

## 以联吡啶二羧酸及邻菲咯啉衍生物为配体的两种锌(II) 配合物的水热合成及晶体结构

王倩倩<sup>1</sup> 刘春波<sup>1,2</sup> 李秀颖<sup>1,2</sup> 王 星<sup>1</sup> 王申堂<sup>1</sup> 车广波<sup>\*,1,2</sup> 李春香<sup>\*,1</sup>

(<sup>1</sup> 江苏大学化学化工学院, 镇江 212013)

(<sup>2</sup> 环境友好材料制备与应用教育部重点实验室, 四平 136000)

**摘要:** 在水热条件下合成了两种配合物  $[\text{Zn}(\text{bpdc})(\text{pyip})_2] \cdot 3\text{H}_2\text{O}$  (**1**) 和  $[\text{Zn}(\text{pip})_2(\text{Hpip})] \cdot 3\text{H}_2\text{O}$  (**2**) ( $\text{H}_2\text{bpdc}$ =2,2'-联吡啶-3,3'-二羧酸,  $\text{pyip}$ =2-(3-吡啶基)-1*H*-咪唑并[4,5-*f*][1,10]邻菲咯啉,  $\text{Hpip}$ =2-苯基-1*H*-咪唑并[4,5-*f*][1,10]邻菲咯啉), 并利用红外和 X 射线单晶衍射对其结构进行了表征。配合物 **1** 属单斜晶系,  $P2_1/c$  空间群, 晶胞参数  $a=1.656\ 9(5)$  nm,  $b=1.361\ 4(4)$  nm,  $c=1.863\ 7(6)$  nm,  $\beta=93.128\ (6)^\circ$ ,  $V=4.198\ (2)$  nm<sup>3</sup>,  $Z=4$ ,  $\text{ZnC}_{48}\text{H}_{34}\text{N}_{12}\text{O}_7$ ,  $M_r=955.99$ ,  $D_c=1.513\ \text{g} \cdot \text{cm}^{-3}$ ,  $\mu(\text{Mo } K\alpha)=0.657\ \text{mm}^{-1}$ ,  $F(000)=1\ 968$ ,  $\text{GOOF}=1.008$ ,  $R=0.057\ 7$ ,  $wR=0.107\ 5$ , 其中 4 622 个可观测衍射点 ( $I>2\sigma(I)$ )。配合物 **2** 属单斜晶系,  $P2_1/c$  空间群, 晶胞参数  $a=1.797\ 7(4)$  nm,  $b=1.527\ 0(3)$  nm,  $c=1.767\ 6(4)$  nm,  $\beta=102.84(3)^\circ$ ,  $V=4.730\ 9(19)$  nm<sup>3</sup>,  $Z=4$ ,  $\text{ZnC}_{57}\text{H}_{40}\text{N}_{12}\text{O}_3$ ,  $M_r=1\ 006.36$ ,  $D_c=1.410\ \text{g} \cdot \text{cm}^{-3}$ ,  $\mu(\text{Mo } K\alpha)=0.581\ \text{mm}^{-1}$ ,  $F(000)=2\ 072$ ,  $\text{GOOF}=1.134$ ,  $R=0.089\ 5$ ,  $wR=0.208\ 4$ , 其中 6 558 个可观测衍射点 ( $I>2\sigma(I)$ )。结构分析表明配合物 **1** 和 **2** 均为零维结构, 氢键和  $\pi$ - $\pi$  相互作用在加固配合物的结构中起到重要作用。此外, 对化合物的热稳定性和荧光性质也进行了研究。

**关键词:** 锌(II)配合物; 2,2'-联吡啶-3,3'-二羧酸; 邻菲咯啉衍生物; 水热合成; 晶体结构

中图分类号: O614.24<sup>1</sup>

文献标识码: A

文章编号: 1001-4861(2012)03-0619-07

## Hydrothermal Synthesis and Crystal Structure of Two Zinc (II) Complexes with 2,2'-Bipyridine-3,3'-dicarboxylic Acid and Phenanthroline Derivative Ligands

WANG Qian-Qian<sup>1</sup> LIU Chun-Bo<sup>1,2</sup> LI Xiu-Ying<sup>1,2</sup> WANG Xing<sup>1</sup>

WANG Shen-Tang<sup>1</sup> CHE Guang-Bo<sup>\*,1,2</sup> LI Chun-Xiang<sup>\*,1</sup>

(<sup>1</sup>School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, Jiangsu 212013, China)

(<sup>2</sup>Key Laboratory of Preparation and Applications of Environmental Friendly Materials,  
Chinese Ministry of Education, Siping, Jilin 136000, China)

**Abstract:** The title complexes,  $[\text{Zn}(\text{bpdc})(\text{pyip})_2] \cdot 3\text{H}_2\text{O}$  (**1**) and  $[\text{Zn}(\text{pip})_2(\text{Hpip})] \cdot 3\text{H}_2\text{O}$  (**2**) ( $\text{H}_2\text{bpdc}$ =2,2'-bipyridine-3,3'-dicarboxylic acid,  $\text{pyip}$ =2-(pyridin-3-yl)-1*H*-imidazo[4,5-*f*][1,10] phenanthroline,  $\text{Hpip}$ =2-phenyl-1*H*-imidazo[4,5-*f*][1,10]phenanthroline) have been synthesized under hydrothermal conditions and characterized by IR spectrum and X-ray single-crystal diffraction. Complex **1** is of monoclinic, space group  $P2_1/c$  with  $a=1.656\ 9(5)$  nm,  $b=1.361\ 4(4)$  nm,  $c=1.863\ 7(6)$  nm,  $\beta=93.128(6)^\circ$ ,  $V=4.198(2)$  nm<sup>3</sup>,  $Z=4$ ,  $\text{ZnC}_{48}\text{H}_{34}\text{N}_{12}\text{O}_7$ ,  $M_r=955.99$ ,  $D_c=1.513\ \text{g} \cdot \text{cm}^{-3}$ ,  $\mu(\text{Mo } K\alpha)=0.657\ \text{mm}^{-1}$ ,  $F(000)=1\ 968$ ,  $\text{GOOF}=1.008$ , the final  $R=0.057\ 7$  and  $wR=0.107\ 5$  for 4 622 observed reflections ( $I>2\sigma(I)$ ). Complex **2** is of monoclinic, space group  $P2_1/c$  with  $a=1.797\ 7(4)$  nm,  $b=1.527\ 0(3)$  nm,  $c=1.767\ 6(4)$  nm,  $\beta=102.84(3)^\circ$ ,  $V=4.730\ 9(19)$  nm<sup>3</sup>,  $Z=4$ ,  $\text{ZnC}_{57}\text{H}_{40}\text{N}_{12}\text{O}_3$ ,  $M_r=1\ 006.36$ ,  $D_c=1.410\ \text{g} \cdot \text{cm}^{-3}$ ,  $\mu(\text{Mo } K\alpha)=0.581\ \text{mm}^{-1}$ ,  $F(000)=2\ 072$ ,  $\text{GOOF}=1.134$ , the final  $R=0.089\ 5$  and  $wR=0.208\ 4$  for 6 558 observed reflections ( $I>2\sigma(I)$ ). Structural analyses show that the complexes **1** and **2** all present a zero-dimensional unit.

收稿日期: 2011-08-08。收修改稿日期: 2011-10-29。

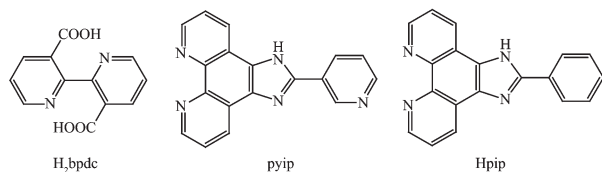
江苏大学自然科学基金(No.09JDC001)资助项目。

\*通讯联系人。E-mail: guangbochejl@yahoo.com; lcx@ujs.edu.cn

Furthermore, the hydrogen-bonding and  $\pi$ - $\pi$  stacking interactions play key roles in consolidating the structures of complexes. Thermal stability and luminescent properties were also investigated. CCDC: 853171, **1**; 853172, **2**.

**Key words:** zinc(II) complex; 2,2'-bipyridine-3,3'-dicarboxylic acid; phenanthroline derivative; hydrothermal synthesis; crystal structure

Metal-organic frameworks (MOFs) remain a considerable focus, since their fascinating structures and properties give rise to gas adsorption, catalytic chemical reaction, molecular selection, magnetic materials, non-linear optics and biological function<sup>[1-10]</sup>. During the past years, many novel and intriguing frameworks have been synthesized and characterized. Among the organic ligands, the chelate 1,10-phenanthroline (phen) and its derivatives have been extensively used in the preparation of a variety of MOFs with versatile topologies. This is because their excellent coordinating capacities, hydrogen bond donors and acceptors, and potential supramolecular recognition sites for  $\pi$ - $\pi$  stacking interactions, which can greatly govern the process of self-assembly, and may link polynuclear discrete units or low-dimensional entities into high-dimensional supramolecular networks<sup>[11-15]</sup>. Following this strategy, herein we report the synthesis, elemental and thermogravimetric analyses, infrared spectra, crystal structures and photoluminescent spectra of two new coordination complexes of formula  $[\text{Zn}(\text{bpdc})(\text{pyip})_2] \cdot 3\text{H}_2\text{O}$  (**1**) and  $[\text{Zn}(\text{pip})_2(\text{Hpip})] \cdot 3\text{H}_2\text{O}$  (**2**) ( $\text{H}_2\text{bpdc}$  = 2,2'-bipyridine-3,3'-dicarboxylic acid,  $\text{pyip}$  = 2-(pyridin-3-yl)-1*H*-imidazo [4,5-*f*] [1,10]phenanthroline,  $\text{Hpip}$  = 2-phenyl-1*H*-imidazo [4,5-*f*] [1,10]phenanthroline). In the crystal structures, **1** and **2** were further assembled to three-dimensional and two-dimensional structures by non-covalent interactions such as hydrogen bonds and  $\pi$ - $\pi$  stacking interactions, respectively.



## 1 Experimental

### 1.1 General

Two phenanthroline derivative ligands ( $\text{pyip}$  and

$\text{Hpip}$ ) were synthesized according to the literature method<sup>[16]</sup> and all other materials were purchased from commercial sources and used without further purification. Elemental analyses were conducted on a Perkin-Elmer 240C analyzer. IR spectra were collected by Fourier transform infrared spectrometer Nicolet Nexus 470. Thermogravimetric analyses (TGA) were carried out under air condition on a NETZSCH STA 449C analyzer. Photoluminescent spectra were obtained from Fluorescence spectrophotometer CaryEclipse while the two compounds were solid-state.

### 1.2 Syntheses and crystal growth

$[\text{Zn}(\text{bpdc})(\text{pyip})_2] \cdot 3\text{H}_2\text{O}$  (**1**): A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.2 mmol, 0.059 5 g),  $\text{H}_2\text{bpdc}$  (0.2 mmol, 0.048 8 g),  $\text{pyip}$  (0.4 mmol, 0.118 9 g),  $\text{NaOH}$  (0.4 mmol, 0.016 0 g) and deionized water (12 mL) was stirred for 30 min in air, then transferred to a 25 mL Teflon-lined stainless steel autoclave and heated to 160 °C for 3 d. After cooling to room temperature at a rate of 5 °C  $\cdot$  h<sup>-1</sup>, yellow block crystals of **1** were obtained. The crystals were filtered, washed with distilled water and dried at ambient temperature to give a yield of about 72% based on Zn(II). Anal. Calcd. for  $\text{ZnC}_{48}\text{H}_{34}\text{N}_{12}\text{O}_7$  (%): C, 60.29; H, 3.58; N, 17.58. Found (%): C, 60.24; H, 3.61; N, 17.53. IR spectrum (KBr,  $\text{cm}^{-1}$ ): 3 398(m), 3 060(m), 1 568(s), 1 509(m), 1 449(s), 1 387(s), 1 361(m), 1 189(m), 1 147(w), 1 077(m), 945(m), 812(s), 735(s), 695(m), 644(w), 422(m).

$[\text{Zn}(\text{pip})_2(\text{Hpip})] \cdot 3\text{H}_2\text{O}$  (**2**): A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.1 mmol, 0.029 7 g),  $\text{Hpip}$  (0.3 mmol, 0.088 9 g),  $\text{NaOH}$  (0.8 mmol, 0.032 0 g) and deionized water (12 mL) was stirred for 30 min in air, then transferred to a 25 mL Teflon-lined stainless steel autoclave and heated to 180 °C for 3 d. After cooling to room temperature at a rate of 5 °C  $\cdot$  h<sup>-1</sup>, yellow block crystals of **2** were obtained. The crystals were filtered, washed with distilled water and dried at ambient temperature to give a yield of

about 69% based on Zn(II). Anal. Calcd. for  $\text{ZnC}_{57}\text{H}_{40}\text{N}_{12}\text{O}_3$  (%): C, 68.02; H, 4.01; N, 16.70. Found (%): C, 68.11; H, 3.98; N, 16.77. IR spectrum (KBr,  $\text{cm}^{-1}$ ): 3 407(m), 3 058(m), 1 567(s), 1 508(m), 1 447(s), 1 403(s), 1 360(m), 1 188(m), 1 077(s), 946(m), 814(s), 735(s), 640(w), 556(w), 421(w).

### 1.3 X-ray structure determination

Crystallographic data of two compounds were collected on Rigaku RAXIS-RAPID single crystal diffractometer equipment. The machine was equipped with a narrow-focus, 5.4 kW sealed tube X-ray source (graphite-monochromated Mo  $K\alpha$  radiation,  $\lambda = 0.071\,073\,\text{nm}$ ) using an  $\omega$  scan mode at room temperature 292(2) K. For **1**, a total of 23 005 reflections were collected in the range of  $1.85^\circ \leq \theta \leq 25.05^\circ$ , of which 7 460 were unique with  $R_{\text{int}} = 0.074\,3$  and 4 622 were observed with  $I > 2\sigma(I)$ . And for **2**, a total of 22 008

reflections were collected in the range of  $2.67^\circ \leq \theta \leq 25.51^\circ$ , of which 8 808 were unique with  $R_{\text{int}} = 0.064\,7$  and 6 558 were observed with  $I > 2\sigma(I)$ . All the structures were solved by direct methods using the program SHELXS-97<sup>[17]</sup> and refined by full-matrix least-squares techniques against  $F^2$  using the SHELXTL-97 crystallographic software package<sup>[18]</sup>. All non-hydrogen atoms were easily found from the difference Fourier map and refined anisotropically, whereas the hydrogen atoms of the organic molecules were placed by geometrical considerations and were added to the structure factor calculation. In compound **2**, the hydrogen atoms attached to water molecule O3W could not be positioned reliably. The detailed crystallographic data and structure refinement parameters for two compounds are summarized in Table 1.

CCDC: 853171, **1**; 853172, **2**.

Table 1 Crystallographic data for compound **1** and **2**

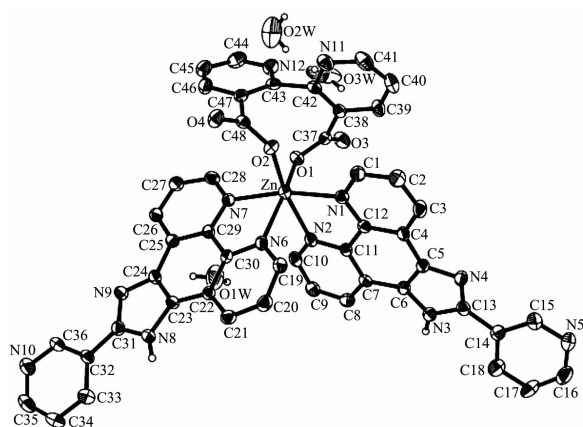
Compound	<b>1</b>	<b>2</b>
Empirical formula	$\text{ZnC}_{48}\text{H}_{34}\text{N}_{12}\text{O}_7$	$\text{ZnC}_{57}\text{H}_{40}\text{N}_{12}\text{O}_3$
Formula weight	955.99	1 006.36
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
$a / \text{nm}$	1.656 9(5)	1.797 7(4)
$b / \text{nm}$	1.361 4(4)	1.527 0(3)
$c / \text{nm}$	1.863 7(6)	1.767 6(4)
$\beta / (^\circ)$	93.128(6)	102.84(3)
$V / \text{nm}^3$	4.198(2)	4.730 9(19)
$Z$	4	4
$R_1 (I > 2\sigma(I))$	0.057 7	0.089 5
$wR_2 (I > 2\sigma(I))$	0.1075	0.2084
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.513	1.410
$\mu / \text{mm}^{-1}$	0.657	0.581
$F(000)$	1 968.0	2 072.0
Unique reflections	7 460	8 808
Observed reflections ( $I > 2\sigma(I)$ )	4 622	6 558
Goodness-of-fit on $F$	1.008	1.134

## 2 Results and discussion

### 2.1 Description of the structure

Compound **1** possesses a discrete zero-dimensional structure that crystallizes in space group  $P2_1/c$ . The asymmetric unit of **1** (show in Fig.1) consists of one  $\text{Zn}^{2+}$  ion, two pyip ligands, one bpdc<sup>2-</sup> ligand and three

free water molecules. The central  $\text{Zn}^{2+}$  ion adopts slightly distorted octahedral geometry coordinated by four nitrogen atoms (N1, N2, N6, N7) from two pyip ligands, and two O atoms (O1, O2) from one bpdc<sup>2-</sup> ligand. The bond distances of Zn-N are similar to the reported with the range of 0.212 0~0.224 0(3) nm, and the Zn-O bond distances are in the range of 0.206 8~



Hydrogen atoms were omitted for clarity

Fig.1 ORTEP view of complex **1** with 30% probability displacement ellipsoids

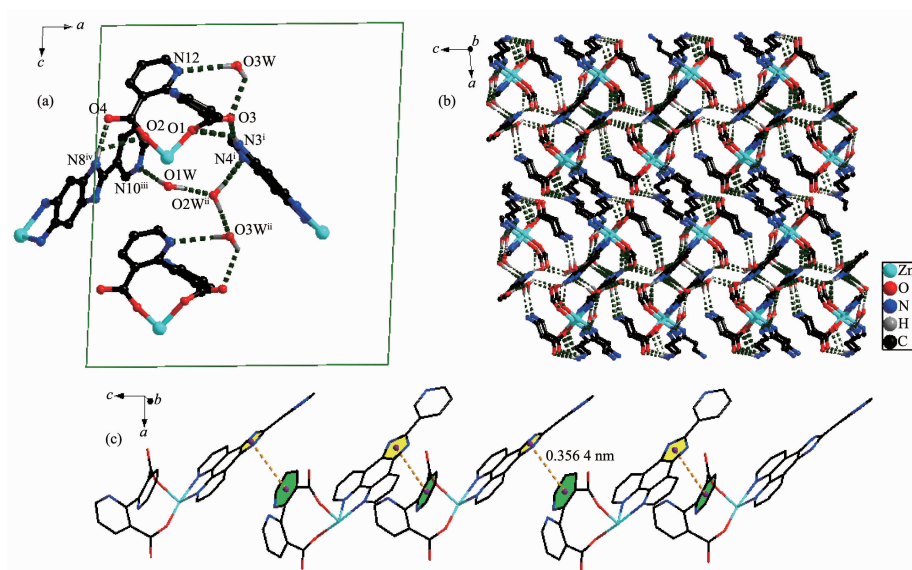
0.209 3(3) nm<sup>[19-22]</sup>. The selected bond lengths and bond angles are given in Table 2. Intramolecular and intermolecular hydrogen bonds are observed in this complex as follows: (i) The hydrogen bonds between the nitrogen atom N atom of pyip and the carboxylate O atom (N3<sup>i</sup>–H8<sup>⋯</sup> O1 0.266 nm, 138.9°). The similar bonds are observed between N3<sup>i</sup> and O3 (N3<sup>i</sup>–H8<sup>⋯</sup> O3 0.190 nm, 164.8°), N8<sup>iv</sup> and O2 (N8<sup>iv</sup>–H15<sup>⋯</sup> O2 0.267 nm, 121.1°), N8<sup>iv</sup> and O4 (N8<sup>iv</sup>–H15<sup>⋯</sup> O4 0.192 nm, 173.9°). (ii) The O–H<sup>⋯</sup> O hydrogen bonds between three water molecules (O1W–H1WA<sup>⋯</sup> O2W<sup>ii</sup> 0.192

nm, 174.4°; O2W<sup>ii</sup>–H2WA<sup>⋯</sup> 3W<sup>iii</sup> 0.200 nm, 154.6°). (iii) The hydrogen bonds between water molecules and N atoms of the pyip or bpd<sup>2-</sup> ligands (O1W–H1WB<sup>⋯</sup> N10<sup>iii</sup> 0.215 nm, 176.4°; O2W<sup>ii</sup>–H2WB<sup>⋯</sup> N4<sup>i</sup> 0.251 nm, 119.4°; O3W–H3WA<sup>⋯</sup> N12 0.251 nm, 162.8°). (iv) The hydrogen bonds between water molecule O3W and the carboxylate oxygen atom O3 (O3W–H3WB<sup>⋯</sup> O3 0.237 nm, 126.2°) (Table 3). Through these hydrogen bonds, the zero-dimensional structures are turned to a three-dimensional supramolecular structure (Fig.2a, Fig.2b). Simultaneously, the neighboring zero-dimensional units are assembled via  $\pi$ - $\pi$  stacking interactions between the pyip ligands (centroid-to-centroid distance=0.356 4 nm) into a steady three-dimensional supramolecular motif (Fig.2c).

Single crystal X-ray determination shows that **2** is also a zero-dimensional configuration, in which Zn center is six-coordinated. As shown in Fig.3, each distorted octahedral Zn(II) center is defined by six N atoms from three different Hpip ligands. It should be noted that the deprotonated N anion of the imidazole rings of two ligands balance the charge of Zn<sup>2+</sup>, generating a neutral complex. All the Zn–N distances are in the range of 0.211 9 (4)~0.220 8(4) nm, which are in agreement with those described in the literature<sup>[19-22]</sup>.

Table 2 Selected bond lengths (nm) and bond angles(°) for **1** and **2**

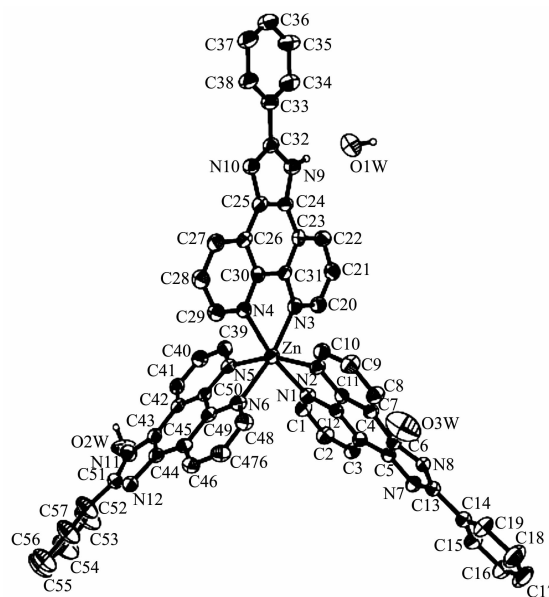
Complex <b>1</b>					
Zn–O1	0.209 3(3)	Zn–N1	0.212 3(3)	Zn–N2	0.221 0(3)
Zn–O2	0.206 8(3)	Zn–N6	0.224 0(3)	Zn–N7	0.212 0(3)
O2–Zn–O1	99.23(10)	O2–Zn–N7	96.17(11)	O1–Zn–N7	90.18(11)
O2–Zn–N1	89.38(10)	O1–Zn–N1	100.02(11)	N7–Zn–N1	167.48(12)
O2–Zn–N2	165.45(11)	O1–Zn–N2	86.65(11)	N7–Zn–N2	97.11(12)
N2–Zn–N2	76.45(12)	O2–Zn–N6	95.50(11)	O1–Zn–N6	160.84(11)
N7–Zn–N6	76.05(12)	N1–Zn–N6	92.29(12)	N2–Zn–N6	82.00(11)
Complex <b>2</b>					
Zn–N1	0.219 4(4)	Zn–N2	0.214 4(4)	Zn–N3	0.215 0(4)
Zn–N4	0.217 3(4)	Zn–N5	0.211 9(4)	Zn–N6	0.220 8(4)
N5–Zn–N2	160.80(15)	N5–Zn–N3	99.26(16)	N2–Zn–N3	96.67(16)
N5–Zn–N4	96.79(16)	N2–Zn–N4	97.28(15)	N3–Zn–N4	76.52(15)
N5–Zn–N1	90.99(16)	N2–Zn–N1	76.76(15)	N3–Zn–N1	95.77(15)
N4–Zn–N1	169.79(16)	N5–Zn–N6	76.88(15)	N2–Zn–N6	89.10(15)
N3–Zn–N6	169.67(15)	N4–Zn–N6	94.30(16)	N1–Zn–N6	93.89(16)



Symmetry code: <sup>i</sup> 1-x, 1+y, 1-z; <sup>ii</sup> x, 0.5-y, 0.5+z; <sup>iii</sup> -x, -y, 1-z; <sup>iv</sup> -x, 1-y, 1-z; Dots are centroid of the rings and some of atoms are omitted for clarity in (c)

Fig.2 (a) Hydrogen bonds of compound **1**, some of atoms are omitted for clarity; (b) Three-dimensional superamolecular structure constructed by hydrogen bonds, some of atoms are omitted for clarity; (c)  $\pi$ - $\pi$  stacking interactions of compound **1**

Selected bond lengths and bond angles of **2** are listed in Table 2. Also, there are three uncoordinated water molecules (O1W, O2W, O3W) per asymmetric unit, which interact with the N atoms of the Hpip ligands through strong hydrogen bonding interactions (N9-H9A  $\cdots$  O1W 0.199 nm, 160.8°; O2W<sup>i</sup>-H2WA  $\cdots$  N11<sup>i</sup> 0.198 nm, 164°; O2W<sup>i</sup>-H2WB  $\cdots$  N8<sup>ii</sup> 0.196 nm, 162°; O1W-H1WA  $\cdots$  N10<sup>iii</sup> 0.241 nm, 128°). Furthermore, intermolecular O-H  $\cdots$  O hydrogen bonds are observed between the free water molecules (O1W-H1WB  $\cdots$  O3W<sup>ii</sup> 0.191 nm, 165°) (Table 3, Fig.4a). As shown in Fig.4b, these discrete fragments are assembled to a two-dimensionally network by hydrogen bonding. The same to complex **1**, the intermolecular  $\pi$ - $\pi$  stacking interactions between Hpip ligands in adjacent mononuclear units (centroid-to-centroid distance = 0.343 4 nm) are contributed to the stabilization of the overall crystal structure (Fig.4c).



Hydrogen atoms were omitted for clarity

Fig.3 ORTEP view of complex **2** with 30% probability displacement ellipsoids

Table 3 Hydrogen bond lengths and bond angles for **1** and **2**

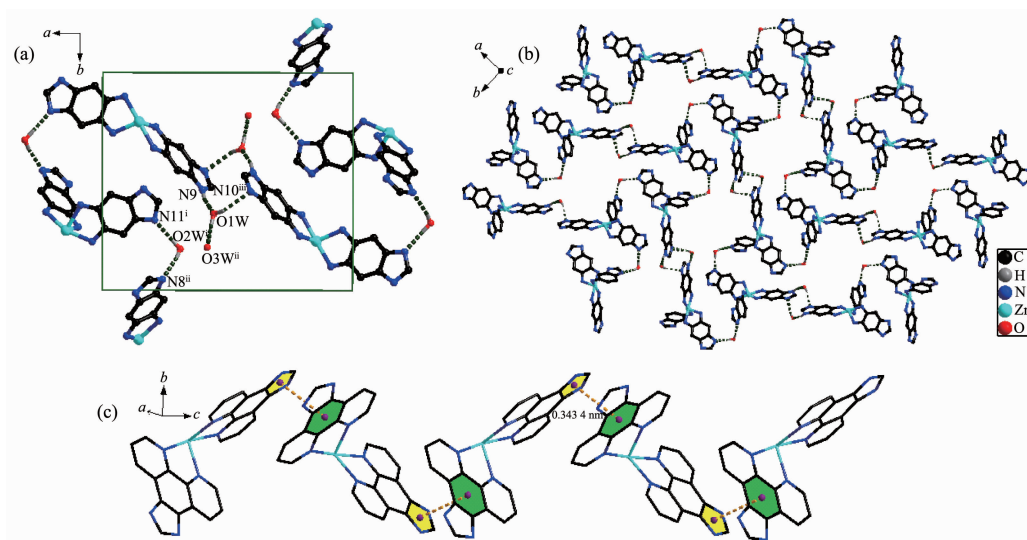
D-H $\cdots$ A	<i>d</i> (D-H) / nm	<i>d</i> (H $\cdots$ A) / nm	<i>d</i> (D $\cdots$ A) / nm	$\angle$ DHA / (°)
Complex <b>1</b>				
N3 <sup>i</sup> -H8 $\cdots$ O1	0.086	0.266	0.335 5	138.9
N3 <sup>i</sup> -H8 $\cdots$ O3	0.086	0.190	0.274 2	164.8
N8 <sup>iv</sup> -H15 $\cdots$ O2	0.086	0.267	0.3202	121.1



Continued Table 3

N8 <sup>iv</sup> -H15...O4	0.086	0.192	0.277 3	173.9
O1W-H1WA...O2W <sup>ii</sup>	0.087	0.192	0.278 5	174.4
O2W <sup>ii</sup> -H2WA...O3W <sup>iii</sup>	0.085	0.200	0.279 1	154.6
O3W-H3WA...N12	0.0897	0.251	0.337 8	162(8)
O1W-H1WB...N10 <sup>iii</sup>	0.087	0.215	0.302 3	176.4
O2W <sup>ii</sup> -H2WB...N4 <sup>i</sup>	0.086	0.251	0.303 0	119.4
O3W-H3WB...O3	0.086	0.237	0.295 5	126.2
Complex 2				
N9-H9A...O1W	0.086	0.199	0.281 6	160.8
O2W <sup>i</sup> -H2WA...N11 <sup>i</sup>	0.085	0.198	0.280 9	164
O2W <sup>i</sup> -H2WB...N8 <sup>ii</sup>	0.085	0.196	0.278 0	162
O1W-H1WA...N10 <sup>iii</sup>	0.086	0.241	0.301 1	128
O1W-H1WB...O3W <sup>ii</sup>	0.086	0.191	0.274 8	165

Symmetry transformations used to generate the equivalent atoms: **1**: <sup>i</sup> 1-x, 1+y, 1-z; <sup>ii</sup> x, 0.5-y, 0.5+z; <sup>iii</sup> -x, -y, 1-z; <sup>iv</sup> -x, 1-y, 1-z; **2**: <sup>i</sup> 2-x, 0.5+y, 1.5-z; <sup>ii</sup> x, 1+y, z; <sup>iii</sup> 1-x, 1-y, 1-z.



Symmetry code: <sup>i</sup> 2-x, 0.5+y, 1.5-z; <sup>ii</sup> x, 1+y, z; <sup>iii</sup> 1-x, 1-y, 1-z; Dots are centroid of the rings and some of atoms are omitted for clarity in (c)

Fig.4 (a) Hydrogen bonds of compound **2**, some of atoms are omitted for clarity; (b) Two-dimensional superamolecular net structure constructed by hydrogen bonds, some of atoms are omitted for clarity; (c)  $\pi$ - $\pi$  stacking interactions of compound **2**

## 2.2 TG analysis

The thermal stability of complexes **1** and **2** was investigated by TGA (Fig.5). Three distinct weight losses were observed for **1**. The first weight loss of 5.80% for **1** is in the range of 52~135 °C, assigned to the release of the free water molecules (calcd. 5.65%). In complex **1**, the second weight loss of 24.97% is ascribable to the loss of bpdc<sup>2-</sup> ligands (calcd. 25.34%) from 380 to 490 °C. The next weight loss may be the decomposition of pyip ligands when the temperature is

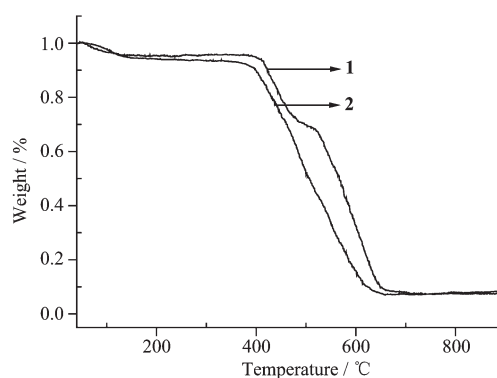


Fig.5 TG curves for complexes **1** and **2**

higher. Compound **2** shows a two-step weight loss. The first weight loss of 5.51% (calcd. 5.37%) is assigned to the liberation of three uncoordinated water molecules which occurred in the range of approximate 70~160 °C. The second loss of 87.53% (calcd. 88.14%) occurs from 355 to 665 °C, which corresponds to the loss of Hpip ligands. After the decomposition, the two complex's final product may all be ZnO.

### 2.3 Photoluminescent properties

Zn(II) can produce a variety of complexes that not only exhibit appealing structures but also possess photoluminescent (PL) properties<sup>[12,20]</sup>. The PL spectra of two complexes were investigated in the solid state at room temperature. As indicated in Fig.6, the emission peaks are 621 (**1**) and 635 nm (**2**) upon excitation at 365 nm, respectively. In order to understand the nature of these emission bands, the PL properties of free ligands pyip and Hpip were analyzed, showing they exhibit the strongest emission peaks at about 551 nm and 475 nm<sup>[23]</sup> from 300 to 800 nm, respectively. Compared with the PL spectra of free ligand, the emission spectra of two complexes are obviously similar to those of ligands, which might be attributable to chelating coordination of the planar ligands in both complexes. The PL emissions of **1** and **2** also mainly originate from the intraligand fluorescent emissions of ligands<sup>[13]</sup>. By comparison, two complexes show different PL spectra. The reason for different emissions of two compounds was presumably owing to the differences of coordination mode of complexes with different ligands.

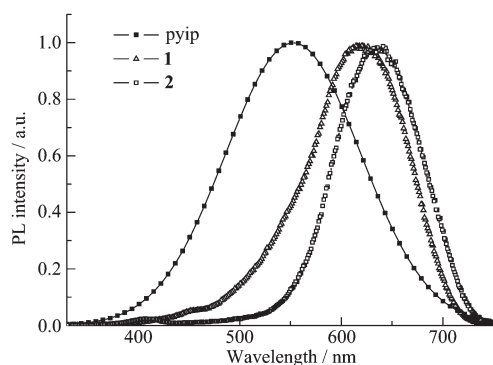


Fig.6 Photoluminescent spectra of complex **1**, **2** and pyip ligand in room temperature

### References:

- [1] Joseph G N, Seth M C. *J. Am. Chem. Soc.*, **2010**,**132**:4560-4561
- [2] Chang Z, Zhang D S, Chen Q, et al. *Inorg. Chem.*, **2011**,**50**: 7555-7562
- [3] Liu T F, Zhang W J, Sun W H, et al. *Inorg. Chem.*, **2011**,**50**: 5242-5248
- [4] Wang X L, Chen Y Q, Gao Q, et al. *Cryst. Growth Des.*, **2010**, **10**:2174-2184
- [5] Kahn O. *Acc. Chem. Res.*, **2000**,**33**:647-657
- [6] Fache F, Schulz E, Tommasino M L, et al. *Chem. Rev.*, **2000**, **100**:2159-2231
- [7] Yaghi O M, O'Keeffe M, Ockwig N W, et al. *Nature*, **2003**, **423**:705-714
- [8] Xiang S L, Huang J, Li L, et al. *Inorg. Chem.*, **2011**,**50**:1743-1748
- [9] CHE Guang-Bo(车广波), LI Xiu-Yin(李秀颖), XU Zhan-Lin(徐占林), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2009**,**25**:556-559
- [10] LIU Chun-Bo(刘春波), CHE GUANG-Bo(车广波), WANG Qing-Wei(王庆伟), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2008**,**24**:835-838
- [11] Wang X L, Chen Y Q, Liu G C, et al. *Inorg. Chim. Acta*, **2010**,**363**:773-778
- [12] Che G B, Liu C B, Liu B, et al. *CrystEngComm*, **2008**,**10**:184-191
- [13] Li X Y, Liu C B, Che G B, et al. *Inorg. Chim. Acta*, **2010**,**363**: 1359-1366
- [14] Che G B, Wang J, Liu C B, et al. *Inorg. Chim. Acta*, **2009**, **362**:2756-2761
- [15] Wang X L, Liu G C, Zhang J X, et al. *Dalton Trans.*, **2009**: 7347-7349
- [16] Steck E A, Day A R. *J. Am. Chem. Soc.*, **1943**,**65**:452-456
- [17] Sheldrick G M. *SHELXS-97, Program for the Solution of Crystal Structure*, University of Göttingen, **1997**.
- [18] Sheldrick G M. *SHELXS-97, Program for the Refinement of Crystal Structure*, University of Göttingen, **1997**.
- [19] Zhang X M, Wu H S, Chen X M, et al. *Eur. J. Inorg. Chem.*, **2003**:2959-2964
- [20] XU Zhan-Lin(徐占林), LI Xiu-Yin(李秀颖), CHE Guang-Bo(车广波), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2008**,**24**:1721-1724
- [21] Chen Y H, Gu X J, Peng J, et al. *J. Mol. Struct.*, **2004**,**692**: 243-247
- [22] Sun C Y, Jin L P. *Polyhedron*, **2006**,**25**:1327-1332
- [23] Yang J, Li G D, Gao J J, et al. *Chem. Eur. J.*, **2007**,**13**:3248-3261