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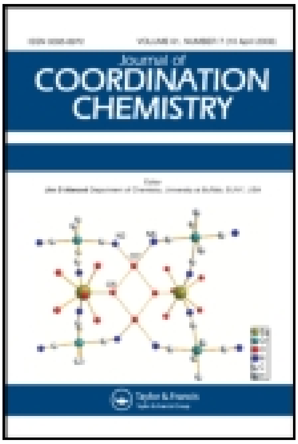

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Fine tuning of the Cd(II)-bis(benzimidazole) networks by changing carboxylate anions

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Fine tuning of the Cd(II)–bis(benzimidazole) networks by changing carboxylate anions

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Three new polymeric frameworks, $[Cd(bbbi)(ita)(H_2O)]\cdot H_2O$ (**1**), [Cd(bbbi)(fma)] (**2**), and $[Cd(bbbi)(fma)(H_2O)]\cdot 2H_2O$ (**3**) (bbbi = 1,1-(1,4-butanediyl)bis-1 H-benzimidazole, H_2ita = itaconic acid, and H_2fma = fumaric acid), have been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction. Complex **1** is a 2-D (4,4) network containing infinite 1-D zigzag Cd(II)-bbbi chains linked by auxiliary ita ligands. In the structure of **2**, infinite 1-D linear Cd(II)-bbbi chains are linked by fma ligands to generate an undulated 2-D (4,4) network. In **3**, an *in situ* ligand transformation occurred with malate converted to H_2fma by dehydration. Thus, a 2-D (4,4) grid network constructed from bbbi and fma was obtained. The carboxylates with different substituents play an important role in the formation of the final frameworks and coordination modes of Cd(II). Thermal stability and luminescent properties of **1–3** were investigated.

Keywords: Hydrothermal synthesis; Crystal structures; Cadmium complexes; Organic carboxylate

1. Introduction

Design and synthesis of coordination polymers (CPs) have attracted extensive attention [1–6] owing to their structural beauty and potential application as functional materials [7–11]. Selection of suitable ligands is the key step in making CPs with fascinating structures. Aliphatic dicarboxylates (such as malonate, succinate, fumarate, glutarate, adipate, etc) are capable of binding metal ions in diverse coordination modes, leading to a wide variety of extended structures [12–16]. In addition, O-donors with different substituents have received much attention, and the final structures of CPs can dramatically change with the change of O-donor [17–20]. There are relatively few reports on the effect of different substituents of aliphatic dicarboxylates on the structures of CPs [21]. To systematically study the influence of the substituents on the structures of CPs, we chose aliphatic carboxylates with different substituents as ligands in this work.

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Benzimidazole-containing flexible ligands have been well-used in crystal engineering and are of particular interest in coordination chemistry, since they are effective bridging ligands; two benzimidazoles as flexible ligands can selectively adjust *via* rotating and bending the $–CH_2–$ group to meet the requirements of the coordination geometries of metals in the assembly process [22–27]. In this work, we select 1,1-(1,4-butanediyl)bis-1 H-benzimidazole (bbbi) as the ligand.

The d^{10} configuration and softness of cadmium(II) permit a wide variety of geometries and coordination numbers [28]. Therefore, to explore the influence of carboxylate on the structures of coordination architectures, three structurally related flexible aliphatic dicarboxylates, itaconic acid (H_2ita), fumaric acid (H_2fma), and malate acid (H_2mal) (scheme 1), have been reacted with $Cd(NO_3)_2 \cdot 4H_2O$ and bbbi, and three new 2-D CPs, $[Cd(bbbi)(ita)(H_2O)] \cdot H_2O$ (**1**), [Cd(bbbi)(fma)] (**2**), and $[Cd(bbbi)(fma)(H_2O)] \cdot 2H_2O$ (**3**), have been obtained. The thermal stability and luminescence of **1–3** are discussed.

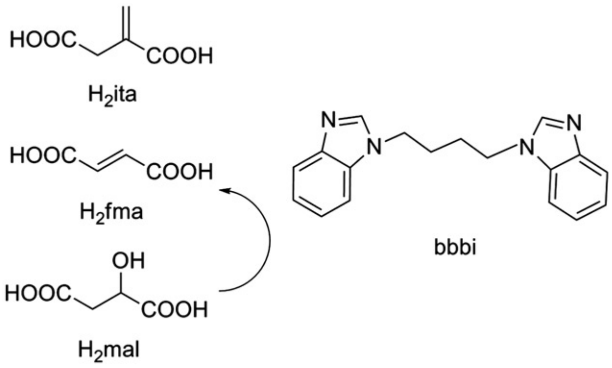
2. Experimental

2.1. *General materials and methods*

Solvents and starting materials for synthesis were commercially available and used as received. Ligand bbbi was prepared according to the literature [29] and characterized by FT-IR spectra and ^{1}H NMR. FT-IR spectra (KBr pellets) were taken on a Magna FT-IR 560 spectrometer. Thermogravimetric data for **1–3** were performed using a Pyris Diamond thermal analyzer. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240 C analyzer. Fluorescence spectra were recorded at room temperature on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer.

2.2. *Syntheses*

2.2.1. $[Cd(bbbi)(ita)(H_2O)] \cdot H_2O$ (1). $Cd(NO_3)_2 \cdot 4H_2O$ (0.031 g, 0.1 mmol), H_2ita (0.013 g, 0.1 mmol), and bbbi (0.015 g, 0.05 mmol) were dissolved in 8 mL of distilled



Scheme 1. Structures of the aliphatic carboxylate and bbbi in this work.

water and stirred for 0.5 h. Then the pH was adjusted to 6.0 by addition of 0.1 mol L^{-1} NaOH. The resulting mixture was transferred and sealed in a 25 mL Teflon-lined stainless steel vessel, which was heated at 150°C for 50 h and cooled to room temperature at a rate of 5°C h^{-1}. Yellow block crystals of **1** suitable for X-ray diffraction were isolated by mechanical separation from amorphous solid in 31% yield (based on Cd(II) salt). Anal. Calcd for $C_{23}H_{26}CdN_4O_6$ (%): C, 48.69; H, 4.59; N, 9.88. Found (%): C, 47.92; H, 4.62; N, 9.56. IR (KBr, cm^{-1}): 3361 (m), 3116 (w), 2956 (w), 2361 (m), 1622 (s), 1558 (s), 1535 (s), 1500 (m), 1464 (m), 1377 (s), 1239 (s), 1074 (s), 754 (s), 704 (w), 681 (m).

2.2.2. [Cd(bbbi)(fma)] (2). The synthetic procedure for **2** is the same as that for **1** except that H_2fma (0.012 g, 0.1 mmol) was used instead of H_2ita. Yellow block crystals of **2** suitable for X-ray diffraction were isolated by mechanical separation from amorphous solid in 27% yield (based on Cd(II) salt). Anal. Calcd for $C_{22}H_{20}CdN_4O_4$ (%): C, 51.08; H, 3.87; N, 10.84. Found (%): C, 51.83; H, 3.71; N, 11.24. IR (KBr, cm^{-1}): 3082 (m), 3043 (m), 2925 (m), 2360 (s), 1606 (s), 1560 (m), 1492 (s), 1461 (s), 1440 (m), 1377 (s), 1195 (s), 1006 (s), 746 (s), 694 (m), 644 (m).

2.2.3. [Cd(bbbi)(fma)(H_2O)] · 2H_2O (3). The synthetic procedure for **3** is the same as that for **1** except that malate (H_2mal) (0.013 g, 0.1 mmol) was used instead of H_2ita. During the reaction, the H_2mal was dehydrated and fma was generated. Yellow block crystals of **3** suitable for X-ray diffraction were isolated by mechanical separation from amorphous solid in 42% yield (based on Cd(II) salt). Anal. Calcd for $C_{22}H_{26}CdN_4O_7$ (%): C, 46.25; H, 4.55; N, 9.81. Found (%): C, 47.26; H, 4.61; N, 9.14. IR (KBr, cm^{-1}): 3365 (m), 3141 (w), 2941 (w), 2360 (s), 1651 (w), 1568 (s), 1510 (s), 1463 (s), 1375 (s), 1296 (m), 1240 (m), 1201 (m), 752 (s), 694 (s).

2.3. *X-ray crystallographic study*

A Bruker Apex CCD diffractometer (Mo-Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å) was used to collect data. The structures were solved by direct methods with SHELXS-97 and Fourier techniques and refined by full-matrix least-squares on F^2 with SHELXS-97 [30, 31]. All non-hydrogen atoms were refined anisotropically, hydrogens of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The hydrogens of water have not been located. All the crystal data and structure refinement details for the three complexes are given in table 1. Relevant bond distances and angles are listed in table S1.

3. Results and discussion

3.1. *Syntheses*

Compounds **1–3** have been prepared by hydrothermal reactions. The reaction of H_2ita and bbbi with $Cd(NO_3)_2 \cdot 4H_2O$ generated a new 2-D network [Cd(bbbi)(ita)(H_2O)] · H_2O (**1**). In order to investigate the influence of carboxylate anion on

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

	1	**2**	**3**
Empirical formula	$C_{23}H_{26}CdN_4O_6$	$C_{22}H_{20}CdN_4O_4$	$C_{22}H_{26}CdN_4O_7$
Formula weight	566.88	516.82	570.87
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P21/c$	$P\bar{1}$	$P21/c$
Unit cell dimensions (Å, °)			
a	9.7238(6)	8.577(5)	9.887(5)
b	15.3548(10)	10.259(5)	15.168(5)
c	16.4393(10)	11.765(5)	16.879(5)
α	90	86.604(5)	90
β	104.7060(10)	87.368(5)	110.742(19)
γ	90	85.602(5)	90
Volume (Å^3), Z	2374.1(3), 4	1029.5(9), 2	2367.2(16), 4
Calculated density (g cm^{-3})	1.586	1.667	1.602
Absorption coefficient, μ (mm^{-1})	0.966	1.098	0.972
$F(000)$	1152	520	1160
Goodness-of-fit on F^2	1.021	1.007	1.074
Final R indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.0298$, $wR_2{}^b = 0.0798$	$R_1{}^a = 0.0209$, $wR_2{}^b = 0.0526$	$R_1{}^a = 0.0226$, $wR_2{}^b = 0.0588$
R indices (all data)	$R_1{}^a = 0.0390$, $wR_2{}^b = 0.0835$	$R_1{}^a = 0.0227$, $wR_2{}^b = 0.0537$	$R_1{}^a = 0.0276$, $wR_2{}^b = 0.0614$

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

the reaction, H_2fma was used to replace H_2ita under the same reaction conditions, and a new complex [Cd(bbbi)(fma)] (**2**) with an undulated 2-D (4,4) network was obtained. When malate acid was selected to prepare **3** in the presence of bbbi and Cd(II), another new 2-D CP [Cd(bbbi)(fma)(H_2O)] · 2H_2O (**3**) was isolated, in which malate acid was converted into fumarate. An *in situ* reaction happened in the formation of **3**, with dehydration of the hydroxyl of malate acid into fumarate under hydrothermal conditions. These fumarates connect Cd(II) into 1-D zigzag chains, whereas bbbi are as bidentate-bridging ligands linking the 1-D chain to form a 2-D (4,4) grid network.

3.2. *Description of crystal structures*

3.2.1. Structural analysis of [Cd(bbbi)(ita)(H_2O)] · H_2O (1).

The polymeric structure of **1** was confirmed by X-ray single-crystal structure determination. The coordination environment around Cd(II) is exhibited in figure 1. Each Cd(II) is seven-coordinate by N1 and N2 from two different bbbi ligands with Cd–N distances of 2.335(2) and 2.312(2) Å and four oxygens (O1, O2, O3, and O4) from two distinct ita ligands and one oxygen from coordinated water, showing a distorted pentagonal bipyramid {CdN_2O_5}. The Cd–O bond lengths are in the range of 2.305(2)–2.552(3) Å.

Both bbbi and ita in **1** are bridging ligands. The Cd(II) and bridging bbbi form an infinite 1-D zigzag chain with Cd–Cd–Cd angle of 135.1°. The two carboxylates of ita are bis(chelating) to connect two Cd(II)s (scheme 2a), leading to the formation of a 2-D grid network with (4,4) topology, which can be seen clearly from a simplified 2-D network (figure 2). In each Cd_4 grid, the Cd$\cdots$Cd edge distances are 9.303 Å for

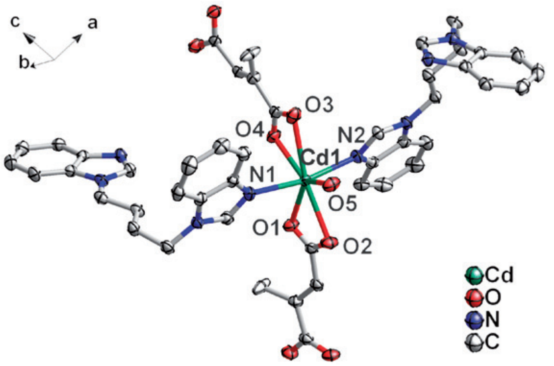
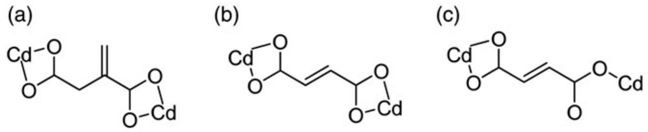


Figure 1. Coordination environment of Cd(II) in **1** (thermal ellipsoids are at the 30% probability level).



Scheme 2. Coordination modes of ita in **1** (a), fma in **2** (b), and in **3** (c).

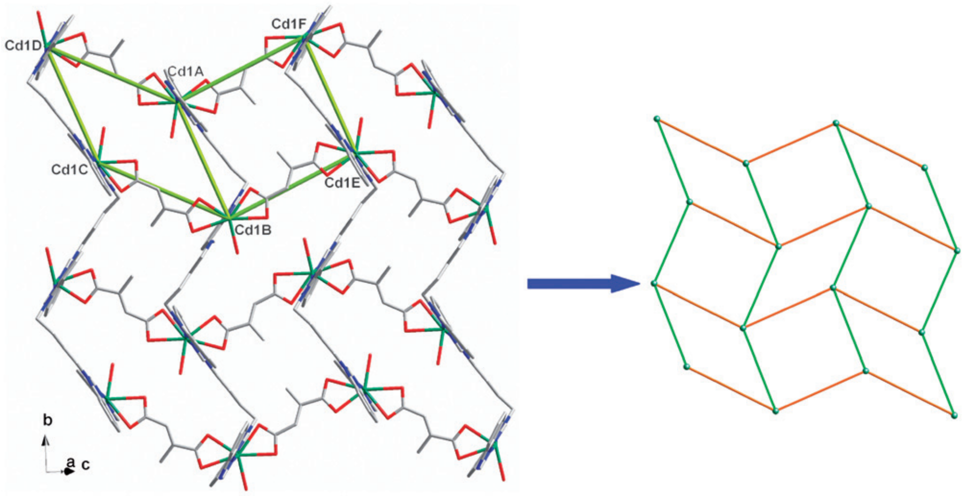


Figure 2. The 2-D layer structure of **1**.

Cd1A ··· Cd1D and Cd1B ··· Cd1C, 8.307 Å for Cd1A ··· Cd1B and Cd1C ··· Cd1D (figure 2).

The remarkable feature of **1** is that there are C–H ··· π interactions (the distance H8B···centroid is 2.945 Å) involved in the stabilization of the crystal lattice [32, 33].

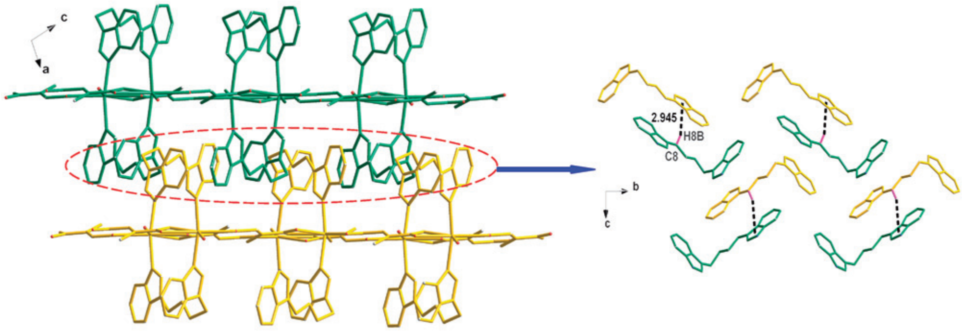


Figure 3. The 3-D supramolecular structure of **1** formed through C–H $\cdots\pi$ interactions between different layers.

The 2-D grid layers are further linked by C–H $\cdots\pi$ hydrogen bonds to generate a 3-D structure (figure 3).

3.2.2. Structural analysis of [Cd(bbbi)(fma)] (2). X-ray diffraction analysis reveals that **2** is an undulated 2-D (4,4) network constructed from bbbi and fma. The coordination environment of Cd(II) is shown in figure 4. Each Cd(II) is six-coordinate with two nitrogens of two bbbi molecules and four oxygens from two fma to complete a distorted octahedral geometry $\{CdN_2O_4\}$. The Cd–O bond lengths are 2.2777(18)–2.427(2) Å and the Cd–N bond lengths are 2.2740(19)–2.2891(19) Å.

Each bbbi links two Cd(II)s in **2** to form an infinite 1-D linear chain, which is different from the 1-D zigzag chain of Cd-bbbi in **1**. Adjacent Cd-bbbi chains are further linked by fma to give an undulated 2-D (4,4) network (figure 5). All fma ligands are bis(chelating) (scheme 2 b). The Cd $\cdots$ Cd distance separated by bbbi and fma are 10.259 and 9.060 Å, respectively.

In addition, π–π stacking interaction between benzimidazole rings in **2** (centroid-to-centroid distances of 3.882, 3.762, 3.691, and 3.671 Å, face-to-face distance of 3.5141 and 3.4488 Å) consolidates the overall structure. Adjacent 2-D architectures are further extended into a 3-D supramolecular network by intermolecular π–π stacking interactions (figure 6).

3.2.3. Structural analysis of [Cd(bbbi)(fma)(H$_2$O)]·2H$_2$O (3). Complex **3** shows a network similar to that of **1**. X-ray crystallographic analysis reveals that **3** is monoclinic with space group $P21/c$. The asymmetric unit of **3** consists of one bbbi, one fma, one Cd(II), one coordinated water molecule, and two uncoordinated water molecules. As displayed in figure 7, each Cd(II) with a distorted octahedral coordination geometry is coordinated by three oxygens (O1, O3B, O4B) from two distinct fma ligands and one oxygen from one coordinated water molecule and N1 and N3A from two different bbbi ligands. O1, O3B, O4B, and O5 comprise the equatorial plane, and the axial positions are occupied by N1 and N3A. The Cd–O distances range from 2.2954(18) to 2.4636(18) Å and the Cd–N distances are 2.304(2) and 2.318(2) Å (table S1).

Cd(II)s are linked into 1-D zigzag [Cd(bbbi)] chains through bridging bbbi. The 1-D chains are connected by fma into 2-D (4,4) grid motifs (figure 8). All fma ligands show

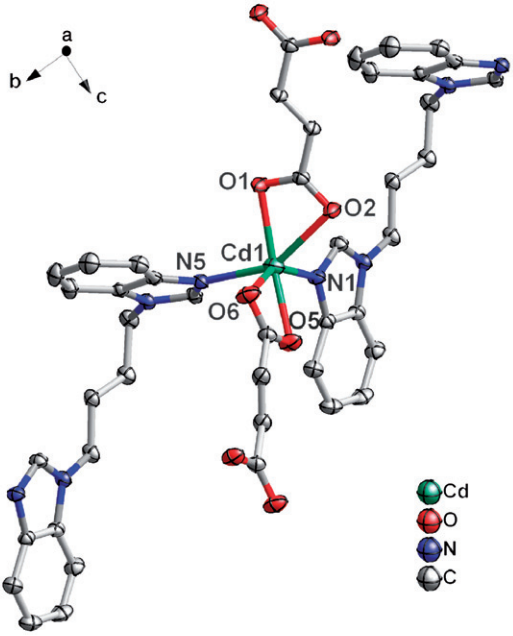


Figure 4. Coordination environment of Cd(II) in **2** (thermal ellipsoids are at the 30% probability level).

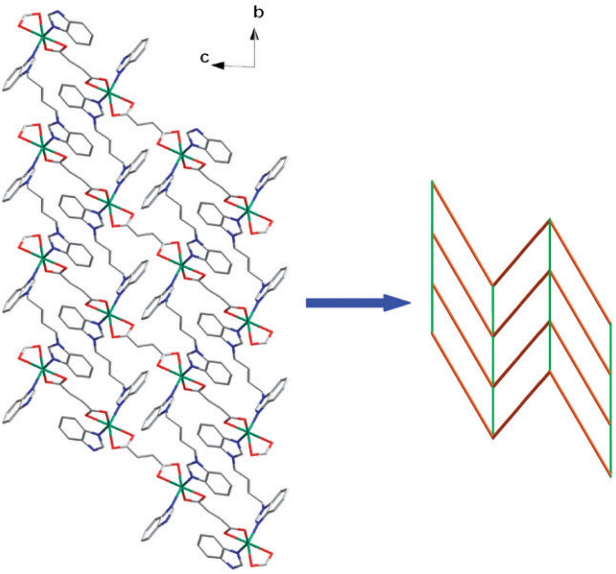


Figure 5. The undulated 2-D (4,4) network of **2**.

two types of coordination, monodentate and chelating bridging (scheme 2c). The perimeter of each grid is outlined by Cd–Cd distances of 8.213 and 9.302 Å through the bbbi and fma ligands, respectively. The 2-D layers are further linked by C–H $\cdots \pi$ hydrogen bonds (the distance H11B···centroid is 2.908 Å) to generate a 3-D

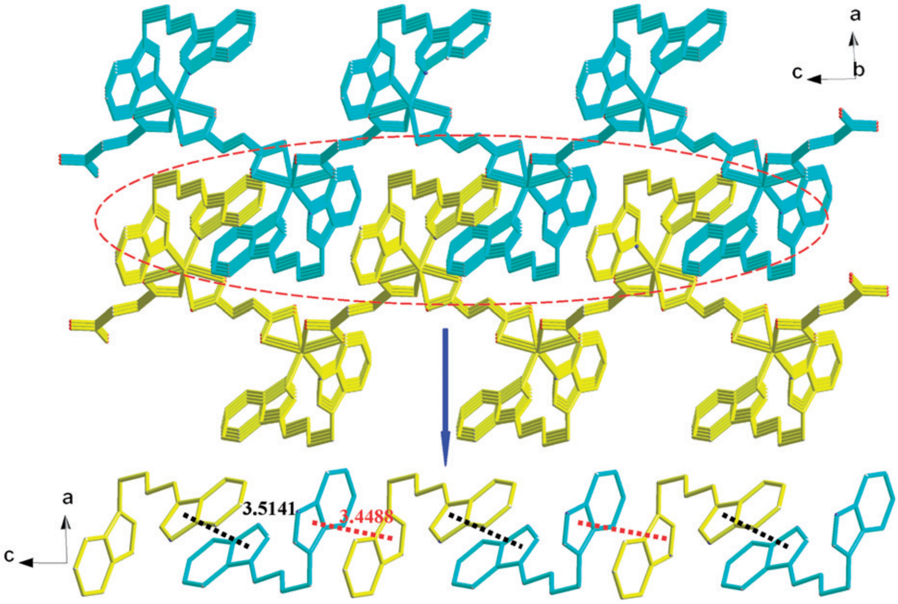


Figure 6. The 3-D supramolecular structure of **2** formed through π–π interactions between different layers.

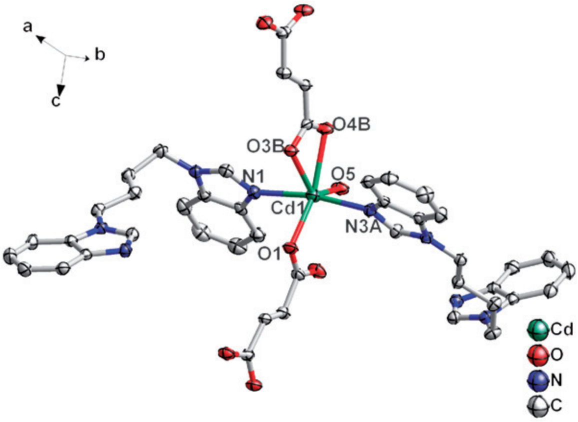


Figure 7. Coordination environment of Cd(II) in **3** (thermal ellipsoids are at the 30% probability level).

supramolecular structure (figure 9). These hydrogen-bonding interactions further stabilize the crystal structure.

3.3. *Effect of the organic carboxylate anions on the structures of the complexes*

The effects of the organic acid on the structures of **1–3** have been clearly demonstrated. Through varying the different succinic acid derivatives under the same conditions, **1–3**

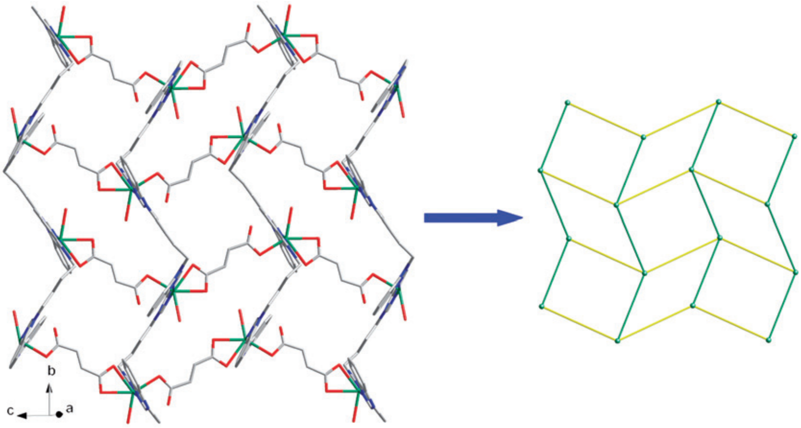


Figure 8. The 2-D layer structure of **3**.

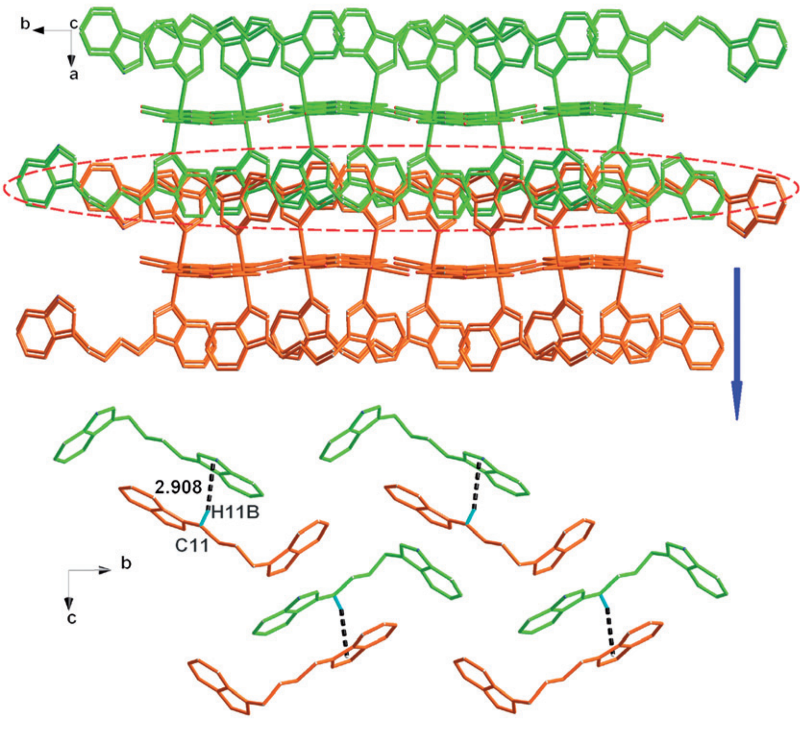


Figure 9. The 3-D supramolecular structure of **3** formed through C–H $\cdots\pi$ interactions between different layers.

exhibit some differences in their architectures. The coordination numbers of Cd(II) in these three complexes decrease from 7 in **1** to 6 in **2** and **3**. The structures display 2-D grid network to undulated 2-D network, and then to 2-D grid network, correspondingly. In **1**, ita adopts bridging bis-chelating coordination as a μ_2-bridge linking the infinite 1-D zigzag Cd(II)-bbbi chains to a 2-D grid network. In **2**, when fumaric acid

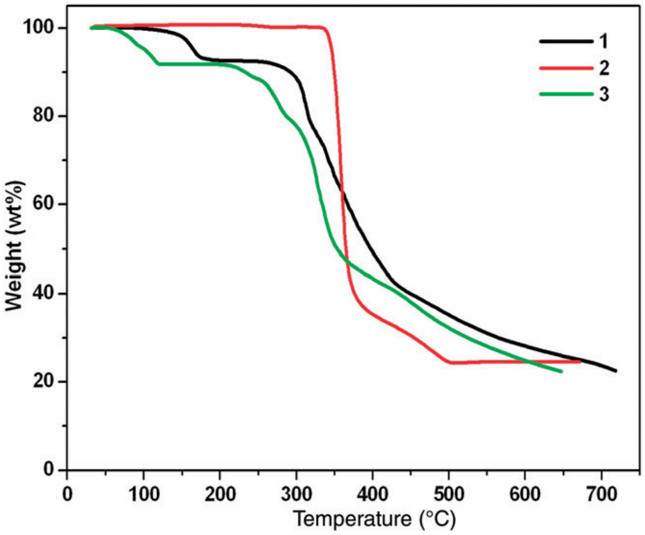


Figure 10. TGA curves of **1–3**.

was used, the coordination numbers of Cd(II) decrease from 7 in **1** to 6 in **2**. The fma anions also serve as a μ_2-bridge linking adjacent linear Cd-bbbi chains to give an undulated 2-D network. In **3**, when malate acid was used, an *in situ* ligand transformation occurred, malate acid was converted to fumaric acid by dehydration, resulting in the construction of a 2-D (4,4) grid network assembled from bbbi and fma. Compared with **2**, **3** contains the same ligands and metal as **2**, however, fma show monodentate and chelating bridging coordination, different from that of fma in **2** (scheme 2).

Some complexes based on Cd(II) ion and bis(2-methylimidazo-1-yl)methane (2-mBIM)/benzimidazole have been reported [34, 35]. In the previously reported related 2-D complex $[Cd_2(2\text{-mBIM})_2(NO_3)_2(C_4H_4O_4)(H_2O)_5]_n$, the Cd-2-mBIM chain showed 1-D helical structure and was connected into 2-D layers by bridging bimonodentate carboxylate [35]. In this work, **2** and **3** also exhibit 2-D networks. However, the carboxylates show bis-chelating/monodentate and a chelating bridging coordination in **2** and **3**, respectively, and Cd-bbbi chains are linear/zigzag in **2** and **3**, different from the reported complex. The results indicate that carboxylates with different substituents in **1–3** play important roles in constructing the final frameworks.

3.4. *Thermal properties of 1–3*

To explore thermal stability of these polymers, thermogravimetric analyses (TGA) for crystalline samples of **1–3** were performed (figure 10). The TGA curve of **1** indicates that uncoordinated and coordinated water molecules are released between 98 and 180°C (Calcd: 6.35%; Found: 6.55%); the framework is stable up to 268°C. Upon further heating, the organic ligands of **1** decompose progressively, leaving CdO as the final product (Calcd: 22.65%; Found: 22.63%). Complex **2** is stable up to 340°C with rapid weight loss from 340°C to 489°C corresponding to the removal of the organic

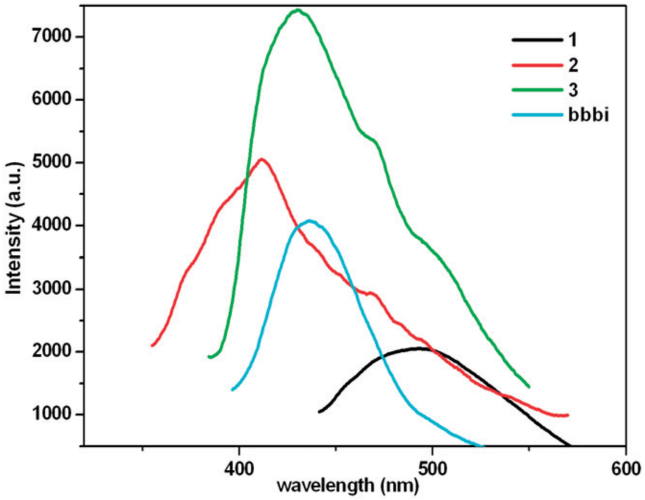


Figure 11. The emission spectra of **1–3** and bbbi in the solid state at room temperature.

components, and the residues are presumed to be CdO (Calcd: 24.84%; Found: 24.58%). For **3**, weight loss from 81°C to 145°C arise from one coordinated and two uncoordinated water molecules (Calcd: 9.46%; Found: 9.13%). Further weight loss is ascribed to the release of the organic ligands and the residual CdO weight is 22.37% (Calcd: 22.49%). Complex **2** is more stable than **1** and **3**, attributed to no water in **2**.

3.5. *Fluorescence of 1–3*

The solid-state luminescence of bbbi and **1–3** are measured at room temperature (figure 11). Fluorescent emissions of aliphatic-dicarboxylates used in this article are very weak compared with bbbi, so the three carboxylates have almost no contribution to the fluorescent emission. Emission bands are observed at 494 nm ($\lambda_{ex} = 324$ nm) for **1**, 411 nm ($\lambda_{ex} = 300$ nm) for **2**, 430 nm ($\lambda_{ex} = 290$ nm) for **3**, and 435 nm ($\lambda_{ex} = 312$ nm) for bbbi. The emission bands of **1** and **2** are 59 nm red-shifted and 24 nm blue-shifted, respectively. Such broad emission bands may be tentatively assigned to ligand-to-metal charge transfer (LMCT) as discussed previously [32, 36, 37]. Complex **3** is much stronger than bbbi, and the maximum emission wavelength of **3** is at 430 nm, which is close to that of bbbi; therefore, it is attributed to Cd(II)-bbbi [38]. From figure 11, we find that the fluorescent intensity of **3** is stronger than that of **1** and **2**, attributed to different rigidity of the crystal packing in the solid state [39, 40]. This suggests that **3** may be an excellent photoactive material.

4. Conclusions

Three new Cd(II) metal–organic frameworks have been isolated under hydrothermal conditions by the reactions of bbbi and Cd(II) salts with flexible aliphatic dicarboxylates. Compounds **1–3** display 2-D (4,4) network structures and show plane and undulated character, respectively. Compounds **1–3** are further extended to 3-D supramolecular structures by C–H $\cdots \pi$ and π–π interactions. The substituents on succinic acid influence the coordination environments of metal ions, and thus determine the structures of the CPs. Carboxylic ligands with different coordination modes and conformations play important roles in the formation of the different structures.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 796589–796591 for **1–3**, respectively.

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