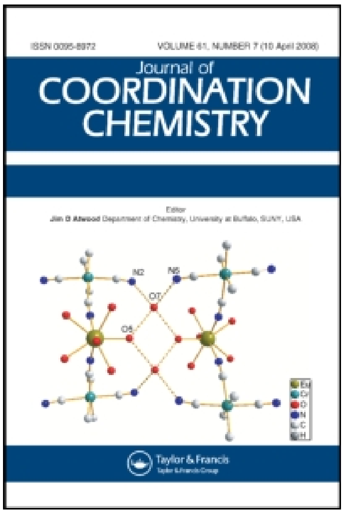

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Supramolecular structures assembled based on mononuclear 2,6-naphthalenedisulfonate zinc(II) complexes

Jin-Hao Song[a]; Xia Li[a]; Ying-Quan Zou[b]
[a] Department of Chemistry, Capital Normal University, Beijing 100048, China [b] Department of Chemistry, Beijing Normal University, Beijing 100875, China

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Supramolecular structures assembled based on mononuclear 2,6-naphthalenedisulfonate zinc(II) complexes

JIN-HAO SONG†, XIA LI*† and YING-QUAN ZOU‡

†Department of Chemistry, Capital Normal University, Beijing 100048, China
‡Department of Chemistry, Beijing Normal University, Beijing 100875, China

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Three complexes, $[Zn(phen)_2(H_2O)(2,6\text{-}NDS)]2H_2O$ (**1**), $[Zn(phen)_2(2,6\text{-}NDS)]H_2O$ (**2**), and $[Zn(2,2'\text{-}bipy)_2(H_2O)(2,6\text{-}NDS)]3H_2O$ (**3**) (2,6-NDS = 2,6-naphthalenedisulfonate; phen = 1,10-phenanthroline; 2,2′-bipy = 2,2′-bipyridine), have been obtained by different methods and structurally characterized by X-ray single crystal diffraction. Compound **1** features mononuclear structure with space group *P1* and further forms a 2-D supramolecular structure by hydrogen bonds and π–π stacking interactions. Compound **2** displays a mononuclear structure with centrosymmetric space group $P\bar{1}$ and extends into a 1-D supramolecular chain through π–π stacking interactions. Compound **3** is also a mononuclear structure that aggregates into a 2-D supramolecular network through hydrogen bonds. The synthetic method has great influence on the structures of the complexes. The three complexes show photoluminescence.

Keywords: Zinc; 2,6-Naphthalenedisulfonate; Mononuclear complex; Supramolecular structure; Luminescence

1. Introduction

Inorganic–organic complexes based on metal centers and multifunctional bridging ligands have versatile architectures and potential applications in catalysis, magnetism, nonlinear optics, fluorescence sensing, separations, etc. [1–5]. A number of transition metal complexes have been reported using a variety of organic acids such as poly-carboxylate, phosphonate, and sulfonate [1–28] showing 1-D, 2-D, and 3-D polymeric structures with the organic acid as bridging ligand linking the metal centers [1–23]. Examples of 0-D metal–organic acid systems are limited [24–28]. Interest has focused on supramolecular architectures based on zero/low-dimensional structures through noncovalent self-assembly such as hydrogen bonds and π–π stacking interactions to further control structures and properties.

2,6-Naphthalenedisulfonate (2,6-NDS), a rigid ligand with multiple coordination sites, high symmetry, and large conjugated system, seems a good ligand for the construction of complexes with the interesting structures [15–17, 24, 25]. Here, three complexes, $[Zn(phen)_2(H_2O)(2,6\text{-}NDS)] \cdot 2H_2O$ (**1**), $[Zn(phen)_2(2,6\text{-}NDS)] \cdot H_2O$ (**2**), and $[Zn(2,2'\text{-}bipy)_2(H_2O)(2,6\text{-}NDS)] \cdot 3H_2O$ (**3**) (phen = 1,10-phenanthroline;

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*Corresponding author. Email: xiali@mail.cnu.edu.cn

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2,2′-bipy = 2,2′-bipyridine), have been synthesized. The complexes are mononuclear and are further assembled into supramolecular structures through noncovalent interactions. Many Zn-carboxylate complexes show coordination polymers with 1-D, 2-D, or 3-D structures through carboxylate bridging Zn^{2+} ions [18–23]. Herein, we present the synthesis, crystal structures, and characterization of the three complexes.

2. Experimental

2.1. *Materials*

$Zn(NO_3)_3 \cdot 6H_2O$ was prepared from the oxide with nitric acid. Other analytical grade chemicals and solvents were purchased and used without purification.

2.2. *Synthesis of complexes*

Preparation for **1**: 2,6-NDS sodium salt (0.0664 g, 0.2 mmol) and 1,10-phen (0.0792 g, 0.4 mmol) were mixed in 20 mL ethanol and heated with stirring. Then aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.0595 g, 0.2 mmol) was added to the solution. The resulting solution was filtered and colorless block single crystals were collected from the mother liquor after 2 weeks. Yield: 62%. $C_{34}H_{28}N_4O_9S_2Zn$ (766.09), Anal. Calcd (%): C, 53.30; H, 3.68; N, 7.31. Found (%): C, 53.12; H, 3.54; N 7.15. Selected IR [KBr pellet, ν (cm^{-1})]: 3456 br, 1516 m, 1428 s, 1233 vs, 1183 vs, 1141 m, 1092 vs, 1038 vs, 865 m, 847 s, 727 vs, 664 vs, 626 s, 570 m, 447 w, 418 w.

Preparation for **2**: A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.0595 g, 0.2 mmol), 2,6-NDS sodium salt (0.0664 g, 0.2 mmol), 1,10-phen (0.0792 g, 0.4 mmol), and deionized water (10 mL) was placed in a 25-mL Teflon-lined stainless steel autoclave and heated at 170°C for 3 days, then slowly cooled to room temperature. Yellow needle single crystals were obtained. Yield: 48%. $C_{34}H_{24}N_4O_7S_2Zn$ (730.06). Anal. Calcd (%): C, 55.94; H, 3.31; N, 7.67. Found (%): C, 55.69; H, 3.23; N, 7.88. Selected IR [KBr pellet, ν (cm^{-1})]: 3450 br, 1519 w, 1431 m, 1183 m, 1166 m, 1083 m, 1026 s, 869 m, 854 m, 726 m, 662 s, 625 s, 445 w, 426 w.

Preparation for **3**: A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.0595 g, 0.2 mmol), 2,6-NDS sodium salt (0.0664 g, 0.2 mmol), 2,2′-bipy (0.0624 g, 0.4 mmol), and deionized water (7 mL) was placed in a 25-mL Teflon-lined stainless steel autoclave and heated at 150°C for 3 days, then slowly cooled to room temperature. The resulting clear solution was filtered and the filtrate was kept undisturbed; colorless block single crystals were obtained from the mother liquor after 2 weeks. Yield: 54%. $C_{30}H_{30}N_4O_{10}S_2Zn$ (736.07). Anal. Calcd (%): C, 48.95; H, 4.11; N, 7.61. Found (%): C, 48.71; H, 4.03; N, 7.43. Selected IR [KBr pellet, ν (cm^{-1})]: 3425 br, 1598 m, 1441 m, 1250 s, 1238 s, 1183 s, 1166 s, 1088 s, 1030 s, 767 m, 664 vs, 624 s, 444 w, 414 w.

2.3. *Single-crystal X-ray diffraction*

The X-ray single crystal data collections were performed on a Bruker Smart Apex II CCD diffractometer (Germany) equipped with graphite monochromated Mo-Kα

radiation ($\lambda = 0.71073$ Å) at 293(2) K. Semiempirical absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL-97 (University of Gottingen, Germany, 1997) [29, 30]. All non-hydrogen atoms in the three complexes were refined anisotropically. Hydrogens of water were located by difference Fourier map and refined with distance restraints for O–H and H $\cdots$ H (0.96 and 1.52 Å, respectively) and one variable isotropic U for all. Other hydrogen atoms were placed in calculation positions. The summary of crystal data for **1**–**3** are listed in table 1 and selected bond distances and angles in tables 2–4.

2.4. *Physical measurement*

Elemental analyses were performed using an Elementar Vario EL analyzer (Germany). IR spectra were recorded with a Bruker EQUINOX-55 spectrometer (Germany) using KBr pellets. Thermogravimetric-differential thermogravimetric analyses (TG-DTA) measurements were carried out on a WCT-1A Thermal Analyzer (Beijing Optical Instrument Factory, China) at a heating rate of 10°C min^{-1} in air. Solid-state luminescence spectra were recorded on an F-4500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) at room temperature.

Table 1. Crystal data and structure refinement for **1**, **2** and **3**.

	1	**2**	**3**
Empirical formula	$C_{34}H_{28}N_4O_9S_2Zn$	$C_{34}H_{24}N_4O_7S_2Zn$	$C_{30}H_{30}N_4O_{10}S_2Zn$
Formula weight	766.09	730.06	736.07
Temperature (K)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P1$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions (Å, °)			
a	7.76450(10)	7.46040(10)	13.3308(2)
b	8.33540(10)	12.70130(10)	15.4330(2)
c	13.2926(2)	16.6160(2)	16.48300(10)
α	105.8420(10)	74.1530(10)	90
β	96.0500(10)	89.5020(10)	107.9330(10)
γ	101.4890(10)	81.6580(10)	90
Volume (Å^3), Z	799.309(19), 1	1497.82(3), 2	3226.37(7), 4
Calculated density (mg m^{-3})	1.592	1.619	1.515
Absorption coefficient (mm^{-1})	0.964	1.020	0.954
F (000)	394	748	1520
Reflections collected	7676	14,509	16,962
Independent reflection	4358 [R(int) = 0.0147]	6823 [R(int) = 0.0188]	7509 [R(int) = 0.0171]
Data/restraints/parameters	4358/3/452	6823/3/440	7509/12/447
Goodness-of-fit on F^2	1.056	1.014	0.999
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0205$, $wR_2 = 0.\ 0.0532$	$R_1 = 0.0348$, $wR_2 = 0.0899$	$R_1 = 0.0501$, $wR_2 = 0.1441$
R indices (all data)	$R_1 = 0.0210$, $wR_2 = 0.0534$	$R_1 = 0.0456$, $wR_2 = 0.0956$	$R_1 = 0.0664$, $wR_2 = 0.1579$
Largest difference peak and hole (e Å^{-3})	0.234 and −0.325	0.425 and −0.354	1.370 and −0.575

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

O(1w)–Zn(1)	2.1305(16)	O(5)–Zn(1)	2.2475(17)
N(1)–Zn(1)	2.118(2)	N(2)–Zn(1)	2.1471(19)
N(3)–Zn(1)	2.158(2)	N(4)–Zn(1)	2.111(2)
N(4)–Zn(1)–N(1)	176.44(9)	N(4)–Zn(1)–O(1w)	92.33(7)
N(1)–Zn(1)–O(1w)	91.15(7)	N(4)–Zn(1)–N(2)	98.49(7)
N(1)–Zn(1)–N(2)	78.28(8)	O(1w)–Zn(1)–N(2)	163.30(6)
N(4)–Zn(1)–N(3)	78.53(8)	N(1)–Zn(1)–N(3)	100.36(8)
O(1w)–Zn(1)–N(3)	96.01(7)	N(2)–Zn(1)–N(3)	98.56(7)
N(4)–Zn(1)–O(5)	89.43(7)	N(1)–Zn(1)–O(5)	91.55(7)
O(1w)–Zn(1)–O(5)	86.11(6)	N(2)–Zn(1)–O(5)	81.35(7)
N(3)–Zn(1)–O(5)	167.83(7)		

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

N(1)–Zn(1)	2.0744(18)	N(2)–Zn(1)	2.1149(16)
N(3)–Zn(1)	2.0736(17)	N(4)–Zn(1)	2.1258(17)
O(1)–Zn(1)	2.0354(15)		
O(1)–Zn(1)–N(3)	116.96(6)	O(1)–Zn(1)–N(1)	109.31(6)
N(3)–Zn(1)–N(1)	133.73(7)	O(1)–Zn(1)–N(2)	88.42(6)
N(3)–Zn(1)–N(2)	100.54(6)	N(1)–Zn(1)–N(2)	79.96(7)
O(1)–Zn(1)–N(4)	88.91(6)	N(3)–Zn(1)–N(4)	79.69(7)
N(1)–Zn(1)–N(4)	102.02(7)	N(2)–Zn(1)–N(4)	177.09(7)

Table 4. Selected bond lengths (Å) and angles (°) for **3**.

O(1)–Zn(1)	2.237(3)	O(7)–Zn(1)	2.067(3)
N(1)–Zn(1)	2.134(3)	N(2)–Zn(1)	2.177(3)
N(3)–Zn(1)	2.122(3)	N(4)–Zn(1)	2.147(3)
O(7)–Zn(1)–N(3)	165.19(13)	O(7)–Zn(1)–N(1)	91.70(13)
N(3)–Zn(1)–N(1)	97.88(11)	O(7)–Zn(1)–N(4)	95.36(13)
N(3)–Zn(1)–N(4)	77.01(11)	N(1)–Zn(1)–N(4)	168.91(12)
O(7)–Zn(1)–N(2)	96.15(14)	N(3)–Zn(1)–N(2)	97.14(11)
N(1)–Zn(1)–N(2)	75.80(12)	N(4)–Zn(1)–N(2)	94.91(12)
O(7)–Zn(1)–O(1)	86.70(12)	N(3)–Zn(1)–O(1)	82.28(10)
N(1)–Zn(1)–O(1)	88.64(10)	N(4)–Zn(1)–O(1)	100.28(10)
N(2)–Zn(1)–O(1)	164.23(10)		

3. Results and discussion

3.1. *Structural description*

The hydrothermal synthesis and conventional solution reaction may lead to diverse structures of metal–carboxylate complexes. Therefore, we expect to construct Zn-complexes with different structures by different syntheses. The complexes $[\mathrm{Zn(phen)_2(H_2O)(2,6\text{-}NDS)}]\cdot 2\mathrm{H_2O}$ (**1**) and $[\mathrm{Zn(phen)_2(2,6\text{-}NDS)}]\cdot \mathrm{H_2O}$ (**2**) were obtained by conventional solution and hydrothermal syntheses, respectively. Using 2,6-NDS and 2,2′-bipy, we tried solvent and hydrothermal methods, but could not get single crystals. However, we obtained single crystals of complex $[\mathrm{Zn(2,2'\text{-}bipy)_2(H_2O)(2,6\text{-}NDS)}]\cdot 3\mathrm{H_2O}$ (**3**) by the combination of hydrothermal reaction and solution evaporation. According to literature [24, 25], we varied conditions such as pH and temperature.

$[Zn(phen)_2(H_2O)(2,6\text{-NDS})]\cdot 2H_2O$ (**1**) was obtained by conventional solution reaction as a mononuclear molecule with space group *P1*, as shown in figure 1(a). The space group *P1* indicates a chiral structure for **1**. The Zn^{2+} is six-coordinate with four nitrogens of two phen, one oxygen of 2,6-NDS anion, and one water in a distorted octahedral coordination environment. Atoms N1, N2, N4, and O1w are in the equatorial plane with mean deviation of 0.128 Å. N3 and O5 are in the axial positions

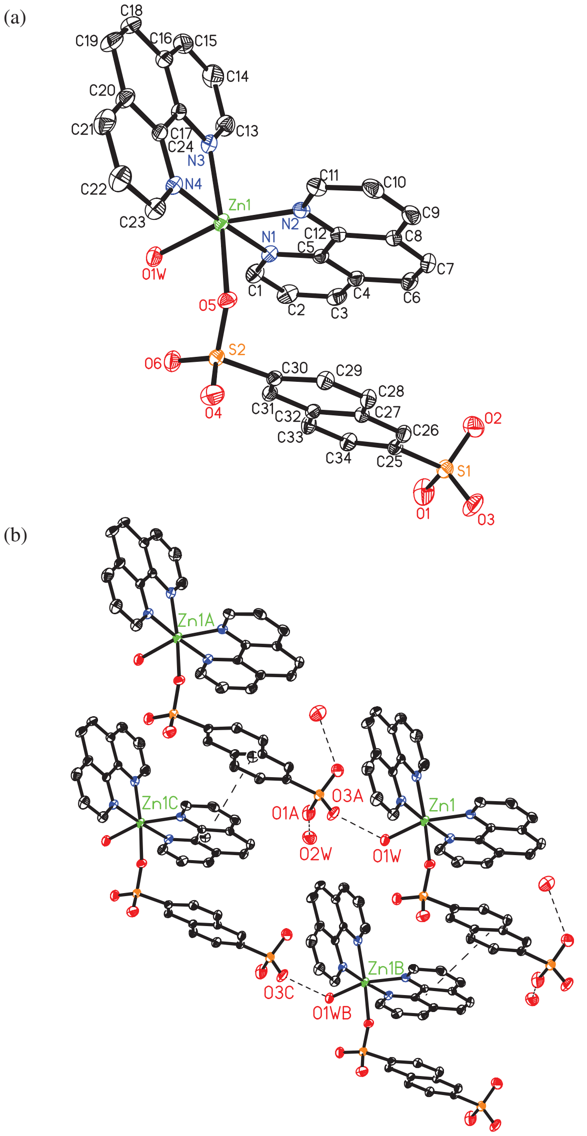

Figure 1. (a) Molecular structure of **1** at 30% probability displacement ellipsoids. Uncoordinated water molecules are omitted. (b) 2-D supramolecular network of **1** by hydrogen bonds and π–π stacking interactions along the *a*-axis.

with the angle N3–Zn1–O5 of 167.82(6)°. The bond angles of N1–Zn1–O5 and O1w–Zn1–O5 are 91.54(7)° and 86.15(6)°, respectively, close to the ideal number of 90°, indicating slight distortion. The Zn–N bond distances vary from 2.1087(19) to 2.1584(19) Å, with an average of 2.145 Å. The Zn–O(water) and Zn–O(sulfonate) bond distances are 2.1307(14) and 2.2474(16) Å, respectively. 2,6-NDS is monodentate. The two chelating phens create steric hindrance around Zn^{2+} with a twisting angle of 103.8°, indicating a greater twist between the two rings. The aromatic rings of phen(N1/N2) and 2,6-NDS are almost parallel with the dihedral angle of 5.2°.

There are intermolecular hydrogen bonds between the coordinated water molecule and the uncoordinated sulfonate, O1W···O3 [x, $y+1$, $z+1$], 2.758 Å, 166.94°; O1W···O6, 2.784 Å, 161.01°, giving a 1-D chain (figure 1a). Free water molecules in **1** are attached to the chain through hydrogen bonds with the uncoordinated sulfonate, O2W···O1 [x, $y+1$, $z+1$], 2.909 Å, 165.70°. In addition, π–π stacking interactions are formed between chains. The centroid–centroid distance between the phen(N1/N2) ring and the 2,6-NDS naphthalene ring from adjacent 1-D chain is 3.61 Å, giving intermolecular π–π stacking interactions. Thus, the molecule unit is connected by hydrogen bonds and π–π stacking interactions and extended into a 2-D supramolecular (4, 4) rectangular grid-like framework as shown in figure 1(b). The dimension of the rectangular grid is about 8.335×13.626 Å^2 based on the Zn···Zn separation.

In the synthesis of **2**, the reactants 2,6-NDS, phen and $Zn(NO_3)_2 \cdot 6H_2O$ are the same as for **1**, but with different reaction conditions. $[Zn(phen)_2(2,6\text{-}NDS)] \cdot H_2O$ (**2**) obtained under hydrothermal condition shows a mononuclear structure, crystallizing in centrosymmetric space group $P\bar{1}$. As shown in figure 2(a), Zn^{2+} is coordinated by four nitrogens of two phen and one oxygen of monodentate 2,6-NDS anion in a slightly distorted square pyramid. The apical position is occupied by Zn–O(sulfonate) [2.0354(15) Å] and the square plane is formed by nitrogens with a mean deviation of 0.4328 Å. The Zn–N distances vary from 2.0744(18) to 2.1258(17) Å with an average of 2.097 Å. The two phen molecules are not coplanar with a dihedral angle of 43.8°; the phen(N3/N4) and the 2,6-NDS naphthalene ring are almost parallel with a dihedral angle of 3.6°. The π–π stacking interactions along the *b*-axis are observed between the phen(N3/N4) and 2,6-NDS naphthalene ring of adjacent molecule, with the centroid–centroid distance of 3.92 Å. The molecules stack to give a 1-D supramolecular chain as shown in figure 2(b). The nearest Zn···Zn distance is 7.460 Å.

$[Zn(2,2'\text{-}bipy)_2(H_2O)(2,6\text{-}NDS)] \cdot 3H_2O$ (**3**) shows a mononuclear structure (figure 3a), crystallizing in monoclinic system $P2_1/n$, different from **1**. However, the Zn^{2+} in **3** has similar coordination as observed in **1**. Zn^{2+} is coordinated by monodentate 2,6-NDS, two chelating 2,2′-bipy, and one water in a ZnN_4O_2 distorted octahedron. Bond angles of N2–Zn1–O1, N1–Zn1–O1, and N3–Zn1–O1 are 164.82(10)°, 88.64(10)°, and 82.28(10)°, respectively, exhibiting deviation from ideal octahedral geometry. The average bond distances of Zn–N, Zn–O(water), and Zn–O(sulfonate) are 2.1332, 2.067(3), and 2.237(3) Å, respectively, comparable to those in **1**. The two 2,2′-bipy ligands bend toward Zn^{2+} with a dihedral angle of 83.4°. However, 2,2′-bipy(N3/N4) pyridyl ring and the 2,6-NDS naphthalene ring are almost parallel with a dihedral angle of 2.2°.

There exist abundant hydrogen bonds in **3** forming the 2-D supramolecular structure (figure 3b). The complex contains three lattice waters (O8, O9, and O10) that participate extensively in hydrogen bond interactions forming $(H_2O)_3$ clusters with O···O distances of 2.708 and 2.737 Å. The $(H_2O)_3$ clusters form hydrogen bonds

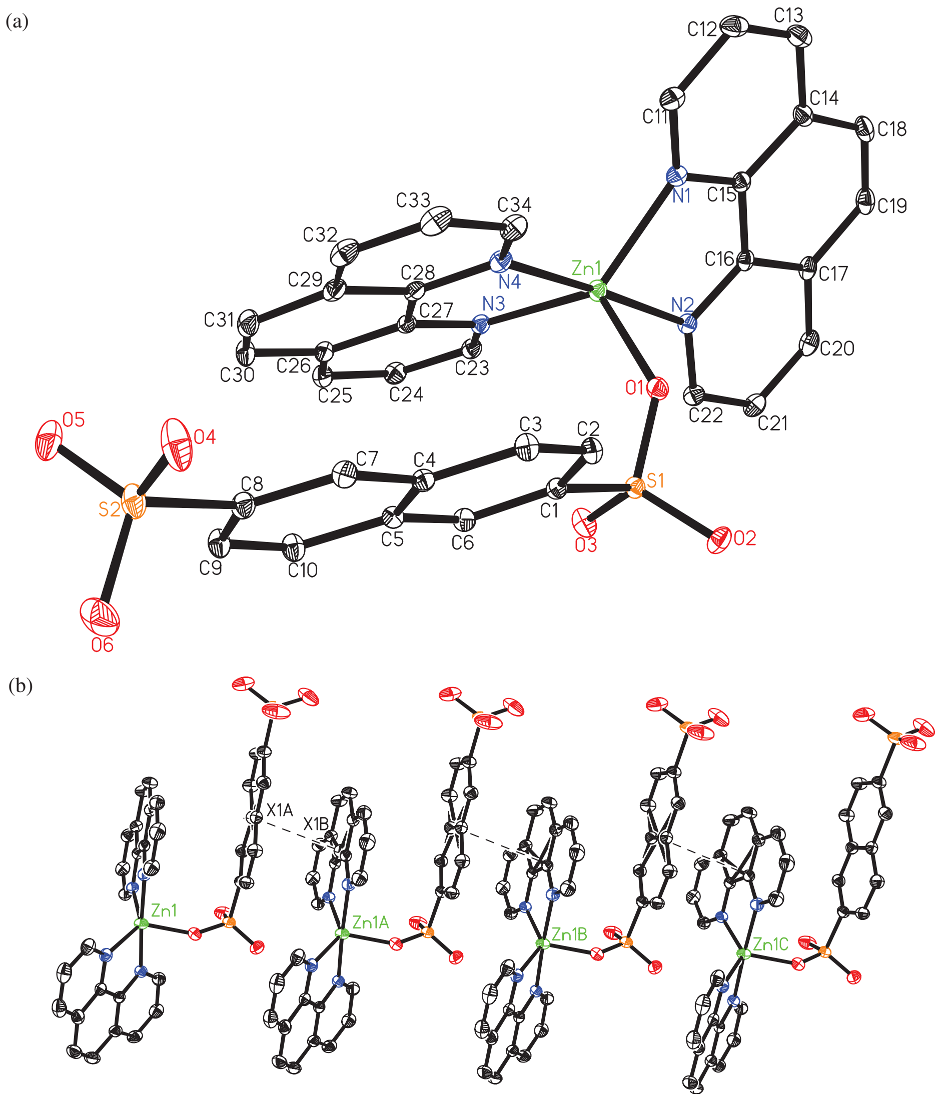

Figure 2. (a) Molecular structure of **2** at 30% probability displacement ellipsoids. Uncoordinated water molecules are omitted. (b) 1-D supramolecular chain of **2** by π–π stacking along the *b*-axis.

with noncoordinated sulfonate and coordinated water: O8 $\cdots$ O5, 2.728 Å; O9 $\cdots$ O6, 2.664 Å; O9 $\cdots$ O2, 2.908 Å; O10 $\cdots$ O4, 2.626 Å; O8 $\cdots$ O7, 2.635 Å, generating a 2-D supramolecular network. In addition, there are intermolecular π–π stacking interactions between 2,2′-bipy(N3/N4) pyridyl ring and the 2,6-NDS naphthalene ring of adjacent units at 3.66 Å, similar to **1**.

Compounds **1** and **2** show different formations and dimensional structures as a result of the different reaction conditions. The different numbers of coordinated and noncoordinated water molecules in **1** and **2** lead to different intermolecular interactions. The hydrogen bonds in **1** link monomers into 1-D chains, which are joined via π–π stacking interactions to afford a 2-D supramolecular network. The 1-D supramolecular

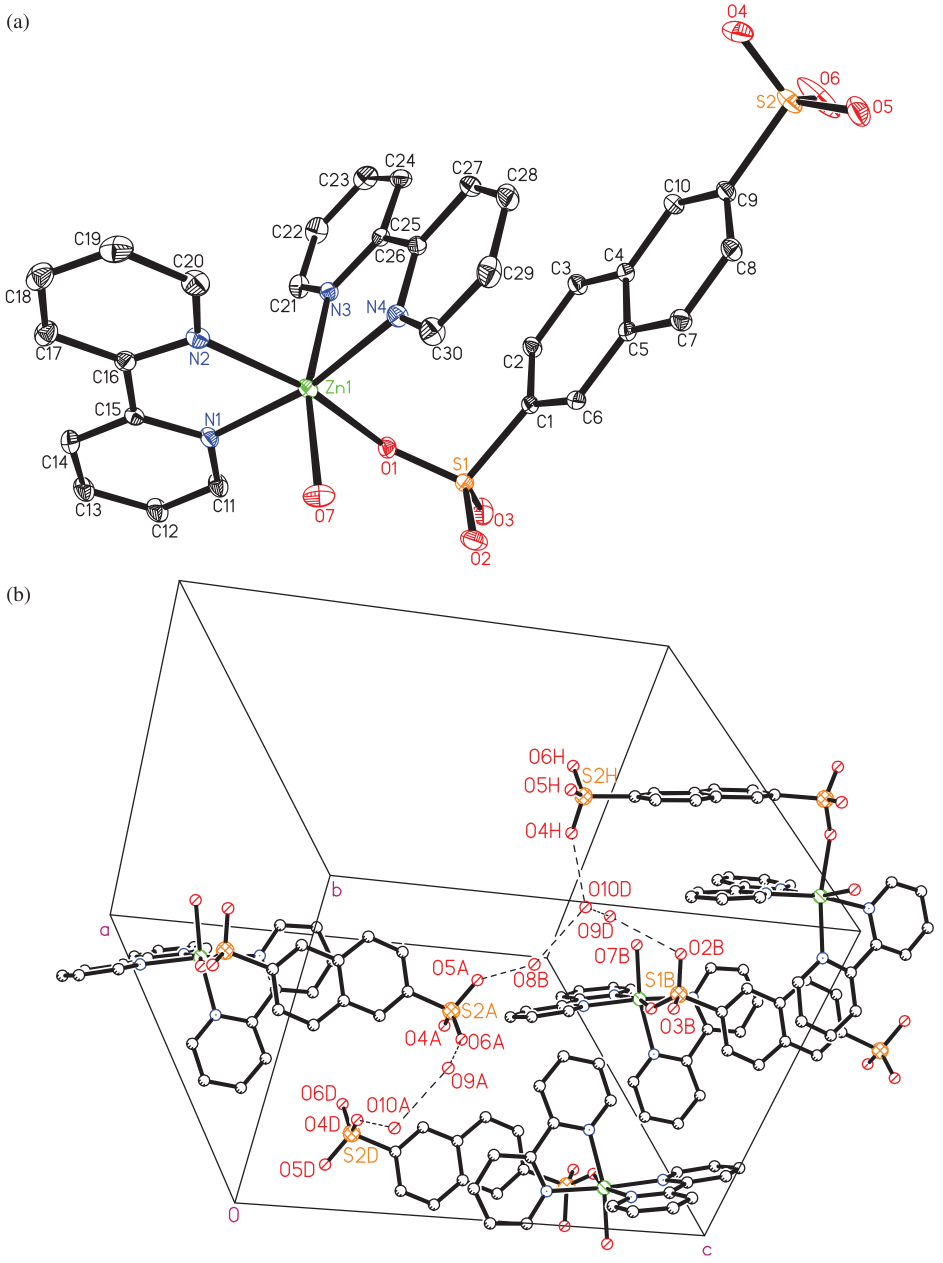

Figure 3. (a) Molecular structure of **3** at 30% probability displacement ellipsoids. Uncoordinated water molecules are omitted. (b) 2-D supramolecular network of **3** by hydrogen bonds.

chain of **2** is formed by π–π stacking interactions. In **1** and **2**, the 2,6-NDS ligand has the same coordination mode but differ by *ca* 0.212 Å for Zn–O(sulfonate) bond, which significantly exceed systematic errors for this parameter. The elongation of the Zn–O(sulfonate) bond in **1** is caused by the hydrogen bonds in the complex.

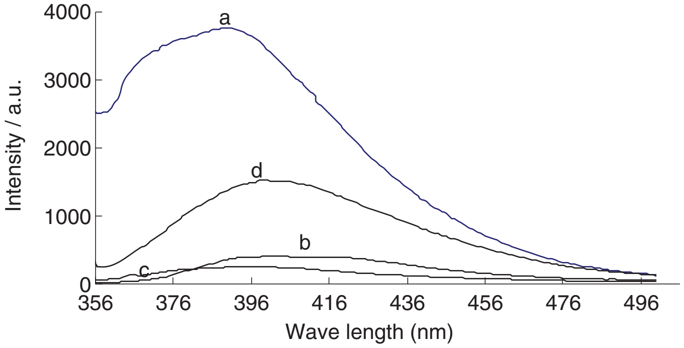

Figure 4. Photoluminescent emission spectra of 2,6-NDS (a), **1** (b), **2** (c), and **3** (d) in solid state at room temperature ($\lambda_{ex} = 335$ nm).

However, the Zn–N(phen) bond distances are almost equal for **1** and **2** with differences of *ca* 0.048 Å. The structures and metal–ligand bond distances of **1** and **3** are similar. Compounds **1–3** are a few examples of complexes with 2,6-NDS.

3.2. *Luminescence properties*

Solid-state fluorescence spectra of the complexes and 2,6-NDS were measured upon the excitation of 335 nm at room temperature, as shown in figure 4. The fluorescence emission spectrum of free 2,6-NDS shows strong and broad emission at 391 nm. The three complexes exhibit broad emission bands at about 400, 396, and 399 nm. The fluorescence emission spectra of the complexes blue-shift as for free ligand; however, emission intension is weaker. Therefore, the fluorescence emission of the three complexes is probably due to π^*–π transitions of the ligands and Zn^{2+} ion may quench fluorescence emission of the ligand.

3.3. *Thermogravimetric analysis*

The TG-DTA analyses of the three complexes were studied in air from 20°C to 1000°C. The first weight loss starts at 157°C, 147°C, and 94°C for **1**, **2,** and **3**, respectively, with the loss of all water molecules. The corresponding weight losses are 7.25% (Calcd 7.05%) for **1**, 2.73% (Calcd 2.47%) for **2**, and 9.59% (Calcd 9.79%) for **3**. The organic ligands completely decomposed at 616°C, 578°C, and 582°C for **1**, **2,** and **3**, respectively. The total mass losses are 91.64% (Calcd 89.38%) for **1**, 91.6% (Calcd 88.85%) for **2**, and 88.40% (Calcd 88.95%) for **3**. The residues are ZnO.

4. Conclusions

We have constructed three new complexes by different methods using 2,6-NDS and 1,10-phen or 2,2′-bipy. 2,6-NDS coordinates monodentate to Zn^{2+} leading to mononuclear structures. Supramolecular structures are built up by hydrogen bonds and/or π–π stacking interactions. Reaction methods play important roles in the construction of complexes, the crystal packing is determined by the number of noncovalent interactions, such as hydrogen bonds and π–π stacking interactions, and hydrogen bonds affect metal–ligand bond distances.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Center as supplementary publication: CCDC-711522, 699805, and 699804 for **1**, **2,** and **3**, respectively. These data can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk.

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