

Synthesis, Structures and Photoluminescent Properties of Two Novel Zinc(II) Compounds Constructed from 5-Sulfoisophthalic Acid

Yu-Lan Zhu,^{†,*} Xue-Ling Tang,^{†,‡} Kui-Rong Ma,[†] Hao Chen,[†] Feng Ma,[‡] and Lian-Hua Zhao[‡]

[†]Jiangsu Key Laboratory for the Chemistry of Low-Dimensional Materials, Huaiyin Normal University, Huaian 223300, P. R. China. *E-mail: yulanzhu2008@126.com

[‡]Department of Chemistry, College of Science, Yanbian University, Yanji 133002, P. R. China
Received March 14, 2010, Accepted April 17, 2010

Hydrothermal reaction of zinc(II) salts with 5-sulfoisophthalic acid monosodium salt ($\text{NaO}_3\text{SC}_6\text{H}_3\text{-1,3-(COOH)}_2$, $\text{NaH}_2\text{-SIP}$) and 1,10-phenanthroline (phen) led to two new compounds, $[\text{Zn}(\text{phen})_3]\cdot 2\text{H}_2\text{SIP}\cdot 4\text{H}_2\text{O}$ (**1**) and $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{SIP}\cdot 2\text{H}_2\text{O}$ (**2**). They were characterized by element analysis, IR spectroscopy, thermalgravimetric analysis (TGA), X-ray powder diffraction (XRD), and single-crystal X-ray diffraction. Both compounds **1-2** represent the first example of Zn/phen/SIP system. The Zn (II) ion in **1** is six-coordinated by six nitrogen atoms from three phen molecules, and the H_2SIP^- ligands engage in the formation of hydrogen bond. The Zn(II) ion in **2** is coordinated by four nitrogen atoms from two phen molecules and two oxygen atoms from two water molecules. Moreover, both **1** and **2** are assembled into 3D supramolecular architectures by hydrogen bonds (O-H \cdots O) and π - π interactions. Solvent water molecules occupying voids of the compounds serve as receptors or donors of the extensive O-H \cdots O hydrogen bonds.

Key Words: Hydrothermal synthesis, Crystal structures, Supramolecular, Photoluminescent properties

Introduction

The rational assembly of the supramolecular architectures from organic ligands and metal ions is currently of significant interest due to their interesting properties, versatile intriguing structure and topologies and promising applications in the areas of catalysis, chirality, conductivity, luminescence, magnetism, and porosity.¹⁻¹¹ Supramolecular interactions, which contain hydrogen bond, π - π stacking, electrostatic attraction and so on, play a crucial role in formation of geometry and properties of the architectures as well as potential applications.¹²⁻¹⁵

Many chemists devoted to the study of self-assembly of the supramolecules based on the metal ions and the mixed ligands containing multicarboxyl group and *N*-heterocycle.¹⁶⁻¹⁹ One of self-assembly technique is to combine low-dimensional molecules containing metal with free organic ligands through weak intermolecular interactions under the hydrothermal condition.²⁰ 1,10-Phenanthroline (phen) has attracted enormous interest in complexation of the metal cations because of its structural rigidity, planarity, aromaticity, basicity and chelating capability. Many metal phenanthrolines have been reported.^{21,22} The 5-sulfoisophthalic acid (H_3SIP) ligand including two carboxylate and one sulfonate groups, as a free ligand for supramolecular frameworks, can facilitate the formation of hydrogen bond and achievement of high-dimensional supramolecular networks. In addition, π - π stacking interactions between the aromatic rings may promote supramolecular architectures.²³

To the best of our knowledge, the zinc/phen/SIP system has never been reported in the previous literature. Herein, we prepared zinc/phen/SIP supramolecular compounds. In this context, two 3D supramolecular compounds, $[\text{Zn}(\text{phen})_3]\cdot 2\text{H}_2\text{SIP}\cdot 4\text{H}_2\text{O}$ (**1**) and $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{SIP}\cdot 2\text{H}_2\text{O}$ (**2**) were prepared by hydrothermal reaction and characterized by single-crystal X-ray diffraction, IR, thermalgravimetric analysis (TGA), powder X-

ray diffraction (XRD). The luminescent properties are also discussed.

Experimental Section

All reagents were purchased from commercial sources and used without further purification. Element analyses were performed on a Perkin-Elmer 2400LS elemental analyzer. IR spectra were recorded from 4000 to 400 cm^{-1} with a Nicolet AVATAR360 instrument. The thermal gravimetric analyses (TGA) were carried out with a TGA/SDTA851e differential thermal analyzer with a rate of 10 $^\circ\text{C}/\text{min}$. Power X-ray diffraction patterns were performed on a ARL X'TRA diffractometer using $\text{Cu-K}\alpha$ radiation. Emission spectra in the solid state at room temperature were taken on a Perkin-Elmer LS-55 fluorescence spectrophotometer.

Preparation of $[\text{Zn}(\text{phen})_3]\cdot 2\text{H}_2\text{SIP}\cdot 4\text{H}_2\text{O}$ (1**).** An aqueous water solution (5 mL) of $\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$ (0.043 g, 0.2 mmol), NaH_2SIP (0.053 g, 0.2 mmol) and 1,10-phenanthroline (0.158 g, 0.8 mmol) was placed in a 23 mL Teflon-lined stainless steel vessel. The vessel was sealed and then heated at 413 K for 72 h. The colorless brick-shaped crystals were obtained. Yield: 30%. Anal. Calcd (%) for **1**: C, 53.45; H, 3.62; N, 7.19; Found (%): C, 53.15; H, 3.43; N, 7.05. IR (KBr, cm^{-1}): 3412 s, 1614 m, 1564 m, 1517 w, 1424 m, 1382 s, 1106 s, 1056 s, 1001 s, 848 w, 785 w, 723 w, 622 w, 473 m.

Preparation of $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{SIP}\cdot 2\text{H}_2\text{O}$ (2**).** A mixture of $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ (0.115 g, 0.4 mmol), NaH_2SIP (0.053 g, 0.2 mmol) and 1,10-phenanthroline (0.020 g, 0.1 mmol) with 5 mL distilled water was sealed in a 23 mL Teflon-lined stainless steel vessel and heated to 413 K, kept the temperature for 3 days, and then cool to room temperature. The colorless prism-shaped product was obtained and washed by water and dried in air. Yield: 20%. Anal. Calcd (%) for **1**: C, 48.62; H, 3.47; N, 5.67;

Table 1. Crystallographic data and structure refinement parameters for **1** and **2**

| | 1 | 2 |
|--|--|--|
| Empirical formula | C ₅₂ H ₄₂ N ₆ O ₁₈ S ₂ Zn | C ₄₀ H ₃₄ N ₄ O ₁₈ S ₂ Zn |
| Mr | 1168.41 | 988.20 |
| Crystal system | Triclinic | Monoclinic |
| Space group | <i>P</i> $\bar{1}$ | <i>P</i> 2(1)/ <i>n</i> |
| <i>a</i> /Å | 12.822(2) | 11.4311(1) |
| <i>b</i> /Å | 12.858(2) | 29.519(4) |
| <i>c</i> /Å | 16.156(3) | 13.2321(1) |
| α /° | 67.196(2) | 90.00 |
| β /° | 86.246(2) | 113.4700(1) |
| γ /° | 88.167(3) | 90.00 |
| <i>V</i> /Å ³ | 2450.0(7) | 4095.6(9) |
| <i>Z</i> | 2 | 4 |
| <i>D</i> _c /Mg·m ⁻³ | 1.584 | 1.603 |
| μ /mm ⁻¹ | 0.674 | 0.788 |
| θ range | 2.29 - 21.49 | 2.17 - 24.69 |
| Unique reflections | 8521 | 7226 |
| Observed reflections | 5327 | 5729 |
| Parameters | 721 | 617 |
| <i>F</i> (000) | 1204 | 2032 |
| <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] | 0.0602, 0.1397 | 0.0731, 0.1846 |
| <i>R</i> ₁ , <i>wR</i> ₂ [all data] | 0.1037, 0.1602 | 0.0903, 0.1954 |
| <i>GOF</i> | 1.030 | 1.084 |
| Largest peak and hole (e Å ⁻³) | 0.77 and -0.69 | 1.48 and -1.35 |

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

| 1 | | | |
|-----------|-----------|-----------|-----------|
| Zn1–N1 | 2.184(4) | Zn1–N4 | 2.136(4) |
| Zn1–N2 | 2.136(4) | Zn1–N5 | 2.179(4) |
| Zn1–N3 | 2.152(4) | Zn1–N6 | 2.215(4) |
| N1–Zn1–N2 | 76.96(1) | N2–Zn1–N3 | 94.27(2) |
| N1–Zn1–N3 | 99.04(1) | N2–Zn1–N4 | 165.32(2) |
| N1–Zn1–N4 | 91.95(1) | N2–Zn1–N5 | 97.95(1) |
| N1–Zn1–N5 | 96.30(1) | N2–Zn1–N6 | 94.46(1) |
| N1–Zn1–N6 | 167.72(1) | | |
| 2 | | | |
| Zn1–O1 | 2.116(5) | Zn1–N2 | 2.148(5) |
| Zn1–O2 | 2.107(4) | Zn1–N3 | 2.137(5) |
| Zn1–N1 | 2.146(5) | Zn1–N4 | 2.196(5) |
| O1–Zn1–O2 | 86.71(2) | N1–Zn1–N2 | 78.2(2) |
| O1–Zn1–N1 | 93.41(2) | N1–Zn1–N3 | 173.56(2) |
| O1–Zn1–N2 | 170.53(2) | N1–Zn1–N4 | 97.08(2) |
| O1–Zn1–N3 | 89.45(2) | N2–Zn1–N3 | 99.34(2) |
| O1–Zn1–N4 | 91.61(2) | N2–Zn1–N4 | 93.78(2) |

Found (%): C, 48.57; H, 3.31; N, 5.64. IR (KBr, cm⁻¹): 3405 s, 3089 s, 1688 s, 1624 w, 1606 w, 1519 w, 1450 w, 1428 m, 1195 s, 1112 s, 1046 s, 998 w, 852 m, 727 m, 673 w, 619 m, 487 w.

X-ray crystallography. Single crystal of compounds **1** and **2**

were mounted on a Bruker Smart CCD using Mo K α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator at room temperature. All structure were solved by the direct method and successive Fourier difference syntheses, and refined by the full-matrix least-squares method on *F*² with anisotropic thermal parameters for all non-hydrogen atoms using SHELXS-97²⁴ and SHELXL-97²⁵ programs, respectively. The hydrogen atoms of the ligand were generated theoretically onto the specific atoms and refined isotropically with the fixed thermal factors. H atoms of water were added by the difference Fourier maps and refined with constrained. The details of the crystal structures and refinements are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2. CCDC Nos. 758987 and 758988 contain the supplementary crystallographic data for compounds **1** and **2**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Description of crystal structures.

[Zn(phen)₃·2H₂SIP·4H₂O (1): The crystal structure of [Zn(phen)₃·2H₂SIP·4H₂O] is depicted in Figure 1. The asymmetric unit consists of one Zn(II) ion, three phen molecules, two H₂SIP⁻ ligands and four lattice water molecules. Zn(1) ion, which is bonded to six N atoms from the three 1,10-phen, displays a distorted [ZnN₆] octahedral coordination geometry. The Zn–N (2.136(4)–2.215(4) Å) (see Table 2) bond distances are comparable to those reported in similar compounds.^{26,27} It is different from the previous literature of Zn–SIP system^{28–30} that the SIP units are not coordinated. For the sake of charge balance, the two uncoordinated carboxyl groups of the SIP ligands should be protonated H₂SIP⁻, which forms hydrogen bond with the carboxylate oxygen atoms from neighboring unit (symmetry operator: O(1): 2-x, 1-y, 1-z; O(9): 2-x, 2-y, -z). The O(2)–H(2A)···O(1)ⁱ hydrogen bond length and angle are 2.682(4) Å and 176.2°, respectively. The O(8)–H(8O)···O(9)ⁱⁱⁱ hydrogen bond length and angle are 2.603(4) Å and 170.3°, respectively. The oxygen atoms from carboxyl groups and oxygen atoms of SO₃⁻ groups from neighboring unit (symmetry operator: O(5): 2-x, 1-y, -z) form hydrogen bond (O(4)–H(4)···O(5)ⁱⁱ) with the bond length and angle are 2.634(5) Å and 157.9°, respectively. There are also O–H···O hydrogen bonds between carboxyl groups and free water molecules (O(10)–H(10A)···O(15)^{iv}, 2.542(5) Å, 150.1°) and between free water molecules and SO₃⁻ groups (O(15)–H(15A)···O(12), 2.714(5) Å, 144.2°; O(16)–H(16B)···O(14)^v, 2.734(7) Å, 139(9)°; O(17)–H(17A)···O(6)^{vi}, 2.878(5) Å, 156.9°; O(18)–H(18)C···O(7)^v, 2.636(9) Å, 145.4°). The hydrogen bond lengths and angles are listed in Table 3. Additionally, O–H···O hydrogen bond interactions among the free water molecules play a crucial role in formation of 2D supramolecular layer.

Within the double-chain, there are 10-membered rings (ring 1, O(15)–O(16)–O(14)–S(2)–O(12)–O(15)–O(16)–O(14)–S(2)–O(12), ring 2, O(6)–S(1)–O(7)–O(18)–O(17)–O(6)–S(1)–O(7)–O(18)–O(17), H atoms are omitted.) which are from four lattice water molecules and the sulfonate moieties of two SIP ligands (Figure 2a). 1D anionic double-chain [H₂SIP–H₂O]_n⁻ via the

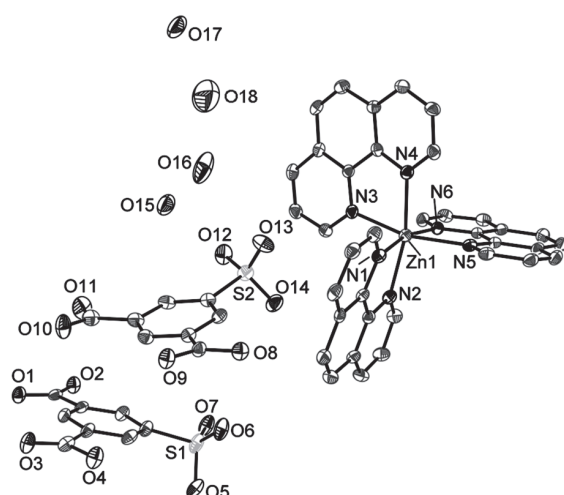


Figure 1. View of **1** with 30% probability displacement ellipsoids (H atoms are omitted for clarity).

hydrogen bonds generate 2D supramolecular anionic layer along the *z*-axis (Figure 2b, 2c). Interestingly, $[\text{ZnN}_6]_n^{2+}$ octahedron are placed in voids between adjacent anionic layers (Figure 2d). So a three-dimensional supramolecular framework is further constructed through electrostatic attraction between the anionic layer and cationic $[\text{ZnN}_6]_n^{2+}$ octahedron. Simultaneously, the extensive hydrogen bond interactions link 2D layers into a three-dimensional supramolecular framework, as illustrated in Figure 2c, which can be also regarded as the alternant stacking of the anionic layers and the $[\text{Zn}(\text{phen})_3]^{2+}$ cationic moieties (Figure 2d).

The three-dimensional supramolecular framework is further stabilized by π - π interactions. The π - π interactions are observed between the aromatic rings of the SIP ligands and the pyridine rings of the phen ligands, with the centroid-to-centroid distances in the range of 3.666(3)-3.917(3) Å. (see Table S1)

$[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{SIP} \cdot 2\text{H}_2\text{O}$ (2**):** X-ray crystallography shows that the structure of **2** consists of 2D supramolecular layers in the *bc* plane, which are further connected into the 3D supramolecular framework *via* rich hydrogen bond and π - π interactions. In comparison to **1**, the structure of **2** is more complicated due to the water molecule involved in coordination to the zinc ion. The Zn(II) ion in **2** is six-coordinated by four N atoms from two phen and two O atoms from coordinated water molecules (Figure 3). The ligand H_2SIP^- is also uncoordinated, similar to that of **1**. The Zn(1) ion has distorted octahedral coordination geometry with the two positions taken up by two water molecules. The Zn-N distances are in the range of 2.137(5)-2.196(5) Å, which are in agreement with ones of compound **1**. The Zn-O bond distances are 2.116(5) Å for O(1), and 2.107(4) Å for O(2), respectively. These bond lengths are similar to those reported previously.^{26,27}

The asymmetric units are self-interconnected into a 3D supramolecular structure through seven types of hydrogen bonds between (a) the coordinated water molecules and sulfonate oxygen atoms (O(2)-H(2A)···O(4)ⁱⁱ, 2.712(14) Å, 167.3°; O(2)-H(2B)···O(10)ⁱⁱⁱ, 2.666(7) Å, 160.6°), (b) the coordinated water molecules and carboxylate oxygen atoms (O(1)-H(1A)···O(15)ⁱ,

Table 3. Hydrogen bond lengths (Å) and angles (°) for **1** and **2**

| | D-H | H···A | D···A | D-H···A |
|-------------------------------|---------|---------|-----------|---------|
| 1 | | | | |
| O2-H2A···O1 ⁱ | 0.82 | 1.86 | 2.682(4) | 176.2 |
| O4-H4···O5 ⁱⁱ | 0.82 | 1.86 | 2.634(5) | 157.9 |
| O8-H8O···O9 ⁱⁱⁱ | 0.82 | 1.79 | 2.603(4) | 170.3 |
| O10-H10A···O15 ^{iv} | 0.92 | 1.70 | 2.542(5) | 150.1 |
| O15-H15A···O12 | 0.88 | 1.95 | 2.714(5) | 144.2 |
| O15-H15B···O16 | 0.87 | 1.84 | 2.699(1) | 175.0 |
| O16-H16B···O14 ^v | 0.86(9) | 2.03(9) | 2.734(7) | 139(9) |
| O16-H16D···O18 | 0.85(1) | 1.96(1) | 2.507(1) | 120(1) |
| O17-H17A···O6 ^{vi} | 0.85 | 2.08 | 2.878(5) | 156.9 |
| O17-H17B···O18 | 0.85 | 1.90 | 2.702(1) | 156.9 |
| O18-H18C···O7 ^v | 0.91 | 1.84 | 2.636(9) | 145.4 |
| 2 | | | | |
| O1-H1A···O15 ⁱ | 0.82 | 1.94 | 2.752(5) | 168.2 |
| O1-H1B···O17 | 0.97 | 1.74 | 2.703(6) | 172.8 |
| O2-H2A···O4 ⁱⁱ | 0.85 | 1.87 | 2.712(14) | 167.3 |
| O2-H2B···O10 ⁱⁱⁱ | 0.85 | 1.85 | 2.666(7) | 160.6 |
| O9-H9A···O11 ^{vii} | 0.82(7) | 1.83(7) | 2.604(6) | 157(7) |
| O16-H16···O3 ^{viii} | 0.82 | 1.81 | 2.620(14) | 168.6 |
| O17-H17A···O8 | 0.86 | 2.11 | 2.905(7) | 152.5 |
| O17-H17B···O18 ^{vii} | 0.86 | 1.97 | 2.751(8) | 150.7 |
| O18-H18A···O5 ^{viii} | 0.87 | 1.92 | 2.71(3) | 152.8 |
| O18-H18B···O12 ⁱⁱⁱ | 0.86 | 1.95 | 2.778(8) | 162.1 |
| O7-H71···O13 ^{vi} | 0.84 | 1.80 | 2.633(6) | 170.5 |
| O14-H141···O6 ^{ix} | 0.85 | 1.74 | 2.593(6) | 173.5 |

Symmetry transformations used to generate equivalent atoms are as follows. Complex **1**: (i) 2-x, -y, 1-z; (ii) 2-x, 1-y, -z; (iii) 2-x, 2-y, -z; (iv) 2-x, 1-y, 1-z; (v) 1-x, 1-y, 1-z; (vi) x, y, 1+z. Complex **2**: (i) -1/2+x, 1/2-y, 1/2+z; (ii) x, y, -1+z; (iii) -1/2+x, 1/2-y, -1/2+z; (vi) 1/2-x, -1/2+y, 1/2-z; (vii) -1+x, y, z; (viii) 1+x, y, -1+z; (ix) 1/2-x, 1/2+y, 1/2-z.

2.752(5) Å, 168.2°), (c) the coordinated water molecules and free water molecules (O(1)-H(1B)···O(17), 2.703(6) Å, 172.8°), (d) the free water molecules and sulfonate oxygen atoms (O(18)-H(18A)···O(5)^{viii}, 2.71(3) Å, 152.8°; O(18)-H(18B)···O(12)ⁱⁱⁱ, 2.778(8) Å, 162.1°), (e) the free water molecules and carboxylate oxygen atoms (O(17)-H(17A)···O8, 2.905(7) Å, 152.5°), (f) the free water molecules (O(17)-H(17B)···O(18)^{vii}, 2.751(8) Å, 150.7°), (g) the carboxylate oxygen atoms (O(7)-H(71)···O(13)^{vi}, 2.633(6) Å, 170.5°; O(14)-H(141)···O(6)^{ix}, 2.593(6) Å, 173.5°), (h) the carboxylate oxygen atoms and sulfonate oxygen atoms (O(9)-H(9A)···O(11)^{vii}, 2.604(6) Å, 157(7)°; O(16)-H(16)···O(3)^{viii}, 2.620(14) Å, 168.6°).

The whole framework structure is further stabilized by π - π stacking. The shortest distance between two parallel phen planes is about 3.8 Å, which is within the common range for π - π interactions between two aryl rings.²³ (Table S1) The hydrogen bonds, involving the coordinated water molecules, the lattice water molecules, carboxylate groups and sulfonate groups of SIP ligands, generate one-dimensional double chains, which combines with weak π - π interactions forms 3D supramolecular structure (Figure 4).

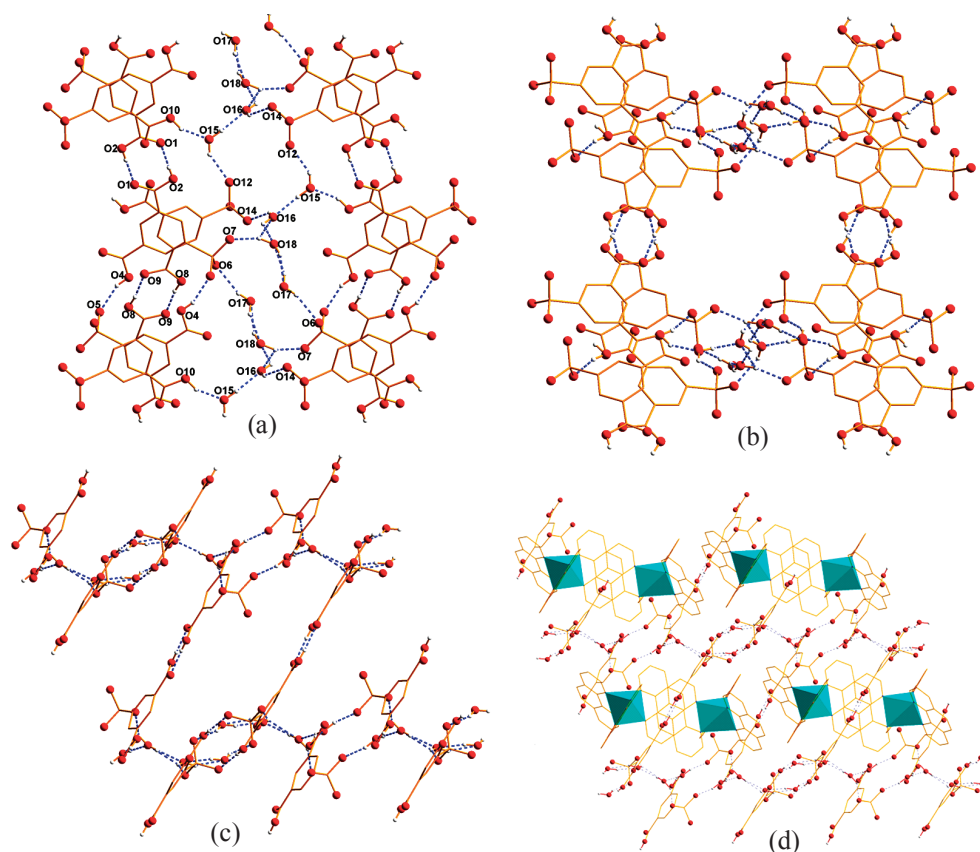


Figure 2. Compound 1: (a) 1D double-chain (b) 3D supramolecular framework in the *ab* plane. (c) 3D supramolecular framework in the *bc* plane ($[\text{Zn}(\text{phen})_3]^{2+}$ moieties are omitted for clarity). (d) the layered extended structure showing the $[\text{Zn}(\text{phen})_3]^{2+}$ cationic moieties occupied voids of the $[\text{H}_2\text{SIP-H}_2\text{O}]_n^-$ anionic layers.

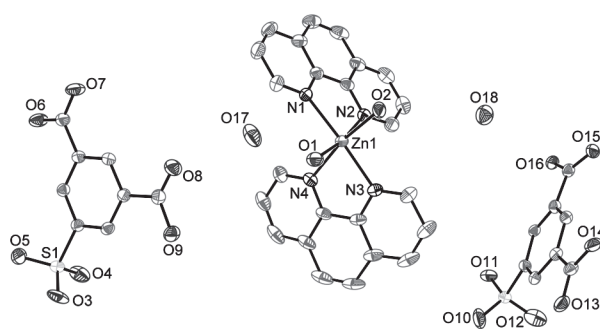


Figure 3. View of **2** with 30% probability displacement ellipsoids (H atoms are omitted for clarity).

XRD analysis. In order to check the phase purity, the XRD patterns of title compounds were checked at room temperature. As shown in Figure S1, the peak positions of the simulated and experimental XRD patterns are in the agreement with each other, demonstrating the good phase purity of the compounds.

Thermal analysis. The thermal stability of these new crystalline materials was investigated by the thermogravimetric (TG) analysis experiments. As shown in Figure 5, the TGA curves of **1** and **2** are different due to their different architectures. The TGA curve of **1** shows that the first weight loss of 1.46% (calcd.

1.54%) from 25 °C to 130 °C corresponds to the loss of one lattice water molecule per formula unit. The weight loss in the temperature range 181 to 330 °C corresponds to the loss of three lattice water molecule (weight loss of 4.62%, calcd. 4.89%). The further weight loss from 330 °C corresponds to the loss of H_2SIP^- molecules, and after 400 °C, the framework of three phen ligands is continuously decomposed. The weight loss is 46.0% (calcd. 46.2%). Finally, the residue is ZnSO_4 and ZnO . Until 800 °C the decomposing process is not complete. Comparably, compound **2** is much stable with the first weight loss of the lattice water and coordinated water molecules 7.05% (calcd. 7.28%) in the temperature range 25 to 140 °C. After a platform in the range of 140 to 330 °C with no weight loss, the H_2SIP^- molecules begin to remove and up to 400 °C two coordinated phen molecules collapse. The residue is ZnO at 650 °C.

Photoluminescent properties. The emission spectra of **1** and **2** in the solid state at room temperature are investigated, as shown in Figure 7. It is reported that free NaH_2SIP and free phen- H_2O display photoluminescent emission in the solid state. The emission bands for free phen- H_2O are at 365 and 388 nm ($\lambda_{\text{ex}} = 310$ nm), which may be attributed to the $\pi^* \rightarrow \pi$ transition.³¹ The free NaH_2SIP displays photoluminescent emission at 320 nm under 286 nm radiation.³² The maximum of the emission bands of **1** is located at 394 nm ($\lambda_{\text{ex}} = 320$ nm), while **2** shows two emission bands at 376 nm and 393 nm ($\lambda_{\text{ex}} = 280$ nm), respectively. In

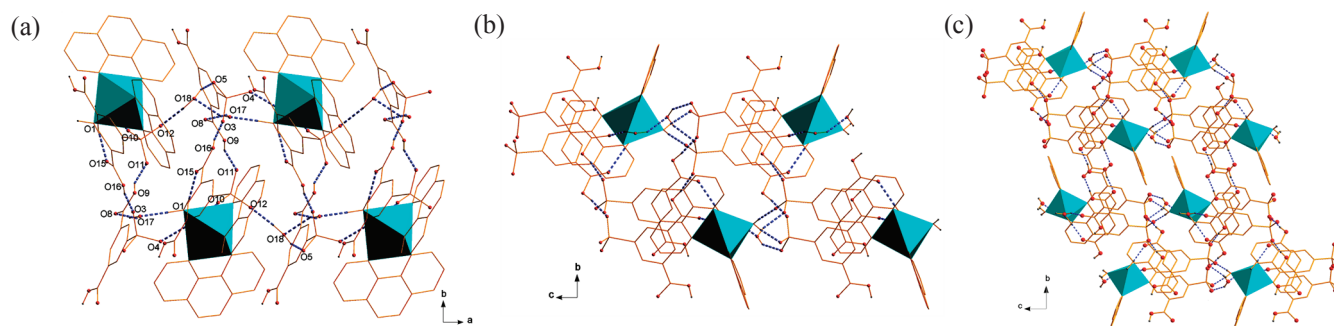


Figure 4. View of **2**: (a) 1D hydrogen-bonded double chain. (b) 2D hydrogen-bonded layer parallel to the *bc* plane. (c) 3D hydrogen-bonded framework.

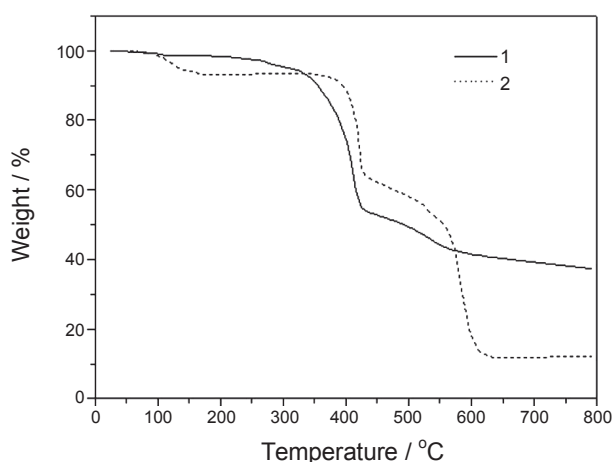


Figure 5. TGA curves of **1** and **2**.

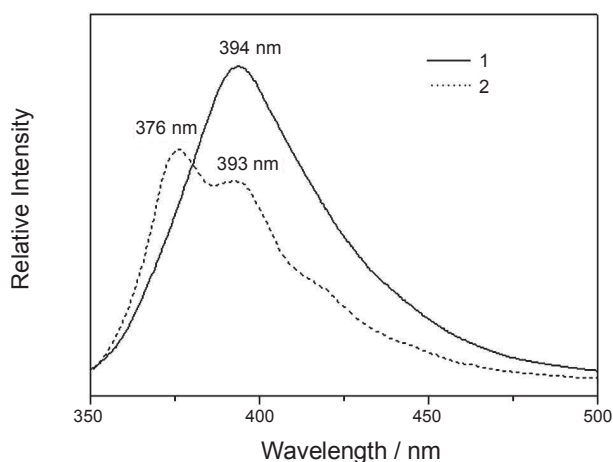


Figure 6. Solid-state emission spectra of **1** and **2**.

addition, the Zn^{2+} ions are different to oxidize or to reduce due to its d^{10} configuration. So compared with those of the free ligands, the emission of **1** and **2** at about 390 nm are assigned to be intra-ligand charge transfer of phen ligands,²⁷ as well as another emission at 376 nm in **2**.

Conclusion

In summary, two new Zn/SIP/phen compounds have been successfully synthesized by a hydrothermal route and structurally determined by X-ray analysis. It is found that not only the reaction conditions play a crucial role in the syntheses, but also the noncovalent interactions influence the final extended structures. The 3D Zn-phen architecture was observed for the first time in the presence of 5-sulfoisophthalic acid. Two extended structures are featured with 3D supramolecular framework. The uncoordinated sulfonate and carboxylate oxygen atoms play an important structural role by participating in a number of hydrogen bonds.

Acknowledgments. This work was supported by National Natural Science Foundation of China (No. 20671038) and the Jiangsu Key Laboratory for the Chemistry of Low-Dimensional Materials (No. JSKC09061).

Supporting Information Available. Supporting Information are available on request from the correspondence author (fax: + 86 517 83525100 email: yulanzhu2008@126.com)

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