

# Synthesis of two-dimensional metal–organic networks from 1,10-phenanthroline-chelated cadmium complex and polycarboxylate

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## Abstract

The design of two 2D metal–organic frameworks using a 1,10-phenanthroline-chelated cadmium complex as precursor and a bridging polycarboxylate as linker is described. The reaction of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  with the chelating ligand 1,10-phenanthroline (phen) at room temperature gave  $[\text{Cd}(\text{phen})(\text{NO}_3)_2]$  (**1**) in high yield. Treatment of the inorganic precursor **1** with the polycarboxylate bridge ligand, benzene-1,4-dicarboxylic acid ( $\text{H}_2\text{BDC}$ ) or benzene-1,2,4,5-tetracarboxylic acid ( $\text{H}_4\text{btcc}$ ), under mild hydrothermal conditions led to the formation of two metal–organic networks  $\{[\text{Cd}(\text{BDC})(\text{phen})]\text{DMF}\}_n$  (**2**) and  $[\text{Cd}_2(\text{btcc})(\text{phen})_2]_n$  (**3**). Single-crystal X-ray diffraction analyses showed that both products have two-dimensional sheet architectures. Compound **2** was constructed via the use of  $[\text{Cd}_2(\text{O}_2\text{C})_4]$  unit and BDC linker, whereas compound **3** involved the use of  $[\text{CdO}_4]$  core and btcc bridge. The cadmium ions in compounds **2** and **3** are hepta- and hexa-coordinated, respectively. Thermogravimetric (TG) analyses showed that **2** and **3** are thermally stable ( $T_{\text{decomp.}} > 360^\circ\text{C}$ ). Photoluminescence studies revealed that compounds **1–3** displayed a strong fluorescent emission in the solid state at room temperature.

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**Keywords:** Cadmium; Metal–organic networks; Chelate ligand; Bridge ligand; Photoluminescence

## 1. Introduction

Over the past decade, low dimensional coordination polymers [1–7] have attracted considerable interest, due to their intriguing structural features and unique electro-conductive, nonlinear optic, and magnetic properties, which are different from those of 3D frameworks [8–10]. The combination of a chelating ligand and polycarboxylate ligands at the metal center has been published as a rational strategy for the preparation of 1D chainlike and 2D layer-like structures [6b,8,11–17], since a bulky aromatic chelating ligand would prevent the occurrence of higher dimensions of the overall framework by “passivating” vacant sites and increasing steric hindrance at the metal center [8]. Herein we report on the synthesis of two 2D

coordination polymers. The strategy for the design lies in the use of a 1,10-phenanthroline-chelated metal complex as a precursor that is terminated in one dimension by a chelating aromatic ligand and the utilization of a bridging polycarboxylate ligand as propagating linker between the inorganic moieties.

## 2. Experimental

### 2.1. General remarks

All reagents were purchased from commercial sources and were used as received without further purification. Elemental analyses were conducted on a Perkin-Elmer 2400 CHN elemental analyzer. All thermogravimetric (TG) analyses were performed under a flow of nitrogen on a Perkin-Elmer TGA-7 analyzer at a heating rate of  $10^\circ\text{C}/\text{min}$ . Photoluminescence spectra were obtained on a Hitachi F-4500 fluorescence spectrophotometer.

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## 2.2. Synthesis of $[Cd(phen)(NO_3)_2]$ (**1**)

A solution of 1,10-phenanthroline (phen, 0.01 mmol) in EtOH (12 mL) was added into a solution of  $Cd(NO_3)_2 \cdot 4H_2O$  (0.01 mmol) in EtOH (45 mL) at room temperature. The mixture was allowed to stir for 3 h. The resulting white precipitates were isolated by filtration and washed with ethanol, and then dried under vacuum. Yield 80%. Anal. Found: C, 35.11; H, 2.09; N, 13.63%. Calcd. for  $C_{12}H_8CdN_4O_6$ : C, 34.59; H, 1.94; N, 13.45%.

## 2.3. Synthesis of $\{[Cd(BDC)(phen)] \cdot DMF\}_n$ (**2**)

A mixture of  $[Cd(phen)(NO_3)_2]$  (0.15 mmol),  $H_2BDC$  (0.15 mmol), and DMF (12 mL) was conducted in an acid digestion bomb at 80 °C for 96 h. Colorless crystals were collected in 76% yield by filtration and washed with ethanol, and then dried at room temperature. Anal. Found: C, 51.62; H, 3.82; N, 8.07%. Calcd. for  $C_{23}H_{19}CdN_3O_5$ : C, 52.14; H, 3.61; N, 7.93%.

## 2.4. Synthesis of $[Cd_2(btec)(phen)_2]_n$ (**3**)

A mixture of  $[Cd(phen)(NO_3)_2]$  (0.15 mmol),  $H_4btec$  (0.32 mmol), and DMF (12 mL) was conducted in an acid digestion bomb at 80 °C for 96 h. Colorless crystals were collected in 84% yield by filtration and washed with ethanol, and then dried at room temperature. Anal. Found: C, 48.66; H, 2.35; N, 7.02%. Calcd. for  $C_{34}H_{18}Cd_2N_4O_8$ : C, 48.89; H, 2.17; N, 6.71%.

## 2.5. X-ray crystallography

Suitable single crystal of **3** was selected for indexing and the collection of intensity data. Measurements were performed using graphite-monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Kappa CCD diffractometer. Compound **3** crystallizes in the monoclinic system with space group  $P2_1/c$ . Intensity data were collected at 298 K within the limits  $2.45^\circ < \theta < 25.05^\circ$ . The structure was solved by direct methods and refined by full-matrix least-squares method on  $F^2$  using the WINGX [18] and SHELX-97 [19] program packages. An empirical absorption correction, based on multi-scan method, was applied. Anisotropic thermal factors were assigned to non-hydrogen atoms. The positions of hydrogen atoms were generated geometrically, assigned isotropic thermal parameters. Basic information pertaining to the crystal parameters and structure refinements for **3** are summarized in Table 1, and selected bond distances and angles are provided in Table 2.

CCDC-600560 (**3**) contains the Supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.htm](http://www.ccdc.cam.ac.uk/conts/retrieving.htm) [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

Table 1

Crystal structure refinement data for **3**

|  |  |
|--|--|
| Empirical formula  | $C_{34}H_{18}Cd_2N_4O_8$                 |
| Formula weight   | 835.338                                  |
| Crystal system   | Monoclinic                               |
| Space group  | $P2_1/c$                                 |
| <i>a</i> (Å)   | 7.5768(2)                                |
| <i>b</i> (Å)   | 20.1802(6)                               |
| <i>c</i> (Å)   | 9.8192(3)                                |
| $\beta$ (°)  | 111.9101(12)                             |
| <i>V</i> (Å <sup>3</sup> )                                     | 1392.93(7)                               |
| <i>Z</i>   | 2  |
| <i>T</i> (Å)   | 298                                      |
| Diffractometer   | Kappa CCD                                |
| $\lambda$ (Å)  | 0.71073                                  |
| <i>D</i> <sub>calcd</sub> (g cm <sup>−3</sup> )                | 1.992                                    |
| $\mu$ (mm <sup>−1</sup> )                                      | 1.594                                    |
| <i>F</i> <sub>000</sub>  | 820                                      |
| $\theta$ (°)   | 2.45–25.05                               |
| Reflns measured  | 8207                                     |
| Reflns indep.  | 2397 ( <i>R</i> <sub>int</sub> = 0.0630) |
| Reflns observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]          | 1933                                     |
| Parameters   | 217                                      |
| <i>R</i> 1 <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]  | 0.0356                                   |
| <i>wR</i> 2 <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] | 0.1010                                   |
| <i>R</i> 1 (all data)  | 0.0535                                   |
| <i>wR</i> 2 (all data)   | 0.1321                                   |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                       | 0.964                                    |
| $\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å <sup>−3</sup> )     | 0.846/−1.077                             |

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \left[ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2) \right]^{1/2}.$$

Table 2

Selected bond lengths (Å) and angles (°) for **3**

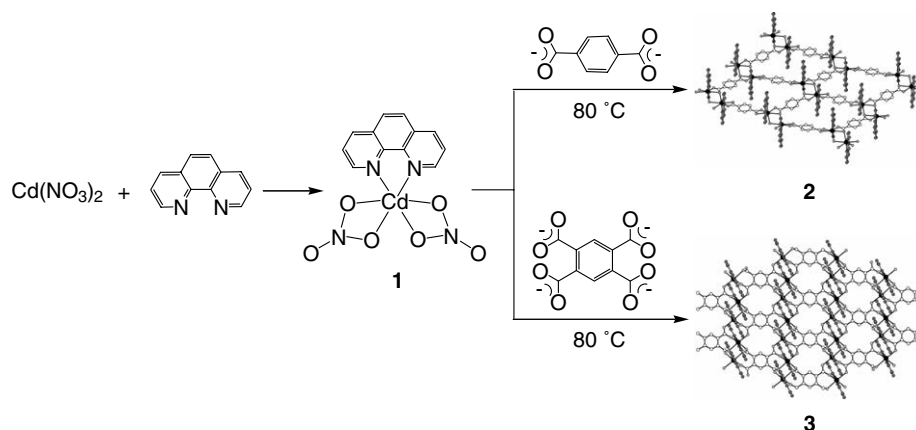
|                   |            |
|-------------------|------------|
| Cd(1)–O(4b)       | 2.225(4)   |
| Cd(1)–O(2a)       | 2.293(4)   |
| Cd(1)–O(3)        | 2.383(4)   |
| O(4b)–Cd(1)–O(1)  | 111.17(16) |
| O(1)–Cd(1)–O(2a)  | 101.31(14) |
| O(1)–Cd(1)–N(2)   | 154.09(14) |
| O(4b)–Cd(1)–O(3)  | 95.57(16)  |
| O(2a)–Cd(1)–O(3)  | 174.53(16) |
| O(4b)–Cd(1)–N(1)  | 149.46(16) |
| O(2a)–Cd(1)–N(1)  | 87.45(17)  |
| O(3)–Cd(1)–N(1)   | 98.02(15)  |
| Cd(1)–O(1)        | 2.255(4)   |
| Cd(1)–N(2)        | 2.354(5)   |
| Cd(1)–N(1)        | 2.384(4)   |
| O(4b)–Cd(1)–O(2a) | 79.47(17)  |
| O(4b)–Cd(1)–N(2)  | 85.08(17)  |
| O(2a)–Cd(1)–N(2)  | 101.46(16) |
| O(1)–Cd(1)–O(3)   | 78.25(13)  |
| N(2)–Cd(1)–O(3)   | 80.25(14)  |
| O(1)–Cd(1)–N(1)   | 98.34(16)  |
| N(2)–Cd(1)–N(1)   | 70.55(15)  |

Symmetry transformations used to generate equivalent atoms: a,  $-x, -y, -z$ ; b,  $-x + 1, -y, -z$ .

## 3. Results and discussion

### 3.1. Synthesis of compounds **2** and **3**

Compound  $[Cd(phen)(NO_3)_2]$  (**1**) was prepared in high yield by treating  $Cd(NO_3)_2 \cdot 4H_2O$  with the chelating ligand, 1,10-phenanthroline (phen), at room temperature.



Compound **1** was characterized by elemental analysis. In order to control the propagating process of a self-assembly reaction, compound **1** is used as an inorganic precursor in assembling polycarboxylate bridging ligands to form extended 2D coordination polymers. The bulky aromatic chelating ligand would be expected to passivate the vacant sites and increase the extent of steric hindrance at the cadmium metal center, thereby reducing the dimensions of the resulting net. Two-dimensional compounds  $\{[\text{Cd}(\text{BDC})(\text{phen})]\cdot\text{DMF}\}_n$  (**2**) and  $[\text{Cd}_2(\text{btec})(\text{phen})_2]_n$  (**3**) were successfully synthesized using this strategy by reacting the cadmium–phen building unit **1** with the bridging aromatic polycarboxylic acid (benzene-1,4-dicarboxylic acid ( $\text{H}_2\text{BDC}$ ) for **2** and benzene-1,2,4,5-tetracarboxylic acid ( $\text{H}_4\text{btec}$ ) for **3**) under mild hydro(solvo)thermal conditions (Scheme 1).

### 3.2. Structural description of $\{[\text{Cd}(\text{BDC})(\text{phen})]\cdot\text{DMF}\}_n$ (**2**)

Compound **2** is crystallographically characterized as a known coordination polymer  $\{[\text{Cd}(\text{BDC})(\text{phen})]\cdot\text{DMF}\}_n$  [20]. This species is constructed from dinuclear  $\text{Cd}_2(\text{O}_2\text{C})_4(\text{phen})_2$  secondary building units (SBUs), in which two  $\text{Cd}^{\text{II}}$  centers, each having seven-coordinated  $\text{CdN}_2\text{O}_5$  cores, are bridged by two carboxylates in a chelating-bridging bidentate mode. Each SBU acts as a building node for connecting four adjacent SBUs through BDC linkers in a head-to-tail arrangement, generating a 2D sheet architecture in a grid-like (4,4)-net, which is stabilized by alternating intra- (av.  $\text{C}\cdots\text{C}$  distance 3.46 Å) and inter-node (av.  $\text{C}\cdots\text{C}$  distance 3.51 Å)  $\pi$ – $\pi$  interactions between the aromatic rings of the phen ligands (Fig. 1a). The crystal packing of **2** shows an inter-digited arrangement of sheets stacked in the  $bc$ -plane, in which the lattice DMF molecules are located in the inter-sheet spaces (Fig. 1b). In **2**, the carboxylate groups of the BDC ligand exhibit two different coordination modes, i.e. bis(chelating bidentate) and bis(chelating–bridging bidentate), as shown in Fig. 2.

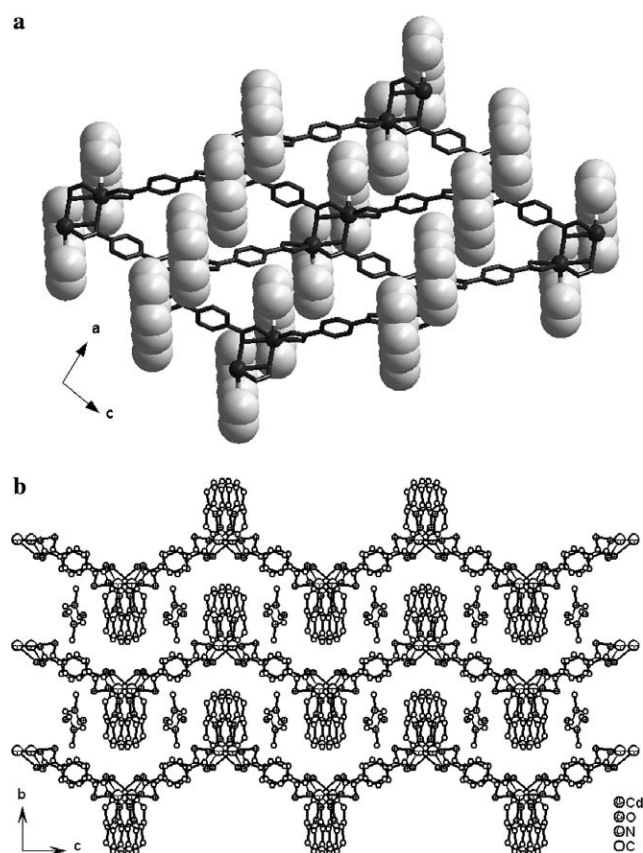


Fig. 1. (a) The 2D sheet architecture of **2** showing the (4,4)-net topology by regarding  $\text{Cd}_2\text{N}_4\text{O}_8$  cores as nodes, which is stabilized by alternative intra- and inter-node  $\pi$ – $\pi$  interactions between aromatic rings of phen ligands (space-filling model). (b) Crystal packing of **2** showing an inter-digited arrangement of stacked sheets with the lattice DMF molecules located between sheets.

### 3.3. Structural description of $[\text{Cd}_2(\text{btec})(\text{phen})_2]_n$ (**3**)

Solid-state structure analysis shows that compound **3** has a 2D sheet architecture and crystallizes in the monoclinic space group  $P2_1/c$ . There is one cadmium atom, one phen ligand, and half of a btec ligand in each

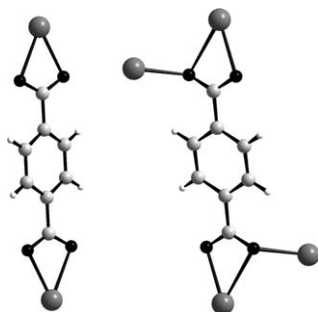


Fig. 2. Coordination modes of BDC in **2**, (left) bis(chelating bidentate) and (right) bis(chelating-bridging bidentate).

asymmetric unit. As shown in Fig. 3, the cadmium atom is coordinated by one chelated phen ligand and four carboxylate oxygen atoms from three distinct btc ligands, forming a distorted octahedral  $\text{CdN}_2\text{O}_4$  core. Each btc ligand bridges to six cadmium atoms in a tetrakis(bidentate) fashion to generate a 2D sheet architecture (Fig. 4), in which the carboxylate groups of the btc ligand all display a *syn, anti*-bidentate bridging mode. Along the crystallographic *a*-axis, the cadmium atoms in the 2D sheet are

maintained in a pseudo-chain arrangement with a  $\text{Cd} \cdots \text{Cd}$  distance of 4.69 Å.

It is noteworthy that the four carboxylates in the btc ligand exhibit different orientations (Fig. 4a). One set of carboxylate groups that are *para* with respect to each other is almost parallel to the central phenyl ring (dihedral angle  $6.59^\circ$ ), while the other set is nearly orthogonal (dihedral angle  $94.42^\circ$ ) to the phenyl plane. The adjacent carboxylate groups are perpendicular to each other with a dihedral angle of  $91.82^\circ$ . This is most likely due to the ring strain of the metal-containing seven-membered ring ( $\text{CdO}_2\text{C}_4$ ) and steric hindrance imposed by two adjacent carboxylate groups in the btc ligand. Owing to the aromatic nature of the chelated phen ligand, adjacent 2D sheets are intercalated with each other to form a 3D supramolecular network through face-to-face  $\pi$ - $\pi$  stacking between phen moieties with a  $\text{C} \cdots \text{C}$  separation of 3.30–3.63 Å (Fig. 5).

### 3.4. Thermogravimetric (TG) analysis of compounds **2** and **3**

As shown in Fig. 6, a thermogravimetric (TG) analysis of compound **2** showed that a weight loss of 14.3% occurred over the temperature range  $75$ – $144^\circ\text{C}$ , which

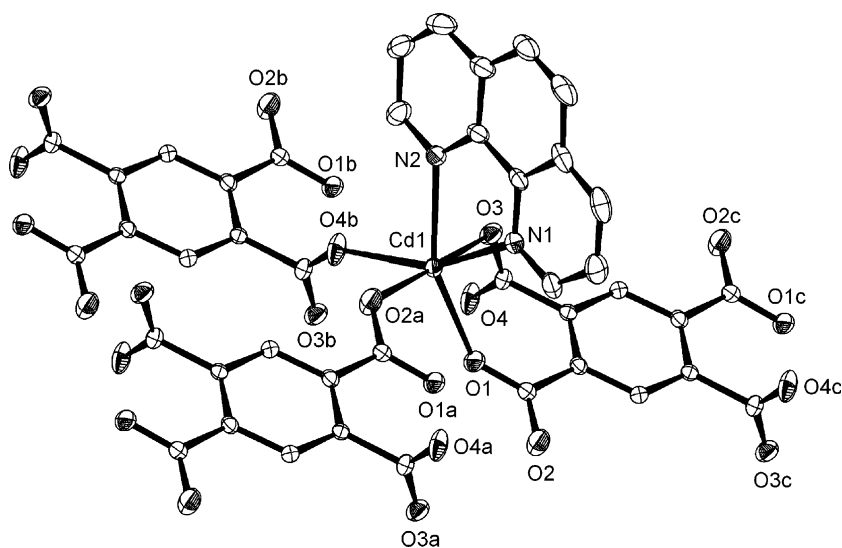


Fig. 3. ORTEP plot of the coordination environment around cadmium ion with the atom-labeling scheme in **3**.

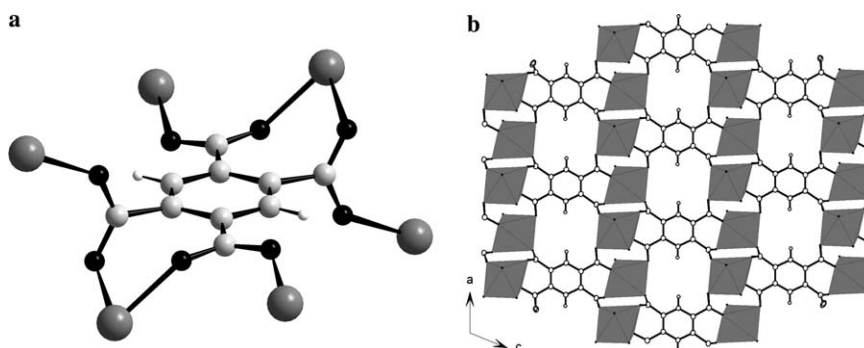


Fig. 4. (a) Coordination mode of btc ligand in **3**. (b) The 2D sheet architecture of **3** constructed by  $[\text{CdN}_2\text{O}_4]$  cores (polyhedra) and btc bridges.



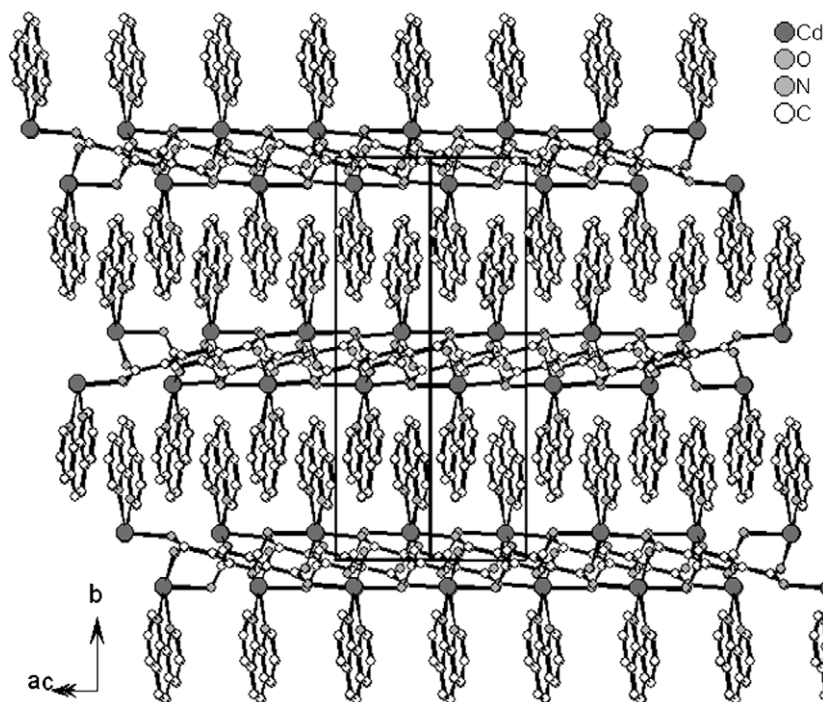


Fig. 5. The 3D supramolecular network of **3** showing the face-to-face  $\pi$ - $\pi$  stacking between aromatic rings of phen ligands.

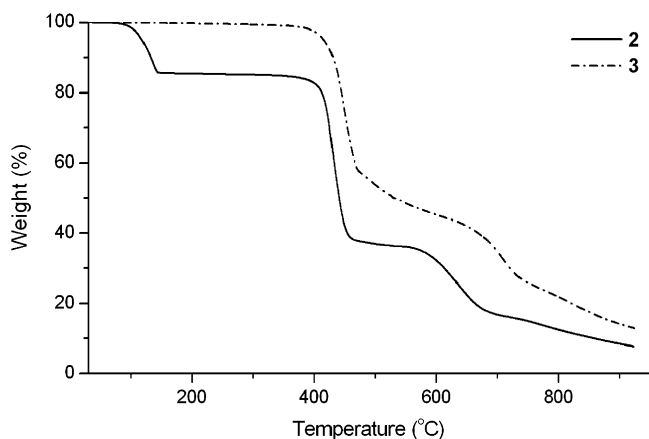


Fig. 6. Thermogravimetric (TG) analysis diagrams of **2** (solid line) and **3** (dash-dot line).

corresponds to the removal of a free DMF molecule per formula unit (calcd. 13.8%). The solvent-free phase,  $[\text{Cd}(\text{BDC})(\text{phen})]$ , subsequently shows no weight loss until the temperature reaches 365 °C. On the other hand, the TG curve for **3** showed that the compound is thermally stable at temperature up to 370 °C, followed by a multi-step decomposition process.

### 3.5. Fluorescent properties of compounds 1–3

The photoluminescent properties of compounds **1–3**, in the solid state, were examined at room temperature and relevant spectra are shown in Fig. 7. The fluorescent emission band for **1** is mainly located at 402 nm with three

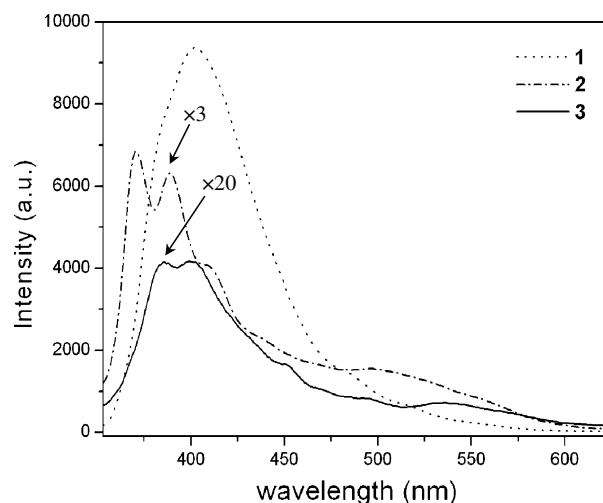


Fig. 7. Photoluminescence spectra of **1–3** in the solid state at room temperature.

shoulder bands at 386, 481, and 508 nm upon excitation at 320 nm. The free 1,10-phenanthroline shows fluorescence emission bands at 365 and 388 nm in the solid state ( $\lambda_{\text{ex}} = 310$  nm), which correspond to  $\pi \rightarrow \pi^*$  transition [15]. Therefore, the strong structureless emission band at 402 nm for **1** is tentatively assigned to the intraligand fluorescence of coordinated phen ligands due to the planar configuration of the excimeric phen molecules maintained by the cadmium metal center [15,20,21]. Compound **2** exhibits structured emission bands at 370, 389, and 405(sh), which are assigned to  $\pi \rightarrow \pi^*$  transition of the coordinated phen ligand, as reported by Qiu and

co-workers [20]. A further weak emission band at 495 nm for **2** may not be related to  $n \rightarrow \pi^*$  transition of the BDC ligand but may simply arise from a charge-transfer transition [22–24], since the free H<sub>2</sub>BDC exhibits only one emission band located at about 390 nm ( $\lambda_{\text{ex}} = 350$  nm) [23]. In the case of **3**, photoluminescence with two main peaks at 386 and 400 nm and several shoulders in the region 450–500 nm, as well as one broad band at 533 nm ( $\lambda_{\text{ex}} = 330$  nm) are observed (Fig. 7). In comparison, the free H<sub>4</sub>btec ligand also shows similar multiple emission bands at 360, 381, 455, and 470 nm with shoulders at 494 and 523 nm upon excitation at 320 nm, which can be attributed to  $n \rightarrow \pi^*$  transition [23]. This indicates that the btec ligands make a significant contribution to fluorescent emission of **3** in addition to that from the coordinated phen ligands. Therefore, the emission bands for **3** are rationally assigned to the combination of strong  $\pi \rightarrow \pi^*$  transition of the coordinated phen ligand [15,20] and weak  $n \rightarrow \pi^*$  transition of the btec ligand.

#### 4. Conclusions

The synthesis of two 2D networks is described. A 1,10-phenanthroline-chelated cadmium metal complex was successfully used as an inorganic subunit to react with polycarboxylate bridging ligands to form 2D coordination polymers in high yields under mildly hydrothermal reaction conditions.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2006.03.078](https://doi.org/10.1016/j.molstruc.2006.03.078).

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