

基于 1,10-邻菲罗啉-5,6-二酮和 Keggin 型多金属氧化物的 化合物的水热合成及性质

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摘要: 在水热条件下, 用 1,10-邻菲罗啉-5,6-二酮(Do)作为中性配体合成了 3 个基于 Keggin 型多金属氧化物的化合物(HDo)₆(PW₁₂O₄₀)₂·H₂O(**1**), [Cu(Do)₂(H₂O)]₂[Cu(Do)₂(PW₁₂O₄₀)(H₂O)](PW₁₂O₄₀)(**2**)和[Pb(Do)₂(PW₁₂O₄₀)](HDo)(**3**), 并对其进行了元素分析、红外光谱、电感耦合等离子体分析、X 射线光电子能谱、热重分析以及荧光光谱等表征。单晶 X 射线衍射分析表明化合物 **1** 和 **2** 为零维结构, 化合物 **3** 是一维链状结构。

关键词: 1,10-邻菲罗啉-5,6-二酮; Keggin 型多金属氧化物; 水热; 晶体结构

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Hydrothermal Syntheses and Properties of Compounds Based on 1,10-Phenanthroline-5,6-dione and Keggin-Type Polyoxometalate

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Abstract: Three compounds based on Keggin-type polyoxometalate (POMs) using 1,10-phen-5,6-dione (Do) as neutral organic ligand, namely, (HDo)₆(PW₁₂O₄₀)₂·H₂O (**1**), [Cu(Do)₂(H₂O)]₂[Cu(Do)₂(PW₁₂O₄₀)(H₂O)](PW₁₂O₄₀)(**2**) and [Pb(Do)₂(PW₁₂O₄₀)](HDo)(**3**), have been synthesized under hydrothermal conditions and characterized by elemental analyses, infrared spectra, inductively coupled plasma analyses, X-ray photoelectron spectroscopy and single-crystal X-ray diffraction. Compounds **1** and **2** are zero-dimensional structures, and compound **3** exhibits one-dimensional chain. The thermal stabilities and photoluminescent properties of three compounds have also been investigated. CCDC: 767622, **1**; 767623, **2**; 767619, **3**.

Key words: 1,10-phenanthroline-5,6-dione; kegginn-type polyoxometalate; hydrothermal; crystal structure

Much effort has been devoted to metal-organic frameworks (MOFs) due to their potential applications in chemical-biology, polyacid nano materials, catalysis, pharmaceutical chemistry and functional applications^[1]. The structure of the resultant framework is mainly influenced by various factors, such as the

ligands, anions, templates, geometric requirements of metal atoms, and so on. Among them, ligand plays an important role in the construction of MOFs with distinctive structures. The derivatives of 1,10-phenanthroline (phen) are one kind of important ligands to form novel supermolecular structures.

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Numerous 1D, 2D and 3D frameworks with derivatives of phen have been reported [2-5]. Among these derivatives, although 1,10-phenanthroline-5,6-dione (Do) could donate both N atoms and O atoms in the self-assembly of complexes, the reports about complexes with Do are still rare [6]. On the other hand, the research based on polyoxometalates (POMs) clusters, especially the α -Keggin-type polyoxometalate, has attracted a lot of interests due to their extensive applications in catalysis, photochemistry, electrochemistry, magnetism, and biochemistry[1,7].

Under these considerations, we selected Keggin-type polyoxometalate α -H₃(PW₁₂O₄₀) and Do as organic ligand for producing complexes to find out the constructing possibilities and optimum conditions. Herein, a series of compounds, namely, (HDo)₆(PW₁₂O₄₀)₂·H₂O (**1**), [Cu(Do)₂(H₂O)]₂[Cu(Do)₂(PW₁₂O₄₀)(H₂O)](PW₁₂O₄₀) (**2**) and [Pb(Do)₂(PW₁₂O₄₀)](HDo) (**3**) were hydrothermally synthesized. Their crystal structures, thermal stabilities and photoluminescent properties are reported in this article.

1 Experimental

1.1 General

The ligand Do was synthesized according to the literature [8] and all other materials were purchased from commercial sources without further purification. Elemental analysis (C, H and N) were performed on a Perkin-Elmer 2400 CHSN elemental analyzer. ICP was done on a Perkin-Elmer Optima 3300 DV spectrometer. The IR spectra were obtained on an Alpha Centaur FT/IR spectrometer with KBr pellets in the range of 4 000~400 cm⁻¹ region. XPS analyses were performed on a VGESCALABMK spectrometer with an Mo K α (1 253.6 eV) achromatic X-ray source. Thermogravimetric Analyses (TGA) were carried out under N₂ condition on a NETZSCH STA 449C analyzer in owing N₂ with a heating rate of 5 °C·min⁻¹. The solid-state luminescent spectroscopy was performed on a Perkin-Elmer LS55 spectrometer.

1.2 Syntheses and crystal growth

(HDo)₆(PW₁₂O₄₀)₂·H₂O (**1**): The starting materials

α -H₃[PW₁₂O₄₀] (0.05 mmol, 1 444 mg), Do (0.1 mmol, 20 mg) and distilled water (12 mL) were mixed. The resulting suspension was stirred for 1 h and the suspension was sealed in the 25 mL Telfon-lined reactor and heated to 150 °C for 4 d. Orange block crystals were obtained after cooling to room temperature with a yield of about 59% based on W. Anal. Calcd. for C₇₂H₄₄N₁₂O₉₃P₂W₂₄ (%): C, 12.29; H, 0.63; N, 2.39; P, 0.88; W, 62.68. Found (%): C, 12.10; H, 0.69; N, 2.22; P, 0.91; W, 62.58. IR spectrum (KBr cm⁻¹): 3 489 (s), 3 093 (w), 1 693(s), 1 620 (m), 1 574 (s), 1 471 (s), 1 300 (s), 1 261(m), 1 211(m), 1 124(m), 1 080(s), 978(s), 895(s), 816(s), 731(s), 596(w), 521(s).

[Cu(Do)₂(H₂O)]₂[Cu(Do)₂(PW₁₂O₄₀)(H₂O)](PW₁₂O₄₀) (**2**): The synthesis of **2** was similar to compound **1**, but the metal salt was Cu(NO₃)₂ and α -H₃[PW₁₂O₄₀] was changed to 0.075 mmol. And other reaction conditions were the same as compound **1**. Green block crystals were filtered and yield 68% based on W. Anal. Calcd. for Cu₃C₇₂H₄₂N₁₂O₉₅P₂W₂₄ (%): Cu, 2.63; C, 11.91; H, 0.58; N, 2.32; P, 0.85; W, 60.77. Found (%): Cu, 2.59; C, 12.10; H, 0.59; N, 2.12; P, 0.85; W, 60.01. IR spectrum (KBr cm⁻¹): 3 481(m), 3 107(w), 1 691(s), 1 614 (m), 1 572 (s), 1 527 (m), 1 470 (s), 1 423(s), 1 298 (s), 1 254 (s), 1 205 (m), 1 120 (m), 1 082(s), 1 020(m), 982(s), 895(s), 804(s), 596(w), 517(s).

[Pb(Do)₂(PW₁₂O₄₀)](HDo) (**3**): Compound **3** was prepared in a manner similar to that described for compound **2**, except the Pb(NO₃)₂ replaced the Cu(NO₃)₂ and the synthesis temperature was 160 °C. Yellow block crystals were filtered and yield 72% based on W. Anal. Calcd. for PbC₃₆H₁₉N₆O₄₆PW₁₂ (%): Pb, 5.58; C, 11.64; H, 0.52; N, 2.26; P, 0.83; W, 59.37. Found (%): Pb, 5.60; C, 11.60; H, 0.55; N, 2.21; P, 0.80; W, 58.99. IR spectrum (KBr cm⁻¹): 3 417(w), 3 244(w), 3089(w), 1 699(s), 1 581(s), 1 527 (s), 1 433(s), 1 377(m), 1 294(s), 1 252(s), 1 078(s), 978(s), 893(s), 810(s), 596(m), 523(s).

1.3 X-ray structure determination

Crystallographic data of compounds **1**~**3** were collected at room temperature on a Rigaku RAXIS-RAPID single crystal diffractometer equipped with a

narrow-focus, 5.4 kW sealed tube X-ray source (graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.071\ 073\ \text{nm}$) by using an ω - 2θ scan mode at 293 (2) K. The structures of these compounds were solved by the direct method of SHELXS-97^[9] and refined with full-matrix least-squares techniques using the SHELXL-97^[10] program. All the nonhydrogen atoms were refined

anisotropically and the hydrogen atoms were calculated theoretically. In compounds **1** and **2**, the hydrogen atoms attached to water molecules could not be positioned reliably. The detailed crystallographic data and structure refinement parameters for compounds **1**~**3** are summarized in Table 1.

CCDC: 767622, **1**; 767623, **2**; 767619, **3**.

Table 1 Crystal data and structure refinements for compounds 1~3

Compound	1	2	3
Empirical formula	C ₇₂ H ₄₄ N ₁₂ O ₉₃ P ₂ W ₂₄	Cu ₃ C ₇₂ H ₄₂ N ₁₂ O ₉₃ P ₂ W ₂₄	PbC ₃₆ H ₁₉ N ₆ O ₄₆ PW ₁₂
Formula weight	7041.53	7 260.14	3 715.67
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1$	Cc
a / nm	1.344 68(9)	1.182 1(2)	2.193 3(4)
b / nm	1.898 85(12)	2.375 7(5)	1.503 9(3)
c / nm	2.545 94(16)	2.292 7(5)	2.045 2(4)
$\alpha / (^\circ)$	81.444(1)	90	90
$\beta / (^\circ)$	75.598(1)	96.38(3)	118.90(3)
$\gamma / (^\circ)$	69.707(1)	90	90
V / nm^3	5.863 6(7)	6.398(2)	5.906(2)
Z	2	2	4
$D_c / (\text{g}\cdot\text{cm}^{-3})$	3.987	3.768	4.179
μ / mm^{-1}	23.580	22.097	26.248
Reflns collected / unique	32 355/22 826	58 373/28 215	14 058/8 613
$F(000)$	6 220	6 422	6 517
$R_1 / wR_2(I > 2\sigma(I))$	0.053 6/0.132 4	0.052 3/0.096 3	0.035 3/0.056 4
R_1 / wR_2 (all data)	0.070 1/0.142 9	0.085 0/0.108 8	0.040 3/0.061 5
GOF (F^2)	1.036	1.031	1.052

2 Results and discussion

2.1 Description of crystal structures

2.1.1 Structural description of 1

Single-crystal X-ray diffraction analysis reveals that there are six organic ligands HDo⁺ and two (PW₁₂O₄₀)³⁻ ions in the asymmetric unit of **1** (Fig.1a). In this compound, there are one uncoordinated water molecule (OW) per asymmetric unit which serves as hydrogen bonding interaction acceptor and interacts with the N atom from the Do ligand (N4-H4...OW). There are four types of hydrogen bonding interactions between Do ligands (N2-H2A...O90^{#1}, N6-H6...O84, N7-H7...O91, N9-H9A...O81^{#2}, symmetry code: #1 –

$x+2, -y+1, -z+1$; #2 $-x+3, -y+1, -z+1$) (Table 2). Among these hydrogen bonds, N2-H2A...O90^{#1} and N9-H9A...O81^{#2} further consolidate the structure of **1**, leading to a 1D supermolecular structure (Fig.1b).

2.1.2 Structural description of 2

Single-crystal X-ray diffraction analysis shows that compound **2** consists of three Cu²⁺ ions, six Do ligands, three water molecules and two (PW₁₂O₄₀)³⁻ ions (Fig.2). In **2**, there are three crystallographically independent Cu²⁺ (Cu1, Cu2 and Cu3). Cu1 is six-coordinated by four N atoms (0.202 5(11) nm for Cu1-N1, 0.202 6 (9) nm for Cu1-N2, 0.226 4 (10) nm for Cu1-N3, 0.2034 (9) nm for Cu1-N4) and two O atoms (0.2007(11) nm for Cu1-O1W, 0.2411(8) nm for Cu1-

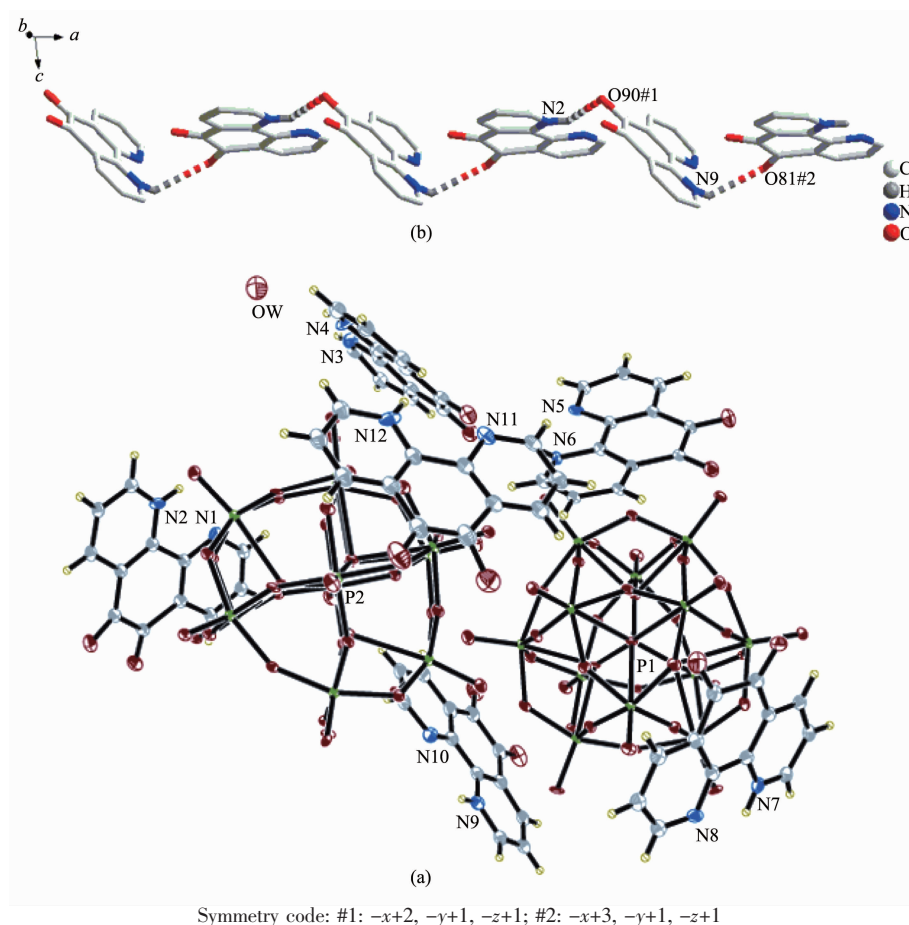


Fig.1 (a) ORTEP view of **1**, showing 30% probability displacement ellipsoids; (b) 1D chain structure built of the hydrogen bonds along *a* axis

Table 2 Hydrogen bond distances (nm) and angles ($^{\circ}$) for **1**

D-H \cdots A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^{\circ})$
N4-H4 \cdots O1W	0.086	0.229	0.3026(15)	143.2
N2-H2A \cdots O90 ^{#1}	0.086	0.263	0.3182(14)	123.1
N6-H6 \cdots O84	0.086	0.253	0.2987(11)	114.0
N7-H7 \cdots O91 ^{#3}	0.086	0.228	0.2968(13)	136.6
N9-H9A \cdots O81 ^{#2}	0.086	0.254	0.3007(10)	114.8

Symmetry codes: #1: $-x+2, -y+1, -z+1$; #2: $-x+3, -y+1, -z+1$; #3: $-x+2, -y+1, -z+2$

O6]. Then Cu2 is five-coordinated by four N atoms (0.1979(9) nm for Cu2-N5, 0.2058(11) nm for Cu2-N6, 0.1993(9) nm for Cu2-N7, 0.2177(9) nm for Cu2-N8) and one O atom (0.2045 (10) nm for Cu2-O2W). The coordination sites of Cu3 are also five (0.2004(11) nm for Cu3-O3W, 0.2042(10) for Cu3-N9, 0.2078(10) nm for Cu3-N10, 0.1968(12) nm for Cu3-N11 and 0.1960 (11) nm for Cu3-N12). All the bond distances are in the range of other similar organic-inorganic compounds^[11].

2.1.3 Structural description of **3**

Compound **3** consists of one Pb^{2+} ion, one $(\text{PW}_{12}\text{O}_{40})^{3-}$ ion and three Do ligands in which one protonated HDo^{+} ligand is free in this structure. As shown in Fig.3a, the central metal bivalence Pb are six-coordinated by two O atoms (0.282 3 (5) nm for Pb-O5 and 0.273 9 (6) nm for Pb-O36) from two $(\text{PW}_{12}\text{O}_{40})^{3-}$ ion and four N atoms from the two Do ligands (0.258 4(8) nm for Pb-N1, 0.251 3(9) nm for Pb-N2, 0.243 9 (7) nm for Pb-N3 and 0.257 7 (8) nm

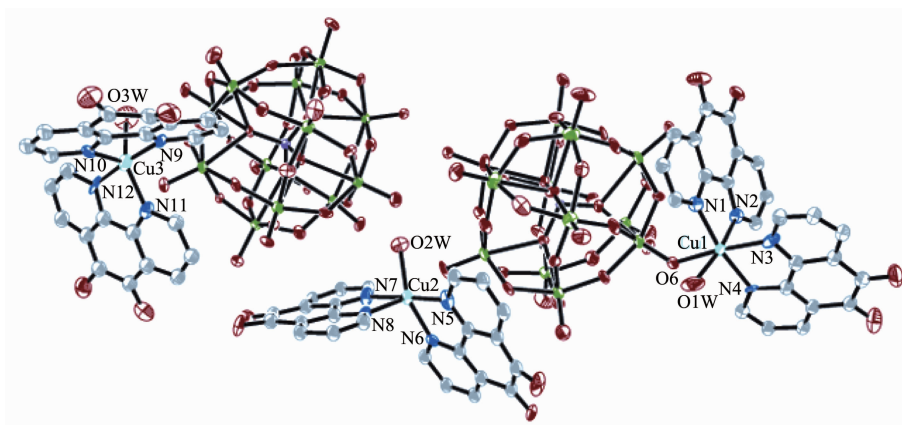


Fig.2 ORTEP plot of the asymmetric unit of **2**, showing 30% probability displacement ellipsoids

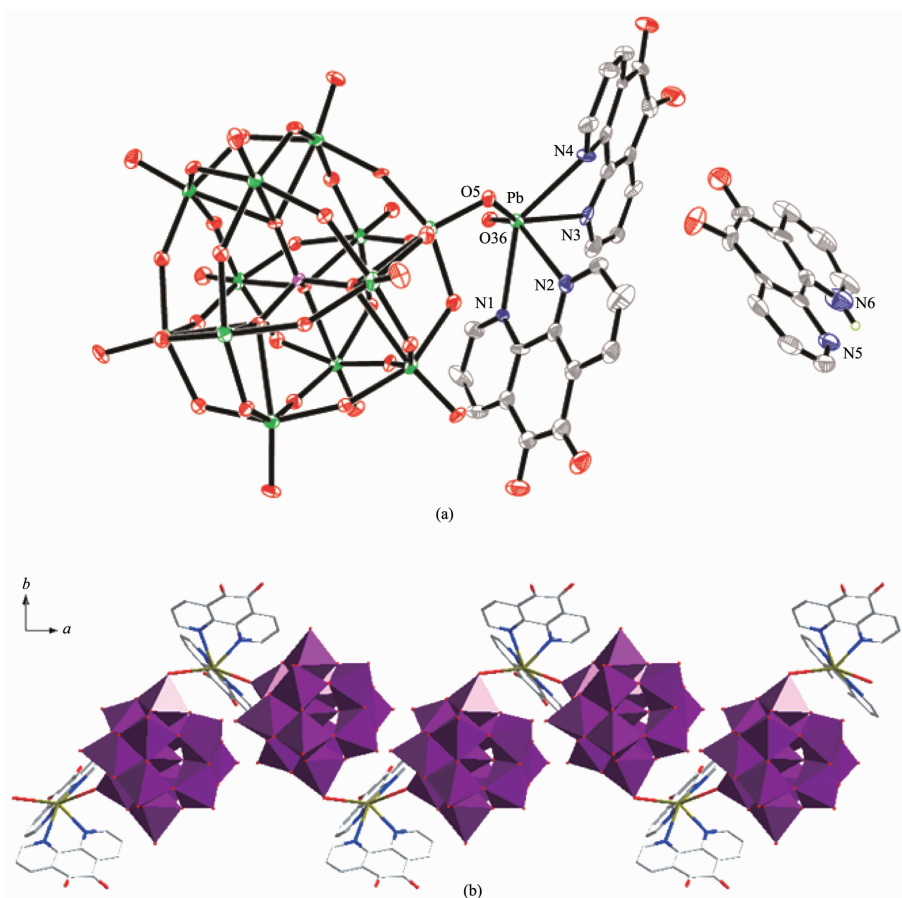


Fig.3 (a) The ORTEP view of compound **3**, showing 30% probability displacement ellipsoids;
(b) 1D twisted Pb-POMs chain along the crystallographic along *a* axis

for Pb-N4), showing a badly distorted octahedral coordinated geometry. The bond distances of Pb-O and Pb-N are within the normal ranges as observed in the other Pb containing compounds [12]. A 1D chain structure is formed by O5 and O36 from POMs (shown in Fig.3b). The neighboring Pb atoms form Z-shaped

chain with Pb...Pb bond distance of 1.360 5 nm.

2.1.4 Effect of reaction conditions on the compounds structures

To investigate the influence of the metallic ion on the structure, any metallic salt was not introduced to the reaction system of **1**. Compound **1** exhibits zero-

dimensional structure in which POMs have not any coordinating O atoms. In contrast with **2** and **3**, the variation of the crystal structures has been observed through selecting metal centers with dissimilar coordination preferences. In despite of the same coordination patterns of Keggin-type POMs (Fig.4), the complex **2** displays zero-dimensional structure and complex **3** shows 1D chain structure. This can presumably be attributed to the metal-controlled assembly and the metal center plays a crucial and steering role in constructing compounds. It should be noted that the reaction temperature is also an important factor in determining the structures of coordination compounds, which is demonstrated by the formation of compounds **2** and **3**.



Fig.4 Coordination patterns of Keggin-type POMs in complexes **2** and **3**

2.2 IR spectra

The IR spectra of compounds **1**~**3** all exhibit characteristic asymmetric vibrations for the α -Keggin structure, namely, P-Oa ($1\,080\text{ cm}^{-1}$ for **1**, $1\,082\text{ cm}^{-1}$ for **2**, $1\,078\text{ cm}^{-1}$ for **3**), W-Ot (978 cm^{-1} for **1**, 982 cm^{-1} for **2**, 978 cm^{-1} for **3**), corner-sharing W-Oc-W (895 cm^{-1} for **1** and **2**, 893 cm^{-1} for **3**), edge-sharing W-Oe-W (816 cm^{-1} for **1**, 804 cm^{-1} for **2**, 810 cm^{-1} for **3**)^[13]. And peaks in the range of $1\,100\sim1\,700\text{ cm}^{-1}$ and wave numbers from $3\,000\sim3\,300\text{ cm}^{-1}$ are indicative of the organic ligands of Do. The peaks about $3\,250\sim3\,740\text{ cm}^{-1}$ are ascribed to the O-H stretching vibration.

2.3 XPS Spectra

In XPS spectra for compounds **1**~**3**. The peaks at

35.73 and 37.12 eV for **1**, 35.20 and 37.10 eV for **2**, 35.65 and 37.79 eV for **3** are attributed to $\text{W}^{6+}(4f_{7/2})$ and $\text{W}^{6+}(4f_{5/2})$ ^[14]. In the XPS spectra of **2**, the similar peaks at about 933.80 and 954.20 eV for **2** are attributed to $\text{Cu}^{2+}(2p_{3/2})$ and $\text{Cu}^{2+}(2p_{1/2})$, respectively^[15]. The peaks at 138.65 and 143.60 eV are attributed to $\text{Pb}^{2+}(4d_{5/2})$ and $\text{Pb}^{2+}(4d_{3/2})$ for **3**^[16]. All these spectra further confirm the valence sum calculations and the structural analyses.

2.4 TGA

In order to characterize more about the compounds, their thermal stabilities were investigated by TGA (Fig. 5). In **1**, a total weight loss of 19.5% is accordant with the calculated value of 18.3% in the range of $40\sim740\text{ }^{\circ}\text{C}$, ascribed to the release of a water molecule and six HDO^{+} ligands. Compound **2** loses water molecules from room temperature to $145\text{ }^{\circ}\text{C}$ about 0.70% (Calcd. 0.74%) firstly, then the 16.9% (Calcd. 17.4%) weight loss attribute to the organic ligand decompose from $399\text{ }^{\circ}\text{C}$. The anhydrous compound **3** only has one step loss of 17.5% (Calcd. 17.0%) from 400 to $747\text{ }^{\circ}\text{C}$ which is ascribed to the loss of organic ligands.

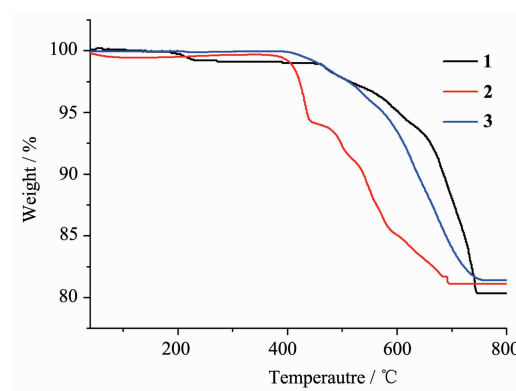


Fig.5 TGA curves of **1**~**3**

2.5 Photoluminescent properties

The luminescent properties of compounds **1**~**3** and free Do ligand are studied in the solid state at room temperature. As shown in Fig.6, very similar wide emission bands (For **1**, $\lambda_{\text{em}}=592\text{ nm}$; **2**, $\lambda_{\text{em}}=596\text{ nm}$) were observed. And then similar wide emission band in compound **3** ($\lambda_{\text{em}}=585\text{ nm}$) were also observed. The free Do ligand possesses the maximum emission at 594 nm. Compared with the PL spectra of **1**~**3** and free ligands, the emission spectra of three

compounds are obviously similar to that of Do, which might be attributable to the intraligand fluorescent emissions of Do^[17]. However, it is not difficult to find that the free counter anion POMs has little influence on the shift of emission bands of Do in compound **1**. Compounds **2** and **3** exhibit red shift of 2 nm and blue shift of 9 nm compared to the emission peak of free ligand Do, respectively. The reason for different emissive peak positions of **2** and **3** was presumably owing to the differences of metal center and coordination mode of complexes.

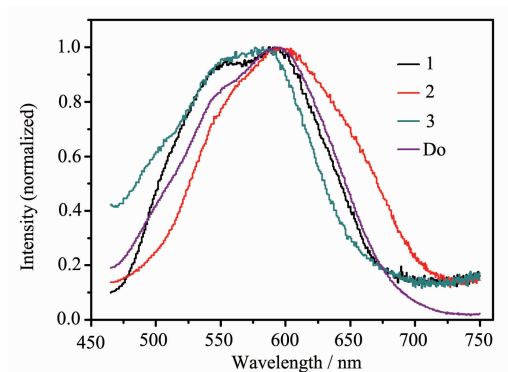


Fig.6 Solid state photoluminescent spectra of Do and **1**~**3**

3 Conclusions

In this work, three new compounds based on Keggin-type POMs and organic ligand Do were achieved under hydrothermal conditions. Compounds **1** and **2** possess zero-dimensional structures, while **3** exhibits one dimensional chain structure. In addition, the N-H...O hydrogen bonding interactions connect the zero-dimensional structures to be one dimensional chains in **1**. Photoluminescent properties of these compounds indicated that they may be employed as candidates for potential solid luminescent materials.

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