

温度控制的原位脱羧 3-氟邻苯二甲酸与铅(II)配位聚合物的合成、晶体结构及荧光性质

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摘要: $\text{Pb}(\text{NO}_3)_2$ 与 3-氟邻苯二甲酸(H_2Fpht)和 2,2'-联吡啶(bpy)在不同水热反应温度下获得了 2 个新的配位聚合物: $[\text{Pb}(\text{Fba})(\text{bpy})(\text{NO}_3)]_n$ (**1**)和 $[\text{Pb}_4\text{O}_2(\text{Fba})_4]_n$ (**2**)。3-氟邻苯二甲酸配体经由原位脱羧生成了 3-氟苯甲酸根(Fba)。配合物 **1** 具有 Pb- NO_3 -Pb 双螺旋链结构,是由硝酸根桥联四方反棱柱 $[\text{PbO}_6\text{N}_2]$ 结构单元而形成,而 Fba 与 bpy 配体螯合配位于中心铅离子。配合物 **2** 为 Pb-OH-Pb 链状结构,包含四面体结构单元 $[\text{Pb}_4(\mu_4\text{-OH})_4]^{4+}$,且具有 4 个晶体学独立的铅离子中心: Pb(1) O_6 、Pb(2) O_6 、Pb(3) O_5 和 Pb(4) O_5 。这两个配合物链分别经氢键作用力自组装为三维超分子网络结构。室温下,测定了配合物的固体荧光光谱,均显示为基于配体的荧光发射。有意思的是,通过荧光淬灭机理配合物 **2** 可以选择性地检测硝基苯。

关键词: 铅配合物; 3-氟邻苯二甲酸; 晶体结构; 荧光

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Temperature-Dependent Formation of Lead(II) Coordination Polymers with 3-Fuorophthalic Acid Involving *in Situ* Decarboxylation: Syntheses, Structures and Fluorescence properties

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Abstract: Hydrothermal reactions of $\text{Pb}(\text{NO}_3)_2$ /3-fluorophthalic acid (H_2Fpht)/2,2'-bipyridine (bpy) involving *in situ* decarboxylation at different temperatures gave two coordination polymers, $[\text{Pb}(\text{Fba})(\text{bpy})(\text{NO}_3)]_n$ (**1**) and $[\text{Pb}_4\text{O}_2(\text{Fba})_4]_n$ (**2**). The 3-fluorobenzoate (Fba) results from the *in situ* decarboxylation of H_2Fpht . Complex **1** shows a Pb- NO_3 -Pb double helical chain structure, which consists of $[\text{PbO}_6\text{N}_2]$ square antiprism polyhedra by tetradentate nitrate bridge. The Fba and bpy as chelating ligands bond to Pb(II) ions. Complex **2** possesses a Pb-OH-Pb chain structure involving tetrahedron $[\text{Pb}_4(\mu_4\text{-OH})_4]^{4+}$ units with four crystallographically independent Pb(II) polyhedral: Pb(1) O_6 , Pb(2) O_6 , Pb(3) O_5 and Pb(4) O_5 . Moreover, hydrogen bonds between infinite chains lead to the formation of interesting 3D supramolecular architectures of **1** and **2**. Fluorescence of complexes **1** and **2** were recorded at room temperature. The two complexes exhibit emission from the ligands. Interestingly, complex **2** can selectively sense to nitrobenzene via a fluorescence quenching mechanism. CCDC: 1055033, **1**; 1055034, **2**.

Keywords: lead complex; 3-fluorophthalic acid; crystal structure; fluorescence

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0 Introduction

Metal-organic frameworks (MOFs) have become one of particularly popular subjects, which is attributed to their intriguing diversity of the structures and potential applications in magnetism, gas adsorption, catalysis, luminescence and so on^[1-6]. The differences of MOFs lie in different properties of metal ions and diverse chemical structure of the ligands. Furthermore, the MOFs self-assembly process can be influenced by solvent system, pH value, reaction temperature and concentration. A variety of MOFs have been constructed by careful selection of the metal ions and multidentate bridging ligands^[7-8]. As a heavy *p*-block metal ion, Pb(II) exhibits unique coordination preferences, such as large ionic radius, flexible coordination environment, variable coordination numbers ranging from 2 to 10^[9-17]. This presents unique opportunities for the assembly and synthesis of Pb(II) complexes with interesting structures and physicochemical properties, such as luminescence, photovoltaic conversion and fluorescence sensing. Hence, there is a great significance in exploring new Pb(II) coordination polymers for their novel structures and fluorescence sensing. However, the recognition and sensing of small organic molecules have important roles in biological and environmental systems^[3,18-20]. Up to now, the aromatic carboxylates have been widely used to construct MOFs because of their excellent coordinating ability, π -conjugated system and a variety of coordination modes^[5,7-8]. However, fluorinated organic ligands may impart a variety of functional properties, such as higher gas affinity and excellent photoluminescence properties^[17,21-24]. 3-Fluorophthalic acid (H_2Fpht) has an interesting conformation: (1) its two carboxylate groups on the aromatic rings are 1,2-positions; (2) the F atom has the electron-withdrawing nature and the electrostatic repulsion between the F atom and the carboxylate oxygen atom. So, H_2Fpht is a good candidate for construction of MOFs with intriguing structural features and properties^[17,21-22].

More recently, we have reported two Pb(II) complexes, $[Pb_2(Fpht)_2(bpy)(H_2O)_2] \cdot 2H_2O$ and $Pb_5(Fpht)$

$_4(Fba)_2$, which derived from H_2Fpht in the presence and absence of 2,2'-bipyridine (bpy) by hydrothermal reaction at 160 °C^[17]. They show interesting structures and photoluminescence. Herein, to further investigate the Pb(II) chemistry with H_2Fpht ligand, hydrothermal reactions of $Pb(NO_3)_2$ and H_2Fpht in the presence of bpy were studied. Interestingly, two new 1D coordination polymers, $[Pb(Fba)(bpy)(NO_3)]_n$ (**1**) and $[Pb_4O_2(Fba)_4]_n$ (**2**) were obtained at 170 °C and 180 °C, respectively. The 3-fluorobenzoate (Fba) results from the *in situ* decarboxylation of H_2Fpht . Herein we report the synthesis and structural characterization of the two complexes obtained from the *in situ* reaction under hydrothermal conditions at different temperatures, and their luminescence property will also be described. Notably, the two complexes exhibit similar fluorescence property, and the fluorescence can be quenched greatly by nitrobenzene, demonstrating its sensing capacity.

1 Experimental

1.1 Materials and physical measurement

All reagents were commercially available and used without purification. Elemental analyses (C, H, and N) were performed on an Elementar Vario EL analyzer. Infrared (IR) spectra were measured on a Bruker Tensor 37 spectrophotometer using KBr pellets from 400 to 4 000 cm^{-1} . Fluorescence spectra were recorded on an FL4500 fluorescence spectrophotometer (Japan Hitachi company) at room temperature. Thermogravimetric analyses (TGA) were carried out using a HCT-2 thermal analyzer under air from room temperature to 800 °C with a heating rate of 10 °C \cdot min⁻¹.

1.2 Syntheses of complexes 1 and 2

Preparation of $[Pb(Fba)(bpy)(NO_3)]_n$ (**1**). A mixture of $Pb(NO_3)_2$ (0.2 mmol), H_2Fpht (0.2 mmol), H_2O (10 mL), bpy (0.1 mmol) and an aqueous solution of NaOH (2 mol \cdot L⁻¹, 0.15 mL) was sealed in a Teflon-lined reactor and heated at 170 °C for 3 days. After slow cooling to room temperature, colorless block crystals of the complex were obtained. Yield: 43% (based on Pb). Elemental analysis Calcd. for $C_{17}H_{12}FN_3O_5Pb$ (%): C, 36.14; N, 7.44; H, 2.12; Found (%): C, 35.64; N,

7.09; H, 2.08. IR(KBr pellet, cm^{-1}): 3 435(s), 1 552(vs), 1 529(vs), 1 468(m), 1 384(vs), 1 243(w), 1 156(w), 1 062(w), 1 014(w), 844(s), 765(s), 734(m), 698(w), 644(w), 573(w), 466 (m).

Preparation of $[\text{Pb}_4\text{O}_2(\text{Fba})_4]_n$ (**2**). Complex **2** was prepared as described for **1** except that the temperature was 180 °C. Colorless block crystals. Yield: 43% (based on Pb). Elemental analysis Calcd. for $\text{C}_{28}\text{H}_{16}\text{F}_4\text{O}_{10}\text{Pb}_4$ (%): C, 23.71; H, 1.13; Found (%): C, 23.48; H, 1.07. IR(KBr pellet, cm^{-1}): 3 433(m), 1 543(vs), 1 473(m), 1 387(vs), 1 266(w), 1 155(w), 1 096(w), 1 008(w), 851(s), 766(s), 691(w), 669(w), 575(w), 465 (m), 432(w).

1.3 X-ray crystal structure determination

The X-ray single-crystal data collections for **1** and **2** were performed on a Bruker Smart Apex II CCD diffractometer equipped with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at 293(2) K. Semiempirical absorption correction was applied on

the complex using SADABS program^[25]. The structure was solved by direct methods and refined by full matrix least squares on F^2 using SHELXS 97 and SHELXL 97^[26-27]. All non-hydrogen atoms in the complexes were refined an isotropically. Hydrogens were generated geometrically and treated by a mixture of independent and constrained refinement. A summary of the crystallographic data and details of the structure refinements are listed in Table 1. Selected bond distances and angles are listed in Table 2.

CCDC: 1055033, **1**; 1055034, **2**.

2 Results and discussion

2.1 Synthesis

The hydrothermal reactions have generated great attention in the past decade because the hydrothermal synthesis can result in the generation of novel coordination compounds, exhibiting structural diversity

Table 1 Crystallographic data and structure refinement of complexes 1~2

	1	2
Empirical formula	$\text{C}_{17}\text{H}_{12}\text{FN}_3\text{O}_3\text{Pb}$	$\text{C}_{28}\text{H}_{16}\text{O}_{10}\text{F}_4\text{Pb}_4$
Formula weight	564.49	1 417.21
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Fdd2$
a / nm	0.655 54(5)	3.714 11(11)
b / nm	0.836 39(6)	3.166 97(10)
c / nm	1.581 88(11)	1.095 48(3)
$\alpha / (^\circ)$	84.626(1)	
$\beta / (^\circ)$	84.651(1)	
$\gamma / (^\circ)$	83.486(1)	
V / nm^3	0.854 9(4)	12.88 56(7)
Z	2	16
$D_c / (\text{Mg}\cdot\text{m}^{-3})$	2.193	2.922
Absorption coefficient / mm^{-1}	9.913	20.918
$F(000)$	532	10 048
Crystal size / mm	0.20×0.11×0.05	0.25×0.18×0.20
θ range for data collection / $(^\circ)$	2.46~25.00	2.56~25.02
Limiting indices	$-7 \leq h \leq 7; -9 \leq k \leq 9; -13 \leq l \leq 18$	$-44 \leq h \leq 40; -34 \leq k \leq 37; -13 \leq l \leq 13$
Reflections collected, unique (R_{int})	4 192, 2 987 (0.025 9)	19 532, 5 603 (0.063 1)
Data, restraints, parameters	2 987, 0, 244	5 603, 1, 416
Goodness-of-fit on F^2	1.025	1.179
Final R indices ($I > 2\sigma(I)$)	$R_1=0.028\ 0, wR_2=0.061\ 8$	$R_1=0.071\ 4, wR_2=0.161\ 6$
R indices (all data)	$R_1=0.031\ 2, wR_2=0.063\ 0$	$R_1=0.079\ 7, wR_2=0.166\ 2$
Largest diff. peak and hole / $(\text{e}\cdot\text{nm}^{-3})$	1 348 and $-1\ 035$	2 709 and $-2\ 828$

Table 2 Selected bond distances (nm) and angles ($^{\circ}$) of complexes **1**~**2**

1					
Pb(1)-O(1)	0.244 8(4)	Pb(1)-O(2)	0.263 0(4)	Pb(1)-O(3)A	0.290 3(5)
Pb(1)-O(3)B	0.287 8(4)	Pb(1)-O(4)B	0.280 7(5)	Pb(1)-O(5)	0.288 2(6)
Pb(1)-N(2)	0.241 9(5)	Pb(1)-N(1)	0.246 1(5)		
O(1)-Pb(1)-O(2)	51.56(12)	N(2)-Pb(1)-N(1)	66.47(15)	O(5)-Pb(1)-O(3)A	124.35(10)
O(3)B-Pb(1)-O(4)B	44.67(4)				
2					
Pb(1)-O(1)	0.247 2(6)	Pb(1)-O(4)	0.255 7(3)	Pb(1)-O(6)A	0.296 0(3)
Pb(1)-O(7)	0.256 9(4)	Pb(1)-O(9)	0.232 3(2)	Pb(1)-O(10)	0.229 1(5)
Pb(2)-O(2)	0.262 6(2)	Pb(2)-O(3)B	0.284 2(3)	Pb(2)-O(5)	0.252 8(4)
Pb(2)-O(8)A	0.253 1(3)	Pb(2)-O(9)	0.220 9(2)	Pb(2)-O(10)	0.231 0(3)
Pb(3)-O(3)	0.249 4(3)	Pb(3)-O(5)	0.272 7(3)	Pb(3)-O(8)A	0.281 6(4)
Pb(3)-O(9)	0.229 6(4)	Pb(3)-O(10)A	0.235 6(4)	Pb(4)-O(6)	0.242 1(2)
Pb(4)-O(7)	0.291 8(4)	Pb(4)-O(8)	0.260 9(4)	Pb(4)-O(9)B	0.236 6(2)
Pb(4)-O(10)	0.222 5(3)				
O(1)-Pb(1)-O(4)	157.5(11)	O(1)-Pb(1)-O(7)	96.4(13)	O(1)-Pb(1)-O(9)	9.40(10)
O(1)-Pb(1)-O(10)	76.8(11)	O(1)-Pb(1)-O(6)A	78.9(5)	O(4)-Pb(1)-O(6)A	119.7(9)
O(4)-Pb(1)-O(7)	74.0(12)	O(4)-Pb(1)-O(9)	81.8(10)	O(4)-Pb(1)-O(10)	80.8(11)
O(6)A-Pb(1)-O(7)	148.5(9)	O(6)A-Pb(1)-O(10)	137.0(2)	O(6)A-Pb(1)-O(9)	71.5(4)
O(7)-Pb(1)-O(9)	139.9(12)	O(7)-Pb(1)-O(10)	69.7(12)	O(10)-Pb(1)-O(9)	75.3(10)
O(2)-Pb(2)-O(3)B	73.4(2)	O(2)-Pb(2)-O(5)	150.8(10)	O(2)-Pb(2)-O(8)A	85.2(1)
O(2)-Pb(2)-O(9)	74.0(9)	O(2)-Pb(2)-O(10)	92.6(10)	O(3)B-Pb(2)-O(5)	133.1(9)
O(3)B-Pb(2)-O(8)A	144.1(3)	O(3)B-Pb(2)-O(9)	135.2(2)	O(3)B-Pb(2)-O(10)	74.6(3)
O(5)-Pb(2)-O(8)A	76.2(8)	O(5)-Pb(2)-O(9)	77.2(10)	O(5)-Pb(2)-O(10)	85.5(11)
O(8)A-Pb(2)-O(9)	60.1(1)	O(8)A-Pb(2)-O(10)	136.1(0)	O(10)-Pb(2)-O(9)	77.1(10)
O(3)-Pb(3)-O(5)	111.5(10)	O(3)-Pb(3)-O(8)A	149.4(0)	O(3)-Pb(3)-O(9)	91.9(10)
O(3)-Pb(3)-O(10)A	81.0(1)	O(5)-Pb(3)-O(8)A	74.5(0)	O(5)-Pb(3)-O(9)	71.9(9)
O(5)-Pb(3)-O(10)A	145.8(10)	O(8)A-Pb(3)-O(9)	60.6(1)	O(8)A-Pb(3)-O(10)A	79.4 (8)
O(9)-Pb(3)-O(10)A	76.1(10)	O(6)-Pb(4)-O(7)	148.6(9)	O(6)-Pb(4)-O(8)	145.0(13)
O(6)-Pb(4)-O(9)B	81.7(10)	O(6)-Pb(4)-O(10)	85.5(11)	O(7)-Pb(4)-O(8)	45.3(5)
O(7)-Pb(4)-O(9)B	96.9(6)	O(7)-Pb(4)-O(10)	63.8(7)	O(8)-Pb(4)-O(9)B	63.2(13)
O(8)-Pb(4)-O(10)	86.7(13)	O(9)B-Pb(4)-O(10)	77.4(10)		

Symmetry codes: A: $-1+x, y, z$; B: $2-x, 1-y, -z$ for **1**; A: $2-x, 1.5-y, -0.5+z$; B: $2-x, 1.5-y, 0.5+z$ for **2**.

and unique properties for potential applications. In our previously reported reaction systems containing $\text{Pb}(\text{NO}_3)_2$ and H_2Fpht in the presence and absence of bpy, we have prepared two complexes, $[\text{Pb}_2(\text{Fpht})_2(\text{bpy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ and $\text{Pb}_5(\text{Fpht})_4(\text{Fba})_2$, by the hydrothermal reactions at $160\text{ }^{\circ}\text{C}$. In absence of secondary ligand bpy, H_2Fpht was partly converted into HFba by the loss of one carboxyl group, and resulted in the formation of $\text{Pb}_5(\text{Fpht})_4(\text{Fba})_2$. In order to further investigate

reaction system of $\text{Pb}(\text{NO}_3)_2\text{-H}_2\text{Fpht}$ in the presence of bpy, we change the hydrothermal reaction to $170\text{ }^{\circ}\text{C}$ and $180\text{ }^{\circ}\text{C}$. Interestingly, two new coordination polymers $[\text{Pb}(\text{Fba})(\text{bpy})(\text{NO}_3)]_n$ (**1**) and $[\text{Pb}_4\text{O}_2(\text{Fba})_4]_n$ (**2**) were obtained. H_2Fpht ligand turned into 3-fluorobenzoate (Fba) by decarboxylation reaction. The result shows that the $\text{Pb}(\text{II})$ complexes containing H_2Fpht depend on the reaction temperature. The TGA curves are unchanged from room temperature to $182\text{ }^{\circ}\text{C}$ for **1** and

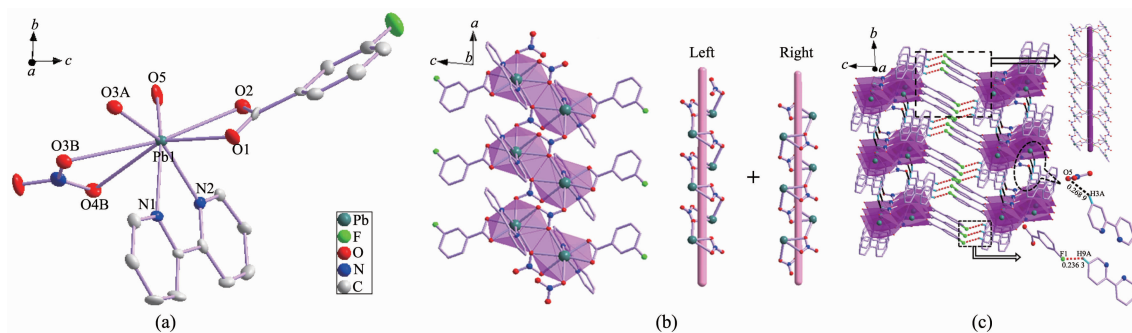
164 °C for **2**, indicating thermal stability. Then, the frameworks begin to decompose until 462 °C for **1** and 449 °C for **2**, corresponding to release of ligands.

2.2 Structural description of **1** and **2**

Structural description of $[\text{Pb}(\text{Fba})(\text{bpy})(\text{NO}_3)]_n$ (**1**). X-ray crystallographic analysis reveals that complex **1** crystallizes in triclinic space group $P\bar{1}$ and has a 1D zigzag chain (Fig.1). The asymmetric unit of **1** contains one Pb(II) ion, one bpy ligand, one Fba ligand, and one NO_3^- group. Central Pb(II) ion is eight-coordinated by two nitrogen atoms (N1 and N2) of bpy, two oxygen atoms (O1 and O2) of Fba, and four oxygen atoms (O3A, O3B, O4B and O5) of three nitrate groups and is in a distorted square antiprism geometry (Fig.1a). The bpy molecule chelates Pb(II) ion forming a five-membered ring with Pb-N bond lengths of 0.241 9(5) and 0.246 1(5) nm. The Fba ligand adopts $\mu^1:\eta^1 \eta^1$ bidentate chelating mode and coordinates Pb(II) ion, in which the bond distances of Pb-O are 0.263 0(4) and 0.244 8(4) nm. The NO_3^- adopts $\mu^3:\eta^1 \eta^1 \eta^2$ coordination mode and acts as a tetradentate ligand to link three different Pb(II) ions, in which the bond distances of Pb-O are 0.280 7(5), 0.287 8(4), 0.288 2(6) and 0.290 3(5) nm. The bond distances of Pb-O (NO_3) are longer than those of Pb-O (Fba). Comparable to the reported literatures, the distances of Pb-N and Pb-O are close to the values in the literature^[9]. The bond angle of N-Pb-N is 66.47 (15)°. The bond angles of O-Pb-O are range from 44.67(4)° to 124.35(2)°. The four atoms of the NO_3^- are almost coplanar with the mean deviations of 0.000 4

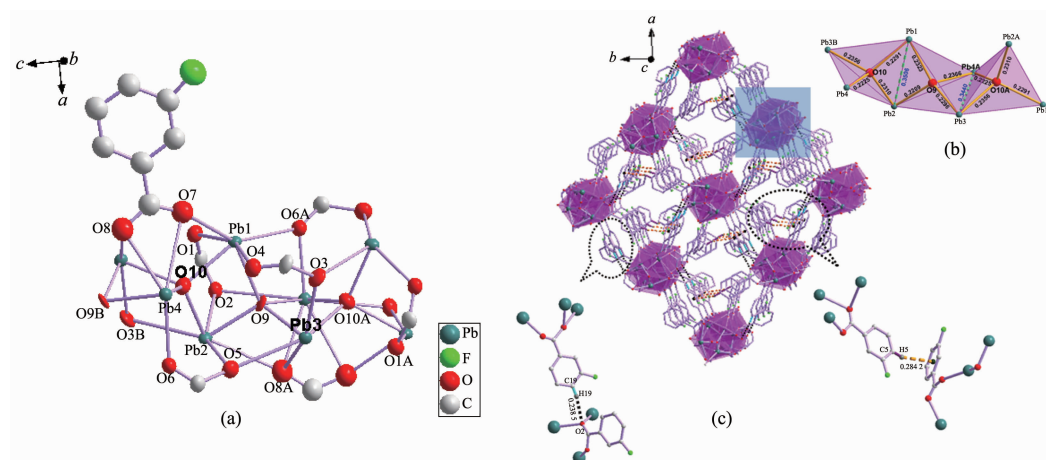
nm. The adjacent Pb(II) ions are connected by NO_3^- groups resulting in a 1D zigzag chain structure. The angle of $\text{Pb}\cdots\text{Pb}\cdots\text{Pb}$ is 75.70(4)° and the distances of $\text{Pb}\cdots\text{Pb}$ are 0.498 3(3) and 0.566 6(2) nm. The bpy and Fba ligands lie at both side of the chain and are almost perpendicular with the dihedral angle of 96.1(3)°, which may decrease steric hindrances of the two chelating ligands around the Pb(II) ion. Interestingly, the $\text{Pb}-\text{NO}_3-\text{Pb}$ chain forms double helical architecture with the screw of pitch being 0.655 5 nm, which has a repeat unit consisting of two Pb(II) centers, two NO_3 groups along a axis (Fig.1b). It is noteworthy that such 1D structure by tetradentate nitrates linking metal centers is rare^[10]. The adjacent chains are connected by $\text{C}-\text{H}\cdots\text{F}$ hydrogen bonds ($d(\text{C}\cdots\text{F})=0.236\ 3(4)$ nm) between bpy and Fba ligands to form the 2D network paralleling the ac plane, which is further extended into a 3D supramolecular assembly by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds ($d(\text{C}\cdots\text{O})=0.268\ 9(3)$ nm) between bpy and NO_3^- ligands (Fig.1c). Interestingly, new helical motifs are observed by using $\text{C}-\text{H}\cdots\text{F}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds as linkers, respectively.

Structural description of $[\text{Pb}_4\text{O}_2(\text{Fba})_4]_n$ (**2**). Complex **2** crystallizes in orthorhombic space group $Fdd2$ and possesses an infinite Pb-OH-Pb chain structure (Fig.2). There are four crystallographically independent Pb(II) ions: Pb1O_6 , Pb2O_6 , Pb3O_5 and Pb4O_5 (Fig. 2a). Pb1 is six-coordinated by four oxygen atoms of Fba ligands and two μ_4 -O atoms. The bond distances of Pb1-O vary from 0.229 1(5) to 0.296 0(3) nm. Pb2



All hydrogen atoms are omitted for clarity in (a); Symmetry codes: A: $-1+x, y, z$; B: $2-x, 1-y, -z$

Fig.1 View of the structure of **1**: (a) Coordination environment of Pb(II) ion with 50% thermal ellipsoids; (b) 1D $\text{Pb}-\text{NO}_3-\text{Pb}$ zigzag chain; (c) 3D network by $\text{C}-\text{H}\cdots\text{F}$ and $\text{C}-\text{H}\cdots\text{O}$ weak interactions



All hydrogen atoms are omitted for clarity in (a); Symmetry codes: A: $2-x, 1.5-y, -0.5+z$; B: $2-x, 1.5-y, 0.5+z$

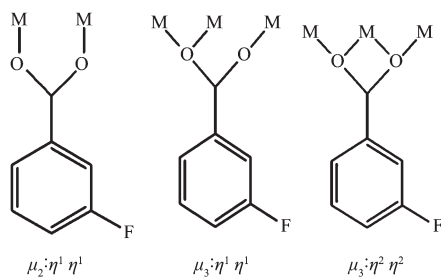
Fig.2 View of the structure of **2**: (a) Coordination environments of Pb(II) ion with 30% thermal ellipsoids; (b) 1D chain structure embracing a tetrahedron-like cluster $[\text{Pb}_4(\mu_4\text{-OH})_4]^{4+}$; (c) 3D network formed via C-H \cdots O and C-H $\cdots\pi$ noncovalent interactions

is six-coordinated by four oxygen atoms of Fba ligands and two $\mu_4\text{-O}$ atoms. The bond distances of Pb2-O vary from 0.220 9(2) to 0.284 2(3) nm. Pb3 is five-coordinated by three oxygen atoms of Fba ligands and two $\mu_4\text{-O}$ atoms. The bond distances of Pb3-O vary from 0.229 6(4) to 0.281 6(4) nm. Pb4 is five-coordinated by three oxygen atoms of Fba ligands and two $\mu_4\text{-O}$ atoms. The bond distances of Pb4-O vary from 0.222 5(3) to 0.291 8(4) nm. Thereinto, the Pb1-O6A, Pb2-O3B, Pb3-O8A and Pb4-O7 bonds are significantly longer and the distances are 0.296 0(3), 0.284 2(3), 0.281 6(4) and 0.291 8(4) nm, respectively. All the distances of Pb-N and Pb-O are close to the values in the literatures^[9]. In **2**, Fba ligands adopt three different coordination modes, $\mu_2:\eta^1\eta^1$, $\mu_3:\eta^1\eta^1$ and $\mu_3:\eta^2\eta^2$ to link two or three different Pb(II) ions (Scheme 1). Each Pb(II) and its three nearest Pb(II) ions are connected together by μ_4 -hydroxyl bridging ligands (O9 or O10), forming a tetrahedron-like cluster $[\text{Pb}_4(\mu_4\text{-}$

$\text{OH})_4]^{4+}$ with the Pb \cdots Pb distances of 0.344 0(3)~0.398 5(3) nm, in which four Pb(II) ions are located at the corner angles of the neighbouring tetrahedron (Fig. 2b). The tetrahedron $[\text{Pb}_4(\mu_4\text{-OH})_4]^{4+}$ unit distorts, in which the Pb-O-Pb angles vary from 95.2(8) $^\circ$ to 123.0(1) $^\circ$. The tetrahedron $[\text{Pb}_4(\mu_4\text{-OH})_4]^{4+}$ units further extended into a Pb-OH-Pb chain structure, in which the octanuclear Pb(II) clusters act as secondary building blocks (SBUs). The 1D chain motifs are further connected into 3D supramolecular network by C-H \cdots O and C-H $\cdots\pi$ noncovalent interactions (Fig.2c). The C-H \cdots O hydrogen bond formed between C-H of Fba and carboxylate oxygen atom of Fba with the C \cdots O distance of 0.330 1(3) nm. The C-H $\cdots\pi$ interaction exists between adjacent Fba ligands with the distance of 0.284 2(4) nm.

2.3 Photoluminescence properties

Luminescence properties of MOFs are very important because of their potential applications in photochemistry, chemical sensors, and electroluminescent displays. Solid-state photoluminescence spectra of complexes **1~2** and ligands were recorded at room temperature (Fig.3). The free ligands display emission bands at 432 nm with a shoulder at 455 nm for H₂Fpht (λ_{ex} =377 nm) and at 432 nm with a shoulder at 453 nm for bpy (λ_{ex} =377 nm). The emission of the free ligands is attributable to the $\pi^*\text{-}\pi$ transitions.



Scheme 1 Coordination modes of Fba in **2**

The emission bands of complexes **1**~**2** occur at 431 nm with a shoulder of 456 nm for **1** ($\lambda_{\text{ex}}=378$ nm) and at 432 nm with a shoulder of 458 nm for **2** ($\lambda_{\text{ex}}=332$ nm). The two complexes exhibit the emission maxima (centered at 431 nm for **1** and 432 nm for **2**) similar to that of the free ligands and we assume that the emissions of **1**~**2** come from the ligands. To investigate the influence of different solvent molecules on the luminescent intensities, complex **2** was immersed in dimethyl formamide (DMF), methanol, triethylamine, acetonitrile and nitrobenzene(NB) to form the suspensions. The luminescence intensity of the suspensions depends on the nature of solvent molecules (Fig.4). It was found that the locations of the maximum emissions for all of the samples have the minor shifts, compared with that of compound **2** in the solid state. This may be caused by the solvent effect. Significant quenching of fluorescence intensity of **2** was observed

in the case of nitrobenzene, which almost disappeared, providing room for selective sensing. The mechanism of fluorescence sensing can be attributed to the photoinduced electron transfer from complex **2** to the electron-withdrawing nitrobenzene through interspecies contacts^[18-20]. The solvent-dependent luminescent properties are of interest for the sensing of NB, which is very harmful to human beings as a pollution molecule. Therefore, we provide promising MOF-based sensor for selective detection of nitrobenzene.

3 Conclusions

Temperature-dependent hydrothermal synthetic reactions of Pb(II) salts with H₂Fpht in the presence and absence of bpy afforded four different metal-organic framework species, namely two reported complexes [Pb₂(Fpht)₂(bpy)(H₂O)₂]·2H₂O and Pb₅(Fpht)₄(Fba)₂^[17] and two title complexes [Pb(Fba)(bpy)(NO₃)₃]_n (**1**) and [Pb₄O₂(Fba)₄]_n (**2**). Complexes **1** and **2** obtained from the in situ Pb(II)/H₂Fpht reaction under hydrothermal conditions at different temperatures. Fba ligand exhibits versatile coordination modes: $\mu_1:\eta^1 \eta^1$ in **1** and $\mu_2:\eta^1 \eta^1$, $\mu_3:\eta^1 \eta^1$ and $\mu_3:\eta^2 \eta^2$ in **2**. Pb(II) ions have different coordination numbers of 8 in **1** and 5, 6 in **2**. Complex **1** has a 1D chain architecture by tetradentate nitrates as connectors while complex **2** is constructed from μ_4 -OH bridged octanuclear Pb(II) clusters as SBUs. Notably, the solvent-dependent luminescence behavior of Pb(II) complex **2** was discussed. The selective sensing nitrobenzene might lead to its application in environmental system.

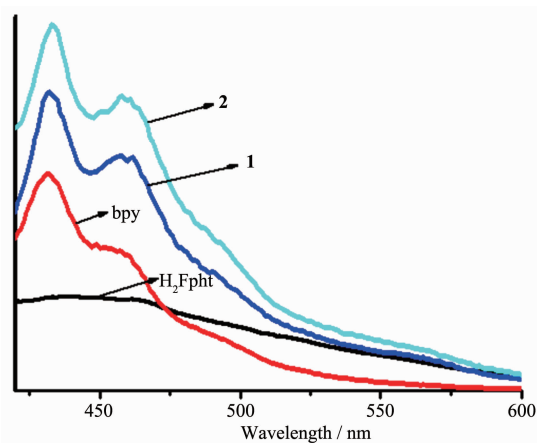


Fig.3 Emission spectra of complexes **1**~**2** and free ligands in the solid state

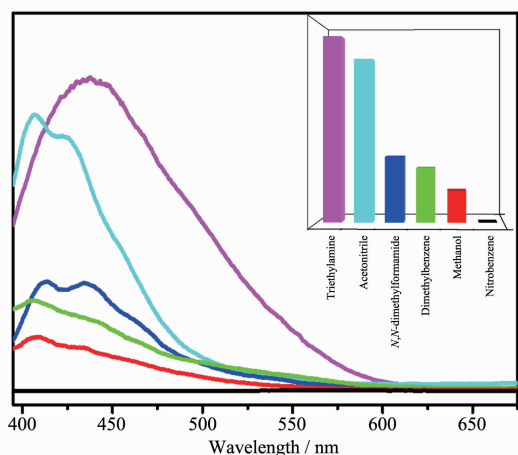


Fig.4 Emission spectra of **2** dispersed in different solvent

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