

## 基于 2-(4'-羧基苯基)咪唑-4,5-二羧酸构筑的三个镉/锌配位聚合物的合成、拓扑结构、荧光光谱及 DNA 作用

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**摘要:** 以 2-(4'-羧基苯基)咪唑-4,5-二羧酸( $\text{H}_4\text{CPhIDC}$ ,  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_6$ )为配体,用溶剂热合成了 3 种配位聚合物 $\{[\text{Cd}_2(\text{CPhIDC})(\text{bimb})]\cdot\text{H}_2\text{O}\}_n$  (**1**)、 $\{[\text{Cd}_2(\text{CPhIDC})(\text{phen})_2]\cdot 3\text{H}_2\text{O}\}_n$  (**2**)、 $\{[\text{Zn}_2(\text{CPhIDC})(\text{bpp})]\cdot 1.5\text{H}_2\text{O}\}_n$  (**3**)( $\text{bimb}$ =1,4-双咪唑基-丁烷,  $\text{phen}$ =1,10-菲咯啉,  $\text{bpp}$ =1,3-双(4-吡啶基)-丙烷)。用元素分析、红外光谱、粉末 X 射线衍射和单晶 X 射线衍射对配合物进行了表征和结构分析。结构分析表明,主配体以完全去质子化  $\text{CPhIDC}^{4-}$  的形式与中心金属离子形成以  $\mu_4$  和  $\mu_5$  为配位模式的二维及三维聚合物。配合物 **1** 和 **3** 是三维网络结构,同时呈现(3,4,5)-连接的 $(5\cdot 6\cdot 7)(4\cdot 5^2\cdot 6\cdot 7^2)(4\cdot 5^2\cdot 6\cdot 7^4\cdot 8^2)$ 拓扑结构,两者的不同之处是中心离子和辅助配体。配合物 **2** 是二维波纹状渔网结构,呈现  $4^4\cdot 6^2$  拓扑结构,在其空间填充上又类似于 DNA 双螺旋链的单螺旋结构。测定了产物的固体荧光光谱;用 EtBr 荧光探针法研究了配体及配合物与 ct-DNA 的相互作用。

**关键词:** 2-(4'-羧基苯基)咪唑-4,5-二羧酸; 镉/锌配位聚合物; 拓扑结构; 荧光光谱; DNA 作用

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## Three Cd(II) and Zn(II) Coordination Polymers Based on 2-(4'-Carboxyphenyl)-1H-imidazole-4,5-dicarboxylic Acid: Syntheses, Topological Structures, Fluorescent Spectra and DNA Binding

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**Abstract:** Three coordination polymers of cadmium and zinc  $\{[\text{Cd}_2(\text{CPhIDC})(\text{bimb})]\cdot\text{H}_2\text{O}\}_n$  (**1**),  $\{[\text{Cd}_2(\text{CPhIDC})(\text{phen})_2]\cdot 3\text{H}_2\text{O}\}_n$  (**2**),  $\{[\text{Zn}_2(\text{CPhIDC})(\text{bpp})]\cdot 1.5\text{H}_2\text{O}\}_n$  (**3**), ( $\text{H}_4\text{CPhIDC}$ =2-(4'-carboxyphenyl)-1H-imidazole-4,5-dicarboxylic acid,  $\text{bimb}$ =1,4-bis(imidazol-1-yl)butane,  $\text{phen}$ =1,10-phenanthroline,  $\text{bpp}$ =1,3-di(pyridin-4-yl)propane) have been synthesized by solvothermal reaction and characterized by IR, EA and PXRD. Single crystal X-ray diffraction shows that the  $\text{H}_4\text{CPhIDC}$  ligand presents fully deprotonated motifs of  $\text{CPhIDC}^{4-}$  in three corresponding polymers. Moreover, the fully deprotonated ligands coordinate in the  $\mu_4$  and  $\mu_5$  manner to generate 2D and 3D polymers, displaying three different coordination modes. Complexes **1** and **3** exhibit 3D structures with (3,4,5)-connected frameworks with  $(5\cdot 6\cdot 7)(4\cdot 5^2\cdot 6\cdot 7^2)(4\cdot 5^2\cdot 6\cdot 7^4\cdot 8^2)$  topology, but the metal ions and auxiliary ligands are different. **2** displays a 2D wave-like fishing nets structure with  $4^4\cdot 6^2$  topology. The fluorescence spectra in the solid state and DNA binding properties of the polymers and ligand are investigated. CCDC: 969814, **1**; 937738, **2**; 937741, **3**.

**Keywords:** 2-(4'-carboxyphenyl)-1H-imidazole-4,5-dicarboxylic acid; Cd and Zn coordination polymers; topological structure; fluorescence spectra; DNA binding

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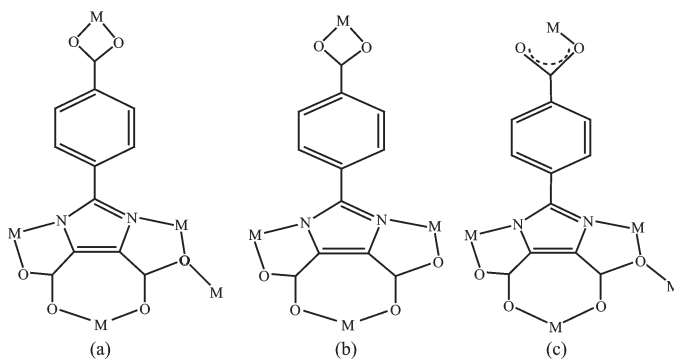
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Coordination polymers, as a type of important materials, exhibits attractive application prospects in the fields of gas adsorption, storage and separation, adsorption of dyes, electrical conductivity, optical materials, magnetic materials, catalyzer, and so on<sup>[1-14]</sup>. Those applications bring the new dawn for the porous materials science. Multifunctional organic ligands, especially the N-heterocyclic carboxylates, contain multi-oxygen and nitrogen atoms, and possess the ability to coordinate with metal ions in versatile ways. These building blocks lead to the formations of various coordination polymers with specific topologies and useful properties<sup>[16-17]</sup>.

Imidazole-4,5-dicarboxylic acid ( $H_3IDC$ ), which can be partially or fully deprotonated to generate  $H_2IDC^-$ ,  $HIDC^{2-}$ ,  $IDC^{3-}$  at different pH values and afford various coordination modes, is favored by multitudinous research groups. According to the reported coordination polymers<sup>[18-23]</sup> constructed from  $H_3IDC$ , this kinds of ligand still remain extremely widely researched. Recently, according to purposefully changing the substituent group on the 2-position of imidazole-4,5-dicarboxylic acid, excellent ligands has been obtained, which can be used to construct coordination

polymers with rapidly changing topological structures and useful properties, such as 2-methyl-1*H*-imidazole-4,5-dicarboxylic acid, 2-ethyl-1*H*-imidazole-4,5-dicarboxylic acid, 2-propyl-1*H*-imidazole-4,5-dicarboxylic acid, 2-phenyl-1*H*-imidazole-4,5-dicarboxylic acid, 2-hydroxymethyl-1*H*-imidazole-4,5-dicarboxylic acid and 2-(pyridyl)-1*H*-imidazole-4,5-dicarboxylic acid.

Herein, taking into account the factors mentioned above, a new  $H_3IDC$  derivative, 2-(4'-carboxyphenyl)-1*H*-imidazole-4,5-dicarboxylic acid ( $H_4CPhIDC$ ), was purposely synthesized by condensation and oxidation reactions. Three coordination polymers of cadmium and zinc  $\{[Cd_2(CPhIDC)(bimb)] \cdot H_2O\}_n$  (**1**),  $\{[Cd_2(CPhIDC)(phen)_2] \cdot 3H_2O\}_n$  (**2**),  $\{[Zn_2(CPhIDC)(bpp)] \cdot 1.5H_2O\}_n$  (**3**), (bimb=1,4-bis(imidazol-1-yl)butane, phen=1,10-phenanthroline, bpp=1,3-di(pyridin-4-yl)propane) have been synthesized by solvothermal reaction and characterized. The carboxyl containing group on the 2-position<sup>[24]</sup> of  $H_4CPhIDC$  is successfully applied to construct coordination polymers. Its fully deprotonated motifs of  $CPhIDC^{4-}$  can exhibit very flexible coordination modes (Scheme 1), and form a large diversity of supramolecular architectures.



Scheme 1 Coordination modes of  $CPhIDC^{4-}$  for the three polymers

## 1 Experimental

### 1.1 Materials and measurements

$H_4CPhIDC$  was prepared according to literature<sup>[25-28]</sup> with some proper modification. The other reagents were of analytical grade and used without further purification. Calf thymus DNA (ct-DNA) was prepared with  $0.1 \text{ mol} \cdot \text{L}^{-1}$  NaCl. The concentration of ct-DNA

was  $200 \text{ } \mu\text{g} \cdot \text{mL}^{-1}$  ( $c_{\text{DNA}}=0.372 \text{ mmol} \cdot \text{L}^{-1}$ ). The ct-DNA solutions were stored at  $4 \text{ } ^\circ\text{C}$  and gave a ratio of UV-Vis absorbance at 260 and 280 nm,  $A_{260}/A_{280}=1.8$ , indicating that DNA was sufficiently free of protein. The buffer solution,  $0.01 \text{ mol} \cdot \text{L}^{-1}$  Tris-HCl (tris (hydroxymethyl) aminomethane hydrochloride, pH = 7.4), was prepared with double-distilled water.

Elemental analysis was performed on C, H, N

elemental analyzer, Elementar Vario EL III. FTIR spectra were recorded on a Nicolet NEXUS 670 FTIR spectrophotometer using KBr discs in the range of 4 000~400  $\text{cm}^{-1}$ . A Mettler Toledo thermal analyzer TGA/SDTA 851<sup>e</sup> was used to carry out the thermogravimetric analysis with a heating rate of 10  $^{\circ}\text{C}\cdot\text{min}^{-1}$  from 30~800  $^{\circ}\text{C}$  in air atmosphere. Powder X-ray diffraction (PXRD) data were collected on a PW 3040/60 Focus X-ray diffractometer using Cu  $K\alpha$  radiation ( $\lambda=0.154\ 06\ \text{nm}$ ,  $2\theta=2^{\circ}\sim 60^{\circ}$ ) at room temperature with acceleration voltage of 40 kV and current of 40 mA. Fluorescence spectra were measured at room temperature with an Edinburgh FL-FS920 TCSPC system.

## 1.2 Synthesis of the polymers

### 1.2.1 Synthesis of $[\{\text{Cd}_2(\text{CPhIDC})(\text{bimb})\}\cdot\text{H}_2\text{O}]_n$ (**1**)

A mixture of  $\text{H}_4\text{CPhIDC}$  (0.140 g, 0.5 mmol), bimb (0.147 g, 0.75 mmol),  $\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$  (0.170 g, 0.75 mmol), and  $\text{H}_2\text{O}/\text{EtOH}$  (15 mL, 4:1,  $V/V$ ) with the pH value of 8 adjusted by 0.5  $\text{mol}\cdot\text{L}^{-1}$  NaOH was sealed in a 20 mL Teflon-lined stainless steel vessel and heated at 160  $^{\circ}\text{C}$  for 3 d. After the mixture was cooled to room temperature at a rate of 10  $^{\circ}\text{C}\cdot\text{h}^{-1}$ , colorless crystals suitable for single-crystal analysis and physical measurements were obtained, washed with distilled water, and dried in air. Yield: 41% (based on  $\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$ ). Anal. Calcd. for  $\text{C}_{44}\text{H}_{40}\text{N}_{12}\text{O}_{13}\text{Cd}_4$  (%): C 37.46, H 2.86, N 11.92; Found(%): C 37.71, H 2.83, N 11.98. IR (KBr,  $\text{cm}^{-1}$ ): 3 538 (m), 2 943(w), 2 860(w), 1 588(s), 1 542(s), 1 525(s), 1 440(s), 1 405(s), 1 375(m), 1350(m), 1 293(s), 1 229(s), 1 113(s), 1 097(s), 941(s), 862(s), 823(s), 789(s), 785(s), 652(s), 570(m), 499(m), 462(s).

### 1.2.2 Synthesis of $[\{\text{Cd}_2(\text{CPhIDC})(\text{phen})_2\}\cdot 3\text{H}_2\text{O}]_n$ (**2**)

The synthesis method is similar to **1**, where the metal source is  $\text{Cd}(\text{OH})_2$ , the auxiliary ligand is changed to phen, the pH value is not adjusted, the solvents are  $\text{H}_2\text{O}/i\text{-PrOH}/\text{acetone}$  (15 mL, 2:1:1,  $V/V$ ). Yield: 36% (based on  $\text{Cd}(\text{OH})_2$ ). Anal. Calcd. for  $\text{C}_{36}\text{H}_{26}\text{N}_6\text{O}_9\text{Cd}_2$  (%): C 47.44, H 2.88, N 9.22; Found: C 47.28, H 2.83, N 9.29. IR(KBr,  $\text{cm}^{-1}$ ): 3 499(m), 1 603(s), 1 588(s), 1 542(s), 1 514(s), 1 429(s), 1 392(s), 1 279(m), 1 223(w), 1 145(m), 1 013(w), 970(m), 859(s), 842(s),

792(m), 727(s), 547(m), 506(m), 457(m).

### 1.2.3 Synthesis of $[\{\text{Zn}_2(\text{CPhIDC})(\text{bpp})\}\cdot 1.5\text{H}_2\text{O}]_n$ (**3**)

The synthesis method is roughly the same as **1**, where the metal source is changed to zinc acetate, the auxiliary ligand is changed to bpp, the pH value is adjusted to close to 6.5, the solvents are  $\text{H}_2\text{O}/\text{EtOH}$  (15 mL, 3:2,  $V/V$ ). Yield: 44% (based on  $\text{Zn}(\text{CH}_3\text{COO})_2$ ). Anal. Calcd. for  $\text{C}_{25}\text{H}_{21}\text{N}_4\text{O}_{7.5}\text{Zn}_2$  (%): C 47.79, H 3.37, N 8.92; Found (%): C 47.72, H 3.25, N 9.17. IR(KBr,  $\text{cm}^{-1}$ ): 3 480(m), 2 936(w), 2 874(w), 1 608(s), 1 590(s), 1 550(s), 1 430(s), 1 403(s), 1 381(s), 1 352(m), 1 271(s), 1 224(m), 1 175(m), 1 122(s), 1 068(m), 1 028(s), 872(m), 830(s), 813(s), 796(s), 789(s), 749(s), 727(s), 664(w), 634(w), 574(w), 525(m), 489(m), 463(s).

## 1.3 X-ray diffraction analysis

The single crystals of the polymers with approximate dimensions were mounted on a Bruker Smart Apex II CCD diffractometer. The diffraction data were collected using a graphite monochromated Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073\ \text{nm}$ ) at 296(2) K. Absorption corrections were applied using SADABS<sup>[29]</sup>. The structure was solved by using the SHELXS-97<sup>[30]</sup> program package and refined with the full-matrix least-squares technique based on  $F^2$  using the SHELXL-97<sup>[31]</sup> program package. Remaining hydrogen atoms were added in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Hydrogen atoms on water molecules were located in a difference Fourier map and included in the subsequent refinement using restraints ( $d_{\text{O-H}}=0.085\ \text{nm}$ ,  $d_{\text{H}\cdots\text{H}}=0.130\ \text{nm}$ ) with  $U_{\text{iso}}(\text{H})=0.15U_{\text{eq}}(\text{O})$ . Other hydrogen atoms were added theoretically. The detail about the crystal data is summarized in Table 1. Selected bond distances and bond angles are given in Table S1 to Table S3 (Supporting information).

CCDC: 969814, **1**; 937738, **2**; 937741, **3**.

## 1.4 DNA binding

1.0 mL of 200  $\mu\text{g}\cdot\text{mL}^{-1}$  DNA solution, 1.0 mL of 200  $\mu\text{g}\cdot\text{mL}^{-1}$  EB solution and 2.0 mL of Tris-HCl buffer solution with pH=7.40 were added to a 10 mL colorimetric tube and allowed to stand at room temperature for 2 h. Then, a solution of 0.50 or 0.10  $\text{mmol}\cdot\text{L}^{-1}$  compound was added to the mixed solution

**Table 1** Crystal data and structure refinement parameters for polymers 1~3

Complex	1	2	3
Empirical formula	C <sub>22</sub> H <sub>30</sub> N <sub>6</sub> O <sub>7</sub> Cd <sub>2</sub>	C <sub>36</sub> H <sub>26</sub> N <sub>6</sub> O <sub>9</sub> Cd <sub>2</sub>	C <sub>25</sub> H <sub>21</sub> N <sub>4</sub> O <sub>7.5</sub> Zn <sub>2</sub>
Formula weight	705.24	911.43	628.20
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> / nm	1.437 68(3)	1.500 72(4)	1.362 92(9)
<i>b</i> / nm	0.942 50(2)	1.035 98(3)	0.973 17(7)
<i>c</i> / nm	1.827 64(4)	2.277 75(7)	1.818 30(12)
$\beta$ / (°)	90.441 0(10)	91.197(2)	90.642(4)
<i>V</i> / nm <sup>3</sup>	2.476 40(9)	3.540 48(18)	2.411 6(3)
<i>Z</i>	4	4	4
<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	1.892	1.710	1.730
Absorption coefficient / mm <sup>-1</sup>	1.772	1.265	2.047
Crystal size / mm	0.220×0.200×0.180	0.326×0.253×0.188	0.336×0.272×0.157
Crystal color	Colorless	Colorless	Red
<i>F</i> (000)	1 384	1 808	1 276
Reflection collected	38 716	31 171	24 514
Unique reflection ( <i>R</i> <sub>int</sub> )	5 705 (0.046 9)	8 146 (0.058 2)	6 664 (0.052 4)
Reflection with <i>I</i> >2σ( <i>I</i> )	4 570	4 852	4 544
$\theta$ range / (°)	1.80~27.55	1.61~27.56	1.86~29.62
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> >2σ( <i>I</i> )]	0.028 1, 0.063 7	0.042 5, 0.079 3	0.044 1, 0.111 9
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.039 8, 0.068 6	0.094 3, 0.094 1	0.076 0, 0.127 2
Goodness-of-fit (on <i>F</i> <sup>2</sup> )	1.011	1.014	1.023
(Δρ) <sub>max</sub> , (Δρ) <sub>min</sub> / (e·nm <sup>-3</sup> )	571, -615	468, -605	651, -845

and diluted to a scale with distilled water. After 4 h at room temperature, the fluorescence spectra of the composite system in 520~700 nm range are recorded by exciting at 251 nm.

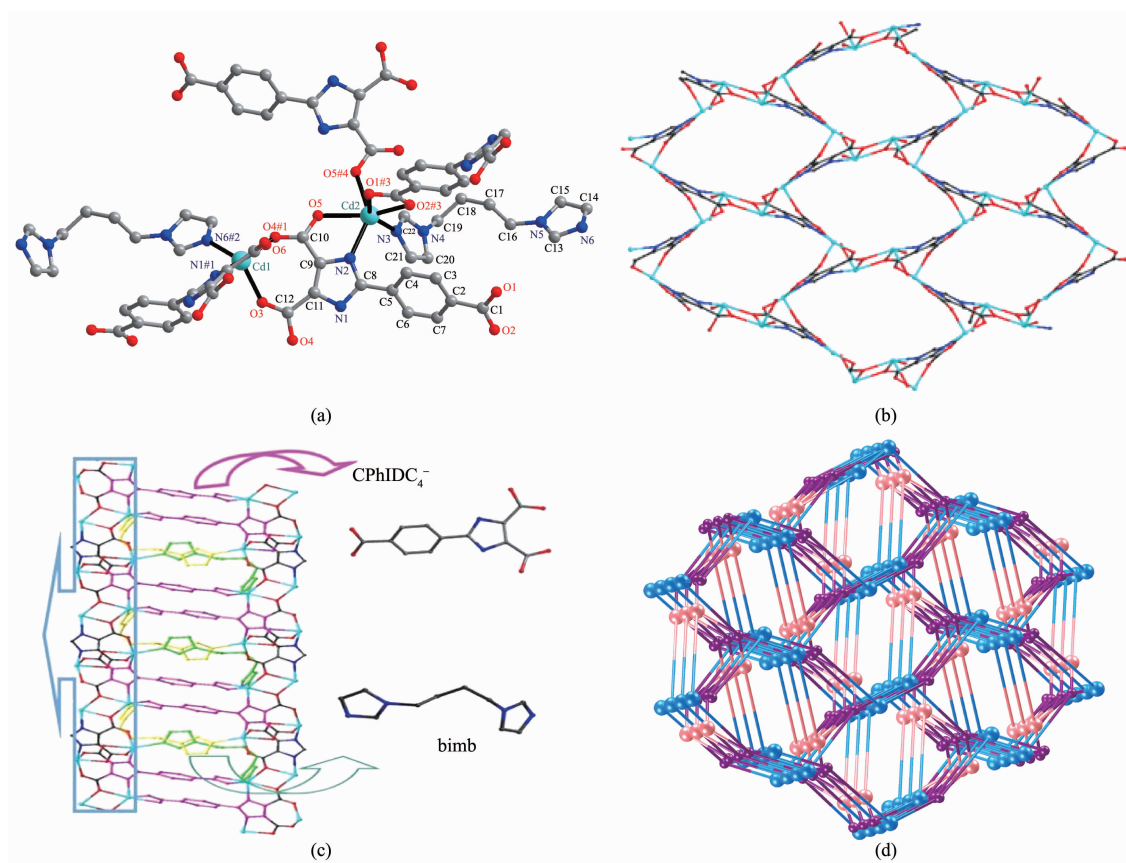
## 2 Results and discussion

### 2.1 Crystal structures of the complexes

#### 2.1.1 Crystal structure of {[Cd<sub>2</sub>(CPhIDC)(bimb)]·H<sub>2</sub>O}<sub>n</sub> (**1**)

Single-crystal analysis shows polymer **1** crystallizes in the monoclinic system with space group *P*2<sub>1</sub>/*n* and the asymmetric unit cell contains two Cd<sup>2+</sup> ions, one CPhIDC<sup>4-</sup> anion, one 1,4-bis(imidazol-1-yl)butane molecule and one lattice water molecule. As shown in Fig.1a, the Cd(2) adopts distorted octahedral geometry with a six-coordinated mode by four oxygen atoms (O5, O1#3, O2#3, O5#4, *d*<sub>Cd-O</sub>=0.223 6(2)~0.251 9(3) nm) and one nitrogen atom (N2, *d*<sub>Cd-N</sub>=0.227 4(3) nm) from three CPhIDC<sup>4-</sup> ligands and one nitrogen atom

(N3, *d*<sub>Cd-N</sub>=0.225 2(3) nm) from one bimb molecule. The Cd (1) adopts distorted trigonal bipyramid coordinated with three oxygen atoms (O3, O6, O4#1, *d*<sub>Cd-O</sub>=0.221 0(2)~0.236 3(2) nm), one nitrogen atom (N1#1, *d*<sub>Cd-N</sub>=0.221 2(3) nm) from two CPhIDC<sup>4-</sup> ligands and one nitrogen atom (N6#2, *d*<sub>Cd-N</sub>=0.223 3(3) nm) from one bimb molecule. From Cd-O, Cd-N bond distances and O3-Cd1-N6#2, O3-Cd1-O4#1, N6#2-Cd1-O4#1 bond angles for **1**, we could know that the five atoms are practically in the same plane while the O1 and N3 atoms are at the side of it. Thus the two Cd<sup>2+</sup> ions are bridged by the ends of one bimb molecule respectively. The CPhIDC<sup>4-</sup> ligand adopt conformations with μ<sub>5</sub>-κO:κ<sup>2</sup>O', N:κ<sup>2</sup>O'', N':κ<sup>2</sup>O''', O''':κO'''''. The two Cd<sup>2+</sup> ions are bridged by the ends of one bimb molecule respectively. The CPhIDC<sup>4-</sup> ligand adopts conformations with μ<sub>5</sub>-κO:κ<sup>2</sup>O', N:κ<sup>2</sup>O'', N':κ<sup>2</sup>O''', O''':κO''''' coordination fashion (Scheme 1a) to connect Cd(1) and Cd(2) ions. The selected distances and bond angles



Symmetry codes: #1:  $-x+3/2, y-1/2, -z+3/2$ ; #2:  $x+1, y-1, z$ ; #3:  $-x+1/2, y-1/2, -z+3/2$ ; #4:  $-x+1, -y+1, -z+1$

Fig.1 (a) Ball-and-stick structural view of **1**; (b) 2D plane structure for **1** viewed along *a* axis; (c) 3D framework for **1** viewed along *b* axis; (d) (3,4,5)-topological connected for **1**

fall in the normal regions which are comparable to the values reported in literatures<sup>[32]</sup>. For **1**, the  $\text{Cd}^{2+}$  ion is bridged by the imidazole ring to form a 2D plane ellipsoid lattice ( $0.785\ 6(4)\ \text{nm} \times 0.922\ 3(3)\ \text{nm}$ ) (Fig. 1b). The 2D surface adopts staggered conformations connected with bimb molecules and  $\text{CPhIDC}^{4-}$  anions to build up a 3D  $[\text{Cd}_2(\text{CPhIDC})(\text{bimb})]$  framework (Fig. 1c). Both bimb molecules reside in the tunnels and the extensive hydrogen bonds (Table S4) contribute themselves to stabilize the crystal structure.

In the 3D  $[\text{Cd}_2(\text{CPhIDC})(\text{bimb})]$  frameworks, from the topological point of view,  $\text{CPhIDC}^{4-}$  anions ligand are each bonded to five  $\text{Cd}(\text{II})$  ions (three  $\text{Cd}(1)$  and two  $\text{Cd}(2)$ ), while  $\text{Cd}(1)$  ions are each coordinated to five atoms ( $\text{O}1, \text{O}2, \text{O}3, \text{O}3\#2, \text{N}2$ ) from three  $\text{CPhIDC}^{4-}$  anions in a  $\kappa\text{O}:\kappa^2\text{O}'$ ,  $\text{N}:\kappa\text{O}''$  coordination fashion and one nitrogen atom ( $\text{N}3$ ) from bimb molecule in  $\kappa\text{N}$  coordination fashion.  $\text{Cd}(2)$  ions are each coordinated to four atoms ( $\text{O}6, \text{O}4, \text{O}5, \text{N}1$ ) from two  $\text{CPhIDC}^{4-}$

ligand anions in a  $\kappa^2\text{O}, \text{O}':\kappa^2\text{O}''$ ,  $\text{N}$  and one atom from one bimb ligand in  $\kappa\text{N}$  coordination fashion. From topological point of view the 3D framework can be simplified in some underlying net, where  $\text{Cd}(1)$  and  $\text{Cd}(2)$  atoms,  $\text{CPhIDC}^{4-}$  anions and bridge bimb ligands are presented by 4-coordinated, 3-coordinated, 5-coordinated nodes, respectively.

Viewed along *a* axis for **1** without bimb and benzeneedge, respectively (Fig.1d), topology of the 3,4,5-coordinated trinodal underlying net can be described with point symbol  $(5 \cdot 6 \cdot 7)(4 \cdot 5^2 \cdot 6 \cdot 7^4 \cdot 8^2)(4 \cdot 5^2 \cdot 6 \cdot 7)$ . The structure of **1** is completely different from the reported (3,4,5)-connected frameworks with  $(6 \cdot 8 \cdot 10)(6 \cdot 8^2)(6^3)_4(6^4 \cdot 10^2)(6^4 \cdot 8^4 \cdot 10^2)$ ,  $(6^3)_2(6^6)(6^8 \cdot 8^2)$ ,  $(4 \cdot 6^2)_2(4^3 \cdot 6^7)_2(4^4 \cdot 6^2)$ ,  $(4^2 \cdot 6)(4^4 \cdot 6^2)(4^4 \cdot 6^3 \cdot 8^3)$ ,  $(5 \cdot 6 \cdot 7)(5^4 \cdot 6 \cdot 8)(5^4 \cdot 6^3 \cdot 8^3)$ ,  $(4 \cdot 6 \cdot 8)_2(4 \cdot 8^2)(4 \cdot 6^4 \cdot 8^5)(4^2 \cdot 6^2 \cdot 8^2)$ ,  $(4 \cdot 6^2)(4^2 \cdot 6)(4^2 \cdot 8^4)(4^3 \cdot 6 \cdot 8^6)(4^2 \cdot 6^5 \cdot 8^3)$ ,  $(4 \cdot 6 \cdot 8)_2(4^2 \cdot 6^2 \cdot 8^2)(4^2 \cdot 6^5 \cdot 8^3)_2$ , and  $(4 \cdot 6^2)_2(4 \cdot 6^7 \cdot 8^2)^2(6^5 \cdot 10)$  topologies<sup>[33-34]</sup>, which presents a new trinodal (3,4,5)-connected 3D



network topology.

### 2.1.2 Crystal structure of $\{\text{Cd}_2(\text{CPhIDC})(\text{phen})_2\} \cdot 3\text{H}_2\text{O}\}_n$ (**2**)

Single-crystal analysis shows polymer **2** crystallizes in the monoclinic system with space group  $P2_1/n$  and the asymmetric unit cell contains two  $\text{Cd}^{2+}$  ions, one  $\text{CPhIDC}^{4-}$  anion, two 1,10-phenanthroline mole-

cules and three lattice waters. As shown in Fig.2a, polymer **2** is a double-core structure bridged by the  $\text{CPhIDC}^{4-}$  anions and adopt six-coordinated with two  $\text{Cd}^{2+}$  ions ( $\text{Cd1}$  and  $\text{Cd2}$ ). The  $\text{Cd1}$  is connected with three oxygen atoms ( $\text{O3\#1}$ ,  $\text{O4}$ ,  $\text{O6}$ ,  $d_{\text{Cd-O}}=0.222\ 0(3)\sim 0.235\ 1(3)\ \text{nm}$ ), one nitrogen atom ( $\text{N1\#1}$ ,  $d_{\text{Cd-N}}=0.223\ 0(3)\ \text{nm}$ ) from two  $\text{CPhIDC}^{4-}$  ligands and two

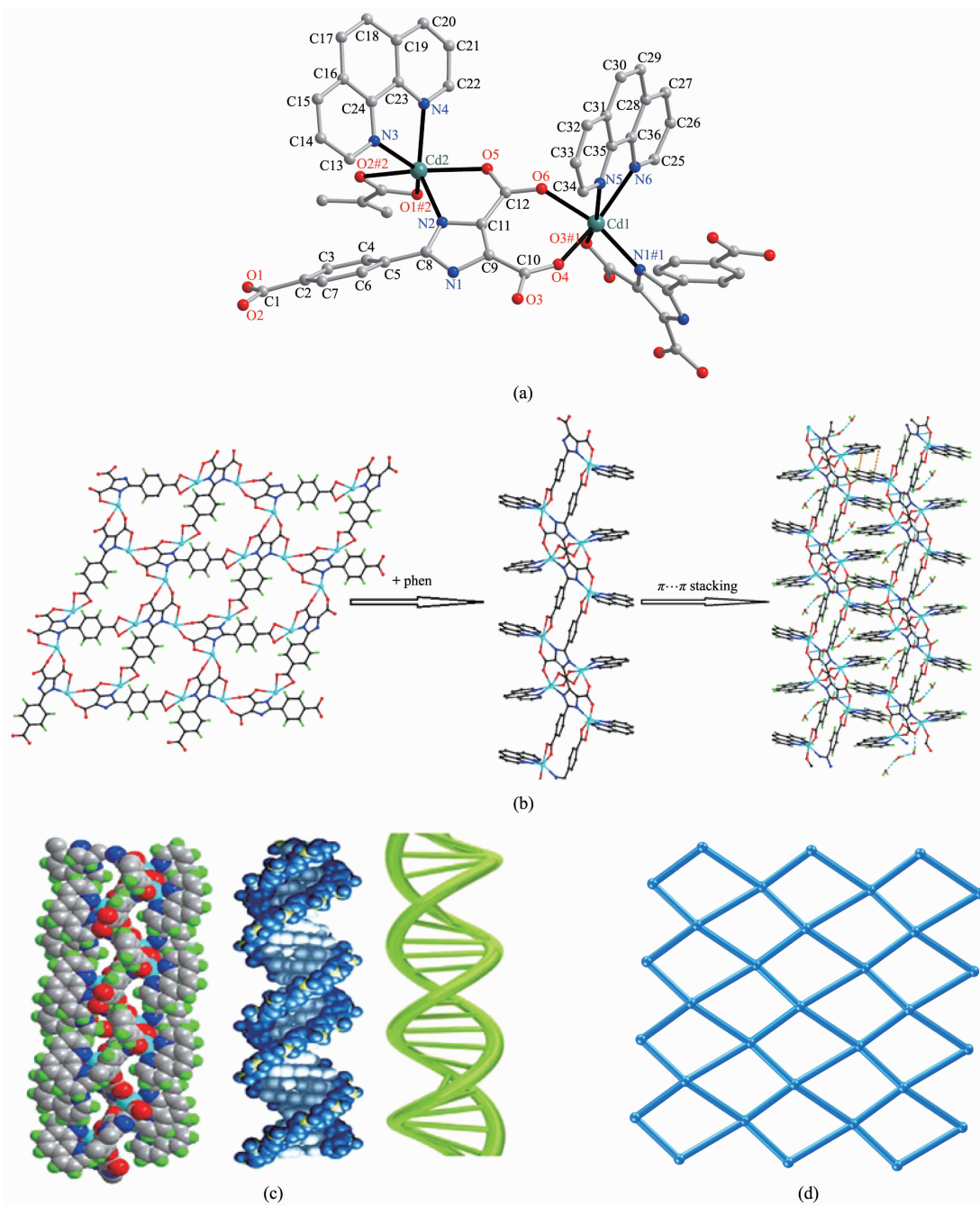


Fig.2 (a) Ball-and-stick structural view of **2**; (b) 3D stacking structure for **2** with hydrogen bond and  $\pi \cdots \pi$  from phen molecules; (c) Single-screw structure of **2** and the double-helix structure for DNA; (d) (4,4)-topological connected for **2**

nitrogen atoms (N5, N6,  $d_{\text{Cd-N}}=0.236\ 9(4)\sim 0.238\ 8(4)$  nm) from one 1,10-phenanthroline molecule to form a distorted octahedral geometry. Cd2 is practically identical to Cd1, but the six-coordinated atoms form a different severe flattening octahedral geometry. Cd-O distances, Cd-N distances and bond angles for **2** (Table S2) fall in the normal regions which are comparable to the values reported in literatures<sup>[35]</sup>. The CPhIDC<sup>4-</sup> anions adopt conformations with each bridging four Cd<sup>2+</sup> ions in  $\mu_4\text{-}\kappa^2\text{O}, \text{O}':\kappa^2\text{N}, \text{O}'':\kappa^2\text{N}', \text{O}''':\kappa^2\text{O}''', \text{O}''''$  coordination fashion (Scheme 1b) to form a ternary-chelate ring, two five-chelate rings and a seven-chelate ring.

Viewed along *c* axis without phen molecular, the Cd<sup>2+</sup> ion is bridged by the CPhIDC<sup>4-</sup> to form a 2D plane grid. Viewed along *b* axis only, the Cd<sup>2+</sup> ions bridging by ligands to form a bent long chain with phen molecules connected in the two sides of it. Meanwhile, the two adjacent chains stack with the function of  $\pi\cdots\pi$  from phen molecules to form a 3D network (Fig.2b). In addition, the hydrogen bonds (O2B-H2C $\cdots$ O3W#1) connected by the oxygen atom from free water molecules and hydrogen bond (O2W-H2A $\cdots$ O3, O2B-H2C $\cdots$ O3W#1, O2B-H2D $\cdots$ O1#2, O3W-H3C $\cdots$ O2), which is shown in Table S5, connected by oxygen atom from carboxylic acid and free water and thus contribute themselves to stabilize the crystal structure.

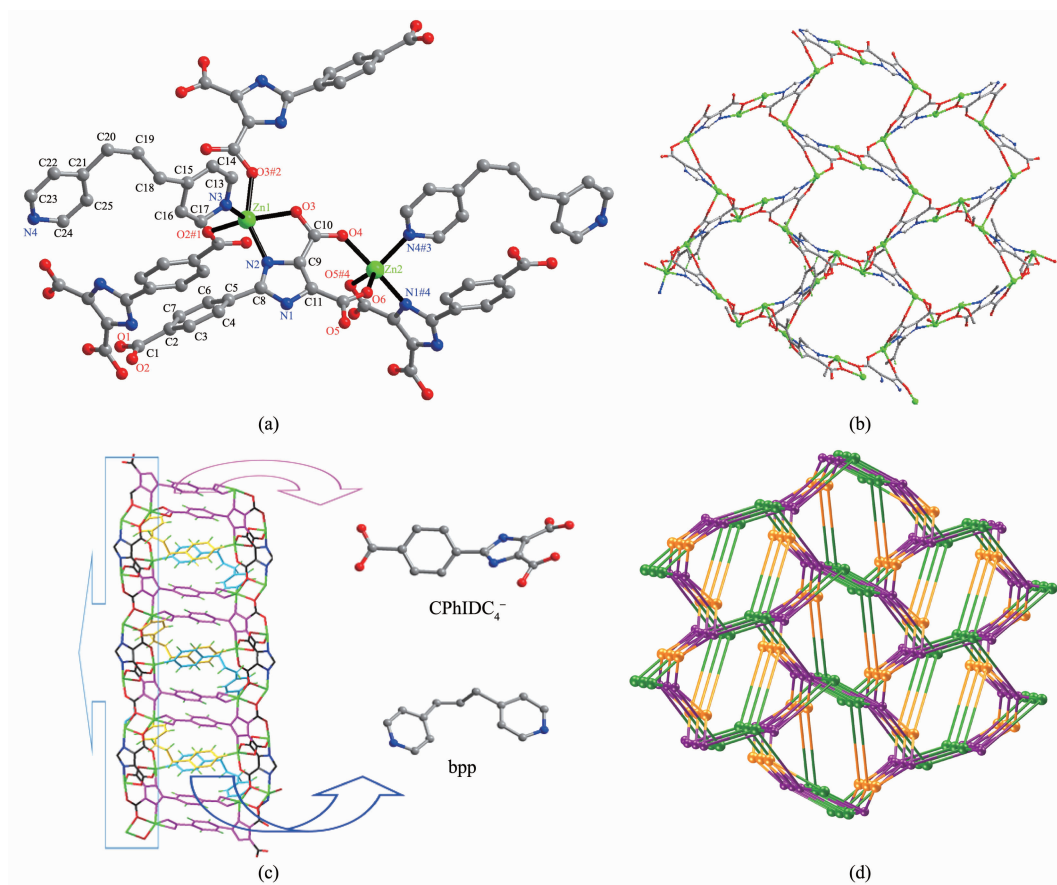
Interestingly, comparing the space filling figure for **2** with the structure of DNA, the single-screw structure of **2** is quite similar to the double-helix structure for DNA (Fig.2c). The inner hydrogen bond from the spiral chain and the phen molecules reside in the tunnel contribute the framework to stabilize the spiral chain structure. From the topological point of view, each CPhIDC<sup>4-</sup> ligand, linked to four Cd<sup>2+</sup> ions (two Cd1 and two Cd2), represents a 4-connected node while each Cd(II) ion connects to two CPhIDC<sup>4-</sup> anions as an edge of underlying net. Thus the chelating effect in **2** leads to 4-coordinated 2D underlying net with point symbol (4<sup>4</sup>)(6<sup>2</sup>) and vertex symbol (4 $\cdot$ 4 $\cdot$ 4 $\cdot$ 4) (Fig.2d).

### 2.1.3 Crystal structure of $\{[\text{Zn}_2(\text{CPhIDC})(\text{bpp})]\cdot$

$1.5\text{H}_2\text{O}]_n$  (**3**)

Single-crystal analysis shows polymer **3** crystallizes in the monoclinic system with space group  $P2_1/n$  and the asymmetric unit cell contains two Zn<sup>2+</sup> ions (Zn(1) and Zn(2)), one CPhIDC<sup>4-</sup> anion, one bpp molecule, one and a half lattice water. As shown in Fig.3a, Zn(1) is five-coordinated by three oxygen atoms (O2#1, O3#2, O3,  $d_{\text{Zn-O}}=0.199\ 4(2)\sim 0.213\ 7(2)$  nm) and one nitrogen atom (N2,  $d_{\text{Zn-N}}=0.210\ 8(2)$  nm) from three imidazole carboxylic acid ligands and one nitrogen atom (N3,  $d_{\text{Zn-N}}=0.205\ 3(3)$  nm) from one bpp molecule. Zn(1) is only 0.000 03 nm away from the O2#1, O3 and N3 plane, whereas the N2, O3#2 are at the side of the plane with the N2-Zn1-O3#2 bond angle of 149.28(8)°, which deviates from the straight line about 30.72° and thus the six atoms form a distorted trigonal bipyramid geometry. Zn(2) adopts the five-coordinated mode to form a distorted trigonal bipyramid geometry by three oxygen atoms (O6, O4, O5#4,  $d_{\text{Zn-O}}=0.203\ 5(3)\sim 0.209\ 1(2)$  nm) and one nitrogen atom (N1#4,  $d_{\text{Zn-N}}=0.209\ 8(3)$  nm) from one CPhIDC<sup>4-</sup> ligand and one nitrogen atom (N4#3,  $d_{\text{Zn-N}}=0.208\ 9(3)$  nm) from one bpp molecule. The bond angles of O6-Zn2-N4#3, O6-Zn2-O5#4, N4#3-Zn2-O5#4 are 117.31(13)°, 117.69(11)°, 124.90(13)°, respectively, and the sum of the three is 359.90°, which shows that O6, N4#3, O5#4 and Zn(2) are almost in the same plane, the bond angle (N1#4-Zn2-O4) is 169.54(10)°. In addition, two Zn<sup>2+</sup> ions are linked by the two sides of the bpp molecule. The ligand adopts conformations with  $\mu_5\text{-}\kappa\text{O}:\kappa^2\text{O}', \text{N}:\kappa^2\text{O}'', \text{N}':\kappa^2\text{O}''', \text{O}''':\kappa\text{O}''''$  coordination fashion (Scheme 1c) to connect Zn1 and Zn2 to form a five-member chelate ring and a seven-member chelate ring, respectively. The imidazole carboxylic acid ligand in the **3** adopt single dentate and bidentate chelate coordination mode connected to the metal ions. The Zn-O distances and the Zn-N distances and bond angles fall in the normal regions which are comparable to the values reported in literatures<sup>[36]</sup>.

Viewed along *c* axis without bpp, the Zn<sup>2+</sup> ion is bridged by the imidazole ring to form a 2D-grid sheet structure (Fig.3b). The 2D-grid sheet staggered conby the CPhIDC<sup>4-</sup> anions, bpp molecules expands to 3D Zn<sub>2</sub>(CPhIDC)(bpp) framework (Fig.3c). The 3D



Symmetry codes: #1:  $-x+1/2, y-1/2, -z+3/2$ ; #2:  $-x+1, -y+1, -z+1$ ; #3:  $x+1, y-1, z$ ; #4:  $-x+3/2, y-1/2, -z+3/2$

Fig.3 (a) Ball-and-stick structural view of **3**; (b) 2D plane structure for **3** viewed along  $a$  axis; (c) 3D framework for **3** viewed along  $b$  axis; (d) (3,4,5)-topological connected for **3**

$\text{Zn}_2(\text{CPhIDC})(\text{bpp})$  framework is found to be stabilized by the bpp padding molecules and the abundant hydrogen bonds (Table S6).

As the 3D topological connected for **3** in Fig.3d, the  $\text{CPhIDC}^{4-}$  anions are each bonded to four Zn(II) ions (two Zn1 and two Zn2). The Zn (1) ions are each coordinated to six atoms (O3#2, O2#1, O1#1, O3, N2, N3) from three  $\text{CPhIDC}^{4-}$  anions in a  $\kappa\text{O}:\kappa^2\text{O}'$ ,  $\text{N}:\kappa^2\text{O}''$ ,  $\text{O}'''$  coordination fashion and one bpp molecule in  $\kappa\text{N}$  coordination fashion. The Zn(2) ions are each coordinated to four atoms (O6, O4, O5, N1) from two  $\text{CPhIDC}^{4-}$  ligand anions in  $\kappa^2\text{O}$ ,  $\text{O}':\kappa^2\text{O}''$ ,  $\text{N}$  coordination fashion and one nitrogen atom from one bpp ligand in  $\kappa\text{N}$  coordination fashion. Therefore, each Zn1 ion, Zn2 ion and  $\text{CPhIDC}^{4-}$  anion can now be viewed as 4-connected nodes, 3-connected nodes and 5-connected nodes, respectively and leads to trinodal net with point symbol  $(4\cdot5^2\cdot6\cdot7^3)(5\cdot6\cdot7)(4\cdot5^2\cdot6\cdot7^4\cdot8^2)$ , which

is same as **1** (Fig.3d).

## 2.2 Analysis of FTIR spectra and PXRD

A broad absorption peak at  $3\,435\text{ cm}^{-1}$  in the free ligand can be assigned to the stretching vibration of phenolic hydroxyl group  $\nu_{\text{O-H}}$  in the carboxyl group. The absorption peak at  $3\,012\sim3\,109\text{ cm}^{-1}$  is the stretching vibration peak of  $\nu_{\text{N-H}}$  on the imidazole ring. The stretching vibration peak of the carbonyl group  $\nu_{\text{C=O}}$  appears at  $1\,716\text{ cm}^{-1}$ , and the stretching vibration peak of  $\nu_{\text{C=N}}$  in imidazole ring is located at  $1\,614\text{ cm}^{-1}$ . The infrared spectra of polymers **1**~**3** are similar, indicating that they have similar coordination modes. The broad peaks appear from  $3\,403$  to  $3\,538\text{ cm}^{-1}$  in the three polymers due to the O-H stretching vibration of water. The characteristic absorption peaks of carboxyl groups at  $1\,716\text{ cm}^{-1}$  disappear in polymers. The asymmetric stretching vibration  $\nu_{\text{as}}(-\text{COO}-)$  peaks appear at  $1\,542\sim1\,550\text{ cm}^{-1}$ , and symmetrical stretching



vibration peaks  $\nu_s(\text{-COO-})$  appear at  $1\,428\sim 1\,440\text{ cm}^{-1}$  and  $1\,375\sim 1\,395\text{ cm}^{-1}$ , indicating that the carboxyl group of ligand are in the form of bidentate chelating, bridging and monodentate coordination<sup>[19,37]</sup>.  $\nu_{\text{C=N}}$  stretching vibration of imidazole ring in ligand has red-shift from  $1\,614$  to  $1\,588\sim 1\,590\text{ cm}^{-1}$ . Two vibration peaks at  $2\,943\text{ cm}^{-1}$  (**1**),  $2\,936\text{ cm}^{-1}$  (**3**) and  $2\,860\text{ cm}^{-1}$  (**1**),  $2\,874\text{ cm}^{-1}$  (**3**) are C-H stretching vibration of  $\text{-CH}_2\text{-}$  group in auxiliary ligands bimp and bpp. However, polymer **2** don't have these two peaks. Another two absorption peaks at  $499\sim 506\text{ cm}^{-1}$  and  $457\sim 463\text{ cm}^{-1}$  can be attributed to the stretching vibration of  $\nu_{\text{M-O}}$  and  $\nu_{\text{M-N}}$ . All of above are consistent with the results of single crystals structure analysis.

The simulated and experimental PXRD patterns of coordination polymers **1~3** are given in Fig.S1~S3. The results suggest that the crystal structures are truly representative of the bulk materials. The differences in intensity are due to the preferred orientation of the powder samples.

### 2.3 Luminescent properties

There are few reports about the strong luminescent properties in imidazole-4,5-dicarboxylic acid. However, 2-(4'-carboxyphenyl)-1*H*-imidazole-4, 5-dicarboxylic acid ( $\text{H}_4\text{CPhIDC}$ ) has strong luminescent property at room temperature.

As illustrated in Fig.4, the solid-state luminescence spectra at room temperature for  $\text{H}_4\text{CPhIDC}$  ligand, polymers **1**, **2** and **3** are observed to have their main emission at 524, 527, 526 and 524 nm (609 nm) ( $\lambda_{\text{ex}}=467\text{ nm}$ ), respectively. The imidazole ligand, **1** and **2** can emit a certain intensity green luminescent while **3** can not only emit green but also emit orange luminescent. The green luminescent for **1**, **2** and **3** are from imidazole ligand and stronger than the free ligand, which can be ascribed to the luminescent of  $\text{H}_4\text{CPhIDC}$  ligand sensitized by metal ions. In addition, we can presume that the emission for **3** is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature, because the  $\text{Zn(II)}$  ion is difficult to be oxidized or reduced due to its  $d^{10}$  configuration. Thus, emissions observed at 609

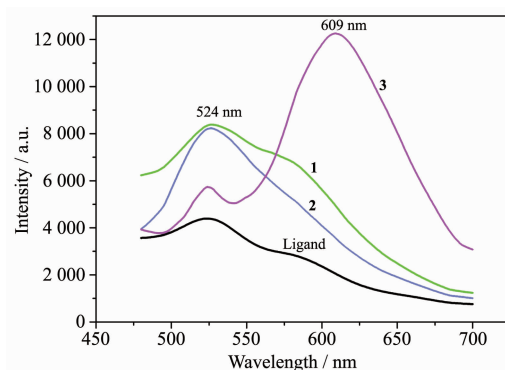


Fig.4 Fluorescence spectra for the  $\text{H}_4\text{CPhIDC}$  ligand and polymers **1~3**

nm for **3** may be assigned the band to an intra-ligand ( $\pi^*\text{-}\pi$ ) fluorescent emission of bpp auxiliary ligand<sup>[38]</sup>.

### 2.4 DNA binding

The interaction of ligand and polymers with calf thymus DNA (CT-DNA) was studied by an EB fluorescent probe. Fig.5 shows the emission spectra of EB bonded to DNA with compounds or not. As the increasing concenof the compounds, the emission intensity at 592 nm of EB-DNA system changed in different degrees. According to the classical Stern-Volmer equation<sup>[39]</sup>:  $I_0/I=1+K_{\text{sq}}r$ , where  $I_0$  and  $I$  represent the fluorescence intensities in the absence or presence of the compounds, respectively;  $r$  is the concentration ratio of the compounds to DNA;  $K_{\text{sq}}$  is a linear Stern-Volmer quenching constant, the  $K_{\text{sq}}$  value was obtained as the slope of  $I_0/I$  versus  $r$  linear plot.

From the inset in Fig.5, the  $K_{\text{sq}}$  value were 16.53, 0.88, 21.77 and 1.07 for  $\text{H}_4\text{CPhIDC}$  ligand, polymers **1**, **2** and **3**. It suggested that the interaction of the ligand with DNA are strong and can release more free EB molecules from EB-DNA, because of the present of benzene and imidazole rings. Especially, polymer **2** has the strongest interaction with the DNA, which is attributed to not only big planar molecules phen but also its similar double-helix structure with DNA (Fig. 2c). Thus, its molecules are more likely to enter the double helix structure of the DNA molecules. While the other two polymers are weaker than that of  $\text{H}_4\text{CPhIDC}$  ligand, which could be ascribed to that the planarity of molecules of **1** and **3** is not as good as  $\text{H}_4\text{CPhIDC}$  ligand and **2**.

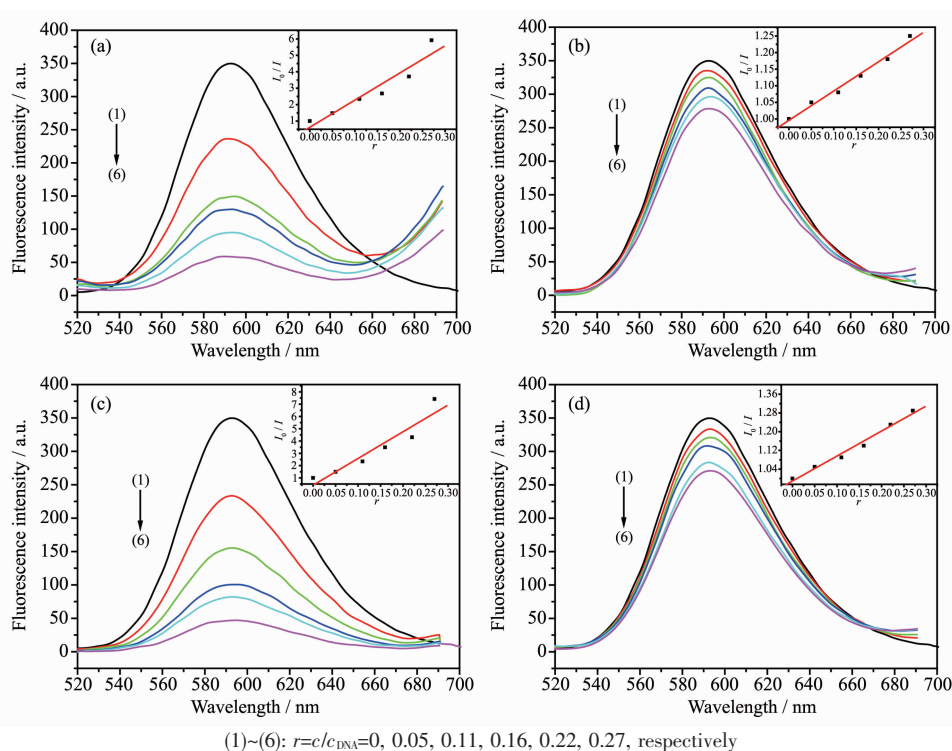


Fig.5 Emission spectra of EB-DNA system in the absence and presence of the  $\text{H}_4\text{CPhIDC}$  ligand (a), polymers **1** (b), **2** (c) and **3** (d)

### 3 Conclusions

$\text{H}_4\text{CPhIDC}$  was purposely synthesized by condensation and oxidation reactions and successfully applied to constructing three novel coordination polymers  $\{[\text{Cd}_2(\text{CPhIDC})(\text{bimb})] \cdot \text{H}_2\text{O}\}_n$  (**1**),  $\{[\text{Cd}_2(\text{CPhIDC})(\text{phen})_2] \cdot 3\text{H}_2\text{O}\}_n$  (**2**),  $\{[\text{Zn}_2(\text{CPhIDC})(\text{bpp})] \cdot 1.5\text{H}_2\text{O}\}_n$  (**3**). Complexes **1** and **3** exhibit analogous 3D  $[\text{Cd}_2(\text{CPhIDC})(\text{bimb})]$  and 3D  $[\text{Zn}_2(\text{CPhIDC})(\text{bpp})]$  frameworks with  $(5 \cdot 6 \cdot 7)(4 \cdot 5^2 \cdot 6 \cdot 7^2)(4 \cdot 5^2 \cdot 6 \cdot 7^4 \cdot 8^2)$  topology, but the metal ions and auxiliary ligands are different. Complex **2** is 2D wave-like fishing net structure with  $4^4 \cdot 6^2$  topology. Moreover, the luminescent properties shows that polymer **3** can emit green and orange luminescence, while the imidazole ligand and the other two polymers can emit a certain intensity green luminescence. In addition, the interaction of the ligands with DNA is strong and could release more free EB molecules from EB-DNA, because of the present of benzene and imidazole rings. Among the four compounds, the polymer **2** has the strongest interaction with the DNA due to the addition of the big planar molecules phen and the particularity of its structure.

This class of materials provides a new impetus to the construction of novel multifunctional coordination polymers materials.

Supporting information is available at <http://www.wjhxsb.cn>

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