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两个由醋酸根和含吡啶基配体构筑的 Zn(Ⅱ) 配聚物的合成、晶体结构及其荧光性质

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摘要:以醋酸锌、异烟肼(INH)、2-氨基吡啶(2-APy)为原料在 *N*,*N*-二甲基甲酰胺(DMF)溶液中合成了 2 个 Zn(Ⅱ)配位聚合物 $[Zn(CH_3COO)_2(INH)]_n$ (**1**),$[Zn(CH_3COO)_2(2\text{-}APy)]_n$ (**2**),用红外光谱、元素分析、粉末 X 射线衍射、X 射线单晶衍射对配合物进行了表征。晶体结构测试表明,配聚物 **1** 属单斜晶系,空间群 $P2_1/c$,晶胞参数:a=0.914 44(17) nm,b=0.161 86(3) nm,c=0.871 75(16) nm,β=96.181(3)°,V=1.282 8(4) nm^3,Z=4;配聚物为 2D 层状结构,该层状结构通过氢键弱相互作用,进一步形成 3D 超分子结构。配聚物 **2** 属三斜晶系,空间群 $P\bar{1}$,晶胞参数:a=0.747 0(4) nm,b=0.814 5(5) nm,c=1.895 7(11) nm,α=88.276(8)°,β=86.202(8)°,γ=84.334(8)°,V=1.144 9(11) nm^3,Z=2;配聚物 **2** 为一维 zig-zag 链状结构。室温固态荧光测试显示,配聚物 **1**、**2** 分别在最大波长 382.6 和 367.5 nm 处具有较强的荧光发射。

关键词:锌;配位聚合物;晶体结构;荧光性质
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Syntheses, Structures and Luminescent Properties of Two Zinc(Ⅱ) Coordination Polymers Constructed by Acetate and Pyridyl-Containing Ligands

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Abstract: Two coordination polymers, $[Zn(CH_3COO)_2(INH)]_n$ (INH=isonicotinic acid hydrazid; isoniazid) (**1**) and $[Zn(CH_3COO)_2(2\text{-}APy)]_n$ (2-APy=2-aminopyridine) (**2**) have been synthesized in DMF solution and structurally characterized by elemental analysis, IR spectra, single-crystal and powder X-ray diffractions. Structural analyses reveal that polymer **1** exhibits a 2-dimensional (2D) infinite layer framework, and the resulting 2D structure is interconnected by hydrogen-bond interactions to lead to a 3D supramolecular architecture. It crystallizes in the monoclinic system, space group $P2_1/c$, with cell parameters a=0.914 44(17) nm, b=0.161 86(3) nm, c=0.871 75(16) nm, β=96.181(3)°, V=1.282 8(4) nm^3, Z=4. Polymer **2** is an infinite 1D zig-zag chain. Polymer **2** crystallizes in the triclinic system, space group $P\bar{1}$, with cell parameters a=0.747 0(4) nm, b=0.814 5(5) nm, c=1.895 7(11) nm, α=88.276(8)°, β=86.202(8)°, γ=84.334(8)°, V=1.144 9(11) nm^3, Z=2. The solid-state luminescent properties of two polymers have also been investigated at room temperature. CCDC: 870030, **1**; CCDC: 1524913, **2**.

Keywords: zinc; coordination polymer; crystal structure; luminescent property

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0 Introduction

In recent years, coordination polymers have increasingly attracted considerable attention for their structural and topological diversities as well as their potential applications in the fields including luminescence[1-7], gas storage/separation[8-10], magnetic properties[11], catalysis[12-13], drug delivery[14] and precursors for nanoparticles[15], *etc*. The assembly of coordination polymers can be influenced by some external factors, such as temperature, solvent, reactant concentration, and pH value, etc., and some internal factors, such as coordination geometries of the central metals, configurations, and nature of the organic ligands[16-17]. Among these factors, the choice of the organic ligands is the greatest influence in determining the type and topology of the product. Properties of organic ligands, such as solubility, coordination activity, length, geometry, and relative orientation of the donor groups, play a very important role in dictating polymer framework topology[17]. So, it is very important to design the organic ligands or regulate the synthesis conditions. To realize the infinite extension of structure, organic ligands with two or more coordination atoms, such as N, O, and S atoms, are often employed[5,18]. Therefore, most coordination polymers are constructed from metal ions and carboxylic acid- or nitrogen-containing ligands. Lewis base coordinated zinc(Ⅱ) carboxylate polymers are an important class of coordination polymers, which have been known for many years[19-21]. The spherical d^{10} configuration of the Zn(Ⅱ) cation has associated with it a highly flexible coordination sphere which allows it to adopt multiple geometries to suit the demands of its environment. As a result, Zn is an ideal metal for use in constructing extended coordination networks with ligands that can bridge the metal centers in one or multiple directions. On the other hand, the properties and structures of such materials are easily variable with changes in the counterion present. Anionic carboxylates are highly flexible and versatile O-donor ligands in that a range of substituents may be introduced on the carbonyl carbon to modulate its reactivity and coordination propensity to result in a variety of coordination modes such as monodentate, chelating, bidentate bridging, monoatomic bridging, and chelating bridging[4]. Moreover, the choice of the organic ligands is the greatest influence in determining the type and topology of the product. So, the properties and structures of such materials are easily variable with changes in ligand ratio, ligand type and the counterion present. Pyridyl-containing ligand, such as INH or 2-APy, being an interesting N-type of heterocyclic system, has attracted much attention of many researchers[21-23]. In earlier efforts, we have used INH ligand with Cu(I) ions to form metal-organic coordination polymers[22-23]. As part of our ongoing research in this area, we herein report the synthesis, structures and luminescent properties of two Zinc(Ⅱ) coordination polymers constructed by acetate and pyridyl-containing ligands: $[Zn(CH_3COO)_2(INH)]_n$ (**1**) and $[Zn(CH_3COO)_2(2\text{-APy})]_n$ (**2**).

1 Experimental

1.1 Materials and measurements

INH (Isonicotinic acid hydrazide; Isoniazid) and 2-APy (2-Aminopyridine) were purchased from Alfa Aesar, UK. All solvents and other chemicals were purchased and use received. Element analyses were performed on a Perkin-Elmer 2400LS elemental analyzer. Powder X-ray diffraction (PXRD) patterns were measured on an ARL/X′PRA powder diffractometer at 40 kV, 40 mA using a Cu $K\alpha$ radiation (λ=0.154 06 nm) in 2θ range of 5°~40°. IR spectra were measured in KBr pellets on a Nicolet AVATAR360 FT-IR spectrometer in the range of 4 000 ~400 cm^{-1}. Fluorescence spectra were recorded on a Perkin-Elmer LS55 spectrometer.

1.2 Synthesis of the polymer 1

$Zn(CH_3COO)_2\cdot 2H_2O$ (0.439 g, 2 mmol) was dissolved in 10 mL DMF solvent at room temperature. INH (0.274 g, 2 mmol) was added to this solution with stirring, during which time white precipitate formed. Then, NH_4SCN was added to the reaction mixture until the precipitate dissolved and a colorless solution formed. The colorless solution obtained was filtered and the filtrate was then transfered to two test tubes

and carefully layered by *i*-PrOH. Three weeks later, the products were collected and colorless block crystals of $[Zn(CH_3COO)_2(INH)]_n$ suitable for X-ray measurements were obtained. Anal. Calcd. for $C_{10}H_{13}N_3O_5Zn$ (%): C, 37.46; H, 4.09; N, 13.11. Found(%): C, 37.22; H, 4.20; N, 13.28. IR (KBr, cm^{-1}): 3 445(m), 3 308(m), 3 098(m), 3 004(m), 1 666(s), 1 620(s), 1 559(vs), 1 415(s), 1 349(m), 1 215(m), 1 090(m), 1 021(m), 693(s), 684(m).

1.3 Synthesis of the polymer 2

Compound **2** was synthesized by the same procedure as described for **1** except the addition of 2-APy (0.188 g, 2 mmol) instead of INH (0.274 g, 2 mmol). Colorless block crystals were obtained and collected in the same way as for compound **1**. Anal. Calcd for $C_{18}H_{24}N_4O_8Zn_2$(%): C, 38.94; H, 4.36; N, 10.09. Found(%): C, 38.62; H, 4.55; N, 10.21. IR (KBr, cm^{-1}): 3 432(s), 3 328(s), 3 312(s), 1 653(s), 1 614(s), 1 589(vs), 1 557(s), 1 501(m), 1 444(m), 1 396(s), 1 332(m), 1 058(m), 1 002(m), 950(m), 857(m), 768(m), 687(m), 607(m), 478(m), 437(m).

1.4 Powder X-ray diffraction

The phase purity of the as-synthesized compounds was confirmed by PXRD patterns, which are consistent with the simulated patterns using the Mercury program (version 1.4.2, Cambridge Crystallographic Data Centre, Cambridge, UK) from the single-crystal X-ray diffraction data. Fig.1 (**1** and **2**) show the PXRD patterns of as-synthesized compounds and the simulated patterns on the basis of single-crystal structures of **1** and **2**, respectively.

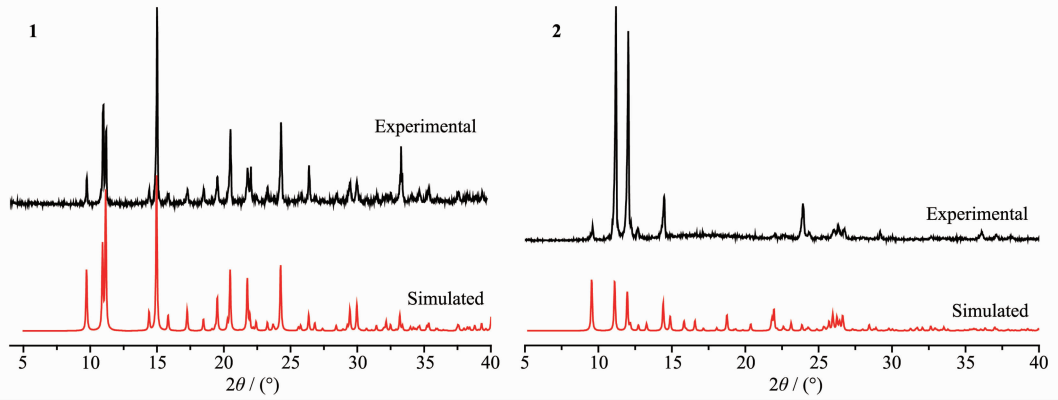


Fig.1　Experimental (upper trace) and simulated (lower trace) PXRD patterns of the polymers **1** and **2**

1.5 Determination of crystal structures

The X-ray diffraction measurement for the two compounds were performed on a Bruker Smart APEX Ⅱ CCD diffractometer equipped with a graphite monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) by using φ-ω scan mode at 296(2) K. The crystal parameters and experimental details of the data collection are summarized in Table 1. Semi-empirical absorption correction was applied to the intensity data using the SADABS program[24]. The structures were solved by direct methods of SHELXS-97 program and refined by full matrix least-square on F^2 using the SHELXTL-97 program[25-26]. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms.

CCDC: 870030, **1**; 1524913, **2**.

2 Results and discussion

2.1 Description of crystal structure

Single-crystal structure analysis reveals that the polymer **1** crystallizes in the monoclinic system, space group $P2_1/c$ with 4 asymmetric units in one unit cell, and exhibits a 2D layer network. The structure of the polymer **1** is depicted in Fig.2 (**1**) and Fig.3. Some selected bond lengths and bond angles are listed in Table 2. As depicted in Fig.2, the asymmetric unit contains two acetate anions, an INH ligand and one Zn(Ⅱ) ion. In the polymer **1**, zinc(Ⅱ) is coordinated by

Table 1 Crystallographic collection and refinement parameters for the title polymers

Polymer	1	2
Empiric formula	$C_{10}H_{13}N_3O_5Zn$	$C_{18}H_{24}N_4O_8Zn_2$
Formula weight	320.60	555.15
Color	Colorless	Colorless
Size / mm	0.20×0.22×0.26	0.20×0.22×0.26
Temperature / K	296(2)	296(2)
θ range for data collection / (°)	2.24~25.5	1.08~25.5
Wavelength / nm	0.071 073	0.071 073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a / nm	0.914 44(17)	0.747 0(4)
b / nm	1.618 6(3)	0.814 5(5)
c / nm	0.871 75(16)	1.895 7(11)
α / (°)		88.276(8)
β / (°)	96.181(3)	86.202(8)
γ / (°)		84.334(8)
V / nm^3	1.282 8(4)	1.144 8(11)
Z	4	2
D / (g·cm^{-3})	1.660	1.610
μ(Mo $K\alpha$) / mm^{-1}	1.935	2.145
F(000)	656	568
Limiting indices	$-11 \leqslant h \leqslant 10, -19 \leqslant k \leqslant 19, -9 \leqslant l \leqslant 10$	$-8 \leqslant h \leqslant 9, -9 \leqslant k \leqslant 9, -22 \leqslant l \leqslant 22$
Reflection collected, unique	7 380, 2 328 (R_{int}=0.062)	8 323, 4 159 (R_{int}=0.034)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data, restraints, parameters	2 328, 96, 174	4 159, 0, 293
GOF on F^2	1.02	1.00
R_1, wR_2[a] [$I>2\sigma(I)$]	R_1=0.050 3, wR_2=0.121 7	R_1=0.042 1, wR_2=0.080 3
R_1, wRa (all data)	R_1=0.080 5, wR_2=0.147 9	R_1=0.076 9, wR_2=0.091 9
Largest difference peak and hole / (e·nm^{-3})	719 and −510	542 and 334

[a] $w=1/[\sigma^2(F_o^2)+(0.079\ 0P)^2+0.348\ 2P]$ where $P=(F_o^2+2F_c^2)/3$, **1**; $w=1/[\sigma^2(F_o^2)+(0.035\ 4P)^2+0.504\ 7P]$ where $P=(F_o^2+2F_c^2)/3$, **2**.

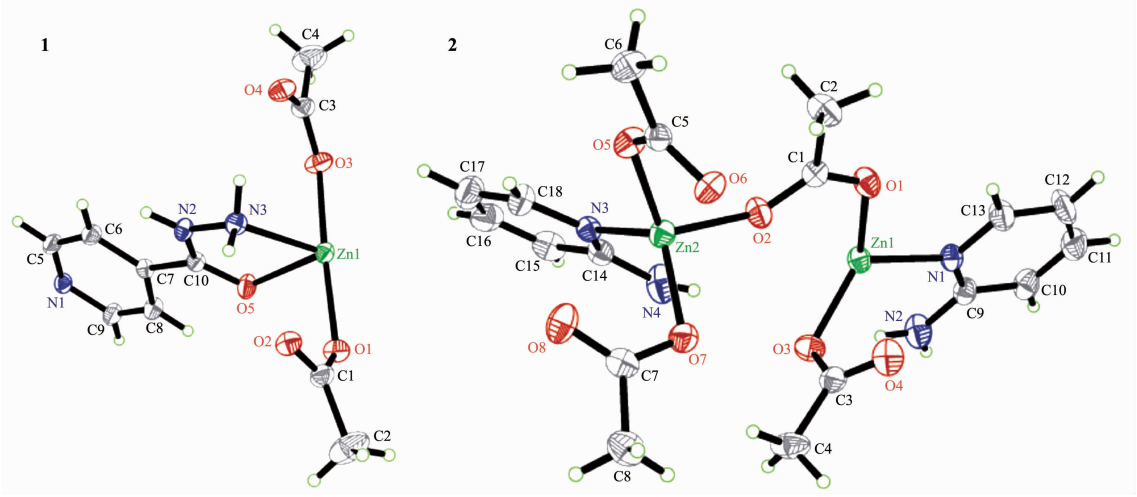


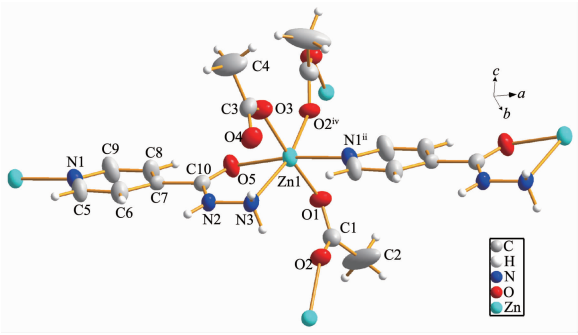
Fig.2 Asymmetric units of the title polymers and the labeling scheme used with 30% ellipsoidal probability

Table 2　Selected bond lengths (nm) and angles (°) for the polymers

Polymer **1**					
Zn(1)-O(1)	0.210 2(3)	Zn(1)-O(5)	0.218 0(4)	Zn(1)-N(1)^{ii}	0.215 1(5)
Zn(1)-O(3)	0.209 0(5)	Zn(1)-N(3)	0.215 9(4)	Zn(1)-O(2)^{iv}	0.206 9(4)
O(1)-Zn(1)-O(3)	173.16(16)	O(2)^{ii}-Zn(1)-O(3)	90.75(15)	Zn(1)^{iii}-O(2)-C(1)	143.9(3)
O(1)-Zn(1)-O(5)	86.91(13)	O(5)-Zn(1)-N(3)	75.47(15)	Zn(1)-O(3)-C(3)	134.7(4)
O(1)-Zn(1)-N(3)	100.82(16)	O(2)^{ii}-Zn(1)-O(5)	88.20(15)	Zn(1)-O(5)-C(10)	111.1(3)
O(1)-Zn(1)-N(1)^{ii}	86.69(16)	O(5)-Zn(1)-N(1)^{ii}	172.24(17)	Zn(1)^{i}-N(1)-C(5)	126.3(4)
O(1)-Zn(1)-O(2)iv	82.50(13)	N(1)^{ii}-Zn(1)-N(3)	101.47(17)	Zn(1)^{i}-N(1)-C(9)	115.8(4)
O(3)-Zn(1)-O(5)	91.75(15)	O(2)^{iv}-Zn(1)-N(3)	163.04(15)	Zn(1)-N(3)-N(2)	109.4(3)
O(3)-Zn(1)-N(3)	85.31(18)	O(2)^{iv}-Zn(1)-N(1)^{ii}	95.30(17)		
O(3)-Zn(1)-N(1)^{ii}	95.12(18)	Zn(1)-O(1)-C(1)	124.8(3)		
Polymer **2**					
Zn(1)-O(1)	0.197 0(3)	Zn(1)-O(6)^{i}	0.201 3(3)	Zn(2)-O(7)	0.195 5(3)
Zn(1)-O(3)	0.194 5(3)	Zn(2)-O(2)	0.200 9(3)	Zn(2)-N(8)	0.203 1(3)
Zn(1)-N(1)	0.202 4(4)	Zn(2)-O(5)	0.196 8(3)		
O(1)-Zn(1)-O(3)	124.32(13)	O(2)-Zn(2)-O(5)	109.89(13)	Zn(1)-O(1)-C(1)	118.8(3)
O(1)-Zn(1)-N(1)	103.58(13)	O(2)-Zn(2)-O(7)	99.58(13)	Zn(2)-O(2)-C(1)	140.7(3)
O(1)-Zn(1)-O(6)^{ii}	108.83(12)	O(2)-Zn(2)-N(3)	103.11(12)	Zn(2)-O(5)-C(5)	114.8(2)
O(3)-Zn(1)-N(1)	120.77(13)	O(5)-Zn(2)-O(7)	126.91(12)	Zn(2)-O(7)-C(7)	107.4(3)
O(3)-Zn(1)-O(6)^{ii}	97.59(12)	O(5)-Zn(2)-N(3)	100.83(12)		
O(6)^{i}-Zn(1)-N(1)	97.53(12)	O(7)-Zn(2)-N(3)	114.44(13)		

Symmetry codes: ^{i} −1+x, y, z; ^{ii} 1+x, y, z; ^{iii} x, 1/2−y, −1/2+z; ^{iv} x, 1/2−y, 1/2+z

four oxygen atoms from two bridging acetate groups, a non-bridge acetate group and a carbonyl group of INH ligand, a terminal hydrazide nitrogen atom and a pyridine nitrogen atom from two different INH ligands (Fig.3). The coordination geometry of zinc can be described as a distorted octahedral coordination geometry with Zn-N bond lengths ranging 0.215 1(5)~0.215 9(4) nm and Zn-O bond lengths ranging 0.206 9(4)~0.218 0(4) nm, which are comparable to the values in related zinc(Ⅱ) polymers[4,21]. In the polymer **1**, the Zn-N (pyridine nitrogen) bond length is 0.215 1(5) nm, which is similar to the Zn-N (from hydrazide) bond length (0.215 9(4) nm). Also, the Zn-O (from CH_3COO^-) bond lengths are 0.210 2(3), 0.209 0(5), and 0.206 9(4) nm, respectively, which are similar to each other. However, the Zn-O bond (from carbonyl group of INH) length is 0.218 0(4) nm, which is slightly longer. As shown in Fig.3, in the polymer **1**, one INH molecule is coordinated to a metal center by an oxygen atom of carbonyl group and a terminal nitrogen atom of the hydrazide, thereby forming a five-membered ring (Zn(1)-O(5)-C(10)-N(2)-N(3)). The pyridine nitrogen of this INH is coordinated to the other metal center. For the polymer **1**, the bond angles of O-Zn-N and O-Zn-O (three atoms in the axial direction) are within 163.04(15)° (O(2)^{iv}-Zn(1)-N(3)) 173.16(16)° (O(1)-Zn(1)-O(3)), which are decreased compared to the bond

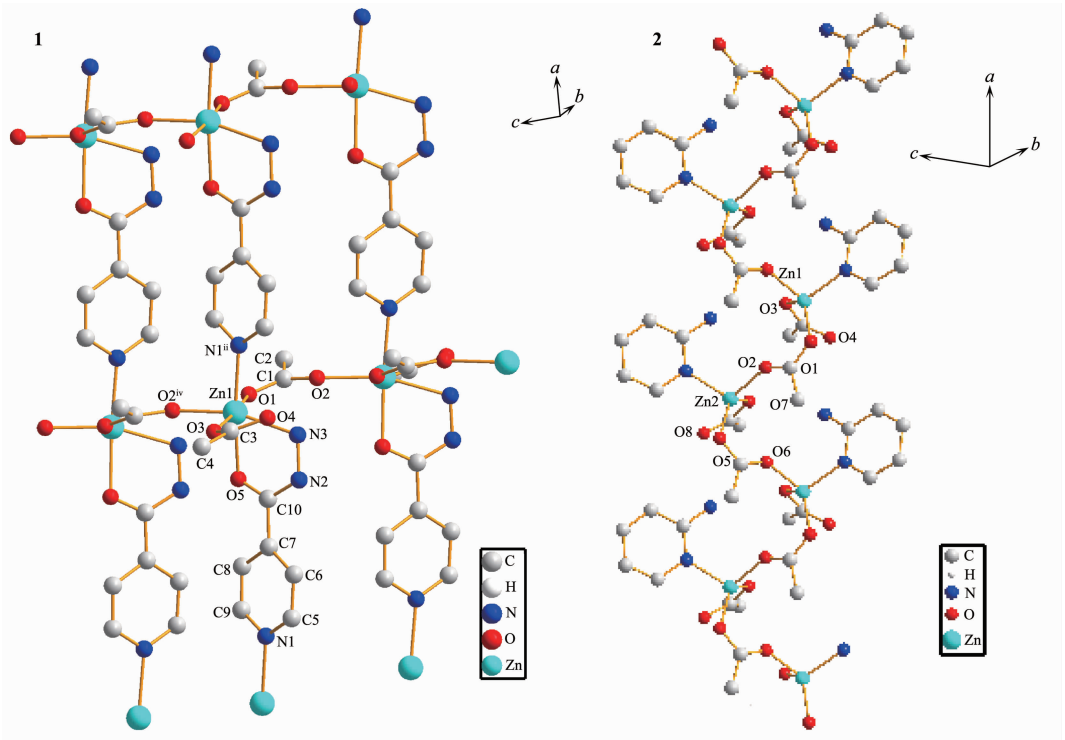


Symmetry codes: ^{ii} 1+x, y, z; ^{iv} x, 1/2−y, 1/2+z

Fig.3　Coordination environment of Zn(Ⅱ) atom in the polymer **1** with the ellipsoids drawn

angle of 180° for an ideal octahedron. Additionally, the bond angles of the *cis* O-Zn-N and O-Zn-O are within 75.47(15)° (O(5)-Zn(1)-N(3)) 101.47(17)° (N(1)^{ii}-Zn(1)-N(3)), which are different from the bond angle of 90° for an ideal octahedron. These are in accordance with the distorted octahedron configuration. The deviation can be explained by steric effects because the INH acts as a bridge between Zn(Ⅱ) centers and the approximation of the metal centers is accompanied by a geometric distortion in the INH molecule[21]. In the polymer **1**, there are two different types of CH_3COO^- groups, which are bridging (bidentate bridging) and non-bridging (monodentate) CH_3COO^- ligands. Two adjacent Zn(Ⅱ) atoms are bridged by a CH_3COO^- ligand, forming a 1D chain. The nonbonded Zn⋯Zn separation within the 1D chain is 0.504 67 (11) nm. These 1D chains extend in the *c* direction. The INH molecules act as bridges to link the Zn(Ⅱ) atoms (Zn⋯Zn separation is 0.914 44(19) nm) of two neighboring 1D chains, which further construct a layer network (Fig.4 (**1**)).

The polymer **2** crystallizes in the triclinic system, space group $P\bar{1}$ with 2 asymmetric units in one unit cell, and exhibits a 1D zig-zag chain. The structure of the polymer **2** is depicted in Fig.2. Some selected bond lengths and bond angles are listed in Table 2. As depicted in Fig.2, the asymmetric unit contains four acetate anions, two 2-APy ligands and two Zn(Ⅱ) ions. In the polymer **2**, the Zn(Ⅱ) (2) is tetrahedrally surrounded by N(3) of 2-APy, O(7) of the monodentate acetate, O(2), O(5) of the two *syn-anti* bridging acetate. The Zn(Ⅱ) (1) is also tetrahedrally surrounded by N(1) of 2-APy, O(3) of the monodentate acetate, O(1) of the *syn-anti* bridging acetate and another O of the *syn-anti* bridging acetate from the next repeating unit of the polymer. In the polymer **2**, the coordination geometry of zinc can be described as a distorted tetrahedral coordination geometry with Zn-N bond lengths ranging 0.202 4(3)~0.203 1(3) nm and Zn-O bond lengths ranging 0.194 5(3)~0.201 3(3) nm, which are comparable to the values in related zinc(Ⅱ) polymers[4]. However, the Zn-N bond lengths and the Zn-O bond lengths are slightly longer than those of the polymer **1**. The nonbonded Zn ⋯ Zn separations within the repeating unit and between the repeating units are 0.477 32(20) and 0.461 17(19) nm, and these distances

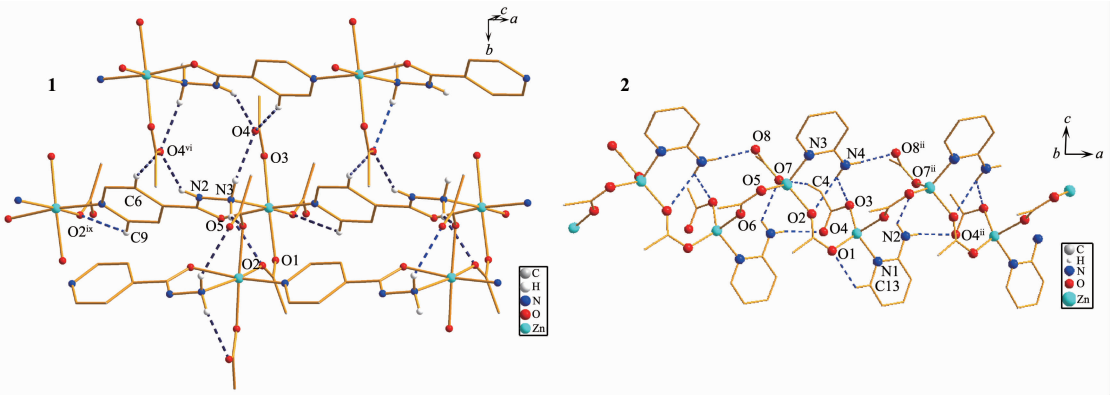


Hydrogen atoms are omitted for clarity; Symmetry codes: ^{ii} 1+*x*, *y*, *z*; ^{iv} *x*, 1/2−*y*, 1/2+*z*

Fig.4 Single 2D coordination sheet for **1** and an 1D zig-zag chain for **2**

are longer than those of the related reported (0.441 5(1) nm)[4]. Another, in the polymer **2**, the 2-APy is situated on the opposite side of the growing polymer and thus renders a syndiotactic stereo chemistry, as shown in Fig.4. This structure arise can due to the steric and basic properties of Lewis bases.

Significant hydrogen-bond parameters observed in the polymer **1** and **2** are listed in Table 3. In the crystal lattice of the polymer **1**, there exist some week intermolecular and intramolecular interactions, including non-classic C–H⋯O hydrogen bond. All of the N-terminals are involved in weak hydrogen bonds. The non-bridging CH_3COO^- ligands are involved in hydrogen bonding, with the hydrazide groups and pyridine ring of neighboring layers, thereby forming a 3D supramolecular arrangement. The bridging CH_3COO^- ligands are only involved in hydrogen bonding with the N-terminals of the same layer (Fig.5 (**1**)). These week interactions help to stabilize the crystal structure. Also, the polymer **2** is stabilized by some week intermolecular and intramolecular interactions in the crystal lattice (Fig.5 (**2**)). In the crystal lattice of the polymer **2**, including intramolecular H-bonding interactions (N(4)–H(4A)⋯O(2), N(4)–H(4A)⋯O(3), non-classic C–H⋯O) and intermolecular interactions (N(2)–H(2A)⋯O(7)^{ii}, N(2)–H(2B)⋯O(4)^{ii}, N(4)–H(4B)⋯



Only hydrogen atoms involved in the hydrogen bonds are shown; Symmetry codes: ^{vi} 1–x, –y, –z; ^{ix} –1+x, 1/2–y, 1/2+z for **1**; ^{ii} 1+x, y, z for **2**

Fig.5　Selected hydrogen bonds for the polymers shown in dashed line

Table 3　Hydrogen bond parameters for polymers 1 and 2

D–H⋯A / nm	*d*(D-H) / nm	*d*(H⋯A) / nm	*d*(D⋯A) / nm	∠DHA / (°)
Polymer **1**				
N(2)–H(2)⋯O(4)^{vi}	0.086 00	0.197 00	0.273 1(6)	148.00
N(3)–H(3A)⋯O(2)	0.090 00	0.229 00	0.297 7(6)	133.00
N(3)–H(3A)⋯O(1)^{iii}	0.090 00	0.229 00	0.297 7(6)	133.00
N(3)–H(3B)⋯O(4)	0.090 00	0.214 00	0.288 5(6)	139.00
C(6)–H(6)⋯O(4)^{vi}	0.093 00	0.240 00	0.329 5(7)	161.00
C(9)–H(9)⋯O(2)^{ix}	0.093 00	0.259 00	0.315 8(7)	120.00
Polymer **2**				
N(2)–H(2A)⋯O(7)^{ii}	0.086 00	0.251 00	0.307 3(5)	124.00
N(2)–H(2B)⋯O(4)^{ii}	0.086 00	0.221 00	0.302 6(5)	159.00
N(4)–H(4B)⋯O(8)^{ii}	0.086 00	0.208 00	0.293 8(5)	174.00
N(4)–H(4A)⋯O(2)	0.086 00	0.243 00	0.310 6(5)	135.00
N(4)–H(4A)⋯O(3)	0.086 00	0.248 00	0.310 1(6)	129.00
C(4)–H(4E)⋯O(7)	0.096 00	0.247 00	0.335 2(6)	153.00
C(13)–H(13)⋯O(1)	0.093 00	0.257 00	0.317 8(6)	123.00

Symmetry codes: ^{iii} x, 1/2–y, –1/2+z; ^{vi} 1–x, –y, –z; ^{ix} –1+x, 1/2–y, 1/2+z for **1**; ^{ii} 1+x, y, z for **2**

O(8)^{ii}). These interactions exist in the zig-zag chain. The parameters of the H-bonds are listed in Table 3.

2.2 Luminescent properties

Inorganic-organic hybrid coordination polymers, constructed with d^{10} metal centers and conjugated organic linkers, have received remarkable attention in view of various potential applications, such as in chemical sensors, photochemistry, and so on[5,27-30]. The fluorescence properties of the polymer **1** and **2**, as well as free ligands INH and 2-APy, have been investigated in the solid state at room temperature, as depicted in Fig.6. Upon excitation at 211 nm, both the microcrystalline free ligand INH and the polymer **1** samples show broad emission bands with the maximum peaks at 369.5 nm for INH, 382.6 nm for the polymer **1**, respectively (Fig.6 (**1**)). As shown in Fig.6, coordination of the INH ligand with Zn (Ⅱ) results in a 13.1 nm red shift of the emission maximum. The emission spectra have broad peaks with maxima at 367.5 nm for polymer **2**, and 396.5 nm for 2-APy (λ_{ex}=250 nm), respectively. Coordination of the free ligand 2-APy with Zn(Ⅱ) results in a 29.0 nm blue shift of the emission maximum. These emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature, since the Zn^{2+} ions are difficult to oxidize or to reduce due to their d^{10} configuration. The emissions of polymers **1**, **2** may be a mixture of characters of intra-ligand and ligand-to-ligand charge transition (LLCT). And the observed red or blue shift of the emission maximum between the polymers and the ligands is considered to mainly originate from the influence of the coordination of the ligand to metal atom[27-30]. The results indicate that these polymers may be potential candidates of fluorescent materials.

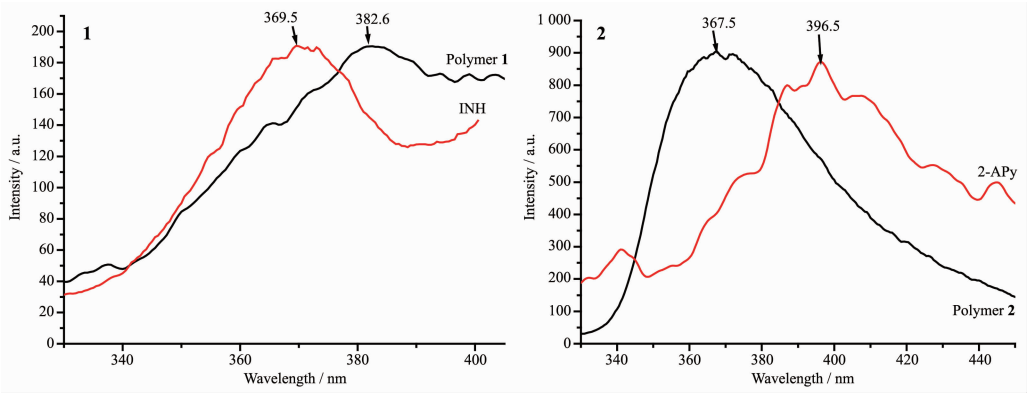


Fig.6 Solid-state emission spectra of the polymers and the free ligands

3 Conclusions

Two zinc (Ⅱ) coordination polymers constructed by acetate and pyridyl-containing ligands have been successfully synthesized and structurally characterized. Polymer **1** is a 2D infinite layer framework, and the resulting 2D structure is interconnected by hydrogen-bond interactions to lead to a 3D supramolecular architecture. Polymer **2** is an infinite one-dimensional (1D) zig-zag chain. The results of our present research, together with those in the previous study[21-23], demonstrate that the structural diversity in composition and dimensionality of the coordination compounds can be achieved by the adjustments of ligands, metal centers and/or coordinated anions. In addition, the photoluminescence investigation shows that two coordination polymers appear potentially applied as luminescent materials.

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