

# Three New Complexes Based on a Flexible Bis(benzimidazole) Ligand and Rigid/Flexible Organic Carboxylates

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**Abstract** Three new polymeric frameworks,  $[\text{Ni}(\text{bbbm})(\text{L1})_2]_n$  (**1**),  $[\text{Ni}(\text{bbbm})(\text{L2})_2]_n$  (**2**), and  $\{[\text{Co}(\text{bbbm})(\text{L3})] \cdot \text{H}_2\text{O}\}_n$  (**3**) (bbbm = 1,4-bis(*N*-benzimidazolyl) butane, HL1 = 4-bromobenzoic acid, HL2 = 3-methylbenzoic acid, and H<sub>2</sub>L3 = glutaric acid) have been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction. Complex **1** features a one-dimensional (1D) linear chain structure bridged by bbbm ligands, which is further connected into a supramolecular double chain structure through intermolecular  $\pi$ - $\pi$  stacking interactions. Complex **2** contains 1D zigzag chain, which is further arranged into a 2D supramolecular architecture by hydrogen bonding and  $\pi$ - $\pi$  stacking interactions. In the structure of **3**, there are infinite 1D zigzag Co(II)-bbbm chains linked together by L3 ligands to generate an undulated 2D (4,4) sheet, which is further connected by intermolecular  $\pi$ - $\pi$  stacking interactions to form a 3D supramolecular network. Furthermore, thermal stability and luminescent property of **1–3** were investigated.

**Keywords** Hydrothermal synthesis · Crystal structures · Benzimidazole · Organic carboxylate · Luminescent property

## Introduction

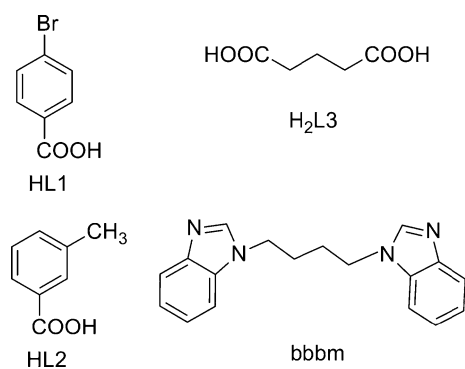
The assembly of metal–organic coordination polymers has been a rapidly expanding research field [1–5]. This is due

to their potential as functional materials with specific properties, such as luminescence, magnetism, absorption, catalysis, ion-exchange, etc. [6–11]. To date, the rational and controllable synthesis of coordination networks and supramolecular architectures is still a difficult challenge in most cases. Several factors, such as  $\pi$ - $\pi$  stacking and H-bonding interactions etc., may affect assembly of the compounds [12, 13]. Thus, a key step for the construction of such complexes is to select suitable functional ligands which possess strong coordination ability and can provide the hydrogen bond acceptors/donors and  $\pi$ -conjugated system for extending their networks [14–16].

On the basis of the aforementioned points, we select flexible multidentate ligand 1,4-bis(*N*-benzimidazolyl) butane (bbbm) with aliphatic core and benzimidazole nitrogen donors as main ligand because of its remarkable advantages (Scheme 1): (i) the bis(benzimidazole) nitrogens have strong coordination ability and the  $-(\text{CH}_2)_n-$  group is flexible [17–19]; (ii) bbbm ligand contains both an imidazole ring and a larger conjugated  $\pi$ -system, capable of acting as hydrogen bond donors and for  $\pi$ - $\pi$  stacking interactions. For example, Lang and co-workers have designed and synthesized a series of coordination polymers based on a series of flexible bidentate benzimidazole-containing organic ligands [20]. Hou and co-workers have also reported some coordination polymers based on flexible bbbm ligand [21–24]. To our knowledge, the reports on the bbbm-based compounds with organic carboxylates as the secondary ligands are relatively limited.

Here, we select three structurally representative organic carboxylate ligands 4-bromobenzoic acid (HL1), 3-methylbenzoic acid (HL2), and glutaric acid (H<sub>2</sub>L3) acting as secondary ligands. Three new coordination polymers  $[\text{Ni}(\text{bbbm})(\text{L1})_2]_n$  (**1**),  $[\text{Ni}(\text{bbbm})(\text{L2})_2]_n$  (**2**), and  $\{[\text{Co}(\text{bbbm})(\text{L3})] \cdot \text{H}_2\text{O}\}_n$  (**3**) have been successfully synthesized under

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**Scheme 1** Structures of the carboxylates and bbbm ligand in this work

hydrothermal conditions. In addition, the thermal stability and luminescent property of **1–3** have also been investigated in the solid state.

## Experimental Procedures

### Materials and Methods

Solvents and starting materials for synthesis were commercially available and used as received. Ligand bbbm was prepared according to the literature [25]. FT-IR spectra (KBr pellets) were taken on a Magna FT-IR 560 spectrometer. Thermogravimetric data were performed using a Pyris Diamond thermal analyzer. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer. Fluorescence spectra were recorded at room temperature on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer.

### Synthesis of $[Ni(bbbm)(L1)_2]_n$ (**1**)

A mixture of  $Ni(NO_3)_2 \cdot 6H_2O$  (0.029 g, 0.1 mmol), HL1 (0.04 g, 0.2 mmol) and bbbm (0.015 g, 0.05 mmol) was dissolved in 8 mL of distilled water and stirred for 0.5 h. Then the pH was adjusted to 6.0 by the addition of 0.1 M NaOH solution. Consequently, 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 then, the reaction system was cooled to room temperature at a rate of 5 °C h<sup>-1</sup>. Green block crystals of **1** suitable for X-ray diffraction were isolated by mechanical separation from amorphous solid in 28% yield (based on Ni(II) salt). Anal. Calcd for  $C_{32}H_{26}Br_2NiN_4O_4$ : C 51.26, H 3.47, N 7.48%. Found: C 51.46, H 3.43, N 7.54%. IR (KBr, cm<sup>-1</sup>): 3101 (m), 3060 (w), 2945 (w), 2360 (s), 1587 (s), 1533 (s), 1508 (w), 1461 (s), 1421 (s), 1294 (m), 1245 (s), 1201 (s), 856 (s), 773 (s), 748 (s), 671 (m).

### Synthesis of $[Ni(bbbm)(L2)_2]_n$ (**2**)

The synthetic procedure for **2** is the same as that for **1** except that HL2 (0.027 g, 0.2 mmol) was used instead of HL1. Green crystals of **2** suitable for X-ray diffraction were isolated by mechanical separation from amorphous solid in 31% yield (based on Ni(II) salt). Anal. Calcd for  $C_{34}H_{32}NiN_4O_4$ : C 65.88, H 5.17, N 9.04%. Found: C 65.69, H 5.13, N 9.11%. IR (KBr, cm<sup>-1</sup>): 3114 (w), 3058 (w), 2923 (w), 2360 (s), 1593 (w), 1525 (s), 1440 (s), 1392 (s), 1296 (m), 1263 (w), 1220 (s), 808 (m), 761 (s), 742 (s), 675 (m).

### Synthesis of $\{[Co(bbbm)(L3)] \cdot H_2O\}_n$ (**3**)

The synthetic procedure for **3** is the same as that for **1** except that H<sub>2</sub>L3 (0.013 g, 0.1 mmol) and  $CoCl_2 \cdot 6H_2O$  (0.024 g, 0.1 mmol) were used instead of HL1 and  $Ni(NO_3)_2 \cdot 6H_2O$ . Purple-red crystals of **3** suitable for X-ray diffraction were isolated by mechanical separation from amorphous solid in 45% yield (based on Co(II) salt). Anal. Calcd for  $C_{23}H_{26}CoN_4O_5$ : C 55.49, H 5.23, N 11.26%. Found: C 55.65, H 5.21, N 11.34%. IR (KBr, cm<sup>-1</sup>): 3329 (m), 3095 (m), 3002 (w), 2937 (w), 2360 (s), 1637 (m), 1541 (s), 1509 (s), 1429 (m), 1396 (s), 1298 (s), 1254 (s), 1206 (m), 757 (s), 740 (s), 668 (m).

### X-ray Crystallographic Study

A Bruker Apex CCD diffractometer (Mo-K $\alpha$  radiation, graphite monochromator,  $\lambda = 0.71073 \text{ \AA}$ ) was used to collect data. The structures were solved by direct methods with *SHELXS-97* and Fourier techniques and refined by the full-matrix least-squares method on  $F^2$  with *SHELXL-97* [26, 27]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The H-atoms of water molecules have not been localized. All the crystal data and structure refinement details for the three complexes are given in Table 1. The data of relevant bond distances and angles are listed in Table 2.

## Results and Discussion

### Description of the Structure

$[Ni(bbbm)(L1)_2]_n$  (**1**) The asymmetric unit of **1** consists of one bbbm, two L1 ligands, one Ni(II) ion. As displayed in Fig. 1, each Ni(II) ion with a distorted octahedral coordination geometry is coordinated by four oxygen atoms (O1, O2, O1A, O2A) from two distinct L1 ligands and two N

**Table 1** Crystal data and structure refinement parameters for compounds **1–3**

	<b>1</b>	<b>2</b>	<b>3</b>
Formula	C <sub>32</sub> H <sub>26</sub> Br <sub>2</sub> NiN <sub>4</sub> O <sub>4</sub>	C <sub>34</sub> H <sub>32</sub> NiN <sub>4</sub> O <sub>4</sub>	C <sub>23</sub> H <sub>26</sub> CoN <sub>4</sub> O <sub>5</sub>
Fw	749.10	619.35	497.41
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>Pbcn</i>	<i>Pbcn</i>	<i>C2/c</i>
<i>a</i> (Å)	25.305(5)	11.324(5)	31.746(5)
<i>b</i> (Å)	10.665(5)	20.242(5)	8.750(5)
<i>c</i> (Å)	11.487(5)	27.061(5)	16.279(5)
$\alpha$ (°)	90.000	90.000	90.000
$\beta$ (°)	90.000	90.000	91.348(5)
$\gamma$ (°)	90.000	90.000	90.000
<i>V</i> (Å <sup>3</sup> )	3100(2)	6203(3)	4521(3)
<i>Z</i>	4	8	8
<i>T</i> (K)	293(2)	293(2)	293(2)
$\rho$ calcd (g cm <sup>-3</sup> )	1.605	1.326	1.462
$\mu$ (mm <sup>-1</sup> )	3.247	0.669	0.802
$\theta$ range (°)	2.73–26.00	2.51–26.00	2.41–25.00
Observed data	3043	6075	3966
No. of parameters	195	376	298
GOOF	1.047	1.026	1.132
$R_1^a$ [ $I > 2\sigma(I)$ ]	0.0428	0.0724	0.0602
$wR_2^b$ (all data)	0.1174	0.2560	0.1986
Max, min peaks (e Å <sup>-3</sup> )	1.236, -1.125	1.089, -0.375	1.437, -0.601

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

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

atoms (N1, N1A) from two different bbbm ligands. The N1A, O1, O2, and O2A atoms comprise the equatorial plane, and the axial positions are occupied by N1 and O1A. The Ni–O distances range from 2.052(2) to 2.215(2) Å, and the Ni–N distance is 2.040(3) Å (Table 2).

The Ni(II) ions are linked into one-dimensional (1D) linear chain [Ni(bbbm)] through bridging bbbm ligands. The crossed L1 ligands are attached to one side of 1D linear chain. Interestingly, the two adjacent linear chains are further connected into a supramolecular double chain through intermolecular  $\pi$ – $\pi$  stacking interactions between the aromatic ring of the carboxylate ligand and the benzimidazole ring of the neighboring chain (3.987 Å) (Fig. 2).

$[Ni(bbbm)(L2)_2]_n$  (**2**) The structure of **2** is a 1D zigzag chain. The asymmetric unit of **2** is composed of one Ni(II) ion, one bbbm ligand, and two L2 ligands (Fig. 3). Each Ni(II) ion is six-coordinated by two nitrogen atoms from two bbbm ligands and four oxygen atoms from two L2 ligands, showing a distorted octahedral geometry. The Ni–O bond lengths range from 2.047(3) to 2.242(3) Å, and the Ni–N bond lengths are 2.011(4) and 2.046(4) Å, respectively. Each Ni(II) is linked to adjacent Ni(II) through the bridging bbbm, forming a 1D zigzag chain structure (Fig. 4a), where the Ni–Ni–Ni angle, defined by

the orientation of the bbbm ligands in the chain, is 101.51°. To be noticed, the L2 ligands in **2** are arranged at both sides of the chain.

In addition, the adjacent 1D chains are further arranged into a 2D supramolecular architecture by the intermolecular  $\pi$ – $\pi$  stacking interactions between the aromatic ring of the carboxylate ligand and the benzimidazole ring of the neighboring chain (3.975 Å) and one kind of hydrogen bonding interactions [C(8)–H(8A)···O(4) 3.1808 Å, 134° and C(18)–H(18A)···O(2) 3.1079 Å, 121°] (Fig. 4b). The weak noncovalent interactions are important in the formation of the final supramolecular structure of **2**.

$\{[Co(bbbm)(L3)] \cdot H_2O\}_n$  (**3**) The fundamental building unit of **3** contains one cobalt ion, one bbbm ligand, one L3 ligand and one interstitial water molecule. Each Co(II) cation exhibits a distorted trigonal–bipyramidal geometry with a CoN<sub>2</sub>O<sub>3</sub> coordination environment, and is coordinated by three oxygen atoms from two L3 ligands and two nitrogen atoms from two bbbm ligands, as shown in Fig. 5. The Co–O bond lengths in **3** are in the range of 2.023(4) to 2.392(4) Å, and the Co–N distances are 2.033(4) and 2.076(3) Å, which is comparable with those observed in other cobalt(II)-containing complexes [28].

Each bbbm ligand links two Co(II) ions in **3** to form an infinite 1D zigzag chain. The adjacent Co–bbbm chains are further linked by L3 ligands to give an undulated 2D (4,4) sheet (Fig. 6a, b). Each L3 ligand shows both a monodentate and chelating coordination mode. The Co···Co distances separated by bbbm and L3 are 13.916, 13.646, and 8.750 Å, respectively.

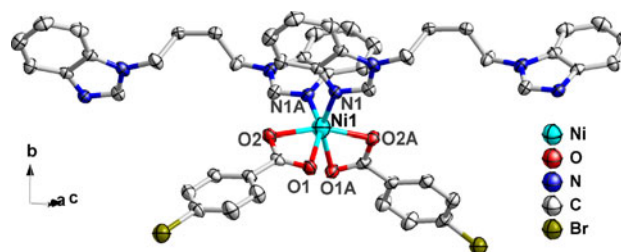
Furthermore, a kind of  $\pi$ – $\pi$  interactions between benzimidazole rings in **3** (centroid-to-centroid distances of 3.983 and 3.714 Å) consolidate the overall structure. The adjacent 2D architectures are further connected by the intermolecular  $\pi$ – $\pi$  stacking interactions between benzimidazole ring of bbbm ligand and the benzimidazole ring of the neighboring 2D layer to form a 3D supramolecular network (Fig. 7).

In the previously reported related complexes, a 2D  $[(CuSCN)_4(bbbm)_3]_n$  with a kind of  $[CuSCN]_n$  double chain has been reported by Lang et al. [20]. One 3D  $\{[Cd(bbbm)(SO_4)(H_2O)_2]CH_3OH\}_n$  and two 2D  $\{[Ni(bbbm)_2(H_2O)_2](NO_3)_2 \cdot 2CH_3OH \cdot 6H_2O\}_n$  and  $\{[Co(bbbm)_2(H_2O)_2](NO_3)_2 \cdot 2CH_3OH \cdot 6H_2O\}_n$  have been reported by Hou et al. [23]. To our knowledge, the reports on the bbbm-based compounds with organic carboxylates as the secondary ligands are relatively limited. In this work, we selected flexible bis(benzimidazole) bbbm as the main ligand and different carboxylate ligands as the secondary ligands, intending to observe carboxylate ligand effect on the assembly of the coordination polymers. From the structures of **1–3**, it can be seen that the different carboxylate ligands result in the corresponding structural changes. The

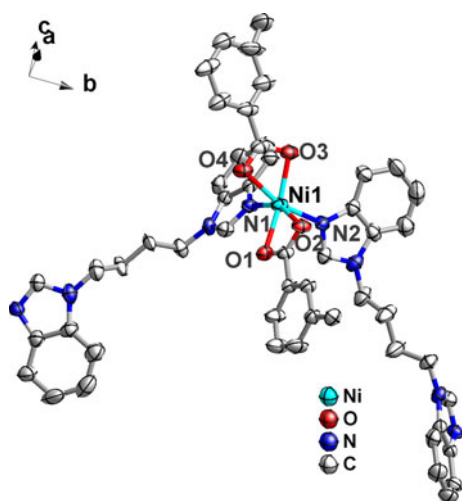
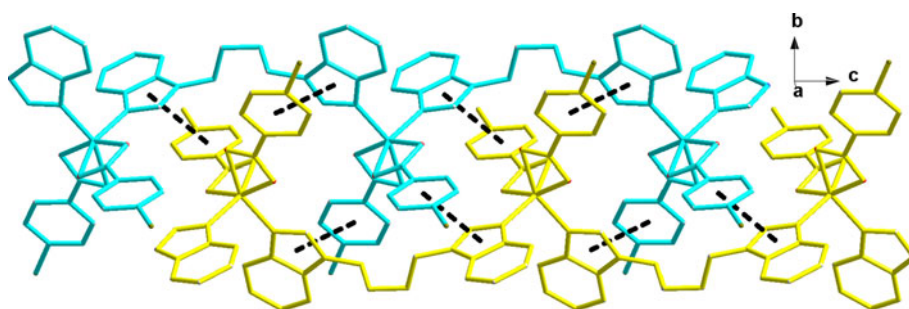
**Table 2** Selected bond distances (Å), angles (°) for compounds **1–3** and selected hydrogen-bonding geometry (Å, °) for **2**

<b>Compound 1</b>			
Ni(1)–N(1)	2.040(3)	Ni(1)–N(1A)	2.040(3)
Ni(1)–O(2)	2.052(2)	Ni(1)–O(2A)	2.052(2)
Ni(1)–O(1)	2.215(2)	Ni(1)–O(1A)	2.215(2)
N(1)–Ni(1)–N(1A)	100.30(16)	N(1)–Ni(1)–O(2)	99.92(10)
N(1A)–Ni(1)–O(2)	92.53(10)	N(1)–Ni(1)–O(2A)	92.53(10)
N(1A)–Ni(1)–O(2A)	99.92(10)	O(2)–Ni(1)–O(2A)	160.57(14)
N(1)–Ni(1)–O(1)	90.22(11)	N(1A)–Ni(1)–O(1)	153.68(10)
O(2)–Ni(1)–O(1)	61.74(10)	O(2A)–Ni(1)–O(1)	103.67(10)
N(1)–Ni(1)–O(1A)	153.68(10)	N(1A)–Ni(1)–O(1A)	90.22(11)
O(2)–Ni(1)–O(1A)	103.67(10)	O(2A)–Ni(1)–O(1A)	61.74(10)
O(1)–Ni(1)–O(1A)	90.75(14)		
Symmetry code: A: $-x + 1, y, -z + 1/2$			
<b>Compound 2</b>			
Ni(1)–N(2)	2.011(4)	Ni(1)–N(1)	2.046(4)
Ni(1)–O(1)	2.047(3)	Ni(1)–O(3)	2.059(4)
Ni(1)–O(4)	2.174(4)	Ni(1)–O(2)	2.242(3)
N(2)–Ni(1)–N(1)	93.50(16)	N(2)–Ni(1)–O(1)	92.36(14)
N(1)–Ni(1)–O(1)	94.32(14)	N(2)–Ni(1)–O(3)	100.77(19)
N(1)–Ni(1)–O(3)	95.32(15)	O(1)–Ni(1)–O(3)	163.18(16)
N(2)–Ni(1)–O(4)	162.34(17)	N(1)–Ni(1)–O(4)	91.70(16)
O(1)–Ni(1)–O(4)	104.07(14)	O(3)–Ni(1)–O(4)	61.91(16)
N(2)–Ni(1)–O(2)	87.75(15)	N(1)–Ni(1)–O(2)	155.36(14)
O(1)–Ni(1)–O(2)	61.05(12)	O(3)–Ni(1)–O(2)	108.63(14)
O(4)–Ni(1)–O(2)	94.51(14)		
<b>Compound 3</b>			
Co(1)–O(1)	2.023(4)	Co(1)–N(2)	2.033(4)
Co(1)–O(3A)	2.065(4)	Co(1)–N(1)	2.076(3)
Co(1)–O(4A)	2.392(4)	O(1)–Co(1)–N(2)	105.71(17)
O(1)–Co(1)–O(3A)	144.97(18)	N(2)–Co(1)–O(3A)	98.13(15)
O(1)–Co(1)–N(1)	91.03(18)	N(2)–Co(1)–N(1)	101.23(14)
O(3A)–Co(1)–N(1)	109.29(15)	O(1)–Co(1)–O(4A)	94.65(16)
N(2)–Co(1)–O(4A)	155.57(14)	O(3A)–Co(1)–O(4A)	57.76(13)
N(1)–Co(1)–O(4A)	91.59(13)		
Symmetry code: A: $x, y - 1, z$			
<b>Compound 2</b>			
D–H...A	d(D...A)/Å	D–H...A/°	
C(8)–H(8A)...O(4)	3.1808	134	
C(18)–H(18A)...O(2)	3.1079	121	

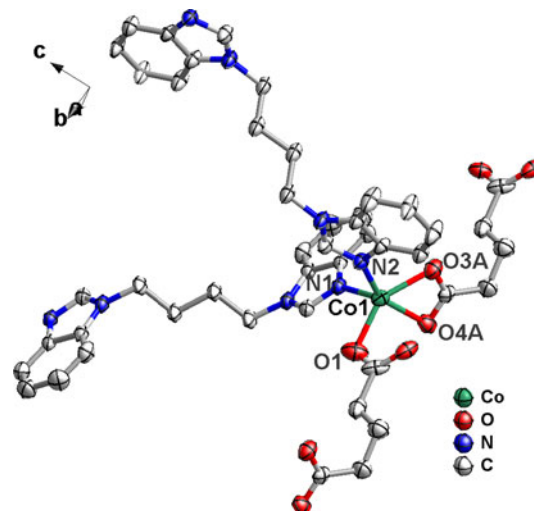
different 1D linear/zigzag chain structures of **1** and **2** are formed, and the 2D sheet structure of **3** is obtained. Complexes **1**, **2** and **3** are ultimately extended to supramolecular double chain, 2D and 3D networks by hydrogen bonding and  $\pi$ – $\pi$  stacking interactions, which is different from the above reported complexes. As can be seen from the description of structures, the bbbm can rotate and bend around the  $-\text{CH}_2-$  group freely when coordinating to the central metals. Thus, different structures have been obtained with the change of conformations of bbbm ligands. As shown in Fig. 8, the flexible bbbm ligands

**Fig. 1** Coordination environment of the Ni(II) ion in **1** (thermal ellipsoids are at the 30% probability level)

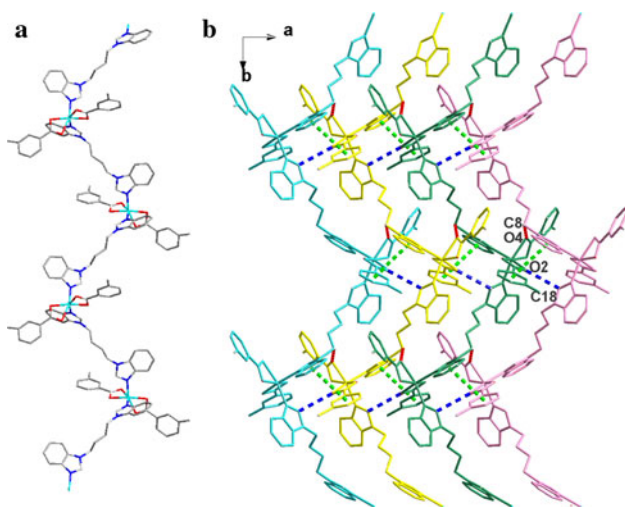
**Fig. 2** The 1D supramolecular double-chain of **1** formed through  $\pi$ - $\pi$  interactions between different 1D chains



**Fig. 3** Coordination environment of the Ni(II) ion in **2** (thermal ellipsoids are at the 30% probability level)

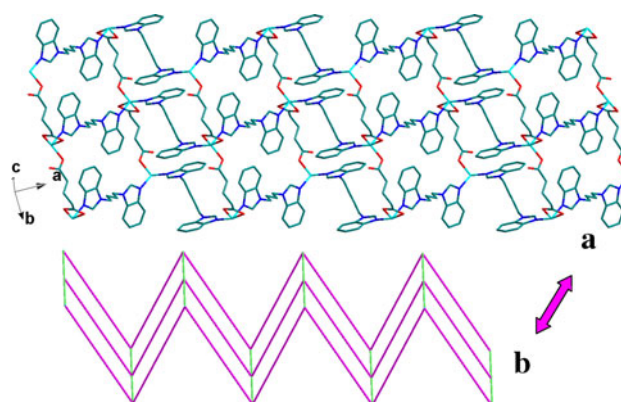


**Fig. 5** Coordination environment of the Co(II) ion in **3** (thermal ellipsoids are at the 30% probability level)



**Fig. 4** **a** View of the 1D zigzag chain of **2**. **b** 2D supramolecular layer of **2** formed through hydrogen bonding and  $\pi$ - $\pi$  interactions between different 1D chains

adopt three conformations in compounds **1–3**, [with M...M separation 11.487(5), 13.0688(30) and 13.9155(30) Å]. The C–C–C torsion angle for each compound is 79.013, 157.073 and 180.00. It is obvious that different

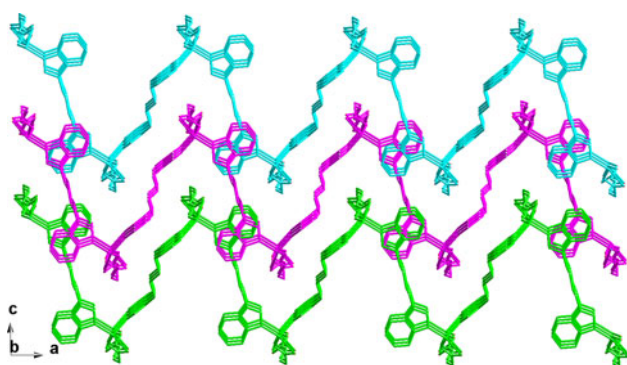


**Fig. 6** **(a, b)** View of an undulated 2D (4,4) sheet in **3**

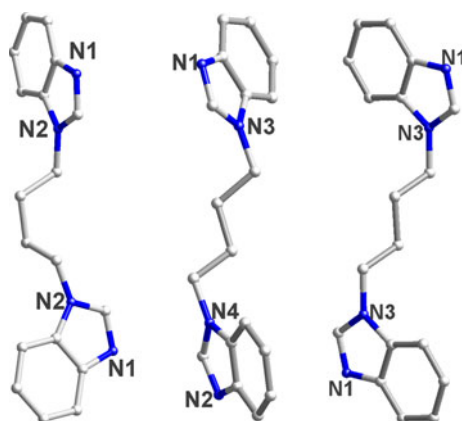
conformations can lead to different lengths of the bbbm, which play important roles in the formation of different structures.

#### Thermal Stability Analysis

Thermogravimetric analyses (TGA) are performed to measure the thermal stabilities of **1–3** as shown in Fig. 9. In compounds **1** and **2**, a rapid weight loss of 290–650 and



**Fig. 7** 3D supramolecular structure of **3** formed through  $\pi$ - $\pi$  interactions between different layers

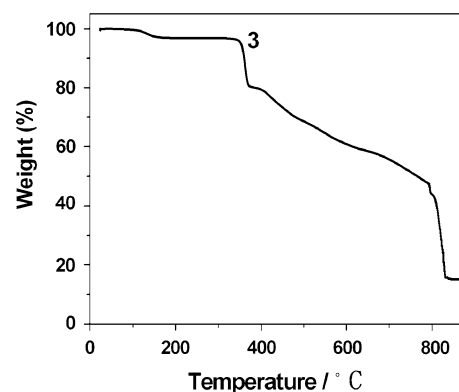
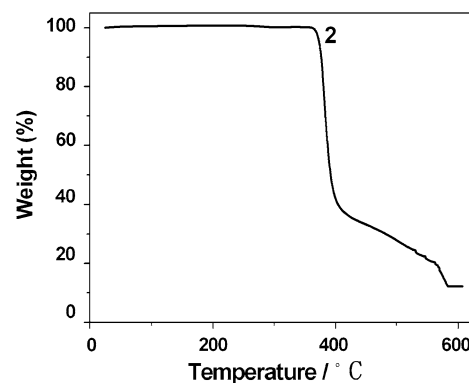
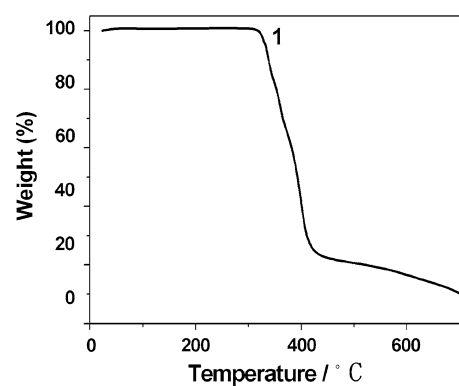


**Fig. 8** Three conformation modes of bbbm ligand in complexes **1–3**

330–555 °C corresponds to the organic ligands and the remaining residue is NiO (calcd: 9.97%; found: 9.63% for **1**; calcd: 12.06%; found: 12.16% for **2**). Polymer **3** lost the interstitial water at 102–164 °C (calcd: 3.62%; found: 3.32%). Upon further heating, the organic mixed-ligands of **3** are observed to be decomposed progressively, leaving CoO as the final product (calcd: 15.06%; found: 14.95%).

#### Luminescent Property

The luminescent behaviors of polymers **1–3** and free ligand bbbm were studied in the solid state at room temperature (Fig. 10). The free ligand bbbm displays luminescence with emission band at 435 nm ( $\lambda_{\text{ex}} = 312$  nm). Meanwhile, the emission for the complexes **1–3** can be observed, where the emission bands appear at 368 nm ( $\lambda_{\text{ex}} = 235$  nm) for **1**, 470 nm ( $\lambda_{\text{ex}} = 250$  nm) for **2** and 494 nm ( $\lambda_{\text{ex}} = 324$  nm) for **3**. Compared with that of the free ligand bbbm, the emission peaks of **1–3** are 67 nm blue-shifted for **1**, 35 nm red-shifted for **2** and 59 nm red-shifted for **3**, which may be due to the increase of conjugation upon metal coordination and originate from the ligand-to-metal charge-transfer (LMCT) [29–32].

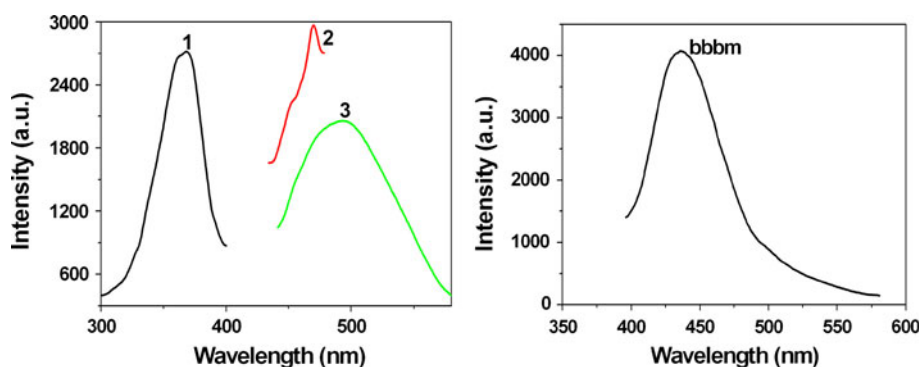


**Fig. 9** Thermogravimetric analyses (TGA) curves of complexes **1–3**

#### Conclusions

In this article, the assembly reactions of the flexible ligand bbbm and nickel(II) or cobalt(II) salts with auxiliary carboxylate ligands produce three coordination polymers  $[\text{Ni}(\text{bbbm})(\text{L}1)_2]_n$  (**1**),  $[\text{Ni}(\text{bbbm})(\text{L}2)_2]_n$  (**2**), and  $\{[\text{Co}(\text{bbbm})(\text{L}3)] \cdot \text{H}_2\text{O}\}_n$  (**3**) under hydrothermal conditions. Complexes **1** and **2** feature linear and zigzag chain structures, respectively. Complex **3** has an undulated 2D (4,4) network. Complexes **1–3** are further connected by intermolecular interactions to form supramolecular double chain, 2D and 3D supramolecular networks, respectively. The flexibility of bbbm, the diversity of the carboxylate and the different coordination preferences of the Co(II) and Ni(II) metal ions lead

**Fig. 10** The emission spectra of **1–3** and bbbm ligand in the solid state at room temperature



cooperatively to the different architectures from 1D chain to 2D layer.

### Supplementary Material

CCDC 798761–798763 for complexes **1–3** contain the supplementary crystallographic data for this article. The data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> [or from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2, 1EZ, UK; fax: +44 (0) 1223-336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

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