

基于四氟对苯二甲酸为配体的两个锌(II)的 配合物的合成、晶体结构和荧光性质

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摘要: 本文以四氟对苯二甲酸(H₂tfbdc)和 2,2'-联吡啶(bpy)为配体, 合成了 2 个锌(II)的配合物[Zn₂(bpy)₄(Htfbdc)₂(tfbdc)] (**1**) and [Zn(bpy)(H₂O)₂(tfbdc)] (**2**)。并用元素分析、红外光谱、X-射线单晶衍射结构分析、热重分析等对其进行了表征。化合物 **1** 和 **2** 均属于三斜晶系, 空间群为 $P\bar{1}$ 。配合物 **1** 和 **2** 中的锌(II)离子分别位于畸变的八面体和畸变的三角双锥构型中。配合物 **1** 为双核结构, 它们通过分子间氢键进一步形成一个二维的结构; 配合物 **2** 是一个单核的两性离子, 两性离子间通过氢键形成一个三维的空间网状超分子结构。考察了两种配合物的固体荧光性质。

关键词: 锌; 四氟对苯二甲酸; 晶体结构; 荧光性质

中图分类号: O614.24¹ 文献标识码: A 文章编号: 1001-4861(2013)09-1999-08

DOI: 10.3969/j.issn.1001-4861.2013.00.268

Synthesis, Crystal Structures and Photoluminescent Properties of Two Zinc(II) Complexes Based on Tetrafluoroterephthalate Ligand

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Abstract: Two new Zinc(II) complexes, [Zn₂(bpy)₄(Htfbdc)₂(tfbdc)] (**1**) and [Zn(bpy)(H₂O)₂(tfbdc)] (**2**) (2,2'-bpy=2,2'-bipyridine, tfbdc=tetrafluoroterephthalate) have been synthesized and characterized by elemental analysis, IR spectra, thermogravimetric and X-ray single crystal structure analyses. Structure analysis reveals that **1** and **2** possess same crystal system and space group: triclinic, $P\bar{1}$. In **1**, Zn(II) ion has distorted octahedral geometry, while in **2**, Zn(II) ion has geometry of distorted trigonal bipyramid. Complex **1** is a dinucleate structure, which is further assembled to a 2D supramolecular network through intermolecular hydrogen bonds. Complex **2** is a mononucleate zwitterion, which is further assembled to a 3D supramolecular network via hydrogen bonds interactions. Photoluminescent properties of complexes **1** and **2** in the solid state have also been investigated. CCDC: 900443, **1**; 900444, **2**.

Key words: zinc(II); 2,3,5,6-tetrafluoroterephthalic acid; crystal structure; photoluminescent property

收稿日期: 2012-11-16。收修改稿日期: 2013-03-03。

国家自然科学基金(No.20971060;21101018);南京大学配位化学国家重点实验室开放课题;江苏高校优势学科建设工程资助项目。

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Recently, the design and synthesis of supramolecular metal-organic crystalline materials or crystal engineering is an important and rapidly growing research area owing to their intriguing structural features and potential applications in electrical and magnetic materials, catalysis, adsorption, molecular recognition and gas storage^[1-16]. The assembly of these supramolecular complexes strongly depends on the selection of both the metallic centers and ligands. Aromatic multicarboxylic acid, such as 1,4-benzenedicarboxylic acid, 1,3-benzenedicarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid^[17-23] are good building blocks in the design of supramolecular compounds and multi-dimensional coordination polymers owing to their rich coordination modes. As with most other classes of ligands used in the synthesis of hybrid framework materials, perfluorinated ligands, such as 2,3,5,6-tetrafluoroterephthalic acid (H_2tfbdc) can be used to make a diverse and interesting range of structures and properties^[24-31]. For example, recently, we reported two zinc coordination polymers with obvious fluorescent properties based on tetrafluoroterephthalic acid^[32]. Moreover, due to the presence of fluorine atom with high electro-negativity, these ligands presented a number of opportunities for creating supramolecular arrangement via weak intermolecular contacts. But, to date, such supramolecular frameworks constructed by zwitterionic complexes containing tetrafluoroterephthalate have been less explored; only two tetrafluoroterephthalate zwitterionic complexes are reported by us^[33]. To extend our research in constructing functional coordination polymers and supramolecular compounds with tetrafluoroterephthalic acid^[34-35] and also to consider the promising luminescent properties of many Zinc(II) carboxylate complexes^[32]. We deliberately chose $Zn(NO_3)_2 \cdot 6H_2O$ to react with H_2tfbdc and 2,2'-bpy in different ratio and isolated two novel complexes $[Zn_2(bpy)_4(Htfbdc)_2(tfbdc)]$ (**1**) and $[Zn(bpy)(H_2O)_2(tfbdc)]$ (**2**).

1 Experimental

1.1 Materials

Tetrafluoroterephthalic acid (H_2tfbdc) was synthe-

sized according to literature methods. All chemicals employed were commercially available and used as received without further purification.

1.2 Physical measurements

Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 Series II element analyzer. FTIR spectra were recorded on a Nicolet 460 spectrophotometer in the form of KBr pellets. Single-crystal X-ray diffraction measurements of the two complexes were carried out with a Bruker Smart Apex CCD diffractometer at 293(2) K. Thermogravimetric analysis (TGA) experiments were carried out on a DuPont thermal analyzer from room temperature to 800 °C under N_2 atmosphere at a heating rate of 10 °C·min⁻¹. Luminescence spectra of solid samples were recorded on a Varian Cary Eclipse spectrometer.

1.3 Preparation of $[Zn_2(bpy)_4(Htfbdc)_2(tfbdc)]$ (**1**)

$Zn(NO_3)_2 \cdot 6H_2O$ (0.029 7 g, 0.1 mmol), H_2tfbdc (0.047 6 g, 0.2 mmol) and 2,2'-bipyridine (0.015 6 g, 0.1 mmol) were added into a mixed solvent of 4 mL anhydrous ethanol and 3 mL deionized water and stirred for 1h. The resulting colorless solution was allowed to stand at ambient temperature for 3 d to afford colorless crystals. Yield 62.48% (based on Zn). Anal. Calcd. for $C_{64}H_{34}F_{12}N_8O_{12}Zn_2$ (%): C, 52.44; H, 2.34; N, 7.64. Found (%): C, 52.10; H, 2.53; N, 7.50. IR spectrum (cm⁻¹, KBr pellet) ν : 3 405(w), 3 118(m), 3 075(m), 1 730(s), 1 634(vs), 1 607(vs), 1 465(vs), 1 442(vs), 1 367(vs), 1 180(s), 1 160(s), 1 063(w), 1 044(w), 1 022(m), 992(vs), 985(s), 868(w), 767(vs), 738(s), 704(s), 651(m), 630(w), 505(w), 416(w).

1.4 Preparation of $[Zn(bpy)(H_2O)_2(tfbdc)]$ (**2**)

$Zn(NO_3)_2 \cdot 6H_2O$ (0.029 7 g, 0.1 mmol), H_2tfbdc (0.011 75 g, 0.05 mmol), adenine (0.1 mmol) and 2,2'-bipyridine (0.015 6 g, 0.1 mmol) were added into a mixed solvent of 3 mL anhydrous ethanol and 4 mL deionized water and stirred for 1 h. The resulting colorless solution was allowed to stand at ambient temperature for one week to afford colorless crystals. Yield 65.31% (based on Zn). Anal. Calcd. for $C_{18}H_{12}F_4N_2O_6Zn$ (%): C, 43.79; H, 2.43; N, 5.67. Found (%): C, 43.54; H, 2.52; N, 5.82. IR spectrum (cm⁻¹, KBr pellet) ν : 3 415(m), 3 098(m), 3 033(m), 2 926

(m), 2 850(m), 2 812(m), 2 682(m), 2 555(w), 2 005(w), 1 934(w), 1 893(w), 1 826(w), 1 681(vs), 1 614(s), 1 599(s), 1 460(s), 1362(vs), 1248(m), 1143(w), 1125(w), 986(vs), 952(m), 883 (s), 787 (m), 736(vs), 648(m), 558 (m), 530 (m), 473 (m).

1.5 X-ray crystallography

Single-crystal X-ray diffraction measurements of **1** and **2** were carried out with a Bruker Smart Apex CCD diffractometer at 293 (2) K. Intensities of reflections were measured using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) with the ψ - ω scans mode in the range of $1.39^\circ \leq \theta \leq 25.00^\circ$ (**1**) and $1.78^\circ \leq \theta \leq 25.00^\circ$ (**2**). The structure was solved by direct

methods using the SHELXS program of the SHELXTL package and refined with SHELXL^[36]. 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. H atoms attached to O atoms from the water molecules were first located in difference Fourier maps and then placed in the calculated sites and included in the refinement. Crystallographic data parameters for structural analyses were summarized in table 1.

CCDC: 900443, **1**; 900444, **2**.

Table 1 Crystal structure parameters of the complex **1** and **2**

Compound	1	2
Empirical formula	$\text{C}_{64}\text{H}_{34}\text{Zn}_2\text{N}_8\text{O}_{12}\text{F}_{12}$	$\text{C}_{18}\text{H}_{12}\text{ZnN}_2\text{O}_6\text{F}_4$
Formula weight	1 465.73	493.67
Color	Colorless	Colorless
Crystal size / mm	0.26×0.24×0.20	0.28×0.24×0.22
Temperature / K	293(2)	293(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	0.978 91(7)	0.828 55(8)
b / nm	1.009 45(8)	0.968 08(8)
c / nm	1.600 33(12)	1.167 36(10)
α / (°)	102.891(2)	90.161(2)
β / (°)	107.641(10)	100.501(2)
γ / (°)	96.569(10)	102.486(2)
V / nm ³	1.440 56(19)	0.898 02(14)
Z	1	2
D_c / (g·cm ⁻³)	1.690	1.826
μ (Mo $K\alpha$) / mm ⁻¹	0.947	1.451
Index ranges (h, k, l)	-11 / 11, -11 / 11, -19 / 15	-5 / 9, -11 / 11, -13 / 13
$F(000)$	738	496
θ range for data collection / (°)	1.39 to 25.00	1.78 to 25.00
Reflections collected	8 055	4 988
Independent reflections (R_{int})	4 993	3 103
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4 993 / 1 / 443	3 103 / 0 / 280
Goodness-of-fit on F^2	1.014	1.059
R_1, wR_2 ($I > 2\sigma(I)$)	0.040, 0.124	0.028, 0.093
R_1, wR_2 (all data)	0.055, 0.187	0.030, 0.096
Largest diff. Peak and hole / (e·nm ⁻³)	890, -1 150	480, -430

2 Results and discussion

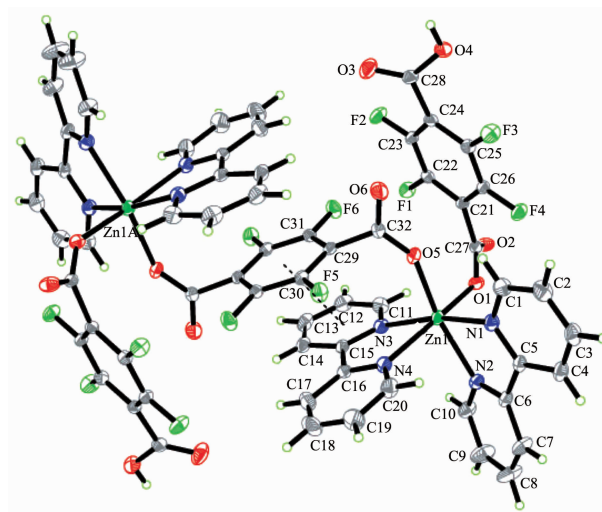
2.1 Synthesis

Compound **1** was obtained by slow evaporation of EtOH-H₂O solution of Zn(NO₃)₂·6H₂O, 2,2'-bpy and H₂tfbdc in the molar ratio 1:1:2. It was isolated in a good yield in a shorter period of crystallization. Compound **2** was obtained by slow evaporation of EtOH-H₂O solution of Zn(NO₃)₂·6H₂O, 2,2'-bpy and H₂tfbdc in the molar ratio 2:2:1 in the presence of adenine; however, in the absence of adenine and other reaction conditions were same with that above mentioned, compound **2** was not obtained, indicating the adenine may play a role of base/template. Besides, the molar ratios of Zn(NO₃)₂·6H₂O, 2,2'-bpy and H₂tfbdc in the synthesis of **1** and **2** are different from that of Zn(II), 2,2'-bpy and tfbdc²⁻ in **1** (1:2:1) and **2** (1:1:1). This result may be relevant to 2,2'-bpy acting as a ligand and a base roles in the reactions. They are stable in air and insoluble in H₂O, C₂H₅OH, CH₃CN, and ether; but compound **1** is soluble in DMF, **2** insoluble in DMF. All the crystals of compounds **1** and **2** were well-shaped, which are suitable for single crystal X-ray diffraction and successive characterizations.

2.2 Crystal structures of **1** and **2**

X-ray crystal structure analysis reveals that **1**

crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit of **1** contains one Zn(II), one Htfbdc⁻, half of a tfbdc²⁻ and two 2,2'-bpy molecules. As illustrated in Fig.1, two crystallographically equivalent Zn(II) ions are bridged by one tfbdc²⁻ with bridging bis-monodentate fashion. The distance between Zn1 and Zn1A is 0.931 55(6) nm. The coordination sphere of Zn(II) is defined by two carboxylic oxygen atoms (O1, O5), four nitrogen atoms (N1, N2, N3 and N4) from two 2,2'-bpy molecules, leading to a distorted octahedral geometry. The equatorial position are



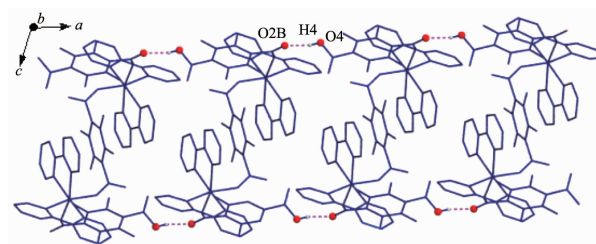
Symmetry code: A: 2-x, 1-y, -z

Fig.1 Crystal structure of complex **1** with thermal ellipsoid at 30% probability level

Table 2 Selected bond lengths (nm) and angles (°) for complex **1** and **2**

Complex 1					
Zn(1)-O(5)	0.205 39(15)	Zn(1)-O(1)	0.209 30(14)	Zn(1)-N(1)	0.216 05(18)
Zn(1)-N(2)	0.218 38(17)	Zn(1)-N(3)	0.219 85(18)	Zn(1)-N(4)	0.222 71(18)
O(5)-Zn(1)-O(1)	93.86(6)	O(5)-Zn(1)-N(1)	87.05(6)	O(1)-Zn(1)-N(1)	100.00(6)
O(5)-Zn(1)-N(2)	163.04(7)	O(1)-Zn(1)-N(2)	89.67(6)	N(1)-Zn(1)-N(2)	76.00(7)
O(5)-Zn(1)-N(3)	97.73(6)	O(1)-Zn(1)-N(3)	90.65(6)	N(1)-Zn(1)-N(3)	168.04(7)
N(2)-Zn(1)-N(3)	98.80(7)	O(5)-Zn(1)-N(4)	94.56(6)	O(1)-Zn(1)-N(4)	163.20(7)
N(1)-Zn(1)-N(4)	94.92(7)	N(2)-Zn(1)-N(4)	86.49(7)	N(3)-Zn(1)-N(4)	73.84(7)
Complex 2					
Zn(1)-O(5)	0.199 87(17)	Zn(1)-O(1)	0.201 05(18)	Zn(1)-O(6)	0.202 78(18)
Zn(1)-N(2)	0.212 9(2)	Zn(1)-N(1)	0.214 3(2)		
O(5)-Zn(1)-O(1)	124.49(8)	O(5)-Zn(1)-O(6)	102.60(8)	O(1)-Zn(1)-O(6)	90.37(8)
O(5)-Zn(1)-N(2)	99.97(7)	O(1)-Zn(1)-N(2)	134.12(8)	O(6)-Zn(1)-N(2)	90.37(8)
O(5)-Zn(1)-N(1)	94.16(8)	O(1)-Zn(1)-N(1)	88.91(8)	O(6)-Zn(1)-N(1)	160.08(9)
N(2)-Zn(1)-N(1)	76.03(8)				

occupied by N(1), N(4), N(3), and O(5) atoms, N(4) and O(1) atoms are located in the axial positions, and the bond angles of O(5)-Zn(1)-N(2), O(1)-Zn(1)-N(4), N(1)-Zn(1)-N(3) are $163.04(7)^\circ$, $163.20(7)^\circ$ and $168.04(7)^\circ$ respectively, deviating from 180° (Table 2). In addition, the average bond length of Zn-N (0.219 2 nm) is longer than that of Zn-O (0.207 3 nm), indicating that the strength of Zn(II) ion coordinated with nitrogen atoms from two 2,2'-bpy molecules are weaker than that of oxygen atoms from tetrafluoroterephthalate. The Zn-O bond distances in the range of 0.205 39(15) to 0.209 30(14) nm are comparable to those found in other Zn(II) complexes reported^[32]. The discrete dinuclear structure is further cross-linked via the intermolecular hydrogen bonds O(4)-H(4)⋯O(2)B to form 1D chains (Fig.2). And these infinite chains interlinked via the interaction of four kinds of intermolecular hydrogen bonds C(7)-H(7)⋯O(2)C, C(9)-H(9)⋯O(6)D, C(11)-H(11)⋯O(1) and C(20)-H(20)⋯F(1)C, resulting in the formation of a two-dimensional (2D) layer. The lengths and angles of the hydrogen bonds for **1** are listed in table 3. Besides, the separation of 0.359 4(2) nm between the centroids of the pyridine ring and benzene ring, indicates the existence of the significant intramolecular π - π interactions (Fig.1).



Symmetry code: B: $1+x, y, z$; Hydrogen bonds are indicated by dashed lines

Fig.2 1D chain of **1** along the a axis linked by hydrogen bonds

As shown in Fig.3, the coordination sphere of the Zn(II) ion is defined by three oxygen atoms (O1, O5, O6) from one tfbdc²⁻ ligand and two water molecules as well as two nitrogen atoms (N1, N2) from one 2,2'-bipyridine molecule. The Zn(II) ion is five-coordinated

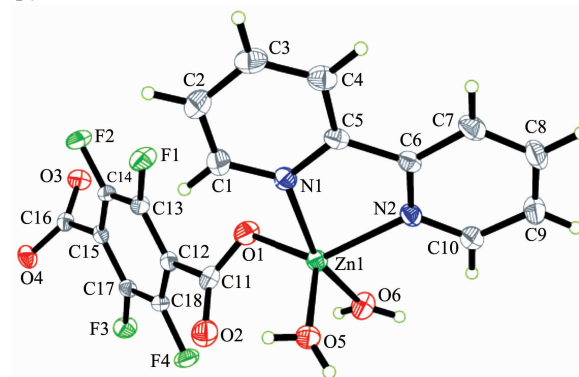


Fig.3 Crystal structure of complex **2** with thermal ellipsoid at 30% probability level

Table 3 Hydrogen bond distances and angles for complex **1** and **2**

D-H⋯A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}⋯\text{A}) / \text{nm}$	$d(\text{D}⋯\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
Complex 1				
O(4)-H(4)⋯O(2)B	0.082	0.178	0.258 3(2)	164
C(7)-H(7)⋯O(2)C	0.093	0.254	0.343 2(4)	161
C(9)-H(9)⋯O(6)D	0.093	0.246	0.309 6(4)	125
C(11)-H(11)⋯O(1)	0.093	0.257	0.314 1(3)	120
C(20)-H(20)⋯F(1)C	0.093	0.251	0.323 2(3)	134
Complex 2				
O(5)-H(5X)⋯F(2)A	0.082	0.250	0.316 6(2)	139
O(5)-H(5X)⋯O(3)A	0.082	0.221	0.273 6(3)	123
O(5)-H(5Y)⋯O(4)B	0.082	0.186	0.266 5(3)	166
O(6)-H(6X)⋯F(2)C	0.082	0.253	0.324 9(2)	147
O(6)-H(6Y)⋯O(3)D	0.082	0.192	0.266 6(3)	152
C(4)-H(4)⋯O(4)E	0.093	0.253	0.342 8(3)	163
C(7)-H(7)⋯O(4)E	0.093	0.234	0.325 4(3)	166

Symmetry code: B: $1+x, y, z$; C: $x, 1+y, z$; D: $-1+x, y, z$ for **1**; A: $1+x, 1+y, z$; B: $1-x, -y, 1-z$; C: $x, -1+y, z$; D: $-x, -y, 1-z$; E: $1+x, 1+y, 1+z$ for **2**.

with a geometry of distorted trigonal bipyramid. Zn-N bond lengths lie in the range of 0.212 9(2)~0.214 3(2) nm. Zn-O bond distances in the range of 0.199 87(17)~0.202 78(18) nm is somewhat shorter than those found in $[\text{Zn}_2(\text{tfbdc})_2(\text{DMF})_2(\text{EtOH})]_n$ and $[\text{Zn}(\text{tfbdc})(\text{MeOH})_4]_n$ ^[32].

It is interesting that complex **2** is a zwitterionic complex; Fig.3 clearly shows that two carboxylic groups of tetrafluoroterephthalic acid are all deprotonated, but only one carboxylate group coordinates with Zn(II) ion, resulting in $[\text{Zn}(\text{bpy})(\text{H}_2\text{O})_2(\text{tfbdc})]$ acquiring a zwitterionic nature. Similar case has been found in the complexes $[\text{M}(\text{ImH})_4(\text{tfbdc})(\text{H}_2\text{O})]$ (M=Co and Ni) (ImH=imidazole)^[33]. To our knowledge, it is the third zwitterionic complex containing tetrafluoroterephthalate. The independent components $[\text{Zn}(\text{bpy})(\text{H}_2\text{O})_2(\text{tfbdc})]$ are connected through five kinds of intermolecular hydrogen bonds O(5)–H(5X)⋯F(2)A, O(5)–H(5X)⋯O(3)A, O(5)–H(5Y)⋯O(4)B, O(6)–H(6X)⋯F(2)C and O(6)–H(6Y)⋯O(3)D, resulting in the formation of a two-dimensional (2D) layer, as shown in Fig.4. The 2D grid-like layers are further packed into a three-dimensional supramolecular architecture with channels

through hydrogen bonding interactions (C(4)–H(4)⋯O(4)E and C(7)–H(7)⋯O(4)E between the adjacent layers. The lengths and angles of the hydrogen bonds for **2** are listed in table 3.

2.3 Infrared spectrum

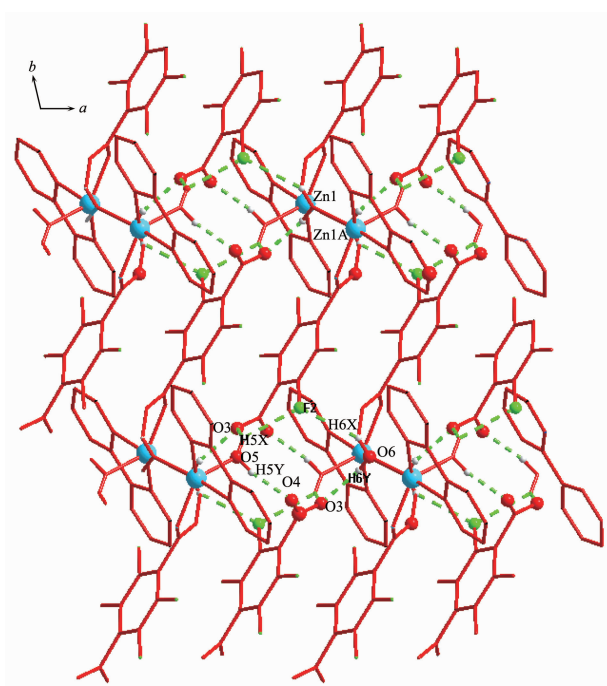
IR spectra of complexes **1** and **2** reflect the binding patterns of H_2tfbdc and 2,2'-bpy (see Supplementary materials Fig.S1 and S2). For compound **1**, the peaks at 1 634, 1 607 and 1 442, 1 366 cm^{-1} are the $\nu_{\text{as}}(\text{OCO})$, and $\nu_{\text{s}}(\text{OCO})$ stretching modes of $\text{Htfbdc}^-/\text{tfbdc}^{2-}$ ^[37], respectively, while stronger absorption at 737 cm^{-1} is the $\delta(\text{OCO})$ bent vibration of $\text{Htfbdc}^-/\text{tfbdc}^{2-}$. For compound **2**, the strong peak around 3 400 cm^{-1} is the $\nu(\text{OH})$ stretching mode of water; no absorption peak around 1 690~1 730 cm^{-1} shows that the protons from carboxylic acid (–COOH) are deprotonated. The peaks at 1 681, 1 614 and 1 459, 1 362 cm^{-1} are the $\nu_{\text{as}}(\text{COO}^-)$, and $\nu_{\text{s}}(\text{OCO})$ stretching modes of tfbdc^{2-} ^[25] respectively, while stronger absorption at *ca.* 735 cm^{-1} is the $\delta(\text{OCO})$ bent vibration of tfbdc^{2-} . For Compounds **1** and **2**, the weak absorption at 3 000 cm^{-1} is the $\nu(\text{C-H})$ bent vibration of bpy.

2.4 Thermal analysis

Thermal stability of the title complexes $[\text{Zn}_2(\text{bpy})_4(\text{Htfbdc})_2(\text{tfbdc})]$ (**1**) and $[\text{Zn}(\text{bpy})(\text{H}_2\text{O})_2(\text{tfbdc})]$ (**2**) have been investigated by TG technique. (see Supplementary materials Fig.S3) For **1**, the TG analysis shows that the weight loss begins at 155 °C, showing its 2D framework is maintained up to 155 °C. Four 2,2'-bpy decomposed gradually from 155 to 205 °C (Calcd. 42.59% ; Found, 45.12%). The next weight loss of 14.89% (Calcd. 16.10%) occurs from 205 to 376 °C, corresponding to loss of one tfbdc^{2-} ligand, then the residual substance is decomposed gradually. For **2**, the initial weight loss of 8.0% (7.2%) occurs from 107 to 186 °C, corresponding to loss of two coordinated water molecules. Then the remaining substance is decomposed gradually.

2.5 Photoluminescent properties

The solid-state fluorescence of free H_2tfbdc , compounds **1** and **2** were investigated at room temperature. In the emission spectra of compounds **1** and **2**, they have a band at *ca.* 424 nm (λ_{ex} =372 nm),



Symmetry code: A: 1+x, 1+y, z; Hydrogen bonds are indicated by dashed lines

Fig.4 2D grid layers of the complex **2**

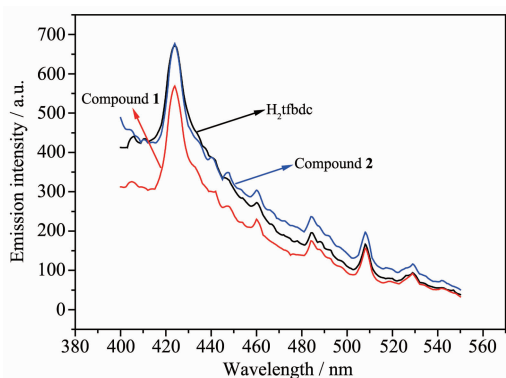


Fig.5 Solid-state emission spectra for complexes **1**, **2** and ligand H_2tfbdc ($\lambda_{ex}=372$ nm) at room temperature

which is quite similar to that of the free H_2tfbdc . Therefore the origin of the emissions of compounds **1** and **2** may be attributable to the internal charge transfer ($\pi \rightarrow \pi^*$ transitions) of the ligand (IL)^[32].

3 Conclusions

In summary, we have successfully synthesized two new complexes $[Zn_2(bpy)_4(Htfbdc)_2(tfbdc)]$ (**1**) and $[Zn(bpy)(H_2O)_2(tfbdc)]$ (**2**) under slow evaporation condition. In complex **1**, the discrete dinuclear units $[Zn_2(bpy)_4(Htfbdc)_2(tfbdc)]$ are linked via hydrogen-bonding to generate a 2D framework. The framework of **1** is stable under 155 °C. Complex **2** is a mononucleate zwitterion, further assembled to a 3D supramolecular network via hydrogen-bonding interactions. Besides, complexes **1** and **2** display significant purple fluorescence at room temperature.

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