

## 两种具有三维孔道结构有机模板稀土硫酸盐的合成、表征及性质研究

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**摘要:** 本文分别采用水热和溶剂热的方法, 以乙二胺和哌嗪为有机模板剂分别合成了两种新的三维孔道结构的稀土硫酸盐  $[\text{Gd}_2(\text{SO}_4)_5(\text{H}_2\text{O})_2][\text{C}_2\text{N}_2\text{H}_{10}]_2$  (**1**),  $[\text{Eu}_2(\text{SO}_4)_5(\text{H}_2\text{O})_2][\text{C}_4\text{N}_2\text{H}_{12}]_2$  (**2**), 并且通过单晶 X 射线衍射、元素分析、红外、热重对两种化合物进行了表征。化合物 **1** 和 **2** 都属于单斜晶系,  $P2_1/c$  空间群。化合物 **1**:  $a=0.652\ 1(4)\ \text{nm}$ ,  $b=1.692\ 0(9)\ \text{nm}$ ,  $c=2.023\ 3(11)\ \text{nm}$ ,  $\beta=95.168(7)^\circ$ ,  $Z=4$ 。化合物 **2**:  $a=1.972\ 1(2)\ \text{nm}$ ,  $b=1.927\ 1(2)\ \text{nm}$ ,  $c=1.323\ 20(14)\ \text{nm}$ ,  $\beta=92.307\ 0(10)^\circ$ ,  $Z=8$ 。单晶结构分析表明, 这两种化合物的无机骨架都是由  $\text{SO}_4$  连接具有交替十六元环与八元环二维层形成的三维孔道结构。化合物 **2** 的固体荧光分析表明, 在 396 nm 的激发波长下表现出  $\text{Eu}^{3+}$  的特有发光性质。

**关键词:** 水热; 溶剂热; 稀土硫酸盐; 三维结构; 荧光性质

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## Synthesis, Structural Characterization and Properties of Two Organic Amine Templated Lanthanide Sulfates with Three Dimensional Channels

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**Abstract:** Employing hydrothermal/solvothermal method and ethylenediamine or piperazine as organic template, two lanthanide sulfates  $[\text{Gd}_2(\text{SO}_4)_5(\text{H}_2\text{O})_2][\text{C}_2\text{N}_2\text{H}_{10}]_2$  (**1**),  $[\text{Eu}_2(\text{SO}_4)_5(\text{H}_2\text{O})_2][\text{C}_4\text{N}_2\text{H}_{12}]_2$  (**2**), with three-dimensional channels have been synthesized and characterized by single-crystal XRD, ICP, IR and TGA. Both of the two compounds crystallize in the monoclinic space group  $P2_1/c$ . Crystal data for **1**,  $a=0.652\ 1(4)\ \text{nm}$ ,  $b=1.692\ 0(9)\ \text{nm}$ ,  $c=2.023\ 3(11)\ \text{nm}$ ,  $\beta=95.168(7)^\circ$ ,  $Z=4$ . For **2**,  $a=1.972\ 1(2)\ \text{nm}$ ,  $b=1.927\ 1(2)\ \text{nm}$ ,  $c=1.323\ 20(14)\ \text{nm}$ ,  $\beta=92.307\ 0(10)^\circ$ ,  $Z=8$ . Crystal structure analysis reveals that both of the inorganic frameworks of compounds **1** and **2** have three-dimensional architectures which are formed by connecting of the two-dimensional layers possessing 8-membered rings and 16-membered rings with  $\text{SO}_4$ . The solid state luminescent properties of compounds **2** were investigated and it displays a typical luminescent property of  $\text{Eu}^{3+}$  with excitation wavelength at 396 nm. CCDC: 874219, **1**; 874220, **2**.

**Key words:** hydrothermal; solvothermal; lanthanide sulfate; three-dimensional structure; luminescent properties

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## 0 Introduction

As the study focus, microporous materials with inorganic open framework have received great attentions because of their widespread applications in catalysis<sup>[1-3]</sup>, ion-exchange<sup>[4-5]</sup>, magnetic properties<sup>[6]</sup> and luminescence properties<sup>[7-8]</sup>. As a building unit, the sulfate tetrahedron can be effectively used to construct new solid state materials with novel structures and interesting properties<sup>[9]</sup>. Compared with other transition metals, the rare-earth elements adopt more flexible coordination numbers, which makes it possible to form novel topological framework. One of the strategies used in the synthesis of solid state materials is to employ a special organic amine as the structure-directing agent (SDA)<sup>[10]</sup>. Recently, rare-earth sulfates with organic amine as the template showing 1D, 2D and 3D structures have been prepared by hydrothermal method<sup>[11-16]</sup>. By employing solvothermal method, some new organically templated lanthanide sulfates have also been prepared<sup>[17-27]</sup>. Even though many lanthanide sulfates have been described in the literatures, the reports of structural information for 3D open frameworks with organic component are comparatively limited.

Due to the excellent luminescence property, europium becomes the important member in the rare-earth elements. Till now, europium sulfates with organic amine showing 3D structure have been less reported<sup>[14-15,28]</sup>. Therefore, it is vital to synthesize europium sulfates in order to explore their potential application in ion exchange and luminescence. In this paper, we present the hydrothermal/solvothermal synthesis and structural investigations of two novel 3D open-framework lanthanide sulfates  $[\text{Gd}_2(\text{SO}_4)_5(\text{H}_2\text{O})_2][\text{C}_2\text{N}_2\text{H}_{10}]_2$  (**1**),  $[\text{Eu}_2(\text{SO}_4)_5(\text{H}_2\text{O})_2][\text{C}_4\text{N}_2\text{H}_{12}]_2$  (**2**).

## 1 Experimental

### 1.1 Reagents and measurements

All chemicals purchased were of reagent grade and used without further purification. The elemental analyses for Ln (Ln=Ga **1**; Eu **2**) were performed on a Zeeman inductively coupled plasma (ICP) spectrometer, while the C, H, and N analyses were performed on a

Perkin-Elmer 2400 elemental analyzer. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. Thermogravimetric analyses (TGA) were carried out in a  $\text{N}_2$  atmosphere on a Diamond thermogravimetric analyzer from 50 to 1000 °C at a heating rate of 10 °C·min<sup>-1</sup>.

### 1.2 Synthesis of compounds

In a typical synthesis of compound **1**, a solution was prepared by dissolving  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.443 7 g, 0.983 mmol) into distilled water (3.998 9 g, 221.972 mmol), en (0.217 9 g, 3.626 mmol) and sulfuric acid (0.386 5 g, 3.865 mmol, 98%) under constant stirring for an hour. The resulting mixture was transferred into a 24 mL Teflon-lined stainless-steel autoclave and heated at 453 K for 6 d. After cooling to room temperature, the product was washed with deionized water and dried in air for one day. Finally, the rodlike colorless crystals (yield 56%, with respect to Gd) were obtained. The elemental analysis found (%): C, 5.41; H, 2.74; N, 5.68 (calcd.(%): C, 5.03; H, 2.53; N, 5.87). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3 566 (m), 3 372 (b), 3 162 (m), 1 615 (w), 1 513 (m), 1 386(vs), 1 170 (m), 1 094 (m), 663 (w), 606 (w).

Compound **2** were prepared by solvothermal method.  $\text{Eu}_2\text{O}_3$  (0.189 0 g, 0.537 mmol) was dissolved in a mixture of  $\text{H}_2\text{O}$  (0.972 2 g, 53.965 mmol) and *n*-butanol (5.177 1 g, 69.846 mmol), which was stirred for 1 hour. Then sulfuric acid (0.342 3 g, 3.423 mmol, 98%) and piperazine (0.217 6 g, 2.526 mmol) were added. The final pH was 1.5. This solution was sealed in a 24 mL Teflon-lined autoclave and heated at 433 K for 6 d. The product was washed with deionized water, dried at room temperature for one day to give the colorless block crystals (yield 22%, with respect to Eu). The elemental analysis found (%) C, 9.42; H, 2.79; N, 5.58 (calcd.(%): C, 9.64; H, 2.83; N, 5.62). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3 437 (m), 3 069 (s), 2 827 (m), 1 597(s), 1 082(vs), 646(w), 605(s).

### 1.3 X-ray structure determination

The single crystals of compound **1**, **2** were chosen onto a thin glass fiber by epoxy glue in air for data collection. The diffraction data were collected on a Bruker Apex 2 CCD with  $\text{Mo K}\alpha$  radiation ( $\lambda=0.071\ 073$  nm) at 296 K using  $\varphi$ - $\omega$  scan method. An empirical

absorption correction was applied. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of organic molecule were refined in calculated positions, assigned isotropic thermal parameters, and allowed to ride on their parent atoms, while the H atoms of the water molecule were located

from different map. All calculations were performed using the SHELX97 program package<sup>[29]</sup>. Further details of the X-ray structural analyses for compounds **1** and **2** are given in Table 1 and selected bond lengths are listed in Table 2.

CCDC: 874219, **1**; 874220, **2**.

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

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>4</sub> H <sub>24</sub> Gd <sub>2</sub> N <sub>4</sub> O <sub>22</sub> S <sub>5</sub>	C <sub>8</sub> H <sub>28</sub> Eu <sub>2</sub> N <sub>4</sub> O <sub>22</sub> S <sub>5</sub>
Formula weight	955.07	996.56
Temperature / K	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> / nm	0.652 1(4)	1.972 1(2)
<i>b</i> / nm	1.692 0(9)	1.927 1(2)
<i>c</i> / nm	2.023 3(11)	1.323 20(14)
$\beta$ / (°)	95.168(7)	92.307 0(10)
<i>V</i> / nm <sup>3</sup>	2.223(2)	5.024 8(9)
<i>Z</i>	4	8
<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	2.853	2.635
Absorption coefficient / mm <sup>-1</sup>	6.498	5.471
<i>F</i> (000)	1 840	3 888
Theta range for data collection / (°)	2.02 to 25.50	2.07 to 25.00
Limiting indices	-7 ≤ <i>h</i> ≤ 7, -20 ≤ <i>k</i> ≤ 20, -24 ≤ <i>l</i> ≤ 11	-23 ≤ <i>h</i> ≤ 19, -22 ≤ <i>k</i> ≤ 22, -15 ≤ <i>l</i> ≤ 15
Reflections collected / unique ( <i>R<sub>int</sub></i> )	0 986 / 4 127 (0.042 2)	24 852 / 8 812 (0.036 4)
Completeness to $\theta=25.00^\circ$ / %	99.9	99.7
Max. and min. transmission	0.509 4 and 0.442 3	0.610 7 and 0.559 7
Data / restraints / parameters	4 127 / 6 / 347	8 812 / 63 / 764
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.009	1.051
Final <i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> <sub>1</sub> =0.029 0, <i>wR</i> <sub>2</sub> =0.066 0	<i>R</i> <sub>1</sub> =0.030 7, <i>wR</i> <sub>2</sub> =0.078 6
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.036 9, <i>wR</i> <sub>2</sub> =0.068 5	<i>R</i> <sub>1</sub> =0.033 9, <i>wR</i> <sub>2</sub> =0.080 8

**Table 2** Selected bond lengths (nm) for compound **1** and **2**

Compound <b>1</b>					
Gd(1)-O(6)#1	0.238 0(4)	Gd(1)-O(19)#2	0.239 2(4)	Gd(1)-O(2W)	0.240 7(4)
Gd(1)-O(9)	0.252 3(4)	Gd(1)-O(8)	0.253 1(4)	Gd(1)-O(2)	0.260 3(4)
Gd(2)-O(20)#3	0.237 1(4)	Gd(2)-O(1W)	0.239 5(4)	Gd(2)-O(5)	0.240 9(4)
Gd(2)-O(7)	0.243 1(4)	Gd(2)-O(1)	0.246 3(4)	Gd(2)-O(15)#4	0.248 7(4)
Gd(2)-O(3)	0.250 6(4)	Gd(2)-O(14)#4	0.251 7(4)	Gd(2)-O(18)	0.269 5(4)
Compound <b>2</b>					
Eu(1)-O(21)#1	0.243 0(3)	Eu(1)-O(31)	0.253 2(3)	Eu(2)-O(3W)	0.239 3(3)
Eu(1)-O(1W)	0.243 5(3)	Eu(1)-O(35)	0.254 9(3)	Eu(2)-O(9)	0.242 4(2)
Eu(1)-O(28)	0.245 2(2)	Eu(1)-O(26)	0.261 6(3)	Eu(2)-O(14)#3	0.244 2(2)
Eu(1)-O(23)	0.250 4(3)	Eu(2)-O(36)#2	0.232 5(3)	Eu(2)-O(10)	0.246 1(2)
Eu(2)-O(13)	0.251 9(2)	Eu(3)-O(30)#2	0.241 0(3)	Eu(3)-O(5)	0.246 1(2)
Eu(2)-O(2)	0.254 0(3)	Eu(3)-O(2W)	0.243 2(3)	Eu(3)-O(22)	0.248 8(3)

Continued Table 2

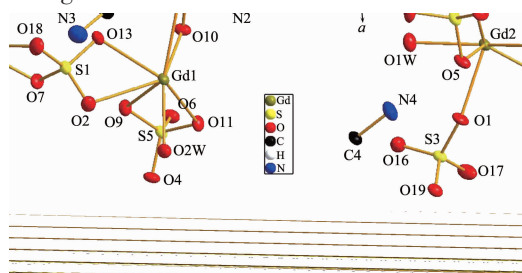
Eu(3)-O(7)	0.239 8(3)	Eu(4)-O(6)	0.255 1(3)	Eu(4)-O(40)#5	0.296 4(4)
Eu(3)-O(15)	0.255 9(3)	Eu(4)-O(1)	0.238 3(3)	Eu(4)-O(24)#6	0.245 9(3)
Eu(3)-O(25)	0.258 8(3)	Eu(4)-O(11)	0.242 6(2)	Eu(4)-O(4W)	0.248 0(3)
Eu(4)-O(27)#4	0.237 8(2)	Eu(4)-O(39)#5	0.243 3(3)	Eu(4)-O(18)#6	0.250 8(2)

Symmetry transformations used to generate equivalent atoms for **1**: #1:  $x-1, y, z$ ; #2:  $x, -y+3/2, z+1/2$ ; #3:  $x+1, y, z$ ; #4:  $-x+1, -y+2, -z+1$ ; #5:  $x, y, z-1$ ; #6:  $x, -y+1/2, z+1/2$ ; #7:  $-x+1, y-1/2, -z+3/2$ ; #8:  $x, -y+3/2, z-1/2$ ; #9:  $-x, -y+1, -z+2$ ; #10:  $-x, y+1/2, -z+5/2$ .

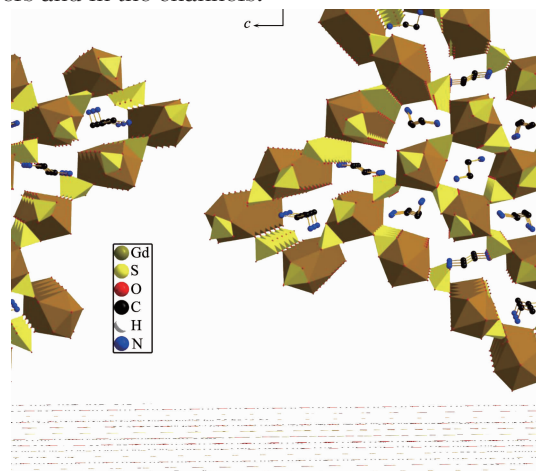
## 2 Results and discussion

### 2.1 Crystal structure

As shown in Fig.1, the asymmetric unit of compound **1** contains 37 non-hydrogen atoms, 29 of which belong to the inorganic framework, including two crystallographically distinct gadolinium atoms, five sulfate groups, two coordination water molecules and two ethylenediamine molecules (4 carbon atoms and 4 nitrogen atoms). The crystallographically distinct Gd(1) and Gd(2) are both coordinated by three bidentate sulfate anions, two monodentate sulfate anions and one water molecule. In the framework of  $[\text{Gd}_2(\text{SO}_4)_5(\text{H}_2\text{O})_2][\text{C}_2\text{H}_{10}\text{N}_2]_2$ , five crystallographic independent S atoms can be divided into three types: S(3) link two Gd atoms to make two Gd-O-S linkages; S(4) and S(5) connect two Gd atoms to form three Gd-O-S linkages; S(1) and S(2) make four Gd-O-S linkages to connect two Gd atoms. The distance of Gd-O vary from 0.237 1(4) to 0.269 5(4) nm, while the angles O-Gd-O are between  $54.11(12)^\circ$  and  $151.51(13)^\circ$ , which are similar to those reported gadolinium sulfates<sup>[26]</sup>. The O-S-O angles are within the expected range for tetrahedral geometry. The bridging  $\text{SO}_4$  tetrahedra link the  $\text{GdO}_9$  polyhedra by sharing the corners or edges to generate 2D layers which consist of 8-membered rings and 16-membered rings along a-axis, as shown in Fig.2. Then the 2D layers are stacked over one another in AAAA... fashion to forming 3D structure containing 8- and 16-membered channels. Protonated

Fig.1 Asymmetric unit of compound **1**

ethylenediamine cations are located between the 2D layers and in the channels.

Fig.2 Projection of the three dimensional structure along the  $a$  axis, the protonated amine units are shown in 8-membered and 16-membered channels

As shown in Fig.3, the asymmetric unit of compound **2** contains 82 non-hydrogen atoms, 58 of which belong to the inorganic framework, including four europium atoms, ten sulfate groups, four coordination water molecules and four protonated piperazine cations (16 carbon atoms and 8 nitrogen atoms). The Eu(1), Eu(3) and Eu(4) are coordinated by nine oxygen atoms from five sulfate groups and one coordinated water, while the Eu(2) is coordinated by eight oxygen atoms from five sulfate groups and one coordinated water. In the framework of compound **2**, ten crystallographic independent S atoms can be divided into three types: S(3), S(9) and S(10) link two Eu atoms to make two Eu-O-S linkages; S(1), S(4) and S(8) connect two Eu atoms to form three Eu-O-S linkages; S(2), S(5), S(6) and S(7) make four Eu-O-S linkages to connect two Eu atoms. The distance of Eu-O vary from 0.232 5(3) to 0.296 4(4) nm, while the angles O-Eu-O are between  $50.41(10)^\circ$  and  $157.88(9)^\circ$ , which are similar to those reported europium sulfates<sup>[26-27]</sup>. The O-S-O angles are within the

expected range for tetrahedral geometry. The bridging  $\text{SO}_4$  tetrahedra link the  $\text{EuO}_9$  and  $\text{EuO}_8$  polyhedra by sharing the corners or edges to generate 2D layers which consist of 8-membered rings and 16-membered rings along  $c$  axis. The adjacent layers are connected by  $\text{SO}_4$  tetrahedra forming a 3D structure, which is similar to compound **1**. In the compound **1**, the 2D layers are linked by  $\text{SO}_4$  tetrahedra constructing a 3D open framework, the 8- and 16-membered rings are stacked over one another in AAAA... fashion, forming the 8- and 16-membered channels, but in the compound **2**, the 2D layers are linked by  $\text{SO}_4$  tetrahedra with a stagger position. As a result, the 8- and 16-membered rings are stacked over one another in ABAB... fashion, so only the 8-membered channels along  $c$  axis are observed, the

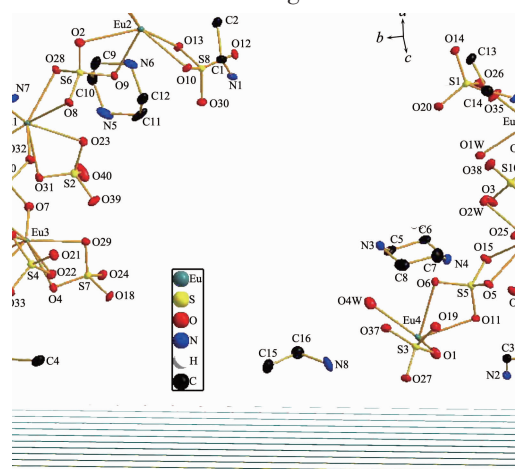


Fig.3 Asymmetric unit of compound **2**

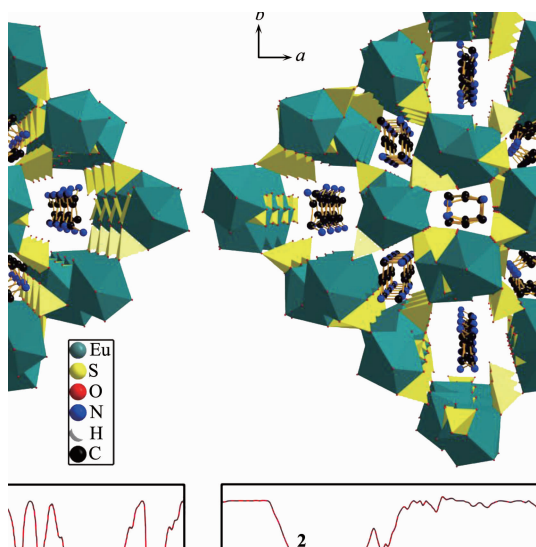


Fig.4 Projection of the three dimensional structure along  $c$  axis, the protonated amine units are shown in 8-membered channels

fully protonated piperazine molecules are located in the 8-membered channels and involved in the hydrogen bond interaction with the oxygen atoms from the framework, as shown in Fig.4.

## 2.2 IR property

The IR spectrum of compound **1** shows that the band around  $3\,500\text{ cm}^{-1}$  can be attributed to the presence of water. The typical sharp peaks for ethylenediamine are in the region  $1\,386\sim 1\,615\text{ cm}^{-1}$ . Characteristic bands due to the  $\text{SO}_4^{2-}$  are in the  $1\,094$  and  $606\text{ cm}^{-1}$  region. The bands at  $3\,162$  and  $3\,053\text{ cm}^{-1}$  are due to O-H bonding and N-H bonding vibrations, respectively. Similarly, The IR spectrum of compound **2** shows that the band around  $3\,500\text{ cm}^{-1}$  can be attributed to the presence of water. The typical sharp peaks for piperazine are in the region  $1\,430\sim 1\,597\text{ cm}^{-1}$ . Characteristic bands due to the  $\text{SO}_4^{2-}$  are in the  $1\,082$  and  $605\text{ cm}^{-1}$  region. The bands at  $3\,150$  and  $3\,069\text{ cm}^{-1}$  are due to O-H bonding and N-H bonding vibrations, respectively.

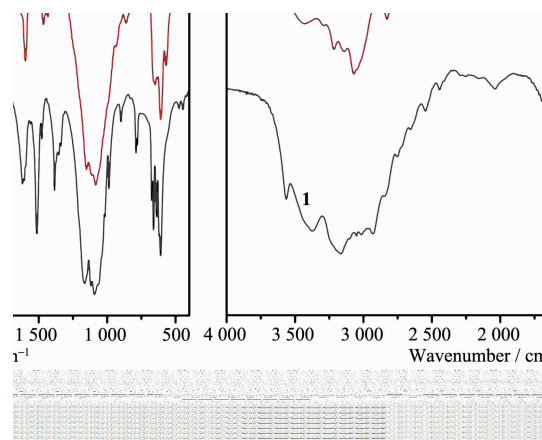


Fig.5 FTIR spectrum of compound **1** and **2**

## 2.3 TG analysis

For compound **1**, Thermal analysis shows that the total weight loss is 69.2% and the calculated value is 62.1%. As shown in Fig.6a, the weight loss of 8.5% in the range of  $50\sim 300\text{ }^{\circ}\text{C}$  corresponds to the removal of the coordinated water (the calculated value is 3.8%). Reason may be that the sample is wet. The weight loss of 58.3% in the range  $300\sim 900\text{ }^{\circ}\text{C}$  can be attributed to the loss of ethylenediamine and  $\text{SO}_3$  (the calculated value is 61.1%).

Thermal analysis shows that the total weight loss of compound **2** is 66.9%, which is close to the calculated





Fig.6 (a) TG Curve for the decomposition of compound **1** in  $N_2$  atmosphere; (b) TG Curve for the decomposition of compound **2** in  $N_2$  atmosphere

value (64.7%). As shown in Fig.6b, the weight loss of 3.2% in the range of 50 ~330 °C corresponds to the removal of the coordinated water (the calculated value is 3.6%). The weight loss of 63.7% in the range 330 ~ 900 °C can be attributed to the loss of piperazine and  $SO_3$  (the calculated value is 61.1%).

## 2.4 Luminescence property

Luminescent properties of compounds **2** were investigated because of existence of  $Eu^{3+}$ . The solid-state emission spectra of the compound at room temperature were measured under excitation at 396 nm for  $Eu^{3+}$ . As shown in Fig.7, compound **2** shows four emission bands at 595 nm ( $^5D_0 \rightarrow ^7F_1$ ), 616 nm ( $^5D_0 \rightarrow ^7F_2$ ), 653 nm ( $^5D_0 \rightarrow ^7F_3$ ), 696 nm ( $^5D_0 \rightarrow ^7F_4$ ), which is in agreement with the reported  $Eu^{3+}$  compounds<sup>[26-27]</sup>.

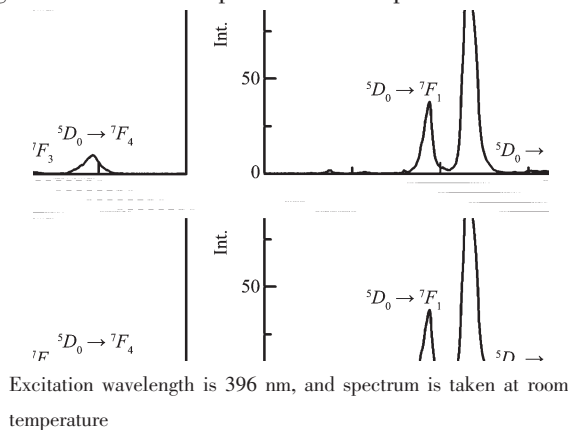


Fig.7 Photoluminescence of compound **2**

## 3 Conclusions

In summary, we have successfully synthesized two 3D organic-templated lanthanide sulfates  $[Gd_2(SO_4)_5$

$(H_2O)_2][C_2N_2H_{10}]_2$  (**1**),  $[Eu_2(SO_4)_5(H_2O)_2][C_4N_2H_{12}]_2$  (**2**). Though the two compounds employing different amines and unlike experiment condition such as temperature and solvent, they have similar inorganic framework. The  $LnO_x$  are linked by  $SO_4$  to form the layers in which each 8-membered ring is surrounded by four 16-membered rings. Further, the adjacent layers are connected by  $SO_4$  groups in AAAA... fashion to form a 3D structure containing 8- and 16-membered channels in **1**, but the adjacent layers are connected by  $SO_4$  groups in ABAB... fashion to form a 3D structure containing only 8-membered channels in **2**. The luminescent spectra of **2** reveal that the rare-earth organic template sulfates not only possess luminescence nature and are promising photoluminescence materials.

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