

## 由4,4'-二甲基-2,2'-联苯二甲酸配体构筑的锌(II)和镉(II) 双核配合物的合成、晶体结构、荧光及光催化性质

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**摘要:** 采用水热方法, 用4,4'-二甲基-2,2'-联苯二甲酸配体(H<sub>2</sub>dbda)和非咯啉(phen)、2,2'-联吡啶(2,2'-bipy)分别与ZnCl<sub>2</sub>或CdCl<sub>2</sub>·H<sub>2</sub>O反应, 合成了3个零维双核配合物[Zn<sub>2</sub>(μ-dbda)<sub>2</sub>(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (**1**)、[Zn<sub>2</sub>(μ-dbda)<sub>2</sub>(2,2'-bipy)<sub>2</sub>] (**2**)和[Cd<sub>2</sub>(μ-dbda)<sub>2</sub>(2,2'-bipy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (**3**), 并对其结构、荧光和光催化性质进行了研究。结构分析结果表明3个配合物分别属于三斜和单斜晶系的P $\bar{1}$ 和P2<sub>1</sub>/n空间群。配合物**1**~**3**都具有零维双核结构, 而且这些双核单元通过O-H...O氢键作用进一步形成了三维超分子框架。研究表明, 配合物**1**~**3**在室温下能发出蓝色荧光。另外, 研究了3个配合物对有机染料亚甲基蓝的光催化降解性能, 结果表明配合物**3**可以高效地降解亚甲基蓝。

**关键词:** 配位化合物; 4,4'-二甲基-2,2'-联苯二甲酸; 荧光; 光催化

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## Syntheses, Crystal Structures, Luminescence and Photocatalytic Activity of Three Dinuclear Zinc(II) and Cadmium(II) Coordination Compounds Based on 4,4'-Dimethyl-2,2'-biphenyldicarboxylic Acid

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**Abstract:** Three 0D dinuclear zinc(II) and cadmium(II) coordination compounds, namely [Zn<sub>2</sub>(μ-dbda)<sub>2</sub>(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (**1**), [Zn<sub>2</sub>(μ-dbda)<sub>2</sub>(2,2'-bipy)<sub>2</sub>] (**2**), and [Cd<sub>2</sub>(μ-dbda)<sub>2</sub>(2,2'-bipy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (**3**), have been constructed hydrothermally using H<sub>2</sub>dbda (H<sub>2</sub>dbda=4,4'-dimethyl-2,2'-biphenyldicarboxylic acid), phen (phen=1,10-phenanthroline), 2,2'-bipy (2,2'-bipy=2,2'-bipyridine), and zinc or cadmium chlorides. Single-crystal X-ray diffraction analyses reveal that three compounds crystallize in the triclinic or monoclinic systems, space groups P $\bar{1}$  or P2<sub>1</sub>/n. All compounds disclose a discrete dimer structure, which is assembled to a 3D supramolecular framework through O-H...O hydrogen bonds. The luminescent and photocatalytic properties of three compounds were investigated, showing that com-

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pound **3** is a promising photocatalyst for the UV-light-driven degradation of methylene blue as a model organic dye pollutant. CCDC: 1962704, **1**; 1962705, **2**; 1962706, **3**.

**Keywords:** coordination compound; 4,4'-dimethyl-2,2'-biphenyldicarboxylic acid; luminescence; photocatalysis

## 0 Introduction

During the past few decades, extensive endeavors have been focused on the rational design and controllable synthesis of coordination compounds, since they displaying intriguing network structures and potential applications in gas adsorption and separation, catalysis, sensing, luminescence, and magnetism<sup>[1-7]</sup>. From the viewpoint of the synthetic strategy of crystal engineering, the suitable selection of organic ligands and metal ions plays a dominating role on the construction of coordination compounds<sup>[8-9]</sup>. Moreover, other factors will also be taken into account, such as solvent, template, temperature, and pH value<sup>[10-13]</sup>.

In this context, biphenyl polycarboxylate ligands have been extensively utilized to synthesize various functional coordination compounds owing to their strong coordination ability in diverse modes and the fact that they are able to satisfy the geometric requirement of the metal centers, which leads to higher dimensional frameworks<sup>[11,13-15]</sup>.

In this work, we selected 4,4'-dimethyl-2,2'-biphenyldicarboxylic acid (H<sub>2</sub>dbda) as an organic ligand owing to the following features: (1) it can twist and rotate freely to generate different angles between the two phenyl planes via the C-C single bond to furnish a subtle conformational adaptation; (2) it has four potential coordination sites (four carboxylate O donors), which can lead to diverse coordination patterns and high dimensionalities; (3) this acid ligand remains poorly used for the generation of coordination compounds. Given these features, the main objective of the present study consisted in the exploration of H<sub>2</sub>dbda as a biphenyl dicarboxylate ligand for the assembly of diverse coordination compounds.

Hence, in this work, we report the syntheses, crystal structures, luminescent and photocatalytic properties of three Zn(II) and Cd(II) coordination compounds

constructed from the biphenyl dicarboxylate ligand.

## 1 Experimental

### 1.1 Reagents and physical measurements

All chemicals and solvents were of AR grade and used without further purification. Carbon, hydrogen and nitrogen contents 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) data were collected on a LINSEIS STA PT1600 thermal analyzer with a heating rate of 10 °C·min<sup>-1</sup>. Excitation and emission spectra were recorded on an Edinburgh FLS920 fluorescence spectrometer using the solid samples at room temperature.

### 1.2 Synthesis of [Zn<sub>2</sub>(μ-dbda)<sub>2</sub>(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (**1**)

A mixture of ZnCl<sub>2</sub> (0.027 g, 0.20 mmol), H<sub>2</sub>dbda (0.054 g, 0.20 mmol), phen (0.040 g, 0.20 mmol), NaOH (0.016 g, 0.40 mmol), and H<sub>2</sub>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<sup>-1</sup>. Yellow block-shaped crystals of **1** were isolated manually, and washed with distilled water. Yield: 44% (based on H<sub>2</sub>dbda). Anal. Calcd. for C<sub>56</sub>H<sub>44</sub>Zn<sub>2</sub>N<sub>4</sub>O<sub>10</sub>(%): C 63.23, H 4.17, N 5.27; Found(%): C 63.47, H 4.16, N 5.30. IR (KBr, cm<sup>-1</sup>): 3 435w, 3 020w, 1 590s, 1 558m, 1 475w, 1 413m, 1 356m, 1 253w, 1 216w, 1 148w, 1 102w, 1 055w, 1 018w, 868w, 838w, 807w, 770m, 728w, 676w, 552w.

### 1.3 Synthesis of [Zn<sub>2</sub>(μ-dbda)<sub>2</sub>(2,2'-bipy)<sub>2</sub>] (**2**)

The preparation of **2** was similar to that of **1** except using 2,2'-bipy (0.031 g, 0.20 mmol) instead of phen. After being cooled to room temperature, yellow block-shaped crystals of **2** were isolated manually, and washed with distilled water. Yield: 41% (based on H<sub>2</sub>dbda). Anal. Calcd. for C<sub>52</sub>H<sub>40</sub>Zn<sub>2</sub>N<sub>4</sub>O<sub>8</sub>(%): C 63.75,

H 4.12, N 5.72; Found(%): C 63.49, H 4.10, N 5.76. IR (KBr,  $\text{cm}^{-1}$ ): 1 594s, 1 557w, 1 475w, 1 413m, 1 356w, 1 253w, 1 211w, 1 154w, 1 097w, 1 050w, 1 019w, 874w, 807w, 764m, 734w, 681w, 656w, 547w.

#### 1.4 Synthesis of $[\text{Cd}_2(\mu\text{-dbda})_2(2,2'\text{-bipy})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**3**)

A mixture of  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  (0.040 g, 0.20 mmol),  $\text{H}_2\text{dbda}$  (0.054 g, 0.20 mmol), 2,2'-bipy (0.031 g, 0.20 mmol), NaOH (0.016 g, 0.40 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  $^\circ\text{C}$  for 3 days, followed by cooling to room temperature at a rate of 10  $^\circ\text{C} \cdot \text{h}^{-1}$ . Yellow block-shaped crystals of **3** were isolated manually, and washed with distilled water. Yield: 38% (based on  $\text{H}_2\text{dbda}$ ). Anal. Calcd. for  $\text{C}_{52}\text{H}_{48}\text{Cd}_2\text{N}_4\text{O}_{12}$ (%): C 54.51, H 4.22, N 4.89; Found(%): C 54.77, H 4.20, N 4.93. IR (KBr,  $\text{cm}^{-1}$ ): 3 430m, 2 916w, 1 548s, 1 475w, 1 418

m, 1 376m, 1 252w, 1 216w, 1 154w, 1 101w, 1 060w, 1 008w, 910w, 807m, 770m, 728w, 676w, 552w.

The compounds are insoluble in water and common organic solvents, such as methanol, ethanol, acetone, and DMF.

#### 1.5 Structure determination

Three single crystals with dimensions of 0.26 mm $\times$ 0.24 mm $\times$ 0.23 mm (**1** and **3**) and 0.25 mm $\times$ 0.24 mm $\times$ 0.23 mm (**2**) were collected at 293(2) K on a Bruker SMART APEX II CCD diffractometer with Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073$  nm). The structures were solved by direct methods and refined by full matrix least-square on  $F^2$  using the SHELXTL-2014 program<sup>[16]</sup>. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were positioned geometrically and refined using a riding model. A summary of the crystallography data and structure refinements for **1**~**3** is given in Table 1. The selected bond lengths and angles for

Table 1 Crystal data for compounds **1**~**3**

Compound	<b>1</b>	<b>2</b>	<b>3</b>
Chemical formula	$\text{C}_{56}\text{H}_{44}\text{Zn}_2\text{N}_4\text{O}_{10}$	$\text{C}_{52}\text{H}_{40}\text{Zn}_2\text{N}_4\text{O}_8$	$\text{C}_{52}\text{H}_{48}\text{Cd}_2\text{N}_4\text{O}_{12}$
Formula weight	1 063.69	979.62	1 145.74
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
$a$ / nm	1.001 64(8)	1.051 03(10)	1.007 26(10)
$b$ / nm	1.090 88(8)	1.117 77(9)	2.154 64(12)
$c$ / nm	1.192 72(9)	1.143 45(12)	1.210 50(12)
$\alpha$ / ( $^\circ$ )	67.098(7)	101.385(8)	
$\beta$ / ( $^\circ$ )	88.235(7)	109.947(9)	113.531(12)
$\gamma$ / ( $^\circ$ )	89.044(6)	109.873(8)	
$V$ / $\text{nm}^3$	1.199 93(17)	1.110 4(2)	2.408 7(4)
$Z$	1	1	2
$F(000)$	548	504	1 160
$\theta$ range for data collection / ( $^\circ$ )	3.468~25.049	3.374~25.048	3.379~25.049
Limiting indices	$-11 \leq h \leq 11$ , $-12 \leq k \leq 12$ , $-14 \leq l \leq 14$	$-12 \leq h \leq 11$ , $-13 \leq k \leq 13$ , $-11 \leq l \leq 13$	$-11 \leq h \leq 10$ , $-25 \leq k \leq 14$ , $-14 \leq l \leq 14$
Reflection collected, unique ( $R_{\text{int}}$ )	7 187, 4 227 (0.044 2)	6 910, 3 923 (0.036 4)	8 208, 4 264 (0.060 5)
$D_c$ / ( $\text{g} \cdot \text{cm}^{-3}$ )	1.472	1.465	1.580
$\mu$ / $\text{mm}^{-1}$	1.066	1.142	0.951
Data, restraint, parameter	4 227, 0, 327	3 923, 0, 300	4 264, 7, 318
Goodness-of-fit on $F^2$	1.075	1.065	1.040
Final $R$ indices [ $I \geq 2\sigma(I)$ ] $R_1, wR_2$	0.057 8, 0.084 3	0.049 1, 0.085 6	0.054 8, 0.078 4
$R$ indices (all data) $R_1, wR_2$	0.089 3, 0.102 8	0.076 1, 0.098 9	0.093 1, 0.099 9
Largest diff. peak and hole / ( $\text{e} \cdot \text{nm}^{-3}$ )	515 and -351	384 and -402	893 and -572

compounds **1**~**3** are listed in Table 2. Hydrogen bond parameters of compounds **1** and **3** are given in Tables 3 and 4. CCDC: 1962704, **1**; 1962705, **2**; 1962706, **3**.

**Table 2 Selected bond distances (nm) and bond angles (°) for compounds 1~3**

<b>1</b>					
Zn(1)-O(1)	0.196 1(3)	Zn(1)-O(4)A	0.197 3(3)	Zn(1)-O(5)	0.214 8(3)
Zn(1)-N(1)	0.209 8(3)	Zn(1)-N(2)	0.212 9(4)		
O(1)-Zn(1)-O(4)A	109.16(13)	O(1)-Zn(1)-N(1)	121.82(12)	O(4)A-Zn(1)-N(1)	128.42(13)
O(1)-Zn(1)-N(2)	93.82(13)	N(2)-Zn(1)-O(4)A	91.67(13)	N(1)-Zn(1)-N(2)	78.41(15)
O(1)-Zn(1)-O(5)	94.93(12)	O(5)-Zn(1)-O(4)A	95.01(11)	N(1)-Zn(1)-O(5)	88.35(13)
N(2)-Zn(1)-O(5)	166.60(12)				
<b>2</b>					
Zn(1)-O(1)	0.191 1(2)	Zn(1)-O(3)A	0.189 8(3)	Zn(1)-N(1)	0.205 2(3)
Zn(1)-N(2)	0.205 5(3)				
O(1)-Zn(1)-O(3)A	112.69(12)	N(1)-Zn(1)-O(3)A	108.18(12)	O(1)-Zn(1)-N(1)	118.51(13)
N(2)-Zn(1)-O(3)A	107.62(12)	O(1)-Zn(1)-N(2)	125.20(11)	N(1)-Zn(1)-N(2)	80.01(13)
<b>3</b>					
Cd(1)-O(2)	0.222 3(4)	Cd(1)-O(4)A	0.218 1(4)	Cd(1)-O(5)	0.229 1(4)
Cd(1)-N(1)	0.231 9(5)	Cd(1)-N(2)	0.233 4(5)		
O(4)A-Cd(1)-O(2)	125.23(17)	O(4)A-Cd(1)-O(5)	99.32(15)	O(2)-Cd(1)-O(5)	81.75(15)
O(4)A-Cd(1)-N(1)	96.99(18)	O(2)-Cd(1)-N(1)	99.52(17)	O(5)-Cd(1)-N(1)	159.0(2)
O(4)A-Cd(1)-N(2)	134.18(17)	O(2)-Cd(1)-N(2)	100.48(17)	O(5)-Cd(1)-N(2)	89.26(18)
N(1)-Cd(1)-N(2)	69.8(2)				

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

**Table 3 Hydrogen bond parameters of compound 1**

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle\text{DHA} / (^\circ)$
O(5)-H(1W)···O(3)A	0.078 7	0.199 0	0.266 1	143.1
O(5)-H(2W)···O(2)	0.091 1	0.173 2	0.261 4	175.6

Symmetry code: A:  $-x+2, -y, -z+1$ .

**Table 4 Hydrogen bond parameters of compound 3**

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle\text{DHA} / (^\circ)$
O(5)-H(1W)···O(4)	0.096 2	0.199 1	0.276 0	135.4
O(5)-H(2W)···O(1)A	0.069 5	0.218 8	0.286 6	165.5
O(6)-H(3W)···O(3)	0.084 9	0.200 0	0.283 1	166.1

Symmetry code: A:  $-x+1, -y, -z+1$ .

## 1.6 Photocatalytic activity study

Photocatalytic degradation of methylene blue (MB) in the presence of catalysts **1**~**3** was investigated using a Cary 5000 UV - Vis - NIR spectrophotometer. The catalyst (50 mg) was dispersed in 100 mL aqueous solution of MB ( $10 \text{ mg} \cdot \text{L}^{-1}$ ) under stirring for 30 min in

the dark, aiming to ensure an adsorption - desorption equilibrium. The obtained mixture was then exposed to a continuous UV irradiation using an Hg lamp (125 W) for 150 min with continuous stirring. Reaction samples (5 mL) were taken out every 15 min, centrifuged, and then analyzed by UV - Vis spectrophotometry, monitor-

ing an intensity decrease of the MB absorption band at 668 nm. A control experiment was also performed under the same reaction conditions, showing that no MB degradation takes place in the absence of catalyst.

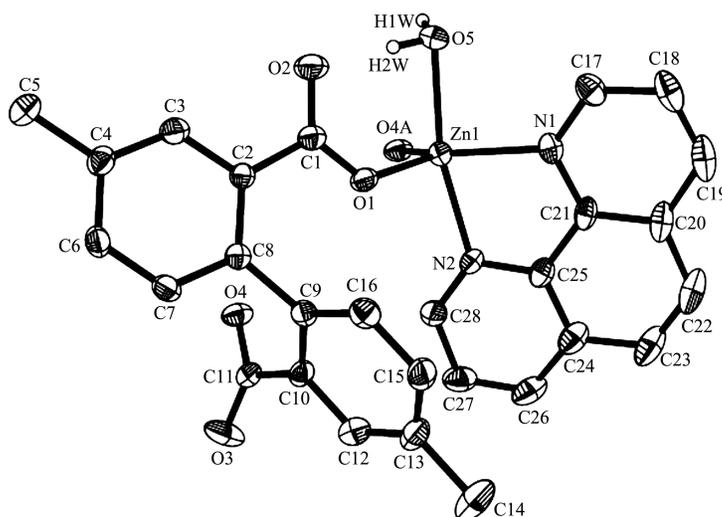
## 2 Results and discussion

### 2.1 Description of the structure

#### 2.1.1 Structure of $[\text{Zn}_2(\mu\text{-dbda})_2(\text{phen})_2(\text{H}_2\text{O})_2]$ (**1**)

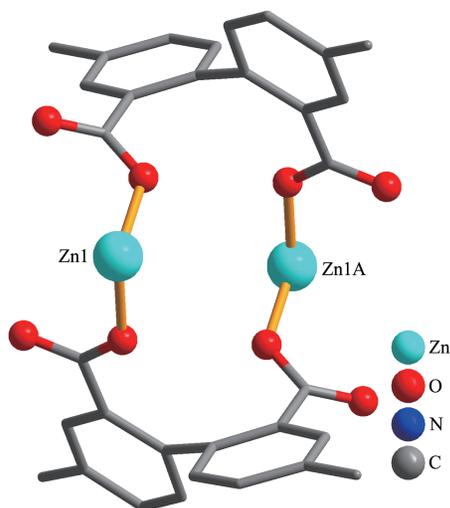
This compound reveals a discrete dimeric structure with the asymmetric unit containing a Zn(II) ion, a  $\mu\text{-dbda}^{2-}$  ligand, a phen moiety, and one coordinated water molecule. The Zn(II) center is penta-coordinated and reveals a trigonal bipyramidal  $\{\text{ZnN}_2\text{O}_3\}$  environment, which is completed by two O atoms from two  $\mu\text{-}$

$\text{dbda}^{2-}$  blocks, one O atom from the  $\text{H}_2\text{O}$  ligand, and a pair of N atoms from the phen moiety (Fig. 1). The lengths of the Zn-O and Zn-N bonds are 0.196 1(3)~0.214 8(3) and 0.209 8(3)~0.212 9(4) nm, respectively; these are within the normal values for related Zn(II) derivatives<sup>[11,17-18]</sup>. The  $\mu\text{-dbda}^{2-}$  block acts as a  $\mu$ -linker via monodentate  $\text{COO}^-$  groups (Fig. 2). In the  $\mu\text{-dbda}^{2-}$  block, the dihedral angle of two benzene rings is  $68.36^\circ$ . The  $\mu\text{-dbda}^{2-}$  blocks connect two Zn1 ions to give a  $\text{Zn}_2$  molecular unit having a  $\text{Zn}\cdots\text{Zn}$  distance of 0.574 3(3) nm (Fig. 2). These discrete  $\text{Zn}_2$  units are interconnected by  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds to form a 3D supramolecular framework (Fig. 3).



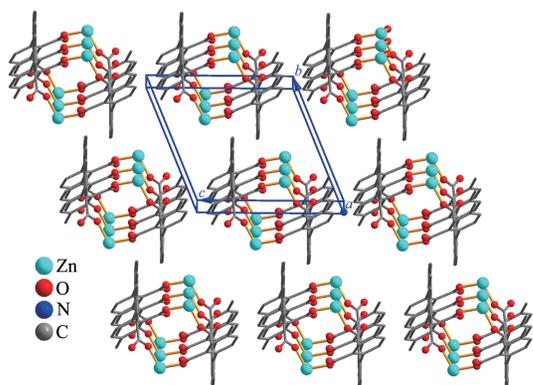
H atoms are omitted for clarity except those bonding to oxygen atoms; Symmetry code: A:  $-x+2, -y, -z+1$

Fig.1 Drawing of the asymmetric unit of compound **1** with 30% probability thermal ellipsoids



Symmetry code: A:  $-x+2, -y, -z+1$

Fig.2 Di-zinc(II) unit in **1**

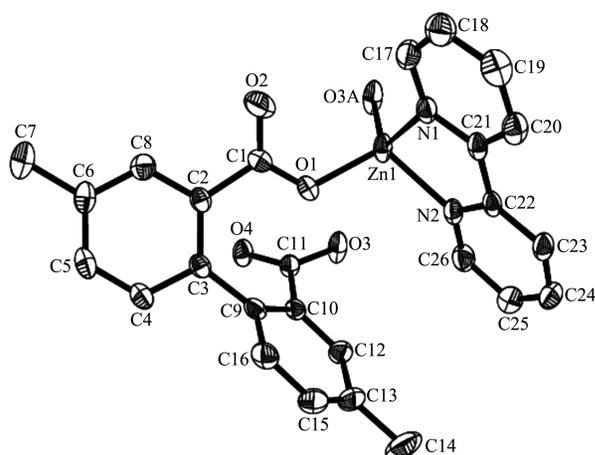


Ligands phen and H<sub>2</sub>O are omitted for clarity

Fig.3 Perspective of 3D supramolecular framework along *b* and *c* axes in **1**

### 2.1.1.2 [Zn<sub>2</sub>(μ-dbda)<sub>2</sub>(2,2'-bipy)<sub>2</sub>] (**2**)

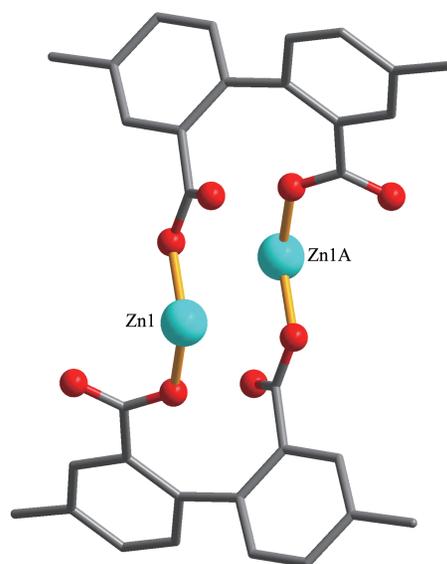
This compound also has a discrete dimeric structure. Its asymmetric unit containing one Zn(II) ion, a μ-dbda<sup>2-</sup> ligand, and a 2,2'-bipy moiety. The Zn1 center is tetra-coordinated and reveals a distorted tetrahedral {ZnN<sub>2</sub>O<sub>2</sub>} geometry formed by two carboxylate O donors from two individual μ-dbda<sup>2-</sup> moieties and two N donors from the 2,2'-bipy moiety (Fig. 4). The Zn - O (0.189 8(3)~0.191 1(2) nm) and Zn - N (0.205 2(3)~0.205 5(3) nm) bonds are within standard values<sup>[17-19]</sup>. The dbda<sup>2-</sup> block acts as a μ-linker with its carboxylate groups adopting a monodentate mode (Fig. 5). Within the μ-dbda<sup>2-</sup> block, the dihedral angle between two aromatic rings is 64.00°. The μ-dbda<sup>2-</sup> blocks link two Zn1 ions to give a Zn<sub>2</sub> unit having a Zn···Zn distance of 0.393 0(3) nm (Fig. 5). These discrete Zn<sub>2</sub> units are in-



H atoms are omitted for clarity; Symmetry code: A:  $-x+1, -y, -z+1$

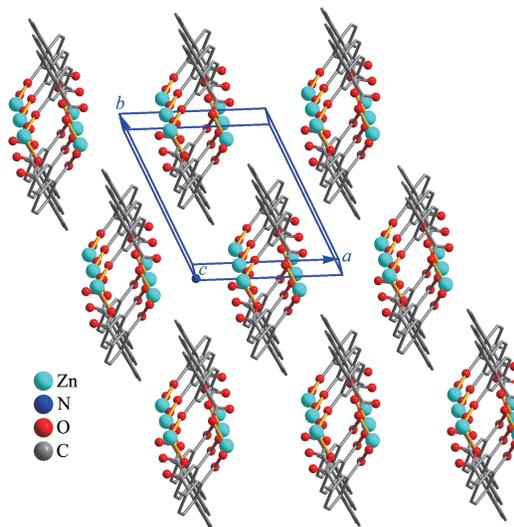
Fig.4 Drawing of the asymmetric unit of compound **2** with 30% probability thermal ellipsoids

terconnected to form a 3D supramolecular framework (Fig.6).



Symmetry code: A:  $-x+1, -y, -z+1$

Fig.5 Di-zinc(II) unit in **2**



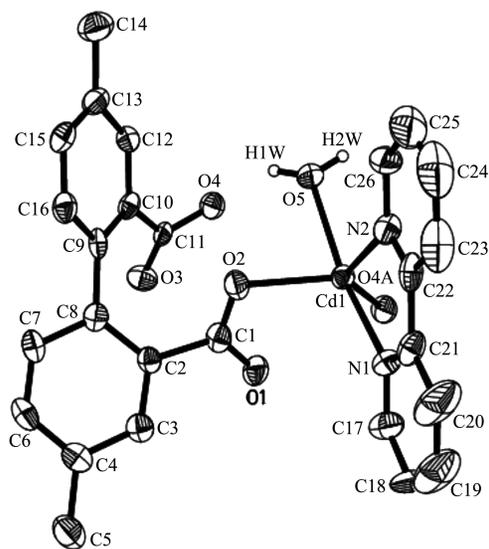
2,2'-bipy ligands are omitted for clarity

Fig.6 Perspective of 3D supramolecular framework along *a* and *b* axes in **2**

### 2.1.1.2 [Cd<sub>2</sub>(μ-dbda)<sub>2</sub>(2,2'-bipy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (**3**)

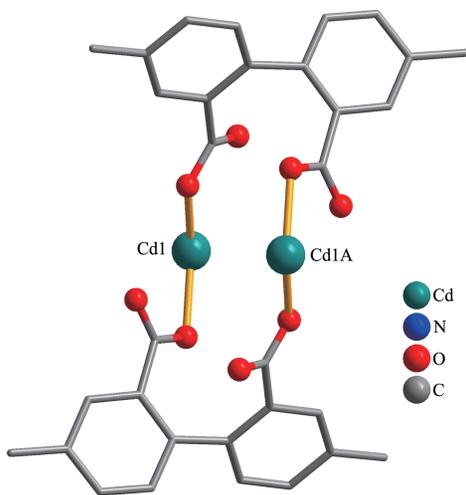
This compound has a discrete Cd(II) dimer structure. There are one Cd1 ion, one μ-dbda<sup>2-</sup> block, one 2,2'-bipy moiety, one H<sub>2</sub>O ligand, and one lattice water molecule in the asymmetric unit of **3** (Fig. 7). The Cd1 ion is penta-coordinated with a distorted {CdN<sub>2</sub>O<sub>3</sub>} trigonal bipyramidal environment. It is filled by two carboxylate O atoms from two μ-dbda<sup>2-</sup> blocks, one O atom

from the  $\text{H}_2\text{O}$  ligand, and a pair of N atoms from the 2, 2'-bipy moiety. The Cd-O (0.218 1(4)–0.229 1(4) nm) and Cd-N (0.231 9(5)–0.233 4(3) nm) bond lengths are in good agreement with those distances observed in some other Cd(II) compounds<sup>[9,11,13]</sup>. The  $\mu$ -dbda<sup>2-</sup> block is bidentate and behaves as a  $\mu$ -linker, interconnecting the adjacent Cd1 ions into a dicadmium(II) molecular with a Cd···Cd separation of 0.463 3(5) nm. Discrete Cd<sub>2</sub> units are further assembled into a 3D supramolecular framework (Fig.9).



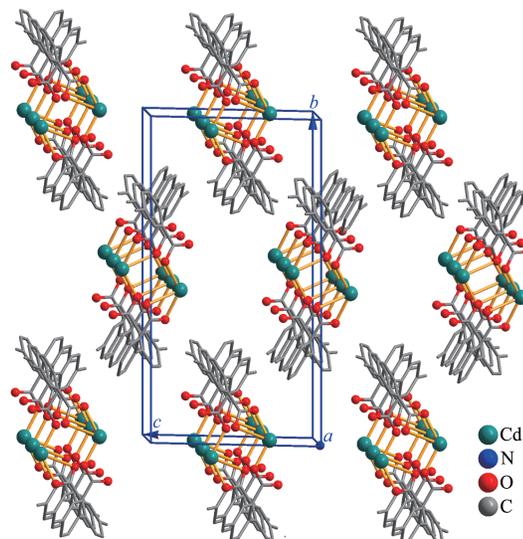
H atoms except those bonding to oxygen atoms and lattice water molecules are omitted for clarity; Symmetry codes: A:  $-x+1, -y, -z+1$

Fig.7 Drawing of the asymmetric unit of compound **3** with 30% probability thermal ellipsoids



Symmetry code: A:  $-x+1, -y, -z+1$

Fig.8 Di-cadmium(II) unit in **3**



2,2'-bipy ligands are omitted for clarity

Fig.9 Perspective of 3D supramolecular framework along *b* and *c* axes in **3**

## 2.2 TGA analysis

To determine the thermal stability of compounds **1**–**3**, their thermal behaviors were investigated under nitrogen atmosphere by thermogravimetric analysis (TGA). As shown in Fig.10, TGA curve of compound **1** showed that there was a loss of two  $\text{H}_2\text{O}$  ligands between 78 and 126 °C (Obsd. 3.6%, Calcd. 3.4%); further heating above 231 °C led to a decomposition of the dehydrated sample. Compound **2** did not contain solvent of crystallization or  $\text{H}_2\text{O}$  ligands and remained stable up to 210 °C, followed by a decomposition on further heating. Compound **3** lost its two lattice water molecules and two  $\text{H}_2\text{O}$  ligands in a range of 46–129 °C (Obsd. 6.6%, Calcd. 6.3%), followed by the decomposition at 245 °C.

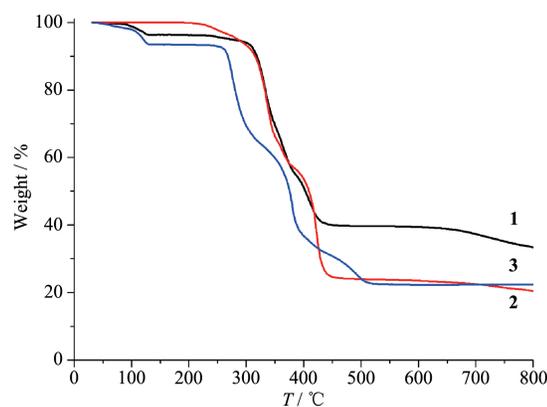


Fig.10 TGA curves of compounds **1**–**3**

### 2.3 Luminescent properties

Solid-state emission spectra of H<sub>2</sub>dbda and compounds **1**~**3** were measured at room temperature (Fig. 11). The spectrum of H<sub>2</sub>dbda revealed a weak emission with a maximum at 453 nm ( $\lambda_{\text{ex}}=310$  nm). In comparison with H<sub>2</sub>dbda, the coordination compounds **1**~**3** exhibited more extensive emissions, namely at 390 nm for **1**, 411 nm for **2**, and 387 nm for **3** ( $\lambda_{\text{ex}}=310$  nm). These emissions correspond to intraligand  $\pi-\pi^*$  or  $n-\pi^*$  transition of H<sub>2</sub>dbda<sup>[9,11,18]</sup>. Enhancement of the luminescence in **1**~**3** vs H<sub>2</sub>dbda can be explained by the coordination of ligands to Zn(II) or Cd(II). The coordina-

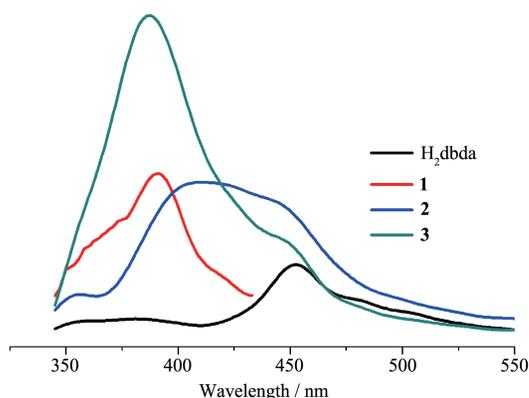


Fig. 11 Solid-state emission spectra of H<sub>2</sub>dbda and compounds **1**~**3** at room temperature

tion can augment a rigidity of ligands and reduce an energy loss due to radiationless decay<sup>[13,17,19]</sup>.

### 2.4 Photocatalytic activity for dye degradation

Prior research showed that various transition metal coordination polymers are promising photocatalysts for the degradation of different organic dye pollutants<sup>[20-24]</sup>. To study the photocatalytic activity of **1**~**3**, we selected methylene blue (MB) as a model dye contaminant in wastewater. The obtained results (Fig. 12 and 13) indicated that the MB degradation rate attained 81.4% after 150 min in the presence of **3** that is the

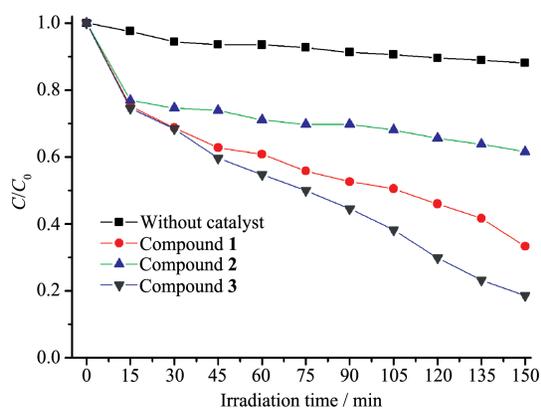


Fig. 12 Photocatalytic degradation of MB solution under UV light using catalysts **1**~**3** and the blank experiment

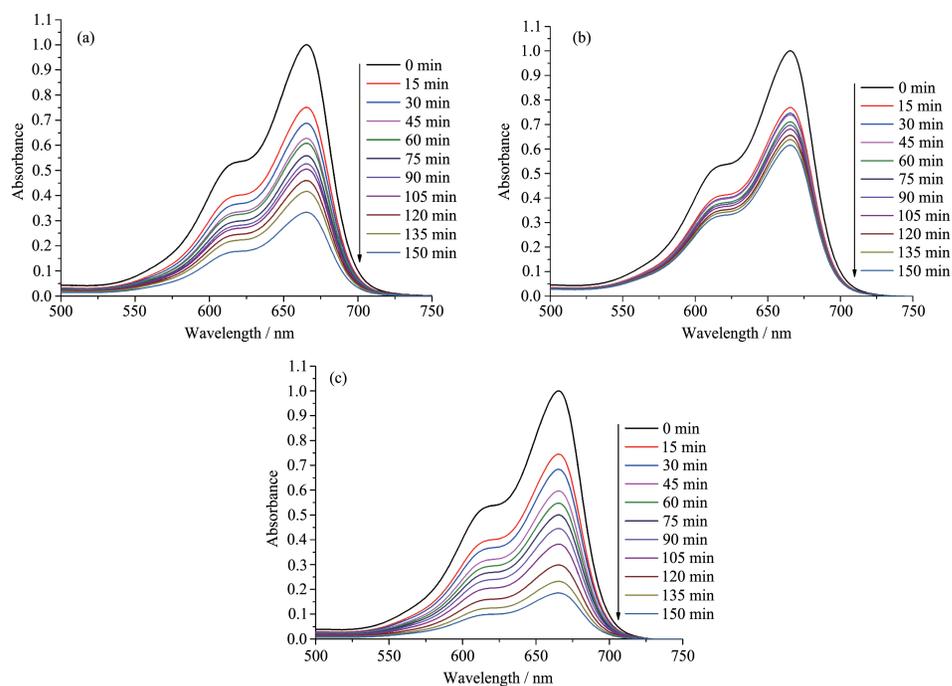


Fig. 13 Time-dependent UV-Vis spectra of the reaction mixtures in the course of MB photodegradation catalyzed by **1** (a), **2** (b), and **3** (c)

most active catalyst. For **1** and **2**, the MB degradation rates were inferior, being 66.7% and 38.5%, respectively. Under similar conditions, blank test showed that the MB degradation efficiency was only 11.8% after 150 min. The research demonstrates that the photocatalytic activity depends on various factors, such as the number of water ligands, the coordination environment of metal centers, and the optical band gap of catalyst<sup>[21,24-25]</sup>.

### 3 Conclusions

In summary, we have successfully synthesized and characterized three new zinc and cadmium coordination compounds by using one unexplored biphenyl dicarboxylic acid as ligand under hydrothermal condition. All compounds feature a 0D dimeric structure. Besides, the luminescence and photocatalytic properties were also investigated and discussed. The results show that compound **3** can degrade methylene blue efficiently.

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