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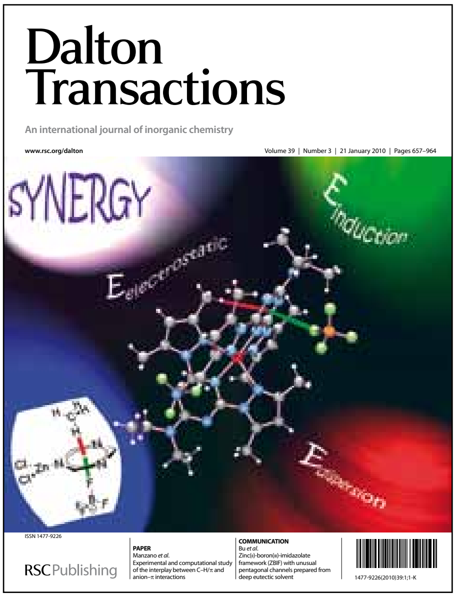
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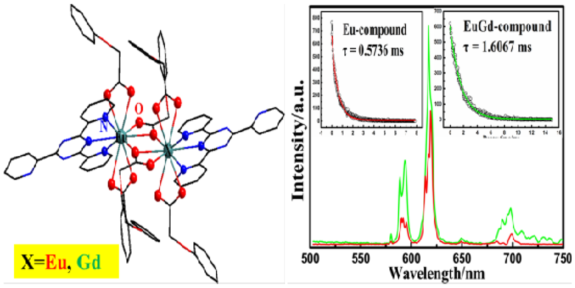

Two europium crystals with HPOA and TPTZ were prepared and the heteronuclear compound exhibits superior luminescent properties to the homonuclear.

Crystal structure and photoluminescence of two europium compounds with phenoxyacetic acid and 2,4,6-tri(2-pyridyl)-s-triazine

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Abstract

Two novel crystal compounds of Eu^{3+} and Gd^{3+}/Eu^{3+} with phenoxyacetic acid (HPOA) and 2,4,6-tri(2-pyridyl)-s-triazine (TPTZ) have been synthesized. The two compounds are characterized by elemental analysis, rare earth coordination titrations, molar conductivity measurement, UV–vis absorption spectroscopy and IR spectroscopy. The crystal structures of compound **1** $Eu_2(TPTZ)_2(POA)_6\cdot 2CH_3OH$ and **2** $EuGd(TPTZ)_2(POA)_6\cdot 2CH_3OH$ were determined by single-crystal X-ray diffraction. The two monocrystals belong to the triclinic system, and space group P-1 with the following unit cell parameters a=12.2448(10), 12.2476(6) Å; b=13.2214(11), 13.2260(7) Å; c=13.5248(12), 13.5210(7) Å; α=74.8544(15),74.8810(10)°; β=83.0605(16), 83.0465(8)°; γ=87.1996(14), 87.2126(8)°; V=2097.7(7), 2098.5(19) $Å^3$ and Z=1, respectively. They are both dinuclear, one is homonuclear and the other is heteronuclear compound. Each metal ion coordinately bonded to three nitrogen atoms of one TPTZ, seven oxygen atoms of three phenoxyacetate ions. Furthermore, there exist two coordinate forms between $C_6H_5OCH_2COO^-$ and metal ions. One is chelating bidentate, the other is chelating and bridge coordinating. The triplet energy level of phenoxyacetic acid was measured, which is approximately 22500 cm^{-1}, indicating that the lowest excitation state energy level of Eu(Ш) and the triplet state energy level of phenoxyacetic acid match well with each other. The luminescent emission intensity of both compounds was very strong. Besides, the results indicated that the luminescent emission intensity, luminescence lifetimes and the emission quantum efficiencies of Gd^{3+}/Eu^{3+} compound **2** are remarkably superior to those of the compound **1**, respectively. This phenomenon may mainly result from the decrease of the concentration quenching effect of Eu^{3+} ions, and intramolecular energy transfer from the ligands coordinated with Gd^{3+} ions to Eu^{3+} ions.

Keyword: phenoxyacetic acid, 2,4,6-Tri(2-pyridyl)-s-triazine, europium compounds, crystal structure, luminescent property

1. Introduction

The preparation of coordination clusters and donor molecules via coordination bonds or secondary bonding interactions is of increasing importance in the field of crystal engineering.[1-10] For a long time, researchers have a problem whether the doped compounds are the mixed compounds of different pure compounds or the heteronuclear compounds which have different coordinated metal ions in one molecule. In order to give an answer, two crystals of Eu^{3+} and Gd^{3+}/Eu^{3+} are synthesized with anion ligand phenoxyacetic acid (HPOA) and neutral ligand 2,4,6-tris-(2-pyridyl)-s-triazine (TPTZ). One of the two crystals is homonuclear and the other is heteronuclear.

As a superior class of neutral ligand, TPTZ has three different “coordination sites” in the molecule. It is a nearly planar molecule possessing soft π-donor. And it presents a specific atomic grouping, α,α’-diimine structure, constituting part of the aromatic system which is capable of forming stable five-membered chelated rings with the metal ions.[11,12] The interest in this ligand lay principally in its promise and versatility.

Based on the investigation of the luminescence of series of rare earth organic chelates, some relationships between the luminescence and the structure of the chelates were proposed. The suitability of the energy gap between the triplet level of ligand and the lowest excited state energy of rare earth ion is critical for efficient energy transfer.[13, 14] The triplet energy level of TPTZ is measured to be 21277 cm^{-1} in our previous work,[15] therefore, we choose Eu^{3+} to coordinate with the ligand. Besides, we also select HPOA as the anion ligand to form the crystal. However, there exist some restrictions for the practical application of the europium compounds, essentially owing to their expensive price, weak luminescent intensity, short lifetime and low quantum efficiency.[16, 17] In order to overcome these drawbacks, rare earth compounds should be incorporated with some cheap rare earths, for example, Gd^{3+}, Y^{3+} and La^{3+}.[18, 19] Recently, our group has reported the synthesis of introducing inertia rare earth ion into luminescent rare earth complexes. It is shown that the promising luminescent properties can be obtained by introducing inertia rare earth. However, the synthesis and luminescence properties of doping Gd^{3+} to Eu^{3+} coordinated with TPTZ and anion organic ligand, and especially the crystal structure of Gd^{3+}/Eu^{3+} compound have not been reported until now. Herein, the synthesis, characterization, and luminescent property of two dinuclear clusters $EuLn(TPTZ)_2(POA)_6{\cdot}2CH_3OH$ (Ln = Eu, Gd) are reported. All measurements reveal that the Gd^{3+}/Eu^{3+} compound shows more remarkable luminescent intensity, longer luminescence lifetime and higher quantum efficiencies than the Eu^{3+} compound.

2. Experimental sections

2.1. Chemical reagents and instruments

Purities of rare earth oxides Eu_2O_3 and Gd_2O_3 are 99.99%. HPOA, TPTZ, anhydrous ethanol and other reagents are all of analytical grade and used as received.

The molar concentration of rare-earth ions was analyzed by titration with EDTA complexometric titration method with xylenol orange as the indicator in hexamethylenetetramine-HCl buffer solution.[20-21] Elemental analysis of C, H and N was performed on a Vario EL Cube elemental analyzer. The contents of europium and gadolinium in the compounds were measured by a Varian Vista-MPX inductively coupled plasma atomic emission spectrometry (ICP-AES). Molar conductivity (Λ_m) was measured on a DDS-11A conductivity meter with DJS-I platinum black electrode at room temperature using dimethylformamide (DMF) as solvent, and the concentration of the compounds was 1.0×10^{-5} $mol{\cdot}L^{-1}$. Crystals X-ray diffraction patterns were recorded on a Bruker SMART 1000 CCD diffractometer with a monochromator in the Mo Kα radiation (λ=0.071073Å) incident beam at a temperature of 293 (2) K. The θ range of data collection was from 1.05 to 25.02°. The UV spectra were recorded on Shimadzu UV-265 spectrophotometer. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR spectrometer as KBr pellets. The phosphorescence spectrum of the complex $Gd(POA)_3$ was recorded on the Edinburgh Analytical Instruments FLS-920 spectrophotometer at 77 K. Luminescence spectra and luminescence lifetime of the two compounds in the ethanol solution were determined on the FLS-920 fluorescence spectrophotometer at room temperature.

2.2. Synthesis of compounds

2.2.1. Preparation of rare earth chloride.

1.76 g Eu_2O_3 was dissolved in a certain amount of hydrochloric acid. The mixture was heated until crystallized film appeared above the solution, after which the mixture was cooled to room temperature. The white powdered solid appeared. The powder was dissolved in anhydrous ethanol to get 0.1mol·L^{-1} $EuCl_3$ ethanol solution. The preparation of 0.1 mol·L^{-1} $GdCl_3$ ethanol solution was similar to that of $EuCl_3$.

2.2.2. Preparation of the crystals.

TPTZ (1 mmol, 0.312g) and HPOA (3 mmol, 0.4565g) were first dissolved in 10 ml ethanol solution with stirring at 60 °C. 10 ml $EuCl_3$ (0.1 mol·L^{-1}) ethanol solution was added into above solution. Then the pH value of the solution was adjusted to be 6.4～6.7 with $NH_3{\cdot}H_2O$. After stirring at 60 °C for 3h, the solution was left still at room temperature overnight. The mixture was separated by filtering and washing with the mixture of methanol and ethanol, and the filtrate was collected. The crystals were obtained after the filtrate had been kept for five weeks at room temperature. Anal. Calcd (%) for $C_{86}H_{74}Eu_2N_{12}O_{20}$: C 54.38; H 3.93; N 8.85; Eu 16.00; found (%): C 54.64; H 3.72; N 8.59; Eu 15.81.

The preparation of the crystal $C_{86}H_{74}EuGdN_{12}O_{20}$ **2** was similar to that of $C_{86}H_{74}Eu_2N_{12}O_{20}$ **1** except that an equimolar amount of $EuCl_3$ and $GdCl_3$ was added. Anal. Calcd (%) for $C_{86}H_{74}EuGdN_{12}O_{20}$: C 54.23; H 3.92; N 8.82; Eu 7.98; Gd 8.26; found (%): C 54.47; H 4.18; N 8.69; Eu 8.01; Gd 8.08.

The two crystals are slightly soluble in DMF and dimethyl sulfoxide (DMSO) and insoluble in methanol, ethanol and acetonitrile. The Λ_m of compound **1** is 14.5 S•cm^2•mol^{-1} and 15.5 S•cm^2•mol^{-1} for compound **2** in DMF. This small value of molar conductivity reveals that only a small section of the compounds ionizes and they are all non-electrolytes.[22, 23]

2.3. Crystal structure determinations

The structures of the compounds **1** and **2** were solved by direct methods, and refined against F^2 by full-matrix least-squared method using the SHELXL-97.[24] All of the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located in a different Fourier map. The crystallographic data for the two crystals are listed in Table 1. Structural information was deposited at the Cambridge Crystallographic Data Center (CCDC reference numbers 911888 for **1**, 911887 for **2**).

Table 1 Crystal data and details of the structure determination

Compound	$Eu_2(TPTZ)_2(POA)_6\cdot 2CH_3OH$ **1**	$EuGd(TPTZ)_2(POA)_6\cdot 2CH_3OH$ **2**
Empirical formula	$C_{86}H_{74}Eu_2N_{12}O_{20}$	$C_{86}H_{74}EuGdN_{12}O_{20}$
Formula weight	1899.49	1904.78
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	12.2448(10)	12.2476(6)
b (Å)	13.2214(11)	13.2260(7)
c (Å)	13.5248(12)	13.5210(7)
α (deg)	74.8544(15)	74.8811(9)
β (deg)	83.0605(16)	83.0465(8)
γ (deg)	87.1996(14)	87.2126(8)
V ($Å^3$)	2097.7(3)	2098.53(19)
Z	1	1
$D_{calcd.}$(g/cm^3)	1.504	1.507
μ (mm^{-1})	1.560	1.602
θ range for data collection (deg)	1.05 to 25.02	1.05 to 25.02
T (K)	293(2)	293(2)
Wavelength(Å)	0.71073	0.71073
R1	0.0376	0.0243

wR2	0.0936	0.0705

3. Results and discussions

3.1. Absorption spectra

As shown in Fig.1, the ligands HPOA and TPTZ show strong absorption bands at 272 nm and 282 nm, respectively, and intense bands ($\varepsilon \approx 8.0 \times 10^4$ and 1.3×10^5 $L\cdot mol^{-1}\cdot cm^{-1}$, respectively for the ligands HPOA and TPTZ) are assigned to π-π^* transition localized on both HPOA and TPTZ ligands. After coordinating to rare earth ions, the absorption bands obviously shift to 278-279 nm and exhibit an increase in absorptions intensity ($\varepsilon \approx 2.3 \times 10^5$ and 2.9×10^5 $L\cdot mol^{-1}\cdot cm^{-1}$, respectively for compound **1** and **2**). The increasement of the molar extinction coefficients can be attributed to the increased conjugations after coordination.[25] Besides, the similarity of the absorption spectra of the two compounds suggests they have a similar structure.

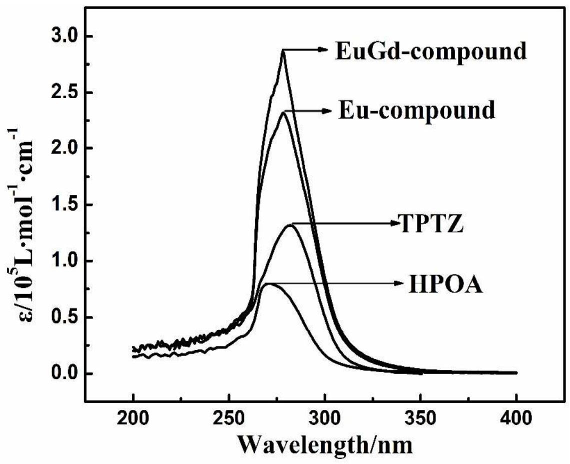

Fig. 1 Absorption spectra of the ligands and the compounds

3.2. Infrared spectroscopy

Within the scope of 4000-400 cm^{-1}, the IR spectra of the crystals, TPTZ and HPOA ligands were determined as Fig. 2. It is assumed that the two crystals have similar coordination structure. In the IR spectrum of TPTZ ligand, the band at 1373 cm^{-1} was attributed to breathing vibration of the center ring and the band at 994 cm^{-1} was attributed to bending vibration of pyridyl ring. The two bands upshifted by 6-10 and 12-14 cm^{-1}, respectively, in the compounds, indicating that nitrogen atoms of the center ring and the pyridyl ring coordinated with the metal ions. The ligand HPOA showed absorption bands around 1700 cm^{-1} and 1095 cm^{-1}, which could be ascribed to the stretching vibration ($\nu_{(C=O)}$(COOH)) and bending vibration $\delta_{(O\text{-}H)}$(COOH) of carboxylic acid, respectively. These two bands disappeared in the compounds. And the new bands around 1600 cm^{-1} and 1429~1430 cm^{-1} appeared, which could be ascribed to the asymmetric and symmetric stretching vibration of carboxylate in the compounds, respectively. Thus, the carboxylate groups of HPOA ligand were involved into the coordination of the two compounds.[26] It is worth noting that the difference $\Delta\nu$ between $\nu_{as(COO-)}$ and $\nu_{s(COO-)}$ is important because $\Delta\nu$ can be used to determine the coordination mode between the metal and carboxylate ligand.[27, 28] It is generally believed that unidentate complexes are expected to exhibit a larger $\Delta\nu$ (>200 cm^{-1}) than the corresponding ionic species. On the contrary, bidentate chelate coordination leads to lower $\Delta\nu$ (<200 cm^{-1}) than that in the unidentate species and $\Delta\nu$ for bridging complexes should be close to the ionic values.[29-33]

The $\Delta\nu$ values are 171 cm^{-1} and 170 cm^{-1}, respectively for compound **1** and compound **2**, which are obviously lower than 200 cm^{-1} and somewhat lower than the corresponding ionic value (173 cm^{-1}).[29] Indeed, in the spectra of the compounds, ionic and bridging carboxylates are not distinguishable. This would suggest that the carboxylate groups are coordinated via bridging and bidentate coordination to the metal ions.

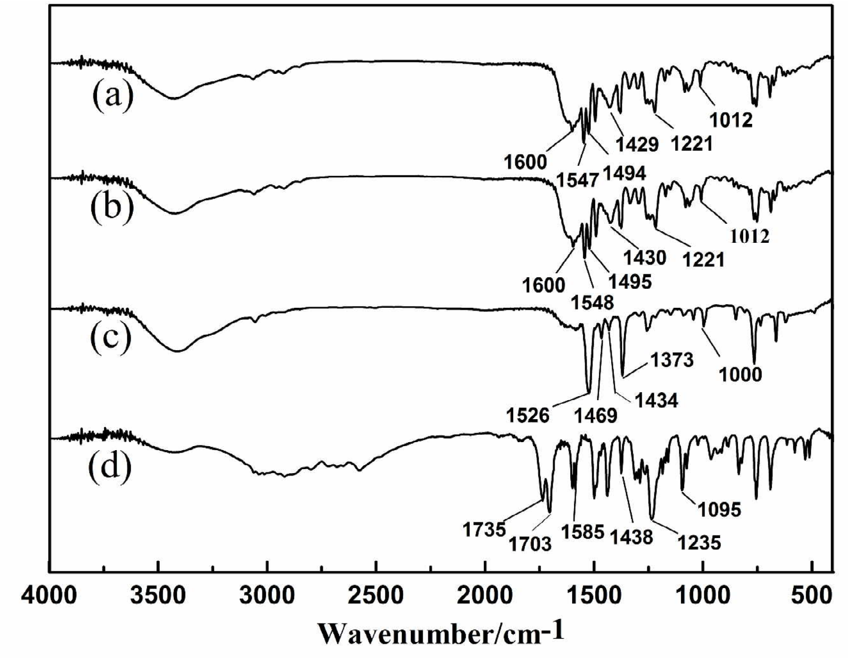

Fig. 2 IR spectra: (a) compound **1,** (b) compound **2**, (c). TPTZ, (d). HPOA.

3.3. Crystal Structure

The structures of the two crystals were established by single-crystal X-ray structure determination and X-ray data parameters have been given in Table 1. Selected band distances and angles are given in Table 2(a), Table 2(b) and Table 2(c), respectively. Structural elucidation reveals the formation of a new series of dinuclear clusters [EuLn(TPTZ)$_2$(POA)$_6$] where Ln = Eu(1) and Gd(2). The two crystals show similar structures. The structure of **1** can be visualized in Fig. 3. Each asymmetric unit contains one TPTZ ligand, three POA$^-$ anions and one metal atom. Each carboxylate group of the POA$^-$ in tridentate (κ^1–κ^2-μ_2) fashion bridges between two metal(Ш) ions, coordinating κ^1– to one and κ^2– to the other (see Fig. 3). Each metal(Ш) ion is 10-coordinate and bonds to one κ^1– carboxylates, one κ^2-carboxylates, two chelate POA$^-$ anion ligands and one tridentate TPTZ.[34] Crystals **1** and **2** crystallize in the triclinic space group P-1 with Z value of 1. Unit cell parameters is that a=12.2448(10), 12.2476(6) nm; b=13.2214(11), 13.2260(7) nm; c=13.5248(12), 13.5210(7) nm; α=74.8544(15), 74.8810(10)°; β=83.0605(16), 83.0465(8)°; γ=87.1996(14), 87.2126(8)°; V=2097.7(7), 2098.5(19) nm^3 for compound **1** and **2**, respectively. Unit cell packing diagrams for two compounds are similar, and only the cell packing of compound

1 is shown in Fig. 5. Because of the different radii of metal ions (r_{Eu3+} = 96 pm, r_{Gd3+} = 94 pm), the corresponding bond lengths are varied, with bond lengths Eu(1)-O(4) = 2.397(3) Å, Eu(1)-O(2) = 2.461(4) Å, Eu(1)-N(1)=2.608(4)Å… for compound **1** and Eu|Gd-O(4) = 2.3897(15) Å, Eu(1)-O(2) = 2.4615(17) Å, Eu(1)|Gd(1)-N(1)=2.6011(18)Å… for compound **2.** Generally, the bond lengths of compound **2** are a little shorter than those of compound **1**.

Table 2 (a) Selected bond lengths [Å] for crystals

bond lengths(Å)			
Compound **1**		Compound **2**	
Eu(1)—O(4)'	2.397(3)	Eu(1)|Gd(1)—O(4)'	2.3897(15)
Eu(1)—O(2)	2.461(4)	Eu(1)|Gd(1)—O(2)	2.4615(17)
Eu(1)—O(1)	2.495(4)	Eu(1)|Gd(1)—O(1)	2.4852(17)
Eu(1)—O(7)	2.508(4)	Eu(1)|Gd(1)—O(7)	2.4896(17)
Eu(1)—O(5)	2.525(4)	Eu(1)|Gd(1)—O(5)	2.5165(16)
Eu(1)—O(8)	2.565(5)	Eu(1)|Gd(1)—O(8)	2.5668(19)
Eu(1)—N(1)	2.608(4)	Eu(1)|Gd(1)—N(1)	2.6011(18)
Eu(1)—N(2)	2.610(4)	Eu(1)|Gd(1)—N(2)	2.6078(18)
Eu(1)—O(4)	2.613(4)	Eu(1)|Gd(1)—O(4)	2.6113(15)
Eu(1)—N(6)	2.698(4)	Eu(1)|Gd(1)—N(6)	2.6931(19)

Table 2(b) Selected bond angles [°] for compound **1**

bond Angle(°)			
O(4)'—Eu(1)—O(2)	91.46(13)	O(1)—Eu(1)—N(2)	71.02(14)
O(4)'—Eu(1)—O(1)	136.84(13)	O(7)—Eu(1)—N(2)	110.13(14)
O(2)—Eu(1)—O(1)	52.84(12)	O(5)—Eu(1)—N(2)	131.70(12)
O(4)'—Eu(1)—O(7)	79.75(13)	O(8)—Eu(1)—N(2)	66.93(14)
O(2)—Eu(1)—O(7)	135.69(13)	N(1)—Eu(1)—N(2)	62.44(13)
O(1)—Eu(1)—O(7)	141.87(13)	O(4)'—Eu(1)—O(4)	66.05(14)
O(4)'—Eu(1)—O(5)	116.46(12)	O(2)—Eu(1)—O(4)	69.18(13)
O(2)—Eu(1)—O(5)	70.49(14)	O(1)—Eu(1)—O(4)	112.20(12)
O(1)—Eu(1)—O(5)	77.35(13)	O(7)—Eu(1)—O(4)	67.57(13)
O(7)—Eu(1)—O(5)	74.99(14)	O(5)—Eu(1)—O(4)	50.47(11)
O(4)'—Eu(1)—O(8)	72.21(14)	O(8)—Eu(1)—O(4)	109.97(13)
O(2)—Eu(1)—O(8)	161.55(15)	N(1)—Eu(1)—O(4)	117.92(12)

O(1)—Eu(1)—O(8)	136.30(13)	N(2)—Eu(1)—O(4)	176.78(12)
O(7)—Eu(1)—O(8)	51.29(14)	O(4)’—Eu(1)—N(6)	71.53(13)
O(5)—Eu(1)—O(8)	124.10(14)	O(2)—Eu(1)—N(6)	71.66(14)
O(4)’—Eu(1)—N(1)	143.35(15)	O(1)—Eu(1)—N(6)	74.15(13)
O(2)—Eu(1)—N(1)	124.75(14)	O(7)—Eu(1)—N(6)	141.24(14)
O(1)—Eu(1)—N(1)	77.98(14)	O(5)—Eu(1)—N(6)	141.42(14)
O(7)—Eu(1)—N(1)	70.31(14)	O(8)—Eu(1)—N(6)	94.47(14)
O(5)—Eu(1)—N(1)	76.11(13)	N(1)—Eu(1)—N(6)	121.53(13)
O(8)—Eu(1)—N(1)	72.66(15)	N(2)—Eu(1)—N(6)	60.18(13)
O(4)’—Eu(1)—N(2)	111.61(13)	O(4)—Eu(1)—N(6)	120.02(12)
O(2)—Eu(1)—N(2)	113.44(14)		

Table 2(c) Selected bond angles [°] for compound **2**

bond Angle(°)			
O(4)’—Eu(1)|Gd(1)—O(2)	91.11(6)	O(1)—Eu(1)|Gd(1)—N(2)	71.15(6)
O(4)’—Eu(1)|Gd(1)—O(1)	136.76(6)	O(7)—Eu(1)|Gd(1)—N(2)	110.06(6)
O(2)—Eu(1)|Gd(1)—O(1)	52.93(6)	O(5)—Eu(1)|Gd(1)—N(2)	131.66(6)
O(4)’—Eu(1)|Gd(1)—O(7)	79.97(6)	O(8)—Eu(1)|Gd(1)—N(2)	66.81(6)
O(2)—Eu(1)|Gd(1)—O(7)	135.60(6)	N(1)—Eu(1|)Gd(1)—N(2)	62.36(6)
O(1)—Eu(1)|Gd(1)—O(7)	141.64(6)	O(4)’—Eu(1)|Gd(1)—O(4)	65.65(6)
O(4)’—Eu(1)|Gd(1)—O(5)	116.29(5)	O(2)—Eu(1)|Gd(1)—O(4)	69.34(5)
O(2)—Eu(1)|Gd(1)—O(5)	70.60(6)	O(1)—Eu(1)|Gd(1)—O(4)	112.39(5)
O(1)—Eu(1)|Gd(1)—O(5)	77.28(6)	O(7)—Eu(1)|Gd(1)—O(4)	67.37(5)
O(7)—Eu(1)|Gd(10—O(5)	74.80(6)	O(5)—Eu(1)|Gd(1)—O(4)	50.69(5)
O(4)’—Eu(1)|Gd(1)—O(8)	72.29(6)	O(8)—Eu(1)|Gd(1)—O(4)	109.75(6)
O(2)—Eu(1)|Gd(1)—O(8)	161.22(7)	N(1)—Eu(1)|Gd(1)—O(4)	117.98(5)
O(1)—Eu(1)|Gd(1)—O(8)	136.37(6)	N(2)—Eu(1)|Gd(1)—O(4)	176.45(5)
O(7)—Eu(1)|Gd(1)—O(8)	51.58(6)	O(4)’—Eu(1)|Gd(1)—N(6)	71.43(6)
O(5)—Eu(1)|Gd(1)—O(8)	124.26(6)	O(2)—Eu(1)|Gd(1)—N(6)	71.63(6)
O(4)’—Eu(1)|Gd(1)—N(1)	143.55(6)	O(1)—Eu(1)|Gd(1)—N(6)	74.35(6)
O(2)—Eu(1)|Gd(1)—N(1)	124.87(6)	O(7)—Eu(1)|Gd(1)—N(6)	141.31(6)
O(1)—Eu(1)|Gd(1)—N(1)	77.94(6)	O(5)—Eu(1)|Gd(1)—N(6)	141.51(6)
O(7)—Eu(1)|Gd(1)—N(1)	70.22(6)	O(8)—Eu(1)|Gd(1)—N(6)	94.22(6)
O(5)—Eu(1)|Gd(1)—N(1)	76.07(5)	N(1)—Eu(1)|Gd(1)—N(6)	121.64(6)
O(8)—Eu(1)|Gd(1)—N(1)	72.85(6)	N(2)—Eu(1)|Gd(1)—N(6)	60.36(6)
O(4)’—Eu(1)|Gd(1)—N(2)	111.82(6)	O(4)—Eu(1)|Gd(1)—N(6)	119.91(5)
O(2)—Eu(1)|Gd(1)—N(2)	113.59(6)		

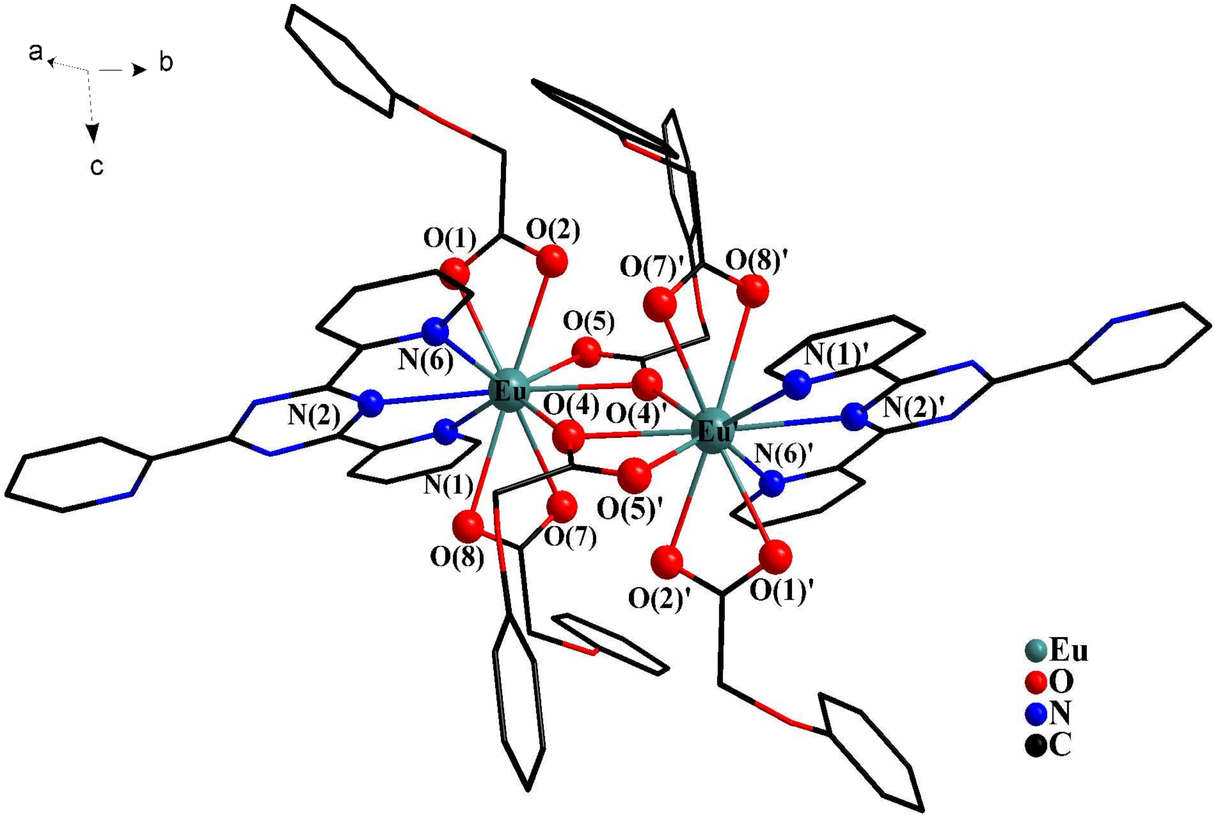

Fig. 3 The crystal structure of $Eu_2(TPTZ)_2(POA)_6{\cdot}2CH_3OH$ (compound **1**)

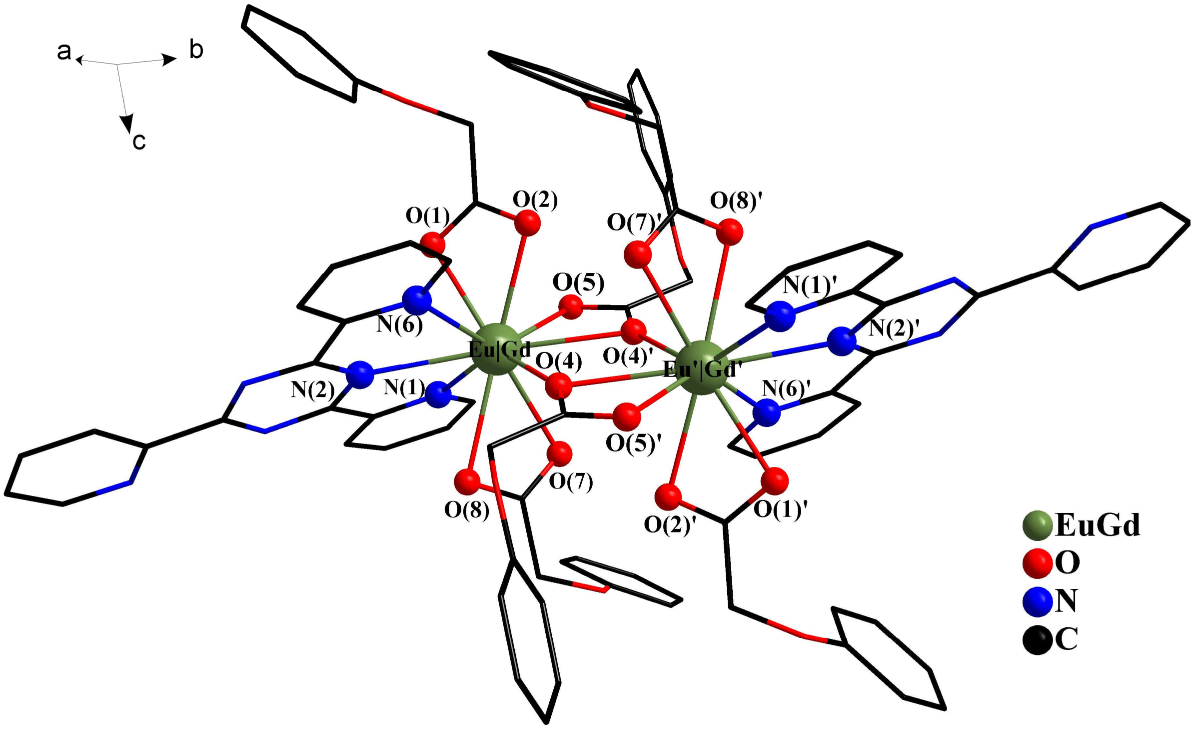

Fig. 4 The crystal structure of $EuGd(TPTZ)_2(POA)_6{\cdot}2CH_3OH$ (compound **2**)

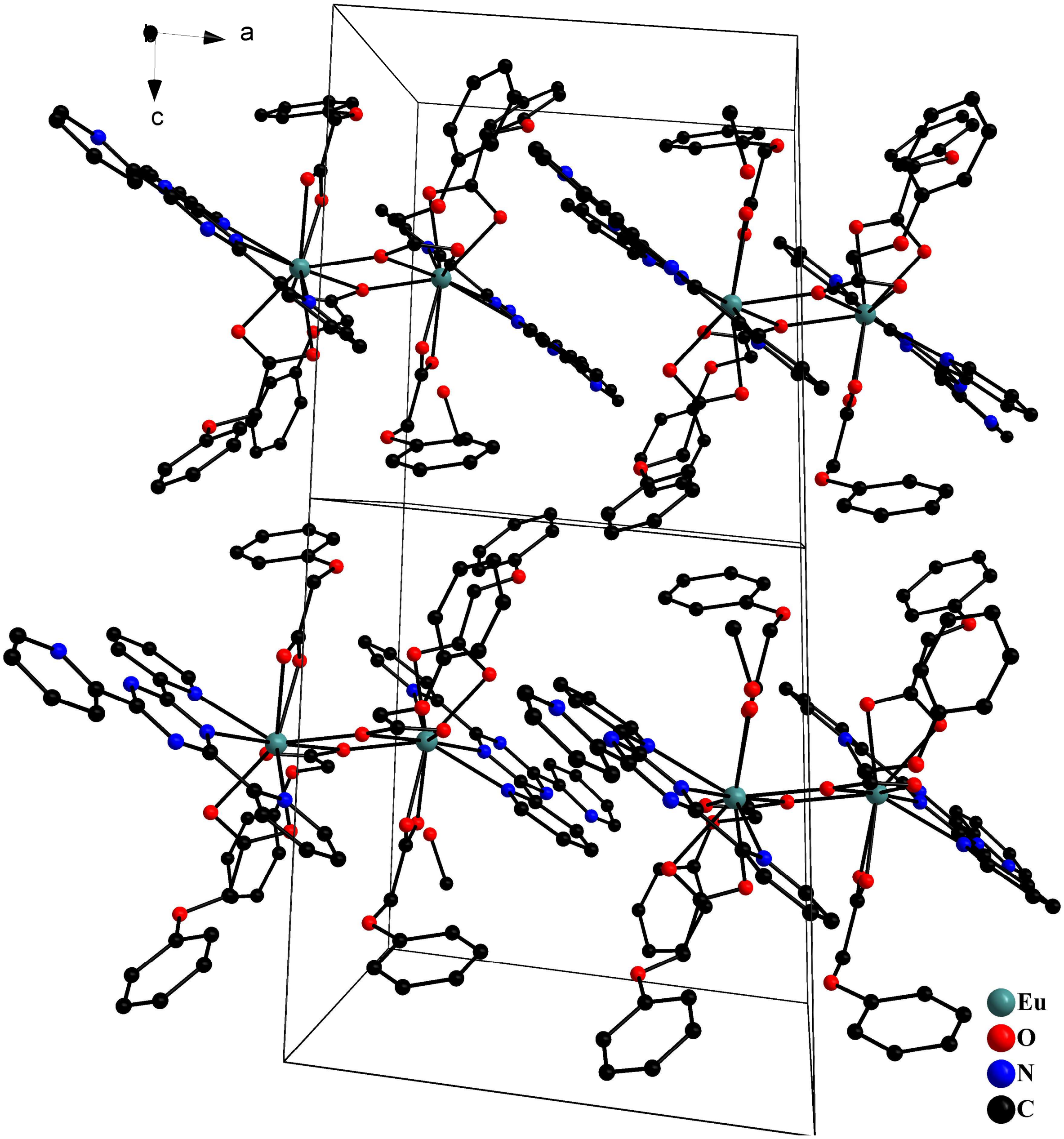

Fig. 5 Crystal cell packing diagram of $Eu_2(TPTZ)_2(POA)_6\cdot2CH_3OH$ (compound **1**)

3.4. Luminescence spectra

3.4.1. Determination of the triplet energy level of ligand HPOA

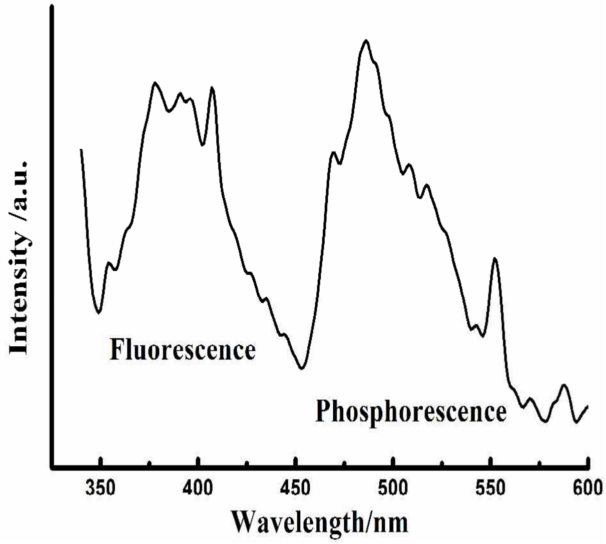

Fig. 6 Emission spectrum of Gd(POA)$_3$ at 77 K

The triplet energy level of coordinated ligands plays key roles in the energy transfer (ET) process.[35-37] Generally, the lanthanide ions cannot obviously affect the triplet energy level of the ligands. The lowest level of Gd^{3+} ($^6P_{7/2}$→$^8S_{7/2}$) is located at 32150 cm^{-1},[38, 39] which is so high that there may be no energy transfer between central Gd^{3+} ion and its coordinated ligands. Therefore, the phosphorescence spectrum of a gadolinium complex allows one to evaluate the triplet energy level of the corresponding coordinated ligand.[40] The emission spectrum of the complex Gd(POA)$_3$ was measured in a solution of EtOH at 77 K by making the optimal excitation wavelength of 300 nm, and was shown in Fig. 6. From the emission spectra, the triplet energy level can be evaluated. Using the method of fitting a tangent on the edge of the highest energy band, the interception between the tangent and the baseline is the triplet state energy.[41] Hence, the triplet energy level of HPOA is estimated to be 2.25×10^4 cm^{-1} (444 nm).

3.4.2 Luminescence spectra, luminescence lifetimes and quantum efficiencies of the compounds

Luminescence spectra of the compounds were obtained under the excitation slit and emission slit widths were all 0.5 nm at room temperature, and the concentration of the two compounds in the ethanol solution was both 1×10^{-4} mol·L^{-1}. The excitation spectra were measured by monitoring the emission wavelength at 616 nm within the scope of 220~450 nm. The emission spectra were determined at room temperature, and the most efficacious excitation wavelength was at 351 nm and 354 nm, respectively, as shown in Fig. 7. And the emission spectra of the compounds are essentially similar. Due to the strong emission intensities of the $^5D_0 \rightarrow ^7F_1$ (around 590 nm) and $^5D_0 \rightarrow ^7F_2$ (around 618 nm) transitions, the two compounds emit the orange light. The emission spectra show five typical emission bands at 580, 593, 618 nm, 650 nm and 705 nm, corresponding to the $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ transitions of the Eu^{3+} ion, respectively. Among them the luminescence intensity of $^5D_0 \rightarrow ^7F_2$ transition is the strongest for the both compounds. It can be seen from Fig. 7 that the two compounds present characteristic and strong luminescent emission. The emission intensity of Gd^{3+}/Eu^{3+} compound is much stronger than that of the undoped europium compound. Furthermore, the positions of Eu^{3+} emission bands in the Gd^{3+}/Eu^{3+} compound do not change but exhibit different splits of the emission bands, indicating that the symmetry around the emitting ion is different from the Eu^{3+} compound. This is because that adding Gd^{3+} may increase in the point symmetry, change the energy level and the micro-environment of Eu^{3+}.[41, 42]

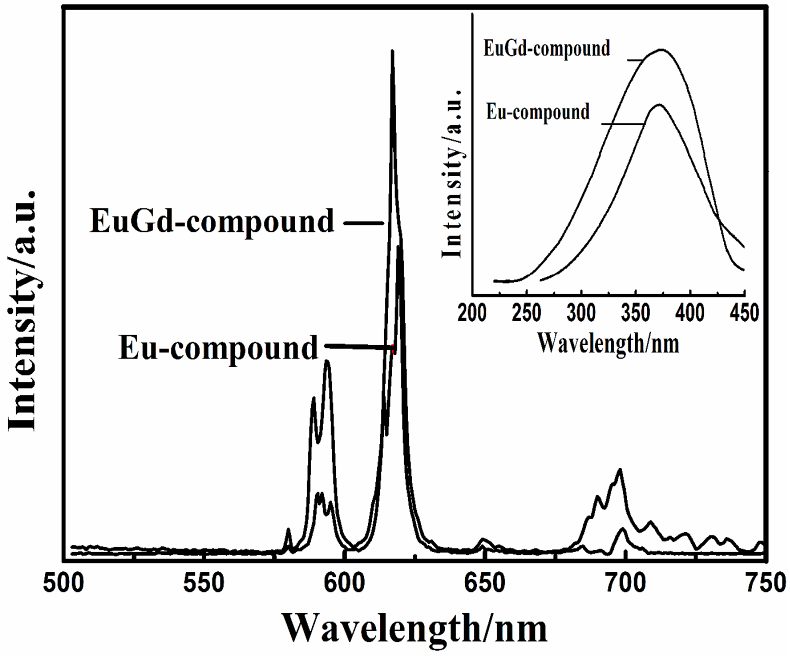

Fig. 7 Luminescence emission spectra of the compounds with the excitation spectra as inset

The luminescence lifetime of the compounds was determined, and their data were shown in Table 3, and corresponding luminescence decay curves and fit curves are shown in Fig. 8. The decay profile is well reproduced by a single exponential $Ln(I(t)/I_0 = -k/t = -t/\tau$ (I_0 is initial luminescence intensity, τ is the luminescence lifetime), indicating that all Eu^{3+} ions occupy the same average coordination environment.[19, 43] The luminescence lifetime of Gd^{3+}/Eu^{3+} compound is longer than that of the Eu^{3+} compound. Also, the lifetime (typically>1.0 ms) is much longer than the reported values in the literatures,[19, 24, 44-47] which indicating that doping Gd^{3+} ion not only enhances the luminescence efficiencies of Eu^{3+} ions but also prolongs the luminescence lifetimes.

Table 3 Luminescent lifetime and χ^2 of the compounds

Compound	Luminescent lifetime (μs)	χ^2
1	573.60	0.990
2	1606.70	0.994

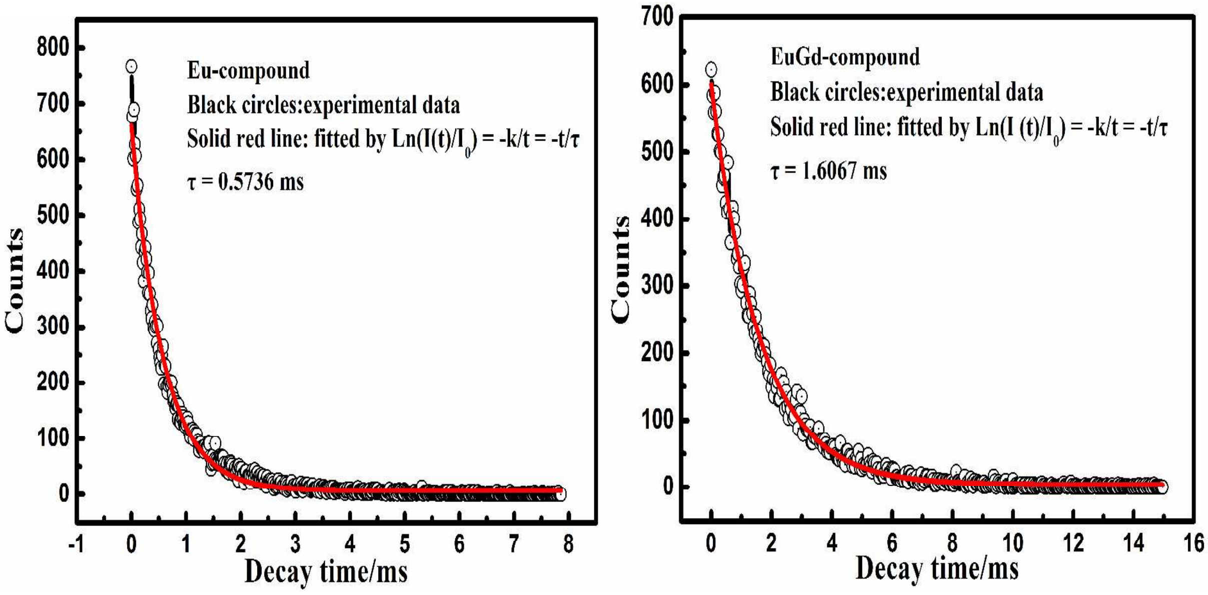

Fig. 8 Luminescence decay and fit curves for the compounds

The typical curves of the Eu^{3+} compounds were measured and have been fitted well into a single exponential function. Assuming that only nonradiative and radiative processes are essentially involved in the depopulation of the $^5D_0$ state, and according to the emission spectra and lifetime of Eu^{3+} (τ, $^5D_0$), the emission quantum efficiency (η) can be calculated. The η can be defined as follows:[48-50]

$$\eta = \frac{A_{rad}}{(A_{rad} + A_{nrad})} \qquad (1)$$

Where A_{rad} and A_{nrad} are radiative and nonradiative transition rates, respectively. A_{rad} can also be obtained by summing over the radiative rates A_{0J} for each $^5D_0 \rightarrow {}^7F_J$ (J = 0-4) transition of Eu^{3+}:

$$A_{\mathrm{rad}} = \sum A_{0J} = A_{00} + A_{01} + A_{02} + A_{03} + A_{04} \qquad (2)$$

In the above Eq. (2), A_{0J} can be calculated from the following equation:

$$A_{0J} = A_{01}\left(\frac{I_{0J}}{I_{01}}\right)\left(\frac{\nu_{01}}{\nu_{0J}}\right) \qquad (3)$$

Here, A_{0J} is the experimental coefficients of spontaneous emission. A_{01} is the Einstein's coefficient of spontaneous emission between the $^5D_0$ and $^7F_1$ energy levels. A_{01} can be determined to be about 50 s^{-1}, which can be considered as a reference for the whole spectra.[51] I_{0J} corresponds to the intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions (J = 0-4). I_{01} corresponds to the intensity of transition $^5D_0 \rightarrow {}^7F_1$ with ν_{0J} ($\nu_{0J} = 1/\lambda_J$) energy centers, respectively.

The lifetime (τ), radiative (A_{rad}), and nonradiative (A_{nrad}) transition rates are related via the following equation:

$$A_{tot} = \left(\frac{1}{\tau}\right) = A_{\mathrm{rad}} + A_{nrad} \qquad (4)$$

On the basis of the above four equations, the quantum efficiencies of the two kinds of europium compounds are calculated and shown in Table 4. It can be seen that the quantum efficiencies (η) of the compounds mainly depend on the values of two factors: one is lifetimes (τ) and the other is I_{02}/I_{01}. As can be seen from Table 4, the quantum efficiency of Gd^{3+}/Eu^{3+} compound is higher than that of europium compound, which shows that the inert rare earth ion Gd^{3+} may greatly sensitize the luminescence of europium compound. Compared with some europium complexes reported (the quantum efficiencies are typically in the range of 1 – 25%), [17, 52] the quantum efficiency of the Gd^{3+}/Eu^{3+} compound reported here is much higher.

Table 4 Luminescence data of the compounds

	1	**2**
υ_{00}(cm^{-1})	17241	17241
υ_{01}(cm^{-1})	16949	16949
υ_{02}(cm^{-1})	16155	16207
υ_{03}(cm^{-1})	14306	14306
I_{01}	603	1475

I_{02}	2808	4595
I_{02}/I_{01}	4.66	3.12
τ (μs)	573.60	1606.70
$1/\tau$ (μs)$^{-1}$	1743.38	622.39
A_r	319.00	252.45
A_{nr}	1424.38	369.94
η (%)	18.30	40.56

Above all, the two compounds behave strong luminescent intensity, and the Gd^{3+}/Eu^{3+} compound presents different splits of the emission band, show stronger luminescent intensity, longer lifetimes and higher quantum efficiencies compared with undoped compound.

In general, the sensitization way in luminescent europium series compounds is composed by the following process. First, the ligands are excited into their excited singlet states, followed by intersystem crossing of the ligands to their triplet states and energy transfer from the triplet state to the ^5D_J (J=0~4) of the Eu^{3+} ion. And then internal conversion to the emitting $^5D_0$ state and transition to the ground state takes place.[53-54] The electron transitions from the higher excited states, such as $^5D_3$ (24800 cm^{-1}), $^5D_2$ (21200 cm^{-1}) and $^5D_1$ (19000 cm^{-1}), to $^5D_0$ (17500 cm^{-1}) are feasible by internal conversion, and most of the photophysical processes occur in this course. Therefore, the two europium compounds give rise to typical Eu(Ш) emission bands at about 580, 590, 650, 614 and 700 nm, which are corresponding to the deactivation of the excited state $^5D_0$ to the ground states ^7F_J(J=0-4). The two compounds behave excellent luminescence properties. This phenomenon may result from the following reasons. (1) The difference between the triplet state of the ligand and $^5D_0$ of Eu^{3+} is one of the important factors which can affect the luminescent properties of the europium complexes. The triplet energy level of the anion ligand HPOA (22500 cm^{-1}) and the neutral ligand TPTZ (21277 cm^{-1}) is higher than the lowest energy level of Eu^{3+} (17500 cm^{-1}),[55] therefore, the energy absorbed by the ligands can effectively transfer to Eu^{3+}. (2) It can be seen from the crystallographic data and IR spectra of the compounds that as a bridging ligand, HPOA ligand links with Eu^{3+} ions in the homonuclear, and Eu^{3+} ions and Gd^{3+} ions in the heteronuclear compound, which may help the intermolecular energy transfer from the ligands to emitting ions. (3) TPTZ could make coordination saturation of Eu^{3+} ions and increase steric hindrance of the compounds. As a result, no water molecules are involved in the coordination of central metal ions, and luminescence quenching effect induced by water molecules can be effectively reduced.[56] As compared with the Eu^{3+} compound, the Gd^{3+}/Eu^{3+} compound exhibits superior luminescence properties, which is mainly due to that high concentration of Eu^{3+} ions leads to the concentration quenching in the undoped europium compound. The introduction of Gd^{3+} can largely dilute the Eu^{3+} ions, which can decrease the concentration quenching. Also, the addition of Gd^{3+} would increase the point symmetry of the compound which decreases the relaxation of Laporte's and decreases the oscillator strengths of transitions, thus can increase the lifetime.[42] There might be other reasons leading to the above mentioned phenomena.[57-60] Further investigations need to be conducted in our laboratory.

4. Conclusion

In summary, two ternary compounds of rare earth ions Eu^{3+} and Gd^{3+}/Eu^{3+} with HPOA and TPTZ have been synthesized, and the triplet energy level of phenoxyacetic acid has been measured to be approximately 22500 cm^{-1}. The structures of the compounds are established by single-crystal X-ray diffraction. Both Gd^{3+} and Eu^{3+} ion in the crystals contain the similar kinds of coordinate environment. Besides, the doped complex is not the physical mixture of europium compound and gadolinium compound, but the formation of heteronuclear compound. The study on the luminescence properties of the two compounds shows that the characteristic luminescence of the corresponding Eu^{3+} is due to the intramolecular energy transfer from the ligands to the central Eu^{3+} ions. And the introduction of Gd^{3+} can largely enhance luminescent intensity, prolong the luminescent lifetime and increase the luminescence quantum efficiency of the compound. Finally, if we can reasonably and effectively introduce the cheap inert rare earth ions, the doped rare earth compounds may find a wide range of applications.

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