures [11]. A family of linkers $[(bzim)(CH_2)_n(bzim)]$

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($n = 3$, prbbm; $n = 4$, bbbm; $n = 5$, pbbm) was employed to assemble Zn(II) and Cd(II) coordination polymers [12–14].

In contrast, the most prominent benzimidazole derivative is 5,6-dimethylbenzimidazole, which serves as an axial ligand for cobalt in vitamin B_{12} [15]. Coordination polymers based on flexible bis(5,6-dimethylbenzimidazoles) have been rarely studied [16]. Three bis(benzimidazole) derivatives with different flexible spacers, 1,3-bis(5,6-dimethylbenzimidazole)propane (L_1), 1,4-bis(5,6-dimethylbenzimidazole)butane (L_2), and 1,6-bis(5,6-dimethylbenzimidazole)hexane (L_3), have been synthesized and reacted with Cd(II) salts under hydrothermal conditions, yielding $[CdBr_2(L_1)]_n$ (**1**), $[CdI_2(L_2)]_n$ (**2**), and $Cd_2Br_4(L_3)_2$ (**3**), which exhibit structural diversity from discrete dinuclear to 1-D frameworks.

2. Experimental

2.1. *Materials and physical measurements*

All starting reagents commercially obtained were of analytical grade and used without purification. L_1, L_2, and L_3 were prepared according to the literature method [17]. Elemental analyses were made on a Perkin-Elmer automatic analyzer. IR spectra were recorded on a Nicolet FT-IR Avatar 360 spectrophotometer from 4000 to 400 cm^{-1} using KBr pellets. TG measurements were carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 800°C under N_2 with a heating rate of 10°C min^{-1}. X-ray powder diffraction measurement was executed on a D/MAX 2500PC X-ray diffractometer using Cu-Kα radiation ($\lambda = 0.1542$ nm) from 2θ of 5–50° with a step size of 0.02° and a scanning rate of 10°min^{-1}. Fluorescence spectra were performed with a Hitachi F-7000 fluorescence spectrophotometer at room temperature.

2.2. *Synthesis of the complexes*

2.2.1. Synthesis of $[CdBr_2(L_1)]_n$ (1). A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (15.5 mg, 0.05 mmol), KBr (11.9 mg, 0.1 mmol), L_1 (16.6 mg, 0.05 mmol), MeOH (3 mL), and H_2O (3 mL) was placed in a Teflon-lined stainless steel vessel and heated to 140°C for 72 h under autogenous pressure, and then cooled to room temperature at a rate of 5°C h^{-1}. Colorless crystals of **1** were obtained in 72% yield based on $Cd(NO_3)_2 \cdot 4H_2O$. Calcd for $C_{21}H_{24}Br_2CdN_4$ ($Fw = 604.66$) (%): C, 41.71; H, 4.00; N, 9.27. Found (%): C, 41.61; H, 4.16; N, 9.13. FTIR (KBr pellet, cm^{-1}): 3080 (m), 2930 (m), 1630 (m), 1490 (vs), 1440 (m), 1370 (m), 1270 (m), 1210 (m), 1150 (m), 843 (m).

2.2.2. Synthesis of $[CdI_2(L_2)]_n$ (2). A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (15.5 mg, 0.05 mmol), KI (16.6 mg, 0.1 mmol), L_2 (17.3 mg, 0.05 mmol), DMF (1 mL), and H_2O (5 mL) was placed in a Teflon-lined stainless steel vessel and heated to 140°C for 72 h under autogenous pressure, and then cooled to room temperature at a rate of 5°C h^{-1}. Colorless crystals of **2** were obtained in 68% yield based on $Cd(NO_3)_2 \cdot 4H_2O$. Calcd for $C_{22}H_{26}CdI_2N_4$ ($Fw = 712.67$) (%): C, 37.08; H, 3.68; N, 7.86. Found (%): C, 37.12;

H, 3.51; N, 7.93. FTIR (KBr pellet, cm^{-1}): 3100 (m), 2930 (m), 1630 (m), 1500 (vs), 1470 (m), 1370 (m), 1270 (m), 1210 (m), 1150 (m), 843 (m).

2.2.3. Synthesis of $Cd_2Br_4(L_3)_2$ (3). Complex **3** was prepared using a similar method as for **1** but using L_3 (18.7 mg, 0.05 mmol) rather than L_1 (17.3 mg, 0.05 mmol). Colorless crystals of **3** were obtained in 78% yield based on $Cd(NO_3)_2 \cdot 4H_2O$. Calcd for $C_{48}H_{60}Br_4Cd_2N_8$ ($Fw = 1293.48$) (%): C, 44.57; H, 4.68; N, 8.66. Found (%): C, 44.41; H, 4.76; N, 8.53. FTIR (KBr pellet, cm^{-1}): 3100 (m), 2930 (m), 1630 (m), 1510 (vs), 1450 (m), 1380 (m), 1270 (w), 1210 (m), 1140 (m), 852 (m).

2.3. *X-ray crystallography*

Suitable single crystals of **1**–**3** were mounted on glass fibers with epoxy cement for X-ray measurements. The crystallographic data collections were carried out on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and ω–2θ scan mode at 293 K. All absorption corrections were applied using SADABS [18]. The structures were solved by direct methods and refined anisotropically by full-matrix least-squares using the Bruker SHELXTL program package [19]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on the corresponding parents. Crystallographic data and experimental details for structural analyses are summarized in table 1. Selected bond lengths and angles for **1**–**3** are listed in table 2.

3. Results and discussion

3.1. *Description of crystal structures*

3.1.1. Crystal structure of $[CdBr_2(L_1)]_n$ (1). X-ray diffraction analysis indicates that **1** crystallizes in the monoclinic space group $P2_1/n$. The independent unit consists of one Cd(II), two bromides, and one L_1. The coordination environment of Cd(II), shown in figure 1(a), is four-coordinate with two bromides (Br1 and Br2) and two nitrogen atoms (N2 and N3) from two distinct L_1, with distances of Cd–Br = 2.6948(11)–2.7408(5) Å and Cd–N = 2.249(7)–2.281(8) Å. The *cis*-coordination bond angles range from 106.0(3)° to 127.05(4)°, showing distortion of tetrahedral geometry in **1**.

In **1**, L_1 is a bridging bis(monodentate) ligand, taking a *trans–trans* conformation, and connects $CdBr_2$ forming a 1-D helical chain, as shown in figure 1(b). The distance between two adjacent Cd(II) atoms is 10.7658(10) Å. Furthermore, two neighboring chains are nearly parallel with dihedral angle of 0.273(3)°, resulting in formation of π–π stacking interactions between benzimidazole rings of L_1. Thus, the helical chains are expanded to a 2-D supramolecular network by π–π stacking interactions, with a center-to-center distance of 3.656(5) Å, as shown in figure 1(c).

Table 1. Crystal data and structure refinements for **1**–**3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{21}H_{24}Br_2CdN_4$	$C_{22}H_{26}CdI_2N_4$	$C_{48}H_{60}Br_4Cd_2N_8$
Formula weight	604.66	712.67	1293.48
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions (Å, °)			
a	10.9075(8)	9.2089(6)	11.0305(8)
b	14.5591(10)	10.5917(7)	14.4886(10)
c	15.2928(11)	14.3096(11)	16.3552(12)
α	90	85.9350(12)	90
β	107.2890(10)	76.8730(11)	98.6770(10)
γ	90	70.6070(10)	90
Volume (Å^3), Z	2318.8(3), 4	1282.12(15), 2	2583.9(3), 2
Absorption coefficient (mm^{-1})	4.401	3.274	3.956
Calculated density (g cm^{-3})	1.732	1.846	1.662
$F(000)$	1184	680	1280
Crystal size (mm^3)	$0.16 \times 0.16 \times 0.14$	$0.22 \times 0.17 \times 0.16$	$0.18 \times 0.16 \times 0.15$
θ range for data collection (°)	2.04–25.02	2.04–25.02	2.09–25.02
Limiting indices	$-12 \le h \le 12$; $-17 \le k \le 17$; $-18 \le l \le 17$	$-10 \le h \le 10$; $-12 \le k \le 12$; $-17 \le l \le 16$	$-13 \le h \le 13$; $-17 \le k \le 17$; $-19 \le l \le 19$
Reflections collected	17,432	9946	19,402
Independent reflections θ	4084 [R(int) = 0.0387]	4515 [R(int) = 0.0555]	4550 [R(int) = 0.0439]
Completeness to $\theta = 25.02$ (%)	100	99.8	99.9
Goodness-of-fit on F^2	1.052	1.059	0.812
Final R indices $[I > 2\sigma(I)]^{a,b}$	$R_1 = 0.0583$, $wR_2 = 0.1933$	$R_1 = 0.0423$, $wR_2 = 0.1245$	$R_1 = 0.0376$, $wR_2 = 0.0954$
R indices (all data)^{a,b}	$R_1 = 0.0704$, $wR_2 = 0.2051$	$R_1 = 0.0552$, $wR_2 = 0.1331$	$R_1 = 0.0606$, $wR_2 = 0.1129$
$\Delta\rho_{max}$ (e Å^{-3})	2.820	1.331	0.785
$\Delta\rho_{min}$ (e Å^{-3})	−1.399	−1.411	−0.502

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**3**.

1			
Cd1–N3	2.249(7)	Cd1–N2	2.281(8)
Cd1–Br1	2.6948(11)	Cd1–Br2	2.7252(11)
N3–Cd1–N2	106.0(3)	N3–Cd1–Br1	108.75(19)
N2–Cd1–Br1	100.6(2)	N3–Cd1–Br2	104.94(19)
N2–Cd1–Br2	107.9(2)	Br1–Cd1–Br2	127.05(4)
2			
I1–Cd1	2.7160(7)	I2–Cd1	2.7251(6)
Cd1–N3	2.265(5)	Cd1–N1	2.236(5)
I1–Cd1–I2	124.10(2)	N3–Cd1–N1	105.42(19)
N3–Cd1–I1	111.30(13)	N1–Cd1–I1	104.70(13)
N3–Cd1–I2	101.39(13)	N1–Cd1–I2	108.67(13)
3			
Cd1–N3	2.258(4)	Cd1–N1	2.267(4)
Cd1–Br1	2.5416(7)	Cd1–Br2	2.5349(7)
N3–Cd1–N1	103.54(15)	N3–Cd1–Br2	115.28(11)
N1–Cd1–Br2	100.88(11)	N3–Cd1–Br1	108.02(12)
N1–Cd1–Br1	108.33(11)	Br1–Cd1–Br2	119.17(3)

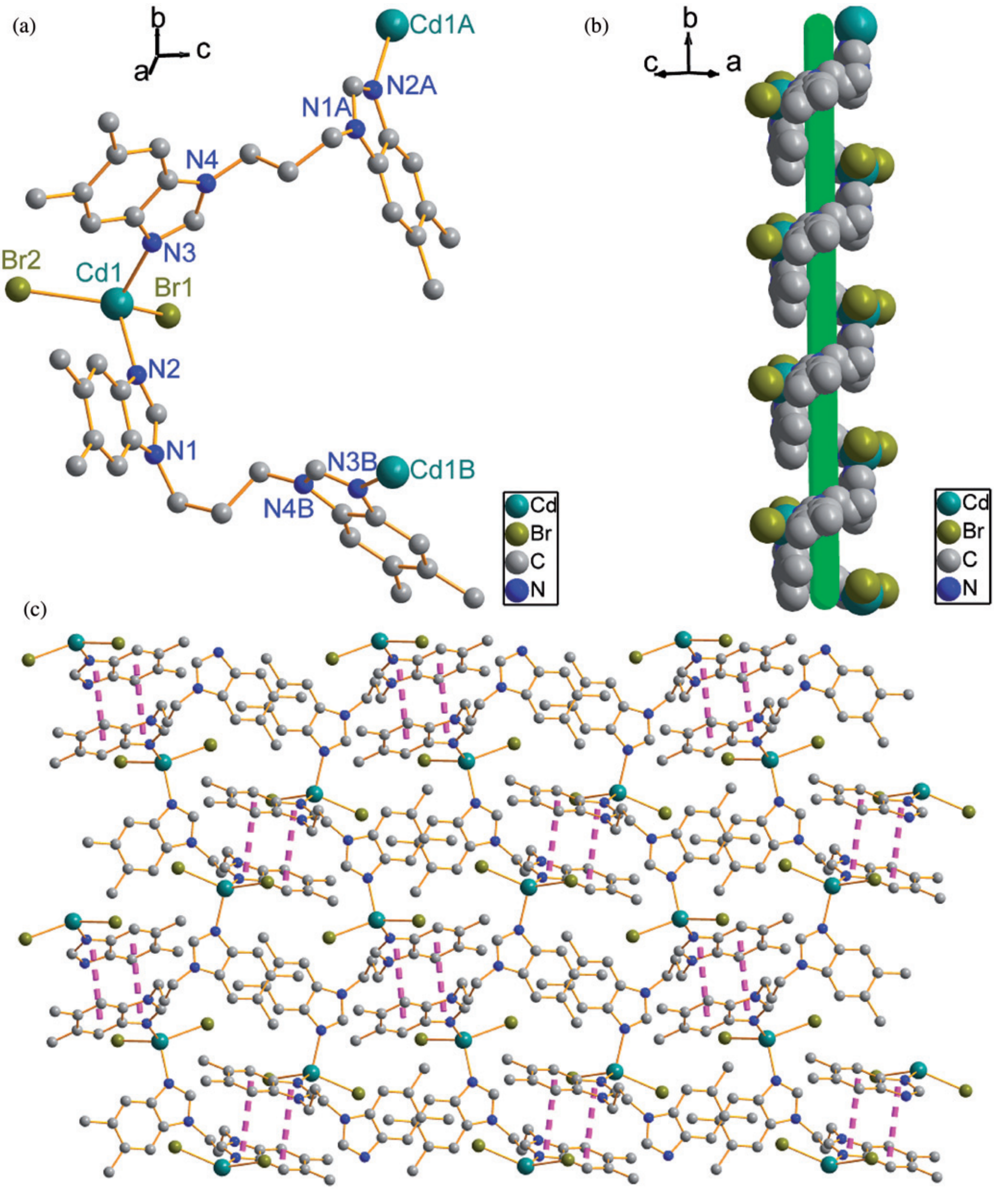

Figure 1. (a) The coordination environment around Cd(II) in **1**; all hydrogen atoms were omitted for clarity. Symmetry transformations used to generate equivalent atoms: A = $-x+1.5$, $y+0.5$, $-z+0.5$; B = $-x+1.5$, $y-0.5$, $-z+0.5$. (b) 1-D helical chain connected by bromides and **L1** in **1**. (c) 2-D supramolecular network connected by π–π stacking interactions in **1**.

3.1.2. Crystal structure of [CdI$_2$(L$_2$)]$_n$ (2). Complex **2** crystallizes in the triclinic space group $P\bar{1}$ with the asymmetric unit consisting of one crystallographically independent Cd(II), two iodides, and one L$_2$. Figure 2(a) illustrates the coordination environment of the metal center, located in a distorted tetrahedron, surrounded by two iodides (I1 and I2) and two nitrogen atoms (N1 and N3) from two separated L$_2$. The Cd–N and Cd–I

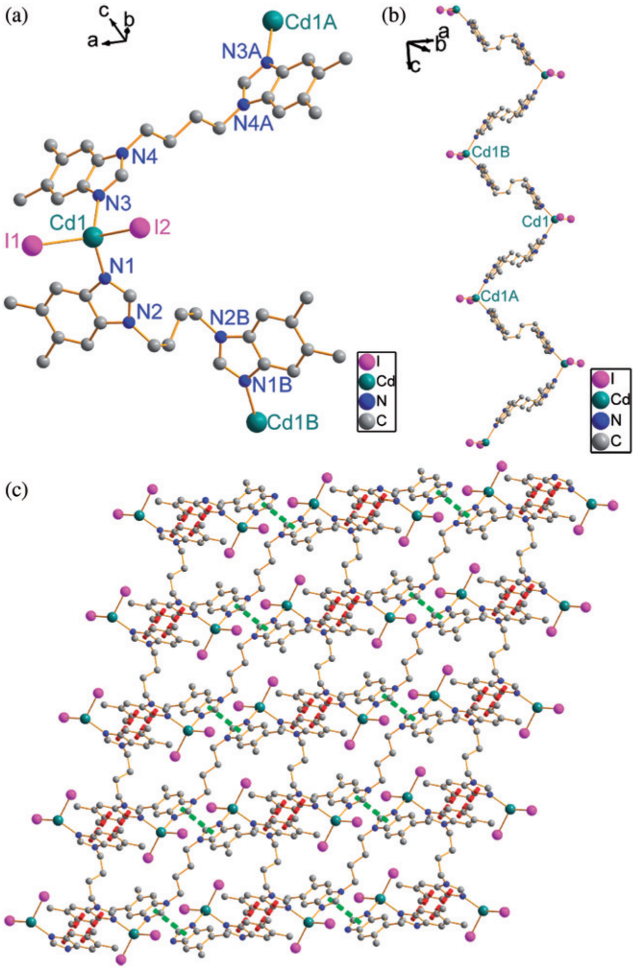

Figure 2. (a) Coordination environment around Cd(II) in **2**; all hydrogen atoms were omitted for clarity. Symmetry transformations used to generate equivalent atoms: A = $-x$, $-y+1$, $-z+1$; B = $-x+1$, $-y$, z. (b) 1-D zigzag chain connected by iodides and **L2** in **2**. Symmetry transformations used to generate equivalent atoms: A = $-x$, $-y+1$, $-z+1$; B = $-x+1$, $-y$, z. (c) 2-D supramolecular structure connected by π–π stacking interactions in **2**.

bond lengths are 2.236(5)–2.265(5) and 2.716(7)–2.7251(6) Å, respectively, and the corresponding bond angles are 101.39(13)–124.1(2)°.

L_2 shows two coordination conformations in **2** with coordinated N···N separations of 8.716(9) and 10.1555(7) Å, respectively. One L_2 adopts *cis–trans–cis* conformation and the other L_2 exhibits *trans–trans–trans* conformation, and is longer in length. Cd(II) linking two L_2 with different conformations leads to a 1-D zigzag chain, where the Cd1A–Cd1–Cd1B angle is 80.438(4)°, as shown in figure 2(b). The distances between Cd(II) linked by two L_2 are 12.7457(9) and 13.9764(10) Å, respectively. In **2**, there are two kinds of π–π stacking interactions: between the benzimidazole rings from two parallel *cis–trans–cis* conformation L_2 with face-to-face distance of 3.694(4) Å and two parallel *trans–trans–trans* conformation L_2 with center-to-center distance of 3.592(4) Å.

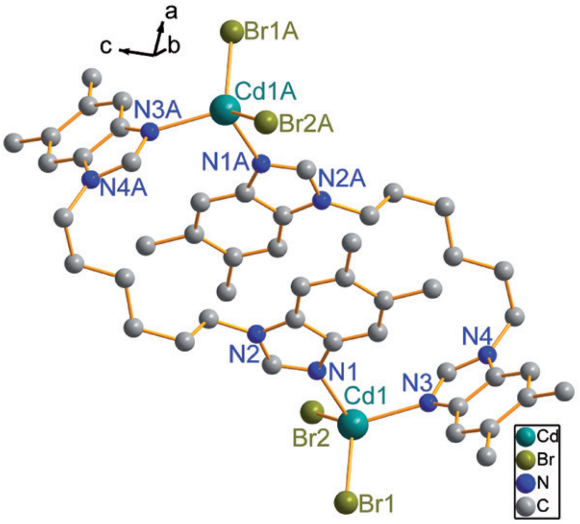

Figure 3. Coordination environment around Cd(II) in **3**; all hydrogen atoms were omitted for clarity. Symmetry transformations used to generate equivalent atoms: $A = -x + 1, -y, -z + 2$.

Thus, neighboring 1-D chains are further extended into a 2-D supramolecular framework through π–π stacking interactions, as shown in figure 2(c).

3.1.3. Crystal structure of $Cd_2Br_4(L_3)_2$ (3). Compared with **1** and **2**, **3** exhibits a dinuclear structure. The independent unit of **3** contains one Cd(II), two bromides, and one L_3. As shown in figure 3, Cd(II) is four-coordinate with two bromides (Br1 and Br2) and two nitrogen atoms (N2 and N3) from two different L_3, showing distorted tetrahedral geometry. The Cd–Br and Cd–N bond lengths are 2.5349(7), 2.5416(7), 2.258(4), and 2.267(4) Å, respectively. The corresponding bond angles are 100.88(11)–119.17(3)°. In **3**, L_3 is bis-monodentate bridging, adopting a *trans–trans* conformation, and connecting neighboring $CdBr_2$ units to form a dinuclear metallomacrocycle, with 10.455(7) Å between adjacent Cd(II) atoms.

3.1.4. Structural comparison of the coordination polymers. A metallomacrocycle and two coordination polymers from reactions of Cd(II) salts with 5,6-dimethylbenzimidazole bearing different spacer length ($-(CH_2)_n-$, $n = 3, 4, 6$) are presented. X-ray analysis reveals that **1** consists of a 1-D helical chain in which $CdBr_2$ units are linked by L_1 bridges and the helical chains are expanded to a 2-D supramolecular network by π–π stacking interactions. For **2**, each CdI_2 unit is connected by two different conformations of L_2 bridges to form 1-D zigzag chains, which are further extended into a 2-D supramolecular framework through π–π stacking interactions. Complex **3** contains a dinuclear metallomacrocycle in which each $CdBr_2$ unit is linked by L_3 bridges. For **1**–**3**, Cd(II) centers have a tetrahedral coordination geometry and each halide is terminal. These results provide insight into how Cd(II) coordination polymers assembly is affected by spacer length of the ligands. In crystal structures of related bis-benzimidazole coordination polymers $[Cd(bbbi)(ita)(H_2O)] \cdot H_2O$ (**4**), [Cd(bbbi)(fma)]

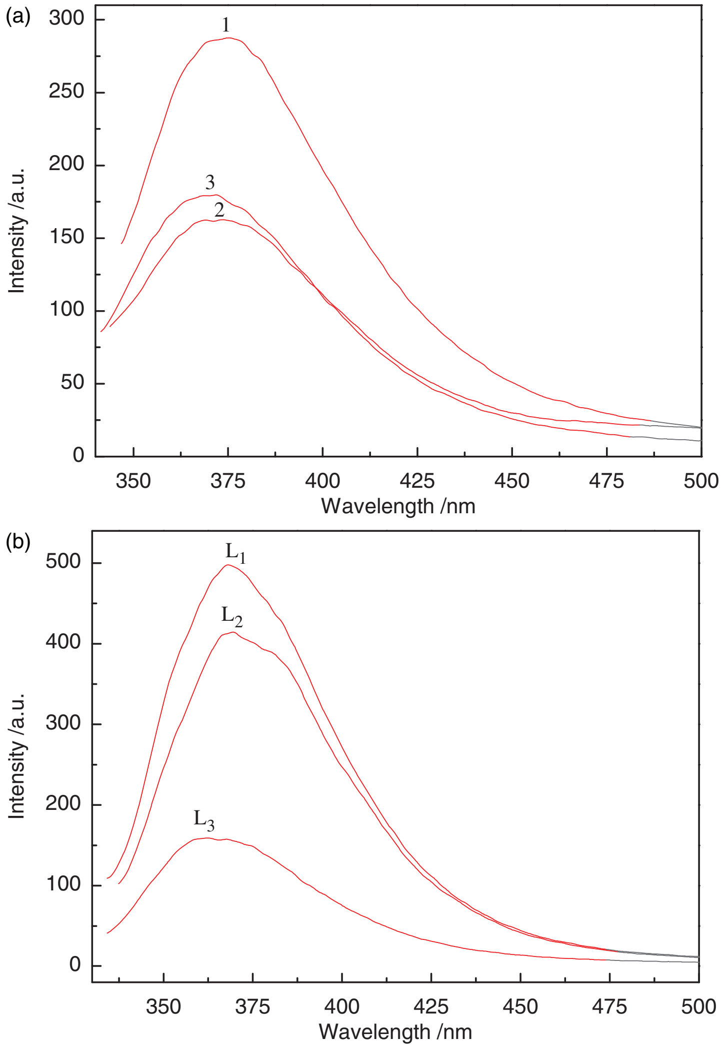

Figure 4. (a) Fluorescent emission spectra of **1–3** in the solid state at room temperature. (b) Fluorescent emission spectra of L_1, L_2, and L_3 in the solid state at room temperature.

(**5**), and $[Cd(bbbi)(fma)(H_2O)] \cdot 2H_2O$ (**6**) (H_2ita = itaconic acid, bbbi = 1,1-(1,4-butanediyl)bis-1H-benzimidazole, and H_2fma = fumaric acid), the significant differences of these metal–organic frameworks indicate that carboxylates with different substituents also play an important role in formation of the final frameworks and coordination modes of Cd(II) [10i].

3.2. *Thermal properties*

Thermogravimetric experiments were carried out to study the thermal stability of **1**–**3**. The results are presented in "Supplementary material." Complexes **1**–**3** had only one weight loss step of 80.09% for **1**, 82.13% for **2**, and 81.29% for **3** between 323.02 and

480.52°C (**1**), 348.44 and 533.44°C (**2**), and 426.51 and 581.51°C (**3**), attributed to loss of ligands and X (X = Br or I) (Calcd 84.23% for **1**, 81.41% for **2,** and 82.62% for **3**). In all cases, the residue was assumed to be Cd.

3.3. *Photoluminescent properties*

Photoluminescence properties of **1**–**3**, L_1, L_2, and L_3 in the solid state at room temperature are provided in figure 4(a) and (b). Upon excitation at 320 nm (L_1, L_2, L_3, and **3**) and 325 nm (**1** and **2**), L_1, L_2, L_3, and **1**–**3** exhibit photoluminescence with emission maxima at 368 nm (L_1), 370 nm (L_2), 363 nm (L_3), 375 nm (**1**), 374 nm (**2**), and 369 nm (**3**). Emission maxima of **1**–**3** are red-shifted compared to the corresponding ligand. The bands might be assigned to metal-to-ligand charge transfer with electrons being transferred from Cd(II) to the unoccupied π^* orbitals of the benzimidazolyl groups [20].

4. Conclusion

Three coordination polymers were obtained by the reaction of Cd(II) and three flexible bis(benzimidazole) ligands under hydrothermal conditions. X-ray analysis revealed that **1**–**3** exhibit 1-D helical chain, 1-D zigzag chain, and a binuclear structure, respectively. These results provide insight into how the assembly of Cd(II) coordination polymers is affected by the spacer length of the ligands. The luminescent behaviors of the complexes are also described.

Supplementary material

CCDC 870004–870006 contain the supplementary crystallographic data for coordination polymers **1**–**3**. 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

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