Syntheses, structures, and luminescence of three metal carboxylate polymers of 2,5-dibenzoylterephthalic acid and N-donor auxiliary ligands

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Syntheses, structures, and luminescence of three metal carboxylate polymers of 2,5-dibenzoylterephthalic acid and N-donor auxiliary ligands

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Three coordination polymers, [CdL(2,2′-bpy)] (**1**), [ZnL(phen)$_2$] (**2**), and [ZnL(2,2′-bpy)] (**3**) (H$_2$L = 2,5-dibenzoylterephthalic acid, 2,2′-bpy = 2,2′-bipyridine, and phen = 1,10-phenanthroline), were synthesized and crystallographically characterized. The compounds were further characterized by elemental analyses, FTIR, thermogravimetric analyses, and powder X-ray diffraction. Complex **1** exhibits a 2D sheet structure with (4,4) grid units, while **2** and **3** present infinite 1D zig–zag chain structures. The complexes are all extended into high-dimensional supramolecular networks through intermolecular hydrogen bonds and π–π stacking interactions. A structural comparison of **1**–**3** demonstrates that the characteristics of subsidiary ligands and slight difference in coordination models of L play a very important role in construction of the complexes. Additionally, luminescence of the complexes is also investigated at room temperature.

Keywords: Coordination polymer; 2,5-Dibenzoylterephthalic acid; 2,2′-bpy; Phen; Luminescence

1. Introduction

Coordination polymers have interesting structures and potentially useful properties (e.g. luminescence, catalysis, and magnetism) [1]. Noncovalent interactions, like H-bonds, C–H$\cdots\pi$, and $\pi\cdots\pi$ interactions, are steering forces of molecular self-assembly [2]. Multicarboxylic ligands are widely used in development of networks organized through coordination bonds, hydrogen bonds, and $\pi\cdots\pi$ stacking interactions [3]. Many investigations have paid attention to coordination polymers containing asymmetric rigid benzene polycarboxylates such as 1,2,3-benzenetricarboxylic acid (1,2,3-H$_3$btc) [4], 1,4-benzenedicarboxylic acid [5], 1,3,5-benzenetricarboxylic acid (1,3,5-H$_3$btc) [6], and 1,2,4,5-benzenetetracarboxylic acid (1,2,4,5-H$_4$btc) [7]. Compared with those rigid multicarboxylates 2,5-dibenzoylterephthalic acid, grafting benzoyl on terephthalic exhibits more steric

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hindrance than 1,4-benzenedicarboxylic and the aromatic substituent may rotate around the central phenyl ring. The resulting steric hindrance can play important roles in directing the extended structures of coordination polymers. Structural sophistication can be further enhanced through ancillary co-ligands. The multicarboxylate 2,5-dibenzoylterephthalic acid (Scheme 1) is relatively rare [8]. A series of Sn complexes based on such ligands show discrete mononuclear molecular structures by virtue of terminal ligands that hinder the extension of higher dimensional structures.

To seek possible structural variations and property changes of substituents on mono-aromatic polycarboxylates [9], we introduced 2,2′-bpy and phen (2,2′-bpy=2,2′-bipyridine and phen=1,10-phenanthroline) as auxiliary ligands to adjust the network structure. As a result, [CdL(2,2′-bpy)] (**1**), [ZnL(phen)$_2$] (**2**), and [ZnL(2,2′-bpy)] (**3**) (H$_2$L=2,5-dibenzoylterephthalic acid) with high-dimensional supramolecular networks were obtained via hydrothermal reaction of Cd^{2+} (or Zn^{2+}) salts with 2,2′-bpy and phen. The luminescence of the three compounds is also studied.

2. Experimental

2.1. *Materials and instrumentation*

Reagents were purchased commercially and used without purification. The FTIR spectra were recorded from KBr pellets (4000–400 cm^{-1}) on a Mattson Alpha-Centauri spectrometer. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 2400 Elemental Analyzer. Thermogravimetric analyses (TGA) were investigated on a Netzsch Sta449C thermoanalyzer under N$_2$ with a ramp rate of 5 °C min^{-1}. The fluorescence spectra were obtained using a Cary Eclipse luminescence spectrophotometer (VARIAN, USA). Diamagnetic corrections were estimated from Pascal's constants for all constituent atoms.

2.2. *Syntheses*

2.2.1. Synthesis of [CdL(2,2′-bpy)] (**1**). A mixture of Cd(NO$_3$)$_2$·4H$_2$O (30.8 mg, 0.1 mmol), L (37.4 mg, 0.1 mmol), 2,2′–bpy (15.8 mg, 0.1 mmol), and H$_2$O (15 mL) was stirred for 30 min at room temperature and the pH of the solution was adjusted to 4.5 with 0.1 M NaOH. The mixture was kept stirring for another 30 min, sealed in a 25 mL Teflon-lined stainless steel vessel, heated at 160 °C for 72 h, and then cooled to 40 °C at a rate of 4 °C h^{-1}. Colorless block crystals were obtained after washing with deionized water and drying in air, in ∼61% yield based on cadmium. Elemental analysis (%) calcd for C$_{32}$H$_{20}$CdN$_2$O$_6$ (640.91): C, 59.97; H, 3.15; N, 4.37. Found (%): C, 60.04; H, 3.13; N,
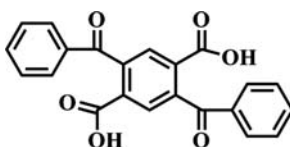
Scheme 1. The structure of 2,5-dibenzoylterephthalic acid.

4.36; IR (KBr pellet, cm^{-1}): 1679 (m), 1665 (s), 1574 (w), 1491 (w), 1478 (s), 1342 (s), 1014 (m), 948 (s), 916 (s), 890 (m), 681 (m), 621 (w).

2.2.2. Synthesis of [ZnL(phen)$_2$] (**2**). A mixture of Zn(NO$_3$)$_2$·4H$_2$O (29.7 mg, 0.1 mmol), L (37.4 mg, 0.1 mmol), 1,10′–phen (39.64 mg, 0.2 mmol), and H$_2$O (15 mL) was stirred for 30 min at room temperature and the pH of the solution was adjusted to 4.0 with 0.1 M NaOH. The mixture was kept stirring for another 30 min, sealed in a 25 mL Teflon-lined stainless steel vessel, heated at 160 °C for 72 h, and then cooled to 40 °C at a rate of 4 °C h^{-1}. Colorless block crystals were obtained after washing with deionized water and drying in air, in ∼56% yield based on zinc. Elemental analysis (%) calcd for C$_{46}$H$_{28}$ZnN$_4$O$_6$ (798.11): C, 69.23; H, 3.54; N, 7.02. Found (%): C, 68.97; H, 3.68; N, 7.04; IR (KBr pellet, cm^{-1}): 1672 (s), 1604 (w), 1550 (m), 1418 (s), 1388 (w), 1255 (m), 1069 (s), 1017 (w), 937 (m), 853 (s), 698 (m).

2.2.3. Synthesis of [ZnL(2,2′-bpy)] (**3**). The procedure is similar to the synthesis of **2** except that 2,2′-bpy (15.8 mg, 0.1 mmol) was used instead of 1,10′-phen. Colorless block crystals were obtained in ∼58% yield based on zinc. Elemental analysis (%) calcd for C$_{32}$H$_{20}$ZnN$_2$O$_6$ (593.89): C, 64.72; H, 3.40; N, 4.72. Found (%): C, 64.46; H, 3.32; N, 4.97; IR (KBr pellet, cm^{-1}): 1670 (m), 1627 (s), 1546 (w), 1449 (s), 1312 (w), 1245 (m), 1175 (w), 1020 (m), 919 (m), 796 (s), 692 (s), 511 (w).

2.3. *X-ray crystallography*

Appropriate colorless block crystals of **1**, **2**, and **3** with dimensions of 0.20 mm × 0.05 mm × 0.05 mm, 0.16 mm × 0.13 mm × 0.10 mm, and 0.16 mm × 0.14 mm × 0.10 mm were attached to a glass fiber for data collections on a SMART (Bruker, 2002) diffractometer equipped with MoKα radiation ($\lambda_1 = 0.71073$ Å, $\lambda_2 = 0.71073$ Å, $\lambda_3 = 0.71073$ Å) at 293(2) K from $1.72° < \theta_1 < 25.00°$, $1.95° < \theta_2 < 25.02°$, and $1.82° < \theta_3 < 25.02°$. Empirical absorption corrections were applied to the data using ABSCOR [12]. The structure was solved by direct methods followed by difference Fourier method and refined by full-matrix least-squares on F^2 using the SHElXTL-97 package [13]. All nonhydrogen atoms were refined anisotropically. The polymer **1** gave $R = 0.0459$ and $wR = 0.1163$ ($w = 1/[\sigma^2(F_0^2)$ + $(0.0918P)^2 + 0.0000P]$, where $P = (F_0^2 + 2F_c^2)/3)$. $GOF = 1.041$, $(\Delta\rho)_{max} = 0.769$, $(\Delta\rho)_{min} = -0.789$e/Å^3 and $(\Delta/\sigma)_{max} = 0.191$. **2** gave $R = 0.0317$ and $wR = 0.0867$ ($w = 1/[\sigma^2(F_0^2)$ + $(0.0505P)^2 + 0.7251P]$, where $P = (F_0^2 + 2F_c^2)/3)$. $GOF = 1.061$, $(\Delta\rho)_{max} = 0.673$, $(\Delta\rho)_{min} = -0.373$e/Å^3 and $(\Delta/\sigma)_{max} = 0.047$. **3** gave $R = 0.0599$ and $wR = 0.1621$ ($w = 1/[\sigma^2(F_0^2) + (0.1245P)^2 + 0.0000P]$, where $P = (F_0^2 + 2F_c^2)/3)$. $GOF = 1.003$, $(\Delta\rho)_{max} = 0.483$, $(\Delta\rho)_{min} = -0.420$e/Å^3 and $(\Delta/\sigma)_{max} = 0.093$. Details of crystal data collection and structure refinements for **1**–**3** are listed in table 1 and selected bond parameters are listed in table 2. In addition, tables 3 and 4 show $\pi\cdots\pi$ interactions in **1** and **2** and hydrogen-bonding geometry parameters for **3**, respectively. The CCDC reference numbers for **1**–**3** are 843,558, 843,560, and 726,169, respectively. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax:+44(1223)336–033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Details of crystal data collection and structure refinement for **1**–**3**.

Polymers	1	2	3
Formula	$C_{32}H_{20}CdN_2O_6$	$C_{46}H_{28}ZnN_4O_6$	$C_{32}H_{20}ZnN_2O_6$
M	640.91	798.11	593.89
Color	Colorless	Colorless	Colorless
Temperature/K	293(2)	293(2)	293(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	$P2_1/c$	P-1
a/Å	10.0065(14)	9.8650(8)	10.3643(18)
b/Å	11.5311(16)	20.8697(17)	11.972(2)
c/Å	12.5543(17)	17.5587(14)	12.052(2)
α/°	70.960(2)	90	109.389(2)
β/°	82.651(2)	101.278(1)	94.847(3)
γ/°	82.555(2)	90	101.401(3)
V/Å^3	1352.1(3)	3545.2(5)	1364.4(4)
Z	2	4	2
ρ_{calcd}/g cm^{-3}	1.574	1.495	1.446
μ/mm^{-1}	0.857	0.754	0.949
$F(0\,0\,0)$	644.0	1640.0	608.0
Crystal size/mm	$0.20 \times 0.05 \times 0.05$	$0.16 \times 0.13 \times 0.10$	$0.16 \times 0.14 \times 0.10$
θ Range/°	1.72–25.00	1.95–25.02	1.82–25.02
Reflections collected	6878	17,631	6858
Independent reflections	4705	6232	4748
R_{int}	0.0276	0.0263	0.0312
GOF on F^2	1.041	1.061	1.003
Final R indices [$I>2\sigma(I)$]	[a]$R_1 = 0.0459$, [b]$wR_2 = 0.1163$	$R_1 = 0.0317$, $wR_2 = 0.0867$	$R_1 = 0.0599$, $wR_2 = 0.1621$
Largest diff. peak and hole/ e·Å^3	0.0641, 0.1481	0.0402, 0.0917	0.0980, 0.2046

[a]$R_1 = \sum ||F_0| - |F_c||/\sum|F_0|$; [b]$wR_2 = \sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]^{1/2}$.

3. Results and discussion

3.1. *Synthesis and IR spectroscopy*

Colorless crystals of **1**–**3** were hydrothermally synthesized by assembly of metal (cadmium and zinc) salt with 2,5-dibenzoylterephthalic acid and co-ligands (phen or 2,2′-bpy) in H_2O, and furthermore, structurally determined by single-crystal X-ray diffraction.

The IR spectra of **1**–**3** exhibit absorptions from 1600–1450 cm^{-1}, ascribed to skeletal vibrations of the aromatic rings. The $v_{as}(COO)$ and $v_s(COO)$ bands at 1665, 1574, 1478, and 1342 cm^{-1} for **1** and 1604, 1550, 1418, and 1388 cm^{-1} for **2,** and 1627, 1546, 1449, and 1312 cm^{-1} for **3** are from carboxylates. The Δv values [$\Delta v = v_{as}(COO) - v_s(COO)$] (187, 232 cm^{-1} in **1** and 178, 234 cm^{-1} in **3**) indicate two different coordination modes of carboxylates of O_2N-btc^{3-} [10]. Absorptions $v_{as}(COO)$ at 1604 and 1550 cm^{-1} and $v_s(COO)$ at 1418 and 1388 cm^{-1} in IR spectra of **2** with Δv values of 186 cm^{-1} and 162 cm^{-1} indicate monodentate and chelating coordination of carboxylates in **2**.

3.2. *Description of the structures*

3.2.1. [CdL(2,2′-bpy)] (**1**). X-ray single-crystal diffraction reveals that **1** contains binuclear Cd(II) with nonbonding Cd···Cd distances of 3.831(7) Å. As shown in figure 1(a),

Table 2.   Selected bond lengths /Å and angles /° for **1–3**.

1

Cd(1)–O(4)	2.324(4)	N(1)–Cd(1)–O(5)#1	83.02(16)
Cd(1)–N(1)	2.337(5)	O(2)–Cd(1)–O(5)#1	86.11(15)
Cd(1)–O(2)	2.347(4)	N(2)–Cd(1)–O(5)#1	120.34(16)
Cd(1)–N(2)	2.371(5)	O(4)–Cd(1)–O(1)	83.86(14)
Cd(1)–O(5)#1	2.385(4)	N(1)–Cd(1)–O(1)	147.97(18)
Cd(1)–O(1)	2.433(4)	O(2)–Cd(1)–O(1)	54.87(15)
Cd(1)–O(4)#1	2.512(4)	N(2)–Cd(1)–O(1)	91.74(19)
O(4)–Cd(1)–N(1)	80.71(16)	O(5)#1–Cd(1)–O(1)	128.97(15)
O(4)–Cd(1)–O(2)	135.63(15)	O(4)–Cd(1)–O(4)#1	75.30(14)
N(1)–Cd(1)–O(2)	143.05(18)	N(1)–Cd(1)–O(4)#1	112.46(16)
O(4)–Cd(1)–N(2)	112.43(16)	O(2)–Cd(1)–O(4)#1	88.10(15)
N(1)–Cd(1)–N(2)	68.9(2)	N(2)–Cd(1)–O(4)#1	172.19(14)
O(2)–Cd(1)–N(2)	86.87(18)	O(5)#1–Cd(1)–O(4)#1	53.28(13)
O(4)–Cd(1)–O(5)#1	113.36(14)	O(1)–Cd(1)–O(4)#1	90.24(15)

2

Zn(1)–O(3)	2.0377(13)	N(1)–Zn(1)–N(4)	159.15(6)
Zn(1)–O(1)	2.0636(13)	O(3)–Zn(1)–N(2)	170.97(6)
Zn(1)–N(1)	2.1711(17)	O(1)–Zn(1)–N(2)	95.22(6)
Zn(1)–N(4)	2.1930(17)	N(1)–Zn(1)–N(2)	75.34(6)
Zn(1)–N(2)	2.2332(17)	N(4)–Zn(1)–N(2)	89.58(6)
Zn(1)–N(3)	2.2939(17)	O(3)–Zn(1)–N(3)	90.72(6)
O(3)–Zn(1)–O(1)	92.22(6)	O(1)–Zn(1)–N(3)	175.20(6)
O(3)–Zn(1)–N(1)	99.08(6)	N(1)–Zn(1)–N(3)	89.36(6)
O(1)–Zn(1)–N(1)	93.92(6)	N(4)–Zn(1)–N(3)	74.15(6)
O(3)–Zn(1)–N(4)	93.90(6)	N(2)–Zn(1)–N(3)	82.22(6)
O(1)–Zn(1)–N(4)	101.84(6)		

3

Zn(1)–O(3)	1.914(4)	O(3)–Zn(1)–O(2)	106.75(17)
Zn(1)–N(2)	2.048(5)	N(2)–Zn(1)–O(2)	129.19(18)
Zn(1)–N(1)	2.067(5)	N(1)–Zn(1)–O(2)	91.90(17)
Zn(1)–O(2)	2.114(4)	O(3)–Zn(1)–O(1)	109.67(18)
Zn(1)–O(1)	2.193(4)	N(2)–Zn(1)–O(1)	93.89(17)
O(3)–Zn(1)–N(2)	123.7(2)	N(1)–Zn(1)–O(1)	138.99(18)
O(3)–Zn(1)–N(1)	107.49(19)	O(2)–Zn(1)–O(1)	61.25(15)
N(2)–Zn(1)–N(1)	79.4(2)		

Symmetry transformations used to generate equivalent atoms: #1 −x+1,−y, −z+1; #2 −x+1, −y, −z+2; #3 −x+2, −y, −z+1 for **1**.

Table 3.   π···π Interactions in **1** and **2**.

Complex	Two rings	Symmetry code	Centroid-to-centroid distance (Å)
1	Cg(2)>Cg(2)	1−x, 1−y, 1−z	3.5999
2	Cg(11)>Cg(12)	x, 1/2−y, −1/2+z	3.5722

Complex	Dihedral angle (°)	Perpendicular distance of Cg(I) on ring J (Å)	Perpendicular distance of Cg(J) on ring I (Å)
1	0	3.546	3.546
2	2.66	3.361	3.411

Cg(2): N(2)>C(28)>C(29)>C(30)>C(31)>C(32) Cg(11): C(26)>C(27)>C(28)>C(29)>C(30)>C(31) Cg(12): C(38)>C(39)>C(40)>C(41)>C(42)>C(43).

Cd1 lies at an inversion center in a pentagonal bipyramidal environment, seven-coordinate by five oxygens from three L1 (Cd–O 2.325(4)–2.511(4) Å) and two nitrogens (Cd–N

Table 4. Hydrogen-bonding parameters (Å, °) for **3**.

D−H⋯A	d(D−H)	d(H⋯A)	d(D⋯A)	∠ (DHA)
C(14)−H(14)⋯O(5)	0.93	2.39	3.1811	143.57

2.337(5)–2.371(5) Å) from two 2,2′-bpy ligands. In **1**, two Cd1 ions are linked by a μ^2:η^1:η^2-L, resulting in a binuclear [Cd$_2$(COO)$_2$] building unit; binuclear units are further connected by four L1 to construct a 2D layer [figure 1(b)] with 36-membered macrocyclic rings. The 2D layer shows large rhombic (4,4) grids with approximate size of 15.617 × 14.460 Å^2. Consequently, a 3D supramolecular framework is formed in **1** through π⋯π interactions between two benzene rings of 2,2′-bpy. The centroid to centroid distances between the benzene rings are 3.599 Å (table 3).

3.2.2. [ZnL(phen)$_2$] (**2**). Compound **2** crystallizes in monoclinic space group $P2_{(1)}$/c with a zinc ion, a L, and two phen in the asymmetric unit. Zn1 displays octahedral geometry surrounded by two oxygens (Zn–O 2.0636(13)–2.0377(13) Å) from two bridging L and four chelating nitrogens (Zn–N 2.1710(18)–2.2938(17) Å) from different phen ligands. Each Zn(II) is further connected via L to generate a 1D zig–zag chain structure [figure 2(b)] and also, show π–π interactions between arene cores of adjacent phen from a neighboring chain (3.572(2) Å) [figure 2(c)] (table 3).

3.2.3. [ZnL(2,2′-bpy)] (**3**). When phen was replaced by 2,2′-bpy, a different 2D net was formed in **3**. The structure of **3** is a 1D zig–zag chain and crystallizes in the triclinic space group P-1. The asymmetric unit of **3** is composed of one Zn(II), one 2,2′-bpy, and one L. Each Zn(II) is five-coordinate by three oxygens (Zn–O 1.914(4)–2.193(4) Å) from one chelating and one bridging L and two nitrogens (Zn–N 2.067(5)–2.048(5) Å) from a chelating 2,2′-bpy. Each Zn(II) is linked to adjacent Zn(II) through bridging L which adopts a chelating and bridging coordination mode alternately forming a unique 1D zig–zag chain structure [figure 3(b)], and the 1D zig–zag chains are extended into a 2D structure via hydrogen bonds (C(14)−H(14)⋯O(5) 2.390 Å, C(14)−H(14)⋯O(5) 143.57°) [figure 3(c)] (table 4).

3.3. *Thermal stability*

TGA measurements are performed for crystalline samples of **1–3** from 25–900 °C in N$_2$ at a heating rate of 5 °C min^{-1}. A weight loss at 280–420 °C corresponds to release of the organic groups and the remaining product is CdO (obsd. 21.90%, Calcd 20.00%) for **1**. Complex **2** begins to decompose at 300 °C and ends above 490 °C, attributed to loss of organic ligands. The remaining weight (Obsd. 11.15%) indicates that the final product is ZnO (Calcd 10.20%). Complex **3** is stable to 320 °C and then, the organic groups decompose gradually from 320 to 540 °C, with the remaining product ZnO (Obsd. 14.10%, Calcd 13.70%) (Supplementary material).
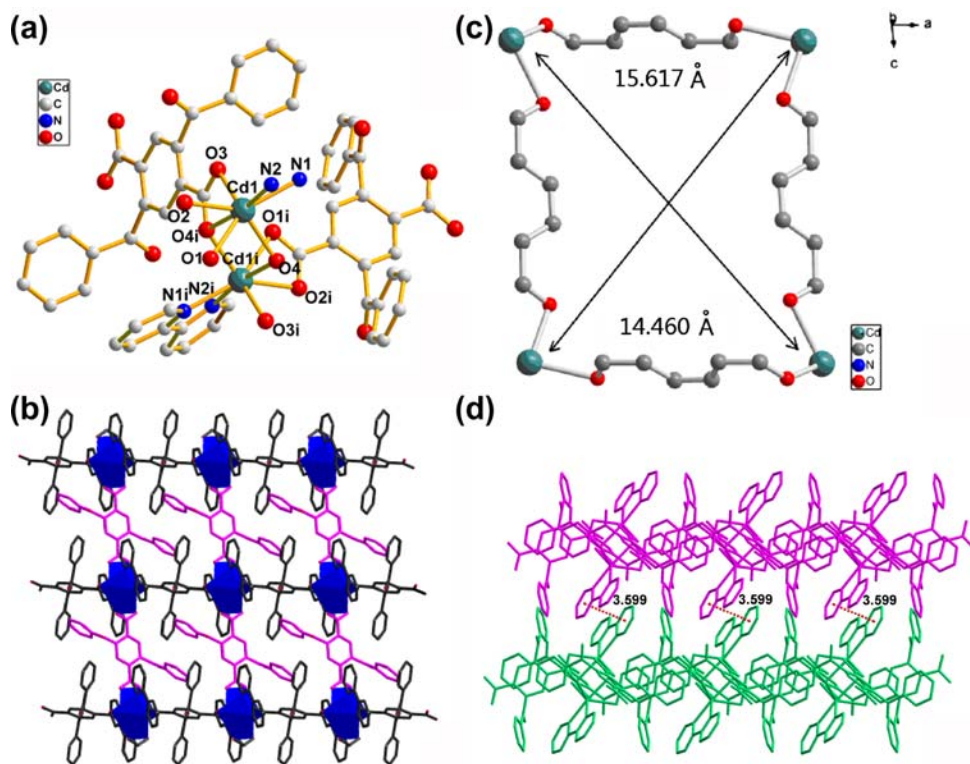
Figure 1. (a) Coordination environments of cadmium(II) centers in **1**. Hydrogens are omitted for clarity. Symmetry codes: $i = -x + 1, -y, -z + 1$. (b) Views showing the (4,4) networks formed by connecting the clusters with L linkers. (c) The Cd···Cd distances in the 36-membered macrocyclic ring. (d) Perspective view of abutting layers. Hydrogen bonds are indicated by dotted lines.

3.4. *The powder X-ray diffraction analysis (PXRD)*

In order to check phase purity of the complexes, powder X-ray diffraction (PXRD) patterns of **1**–**3** were determined at room temperature. The peak positions of the measured PXRD patterns are in agreement with patterns simulated from single-crystal data for the three compounds, confirming the good phase purity of the samples (Supplementary material).

3.5. *Luminescent property*

The solid-state photoluminescence spectra of **1**–**3** and L were measured at room temperature as depicted in figure 4. All of the measurements were performed at excitation wavelength 380 nm. L displays a strong emission peak at 472 nm, while **1**–**3** exhibit intense emission at 425 nm, 420 nm, and 457 nm, respectively [11]. These emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT), since it is difficult to oxidize or reduce Zn(II) and Cd(II). Compared with L, the significantly shifted emissions for **1**–**3** may be attributed to deprotonation of the ligand and the coordination interaction between L and the metal cations (Zn^{II}/Cd^{II}) [11].
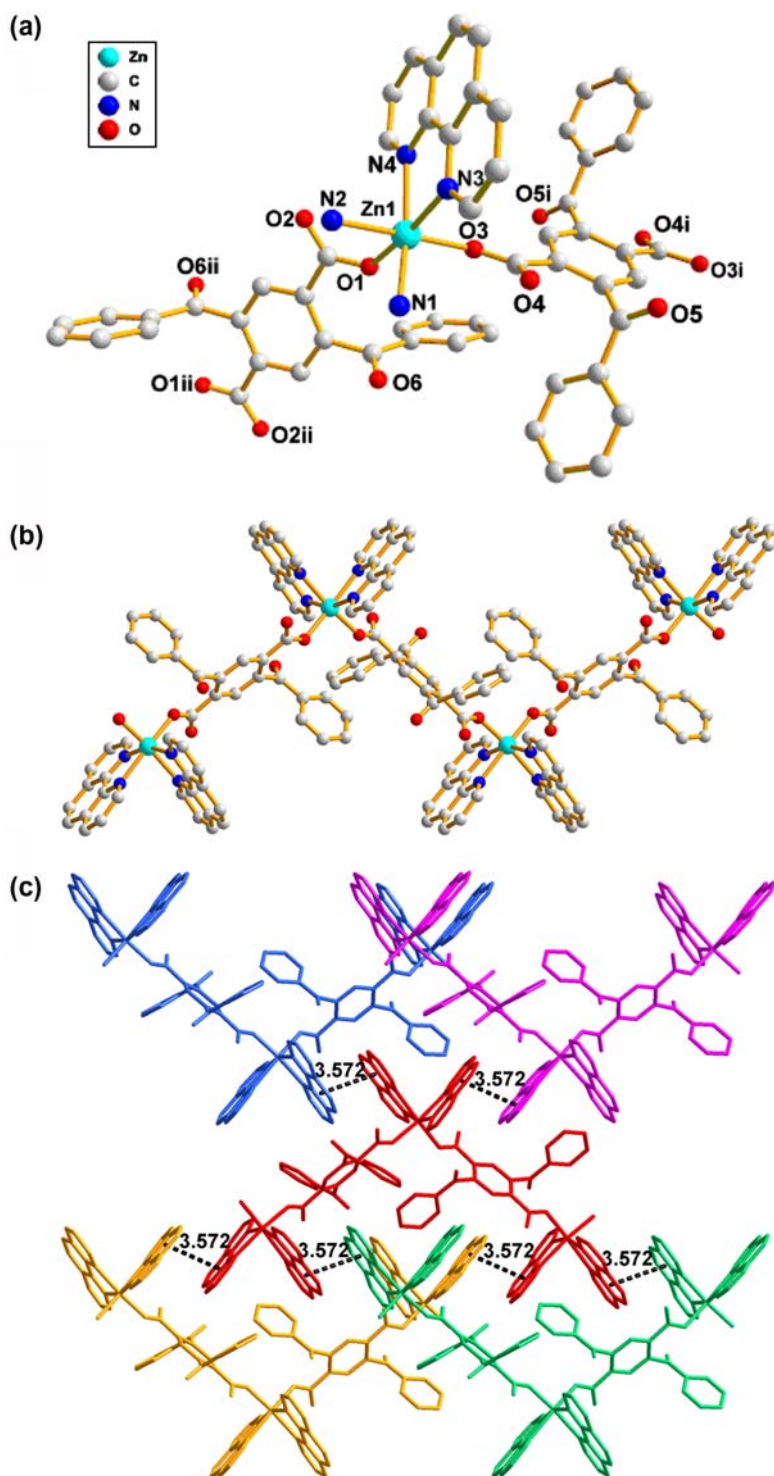
Figure 2. (a) Coordination environments of zinc(II) centers in **2**. Hydrogens are omitted for clarity. Symmetry codes: $i = -x+1, -y+1, -z+2$; $ii = -x, -y+1, -z+1$. (b) The 1D polymeric structure of **2**. (c) Perspective view of abutting chains; hydrogen bonds are indicated by dotted lines.

Figure 3. (a) Coordination environments of Zn(II) in **3**. Hydrogens are omitted for clarity. Symmetry codes: i = – x + 2, −y, −z; ii = −x + 1, −y + 1, −z + 1. (b) The 1D polymeric structure of **2**. (c) Perspective view of abutting chains. Hydrogen bonds are indicated by dotted lines.
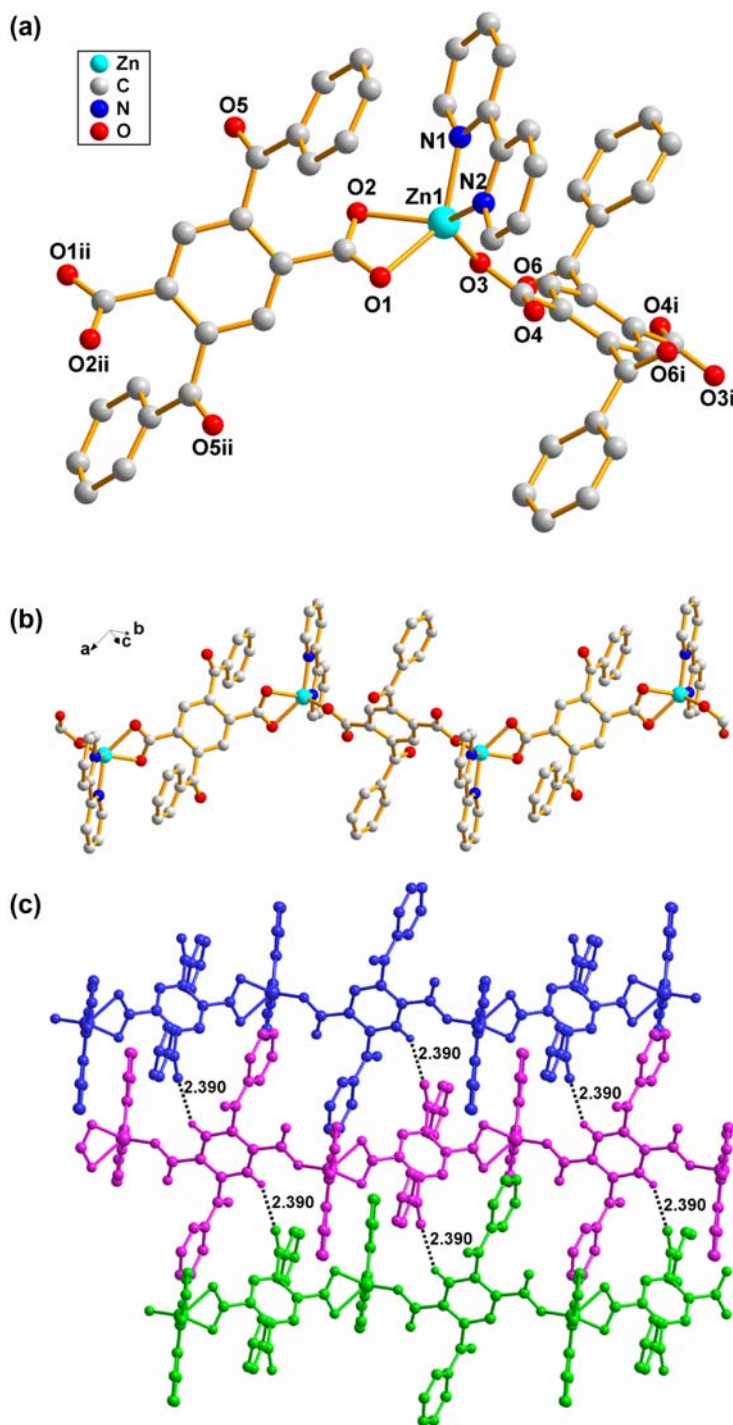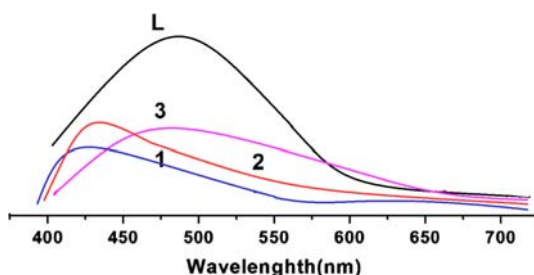
Figure 4. The emission spectra of **1**–**3** and L at room temperature.

4. Conclusion

Three new coordination polymers containing 2,5-dibenzoylterephthalic acid and 2,2′-bpy or phen with Zn^{II} and Cd^{II} have been hydrothermally prepared and isolated. Comparing the three Zn^{II} and Cd^{II} complexes with previously reported similar ones containing Zn^{II} and Cd^{II} metals [14] indicates that *p*-benzenedicarboxylates, rather than *o*- and *m*-ones, have the innate ability to provide a 3D structure with or without auxiliary ligands. Thus, terminal ligands phen and 2,2′-bipy are utilized to tailor the preferential 3D structures to generate low-dimensional structures and one 2D and two zig–zag ones as expected. The compounds display different photoluminescent properties influenced by structures and bridging modes. Comparison of the crystal structures of **1**–**3** demonstrates that both the multicarboxylate and the chelate ligands are efficient for construction of high-dimensional supramolecular structures based on noncovalent interactions (π–π and C–H$\cdots\pi$). It is challenging to further research 2,5-dibenzoylterephthalic acid or more auxiliary ligands which may result in high-dimensional frameworks.

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