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In situ hydrothermal syntheses, crystal structures and luminescent properties of two novel zinc(II) coordination polymers based on tetrapyridyl ligand

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ABSTRACT

Two novel Zn(II) coordination polymers, $[Zn(2\text{-pytpy})(fum)]_n \cdot nH_2O$ (**1**) and $[Zn_6(4\text{-pytpy})_3(mal)_4]_n \cdot 5n(H_2O)$ (**2**), (2-pytpy = 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine, 4-pytpy = 4′-(4-pyridyl)-4,2′:6′,4″-terpyridine, H_2fum = fumaric acid and H_2mal = malic acid) have been hydrothermally synthesized and structurally characterized. Notably, *in situ* ligand reactions occur in the formation of complexes **1** and **2**, in which maleic acid is converted into fumaric acid and malic acid, respectively. Complex **1** is a 1D infinite chain structure, which is extended into a supramolecular layer by intermolecular $\pi \ldots \pi$ stacking interactions. Complex **2** is a 3D network structure, in which the bidentate-bridging 4-pytpy ligands link the layers based on the tetranuclear Zn(II) subunits to form the (4,10)-connected network. The luminescent properties of **1** and **2** have been investigated with emission spectra and UV–Vis diffuse reflectance spectra in the solid state. Additionally, these two complexes possess great thermal stabilities.

1. Introduction

The design of coordination polymer architectures is an important goal for synthetic chemistry as it provides an opportunity to control the properties of materials at the molecular level [1–3]. The most successful strategies for the design of coordination polymers are based on a building block approach because final structural frameworks can dramatically change when the organic building blocks vary [4,5]. Recently, the *in situ* ligand synthesis as a new approach to prepare coordination polymers has been noted extensively, in which ligand precursor is used to react with metal salts directly to produce single crystals containing new organic ligand [6,7]. *In situ* hydrothermal reactions usually provide not only very stable materials for potential applications, such as luminescence, magnetism, absorption, catalysis and ion-exchange [8–12], but also products that are inaccessible or not easily obtainable by conventional methods [13].

Maleic acid, as O-donor ligand, has received much more attention. It is frequently employed in the construction of polynuclear metal carboxylate clusters due to the isomerization and the hydroxylation of the ethylene group by the *in situ* hydrothermal reactions [14,15]. An interesting Co(II) complex was synthesized by the reaction of the hydroxylation of the ethylene group in maleic acid, which exhibits complicated magnetic properties tunable by guest water removal and exchange [16]. The 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine (2-pytpy, see Scheme 1), as a potentially tetradentate ligand, has been intensively explored because of its versatility as building blocks for coordination polymers [17–23]. However, its isomeric compound, 4′-(4-pyridyl)-4,2′:6′,4″-terpyridine (4-pytpy, see Scheme 1), as a rigid trigonal ligand, has been rarely reported in the realm of coordination chemistry [24,25]. Its rigidity and trigonal geometry may lead to the formation of nanosized cages, porous frameworks enclosing cavities, and channels [26,27].

Our crucial aim of this work is to explore the *in situ* hydrothermal reactions for tuning the structural assembly, which may provide further insights in designing novel hybrid crystalline materials. In this paper, we present the *in situ* hydrothermal syntheses and crystal structures of two novel Zn(II) coordination polymers, $[Zn(2\text{-pytpy})(fum)]_n \cdot nH_2O$ (**1**) and $[Zn_6(4\text{-pytpy})_3(mal)_4]_n \cdot 5n(H_2O)$ (**2**), as well as their luminescent properties and thermal stabilities.

2. Experimental

2.1. General methods

2-Pytpy and 4-pytpy ligands were prepared according to the literature method with some modifications [28,29], other chemicals were of reagent grade and used without further purification. Elemental analyses (C, H, N) were performed on an elementar Vario EL III elemental analyzer. Infrared spectra were recorded on a Bruker EQUINOX 55 spectrometer as KBr pellets in the range of

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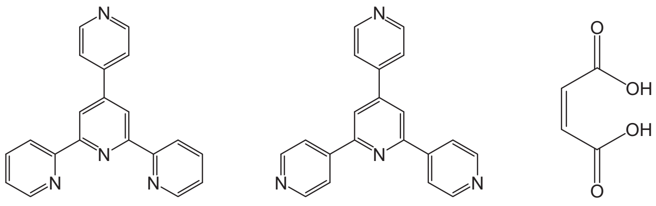


2-pytpy 4-pytpy maleic acid

Scheme 1. Molecular structures of the ligands used in the paper.

400–4000 cm^{-1}. Luminescence spectra were measured on a HitachiF-4500 spectrophotometer at room temperature. Thermal gravimetry analyses (TGA) were carried out with a Universal V2.6 DTA system at a rate of 10 °C/min in a nitrogen atmosphere.

2.2. Preparation of 2-pytpy

A mixture of 2-acetylpyridine (3.21 g, 26.7 mmol), pyridine-4-carboxaldehyde (3.26 g, 26.7 mmol) and NaOH (1.60 g, 40.0 mmol) was dissolved in ethanol (50 mL) with stirred at 0 °C for 2 h, resulted in the formation of a light yellow solution. Then, added 2-acetylpyridine (3.21 g, 26.7 mmol) and excessive ammonium acetate (10.00 g, 129.7 mmol), stirred at 80 °C under nitrogen atmosphere for 5 h. After the mixture was cooling to room temperature, the resulting white precipitate was filtered off, recrystallized with methanol, and dried in vacuo to give colourless needle crystals in 31.7% yield based on pyridine-4-carboxaldehyde (3.06 g). *Anal.* Calc. for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55; N, 18.05. Found: C, 77.57; H, 4.34; N, 18.09. IR (KBr, cm^{-1}): 3418 w, 3049 m, 1703 m, 1585 s, 1530 s 1468 s, 1407 w, 1391 s, 1264 m, 1069 m, 985 m, 901 m, 893 w, 809 s, 735 w, 616 m, 521 m.

2.3. Preparation of 4-pytpy

The preparation of 4-pytpy was similar to that of 2-pytpy except that 4-acetylpyridine was used instead of 2-acetylpyridine. The colourless block crystals were obtained in 35.3% yield based on pyridine-4-carboxaldehyde (3.42 g). *Anal.* Calc. for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55; N, 18.05. Found: C, 77.34; H, 4.69; N, 17.98. IR (KBr, cm^{-1}): 3422 w, 3026 m, 1706 m, 1590 s, 1534 s, 1424 w, 1396 s, 1319 m, 1218 m, 1062 w, 989 m, 891 m, 817 s, 743 w, 672 w, 622 m, 580 m, 493 m.

*2.4. Preparation of [Zn(2-pytpy)(fum)]$_n$·nH$_2$O (**1**)*

A mixture of $ZnCl_2 \cdot 2H_2O$ (0.0136 g, 0.1 mmol), 2-pytpy (0.0312 g, 0.1 mmol), maleic acid (0.0232 g, 0.2 mmol) in distilled water (10 mL) was placed in a Teflon-lined stainless steel vessel and adjusted the pH value of the mixture to 6.0 with 0.5 mol L^{-1} NaOH aqueous solution. The reaction system was heated at 160 °C for 72 h, followed by slowly cooling down to room temperature at a rate of 5 °C h^{-1}. The colourless block crystals were obtained and dried in air to give 0.0327 g, yield: 64.3% based on Zn. *Anal.* Calc. for $C_{24}H_{18}N_4O_5Zn$: C, 56.76; H, 3.57; N, 11.03. Found: C, 56.53; H, 3.42; N, 11.16. IR (KBr, cm^{-1}): 3359 m, 3250 m, 3071 m, 1691 w, 1572 s, 1471 m, 1394 s, 1249 m, 1209 m, 1158 m, 1095 w, 996 w, 962 m, 897 m, 811 m, 794 s, 744 m, 694 m, 621 w, 578 w , 509 w.

*2.5. Preparation of [Zn$_6$(4-pytpy)$_3$(mal)$_4$]$_n$·5n(H$_2$O) (**2**)*

Complex **2** was prepared in a similar procedure as **1**, by using 4-pytpy (0.0312 g, 0.1 mmol) in place of 2-pytpy, and the reaction system was heated at 180 °C. The yellow rhombus crystals were obtained, washed with distilled water (5 mL), and dried in air to give 0.0204 g, yield: 63.1% based on Zn. *Anal.* Calc. (for $C_{76}H_{64}N_{12}O_{25}Zn_6$: C, 47.10; H, 3.32; N, 8.67. Found: C, 47.19; H, 3.21; N, 8.61. IR (KBr, cm^{-1}): 3423 m, 1631 s, 1597 m, 1419 w, 1399 s, 1350 m, 1288 w, 1121 m, 1070 w, 1028 w, 836 m, 818 m, 669 w, 640 m, 629 w, 591 w, 502 m.

2.6. The solid-state UV–Vis diffuse reflectance spectra

The solid-state UV–Vis diffuse reflectance spectra were performed at room temperature using a Shimadzu UV-2550 double monochromator spectrophotometer. The instrument is equipped with an integrating sphere and controlled by a personal computer. $BaSO_4$ was used as a 100% reflectance standard for all materials. The UV–Vis diffuse reflectance measurements were taken in the range of 200–700 nm. Data were collected in reflectance (%*R*) mode. Samples were prepared by grinding them to a fine powder and spreading them on a compacted surface of the powdered standard material, preloaded into a sample holder.

2.7. X-ray crystallography

Intensity data of **1** and **2** were collected on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Empirical absorption corrections were applied using the SADABS program. The structures were solved by the direct method and refined by the full-matrix least-squares on F^2 with SHELX-97 program package [30,31]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms of organic ligands were generated geometrically. The crystal data and structural refinement results are summarized in Table 1. The selected bond distances and angles are listed in Table S1 (Supplementary information).

Table 1
Crystallographic data and structural refinement parameters for **1**and **2**.[a]

Complexes	**1**	**2**
Empirical formula	$C_{24}H_{18}N_4O_5Zn$	$C_{76}H_{64}N_{12}O_{25}Zn_6$
Formula weight	507.79	1937.61
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	monoclinic, $P2_1/n$	monoclinic, $C2/c$
a (Å)	8.6622(5)	34.471(5)
b (Å)	24.636(1)	10.926(1)
c (Å)	10.9851(5)	22.395(3)
α (°)	90	90
β (°)	115.560(3)	120.743(2)
γ (°)	90	90
V (Å^3)	2114.8(2)	7249(2)
Z	4	4
Calculated density (g cm^{-3})	1.595	1.775
Absorption coefficient (mm^{-1})	1.208	2.048
$F(0\,0\,0)$	1040	3936
θ range for data collection (°)	2.22–25.05	1.99–25.05
Index range	$-5 \le h \le 10$ $-29 \le k \le 29$ $-13 \le l \le 12$	$-31 \le h \le 40$ $-12 \le k \le 13$ $-26 \le l \le 25$
Reflections collected	10 512	17 546
Reflections unique	3738	6385
Completeness to $\theta = 25.05$	99.7%	99.5%
Goodness-of-fit (GOF) on F^2	1.048	1.017
Independent reflections (R_{int})	0.0190	0.0577
R_1, wR_2 [$I > 2\sigma(I)$]	0.0248, 0.0662	0.0565, 0.1362
R_1, wR_2 (all data)	0.0306, 0.0685	0.0917, 0.1542
Largest difference in peak, hole (e Å^{-3})	0.247, −0.230	0.957, −0.739

[a] $R = \Sigma||F_0| - |F_C||/\Sigma|F_0|$, $wR_2 = [\Sigma[w(F_0^2 - F_C^2)^2]/\Sigma[(F_0^2)^2]]^{1/2}$.

3. Results and discussion

3.1. Syntheses

2-Pytpy and 4-pytpy were synthesized in high purity and acceptable yield according to the method reported by Kröhnke with some modifications. The reaction time was shortened from 24 h to 7 h. Therefore, our modified procedure is a more convenient method to prepare 2-pytpy and 4-pytpy ligands, as well as its isomeric compounds.

Complexes **1** and **2** have been successfully prepared under hydrothermal conditions. It is noteworthy that the *in situ* reactions occur in the formation of **1** and **2**, in which maleic acid was converted into fumaric acid and malic acid, respectively (see Scheme 2). We used maleic acid as the ligand precursor to react with $ZnCl_2{\cdot}2H_2O$ in the presence of 2-pytpy ligand to obtain $[Zn(2\text{-}pytpy)(fum)]_n{\cdot}nH_2O$ (**1**), in which maleic acid was converted into fumaric acid by the isomerization reaction. To our knowledge, the key influencing factor for the *in situ* reactions is temperature. The *in situ cis–trans* isomeric transformation of substituted ethylene was occurred under 140 °C, because fumaric acid is much stable than maleic acid at high temperature [32–36]. At the same time, the *in situ cis–trans* isomerization can occur with several metal salts, such as Cu(I), Cd(II) and Zn(II) ions [37–39], which indicates metal ion is not one of the key factors for the *in situ cis–trans* isomerization of maleic acid. While in the formation of **2**, the hydroxylation of the ethylene group of maleic acid has been observed. It has long been known that HCl could catalyze the conversion of maleic acid into malic acid with addition of water. The mechanism of the *in situ* ligand synthesis of malic acid is probably similar to that of ethylene hydration reactions to form alcohols in acidic conditions [40,41]. It must be mentioned that if the Zn(II) salts directly react with the malate and 4-pytpy ligands, we only obtained Zn(II) coordination polymers with 4-pytpy ligands and without malate anions [15], which suggests that the *in situ* ligand synthesis is favorable to form coordination polymers with mixed ligands.

3.2. IR spectra

The IR spectra of 2-pytpy, 4-pytpy, **1** and **2** exhibit characteristic bands of the 4′-(4-pyridyl)-terpyridine (2-pytpy and 4-pytpy) at about 1590 cm^{-1} ν(C═C), 1390 cm^{-1} (ring deformation mode C–C) and 810 cm^{-1} (out-of-ring bend C–H). In the IR spectra of **1** and **2**, the absence of any strong bands around 1700 cm^{-1} indicates that the carboxylate groups of organic-acid are completely deprotonated [42,43]. The differences between ν_{as}(COO) and ν_s(COO) ($\Delta = 208\ cm^{-1}$ for **1**, 232 cm^{-1} for **2**) suggest that the carboxylate groups coordinate to the Zn(II) ions in monodentate coordination modes [44,45]. These IR spectra are in good agreement with the results of X-ray structural analyses.

3.3. Description of crystal structures

3.3.1. $[Zn(2\text{-}pytpy)(fum)]_n{\cdot}nH_2O$ (1)

Complex **1** crystallizes in the monoclinic $P2_1/n$ space group. The asymmetric unit of **1** contains one crystallographically independent Zn(II) atom, two half μ_2-fum^{2-} anion, one tridentate-chelating 2-pytpy ligand and one lattice water molecule. As shown in Fig. 1a, the Zn1 center is five-coordinated to three nitrogen atoms (N1, N2, N3) from the same 2-pytpy ligand, and two oxygen atoms (O1 and O3) from different fum^{2-} ligands, respectively. The coordination geometry of Zn1 center can be described as a distorted square-pyramid, the N1, N2, N3, O3 atoms comprise the equatorial plane and the O1 atom occupies the axial position. The distances of Zn–N fall in the range of 2.086(2)–2.177(2) Å, and the Zn–O bond lengths

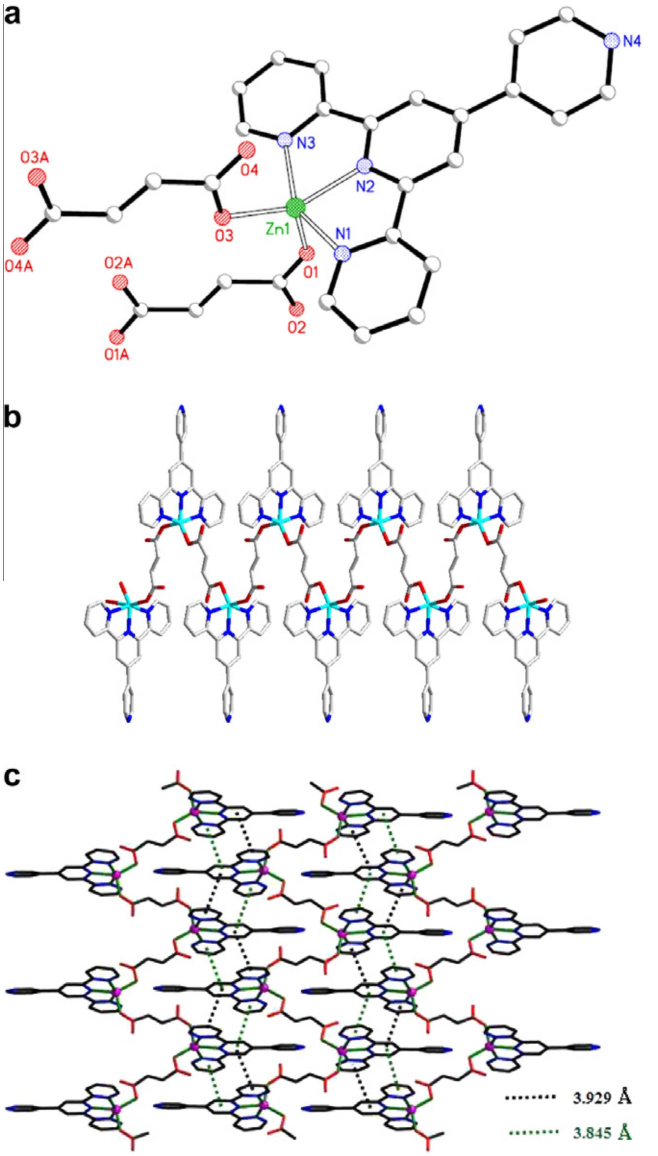
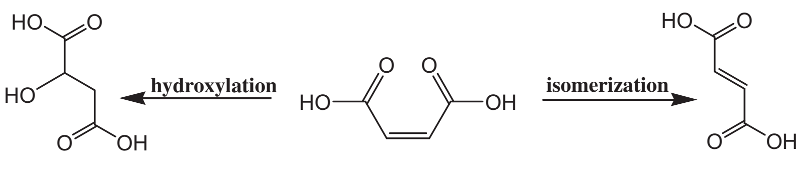


Fig. 1. (a) The coordination environment of the Zn(II) in **1** with partial atom numbering schemes (symmetric code A: −x + 2, −y + 2, −z + 2). Hydrogen atoms and uncoordinated water molecules are omitted for clarity. (b) The view of the 1D chain in **1**. (c) Packing diagram of the 2D layer supported by two types of intermolecular π…π stacking interactions in **1**.



Scheme 2. The *in situ* hydrothermal reactions occur in the formation of **1** and **2**.

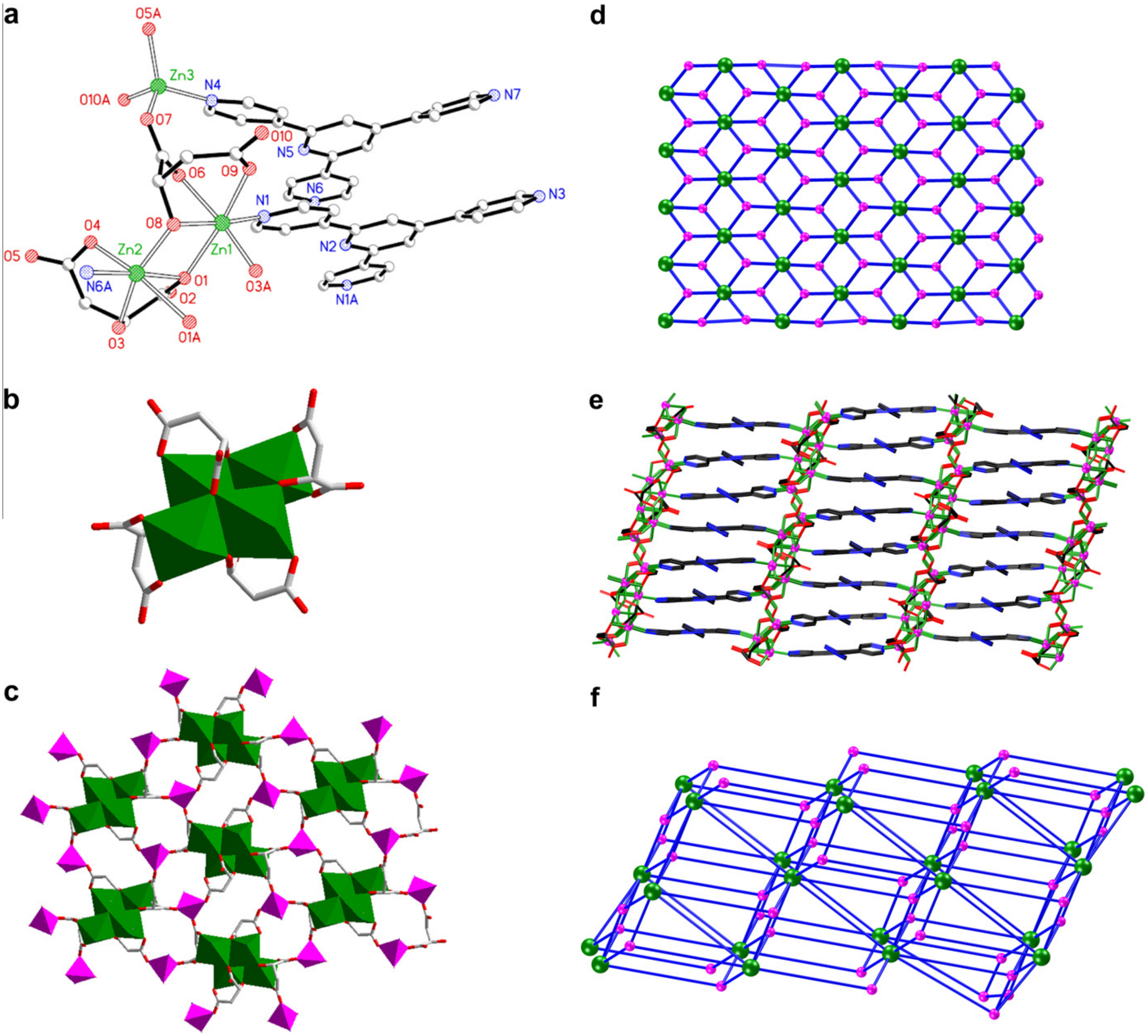


Fig. 2. (a) The coordination environment of the Zn(II) in **2** with partial atom numbering schemes (symmetric code A: $x + 1/2$, $-y + 5/2$). Hydrogen atoms and uncoordinated water molecules are omitted for clarity. (b) The view of the tetranuclear Zn(II) subunit in **2**. (c) The view of the 2D layer constructed from Zn(II) centers and mal^{2-} anions in **2**. (d) The topological network of 2D layer in **2**. The 6-connected tetranuclear Zn(II) subunits are marked as green balls , and 3-connected mononuclear Zn(II) tetrahedron are marked as pink balls, respectively. (e) The view of the 3D structure of **2**. (f) The view of the 3D topological network of **2**. The 10-connected tetranuclear Zn(II) subunits are marked as green balls , and 4-connected mononuclear Zn(II) tetrahedron are marked as pink balls, respectively.

vary from 1.982(1) Å to 1.986(1) Å, which are consistent with the corresponding values reported for Zn-fumaric and Zn-pyridyl complexes [46–48].

In complex **1**, four pyridyl rings of the 2-pytpy ligand are nonplanar, N4 pyridyl ring is twisted relative to the central one (N2 pyridyl ring) with a large angle of 32.27°, while the other two pyridyl rings are nearly co-planar with the central one, the corresponding dihedral angles are 3.03° (N1 pyridyl ring) and 4.63° (N3 pyridyl ring), respectively. In **1**, the rotation of the N4 pyridyl ring with the central one is larger than others. The reasons for this phenomenon are the repulsion force arising from the central pyridine-β-hydrogen atoms and the formation of intermolecular hydrogen bonds to stabilize the compound [49,50]. The other reason may be N1, N2 and N3 pyridyl rings coordinated to Zn(II) center in the same equatorial plane of square-pyramidal coordination geometry.

Notably, H_2fum is completely deprotonated and acts as a bis-monodentate bridging ligand bonding with Zn(II) ions to form a 1D infinite chain structure (Fig. 1b), and the minimum intrachain Zn…Zn distance is 8.080(2) Å. In the solid state, two types of π…π stacking interactions are observed, as illustrated in Fig. 1c. The central and one terminal pyridyl rings of 2-pytpy interact with the terminal and central pyridyl rings from the adjacent chains [3.929(2) Å and 3.845(2) Å for centroid–centroid distances]. Therefore, these 1D chains are linked to each other to form a 2D layer by these two types of intermolecular π…π stacking interactions.

It should be pointed out that although different pyridyl ligands (py = pyridine, phen = 1,10-phenanthroline) were used in the formation of $[Zn(fum)(py)_3]_n{\cdot}n(py){\cdot}n(H_2O)$ [51,52], $[Zn(phen)(fum)]_n{\cdot}n(H_2fum)$ [46] and **1**, they all show 1D zigzag chain structures. However, some differences exist between these complexes. The average Zn–N and Zn–O bond distances in $[Zn(fum)(py)_3]_n$

$\cdot n(\mathrm{py})\cdot n(\mathrm{H_2O})$ [2.175(3) Å and 1.998(3) Å] are longer than the corresponding values in $[\mathrm{Zn(phen)(fum)}]_n\cdot n(\mathrm{H_2fum})$ [(2.049(2) Å and 1.961(2) Å] and **1** [2.147(1) Å and 1.988 (1) Å)], which indicate that chelating ligands are coordinated to metal centers much more stably than that of the monodentate ligands. Additionally, π…π stacking interactions were not observed in $[\mathrm{Zn(fum)(py)_3}]_n\cdot n(\mathrm{py})\cdot n(\mathrm{H_2O})$. However, in $[\mathrm{Zn(phen)(fum)}]_n\cdot n(\mathrm{H_2fum})$ and **1**, they all extended into supramolecular layers by intermolecular π…π stacking interactions. In all, ligands containing big conjugated systems are apt to form more stable complexes than the corresponding complexes with monodentate ligands.

3.3.2. $[\mathrm{Zn_6(4\text{-}pytpy)_3(mal)_4}]_n\cdot 5n(\mathrm{H_2O})$ (**2**)

X-ray structural analysis revealed that **2** is a 3D polymeric network. In **2**, the asymmetric unit contains three crystallographically independent Zn(II) atoms, two μ_3-mal^{2-} anions, one and a half bidentate-bridging 4-pytpy ligand and five lattice water molecules. As shown in Fig. 2a, the Zn1 center is coordinated to five oxygen atoms (O1, O6, O8, O9, and O3A) from mal^{2-} anions and one nitrogen atom (N1) from 4-pytpy ligand. The coordination geometry of Zn1 center can be described as a distorted octahedron, the O1, O6, O9, O3A atoms comprise the equatorial plane and the N1, O8 atoms occupy the axial positions [N1–Zn1–O8 = 173.4(2)°]. Zn2 is also six-coordinated with a distorted octahedral geometry. The basal positions are occupied by O3, O4, O8 and O1A, O1 and N6A atoms occupy the axial positions [O1–Zn2–N6A = 176.8(2)°]. While Zn3 center is four-coordinated to O7, O5A, O10A, N4 with a distorted tetrahedral geometry, the corresponding angles are 101.7(2)° (O5A–Zn3–O7), 112.1(2)° (O5A–Zn3–O10A), 114.7(2)° (O7–Zn3–O10A), 119.3(2)° (O5A–Zn3–N4), 114.2(2)° (O7–Zn3–N4) and 95.5(2)° (O10A–Zn3–N4).

The most interesting feature of **2** is its tetranuclear Zn(II) subunit, which is composed of four edge-sharing $\mathrm{ZnNO_5}$ octahedra (Fig. 2b). In **2**, the tetranuclear Zn(II) subunits are linked through six $\mathrm{ZnNO_3}$ tetrahedra to construct a 2D layer (Fig. 2c). If the tetranuclear Zn(II) subunit is as a six-linked node and the mononuclear Zn(II) tetrahedron as a three-linked node, the 2D layer can be simplified to a 2D topological network with Schläfli symbol of $(4^6.6^6.8^3)(4^3)_2$ (Fig. 2d). The 2D layers are further connected with the bidentate-bridging 4-pytpy ligands to generate a 3D network (Fig. 2e). To simplify this 3D structure, we can consider the tetranuclear subunit as a 10-linked node and the mononuclear Zn(II) tetrahedron as a four-linked node, thus, the 3D structure can be formulated as a (4,10)-connected network with Schläfli symbol of $(3^4.4^{12}.5^{11}.6^{14}.7^3.8^1)(3.4^5)_2$ (Fig. 2f). Notably, this is the first structural paradigm for a coordination polymer with such a (4,10)-connected topological net.

3.4. The solid-state UV–Vis properties

The UV–Vis diffuse reflectance spectra of the complexes **1** and **2** were carried out in the solid state at room temperature. As shown in Fig. 3, the spectra of 2-pytpy and 4-pytpy shows intense peaks at 324 nm and 338 nm, respectively, which can be ascribed to $\pi \to \pi^*$ transitions of pytpy ligand [53,54]. The solid-state UV–Vis diffuse reflectance spectra of **1** and **2** are also depicted in Fig. 3. The bands are located at 265 nm (broad band) and 322 nm for **1**, 260 nm (broad band) and 320 nm for **2**, respectively. They all possess similar absorption spectra and tentatively assigned to ligand-based $\pi \to \pi^*$ transitions.

3.5. Luminescent properties

The Zn(II) terpyridyl complexes are well known for their versatile luminescent properties at room temperature [55,56]. The emission spectra of 2-pytpy and **1**, 4-pytpy and **2** in the solid state are depicted in Fig. 4. 2-Pytpy and 4-pytpy are isomeric conjugated organic compounds, they both exhibit strong emission band at 375 nm upon excitation at 310 nm. In contrast with terpyridyl derivatives, the emission energy is expectable [57]. At room temperature, the similar emission at 383 nm and 385 nm were observed for **1** and **2** at the same excitation condition. It is suggested that the emission of **1** and **2** originated from ligand-based intramolecular charge transfer (ICT) [58]. Notably, a lower energy emission was also detected at 522 nm for **1**, which indicates that the intermolecular π…π stacking interactions exist. The enhancement of luminescence may be attributed to ligand chelation to the Zn(II) centers, which effectively increases the rigidity of the coordination polymers and reduces the loss of energy by radiationless decay [59].

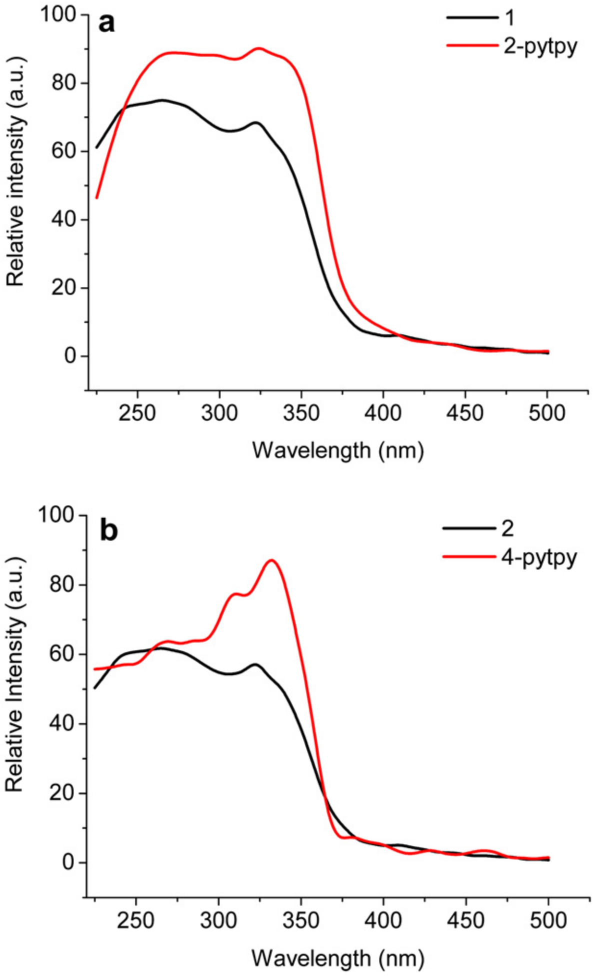


Fig. 3. The solid-state diffuse reflectance spectra of 2-pytpy and **1** (**a**), 4-pytpy and **2** (**b**) at room temperature.

3.6. Thermogravimetric analysis and PXRD patterns

Thermal gravimetry analyses (TGA) were performed to gauge the thermal stabilities of complexes **1** and **2**. As shown in Fig. S1, the TGA curve of **1** and **2** are divided into three stages. The first weight loss of 3.11% occurs under 175 °C for **1** and 4.43% under 190 °C for **2**, which can be attributed to the loss of lattice water molecule (calcd 3.55% for **1** and 4.66% for **2**). The second step weight loss of 61.05% between 385 °C and 452 °C for **1** and 48.53% between 301 °C and 412 °C for **2** indicated the decomposition of pytpy ligands (2-pytpy

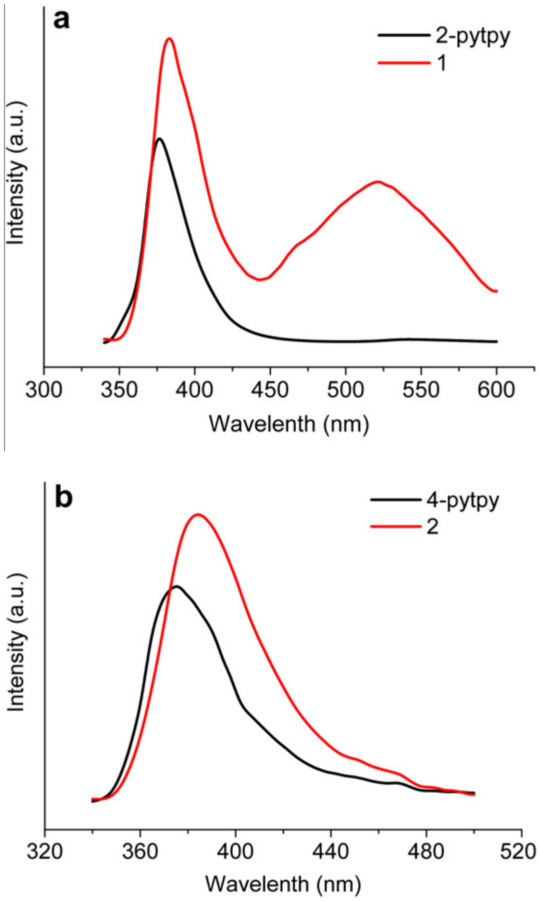


Fig. 4. The solid-state emission spectra of 2-pytpy and **1** (**a**), 4-pytpy and **2** (**b**) at room temperature.

for **1**, calcd 61.18%; 4-pytpy for **2**, calcd 48.05%). The weight loss of 19.48% from 452 °C to 655 °C for **1** and 21.95% from 412 °C to 700 °C for **2** were attributed to the loss of the second ligands (fum^{2-} ligands for **1**, calcd 19.31%; malate anions for **2**, calcd 22.21%). The residue product of 16.16% for **1** and 21.37% for **2** are ZnO (calcd 16.03% for **1** and 21.03% for **2**). TGA results of these two coordination frameworks indicate they possess great thermal stability, especially for **1**, the framework is stable up to 380 °C. The purity of the complexes **1** and **2** is confirmed by powder X-ray diffraction (PXRD). As shown in Fig. S2, the as-synthesized patterns of complexes **1** and **2** match well with their corresponding simulated patterns from single-crystal data.

4. Conclusion

In summary, two novel Zn(II) coordination polymers have been *in situ* hydrothermally synthesized by the reaction of zinc chloride with maleic acid and 4′-(4-pyridyl)-terpyridine mixed ligands. Interestingly, maleic acid is converted into fumaric and malic acid by *in situ* reactions in **1** and **2**, respectively. Complex **1** is a 1D infinite chain structure, and complex **2** is a 3D network structure. The luminescent properties of **1** and **2** have been investigated with emission spectra and the solid-state UV–Vis diffuse reflectance spectra in crystalline state. These complexes display excellent luminescent properties and possess high thermal stability.

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Appendix A. Supplementary material

CCDC 747632(**1**) and 747633(**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.10.020.

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