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Hydrothermal synthesis, crystal structure and luminescence of four novel metal–organic frameworks

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Abstract

Using the principle of crystal engineering, four novel metal–organic coordination polymers, $\{[Cd_1(nic)2(H_2O)]2[Cd_2(nic)2(H_2O)2]\}_n$ (1), $[Cd_2(fma)2(phen)2]_n$ (2), $[Cd(fma)(bipy)(H_2O)]_n$ (3) and $[Zn(mal)(bipy)\cdot 3H_2O]_n$ (4) (nic = nicotinate, fma = fumarate, mal = malate, phen = phenanthroline, bipy = 2,2′-bipyridine) have been synthesized by hydrothermal reaction of $M(CH_3COO)2\cdot 2H_2O$ (M = Zn, Cd) with nicotinic acid, fumaric acid and cooperative L (L = phen, bipy), respectively. X-ray analysis reveals that complex 1 possesses an unprecedented two-dimensional topology structure constructed from three-ply-like layers, complex 2 is an infinite 2D undulating network, complex 3 is a 1D zigzag chain and complex 4 belongs to a 1D chain. The results indicate a transformation of fumarate into malate during the course of hydrothermal treatment of complex 4. The photophysical properties have been investigated with luminescent excitation and emission spectra.

Keywords: Metal–organic coordination polymer; Crystal structure; Hydrothermal; Luminescence

1. Introduction

Transition metal–organic frameworks (MOFs), which are diverse in structure and property, are currently attracting increasing attention not only owing to their fascinating applications in the areas of catalysis, co-operative magnetic behavior, non-linear optical activity and electrical conductivity, but also to their interesting topologies [1–9]. To exquisitely design the MOFs from transition metals and organic ligands with novel architectures and desired functionalities by using of the principles of crystal engineering has been one of the most challenging subject in coordination chemistry areas today [10,11].

One of the efficient routes to coordination polymers is to employ a multifunctional ligand to link metal ions to give an infinite framework. The flexible carboxylic acids are good candidates for the construction of novel metal–organic complexes: the carboxyl groups can form C–O–M–O four-member ring structure with central metal ions improving the stability of transition MOFs; they can act not only as a hydrogen-bond acceptor but also as a hydrogen-bond donor to generate supramolecular topology; the pyridine–carboxylic acids have two types of coordinating atoms (N and O) exhibiting a strong tendency to coordinate to transition metal ions since most of transition metal ions are borderline acids; the dicarboxylic acids have two carboxyl groups that may be completely or partially deprotonated, inducing rich coordination modes and many interesting structures with higher dimensions. There are a large amounts of MOFs constructed from carboxylate acids having been reported [12–17].

In addition, the hydrothermal method is effective to the crystal growth of many coordination polymers. Under hydrothermal conditions, the properties of the reactants and the interactions between organic and inorganic partners are quite different from those under conventional conditions in water. Therefore, various simple precursors and metastable compounds may be produced by hydrothermal reactions, and it facilitates crystal growth from solution [18–20]. Taking advantage of the interesting properties of carboxylic acid and hydrothermal reaction,

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we present the synthesis, structural characterization, and luminescent properties of four novel carboxylate coordinated transition MOFs.

2. Experimental section

2.1. Preparation of complexes

$Zn(CH_3COO)_2 \cdot 2H_2O$, $Cd(CH_3COO)_2 \cdot 2H_2O$, nicotinic acid and fumaric acid were purchased from Aldrich and used without further purification. All the other reagents were commercially available and used as received.

$\{[Cd^1(nic)_2(H_2O)]_2[Cd^2(nic)_2(H_2O)_2]\}_n$ (1): Nicotinic acid (1 mmol) and $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.5 mmol) were mixed in 15 mL deionized water. After stirring half an hour, the mixture was placed in 25 mL Teflon-lined reactor and heated at 160 °C in an oven for 4 d. The resulting solution was cooled slowly to room temperature; the light colorless single crystals of title complex suitable for X-rays four-circle diffraction analysis were obtained. Yield: 64%. Anal. Calcd for $C_{18}H_{16}Cd_{1.50}N_3O_8$: C, 37.83; H, 2.80; N, 7.36%; Found: C, 37.75; H, 2.87; N, 7.28%.

$[Cd_2(fma)_2(phen)_2]_n$ (2): Fumaric acid (1 mmol), phen (1 mmol) and $Cd(CH_3COO)_2 \cdot 2H_2O$ (1 mmol) were mixed in 15 mL deionized water. After stirring half an hour, the mixture was placed in 25 m· Teflon-lined reactor and heated at 160 °C in an oven for 4 d. The resulting solution was cooled slowly to room temperature; the light colorless single crystals of title complex suitable for X-rays four-circle diffraction analysis were obtained. Yield: 72%. Anal. Calcd for $C_{32}H_{20}Cd_2N_4O_8$: C, 47.21; H, 2.46; N, 6.89%; Found: C, 47.14; H, 2.51; N, 6.79%.

$[Cd(fma)(bipy)(H_2O)]_n$ (3): Fumaric acid (1 mmol), bipy (1 mmol) and $Cd(CH_3COO)_2 \cdot 2H_2O$ (1 mmol) were mixed in 15 mL deionized water. After stirring half an hour, the mixture was placed in 25 mL Teflon-lined reactor and heated at 160 °C in an oven for 4 d. The resulting solution was cooled slowly to room temperature; the light colorless single crystals of title complex suitable for X-rays four-circle diffraction analysis were obtained. Yield: 86%. Anal. Calcd for $C_{14}H_{12}CdN_2O_5$: C, 41.93; H, 3.00; N, 7.00%; Found: C, 41.87; H, 3.12; N, 6.95%.

$[Zn(mal)(bipy) \cdot 3H_2O]_n$ (4): Fumaric acid (1 mmol), bipy (1 mmol) and $Zn(CH_3COO)_2 \cdot 2H_2O$ (1 mmol) were mixed in 15 mL deionized water. After stirring half an hour, the mixture was placed in 25 mL Teflon-lined reactor and heated at 160 °C in an oven for 4 d. The resulting solution was cooled slowly to room temperature; the light colorless single crystals of title complex suitable for X-rays four-circle diffraction analysis were obtained. Yield: 76%. Anal. Calcd for $C_{14}H_{18}N_2O_8Zn$: C, 41.21; H, 4.42; N, 6.87%; Found: C, 41.07; H, 4.49; N, 6.75%.

2.2. Measurements and apparatus

Elemental analyses (C, H, N) were determined with an *Elementar Cario EL* elemental analyzer. IR spectra were recorded with a *Nicolet Nexus 912 AO446* spectrophotometer (KBr pellet), 4000–400 cm^{-1} region. The luminescence (excitation and emission) spectra for the solid complex samples were determined with a Perkin–Elmer LS-55 spectrophotometer, whole excitation and emission slit width were 10 and 5 nm, respectively.

2.3. Crystal structure determination

X-ray single-crystal diffraction data for complexes **1–4** were performed with graphite-monochromated Mo$K\alpha$ radiation (λ 0.71073 Å). Reflection was collected with a Bruker SNART APEX detector. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. The hydrogen atoms were added geometrically and not refined. All calculations were performed using SHELXS-97 and SHELXL-97 [21,22]. A summary of crystallographic data and refinement parameters are given in Table 1.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited into the Cambridge Crystallographic Data center as supplementary publication no. CCDC-288902 for complex **1**, CCDC-288901 for complex **2**, CCDC-288900 for complex **3** and CCDC-273873 for complex **4**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Description of crystal structure

(a) $\{[Cd^1(nic)_2(H_2O)]_2[Cd^2(nic)_2(H_2O)_2]\}_n$ (1). A single-crystal X-ray analysis reveals that complex **1** is an unprecedented two-dimensional topology structure constructed from three-ply-like layers. The structure contains two crystallographically unique cadmium centers. The Cd^1 center is seven-coordinated by five oxygen atoms and two nitrogen atoms, and the coordination geometry of Cd^1 center can be described as a distorted monocapped octahedral coordination geometry. Among above-mentioned oxygen atoms, four are from four different nicotinate anions with a Cd1–O3 distance of 2.487(3) Å, a Cd1–O4 distance of 2.361(3) Å, a Cd1–O5 distance of 2.348(3) Å and a Cd1–O6 distance of 2.530(3) Å; another one is from one coordinated water molecule with a Cd1–O7 distance of 2.298(4) Å. The two nitrogen atoms locating at neighboring positions are from two different nicotinate anions with a Cd1–N1 distance of 2.422(4) Å, a Cd1–N2 distance of 2.394(4) Å and and a N1–Cd1–N2 angle of 86.08(12)°. The Cd^2 center is six-coordinated with two nitrogen atoms and two oxygen atoms from four different nic anions and two oxygen atoms from two coordinated water molecules, and the coordination geometry of Cd^2 center can be described as a light-distorted octahedral

Table 1
Crystal data and structure refinement for complexes **1**, **2**, **3** and **4**

Complex	Complex 1	Complex 2	Complex 3	Complex 4
Formula	$C_{18}H_{16}Cd_{1.50}N_3O_8$	$C_{32}H_{20}Cd_2N_4O_8$	$C_{14}H_{12}CdN_2O_5$	$C_{14}H_{18}N_2O_8Zn$
Relative molecular weight M	570.94	813.32	400.66	407.67
Temperature	298(2) K	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Radiation	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$
Crystal system	P2(1)/c	P2(1)/c	Pbca	P2(1)/c
Space group	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Unit dimensions	$a = 11.813(4)$ Å $b = 8.191(3)$ Å $c = 20.167(7)$ Å $\beta = 95.316(5)°$	$a = 11.180(4)$ Å $b = 20.111(7)$ Å $c = 13.894(5)$ Å $\beta = 107.582(4)°$	$a = 9.148(2)$ Å $b = 16.268(4)$ Å $c = 19.862(5)$ Å	$a = 7.063(5)$ Å $b = 19.956(13)$ Å $c = 11.765(7)$ Å $\beta = 92.443(9)°$
Volume	1943.0(12) Å^3	2978.0(18) Å^3	2955.8(13) Å^3	1656.9(18) Å^3
Z	4	4	8	4
Calculated density	1.952 mg/m^3	1.814 mg/m^3	1.801 mg/m^3	1.634 mg/m^3
F(000)	1124	1600	1584	840
Θ range for data collection	1.92–27.14°	1.84–27.01°	2.05–27.01°	2.01–26.01°
Reflections/collected/unique	9432/4213 [R(int) = 0.0655]	14643/6463 [R(int) = 0.0334]	13693/3213 [R(int) = 0.0351]	7490/3256 [R(int) = 0.0301]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4213/4/293	6463/0/434	3213/2/207	3256/9/254
Goodness-of-fit on F^2	0.804	0.991	0.958	1.035
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0380$, w$R2 = 0.0648$	$R1 = 0.0360$, w$R2 = 0.0820$	$R1 = 0.0272$, w$R2 = 0.0613$	$R1 = 0.0374$, w$R2 = 0.0883$
Largest diff. peak and hole	1.296 and −0.820 eÅ^{-3}	1.208 and −0.687 eÅ^{-3}	0.773 and −0.412 eÅ^{-3}	0.561 and −0.298 eÅ^{-3}

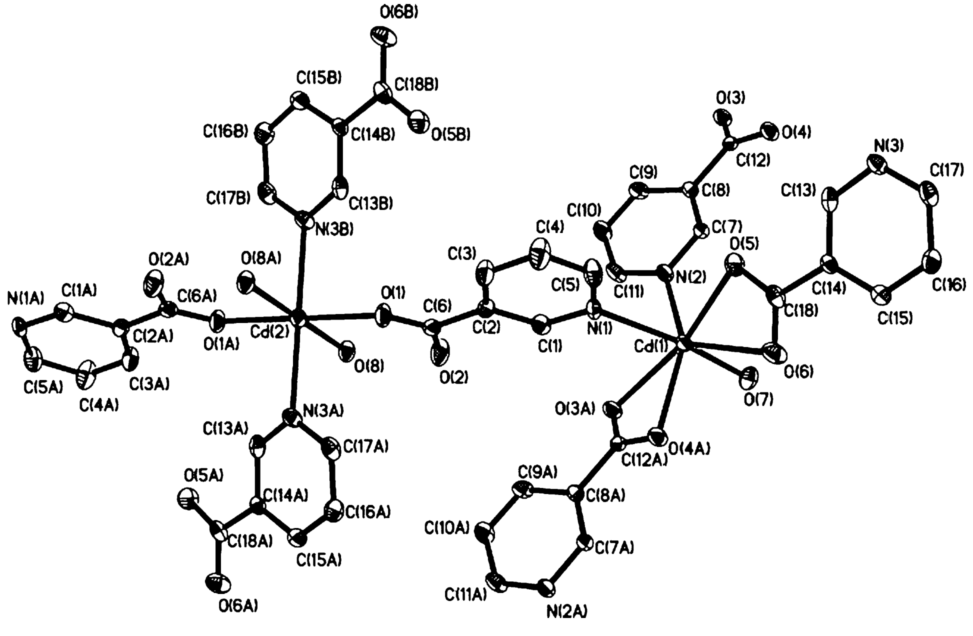


Fig. 1. The ORTEP drawing for complex **1**.

coordination geometry. Especially, O2 and O2(A), O8 and O8(A), N3 and N3(A) locate at the opposite respectively for the O2–Cd–O2(A), O8–Cd–O8(A) and N3–Cd–N3(A) bonds are completely linearity. In addition, the distance of Cd2–O2, Cd2–O8, Cd2–N3 are 2.268(3), 2.381(4) and 2.328(4) Å, respectively. Fig. 1 gives the ORTEP drawing of the coordination environments around the cadmium centers in complex **1**. The selected bond lengths and angles for complexes **1**, **2**, **3** and **4** are listed in Table 2.

The carboxylate groups adopt the bidentate- and tridentate-bridging coordination fashion, and there are three coordination modes of nic anions existing in the structure: (a) The nic anion acts as bridging-bidentate ligand towards Cd centers with pyridine nitrogen atom connecting Cd^1 center and the carboxylate connecting Cd^2 center, and the distance of $Cd^1 \cdots Cd^2$ is 8.9175(23) Å; (b) the nic anion acts as bridging-tridentate ligand towards Cd centers with pyridine nitrogen atom connecting

Table 2
Selected bond distances (Å) and bond angles (⊕) for complexes **1**, **2**, **3** and **4**

(**1**)		(**2**)	
Cd(1)–O(7)	2.298(4)	Cd(1)–O(1)	2.295(2)
Cd(1)–O(5)	2.348(3)	Cd(1)–O(6)	2.326(3)
Cd(1)–O(4)^a	2.361(3)	Cd(1)–N(2)	2.342(3)
Cd(1)–N(2)	2.394(4)	Cd(1)–O(5)	2.355(3)
Cd(1)–N(1)	2.422(4)	Cd(1)–N(1)	2.367(3)
Cd(1)–O(3)^a	2.487(3)	Cd(1)–O(3)	2.395(2)
Cd(1)–O(6)	2.530(3)	Cd(1)–O(2)	2.702(3)
Cd(1)–C(12)^a	2.752(5)	Cd(2)–O(4)	2.250(3)
Cd(2)–O(1)^b	2.268(3)	Cd(2)–O(7)	2.255(11)
Cd(2)–O(1)	2.268(3)	Cd(2)–O(1)	2.313(2)
Cd(2)–N(3)^c	2.328(4)	Cd(2)–N(4)	2.331(3)
Cd(2)–N(3)^d	2.328(4)	Cd(2)–N(3)	2.352(3)
Cd(2)–O(8)^b	2.381(4)	Cd(2)–O(8)	2.439(8)
Cd(2)–O(8)	2.381(4)	Cd(2)–O(3)	2.801(7)
O(7)–Cd(1)–O(5)	104.79(13)	O(1)–Cd(1)–O(5)	153.87(11)
O(7)–Cd(1)–N(2)	84.82(12)	O(6)–Cd(1)–O(5)	55.51(11)
O(5)–Cd(1)–N(2)	83.72(12)	N(2)–Cd(1)–N(1)	71.08(10)
O(7)–Cd(1)–N(1)	164.12(12)	O(1)–Cd(1)–O(3)	82.28(9)
O(5)–Cd(1)–N(1)	87.09(12)	O(6)–Cd(1)–O(3)	80.54(10)
N(2)–Cd(1)–N(1)	86.08(12)	O(5)–Cd(1)–O(3)	104.83(10)
O(4)–Cd(1)–O(3)	54.07(10)	O(4)–Cd(2)–O(1)	91.88(10)
O(5)–Cd(1)–O(6)	53.47(11)	O(7)–Cd(2)–O(1)	94.3(3)
N(2)–Cd(1)–O(6)	128.96(12)	N(4)–Cd(2)–N(3)	71.61(10)
N(1)–Cd(1)–O(6)	114.24(12)	O(7)–Cd(2)–O(8)	54.6(3)
(**3**)		(**4**)	
Cd(1)–O(5)	2.300(2)	Zn(1)–O(5)^a	1.971(2)
Cd(1)–N(2)	2.336(2)	Zn(1)–O(1)	2.037(2)
Cd(1)–O(2)	2.347(2)	Zn(1)–N(1)	2.072(3)
Cd(1)–N(1)	2.365(2)	Zn(1)–O(3)	2.093(2)
Cd(1)–O(4)^a	2.3948(19)	Zn(1)–N(2)	2.106(3)
Cd(1)–O(3)^a	2.410(2)		
O(5)–Cd(1)–O(4)^a	99.02(8)	O(5)^a–Zn(1)–O(1)	98.20(11)
O(2)–Cd(1)–O(4)^a	83.95(7)	O(1)–Zn(1)–N(1)	95.22(9)
O(5)–Cd(1)–O(3)^a	81.98(8)	O(5)^a–Zn(1)–O(3)	97.09(11)
O(2)–Cd(1)–O(3)^a	138.20(7)	O(1)–Zn(1)–O(3)	77.38(8)
O(4)^a–Cd(1)–O(3)^a	54.26(6)	N(1)–Zn(1)–O(3)	122.35(9)
O(2)–Cd(1)–O(1)	53.76(7)	O(1)–Zn(1)–N(2)	163.71(10)
N(2)–Cd(1)–N(1)	70.00(8)	N(1)–Zn(1)–N(2)	78.00(9)

Symmetry transformations used to generate equivalent atoms:
For complex **1**: ^{a}: x, $y-1$, z; ^{b}: $-x+2$, $-y$,$-z$; ^{c}: $-x+1$, $-y+1$, $-z$; ^{d}: $x+1$, $y-1$, z.
For complex **3**: ^{a}: $-x$, $y-1/2$, $-z+1/2$.
For complex **4**: ^{a}: $x-1$, y, z.

Cd^2 center and the carboxylate connecting Cd^1 center, and the distance of neighboring Cd$^1\cdots$Cd^2 is 7.9108(18) Å; (c) the nic anion acts as bridging-tridentate ligand towards two Cd^1 centers with pyridine nitrogen atom connecting Cd^2 center and the carboxylate connecting Cd^1 center, and the distance of Cd$^1\cdots$Cd^1 is 8.191(3) Å. Its interesting that carboxyl oxygen atoms adopt only the bidentate-chelating coordination mode to Cd^1 centers and only monodentate mode to Cd^2 centers.

An important feature of complex **1**, which does not occur in other MOF structures to our best knowledge, is that complex **1** possesses an unprecedented two-dimensional topology structure constructed from three-ply layers, the detailed links can be described stepwise: Cd^1 centers are linked by bridging nic(c) ligands to form two types of opposite directional chains along the *b*-axis, and then these discrete chains are further cross-linked into two layers paralleling to the *ab* plane by nic(a)$_2$-Cd^2-nic(b)$_2$ groups, while the plane forming by Cd^2 centers is sandwiched in the interlayer regions of the two Cd^1-planes alternately along the *c*-axis (Fig. 2). In the three-ply-like layer, the nic(a)$_2$-Cd^2-nic(b)$_2$ groups act as an important role, all Cd^1-chains are linked by them via a nic(a)$_2$-Cd^2-nic(b)$_2$ group connecting four chains. Very intriguingly, a careful examination shows that there exist two types of helical chains formulated [Cd^1-nic(a)-Cd^2-nic(a)-Cd^1]$_n$ and [Cd^1-nic(b)-Cd^2-nic(b)-Cd^1] in the interlayer regions, those chains are interlaced to give honeycomb-like motifs (Fig. 3). In addition, all three-ply like layers are further linked by interlayer hydrogen bonds with both the coordinated water molecules of Cd^1 and Cd^2 serving not only as donors but also acceptors. The interlayer hydrogen bonds are in a novel alternate fashion, and consolidate the stacked arrangement leading to a 3D supramolecular architecture.

(b) [Cd$_2$(fma)$_2$(phen)$_2$]$_n$ (2). A single-crystal X-ray analysis reveals that complex **2** is a 2D undulating network. In the asymmetric unit of complex **2**, there are two cadmium atoms, two fma ligands, and two phen ligands (Fig. 4). The Cd1 center is seven-coordinated by two nitrogen atoms and five oxygen atoms, and the coordination geometry of Cd1 center can be described as a distorted monocapped octahedral coordination geometry. Among above-mentioned oxygen atoms, three are from two different μ_2-O carboxylate groups with a Cd1–O1 distance of 2.295(2) Å, a Cd1–O2 distance of 2.702(3) Å and a Cd1–O3 distance of 2.395(2) Å; other two oxygen atoms are from one chelating carboxylate group with a Cd1–O5 distance of 2.355(3) Å, a Cd1–O6 distance of 2.326(3) Å and a O5–Cd1–O6 angle of 55.51(11)°, respectively. The two nitrogen atoms are from the cooperative phen ligand with Cd1–N1 distance of 2.3675(3) Å, a Cd1–N2 distance of 2.342(3) Å and a N1–Cd1–N2 angle of 71.08(10)°, respectively. Here, we consider that O2 is coordinated to Cd1 center despite Cd1–O2 is much longer than Cd1–O1 because the μ_2-O coordination mode of carboxyl is very steady and the Cd1–O2 distance 2.702(3) Å is within reasonable range of M(metal)–O bonds. The coordination environment of Cd2 is the same as that of Cd1 while the distances of Cd2–O and Cd2–N are little shorter than corresponding Cd1 bonds.

All fma molecules are protonated and taken part in the coordination to the Cd centers, and there are two coordination modes of fma anions existing in the structure: (1) the fma ligand contains two chelating bidentate carboxylate groups towards two Cd centers (Fig. 5a); (2) the fma ligand contains two bridging tridentate μ_2-O carboxylate groups towards four Cd centers (Fig. 5b). Two distorted octahedrons, which are separately formed by Cd1 and Cd2, are bridged by two μ_2-O carboxylate groups from two different fma ligands to generate a double cadmium

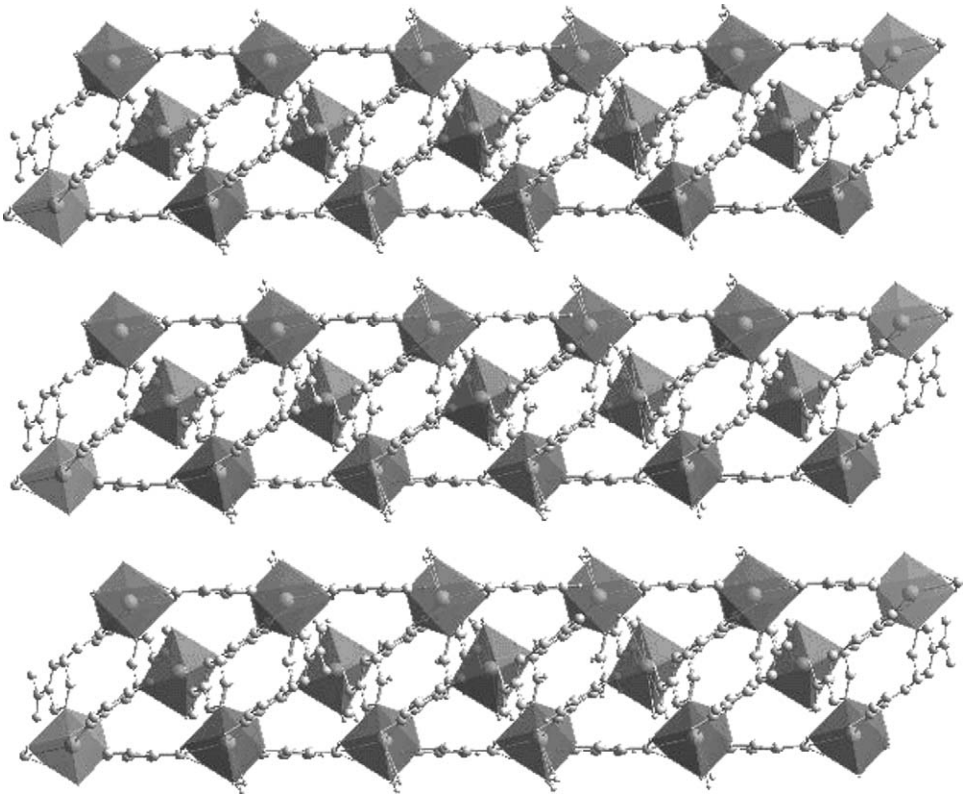


Fig. 2. Viewed along the *a*-axis: the three-ply-like structure for complex **1**.

Fig. 3. The helical chains in the three-ply layer. For clarity, only Cd centers and nicotinate ligands are shown.

cluster, the distance of Cd1···Cd2 is 3.7563 (14) Å. The bimetallic units are each linked by mode (1) and mode (2) ligands to form two type chains, respectively. All chains are further across linked into a 2D undulating network along the *ac* plane (Fig. 6). It's interesting that in the undulating network, there are distorted rectangular pores with sides of 12.051, 12.450, 8.377 and 8.598 Å, respectively (based on the Cd···Cd distance), which are enclosed by four bimetallic units, two mode (1) and two mode (2) fma ligands.

Commonly, the multicarboxylate MOFs always show the 2D or 3D structure. In order to obtain the one-dimensional complexes, one approach is to introduce the terminal ligands such as 2,2′-bipyridine or phen into the carboxylate system because the terminal ligands reduce the available metal–ion binding sites to interdict polymer growth in other directions [23,24]. Many metal–organic polymers containing mixed ligands of multicarboxylate and 2,2′-bipyridine or phen show 1D structure [25–29]. Interestingly, complex **2** shows a 2D structure despite one phen terminal ligand is coordinated to Cd center.

Previously, the Cd complex $[Cd_2(fma)_2(phen)_2]_n$ has been reported, which shows the same structural formula but different from complex **2** [30]. In the citing structure, both Cd1 and Cd2 centers are six-coordinated with two nitrogen atoms and four oxygen atoms, and the coordination geometry of which can be described as a distorted octahedral geometry. Especially, fma ligands exhibit three coordination modes (Fig. 6c), and only the mode (I) is appeared in complex **2**.

In the structure of complex **2**, the aromatic π–π stacking interactions can be found. In the bimetallic unit, the plane–plane distance between two adjacent phen ligands is 3.562 Å, and the plane–plane distance between two adjacent phen ligands from two neighboring undulating layers is 3.732 Å (Fig. 7). Both of two distances are within reasonable ranges, so there exist two type π–π stacking interactions in the structure, intralayer and interlayer π–π stacking interactions, they act as an importance role in the formation of the bimetallic unit and 2D network, respectively. The π–π stacking interactions are in a novel alternate fashion, and consolidate the stacked arrangement leading to a 3D supramolecular architecture.

(c) $[Cd(fma)(bipy)(H_2O)]_n$ (3). A single-crystal X-ray analysis reveals that complex **3** is a zigzag 1D polymeric coordination chain. In the asymmetric unit of complex **3**, there are one cadmium atom, one fumaric ligand, one coordinated water molecule and one bipy ligand (Fig. 8). The Cd center is seven-coordinated by two nitrogen atoms and five oxygen atoms, and the coordination geometry of

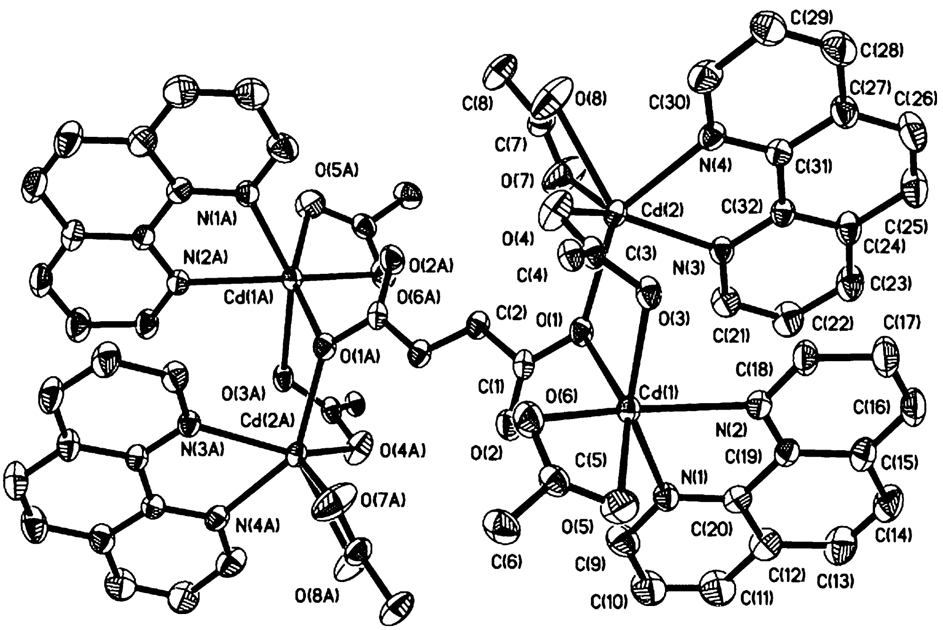


Fig. 4. The ORTEP drawing for complex **2**.

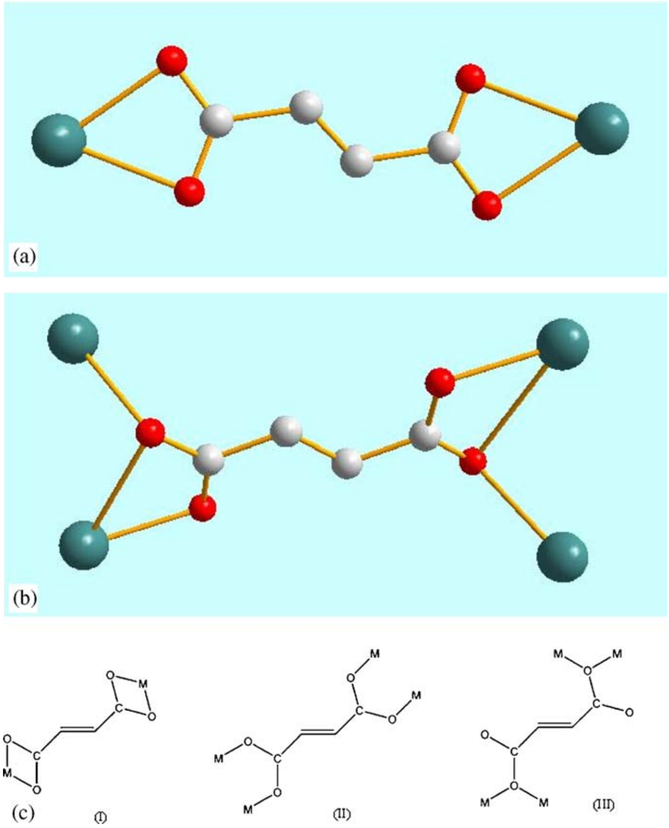


Fig. 5. The coordination mode of fma ligands.

Cd center can be described as a distorted monocapped octahedral coordination geometry. Among above mentioned oxygen atoms, four are from two different chelating carboxylate groups with a Cd–O1 distance of 2.447(2) Å, a Cd1–O2 distance of 2.347(2) Å, a Cd1–O3 distance of 2.410(2) Å, a Cd1–O4 distance of 2.3948(19) Å, a O1–Cd–O2 angle of 53.76(7)° and a O3–Cd–O4 angle of 54.26(6)°; another one oxygen atoms is from one coordinated water molecule with a Cd1–O5 distance of 2.300(2) Å. The two nitrogen atoms (N1, N2) are from the cooperative phen ligand with Cd1–N1 distance of 2.3675(3) Å, a Cd1–N2 distance of 2.342(3) Å and a N1–Cd1–N2 angle of 70.00(8)°, respectively.

For complex **3**, fma ligand shows one coordination mode alike mode(1) of complex **1**, Cd centers are linked into a zigzag chain with a Cd···Cd distance of 9.2033(18) Å (Fig. 9). The bipy planes are coordinated with Cd centers in a chelating fashion, and the benzene rings are on two sides of the one-dimensional alternately. In addition, the coordinated water molecule causes strong O–H···O hydrogen bonds existing in the structure: the oxygen atom with hydrogen atoms (O5–H5) of water molecule can form O–H···O hydrogen bonds (O5–H5···O2, O5–H5···O4) with the carboxylate oxygen atoms (O2, O4) from neighboring zigzag chain. The O–H···O hydrogen bonds are in a novel alternate fashion, and consolidate the stacked arrangement leading to a 3D supramolecular architecture.

(d) [Zn(mal)(bipy)·3H_2O]$_n$ (4). A single-crystal X-ray analysis reveals that complex **4** is a 1D chian-like supramolecular framework constructed from the connections of Zn(II) ions and malate ligands alternately along the a axis. The least asymmetric unit of complex **4** contains one zinc atom, one malate ligand, one bipy ligand and three lattice water molecules (Fig. 10). Each Zn ion is five-coordinated by two nitrogen atoms and three oxygen atoms, and the coordination geometry of Zn center can be described as a distorted trigonal bipyramidal coordination geometry. Among above mentioned five coordination

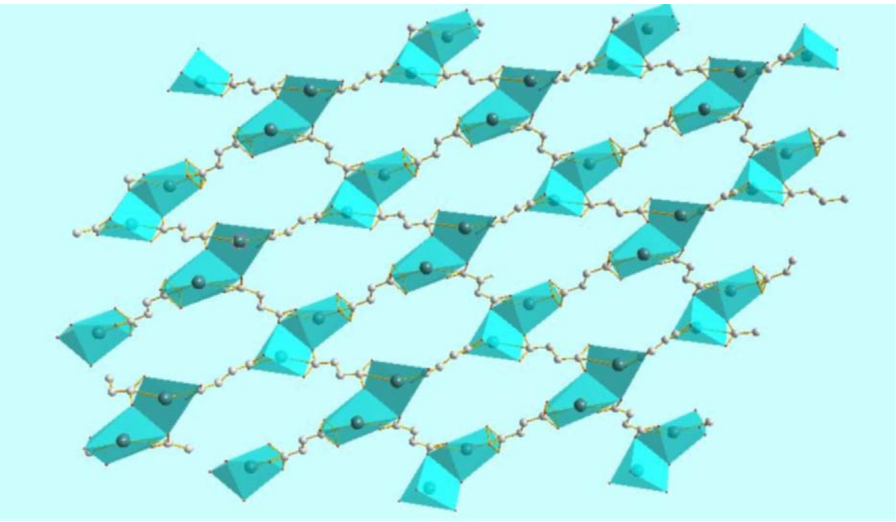


Fig. 6. The 2D undulating network drawing for complex **2**.

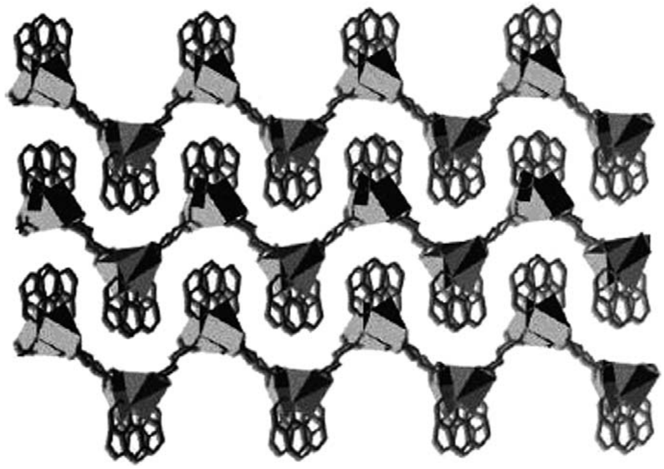
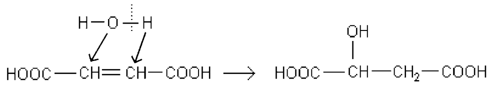


Fig. 7. View of the packing structure of the 2D undulating network along the (100) direction.

atoms, the two nitrogen atoms are from one bipy ligand with a Zn1–N1 distance of 2.072(3) Å, a Zn1–N2 distance of 2.106(3) Å, and a N1–Zn1–N2 angle of 78.00(9)°, respectively; One oxygen atom is from the birdging carboxylate groups with a Zn1–O5 distance of 1.971(2) Å; Especially, the oxygen atom of hydroxyl and one oxygen atom of the birdging carboxylate groups are coordinated to Zn(II) ion forming a pentacircle with a Zn1–O3 distance of 2.093(2) Å and a Zn1–O1 distance of 2.037(2) Å, a O1–Zn1–O3 angle of 77.38(8)°, respectively.

Interestingly, although fumaric acid was used as the original organic reagent in the preparation of the title complex the malate ligand was unexpectedly found in the final products, which indicates a transformation of fumarate into malate during the course of hydrothermal treatment. In literature, the ligation of the metal ion will cause some decrease of electron density on the unsaturated chemical bonds of the organic ligands under hydrothermal conditions, hence promote nucleophilic attack by water molecules or hydroxy groups [31]. In this case, it seems most probable that the solvent aqua molecules act effectively as nucleophiles, attacking the ethylenic carbon atoms of fumaric acid. As a result, the hydration of ethylenic linkage groups of fumarates furnishes the malate ligand. Here we give the reaction scheme:



$$\mathrm{HOOC{-}CH{=}CH{-}COOH} \xrightarrow{} \mathrm{HOOC{-}\overset{OH}{CH}{-}CH_2{-}COOH}$$

It is worthy pointing out that the transformation of fumarate into malate only happened in the course of hydrothermal treatment of complex **4**, in spite of the similar reactant and reaction conditions comparing with complexes **2** and **3**. As previous report, the similar occurrence is also found in the hydrothermal synthetic course of complex $[\mathrm{Zn(mal)(phen)}]_n$ [32], all these indicates that Zn^{2+} affects unsaturated C=C bond more than Cd^{2+}. The reason maybe is that the ionic radius of Zn^{2+} is 0.74 Å and ionic radius of Cd^{2+} is 0.97 Å, therefore zinc ion is easier to approach the C=C (1.34 Å) bond.

The malate ligand exhibits the tridentate-bridging coordination mode towards the Zn centers, since five-member ring is stable than four-member ring, the hydroxyl oxygen atom coordinating metal ions is chose, the Zn centers are connect into a one-dimensional chain-like structure by such mode (Fig. 11). Unlike complex **3**, the bipy planes are on one side of the one-dimensional chain paralleling each other.

The existence of three water molecules causes a lot of the hydrogen bonding in the structure, and there exist four types of O–H⋯O intermolecular hydrogen bonds: one is the O–H⋯O intermolecular hydrogen bonding between the oxygen atoms of the lattice water molecules and the uncoordinated oxygen atoms of the bridging carboxylic groups, the bond angle of which is 174(7)°

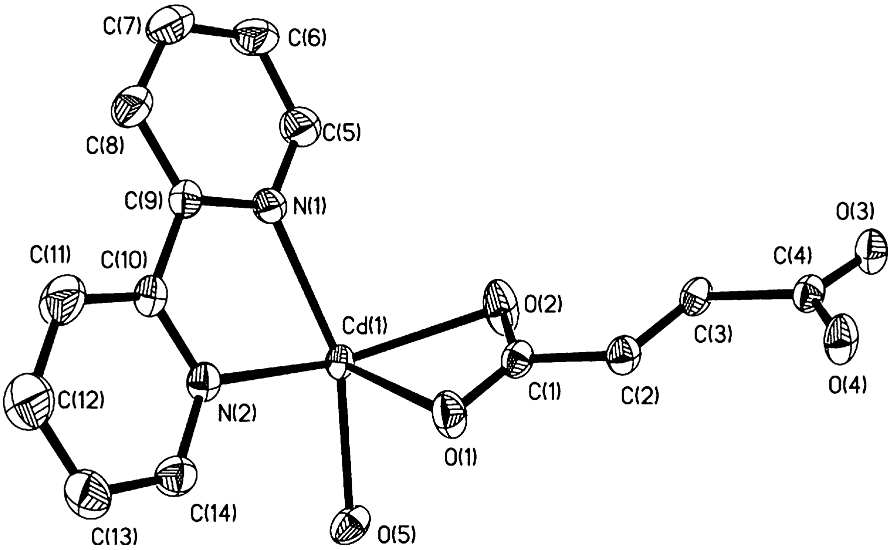


Fig. 8. The ORTEP drawing for complex **3**.

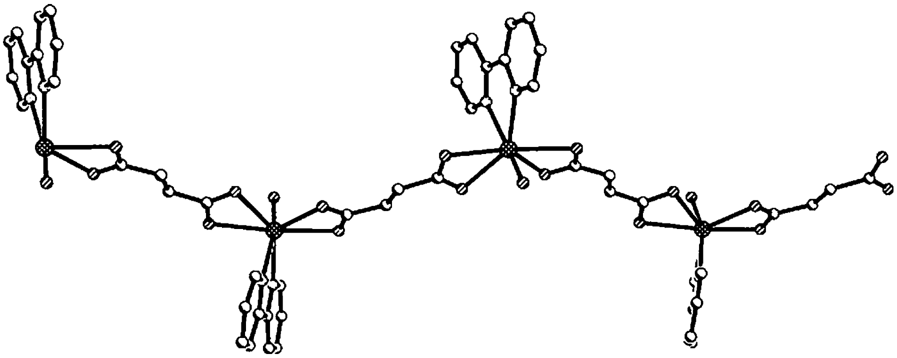


Fig. 9. The zigzag chain of complex **3**.

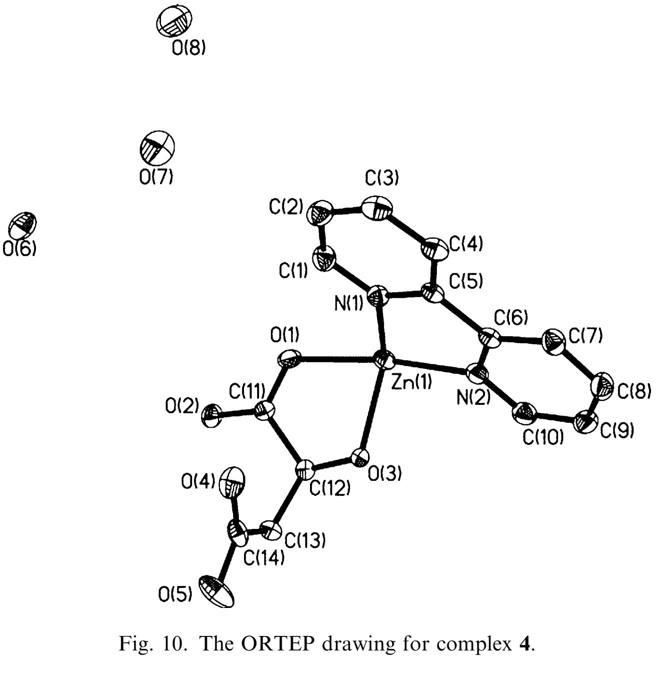


Fig. 10. The ORTEP drawing for complex **4**.

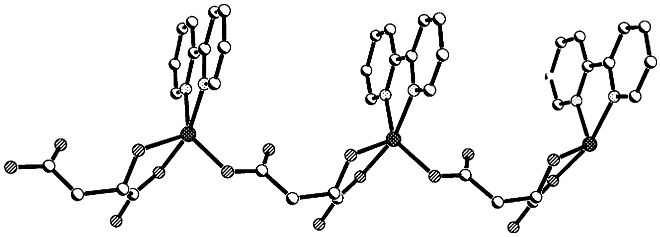


Fig. 11. The 1D chain of complex **4**.

(O8–H8B···O4^{c}); the second is the O–H···O intermolecular hydrogen bonding between the lattice water molecules, the bond angle of which are 155(6)° (O6–H6B···O8^{d}), 118(17)° (O8–H8A···O6^{e}), 162(5)° (O7–H7B···O6^{f}), 160(6)° (O7–H7A···O7^{c}), respectively; the third is the O–H···O intermolecular hydrogen bonding between the oxygen atoms of the lattice water molecules and the coordinated oxygen atoms of the bridging carboxylic groups, the bond angle of which is 169(5)° (O6–H6A···O1^{g}); the last is the O–H···O intermolecular hydrogen bonding between the coordinated oxygen atoms of the bridging carboxylic groups and the uncoordinated oxygen atoms of the bridging carboxylic groups, the bond angle of which is 168(4)° (O3–H3A⋯$O2^h$). The interchain hydrogen bonds are in a novel alternate fashion, and consolidate the stacked arrangement leading to a 3D supramolecular architecture.

3.2. *Luminescent properties of four MOFs*

All complexes **1**–**4** exhibit intense blue photoluminescence upon the radiation of UV light in the crystalline state at room temperature. The excitation band of complex **1** under the emission wavelength 440 nm possesses one main peak at 300 nm. The emission spectrum under the excitation wavelength 300 nm shows a broad band mainly ranging from 400 to 550 nm, and the maximum emission wavelength is at 437 nm. We further measured the emission spectrum of the free nicotinic acid molecules, which shows one emission at 390 nm, indicating that the nicotinate ligand has no emission in the visible region but when it is bound to a cadmium center, blue luminescence is observed, as shown in Fig. 12a. The lower energy band presumably may be ascribed to the smaller electronic delocalization (the electrostatic force between Zn^{2+} and O^{2-}) which cause the pyridine circle of ligands is more conjugated, and the observed luminescence of the complex is attributed to the coordinated nicotinate ligand [33].

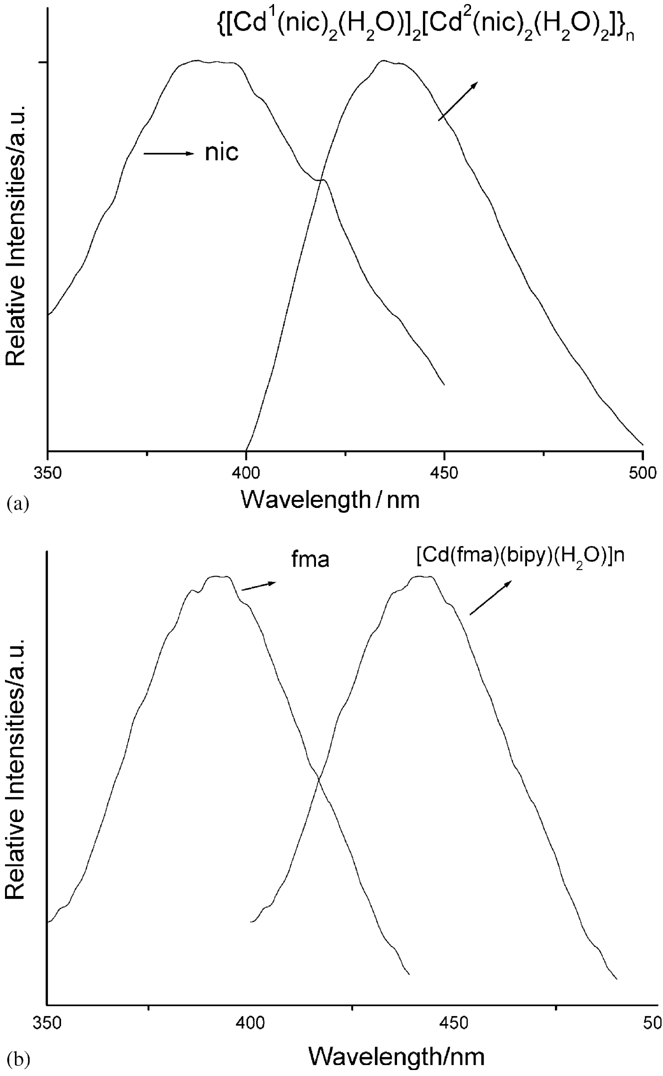


Fig. 12. Luminescent emission spectra of complexes **1** and **3**.

Complexes **2**–**4** are similar to complex **1**. The emission spectra of them shows a broad band mainly ranging from 400 to 500 nm with the maximum emission wavelength is at 440, 443 and 443 nm, respectively. In addition, the emission spectrum of the free fumaric acid molecules shows one emission at 392 nm. The emission spectrum of complex **3** is shown in Fig. 12b. Since hydrothermal products are usually stable and insoluble in common solvents arising from their polymeric structures, those complexes may be potential candidates for photoactive materials.

Acknowledgments

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