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Construction of three low dimensional Zn(II) complexes based on different organic-carboxylic acids

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ABSTRACT

Three new Zn(II) complexes based on different organic-carboxylic acids, $[Zn(mba)_2(2,2'\text{-bipy})]$ (**1**), $[Zn(mpdaH)_2(H_2O)_4]\cdot 4H_2O$ (**2**) and $[Zn(cda)_2(H_2O)_2]_n$ (**3**) (Hmba = 4-methylbenzoic acid, H_2mpda = 2,6-dimethylpyridine-3,5-dicarboxylic acid and H_2cda = chelidonic acid) have been synthesized successfully under hydrothermal conditions. X-ray single crystal diffractions show that compounds **1** and **2** are the mononuclear and **3** is one-dimensional chain, in which the Zn(II) centers have different coordination geometries with octahedron for **1** and **2** and tetrahedron for **3**. Through π–π stacking and/or hydrogen bonding (O–H···O and O–H···N) interactions, different supramolecular structures are assembled, namely, 2D supramolecular layer for **1** and 3D supramolecular networks for **2** and **3**. Furthermore, the IR, TGA and luminescent properties are also investigated in this work.

1. Introduction

The rational design and synthesis of metal-organic frameworks (MOFs) with carboxylic acids using various secondary building units (SBUs) connected through coordination bonds, supramolecular contacts (hydrogen bonding, π···π stacking, etc.), or their combination, continue to be interesting and attractive due to not only their potential properties in catalysis, magnetic behavior, optical material and adsorption, but also their intriguing network architectures [1–5]. A large number of different dimensional coordination polymers have been prepared and characterized using a variety of carboxylic acids. Of the many such kinds of compounds investigated, those containing benzene-core carboxylic acids constitute an important family as they have proven to be good candidates for the rich coordination modes, such as terminal monodentate, chelating to one metal center and various modes of bridging coordination of two, three, four or even five metal centers [6], and also function as hydrogen-bond acceptors as well as donors in assembling supramolecular complexes [7–8]. In recent years, the scope of the investigations on benzene-core carboxylic acids has been enhanced enormously by using N- or O-heterocyclic dicarboxylic acids such as pyridine-, pyran-dicarboxylic acids which can use their carboxylate oxygens and nitrogen or oxygen atoms on the heterocycle to approach metal ions, to form interesting frameworks [9–10]. Although quite a number of compounds have been prepared and explored by the use of such heterocyclic dicarboxylic acids, there are still a great deal of uncharacterized compounds with novel crystal structures emerged under various reaction conditions, and these new compounds mostly are serendipitous, especially the emergence of fancy and intricate supramolecular architectures assembled by small building blocks through hydrogen bonding and π···π stacking interactions, which greatly attract chemists' attention.

In the past years, we have prepared a series of new metal-organic frameworks in the presence of heterocyclic multi-carboxylic acids via the hydrothermal synthesis, and their supramolecular architectures have also been investigated [11]. In order to continue and extend our work, we have recently synthesized three new Zn(II) complexes with 4-methylbenzoic acid, pyridine- and pyran-dicarboxylic acids, that is, $[Zn(mba)_2(2,2'\text{-bipy})]$ (**1**), $[Zn(mpdaH)_2(H_2O)_4]\cdot 4H_2O$ (**2**) and $[Zn(cda)_2(H_2O)_2]_n$ (**3**). Compounds **1** and **2** are prepared from 4-methylbenzoic acid (Hmba) and 2,6-dimethylpyridine-3,5-dicarboxylic acid (H_2mpdc), respectively, and they are both zero-dimensional structures, while compound **3** is synthesized from chelidonic acid (H_2cda) and it possesses a one-dimensional linear structure. Through π···π stacking or hydrogen bonding (O–H···O) interactions, compounds **1** and **3** are further assembled into 2D layer and 3D network supramolecular structures, respectively. However, compound **2** is connected into three-dimensional supramolecular structure through hydrogen bonding (O–H···O and O–H···N) and π···π stacking interactions. To the best of our knowledge, these three carboxylic acids (Hmba, H_2mpdc and H_2cda) and their supramolecular coordination

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chemistry have been less explored up to now [9]. Thus, it is interesting to study the hydrothermal synthesis and coordination chemistry of these ligands and explore the photoluminescence of the resulted coordination frameworks. In this work, we describe the synthesis, characteristic and properties of the three new complexes.

2. Experimental

2.1. Materials and measurements

All materials were reagent grade, obtained from commercial sources and used without further purification. Elemental analyses were performed on a Perkin–Elmer 240C analytical instrument. The metal analysis was performed on an ICP AES Liberty Series II Varian apparatus. IR spectra in the 4000–400 cm^{-1} range were measured with a Thermo Nicolet 320 FT-IR spectrometer using KBr discs. Thermal analyses (under nitrogenated atmosphere, heating rate of 5 °C/min) were carried out in a Labsys NETZSCH TG 209 Setaram apparatus. The luminescent spectra for the solid-state were recorded at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5.0 nm.

2.2. Preparation of complex [Zn(mba)$_2$(2,2′bipy)] (**1**)

A mixture of Hmba (0.135 g, 1.0 mmol), $Zn(ClO_4)_2 \cdot 6H_2O$(0.186 g, 0.50 mmol), 2,2′-bipy (0.078 g, 0.50 mmol) and H_2O (10 cm^3) was placed in a 20 cm^3 Teflon reactor and kept under autogenous pressure at 160 °C for 3 days, and then slowly cooled to room temperature at a rate of 0.5 °C min^{-1}. Colourless block crystals of **1** suited for single crystal X-ray diffraction analyses were formed with a yield of approximately 22% (based on Zn). *Anal.* calc. for $C_{26}H_{22}N_2O_4Zn$: C, 63.49; H, 4.51; N, 5.70. Found: C, 63.46; H, 4.55; N, 5.63; Zn, 13.32%. Zn, 13.29%. Selected IR data (KBr, cm^{-1}): 3035(w), 2937(m), 1632(s), 1553(s), 1472(w), 1435(m), 1401(m), 1376(m), 1313(s), 1276(m), 1192(m), 1160(w), 1121(w), 1089(s), 1017(vs), 926(s), 793(w), 768(s), 661(m).

2.3. Preparation of complex $[Zn(mpdcH)_2(H_2O)_4] \cdot 4H_2O$ (**2**)

Similar to the preparation of **1**, the hydrothermal reaction of H_2mpdc (0.181 g, 1.0 mmol), $Zn(ClO_4)_2 \cdot 6H_2O$ (0.186 g, 0.50 mmol), 2,2′-bipy (0.078 g, 0.50 mmol) and H_2O (10 cm^3) in a 20 cm^3 Teflon reactor under autogenous pressure was performed at 160 °C for 72 h and then was cooled to room temperature at a rate of ca. 0.5 °C min^{-1} to give colorless prism crystals of **2** (yield: 31% based on Zn). Zn, 11.02. *Anal.* calc. for $C_{18}H_{32}N_2O_{16}Zn$: C, 36.16; H, 5.40; N, 4.69; Zn, 10.94. Found: C, 36.09; H, 5.49; N, 4.72%. Selected IR data (KBr, cm^{-1}): 3439(br), 1645(s), 1595(s), 1434(m), 1385(s), 1359(s), 1196(m), 1124(w), 1060(w), 1029(w), 932(w), 794(w), 746(m).

2.4. Preparation of complex $[Zn(cda)_2(H_2O)_2]_n$ (**3**)

Compound **3** was obtained using the same reaction procedure as described for compound **2** taking H_2cda in place of H_2mpdc. The colorless block crystals of **3** were isolated in about 38% yield (based on Zn). *Anal.* calc. for $C_7H_6O_8Zn$: C, 29.66; H, 2.13; Zn, 23.06. Found: C, 29.62; H, 2.25; Zn, 23.12%. Selected IR data (KBr, cm^{-1}): 3419(br), 1625(s), 1575(m), 1520(m), 1429(s), 1387(s), 1337(m), 1202(w), 1190(m), 1120(m), 1060(m), 856(m), 748(m), 726(m).

2.5. X-ray crystallography

The three complexes **1–3** were determined by single crystal X-ray diffraction. Suitable single crystals were mounted on a glass fiber and the intensity data were collected on a Bruker APEX II diffractometer at 298 K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were performed using the SADABS program [12]. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 of data using SHELXTL software [13]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically, the aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors. A summary of parameters for the data collection and refinements for three complexes are given in Table 1. Selected bond lengths and angles for complexes **1–3** are listed in Table 2. Hydrogen-bonding data of complexes **1–3** are listed in Table 3.

Table 1
Crystal data and structure refinement for compounds **1–3**

Complex	**1**	**2**	**3**
Empirical formula	$C_{26}H_{22}N_2O_4Zn$	$C_{18}H_{32}N_2O_{16}Zn$	C_7H6O_8Zn
Formula weight	491.83	597.83	283.49
Temperature (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	7.6208(4)	7.6312(4)	5.1098(2)
b (Å)	9.8140(6)	8.6555(4)	9.3271(4)
c (Å)	15.7439(9)	10.7260(5)	9.8661(4)
α (°)	79.148(3)	69.635(2)	104.937(2)
β (°)	83.929(3)	69.686(2	95.279(2)
γ (°)	79.936(3)	83.593(2)	93.442(2)
V (Å^3)	1135.4(1)	622.9(1)	450.7(1)
Z	2	1	2
$\rho_{calc.}$ (mg m^{-3})	1.439	1.594	2.089
μ (m^{-1})	1.117	1.067	2.753
F(000)	508	312	284
Crystal size (mm)	0.26 × 0.22 × 0.17	0.22 × 0.20 × 0.17	0.28 × 0.26 × 0.22
θ Range for data collection (°)	2.70–25.50	2.71–25.50	2.15–27.50
$h/k/l$ (maximum, minimum)	−9,9/−11,7/ −19,18	−9,9/−10,10/ −12,12	−6,6/−12,11/ −12,12
Reflections collected	5245	3767	5675
Unique (R_{int})	3766 (0.0227)	2284 (0.0207)	2033 (0.0178)
Completeness to q = 27.13 (%)	99.10	98.10	98.10
Absorption correction	empirical	empirical	empirical
Maximum and minimum transmission	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/ parameters	3766/0/300	2284/12/196	2033/6/158
Goodness-of-fit on F^2	1.046	1.081	1.028
Final R_1[a], wR_2[b] indices [$I > 2\sigma(I)$]	0.0424, 0.0975	0.0274, 0.0753	0.0203, 0.0534
R_1, wR_2 indices (all data)	0.0596, 0.1072	0.0276, 0.0756	0.0211, 0.0538
Largest difference in peak and hole (e Å^{-3})	0.341/−0.306	0.354/−0.334	0.366/−0. 502

[a] $R = \sum|F_o| - |F_c|/S|F_o|$.

[b] $wR = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o^2)2]1/2$. $w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.3107P]$ for **1**, $w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 0.2999P]$ for **2**, $w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 0.2805P]$ for **3**, $P = (F_o^2 + 2F_c^2)/3$.

Table 2
Selected atomic distances (Å) and bond angles (°) for compounds **1**–**3**[a]

*Compound **1***			
Zn(1)–O(1)	1.985(2)	O(1)–Zn(1)–O(3)	145.1(1)
Zn(1)–O(2)	2.509(3)	O(1)–Zn(1)–N(1)	105.6(1)
Zn(1)–O(3)	2.066(2)	O(3)–Zn(1)–N(1)	96.5(1)
Zn(1)–O(4)	2.202(2)	O(1)–Zn(1)–N(2)	103.1(1)
Zn(1)–N(1)	2.088(3)	O(3)–Zn(1)–N(2)	107.8(1)
Zn(1)–N(2)	2.103(3)	N(1)–Zn(1)–N(2)	78.1(1)
O(1)–Zn(1)–O(4)	100.99(9)	N(1)–Zn(1)–O(4)	153.4(1)
O(3)–Zn(1)–O(4)	61.24(9)	N(2)–Zn(1)–O(4)	94.4(1)
*Compound **2***			
Zn(1)–O(3)	2.0240(13)	O(3)–Zn(1)–O(6)#1	90.5(1)
Zn(1)–O(3)#1	2.0240(13)	O(3)–Zn(1)–O(6)	89.5(1)
Zn(1)–O(6)#1	2.0764(14)	O(3)#1–Zn(1)–O(6)	90.5(1)
Zn(1)–O(6)	2.0764(14)	O(3)–Zn(1)–O(5)	88.3(1)
Zn(1)–O(5)	2.1864(14)	O(6)–Zn(1)–O(5)	88.3(1)
Zn(1)–O(5)#1	2.1864(14)		
*Compound **3***			
Zn(1)–O(7)	1.9296(12)	O(7)–Zn(1)–O(2)#2	124.5(1)
Zn(1)–O(2)#2	1.9541(12)	O(7)–Zn(1)–O(6)	121.1(1)
Zn(1)–O(6)	1.9723(12)	O(2)#2–Zn(1)–O(6)	95.3(1)
Zn(1)–O(8)	1.9910(14)	O(7)–Zn(1)–O(8)	104.8(1)
O(3)–C(6)	1.3518(18)	O(2)#2–Zn(1)–O(8)	105.3(1)
O(3)–C(2)	1.3554(18)	O(6)–Zn(1)–O(8)	103.3(1)
C(2)–C(3)	1.340(2)	C(6)–O(3)–C(2)	118.2(1)
C(3)–C(4)	1.443(2)	C(3)–C(2)–O(3)	123.1(1)
O(4)–C(4)	1.243(2)	C(2)–C(3)–C(4)	120.4(1)
C(4)–C(5)	1.443(2)	C(5)–C(4)–C(3)	114.5(1)
C(5)–C(6)	1.339(2)	C(6)–C(5)–C(4)	120.4(1)
		C(5)–C(6)–O(3)	123.1(1)

[a] Symmetry transformations used to generate equivalent atoms: #1 −*x*, −*y*, −*z* + 2; #2 *x*, *y*, *z* − 1.

Table 3
Distances (Å) and angles (°) of hydrogen bonds for compounds **1**–**3**

D–H···A	Distance (D–H)	Distance (H···A)	Distance (D···A)	Angle (D–H···A)
*Compound **2***				
O(5)–H(5A)···O(7)#2	0.847(9)	1.928(10)	2.773(2)	176(2)
O(5)–H(5B)···O(4)#1	0.846(9)	1.890(10)	2.713(2)	164(2)
O(6)–H(6D)···O(2)#3	0.836(9)	1.934(12)	2.7518(19)	166(2)
O(6)–H(6E)···O(2)#4	0.842(9)	1.917(12)	2.7478(19)	168(2)
O(7)–H(7A)···O(1)#5	0.850(9)	2.055(14)	2.863(2)	159(2)
O(7)–H(7B)···O(1)	0.850(10)	1.998(14)	2.812(2)	160(2)
O(8)–H(8A)···O(5)#6	0.843(10)	2.029(12)	2.858(2)	168(2)
O(8)–H(8B)···O(2)#5	0.836(10)	2.098(12)	2.919(2)	167(2)
N(1)–H(1)···O(8)#4	0.861(9)	1.875(11)	2.729(2)	175(2)
*Compound **3***				
O(7)–H(7A)···O(1)#7	0.844(9)	1.868(10)	2.7103(18)	175(2)
O(7)–H(7A)···O(3)#7	0.844(9)	2.66(2)	3.0407(16)	109(2)
O(7)–H(7B)···O(5)#7	0.846(9)	1.879(10)	2.7193(18)	172(2)
O(8)–H(8B)···O(4)#8	0.842(9)	1.788(10)	2.6207(18)	169(2)
O(8)–H(8A)···O(6)#9	0.832(9)	2.018(11)	2.8172(18)	161(2)

Symmetry transformation used to generate equivalent atoms: #1 −*x*, −*y*, −*z* + 2; #2 *x*, *y* − 1, *z*; #3 *x*, *y* − 1, *z* + 1; #4 −*x* + 1, −*y* + 1, −*z* + 1; #5 −*x* + 1, −*y* + 2, −*z* + 1; #6 *x* + 1, *y* + 1, *z*; #7 −*x* + 1, −*y* + 1, −*z*; #8 −*x*, −*y* + 2, −*z*; #9 *x* + 1, *y*, *z*.

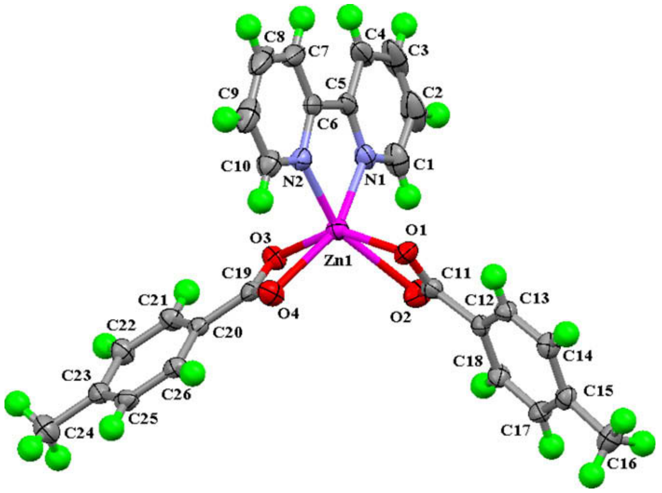


Fig. 1. Coordination environment of Zn(II) ion in **1** with 50% probability thermal ellipsoids.

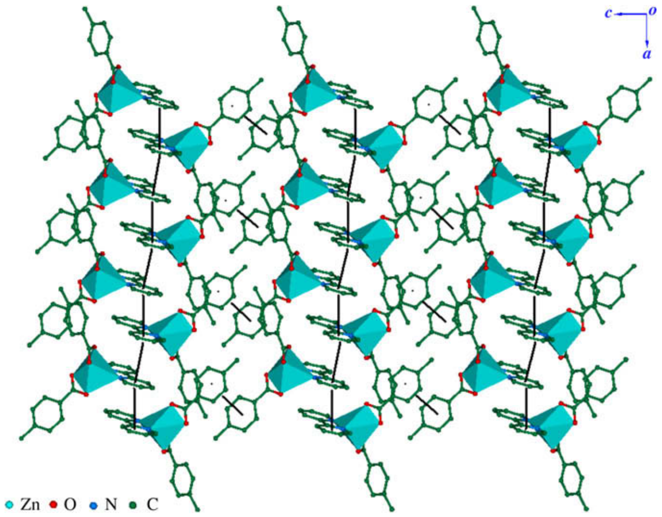


Fig. 2. 2D supramolecular layer of **1** constructed through π···π packing interactions viewed along *a*-axis.

3. Results and discussion

3.1. Description of crystal structures

*3.1.1. [Zn(mba)$_2$(2,2′bipy)] (**1**)*

Single crystal X-ray diffraction analysis reveals that complex **1** consists of [Zn(mba)$_2$(2,2′bipy)] and coordination environment of Zn(II) ion is shown in Fig. 1. Zn(II) ion is six-coordinated by four oxygen atoms (O1, O2 and O3, O4) from two different carboxylic groups of two mba$^-$ ligands and two nitrogen atoms (N1 and N2) of one 2,2′-bipy molecule, exhibiting a distorted octahedral coordination geometry. The Zn–O distances range from 1.985 to 2.509 Å and the Zn–N distances from 2.088 to 2.103 Å (Table 2).

In complex **1**, mba$^-$ and 2,2′-bipy acting as terminal ligands adopt chelating modes ($\hat{O}O/\hat{N}N$) to coordinate with one Zn(II) ion, forming mononuclear unit with three bite angles of O1–Zn1–O2 57.12°, O3–Zn1–O4 61.24° and N1–Zn1–N2 78.05° as secondary building units (SBUs), and then these SBUs are further linked by the π···π stacking interactions among the adjacent parallel 2,2′-bpy molecules or benzene rings with the distance of 3.918 Å, 3.923 Å for 2,2′-bipy rings and 4.058 Å for benzene rings to give rise to 2D layer supramolecular structure which is shown in Fig. 2.

*3.1.2. [Zn(mpdcH)$_2$(H$_2$O)$_4$] · 4H$_2$O (**2**)*

The monocarboxylate ligand mba$^-$ in **1** is replaced by dicarboxylate ligand mpdc^{2-}, giving complex **2**. Single crystal X-ray diffraction analysis shows that the complex **2** is still mononuclear with space group $P\bar{1}$, and the molecular ORTEP plot is shown in Fig. 3. Each dicarboxylate ligand mpbc^{2-} gives one oxygen atom (η^1-O3/O3a) to coordinate to the central Zn(II) atom, and the octahedral coordination environments of the Zn(II) ions are further satisfied by the coordination of four water molecules (O5, O6, O5a and

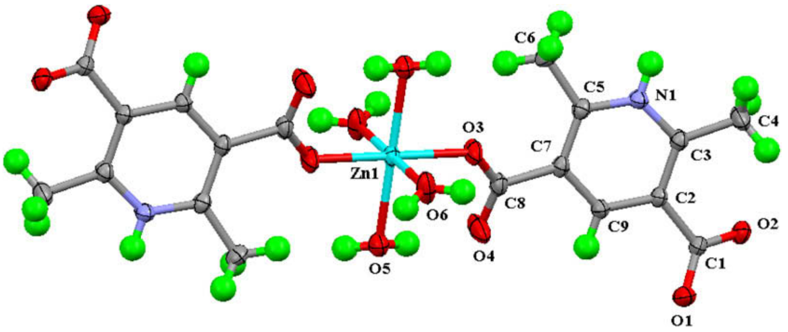


Fig. 3. The molecular structure of complex **2**, shown with 50% probability displacement ellipsoids. Uncoordinated water molecules have been omitted for clarity. Unlabelled atoms are related to labelled atoms by $-x$, $-y$, $-z + 2$.

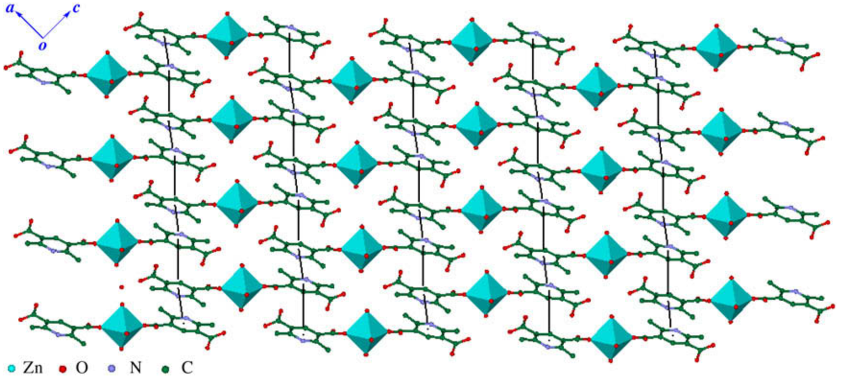


Fig. 4. 2D supramolecular layer of **2** assembled by $\pi\cdots\pi$ packing interactions viewed along *b*-axis.

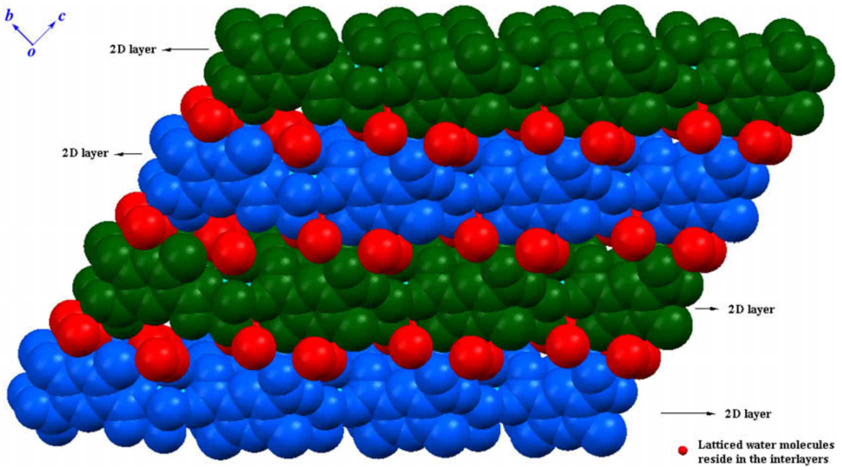


Fig. 5. 3D supramolecular network of **2** fabricated through $\pi\cdots\pi$ packing and hydrogen bonding O–H···O and N–H···O interactions viewed along *a*-axis.

O6a). O3 and O3a are at the axis, while the other four oxygen atoms are located on the plane. The average distances of Zn–O are 2.0956(14) Å. The angles of O(3)–Zn(1)–O(3)#1, O(3)–Zn(1)–O(6) and O(3)–Zn(1)–O(5) are 180°, 89.54(6)° and 88.31(5)°, respectively (Table 2). So the coordination geometry of the central Zn(II) ion may be accurately described as the canonical octahedron.

The intermolecular interactions play significant roles in the formation and stability of compound **2**. As shown in Fig. 4, at first, these discrete Zn1 units (as SBUs) are packed through the $\pi\cdots\pi$ stacking interactions between pyridine rings of the adjacent Zn1 units with the centroid-to-centroid distance of 3.717 Å or 4.035 Å, which results in 2D layer-like supramolecular structure, and latticed water molecules reside in the interlayers (Fig. 5). The nitrogen atom in the central pyridinyl ring is protonated without coordinating under the reaction conditions employed and may be attributed to the steric hindrance of two methyl groups situated *ortho*- to nitrogen atom. Considering ligand mpbc^{2-} in **2** adopting monodentate η^1 mode to coordinate to one Zn(II) ion and the second carboxyl group of ligand mpbc^{2-} remaining free, consequently there are a lot of versatile hydrogen bonds in the crystal lattice of compound **2** (see Table 3): between the lattice water molecules and the uncoordinated carboxylate oxygen atoms, the lattice water

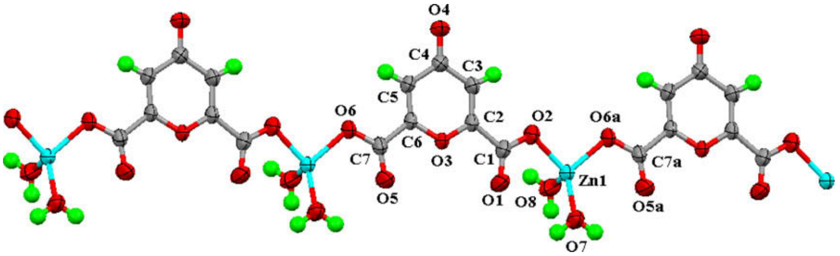


Fig. 6. Coordination environment of Zn(II) ion in 1D compound **3** with 50% probability thermal ellipsoids.

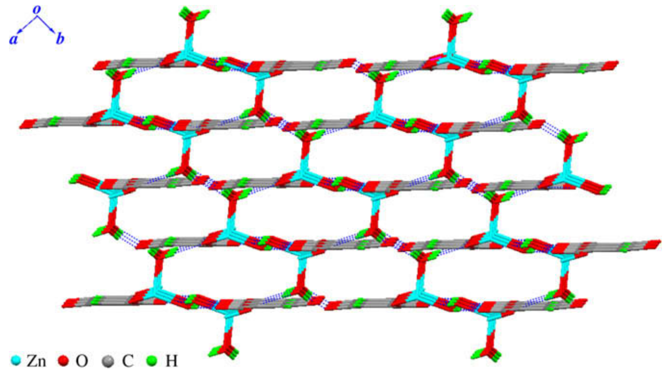


Fig. 7. A view of 3D molecular network with 1D channels constructed by intermolecular O–H$\cdots$O hydrogen interactions viewed along *c*-axis.

molecules and the coordinated carboxylate oxygen atoms, the lattice water molecules and the coordinated water molecules, the coordinated water molecules and the uncoordinated carboxylate oxygen atoms as well as among the lattice water molecules. One the right side of these hydrogen bonding interactions, 2D layers are assembled into 3D supramolecular network (see Fig. 5).

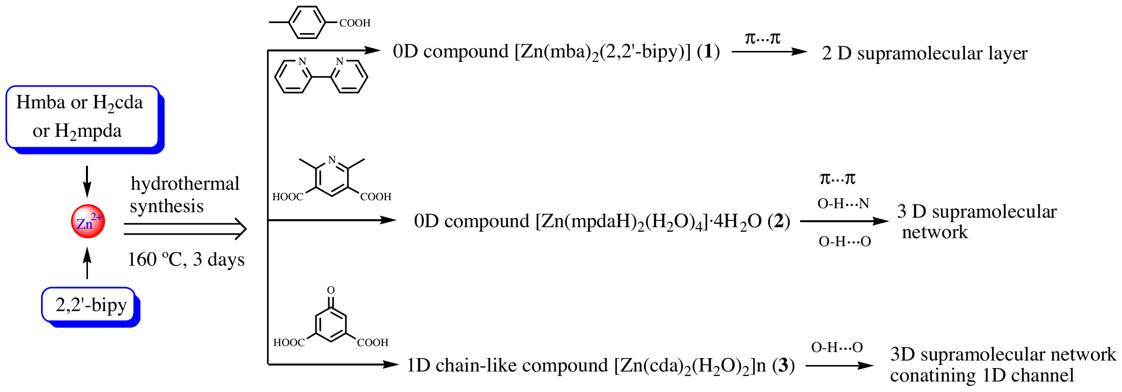
3.1.3. [Zn(cda)$_2$(H$_2$O)$_2$]$_n$ (**3**)

Compound **3** is a one-dimensional chain-like structure, which is constructed by hybridization of organic ligands cda^{2-} with inorganic units Zn(H$_2$O)$_2^{2+}$ (Fig. 6). The selected bond angles and lengths are depicted in Table 2. The coordination geometry of Zn(II) ion, which completely differs from the ones in compounds **1** and **2**, is a slightly distorted tetrahedron with two oxygen atoms from two water molecules and the other two oxygen atoms from different bridging ligands cda^{2-}. The bond angles around the Zn(II) ion are in the range of 95.28–124.54°, and the Zn–O bond lengths range from 1.930 to 1.991 Å.

As shown in Table 2 and Fig. 6, the average lengths of C–C and C–O bonds in the central γ-pyranone ring are 1.391 and 1.354 Å, respectively. Six internal angles of γ-pyranone ring range from 114.54 to 123.14° with a mean of 119.96° very close to 120°. Seven atoms of C2, C3, C4, C5, C6, O3, O4 are almost in the same plane with mean deviation of 0.0296 Å. These data lead to the conclusion that there is a delocalization of the electrons in seven atoms C2–C3–C4–C5–C6–O3–O4 γ-pyranone portion.

As compared with compound **2**, although there are no free water molecules in crystal lattice, two coordinated water molecules in compound **3** with five oxygen atoms of multifunctional chelidonate ligand cda^{2-} are equally engaged in the rich hydrogen bonding network (Table 3). Through these hydrogen bonding interactions between the coordinated water molecules and the coordinated/uncoordinated carboxylate O atoms, the 1D chains are packed alternatively to brick-wall-like three-dimensional network containing 1D channels with the pore size of 3×9 Å^2 (Fig. 7). Unlike **1** and **2**, no significant $\pi\cdots\pi$ stacking interactions are observed in **3**.

It is obvious from the above descriptions that the organic carboxylate ligands have significant effect on the formation and architecture of the resulting Zn(II) complexes (Scheme 1). In complexes **1**, mba^{2-} acts as terminal ligand adopting chelate mode (ÔO) to coordinate with Zn(II) ion cooperated with the co-ligand 2,2′-bipy, which prevents the structure from being extended into higher dimensionality. Compared to the terminal ligand mba^{2-} in **1**, the multidentate dicarboxylate ligands mpbc^{2-} in **2** and cda^{2-} in **3** exclude the co-ligand 2,2′-bipy from coordination to Zn(II) ions, resulting in the existence of the coordinated water molecules and plentiful hydrogen bonds in crystal lattice, which further conduce the differences of the supramolecular structures of compounds **1**–**3**. Both compounds **2** and **3** have 3D spramolecular networks; however, compound **1** is only assembled into 2D supramolecular structure by $\pi\cdots\pi$ stacking interactions between two benzene rings.



Scheme 1.

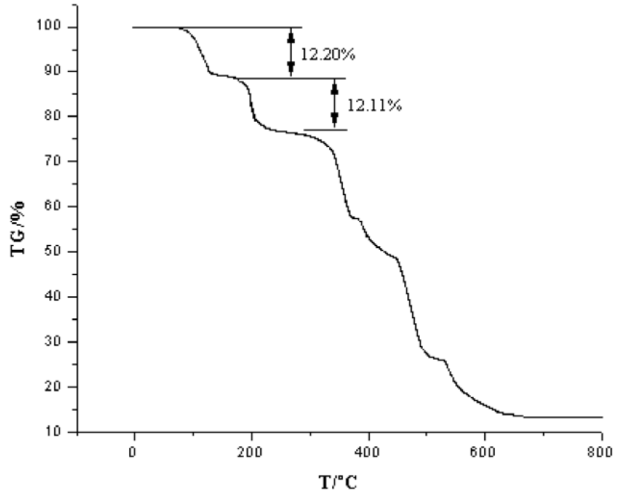


Fig. 8. TG curve of complex **2**.

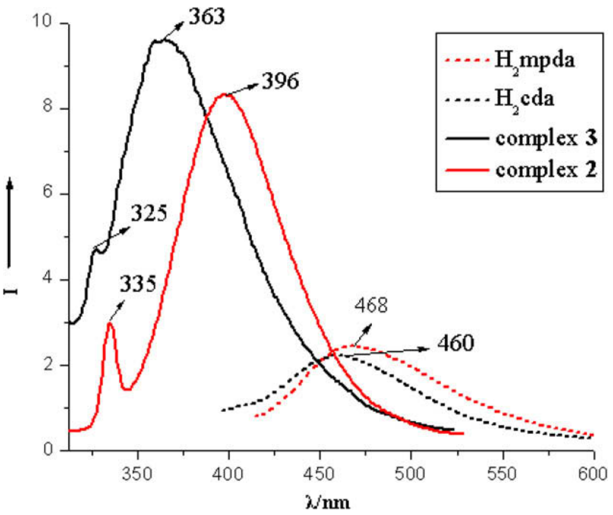


Fig. 9. Luminescent emission spectra: (a) for compound **2** (Em = 396 nm, Ex = 291 nm) and (b) for compound **3** (Em = 363 nm, Ex = 291 nm) in the solid state at room temperature. Em, emission; Ex, excitation.

3.2. Thermal properties

To examine the thermal stability of the complexes, the thermogravimetric analyses of complexes **2** and **3** were carried out from 20 to 800 °C. In **2** and **3**, uncoordinated and coordinated water molecules were lost at first. And then, complicated decomposition reaction took place when the heating continued. Take complex **2** as an example. The TG curve of complex **2** showed that the first weight loss of 12.20% (calc. 12.05%) from 88 to 142 °C corresponds to the loss of four uncoordinated water molecules, the residue weight approximates to the formula of [Zn(mpdaH)$_2$(H$_2$O)$_4$]. And then the weight loss of 12.11% (calc. 12.05%) between 154 and 255 °C ascribes to the loss of four coordinated water molecules, and the residue weight corresponds to Zn(mpdaH)$_2$. Another major weight loss occurred in the range 295–800 °C, which may correspond to complete burning of mpdaH group. The final residue weight is 14.08% (calc. 13.56%) corresponding to ZnO (Fig. 8).

3.3. IR spectra

The IR spectrum of **1** indicates the typical bands of carboxylic groups at 1632 cm^{-1} for the antisymmetric stretching and at 1553 cm^{-1} for symmetric stretching. The values of ($\nu_{\text{asym}} - \nu_{\text{sym}}$) clearly indicate the presence of chelating (79 cm^{-1}) coordination mode of carboxylic groups [14], which is consistent with the single crystal X-ray diffraction. While the IR spectra of complexes **2** and **3** show the common characteristic absorption, such as $\nu_{\text{H}_2\text{O}}$ absorption in the wide range of about 3600–3100 cm^{-1}, centered at 3439 cm^{-1} for **2**, 3419 cm^{-1} for **3**, which approves the existence of water molecules in **2** and **3**. In complex **2**, the ν_{sCOO^-} absorptions appear at 1412–1345 cm^{-1}, while the unco-ordinated carboxyl absorption of the ligand is not presented, which may be caused by the strong hydrogen-bonding. In complex **3**, the ν_{sCOO^-} absorptions appear at 1432–1358 cm^{-1}. It is really a pity that the ν_{asCOO^-} absorptions in complexes **2** and **3** are submerged in the range of 1650–1500 cm^{-1} because the skeleton vibrations of C=O and C=N bonds of aromatic rings appear at the same range. The absence of strong bands ranging from 1690 to 1730 cm^{-1} in compounds **1**–**3** indicates that all ligands are deprotonated.

3.4. Luminescent properties

Room-temperature solid-state luminescent studies performed on powdered samples of complexes **2** and **3** are presented in Fig. 9. The results exhibit that every compound has two peaks (at 335 nm and 396 nm for **2**, 325 nm and 363 nm for **3**) with strong maximal emission bands at 396 nm and 363 nm, respectively, upon excitation at 291 nm in the same experimental environment. The lifetime, τ, for the emissions is 0.027 and 0.035 ns for **2** and **3**, respectively. This indicates that the luminescence should be assigned to fluorescence. As a comparison, luminescence of the corresponding ligands H$_2$mpda and H$_2$cda has been measured, and their emission spectra are also demonstrated in Fig. 9, from which, the emission maximum at 468 nm for H$_2$mpda and 460 nm for H$_2$cda can be attributable to the $\pi^* \rightarrow$ n transition [8]. Thus, the blue-shifted fluorescent emission of compounds **2** and **3** compared to the free corresponding ligands can be assigned as ligand-to-metal charge transfer (LMCT) [15]. The much more enhanced fluorescent intensities of **2** and **3** are presumably attributed to more rigidity of the ligand coordinating to Zn(II) ions than that of the free ligands, which effectively reduces the loss of energy [16]. As can be seen, the main emission bands of **2** and **3** are similar in the band shapes but with differences in the positions of the located emission bands, which have been attributed to the same coordinated mode (η^1) of two heterocyclic dicarboxylate ligands. The differences in the band positions might also be due to the differences in the structures of the central heterocycles of two dicarboxylate ligands and coordination environment around central Zn(II) ions, because luminescence behavior is closely associated with the local environments around metal ions [17–19]. In addition, the different topologies (0D and 1D) and the intricate hydrogen bonds may also influence the emission spectra. Considering that the luminescence properties of the two complexes exhibit a broad range of visible light, giving the observed blue luminescence, therefore, both **2** and **3** may have potential application as luminescent materials in organic light-emitting devices.

In summary, three new low dimensional Zn(II) complexes containing organic-carboxylic acids have been successfully demonstrated. X-ray single crystal diffraction displays that three compounds **1**–3 have the different topologies and supramolecular architectures, which may be attributed to the organic carboxylate ligands having significant effect on the formation and architecture of the resulting Zn(II) complexes. Obviously the results presented here offer the intriguing strategy of constructing the complexes with the different topologies and supramolecular architectures. Furthermore, the intense blue luminescent properties of complex

2 and **3** at room temperature suggest that they have great potential application as luminescent materials.

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Appendix A. Supplementary material

CCDC 677378, 677379 and 677380 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. X-ray crystallographic files in CIF format for compounds **1**–**3** are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.07.015.

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