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Ligand-dependent assembly of dinuclear, linear tetranuclear and one-dimensional Zn(II) complexes with aroylhydrazone Schiff base †

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Three complexes  $[Zn(H_2L^1)(CH_3COO)]_2 \cdot CH_3OH$  (1),  $[Zn_4(H_2L^2)_2(CH_3COO)_4] \cdot 4DMF$  (2) and  $\{[Zn_4(L^3)_2(CH_3COO)_4] \cdot DMSO\}_n$  (3)  $(H_3L^1 = 4$ -hydroxy-benzoic acid (2-hydroxy-5-nitro-benzylidene)-hydrazide,  $H_4L^2 = 4$ -hydroxy-3-methoxy-benzoic acid (2,3-dihydroxy-benzylidene)-hydrazide,  $H_2L^3 = (4$ -nitro-phenoxy)-acetic acid (2-hydroxy-3-methoxy-benzylidene)-hydrazide)) have been synthesized and studied, in which three kinds of ligands have been designed by introducing diversified bridging-functional groups. The X-ray single-crystal diffraction analysis showed that the **1**, **2** and **3** are dinuclear, linear tetranuclear and 1D chain coorddination complexes, respectively, which achieved the controlled synthesis of multinuclear complexes through ligand design. The luminescent properties of these crystalized complexes have been investigated both in solution and solid state.

## Introduction

Multinuclear metal complexes have received enormous attentions for decades, not only for their structural diversity,<sup>1</sup> but also for their fascinating potential application in various fields such as water splitting, fluorescent recognition, biological activity, single-molecule magnets, gas absorption, and catalysis.<sup>2-4</sup> In this regard, multidentate Schiff base ligands can serve as excellent candidates to construct the above mentioned complexes. Very recently, by using the chelating Schiff base ligands, a wide variety of resultant structural motifs have been obtained, such as cage,<sup>5</sup> cubane,<sup>6</sup> linear,<sup>7</sup> helicates<sup>8</sup> and so on. Although the earlier predesign and assembly of novel crystalline material by structure directing factors, such as central metal ions, metal-ligand ratio, solvents, temperature, pH value, and templates, have been validated and summarized, the most effective way to realize the structural diversity of Schiff base complexes is the design of novel chelating ligands, which might provide further insights in designing new crystalline materials.

In our previous work, by using aroylhydrazone Schiff base ligands, we have successfully obtained linear tetranuclear Zn( $\rm II$ ) complex and "less common" cubane  $\rm Zn_4O_4$  clusters, and the novel luminescent properties of these complexes have been studied in detail.<sup>6a,9</sup> Our preliminary study and related

literature reports<sup>10</sup> have indicated that aroylhydrazone ligands have the potential to construct multinuclear complexes. As an extension of our research, three novel aroylhydrazone ligands ( $H_3L^1 = 4$ -hydroxy-benzoic acid (2-hydroxy-5-nitro-benzylidene) -hydrazide,  $H_4L^2 = 4$ -hydroxy-3-methoxy-benzoic acid (2,3dihydroxy-benzylidene)-hydrazide,  $H_2L^3 = (4$ -nitro-phenoxy)acetic acid (2-hydroxy-3-methoxy-benzylidene)-hydrazide) have been successfully designed and synthesized, which possess different substituent groups and chelating/bridging mode (Scheme 1,2).

Herein, we choose the combination of aroylhydrazone ligand and zinc acetate as a precursory binary system, and focus on the effect of different substituent groups of ligands on mediating the conditions of crystallization under room temperature synthesis conditions. And three new coordination complexes  $[Zn(H_2L^1)(CH_3COO)]_2 \cdot CH_3OH$  (1),  $[Zn_4(H_2L^2)_2 \cdot (CH_3COO)_4] \cdot 4DMF$  (2) and  $\{[Zn_4(L^3)_2(CH_3COO)_4] \cdot DMSO\}_n$  (3) were obtained.

Complex **1** display a binuclear structure, by comparison, complex **2** presented a discrete linear tetranuclear cluster when additional hydroxyl group was introduced at the 3-position of the benzylidene part, which provided suitable, disposable bridging groups to control the stereochemistry of the metallic centers as well as the number of metal ions within the cluster motifs.<sup>6a</sup> What's more, the introduction of the potential coordination atom (phenoxy O atom) in major skeleton of the ligand is beneficial to the construction of one-dimensional (1D) coordination polymer **3**. Particularly worth mentioning that, the amido (–NH–) group of the ligand in **3** was induced to coordinate with metal ion by the phenoxy O atom of major skeleton, which is still comparatively rare in previous reports.<sup>11</sup> Furthermore, the luminescent properties of

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<sup>†</sup> Electronic Supplementary Information (ESI) available: CCDC 941209, 938714 and 938713. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x



**Scheme 1** Representation of the effect of substituent of ligand on the structure of complexes 1-3. The turquoise, red, blue and grey balls represent the zinc, oxygen, nitrogen and carbon, respectively.

three complexes in the solid state and MeOH solution have been investigated in detail.

## Experimental

## Materials and measurements

All starting materials and solvents used in this work were of analytical grade and used as purchased from Alfa Aesar Chemical Company without further purification. Organic solvents with analytical purity were supplied by commercial sources and used as received. Elemental analyses (C, H, N) were performed on a Flash EA1112 microanalyzer at the Beijing Institute of Technology. FT-IR spectrum is recorded in the Nicolet-360 FT-IR spectrometer as KBr pellets in the 4000-400 cm<sup>-1</sup> region. The UV-vis absorption spectra were examined on a JASCO UV-1901 spectrophotometer in the wavelength range of 200-800 nm. The photoluminescent (PL) spectra were recorded by using a Hitachi F-7000 luminescence spectrophotometer equipped with a 450 W xenon lamp as the excitation source, and the measurements were performed at room temperature. The photomultiplier tube voltage was 700 V, the scan speed was 1200  $\text{nm}\cdot\text{min}^{-1}$ , and the slit width was 2.5 nm (5.0 nm). Thermo-gravimetric analyses (TGA) were carried out on a SEIKO TG/DTA 6200 thermal analyzer from room temperature to 800 °C at a ramp rate of 10 °C/min in a flowing 50 mL/min nitrogen atmosphere. X-ray powder diffraction (XPRD) of samples were measured using a Japan Rigaku D/Max  $\gamma$  A X-ray diffractometer equipped with graphite-monochromatized Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker Avance III HD (400 and 175 MHz, respectively) spectrometers in DMSO- $d^{\circ}$  with Me<sub>4</sub>Si as the internal standard.

## Synthetic procedures

Synthesis of the ligand  $H_3L^1$ . The ethanol (20mL) solution of 5-Nitrosalicylaldehyde (1.671g, 0.01mol) was added dropwise to the ethanol (20mL) solution of 4-Hydroxybenzhydrazide (1.522g, 0.01mmol) with stirring. The addition of 1 drop of concentrated hydrochloric acid induced a colour change along with immediate precipitation. Then, the mixture was refluxed for 8 hours with vigorous stirring and subsequently cooled to room temperature. The yellow solid was collected by vacuum

filtration, washed with ethanol and diethyl ether, and dried in air (Scheme S1). Yield: (69%). Selected IR (KBr pellet, cm<sup>-1</sup>): v(O–H) 3202; v(C=O) 1656 ; v(C=N) 1603(s). <sup>1</sup>H NMR (400 MHz, DMSO- $d^6$ )  $\delta$  (ppm) 12.45 (s, 1H), 12.11 (s, 1H), 10.22 (s, 1H), 8.71 (s, 1H), 8.58 (s, 1H), 8.17 (d, *J* = 7.4, 1H), 7.85 (s, 2H), 7.12 (d, *J* = 6.7, 1H), 6.89 (s, 2H). <sup>13</sup>C NMR (175 MHz, DMSO- $d^6$ )  $\delta$  (ppm) 163.16, 163.08, 161.52, 144.27, 140.32, 130.32, 126.74, 124.51, 123.47, 120.35, 117.54, 115.59.

Synthesis of the ligands  $H_4L^2$  and  $H_2L^3$ . The procedure for synthesis of the ligands  $H_4L^2$  and  $H_2L^3$  are similar to that of  $H_3L^1$ except for the replacement of 5-Nitrosalicylaldehyde and 4-Hydroxybenzhydrazide with 2, 3-dihydroxybenzaldehyde and vanillic acid hydrazide in H<sub>4</sub>L<sup>2</sup> and 2-hydroxy-3methoxybenzaldehyde and (4-Nitro-phenoxy)-acetic acid hydrazide in  $H_2L^3$ , respectively. For  $H_4L^2$ : Yield: (76%). Selected IR (KBr pellet,cm<sup>-1</sup>): v(O−H) 3490, 3272; v(C=O) 1636 ; v(C=N) 1598. <sup>1</sup>H NMR (400 MHz, DMSO- $d^6$ )  $\delta$  (ppm) 11.90 (s, 1H), 11.31 (s, 1H), 9.80 (s, 1H), 9.20 (s, 1H), 8.57 (s, 1H), 7.49 (m, 2H), 6.95 - 6.75 (m, 4H), 3.86 (s, 3H). <sup>13</sup>C NMR (175 MHz, DMSO- $d^6$ )  $\delta$  (ppm) 162.90, 150.87, 148.76, 147.86, 146.50, 146.05, 123.92, 121.90, 120.58, 119.60, 119.27, 117.74, 115.54, 112.08, 56.20. For H<sub>2</sub>L<sup>3</sup>: Yield: (65%). Selected IR (KBr pellet,cm<sup>-1</sup>): v(O–H) 3090; v(C=O) 1674 ; v(C=N) 1612. <sup>1</sup>H NMR (400 MHz, DMSO- $d^6$ ):  $\delta$  (ppm) 11.85 (s, 1H), 11.66 (s, 1H), 10.60 (s, 1H), 9.37 (s, 1H), 8.56 (s, 1H), 8.36 (s, 1H), 8.25 - 8.20 (m, 2H), 7.42 - 7.09 (m, 3H), 7.09 - 6.94 (m, 1H), 6.87 - 6.82 (m, 1H), 5.33 (s, 1H), 4.89 (s, 1H), 3.83 (s, 3H). <sup>13</sup>C NMR (175 MHz, DMSO-*d*<sup>6</sup>) δ (ppm) 168.32, 164.11, 163.74, 163.41, 148.50, 148.43, 148.40, 147.50, 146.45, 141.91, 141.82, 141.40, 126.29, 126.16, 120.87, 120.84, 119.59, 119.55, 119.38, 118.21, 115.81, 115.65, 114.29, 113.42, 67.05, 65.91, 56.30, 56.26.

Synthesis of  $[Zn(H_2L^1)(CH_3COO)]_2$ ·CH<sub>3</sub>OH (1). The solution of  $Zn(CH_3COO)_2$ ·2H<sub>2</sub>O (44 mg, 0.2 mmol) in 2 mL acetonitrile was added to methanol solution (14mL) of  $H_3L^1$  (15mg, 0.05 mmol) with continuous stirring ca. 30 min. The result solution was then filtered and left at room temperature to give a yellow solution. Yellow single crystal suitable for X-ray analysis was produced by slow evaporation of the mother liquor for two days. Yield: 68%. Anal. Calc. for  $C_{33}H_{30}N_6O_{15}Zn_2$ : C, 44.93; H, 3.40; N, 9.53. Found: C, 44.85; H, 3.43; N, 9.48. Selected IR (KBr pellet, cm<sup>-1</sup>): v(O–H) 3434, 3178; v(C=O) 1598; v(C=N) 1533; v<sub>asym</sub> (COO<sup>-</sup>) 1612; v<sub>sym</sub> (COO<sup>-</sup>) 1362.

Synthesis of  $[Zn_4(H_2L^2)_2(CH_3COO)_4]$ ·4(DMF) (2). The solution of  $Zn(CH_3COO)_2$ ·2H<sub>2</sub>O (44 mg, 0.2 mmol) in 6 mL methanol was added to DMF solution (4mL) of H<sub>4</sub>L<sup>2</sup> (15mg, 0.05 mmol) with continuous stirring ca. 30 min. The result solution was then filtered and left at room temperature to give a yellow solution. Yellow single crystal suitable for X-ray analysis was produced by slow evaporation of the mother liquor for one day. Yield: 60%. Anal. Calc. for C<sub>50</sub>H<sub>64</sub>N<sub>8</sub>O<sub>22</sub>Zn<sub>4</sub>: C, 43.21; H, 4.47; N, 8.07. Found: C, 43.25; H, 4.46; N, 8.03.Selected IR (KBr pellet, cm<sup>-1</sup>): v(O–H) 3225; v(C=O) 1609 ; v(C=N) 1556; v<sub>asym</sub> (COO<sup>-</sup>) 1653; v<sub>sym</sub> (COO<sup>-</sup>) 1391.

Synthesis of {[ $Zn_4(L^3)_2(CH_3COO)_4$ ]·DMSO}<sub>n</sub> (3). The solution of Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (88 mg, 0.4 mmol) in 9 mL isopropanol was added to DMSO solution (1.6mL) of H<sub>2</sub>L<sup>3</sup> (34mg, 0.1 mmol) with continuous stirring ca. 1 hour. The result solution was

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then filtered and left at room temperature to give a yellow solution. Yellow single crystal suitable for X-ray analysis was produced by slow evaporation of the mother liquor for five days. Yield: 76%. Anal. Calc. for C42H44N6O21SZn4: C, 39.92; H, 3.49; N, 6.65. Found: 39.88; H, 3.44; N, 6.68. Selected IR (KBr pellet, cm<sup>-1</sup>): v(O–H) 3411; v(C=O) 1595 ; v(C=N) 1553; v<sub>asvm</sub> (COO<sup>-</sup>) 1627; v<sub>sym</sub> (COO<sup>-</sup>) 1341.

## X-ray crystallography

Suitable single crystals with dimensions of  $0.44 \times 0.17 \times 0.09$ mm, 0.41  $\times$  0.17  $\times$  0.05 mm and 0.17  $\times$  0.11  $\times$  0.06 mm for complexes 1, 2 and 3 were selected for single-crystal X-ray diffraction analysis, respectively. Diffraction intensities for the three complexes were collected on a Rigaku RAXIS-RAPID CCD diffractometer equipped with a graphite-monochromatic Mo-Kα radiation ( $\lambda$  =0.71073Å) using a  $\omega$  scan mode for complexes 1 at 296(2) K and 2, 3 at 153(2) K. Diffraction intensity data were collected in the  $\theta$  range of 1.71 ${\sim}25.01^{\circ}$  for 1, 2.44 ${\sim}$ 26.00° for 2 and 1.92 $\sim$ 29.19° for 3. The collected data were reduced using the SAINT program, and empirical absorption corrections were performed using the SADABS program.<sup>12</sup> Three structures were solved by direct methods<sup>13</sup> and refined using full-matrix least square techniques on  $F^2$  (ref. 14) with the program SHELXL-97.<sup>12</sup> All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. Some of hydrogen atoms were placed in their geometrically generated positions and other hydrogen atoms



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were located from the different Fourier map and refined isotropically. Crystallographic data are given in Table 1. Selected bond distances and angles are given in Table S1, ESI.<sup>†</sup> CCDC 941209 (1), CCDC 938714 (2) and CCDC 938713 (3) contain the supplementary crystallographic data for this paper.

## **Results and Discussion**

## Crystal structure of [Zn(H<sub>2</sub>L<sup>1</sup>)(CH<sub>3</sub>COO)]<sub>2</sub>·CH<sub>3</sub>OH (1)

X-ray crystallographic analysis revealed that 1 is a binuclear molecule and crystallizes in the triclinic space group of P-1, and its asymmetric unit contains one Zn(II) ion, one partially

Complexes	1	2	3	
Formula	$C_{33}H_{30}N_6O_{15}Zn_2$	$C_{50}H_{64}N_8O_{22}Zn_4$	$C_{42}H_{44}N_6O_{21}SZn_4$	
<i>M</i> /mol <sup>-1</sup>	881.41	1390.56	1262.37	
Crystal system	Triclinic	Triclinic	Monoclinic	
Space group	<i>P</i> -1	<i>P</i> -1	C2/c	
a/Å	8.8740(18)	8.4550(17)	38.142(8)	
b/Å	9.5171(18)	13.485(3)	11.411(2)	
c/Å	11.986(2)	14.017(3)	29.647(6)	
α <b>/°</b>	84.921(3)	115.54(3)	90	
β/°	85.114(4)	95.02(3)	129.94(3)	
γ/°	74.714(4)	94.99(3)	90	
V/Å <sup>3</sup>	970.6(3)	1422.6(5)	9893(3)	
Ζ	1	1	8	
<i>Т</i> (К)	296(2)	153(2)	153(2)	
ρ <b>/g·cm</b> ⁻³	1.508	1.621	1.695	
$\mu/\text{mm}^{-1}$	1.311	1.752	2.044	
F(000)	450	714	5136	
$ heta_{\min},  heta_{\max}$ /°	1.71, 25.01	2.44 , 26.00	1.92, 29.19	
S	1.171	1.023	1.061	
R <sub>int</sub>	0.0347	0.0336	0.0514	
$R_1[I>2\sigma(I)]$	0.0845	0.0332	0.0730	
wR <sub>2</sub> [ <i>I</i> >2σ( <i>I</i> )]	0.2257	0.0797	0.2008	
$\Delta  ho_{ m max,min}$ (e Å <sup>-3</sup> )	1.137, -1.135	0.568 , -0.432	1.514, -1.798	

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**Fig. 1** (a) ORTEP picture showing the coordination environment of the Zn(II) ion and ligand in complex **1** (50% probability ellipsoids, hydrogen atoms are omitted for clarity). (b) The polyhedral representations of the 1D chain structure in **1** by H-bonding (O3–H3···O4: 1.871, 2.662, 161.73, dashed line). (c) The 2D layer structure of **1** by H-bonding (N1–H1···O5: 1.961, 2.741, 150.17, pink dashed line). (d) Packing diagram of **1** showing non-conventional H-bonding between different 2D layers (C2–H2B···O6: 2.473, 3.274, 151.3: (12–H12B···O7: 2.477, 3.338, 154.1, blue dashed line).

deprotonated  $[H_2L^1]^-$  ligand and one acetate. As shown in Fig. 1a, Each Zn(II) center is in a NO4 distorted square pyramidal coordination geometry with one oxygen atom (O4) from acetate in axis positions with Zn-O4 of 2.003(7) Å and three oxygen atoms (O1, O2, O2<sup>#1</sup>; #1: -x+1,-y+1,-z+2) and one nitrogen atom (N2) from two equivalent  $[H_2L^1]^-$  ligands in the equatorial positions, which is reflected by the  $\tau$  value (0.317) defined by Addison et al. ( $\tau$ = 0 for an ideal square pyramid, and 1 for an ideal trigonalbipyramid).<sup>15</sup> The basal plane of the square pyramid is defined by O1, O2, N2 and O2#1 atoms, with the bond distances ranging from 2.015(6) to 2.095(7) Å and bond angles ranging from 77.0 to 155.1°. The Zn(II) ion lies approximately in the equatorial position with a deviation (0.2084 Å) from the basal plane. The coordination mode of the  $[H_2L^1]^-$  ligand in **1** displays  $\eta^2:\eta^1:\eta^1:\mu_2$  chelating/bridging mode (Scheme 2a). The Zn(1)-Zn(1)#1 distance is 3.146 Å, implying the existence of d<sup>10</sup>-d<sup>10</sup> weak interactions.<sup>16</sup> The benzene rings of one ligand are non-coplanar and the dihedral angle is 13.1°.

As expected, each molecule of **1** interacts with two neighbours to form 1D chains by H-bonding between uncoordinated hydroxyl and acetate (O3–H3…O4: 1.871, 2.662, 161.73, Fig. 1b). In addition, the adjacent 1D chains were further assembled by N1–H1…O5 between acetate group and amido to form 2D layer structure (Fig. 1c). Further, the 2D layers aggregate together through non-conventional H-bonding between aromatic rings (C-H) and terminal nitro groups (Fig. 1d).

## Crystal structure of [Zn<sub>4</sub>(H<sub>2</sub>L<sup>2</sup>)<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>]·4(DMF) (2)

To investigate the influence of substituent (-OH) at the 3position of salicylaldehyde ring on the structure of resulting complex, reaction of the ligand  $H_4L^2$  and  $Zn(CH_3COO)_2 \cdot 2H_2O$ was carried out and complex **2** was isolated. Complex **2** is a linear tetranuclear cluster crystallizes in triclinic space group *P*-1, and its asymmetric unit contains two Zn(II) ions (Zn1, Zn2), one partially deprotonated  $[H_2L^2]^{2-}$  ligand and two acetates.



**Fig. 2** (a) ORTEP picture showing the coordination environment of the Zn(II) ion and ligand in complex **2** (50% probability ellipsoids, hydrogen atoms are omitted for clarity). (b) The polyhedral representations of the 1D chain structure in **2** by H-bonding (O8–H8B···O11: 1.901, 2.635, 148.5, C24–H24F···O5: 2.586, 3.451, 150, dashed line).

Different to the complex 1, the two asymmetrical units  $[Zn_2(H_2L^2)(CH_3COO)_2]$  in **2** are bridged through the 3-position deprotonated hydroxyl group oxygen atom (O1) in the ligand to form linear Zn4 cluster, and each  $[H_2L^2]^{2-}$  ligand coordinates to three Zn(II) ions with the imine-N, carbonyl-O and the two bridging phenoxo-O atoms combining with two bridging acetate ligands (syn-syn mode). The distance of Zn1-Zn2 in the asymmetrical unit is 3.2973Å and that of Zn2-Zn2# between the two asymmetrical units is 3.2280 Å. The coordination mode of  $[H_2L^2]^{2-}$  ligand in **2** displays  $\eta^2$ :  $\eta^2$ :  $\eta^1$ :  $\eta^1$ :  $\mu_3$ chelating/bridging mode (Scheme 2b). The Zn(II) centers are also five coordinated with slightly different coordination environments of Zn1-NO4 and Zn2-O5, respectively. Alternatively, the coordination geometry of Zn(II) in 2 can be regarded as intermediate between a squared-based pyramid and a trigonal bipyramid (Zn(1):  $\tau$ = 0.54; Zn(2):  $\tau$ = 0.43). The coordination mode of acetate in 2 is different from that in 1, which plays the role of bridge ligand in the  $[Zn_2(H_2L^2)(CH_3COO)_2]$  fragment. The linear  $Zn_4(H_2L^2)_2$  fragment is almost coplanar (Fig. S10, ESI<sup>†</sup>). The coordinated acetate ligands are located up and down the plane, which is similar to tetranuclear Zn(II) complex in our previous report.<sup>6a</sup>

The linear Zn4 clusters are linked by H-bonding between solvent DMF molecules and neighboring  $[Zn_2(H_2L^2)(CH_3COO)_2]_2$  fragments to 1D chains (Fig. 2b), which are extended to a 2D layer by non-conventional H-bonding between acetates and terminal  $-OCH_3$  groups of neighbouring fragments (Fig. S11a, ESI†). It is worth mentioning that the solvent molecule and terminal  $-OCH_3$  group in the ligand  $(H_4L^2)$  influence the supramolecular structure of **2**, which is different from tetranuclear Zn(II) complex reported in literature.<sup>6a</sup>

Complex **2** is different from **1**, which indicated that the additional hydroxyl group at the 3-position of salicylaldehyde ring can play a bridging role to control the stereochemistry of metallic centers as well as the number of metal ions within the cluster motifs. On the other hand, the methoxy group at hydrazide ring can only be involved in H-bonding to contributing the supramolecular structure.

## Crystal structure of $\{[Zn_4(L^3)_2(CH_3COO)_4] \cdot DMSO\}_n$ (3)

In complexes 1 and 2, the amido (-NH-) group of ligand does not coordinate with metal ion as in previous reports,<sup>10</sup> and has no contribution to the expansion of the coordination

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Fig. 3 (a) ORTEP picture showing the coordination environment of the Zn(II) ion and ligand in complex 3 (50% probability ellipsoids, hydrogen atoms are omitted for clarity). (b) The polyhedral representations of the 1D chain structure in 3.

polymer. Complex **3** with 1D chain structure was successfully obtained by the self-assembly of ligand  $H_2L^3$  and  $Zn(CH_3COO)_2 \cdot 2H_2O$ . The phenoxy group at the major skeleton and the methoxy group at the 3-positon of salicylaldehyde ring have significant effects on the coordination geometry of Zn(II) ions and the coordination mode of the ligand, which leads to different connections of Zn(II) ions relative to the complexes **1** and **2**.

X-ray crystallographic analysis revealed that 3 crystallizes in the monoclinic space group of C2/c. The asymmetric unit of **3** contains four Zn(II) ions, two completely deprotonated  $[L^3]^{2-1}$ ligand, four acetate groups (syn-syn mode) and one DMSO molecule. The amido (–NH–) group of  $H_2L^3$  is also deprotonated and coordinate with Zn(II) ion. The Zn1 and Zn4 ions are all five coordinated with coordination environments of Zn-NO4 (imine-N, carboxide-O, phenolic-O and acetate-O). The coordination geometry of Zn1 can be regarded as distorted square pyramidal geometry (Zn1:  $\tau$ = 0.231), where the oxygen atom of acetate group (O2) occupies the apical position. The Zn1 ion is placed at 0.4122 Å from the basal plane. The coordination geometry of Zn4 can be regarded as intermediate between a squared-based pyramid and a trigonal bipyramid (Zn4:  $\tau$ = 0.566). The Zn2 and Zn3 ions are all six coordinated with coordination environments of Zn-NO5 (amido-N, methoxy-O, phenoxy-O, phenolic-O and acetate-O) and can be regarded as a distorted octahedral geometries. The distance of Zn1-Zn2, Zn2-Zn4 and Zn1-Zn3 in asymmetrical unit is 4.8134Å, 3.2084 Å and 3.1463 Å, respectively. The coordination mode of  $[L^3]^{2-}$  ligand in 3 displays  $\eta^{1}$ : $\eta^{2}$ : $\eta^{1}$ : $\eta^{1}$ : $\eta^{1}$ : $\eta^{1}$ : $\mu_{3}$  chelating/bridging mode (Scheme 2c). Each  $[L^3]^{2-}$  ligand acts as a double-chelating and bridging ligand linking Zn(II) ions to form 1D chains, which is very unusual coordination mode for aroylhydrazone ligands. Again, these 1D chains are assembled through non-conventional H-bonding between aromatic rings (C-H) with terminal nitro groups and methylene groups (C-H) with acetates to 2D layer structure (Fig. S12, ESI<sup>+</sup>).

## Luminescent Properties

Metal-organic complexes have been reported to have abilities that affect the emission wavelength and intensity of the organic material through metal coordination.<sup>17</sup> Therefore, it is important to investigate the luminescent properties of metal-organic complexes in view of potential applications. Therefore, the photoluminescent properties of complexes 1-3 as well as the relative ligands were investigated at room temperature in the solid state (Fig. 4). It is shown that complex 1 has a broad emission with maximum at 498 and 524 nm, accompanied by a shoulder peak at 400nm ( $\lambda_{ex}$  = 293 nm), while the H<sub>3</sub>L<sup>1</sup> ligand displays a broad emission at 494 and 542 nm ( $\lambda_{ex}$  = 293 nm). Apparently, the emission at 498 and 524 nm of complex **1** is similar to that of the ligand  $H_3L^1$ , indicating that the dinuclear complex 1 is L-based emission, and the relatively lower peak at 400 nm can be attributed to ligand-tometal charge transfer (LMCT) transition. Meanwhile, under  $\lambda_{ex}$ = 316 nm excitation, the emission for molecular cluster 2 is at 548 nm, accompanied by a lower peak at 388 nm, compared to the emission of the ligand  $H_4L^2$  ( $\lambda_{em}$  = 436, 470 and 552 nm,  $\lambda_{ex}$ = 316 nm), the peaks at 388 and 548 nm can be attributed to ligand-to-metal charge transfer (LMCT) and  $\pi$ - $\pi$ \* intraligand (IL) transitions, respectively. In the same way, when  $\lambda_{ex}$  = 312 nm, the complex 3 exhibits green luminescence with the peak at 533 nm, accompanied by a shoulder peak at 379 nm, compared to the emission of the ligand  $H_2L^3$  ( $\lambda_{em}$  = 413, 468 and 521 nm,  $\lambda_{ex}$  = 312 nm). In a word, complexes **1–3** display ligand-based fluorescence emissions mainly and accompanied by a ligand-to-metal charge transfer (LMCT) transition in the solid state.

The UV-vis spectra and photoluminescent properties of ligands  $H_3L^1$ ,  $H_4L^2$ ,  $H_2L^3$  and complexes 1-3 in the MeOH solution were also studied to further understand their solution fluorescent behaviour (section 6, ESI<sup>†</sup>). It is shown that complexes 1-3 have a broad emission with maxima at 443, 498 and 458 nm respectively, while the ligands  $H_3L^1$ ,  $H_4L^2$  and  $H_2L^3$  have a broad emission at 488, 431 and 415 nm respectively. Compared with the ligands, a blue-shift (45 nm) for 1 and red-shift (67 nm and 43 nm) for 2 and 3 emissions are observed.



Fig. 4 Normalized emission spectra of the  $H_3L^1$ ,  $H_4L^2$ ,  $H_2L^3$ , 1, 2 and 3 in the solid state at room temperature ( $\lambda_{ex} = 293$  nm for  $H_3L^1$  and 1,  $\lambda_{ex} = 316$  nm for  $H_4L^2$  and 2 and  $\lambda_{ex} = 312$  nm for  $H_2L^3$  and 3).

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Combining previous studies, these red-shifts and blue-shift may be caused by a ligand-to-metal charge-transfer (LMCT) transition. Complexes **1-3** display ligands-based fluorescence emissions in MeOH solution.

## Conclusions

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In summary, three aroylhydrazone ligands and their Zn(II) coordination complexes have been synthesized in this work. The complex 1 displayed a binuclear Zn(II) structure, 2 presented a discrete linear tetranuclear Zn(II) structure and 3 is 1D coordination polymer. It is a successful story to control the nuclear number and molecular structures of multi-nuclear coordination complex based on rational ligand design. Importantly, it is the first time to realize the amido (-NH-) group of aroylhydrazone ligand can coordinate to metal ion and exhibits a double-chelating and bridging coordination mode. So, the substituent at the 3-position of salicylaldehyde ring can provide potential coordination donors (phenoxy O atom) will be beneficial to the construction of coordination polymers. The ligand-based fluorescence emissions of complexes 1-3 in the solid state and MeOH solution have been studied according to their crystal strcutures. We believe that the three complexes presented here can provide us an opportunity to further design and construct coordination polymers with specific structures and photoluminescent properties, which are now underway.

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