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Qi Feng^a, Yun Tang^a, Huihua Song^a & Jixue Han^a

^a College of Chemistry and Material Sciences, Hebei Normal University, Shijiazhuang, P. R. China

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Concentration-controlled Zn(II) compounds constructed from *N*-tosyl-*L*-glutamic acid and 1,10-phenanthroline

QI FENG, YUN TANG, HUIHUA SONG* and JIXUE HAN

College of Chemistry and Material Sciences, Hebei Normal University, Shijiazhuang, P. R. China

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By controlling the concentration of the reaction system, two novel zinc(II) complexes, $[\text{Zn}_2(\text{tsgluO})_2(\text{phen})_2]_n$ (**1**) and $[\text{Zn}_2(\text{tsgluO})_2(\text{phen})_2(\text{H}_2\text{O})_2]$ (**2**) ($\text{H}_2\text{tsgluO} = N$ -tosyl-*L*-glutamic acid, phen = 1,10-phenanthroline), have been synthesized under hydrothermal conditions and characterized by elemental analysis, infrared spectra, thermogravimetric analysis, and single-crystal X-ray diffraction. Complexes **1** and **2** both crystallize in the triclinic space group P-1. Complex **1** exhibits a 1-D double-chain structure. Complex **2** has a dinuclear structure which is extended by hydrogen-bonding interactions to form a 2-D supramolecular network. The structural difference indicates that the concentration plays a crucial role in modulating structures of coordination complexes. The two compounds also show intense fluorescence at room temperature.

Keywords: Zn(II) Compounds; Crystal structure; Fluorescent properties

1. Introduction

The rational design and syntheses of metal–organic frameworks (MOFs) are of interest in supramolecular chemistry and crystal engineering owing to their variety of architectures and topological networks [1–4], as well as due to their potential applications in adsorption, catalysis, luminescence, magnetism, nonlinear optics, or porous materials [5–11]. Thus so far, much attention has been drawn to the rational design of new networks structures and a variety of extended frameworks has been obtained. However, synthesis of MOFs with desirable structures and properties is still a challenge with many efforts devoted to fundamental structural aspects to understand and control the factors that affect assembly of supramolecular architectures, such as coordination geometry of metal ions [12, 13], the structure of organic ligands [14–18], the solvent system [19–21], pH [22–24], temperature [25–27], counter anion [28], ligand-to-metal ratio [29], etc. In some cases, a small change in any of these factors can lead to new complexes with different topologies and functions. Therefore, understanding the relationships between the structures of complexes and these factors is very important.

Amino acid derivatives have been widely used for fabricating many interesting coordination networks [30, 31], not only for their ready availability from the inexpensive simple amino acid and potential practical applications such as good catalytic properties, but also

*Corresponding author. Email: songhuihua@hebtu.edu.cn

because of their versatile bonding modes with metal ions. On the other hand, transition metal ions with filled d-shell orbitals have no unpaired electrons and facilitate linker-based photoemission. MOFs based on transition metal ions with d^{10} electronic configuration (especially Zn(II)) have been an area of intense research, primarily due to photoluminescence [32, 33]. In our previous work, we reported a series of coordination polymers constructed by the *N*-tosyl-*L*-glutamic acid ligand. As an extension of our previous work, we report here two new Zn(II) coordination polymers, $[\text{Zn}_2(\text{tsgluO})_2(\text{phen})_2]_n$ (**1**) and $[\text{Zn}_2(\text{tsgluO})_2(\text{phen})_2(\text{H}_2\text{O})_2]$ (**2**) ($\text{H}_2\text{tsgluO} = N$ -tosyl-*L*-glutamic acid, phen = 1,10-phenanthroline), which are influenced by the concentration of the reaction system. To the best of our knowledge, concentration effects have seldom been reported. In addition, fluorescence of **1** and **2** has also been studied.

2. Experimental

2.1. Materials and methods

All commercially available chemicals and solvents are of reagent grade and were used without purification. Infrared (IR) spectra were recorded using KBr pellets from 4000 cm^{-1} to 400 cm^{-1} on a Fourier-transform infrared-8900 spectrometer. Elemental analyzes (C, H, and N) were performed on a Vario EL analyzer. Thermogravimetric analyzes (TGA) were carried out on a simultaneous STA 449F3/TENSOR 27 thermal analyzer under nitrogen with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from room temperature to $850\text{ }^\circ\text{C}$. Luminescence spectra were recorded on a Hitachi F-4500 Luminescence spectrometer at room temperature.

2.2. Syntheses of the complexes

2.2.1. $[\text{Zn}_2(\text{tsgluO})_2(\text{phen})_2]_n$. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.0440 g, 0.2 mM), H_2tsgluO (0.1206 g, 0.4 mM), phen (0.0396 g, 0.2 mM), and NaF (0.0042 g, 0.1 mM) were mixed in solution containing H_2O (9.0 mL). The mixture was placed in a 23-mL Teflon reactor, which was then heated to $120\text{ }^\circ\text{C}$ for five days. The resulting solution was left to cool slowly to room temperature. Colorless block-shaped crystals of **1** suitable for X-ray determination were obtained, collected by filtration, and washed with water in 61% yield (based on Zn). Anal. Calcd for $\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}_6\text{SZn}$ (%): C, 52.9; H, 3.9; N, 7.7. Found: C, 52.8; H, 3.7; N, 7.9. IR data (KBr, cm^{-1}): 3419 w, 3189 w, 3078 m, 3056 m, 2968b, 2935b, 1616 m, 1583 m, 1518 s, 1404 m, 1398 m, 1325 s, 1257 m, 1213 m, 1159 s, 1091 s, 1037 m, 983 m, 908 m, 847 s, 816 s, 773 m, 727 s, 659 b, 661 b, 568 s, 426 m, 424 m.

2.2.2. $[\text{Zn}_2(\text{tsgluO})_2(\text{phen})_2(\text{H}_2\text{O})_2]$. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.0550 g, 0.25 mM), H_2tsgluO (0.1507 g, 0.5 mM), phen (0.0495 g, 0.25 mM), and NaF (0.0042 g, 0.1 mM) were mixed in solution containing H_2O (9.0 mL). The mixture was placed in a 23-mL Teflon reactor, which was then heated to $120\text{ }^\circ\text{C}$ for five days. The resulting solution was left to cool slowly to room temperature. Yellow block-shaped crystals of **2** suitable for X-ray determination were obtained, collected by filtration, and washed with water in 65% yield (based on Zn). Anal. Calcd for $\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}_6\text{SZn}$ (%): C, 51.2; H, 4.1; N, 7.5. Found: C, 51.4; H, 4.0; N, 7.3. IR data (KBr, cm^{-1}): 3419w, 3268 m, 3060 m, 2963 m, 1614 m, 1517 s, 1494 m, 1423 m, 1390 m, 1322 s, 1220 m, 1163 s, 1091s, 980 m, 901 m, 850 s, 814 m, 775 m, 727s, 665 s, 571 m, 547 m, 486 m, 430 m, 424 m.

2.3. X-ray crystallography

Colorless block-shaped crystals of **1** ($0.49 \times 0.35 \times 0.29$ mm) and yellow block-shaped crystals of **2** ($0.32 \times 0.27 \times 0.18$ mm) were subjected to single-crystal X-ray diffraction analysis on a Bruker SMART-CCD area detector diffractometer with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) at 298(2) K by the ω - ϕ scan technique. The structure was solved by direct methods using SHELXS-97. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using SHELXL-97 [34]. Hydrogens were added in geometrical positions and were not refined. A semi-empirical absorption correction was applied to the intensity data using SADABS [35]. A summary of the crystallographic data and refinement parameters are given in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. Crystal structure

3.1.1. Crystal structure of $[\text{Zn}_2(\text{tsgluO})_2(\text{phen})_2]_{\text{n}}$. Single-crystal X-ray diffraction analysis reveals that the two complexes crystallize in the triclinic system, space group P-1. As shown in figure 1(a), the asymmetric unit of **1** consists of one $\text{Zn}(\text{II})^-$, one tsgluO^{2+} , and one phen molecule. Zn1 is five-coordinate in a slightly distorted trigonal bipyramidal geometry, in which the coordination sphere of Zn is O_3N_2 . Zn(II) is coordinated from O1, O2A

Table 1. Crystal data and structure refinement of **1** and **2**.

Complex	1	2
Empirical formula	$\text{C}_{24}\text{H}_{21}\text{N}_3\text{ZnO}_6\text{S}$	$\text{C}_{48}\text{H}_{46}\text{N}_6\text{O}_{14}\text{S}_2\text{Zn}_2$
Formula weight	544.87	1125.77
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	9.6048(14)	10.044(2)
b (Å)	10.2230(15)	11.392(2)
c (Å)	12.6536(19)	11.606(2)
α (°)	77.235(2)	105.233(3)
β (°)	70.751(2)	95.449(3)
γ (°)	81.346(2)	102.970(3)
V (Å ³)	1139.9(3)	1231.8(4)
Z	2	1
D_{Calcd} ($\text{Mg}\cdot\text{m}^{-3}$)	1.587	1.518
$F(000)$	560	580
Crystal size (mm)	$0.49 \times 0.35 \times 0.29$	$0.32 \times 0.27 \times 0.18$
θ range (°)	1.73–25.49	1.84–25.49
Reflections collected/unique (R_{int})	6014/4180(0.0178)	6487/4485(0.0165)
Max. and min. transmission	0.7192–0.5870	0.816–0.703
Completeness to $\theta=25.49$ (%)	98.3	98.1
Data/restraints/parameters	4180/0/317	4485/1/326
Goodness-of-fit on F^2	1.036	1.051
R_1 , wR_2 [$I > 2\sigma(I)$] ^a	0.0322, 0.0857	0.041 3, 0.1032
R_1 , wR_2 (all data) ^a	0.0350, 0.0873	0.0495, 0.1092
Largest diff. peak and hole ($\text{e}\cdot\text{nm}^{-3}$)	443 and -420	476 and -368

^a $R_1 = |F_o - F_c|/\Sigma F_o$, $wR_2 = \Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^{1/2}$.

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

Compound 1					
N(1)–Zn(1)	2.165(2)	N(2)–Zn(1)	2.1260(19)	O(1)–Zn(1)	2.0131(17)
O(2)–Zn(1)#1	2.0461(18)	O(4)–Zn(1)#2	1.9740(16)		
O(4)#3–Zn(1)–O(1)	98.40(7)	O(4)#3–Zn(1)–O(2)#1	95.02(8)	O(1)–Zn(1)–O(2)#1	122.58(8)
O(4)#3–Zn(1)–N(2)	97.45(7)	O(1)–Zn(1)–N(2)	99.99(7)	O(2)#1–Zn(1)–N(2)	133.08(8)
O(4)#3–Zn(1)–N(1)	171.65(7)	O(1)–Zn(1)–N(1)	88.84(8)	O(2)#1–Zn(1)–N(1)	84.45(8)
N(2)–Zn(1)–N(1)	77.08(7)				
Compound 2					
N(2)–Zn(1)	2.155(2)	N(3)–Zn(1)	2.120(2)	O(1)–Zn(1)#1	2.036(2)
O(3)–Zn(1)	2.521(2)	O(4)–Zn(1)	2.060(2)	O(7)–Zn(1)	2.059(2)
O(1)#1–Zn(1)–O(7)	90.50(9)	O(1)#1–Zn(1)–O(4)	91.87(10)	O(7)–Zn(1)–O(4)	142.86(10)
O(1)#1–Zn(1)–N(3)	90.37(10)	O(7)–Zn(1)–N(3)	114.96(10)	O(4)–Zn(1)–N(3)	102.08(10)
O(1)#1–Zn(1)–N(2)	168.03(10)	O(7)–Zn(1)–N(2)	92.58(9)	O(4)–Zn(1)–N(2)	92.64(10)
N(3)–Zn(1)–N(2)	77.84(9)	O(1)#1–Zn(1)–O(3)	104.43(9)	O(7)–Zn(1)–O(3)	88.04(9)
O(4)–Zn(1)–O(3)	55.55(9)	N(3)–Zn(1)–O(3)	152.79(9)	N(2)–Zn(1)–O(3)	87.24(9)

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

and O4A of two tsgluO^{2-} , and N1 and N2 of one phen. The Zn–O bond lengths range from 1.9740(16) to 2.0461(18) Å and the Zn–N distances are 2.1260(19) Å and 2.165(2) Å, all of which fall within the normal ranges [36]. Each tsgluO^{2-} is a μ_3 ($\kappa^1\text{O}:$ $\kappa^1\text{O}:$ $\kappa^1\text{O}$) coordination mode [scheme 1(a)] to bridge three Zn atoms, in which the α -carboxylate is μ_2 ($\kappa^1\text{O}:$ $\kappa^1\text{O}$) coordination, while the γ -carboxylate is μ_1 ($\kappa^1\text{O}:$ $\kappa^0\text{O}$) coordination. Adjacent Zn(II) cations are doubly bridged by two α -carboxylates with Zn \cdots Zn separation of 4.026 Å to form a centrosymmetric dinuclear $\text{C}_2\text{O}_4\text{Zn}_2$ [figure 1(b)]. Such dinuclear units are linked by tsgluO^{2-} to generate a 1-D double chain running along the a -axis [figure 1(c)]. Worthy of mention is that the phen ligands are arranged on both sides of the chain to form a “wing-like” structure.

3.1.2. Crystal structure of $[\text{Zn}_2(\text{tsgluO})_2(\text{phen})_2(\text{H}_2\text{O})_2]$. X-ray structure analysis reveals that the asymmetric unit of **2** consists of one Zn(II) $^+$, one tsgluO^{2-} , one phen molecule, and one coordinated water molecule. As illustrated in figure 2(a), the coordination environment around Zn1 presents a distorted $\text{O}_w\text{O}_3\text{N}_2$ octahedral geometry, defined by three oxygens (O1A, O3, and O4) from two different tsgluO^{2-} , one oxygen (O7) from coordinated water, and two nitrogens (N2 and N3) from a chelating bidentate phen. The Zn–O (tsgluO^{2-}) distances range from 2.036(2) Å to 2.521(2) Å, while the Zn–O (H_2O) distance is 2.059(2) Å, and the Zn–N distances are 2.155(2) Å and 2.120(2) Å, respectively. The 2.521(2) Å value of Zn(1)–O(3) indicates strong steric hindrance from phen. The tsgluO^{2-} is a μ_2 ($\kappa^1\text{O}:$ $\kappa^1\text{O}:$ $\kappa^1\text{O}$) coordination mode [scheme 1(b)], in which the α -carboxylate is μ_1 ($\kappa^1\text{O}:$ $\kappa^0\text{O}$) coordination, while the γ -carboxylate is μ_1 ($\kappa^1\text{O}:$ $\kappa^1\text{O}$) coordination. In this fashion, the tsgluO^{2-} connects adjacent Zn(II) cations forming a binuclear unit (Zn \cdots Zn distance = 8.410 Å) [figure 2(b)]. These binuclear units are further connected into a 2-D supramolecular network through hydrogen-bonding interactions (table 3) between coordinated water (O7) and O3, O5 or N1 of tsgluO^{2-} [O(7)–H(7A) \cdots O(3)#2 ($-x + 2, -y + 1, -z + 2$) 2.703(3) Å; N(1)–H(1) \cdots O(5)#3 ($-x + 2, -y + 1, -z + 1$) 2.952(4) Å] [figure 2(c)].

The (+)-*N*-tosyl-*L*-glutamic acid is chiral, but the two compounds are achiral. This may be caused by the hydrothermal condition. During the synthetic procedure, half of the ligands underwent inversion and are present as the D enantiomer, so the tsgluO^{2-} groups racemized and the compounds are achiral. The racemization of amino acids in this way has been reported previously [37].

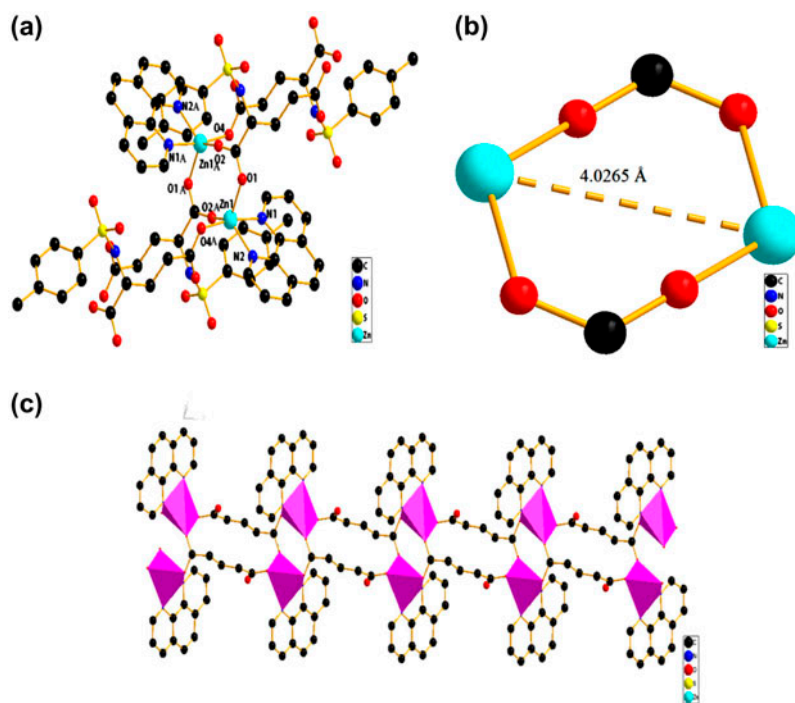
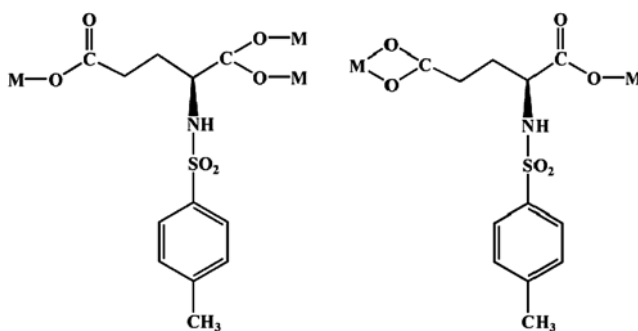


Figure 1. (a) The coordination environment of Zn(II) for **1**. All hydrogens have been omitted for clarity. (b) The eight-membered ring for **1**. (c) The one-dimension double chain structure for **1** (tosyl groups of tsgluO^{2-} have been omitted for clarity).



Scheme 1. (a) The observed coordination modes of H_2tsgluo for **1**. (b) The observed coordination modes of H_2tsgluo for **2**.

In our previous studies, we reported a series of coordination polymers constructed by *N*-tosyl-*L*-glutamic acid, and it is interesting to compare our present results with the related complexes involving *N*-tosyl-*L*-glutamic acid and chelating nitrogen donor ligands. The crystal structures of two coordination complexes, $[\text{Cu}(\text{tsgluO})(2,2'\text{-bipy})]_n$ (a) and $[\text{Mn}(\text{tsgluO})(2,2'\text{-bipy})]_n$ (b), synthesized under different reaction conditions have been reported [38, 39]. In complex (a), Cu(II) is five-coordinate in a square pyramidal geometry with tsgluO^{2-} a μ_3 ($\kappa^1\text{O}:$ $\kappa^1\text{O}:$ $\kappa^1\text{O}$) coordination mode, generating a ladder-like 1-D double

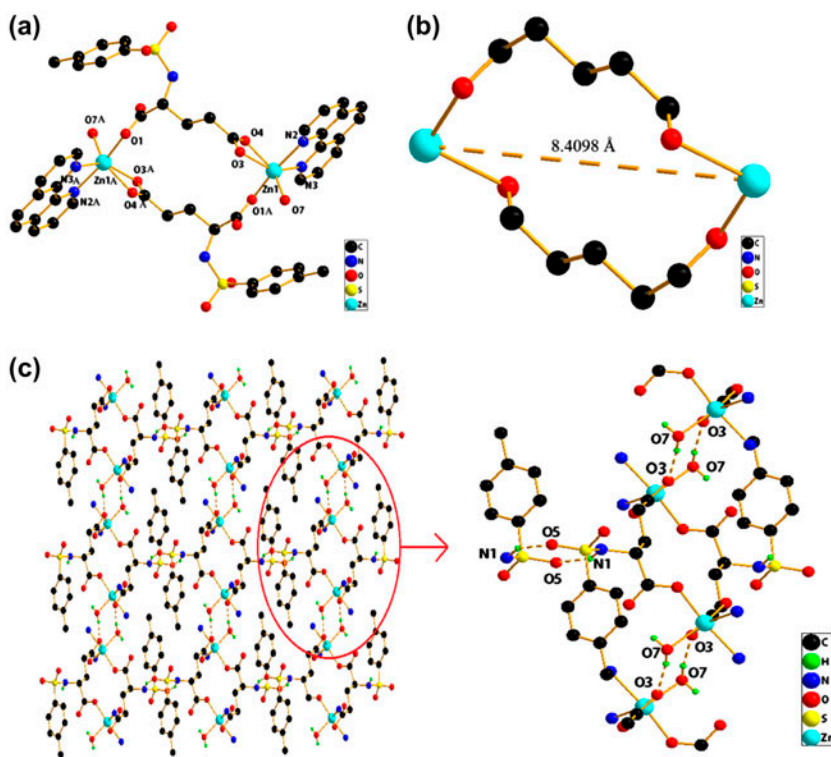


Figure 2. (a) The coordination environment of Zn(II) for **2**. All hydrogens have been omitted for clarity. (b) The sixteen-membered ring for **2**. (c) The two-dimension layer structure formed by hydrogen-bonding interactions (phen molecules have been omitted for clarity).

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

D-H	d(D-H)/nm	d(H \cdots A)/nm	d(D \cdots A)/nm	\angle DHA/°
O(7)–H(7A) \cdots O(3)#2	0.85	1.86	2.703(3)	172.1
O(7)–H(7B) \cdots O(2)#1	0.85	1.89	2.710(3)	161.1
N(1)–H(1) \cdots O(5)#3	0.84	2.17	2.952(4)	153.9

Symmetry codes: #1 $-x + 2, -y + 1, -z + 2$; #2 $-x + 1, -y + 1, -z + 2$; #3 $-x + 2, -y + 1, -z + 1$.

chain structure. In complex (b), Mn(II) is six-coordinate and exhibits a distorted octahedral coordination sphere with $\text{tsgluO}^{2-} - \mu_3$ ($\kappa^1\text{O} : \kappa^1\text{O} : \kappa^1\text{O}$) coordination in a ladder-like 1-D double chain structure. While in **1**, Zn(II) is five-coordinate and displays a slightly distorted trigonal bipyramid geometry, the tsgluO^{2-} is a μ_3 ($\kappa^1\text{O} : \kappa^1\text{O} : \kappa^1\text{O}$) coordination and adjacent Zn(II) cations are doubly bridged by two α -carboxylates forming a dinuclear unit which is further connected by tsgluO^{2-} groups to generate a 1-D double chain structure. The 1-D double chain structure in **1** is different from those in (a) and (b). Crystal structures of $[\text{Pb}_2(\text{tsgluo})_2(\text{phen})_2]$ (c) and $[\text{Pb}_2(\text{tsgluo})_2(2,2'\text{-bipy})_2]$ (d), synthesized under different reaction conditions, have been reported recently [40]. Complexes (c) and (d) both exhibit a dinuclear structure and have a similar coordination mode with Pb(II) six-coordinate in a

distorted pentagonal pyramid; tsgluO^{2-} is μ_2 ($\kappa^1\text{O}:$ $\kappa^1\text{O}:$ $\kappa^1\text{O}:$ $\kappa^1\text{O}$) coordination, whereas complex (d) further forms a 1-D chain by hydrogen bond interactions. The dinuclear structure of **2** is similar to that of (c) and (d), but Zn(II) in **2** is six-coordinate with a distorted octahedral geometry and tsgluO^{2-} has μ_2 ($\kappa^1\text{O}:$ $\kappa^1\text{O}:$ $\kappa^1\text{O}$) coordination in a dinuclear complex, which is further connected into a 2-D supramolecular network through hydrogen-bonding interactions. A comparison of **1** and **2** reveals that they are synthesized under similar conditions except for using different concentrations. Under the different concentrations, the same metal cation exhibits different coordination environments, and the same tsgluO^{2-} generates different coordination modes. Obviously, different concentrations are responsible for the structural diversities of the two complexes. The comparative structural studies of the mixed ligand complexes involving *N*-tosyl-*L*-glutamic acid and chelating nitrogen donors with transition metals clearly indicate that the reaction conditions, coordination geometries of the transition metals, and different coordination modes of tsgluO^{2-} play a crucial role in the structural diversity.

3.2. Thermal analysis

TGAs of **1** and **2** were carried out at a heating rate of $15\text{ }^\circ\text{C min}^{-1}$. The TGA curve of **1** exhibits a stable plateau from 25 to $282\text{ }^\circ\text{C}$, and then the first lost weight corresponds to *N*-tosyl-*L*-glutamic ligands (observed 51.17%, calculated 54.87%) from 282 to $578\text{ }^\circ\text{C}$. Further weight loss, responsible for phen molecules (observed 33.64%, calculated 33.03%), was observed between 578 and $720\text{ }^\circ\text{C}$. The remaining weight of 15.19% corresponds to the percentage (14.86%) of Zn and O components, indicating that the final product is ZnO. TG curve of **2** shows first mass loss of 2.84% at $150\text{--}163\text{ }^\circ\text{C}$ from loss of two coordinated waters (calcd 3.20%). Then, it shows a relatively stable plateau from 163 to $290\text{ }^\circ\text{C}$. Upon further heating, a sharp drop in weight is observed from 290 to $590\text{ }^\circ\text{C}$ (observed 50.24%, calculated 53.12%), suggesting decomposition of the *N*-tosyl-*L*-glutamic ligands. Mass loss from 590 to $730\text{ }^\circ\text{C}$ was attributed to decomposition of phen (observed 32.22%, calculated 31.98%). The total weight loss is about 85.37%, very close to the theoretical value of 85.61%, and the final residue is ZnO. TGA traces for **1** and **2** are depicted in figure 3.

3.3. Fluorescence

Emission spectra of **1** and **2** in $\text{H}_2\text{O}/\text{MeOH}$ at room temperature are depicted in figure 4. Compounds **1** and **2** exhibit the same emission bands when excited at 273 nm. To understand the nature of these emission bands, we first analyzed the photoluminescence properties of free H_2tsgluO . Upon excitation at 276 nm, the strongest emission peak is at 315 nm due to a $\pi\text{--}\pi^*$ and/or $\pi^*\text{--n}$ transition [36, 41]. We then investigated the emission spectrum of free phen with emission bands located at 365 nm and 388 nm upon excitation at 310 nm [42, 43]. Therefore, the characteristic emission bands at 304 and 315 nm can be assigned to emission of H_2tsgluO ligands [44], while the emission bands at 367 nm with a shoulder at 383 nm are probably due to $\pi\text{--}\pi^*$ transitions [45] of phen because similar peaks also appear for free phen. Different intensities of **1** and **2** may be attributed to different coordination modes of H_2tsgluO and different structures of the complexes.

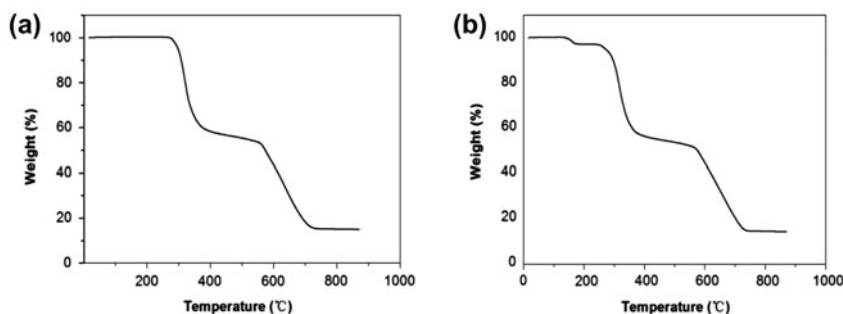


Figure 3. Thermal analyzes for (a) **1** and (b) **2**.

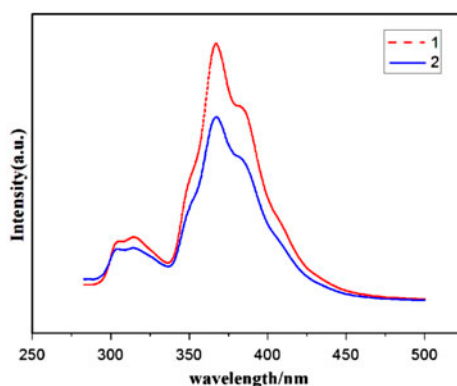


Figure 4. The emission spectra of **1** and **2** at room temperature.

4. Conclusion

Two new Zn(II) compounds have been synthesized under hydrothermal conditions by reaction of *N*-tosyl-*L*-glutamic acid, 1,10-phenanthroline, and zinc salts. Compound **1** exhibits a 1-D double-chain structure. Complex **2** is a dinuclear complex which is extended by hydrogen-bonding interactions to form a 2-D supramolecular network. The different structures indicate that concentration plays an important role in modulating the formation of structures of coordination complexes. Compounds **1** and **2** exhibit similar fluorescence emission, but the fluorescence intensity for **1** is higher than that for **2**, which may be due to the different coordination and structures of the two complexes.

Supplementary material

CCDC-760114 (**1**) and -760115 (**2**) contain the supplementary crystallographic data. Copies of the data can be obtained free of charge via the Internet at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or by post from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336,033, E-mail: deposit@ccdc.cam.ac.uk).

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