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# Hydrogen bonded supra-molecular framework in inorganic–organic hybrid compounds: Syntheses, structures, and photoluminescent properties

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# HIGHLIGHTS

▶ Two cadmium complexes were prepared and characterized by IR, X-ray diffraction and TGA techniques.

▶ The two complexes show distorted octahedral geometries.

▶ Different intermolecular interactions lead to various crystalline aggregates in 1–2.

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# ABSTRACT

Two novel compounds constructed from aromatic acid and *N*-Heterocyclic ligands have been synthesized by hydrothermal reaction:  $[Cd(mip)(1,8-NDC)(H_2O)]_2$  (1) [mip = 2-(3-methoxyphenyl)-1H-imidazo[4,5-f] [1,10]phenanthroline, 1,8-NDC = naphthalene-1,8-dicarboxylic acid] and  $Cd(mip)_2(NTC)_2$  (2) [NTC = nicotinic acid]. Compounds 1 and 2 are characterized by elemental analysis, IR, single crystal X-ray diffraction and thermogravimetric analysis (TGA). Single-crystal X-ray investigation reveals that compounds 1–2 are 0 dimensional (0D) structures, and the existence of hydrogen bonds and  $\pi$ - $\pi$  interactions lead the 0D to 2D novel framework. Hydrogen bonds and  $\pi$ - $\pi$  interactions are powerful non-covalent intermolecular interactions for directing supra-molecular architectures. TG analysis shows clear courses of weight loss, which corresponds to the decomposition of different ligands. At room temperature, compound 1 exhibits emission at 449 nm upon excitation at 325 nm, and compound 2 shows a strong emission at 656 nm upon excitation at 350 nm. Fluorescent spectrum displays that compounds 1 and 2 are potential luminescent materials.

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1. Introduction

The design and construction of metal-organic frameworks (MOFs) has become a very attractive research field. The motive comes not only from the interesting network topologies, but also from the demand for potential applications as catalysis, porosity, sensors, magnetism, luminescence, molecular recognition, nonlinear optics and electrical conductivity [1–7]. In this regard, much progress has been made on the design and synthesis of novel coordination frameworks and the relationships between their structures and properties. Therefore, systematic research on this topic is still very necessary and important. However, rational design and controllable preparation of metal-organic coordination polymers still remains a long-term challenge for the chemists. The structures of coordination polymers are determined by several

\* Corresponding author. Tel.: +86 15844440698. *E-mail address:* yanli820618@163.com (L. Yan). factors, such as the coordination nature of metal ions, ligand structures, pH value, the counter anion, temperature [8]. Generally, there are two different types of interactions: covalent bonds and non-covalent interactions, which can be used to construct varied supramolecular architectures. To date, relatively less attention has been given to non-covalent interactions, although, noncovalent interactions can be one of the most powerful force for instructing and directing the supramolecular architectures [9-12]. Select suitable multi-dentate ligands such as polycarboxylate and N-heterocyclic ligands is a successful approach to design and controlled synthesis of coordination polymers. Multi-carboxylate ligands have been demonstrated as top-rank candidates, because of their versatile coordination modes and strong coordination ability, for the formation of 1D, 2D or 3D frameworks. However, naphthalene-1,8-dicarboxylic acid (1,8-NDC) and nicotinic acid (NTC) are rarely reported, which inspirits our interest in it. NTC ligand exhibits strong coordination ability and different kinds of coordination modes. It possesses





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donor nitrogen atom and carboxylate oxygen atom simultaneously in the structure of NTC, which can be used as excellent ligand to construct intriguing structural topologies. As for the N-heterocyclic ligands, the chelating ligands 2-(pyridin-2-yl) pyridine, 4-(pyridin-4-yl) pyridine, 1,10-phenanthroline, and their substituted derivatives have played an important role in the construction of coordination polymers. In this paper, we synthesize a novel *N*-heterocyclic ligand: 2-(3-methoxyphenyl)-1H-imidazo[4,5-f] [1,10] phenanthroline (mip) in view of the following characteristics: (1) it possesses extended long-conjugated unsymmetrical aromatic system to provide supramolecular interactions; (2) it has two nitrogen atoms, which is similar with 2,2'-bipyridyl-like bidentate chelating molecules; (3) it is a planar rigid bidentate chelating ligand, which can provide supramolecular interactions such as aromatic stacking to construct intriguing structures; and (4) it possesses strong coordination ability[13]. The synthesis of mip is shown in Scheme 1.

For the past several years, we have worked on the synthesis of the mip similar ligands [14–16]. However, the investigation for this type of *N*-heterocyclic ligands is not enough. In this paper, we design and synthesize two novel Cd(II) coordination polymers, namely: [Cd(mip)(1,8-NDC)(H<sub>2</sub>O)]<sub>2</sub> **1**, and Cd(mip)<sub>2</sub>(NTC)<sub>2</sub> **2**. Non-covalent intermolecular interactions (coordination bonds, hydrogen bonds and  $\pi$ – $\pi$  interactions) play an important role in the architectures, which favor construction of higher dimensional super-molecular framework and reinforce the structural stability. The research shows that **1** and **2** are good luminescent material.

# 2. Experimental section

#### 2.1. Materials

The ligands mip was prepared according to the description in the literature procedures [17]. The metallic salt, 1,8-NDC, NTC and NaOH, were purchased commercially and used without further purification.

#### 2.2. Physical measurements

The FT-IR spectrum was measured with KBr pellets in the range of 4000–400 cm<sup>-1</sup> on a Perkin–Elmer 240C spectrometer. TGA was performed using a Perkin–Elmer TG-7 analyzer at the rate of 10 °C/ min rise of temperature in nitrogen atmosphere. Crystal structures were determined on a Bruker SMART APEX II CCD X-ray diffractometer. Carbon, hydrogen and nitrogen Elemental analyses were performed with a PE-2400 elemental analyzer. <sup>1</sup>H NMR spectra of mip ligand was carried out with Bruker AV 300 MHz spectrometers and chemical shifts are referenced to internal TMS. UV–Vis spectra were obtained on a JASCO V-570 spectrometer.

#### 2.3. Syntheses

Ligand mip: A mixture of 3-methoxybenzaldehyde, 1,10-phenanthroline-5,6-dione (0.525 g, 2.5 mmol), ammonium acetate (3.88 g, 50 mmol) and glacial acetic acid was refluxed for 4 h, then cooled to room temperature. Yellow precipitate was obtained when addition of concentrated aqueous ammonia to neutralize, which was collected and washed with water. The crude product dissolved in ethanol was purified by filtration on silica gel. The principal yellow band was obtained. Then evaporation of the solution gave yellow products. Yield 0.57 g, 70%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 3.25 (s, 3H, CH<sub>3</sub>–O–Ar), 3.58 (s, 1H, NH), 6.73–7.65 (m, 4H, Ar–H), 7.90–9.10 (m, 6H, aromatic protons in the moiety of phenanthroline, Ar–H).

[Cd(mip)(1,8-NDC)(H<sub>2</sub>O)]<sub>2</sub> (**1**): A mixture of mip (0.100 g, 0.3 mmol), Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.098 g, 0.3 mmol), 1,8-NDC (0.130 g, 0.6 mmol) in distilled H<sub>2</sub>O (18 mL) was stirred at room temperature and adjusted the pH value to about 7.0 with NaOH. We put the cloudy solution into a 30-mL Teflon-lined stainless vessel at 170 °C for 3 days and afterwards cooled to room temperature at a rate of 5 °C/h. The yellow crystals of compound **1** were obtained in 71% yield based on Cd. C<sub>64</sub>H<sub>44</sub>Cd<sub>2</sub>N<sub>8</sub>O<sub>12</sub>: calcd. C 57.28, H 3.30, N 8.35%; found: C 56.69, H 3.11, N 8.39%. IR (KBr, cm<sup>−1</sup>): 3139(s), 1621(vs), 1559(vs), 1384(vs), 1226(s), 1050(s), 843(s), 520(m), 419(m).

Cd(mip)<sub>2</sub>(NTC)<sub>2</sub> (**2**): A mixture of mip (0.100 g, 0.3 mmol), Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.098 g, 0.3 mmol), NTC (0.073 g, 0.6 mmol) in distilled H<sub>2</sub>O (18 mL) was stirred at room temperature and adjusted the pH value to about 7.0 with NaOH. We put the cloudy solution into a 30-mL Teflon-lined stainless vessel at 170 °C for 3 days. The reaction was cooled to room temperature at a rate of 5 °C/h, and then small yellow crystals of compound **2** were collected in 89% yield based on Cd. C<sub>52</sub>H<sub>36</sub>CdN<sub>10</sub>O<sub>6</sub>: calcd. C 61.87, H 3.59, N 13.87%; found: C 61.69, H 3.11, N 13.92%. IR (KBr, cm<sup>-1</sup>): 1600(vs), 1390(vs), 1241(s), 1058(s), 706(m), 542(m).

#### 2.4. X-ray crystallography

Single-crystal X-ray diffraction data for compounds **1** and **2** were collected at 292(2) K with a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K in the range of  $1.67 \le \theta \le 26.07^{\circ}$  for **1** and  $1.46 \le \theta \le 26.04^{\circ}$  for **2**. Absorption corrections were applied using multi-scan technique and all the structures were solved by direct methods and refined by full-matrix least-squares based on  $F^2$  using the programs SHELXS-97 [18] and SHELXTL-97 [19]. Non-hydrogen atoms were refined with anisotropic temperature parameters and all hydrogen atoms were refined isotropically. Experimental details for crystallographic data and structure refinement parameters for compounds **1** and **2** are listed in Table 1.



Scheme 1. The synthesis of mip ligand.

Table	1
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Crystal data and details of structure refinement parameters for **1** and **2**.

Compound	1	2
Empirical formula	$C_{64}H_{44}Cd_2N_8O_{12}$	C <sub>52</sub> H <sub>36</sub> CdN <sub>10</sub> O6
Formula weight	1341.89	1009.31
Crystal system	triclinic	orthorhombic
Space group	P-1	pbcn
<i>a</i> (nm)	1.11999(4)	1.53142(1)
<i>b</i> (nm)	1.17767(5)	1.10794(1)
<i>c</i> (nm)	1.39283(6)	2.7814(3)
β(0)	71.1350(10)	90
Volume (nm <sup>3</sup> )	1.59567(1)	4.7193(9)
Ζ	1	4
Density (Mg/m <sup>3</sup> ) (calculated)	1.396	1.421
Absorption coefficient (mm <sup>-1</sup> )	0.731	0.525
F(000)	676	2056
Crystal size (mm <sup>3</sup> )	$0.45\times0.30\times0.21$	$0.53 \times 0.38 \times 0.21$
Theta range (o)	1.67 to 26.07	1.46 to 26.04
Reflections collected	8831	27912
Unique reflections (R <sub>int</sub> )	6247 [0.0123]	4658 [0.0592]
Goodness-of-fit on $F^2$	1.121	1.034
Final R indices $(I > 2\sigma)$	R1 = 0.0771	R1 = 0.0563
	wR2 = 0.2581	wR2 = 0.1472
R indices (all data)	R1 = 0.0829wR2 = 0.2672	R1 = 0.0865 wR2 = 0.1678
Largest difference peak and hole $(e \text{ Å}^{-3})$	4.223, -0.585	1.596, -0.241

#### 3. Results and discussion

#### 3.1. Structural analysis of compound 1

The molecular structure is shown in Fig. 1. The 1 D chain structure is shown in Fig. 2, and the 2D layer structure is suggested in Fig. 3. Selected bond lengths and bond angles are given in Table 2.

Single-crystal X-ray structural analysis reveals that the asymmetric unit of compound **1** contains two Cd(II) atoms, two mip ligands, two 1,8-NDC ligands and two lattice H<sub>2</sub>O molecules. The Cd(II) atom is hexa-coordinated with two nitrogen atoms (N(1), N(2)) from one chelating mip ligand and four oxygen atoms ((O(1W) from one lattice water molecule, O(1), O(2) from one chelating bidentate 1,8-NDC, O(3A) from another distinct bridging monodentate 1,8-NDC ligand). For the coordination environment of Cd(1), the Cd(1), O1W, O1, N1, N2 atoms define the basal plane, and the O2, O3 atoms occupy the apical axial positions, forming a distorted octahedral geometry. The N(O)–Cd–O(N) angles range are from 83.18(1) to155.01(1)°. The bond distances of Cd–O<sub>carboxylic</sub> = 2.193(5)–2.471(5) Å, Cd–O<sub>water</sub> = 2.414(5) Å, and those of Cd–N bond distances fall in the 2.326(6)–2.352(6) Å range, which are similar with the values reported [20–25].



Fig. 1. The molecular structure of compound 1 (hydrogen atoms were omitted).

Each pair of adjacent Cd(II) atoms are bridged by two 1,8-NDC ligands to form a dinuclear structure [26,27]. The 1,8-NDC ligands take bis-chelating and monodentate bridging coordination modes to link two metal Cd(II) atoms, and this lead to the formation of 0D network. There is 14-membered ring in the asymmetric unit of compound 1, and the distance of adjacent Cd atoms is 5.0859 Å. There are three kinds of H-bonds interactions in compound 1:  $N-H\cdots O$ ,  $C-H\cdots O$  and  $O-H\cdots O$  interactions. The most interesting aspect of the structure in 1 concerns the intermolecular of N-H···O  $[H(4A) \cdots O(4) = 1.98 \text{ Å}, N(4) \cdots O(4) = 2.793 \text{ Å}$ and  $N(4)-H(4A)\cdots O(4) = 159^{\circ}$  interactions, which helps in the construction of the 1 D chain structure (Fig. 2). The N-heterocyclic mip ligands are attached to both sides of this chain regularly, and mip ligands on the same sides are parallel nearly. Moreover, in compound **1**, adjacent dimers are linked together through  $\pi$ - $\pi$  stackings (centroid-to-centroid distance of 3.661 Å and faceto-face distance of 3.575 Å) between two 1.8-NDC ligands. Surprisingly, the existence of H-bonds interactions and  $\pi$ - $\pi$  stackings lead to the 2D supramolecular framework (Fig. 3). Clearly, intermolecular  $\pi$ - $\pi$  stacking and H-bonds interactions contribute to the stabilization of the structure of compound 1.

#### 3.2. Structural analysis of compound 2

The molecular structure is shown in Fig. 4, and the 1D chain structure is shown in Fig. 5. The 2D layer structure is shown in Fig. 6. Selected bond lengths and bond angles are listed in Table 3, and Hydrogen bond lengths and angles for the compounds **1** and **2** are listed in Table 4.

Single-crystal X-ray structural analysis reveals that the asymmetric unit of compound **2** contains one Cd(II) atom, two mip ligands, and two NTC ligands. The Cd(II) atom is six-coordinated by four N-Heterocyclic nitrogen atoms from two different mip ligands (Cd(1)-N = 2.390-2424 Å) and two oxygen atoms from two NTC molecule (Cd(1)-O = 2.262 Å), which are similar with the values reported [20-25]. The N(O)-Cd-O(N) angles range are from 83.67(1) to 152.78(1)°. The angle of N(2)-Cd(1) -N(1),  $N(2)^{\#1}-Cd(1)-N(1)$ ,  $O(2)-Cd(1)-N(2)^{\#1}$ , and O(2)-Cd(1)-N(2) $(^{\#1} = -x, y, -z+1/2)$  is 69.24, 82.86, 122.36 and 83.67°, and the sum is 358.13°. For the coordination environment of Cd(1), the Cd(1), O(2), N(2), N(1) and  $N(2)^{\#1}$  atoms define the basal plane, and  $N(1)^{\#1}$  and  $O(2)^{\#1}$  atoms occupy the apical axial positions to form a distorted octahedral environment. In compound 2, the NTC ligand coordinates to one Cd(II) atom in bridging coordination mode to form 0D structure. Interesting, the existence of N4–H4A···O1 hydrogen bonds interactions  $[H(4A) \cdots O(1) =$ 1.940 Å, N(4)...O(1) = 2.785 Å and N(4)–H(4A)...O(1) = 167°] lead the 0D to 1D chain structure with the distances of Cd...Cd are 9.4509 Å. The *N*-heterocyclic ligands mip are attached to both sides of this chain regularly, see Fig. 5. Moreover, there is another type of hydrogen bonds interactions:  $C(17)-H(17A)\cdots O(3)$  [H(17A) $\cdots O(3)$ = 2.430 Å,  $C(17) \cdots O(3) = 3.342$  Å and  $C(17) - H(17A) \cdots O(3) = 168^{\circ}$ ], which lead the 1D chain to 2D layer structure, see Fig. 6. Moreover, there are  $\pi - \pi$  interactions between the aryl ring of mip ligands with distances between  $cg(1) \rightarrow cg(2)$  ring centroid is 3.696 Å. Cg(1): C5  $\rightarrow$  C6  $\rightarrow$  N3  $\rightarrow$  N4  $\rightarrow$  C13, Cg(2): C14  $\rightarrow$  C15  $\rightarrow$  C16  $\rightarrow$  C17  $\rightarrow$  C18  $\rightarrow$  C19. It is noteworthy that the existence of hydrogen bonds and  $\pi$ - $\pi$  interactions reinforce the structural stability of compound **2**, which can be proved by TG analysis.

The Cd(II) atom is hexa-coordinated in the compound **1** with two nitrogen atoms from one chelating mip ligand and four oxygen atoms ((O(1W) from one lattice water molecule). The 1,8-NDC ligands take bis-chelating and monodentate bridging coordination modes to link two metal Cd(II) atoms. The Cd(II) atom is hexacoordinated in the compound **2** with four nitrogen atoms from two chelating mip ligands and two oxygen atoms from two



Fig. 2. 1D chain structure by  $N-H\cdots O$  hydrogen bonds of compound 1 (dotted lines represent hydrogen bonds).



Fig. 3. 2D supramolecular structure by N-H···O hydrogen bonds and  $\pi$ - $\pi$  interactions of compound 1 (dotted lines represent hydrogen bonds).

Selected bond lengths (Å) and bond angles (°) for compound <b>1</b> .				
bond	Dist.	bond	Dist.	
Cd(1)-O(3) <sup>#1</sup>	2.193(5)	Cd(1)-O(2)	2.297(5)	
Cd(1)-O(1)	2.471(5)	Cd(1)-O(1W)	2.414(5)	
Cd(1)-N(1)	2.352(6)	Cd(1)-N(2)	2.326(6)	
Angle	(°)	Angle	(°)	
$O(3)^{\#1}-Cd(1)-O(2)$	141.9(2)	$O(3)^{\#1}-Cd(1)-O(1W)$	79.36(1)	
O(2)-Cd(1)-O(1W)	78.06(1)	$O(3)^{\#1}-Cd(1)-O(1)$	109.64(1)	
O(2)-Cd(1)-O(1)	54.64(1)	O(1W)-Cd(1)-O(1)	113.90(1)	
$O(3)^{\#1}-Cd(1)-N(2)$	106.5(2)	N(2)-Cd(1)-O(1W)	84.80(1)	
N(1)-Cd(1)-O(1W)	155.01(1)	N(2)-Cd(1)-O(1)	141.6(2)	
O(2)-Cd(1)-N(2)	101.5(2)	$O(3)^{\#1}-Cd(1)-N(1)$	113.2(2)	

Symmetry transformations used to generate equivalent atoms: #1 - x, -y+1, -z.

different NTC, and donor nitrogen atom in the structure of NTC is absent in the coordination. The structures of adjacent Cd(II) atoms in **1** are symmetric, and the most interesting aspect of the structure in **1** concerns the intermolecular of  $O1W-H1WB\cdots O1$  interactions, which strengthen the stability of the dimer structure.

# 3.3. IR spectra

Table 2

In compound **1**, the two peaks at 1621 and 1559 cm<sup>-1</sup> correspond to the antisymmetric stretching of carboxyl, the peak at 1384 cm<sup>-1</sup> corresponds to the stretching of carboxyl. The  $\Delta v$  ( $v_{as}(COO^{-})-v_{s}(COO^{-})$ ) are 237 and 175 cm<sup>-1</sup>, indicating that the carboxyls adopt bidentate and monodentately coordinated with Cd(II) atoms. In compound **2**, the strong absorption peaks at 1600 cm<sup>-1</sup> is the antisymmetric stretching of carboxyl, and the



Fig. 4. The molecular structure of compound 2 (hydrogen atoms were omitted).

absorption at  $1390 \text{ cm}^{-1}$  is the symmetric stretching of carboxyl. The separation is  $210 \text{ cm}^{-1}$  (larger than  $200 \text{ cm}^{-1}$ ), which indicates the carboxyls adopt monodentate coordination mode. The IR results are good agreement with their solid structural features from the results of their crystal structures.

#### 3.4. UV–Vis absorption spectra

The UV–Vis absorption spectra of mip ligand and compounds **1** and **2** are determined in the solid state at room temperature



Fig. 5. The 1D chain structure by N-H···O hydrogen bonds of compound 2 (dotted lines represent hydrogen bonds).



Fig. 6. The 2D layer structure by N-H···O and C-H···O hydrogen bonds of compound 2 (dotted lines represent hydrogen bonds).

#### Table 3

Selected bond lengths (Å) and bond angles (°) for compound  $\boldsymbol{2}.$ 

Bond	Dist.	Bond	Dist.
Cd(1)–O(2) Cd(1)–N(1) Cd(1)–N(2)	2.262(3) 2.424(4) 2.390(3)	$Cd(1)-O(2)^{#1}$ $Cd(1)-N(1)^{#1}$ $Cd(1)-N(2)^{#1}$	2.262(3) 2.424(4) 2.390(3)
Angle $O(2)-Cd(1)-O(2)^{#1}$ $O(2)^{#1}-Cd(1)-N(2)^{#1}$ $O(2)^{#1}-Cd(1)-N(2)$ $O(2)^{#1}-Cd(1)-N(1)^{#1}$ $O(2)^{#1}-Cd(1)-N(1)$ $N(2)^{#1}-Cd(1)-N(1)$	(°) 98.88(1) 83.67(1) 122.36(1) 152.78(1) 93.64(1) 69.24(1) 82.86(1)	Angle $O(2)-Cd(1)-N(2)^{\#1}$ O(2)-Cd(1)-N(2) $O(2)-Cd(1)-N(1)^{\#1}$ O(2)-Cd(1)-N(1) $N(2)^{\#1}-Cd(1)-N(2)$ $N(2)-Cd(1)-N(1)^{\#1}$ N(2)-Cd(1)-N(1)	(°) 122.36(1) 83.67(1) 93.64(1) 152.78(1) 141.85(1) 82.86(1) 69.24(1)

Symmetry transformations used to generate equivalent atoms: #1 - x, y, -z+1/2.

#### Table 4

Hydrogen bond lengths (nm) and angles (°) for the compounds 1 and 2.

D−H· · ·A	D-H	$H{\cdot}{\cdot}{\cdot}A$	$D{\cdots}A$	$D{-}H{\cdot}{\cdot}{\cdot}A$
1				
01W–H1WB ···· 01	0.0960	0.1890	0.2676	138
N4-H4A···O4	0.0860	0.1980	0.2793	159
C8–H8A···O2	0.0930	0.2510	0.3121	123
C19-H19A···O4	0.0930	0.2440	0.3327	159
2				
$N(4)-H(4A)\cdots O(1)$	0.0860	0.1940	0.2785	167
$C(8)-H(8A)\cdots O(1)$	0.0930	0.2540	0.3413	155
C(17)-H(17A) - O(3)	0.0930	0.2430	0.3342	168

(Fig. 7). The result suggests that the ligand mip shows two absorption bands at 275 nm and 233 nm. Absorption bands for

compounds **1** and **2** are between 404 nm and 410 nm, which are red-shifted by 129–177 nm relative to that of free ligand. After coordination, the formation of the more large conjugated system may be the reason for the strong red-shift. The above analyses for UV–Vis spectral are in agreement with the determined crystal structure of **1** and **2**.

# 3.5. Thermal properties

To examine the stability of compounds **1** and **2**, we examined the TGA curves of crystalline samples in the flowing nitrogen atmosphere at a heating rate of 10 °C/min (Fig. 8). As expected, in compound **1**, the first weight loss corresponding to the removal of lattice H<sub>2</sub>O is 2.90% (calcd. 2.68%) from 107 to 145 °C. The second weight loss of 31.80% from 145 to 438 °C corresponds to the loss of 1,8-NDC ligands (calcd. 32.22%). The last weight loss of 47.20% in the temperature range of 438–564 °C can be ascribed to the release of mip ligands (calcd. 48.60%). In compound **2**, the first weight loss of 24.00% from 312 to 363 °C corresponds to the loss of NTC ligands (calcd. 24.38%). The second weight loss in the temperature range of 380–620 °C can be ascribed to the release of mip ligands (obsd 62.50%, calcd 64.64%). The final formation may be the metal oxide CdO. The analysis results indicate that the frameworks of compounds **1**–**2** are very stable.

# 3.6. Photoluminescent properties

Luminescence property is very important in photochemistry and photophysics [28,29]. So in this study, we research the luminescence of compounds **1** and **2**, as well as the free ligand mip (Figs. 9 and 10). The free ligand exhibits emission at 539 nm (excitation at 347 nm) for mip. Compound **1** exhibits one broad



Fig. 7. UV–Vis spectrum of compound 1 and 2 in solid state at room temperature.



Fig. 8. TGA curves of compounds 1 and 2.



Fig. 9. Luminescent spectrum of ligand mip and compound 1 in solid state at room temperature.

emission band with the maximum intensity at 449 nm upon excitation at 325 nm, which is blue-shifted by 90 nm relative to the



Fig. 10. Luminescent spectrum of ligand mip and compound 2 in solid state at room temperature.

emission wavelength of free ligand mip. While compound **2** shows one broad emission band with the maximum intensity at 656 nm upon excitation at 350 nm, which is red-shifted by 117 nm relative to the emission wavelength of free ligand mip. It is worth to mention that the heavy atom effect is quenching to some extent, so the luminescent of compound **1** is weaker than mip ligand. Compounds **1–2** exhibit strong emissions, which may be attributed to the ligand rigidity. The rigidity is favor of energy transfer and reduces the loss of energy through a radiationless pathway. However, the effect of the microenvironment between ligands and compounds on the luminescence properties still needs further investigations. The coordination polymer **2** may be good candidate for potential photoluminescence material because it is highly thermally stable and insoluble in water and common organic solvents.

# 4. Conclusions

In conclusion, two unique compounds have been synthesized by using plane multifunctional ligands mip, 1,8-NDC and NTC. It is noteworthy that non-covalent interactions ( $\pi \cdots \pi$  interactions, H-bond and coordination bonds) can be one of the most powerful force for instructing and directing the supra-molecular architectures, as well as reinforcing the structural stability of the title compounds. TG analysis reveals that the title compounds are very stable and worthy of further study as candidate of potential photoluminescence material.

#### Supplementary material

CCDC 859084 and 859139 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data request. cif.

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