



# Syntheses, Crystal Structures and NBO Calculation of Two New Zinc(II) Coordination Polymers

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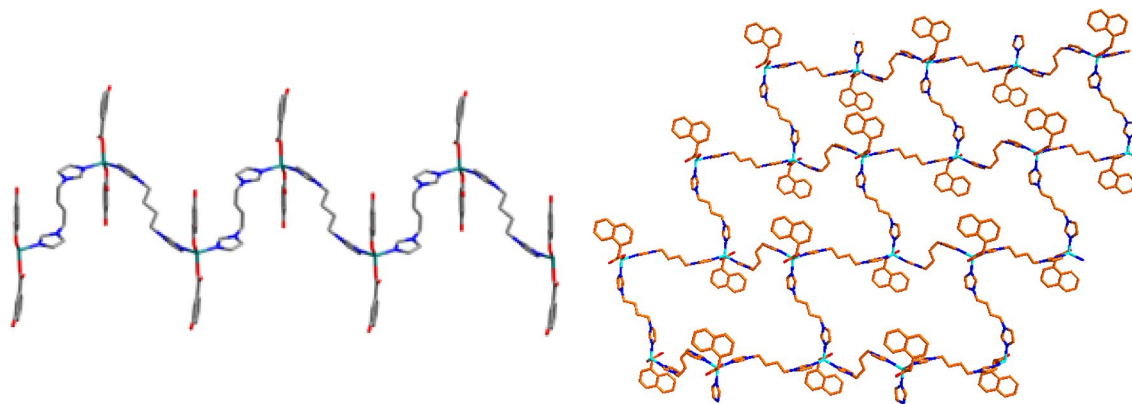
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## Abstract

Two new Zn(II) coordination polymers based on bis(imidazol), namely,  $[\text{Zn}(\text{hba})_2(\text{bib})]_n$  (**1**) and  $[\text{Zn}(\text{NAA})(\text{bib})_{1.5}]_n \cdot n\text{NO}_3^- \cdot 3n\text{H}_2\text{O}$  (**2**) (Hhba = 3-hydroxybenzoic acid, HNAA = 1-naphthyl acetic acid, bib = 1,4-bis(imidazol-1-yl)-butane) have been successfully synthesized under hydrothermal conditions. Their structures have been determined by single crystal X-ray diffraction analyses, elemental analyses, IR, TG and fluorescence spectrums. Complex **1** shows a one-dimensional *zigzag* chain structure. Complex **2** exhibits two-dimensional network structure. The intermolecular hydrogen bonding and  $\pi$ - $\pi$  stacking interactions extend the complexes **1** and **2** into supramolecular architectures and play an important role in stabilizing complexes **1** and **2**. Furthermore, complex **1** exhibits intense blue luminescence and appears to be a good candidate for novel hybrid inorganic–organic photoactive materials, while no photoluminescent response was observed for complex **2**. In addition, we analyzed the Natural Bond Orbitals (NBO) of **1** and **2** using the PBE0/LANL2DZ method in the Gaussian 09 Program. The calculations showed the obvious covalent interaction between the coordinated atoms and Zn(II) ion.

## Graphic Abstract

Two new Zn(II) coordination polymers based on bis(imidazol), namely,  $[\text{Zn}(\text{hba})_2(\text{bib})]_n$  (**1**) and  $[\text{Zn}(\text{NAA})(\text{bib})_{1.5}]_n \cdot n\text{NO}_3^- \cdot 3n\text{H}_2\text{O}$  (**2**) have been successfully synthesized under hydrothermal conditions. Their structures have been determined by single crystal X-ray diffraction analyses, elemental analyses, IR, TG and fluorescence spectrum. Complex **1** shows a one-dimensional *zigzag* chain structure. Complex **2** exhibits two-dimensional network structure. The intermolecular hydrogen bonding and  $\pi$ - $\pi$  stacking interactions extend the complex **1** and **2** into supramolecular architectures and play an important role in stabilizing complex **1** and **2**. In addition, we analyzed Natural Bond Orbital (NBO) of **1** and **2** in using the PBE0/LANL2DZ method built in Gaussian 09 Program. The calculation results showed the obvious covalent interaction between the coordinated atoms and Zn(II) ion.



**Keywords** Hydrothermal synthesis · Crystal structure · Zn(II) complex · Natural bond orbital · Luminescent property

## Introduction

The design and synthesis of metal–organic coordination polymers relies on the selection of ligands and metal ions and has become a very attractive research field. This is motivated not only by the intriguing structural diversity but also by the demand of applying functional materials into the fields of catalysis, porosity, magnetism, luminescence and nonlinear optics [1–3]. In general, grids with various sizes and shapes can be synthesized by choosing suitable single metal ions and organic ligands such as carboxylates and N-donor groups [4–6]. Self-assembly is a complex process, highly influenced by many factors, such as the coordination geometry of metal ions, the nature of organic ligands, solvent system, temperature, pH value of the solution, the ratio between metal salt and ligand, the templates and the counter anions [7–14].

These factors have been well-studied, but there are other forces such as hydrogen-bonding,  $\pi$ – $\pi$  interactions, metal–metal interactions that can greatly influence the supramolecular topology and its dimensionality [15–17]. These considerations made us investigate new coordination structures with 3-hydroxybenzoic acid (Hhba), 1-naphthyl acetic acid (HNAA) and bridging ligands (bib). In this manuscript, we report the syntheses, crystal structures, IR, fluorescence, and TG properties of two new complexes,  $[\text{Zn}(\text{hba})_2(\text{bib})]_n$  (**1**) and  $[\text{Zn}(\text{NAA})(\text{bib})_{1.5}]_n \cdot n\text{NO}_3^- \cdot 3n\text{H}_2\text{O}$  (**2**). Complex **1** exhibits intense blue luminescence and appears to be good candidate for novel hybrid inorganic–organic photoactive materials, while no photoluminescent response was observed for complex **2**. We also analyzed the Natural Bond Orbitals (NBO) using the PBE0/LANL2DZ method in the Gaussian 09 Program.

## Experimental Section

### General Procedures

All solvents and chemicals were commercial reagents and used without further purification. Elemental analyses (carbon, hydrogen, and nitrogen) were performed with a Vario EL(III) Elemental Analyzer. IR spectra ( $4000$ – $400$   $\text{cm}^{-1}$ ) were measured from KBr pellet on a Nicolet 6700 FT-IR spectrometer. TG studies were carried on a STA7300 analyzer under nitrogen at a heating rate of  $10$   $^\circ\text{C min}^{-1}$ . The fluorescent studies were carried out on a computer-controlled JY Fluoro-Max-3 spectrometer at room temperature. The crystal structure was determined using a Bruker D8 QUEST CMOS diffractometer. Power X-ray diffraction (PXRD) patterns were obtained on Bruker D8 Advance

X-ray diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.54056$   $\text{\AA}$ ) at room temperature.

### Syntheses

#### $[\text{Zn}(\text{hba})_2(\text{bib})]_n$ (**1**)

A mixture of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.044 g, 0.2 mmol), Hhba (0.014 g, 0.1 mmol), bib (0.019 g, 0.1 mmol) and 10 mL  $\text{H}_2\text{O}$  was stirred for 15 min at room temperature, then sealed in a 20 mL Teflon-lined stainless steel vessel, and heated to  $110$   $^\circ\text{C}$  for 5 days, followed by slow cooling (a descent rate of  $5$   $^\circ\text{C h}^{-1}$ ) to room temperature. Colorless prism-shaped crystals were obtained. Yield of 26% (based on bib). Anal. Calcd. For  $\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_6\text{Zn}$ : C, 54.61; H, 4.20; N, 10.61. Found C, 54.03; H, 3.94; N, 10.08. IR ( $\text{cm}^{-1}$ ): 3274(w), 1630(w), 1576(s), 1450(m), 1387(m), 1230(m), 1216(w), 1081(m), 936(w), 892(w), 785(w), 713(w), 641(w), 462(w).

#### $[\text{Zn}(\text{NAA})(\text{bib})_{1.5}]_n \cdot n\text{NO}_3^- \cdot 3n\text{H}_2\text{O}$ (**2**)

A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.029 g, 0.1 mmol), HNAA (0.019 g, 0.1 mmol), bib (0.019 g, 0.1 mmol),  $\text{C}_2\text{H}_5\text{OH}$  (5 mL) and 5 mL  $\text{H}_2\text{O}$  was stirred for 15 min at room temperature, then sealed in a 20 mL Teflon-lined stainless steel vessel, and heated to  $120$   $^\circ\text{C}$  for 5 days, followed by slow cooling (a descent rate of  $5$   $^\circ\text{C h}^{-1}$ ) to room temperature. Colorless prism-shaped crystals were obtained. Yield of 27% (based on Zn). Anal. Calcd. For  $\text{C}_{27}\text{H}_{36}\text{N}_7\text{O}_8\text{Zn}$ : C, 49.74; H, 5.57; N, 15.04. Found C, 49.01; H, 5.23; N, 14.67. IR ( $\text{cm}^{-1}$ ): 3423(w), 3127(w), 1586(m), 1528(m), 1390(s), 1231(m), 1094(s), 949(w), 797(w), 659(w).

### Structure Determinations

The X-ray diffraction data collection was performed on two single crystals with the dimensions of  $0.14 \times 0.11 \times 0.08$   $\text{mm}^3$  for **1** and  $0.15 \times 0.13 \times 0.09$   $\text{mm}^3$  for **2** respectively, were collected at 293(2) K on a Bruker D8 QUEST CMOS diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.71073$   $\text{\AA}$ ). The structures were solved by direct method and refined by full-matrix least-squares on  $F^2$  using the SHELXL-97 program [18, 19]. The non-hydrogen atoms of the complexes were refined with anisotropic temperature parameters. The hydrogen atoms were positioned geometrically and refined using a riding model. Crystallographic parameters and the data collection statistics for structures **1** and **2** are shown in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bond parameters of **1** and **2** are listed in Table 3. Further crystallographic parameters have been deposited with the Cambridge Crystallographic Data Centre (no. 1535330 (**1**), 1567036 (**2**); deposit@ccdc.cam.ac.uk or [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)).

**Table 1** Crystallographic parameters and summary of data collection for **1** and **2**

Parameter	Complex <b>1</b>	Complex <b>2</b>
Empirical formula	C <sub>24</sub> H <sub>22</sub> N <sub>4</sub> O <sub>6</sub> Zn	C <sub>27</sub> H <sub>36</sub> N <sub>7</sub> O <sub>8</sub> Zn
Fw (g mol <sup>-1</sup> )	527.83	652.00
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/n	P-1
<i>a</i> (Å)	11.6540(16)	8.2730(7)
<i>b</i> (Å)	10.6204(15)	12.1149(11)
<i>c</i> (Å)	19.092(3)	15.8143(13)
$\alpha$ (°)	90.00	107.7310(10)
$\beta$ (°)	93.783(2)	92.0640(10)
$\gamma$ (°)	90.00	90.0410(10)
Volume (Å <sup>3</sup> )	2357.9(6)	1508.6(2)
<i>Z</i>	4	2
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.487	1.435
GOF	1.027	1.056
Reflns collected/unique	4649/3836	5761/5128
<i>R<sub>int</sub></i>	0.0206	0.0120
<i>R</i> [I > 2σ(I)]	0.0345	0.0411

## Results and Discussion

### Structure Description

Complex **1** exhibits a one-dimensional *zigzag* chain structure. The asymmetric unit of **1** contains one

crystallographically unique Zn(II) ion, two hba ligands and one bib molecule. As shown in Fig. 1, the Zn(1) ion is four-coordinated and displays a distorted tetrahedral {ZnN<sub>2</sub>O<sub>2</sub>} geometry completed by two carboxylate oxygen atoms from two different hba ligands and two nitrogen donors from two flexible bib molecules. The Zn–O bond distances are in the range of 1.9384(18)–1.9432(18) Å, and those of Zn–N are between 1.999(2) and 2.012(2) Å. The N(O)–Zn–O(N) angles fall in the 101.80(9)°–119.27(8)° range.

It is interesting to note that the deprotonated carboxylates of the hba anion coordinate Zn(II) in a monodentate bridging mode and the bib ligands feature a *trans*-conformation bridging mode with a dihedral angle between the two imidazole rings of 0°. The bib ligands link adjacent Zn(II) ions to generate a 1D *zigzag* chain structure with a Zn···Zn distance of 12.218 and 13.478 Å (Fig. 2). These neighboring chains are linked via C–H···O hydrogen bonding interactions (between C atoms of hba, bib ligands and carboxyl O, nitro O atoms), forming a 2D network structure (Fig. 3). In addition,  $\pi$ – $\pi$  interactions are observed between the imidazole rings of bib ligands. The centroid-to-centroid distance between adjacent rings is 3.6246(17) Å for N1, C15, N2, C17, C16 and N3, C20, N4, C22, C21 (symmetry codes: 1/2–*x*, –1/2+*y*, 1/2–*z*) imidazole rings. The plane-to-plane distance is 3.5355(12) Å for N1, C15, N2, C17, C16 and N3, C20, N4, C22, C21 (symmetry codes: 1/2–*x*, –1/2+*y*, 1/2–*z*) imidazole rings. Thus, through C–H···O hydrogen bonding and  $\pi$ – $\pi$  interactions, a 3D supramolecular architecture is achieved.

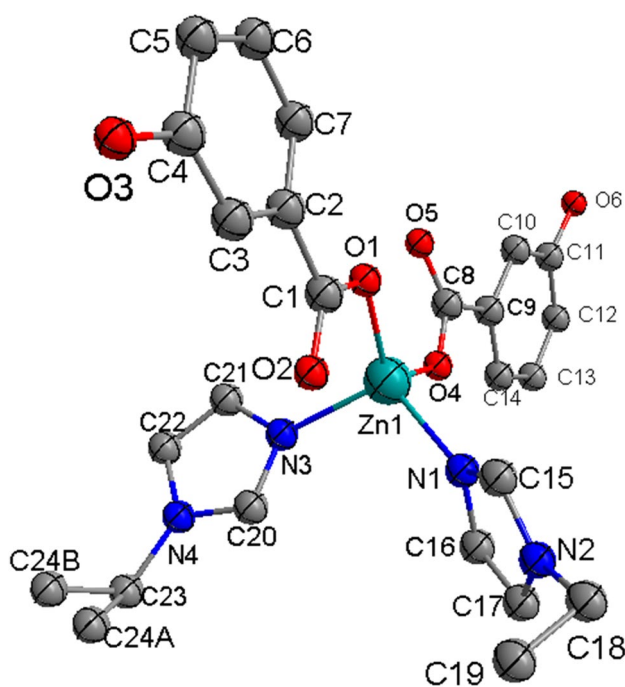
**Table 2** Selected bond lengths (Å) and bond angles (°) for **1** and **2**

<b>1</b>			
Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Zn(1)–O(1)	1.9432(18)	Zn(1)–O(4)	1.9384(18)
Zn(1)–N(1)	1.999(2)	Zn(1)–N(3)	2.012(2)
Angle	$\omega$ , °	Angle	$\omega$ , °
O(4)–Zn(1)–O(1)	119.27(8)	O(4)–Zn(1)–N(1)	101.80(9)
O(1)–Zn(1)–N(1)	114.21(8)	O(4)–Zn(1)–N(3)	103.10(9)
O(1)–Zn(1)–N(3)	109.81(8)	N(1)–Zn(1)–N(3)	107.50(8)
<b>2</b>			
Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Zn(1)–O(1)	1.9518(19)	Zn(1)–N(1)	1.993(2)
Zn(1)–N(3)	1.999(2)	Zn(1)–N(5)	2.037(2)
Angle	$\omega$ , °	Angle	$\omega$ , °
O(1)–Zn(1)–N(1)	117.64(9)	O(1)–Zn(1)–N(3)	117.64(9)
N(1)–Zn(1)–N(3)	109.06(9)	O(1)–Zn(1)–N(5)	97.87(9)
N(1)–Zn(1)–N(5)	103.36(9)	N(3)–Zn(1)–N(5)	109.34(9)

**Table 3** Hydrogen bonds for complexes **1** and **2**

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠DHA
<b>1</b>				
C(3)–H(3)...O(2)	0.93	2.45	2.761(3)	100
C(3)–H(3)...O(2) <sup>#1</sup>	0.93	2.59	3.281(3)	131
C(7)–H(7)...O(6) <sup>#2</sup>	0.93	2.56	3.480(3)	168
C(17)–H(17)...O(6) <sup>#3</sup>	0.93	2.51	3.372(4)	155
C(20)–H(20)...O(3) <sup>#1</sup>	0.93	2.54	3.198(3)	128
<b>2</b>				
O(1 W)–H(1 WC)...O(3)	0.85	2.38	3.040(6)	135
O(1W)–H(1WC)...O(5)	0.85	2.34	3.067(7)	143
O(3 W)–H(3WB)...O(3) <sup>#1</sup>	0.85	2.26	2.551(19)	100
C(13)–H(13)...O(3) <sup>#2</sup>	0.87(3)	2.60(4)	3.402(5)	155(3)
C(16)–H(16B)...O(2) <sup>#3</sup>	0.97	2.49	3.450(4)	169
C(18)–H(18)...O(1 W) <sup>#2</sup>	0.85(4)	2.51(4)	3.293(6)	153(3)
C(21)–H(21B)...O(5) <sup>#4</sup>	0.93(5)	2.52(5)	3.140(8)	124(4)

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



**Fig. 1** View of the asymmetric unit of the complex **1**. Hydrogen atoms are omitted for clarity

Complex **2** exhibits a two-dimensional network architecture. Its asymmetric unit consists of one Zn(II) ion, one NAA ligand, one and a half bib molecules, one counterion nitrate and three crystal water molecules. As depicted in Fig. 4, the four-coordinated Zn(II) ion displays a distorted tetrahedral  $\{ZnON_3\}$  geometry coordinating one carboxylate

oxygen atom from the NAA ligand and three nitrogen donors from three flexible bib molecules. The Zn–O distance is 1.9518(19) Å, the Zn–N distances are between 1.993(2) and 2.037(2) Å. In **2**, the NAA ligand features a monodentate bridging mode, while the bib ligands are in *trans*-conformation bridging mode with dihedral angles between the two imidazole rings of 0°. The bib ligands link neighboring Zn(II) ions to produce a 2D network architecture with seventy-two membered metalla-macrocycle (Fig. 5). The extended structure of complex **2** includes two kinds of O–H...O and C–H...O hydrogen bonding interactions between carboxylate oxygen atoms, coordinated water molecules and carbon atoms (Table 3). Moreover,  $\pi$ – $\pi$  interactions between benzene rings of the NAA ligands are observed. The centroid-to-centroid distances between adjacent rings is 3.690(2) Å for C3, C4, C5, C6, C7, C12 and C3', C4', C5', C6', C7', C12' ( $2-x, -y, 1-z$ ) benzene rings with the plane-to-plane distance of 3.4751(17) Å and 3.841(2) Å for C3, C4, C5, C6, C7, C12 and C7, C8, C9, C10, C11, C12 ( $2-x, -y, 1-z$ ) benzene rings with their plane-to-plane distance to be 3.4767(16) Å. Thus, through hydrogen bonds and  $\pi$ – $\pi$  interactions, the two-dimensional network is further expanded into a three-dimensional supramolecular architecture.

## IR Analysis of Complexes **1** and **2**

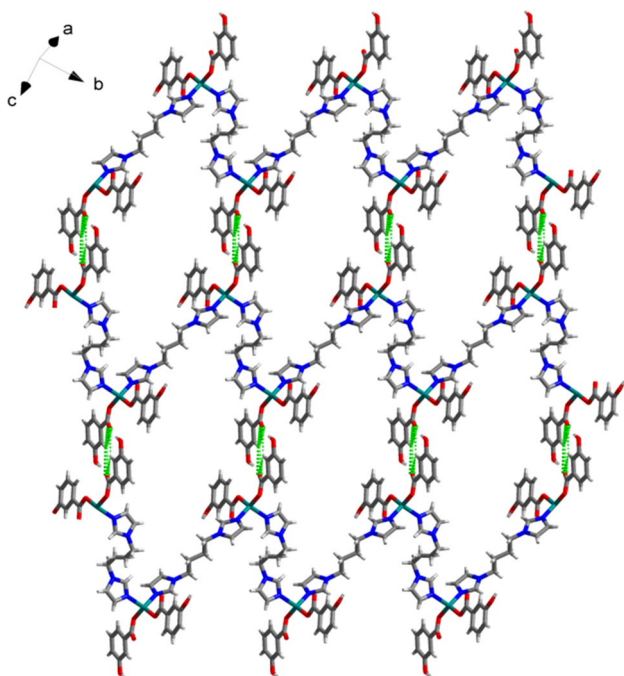
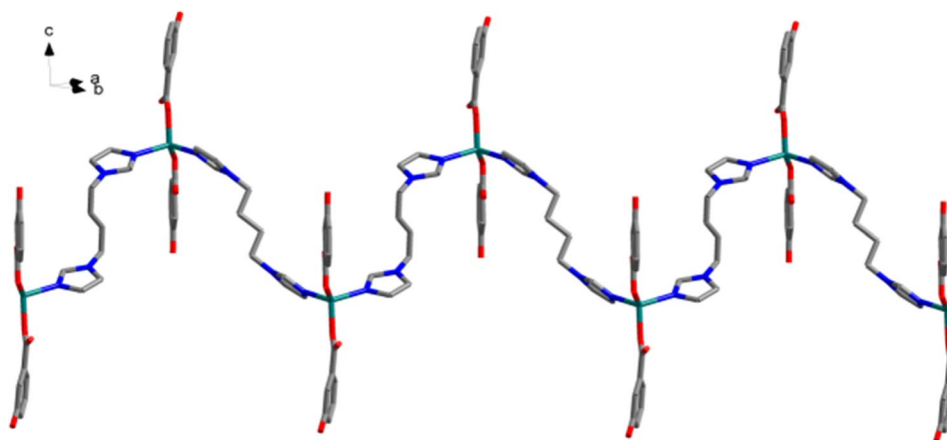
In **1**, the C–N absorption peaks of imidazole can be observed at 1230  $\text{cm}^{-1}$ . Asymmetric and symmetric  $\text{COO}^-$  stretching modes of the lattice hba anion were evidenced by very strong, slightly broadened bands at 1576 and 1387  $\text{cm}^{-1}$  [20], which is consistent with the results of X-ray analysis.

The IR spectrum of **2** shows a broad absorption band at 3423  $\text{cm}^{-1}$  corresponding to the H...O stretching of crystal water molecules in the complex. The C–N absorption peaks of imidazole can be observed at 1231  $\text{cm}^{-1}$ . Asymmetric and symmetric  $\text{COO}^-$  stretching modes of the lattice NAA anion were evidenced by very strong, slightly broadened bands at 1586 and 1390  $\text{cm}^{-1}$  [20], which is consistent with the results of X-ray analysis.

## Thermal Stability and Powder X-Ray Diffraction (PXRD)

To determine the thermal stability of complexes **1** and **2**, their thermal behaviors were investigated under a nitrogen atmosphere by thermogravimetric analysis (TG). As depicted in Fig. 6, the TG curve of **1** shows that the complex is stable up to 230 °C, and then decomposes upon further heating. The TG curve of **2** (Fig. 7) reveals that three crystal water molecules are released between 65 and 320 °C (Obsd. 7.8%; Calcd. 8.3%), and the dehydrated solid begins to decompose at 361 °C. The powder XRD patterns for the

**Fig. 2** View of the one-dimensional zigzag chain of complex **1**



**Fig. 3** View of the 2D network structure of complex **1** formed by C–H...O hydrogen bonding

as-synthesized bulk material closely match the simulated ones from the single-crystal structure analysis, which is evidence that we obtain a pure solid-state phase (Fig. 8).

### Photoluminescent Properties

Metal–organic coordination polymers, especially  $d^{10}$  metal centers, such as  $\text{Ag}^{\text{I}}$ ,  $\text{Au}^{\text{I}}$ ,  $\text{Zn}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$ , and conjugated organic linkers have been researched because of their fluorescent properties and potential applications as fluorescent-emitting materials, chemical sensors and electroluminescent displays [21]. The solid-state photoluminescent emission spectrum of complex **1** was investigated in at room

temperature (Fig. 9). When excited at 330 nm, and complex **1** exhibits intense blue luminescence and shows an emission peak at 367 nm. The free ligands Hhba and bib show photoluminescence with the emission maxima at 410 nm and 438 nm, respectively ( $\lambda_{\text{ex}} = 315$  nm), which can be assigned to intraligand ( $\pi^* \rightarrow \pi$ ) transitions [22]. Thus, the emission band of complex **1** could be assigned to the emission of ligand-to-ligand charge transfer [23, 24]. Owing to the strong fluorescent intensity, **1** appears to be a good candidate for novel hybrid inorganic–organic photoactive materials.

However, no photoluminescent response was observed for complex **2**.

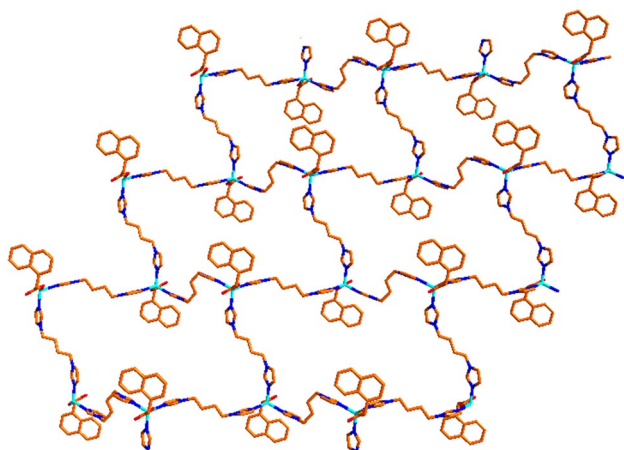
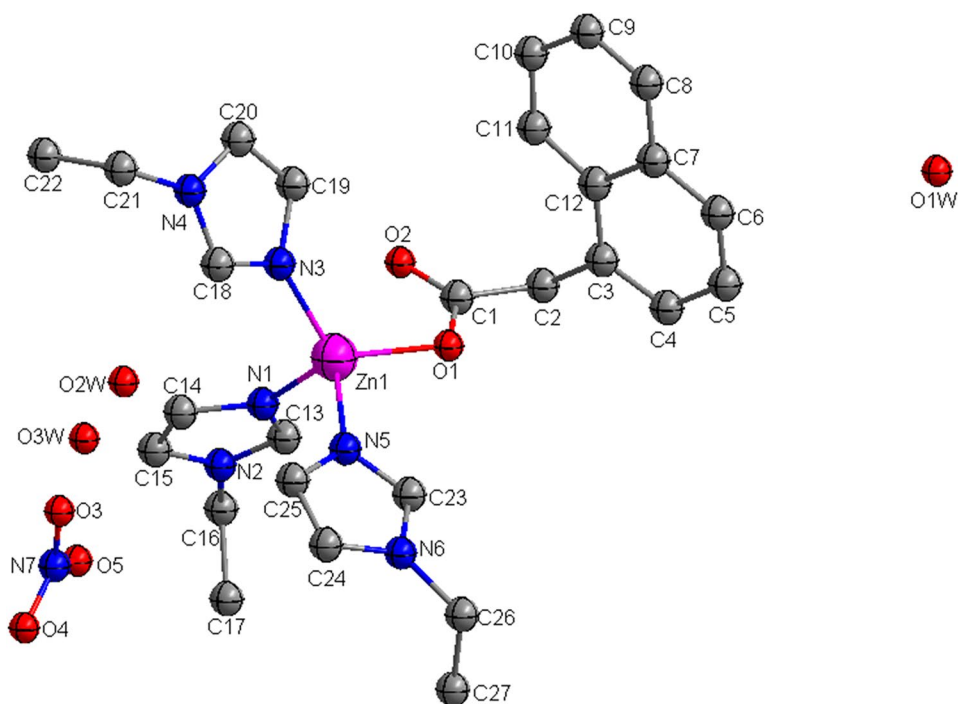
### Theoretical Calculations

The presented calculations were performed with the Gaussian 09 program [25]. Experimental data of the complexes **1** and **2** provided the start geometries of the molecular structures for calculation. We analyzed the NBO by DFT [26] with the PBE0 [27–30] hybrid functional and the LANL2DZ basis set [31].

The selected natural atomic charges, natural electron configuration, Wiberg bond indices and NBO bond orders (a.u) for the compound **1** are listed in Table 4 with the electronic configurations of Zn(II) ion, nitrogen, and oxygen atoms being  $4s^{0.31}3d^{9.97}4p^{0.39}$ ,  $2s^{1.37}2p^{4.21-4.24}$  and  $2s^{1.66-1.68}2p^{5.11-5.17}$ , respectively. We infer that the Zn(II) ion coordination with nitrogen and oxygen atoms is mainly on  $3d$ ,  $4s$ , and  $4p$  orbitals. Both nitrogen and oxygen atoms form coordination bonds with Zn(II) ion using  $2s$  and  $2p$  orbitals and the Zn(II) ion gained electrons from two nitrogen atoms of bib ligand and two oxygen atoms of hba ligands [32, 33]. On the basis of valence-bond theory, the atomic net charge distribution and the NBO bond orders of the compound **1** (Table 4) exhibits the obvious covalent interaction between Zn(II) and its coordination partners.

As can be seen from Fig. 10, lowest unoccupied molecular orbital (LUMO) is mainly composed of bib molecule,

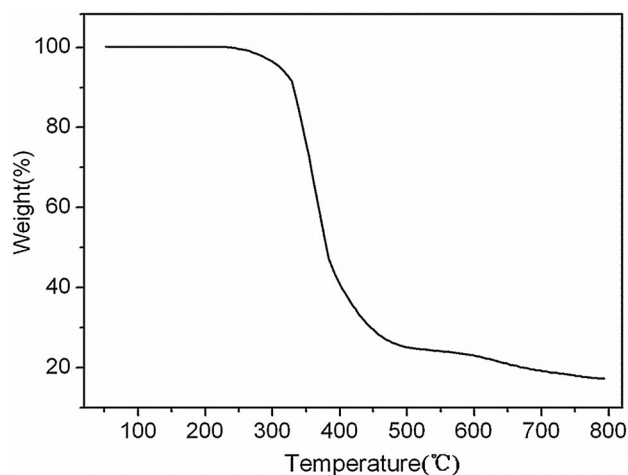
**Fig. 4** View of the asymmetric unit of the complex **2**. Hydrogen atoms are omitted for clarity



**Fig. 5** View of the 2D network structure of complex **2**

highest occupied molecular orbital (HOMO) mainly consists of bib ligand too. So, the ILCT (intraligand charge-transfer) may be inferred from some contours of molecular orbital of complex **1**.

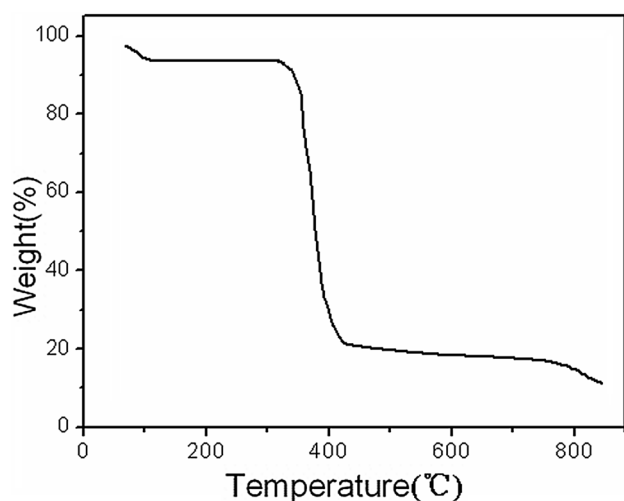
The selected natural atomic charges and natural electron configuration for the complex **2** is shown in Table 4. It is indicated that the electronic configurations of Zn(II) ion, N and O atoms are  $4s^{0.31}3d^{9.97}4p^{0.39}$ ,  $2s^{1.68}2p^{5.14}$  and  $2s^{1.36}2p^{4.24-4.28}$ , respectively. Based on the above results, one can conclude that the Zn(II) ion coordination with N and O atoms is mainly on  $3d$ ,  $4s$ , and  $4p$  orbitals. N atoms form coordination bonds with Zn(II) ion using  $2s$  and  $2p$  orbitals. All O atoms supply electrons of  $2s$  and  $2p$  to Zn(II) ion



**Fig. 6** TG curve of complex **1**

and form the coordination bonds. Therefore, the Zn(II) ion obtained some electrons from three N atoms of bib ligand, one O atom of NAA ligand [32, 33]. Thus, according to valence-bond theory, the atomic net charge distribution and the NBO bond orders of the complex **2** (Table 4) shows the obvious covalent interaction between the coordinated atoms and Zn(II) ion. The differences of the NBO bond orders for Zn–O and Zn–N bonds make their bond lengths be different [33], which is in good agreement with the X-ray crystal structural data of complex **2**.

As can be seen from Fig. 11, both the lowest unoccupied molecular orbital (LUMO) and the highest occupied

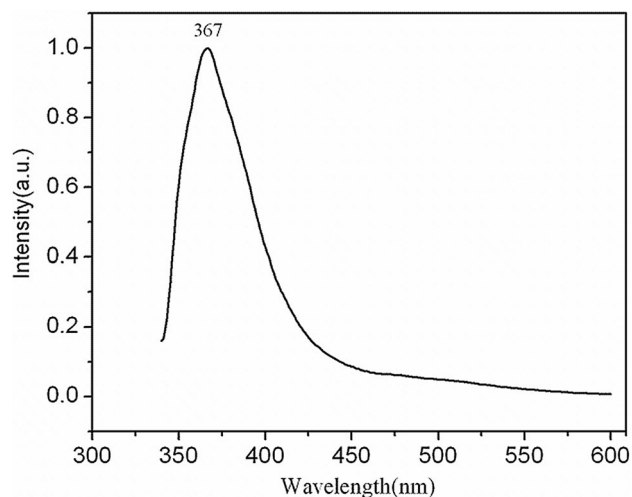


**Fig. 7** TG curve of complex **2**

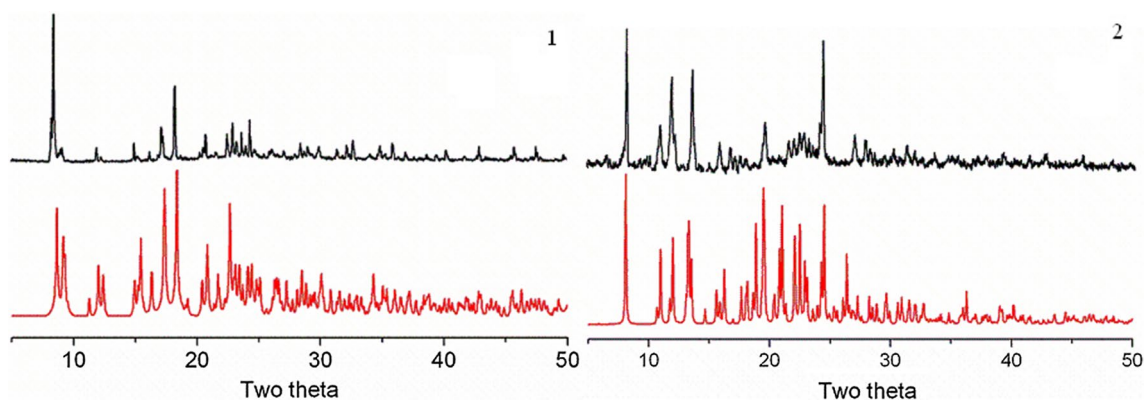
molecular orbital (HOMO) are mainly located on the bib ligand, and LLCT (ligand-to-ligand charge-transfer) may be inferred from some contours of the molecular orbital of complex **2**.

## Conclusions

We have presented two new Zn complexes with hba/NAA and bib ligands. The hba and NAA ligands adopt monodentate bridging modes, while the bib ligands exhibit *trans*-conformation bridging mode and link neighboring Zn(II) ions to generate a 1D zigzag chain in **1** and a 2D network in **2**. Furthermore, 3D supramolecular architectures are formed via hydrogen bonding and  $\pi$ - $\pi$  interactions. A NBO study confirms the obvious covalent interaction between the Zn(II) ions and the coordinated O and N atoms.



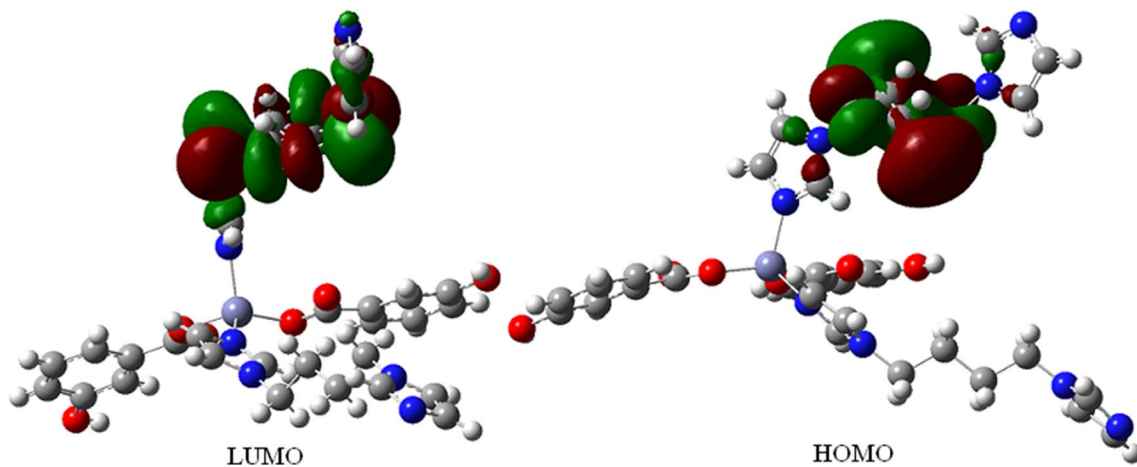
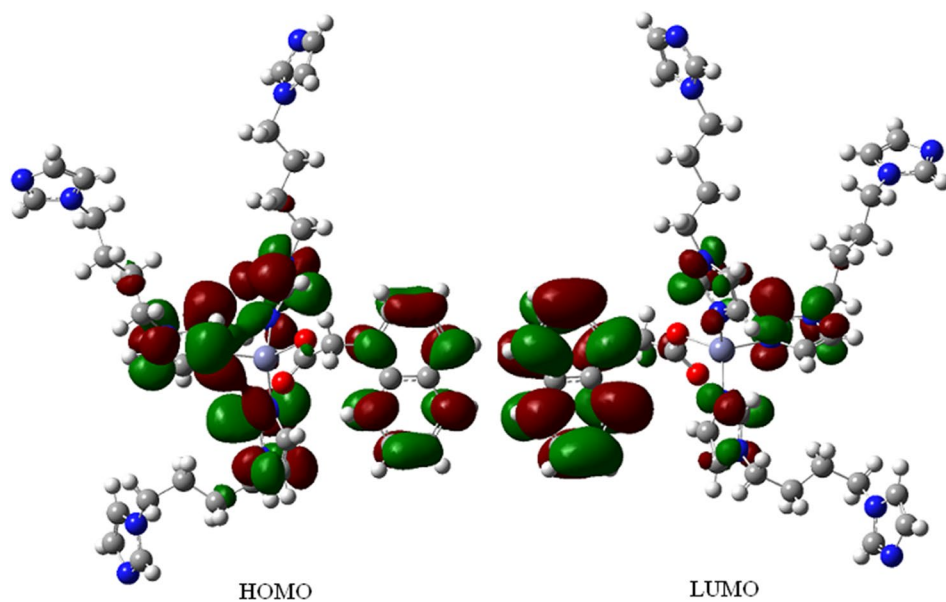
**Fig. 9** Solid-state emission spectrum of **1** at room temperature



**Fig. 8** PXRD patterns of complexes **1** and **2** at room temperature; red simulation and black experimental data (Color figure online)

**Table 4** Natural atomic charges, natural valence electron configurations, Wiberg bond indexes and NBO bond orders (a.u) for **1** and **2**

Atom	Net charge	Electron configuration	Bond	Wiberg bond index	NBO bond orders
<b>1</b>					
Zn(1)	1.32744	[core]4 <i>s</i> (0.31)3 <i>d</i> (9.97)4 <i>p</i> (0.39)			
O(1)	−0.80113	[core]2 <i>s</i> (1.68)2 <i>p</i> (5.11)	Zn(1)–O(1)	0.2924	0.3378
O(4)	−0.84085	[core]2 <i>s</i> (1.66)2 <i>p</i> (5.17)	Zn(1)–O(4)	0.3035	0.3509
N(1)	−0.62138	[core]2 <i>s</i> (1.37)2 <i>p</i> (4.24)	Zn(1)–N(1)	0.2241	0.3379
N(3)	−0.59350	[core]2 <i>s</i> (1.37)2 <i>p</i> (4.21)	Zn(1)–N(3)	0.2144	0.3278
<b>2</b>					
Zn(1)	1.31568	[core]4 <i>s</i> (0.31)3 <i>d</i> (9.97)4 <i>p</i> (0.39)			
O(1)	−0.83190	[core]2 <i>s</i> (1.68)2 <i>p</i> (5.14)	Zn(1)–O(1)	0.2986	0.3374
N(1)	−0.65489	[core]2 <i>s</i> (1.36)2 <i>p</i> (4.28)	Zn(1)–N(1)	0.2596	0.3662
N(3)	−0.65019	[core]2 <i>s</i> (1.36)2 <i>p</i> (4.27)	Zn(1)–N(3)	0.2630	0.3663
N(5)	−0.62372	[core]2 <i>s</i> (1.36)2 <i>p</i> (4.24)	Zn(1)–N(5)	0.2389	0.3409

**Fig. 10** Frontier molecular orbitals of the complex **1****Fig. 11** Frontier molecular orbitals of the complex **2**



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