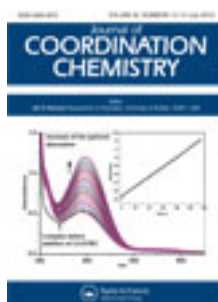


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Cui-Hong He^a, Cui-Huan Jiao^a, Jian-Chen Geng^a & Guang-Hua Cui^a

^a College of Chemical Engineering, Hebei United University, Tangshan 063009, Hebei, P. R. China

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Synthesis, structures, and fluorescence of two cadmium(II) coordination polymers with a semirigid bis-benzimidazole

CUI-HONG HE, CUI-HUAN JIAO, JIAN-CHEN GENG and GUANG-HUA CUI*

College of Chemical Engineering, Hebei United University,
Tangshan 063009, Hebei, P. R. China

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Compounds $[\text{CdLCl}_2]_n$ (**1**) and $\{[\text{Cd}(\text{L})_2(\text{ClO}_4)]\cdot\text{ClO}_4\}_n$ (**2**), where L = 1,3-bis(5,6-dimethylbenzimidazol-1-ylmethyl)benzene, have been synthesized by hydrothermal method, and characterized by element analysis, IR spectra, Powder XRD, and X-ray crystallographic diffraction. Cd(II) in **1** and **2** are both trigonal bipyramidal. Different cadmium salts of chloride and perchlorate lead to different configurations of $[\text{Cd}_2\text{L}_2]^{2+}$, *trans*-form in **1** but *trans* and *cis*-forms in **2**. The 1-D beaded chains of **1** are further linked to generate a 3-D supramolecular architecture by strong π - π stacking interactions as well as intermolecular C-H \cdots Cl hydrogen bonds. In **2**, the 1-D beaded chains are further assembled by intermolecular C-H \cdots O hydrogen bonds to form a 2-D layer. Solid-state fluorescent properties of **1** and **2** were investigated at room temperature.

Keywords: Bis(benzimidazole) ligand; Cadmium(II) polymers; Fluorescence; Supramolecular architecture

1. Introduction

Metal-organic coordination polymers have become a major focus in crystal engineering and supramolecular chemistry because of exceptional structures and potential as functional materials with specific properties, such as luminescence, magnetism, absorption, catalysis, ion-exchange, etc. [1–4]. Rational and controllable synthesis of coordination networks and supramolecular (π - π stacking and hydrogen bonds) architectures is still a challenge, since the assembly of such polymers can be easily influenced by the selection of metal ions with different coordination geometries, ligands, counteranions with different coordination abilities, solvent, etc. Controlling the properties and structures of metal-organic frameworks (MOFs) by the selection of proper organic ligands has attracted most interest in metal-organic architectures [5].

We select flexible multidentate 1,3-bis(5,6-dimethylbenzimidazol-1-ylmethyl)benzene (L) with arylaliphatic core and benzimidazole nitrogen donors as main ligand because of remarkable advantages: (i) the bis(benzimidazole) nitrogens have strong coordination ability and the $-(\text{Ph}-\text{CH}_2)-$ group is semirigid; (ii) L contains both the imidazole ring and a larger conjugated π -system, capable of acting as hydrogen bond donors and

*Corresponding author. Email: tscghua@126.com

for π - π stacking interactions; (iii) among the series of benzimidazole derivatives, 5,6-dimethylbenzimidazole serves as an axial ligand for cobalt in vitamin B₁₂ [6]. Bis(5,6-dimethylbenzimidazole) as a bridging ligand participates in the construction of coordination polymers, allowing us to investigate the influences of methyl-substituted derivative of benzimidazole on the structures and properties of complexes. Such coordination polymers based on bis(5,6-dimethylbenzimidazole) with various metal salts have been studied little [7]. Cd(II)-connecting coordination polymers have attracted considerable interest owing to the large radius, various coordination modes, and unique physical properties of Cd^{II} [8]. So, we and other groups have focused on the synthesis and structural exploration of coordination polymers with flexible bis-benzimidazole ligands [9–13], with a view to make good progress in understanding how the nature of metal ions and the structures of ligands affect the architectures. For our ongoing work, the semirigid bis-benzimidazole, 1,3-bis(5,6-dimethylbenzimidazol-1-ylmethyl)benzene (L), was synthesized. Herein, we reported the synthesis, structures, and fluorescent properties of two coordination polymers constructed by L with cadmium(II) salt with two different counteranions.

2. Experimental

2.1. Materials and physical measurements

L was prepared according to the literature [14]. All other reagents were purchased commercially and used without purification. Elemental analysis was performed on a Perkin-Elmer 240C automatic analyzer. FT-IR spectra were recorded from 4000 to 400 cm⁻¹ on a FT-IR AVATAR 360 (Nicolet) spectrophotometer using KBr pellets. Powder X-ray diffraction (XRD) measurement was executed on a D/MAX 2500PC X-ray diffractometer using Cu-K α radiation ($\lambda = 0.1542$ nm) in the 2θ range 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 polymers

2.2.1. Synthesis of [CdCl₂L]_n (1). A mixture of CdCl₂ · 2.5H₂O (1.0 mmol, 228.4 mg), L (1.0 mmol, 394.5 mg), DMF (2 mL), and H₂O (8 mL) was stirred for 20 min in air, then transferred to a 25 mL Teflon-lined stainless vessel and kept at 140°C for 3 days under autogenous pressure and then cooled to room temperature at 5°C h⁻¹. Colorless block crystals of **1** were obtained (yield: 55% based on CdCl₂ · 2.5H₂O). Elemental Anal. Calcd for C₂₆H₂₆CdCl₂N₄ (%): C, 53.97; H, 4.53; N, 9.69. Found (%): C, 53.93; H, 4.50; N, 9.61. IR data (KBr pellet, cm⁻¹): 3420m, 3091m, 2915m, 1624w, 1494m, 1440m, 1372m, 1089m, 845 m, 707w, 623w, 539w.

2.2.2. Synthesis of {[Cd(ClO₄)(L)₂] · ClO₄}_n (2). A mixture of Cd(ClO₄)₂ · 6H₂O (1.0 mmol, 419.4 mg), L (1.0 mmol, 394.5 mg), MeOH (3 mL), and H₂O (6 mL) was placed in a 25 mL Teflon-lined stainless vessel and kept at 140°C for 3 days under autogenous pressure and then cooled to room temperature at a rate of 5°C h⁻¹.

Colorless block crystals of **2** were obtained (yield: 35% based on $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$). Elemental Anal. Calcd for $\text{C}_{52}\text{H}_{52}\text{CdCl}_2\text{N}_8\text{O}_8$ (%): C, 56.76; H, 4.76; N, 10.18. Found (%): C, 56.73; H, 4.72; N, 10.15. IR data (KBr pellet, cm^{-1}): 3435m, 3121m, 2954m, 1624w, 1502w, 1440m, 1380m, 1303m, 1204m, 1097s, 845 m, 715w, 616 m, 532w, 470w, 432w.

2.3. Crystal structure determination

Crystallographic data collections for **1** and **2** were carried out on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) and ω - 2θ scan mode at 293 K. A semi-empirical absorption correction was applied using SADABS [15a]. The structures were solved by direct methods and refined anisotropically by full-matrix least-squares using Bruker's SHELXTL program package [15b]. Nonhydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions. Details of data collection and structure refinement for **1** and **2** are summarized in table 1 and selected bond lengths and angles

Table 1. Crystallographic data for **1** and **2**.

Compounds	1	2
Empirical formula	$\text{C}_{26}\text{H}_{26}\text{CdCl}_2\text{N}_4$	$\text{C}_{52}\text{H}_{52}\text{CdCl}_2\text{N}_8\text{O}_8$
Formula weight	577.82	1100.32
Temperature (K)	293(2)	293(2)
Wavelength (\AA)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions (\AA , $^\circ$)		
<i>a</i>	10.1267(8)	10.7901(11)
<i>b</i>	10.5972(8)	12.9742(14)
<i>c</i>	13.5576(16)	18.226(2)
α	100.0780(10)	88.318(2)
β	106.8270(8)	85.268(2)
γ	107.4660(10)	86.785(2)
Volume (\AA^{-3}), <i>Z</i>	1272.6(2), 2	2538.0(5), 2
Calculated density (Mg m^{-3})	1.508	1.440
Absorption coefficient (mm^{-1})	1.089	0.598
Crystal size (mm^3)	$0.25 \times 0.22 \times 0.19$	$0.28 \times 0.26 \times 0.24$
<i>F</i> (000)	584	1132
θ range for data collection ($^\circ$)	2.10–25.02	2.24–25.02
Limiting indices	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-16 \leq l \leq 16$	$-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $-21 \leq l \leq 21$
Reflections collected	9621	19,586
Reflections unique	4448 [<i>R</i> (int) = 0.0229]	8934 [<i>R</i> (int) = 0.0655]
Completeness to $\theta = 25.02$ (%)	99.0	99.6
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.041	1.004
Final <i>R</i> indices [$I > 2\sigma(I)$] ^{a,b}	$R_1 = 0.0301$, $wR_2 = 0.0780$	$R_1 = 0.0664$, $wR_2 = 0.1586$
<i>R</i> indices (all data) ^{a,b}	$R_1 = 0.0357$, $wR_2 = 0.0817$	$R_1 = 0.1302$, $wR_2 = 0.1934$
Largest difference peak and hole ($\text{e} \cdot \text{\AA}^{-3}$)	0.503 and -0.507	0.974 and -0.864

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

^b $R_1 = \{ \Sigma [wF_o^2 - F_c^2]^2 / \Sigma [wF_o^2]^2 \}^{1/2}$.

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

Parameter	Value	Parameter	Value
1			
Cd1–N3	2.284(2)	Cd1–N1	2.465(3)
Cd1–Cl1#1	2.4686(8)	Cd1–Cl2	2.5022(9)
Cd1–Cl1	2.7036(8)		
N3–Cd1–N1	71.63(8)	N3–Cd1–Cl1#1	123.40(6)
N1–Cd1–Cl1#1	92.52(6)	N3–Cd1–Cl2	124.54(6)
N1–Cd1–Cl2	108.24(7)	Cl1A–Cd1–Cl2	112.05(3)
N3–Cd1–Cl1	96.30(6)	N1–Cd1–Cl1	153.82(7)
Cl1#1–Cd1–Cl1	74.51(3)	Cl2–Cd1–Cl1	97.76(3)
Cd1–Cl1–Cd1	105.49(3)		
2			
Cd1–N7	2.258(6)	Cd1–N3	2.270(5)
Cd1–N6#1	2.282(5)	Cd1–N1	2.319(6)
Cd1–O3	2.310(6)		
N7–Cd1–N3	134.2(2)	N7–Cd1–N6#1	99.07(19)
N3–Cd1–N6#1	88.62(18)	N7–Cd1–N1	86.8(2)
N3–Cd1–N1	93.53(19)	N6 A–Cd1–N1	169.5(2)
N7–Cd1–O3	107.5(3)	N3–Cd1–O3	117.7(3)
N6#1–Cd1–O3	89.4(2)	N1–Cd1–O3	80.5(2)

Symmetry code for **1**: #1 = $-x, -y + 2, -z + 1$, **2**: #1 = $-x + 1, -y + 2, -z$.

are listed in table 2. In **2**, C50 of aryl and two perchlorates have configurational disorder.

3. Results and discussion

3.1. Description of crystal structures

3.1.1. Crystal structure of $[\text{CdLCl}_2]_n$ (1**).** Solid **1** is stable in air and insoluble in common solvents. Single-crystal XRD analysis reveals that **1** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit consists of one crystallographically independent Cd^{II} , two chlorides, and one L. Each Cd^{II} is surrounded by two nitrogen atoms from two L, a terminal and two μ_2 -bridging chlorides in a slightly distorted trigonal bipyramidal geometry, in which Cl1#1 (symmetry code: #1 = $-x, -y + 2, -z + 1$), N3, and Cl2 occupy the equatorial plane, while N1 and Cl1 complete the apical positions. The Cd–N bond lengths are Cd1–N1 = 2.465(3), Cd1–N3 = 2.284(2) Å, respectively, and the Cd–Cl bond lengths are 2.4686(8)–2.7036(8) Å. L are *trans* forms with dihedral angles between benzimidazole rings within one L of 65.747°.

The Cd(II) ions are linked into a 1-D-beaded chain through bridging L and chlorides. With one terminal chloride and two nitrogen atoms, the two Cd1 atoms are bridged by two $\mu_2\text{-Cl}^-$ using their two residual coordination sites to form the rhomboid [Cd–Cl–Cd1#1–Cl] (symmetry code: #1 = $-x, -y + 2, -z + 1$) binuclear units with a Cd...Cd separation of 4.1191 Å. Adjacent binuclear units $[\text{Cd}_2\text{Cl}_2]$ are linked by two L using a μ_2 -bis(monodentate)-bridging mode to form infinite 1-D chains, as shown in figure 1(a). A 28-member macrocycle of $[\text{Cd}_2\text{L}_2]^{4+}$ with a Cd...Cd separation of

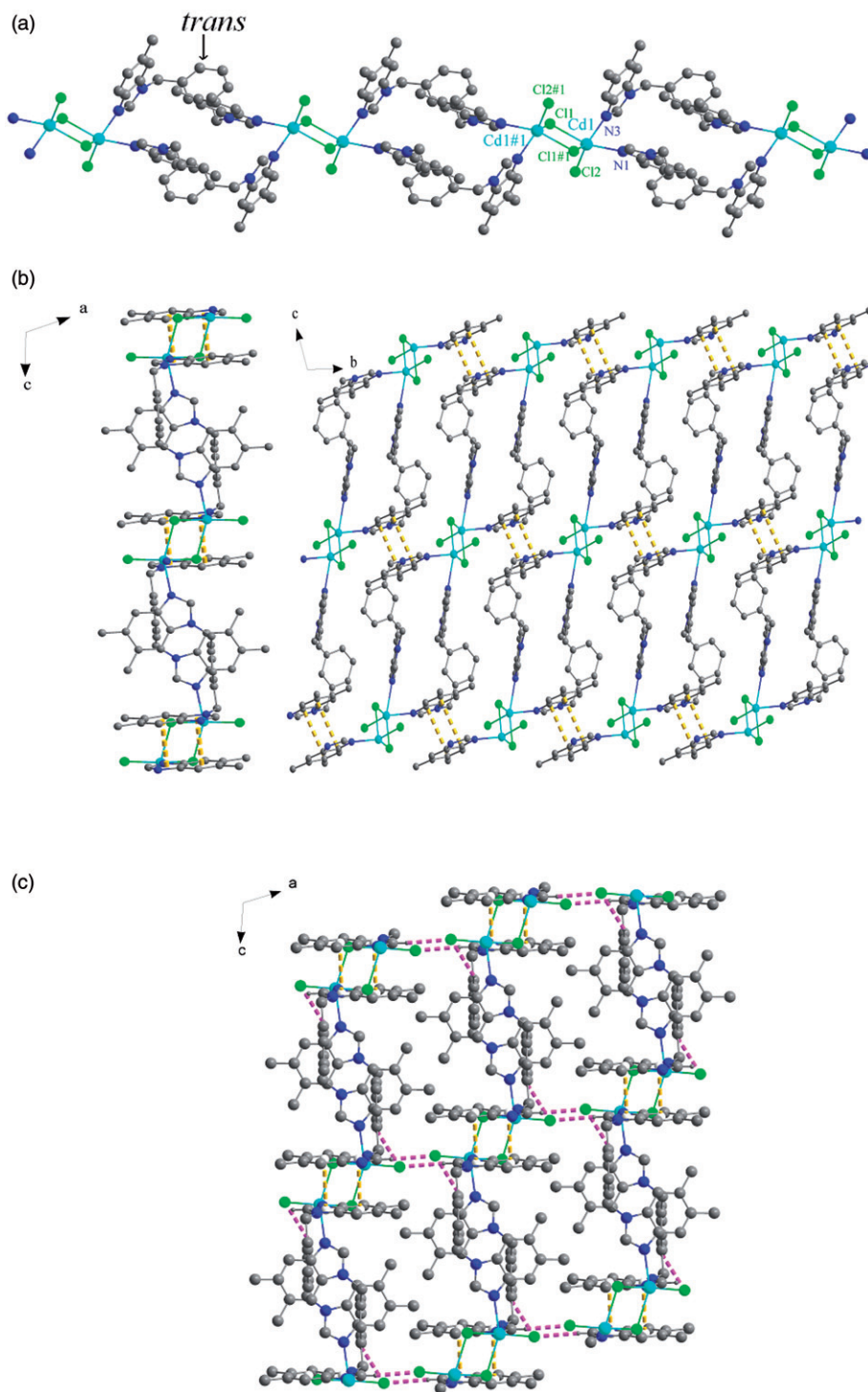


Figure 1. (a) 1-D beaded chain of **1**; all hydrogen atoms were omitted for clarity (symmetry transformations used to generate equivalent atoms: #1 = $-x, 2-y, -z$). (b) The 2-D supramolecular networks by strong aromatic π - π stacking interactions of **1** viewed from *b*- and *a*- axes. (c) 3-D supramolecular framework of **1** constructed by π - π stacking and weak C-H \cdots Cl hydrogen bonding interactions.

Table 3. Non-classical hydrogen bond lengths (Å) and angles (°) for **1** and **2**.

Complex	D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠DHA
1	C14–H14···Cl2C	0.93	2.79	3.585 (4)	144
	C18–H18···Cl2D	0.93	2.75	3.675 (4)	176
2	C1–H1B···O1E	0.96	2.52	3.279 (13)	136
	C17–H17B···O7E	0.97	2.59	3.474 (11)	151
	C30–H30···O4E	0.93	2.48	3.243 (15)	139
	C34–H34···O5E	0.93	2.40	3.249 (9)	151
	C43–H4···O8E	0.93	2.49	3.160 (10)	129

Symmetry code for **1**: C = $-x, 2-y, -z$; D = $1-x, 2-y, 1-z$; **2**: E = $x, 1+y, z$.

2.703 Å exists. The 1-D chains are extended into the final 2-D networks through strong face-to-face π - π stacking interactions between 5,6-dimethylbenzimidazole rings from adjacent chains, with a center-to-center distance of 3.382 Å, an inter-planar angle $\alpha = 0.64^\circ$ and slipping angles β or γ of 13.64° or 13.72° , and an averaged $d_{\pi-\pi}$ distance of 3.285 Å, as depicted in figure 1(b). These 2-D layers are further assembled into 3-D supramolecular frameworks through weak C–H···Cl hydrogen bonding interactions (C14···Cl2C = 3.585(4) Å, C14–H14···Cl2C = 144° ; C18···Cl2D = 3.675(4) Å, C18–H18···Cl2D = 176° , symmetry code: C = $-x, -y+2, -z+1, -z$, D = $-x+1, -y+2, -z+1$) (figure 1c); the main non-classical hydrogen bond data for **1** are listed in table 3.

3.1.2. Crystal structure of $\{[\text{Cd}(\text{L})_2(\text{ClO}_4)] \cdot \text{ClO}_4\}_n$ (2**).** X-ray structural determination reveals that **2** is a 1-D-beaded chain coordination polymer. The structure contains a cadmium, two L, one coordinated and one uncoordinated perchlorate. Each Cd(II) is five-coordinate by four nitrogen atoms from four different L and one oxygen atom from one coordinated perchlorate, showing distorted trigonal bipyramidal geometry. The Cd–O bond length is 2.310(6) Å and the Cd–N bond lengths range from 2.258(6) to 2.319(6) Å.

L shows two kinds of coordination conformations in **2**. One L adopts *cis* conformation, connecting two neighboring Cd²⁺ to a quadrate macrocycle. Another L exhibits a *trans* conformation, linking two adjacent cadmium(II) ions forming a chair-like macrocycle. The dihedral angles between benzimidazole rings within one L are 78.897° for the former and 84.631° for the latter. The distances between Cd(II) linked by the two kinds of L are 11.6026(12) and 10.4786(11) Å, respectively. Each Cd(II) is linked to adjacent Cd(II) through bridging L, forming a 1-D-beaded chain structure (figure 2a), where the Cd–Cd–Cd angle defined by the orientation of L in the chain is $111.158(6)^\circ$. Adjacent 1-D chains are further arranged into a 2-D supramolecular architecture by C–H···O hydrogen bonds between L and ClO₄[−] [C···O 3.243(15)–3.474(11) Å and C–H···O 129 – 151°] (figure 2b). The weak noncovalent interactions are important in the formation of the final supramolecular structure of **2**.

3.1.3. Effect of counteranions on the frameworks. Compounds **1** and **2** are obtained under similar conditions, however, L adopt the *trans* form in **1** and *cis* and *trans*-forms in **2**, thus semirigidity of dipolar ligand could generate cisoid and transoid

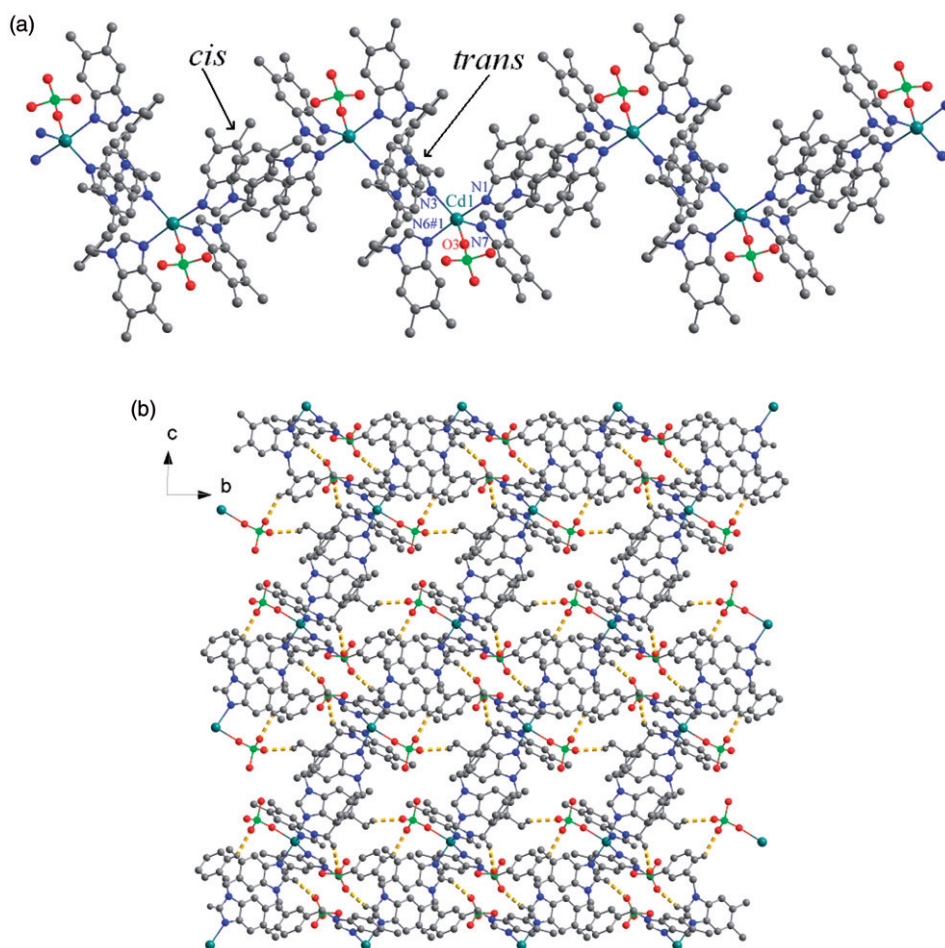


Figure 2. (a) 1-D-beaded chain of **2** (symmetry code: #1 = $-x + 1, -y + 2, -z$), (b) The 2-D supramolecular network by C-H...O interactions of **2**.

isomers when coordinated to metal centers. The conformations of these ligands appear to be anion-dependent. In **1**, Cl^- directly coordinates to Cd^{II} as μ_2 -bridging and terminal ligands and $[\text{Cd}_2\text{Cl}_4]$ are connected by two *trans*-arrangement L forming a 1-D-beaded chain. A 3-D supramolecular architecture is assembled by the cooperative association of coordination interactions as well as non-classical hydrogen bonds C-H...Cl and π ... π packing interactions. The spherical anions ClO_4^- serve as counteranions in **2**; one is weakly coordinated to Cd^{II} and the other resides in the lattice to balance the charge. Both are involved in non-classical hydrogen bonds C-H...O forming higher-dimensional networks with L. The semirigid L and counteranions play an important role in leading to the different structures of coordination and supramolecular architectures. In the crystal structure of the related bis-benzimidazole complexes $\{[\text{HgBr}_2(\text{pbbm})] \cdot \text{DMF}\}_n$ and $[\text{HgI}_2(\text{pbbm})]_2$ (pbbm = 1,1'-(1,5-pentanediy)-bis-1H-benzimidazole), the significant differences of these MOFs indicate that counteranions have similar impact on assembling the MOFs, whereas comparing

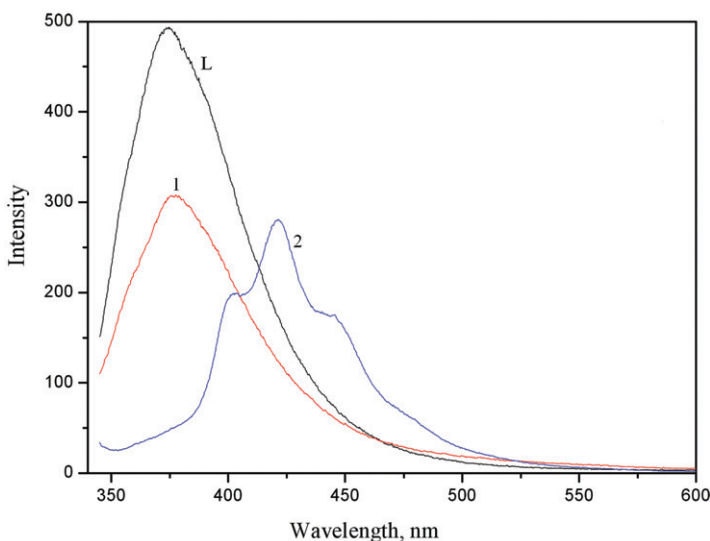


Figure 3. Solid-state photoluminescent spectra of L, **1** and **2**.

[PbI₂(pbbm)]_n with {[HgI₂(pbbm)]·(DMF)_{1/2}]_n differences of the MOFs indicate that metals have remarkable impact on assembling the resultant aggregations [9].

3.2. IR spectra of **1** and **2**

IR spectra of **1** and **2** show strong absorptions around 1494–1624 cm⁻¹, which can be assigned to ν_{C=N}; the strong aromatic ring-vibration absorptions are observed around 738–752 cm⁻¹. The strong band at 1097 cm⁻¹ in **2** is attributed to ClO₄⁻.

3.3. Fluorescence of **1** and **2**

The photoluminescent properties of **1** and **2**, together with L, were studied in the solid state at room temperature; emission spectra are shown in figure 3. Blue emission for **1**, **2**, and L can be observed, where the maximum emission wavelength is at 375 nm (under 330 nm excitation) for L, 377 nm (under 325 nm excitation) for **1**, and 421 nm (under 335 nm excitation) for **2**. Compared with the emission spectrum of L, a slight red shift of 2 nm in **1** with lower intensity is considered to mainly arise from coordination. Red shift of 44 nm in **2** is the result of ligand to metal charge transfer (LMCT) [16] and arises from the incorporation of Cd(II) increasing the conformational rigidity and reducing the loss of energy via vibration motions. Thus, enhanced fluorescence intensity of **2** is detected. Fluorescent intensity of **1** is stronger than that of **2**, possibly from conformational rigidity of **1** with 3-D supramolecular network constructed by the cooperative association of coordination interactions as well as non-classical hydrogen bonds C–H···Cl and π···π packing interactions compared with that of **2** by non-classical C–H···O interactions. The photoluminescence shows that the coordination anions may contribute to the fluorescent emission of the Cd(II) coordination polymers.

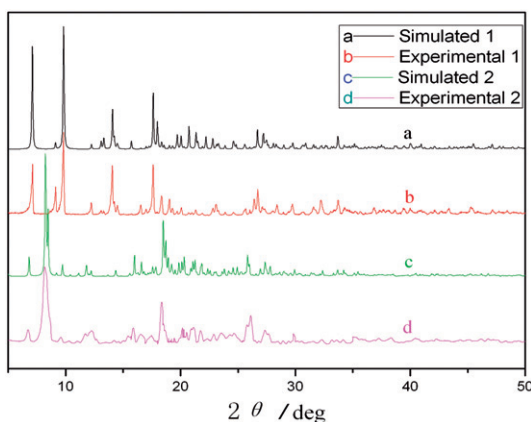


Figure 4. X-ray powder diffraction patterns of **1** and **2**.

3.4. Powder XRD of **1** and **2**

The powder XRD pattern and simulated XRD pattern of **1** and **2** are depicted in figure 4. The measured powder XRD pattern is in good agreement with the simulated pattern by X-ray single crystal data, indicating phase purities of the samples. The difference in reflection intensities between the simulated and the experimental patterns is due to the different orientation of the crystals in the powder samples.

4. Conclusion

Two new polymers have been obtained by hydrothermal reactions of cadmium salts with 1,3-bis(5,6-dimethylbenzimidazol-1-ylmethyl)benzene. Compounds **1** and **2** are both 1-D chain structures with **1** expanded to a 3-D supramolecular architecture, while **2** is expanded to a 2-D supramolecular network. The structures demonstrate that the conformations of L and the counteranions play important roles in the different topologies of supramolecular architectures.

Supplementary material

X-ray crystallographic files in CIF format for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre with CCDC Nos. 855459 and 855460. The data can be freely obtained from the Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

References

- [1] (a) M.L. Zhang, J.J. Wang, Y.X. Ren Lei IV. *J. Coord. Chem.*, **64**, 3585 (2011); (b) J. Chen, Y.L. Feng, Z.G. Jiang, J.W. Cheng. *CrystEngComm*, **13**, 6071 (2011); (c) L. Hou, W.J. Shi, Y.Y. Wang, Y. Guo, C. Jin, Q.Z. Shi. *Chem. Commun.*, 5464 (2011).

- [2] (a) G.H. Cui, J.R. Li, J.L. Tian, X.H. Bu, S.R. Batten. *Cryst. Growth Des.*, **5**, 1775 (2005); (b) T.L. Hu, J.R. Li, C.S. Liu, X.S. Shi, J.N. Zhou, X.H. Bu, J. Ribas. *Inorg. Chem.*, **45**, 162 (2006); (c) R.F. Song, Y.B. Xie, J.R. Li, X.H. Bu. *Dalton Trans.*, 4742 (2003).
- [3] (a) T. Kaczorowski, I. Justyniak, T. Lipinska, J. Lipkowski, J. Lewinski. *J. Am. Chem. Soc.*, **131**, 5393 (2009); (b) M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi. *Chem. Res.*, **34**, 319 (2001); (c) Y. Yamauchi, M. Yoshizawa, M. Fujita. *J. Am. Chem. Soc.*, **130**, 5832 (2008); (d) J. Xu, Z.R. Pan, T.W. Wang, Y.Z. Li, Z.J. Guo, S.R. Batten, H.G. Zheng. *CrystEngComm*, **12**, 612 (2010); (e) F.W. Zhang, Z.F. Li, T.Z. Ge, H.C. Yao, G. Li, H.J. Lu, Y.Y. Zhu. *Inorg. Chem.*, **49**, 3776 (2010).
- [4] (a) D.Z. Wang, T.L. Hu, J.P. Zhao, X.H. Bu. *CrystEngComm*, **12**, 3587 (2010); (b) J.R. Li, Y.G. Ma, M.C. McCarthy, J.L. Sculley, J.M. Yu, H.K. Jeong, P.B. Balbuena, H.C. Zhou. *Coord. Chem. Rev.*, **255**, 1791 (2011); (c) J.R. Li, D.J. Timmons, H.C. Zhou. *J. Am. Chem. Soc.*, **131**, 6368 (2009).
- [5] (a) A.Y. Robin, K.M. Fromm. *Coord. Chem. Rev.*, **250**, 2127 (2006); (b) Y.Y. Liu, J.F. Ma, J. Yang, Z.M. Su. *Inorg. Chem.*, **46**, 3027 (2007); (c) C. Ren, L. Hou, B. Liu, G.P. Yang, Y.Y. Wang, Q.Z. Shi. *Dalton Trans.*, **40**, 793 (2011).
- [6] S.S. Marwaha, R.P. Sethi, J.F. Kennedy. *Enzyme Microb. Technol.*, **5**, 361 (1983).
- [7] X.L. Wang, S. Yang, G.C. Liu, J.X. Zhang, H.Y. Lin, A.X. Tian. *Inorg. Chim. Acta*, **375**, 70 (2011).
- [8] (a) F.N. Dai, H.Y. He, X.L. Zhao, Y.X. Ke, G.Q. Zhang, D.F. Sun. *CrystEngComm*, **12**, 337 (2010); (b) Z.F. Chen, P. Zhang, R.G. Xiong, D.J. Liu, X.Z. You. *Inorg. Chem. Commun.*, **5**, 35 (2002); (c) F.F. Jian, P.S. Zhao, Q.X. Wang, Y. Li. *Inorg. Chim. Acta*, **359**, 1473 (2006); (d) L.N. Yang, Y.X. Zhi, J.H. Hei, J. Li, F.X. Zhang, S.Y. Gao. *J. Coord. Chem.*, **64**, 2912 (2011); (e) J.J. Xu, Z. Zhu, S.M. Shi, J. Zhou, C.M. Jin. *J. Coord. Chem.*, **63**, 2912 (2010).
- [9] (a) B. Xiao, H.W. Hou, Y.T. Fan. *J. Coord. Chem.*, **62**, 1827 (2009); (b) B. Xiao, L.J. Yang, H.Y. Xiao, S.M. Fang. *J. Coord. Chem.*, **64**, 4408 (2011); (c) T.F. Liu, W.F. Wu, C.Q. Wan, C.H. He, C.H. Jiao, G.H. Cui. *J. Coord. Chem.*, **64**, 2296 (2011).
- [10] (a) H. Jiang, Y.Y. Liu, J.F. Ma, W.L. Zhang, J. Yang. *Polyhedron*, **27**, 2595 (2008); (b) X.L. Lü, H. Wu, J.F. Ma, J. Yang. *Polyhedron*, **30**, 1579 (2011).
- [11] (a) S.W. Jin, D.Q. Wang. *J. Coord. Chem.*, **63**, 3042 (2010); (b) J.P. Li, L.K. Li, H.W. Hou, Y.T. Fan. *J. Organomet. Chem.*, **694**, 1359 (2009).
- [12] (a) L.L. Li, Z.G. Ren, X. Lü, H.M. Wang, Y.J. Chang, H.X. Li, B. Wu, J.P. Lang. *Sci. China Chem.*, **53**, 2083 (2010); (b) Q.Y. Wen, J.Q. Chen, H.C. Fang, L. Chen, Z.Y. Zhou, Z.J. Hu, Y.P. Cai. *Z. Anorg. Allg. Chem.*, **635**, 567 (2009); (c) J.Q. Chen, Y.P. Cai, H.C. Fang, Z.Y. Zhou, X.L. Zhan, G. Zhao, Z. Zhang. *Cryst. Growth Des.*, **9**, 1605 (2009).
- [13] M. Arunachalam, P. Ghosh. *CrystEngComm*, **12**, 1621 (2010).
- [14] L.L. Li, H.X. Li, Z.G. Ren, D. Liu, Y. Chen, Y. Zhang, J.P. Lang. *Dalton Trans.*, **40**, 8567 (2009).
- [15] (a) G.M. Sheldrick. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Göttingen, Germany (1997); (b) G.M. Sheldrick. *SHELXL-97, Program for X-ray Crystal Structure Solution and Refinement*, University of Göttingen, Göttingen, Germany (1997).
- [16] Y. Cui, Y. Yue, G. Qian, B. Chen. *Chem. Rev.*, **112**, 1126 (2012).