

由醚氧桥联羧酸配体构筑的铜(II)、锌(II)和锰(II) 配位聚合物的合成、晶体结构、荧光及光催化性质

黎 彧¹ 曾福燃¹ 周 峰^{*,2} 李善吉^{*,3}

(¹广东轻工职业技术学院, 广东省特种建筑材料及其绿色制备工程技术研究中心/

佛山市特种功能性建筑材料及其绿色制备技术工程中心, 广州 510300)

(²佛山职业技术学院机电工程学院, 佛山 528137)

(³广州工程技术职业学院石油化工学院, 广州 510725)

摘要: 采用水热方法, 用醚氧桥联的三羧酸配体(H_3dpna)和四羧酸配体(H_4deta)为主配体, 2, 2'-联吡啶(2, 2'-bipy)和非咯啉(phen)为辅助配体, 分别与 $CuCl_2 \cdot H_2O$ 、 $ZnCl_2$ 和 $MnCl_2 \cdot 4H_2O$ 反应, 合成了 2 个二维配位聚合物 $\{[Cu_3(\mu_4-dpna)_2(2, 2'-bipy)_2] \cdot 4H_2O\}_n$ (**1**) 和 $\{[Zn_3(\mu_4-dpna)_2(2, 2'-bipy)_2(H_2O)_2] \cdot 6H_2O\}_n$ (**2**) 以及 2 个一维配位聚合物 $\{[M_2(\mu_4-deta)(phen)_2(H_2O)] \cdot 3H_2O\}_n$ ($M=Mn$ (**3**), Zn (**4**)), 并对其结构、荧光和光催化性质进行了研究。结构分析结果表明配合物 **1** 和 **2** 属于单斜晶系, $P2_1/c$ 和 $C2/c$ 空间群。由于采用了不同的金属离子, 配合物 **1** 和 **2** 呈现不同的二维层结构。配合物 **3** 和 **4** 为异质同心结构, 均属于单斜晶系, $P2_1/n$ 空间群。配合物 **3** 和 **4** 都具有一维链结构。另外, 研究了这些配合物的荧光和对有机染料亚甲基蓝的光催化降解性能, 结果表明配合物 **2** 和 **4** 可以高效地降解亚甲基蓝。

关键词: 配位聚合物; 醚氧桥联羧酸; 荧光; 光催化

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Syntheses, Crystal Structures, Luminescence and Photocatalytic Activity of Cu(II), Zn(II) and Mn(II) Coordination Polymers Based on Ether-Bridged Carboxylic Acids

LI Yu¹ ZENG Fu-Ran¹ ZHOU Feng^{*,2} LI Shan-Ji^{*,3}

(¹Guangdong Research Center for Special Building Materials and Its Green Preparation Technology/Foshan

Research Center for Special Functional Building Materials and Its Green

Preparation Technology, Guangdong Industry Polytechnic, Guangzhou 510300, China)

(²School of Mechanical and Electrical Engineering, Foshan Polytechnic, Foshan, Guangdong 528137, China)

(³School of Petrochemical Engineering, Guangzhou Institute of Technology, Guangzhou 510725, China)

Abstract: Two 2D coordination polymers, namely $\{[Cu_3(\mu_4-dpna)_2(2, 2'-bipy)_2] \cdot 4H_2O\}_n$ (**1**) and $\{[Zn_3(\mu_4-dpna)_2(2, 2'-bipy)_2(H_2O)_2] \cdot 6H_2O\}_n$ (**2**) as well as two 1D coordination polymers, namely $\{[M_2(\mu_4-deta)(phen)_2(H_2O)] \cdot 3H_2O\}_n$ ($M=Mn$ (**3**), Zn (**4**)) have been constructed hydrothermally using H_3dpna ($H_3dpna=5-(3', 4'-dicarboxylphenoxy)nicotic$ acid) or H_4deta ($H_4deta=2, 3, 2', 3'$ -diphenyl ether tetracarboxylic acid) as a principal building block, 2, 2'-bipy (2, 2'-bipy=2, 2'-bipyridine) or phen (phen=1, 10-phenanthroline) as a auxiliary ligand, and copper, zinc or manganese chlorides. 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 compounds **1** and **2** crystallize in the monoclinic system, space groups $P2_1/c$ or

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*通信联系人。E-mail: 63419822@qq.com, hnlsj2004@163.com

C2/c. Compounds **1** and **2** disclose two different 2D sheet structures. The structural difference of compounds **1** and **2** is driven by the Cu(II)/Zn(II) nodes. Compounds **3** and **4** are isostructural and crystallize in the monoclinic system, space group $P2_1/n$. Both compounds show a 1D chain structure. The luminescent and photocatalytic properties of the compounds were investigated, showing that compounds **2** and **4** can effectively degrade methylene blue as a model organic dye pollutant. CCDC: 2004109, **1**; 2004110, **2**; 2004481, **3**; 2004482, **4**.

Keywords: coordination polymer; ether-bridged carboxylic acid; luminesce; photocatalytic properties

0 Introduction

During the past decades, the design and construction of functional coordination polymers have caught enormous attention of chemical researchers, not only because of their charming architectures and topologies, but also for their various potential applications in gas storage and separation, catalysis, magnetism, luminescence, and biomedicine^[1-12]. However, the design and composition of crystalline complexes with target structures as well as multifunction are of great importance topics and are still the tremendously challenges. The assembly of coordination polymers is mainly affected by many factors, such as metal ions, organic ligands and auxiliary ligands, metal-to-ligand ratio, solvent, and the reaction temperature^[13-22]. The metal ions and organic ligands are the key to get intriguing topologies and functional materials. Multicarboxylate ligands are frequently used for the construction of coordination polymers because they can satisfy the charge-balance and can provide diverse ligands and coordination modes^[5-6,14,16-17,23-24]. Among such polycarboxylate blocks, semirigid biphen ligands are particularly intriguing, since they enable the formation of uncommon metal-organic networks or even topologically unique nets; at the same time, such ligands can also show interesting properties along with flexibility and conformational diversity^[6,14,16-17,25].

Currently, the water pollutant is becoming one serious environment problem in the world. Much effort has been devoted to developing new photocatalytic materials for the green degradation of organic pollutants. Some coordination polymers show good photocatalytic activity for the decomposition of organic dyes^[25-28].

Following our interest in the exploration of novel

and poorly investigated multicarboxylic acids for the design of coordination polymers^[5-6,14,17,25,29], in the present study we selected 5-(3,4-dicarboxylphenoxy)nicotic acid (H_3dpna) or 2,3,2',3'-diphenyl ether tetracarboxylic acid (H_4deta) as a main building block. The selection of H_3dpna and H_4deta has been governed by the following reasons. (1) Both ligands contain two aromatic rings that are interconnected by a rotatable *O*-ether group providing a subtle conformational adaptation. (2) They show three different types of functionalities (*i.e.*, -COOH, *O*-ether or *N*-pyridyl) and have eight or nine potential coordination sites, which can result in diverse coordination patterns and high dimensionalities, especially when acting as a multiply bridging spacer. (3) Two carboxylic acid blocks remain poorly used for the generation of coordination polymers.

Herein, we report the synthesis, crystal structures, and luminescence and photocatalytic properties of Cu(II), Zn(II) and Mn(II) coordination polymers with H_3dpna or H_4deta ligands.

1 Experimental

1.1 Reagents and physical measurements

All chemicals and solvents were of AR grade and used without further purification. The content of 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) data were collected on a LINSEIS STA PT1600 thermal analyzer with a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Excitation and emission spectra were recorded on an Edinburgh FLS920 fluorescence spectrometer using the solid samples at room temperature. Powder X-ray diffraction (PXRD) patterns were measured on a

Rigaku-Dmax 2400 diffractometer using Cu $K\alpha$ radiation ($\lambda=0.154\ 06\ \text{nm}$); the X-ray tube was operated at 40 kV and 40 mA; the data collection range was between 5° and 45° .

1.2 Synthesis of $\{[\text{Cu}_3(\mu_4\text{-dpna})_2(2,2'\text{-bipy})_2] \cdot 4\text{H}_2\text{O}\}_n$ (**1**)

A mixture of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ (0.046 g, 0.3 mmol), H_3dpna (0.061 g, 0.2 mmol), 2,2'-bipy (0.047 g, 0.3 mmol), NaOH (0.024 g, 0.6 mmol), and H_2O (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 $120\ ^\circ\text{C}$ for 3 d, followed by cooling to room temperature at a rate of $10\ ^\circ\text{C} \cdot \text{h}^{-1}$. Blue block-shaped crystals were isolated manually, and washed with distilled water. Yield: 45% (based on H_3dpna). Anal. Calcd. for $\text{C}_{48}\text{H}_{36}\text{Cu}_3\text{N}_6\text{O}_{18}$ (%): C 49.05, H 3.09, N 7.15; Found(%): C 48.93, H 3.07, N 7.16. IR (KBr, cm^{-1}): 3 518w, 3 074w, 1 625m, 1 586s, 1 572s, 1 498w, 1 472w, 1 446m, 1 384s, 1 362s, 1 318w, 1 292w, 1 253w, 1 226w, 1 195w, 1 160w, 1 138w, 1 103w, 1 059w, 1 033w, 989w, 927w, 822w, 795w, 765m, 730w, 699w, 651w, 615w.

1.3 Synthesis of $\{[\text{Zn}_3(\mu_4\text{-dpna})_2(2,2'\text{-bipy})_2(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}\}_n$ (**2**)

Synthesis of **2** was similar to **1** except using ZnCl_2 (0.041 g, 0.3 mmol) instead of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$. Colourless block-shaped crystals of **2** were isolated manually, and washed with distilled water. Yield: 50% (based on H_3dpna). Anal. Calcd. for $\text{C}_{48}\text{H}_{44}\text{Zn}_3\text{N}_6\text{O}_{22}$ (%): C 46.01, H 3.54, N 6.71; Found(%): C 45.86, H 3.55, N 6.74. IR (KBr, cm^{-1}): 3 083w, 1 600s, 1 581s, 1 564s, 1 492w, 1 475w, 1 444m, 1 391s, 1 319w, 1 302w, 1 257w, 1 231w, 1 200w, 1 159w, 1 063w, 1 027w, 987w, 943w, 917w, 828w, 805w, 823w, 774m, 735w, 704w, 655w.

1.4 Syntheses of $\{[\text{M}_2(\mu_4\text{-deta})(\text{phen})_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}\}_n$ ($\text{M}=\text{Mn}$ (**3**), Zn (**4**))

A mixture of $\text{MCl}_2 \cdot x\text{H}_2\text{O}$ ($x=4$ for **3** and $x=0$ for **4**, 0.20 mmol), H_4deta (0.035 g, 0.10 mmol), phen (0.040 g, 0.20 mmol), NaOH (0.016 g, 0.40 mmol), and H_2O (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 d, followed by cooling to room temperature at a rate of $10\ ^\circ\text{C} \cdot \text{h}^{-1}$. Yellow

(**3**) or colourless (**4**) block-shaped crystals were isolated manually, and washed with distilled water. Yield: 52% for **3** and 42% for **4** (based on H_4deta). Anal. Calcd. for $\text{C}_{40}\text{H}_{30}\text{Mn}_2\text{N}_4\text{O}_{13}$ (**3**, %): C 54.31, H 3.42, N 6.33; Found (%): C 54.10, H 3.44, N 6.30. IR (KBr, cm^{-1}): 3 407w, 3 061w, 1 627w, 1 565s, 1 516w, 1 466w, 1 421m, 1 380s, 1 293w, 1 244w, 1 195w, 1 141w, 1 099w, 1 067w, 1 001w, 927w, 902w, 848w, 770w, 729m, 700w, 667w, 639w. Anal. Calcd. for $\text{C}_{40}\text{H}_{30}\text{Zn}_2\text{N}_4\text{O}_{13}$ (**4**, %): C 53.06, H 3.34, N 6.19; Found(%): C 53.27, H 3.32, N 6.23. IR (KBr, cm^{-1}): 3 439w, 3 066w, 1 648s, 1 625s, 1 581m, 1 516w, 1 494w, 1 450w, 1 423w, 1 384s, 1 305w, 1 265w, 1 226w, 1 191w, 1 160w, 1 142w, 1 103w, 1 024w, 984w, 905w, 853w, 804w, 774w, 725m, 707w, 642w, 607w.

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

1.5 Structure determinations

The data for single crystals of compounds **1~4** was collected at 293(2) K on a Bruker SMART APEX II CCD diffractometer with Cu $K\alpha$ radiation ($\lambda=0.154\ 178\ \text{nm}$). The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-2014 program^[30]. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were positioned geometrically and refined using a riding model. Some lattice solvent molecules in **1** are highly disordered and were removed using the SQUEEZE routine in PLATON^[31]. The number of solvent H_2O molecules was obtained on the basis of elemental and thermogravimetric analyses. A summary of the crystallography data and structure refinements for **1~4** is given in Table 1. The selected bond lengths and angles for compounds **1~4** are listed in Table 2. Hydrogen bond parameters of compounds **2~4** are given in Table 3~5.

CCDC: 2004109, **1**; 2004110, **2**; 2004481, **3**; 2004482, **4**.

1.6 Photocatalytic activity studies

Photocatalytic degradation of methylene blue (MB) in the presence of catalysts **1~4** was investigated using a Cary 5000 UV-Vis-NIR spectrophotometer.

Table 1 Crystal data for compounds 1~4

Compound	1	2	3	4
Chemical formula	C ₄₈ H ₃₆ Cu ₃ N ₆ O ₁₈	C ₄₈ H ₄₄ Zn ₃ N ₆ O ₂₂	C ₄₀ H ₃₀ Mn ₂ N ₄ O ₁₃	C ₄₀ H ₃₀ Zn ₂ N ₄ O ₁₃
Molecular weight	1 175.47	1 253.00	884.56	905.42
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / nm	1.813 04(17)	2.024 50(6)	1.268 98(8)	1.246 22(3)
<i>b</i> / nm	1.003 29(8)	0.767 93(2)	1.718 33(12)	1.720 14(5)
<i>c</i> / nm	1.353 58(11)	3.322 33(10)	1.739 32(14)	1.725 40(7)
β / (°)	91.443(9)	100.782(3)	100.857(7)	100.085(3)
<i>V</i> / nm ³	2.461 4(4)	5.074 0(3)	3.724 7(5)	3.641 5(2)
<i>Z</i>	2	4	4	4
<i>F</i> (000)	1 114	2 560	1 808	1 848
Crystal size / mm	0.21×0.20×0.18	0.26×0.24×0.23	0.22×0.21×0.20	0.23×0.19×0.18
θ range for data collection / (°)	4.880~66.600	4.446~69.920	3.648~69.924	3.657~69.969
Limiting indices	-17 ≤ <i>h</i> ≤ 21, -11 ≤ <i>k</i> ≤ 11, -14 ≤ <i>l</i> ≤ 16	-24 ≤ <i>h</i> ≤ 20, -9 ≤ <i>k</i> ≤ 4, -38 ≤ <i>l</i> ≤ 40	-13 ≤ <i>h</i> ≤ 15, -17 ≤ <i>k</i> ≤ 20, -20 ≤ <i>l</i> ≤ 20	-11 ≤ <i>h</i> ≤ 15, -20 ≤ <i>k</i> ≤ 20, -20 ≤ <i>l</i> ≤ 20
Reflection collected, unique (<i>R</i> _{int})	8 795, 4 331 (0.076 5)	9 067, 4 708 (0.027 9)	6 746, 4 196 (0.052 0)	6 769, 4 606 (0.050 5)
<i>D</i> _c / (g·cm ⁻³)	1.586	1.640	1.577	1.651
μ / mm ⁻¹	2.116	2.439	6.171	2.289
Data, restraint, parameter	4 331, 0, 322	4 708, 0, 357	4 196, 0, 534	4 606, 0, 532
Goodness-of-fit on <i>F</i> ²	0.964	1.022	1.031	1.023
Final <i>R</i> indices [<i>I</i> ≥ 2σ(<i>I</i>)] <i>R</i> ₁ , <i>wR</i> ₂	0.068 1, 0.150 8	0.044 2, 0.120 4	0.062 9, 0.154 5	0.075 4, 0.183 9
<i>R</i> indices (all data) <i>R</i> ₁ , <i>wR</i> ₂	0.110 4, 0.186 8	0.058 8, 0.129 8	0.105 6, 0.191 1	0.109 6, 0.206 8
Largest diff. peak and hole / (e·nm ⁻³)	614 and -824	921 and -772	708 and -578	2 058 and -1 275

Table 2 Selected bond distances (nm) and bond angles (°) for compounds 1~4

1					
Cu(1)-O(6)A	0.194 3(4)	Cu(1)-O(6)B	0.194 3(4)	Cu(1)-N(1)	0.203 6(5)
Cu(1)-N(1)C	0.203 6(5)	Cu(2)-O(1)	0.195 7(4)	Cu(2)-O(4)D	0.195 5(5)
Cu(2)-N(2)	0.200 1(5)	Cu(2)-N(3)	0.197 2(5)		
O(6)A-Cu(1)-N(1)C	91.72(19)	O(6)B-Cu(1)-N(1)C	88.28(19)	O(6)A-Cu(1)-N(1)	88.27(19)
O(6)B-Cu(1)-N(1)	91.73(19)	O(4)D-Cu(2)-O(1)	94.31(19)	O(4)D-Cu(2)-N(3)	94.8(2)
N(3)-Cu(2)-O(1)	159.2(2)	O(4)D-Cu(2)-N(2)	158.4(2)	N(2)-Cu(2)-O(1)	96.15(19)
N(2)-Cu(2)-N(3)	81.8(2)				
2					
Zn(1)-O(1)	0.202 4(2)	Zn(1)-O(6)A	0.217 1(3)	Zn(1)-O(7)A	0.241 5(4)
Zn(1)-N(1)B	0.219 1(3)	Zn(1)-N(2)	0.211 2(3)	Zn(1)-N(3)	0.217 8(3)
Zn(2)-O(3)	0.232 9(3)	Zn(2)-O(3)C	0.232 9(3)	Zn(2)-O(4)	0.204 8(3)
Zn(2)-O(4)C	0.204 8(3)	Zn(2)-O(8)	0.201 2(3)	Zn(2)-O(8)C	0.201 2(3)
O(1)-Zn(1)-N(2)	97.45(10)	O(6)A-Zn(1)-O(1)	86.61(11)	N(2)-Zn(1)-O(6)A	89.09(13)
N(3)-Zn(1)-O(1)	165.24(11)	N(2)-Zn(1)-N(3)	75.66(12)	O(6)A-Zn(1)-N(3)	106.07(12)
O(1)-Zn(1)-N(1)B	91.52(10)	N(2)-Zn(1)-N(1)B	132.67(11)	O(6)A-Zn(1)-N(1)B	137.95(12)
N(3)-Zn(1)-N(1)B	84.10(11)	O(7)A-Zn(1)-O(1)	102.35(12)	O(7)A-Zn(1)-N(2)	138.00(12)

Continued Table 2

O(6)A-Zn(1)-O(7)A	56.00(12)	O(7)A-Zn(1)-N(3)	91.20(13)	O(7)A-Zn(1)-N(1)B	83.67(11)
O(8)C-Zn(2)-O(8)	99.0(2)	O(8)-Zn(2)-O(4)	103.74(14)	O(8)C-Zn(2)-O(4)	97.33(14)
O(4)C-Zn(2)-O(4)	147.35(18)	O(8)-Zn(2)-O(3)	87.29(12)	O(8)-Zn(2)-O(3)C	156.47(14)
O(4)-Zn(2)-O(3)	59.14(10)	O(3)-Zn(2)-O(4)C	97.84(11)	O(3)-Zn(2)-O(3)C	95.92(15)
3					
Mn(1)-O(2)	0.222 3(4)	Mn(1)-O(4)	0.208 8(4)	Mn(1)-O(8)A	0.208 0(4)
Mn(1)-N(1)	0.224 2(4)	Mn(1)-N(2)	0.220 2(5)	Mn(2)-O(1)	0.231 7(4)
Mn(2)-O(2)	0.223 9(4)	Mn(2)-O(7)A	0.209 6(4)	Mn(2)-O(10)	0.218 9(4)
Mn(2)-N(3)	0.223 0(5)	Mn(2)-N(4)	0.227 2(5)		
O(4)-Mn(1)-O(8)A	150.42(17)	N(2)-Mn(1)-O(8)A	99.62(17)	O(4)-Mn(1)-N(2)	109.80(16)
O(2)-Mn(1)-O(8)A	89.27(17)	O(2)-Mn(1)-O(4)	84.63(15)	O(2)-Mn(1)-N(2)	96.36(16)
N(1)-Mn(1)-O(8)A	105.16(18)	O(4)-Mn(1)-N(1)	86.16(17)	N(1)-Mn(1)-N(2)	74.34(17)
N(1)-Mn(1)-O(2)	163.81(15)	O(10)-Mn(2)-O(7)A	84.84(16)	N(3)-Mn(2)-O(7)A	103.63(16)
N(3)-Mn(2)-O(10)	99.51(17)	O(2)-Mn(2)-O(7)A	100.13(15)	O(2)-Mn(2)-O(10)	97.90(16)
N(3)-Mn(2)-O(2)	151.59(17)	N(4)-Mn(2)-O(7)A	93.82(15)	N(4)-Mn(2)-O(10)	172.85(16)
N(4)-Mn(2)-N(3)	73.95(16)	N(4)-Mn(2)-O(2)	89.24(15)	O(1)-Mn(2)-O(7)A	154.45(15)
O(1)-Mn(2)-O(10)	87.24(16)	N(3)-Mn(2)-O(1)	101.62(16)	O(2)-Mn(2)-O(1)	57.01(14)
N(4)-Mn(2)-O(1)	96.82(16)	Mn(1)-O(2)-Mn(2)	133.88(18)		
4					
Zn(1)-O(1)	0.215 7(4)	Zn(1)-O(2)	0.229 4(5)	Zn(1)-O(6)A	0.205 6(4)
Zn(1)-O(10)	0.212 7(5)	Zn(1)-N(1)	0.217 1(5)	Zn(1)-N(2)	0.210 5(6)
Zn(2)-O(1)	0.223 6(4)	Zn(2)-O(3)	0.198 8(4)	Zn(2)-O(9)	0.194 7(4)
Zn(2)-N(3)	0.207 3(5)	Zn(2)-N(4)	0.215 4(6)		
O(6)A-Zn(1)-N(2)	105.8(2)	O(6)A-Zn(1)-O(10)	86.98(19)	N(2)-Zn(1)-O(10)	95.4(2)
O(6)A-Zn(1)-O(1)	98.87(18)	N(2)-Zn(1)-O(1)	153.6(2)	O(1)-Zn(1)-O(10)	95.00(19)
O(6)A-Zn(1)-N(1)	93.18(18)	N(2)-Zn(1)-N(1)	78.1(2)	O(10)-Zn(1)-N(1)	173.24(19)
O(1)-Zn(1)-N(1)	91.65(18)	O(6)A-Zn(1)-O(2)	155.56(18)	O(2)-Zn(1)-N(2)	98.2(2)
O(10)-Zn(1)-O(2)	86.66(19)	O(1)-Zn(1)-O(2)	58.29(17)	N(1)-Zn(1)-O(2)	95.86(19)

Symmetry codes: A: $x, -y+3/2, z-1/2$; B: $-x+1, y-1/2, -z+1/2$; C: $-x+1, -y+1, -z$; D: $x, -y+3/2, z+1/2$ for **1**; A: $-x, -y+1, -z$; B: $-x+1, -y+2, -z$; C: $-x, -y, -z+1/2$ for **2**; A: $-x+1, -y, -z+1$ for **3**; A: $-x+1, -y, -z+1$ for **4**.

Table 3 Hydrogen bond parameters of compound 2

D-H $\cdots$ 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(8)-H(1W) $\cdots$ O(9)	0.082 0	0.200 6	0.264 2	133.86
O(8)-H(2W) $\cdots$ O(10)A	0.084 5	0.185 1	0.265 9	159.74
O(9)-H(3W) $\cdots$ O(6)B	0.085 0	0.217 7	0.302 7	179.52
O(9)-H(4W) $\cdots$ O(2)A	0.085 0	0.196 4	0.281 5	179.54
O(10)-H(5W) $\cdots$ O(3)	0.085 0	0.195 1	0.280 1	179.05
O(11)-H(7W) $\cdots$ O(2)A	0.085 5	0.213 2	0.298 7	179.08

Symmetry codes: A: $x, y-1, z$; B: $-x, -y+1, -z$.

Table 4 Hydrogen bond parameters of compound 3

D-H $\cdots$ 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(10)-H(1W) $\cdots$ O(6)A	0.085 0	0.183 9	0.268 8	179.42
O(11)-H(3W) $\cdots$ O(12)B	0.085 0	0.188 7	0.273 6	179.28

Continued Table 4

O(11)–H(4W)···O(4)C	0.088 2	0.213 0	0.280 5	132.73
O(12)–H(5W)···O(3)C	0.085 6	0.192 0	0.274 8	162.66
O(12)–H(6W)···O(6)C	0.085 4	0.197 6	0.277 2	154.70
O(13)–H(7W)···O(10)D	0.068 1	0.209 3	0.277 3	176.73
O(13)–H(8W)···O(11)E	0.084 6	0.216 1	0.280 9	133.27

Symmetry codes: A: $x+1/2, -y+3/2, z-1/2$; B: $-x+2, -y+1, -z+1$; C: $x+1, y, z$; D: $-x+1/2, y-1/2, -z+1/2$; E: $x-1, y, z$.

Table 5 Hydrogen bond parameters of compound 4

D–H···A	$d(\text{D–H}) / \text{nm}$	$d(\text{H···A}) / \text{nm}$	$d(\text{D···A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
O(10)–H(1W)···O(13)	0.082 0	0.213 5	0.277 5	134.94
O(10)–H(2W)···O(6)A	0.086 6	0.180 9	0.267 5	179.01
O(11)–H(3W)···O(3)B	0.086 6	0.199 4	0.286 0	179.47
O(11)–H(4W)···O(12)C	0.085 4	0.189 7	0.275 1	179.72
O(12)–H(5W)···O(4)D	0.085 0	0.186 2	0.271 2	179.69
O(12)–H(6W)···O(7)D	0.086 0	0.192 2	0.278 2	178.37
O(13)–H(7W)···O(8)D	0.085 1	0.191 9	0.277 0	179.00
O(13)–H(8W)···O(11)E	0.084 6	0.204 2	0.288 8	179.14

Symmetry codes: A: $x-1/2, -y+1/2, z+1/2$; B: $x-1, y, z$; C: $x-1, y-1, z$; D: $-x+2, -y+1, -z$; E: $-x+1/2, y+1/2, -z+1/2$.

The catalytic reactions were performed as follows: catalyst ($0.04 \text{ mmol} \cdot \text{L}^{-1}$) was dispersed in 100 mL aqueous solution of MB ($0.031 \text{ mmol} \cdot \text{L}^{-1}$) 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) with continuous stirring for 150 min. Reaction samples (5 mL) were taken out every 15 min, centrifuged, and then analyzed by UV-Vis spectrophotometry, monitoring 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 took place in the absence of catalyst.

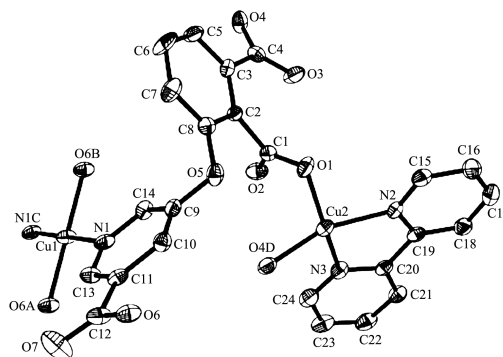
2 Results and discussion

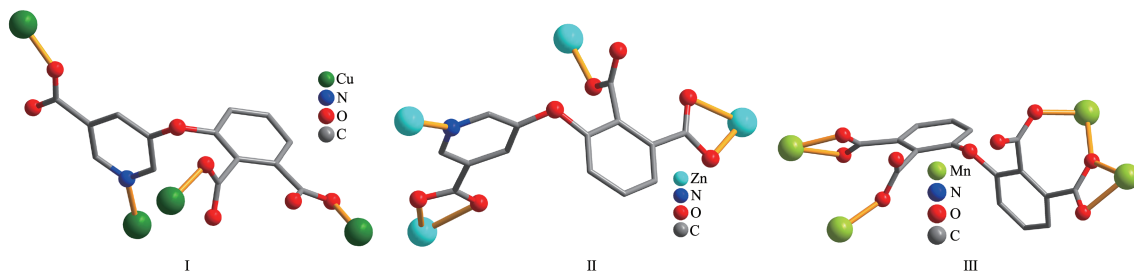
2.1 Description of the structure

2.1.1 $\{[\text{Cu}_3(\mu_4\text{-dpna})_2(2,2'\text{-bipy})_2] \cdot 4\text{H}_2\text{O}\}_n$ (1)

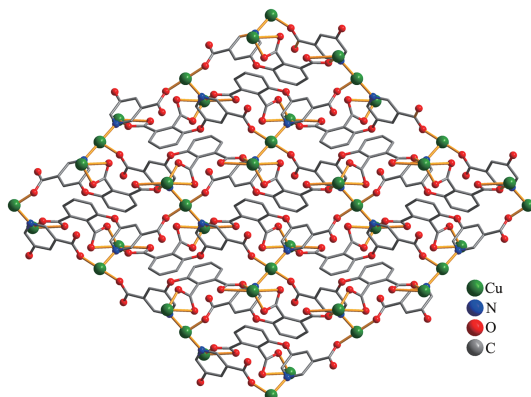
X-ray crystallography analysis reveals that compound **1** crystallizes in the monoclinic system space group $P2_1/c$. As shown in Fig. 1, the asymmetric unit of **1** bears two crystallographically unique Cu(II) ions (Cu1 with half occupancy; Cu2 with full occupancy), one $\mu_4\text{-dpna}^{3-}$ block, one 2,2'-bipy moiety, and two lattice water molecules. The tetra-coordinated Cu1 atom exhibits

a planar tetragonal $\{\text{CuN}_2\text{O}_2\}$ environment, which is occupied by two carboxylate O and two N donors from four different $\mu_4\text{-dpna}^{3-}$ blocks. The Cu2 center is also tetra-coordinated and forms a distorted tetrahedral $\{\text{CuN}_2\text{O}_2\}$ geometry. It is completed by two carboxylate O atoms from two $\mu_4\text{-dpna}^{3-}$ blocks and two N atoms from the 2,2'-bipy moiety. The Cu–O and Cu–N bond distances are $0.194\ 3(4)\sim 0.259\ 9(5)$ and $0.197\ 2(5)\sim 0.203\ 6(5)$ nm, respectively; these are within the normal ranges observed in related Cu(II) compounds^[5,32]. In **1**, the dpna^{3-} ligand adopts coordination mode I (Scheme 1) with carboxylate groups being monoden-

H atoms are omitted for clarity; Symmetry codes: A: $-x, -y+1, -z$; B: $-x+1, -y+2, -z$; C: $-x, -y, -z+1/2$ Fig. 1 Drawing of asymmetric unit of compound **1** with 30% probability thermal ellipsoids

Scheme 1 Coordination modes of dpna^{3-} and deta^{4-} ligands in compounds **1~4**

tate. In the dpna^{3-} ligand, a dihedral angle (between two aromatic rings) and a $\text{C}-\text{O}_{\text{ether}}-\text{C}$ angle are 86.88° and 115.49° , respectively. The μ_4 - dpna^{3-} ligands connect Cu1 and Cu2 atoms to give a 2D sheet (Fig.2).



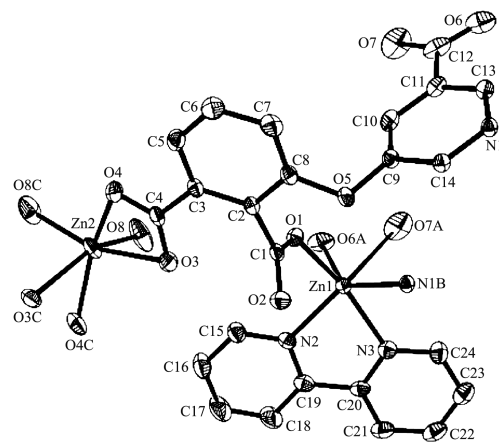
2,2'-bipy ligands are omitted for clarity

Fig.2 Perspective of 2D sheet along b and c axes in **1**

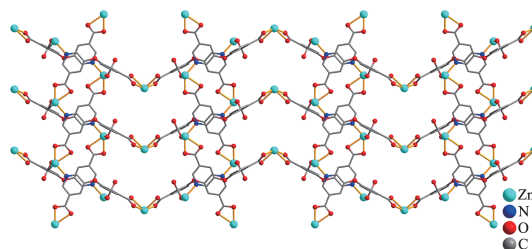
2.1.2 $[\{\text{Zn}_3(\mu_4\text{-dpna})_2(2,2'\text{-bipy})_2(\text{H}_2\text{O})_2\} \cdot 6\text{H}_2\text{O}]_n$ (**2**)

The asymmetric unit of compound **2** contains two crystallographically unique Zn(II) ions (Zn1 with full occupancy and Zn2 with half occupancy), one μ_4 - dpna^{3-} block, one 2,2'-bipy moiety, one H_2O ligand, and three lattice water molecules. As depicted in Fig. 3, six-coordinated Zn1 atom features a distorted octahedral $\{\text{ZnN}_3\text{O}_3\}$ environment, which is filled by three carboxylate O and one N atom of three μ_4 - dpna^{3-} blocks and two N atoms of one 2,2'-bipy moiety. The Zn2 center is also six-coordinated and displays a distorted octahedral $\{\text{ZnO}_6\}$ geometry. It is taken by four carboxylate O atoms from two μ_4 - dpna^{3-} blocks and two O donors from two H_2O ligands. The bond lengths of Zn-O are in a range of $0.201\ 2(3)\sim 0.241\ 5(4)$ nm, while the Zn-N bonds are $0.211\ 2(3)\sim 0.219\ 1(3)$ nm, being comparable to those found in some reported Zn(II) compounds^[14,29,32]. The pyridyl N atom acts as an N-donor for Cu(II)/Zn(II)

centers in both compounds. In **2**, the dpna^{3-} block acts as a μ_4 -linker (mode II, Scheme 1), in which three carboxylate groups adopt monodentate or bidentate modes. Besides, μ_4 - deta^{4-} ligand is considerably bent showing a dihedral angle of 80.43° (between two aromatic rings) and the $\text{C}-\text{O}_{\text{ether}}-\text{C}$ angle of 117.16° . The μ_4 - dpna^{3-} ligands link Zn(II) centers to furnish a 2D sheet (Fig.4). Compounds **1** and **2** were isolated under the same conditions, except for the type of Cu(II)/Zn(II) chloride starting material ($\text{CuCl}_2 \cdot \text{H}_2\text{O}$ for **1** and ZnCl_2 for **2**). Hence,



H atoms are omitted for clarity; Symmetry codes: A: $-x, -y+1, -z$; B: $-x+1, -y+2, -z$; C: $-x, -y, -z+1/2$

Fig.3 Drawing of asymmetric unit of compound **2** with 30% probability thermal ellipsoids

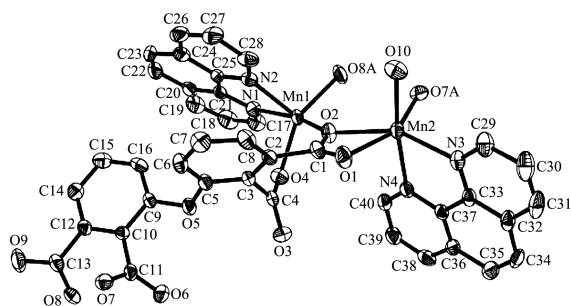
2,2'-bipy moieties are omitted for clarity

Fig.4 View of 2D metal-organic sheet along b and c axes in **2**

structural difference between two products indicate that the assembly process is metal ion-dependent.

2.1.3 $[[M_2(\mu_4\text{-deta})(\text{phen})_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}]_n$ (M=Mn (**3**) and Zn (**4**))

Compounds **3** and **4** are isostructural (Table 1) and the structure of **3** is discussed in detail as an example (Fig.5 and 6). X-ray crystallography analysis reveals that compound **3** crystallizes in the monoclinic system space group $P2_1/n$. As shown in Fig.5, the asymmetric unit of **3** bears two crystallographically unique Mn(II) ions (Mn1 and Mn2), one $\mu_4\text{-deta}^{4-}$ block, two phen moieties, one H_2O ligand and three lattice water molecules. The five-coordinated Mn1 atom exhibits a distorted trigonal bipyramid $\{\text{MnN}_2\text{O}_3\}$ environment, which is occupied by three carboxylate O donors from two different $\mu_4\text{-deta}^{4-}$ blocks and two N atoms from the phen moiety. The Mn2 center is six-coordinated and forms a distorted octahedral $\{\text{MnN}_2\text{O}_4\}$ geometry. It is completed by three carboxylate O atoms from two $\mu_4\text{-deta}^{4-}$ blocks, one O atom for the H_2O ligand, and two N atoms from the phen moiety. The Mn-O and Mn-N bond distances are 0.208 0(4)~0.231 7(4) and 0.220 2(5)~0.227 2(5) nm, respectively; these are within the normal ranges observed in related Mn(II) compounds^[14,17].



sion maximums at 412 and 408 nm ($\lambda_{\text{ex}}=320$ nm). In contrast, compounds **2** and **4** displayed significantly more intense emission bands with the maxima at 406 or 390 nm ($\lambda_{\text{ex}}=320$ nm), respectively. All bands can be assigned to the intraligand ($\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$) emission^[14,17]. The luminescence enhancement in coordination compounds **2** and **4** can be attributed to the binding of ligands to the metal centers, which effectively increases the rigidity of the ligand and reduces the loss

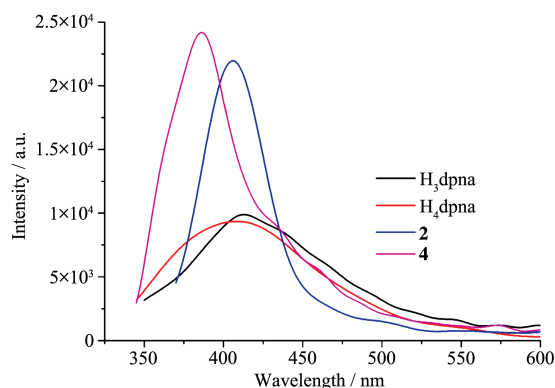


Fig. 8 Solid-state emission spectra of H_3dpna , H_4dpna and compounds **2** and **4** at room temperature

of energy by radiationless decay^[29,32].

2.4 Photocatalytic activity for dye degradation

To study the photocatalytic activity of **1**~**4**, we selected MB as a model dye contaminant in wastewater. The obtained results (Fig. 9 and 10) indicate that the MB degradation rate attained 81.9% after 150 min in the presence of **4** that is the most active catalyst. For **1**~**3**, the MB degradation rates were inferior, being

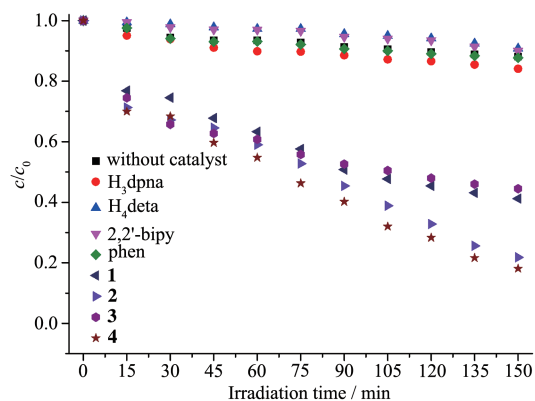


Fig. 9 Photocatalytic degradation of MB solution under UV light using catalysts **1**~**4** and the blank experiments

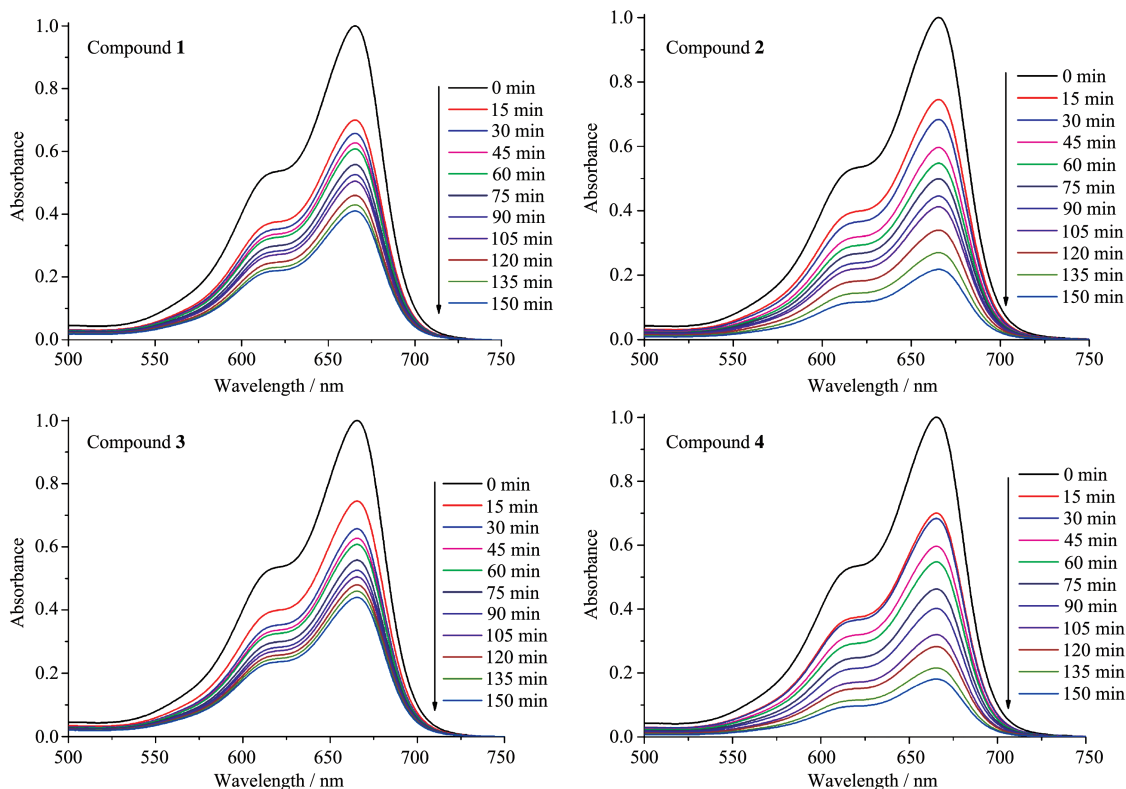


Fig. 10 Time-dependent UV-Vis spectra of the reaction mixtures in the course of MB photodegradation catalyzed by **1**~**4**

58.8%, 78.2% or 55.5%. Under similar conditions, blank tests were also carried out and revealed that the degradation of MB almost did not occur in the absence of catalyst, or using H_3dpna , H_4deta , 2,2'-bipy or phen as catalysts. Besides, to evaluate the stability of compound **4** during the photocatalytic experiments, the catalyst recycling tests were performed (Fig. 11). The obtained results indicated that compound **4** preserved its original catalytic activity even after four reaction cycles, showing only a slight decline of the MB degradation efficiency from 82% to 77%. Moreover, the chemical stability of **4** after photocatalytic experiments can be confirmed by the PXRD pattern of the recovered catalyst (Fig. 12), which well matched that of as-synthesized sample. These results demonstrate that the photocatalytic activity depends on various factors, such as number of water ligands, coordination environment of metal centers, and optical band gap^[25-28,32].

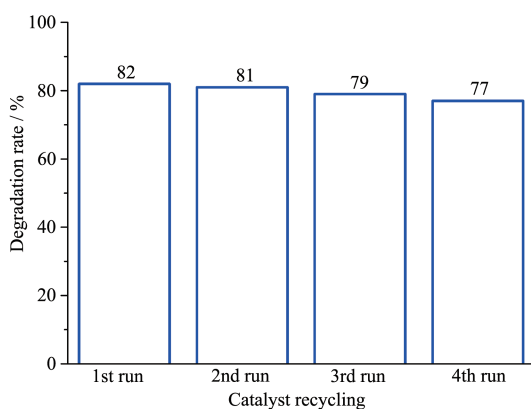


Fig. 11 Catalyst **4** recycling experiments in MB photodegradation

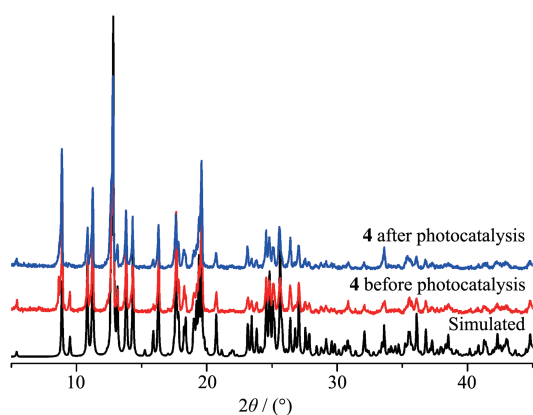


Fig. 12 PXRD patterns for **4**: simulated (red), before (black) and after (blue) photocatalysis

3 Conclusions

In summary, we have synthesized four Cu(II), Zn(II) and Mn(II) coordination polymers based on two unexplored carboxylate ligands. Compounds **1** and **2** possess two different 2D sheet structures. The structural diversity of compounds **1** and **2** is driven by the Cu(II)/Zn(II) node. Compounds **3** and **4** show 1D chain structures.

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