

Syntheses and cofluorescence of complexes of Eu(III)/Y(III) with terephthalic acid, 2-thenoyltrifluoroacetone and trioctylphosphine oxide

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Abstract: A series of Eu(III)/Y(III) complexes of terephthalic acid(TPA) with 2-thenoyltrifluoroacetone(HTTA) and trioctylphosphine oxide(TPPO) were synthesized. Compositions of these complexes are revealed to be $\text{Eu}_{2(1-x)}\text{Y}_{2x}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ or $\text{Eu}_{1-x}\text{Y}_x(\text{TPA})(\text{TTA})(\text{TPPO})_2$. Their IR spectra, fluorescent spectra and the thermal and optical stability were studied. The fluorescent excitation spectra of these complexes show more broad excitation bands than those of $\text{Eu}_2(\text{TPA})_3(\text{TPPO})_4$ and $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$ corresponding to their formations. In addition, both the binuclear complex $\text{EuY}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ and the chain complex $\text{Eu}_{0.4}\text{Y}_{0.6}(\text{TPA})(\text{TTA})(\text{TPPO})_2$ present higher thermal stability and better optical stability than the mononuclear complex $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$ does. And their thermal and optical stabilities are preferably interpreted from the binuclear structure together with the chain polynuclear structure of the complexes. The fluorescence enhancement of cofluorescence Y^{3+} ions to the Eu(III) complexes is clear. The optimum content of Y^{3+} is 0.6 (molar fraction) for the chain complexes $\text{Eu}_{1-x}\text{Y}_x(\text{TPA})(\text{TTA})(\text{TPPO})_2$ and 0.5 for the binuclear complexes $\text{Eu}_{2(1-x)}\text{Y}_{2x}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$. The formation of polynuclear structure of the complex $\text{Eu}_{1-x}\text{Y}_x(\text{TPA})(\text{TTA})(\text{TPPO})_2$ appears to be responsible for the good cofluorescence effect of Y^{3+} ions.

Key words: cofluorescence; europium; terephthalic acid; 2-thenoyltrifluoroacetone; trioctylphosphine oxide

1 Introduction

The organic complexes of rare earth ions having strong luminescent intensity, which have been found important application in light conversion events[1–2], are primarily attributed to both the unique electronic structure of rare earth ions and the antenna effect of organic ligands[3]. Generally, the fluorescence enhancement can be achieved through ligand sensitization. In this process, ultraviolet light is firstly absorbed by the organic ligands, then the absorbed energy may be transferred to the emitting rare earth ions and makes them emit their characteristic light. Organic ligands usually have a broad absorption band in the region of near ultra-violet. If the energy level of the triplet state of the ligand matches well with the emission energy level of rare earth ions, these will result in the

great increase in luminescent intensity of rare earth ions[4–9]. In addition, the fluorescence enhancement can also be realized by the use of the photo-inertia lanthanide ions, such as Y^{3+} , Gd^{3+} and La^{3+} [10–13]. In the presence of these ions, the fluorescence enhancement of some lanthanide complexes can be obtained. This process is referred to cofluorescence, which was extensively studied in the mononuclear complexes of europium(III) ions with β -diketones ligands, such as $\text{Eu}(\text{TTA})_3\text{Phen}$ [10] and $\text{Eu}(\text{TTA})_3\text{TPPO}_2$ [14].

Recently, the syntheses and luminescent properties of the mononuclear complexes of europium(III) with 2-thenoyltrifluoroacetone(HTTA) and trioctylphosphine oxide(TPPO) were studied[1,14]. However, the studies on syntheses and luminescent properties of Eu(III)/Y(III) complexes of 2-thenoyltrifluoroacetone with terephthalic acid (TPA) and trioctylphosphine oxide have not been reported yet.

In this paper, the bridging ligand, terephthalic acid, is reported to be used to link Eu(III)/Y(III) ions to form the binuclear complexes $\text{Eu}_{2(1-x)}\text{Y}_{2x}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ and chain polynuclear complexes $\text{Eu}_{1-x}\text{Y}_x(\text{TPA})(\text{TTA})(\text{TPPO})_2$. The thermal and optical stability and fluorescent properties of above-mentioned complexes were studied, and the fluorescence enhancement of cofluorescence Y^{3+} ion for the Eu(III) complexes was also investigated.

2 Experimental

2.1 Reagents and apparatus

99.99% Eu_2O_3 and 99.98% Y_2O_3 were purchased from Jiangxi South Rare Earth Metals Institute of China. 2-thenoyltrifluoroacetone(HTTA), terephthalic acid (TPA), trioctylphosphine oxide(TPPO) and other reagents were all analytical grade and used without further purification.

C, H analyses were performed on an American Perkin-Elmer 2400 II CHNSLO elemental analyzer. The contents of the rare earth were determined by complexometric titration with EDTA. The infrared spectra were measured at room temperature on Nicolet-550 spectrophotometer (American Perkin-Elmer) using KBr pellets in the spectral range of 4 000–400 cm^{-1} . The scanning electronic microscopy(SEM) was obtained in a microscope JSM-5600LV along with the gold sputtering technique. Differential thermoanalysis (DTA) was performed in a SHDT-40 thermo-analyticmeter using aluminum crucibles with 18.40 mg of sample, under dynamic synthetic air atmosphere (40 mL/min) and heating rate of 10 $^{\circ}\text{C}/\text{min}$ in the temperature range of 30–600 $^{\circ}\text{C}$. The thermogravimetric (TG) curves were recorded with a thermobalance model SHDT-40 in the temperature interval of 30–600 $^{\circ}\text{C}$, using platinum crucibles with 18.0 mg of sample, under dynamic synthetic air atmosphere (40 mL/min) and heating rate of 10 $^{\circ}\text{C}/\text{min}$. A Hitachi F-4500 Spectrometer was used to record excitation and emission spectra of the complex powders. The bandwidth of monochromators was set at 2.5 nm for both excitation and emission.

2.2 Synthesis of complexes

The complex $\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$ was prepared in the following steps. In the first step, standard solution of europium(III) ($1.0 \times 10^{-1} \text{ mol/L}$) was prepared by dissolving Eu_2O_3 in hot hydrochloric acid, evaporating up to syrup and diluting with ethanol to a desired volume. HTTA, TPA and TPPO were dissolved separately in ethanol with molar ratio of 1:1:2. Subsequently the EuCl_3 and HTTA solutions were mixed with molar ratio of 1:1, adjusting pH values to 5.5, stirred and refluxed for 0.6 h

keeping temperature in water-bath. Then according to molar composition of formula $\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$, TPA and TPPO solutions were added dropwise, keeping pH value at 6.5, stirred and refluxed until appearance of a pale yellow precipitate. The solid product was filtered, washed with ethanol and distilled water successively, recrystallized in ethanol, and dried in a vacuum oven.

The $\text{Eu}_2(\text{TPA})_3(\text{TPPO})_4$ and $\text{Eu}_2(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ complexes were prepared by similar process as $\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$, except that the product for $\text{Eu}_2(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ was a yellow precipitate.

The complexes $\text{Eu}_{2(1-x)}\text{Y}_{2x}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ and $\text{Eu}_{1-x}\text{Y}_x(\text{TPA})(\text{TTA})(\text{TPPO})_2$ were prepared by similar process as $\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$, except that the mixture of EuCl_3 and YCl_3 solution was used instead of EuCl_3 . The products obtained were a yellow or pale yellow powder.

The mononuclear complexes $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$, $\text{Eu}_{1-x}\text{Y}_x(\text{TTA})_3(\text{TPPO})_2$ were synthesized by similar process as described in Ref.[1]. The product obtained was a yellow powder.

3 Result and discussion

3.1 Composition of complexes

The rare earth contents were determined by complexometric titration with EDTA. Analytical data of C, H and rare earth contents for complexes are listed in Table 1. The elemental analytical data are consistent with the calculated values of the general formula of the Eu(III) complexes.

3.2 Characterization of complexes

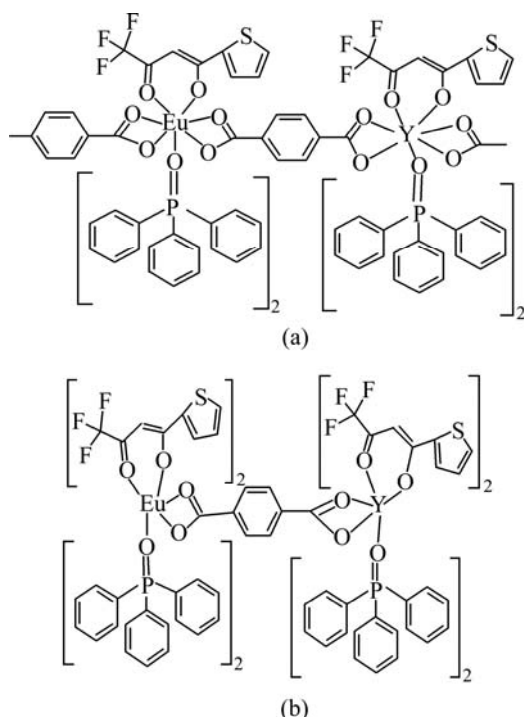
Some results of IR spectra are shown in Table 2. The presence of carboxylate groups in the complexes was definitely confirmed by both the asymmetric stretching bands at 1 541–1 558 cm^{-1} and the symmetric stretching at 1395–1405 cm^{-1} . The differences (Δ) between $\nu_{\text{as}}(\text{COO})$ peaks and $\nu_{\text{s}}(\text{COO})$ peaks are in the range of 142–156 cm^{-1} in the rare earth complexes, which are attributed to the chelating and bridging coordination modes of carboxylate groups with the rare earth since the difference ($\Delta = \nu_{\text{as}} - \nu_{\text{s}}$) in the rare earth complexes is lower than that in Na_2TPA ($\Delta = 168 \text{ cm}^{-1}$). In addition, owing to the great steric hindrance of the complexes $\text{Eu}_{2(1-x)}\text{Y}_{2x}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ and $\text{Eu}_{1-x}\text{Y}_x(\text{TPA})(\text{TTA})(\text{TPPO})_2$, the bridging coordination of carboxylate groups with the rare earth becomes more difficult than the chelating coordination. Thus, the coordination mode of carboxylate groups with rare earth ions is mainly the chelating coordination mode in these complexes, and the proposed chemical structures for the complexes $\text{Eu}_{0.5}\text{Y}_{0.5}(\text{TPA})(\text{TTA})(\text{TPPO})_2$ and $\text{EuY}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ may be given in Fig.1. The IR spectra

Table 1 Elemental analysis data of complexes (mole fraction, %)

Complex	Rare earth		Carbon		Hydrogen	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
$\text{Eu}_2(\text{TPA})_3(\text{TPPO})_4$	15.76	15.92	60.57	60.33	3.60	3.77
$\text{Eu}(\text{TPA})_3(\text{TPPO})_2$	10.84	11.08	52.31	52.49	3.12	3.06
$\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$	14.03	13.89	56.73	57.05	3.25	3.47
$\text{Eu}_2(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$	12.40	12.33	54.25	54.51	3.17	3.24
$\text{Eu}_{0.4}\text{Y}_{0.6}(\text{TPA})(\text{TTA})(\text{TPPO})_2$	10.96	10.81	59.60	59.09	3.52	3.60
$\text{EuY}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$	9.97	10.03	55.86	55.94	3.46	3.36

Table 2 IR spectra data of some complexes

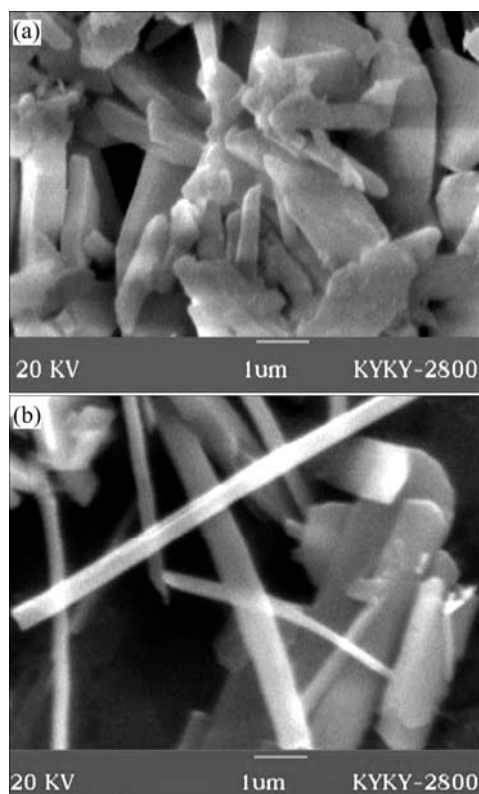
Complex	$\nu_s(\text{COO})/\text{cm}^{-1}$	$\nu_{as}(\text{COO})/\text{cm}^{-1}$	$\Delta(\nu_{as}-\nu_s)/\text{cm}^{-1}$	$\nu_s(\text{CO})/\text{cm}^{-1}$	$\nu(\text{P}=\text{O})/\text{cm}^{-1}$
TTA				1 680	
Na_2TPA	1 395	1 563	168		
TPPO					1 184
$\text{Eu}_2(\text{TPA})_3(\text{TPPO})_4$	1 402	1 558	156		1 152
$\text{Eu}(\text{TTA})_3(\text{TPPO})_2$				1 602	1 153
$\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$	1 395	1 544	149	1 608	1 155
$\text{Eu}_2(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$	1 398	1 541	143	1 599	1 154
$\text{Eu}_{0.5}\text{Y}_{0.5}(\text{TPA})(\text{TTA})(\text{TPPO})_2$	1 403	1 548	146	1 612	1 156
$\text{EuY}(\text{TPA})(\text{TTA})_2(\text{TPPO})_4$	1 405	1 547	142	1 609	1 158

**Fig.1** Chemical structures of complexes $\text{Eu}_{0.5}\text{Y}_{0.5}(\text{TPA})(\text{TTA})(\text{TPPO})_2$ (a) and $\text{EuY}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ (b)

also show the displacement of $\nu(\text{C}=\text{O})$ stretching from about $1\,680\text{ cm}^{-1}$, in free TTA ligand, to approximately $1\,608\text{ cm}^{-1}$ in the complexes, and the displacement of $\nu(\text{P}=\text{O})$ stretching from $1\,184\text{ cm}^{-1}$, in free TPPO ligand, to approximately $1\,155\text{ cm}^{-1}$ in the complexes, indicating that Eu(III)/Y(III) ions are coordinated by the oxygen atoms[15].

The complexes $\text{Eu}_{2(1-x)}\text{Y}_{2x}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$

and $\text{Eu}_{1-x}\text{Y}_x(\text{TPA})(\text{TTA})(\text{TPPO})_2$ present similar configuration, respectively. Fig.2 shows the agglomerated structure of the $\text{Eu}_2(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ complex and the chain/stripe structure of the $\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$ complex. For the binuclear complex $\text{Eu}_2(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$, the formation of the

**Fig.2** SEM images of $\text{Eu}_2(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ (a) and $\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$ (b) complexes

agglomerated structure can be obtained by intermolecular force, while for the $\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$ complex, the chain/stripe presents an infinite configurations, as suggested by the one-dimensional polymeric chain formed.

Fig.3 shows the DTA and TG curves in the temperature range from 50 to 600 °C for the $\text{Eu}_{0.4}\text{Y}_{0.6}(\text{TPA})(\text{TTA})(\text{TPPO})_2$ and $\text{EuY}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$. The DTA curve of the $\text{EuY}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ complex (Fig.3(a)) presents different profile to that of the $\text{Eu}_{0.4}\text{Y}_{0.6}(\text{TPA})(\text{TTA})(\text{TPPO})_2$ complex (Fig.3(b)). $\text{EuY}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ melts at about 213 °C and decomposes approximately in the temperature range from 290 to 385 °C; $\text{Eu}_{0.4}\text{Y}_{0.6}(\text{TPA})(\text{TTA})(\text{TPPO})_2$ melts at about 235 °C and decomposes approximately in the temperature range from 357 to 412 °C, both no decomposition before the melting point. The latter possess better thermal stability than the former. The DTA and TG curves do not present any event relative to water loss, in the interval 50–200 °C, indicating that two complexes are in anhydrous form. This is corroborated by IR spectroscopy and elemental analysis. In addition, the temperature of the thermal decomposition of the mononuclear complex $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$ is approximately in the interval 250 to 330 °C, and the

experiment result corroborates with that reported in Ref.[1]. So the thermal stability for the above mentioned Eu(III) complexes increases in the following order: the mononuclear structure $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$, the binuclear structure $\text{EuY}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$, and the chain polynuclear structure $\text{Eu}_{0.4}\text{Y}_{0.6}(\text{TPA})(\text{TTA})(\text{TPPO})_2$.

3.3 Fluorescent properties of complexes

The fluorescence excitation and emission spectra of the solid state complexes were performed on a Hitachi F-4500 Spectrometer.

The excitation spectra of the Eu(III) complexes, recorded in the spectral range of 220–450 nm by monitoring the emission at the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, are shown in Fig.4. The excitation spectrum of $\text{Eu}_2(\text{TPA})_3(\text{TPPO})_4$ consists of a broad band ranging from 240 to 340 nm with the maximum excitation wavelengths at 327 nm. The excitation spectrum of $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$ shows a strong broad band ranging from 275 to 430 nm with the maximum excitation wavelengths at 383 nm. However, the data of the complexes $\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$ and $\text{Eu}_2(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ exhibit a more broad band with two excitation peaks at about 346 nm and about 366 nm. In addition, in contrast to $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$, the excitation band of TTA in $\text{Eu}_2(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ is shifted to shorter wavelength, and it is the same case for $\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$. This indicates the TTA ligand has different coordination environments in the different complexes. Furthermore, compared with $\text{Eu}_2(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$, the excitation band of $\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$ shows a peak position blue shift. These facts show the presence of the different orientation and different coordination environments for the TPA and TTA ligands in different states, corresponding to the formation of the Eu(III) complexes.

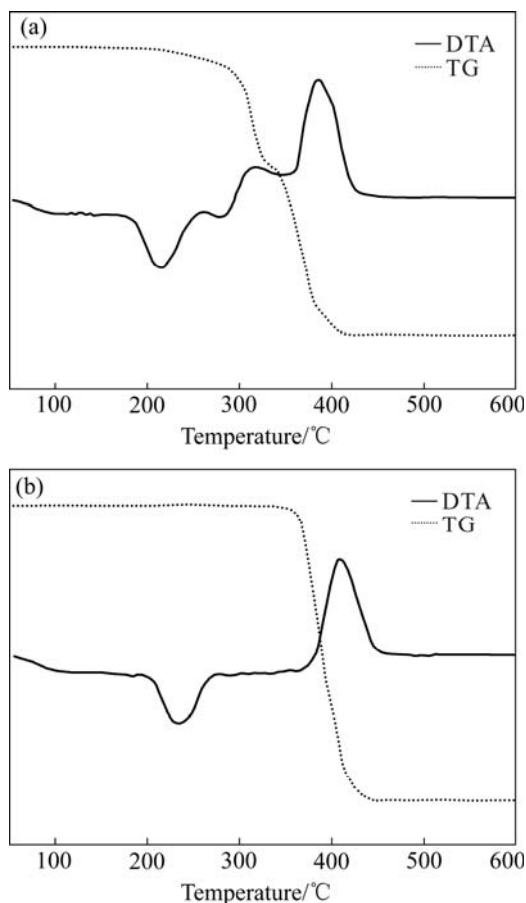


Fig.3 DTA and TG curves of $\text{EuY}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ (a) and $\text{Eu}_{0.4}\text{Y}_{0.6}(\text{TPA})(\text{TTA})(\text{TPPO})_2$ (b) complexes

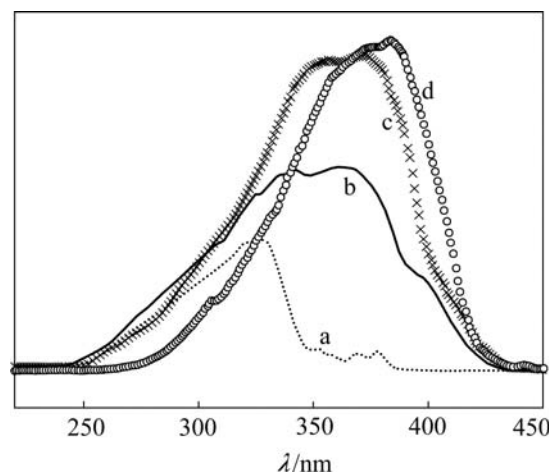


Fig.4 Excitation spectra of complexes $\text{Eu}_2(\text{TPA})_3(\text{TPPO})_4$ (a), $\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$ (b), $\text{Eu}_2(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ (c) and $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$ (d)

The emission spectra were recorded in the range of 550–710 nm with the maximum excitation wavelengths at room temperature, as shown in Fig.5. It is noteworthy that similar emission spectra are observed for the Eu(III) complexes. Five typical Eu(III) emission bands appear approximately at about 583, 594, 616, 653, 703 nm, corresponding to $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$, and $^5D_0 \rightarrow ^7F_4$, respectively. Of all the fluorescent emissions for the Eu(III) complexes, the relative fluorescence intensity of $^5D_0 \rightarrow ^7F_2$ is the strongest.

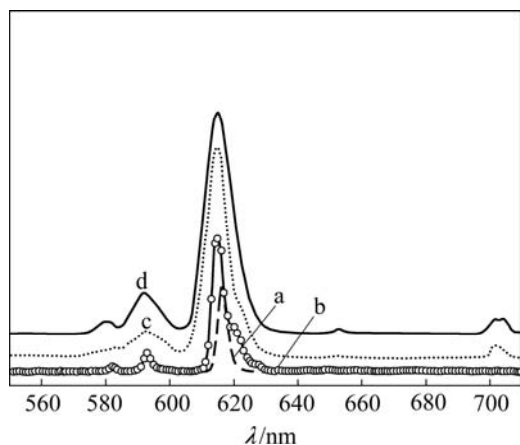


Fig.5 Emission spectra of complexes: (a) $\text{Eu}_2(\text{TPA})_3(\text{TPPO})_4$; (b) $\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$; (c) $\text{Eu}_2(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$; (d) $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$

The data in Table 3 show the relative fluorescence intensity for the interesting Eu(III) complexes studied. And the fluorescence intensity ($^5D_0 \rightarrow ^7F_2$) for the interesting Eu(III) complexes increases in the following order: $\text{Eu}_2(\text{TPA})_3(\text{TPPO})_4$, $\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$, $\text{Eu}_{0.4}\text{Y}_{0.6}(\text{TPA})(\text{TTA})(\text{TPPO})_2$, $\text{Eu}_2(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$, $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$, and $\text{EuY}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$. The results demonstrate that the fluorescence intensity of the Eu(III) complexes is influenced by the structure of complex together with the species and coordination environments of ligand.

The ratios of the relative intensity $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ are also shown in Table 3. By comparison, it can be seen that the symmetry of the new complexes changes much less, i.e. the forced electric dipole

transition ($^5D_0 \rightarrow ^7F_2$) of Eu^{3+} in the complexes is strengthened, and the color purity of the assembly luminescence is significantly improved.

3.4 Effect of cofluorescence Y^{3+} ions on fluorescence intensity

The effects of Y^{3+} , La^{3+} and Gd^{3+} on the fluorescence intensity of the complexes are similar, only the result of Y^{3+} is shown in Fig.6. It can be seen from Fig.6, firstly, that the fluorescence intensity of the complexes $\text{Eu}_{1-x}\text{Y}_x(\text{TPA})(\text{TTA})(\text{TPPO})_2$, $\text{Eu}_{2(1-x)}\text{Y}_{2x}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ and $\text{Eu}_{1-x}\text{Y}_x(\text{TTA})_3(\text{TPPO})_2$ increases with the increment of Y^{3+} content (molar fraction). However, when Y^{3+} content is above 0.6, the fluorescence intensities of the complexes decrease with the increment of Y^{3+} content. But the ability of Y^{3+} for fluorescence enhancement of the Eu(III) complexes is clear. The optimum content of Y^{3+} is 0.6 (molar fraction) for the chain complexes $\text{Eu}_{1-x}\text{Y}_x(\text{TPA})(\text{TTA})(\text{TPPO})_2$, 0.5 for the binuclear complexes $\text{Eu}_{2(1-x)}\text{Y}_{2x}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ and 0.4 for the mononuclear complexes $\text{Eu}_{1-x}\text{Y}_x(\text{TTA})_3(\text{TPPO})_2$. The effect of Y^{3+} on fluorescent enhancement of the above mentioned Eu(III) complexes increases in the following order: $\text{Eu}_{1-x}\text{Y}_x(\text{TTA})_3(\text{TPPO})_2$, $\text{Eu}_{2(1-x)}\text{Y}_{2x}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$, and $\text{Eu}_{1-x}\text{Y}_x(\text{TPA})(\text{TTA})(\text{TPPO})_2$. The ability of Y^{3+} for fluorescence

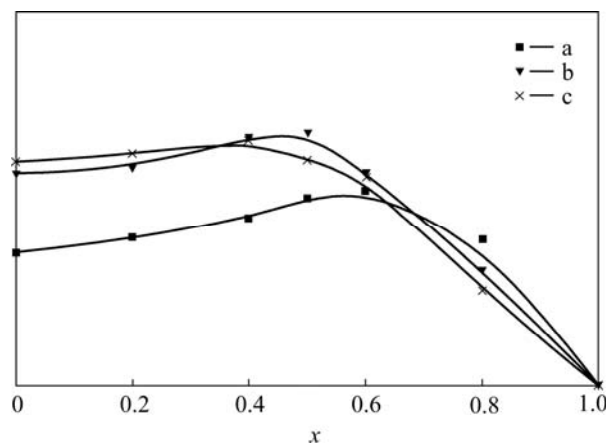


Fig.6 Effect of Y^{3+} content on fluorescence intensity of complexes: (a) $\text{Eu}_{1-x}\text{Y}_x(\text{TPA})(\text{TTA})(\text{TPPO})_2$; (b) $\text{Eu}_{2(1-x)}\text{Y}_{2x}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$; (c) $\text{Eu}_{1-x}\text{Y}_x(\text{TTA})_3(\text{TPPO})_2$

Table 3 Data of fluorescence spectra and ratios of relative intensity $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ for complexes

Complex	$\lambda_{\text{ex}}/\text{nm}$	$\lambda_{\text{ex}}/\text{nm}$ (relative intensity)					$(^5D_0 \rightarrow ^7F_2)/(^5D_0 \rightarrow ^7F_1)$
		$^5D_0 \rightarrow ^7F_0$	$^5D_0 \rightarrow ^7F_1$	$^5D_0 \rightarrow ^7F_2$	$^5D_0 \rightarrow ^7F_3$	$^5D_0 \rightarrow ^7F_4$	
$\text{Eu}_2(\text{TPA})_3(\text{TPPO})_4$	327	583(1.2)	594(5.6)	617(33.8)			6.3
$\text{Eu}(\text{TTA})_3(\text{TPPO})_2$	383	582(5.5)	593(17.1)	616(89.7)	653(2.3)	703(6.4)	5.2
$\text{Eu}(\text{TPA})(\text{TTA})(\text{TPPO})_2$	366	583(2.0)	594(7.5)	616(53.6)	653(0.8)	703(2.7)	7.1
$\text{Eu}_2(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$	370	583(4.6)	594(11.1)	616(85.2)	653(1.4)	703(5.6)	7.7
$\text{Eu}_{0.4}\text{Y}_{0.6}(\text{TPA})(\text{TTA})(\text{TPPO})_2$	369	583(3.5)	594(9.4)	616(78.5)	653(1.1)	703(3.9)	8.3
$\text{EuY}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$	372	583(6.3)	594(12.8)	616(101.4)	653(2.7)	703(8.6)	7.9

enhancement of the above mentioned Eu(III) complexes may be concerned with the mononuclear, binuclear and chain structure of the complexes.

3.5 Optical stability of complexes

Some optical stability tests were also carried out using 360 nm ultraviolet light for complexes $\text{EuY(TPA)(TTA)}_4(\text{TPPO})_4$, $\text{Eu}_{0.4}\text{Y}_{0.6}(\text{TPA})(\text{TTA})(\text{TPPO})_2$ and $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$.

It can be seen in Fig.7 that the optical stability of the Eu(III) complexes increases in this order: mononuclear structure $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$, binuclear structure $\text{EuY(TPA)(TTA)}_4(\text{TPPO})_4$, and chain structure $\text{Eu}_{0.4}\text{Y}_{0.6}(\text{TPA})(\text{TTA})(\text{TPPO})_2$.

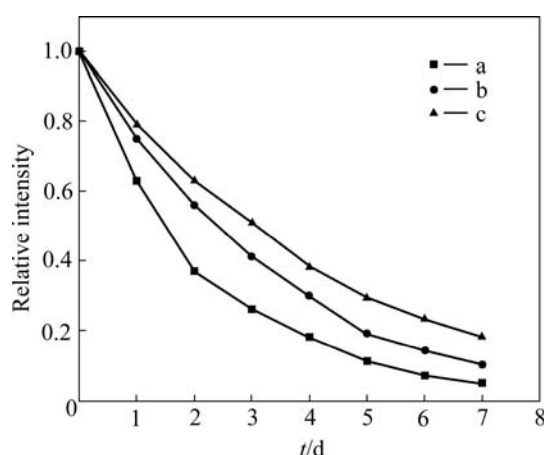


Fig.7 Changes of fluorescence intensity with irradiation time for complexes: (a) $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$; (b) $\text{EuY(TPA)(TTA)}_4(\text{TPPO})_4$; (c) $\text{Eu}_{0.4}\text{Y}_{0.6}(\text{TPA})(\text{TTA})(\text{TPPO})_2$

4 Conclusions

1) A series of relative cheap light conversion complexes of Eu(III)/Y(III) with 2-thenoltrifluoroacetone, terephthalic acid and trioctylphosphine oxide, showing the good thermal and optical stability together with strong red fluorescence, were synthesized. Compositions of these complexes are revealed to be $\text{Eu}_{2(1-x)}\text{Y}_{2x}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ or $\text{Eu}_{1-x}\text{Y}_x(\text{TPA})(\text{TTA})(\text{TPPO})_2$ ($x=0-1$).

2) The thermal and optical stability for the Eu(III) complexes increases in the following order: mononuclear complex $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$, binuclear complex $\text{EuY(TPA)(TTA)}_4(\text{TPPO})_4$, and chain complex $\text{Eu}_{0.4}\text{Y}_{0.6}(\text{TPA})(\text{TTA})(\text{TPPO})_2$. The formation of the binuclear/chain polynuclear structure of the complexes appears to be responsible for the enhancement of the thermal and optical stability of the complexes.

3) The fluorescence enhancement of the Eu(III)

complexes can be obtained by the addition of relative cheap Y^{3+} ions. The optimum content of Y^{3+} is 0.6 (molar fraction) for the chain polynuclear complexes $\text{Eu}_{1-x}\text{Y}_x(\text{TPA})(\text{TTA})(\text{TPPO})_2$, 0.5 for the binuclear complexes $\text{Eu}_{2(1-x)}\text{Y}_{2x}(\text{TPA})(\text{TTA})_4(\text{TPPO})_4$ and 0.4 for the mononuclear complexes $\text{Eu}_{1-x}\text{Y}_x(\text{TTA})_3(\text{TPPO})_2$.

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