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# Synthesis, structure and photoluminescence of two cadmium coordination polymers with 1,3-benzenedicarboxylate and two flexible bis-imidazole ligands

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#### 1. Introduction

In the past decade, a great deal of progress has been made in the synthesis and structural characterization of metal-organic frameworks (MOFs), many of which exhibit novel topological structures, interesting properties, and have the potential for applications in gas adsorption, ion exchange, magnetism, heterogeneous catalysis, luminescence, and nonlinear optics [1–10]. The rational design, synthesis, and characterization of metal-organic compounds with new architectural characteristics has been elusive and still remains a major challenge in this field because the self-assembly process is frequently influenced by various factors such as the number, type, and spatial disposition of binding sites on the ligand; the stereoelectronic preferences of the metal ion; and the metal-ligand ratio, medium, temperature, template, and counterion [1,11–13]. The most effective and facile approach to the controlled preparation of functional MOFs is an appropriate choice of well-designed organic ligands containing multidentate nitrogen and oxygen donor ligands, together with metal centers that have various coordination preferences [14-16].

Generally, multidentate organic ligands containing coordination sites of N and/or O donors play key roles in tailor-made molecular materials as well as in supramolecular self-assembly crystal engineering owing to their molecular geometry and flexibility. For example, the ligands 4,4'-bipyridine and 1,2-bis(4-pyridyl)ethane as well as the ditopic or tripodal imidazole-containing ligands

### ABSTRACT

Two new coordination polymers,  $[Cd_2(2-mBIM)_2(1,3-BDC)_2]_n$  (1) and  $[Cd(BIM)(1,3-BDC)]_n$  (2)  $[BIM = bis(imidazol-1-yl)-methane, 2-mBIM = bis(2-methylimidazol-1-yl)methane], were synthesized by reactions of CdCl<sub>2</sub> with 2-mBIM or BIM ligand in the presence of 1,3-benzenedicarboxylic acid. The polymers were then characterized by elemental analyses, IR, TGA, and X-ray diffraction. Compound 1 is a two-dimensional (2D) twofold parallel interpenetration network with a (4, 4) connected topology. Compound 2 is a 2D double-layer framework containing <math>[Cd_2(COO)_4]$  subunits. The results of this study suggest that subtle changes in the ligand structure may have a great impact on the resulting architectures of the metal–organic frameworks. Solid-state luminescent spectra of compounds 1 and 2 indicate weak fluorescent emissions at *ca*. 389 and 302 nm, respectively.

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1,4-di(1-imidazolyl)benzene and 1,3,5-tris(1-imidazolyl) benzene have been widely used in previously conducted studies [17-20]. On the other hand, polycarboxylates such as benzenedicarboxylate, benzenetricarboxylate, biphenyldicarboxylate, and oxalate  $(OX^{2-})$ are the most extensively studied organic ligands containing O donors in the construction of MOFs because of their versatile coordination modes, structural diversity, and thermodynamic stability [21-25]. Recent studies have further demonstrated that mixed organic ligands with more tunable factors, especially polycarboxylates and N-containing compounds, are good candidates for the construction of novel MOFs [26,27]. The ligand bis(2-methylimidazo-1-yl)methane (2-mBIM) and bis(imidazo-1-yl)methane (BIM) is a novel flexible N-donor ligand that has attracted a great deal of attention in the field of crystal engineering [28-30]. Following such a mixed ligand strategy, in this study, we evaluated reactions of ligand 2-mBIM and BIM with different carboxylate ligands and Cd(II) salts. Specifically, a systematic investigation of the impact of subtle changes in the ligand on the structure of the complexes was carried out. Herein, we report the syntheses, crystal structures, and photoluminescence properties of two novel Cd(II) coordination polymers  $[Cd_2(2-mBIM)_2(1,3-BDC)_2]_n$  (1) and  $[Cd(BIM)(1,3-BDC)]_n$  (2).

#### 2. Experimental section

#### 2.1. Materials and measurements

All chemicals were obtained commercially available and used as received without further purification. Ligand bis(imidazol-1-





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yl)methane (BIM) and bis(2-methyl-imidazol-1-yl)methane (2-mBIM) were prepared by literature's methods [31]. The FT-IR spectra were recorded from KBr pellets in the range of 4500–500 cm<sup>-1</sup> on a Nicolet 5700 infrared spectrometer. Thermogravimetric analysis (TGA) measurements were made using a Pyris diamond TG/DTA Thermogravimetric differential Thermal Analyzer. Samples were heated at 10 °C/min from 40 to 800 °C in a dynamic nitrogen atmosphere. Elemental analyses were performed on a Perkin–Elmer 2400 CHN elemental analyzer. The photoluminescence measurements were carried out on crystalline samples at room temperature and the spectra were collected with a Hitachi F-4500 spectrophotometer.

#### 2.2. Synthesis of $[Cd_2(2-mBIM)_2(1,3-BDC)_2]_n$ (1)

The mixture of CdCl<sub>2</sub>·2.5H<sub>2</sub>O(114 mg, 0.5 mmol), 1,3-benzenedicarboxylic acid (83 mg, 0.5 mmol), NaOH (40 mg, 1.0 mmol) and ligand 2-mBIM (89 mg, 0.5 mmol) were dissolved in the solution of H<sub>2</sub>O (10 mL), and the resulting mixture was transferred and sealed in a 25 mL Teflon-lined stainless steel autoclave, under autogenous pressure at 160 °C for 2 days and then slowly cooled to room temperature at a rate of 10 °C/h. Colorless needle crystals of [Cd<sub>2</sub>(2-mBIM)<sub>2</sub>(1,3-BDC)<sub>2</sub>]<sub>n</sub> suitable for X-ray analysis were obtained in 42% yield. Anal. Calcd for C<sub>34</sub>H<sub>32</sub>Cd<sub>2</sub>N<sub>8</sub>O<sub>8</sub>: C 45.10, H 3.56, N 12.37; Found: C 45.26, H 3.66, N 12.17; IR (KBr, cm<sup>-1</sup>): v = 3445s, 3126m, 2992w, 1608s, 1556s, 1499m, 1442w, 1379s, 1262s, 1194w, 1149m, 1138w, 1077m, 999s, 834w, 747s, 673w, 657s, 517w.

#### 2.3. Synthesis of $[Cd(BIM)(1,3-BDC)]_n$ (2)

The mixture of  $CdCl_2 \cdot 2.5H_2O(114 \text{ mg}, 0.5 \text{ mmol})$ , 1,3-benzenedicarboxylic acid (83 mg, 0.5 mmol), NaOH (40 mg, 1.0 mmol) and ligand BIM (75 mg, 0.5 mmol) were dissolved in the solution of H<sub>2</sub>O (10 mL), and the resulting mixture was transferred and

#### Table 1

Crystallographic data for complexes 1 and 2.

sealed in a 25 mL Teflon-lined stainless steel autoclave, under autogenous pressure at 160 °C for 2 days and then slowly cooled to room temperature at a rate of 10 °C/h. Colorless needle crystals of [Cd(BIM)(1,3-BDC)]<sub>n</sub> suitable for X-ray analysis were obtained in 76% yield. Anal. Calcd for C<sub>15</sub>H<sub>12</sub>CdN<sub>4</sub>O<sub>4</sub>: C 42.42, H 2.85, N 13.19; Found: C 42.79, H 2.96, N 13.27; IR (KBr, cm<sup>-1</sup>): v = 3432s, 3133s, 3113 m, 3006w, 1601s, 1551s, 1474w, 1440m, 1388s, 1284m, 1242m, 1208w, 1103m, 1079s, 1026w, 929m, 849s, 747s, 721s, 658s, 613w.

#### 2.4. X-ray crystallography

Crystals of complexes **1** and **2** were removed from test tube and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber and data for **1** and **2** were collected at 293(2) K using a Bruker/Siemens SMART APEX instrument (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å). An empirical absorption was applied using SADABS program [32]. The structures were solved by direct methods using the program SHELXL 97 and refined by full-matrix least-squares methods on  $F^2$  using the SHELXL 97 crystallographic software package [33]. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from ride mode. The crystal data and structure refinement of compounds **1** and **2** were summarized in Table 1. Selected bond lengths and angles of compounds **1** and **2** were listed in Table 2.

#### 3. Results and discussion

#### 3.1. Description of the crystal structures of 1 and 2

Single crystal X-ray diffraction studies revealed that the asymmetric unit in **1** contains the basic building block of four independent 2-mBIM ligands, four different cadmium centers (Cd1, Cd2, Cd3 and Cd4), and four 1,3-BDC ligands. The most relevant bond lengths and angles for compound **1** are given in Table 2. As shown

Complex code	1	2	
Empirical formula	C <sub>34</sub> H <sub>32</sub> Cd <sub>2</sub> N <sub>8</sub> O <sub>8</sub>	$C_{15}H_{12}CdN_4O_4$	
Formula weight	905.48	424.69	
Temperature (K)	292(2)	294(2)	
Wavelength (Å)	0.71073	0.71073	
Crystal system	Orthorhombic	Monoclinic	
Space group	Pna2(1)	P2(1)/n	
A (Å)	29.1698(11)	9.3613(4)	
B (Å)	10.0178(4)	15.8661(7)	
C (Å)	24.1246(9)	10.1425(4)	
α (°)	90.000(0)	90.000(0)	
β (°)	90.000(0)	101.646(1)	
γ (°)	90.000(0)	90.000(0)	
V (Å <sup>3</sup> )	7049.6(5)	1475.43(11)	
Ζ	8	4	
De (g/cm <sup>3</sup> )	1.706	1.912	
$\mu (\mathrm{mm}^{-1})$	1.27	1.51	
F(000)	3616	840	
Crystal size (mm)	$\textbf{0.20} \times \textbf{0.12} \times \textbf{0.10}$	$0.20 \times 0.10 \times 0.10$	
Crystal color and habit	Colorless block	Colorless needle	
$\theta$ range (°)	2.3–25.3	2.4-28.0	
Index ranges	$-37 \leqslant h \leqslant 37, -12 \leqslant k \leqslant 12, -30 \leqslant l \leqslant 28$	$-12 \leqslant h \leqslant 9, -20 \leqslant k \leqslant 20, -12 \leqslant l \leqslant 13$	
Reflections collected	58772	13765	
Independent reflections	7882 $[R(int) = 0.096]$	3329 [R(int) = 0.028]	
Max. and min. transmission	0.8835 and 0.7853	0.8637 and 0.7522	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	
Data/restraints/parameters	7882/1/945	3329/0/217	
Goodness-of-fit on F <sup>2</sup>	1.03	1.08	
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0536, wR2 = 0.1171	R1 = 0.0312, wR2 = 0.0782	
R indices (all data)	R1 = 0.0649, wR2 = 0.1230 R1 = 0.0358, wR2 = 0.0805		
Largest diff. peak and hole	1.68 and -0.67 eÅ <sup>-3</sup>	0.64 and -0.54 eÅ <sup>-3</sup>	

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

1			
Cd(1)—N(5)	2.246(7)	Cd(1)-O(1)	2.254(7)
Cd(1)-N(3)	2.257(8)	Cd(1)-N(1)	2.283(8)
Cd(1)-O(2)	2.428(9)	Cd(2)-O(8) <sup>iii</sup>	2.233(8)
Cd(2)-O(3) <sup>iv</sup>	2.280(6)	Cd(2)-N(8)	2.313(9)
Cd(2) - O(5)	2.363(8)	Cd(2) - O(6)	2.415(7)
$Cd(2) - O(4)^{iv}$	2.534(8)	$Cd(3) - O(12)^{ii}$	2.256(9)
Cd(3)-N(9)	2.292(10)	Cd(3) - O(9)	2.321(8)
Cd(3) - O(13)	2.339(7)	Cd(3) - O(14)	2.430(7)
Cd(3) - O(10)	2.502(9)	Cd(4) - O(15)	2.224(7)
Cd(4) - N(12)	2.245(8)	$Cd(4) - N(16)^{v}$	2.254(7)
Cd(4) - N(14)	2.257(8)	Cd(4) - O(16)	2.478(9)
$N(16) - Cd(4)^{vi}$	2.254(7)	$O(3) - Cd(2)^{i}$	2.280(6)
$O(4) - Cd(2)^{i}$	2.534(8)	$O(8) - Cd(2)^{ii}$	2.234(8)
$O(12) - Cd(3)^{iii}$	2,256(9)	-(-)	(-)
N(5) - Cd(1) - O(1)	141.8(3)	N(5) - Cd(1) - N(3)	94.5(3)
N(3) - Cd(1) - O(1)	100.1(3)	N(5) - Cd(1) - N(1)	103.6(3)
N(1) - Cd(1) - O(1)	103 3(3)	N(3) - Cd(1) - N(1)	1118(3)
N(5) - Cd(1) - O(2)	897(3)	O(2) - Cd(1) - O(1)	55 7(2)
N(3) - Cd(1) - O(2)	135 7(3)	N(1) - Cd(1) - O(2)	109 9(3)
$O(8)^{iii} - Cd(2) - O(3)^{iv}$	133 3(3)	$O(8)^{iii} - Cd(2) - N(8)$	95 6(3)
$N(8) - Cd(2) - O(3)^{iv}$	87.3(3)	$O(8)^{iii}$ -Cd(2)-O(5)	79.5(3)
$O(5) - Cd(2) - O(3)^{iv}$	141.6(3)	N(8) - Cd(2) - O(5)	111.9(3)
$O(8)^{iii}$ -Cd(2)-O(6)	133.2(3)	$O(6) - Cd(2) - O(3)^{iv}$	91.3(3)
N(8) - Cd(2) - O(6)	100.9(3)	O(5) - Cd(2) - O(6)	53.6(3)
$O(8)^{iii}$ -Cd(2)-O(4) <sup>iv</sup>	110.4(3)	$O(4)^{iv}$ -Cd(2)-O(3) <sup>iv</sup>	54.5(2)
$N(8) - Cd(2) - O(4)^{iv}$	141.8(3)	$O(5) - Cd(2) - O(4)^{iv}$	100.3(3)
$O(6) - Cd(2) - O(4)^{iv}$	81.6(3)	$O(12)^{ii}$ -Cd(3)-N(9)	96.3(4)
$O(12)^{ii}$ -Cd(3)-O(9)	79.6(3)	N(9) - Cd(3) - O(9)	105.5(4)
$O(12)^{ii}$ -Cd(3)-O(13)	141.0(3)	N(9) - Cd(3) - O(13)	83.9(3)
O(13) - Cd(3) - O(9)	138.1(3)	$O(12)^{ii}$ -Cd(3)-O(14)	108.6(3)
N(9) - Cd(3) - O(14)	137.0(3)	O(9) - Cd(3) - O(14)	113.0(3)
O(13) - Cd(3) - O(14)	54.7(3)	$O(12)^{ii}$ -Cd(3)-O(10)	131.1(3)
N(9) - Cd(3) - O(10)	108.2(4)	O(9) - Cd(3) - O(10)	53.6(3)
O(13) - Cd(3) - O(10)	84.5(3)	O(14) - Cd(3) - O(10)	81.3(3)
O(15) - Cd(4) - N(12)	103.8(3)	$O(15) - Cd(4) - N(16)^{v}$	139.6(3)
N(12)-Cd(4)-N(16) <sup>v</sup>	105.3(3)	O(15)-Cd(4)-N(14)	98.5(3)
N(12)-Cd(4)-N(14)	111.6(3)	N(14)-Cd(4)-N(16) <sup>v</sup>	96.2(3)
O(15)-Cd(4)-O(16)	54.4(3)	N(12)— $Cd(4)$ — $O(16)$	108.4(3)
$O(16)-Cd(4)-N(16)^{v}$	89.8(3)	N(14)-Cd(4)-O(16)	136.1(3)
2			
Cd(1) - N(1)	2 352(2)	Cd(1) = O(1)	2,416(2)
$Cd(1) = N(4)^{ii}$	2.332(2) 2.237(2)	Cd(1) = O(2)	2.110(2) 2.345(2)
$Cd(1) = O(5)^{i}$	2.237(2) 2.276(2)	Cd(1) = O(2)	2.515(2) 2465(2)
$Cd(1)^{iii} = O(4)$	2.276(2) 2.465(2)	$Cd(1)^{iv} = O(5)$	2.105(2) 2.276(2)
$Cd(1)^{v} - N(4)$	2.309(2)		21270(2)
$O(5)^{i}$ - Cd(1) - N(4)^{ii}	126 90(9)	O(2) - Cd(1) - O(1)	55 28(7)
$O(5)^{i}$ -Cd(1)-O(2)	84.24(8)	N(1) - Cd(1) - O(1)	88.72(8)
$O(2) - Cd(1) - N(4)^{ii}$	148.35(9)	$O(5)^{i}$ -Cd(1)-O(4) <sup>iii</sup>	100.67(8)
$O(5)^{i}$ -Cd(1)-N(1)	83.14(8)	$O(4)^{iii}$ -Cd(1)-N(4) <sup>ii</sup>	83.30(8)
$N(1)-Cd(1)-N(4)^{ii}$	90.52(9)	$O(2) - Cd(1) - O(4)^{iii}$	85.43(8)
O(2) - Cd(1) - N(1)	99.88(9)	$N(1)-Cd(1)-O(4)^{iii}$	173.81(8)
$O(5)^{i}$ -Cd(1)-O(1)	136.61(8)	$O(1)-Cd(1)-O(4)^{iii}$	91.75(8)
$O(1)-Cd(1)-N(4)^{ii}$	95.58(8)		

Symmetry codes: (i) x + 1/2, -y + 3/2, z; (ii) x, y + 1, z; (iii) x, y - 1, z; (iv) x - 1/2, -y + 3/2, z; (v) x + 1/2, -y + 1/2, z; (vi) x - 1/2, -y + 1/2, z for 1; (i) x, y, z - 1; (ii) x + 1, y, z; (iii) -x + 1, -y, -z + 2; (iv) x, y, z + 1; (v) x - 1, y, z for **2**.



**Fig. 1.** Molecular structure of **1** showing the local coordination environment of the Cd center with thermal ellipsoids at 30% probability. Hydrogen atoms and other similar structures (Cd3 and Cd4) were omitted for clarity.

in Fig. 1, one cadmium atom (Cd1) is coordinated to three nitrogen atoms of three independent 2-mBIM ligands and two oxygen atoms of one 1,3-BDC ligand to give a five-coordinated environment. Another cadmium atom (Cd2) is coordinated to one nitrogen atom of one independent 2-mBIM ligand and five oxygen atoms of three independent 1, 3-BDC ligands (one of them in monodentate and the other two in bidentate mode), forming a six-coordinated environment. The two cadmium centers have different coordinated modes, and two neighboring cadmium atoms with the same coordinated mode are bridged by 2-mBIM and 1,3-BDC ligands, respectively, to form two independent 1D zigzag chains along the direction of the *b*-axis (Fig. 2). In addition, those 1D chains were cross-linked by the other bridging bidenate 2-mBIM and 1,3-BDC ligands alternatively to generate a 2D wavy layer with a 4,4-connected net (Fig. 2). The tetra-coordinated cadmium metal-organic network can be simplified as a (4,4)-connected net topological



Fig. 2. The structure of the 2D wavy layer with a 4,4-connected net in compound 1 (left) and view of the network topology (right).



Scheme 1. The two conformations of ligand 2-mBIM in compound 1.



**Fig. 3.** The 2D twofold parallel interpenetration framework with the (4, 4) connected net topology (left) and schematic representation of the self-penetrating topology (right) in compound **1**.

array with the long and short Schläfli symbols of 4(4).6(2) and  $4^4$ , respectively.

There are two structural characteristics that should be noted. First, the coordination mode of ligand 2-mBIM in compound **1** adopts two types of conformations (*trans*- or *cis*-) as shown in scheme 1. The dihedral angle between the two imidazole rings in the same 2-mBIM ligands with the *trans*- or *cis*- conformation were found to be  $88.2^{\circ}$  and  $57.1^{\circ}$ , respectively. These findings are comparable to previously reported values for corresponding structures [34]. Second, each 2D (4, 4) layer contains enough empty space to allow another 2D (4, 4) layer to interpenetrate and form a twofold parallel interwoven net with the (4, 4) connected topology in the manner shown schematically in Fig. 3. Here, in complex **1**, the flexible structure of 2-mBIM as a V-shaped bidentate nitrogen ligand is likely necessary for formation of the twofold interpenetration.

When ligand 2-mBIM was replaced by BIM in the reaction, complex **2**, which had a different structure, was obtained. Fig. 4 shows the coordination environment of two independent Cd(II) atoms with the atom numbering scheme. It was evident that the Cd1 atom was in a distorted octahedral coordination environment with four oxygen atoms (O1, O2, O4A, and O5B) from three different 1,3-BDC<sup>2-</sup> ligands with Cd1–O1, Cd1–O2, Cd1–O4A, and Cd1–O5B bond distances of 2.416(2), 2.345(2), 2.465(2), and 2.276(2) Å, respectively, and two nitrogen atoms (N1 and N4B) from two different BIM ligands with Cd1-N1 and Cd1-N4B bond distances of 2.352(2) and 2.237(2) Å, respectively (Table 2). One 1,3-BDC<sup>2-</sup> ligand, one BIM ligand, and one Cd center were observed in the asymmetric unit of **2**. One carboxylate group of 1,3-BDC<sup>2-</sup> ligand was coordinated with one Cd center in the bidentate mode, whereas the other carboxylate group was coordinated with two Cd centers in the monodentate mode and bridged two adjacent Cd(II) centers with a Cd-Cd distance of 4.110 Å to form a [Cd<sub>2</sub>(COO)<sub>4</sub>] subunit that was connected through two bridged 1,3-BDC<sup>2-</sup> ligands to make up an infinite  $[Cd_2(1,3-BDC)_2]_n$  1D double chain (Fig. 5). Those 1D double chains were further linked through the BIM ligand-coordinated Cd center in the *cis*-configuration, resulting in formation of a 2D double-layer network (Fig. 6). The coordinated cadmium metal–organic network can be simpli-



**Fig. 4.** ORTEP drawing of **2** showing the local coordination environment of Cd(II) with thermal ellipsoids at 30% probability. Hydrogen atoms were omitted for clarity.



**Fig. 5.** A 1D double chain containing the [Cd<sub>2</sub>(COO)<sub>4</sub>] subunit in **2**.



Fig. 6. A 2D double-layer network in 2 (left) and schematic representation of the network topology (right).



Fig. 7. Solid-state emission spectra at room temperature of 1 (left) and 2 (right) upon photoexcitation at 332 nm and 278 nm, respectively.

fied as a (4, 4)-connected net topological array with the long and short Schläfli symbols of 4(2).6(7).8 and 4.4.6(3).6(3).6(4).6(4).6(3).6(3), respectively.

#### 3.2. The thermal and photoluminescent properties of 1 and 2

The thermal analysis (TGA) under nitrogen atmosphere showed that the complex **1** have the first weight loss of 39.8% from 270 °C to 410 °C corresponds to the loss of 2-mBIM (calcd: 38.8%). Upon further heating, an obvious weight loss occurs in the temperature range of 540 °C to 630 °C, corresponding to the release of organic anionic ligand and indicating the complete decomposition of **1** with 29.8% residual weight corresponds to CdO (calcd: 28.6%). Compound **2** have also weight loss of 35.4% occurred in a temperature range from 192 °C to 296 °C, corresponding to the loss of BIM ligands (calcd: 34.7%). The second-step, which was observed in a temperature range from 370 °C to 410 °C with a residual weight 30.5%, probably corresponds to the completely decomposition of complex **2** at 410 °C.

The photoluminescent properties of **1** and **2** have been investigated. Emission spectra at room temperature in the solid state are shown in Fig. 7. It can be observed that compounds 1 and 2 both exhibit weak photoluminescence upon photoexcitation at 332 nm and 278 nm, respectively. The main emission peaks are located at 389 nm for **1** and 302 nm for **2**. In contrast, the free 2-mBIM and BIM ligand emits at 396 nm and 338 nm upon the 332 nm and 290 nm, respectively. Generally, the intra-ligand fluorescence emission wavelength is determined by the energy gap between the  $\pi$  and  $\pi$ \* molecular orbitals of the free ligand, which is simply related to the extent of  $\pi$  conjugation in the system. As for the metal complexes, the emission peaks of compound 1 are likely assigned to intra-ligand  $\pi$ - $\pi$ \* transitions. Which have also been observed in other polymers [35]. And the blue-shifted emissions of complex 2 compared to free ligand BIM is not only assigned to the intramolecular  $\pi$ - $\pi$ \* and n- $\pi$ \* transitions of the ligands, but are also attributable to ligand-to-metal charge transfers (LMCT) [36].

#### 4. Conclusions

In summary, we synthesized and characterized two new cadmium coordination polymers using 1,3-benzenedicarboxylic acid and two different ligands containing N atoms, BIM, and 2-mBIM. Two interesting different structural motifs were formed in response to only a subtle change in the ligand in which 2-mBIM has a methyl group at the 2-position in the imidazole rings of the BIM ligand. Compound **1** is a 2D twofold parallel interpenetration network with a (4, 4) connected net topology. Compound **2** is a 2D double-layer framework containing  $[Cd_2(COO)_4]$  subunits. These results also suggest that a subtle change in the ligand structure may have a strong influence on the assembly process and the resulting architectural structures of the MOFs.

#### 5. Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference numbers 689345 and 799782. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB21EZ, UK; fax:+44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk).

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