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## ARTICLE

# Effects of Substituent Groups on the Structures and Luminescence Properties of 2D/3D Cd<sup>II</sup> Complexes with Mixed Rigid and Flexible Carboxylate Ligands

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Three new Cd(II) complexes, [Cd(bic)(adp)<sub>0.5</sub>] (1), [Cd(mbic)(adp)<sub>0.5</sub>]·H<sub>2</sub>O (2) and [Cd(hbic)(adp)<sub>0.5</sub>]·H<sub>2</sub>O (3) (Hbic = 1H-benzoimidazole-5-carboxylic acid, Hmbic = 2-methyl-1H-benzoimidazole-5-carboxylic acid, Hhbic = 2-hydroxyethyl-1H-benzoimidazole-5-carboxylic acid, H<sub>2</sub>adp = adipic acid), have been prepared by the hydrothermal reaction of adp<sup>2-</sup> with Cd(II) ions in the presence of different benzimidazole carboxylic acids. **1** exhibits a 3D framework constructed from 1D infinite [Cd(COO)]<sub>n</sub> units which are connected by adp in a *trans*-(κ<sup>2</sup>-κ<sup>1</sup>)-(κ<sup>2</sup>-κ<sup>1</sup>)-μ<sub>4</sub> mode and bic in a novel *trans*-(κ<sup>1</sup>-κ<sup>1</sup>)-(κ<sup>1</sup>)-μ<sub>3</sub>. **2** features an unusual [Cd<sub>2</sub>(COO)<sub>4</sub>] paddle-wheel dinuclear secondary building unit (SBU), which is bridged into a 2D sheet by adp in a (κ<sup>1</sup>-κ<sup>1</sup>)-(κ<sup>1</sup>-κ<sup>1</sup>)-μ<sub>4</sub> mode and mbic in *cis*-(κ<sup>1</sup>-κ<sup>1</sup>)-(κ<sup>1</sup>)-μ<sub>3</sub> mode. For **3**, the metal centre is connected into a 1D double chain by hbic in (κ<sup>1</sup>)-(κ<sup>1</sup>-κ<sup>1</sup>)-μ<sub>2</sub> mode, which is further linked by the *trans*-(κ<sup>2</sup>-κ<sup>1</sup>)-(κ<sup>2</sup>-κ<sup>1</sup>)-μ<sub>4</sub> adp to form a 2D layer architecture. The luminescence property in the solid state at room temperature of compound **1-3** is almost the same as the free ligand.

## Introduction

Coordination polymers have attracted considerable attention in the past decade for their structural features and potential applications as functional materials.<sup>1</sup> Although there are examples where the molecules are assembled in a predetermined fashion, prediction of the crystal structure is largely considered to be serendipitous.<sup>1,2</sup> The structure of the resulting framework is primarily dependent upon the coordination geometry of the metal centres as well as on the functionality and coordinating ability of the bridging ligand.<sup>3</sup> The spherical d<sup>10</sup> configuration of Cd(II) is particularly suited for the construction of coordination polymers.<sup>4</sup> On the one hand, the carboxylate unit is widely used in the synthesis of coordination polymers;<sup>5</sup> for the dicarboxylate entity in particular, and a lot of studies has detailed the synthesis of metal dicarboxylates that exhibit useful properties such as high porosity and magnetism.<sup>6</sup> On the other hand organic ligands consisting of carboxylate and benzimidazole have experienced major development in crystal engineering, and a large number of networks have been reported.<sup>7</sup> Therefore, 1H-benzoimidazole-5-carboxylic acid (Hbic), combining the virtues of both benzimidazole and carboxylic acid, has been selected as the building block due to the special metal-coordinating ability (Chart S1).<sup>8</sup> Though some coordination polymers with Hbic have been reported, they have rarely been used in conjunction with other ligand to construct frameworks.<sup>9</sup>

In the course of ongoing studies on transition metal compounds of carboxylate-aromatic amine or pyridine ligands,<sup>10</sup> we introduced flexible H<sub>2</sub>adp and rigid Hbic and its derivatives in the construction of the new coordination polymers. Hbic with its carboxylate group and

the benzimidazole provides additional coordination sites, which can stabilize the resulting solid networks and its derivatives. By changing the 2-site proton of Hbic by methyl and hydroxyethyl groups in order to introduce bulkiness in the structures and it was possible to follow the effect of these substituent groups to the crystal structures of their complexes (Chart 1). The flexible dicarboxylate adp could supply diverse conformations to control over the stereochemistry of the metallic centres, and create different frameworks.<sup>11</sup>

Herein, we reported the syntheses, structures and luminescence properties of three Cd(II) coordination polymers using the different benzimidazole carboxylic acids and flexible adipic acid (H<sub>2</sub>adp) as auxiliary ligand, which show the effect of substituent groups on the crystal structure.



Chart 1 The ligands Hbic and its derivatives employed.

## Experimental Section

### Materials and Physical Measurements

All the solvents and reagents for syntheses were commercially available and used as received. Hbic, Hmbic and Hhbic were synthesized according to the reported procedure.<sup>8</sup> Elemental analyses of C, H, and N were performed on a Perkin-Elmer 240C analyzer. IR spectra were measured on a TENSOR 27

(Bruker) FT-IR spectrometer by transmission through KBr pellets containing 1% of the compounds. Thermogravimetric Analyses (TGA) were carried out on a Perkin-Elmer Pyris Diamond TG/DTA analyzer at a heating rate of 10 °C·min<sup>-1</sup> from 30 to 1000 °C under N<sub>2</sub>. Luminescence data were recorded on a model F-4500 Luminescence spectrophotometer. X-ray powder diffraction (XRPD) intensities were measured at 293 K on a Rigaku D/max-III A diffractometer (Cu-Kα, λ = 1.54056 Å). The experimental backgrounds were corrected using the Jade 5.0 software package. The simulated PXRD patterns were calculated from the single crystal diffraction data using Powdercell.

## Synthesis

**Synthesis of [Cd(bic)(adp)<sub>0.5</sub>] (1).** A mixture of Hbic (0.081 g, 0.5 mmol) and H<sub>2</sub>adp (0.073 g, 0.5 mmol) was added to an 8 mL aqueous solution of 0.5 mmol NaOH. The mixture was stirred until the solids were completely dissolved, then Cd(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.305 g, 0.5 mmol) was added. After stirring for 5 minutes, the mixture was placed in a 23-mL Teflon-lined stainless steel autoclave and heated at 165 °C for 72 h. The autoclave was cooled over a period of 10 h in air. The yellow crystals of **1** were collected by filtration, washed with ethanol, and dried in air (yield 37% based on Cd). Elemental analyses: calcd. for C<sub>11</sub>H<sub>9</sub>CdN<sub>2</sub>O<sub>4</sub> (%): C, 38.22; H, 2.60; N, 8.10. Found (%): C, 38.59; H, 2.43; N, 7.94. IR data for **1** (KBr, cm<sup>-1</sup>): 3103(w), 2913(w), 2345(m), 1597(m), 1547(m), 1376(vs), 1285(m), 1131(w), 962(m), 779(m), 651(m), 623(w).

**Synthesis of [Cd(mbic)(adp)<sub>0.5</sub>]·H<sub>2</sub>O (2).** The synthesis procedure of **2** was similar to that of **1**, except that Hmbic (0.088 g, 0.5 mmol) replaces Hbic and 0.5 mL triethylamine was added before the mixture was placed into the Teflon-lined autoclave. Some straw yellow cluster-like crystals were collected by filtration, washed with ethanol, and dried in air (yield 38 % based on Cd). Elemental analyses: calcd. for C<sub>12</sub>H<sub>13</sub>CdN<sub>2</sub>O<sub>5</sub> (%): C, 38.15; H, 3.44; N, 7.38. Found (%): C, 38.43; H, 3.41; N, 7.35. IR data for **2** (KBr, cm<sup>-1</sup>): 3396(m), 2905(m), 1629(m), 1605(vs), 1391(vs), 1312(m), 1299(m), 1042(m), 919(w), 805(w), 779(m), 757(m).

**Synthesis of [Cd(hbic)(adp)<sub>0.5</sub>]·H<sub>2</sub>O (3).** The synthesis procedure of **3** was similar to that of **2**, except that Hhbic (0.103g, 0.5 mmol) replaces Hmbic. Some straw yellow sheet-like crystals were collected by filtration, washed with ethanol, and dried in air (yield 41 % based on Cd). Elemental analyses: calcd. for C<sub>13</sub>H<sub>14</sub>CdN<sub>2</sub>O<sub>6</sub> (%): C, 38.29; H, 3.68; N, 6.87. Found (%): C, 38.63; H, 3.36; N, 6.46. IR data for **3** (KBr, cm<sup>-1</sup>): 3417(m), 3091(m), 1602(m), 1571(vs), 1389(vs), 1323(m), 1118(vs), 1057(w), 957(m), 907(w), 817(m), 779(vs), 692(w).

## X-ray Data Collection and Structure Determinations

X-ray single-crystal diffraction data of **1-3** were collected on a Rigaku MM-007/Saturn 70 with graphite monochromatic Mo-Kα radiation (λ = 0.71073 Å). Absorption corrections were applied by using the multi-scan program SADABS.<sup>12</sup> The structures were solved using direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package.<sup>13</sup> Metal atoms in each complex were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F<sup>2</sup>. The hydrogen atoms were generated geometrically. Those weak reflections points at high angle (2θ > 50°) was omitted during refinement. Isotropic refinement for C9 and O3 atoms in compound **3** was performed. Data collection and structural refinement parameters are given

in Table 1 and selected bond distances and angles are given in Table 2. CCDC reference numbers are 924695 - 924697 for complexes **1-3**. The supplementary crystallographic data for the three compounds can be found in the Supporting Information or can be obtained free of charge from the Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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

Complex	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>11</sub> H <sub>9</sub> CdN <sub>2</sub> O <sub>4</sub>	C <sub>12</sub> H <sub>13</sub> CdN <sub>2</sub> O <sub>5</sub>	C <sub>13</sub> H <sub>14</sub> CdN <sub>2</sub> O <sub>6</sub>
Fw	345.60	377.64	406.66
T (K)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P2 <sub>1</sub> /c	P-1	P-1
a (Å)	8.117(1)	8.356(1)	8.603(2)
b (Å)	16.788(3)	9.336(2)	9.066(2)
c (Å)	7.918(1)	9.344(2)	10.120(2)
α (°)	90	62.605(2)	74.826(3)
β (°)	98.491(2)	89.857(3)	73.131(3)
γ (°)	90	85.559(3)	85.128(3)
V (Å <sup>3</sup> )	1067.2(3)	644.8(2)	729.0(2)
Z	4	2	2
D <sub>c</sub> (g cm <sup>-3</sup> )	2.151	1.945	1.853
μ (mm <sup>-1</sup> )	2.055	1.715	1.529
Date collect./ uniq.	4767/2064	5044/2502	4824/2491
R <sub>1</sub> (>2σ)	0.0247	0.0267	0.0279
wR <sub>2</sub> (all data)	0.0615	0.0905	0.0781
GOF	1.079	1.010	1.113
Residues (e Å <sup>-3</sup> )	-0.522/1.168	-0.683/2.144	-0.744/0.981

## Results and Discussion

**Crystal Structure of 1.** Single-crystal X-ray diffraction analysis of **1** reveals an infinite 3D network belonging to the monoclinic space group P2<sub>1</sub>/c. The asymmetric unit consists of one Cd(II) ion, one bic and half of adipate (Fig. 1). The Cd(II) ion has a distorted octahedral geometry, which is equatorially coordinated by three oxygen atoms (O3, O3b and O4b) from two adp, and one bic nitrogen atom (N1), and the axial positions are occupied by two oxygen atoms (O1c and O2a) from two bic. The Cd-N bond length is 2.288(3) Å, and the Cd-O bond lengths range from 2.238(2) to 2.404(2) Å, which are all in accord with those found in the other Cd(II) complexes.<sup>4</sup>

The key feature is the layers of Cd-adipate bridged by the bic ligand to give the 3D framework. The adipate is fully deprotonated and each carboxylate group forms three bonds with two cadmium atoms. Thus it adopts a *syn, syn, anti* mode of coordination. Hbic, potentially can lose two protons, is only deprotonated at the carboxylate group where it bridges two cadmium in a *syn, syn* mode and the imidazole nitrogen is also involved in coordination with a cadmium atom.

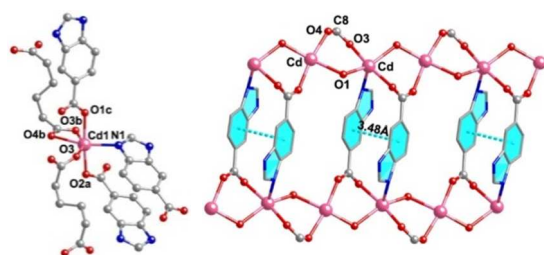
The bic ligand in **1** exhibits a binding mode of *trans*-(κ<sup>1</sup>-κ<sup>1</sup>)-(κ<sup>1</sup>)-μ<sub>3</sub> (IV mode in Chart S1) as found for a Eu(III) complex.<sup>14</sup> The adp acts as the bridge and adopts a *trans*-(κ<sup>2</sup>-κ<sup>1</sup>)-(κ<sup>2</sup>-κ<sup>1</sup>)-μ<sub>4</sub> mode (Chart S2 (XIV)) to link four cadmium ions, similar to that reported for some lanthanide (III) complexes.<sup>15</sup> The mode appears for the first time in the cadmium complexes, but here the carboxyl groups of adp coordinated to Cd<sup>II</sup> ions with *trans* conformation, as discussed in the following. A six-member ring consisting of two Cd<sup>II</sup> ions (Cd...Cd = 3.983 Å), three atoms O3-C8-O4 from the carboxyl group of bic and one μ<sub>2</sub>-O1 atom from the carboxyl group of adp is generated. From the six-member rings, a 1D metallic chain propagates along c axis with Cd(II) ions as nodes (Fig. 1). The adjacent 1D metallic chains extend into 2D network in bc plane by pairs of parallel opposing bic ligands, between which the π-π stacking

interaction with a face-to-face distance of 3.48 Å is observed.<sup>16</sup> Due to the angle between two coordination sites of bic, the 2D network displays wavy plane with a dihedral angle of 115°. Furthermore, 3D structure of **1** is formed by adp bridging the above 2D network (Fig. 2).

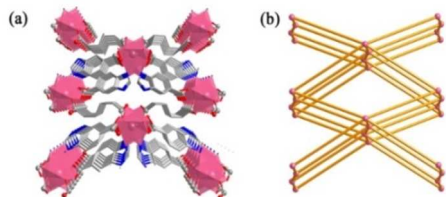
**Table 2** Selected bond lengths (Å) and bond angles (°) for **1-3**.

<b>1</b>			
Cd1-O1 <sup>a</sup>	2.238(2)	O1 <sup>a</sup> -Cd1-O2 <sup>b</sup>	169.51(9)
Cd1-O2 <sup>b</sup>	2.262(2)	O2 <sup>b</sup> -Cd1-O3	97.12(8)
Cd1-O3	2.264(2)	O2 <sup>b</sup> -Cd1-O3 <sup>c</sup>	86.48(8)
Cd1-O3 <sup>c</sup>	2.404(2)	O1 <sup>a</sup> -Cd1-O4 <sup>c</sup>	83.12(9)
Cd1-O4 <sup>c</sup>	2.382(2)	O2 <sup>b</sup> -Cd1-O4 <sup>c</sup>	96.72(9)
Cd1-N1	2.288(3)	O1 <sup>a</sup> -Cd1-N1	88.56(1)
O1 <sup>a</sup> -Cd1-O3	93.28(9)	O3-Cd1-N1	98.18(9)
O3-Cd1-O4 <sup>c</sup>	98.16(8)	N1-Cd1-O4 <sup>c</sup>	162.04(9)
O1 <sup>a</sup> -Cd1-O3 <sup>c</sup>	84.92(8)	N1-Cd1-O3 <sup>c</sup>	109.20(9)
O3-Cd1-O3 <sup>c</sup>	152.48(1)	O2 <sup>b</sup> -Cd1-N1	88.60(9)
O4 <sup>c</sup> -Cd1-O3 <sup>c</sup>	54.34(8)		
<b>2</b>			
Cd1-O1 <sup>b</sup>	2.225(3)	O2 <sup>c</sup> -Cd1-O4 <sup>a</sup>	86.00(1)
Cd1-O2 <sup>c</sup>	2.260(3)	O3-Cd1-O2 <sup>c</sup>	86.54(1)
Cd1-O3	2.242(3)	O3-Cd1-O4 <sup>a</sup>	154.28(1)
Cd1-O4 <sup>a</sup>	2.268(3)	N1-Cd1-O1 <sup>b</sup>	99.91(1)
Cd1-N1	2.208(3)	N1-Cd1-O4 <sup>a</sup>	98.85(1)
O1 <sup>b</sup> -Cd1-O3	86.07(1)	N1-Cd1-O3	106.87(1)
O1 <sup>b</sup> -Cd1-O2 <sup>c</sup>	154.01(1)	N1-Cd1-O2 <sup>c</sup>	106.09(1)
O1 <sup>b</sup> -Cd1-O4 <sup>a</sup>	89.98(1)		
<b>3</b>			
Cd1-O1	2.183(3)	O1-Cd1-O4 <sup>b</sup>	103.73(1)
Cd1-O3 <sup>a</sup>	2.399(4)	O1-Cd1-O5	100.60(1)
Cd1-O4	2.431(3)	O4 <sup>b</sup> -Cd1-O5	128.73(1)
Cd1-O4 <sup>b</sup>	2.283(3)	O5-Cd1-O3 <sup>a</sup>	90.46(2)
Cd1-O5	2.348(3)	O5-Cd1-O4	53.87(1)
Cd1-N1 <sup>a</sup>	2.240(4)	N1 <sup>a</sup> -Cd1-O4	138.59(1)
O1-Cd1-O3 <sup>a</sup>	161.59(2)	O1-Cd1-N1 <sup>a</sup>	93.93(1)
O4 <sup>b</sup> -Cd1-O3 <sup>a</sup>	79.94(2)	N1 <sup>a</sup> -Cd1-O4 <sup>b</sup>	119.14(1)
O1-Cd1-O4	121.84(1)	N1 <sup>a</sup> -Cd1-O5	103.19(1)
O4 <sup>b</sup> -Cd1-O4	74.98(1)	N1 <sup>a</sup> -Cd1-O3 <sup>a</sup>	69.05(1)
O3 <sup>a</sup> -Cd1-O4	76.57(1)		

Symmetry codes for **1**: (a)  $-x, -0.5+y, 0.5-z$ ; (b)  $-x, 1-y, -z$ ; (c)  $x, 0.5-y, -0.5+z$ . for **2**: (a)  $-x, 2-y, 1-z$ ; (b)  $-x, 1-y, 1-z$ ; (c)  $x, 1+y, z$ . for **3** (a)  $1-x, 1-y, -z$ ; (b)  $-x, 1-y, 1-z$ ; (c)  $-1-x, 1-y, 1-z$ .

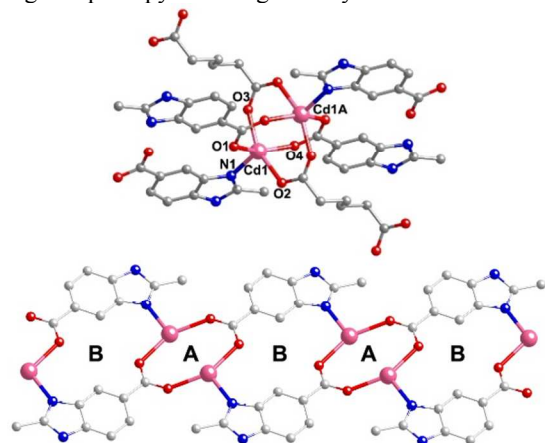


**Fig. 1** (Left): Coordination environment of Cd<sup>II</sup> ion in **1**. (Hydrogen atoms are omitted for clarity; symmetry codes for (a)  $-x, 1-y, -z$ ; (b)  $x, 0.5-y, -0.5+z$ ; (c)  $-x, -0.5+y, 0.5-z$ ). (Right): 1D chain structure along  $c$  axis in **1**.



**Fig. 2** (a) 3D structure of **1** viewed from  $c$  axis. (b) Ball-and-stick style to express 3D connection.

**Crystal Structure of 2.** In contrast to the structure of **1**, that of **2** is based on one-dimensional chains of Cd-adipate bridged by the mbic into a 2D network. In the asymmetric unit of **2**, there are one Cd(II) ion, one mbic, a half adp and one lattice water molecule. The square pyramidal geometry around the Cd centre is coordinated by four oxygen atoms (O1a, O2b, O3 and O4c) from two mbic and two adp with four oxygen square plane and one nitrogen N1 atom from one mbic as vertex of the prism (Fig. 3). The Cd-O bond distances are in the range of 2.225(3) to 2.268(3) Å, which are in good agreement with those of known Cd complexes.<sup>4</sup> The Cd-N bond distance of 2.208(3) Å is shorter than that of **1**. Both adipate carboxylate adopt a *syn-syn* coordinating mode to form pairs of cadmium bridged by the long adipate. The carboxylate group of mbic also bridged two cadmium atoms within a pair by *syn-syn* mode to form paddle-wheel dimers of cadmium. The imidazole nitrogen atom then coordinates the axial position of each cadmium atom resulting in square pyramidal geometry.

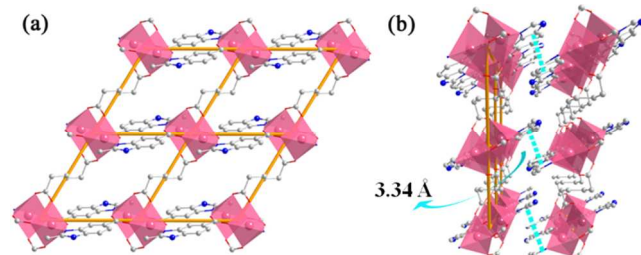


**Fig. 3** (Up): Coordination environment of Cd<sup>II</sup> ions in complex **2**. Symmetry codes: (a)  $-x, 1-y, 1-z$ ; (b)  $x, 1+y, z$ ; (c)  $-x, 2-y, 1-z$ . (Down): 1D dual chain by mbic along  $b$  axis in **2**.

Four equatorial carboxyl groups are from two adp and two mbic, and two axial N-donating atoms from two mbic connected two Cd (II) ions and constructed paddle-wheel structural motif with the Cd...Cd distance of 3.218 Å. A number of transition metals of the 1<sup>st</sup> or 2<sup>nd</sup> transition row transition metals and lanthanides are reported to form homologous paddle-wheel structure.<sup>17</sup> Nevertheless, [Cd<sub>2</sub>(COO)<sub>4</sub>] is less frequently observed and for the five known examples found in the CCDC database nearly all are 0D complexes formed from carboxylate containing large terminal groups, rather than bridging ligands.<sup>18</sup> In these dimeric Cd complexes, the Cd...Cd distance ranges from 3.278 to 3.452 Å, longer than that of **2** probably because of the large spatial encumbrance of CH<sub>3</sub> group of mbic affects the coordination mode of the adp resulting in the unprecedented shortest Cd...Cd distance.

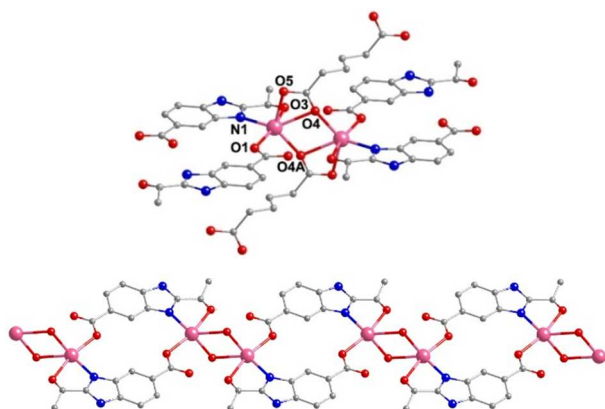
The coordination mode of mbic is described as *cis*-(κ<sup>1</sup>-κ<sup>1</sup>)-(κ<sup>1</sup>)-μ<sub>3</sub>, differing from the *trans*-mode of bic in **1**. Alternatively, 1D dual chain stems from small eight-member-ring **A** and the big fourteen-member-ring **B** by pairs of mbic linking dimeric Cd(II) units along the  $b$  axis (Fig. 3). Pairs of mbic of the 1D dual chain are coplanar, which is distinct from the parallel arrangement of bic in 1D chains of **1**. Such 1D dual chains are extended into 2D layer structure in the  $bc$  plane through adp in the (κ<sup>1</sup>-κ<sup>1</sup>)-(κ<sup>1</sup>-κ<sup>1</sup>)-μ<sub>4</sub> mode (Fig. 4). The existence of torsion angle of the aliphatic chains of the linker adp results in step-like layer for the stacking of parallel 1D chains. Hydrogen bonds

(O1W-H1Wa $\cdots$ N2: 2.736 Å and O1W-H1Wb $\cdots$ O2: 2.825 Å) and  $\pi$ -stacking interactions (face to face distance is 3.34 Å) between mbic of adjacent layers.<sup>16, 19</sup> Furthermore supramolecular link between these 2D layers along the *a* axis results in a 3D framework with a gear-like arrangement.



**Fig. 4** (a) 2D layer in *bc* plane of complex **2**. (b) The  $\pi$ - $\pi$  stacking interactions between 2D layers to form a 3D supramolecular framework in *b* direction.

**Crystal Structure of 3.** The structure of **3** also has a one-dimensional chain of Cd-adipate as in **2** but in this case the bridge is hbic. For **3**, the independent unit also contains one Cd ion, one hbic, a half adp and one lattice water molecule. Cd1 is in a six-coordinated distorted octahedral geometry, made of three O atoms (O4, O4b and O5) from two adp, as well as two O atoms (O1 and O3a) and one N atom (N1a) from two hbic (Fig. 5). The Cd-O bond lengths range from 2.183(3) to 2.431(3) Å, which are also in the range of those found in other Cd complexes.<sup>4</sup> The Cd-N bond distance is 2.240(4) Å, shorter than that of **1** but longer than that of **2**. Such two Cd ions compose of a dimer unit through  $\mu$ -bridged O4 and O4a from different adp with the Cd $\cdots$ Cd distance of 3.741 Å showed in Fig. 8, which is not paddle-wheel structure for complex **2**.

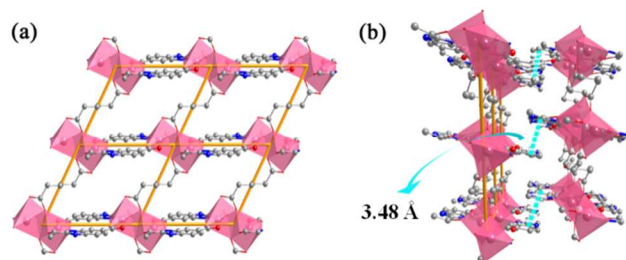


**Fig. 5** (Up): Coordination environment of Cd<sup>II</sup> ions of complex **3**. Symmetry codes: (a) 1-*x*, 1-*y*, -*z*; (b) -*x*, 1-*y*, 1-*z*. (Down): The chain of dimeric units by the hbic ligands.

A pair of hbic in reverse order adopts a  $(\kappa^1)-(\kappa^1-\kappa^1)-\mu_2$  coordination mode to bridge the dinuclear  $\{Cd_2\}$  units into double chains via their carboxylate O, imidazole N and hydroxyethyl O atoms (Fig. 5). The aliphatic chains of adp connects these double chains into a grid-like layer motif parallel to the *ac* crystal plane (Fig. 6).

Two kinds of hydrogen-bonding interactions from the lattice water molecules with the carboxylate oxygen O5 atoms of adp and the imidazole nitrogen N2 atoms of hbic, [O1W-H1A $\cdots$ O5 = 2.750 Å, O1W-H1B $\cdots$ N2 = 2.730 Å] were observed.<sup>19</sup> They join neighbouring layers into a 3D supramolecular structure. Furthermore, the  $\pi$ - $\pi$  stacking interactions between adjacent hbic from adjacent layers intensify the stability of 3D

supramolecular architecture (the face-to-face distance is 3.48 Å).<sup>16</sup>



**Fig. 6** (a) The 2D structure in complex **3**. (b) The  $\pi$ - $\pi$  stacking interactions between 2D layers to form a 3D supramolecular framework.

**Discussion of the Structures.** The organic ligands (bic, mbic and hbic) are the key factors in the formation of the multi-dimensional frameworks.<sup>1</sup> Different conformations adopted by the benzimidazole carboxylate in generating the coordination environment around the metal centres. Firstly, the existence of the 2-site substituent groups alters the coordination modes of benzimidazole for the stereo hindrance. In detail, bic and mbic adopt the *trans*- $(\kappa^1-\kappa^1)-(\kappa^1)-\mu_3$  and *cis*- $(\kappa^1-\kappa^1)-(\kappa^1)-\mu_3$  coordination modes in **1** and **2**, respectively, and 2D grid (**1**) and 1D chain (**2**) structures (Fig. S1 and Fig. 3). The stereo hindrance of methyl substituent modifies the *trans* coordination mode of bic to *cis* mode in mbic. As a result the pair arrangement of bic in **1** being parallel differs from those of mbic in coplanar arrangement in **2**. In complex **3**, the hbic in  $(\kappa^1)-(\kappa^1-\kappa^1)-\mu_2$  mode differs from those of bic and mbic because the hydroxyethyl group adds another coordinating group. The hydroxyethyl group and 3-site N atom form a stable five-member-ring chelate and decrease the chance to coordinate to more cadmium (II) ions. The *cis*  $\mu_2$ -connected mode of hbic results into 1D chain similar to that of complex **2**. The formation of 1D structures based on benzimidazole in **2** and **3** could be attributed to the spatial effect of the substituent groups on 2-site of benzimidazole ligands. Secondly, the 2-site substituent groups affect the coordination abilities of the imidazole N atoms of these ligands. For the distances of Cd-N bonds in the complexes, that of **1** is the longest, which implies that the abilities of 1-site N atoms of bic may be weaker than those of 3-site N atoms of mbic and hbic.

Furthermore, the dimensions of metal-organic frameworks are influenced indirectly by the large stereo hindrance of the 2-site substituent groups. Based on benzimidazole ligands and central metal ions, complex **1** is 2D network, while **2** and **3** are 1D dual chain. Deriving from the 1D or 2D fundamental frameworks, the final dimensions of these complexes are 2D and 3D as adp are introduced. Therefore, the steric hindrance of 2-site substituent groups of mbic and hbic influences their coordination modes and abilities in the formation of complexes, as well as the construction of primary structure.

The diverse coordination modes and conformations of the soft adp is also an important ingredient for the geometry of Cd(II) ion and the construction of the frameworks. It adopts two kinds of  $\mu_4$  binding modes of *trans*- $(\kappa^2-\kappa^1)-(\kappa^2-\kappa^1)-\mu_4$  and  $(\kappa^1-\kappa^1)-(\kappa^1-\kappa^1)-\mu_4$  in **1-3**. In **1** and **3**, adp coordinates to Cd(II) ions in the same mode of *trans*- $(\kappa^2-\kappa^1)-(\kappa^2-\kappa^1)-\mu_4$  and results in the similar octahedral geometry for metal ions. But the adp ligands built the different structures: 2D brick-like grid for **1** and 1D zigzag chain for **3** (Fig. S2(a) and (c)). The first reason might be the similar *gauche-anti* conformation of its aliphatic chains adopted in the complexes, but with the dissimilar

synclinal degree (six C atom torsion angles = 60.6°, 180.0° for **1** and 69.5°, 180.0° for **3**). Secondly, the arrangements of neighbouring adp are completely different, which adopt head-to-tail packing within the 2D grid with longer metallic distance of 3.984 Å for **1** and **3** in uniform head-to-head and tail-to-tail arrangements into 1D chain structure. The main ligands bic and hbc play a crucial role in the formation of high-dimensional MOFs, the auxiliary adp acts only as a linker. While in **2**, adp adopts *bis*(bidentate) mode to connect four Cd(II) ions into 1D bracelet structure with eight-member-ring linked by the aliphatic chains (six C atom torsion angle = 66.1°, 180.0°) (Fig. S2(b)).

**Thermogravimetric Analyses of 1-3.** Thermogravimetric analyses (TGA) were carried out to examine the thermal stability of complexes **1-3** (Fig. S3). The crushed single-crystal samples were heated up to 900 °C in N<sub>2</sub> at a heating rate of 10 °C·min<sup>-1</sup>. The TGA curve for **1** showed that the first weight loss step began from 380 °C. This indicates a high stability of the complex and is accordance with the structure information without lattice water molecule and with strong  $\pi$ -stacking interactions. For **2**, the TGA curve indicated that the first weight loss of 5.8% between 50 and 150 °C corresponds to the loss of one water molecule (calc. 5.2%) per molecular unit. The next stage of this curve from 350 to 500 °C was the completely collapse of the whole skeleton of **2**. The TGA curve for **3** is similar to that of **2**, which is also divided into two stages: (i) departure of one lattice water, with the weight loss of 5.5% from 30 to 200 °C (calc. 4.8%); (ii) the complete decomposition up to 800 °C. The above thermal behaviours may be attributed to their structural features: **1** with 3D structure has higher stability, while **2** and **3** featuring 2D structure with one lattice water have similar thermal decomposition process.<sup>1</sup>

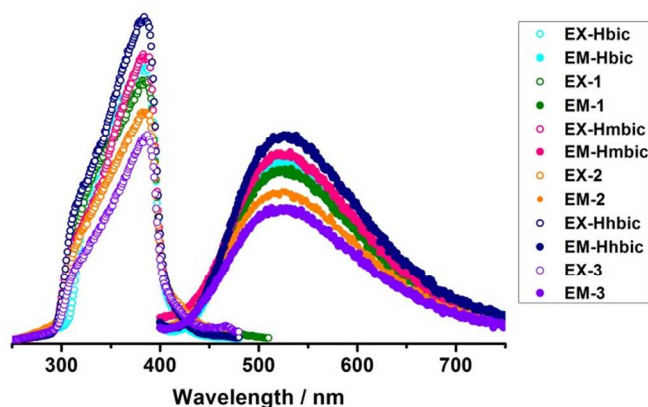


Fig. 7 The excitation (EX) and emission (EM) spectra of the Hbic, Hmbic, Hhbc and complex **1-3**.

**Luminescence Properties of 1-3.** Coordination polymer with a d<sup>10</sup> configuration (such as Zn<sup>2+</sup> or Cd<sup>2+</sup>) has been found to exhibit photoluminescence properties.<sup>20</sup> Therefore, the solid-state luminescence on crushed crystals of **1-3** and the three free benzimidazole carboxylate ligands have been measured. The powder diffraction (XRD) result of **1-3** was recorded before luminescence measurements to ascertain the purity of the samples (Fig. S4). Hbic, Hmbic and Hhbc exhibit emission spectra with a band maximizing at 525, 526 and 529 nm under excitation at 385nm respectively, which is originating from intraligand  $\pi^* \rightarrow \pi$  (Fig. 7) transformation.<sup>8, 14</sup> Under same measurement condition, compound **1-3** displays similar luminescence properties compared to corresponding free ligand. Such result suggest charge transfer between ligand and the

metal center is negligible in compound **1-3** and their luminescence properties is dominated by the intraligand electron transition.

## Conclusions

In summary, we synthesized three 2D/3D frameworks based on Cd(II) with three functionalised benzimidazole carboxylate ligands and flexible hexanedioic acid (adipic, H<sub>2</sub>adp) as auxiliary ligand under hydrothermal conditions. The packing and the structures are directed by the presence of different secondary-building unit in each case. The luminescence is dominated by that of the organic ligands and is influenced by the  $\pi$ - $\pi$  interaction within a pair. Hence, this work further highlights substituent groups of ligand play an important role in the whole structure and properties.

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## Notes and references

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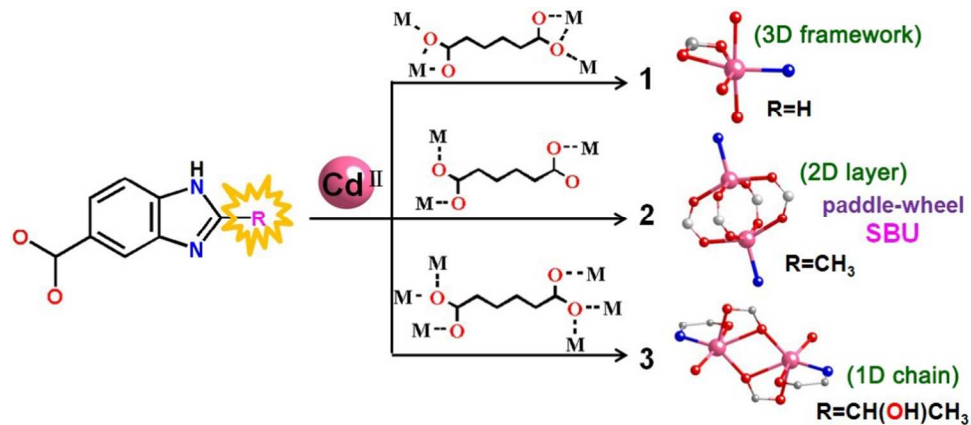
†† Electronic Supplementary Information (ESI) available: the coordination modes of Hbic and H<sub>2</sub>adp, pictures of the structures, TG curves and PXRD patterns for **1-3**. See DOI: 10.1039/b000000x/

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## ARTICLE

## Short text and illustration for table of contents:



Three Cd(II) coordination polymers employing rigid benzimidazole carboxylate and flexible adipate demonstrate the effect of substituent groups on the crystal structures and their luminescence properties.