

## ARTICLE

# Synthesis, Structures, Luminescence and Catalytic Activity in the Knoevenagel Condensation Reaction of Two Cd(II) Coordination Polymers Based on a Biphenyl-dicarboxylic Acid<sup>①</sup>

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**ABSTRACT** Two cadmium(II) coordination polymers, namely  $[\text{Cd}(\mu\text{-dda})(\text{H}_2\text{biim})]_n$  (**1**) and  $[\text{Cd}(\mu\text{-dda})(\text{py})]_n$  (**2**) have been constructed hydrothermally using  $\text{H}_2\text{dda}$  ( $\text{H}_2\text{dda}$  = 4,4'-dihydroxybiphenyl-3,3'-dicarboxylic acid),  $\text{H}_2\text{biim}$  ( $\text{H}_2\text{biim}$  = 2,2'-biimidazole), py (py = pyridine), and cadmium chloride at 160 °C. The products were isolated as stable crystalline solids and were characterized by IR spectra, elemental analyses, thermogravimetric analyses (TGA), and single-crystal X-ray diffraction analyses. Single-crystal X-ray diffraction analyses revealed that both compounds crystallize in the monoclinic system, space group  $C2/c$ . Compound **1** discloses a 1D chain structure. Compound **2** features a 3D framework. The luminescent properties of compounds **1** and **2** were evaluated. Besides, the catalytic activities in the Knoevenagel condensation reaction of two compounds were investigated. Compound **1** exhibits an excellent catalytic activity in the Knoevenagel condensation reaction at room temperature.

**Keywords:** coordination polymer, dicarboxylic acid, luminescence, catalytic properties, Knoevenagel condensation reaction; DOI: 10.14102/j.cnki.0254-5861.2011-3250

## 1 INTRODUCTION

Coordination polymers and derived materials have attracted tremendous attention due to their structural and topological diversity as well as their potential applications as functional materials<sup>[1-15]</sup>. In the last five years, special organic carboxylate ligands have been widely used in synthesizing coordination polymers and derived materials due to strong coordination ability of the carboxyl group and rich coordination modes<sup>[5, 6, 12, 16-19]</sup>. Among them, biphenyl-carboxylic acids have been extensively applied as versatile building blocks towards the assembly of metal-organic architectures<sup>[16, 20, 21]</sup>.

The 4,4'-dihydroxybiphenyl-3,3'-dicarboxylic acid ( $\text{H}_2\text{dda}$ ) is a good bridging ligand for the constructing coordination polymers<sup>[22-24]</sup>, under considering structural semi-rigidity, which has multiple coordinate sites involving four carboxylate oxygen atoms and two hydroxyl O atoms.

Herein, we report the synthesis, crystal structures, luminescence, and catalysis of two Cd(II) coordination

polymers with  $\text{H}_2\text{dda}$  ligand.

## 2 EXPERIMENTAL

### 2.1 General procedures

All chemicals and solvents were of AR grade and used without further purification. Carbon, hydrogen and nitrogen were determined using an Elementar Vario EL elemental analyzer. IR spectra were recorded using KBr pellets and a Bruker EQUINOX 55 spectrometer. Thermogravimetric analysis (TGA) was performed under  $\text{N}_2$  atmosphere with a heating rate of 10 K/min on a LINSEIS STA PT1600 thermal analyzer. Excitation and emission spectra were recorded on an Edinburgh FLS920 fluorescence spectrometer using the solid samples at room temperature. Powder X-ray diffraction patterns (PXRD) were measured on a Rigaku-Dmax 2400 diffractometer using  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ); the X-ray tube was operated at 40 kV and 40 mA. The data were collection in the range of 5–45°. Solution  $^1\text{H}$  NMR spectra were recorded on a JNM ECS 400 M spectrometer.

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## 2.2 Synthesis of compound 1

A mixture of  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  (0.040 g, 0.2 mmol),  $\text{H}_2\text{dda}$  (0.055 g, 0.2 mmol),  $\text{H}_2\text{biim}$  (0.027 g, 0.2 mmol),  $\text{NaOH}$  (0.016 g, 0.4 mmol), and  $\text{H}_2\text{O}$  (10 mL) was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless-steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C/h. Yellow block-shaped crystals of **1** were isolated manually, and washed with distilled water. Yield: 47% (based on  $\text{H}_2\text{dda}$ ). Anal. Calcd. (%) for  $\text{C}_{20}\text{H}_{14}\text{CdN}_4\text{O}_6$ : C, 46.31; H, 2.72; N, 10.80. Found (%): C, 46.41; H, 2.71; N, 10.72. IR (KBr,  $\text{cm}^{-1}$ ): 1628w, 1553m, 1525w, 1473s, 1414s, 1358w, 1278w, 1250w, 1175w, 1155w, 1127w, 1087w, 1039w, 992w, 952w, 920w, 860w, 828m, 801w, 757m, 677w, 562w.

## 2.3 Synthesis of compound 2

Synthesis of **2** was similar to **1** except using py (0.5 mL, 6.3 mmol) instead of  $\text{NaOH}$ . Colourless block-shaped crystals of **2** were isolated manually, and washed with distilled water. Yield: 50% (based on  $\text{H}_2\text{dda}$ ). Anal. Calcd. (%) for  $\text{C}_{19}\text{H}_{13}\text{CdNO}_6$ : C, 49.21; H, 2.83; N, 3.02. Found (%): C, 49.45; H, 2.81; N, 3.00. IR (KBr,  $\text{cm}^{-1}$ ): 1628w, 1599w, 1539w, 1520m, 1478w, 1450w, 1416s, 1341w, 1294w, 1243m, 1220w, 1154w, 1064w, 1036w, 1008w, 952w, 906w, 877w, 821m, 745w, 704m, 637w, 554w.

## 2.4 Structure determination

Two single crystals of the title compounds were mounted on a Bruker CCD diffractometer equipped with a graphite-monochromatic  $\text{Cu-K}\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ) radiation using a  $\varphi$ - $\omega$  scan mode at 293(2) K. The structures were solved by direct methods with SHELXS-97<sup>[25]</sup> and refined by full-matrix least-squares techniques on  $F^2$  with SHELXL-97<sup>[26]</sup>. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms (except those bound to water molecules) were placed in the calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. Compound **1** crystallizes in monoclinic system, space group  $C2/c$  with  $a = 18.4567(4)$ ,  $b = 7.05850(10)$ ,  $c = 28.5221(6) \text{ \AA}$ ,  $V = 3710.03(12) \text{ \AA}^3$ ,  $Z = 8$ ,  $\text{C}_{20}\text{H}_{14}\text{CdN}_4\text{O}_6$ ,  $M_r = 518.75$ ,  $D_c = 1.857 \text{ g/cm}^3$ ,  $F(000) = 2064$ , the final  $R = 0.0231$  and  $wR = 0.0560$  for 3440 observed reflections ( $I > 2\sigma(I)$ ). Compound **2** crystallizes in monoclinic system, space group  $C2/c$  with  $a = 18.4249(11)$ ,  $b = 11.6325(5)$ ,  $c = 7.7798(4) \text{ \AA}$ ,  $V = 1604.40(15) \text{ \AA}^3$ ,  $Z = 4$ ,  $\text{C}_{19}\text{H}_{13}\text{CdNO}_6$ ,  $M_r = 463.70$ ,  $D_c = 1.920 \text{ g/cm}^3$ ,  $F(000) = 920$ , the final  $R = 0.0273$  and  $wR = 0.0691$  for 1491 observed reflections ( $I > 2\sigma(I)$ ). The selected important bond parameters are given in Table 1. The hydrogen bonds in crystal packing of compounds **1** and **2** are listed in Tables 2 and 3.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for **1** and **2**

1					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Cd(1)–O(3)	2.176(2)	Cd(1)–O(5)i	2.177(2)	Cd(1)–N(1)	2.295(2)
Cd(1)–N(4)	2.325(2)				
Angle	(°)	Angle	(°)	Angle	(°)
O(3)–Cd(1)–O(5)i	100.47(7)	N(1)–Cd(1)–O(3)	135.51(7)	O(5)i–Cd(1)–N(1)	107.20(7)
N(4)–Cd(1)–O(3)	113.23(7)	N(4)–Cd(1)–O(5)i	129.76(7)	N(1)–Cd(1)–N(4)	73.63(7)
2					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Cd(1)–O(1)	2.505(2)	Cd(1)–O(1)i	2.505(2)	Cd(1)–O(1)ii	2.451(2)
Cd(1)–O(1)iii	2.451(2)	Cd(1)–O(2)i	2.311(2)	Cd(1)–O(2)iii	2.311(2)
Cd(1)–N(1)	2.241(3)				
Angle	(°)	Angle	(°)	Angle	(°)
O(2)i–Cd(1)–N(1)	140.48(6)	O(2)i–Cd(1)–O(2)iii	79.03(13)	O(1)i–Cd(1)–N(1)	100.99(5)
O(2)i–Cd(1)–O(1)i	54.58(8)	O(2)i–Cd(1)–O(1)ii	106.58(7)	O(1)i–Cd(1)–O(1)ii	158.01(10)
O(1)–Cd(1)–N(1)	82.02(5)	O(2)ii–Cd(1)–O(1)	115.39(8)	O(2)iii–Cd(1)–O(1)	77.61(8)
O(1)i–Cd(1)–O(1)iii	76.52(8)	O(1)ii–Cd(1)–O(1)iii	106.62(8)	O(1)i–Cd(1)–O(1)	164.05(10)

Symmetry codes: i:  $-x+2, y+1, -z+1/2$  for **1**; ii:  $x, -y+1/2, z+1/2$ ; iii:  $-x, y, -z+3/2$ ; iii:  $-x, y, -z+1$  for **2**

Table 2. Geometrical Parameters of Hydrogen Bonds for **1**

D–H...A	d(D–H)/Å	d(H...A)/Å	d(D...A)/Å	∠DHA/°
O(1)–H(1)···O(2)	0.820	1.825	2.549	146
O(4)–H(4)···O(6)	0.820	1.835	2.558	146
N(2)–H(2)···O(2)i	0.830	2.106	2.787	139
N(3)–H(3)···O(6)ii	0.879	1.831	2.702	170

Symmetry codes: (i)  $-x+3/2, -y+3/2, -z+1$ ; (ii)  $x-1/2, -y+3/2, z+1/2$

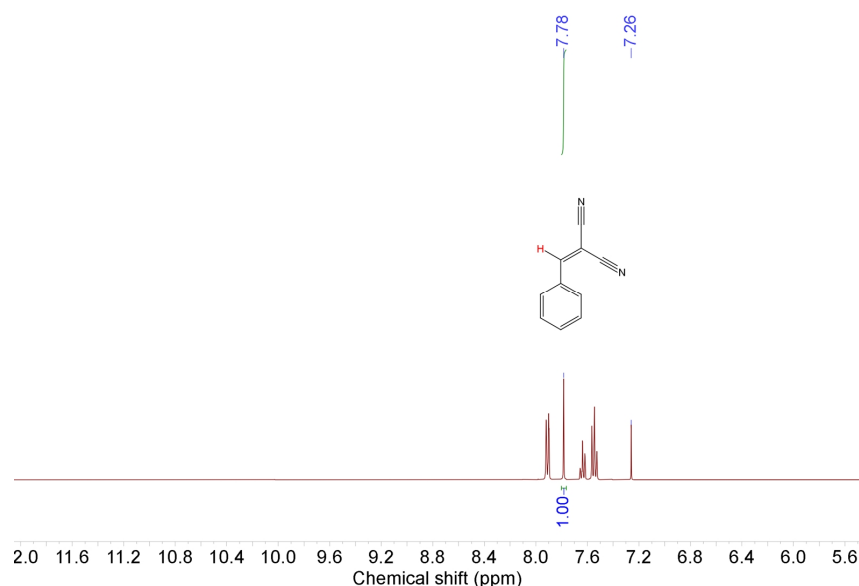
**Table 3. Geometrical Parameters of Hydrogen Bonds for 2**

D–H···A	d(D–H)/Å	d(H···A)/Å	d(D···A)/Å	∠DHA/°
O(3)–H(3)···O(2)	0.820	1.829	2.547	146

## 2.5 Catalytic the Knoevenagel condensation reaction of aldehydes

In a typical test, a suspension of an aromatic aldehyde (0.50 mmol, benzaldehyde as a model substrate), malononitrile (1.0 mmol), and catalyst (typically 2 mol%) in methanol (1.0 mL) was stirred at room temperature. After a desired reaction time, the catalyst was removed by centrifugation, followed by an evaporation of the solvent

from the filtrate under reduced pressure to give a crude solid. This was dissolved in CDCl<sub>3</sub> and analyzed by <sup>1</sup>H NMR spectroscopy for quantification of the products (Fig. 1). To perform the recycling experiment, the catalyst was isolated by centrifugation, washed with dichloromethane, dried at room temperature, and reused. The subsequent steps were performed as described above.



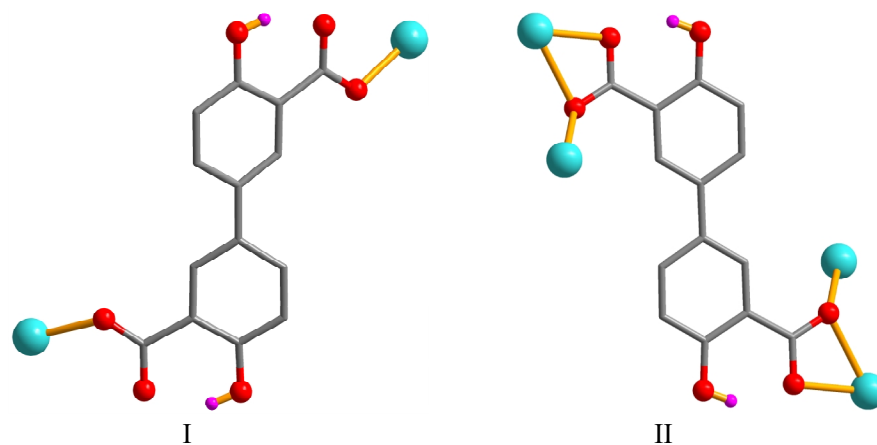
**Fig. 1. Example of integration in the <sup>1</sup>H-NMR spectrum for the determination of the Knoevenagel condensation reaction products (Table 4, Entry)**

## 3 RESULTS AND DISCUSSION

### 3.1 Crystal structure of 1

X-ray crystallography analysis reveals that compound **1** crystallizes in the monoclinic system, space group *C2/c*. As shown in Fig. 2, the asymmetric unit of **1** bears one crystallographically unique Cd(II) atom (Cd(1)), one  $\mu$ -dda<sup>2-</sup> block, and one H<sub>2</sub>biim moiety. The tetra-coordinate Cd(1) atom exhibits a distorted tetrahedral {CdN<sub>2</sub>O<sub>2</sub>} environment, which is occupied by two carboxylate O donors from two different  $\mu$ -dda<sup>2-</sup> blocks and two N atoms from the H<sub>2</sub>biim moiety. The Cd–O and Cd–N bond distances are 2.176(2)~2.177(2) and 2.295(2)~2.325(2) Å, respectively; these are

within the normal ranges observed in related Cd(II) compounds<sup>[12, 20, 27]</sup>. In **1**, the dda<sup>2-</sup> ligand adopts the coordination mode I (Scheme 1) with two COO<sup>-</sup> groups being monodentate. The H<sub>2</sub>biim moiety takes the terminal coordination fashion. In the deta<sup>4-</sup> ligand, a dihedral angle (between two aromatic rings) is 25.17°. The  $\mu$ -dda<sup>2-</sup> blocks connect adjacent Cd atoms to give a 1D chain (Fig. 3). This 1D coordination polymer features double chains built from the 4-connected Cd and  $\mu$ <sub>4</sub>-dda<sup>2-</sup> nodes (Fig. 4). As a result, the chains represent a uninodal 4-connected network with a SP 1-periodic net (4,4)(2,2) topology. The neighboring chains are assembled into a 2D sheet through the N–H···O hydrogen bonds (Table 2 and Fig. 5).



Scheme 1. Coordination modes of the  $\text{dda}^{2-}$  ligands in compounds 1 and 2

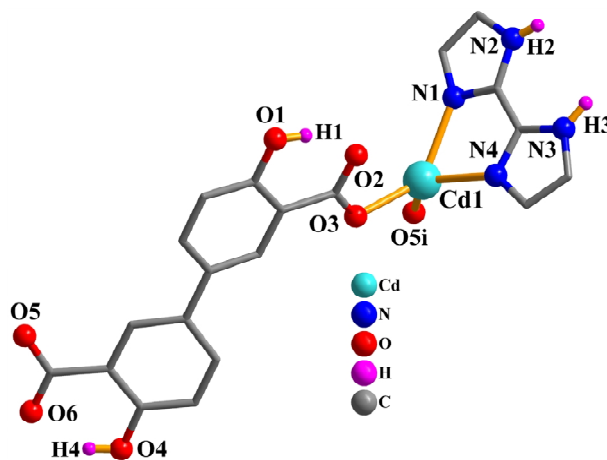


Fig. 2. Coordination environments of the Cd(II) atom in compound 1. The hydrogen atoms are omitted for clarity except in OH and NH groups (Symmetry code: i:  $-x+2, y+1, -z+1/2$ )

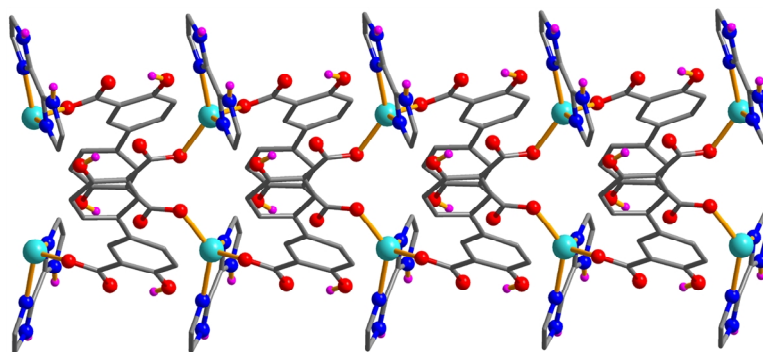


Fig. 3. Perspective view of the 1D chain along the  $c$  axis

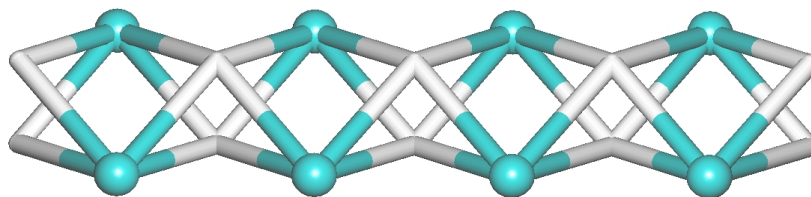


Fig. 4. Topological representation of a uninodal 4-connected network with a SP 1-periodic net (4,4)(2,2) topology; view along the  $c$  axis; 4-linked Cd nodes (green balls), centroids of 4-connected  $\mu_4\text{-dda}^{2-}$  nodes (gray)

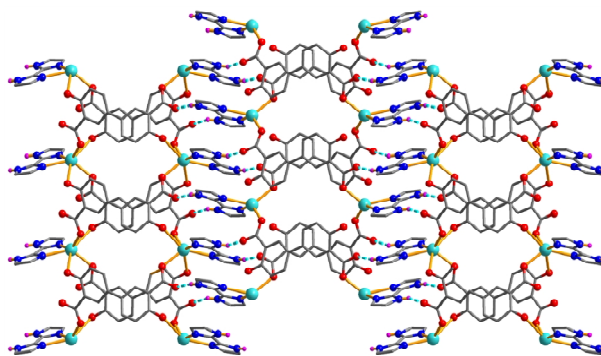


Fig. 5. Perspective view of the 2D sheet along the *bc* plane in **1** (Blue dashed lines present H-bonds)

### 3.2 Crystal structure of **2**

The asymmetric unit of compound **2** contains one crystallographically unique Cd(II) atom (Cd1) with half occupancy), a half of  $\mu_4$ -dda<sup>2-</sup> block, and a half of py moiety. As depicted in Fig. 6, the Cd(1) center is seven-coordinated and displays a distorted pentagonal bipyramidal {CdNO<sub>6</sub>} geometry. It is taken by six carboxylate O atoms from four individual  $\mu_4$ -dda<sup>2-</sup> blocks and one N donor from the py ligand. The bond lengths of Cd–O are in the 2.311(2)~2.505(2) Å range, while the Cd–N bond is 2.241(3) Å, being

comparable to those found in some reported Cd(II) compounds<sup>[20, 27, 28]</sup>. In **2**, the dda<sup>2-</sup> block acts as a  $\mu_4$ -linker (mode II, Scheme 1), in which two carboxylate groups adopt a tridentate mode. Besides, two aromatic rings are coplanar in the  $\mu_4$ -dda<sup>2-</sup> ligand. The  $\mu_4$ -dda<sup>2-</sup> blocks multiply interconnect the neighboring Cd1 centers to generate a 3D metal-organic framework (Fig. 7). This structure is assembled from the 4-connected Cd and  $\mu_4$ -dda<sup>2-</sup> nodes, which are arranged into a binodal 4,4-linked net with a **pts** [PtS, Cooperite] topology and a point symbol of (4<sup>2</sup>.8<sup>4</sup>) (Fig. 8).

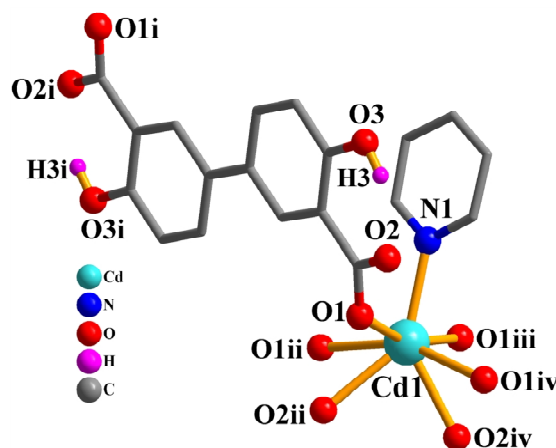


Fig. 6. Coordination environments of the Cd(II) atom in compound **2**. The hydrogen atoms are omitted for clarity except in OH groups (Symmetry codes: i:  $-x+1/2, -y+1/2, -z+2$ ; ii:  $x, -y, z+1/2$ ; iii:  $-x, y, -z+3/2$ ; iv:  $-x, -y, -z+1$ )

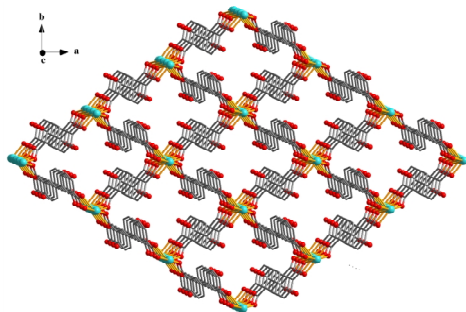


Fig. 7. View of 3D metal-organic framework along the *ab* plane. The py ligands are omitted for clarity

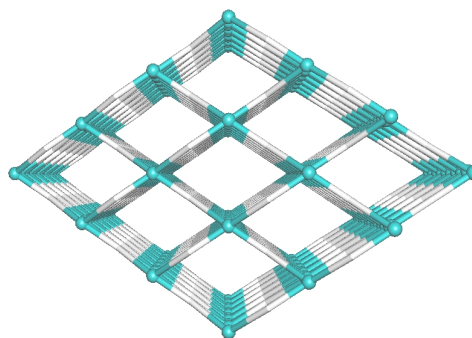


Fig. 8. Topological representation of a binodal 4,4-connected network with a **pts** topology; view along the *ab* plane; 4-linked Cd nodes (green balls), centroids of 4-connected  $\mu_4$ -dda<sup>2-</sup> nodes (gray)

Compounds **1** and **2** were assembled under similar conditions except for the type of auxiliary ligand used ( $\text{H}_2\text{biim}$  for **1** and  $\text{py}$  for **2**). The difference in their structures, 1D chain in **1** vs. 3D sheet in **2**, indicates that the assembly process is dependent on the type of auxiliary ligand.

### 3.3 Thermal analysis

To determine the thermal stability of polymers **1** and **2**,

their thermal behaviors were investigated under nitrogen atmosphere by thermogravimetric analysis (TGA). As shown in Fig. 9, compounds **1** and **2** do not contain solvent of crystallization or  $\text{H}_2\text{O}$  ligands and remain stable up to 245 or 274 °C, followed by a decomposition on further heating.  $\text{CdO}$  is expected as a final decomposition product of **1** (exptl. 25.1%, calcd. 24.8%) and **2** (exptl. 28.0%, calcd. 27.7%).

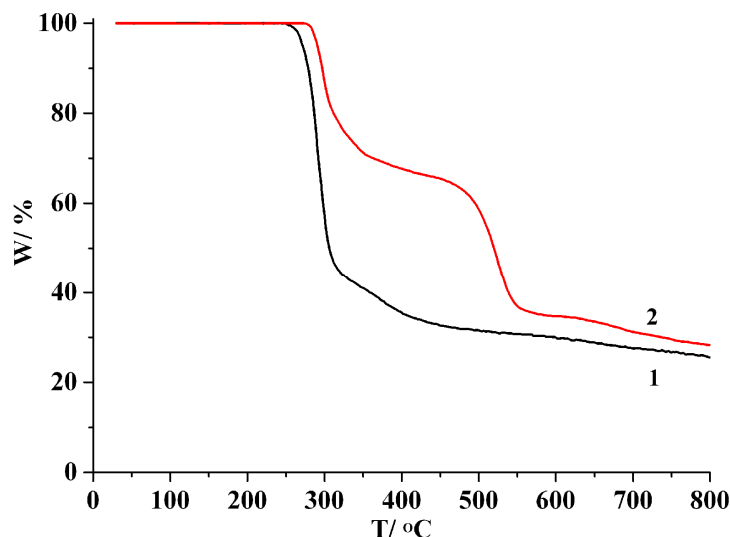


Fig. 9. TGA curves of compounds **1** and **2**

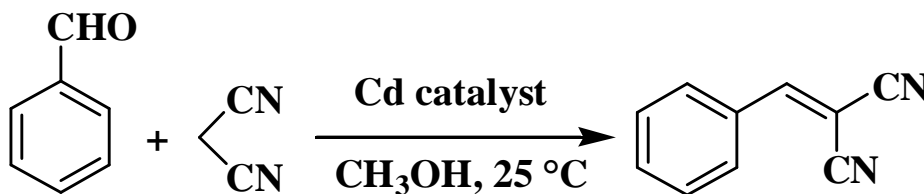
### 3.4 Luminescent properties

The excitation and emission spectra of 4,4'-dihydroxybiphenyl-3,3'-dicarboxylic acid ( $\text{H}_2\text{dda}$ ) and polymers **1** and **2** were measured in the solid state at room temperature (Figs. 10 and 11). The uncoordinated  $\text{H}_2\text{dda}$  shows a weak photoluminescence with an emission maximum at 482 nm ( $\lambda_{\text{ex}} = 366$  nm). In contrast, compounds **1** and **2** display significantly more intense emission bands with the maxima at 455 and 444 nm ( $\lambda_{\text{ex}} = 348$  nm), respectively. The emissions of compounds **1** and **2** are blue-shifted relative to that of the free  $\text{H}_2\text{dda}$  ligand, which can be assigned to the ligand-to-metal charge transfer (LMCT)<sup>[27, 29]</sup>. The luminescence enhancement in the coordination compounds can be attributed to the binding of ligands to the metal centers, which effectively increases the

rigidity of the ligand and reduces the loss of energy by radiationless decay<sup>[27, 28]</sup>. The quantum yield and life time were measured (1.36%, 0.1 ms for **1** and 5.88%, 0.3 ms for **2**).

### 3.5 Catalytic Knoevenagel condensation reaction

Given the potential of cadmium(II) coordination compounds to catalyze the organic reactions<sup>[30-32]</sup>, we explored the application of **1** and **2** as heterogeneous catalysts in the Knoevenagel condensation reaction of benzaldehyde as a model substrate to give 2-(phenylmethylene)-propanedinitrile. Typical tests were carried out by reacting a mixture of benzaldehyde, malononitrile, and a Cd catalyst in methanol at room temperature (Scheme 2, Table 4). Such effects as reaction time, catalyst loading, solvent composition, catalyst recycling, and finally substrate scope were investigated.



Scheme 2. Cd-catalyzed the Knoevenagel condensation reaction of benzaldehyde (model substrate)

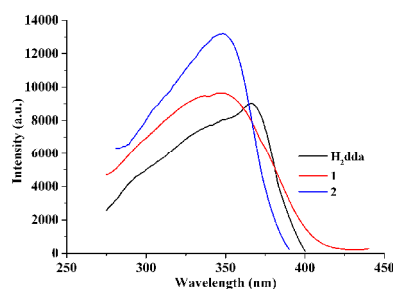


Fig. 10. Solid-state excitation spectra of H<sub>2</sub>dda, and compounds **1** and **2** at room temperature

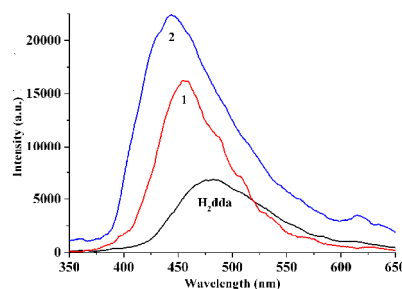


Fig. 11. Solid-state emission spectra of H<sub>2</sub>dda and compounds **1** and **2** at room temperature

Table 4. Co-catalyzed Knoevenagel Condensation Reaction of Benzaldehyde with Malononitrile

Entry	Catalyst	Time, min	Catalyst loading, mol%	Solvent	Yield <sup>a</sup> , %
1	<b>1</b>	10	2.0	CH <sub>3</sub> OH	42
2	<b>1</b>	20	2.0	CH <sub>3</sub> OH	57
3	<b>1</b>	30	2.0	CH <sub>3</sub> OH	63
4	<b>1</b>	40	2.0	CH <sub>3</sub> OH	78
5	<b>1</b>	50	2.0	CH <sub>3</sub> OH	90
6	<b>1</b>	60	2.0	CH <sub>3</sub> OH	100
7	<b>1</b>	60	2.0	H <sub>2</sub> O	100
8	<b>1</b>	60	2.0	C <sub>2</sub> H <sub>5</sub> OH	97
9	<b>1</b>	60	2.0	CH <sub>3</sub> CN	84
10	<b>1</b>	60	2.0	CHCl <sub>3</sub>	67
11	<b>1</b>	60	1.0	CH <sub>3</sub> OH	92
12	<b>2</b>	60	2.0	CH <sub>3</sub> OH	86
13	Blank	60	-	CH <sub>3</sub> OH	23
14	CdCl <sub>2</sub>	60	2.0	CH <sub>3</sub> OH	32
15	H <sub>2</sub> dda	60	2.0	CH <sub>3</sub> OH	31

<sup>a</sup> Calculated by <sup>1</sup>H NMR spectroscopy: mol(product)/mol(aldehyde + product) × 100

Upon using compound **1** as the catalyst (2 mol%), a high conversion of 100% of benzaldehyde into 2-(phenylmethylene)-propanedinitrile was reached after 60 min in methanol at room temperature (Table 4, entry 6).

The results show that compound **1** is more active than compound **2**. Although the relationship between structure and catalytic activity in the present study can not be clearly established, the highest conversion shown by compound **1** may eventually be associated to its 1D structure for easily accessible metal metal centers, together with the presence of the open metal sites<sup>[21, 30]</sup>.

We also compared the activities of catalyst **1** in the reactions of other substituted aromatic aldehydes with malononitrile, and the corresponding yields fall in the range of 55~100% (Table 5). Aryl aldehydes bearing strong electron-withdrawing substituents (e.g., nitro and chloro) exhibited higher reactivities (Table 5, entries 2~5), which may be related to an increase in the electrophilicity of the substrate. Aldehydes containing electron-donating groups (e.g., methyl) showed lower reaction yields (Table 5, entries 6~8), as expected.

Table 5. Knoevenagel Condensation Reaction of Various Aldehydes with Malononitrile Catalyzed by **1**

Entry	Substituted benzaldehyde substrate (R-C <sub>6</sub> H <sub>4</sub> CHO)	Product yield <sup>a</sup> (%)
1	R = H	100
2	R = 2-NO <sub>2</sub>	100
3	R = 3-NO <sub>2</sub>	100
4	R = 4-NO <sub>2</sub>	100
5	R = 4-Cl	100
6	R = 4-OH	55
7	R = 4-CH <sub>3</sub>	98
8	R = 4-OCH <sub>3</sub>	75
9	Cinnamaldehyde	93

<sup>a</sup> Calculated by <sup>1</sup>H NMR spectroscopy: mol(product)/mol(aldehyde + product) × 100



To examine the stability of **1** in the catalytic reaction, we tested the recyclability of this heterogeneous catalyst. For this purpose, upon completion of a reaction cycle, we separated the catalyst by centrifugation, washed it with  $\text{CH}_2\text{Cl}_2$ , and dried it at room temperature before further use. We recycled catalyst **1** repeatedly, and the catalytic system maintained the

higher activity over at least five consecutive cycles (the yields are 100, 100, 99, and 98% for the second to fifth runs, respectively). According to the PXRD data (Fig. 12), the structure of **1** is essentially preserved after five catalytic cycles.

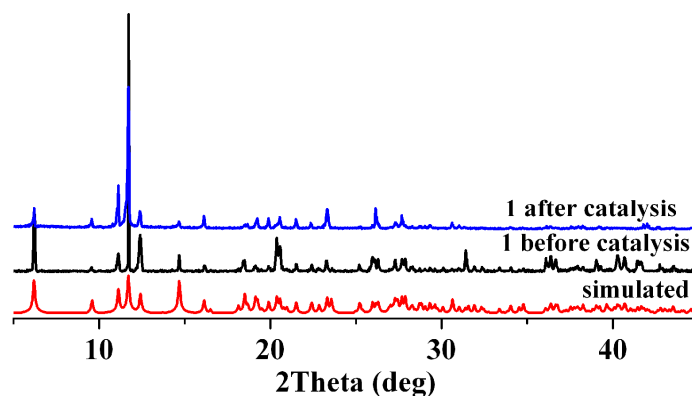


Fig. 12. PXRD patterns for **1**: simulated (red), before (black) and after (blue) catalysis

#### 4 CONCLUSION

In summary, we have synthesized two Cd(II) coordination polymers based on a dicarboxylate ligand. Compound **1** discloses a 1D chain structure, and compound **2** features a 3D

framework. The catalytic properties of both compounds were investigated. Compound **1** revealed an excellent catalytic activity in the Knoevenagel condensation reaction at room temperature.

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