

含有 3,4-吡唑二甲酸的锌(II)配合物:合成、结构和荧光性质

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摘要: 3,4-吡唑二甲酸(H₃pdc)与 Zn(NO₃)₂·6H₂O 在不同的条件下反应制得了 2 个新的配合物:[Zn(H₂pdc)₂(H₂O)₂]·2H₂O (**1**)和[Zn₂(Hpdc)₂(H₂O)₆]·2H₂O (**2**)。X 射线衍射分析表明,**1** 和 **2** 分别是单核和双核结构。H₃pdc 部分脱质子后的阴离子配体在 **1** 和 **2** 中采用的是 N,O-螯合(H₂pdc⁻)以及 μ_2 - κ N,O: κ N 桥联(Hpdc²⁻)配位模式。在这 2 个配合物中,相邻的零维组分通过分子间氢键(O—H···O, N—H···O 和 C—H···O)作用形成三维超分子结构。此外我们还研究了配合物 **1** 和 **2** 的热稳定性和荧光性能。

关键词: 锌; 3,4-吡唑二甲酸; 晶体结构; 荧光; 合成

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Syntheses, Crystal Structures and Luminescent Properties of Zn(II) Complexes Based on 3,4-Pyrazoledicarboxylic Acid

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Abstract: Treatment of H₃pdc with Zn(NO₃)₂·6H₂O under different reaction conditions afforded two complexes, [Zn(H₂pdc)₂(H₂O)₂]·2H₂O (**1**) and [Zn₂(Hpdc)₂(H₂O)₆]·2H₂O (**2**) (H₃pdc=3,4-pyrazoledicarboxylic acid). X-ray diffraction analyses reveal that **1** and **2** contain mono- and dinuclear Zn(II) components, respectively. The partly deprotonated H₃pdc ligand anions in **1** and **2** adopt N,O-chelating fashion (H₂pdc⁻) and μ_2 - κ N,O: κ N' bridging mode (Hpdc²⁻), respectively. In both complexes, the adjacent zero-dimensional components are connected by intermolecular hydrogen bonds (O—H···O, N—H···O and C—H···O) to form a three-dimensional supramolecular architecture. The thermal and luminescent properties of complexes **1** and **2** have also been investigated. CCDC: 1944037, **1**; 1944038, **2**.

Keywords: zinc(II); 3,4-pyrazoledicarboxylic acid; crystal structure; luminescent property; synthesis

Arguably greatest interest has focused on the syntheses and properties of Zn(II) complexes. This reflects the fact that zinc is the second most important metal in the mammalian body, and zinc ions play

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diverse roles in the brain function, gene expression, metalloenzyme regulation, immune function, neural signal transmission and other biological processes^[1-6]. Moreover, the d^{10} configuration of Zn(II) allows the Zn^{2+} to exhibit variable coordination environments, thus forming complexes with tetrahedral to octahedral geometries. The chemistry of Zn(II) complexes is of current interest not only on account of their interesting structures but also because of their photoluminescent properties. In fact, a wide variety of Zn metal-organic frameworks showing interesting photophysical properties have been reported^[7-9]. To synthesize zinc(II) based coordination polymers with fluorescence properties, multi-dentate carboxylate ligands and N,O-mixed ligand systems are widely employed^[7-33]. Especially, N-heterocyclic carboxylic acids, possessing strong coordination ability and multi-coordination modes by the N and O donor atoms on the heterocyclic rings and the carboxylate groups, can coordinate to metal ions in diverse bridging modes as well as different chelating fashions. Until now, numerous Zinc (II) complexes containing five- or six-member N-heterocyclic carboxylic acids, such as pyrazinecarboxylic acid^[10-13], pyridinecarboxylic acid^[14-17], pyrimidine-4,6-dicarboxylic acid^[18], imidazoledicarboxylic acid^[19-23], and pyrazoledicarboxylic acid^[24-29] have been prepared and characterized. Among which, 3,4-pyrazoledicarboxylic acid (H_3pdc) as the multifunctional ligand, possesses the capability to chelate and bridge metal atoms in various coordination modes using two pyrazole nitrogen atoms and four carboxylate oxygen atoms. Meanwhile, it can also act as a donor and/or acceptor in hydrogen bond interactions, depending on the degree of deprotonation, and assemble the complexes into higher supramolecular frameworks. In fact, H_3pdc has been proven to be very effective in constructing supramolecular architectures^[30-33]. So far, H_3pdc has been used to react with trivalent lanthanide salts, generating a series of mononuclear lanthanide complexes, $[Ln(H_2pdc)_3(H_2O)_4] \cdot xH_2O$ and 2D coordination polymers $\{[Ln(\mu_2-Hpdc)(\mu_2-C_2O_4)_{1/2}(H_2O)_2] \cdot H_2O\}_n$ ($Ln=Ce, Pr, Nd$ and Sm)^[30]. Recently, three main group complexes, $[Pb(H_2pdc)_2(H_2O)] \cdot 2H_2O$ and $[M_2$

$(H_2pdc)_4(H_2O)_8] \cdot 2H_2O$ ($M=Sr$ and Ba), as well as three transition metal complexes, $[Cd_2(\mu_2-H_2pdc)_2(H_2O)_8][Cd_2(H_2pdc)_4(H_2O)_2(\mu_2-Cl)_2] \cdot 2H_2O$ and $[M(H_2pdc)_2(H_2O)_2] \cdot 2H_2O$ ($M=Cu$ and Ni) have also been reported by our group^[31-33]. However, to the best of our knowledge, studies of Zn(II) complexes using 3,4-pyrazoledicarboxylic acid ligand have not been explored. Considering outstanding characters of Zn(II) ion and our group's interest in constructing new complexes based on H_3pdc , we carried out the reactions of H_3pdc with $Zn(NO_3)_2 \cdot 6H_2O$ via two different synthetic routes, the routine solution reaction and hydrothermal reaction, isolated two complexes, namely, $[Zn(H_2pdc)_2(H_2O)_2] \cdot 2H_2O$ (**1**) and $[Zn_2(Hpdc)_2(H_2O)_6] \cdot 2H_2O$ (**2**). X-ray diffraction analyses reveal that **1** and **2** contain mono- and dinuclear Zn(II) components respectively, which serve as building blocks to further expand to two 3D inorganic-organic supramolecular assemblies through hydrogen bonds. The results represent an example in which the same reactants produced two different supramolecular assemblies through two different synthetic routes. In this paper, the syntheses, crystal structures and luminescent properties of **1** and **2** were described.

1 Experimental

1.1 Materials

The 3,4-pyrazoledicarboxylic acid was synthesized according to the literature method^[34]. All reagents and solvents employed were commercially available and used as received without further purification.

1.2 Physical measurements

The elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 Series II element analyzer. The infrared spectra were recorded on a Nicolet 460 spectrometer by using KBr pellets. Powder X-ray diffraction (PXRD) determinations were performed on an X-ray diffractometer (D/max 2500 PC, Rigaku) with Mo $K\alpha$ radiation ($\lambda=0.154\ 06\ nm$). The operating voltage and current were 60 kV and 300 mA, respectively, and the PXRD measurements were carried out over a 2θ range of $3^\circ \sim 80^\circ$ in continuous scanning mode. Single-crystal X-ray

diffraction measurements of **1** and **2** were carried out with a Bruker Smart Apex II CCD diffractometer at 293(2) K. Thermogravimetric analysis (TGA) experiments were carried out on a DuPont thermal analyzer from room temperature to 600 °C under N₂ atmosphere at a heating rate of 10 °C · min⁻¹. The luminescent spectra of the solid samples were recorded with a Cary Eclipse spectrometer.

1.3 Preparation of [Zn(H₂pdca)₂(H₂O)₂]·2H₂O (**1**)

To the solution of H₃pdca (0.20 mmol, 0.031 2 g) in deionized water (5 mL), a solution of Zn(NO₃)₂·6H₂O (0.10 mmol, 0.029 1 g) in EtOH (5 mL) was added. After stirring for one hour, the resulting solution evaporated slowly at room temperature. Colorless crystals of **1** were obtained after one week, washed with deionized water and then dried in vacuum. Yield: 34.45% (0.015 3 g, based on H₃pdca). Anal. Calcd. for C₁₀H₁₄ZnN₄O₁₂(%): C, 26.83; H, 3.15; N, 12.51. Found (%): C, 26.45; H, 3.32; N, 12.49. IR spectrum (KBr pellet, cm⁻¹): 3 443 (s), 3 141 (s), 2 852 (s), 1 697(s), 1 585(s), 1 473(s), 1 437(s), 1 400(s), 1 352(s), 1 128 (m), 956(s), 849(m).

1.4 Preparation of [Zn₂(Hpdca)₂(H₂O)₆]·2H₂O (**2**)

A mixture of H₃pdca (0.10 mmol, 0.0160 g), Zn(NO₃)₂·6H₂O (0.10 mmol, 0.029 1 g), imidazole (0.10 mmol, 0.007 0 g) and H₂O (10 mL) was sealed in a 25 mL Teflon-lined autoclave and heated at 150 °C for three days. The reaction mixture was cooled to room temperature at a rate of 2 °C · h⁻¹. After the resulting solution evaporated at ambient temperature for one

week, colorless crystals of **2** suitable for single-crystal X-ray diffraction analysis were obtained. The product was washed with deionized water and then dried in vacuum. Yield: 30.14% (0.017 6 g, based on H₃pdca). Anal. Calcd. for C₁₀H₂₀Zn₂N₄O₁₆(%): C, 20.60; H, 3.46; N, 9.60. Found(%): C, 20.13; H, 3.82; N, 9.34. IR. data (KBr pellet, cm⁻¹): 3 443 (s, br), 3 131 (s), 1 693(s), 1 560(vs), 1 476(s), 1 438(s), 1 394(s), 1 354(s), 1 131 (s), 1 001(m), 848(m), 772(m).

1.5 X-ray crystallography

Single-crystal X-ray diffraction measurements of **1** and **2** were carried out with a Bruker Apex II CCD diffractometer at 293(2) K. Intensities of reflections were measured using graphite-monochromatized Mo K α radiation (λ =0.071 073 nm) with the φ - ω scans mode in a θ range of 2.342°~25.000° (**1**) and 2.513°~24.998° (**2**). The structure was solved by direct methods using the SHELXS and refined with SHELXL of the SHELXTL package^[35]. Anisotropic thermal factors were assigned to all the non-hydrogen atoms. H atoms attached to C were placed geometrically and allowed to ride during subsequent refinement with an isotropic displacement parameter fixed at 1.2 times U_{eq} of the parent atoms. All other hydrogen atoms bonded to O or N atoms were located from difference maps and refined with isotropic thermal parameters 1.5 times of their carrier atoms. The crystallographic data parameters for **1** and **2** are listed in Table 1.

CCDC: 1944037, **1**; 1944038, **2**.

Table 1 Crystal data and structure refinement for **1** and **2**

Complex	1	2
Empirical formula	C ₁₀ H ₁₄ ZnN ₄ O ₁₂	C ₁₀ H ₂₀ Zn ₂ N ₄ O ₁₆
Formula weight	447.62	583.04
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Crystal size / mm	0.24×0.22×0.22	0.24×0.22×0.18
a / nm	0.662 12(9)	0.717 56(14)
b / nm	0.714 09(10)	0.896 24(17)
c / nm	0.935 86(13)	0.918 67(17)
α / (°)	96.482(2)	65.409(3)
β / (°)	107.377(2)	70.213(4)
γ / (°)	108.254(2)	72.009(4)

Continued Table 1

V / nm^3	0.395 0(9)	0.495 66(16)
Z	1	1
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.903	1.953
$\mu(\text{Mo } K\alpha) / \text{mm}^{-1}$	1.652	2.511
$F(000)$	228	296
Independent reflection (R_{int})	1 348	1 701
Data, restraint, parameter	1 348, 2, 125	1 701, 1, 146
Goodness-of-fit on F^2	1.055	1.105
$R_1, wR_2 [I > 2\sigma(I)]$	0.026 7, 0.082 4	0.042 4, 0.120 9
R_1, wR_2 (all data)	0.027 1, 0.089 5	0.047 8, 0.117 5
Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	349 and -424	898 and -599

2 Results and discussion

2.1 Synthesis

Complex **1** was synthesized by slow evaporation of EtOH-H₂O solution of H₃pdC and Zn(NO₃)₂·6H₂O in a molar ratio of 2:1. Complex **2** was isolated under hydrothermal condition of H₃pdC, Zn(NO₃)₂·6H₂O and imidazole (ImH) in a molar ratio of 1:1:1 at 150 °C for three days. ImH may play a role in the crystalline condition of **2**, because only a powder of **2** was obtained under keeping other reaction conditions unchanged and in the absence of ImH. The difference between the structures of **1** and **2** implies that the synthetic route and molar ratio of reactants do affect the structures of complexes. Complexes **1** and **2** were relatively air- and moisture-stable. The elemental analyses of **1** and **2** were consistent with their chemical formulae.

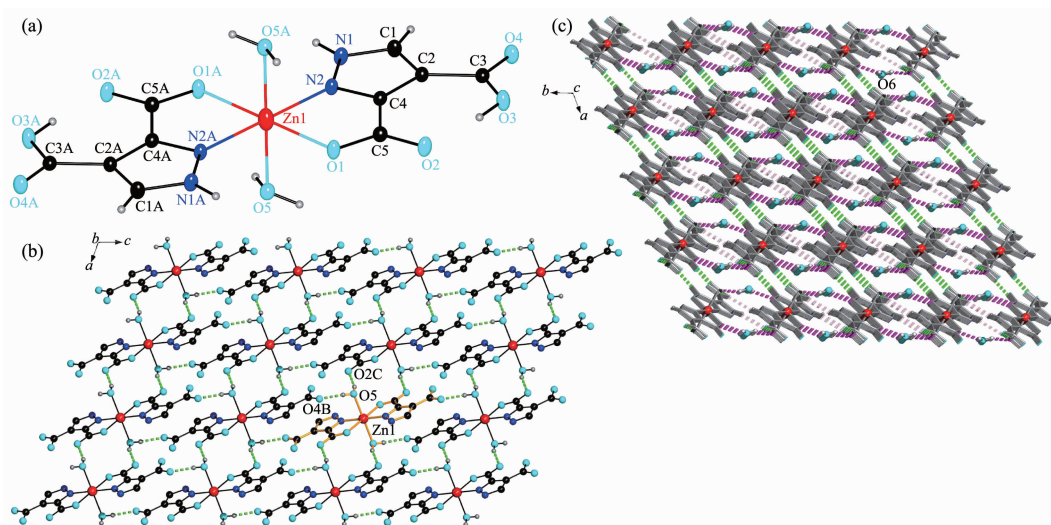
2.2 IR spectra

In the IR spectra of **1** and **2**, the strong and broad bands around 3 200~3 600 cm⁻¹ region are assigned as characteristic peaks of -OH vibration, indicating that water molecules exist in them (Supporting information, Fig.S1). The peaks between 1 680 and 1 710 cm⁻¹ were observed, and it should be attributed to C=O characteristic stretching vibration peaks of carboxylic groups, indicating that the carboxylic groups are not completely deprotonated in **1** and **2**. The vibrations bands at 1 585 and 1 437 cm⁻¹ for **1**, and 1 560 and 1 438 cm⁻¹ for **2** indicate the presence of -COO-. The intense bands in a range of

1 330~1 360 cm⁻¹ are ascribed to the conjugated C=N stretching vibration. The identities of **1** and **2** were finally confirmed by X-ray crystallography.

2.3 Crystal structure of [Zn(H₂pdC)₂(H₂O)₂]·2H₂O (**1**)

X-ray crystal structure analysis reveals that **1** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit consists of half Zn(II) ion, one H₂pdC⁻ ligand, a coordinated water molecule and a lattice aqua molecule. As shown in Fig.1a, the Zn(II) ion is coordinated by a pair of N,O-chelating H₂pdC⁻ ligands, and two additional water molecules, leading to a octahedral geometry with the atoms O(1), O(1A), N(2) and N(2A) on the equatorial position, and the atoms O(5) and O(5A) on the axial position. The bond angles of N(2)-Zn(1)-O(1), N(2A)-Zn(1)-O(1), N(2A)-Zn(1)-O(1A), N(2)-Zn(1)-O(1A) are 78.40(6)°, 101.60(6)°, 78.40(6)°, 101.60(6)°, respectively (Table S1), which are added up to 360°. Moreover, the bond angle of O(5A)-Zn(1)-O(5) is 180°. As a multi-dentate ligand, the H₃pdC partly deprotonated, the resulting H₂pdC⁻ anion chelates to one Zn(II) ion with a pyrazole N atom and a carboxylate O atom to form a five membered ring of Zn(1)-O(1)-C(5)-C(4)-N(2). The bond lengths of Zn-O(1) (0.211 7(16) nm) and Zn-O(5) (0.219 2(15) nm) are longer than those of Zn-N (0.207 4(17) nm), indicating that the strength of Zn(II) ion coordinated with oxygen atoms from H₂pdC⁻ ligands or H₂O molecules is weaker than that of nitrogen atoms from H₂pdC⁻ ligands. The mean length of Zn-O bond in **1** is comparable with that observed in [Zn(HPIDC)(H₂O)]_n.



Only hydrogen atoms involved in the hydrogen bonds are shown; Hydrogen bonds are indicated by dashed lines;
Symmetry codes: A: $1-x, 1-y, 1-z$; B: $1-x, 1-y, -z$; C: $-1+x, y, z$

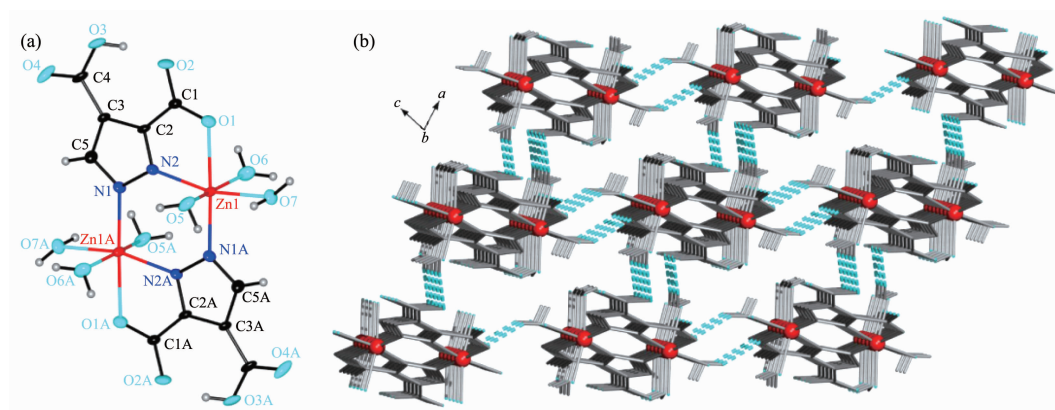
Fig.1 (a) Coordination environment of Zn(II) ion in **1** with thermal ellipsoid at 30% probability level; (b) 2D layer constructed by O-H...O hydrogen-bonding interactions between the coordination units in **1**; (c) 3D supramolecular structure of **1** viewing along c axis

(Zn-O 0.218 90(14) nm, $\text{H}_3\text{PIDC}=\text{2-pyridine-4,5-imidazodiformic acid}$)^[36], while the bond length of Zn-N is shorter than that in $[\text{Zn}(\text{HPIDC})(\text{H}_2\text{O})_n]$ (0.217 48(15) nm). Analysis of the crystal packing of **1** shows that the mononuclear units are extended into 2D structure via O-H...O hydrogen-bonding interactions between coordination water molecule (O(5)) and carboxylate oxygen atoms (O(2C) and O(4B), Symmetry codes: B: $1-x, 1-y, -z$; C: $-1+x, y, z$) (Fig.1b and Table S2). Finally, in the function of two O-H...O hydrogen-bonds between lattice water molecule (O(6)) and carboxylate oxygen atom (O(1A), Symmetry code: A: $1-x, 1-y, 1-z$), coordination water molecule (O(5D), Symmetry code: D: $x, 1+y, z$), along with a weak C(1)-H(1)...O(4E) (Symmetry code: E: $1-x, 2-y, -z$) hydrogen-bonding interaction, these 2D layers are packed along b axis to generate a 3D supramolecular architecture as illustrated in Fig.1c.

2.4 Crystal Structure of $[\text{Zn}_2(\text{Hpdc})_2(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ (**2**)

Complex **2** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit of **2** consists of one Zn(II) ion, one Hpdc²⁻ ligand, three coordination water molecules and one lattice water molecule. As shown in Fig.2a, the structure of **2** consists of a dinuclear

unit with hexa-coordinated Zn(II) ions linked by two $\mu_2\text{-}\kappa\text{N,O}:\kappa\text{O}'$ bridging mode Hpdc²⁻ ligands. The Hpdc²⁻ ligand is both bridging (Zn-N-N-Zn) and chelating (one carboxylate oxygen atom and the adjacent ring nitrogen atom), generating a six-numbered Zn_2N_4 ring, which is also observed in $[\text{Zn}_2(\text{ppca})_2]_n$ ($\text{H}_2\text{ppca}=\text{3-(2-pyridyl)pyrazole-5-carboxylic acid}$)^[37], $[\text{Zn}(\text{pac})(2,2'\text{-bipy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ ($\text{H}_2\text{pac}=\text{pyrazole-3-carboxylic acid}$ and $2,2'\text{-bipy}=\text{2,2'-bipyridine}$)^[24]. The Zn(1)...Zn(1A) separation within Zn_2N_4 ring is 0.395 0(1) nm, which is too long to include any metal-metal interaction. It is close to that in the reported bis(μ -pyrazolato)-bridged dizinc(II) complex, $[\text{Zn}(\text{pac})(2,2'\text{-bipy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (0.393 96(5) nm), but is shorter than that in $[\text{Zn}_2(\text{ppca})_2]_n$ (0.415 5(1) nm). The coordination sphere of Zn(II) is defined by two nitrogen atoms (N(1A) and N(2)) from two Hpdc²⁻ anions, one oxygen atom (O(1)) from one Hpdc²⁻ anion and three oxygen atoms (O(5), O(6) and O(7)) from coordinated water molecules, leading to an octahedral geometry (Fig.2a). The equatorial position are occupied by O(5), O(6), O(7) and N(2) atoms, while O(1) and N(1A) atoms are located in the axial position. The bond angles of N(1A)-Zn(1)-O(1), N(2)-Zn(1)-O(7) and O(5)-Zn(1)-O(6) are 178.04 (12)°, 164.98 (13)° and 167.74(15)° respectively, deviating from 180.00°. The



Only hydrogen atoms involved in the hydrogen bonds are shown; Hydrogen bonds are indicated by dashed lines; Symmetry code: A: $-x, -y, 1-z$

Fig.2 (a) Coordination environment of Zn(II) ions in **2** with thermal ellipsoid at 30% probability level; (b) Dizinc units extended into 3D supramolecular structure through O-H $\cdots$ O hydrogen bonds viewed along b axis

mean Zn-N bond distance (0.207 2(3) nm, Table S1) for **2** is close to the corresponding mean distance of 0.207 3(3) nm in $[\text{Zn}_2(\text{ppca})_2]_n$, and 0.216 2(3) nm in $[\text{Zn}(\text{HPIDC})(\text{H}_2\text{O})]_n$ ($\text{H}_3\text{PIDC} = 2\text{-(pyridin-4-yl)-1H-imidazole-4,5-dicarboxylic acid}$)^[36]. While the length of Zn-O_{Hpdc} (0.224 2(3) nm) is somewhat longer than those in the above two reported Zn(II) complexes containing N-heterocyclic carboxylate (0.205 6(2) and 0.215 6(2) nm). Moreover, it is also longer than the Zn-O_{aq} (from coordinated water) distances (in a range of 0.208 8(3) ~ 0.218 0(3) nm) in **2**, which may be attributed to the unique coordination mode of the Hpdc²⁻ anion. The dizinc units in **2** are extended into 3D structure via O-H $\cdots$ O hydrogen-bonding interactions between coordination water molecules (O(5), O(6) and O(7)) and carboxylate oxygen atoms (O(4B), O(3C) and O(1E), Symmetry codes: B: $-x, -y, 1-z$; C: $1-x, -y, 1-z$; E: $1-x, 1-y, -z$) (Fig.2b and Table S2). Finally, the solvate water molecules (O(8)) are involved in the hydrogen-bonding interactions with carboxylate oxygen atoms (O(1F) and O(2C)) and coordinated water molecules (O(5A) and O(6D), Symmetry codes: A: $-x, 1-y, 1-z$; D: $1-x, 1-y, 1-z$; F: $x, y, 1+z$), respectively, which stabilize the 3D structure of **2**.

2.5 PXRD and thermal analysis

In order to check the phase purity of **1** and **2**, the powder X-ray diffraction patterns were recorded at room temperature. As shown in Fig.S2, the experimental PXRD pattern for each complex correlates well with

its simulated one generated from single-crystal X-ray diffraction data, confirming the phase purity of the bulk materials of **1** and **2**.

In order to examine the thermal stability of **1** and **2**, thermal gravimetric (TG) analyses were carried out from room temperature to 600 °C under nitrogen (Fig. S3). In the TG curve of **1**, the first weight loss of 15.82% in 122~187 °C region corresponds to the loss of four water molecules (Calcd. 16.08%). The second weight loss of 35.17% in the 228~308 °C region corresponds to the loss of one H_2pdc^- ligand (Calcd. 34.45%). Above 308 °C, the remaining substance decomposed gradually, but this degradation did not end upon 600 °C. In the TG curve of **2**, the initial weight loss of 25.36% (Calcd. 24.70%) occurred from 45 to 323 °C, corresponding to the loss of eight water molecules. Above 323 °C, the remaining substance decomposed gradually, but this degradation did not end upon 600 °C.

2.6 Luminescent properties

The luminescent behaviors of Zn(II) complexes **1** and **2** were investigated in the solid state at room temperature (Fig.S4). Upon excitation at 330 nm, the strongest emission peaks for **1** and **2** appeared at 422 and 441 nm, respectively. The emission band for **2** is similar to that of the free ligand with emission maximal at 440 nm upon excitation at 330 nm^[31-32]. While the maximum emission wavelength of **1** underwent a blue-shift of 22 nm, which should be attributed to the ligand-to-metal charge transfer.

3 Conclusions

In summary, two Zn(II) complexes **1** and **2** both contain partly deprotonated H₃pdc ligand anions, H₂pdc⁻ or Hpdc²⁻, but have a remarkable structural and compositional diversity that is achieved through different synthetic routes and molar ratios of reactants. The ligand anions adopt N,O-chelating fashion (H₂pdc⁻ in **1**) and μ_2 - κ N,O: κ N' bridging mode (Hpdc²⁻ in **2**), respectively. By the function of intermolecular hydrogen bonds, mono- and dinuclear complexes **1** and **2** are extended to two 3D supramolecular assemblies, respectively. In addition, two complexes display blue fluorescence in the solid state at room temperature.

Supporting information is available at <http://www.wjhxsb.cn>

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