

以四氟对苯二甲酸为配体构建的两个铅的配位聚合物:合成、晶体结构和荧光性质

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摘要: 在 4-甲基咪唑/三氮唑存在下,利用四氟对苯二甲酸为配体、与 $\text{Pb}(\text{NO}_3)_2$ 作用,得到了 2 种配位聚合物 $[\{\text{Pb}(\text{tfbdc})(\text{H}_2\text{tfbdc})_{0.5}\} \cdot (4\text{-MI}) \cdot (\text{H}_2\text{O})]_n$ (**1**) 和 $[\{\text{Pb}(\text{tfbdc})(\text{H}_2\text{O})_2\}]_n$ (**2**) (tfbdc =四氟对苯二甲酸,4-MI=4-甲基咪唑),并用红外光谱、元素分析和 X-单晶衍射对其进行了表征。化合物 **1** 属于单斜晶系,空间群为 $P2_1/n$,化合物 **2** 属于三斜晶系,空间群为 $P\bar{1}$ 。配合物 **1** 中,铅离子依靠正常的 Pb-O 键和次级键 $\text{Pb} \cdots \text{O}$,与 7 个氧原子配位; tfbdc^{2-} 阴离子和 H_2tfbdc 分别采用不同的配位方式桥联铅离子,导致 1 个具有孔道的三维结构的形成。而 4-甲基咪唑和游离水分子通过氢键作用嵌在这三维结构的孔道中。 π - π 堆积作用的存在增强了 **1** 的稳定性。配合物 **2** 中,铅离子是位于 8 个氧原子的配位环境中, tfbdc^{2-} 阴离子以螯合和桥联的方式与铅离子作用,导致 1 个二维层状结构的形成。此外还考察了 **1** 和 **2** 的热稳定性和固体荧光性质。

关键词: 铅配合物; 四氟对苯二甲酸; 晶体结构; 荧光性质

中图分类号: O614.43⁺3

文献标识码: A

文章编号: 1001-4861(2014)09-2165-09

DOI: 10.11862/CJIC.2014.304

Two Lead-Based Coordination Polymers with 2,3,5,6-Tetrafluoroterephthalic Acid: Synthesis, Crystal Structures and Luminescent Properties

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Abstract: In the present of 4-MI/triazole, Two lead(II) coordination polymers, $[\{\text{Pb}(\text{tfbdc})(\text{H}_2\text{tfbdc})_{0.5}\} \cdot (4\text{-MI}) \cdot (\text{H}_2\text{O})]_n$ (**1**) and $[\{\text{Pb}(\text{tfbdc})(\text{H}_2\text{O})_2\}]_n$ (**2**) (tfbdc =tetrafluoroterephthalate, 4-MI=4-methylimidazole) have been synthesized and characterized by elemental analysis, IR spectra, thermogravimetric and X-ray single crystal structure analyses. Structure analyses reveal that **1** has monoclinic crystal system and space group of $P2_1/n$, and **2** has triclinic crystal system and space group of $P\bar{1}$. In **1**, each Pb(II) ion is coordinated with seven oxygen atoms via the normal Pb-O bond and the secondary bond $\text{Pb} \cdots \text{O}$; tfbdc^{2-} anion and H_2tfbdc ligands are bridged to Pb(II) ions in different coordination fashion, resulting in the formation of a 3D structure with channels. 4-MI and free water molecules are clathrated in the channels via hydrogen bonds interactions. The existence of π - π stacking interactions further enhance the stability of **1**. In **2**, each Pb(II) ion is surrounded by eight oxygens, and tfbdc^{2-} coordinates with Pb(II) ion in chelating and bridging fashion, constructing a 2D layer structure. The thermal stability and solid-state luminescent properties of **1** and **2** have also been studied. CCDC: 977618, **1**; 977147, **2**.

Key words: Pb(II) complex; 2,3,5,6-tetrafluoroterephthalic acid; crystal structure; luminescent property

收稿日期: 2014-02-17。收修改稿日期: 2014-03-24。

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资助项目; 江苏精细石油化工重点实验室资助项目。

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0 Introduction

Coordination polymers and especially their porous congeners, which are frequently termed metal-organic frameworks (MOFs)^[1-2], have received more and more attention in recent years, owing to their easy synthetic accessibility and potential applications in storage and separation media for gases, catalysis, lithium-ion batteries, optic and electric materials and biomedical imaging^[3-11]. To improve these properties, MOFs with fluorinated linker molecules are receiving increasing attention^[12-21]. For MOF with 2,3,5,6-tetrafluoroterephthalic acid (H_2tfbdc) as a linking ligand, superior H_2 adsorption properties have been predicted by theoretical investigations^[22]. However, compared to their nonfluorinated analogues, terephthalic acid (H_2bdc), only some coordination polymers or MOFs employing $tfbdc^{2-}$ ion have been reported^[6,12-13,23-31]. However, due to the presence of fluorine atom with high electro-negativity, 2,3,5,6-tetrafluoroterephthalic acid (H_2tfbdc) may adopt more varied coordination modes and provide more opportunities for creating supramolecular arrangements via weak intermolecular interactions. On the other hand, as is well known, mainly because of $Pb(II)$ ion itself bearing a stereochemically active electron lone pair and large ionic radius, it can adopt variable coordination number and geometry, and thus adding the possibility of constructing novel MOFs. Besides, many $Pb(II)$ -MOFs reported have shown potential applications in the electroluminescence, fluorescent sensors and organic light-emitting diodes^[32-33].

Considering outstanding characters of $Pb(II)$ ion and our group's interest in the MOFs containing $tfbdc^{2-}$ ^[6,23-24,27-30], we tried to synthesize new $Pb(II)$ -based coordination polymers with H_2tfbdc . Luckily, we obtained two new compounds $\{[Pb(tfbdc)(H_2tfbdc)_{0.5}]\cdot(4-MI)\cdot(H_2O)_n\}$ (**1**) and $\{[Pb(tfbdc)(H_2O)_2]\}_n$ (**2**) ($tfbdc$ =tetrafluoroterephthalate, 4-MI=4-methylimidazole). Herein we report their synthesis, crystal structures and properties such as IR spectra, thermal decomposition, and luminescent properties.

1 Experimental

1.1 Materials and methods

All commercially available solvents and reagents were used as received without further purification unless otherwise noted. The ligand H_2tfbdc was prepared according to the literature^[34]. The elemental analysis (C, H and N) was 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. The luminescent spectra of the solid samples were recorded on a Varian Cary Eclipse spectrometer. 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. Single-crystal X-ray diffraction measurement of the complexes **1** and **2** were carried out with a Bruker Apex II CCD diffractometer.

1.2 Synthesis

1.2.1 Preparation of $\{[Pb(tfbdc)(H_2tfbdc)_{0.5}]\cdot(4-MI)\cdot(H_2O)_n\}$ (**1**)

To the solution of H_2tfbdc (0.20 mmol, 0.047 6 g), 4-MI (0.10 mmol, 0.082 0 g) in 2 mL of H_2O and MeOH (1:1, V/V) was added a solution of $Pb(NO_3)_2$ (0.2 mmol, 0.066 2 g) in 2 mL (1:1, V/V) of H_2O and MeOH under oscillation by the ultrasonic-wave reactor (100 W). After 30 min, the solution became turbid slightly, then filtered, and the filtrate allowed to stand at ambient temperature for 3 weeks to afford colorless block crystal **1** (41 % yield based on Pb). Anal. Calcd. for $C_{16}H_9F_6PbN_2O_7$ (%): C, 29.01; H, 1.37; N, 4.23. Found (%): C, 29.00; H, 1.36; N, 4.21. IR data (cm⁻¹, KBr pellet): 3 438 (m), 3 139 (m), 1 721(m), 1 629 (s), 1 475 (s), 1 389 (s), 1 312 (s), 1 225 (s), 994 (s), 713 (s).

1.2.2 Preparation of $\{[Pb(tfbdc)(H_2O)_2]\}_n$ (**2**)

H_2tfbdc (0.10 mmol, 0.023 8 g), triazole (0.25 mmol, 0.017 2 g), $Pb(NO_3)_2$ (0.10 mmol, 0.033 0 g) was dissolved in H_2O (4 mL) and EtOH (6 mL) to give a colorless solution and it was allowed to stand at ambient temperature for one week to afford colorless rod-like crystal **2** (56% yield based on Pb). Anal.

Calcd. for $C_8H_4F_6PbO_6$ (%): C, 20.05; H, 0.84. Found (%): C, 20.01; H, 0.81. IR data (cm^{-1} , KBr pellet): 3 440 (m), 1 673(s), 1 620 (s), 1 476 (s), 1 381 (s), 1 277 (s), 1 151 (s), 991 (s), 743(m).

1.3 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) and 291(2) K, respectively. Intensities of reflections were measured using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 07\ nm$) with the φ - ω scans mode from $1.70^\circ<\theta<25.99^\circ$ (**1**) and $2.05^\circ<\theta<26.00^\circ$ (**2**). The structure was solved by direct methods using Olex 2 for **1** and SHELXTL-

97 for **2** and refined by full-matrix least-squares on F^2 with the SHELXTL-97 program package^[35-36]. Anisotropic thermal factors were assigned to all the non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on the parent atoms. H atoms bonded to O or N were first located in difference Fourier maps and then placed in calculated sites and included in the refinement. Crystallographic data and experimental details for structural analyses are summarized in Table 1. The selected bond lengths and angles for **1** and **2** are listed in Table 2.

CCDC: 977618, **1**; 977147, **2**.

Table 1 Crystals data, experimental conditions and structure refinement parameters of complexes **1** and **2**

	1	2
Empirical formula	$C_{16}H_9F_6N_2O_7Pb$	$C_8H_4F_6O_6Pb$
Formula weight	662.44	479.30
Crystal size / mm	0.12×0.11×0.10	0.13×0.11×0.08
Temperature / K	293(2)	291(2)
Wavelength / nm	0. 071 073	0.071 073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a / nm	1.617 3(11)	0.733 53(10)
b / nm	0.699 9(3)	0.880 64(12)
c / nm	1.647 9(3)	1.043 5(14)
α / (°)		76.449(2)
β / (°)	93.724(3)	73.946(2)
γ / (°)		68.036(2)
V / nm ³	1.861 4(5)	0.594 29(14)
Z	4	2
D_c / (g·cm ⁻³)	2.364	2.679
$F(000)$	1 244	436
$\mu(Mo\ K\alpha)$ / mm ⁻¹	9.168	14.268
θ range for data collection / (°)	1.70 to 25.99	2.05 to 26.00
Independent reflections (R_{int})	3 661	2 282
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3 661/0/293	2 282/0/188
Goodness-of-fit on F^2	1.059	1.095
R_1, wR_2 ($I>2\sigma(I)$)	0.038 7, 0.091 4	0.052 8, 0.137 2
Largest diff. peak and hole / (e·nm ⁻³)	2 511 and -4 441	1 289 and -1 192

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

Complex 1					
Pb(1)-O(1)	0.249 6(4)	Pb(1)···O(1)	0.289 6(5)	Pb(1)-O(2)B	0.268 4(5)
Pb(1)···O(4)A	0.283 6(5)	Pb(1)-O(3)A	0.245 4(5)	Pb(1)···O(2)	0.283 0(5)
Pb(1)-O(6)	0.240 2(5)				
O(1)-Pb(1)-O(2)B	170.03(13)	O(6)-Pb(1)-O(3)A	76.41(19)	O(3)A-Pb(1)-O(1)	83.10(16)
C(1)-O(1)-Pb(1)	140.8(4)	O(3)A-Pb(1)-O(2)B	87.78(14)	C(1)-O(2)-Pb(1)D	130.3(4)
O(6)-Pb(1)-O(1)	78.29(15)	C(8)-O(3)-Pb(1)A	103.0(4)	O(6)-Pb(1)-O(2)B	103.49(16)
C(9)-O(6)-Pb(1)	111.9(4)				
Complex 2					
Pb(1)-O(1)A	0.257 6(8)	Pb(1)-O(1WA)	0.265 9(8)	Pb(1)-O(3)B	0.260 1(8)
Pb(1)···O(2)	0.281 1(8)	Pb(1)-O(2WA)	0.264 3(9)	Pb(1)···O(2)A	0.277 5(8)
Pb(1)-O(1)	0.265 6(8)	Pb(1)···O(4) B	0.278 4(8)		
O(1)A-Pb(1)-O(3)B	86.5(3)	O(3)A-Pb(1)-O(1WA)	73.5(3)	O(1)A-Pb(1)-O(2WA)	97.6(3)
O(2WA)-Pb(1)-O(1WA)	171.2(3)	O(3)B-Pb(1)-O(2WA)	112.2(3)	O(1)-Pb(1)-O(1WA)	81.7(3)
O(1)A-Pb(1)-O(1)	64.0(3)	C(1)-O(1)-Pb(1)A	143.8(7)	O(3)B-Pb(1)-O(1)	145.5(3)
C(1)-O(1)-Pb(1)	97.1(7)	O(2WA)-Pb(1)-O(1)	90.2(3)	Pb(1)A-O(1)-Pb(1)	116.0(3)
O(1)A-Pb(1)-O(1WA)	75.6(3)	C(8)-O(3)-Pb(1)C	98.3(7)		

Symmetry code: A: $-x+1, -y+1, -z+1$; B: $x, y-1, z$; C: $-x+1.5, y-0.5, -z+0.5$; D: $x, y+1, z$ for **1**; A: $-x+2, -y, -z+2$; B: $x, y-1, z+1$; C: $x, y+1, z-1$ for **2**

Table 3 selected hydrogen bond distances and angles in the complex **1**

D-H···A	$d(\text{D-H}) / \text{nm}$	$d(\text{H} \cdots \text{A}) / \text{nm}$	$d(\text{D} \cdots \text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
N(1)-H(1)···F(3)	0.086	0.245	0.306 4(6)	128.0
N(1)-H(1)···O(4)	0.085	0.195	0.275 3(7)	154.0
O(7)-H(F)···O(5)	0.085	0.199	0.283 7(7)	173.0
O(7)-H(G)···O(6)	0.085	0.199	0.280 0(7)	159.0
C(15)-H(B)···O(7)	0.093	0.252	0.328 3(10)	139.0

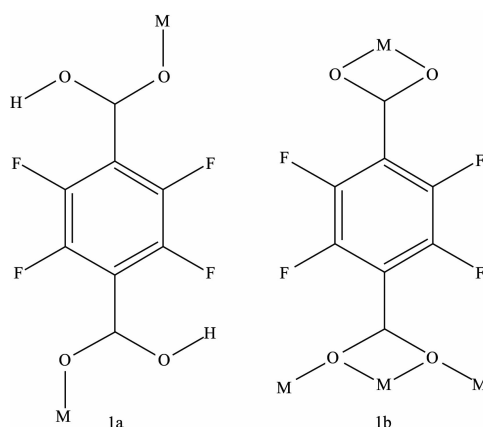
2 Results and discussion

2.1 Synthesis and IR spectra characterization

Complex **1** was synthesized by adding H_2tfbdc , $\text{Pb}(\text{NO}_3)_2$ and 4-MI in a molar ratio of 2:1:2 in $\text{MeOH-H}_2\text{O}$; complex **2** was synthesized by slow evaporation of $\text{EtOH-H}_2\text{O}$ solution including H_2tfbdc , $\text{Pb}(\text{NO}_3)_2$ and triazole in a molar ratio of 1:1:2. 4-MI and triazole may play a role of base/template. **1** and **2** are stable and insoluble in water and common organic solvents.

The IR spectra were determined using KBr pellet method. A strong and broad absorption peak around $3\ 600\sim 3\ 000\ \text{cm}^{-1}$ in **1** and **2** should be attributed to

the stretching vibration of OH, indicating that the Both complexes all include water molecules, and the moderate absorption peak at $3\ 139\ \text{cm}^{-1}$ in **1** shows that it should contain NH from 4-MI^[37]. For **1**, there is a moderate strong peak at $1\ 721\ \text{cm}^{-1}$, indicating that some carboxylic groups are still protonated. For **2**, there are no absorption peaks around $1\ 730\ \text{cm}^{-1}$, indicating that all carboxylic groups are deprotonated. The strong peaks in the range of $1\ 620\sim 1\ 673\ \text{cm}^{-1}$ and $1\ 312\sim 1\ 476\ \text{cm}^{-1}$ of **1** and **2** can be attributed to $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ stretching vibration of tfbdc²⁻ respectively^[38-41], and strong peaks at $713\ \text{cm}^{-1}$ and $991\sim 994\ \text{cm}^{-1}$ for both complexes are attributed to δ



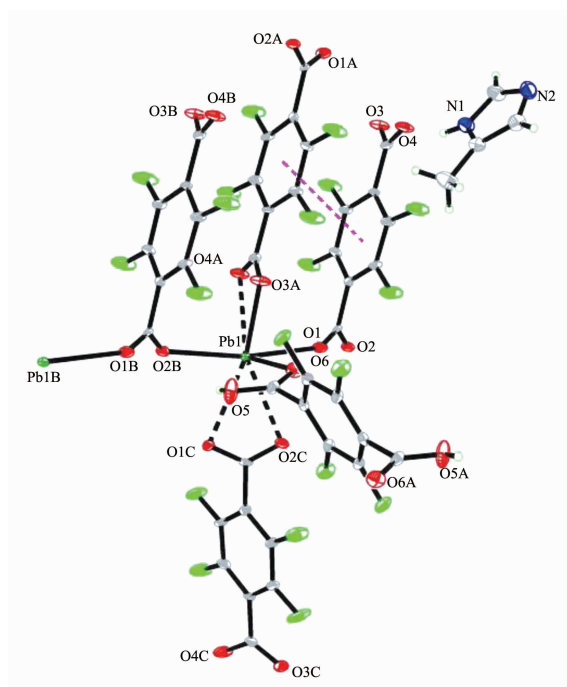
Scheme 1 Coordination modes of the H_2tfbdc (1a) and $tfbdc$ ligand (1b)

(OCO) bending vibration of $tfbdc^{2-}$ [31]. Those assignments are supported by the X-ray crystal structure analysis.

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

Single-crystal X-ray diffraction analysis showed that complex **1** crystallized in the monoclinic space group $P2_1/n$. The coordination sphere of $Pb(II)$ cation is shown in Fig.1. The asymmetric unit of complex **1** contains one $Pb(II)$ cation, one and a half $tfbdc^{2-}$, one free water molecule, and one free 4-MI. The $Pb(II)$ cation, adopting seven-coordinate mode, is surrounded by seven oxygen atoms: two are from two

$tfbdc^{2-}$ anions respectively (O(2)B and O(1)), the $tfbdc^{2-}$ is connected with the other $Pb(II)$ cation in the bridge form with O(1)B/O(2) to form a chain(the angel of O(1)-Pb1-O(2)B is $170.03(13)^\circ$, close to 180°), four separately from bidentately chelating carboxyl groups of two $tfbdc^{2-}$ (O(3)A, O(4)A, O(1)C and O(2)C), and one from monodentately carboxyl groups of H_2tfbdc (O(6)). The Pb-O bond lengths are in the range of $0.240\ 2\ (5) \sim 0.268\ 4(5)$ nm (Table 2), close to the values reported in the literature [12,42]. It is worth mentioning that the bond distances of $Pb \cdots O(4)A$, $Pb \cdots O(1)C$ and $Pb \cdots O(2)C$ lie in the range of $0.277\ 5\ (8) \sim 0.283\ 6(5)$ nm, belonging



Broken lines represent the secondary bands/ π - π interaction; Symmetry code: A: $-x+1, -y+1, -z+1$; B: $x, y-1, z$; C: $-x+1.5, y-0.5, -z+0.5$

Fig.1 Coordination environment of $Pb(II)$ in complex **1** with thermal ellipsoid at 30% probability level

to the secondary bonds^[39]. The bond angles around Pb(II) cation are $76.41(18)^\circ$ to $170.05(15)^\circ$ (Table 2). Besides, the separation of 0.372 3 nm between the centroids of the two benzene rings, indicates the existence of the significant π - π interactions of offset face to face (Fig.1). The tfbdc²⁻ and H₂tfbdc ligands of complex **1** take different coordination fashions (Scheme 1a and 1b). Via fashion 1b, tfbdc²⁻ anion chelates one Pb(II) ion by one carboxyl group, and chelates and bridges three Pb(II) ions with another carboxyl group, resulting in the formation of a 2D layer structure, as shown in Fig.2. The shortest Pb...Pb distance is 0.425 1 nm. These layers are connected

further by H₂tfbdc in fashion 1a (namely amphimono-dentate coordination mode) to construct a stable 3D architecture (Fig.3). The free water molecule and 4-MI are clathrated in the channels, via hydrogen bonds (N(1)-H(1)...F(3), N(1)-H(1)...O(4), O(7)-H(7B)...O(6), Table 3), as listed in Fig.3.

However, owing to the different molar ratio of Pb(II) cation and tfbdc²⁻, the types of auxiliary ligand and the reaction conditions, complex **2** crystallized in the triclinic space group $P\bar{1}$, completely different from the complex **1**. Complex **2** employs eight-coordination mode, in its asymmetric unit, one Pb(II) cation connect one tfbdc²⁻ and two lattice water molecules. As shown

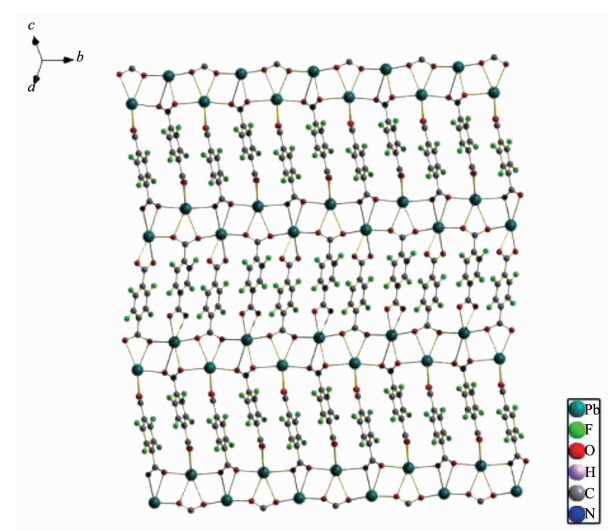
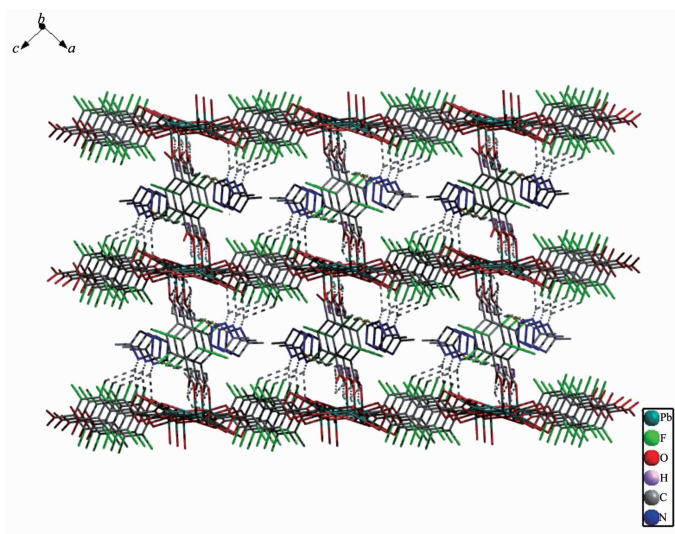


Fig.2 2D grids of complex **1**

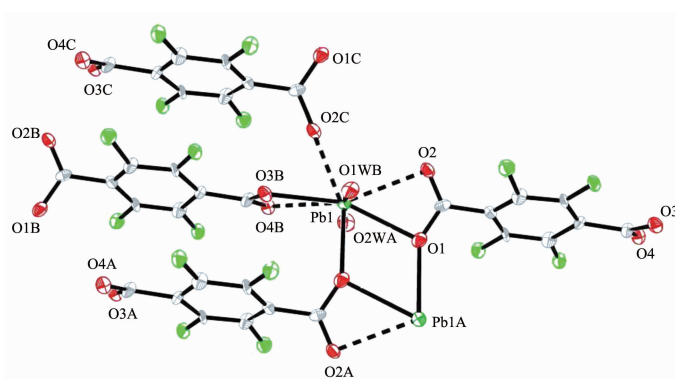


Channels in the structure are filled with the 4-MI and free H₂O guests; Dashed lines represent hydrogen bonds

Fig.3 3D grids of complex **1**

in Fig.4, the Pb(II) cation is surrounded by O(1W)B and O(2W)A atoms from two lattice water molecules, O(1), O(2), O(3)B and O(4B) separately from bidentately chelating carboxyl groups of two tfbdc²⁻, and O(1)A, O(2)C from another two tfbdc²⁻. Similar to complex **1**, the Pb···O(2), Pb···O(2)C, Pb···O(4)B are also secondary bonds^[42]. The Pb-O bond lengths are 0.257 6(8) ~0.265 9(8) nm (Table 2), close to the values reported in the literature^[12,32,43]. The bond angles

around Pb(II) cation are 64.0 (3)° to 171.2 (3)° (Table 2). In **2**, tfbdc²⁻ anion coordinates with Pb(II) cation in fashion 1b (Scheme 1b), resulting in the formation of a 2D layer structure (Fig.5). The shortest Pb···Pb distance is 0.443 7 nm. The 2D layer structure is similar to that of complex **1** (Fig.2), but different from the reported compound [Pb(tfbdc)(MeOH)]_n with 3D structure^[32].



Broken lines represent the secondary bands; Symmetry code: A: $-x+2, -y, -z+2$; B: $x, y-1, z+1$; C: $-x+1, -y, 2-z$.

Fig.4 Coordination sphere of Pb(II) in complex **2** with thermal ellipsoid at 30% probability level

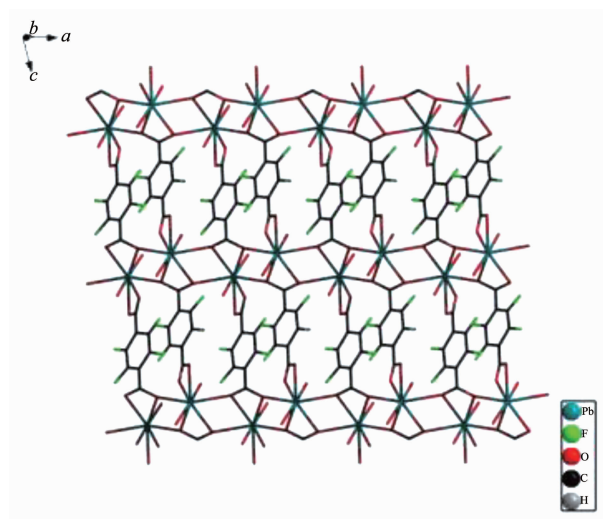


Fig.5 2D grids of Packing diagram of complex **2**

2.3 Thermal analysis

In order to examine the thermal stabilities of complexes **1** and **2**, thermal gravimetric (TG) analyses were carried out from room temperature to 800 °C under nitrogen. For complex **1** (Fig.6), the TG analysis shows that a weight loss about 2.66% from 24 to 161 °C, corresponding to a water molecule loss (the theoretical value calculated 2.72%). Then a greater

mass loss of 12.25% from 160 to 190 °C maybe give the credit to the loss of the free 4-MI (Calcd. 12.39%). Above 190 °C, the residual substance decomposed gradually and the final residue (31.97%) should be PbO (Calcd. 33.66%). For complex **2** (Fig. 6), it shows a mass loss of 7.6% between 35 and 120 °C, corresponding to the loss of water molecules. A theoretical mass loss of two lattice water molecules is

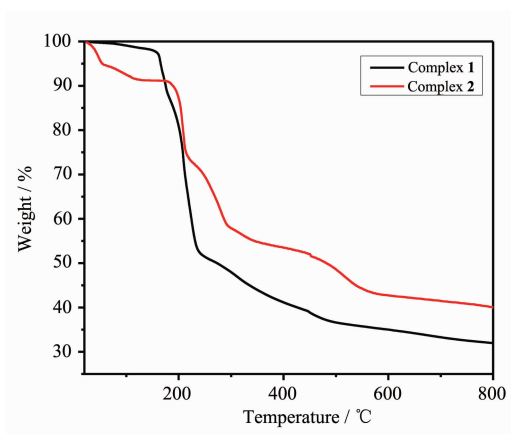


Fig.6 TG curves of complexes **1** and **2**

7.5%, consistent with the experimental result. Above 120 °C, the complex **2** is destroyed gradually. The final residue of 43.7% is in agreement with the percentage of PbO (Calcd. 46.5%).

2.4 Luminescent properties

Luminescent complexes are currently of great interest because of their various applications in chemical sensors, photochemistry, and electroluminescent display [43-44]. Herein, the luminescent behaviors of ligand H₂tfbdc, complexes **1**, and **2** were investigated in the solid state at room temperature owing to excellent luminescent properties of *d*¹⁰ Pb^{II} complexes (Fig.7). Upon excitation at 331 nm, the strongest emission peak for the ligand appears at 362 nm, corresponding to the *n*- π^* / π - π^* transitions. Complexes **1** and **2** all exhibit a emission peak centered at 362 nm, resembling that of the ligand. Therefore the origin of the main emissions of

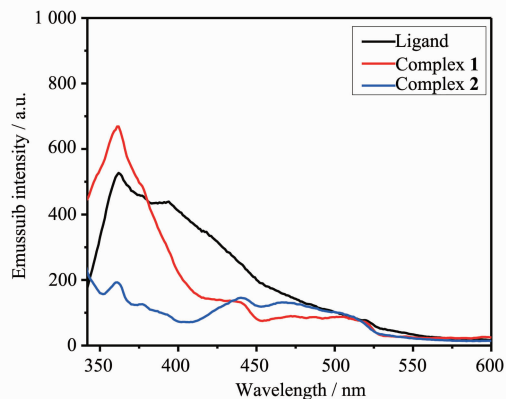


Fig.7 Solid-state emission spectra of the ligand, complexes **1** and **2** under excitation wavelength at 331 nm

compounds **1** and **2** may be attributable to the internal charge transfer of the ligand.

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