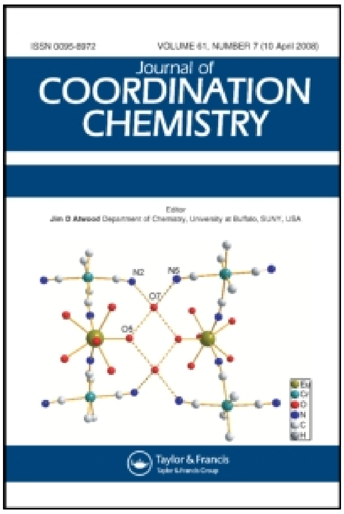

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Synthesis, spectroscopic, and structural characterization of two malate zinc coordination polymers with imidazole or 2,2'-bipyridine

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Synthesis, spectroscopic, and structural characterization of two malate zinc coordination polymers with imidazole or 2,2′-bipyridine

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Zinc(II) coordination polymers, $[Zn(Hmal)(im)(H_2O)]_n \cdot 2nH_2O$ (**1**) and $[Zn(Hmal)(bpy)]_n \cdot 3nH_2O$ (**2**) (H_3mal = malic acid, im = imidazole, bpy = 2,2′-bipyridine), were synthesized from aqueous solution and characterized by elemental analyses, infrared and fluorescence spectra, thermogravimetric analyses, and single-crystal X-ray structural analyses. In **1**, zinc is coordinated by imidazole, water, and tridentate malate in octahedral geometry. The β-carboxy group of malate further bridges with the other zinc forming 1-D polymeric chains. A pair of 1-D chains self-assemble to generate a double chain by strong hydrogen bonds between imidazole and malate. Furthermore, neighboring pairs of double chains are extended to form the final 3-D framework through intermolecular hydrogen bonds. In **2**, the malates link Zn in a bidentate–monodentate fashion to form spiral-shaped chains that extend into a 3-D supramolecular structure by π–π stacking interactions and intermolecular hydrogen bonds. Complex **1** exhibits strong fluorescence at room temperature.

Keywords: Zinc; Malic acid; Imidazole; 2,2′-Bipyridine; Coordination polymer

1. Introduction

Metal–organic coordination compounds have attracted attention because of their intriguing structures, new topologies, and potential applications as functional materials [1–10]. Carboxylate–metal complexes have interesting coordination chemistry, unusual structural features, remarkable physical and chemical properties, and potential applications as dyes, extractants, drugs, pesticides, and catalysts [11–14]. Properties of coordination polymers are heavily influenced by their structures. Therefore, it is important for crystal engineering to investigate the factors influencing the structural construction of functional compounds. The structures of coordination polymers are frequently affected by ligands [15], the nature of metal ions [16], counteranions [17], solvents [18], metal-to-ligand ratio [19], pH [20, 21], and reaction temperature [22]. Malic acid, as an α-hydroxydicarboxylic acid, plays a key role in metabolic pathways of

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plants and animals and is involved in many fundamental biochemical processes, e.g., the Krebs cycle [23, 24]. It is also a versatile ligand in coordination chemistry. However, malate, although important as a polycarboxylate ligand, has been less studied as building blocks to construct metal–organic frameworks (MOFs) [25–35]. A recent advance is the development of a class of MOFs known as zeolitic imidazole frameworks (ZIFs), in which metals such as Zn are linked through nitrogens by ditopic imidazolate or functionalized imidazolate links to form neutral frameworks [15, 36]. These compounds have high chemical and thermal stabilities [37]. In our previous investigation, pH value, metal-to-ligand molar ratio, and reaction temperature have been found to influence the structures of zinc coordination compounds with malate ligand [38]. As part of our ongoing efforts in extension of MOFs with metal salts and α-hydroxycarboxylic acids as well as N-donor ligands, we report herein two coordination polymers, $[Zn(Hmal)(im)(H_2O)]_n \cdot 2nH_2O$ (**1**) and $[Zn(Hmal)(bpy)]_n \cdot 3nH_2O$ (**2**) (H_3mal = malic acid, im = imidazole, bpy = 2,2′-bipyridine). Although **2** has been reported by others [39], we synthesize it by a different method and report it in this article in order to discuss the different coordinations of the ligand.

2. Experimental

2.1. *Materials and general methods*

The pH was measured with the potentiometric method with a digital PHB-8 pH meter. Infrared (IR) spectra were recorded as Nujol mulls between KBr plates using a Nicolet 360 FT-IR spectrometer. Elemental analyses were performed using an EA 1110 elemental analyzer. Thermogravimetric analyses (TGA) were performed on a NETZSCH TG 209 F1 instrument under flowing N_2 with a heating rate of $10^{\circ}C\,min^{-1}$. Fluorescence spectrum of **1** was measured with a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

2.2. *Preparation of $[Zn(Hmal)(im)(H_2O)]_n \cdot 2nH_2O$ (1)*

R,*S*-malic acid (0.67 g, 5 mmol) and imidazole (0.34 g, 5 mmol) were added to a stirred solution of $Zn(NO_3)_2 \cdot 6H_2O$ (1.49 g, 5 mmol) in water (18 mL). The pH of the solution was adjusted to 6.3 with dilute ammonium hydroxide and the mixture heated in a water bath at 60°C for 1 week. The resulting colorless solution was kept for slow evaporation at room temperature. Compound **1** was crystallized after several days. The solid was filtered, washed with water, and air dried to yield white crystals. Yield: 0.99 g (62%). IR (KBr, cm^{-1}): $3336_{s,br}$, 3144_w, 2944_w, 2854_w, 1619_s, 1597_s, 1552_m, 1426_s, 1398_w, 1385_w, 1310_s, 1252_w, 1097_s, 1069_w, 841_m, 756_m, 658_m, 608_w, 579_w; Anal. Calcd for $C_7H_{14}N_2O_8Zn$ (%): C, 26.3; H, 4.4; N, 8.8. Found (%): C, 26.7; H, 4.5; N, 8.8.

2.3. *Preparation of $[Zn(Hmal)(bpy)]_n \cdot 3nH_2O$ (2)*

R,*S*-malic acid (0.27 g, 2 mmol) and 2,2-bpy (0.31 g, 2 mmol) were added to a stirred solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.59 g, 2 mmol) in water (50 mL). The pH of the solution

Table 1. Crystallographic data for **1**.

Empirical formula	$C_7H_{14}N_2O_8Zn$
Formula weight	319.57
Crystal color	Colorless
Crystal size (mm^3)	$0.25 \times 0.15 \times 0.05$
Crystal system	Orthorhombic
Unit cell dimensions (Å)	
a	9.3806(5)
b	8.4077(5)
c	29.127(2)
Volume (Å^3), Z	2297.2(2), 8
Space group	$P\,bca$
Calculated density (g cm^{-3})	1.848
$F(000)$	1312
Reflections collected/unique/R_{int}	16,728
Independent reflection	2814 [R(int) = 0.1276]
Data/restraints/parameters	2814/10/184
θ range (°)	1.40–28.44
Goodness-of-fit on F^2	0.980
$R_1{}^a$, wR_2 [$I > 2\sigma(I)$]^b	0.041, 0.094
$R_1{}^a$, w$R_2{}^b$ (all data)	0.056, 0.099
Largest difference peak and hole (e Å^{-3})	0.757, −0.463

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma(|F_o|)$; $^b\text{w}R_2 = \Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]^{1/2}$.

was adjusted to 4.0 with dilute ammonium hydroxide and the mixture was heated in a water bath at 60°C for several days. Colorless crystals of **2** appeared from the warm solution. The product was isolated by filtration and dried in air. Yield: 0.69 g (84%). IR (KBr, cm^{-1}): $3417_{\text{s,br}}$, 3078_{w}, 1604_{s}, 1493_{w}, 1478_{w}, 1451_{m}, 1417_{s}, 1369_{m}, 1316_{s}, 1296_{m}, 1267_{w}, 1095_{m}, 1045_{w}, 1027_{w}, 787_{m}, 735_{m}, 658_{m}, 562_{w}; Anal. Calcd for $C_{14}H_{18}N_2O_8Zn$ (%): C, 41.2; H, 4.4; N, 6.9. Found (%): C, 41.3; H, 4.3; N, 6.6.

2.4. *X-ray crystallography*

Intensity data of **1** and **2** were collected with Mo-Kα radiation (λ = 0.71073 Å) on a Bruker SMART Apex CCD diffractometer at 296 K. Absorption corrections were applied by using SADABS [40]. The structures were solved by WinGX package [41] and refined by full-matrix least-squares with anisotropic thermal parameters for all the non-hydrogen atoms using SHELXL-97 [42]. Hydrogens were included and located from difference Fourier map but not refined anistropically. Crystal data collections and refinement parameters of **1** are summarized in table 1. Selected bond lengths and angles of **1** are listed in table 2.

3. Results and discussion

3.1. *Synthesis*

Syntheses of **1** and **2** were carried out in aqueous solution. The coordination polymer $[Zn(Hmal)(im)(H_2O)]_n \cdot 2nH_2O$ (**1**) was prepared from the reaction of zinc nitrate hexahydrate, racemic malic acid, and imidazole in a molar ratio of 1 : 1 : 1.

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

Zn(1)–O(1)	2.211(2)	Zn(1)–O(5a)	2.054(2)
Zn(1)–O(2)	2.119(2)	Zn(1)–O(1w)	2.066(2)
Zn(1)–O(4)	2.079(2)	Zn(1)–N(1)	2.016(2)
O(1)–Zn(1)–O(2)	75.56(7)	O(2)–Zn(1)–N(1)	93.67(8)
O(1)–Zn(1)–O(4)	80.53(7)	O(4)–Zn(1)–O(5a)	84.42(7)
O(1)–Zn(1)–O(5a)	82.63(7)	O(4)–Zn(1)–O(1w)	172.70(8)
O(1)–Zn(1)–O(1w)	92.68(8)	O(4)–Zn(1)–N(1)	93.06(8)
O(1)–Zn(1)–N(1)	167.48(8)	O(5a)–Zn(1)–O(1w)	97.43(8)
O(2)–Zn(1)–O(4)	88.77(8)	O(5a)–Zn(1)–N(1)	107.59(8)
O(2)–Zn(1)–O(5a)	157.95(7)	O(1w)–Zn(1)–N(1)	93.11(9)
O(2)–Zn(1)–O(1w)	86.93(8)		
Hydrogen bondings			
O1···O3w	2.659(3)	O1···H···O3w	172(3)
N2···O2(b)	2.787(3)	N2···H···O2	165.0
O1w···O3(c)	2.638(3)	O1w···H···O3(b)	173(3)
O3w···O3(c)	2.729(3)	O3w···H···O3(b)	175(3)
O3w···O2w(d)	2.735(3)	O3w···H···O2w(c)	166(3)

Symmetric transformation for **1**: (a): $-x+1/2$, $y-1/2$, z; (b): $1/2+x$, y, $1.5-z$; (c): $-x-1/2$, $y-1/2$, z; (d): $-x$, $-y+1$, $-z+1$.

The formation of **1** is sensitive to pH of the solution. If the reaction was performed at pH < 5, there is no imidazole binding to Zn and $[Zn_2(Hmal)_2(H_2O)_4]_n \cdot 2nH_2O$ [38] was obtained; while at pH > 7, only $[Zn(Im)_2]_n$ [43] was obtained. The optimal pH is 6.3 for better crystals. The other polymer $[Zn(Hmal)(bpy)]_n \cdot 3nH_2O$ (**2**) was obtained from the reaction of zinc nitrate, racemic malic acid, and 2,2′-bipyridine in a molar ratio of 1 : 1 : 1. It was reported by Song *et al.* [39] that **2** can also be synthesized by hydrothermal reactions of $Zn(CH_3COO)_2{\cdot}2H_2O$, fumaric acid, and 2,2′-bipyridine, in which fumaric acid is transferred to malic acid under hydrothermal condition. The absence of IR absorption bands around 1700 cm^{-1} was attributed to the full deprotonation of carboxy group in the malic acids of **1** and **2**, as revealed by the structural analysis. Strong peaks at 1619, 1597, 1426, and 1310 cm^{-1} for **1**, and 1604, 1417, and 1316 cm^{-1} for **2** correspond to ν_{asym} and ν_{sym} of the coordinated carboxylates, respectively. Both products are insoluble in water, even after heating.

3.2. *Structure description*

The structure of **1** displays a 3-D supramolecular structure composed of 1-D chains. The asymmetric unit of **1** contains one Zn(II), one malate, one imidazole, and one coordinated water. Each zinc is six-coordinate in a distorted octahedral geometry, by four oxygens from two different malates (O1, O2, O4, O5a) and one coordinated water (O1w) and one nitrogen (N1) from imidazole, as shown in figure 1. The Zn–O distances range from 2.054(2) to 2.211(2) Å and the Zn–N distance is 2.016(2) Å. The coordination angles around Zn vary from 75.56(7)° to 172.70(8)° (table 2). Adjacent Zn centers are connected by malate to form a 1-D chain along the *a*-axis, as shown in figure 2. The structure is centrosymmetric and involves both the *R*- and *S*-enantiomers of malate, which are alternatively arranged. Imidazole planes are on one side of the 1-D chain. Two neighboring chains are linked by a hydrogen bond between the uncoordinated nitrogen of imidazole and the coordinated oxygen of the α-carboxy

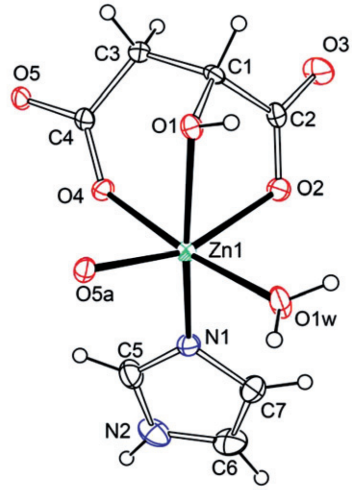

Figure 1. ORTEP plot of the Zn(II) coordination environment in **1**.

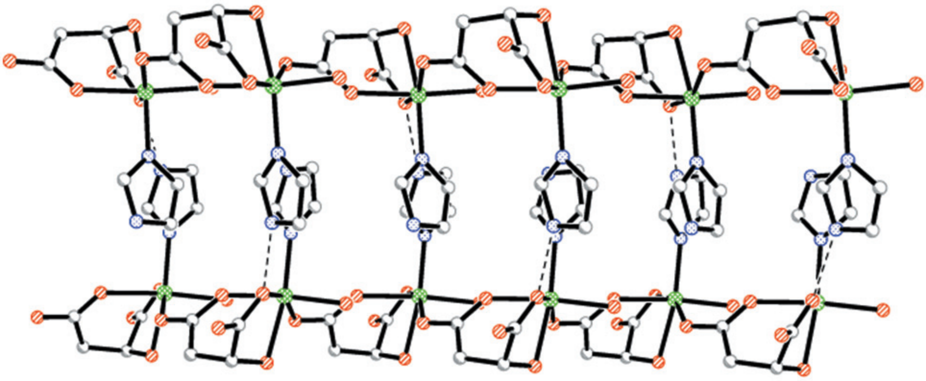

Figure 2. View of the double chain structure composed by H-bond of **1**.

group of malate (with the N2 $\cdots$ O2 = 2.787(3) Å) to form a double chain. Furthermore, strong hydrogen bonds are formed among hydroxy and carboxy oxygens, coordinated, and lattice water molecules (O1 $\cdots$ O3w 2.659(3) Å; O1w $\cdots$ O3(c) 2.638(3) Å; O3w $\cdots$ O3(c) 2.729(3) Å; O3w $\cdots$ O2w(d) 2.735(3) Å; symmetry codes: (a) $-x+1/2$, $y-1/2$, z; (b) $0.5+x$, y, $1.5-z$; (c) $-x-1/2$, $y-1/2$, z; (d) $-x$, $-y+1$, $-z+1$). Through these strong hydrogen bonds, the adjacent double chains are extended to build up a 3-D supramolecular architecture (figure 3).

In **2**, each Zn is five-coordinate in a distorted trigonal bipyramidal coordination geometry, by one hydroxy oxygen and two carboxylate oxygens from two different malates and two nitrogens from a chelating bpy ligand. The detailed structure of **2** has been described in [39]. The malates link the Zn atoms to form spiral-shaped chains and the bpy ligands are arranged uniquely at one side of this chain. Each pair of these spiral-shaped chains recognize others through an aromatic π–π stacking interactions of the bpy ligands to furnish double-stranded chains (figure 4) [44, 45]. In addition, the

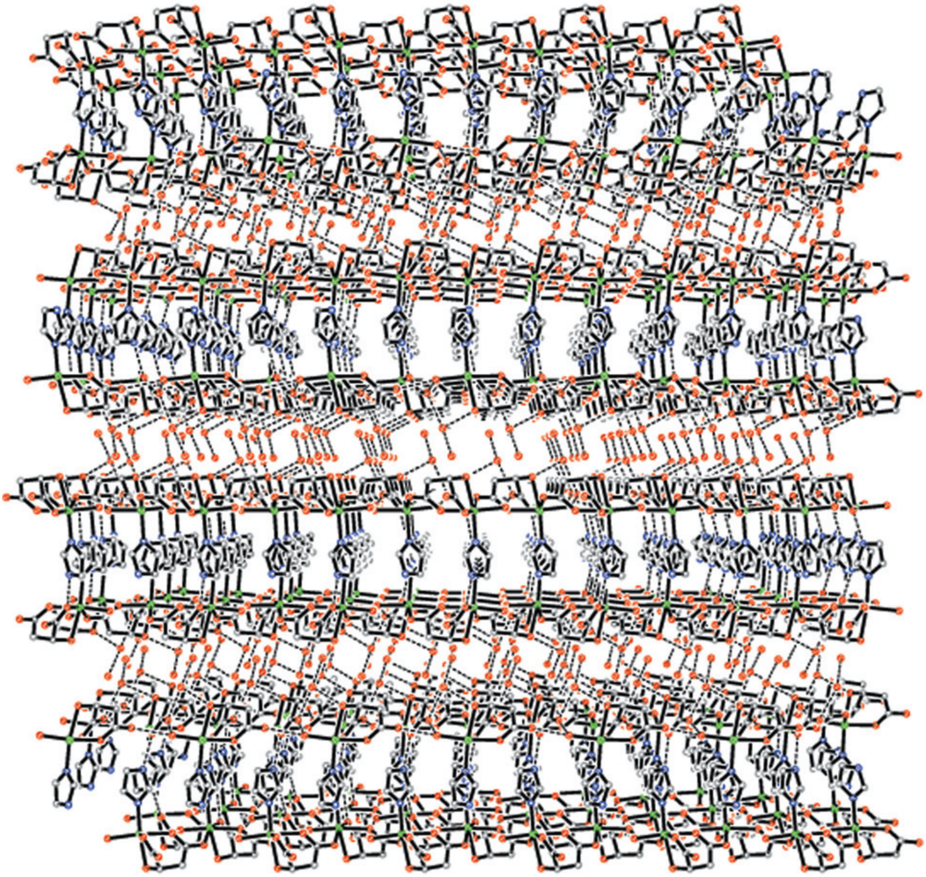

Figure 3. View of the 3-D supramolecular structure of **1**.

double-stranded chains are connected by intermolecular hydrogen bonds to generate a 3-D supramolecular network along the *a*-axis (figure 5).

In **1** and **2**, each malate binds two Zn(II) ions. However, the coordination mode of malate is different in the two complexes. In **1**, malate coordinates to one Zn(II) and is tridentate *via* its hydroxy, α-carboxy, and β-carboxy groups in a *fac*-mode, while the β-carboxy group further coordinates in a monodentate fashion to the other Zn(II) *trans* to the hydroxy. In **2**, the malate is a bidentate–monodentate ligand, coordinating bidentate to one Zn(II) *via* hydroxy and α-carboxy groups, while the β-carboxy coordinates monodentate to the other Zn(II). Perhaps the chelating bpy creates steric hindrance around Zn(II) preventing malate-binding tridentate to one Zn(II) ion as in **1**.

3.3. *Thermogravimetric analysis*

TGA were performed to gauge the thermal stability of **1** and **2** under nitrogen with a heating rate of 10°C $\cdot$ min^{-1}. The weight loss of **1** corresponding to the release of lattice

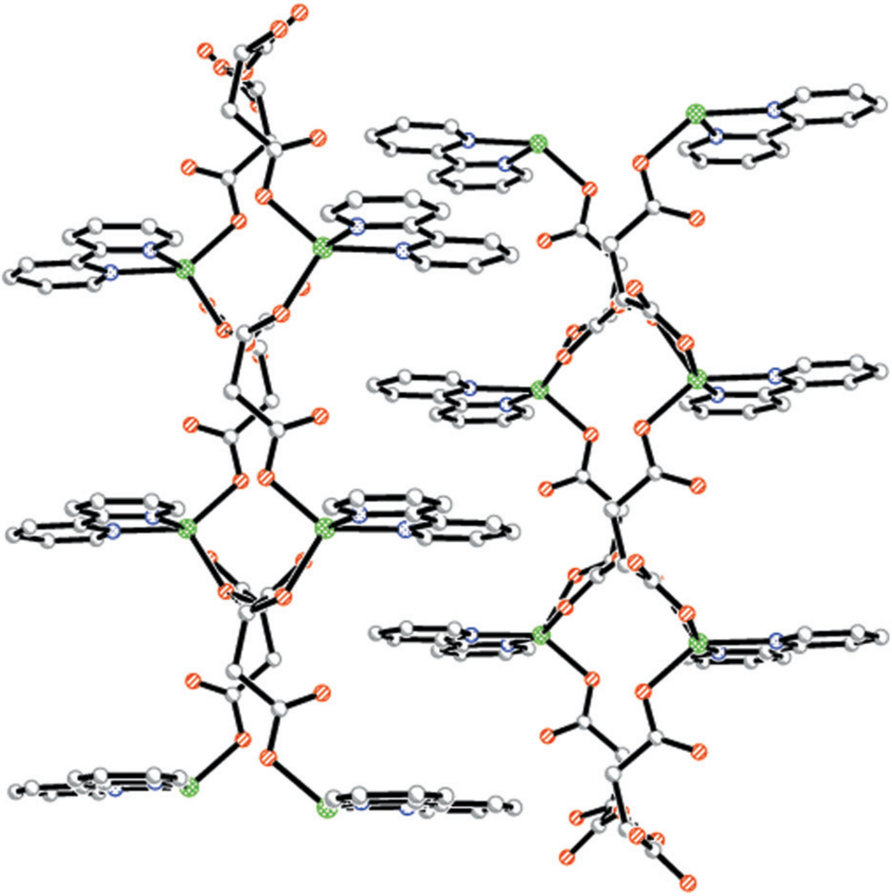

Figure 4. View of the double-stranded chains for **2**. Hydrogens are omitted for clarity.

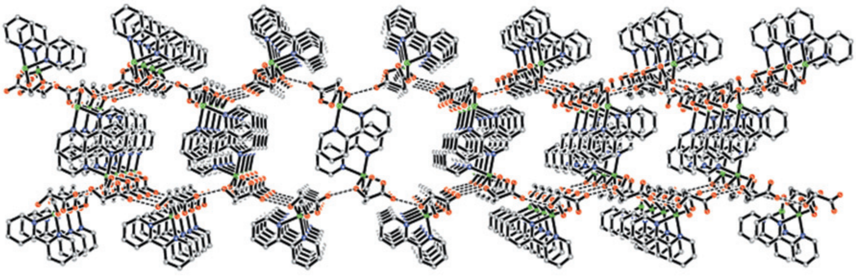

Figure 5. View of the 3-D supramolecular network along the *a*-axis for **2**. Lattice waters are omitted for clarity.

water and coordinated water is observed from 40°C to 130°C (Obsd 18.3%, Calcd 16.9%). The anhydrous material begins to decompose at 210°C. The TGA curve of **2** shows that it undergoes dehydration between 30 and 220°C (Obsd 11.3%, Calcd 13.2%). Decomposition of anhydrous **2** occurs at 225°C.

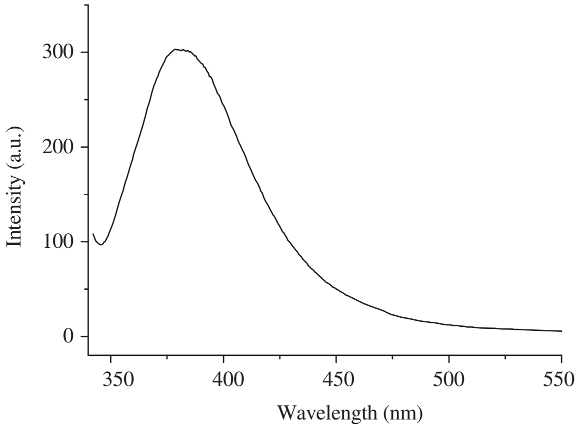

Figure 6. Solid-state emission spectrum of **1** at room temperature.

3.4. *Fluorescent property*

The solid-state fluorescence of **1** was investigated at room temperature. Upon excitation at 330 nm, solid **1** displays strong fluorescent emission at 380 nm (figure 6), exhibiting a blue-shift ($\Delta\lambda = 20$ nm) with respect to free imidazole (400 nm, $\lambda_{ex} = 340$ nm). As reported [46, 47], this emission band of **1** is probably assigned to intraligand fluorescent emission. In addition, the shift of the emission for **1** may be attributed to metal coordination [47, 48].

4. Conclusions

Two 3-D supermolecular frameworks have been synthesized from the reactions of zinc nitrate with malate and imidazole or 2,2′-bipyridine in aqueous solutions. The different coordination modes of malate in **1** and **2** generate two different structures. For **1**, strong hydrogen-bonding interactions exist among polymeric coordination chains, which extend the 1-D double chains to a 3-D supermolecular framework. Moreover, **1** exhibits strong fluorescence at room temperature in the solid state.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 772228 for **1**. CCDC deposition numbers are 772228 and 780689. Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-11223-336033; Email: deposit@ccdc.cam.ac.uk).

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