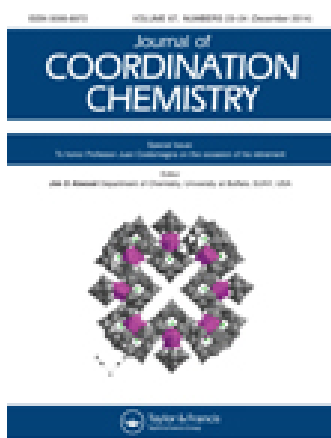


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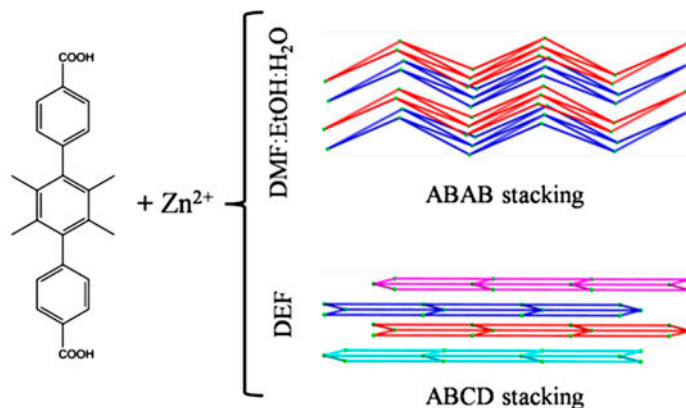
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Solvent-modulated zinc^{II} networks with different stacking arrangements

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Two Zn^{II} complexes, [Zn₂(L)₂(DMF)(H₂O)₂]·DMF (**1**) and [Zn(L)(DEF)]·DEF (**2**), were synthesized by solvothermal reactions using 4,4'-(2,3,5,6-tetramethylbenzene-1,4-diyl)dibenzoic acid (H₂L) and Zn(NO₃)₂·6H₂O in different solvents of DMF, ethanol, and water for **1** and N,N-diethylformamide (DEF) for **2**. The L²⁻ with different coordination modes connect [Zn₂(COO)₂] secondary building units (SBUs) to generate a wavy 2-D (4,4) network of **1** while in **2** there are paddlewheel [Zn₂(COO)₄] SBUs which are connected by L²⁻ to form a planar 2-D (4,4) network. The 2-D layered structures show different stacking arrangements and are further linked by hydrogen bonding or C–H···π interactions to give 3-D architectures. The different structures and stacking arrangements of **1** and **2** result from different reaction solvents. Photoluminescence properties of the complexes were investigated.

Keywords: Zn^{II} complex; Solvothermal reaction; Secondary building unit; Photoluminescence property

1. Introduction

The synthesis of metal-organic frameworks (MOFs) with diverse structures and specific properties remains an intensive research area [1, 2]. Many MOFs with 1-D, 2-D, and 3-D structures have been reported using pre-designed organic ligands to link metal ions or

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secondary building units (SBUs) [3, 4]. It is helpful to recognize the SBUs which determine the final structures while fixing the organic ligands. The geometry of the SBUs is dependent on the bridging groups of the ligands, metal ions, reaction solvent, etc. [5]. Solvent molecules with different sizes, polarities, and coordination abilities usually play important roles in the construction of MOFs from both thermodynamic and kinetic aspects: (i) solvent molecules as ligands coordinate with metal ions; (ii) solvent molecules as guests exist in the voids of frameworks. In fact, the reaction solvent certainly influences the crystal growth and the final structure of MOFs [6].

There are common SBUs, such as dinuclear $[\text{Zn}_2(\text{COO})_2]$, $[\text{Zn}_2(\text{COO})_3]$, paddlewheel $[\text{Zn}_2(\text{COO})_4]$, and tetranuclear $[\text{Zn}_4\text{O}(\text{COO})_6]$, in the Zn^{II} carboxylate systems. The dinuclear SBUs easily form 2-D networks while the tetranuclear ones tend to generate 3-D frameworks due to the geometry of SBUs [7, 8]. For 2-D networks, the layers can adopt different arrangements of parallel stacking and interpenetration [9, 10]. Furthermore, there are different kinds of stacking arrangements for the 2-D layers, such as AAAA, ABAB, ABCD, and ABCDEF, which are induced by non-covalent interactions between the layers [7, 10]. The 2-D networks usually are further connected to generate 3-D supramolecular frameworks through weak C–H $\cdots\pi$, $\pi\cdots\pi$, and/or hydrogen bonding interactions.

Herein we report two solvent-modulated Zn^{II} complexes, $[\text{Zn}_2(\text{L})_2(\text{DMF})(\text{H}_2\text{O})_2]\cdot\text{DMF}$ (**1**) and $[\text{Zn}(\text{L})(\text{DEF})]\cdot\text{DEF}$ (**2**), with 2-D (4,4) network structures constructed from the reactions of 4,4'-(2,3,5,6-tetramethylbenzene-1,4-diyl)dibenzoic acid (H_2L) with zinc nitrate. The 2-D networks are arranged by the ABAB stacking mode of wavy layers in **1** and the ABCD stacking mode of planar layers in **2** due to the different interactions between the layers. The thermal stabilities, powder X-ray diffraction (PXRD), Fourier transform infrared spectra (FT-IR), and photoluminescence properties of the complexes were investigated.

2. Experimental

2.1. Materials and methods

All commercially available chemicals and solvents are of reagent grade and were used as received. H_2L ligand was prepared according to the previously reported method [7a]. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C elemental analyzer. The thermogravimetric analyses (TGA) were performed on a simultaneous SDT 2960 thermal analyzer at a heating rate of 10 °C min⁻¹ under nitrogen. FT-IR spectra were recorded from 400 to 4000 cm⁻¹ on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. PXRD patterns were obtained on a Bruker D8 Advance X-ray diffractometer with Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation at room temperature. Photoluminescence spectra for solid-state samples at room temperature were measured on a Perkin Elmer LS55.

2.2. Syntheses of the complexes

2.2.1. $[\text{Zn}_2(\text{L})_2(\text{DMF})(\text{H}_2\text{O})_2]\cdot\text{DMF}$ (1**).** $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (30 mg, 0.1 mM) and H_2L (8 mg, 0.02 mM) were added to DMF:EtOH:H₂O (V : V : V = 5 : 2 : 1; 6 mL) in a sealed vial (15 mL). The mixture was then heated at 90 °C for three days. After being cooled to room temperature, colorless rod crystals of **1** were obtained in 35% yield. Anal. Calcd for $\text{C}_{54}\text{H}_{58}\text{N}_2\text{O}_{12}\text{Zn}_2$ (%): C, 61.31; H, 5.53; and N, 2.65. Found: C, 61.14; H, 5.58; and N, 2.63. IR (KBr pellet, cm⁻¹): 3390 (s), 2930 (m), 1595 (s), 1514 (s), 1535 (s), 1405 (s), 1170 (w), 1088 (w), 1020 (m), 848 (w), 777 (m), 714 (w), 675 (w), 567 (w), and 510 (w).

Table 1. Crystal data for **1** and **2**.

Complex	1	2
Formula	C ₅₄ H ₅₈ N ₂ O ₁₂ Zn ₂	C ₃₄ H ₄₂ N ₂ O ₆ Zn
Mr	1057.76	640.07
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	13.510(6)	19.7617(14)
<i>b</i> /Å	11.299(5)	19.4852(14)
<i>c</i> /Å	32.958(14)	18.4350(13)
α /°	90	90
β /°	92.484(8)	108.4280(10)
γ /°	90	90
<i>V</i> /Å ³	5026(4)	6734.6(8)
<i>Z</i>	4	8
<i>D_c</i> (g cm ⁻³)	1.398	1.263
μ (mm ⁻¹)	1.019	0.773
<i>F</i> (000)	2208	2704
Reflections collected	37,095	28,542
Independent reflections	13,363	7665
Goodness-of-fit on <i>F</i> ²	1.077	1.103
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0520	0.0546
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^b	0.1161	0.1632

Note: $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$.

2.2.2. [Zn(L)(DEF)]·DEF (2). Zn(NO₃)₂·6H₂O (30 mg, 0.1 mM), H₂L (8 mg, 0.02 mM), and a drop of HBF₄ were added to the solution of DEF (6 mL) in a sealed vial (15 mL). The mixture was then heated at 90 °C for three days. After being cooled to room temperature, colorless rod crystals of **2** were obtained in 56% yield. Anal. Calcd for C₃₄H₄₂N₂O₆Zn (%): C, 63.80; H, 6.61; and N, 4.38. Found: C, 63.66; H, 6.61; and N, 4.34. IR (KBr pellet, cm⁻¹): 2974 (m), 2930 (m), 1659 (s), 1618 (s), 1542 (m), 1402 (s), 1265 (m), 1205 (w), 1164 (w), 1100 (m), 988 (w), 832 (w), 775 (m), 709 (w), 644 (w), and 516 (m).

2.3. X-ray crystallography

Crystallographic data of **1** and **2** were collected on a Bruker Smart Apex CCD with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 293(2) K using the ω -scan technique. The data were integrated using the SAINT program [11(a)], which was also used for intensity corrections for Lorentz and polarization effects. Semiempirical absorption correction was applied using SADABS [11(b)]. The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically on *F*² by full-matrix least-squares using the SHELXL crystallographic software package [11(c)]. The hydrogens of coordinated water molecules in **1** were found directly and all hydrogens of organic ligands were generated geometrically and refined isotropically using the riding model. The details of the crystal parameters, data collection, and refinements of the complexes are summarized in table 1, and selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. Structure description of [Zn₂(L)₂(DMF)(H₂O)₂]·DMF (1)

The asymmetric unit of **1** consists of two Zn^{II} ions, two L²⁻, two coordinated water molecules, and one coordinated and one free DMF. As shown in figure 1(a), Zn1 is surrounded

Table 2. Selected bond lengths [Å] and angles [°] for **1** and **2**.

Complex 1			
Zn(1)–O(4)#1	1.925(2)	Zn(1)–O(1)	1.942(2)
Zn(1)–O(5)	1.945(2)	Zn(1)–O(10)	1.982(2)
Zn(2)–O(2)	2.002(2)	Zn(2)–O(9)	2.014(2)
Zn(2)–O(7)#2	2.064(2)	Zn(2)–O(3)#1	2.110(3)
Zn(2)–O(11)	2.157(3)	Zn(2)–O(8)#2	2.363(3)
O(4)#1–Zn(1)–O(1)	119.02(10)	O(4)#1–Zn(1)–O(5)	120.24(11)
O(1)–Zn(1)–O(5)	100.19(11)	O(4)#1–Zn(1)–O(10)	110.36(11)
O(1)–Zn(1)–O(10)	101.78(10)	O(5)–Zn(1)–O(10)	102.59(10)
O(2)–Zn(2)–O(9)	108.18(10)	O(2)–Zn(2)–O(7)#2	149.55(10)
O(9)–Zn(2)–O(7)#2	101.19(10)	O(2)–Zn(2)–O(3)#1	96.24(10)
O(9)–Zn(2)–O(3)#1	89.52(9)	O(7)#2–Zn(2)–O(3)#1	91.81(10)
O(2)–Zn(2)–O(11)	86.05(10)	O(9)–Zn(2)–O(11)	83.22(10)
O(7)#2–Zn(2)–O(11)	89.63(10)	O(3)#1–Zn(2)–O(11)	172.74(10)
O(2)–Zn(2)–O(8)#2	90.96(10)	O(9)–Zn(2)–O(8)#2	158.19(9)
O(7)#2–Zn(2)–O(8)#2	58.74(9)	O(3)#1–Zn(2)–O(8)#2	98.92(9)
O(11)–Zn(2)–O(8)#2	87.91(10)		
Symmetry transformations used to generate equivalent atoms: (#1) $x, -y + 1/2, z + 1/2$; (#2) $x + 1, -y + 1/2, z + 1/2$.			
Complex 2			
Zn(1)–O(5)	1.984(2)	Zn(1)–O(1)	2.019(2)
Zn(1)–O(3)	2.028(2)	Zn(1)–O(2)#1	2.030(2)
Zn(1)–O(4)#2	2.068(2)		
O(5)–Zn(1)–O(1)	102.70(9)	O(5)–Zn(1)–O(3)	102.77(11)
O(1)–Zn(1)–O(3)	90.48(9)	O(5)–Zn(1)–O(2)#1	97.37(10)
O(1)–Zn(1)–O(2)#1	159.73(12)	O(3)–Zn(1)–O(2)#1	87.80(9)
O(5)–Zn(1)–O(4)#2	97.20(11)	O(1)–Zn(1)–O(4)#2	88.36(9)
O(3)–Zn(1)–O(4)#2	159.75(12)	O(2)#1–Zn(1)–O(4)#2	86.34(9)
Symmetry transformations used to generate equivalent atoms: (#1) $x, y + 1, z$; (#2) $-x + 1, y, -z + 3/2$.			

by four oxygens from three different L²⁻ ligands and one water molecule to give tetrahedral coordination geometry, while Zn2 is surrounded by six oxygens from three distinct L²⁻ ligands, one water molecule, and one DMF to form distorted octahedral coordination geometry. In **1**, two L²⁻ ligands present the different coordination modes as illustrated in scheme 1(a) and (b): (κ^2)-(κ^1)- μ_2 -L²⁻ and (κ^1 - κ^1)-(κ^1 - κ^1)- μ_4 -L²⁻. Two Zn^{II} (one Zn1 and one Zn2) ions are linked by two carboxylate groups each with (κ^1 - κ^1)- μ_2 coordination to give a [Zn₂(COO)₂] SBU. Such SBUs are further connected by L²⁻ ligands to form a 2-D network structure of **1** [figure 1(b)]. From a topological view, each [Zn₂(COO)₂] SBU and L²⁻ can be regarded as 4- [figure S1(a), see online supplemental material at <http://dx.doi.org/10.1080/00958972.2014.971021>] and 2-connectors, respectively. As a result, the topology of **1** is a (4,4) 2-D wavy network [figure 1(c)].

The 2-D wavy layers in **1** adopt ABAB stacking [figure 1(d)] to generate a 3-D supramolecular architecture through O–H...O hydrogen bonding interactions as exhibited in figure 1(e). The hydrogen bonding data are summarized in table S1.

3.2. Structure description of [Zn(L)(DEF)]·DEF (**2**)

When the reaction solvent was changed from the mixed solvents of DMF, EtOH, and H₂O to DEF, **2** was isolated; the asymmetric unit of **2** consists of one Zn^{II}, one L²⁻, one coordinated DEF and one free DEF. As shown in figure 2(a), each Zn^{II} is coordinated by

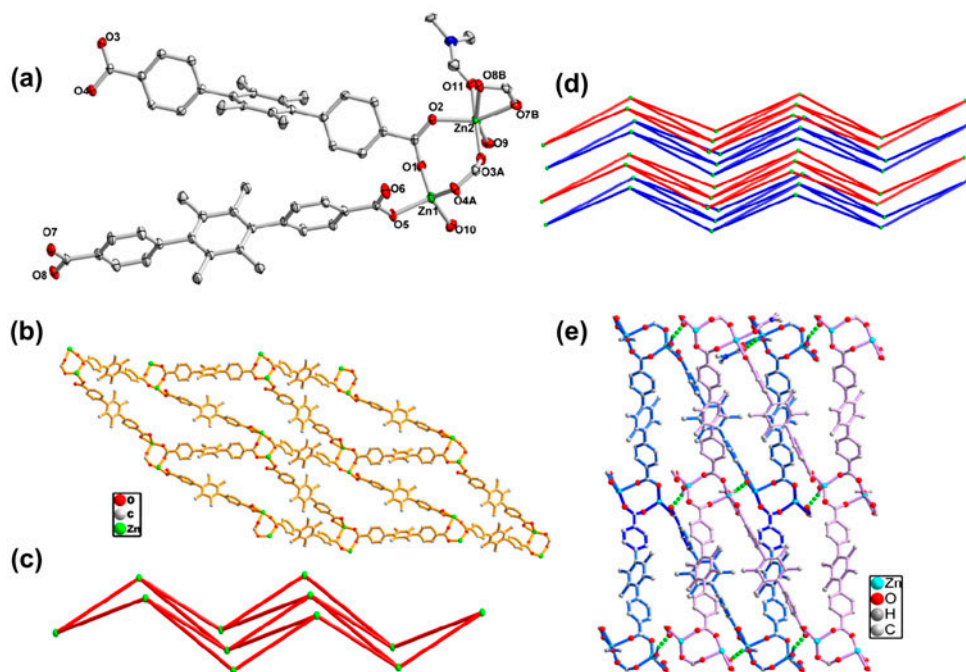
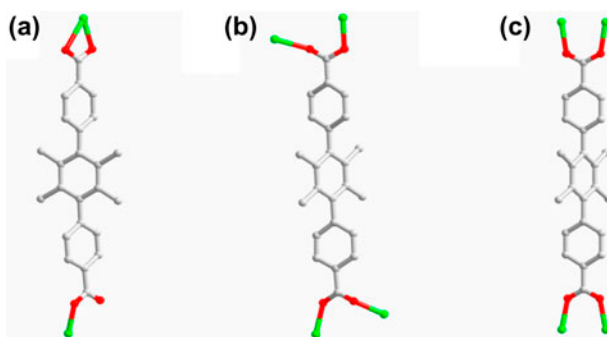


Figure 1. (a) Coordination environment of Zn^{II} ions in **1** with ellipsoids drawn at the 30% probability level. The hydrogens and free solvent molecules are omitted for clarity (symmetry codes: (A) $x, 0.5 - y, 0.5 + z$; (B) $1 + x, 0.5 - y, 0.5 + z$). (b) 2-D wavy layer of **1**. The hydrogens and solvent molecules are omitted for clarity. (c) 2-D (4,4) network of **1**. (d) The ABAB stacking arrangement of the (4,4) wavy layers. (e) Hydrogen bonding interactions are indicated by dashed lines between the adjacent layers in **1**.



Scheme 1. Coordination modes of L²⁻ in **1** (a and b) and **2** (c).

five oxygens from four different L²⁻ ligands and one DEF to give a distorted square pyramidal coordination geometry. The Zn–O lengths are in the range 1.984(2)–2.068(2) Å. The coordination mode of L²⁻ in **2** is also $(\kappa^1-\kappa^1)-(\kappa^1-\kappa^1)-\mu_4-L^{2-}$ as illustrated in scheme 1(c), but with different Zn–O–C–O dihedral angles compared with the one shown in scheme 1(b). Two Zn^{II} ions are joined by four carboxylate groups to give a paddlewheel [Zn₂(COO)₄] SBU, rather than the [Zn₂(COO)₂] one in **1** [figure 1(b)]. The Zn⋯Zn

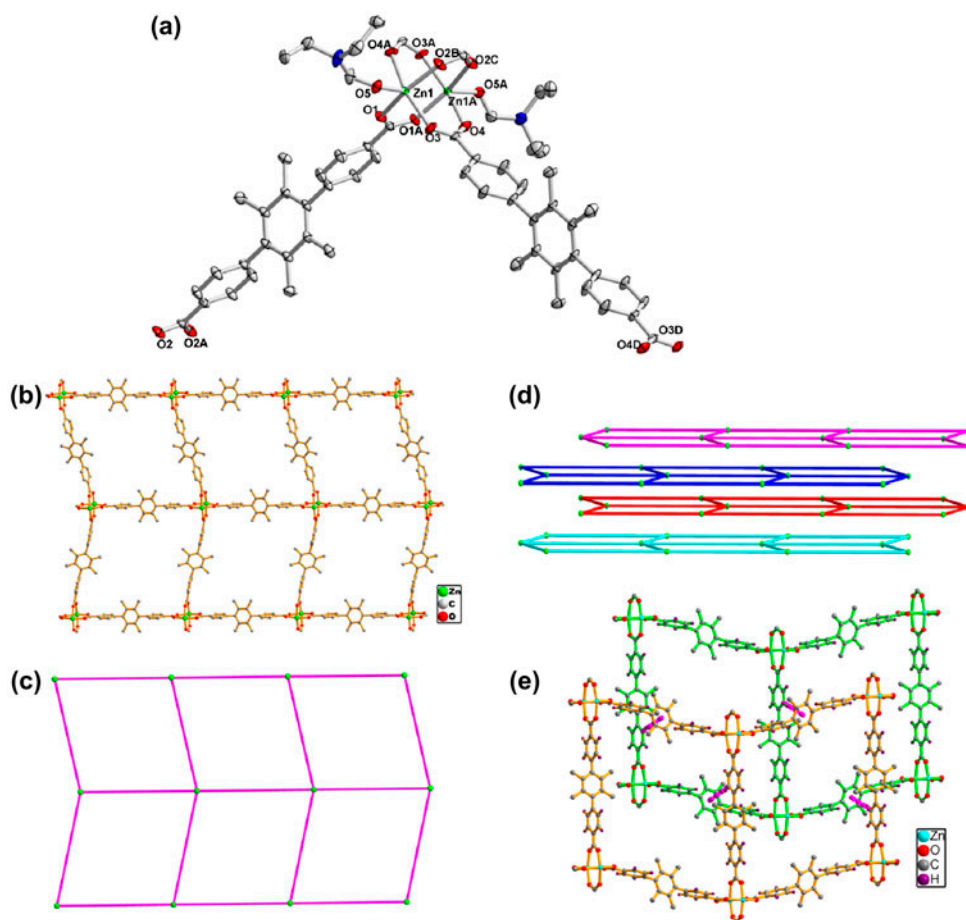


Figure 2. (a) Coordination environment of Zn^{II} ions in **2** with ellipsoids drawn at the 30% probability level. The hydrogens and free solvent molecules are omitted for clarity (symmetry codes: (A) $1-x, y, 1.5-z$; (B) $x, 1+y, z$; (C) $1-x, 1+y, 1.5-z$; (D) $2-x, 2-y, 2-z$). (b) 2-D planar layer of **2**. The hydrogens and solvent molecules are omitted for clarity. (c) The 2-D (4,4) network of **2**. (d) The ABCD stacking arrangement of (4,4) planar layers. (e) C–H \cdots π interactions between the adjacent layers in **2**.

separation in **2** is 2.9464(5) Å, shorter than the value of 2.9939(5) Å in the previously reported Zn^{II} complex with similar paddlewheel SBUs [12]. Each L²⁻ in **2** bridges two SBUs to form a 2-D planar network with (4,4) topology [figure 2(b) and (c)], in which each [Zn₂(COO)₄] SBU can be simplified as a 4-connected node [figure S1(b)]. The 2-D planar layers adopt ABCD stacking [figure 2(d)] to generate a 3-D supramolecular architecture through C–H \cdots π interactions in **2** [figure 2(e)].

3.3. Influence of solvent on structures of the complexes

The reaction solvents for the preparation of **1** and **2** are DMF : EtOH : H₂O (V : V : V = 5 : 2 : 1) and DEF, respectively. The results show that the solvents play an important role in determining the structures of the complexes. DMF and DEF can provide bases, (CH₃)₂NH

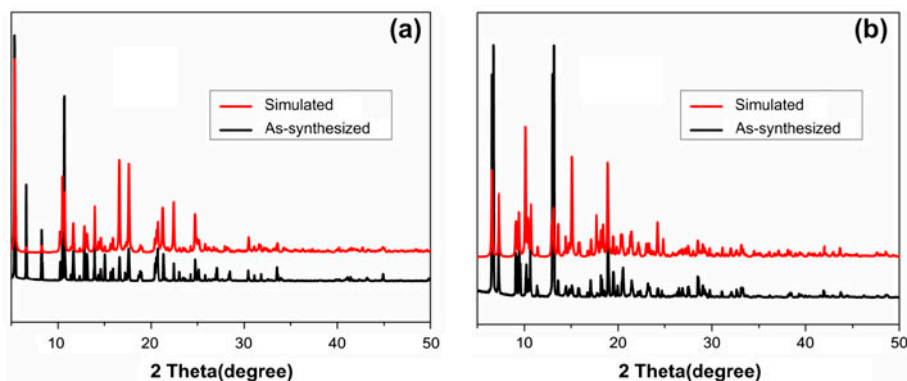


Figure 3. PXRD patterns of **1** (a) and **2** (b).

and $(\text{CH}_3\text{CH}_2)_2\text{NH}$, generated *in situ* by the decomposition of DEF and DMF, respectively [13], which leads to the deprotonation of H_2L to give L^{2-} . The complete deprotonation of H_2L was further confirmed by IR spectral data of **1** and **2** since no vibration bands were observed between 1680 and 1760 cm^{-1} [figure S(2)]. In addition, DMF and DEF serve as both ligands and guests in these two complexes, which may hinder the formation of higher dimensional frameworks [14]. In **1**, there are coordinated H_2O molecules and dinuclear $[\text{Zn}_2(\text{COO})_2]$ SBUs linked by ligands to form a wavy network, while in **2** there are well-known paddlewheel $[\text{Zn}_2(\text{COO})_4]$ SBUs which are joined together by ligands to generate a planar layer structure.

3.4. Powder X-ray diffraction and thermal analysis

The pure phases of **1** and **2** are confirmed by PXRD measurements. As shown in figure 3, the PXRD pattern of the as-synthesized sample is in accord with the simulated one.

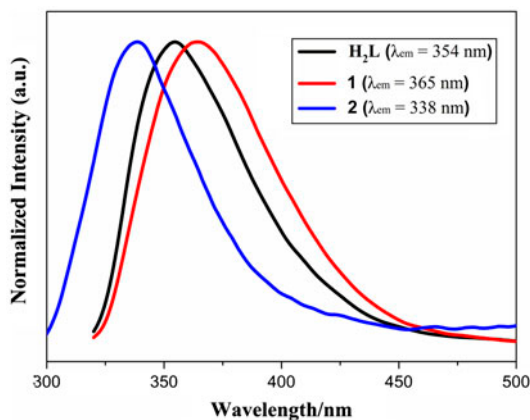


Figure 4. Emission spectra of H_2L , **1**, and **2** in the solid state at room temperature.

TGA was performed in nitrogen for **1** and **2** and the TG curves are shown in figure S3. The TG curve of **1** reveals a weight loss of 17.39% (Calcd 17.21%) between 30 and 280 °C, which corresponds to the loss of two coordinated water molecules, one free DMF, and one coordinated DMF. The TG curve of **2** shows a weight loss of 31.14% (Calcd 31.56%) from 30 to 300 °C, which corresponds to the release of one free DEF and one coordinated DEF.

3.5. Photoluminescence properties

Solid-state emission spectra of **1** and **2** at room temperature are shown in figure 4. Emission bands are observed at 354 nm ($\lambda_{\text{ex}} = 303$ nm) for H₂L, 365 nm ($\lambda_{\text{ex}} = 308$ nm) for **1**, and 338 nm ($\lambda_{\text{ex}} = 282$ nm) for **2**. The emissions of the complexes are neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer due to d¹⁰ electronic configuration of Zn^{II} which is difficult to oxidize or reduce [15]. Therefore, the photoluminescence emissions of the complexes can be assigned to ligand transitions because of their similarity with the free H₂L ligand. Such ligand-based emission is ascribed to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ electronic transitions. The dissimilarity of the emissions of the complexes and the ligands may originate from the coordination of the ligands [16]. Complex **2** has an obvious blue-shift compared with **1**. It may be ascribed to different interactions between the layers, the hydrogen bonds in **1** and the C–H $\cdots\pi$ interactions in **2** [16(b), and (d)].

4. Conclusion

We synthesized and characterized two Zn^{II}-L²⁻ complexes with different [Zn₂(COO)₂] and [Zn₂(COO)₄] SBUs from different solvents. Both are 2-D (4,4) networks but with different stacking arrangements of the layers, an ABAB stacking mode of the wavy layers in **1** and an ABCD stacking mode of the planar layers in **2**. The layers are further connected into 3-D frameworks through weak supramolecular interactions. Complexes **1** and **2** exhibit solid-state emissions at 365 and 338 nm upon excitation at 308 and 282 nm, respectively. The result implies that the reaction solvent plays an important role in determining the structure of the complexes.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication No. CCDC-1011710 (**1**) and 1011711 (**2**). Copies of the data can be obtained at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44 1223336033; E-mail: deposit@ccdc.cam.ac.uk).

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