Fluorescence Properties of Ternary Complexes of Polymer-Bond Triphenylphosphine, Triphenylarsine, Triphenylstibine, and Triphenylbismuthine, Rare Earth Metal Ions, and Thenoyltrifluoroacetone

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ABSTRACT: Rare earth metal ions containing polymer ternary complexes were synthesized and characterized. The functional polymers investigated were polymer-bond triphenylphosphine (PBDP), polymer-bond triphenylarsine (PBDAs), polymer-bond triphenylstibine (PBDSb), and polymer-bond triphenylbismuthine (PBDBi) as polymer ligands. Several substances, such as thenoyltrifluoroacetone (TTA), and 8-hydroxyquinoline (oxin), phenanthroline (phen) were used as low molecular weight ligands. The results show that TTA is the best low molecular weight ligand among them. The fluorescence properties of synthesized complexes were investigated; PBDAs is a better polymer ternary complex that possesses stronger fluorescence intensity coordinated with any low molecular weight ligand. The fluorescence lifetimes of Eu^{3+}-containing polymer ternary complexes are between 0.350 and 0.469 MS. The reaction conditions of the formation and stability of rare earth metal ions—polymer—TTA ternary complexes are discussed. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1605–1611, 1998

Key words: fluorescence; europium; polymer ternary complexes

INTRODUCTION

In the past decades research on the synthesis of rare earth metal containing polymers has attracted a great deal of interest because of their potential applications for fluorescence, laser systems, magnetic and optical materials, and so on.[1-4] We have reported the synthesis, characterization, and fluorescence properties of Eu^{3+}–polymer ligand–thenoyltrifluoroacetone (TTA; where the polymer ligands were PBMAS, PBAAS, and PBAHBAS.[5] In this article we are reporting on the synthesis, characterization, and fluorescence properties of rare earth (Eu, Sm, Tb) ions–polymer ligand–TTA where the polymer ligands are polymer-bond triphenylphosphine (PBDP), polymer-bond triphenylarsine (PBDAs), polymer-bond triphenylstibine (PBDSb), and polymer-bond triphenylbismuthine (PBDBi).

EXPERIMENTAL

Materials

High purity (99.99%) Eu_2O_3, Sm_2O_3, and Tb_2O_3 were purchased from Shanghai Yao Long Chemical Factory. Polymer (*p*-chloromethyl styrene) (PBCS) (Naikai University, crosslink density 6%, Cl content 17.6 wt %) was ground to a fine powder (200 mesh) before reaction. Polymer ligands such as polymer-bond triphenylphosphine (PBDP), polymer-bond triphenylarsine (PBDAs), polymer-bond triphenylstibine (PBDSb), and polymer-

Table I   IR Data of Complexes and Corresponding Ligands

No.	Substance	$\nu_{C=O}$ (cm^{-1})	ν_{M-O} (cm^{-1})	ν_{P-C} (cm^{-1})	ν_{P-ph} (cm^{-1})	ν_{As-C} (cm^{-1})	ν_{As-ph} (cm^{-1})
1	TTA	1659					
2	Eu(TTA)$_4$	1605	440				
3	PBDP			739.694	1434		
4	PBDP–Eu(TTA)$_4$	1606	431	606	1403		
5	PBDAs					732.693	1432
6	PBDAs–Eu(TTA)$_4$	1606	430			602	1402

bond triphenylbismuthine (PBDBi) were pre-pared from PBCS by the method described in the literature.[6] The other chemicals were pure.

Synthesis of Ternary Complexes

One gram of Ln$_2$O$_3$ (Ln = Eu, Sm, Tb) was dissolved in 7 mL of concentrated hydrochloric acid and the mixtures were evaporated to dryness; then ethanol was added to the LnCl$_3$ crystals. A calculated weight of TTA was solved in distilled benzene and was then diluted into a needed volume. A 7-mL solution of LnCl$_3$ (0.4 mmol Ln^{3+}) in ethanol was dripped into a 25-mL Florence flask containing the needed volume of TTA solution. The pH of the mixture solution was adjusted to neutrality (pH 6) by an ethanol solution of NaOH and moved to a three-necked flask. Then a calculated amount of polymer ligand weight was added. The mixture was stirred and refluxed for 8–10 h and evaporated to dryness; the products were filtered, washed with ethanol 3–4 times, and then dried under a vacuum at room temperature for 24 h. The structure of the ternary complexes are as follows:

L = P, As, Sb, Bi
Ln^{3+} = Eu^{3+}, Tb^{3+}, Sm^{3+}
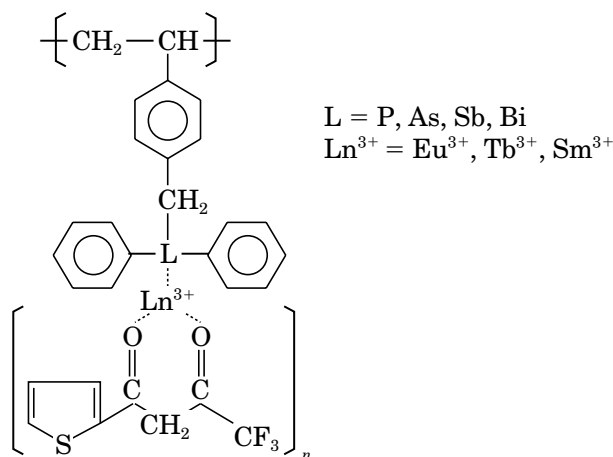
Apparatus

IR spectra were recorded on a Perkin–Elmer PE-983 infrared spectrophotometer, and X-ray photoelectron spectroscopy (XPS) spectra were obtained using a Perkin–Elmer PIII-550/SA instrument. The absorption spectra were measured with a Shimadzu UV-300 automatic recording spectrophotometer. The fluorescence

Table II   XPS Data

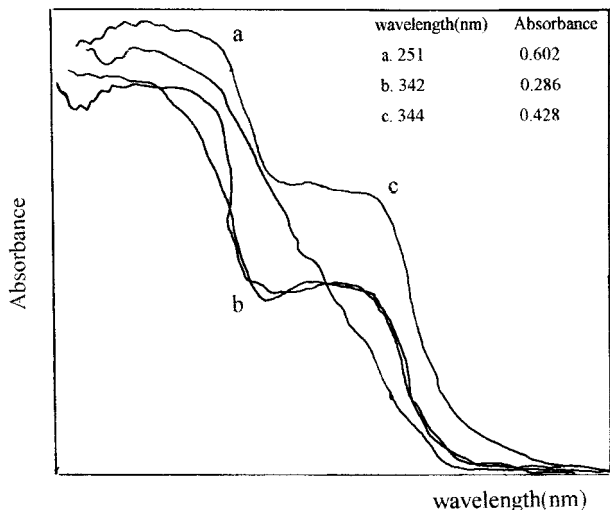| No.	Substance	XPS Peak	Binding Energy, E_b (cV)	ΔE_b (cV)
1	Eu$_2$O$_3$	Eu($3d5/2$)	1136.1	0.0
2	Eu(TTA)$_4$	Eu($3d5/2$)	1134.1	−2.0
3	PBDP	P($2p$)	133.2	
4	PBDAs	As($3d$)	42.7	
5	PBDP–Eu	Eu($3d5/2$)	1135.0	−1.1
		P($2p$)	133.2	
6	PBDP–Eu(TTA)	Eu($3d5/2$)	1135.7	−0.4
		P($2p$)	133.5	+0.3
7	PBDAs–Eu	Eu($3d5/2$)	1134.9	−1.2
		As($3d$)	44.1	+1.4
8	PBDAs–Eu(TTA)	Eu($3d5/2$)	1133.9	−2.2
		As($3d$)	44.9	+2.2

Figure 1   UV-DRS spectra of (a) PBDAs, (b) PBDAs–Eu(III), (c) PBDAs–Eu(III)–(TTA)$_4$.

spectra were obtained at room temperature with an Hitachi MPF-4 spectrofluorimeter equipped with a high-pressure xenon lamp and data processor. The fluorescence lifetime measurements were made on a QJD-9 laser induced fluorescence spectrophotometer.
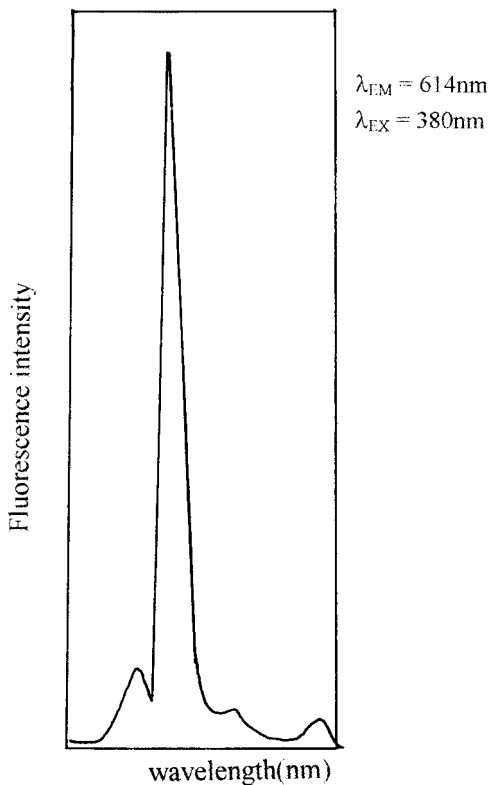
Table III   Fluorescence Intensity of Complex Systems

Complexes	Excitation (nm)	Emission (nm)	Rel. I
PBDP–Eu	380	614	7.0
PBDAs–Eu	379	614	9.0
PBDSb–Eu	373	614	1.9
PBDBi–Eu	375	614	5.8
PBDP–Eu(TTA)$_2$	380	614	34
PBDAs–Eu(TTA)$_2$	380	614	300
PBDSb–Eu(TTA)$_2$	380	614	155
PBDBi–Eu(TTA)$_2$	380	614	90

pH 6, slit ex/em = 10 (nm): ordinate scale × 1. Rel. I, relative intensity.

RESULTS AND DISCUSSION

Characterization

IR spectra results are shown in Table I. The absorption peaks of the ternary complexes are shifted to a lower frequency (from 1659 to 1606 cm^{-1}) indicating the formation of the Eu^{3+}–polymer ligand–TTA ternary complexes.

XPS measurement data are listed in Table II.

Figure 2   The emission spectra of Eu^{3+}–polymer–TTA ternary complexes.
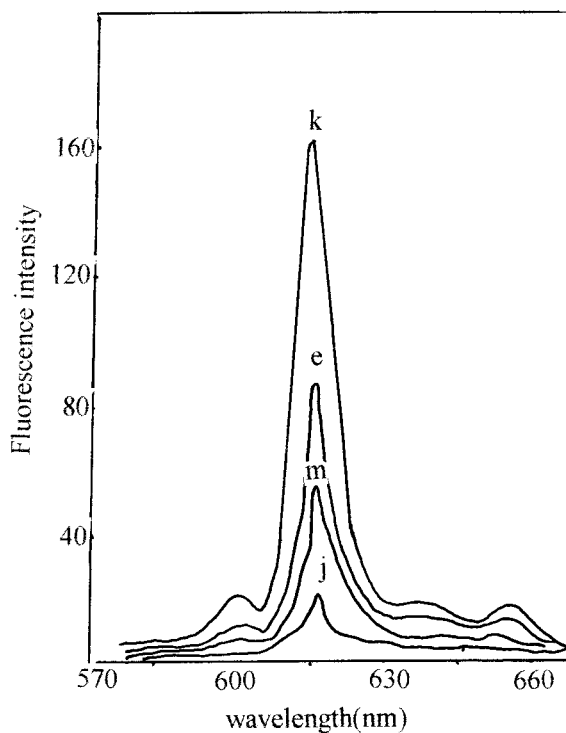

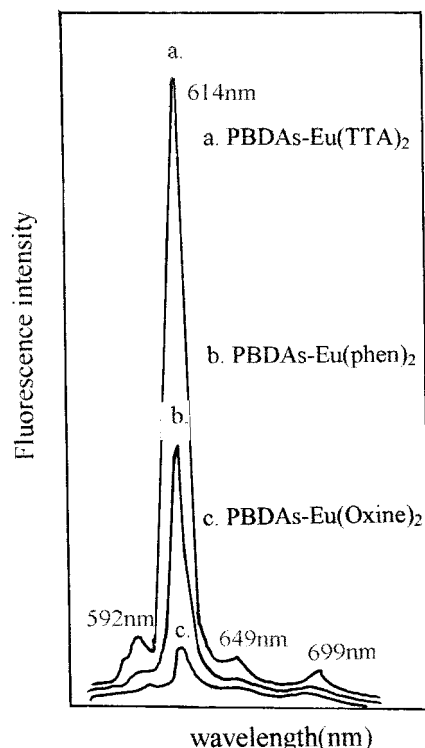**Figure 3**   The emission spectra of different polymer ligand Eu^{3+}-containing ternary complexes.

Figure 4 The emission spectra of different low molecular weight ligand Eu^{3+}-containing ternary complexes.

The binding energies of $Eu(3d5/2)$ in both binary and ternary complexes were lowered. These findings clearly provide evidence for the formation of complexes. The results in Table II show that $Eu(3d5/2)$ binding energy in complexes 5–8 were decreased 1.1, 0.4, and 2.2 eV, respectively, compared with that in Eu_2O_3. These changes indicate that the complex of As with Eu was more stable than the complex of P with Eu.

Fluorescence Properties

Figure 1 shows the absorption spectra of PBDAs, PBDAs–Eu(III), and PBDAs–Eu(III)–$(TTA)_4$.

Table IV   Fluorescence Intensity of Low Molecule Weight Ligands

Complexes	Excitation (nm)	Emission (nm)	Rel. I
PBDP–Eu(TTA)$_2$	380	614	34
PBDP–Eu(phen)$_2$	374	614	3.67
PBDP–Eu(Oxine)$_2$	393	614	0.35
PBDAs–Eu(TTA)$_2$	379	614	300
PBDAs–Eu(Oxine)$_2$	379	614	130
PBDAs–Eu(phen)$_2$	380	614	10

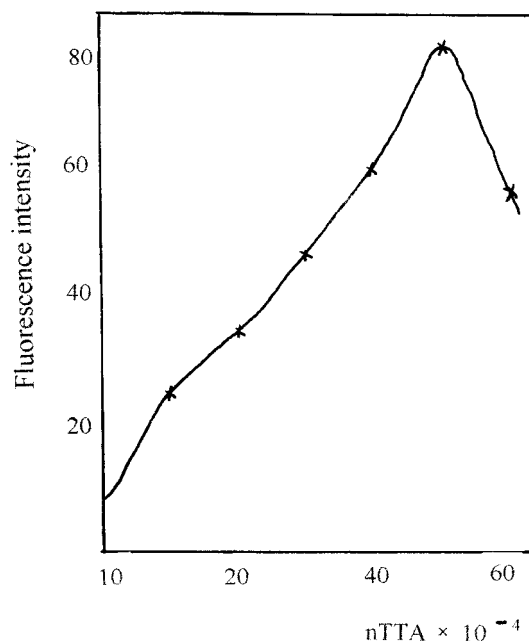pH 6, slit ex/em = 10 (nm): ordinate scale $\times$ 1. Rel. I, relative intensity.

Figure 5 The relationship between fluorescence intensity and the molar ratio of TTA/Eu(III) in the reaction.

The absorption peaks are red shifted from $251 \rightarrow 342 \rightarrow 344$ nm. The 0.428 absorbance of (c) was much higher than that of (b).

The formation of polymer ternary complexes enhanced the fluorescence intensity of the rare earth ions because of the formation of a planar conjugate rigid structure, and the polymer ligand played a role in the immobilization. Variant polymer ligands have different enhancement effects on the fluorescence intensity of rare earth ions. The orange-red fluorescence was observed for all Eu^{3+}-containing complexes. PBDAs was the best ligand. It can form stronger fluorescence ternary complexes with any low molecular weight ligands and rare earth ions.

Table V   Relationship Between Fluorescence Emission Intensity of TTA/Eu(III) Molar Ratio

Complexes	Excitation (nm)	Emission (nm)	Rel. I
PBDP–Eu(TTA)$_2$	380	614	34.0
PBDP–Eu(TTA)$_3$	380	614	46.0
PBDP–Eu(TTA)$_4$	380	614	59.0
PBDP–Eu(TTA)$_5$	380	614	78.5
PBDP–Eu(TTA)$_6$	380	614	54.9

pH 6, slit ex/em = 10 (nm): ordinate scale $\times$ 1. Rel. I, relative intensity.

Table VI   Fluorescence Properties of Different Rare Earth Metal Ions Containing Ternary Complexes

Complexes	Excitation (nm)	Emission (nm)	f	Rel. I
PBDP–Eu(TTA)$_2$	380	614		34
PBDP–Tb(TTA)$_2$	/	/	1	/
PBDP–Sm(TTA)$_2$	321	645		1.0

Rel. I, relative intensity.

The emission peak at 614 nm (Fig. 2, Table III) corresponds to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} (electric dipole transition that is sensitive to the crystalline field). There were high resolution excitation spectra in the region of the $^5D_0-{}^7F_j$ transition.[8] The emission peaks at 592 and 648 nm correspond to the $^5D_1-{}^7F_j$ transition of Eu^{3+}; this is the magnetic dipole transition, which is insensitive to the crystalline field. They are weaker. Different systems and reaction conditions affect the change in fluorescence properties of polymer rare earth metal complexes.

Measurements were made for the fluorescence of polymer binary and ternary complexes. The results of the fluorescence intensity measurements
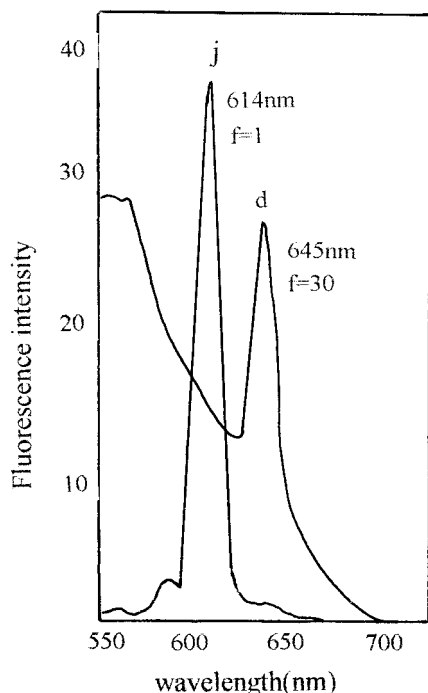
Figure 6   Emission spectra of different rare earth metal ions–polymer–TTA complexes: (j) PBDP–Eu(TTA)$_2$; (d) PBDP–Sm(TTA)$_2$.
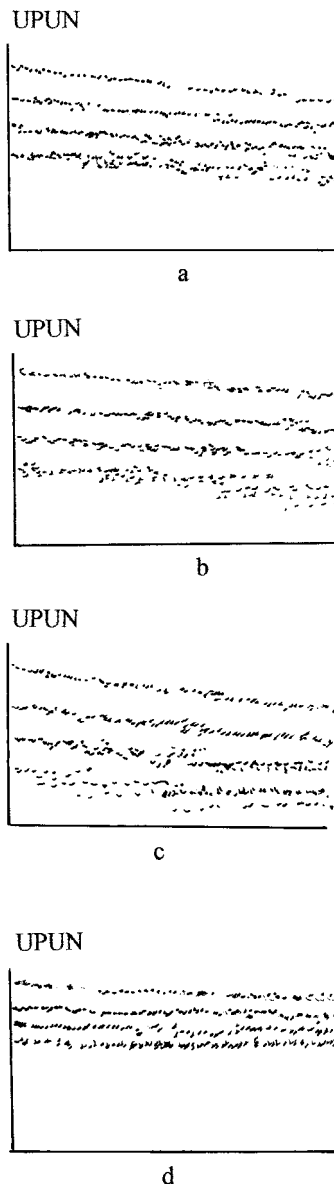
Figure 7   The fluorescence decay curve of the ternary complexes: (a) PBDAs–Eu(TTA)$_2$, (b) PBDSb–Eu-(TTA)$_2$, (c) PBDBi–Eu(TTA)$_2$, (d) PBDP–Eu(TTA)$_2$.

presented in Table III indicate that the fluorescence intensity of polymer rare earth complexes are much higher than binary complexes. For such a change in fluorescence intensity, the only reasonable explanation is the formation of a rigid planar conjugated structure. This may lead to electronic delocalization and may strongly absorb ultraviolet light. It also favors L^*-M energy transfer. Therefore, it greatly enhanced the fluorescence intensity.

In the present study the effect of the polymer ligand on fluorescence intensity was also investi-

Table VII   Fluorescence Lifetime of Complexes

	Complexes			
	PBDP−Eu(TTA)$_2$	PBDAs−Eu(TTA)$_2$	PBDSb−Eu(TTA)$_2$	PBDBi−Eu(TTA)$_2$
MS	0.3054	0.4691	0.3779	0.3502

gated. The emission spectra of different polymer ligand Eu^{3+}-containing ternary complexes were observed as shown in Figure 3 and Table III. The emission spectra of all ternary complexes are sharp peaks and in the visible region. All spectra patterns are similar and their emission wavelengths are the same but their fluorescence intensities are different. The enhancement effect of the PBDAs complex is the strongest.

This article also demonstrates the effect of low molecular weight ligand on fluorescence intensity observed from emission spectra as shown in Figure 4 and Table IV; the emission intensity was at 614 nm for all complexes and originated from the electronic dipole transition emission ($^5D_0 - {}^7F_2$). This means that all the low molecular weight ligands may form ternary complexes with a polymer ligand and a rare earth metal ion.

The different effects on the fluorescence properties of ternary complexes were caused by their different tolerances with the polymer ligand. TTA was the best low molecular weight ligand in our study.
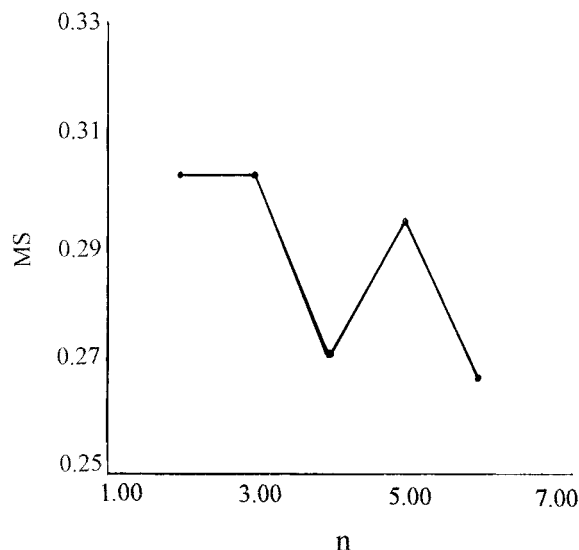
Figure 5 and Table V illustrate the relationship between the molar ratio (n) of TTA/Eu(III) and their fluorescence intensity. The fluorescence intensity was increased with the increase of the molar ratio of TTA/Eu(III); when this ratio approached 5, the fluorescence intensity reached the maximum. A further increase of the molar ratio of TTA/Eu(III) produced a sharp decline. These findings can be interpreted as the fluorescence was relatively quenched upon the addition of TTA concentration. The results in Table VI and Figure 6 show a remarkable difference in the fluorescence intensity enhancement for rare earth metal ions. Eu^{3+}-containing ternary complexes have stronger fluorescence intensity than Sm^{3+}-containing ternary complexes, and the emission of Tb^{3+}-containing ternary complexes completely quenches it. Reaction conditions have a strong influence on formation and stability of complexes. The fluorescence intensity in each system increased with the increase of pH, reached a maximum, and then decreased.

Fluorescence Lifetime of Complexes

The results of the fluorescence lifetime measurements on ternary complexes PBDL−Eu(III)−(TTA)$_2$ ($L = P$, As, Sb, Bi) are shown in Figure 7. The time dependence of the fluorescence in the above ternary complexes are well described in terms of a single exponential function with a lifetime [Fig. 7(a−d)]. The stronger the fluorescence intensity, the longer the fluorescence lifetime. These results provide additional evidence that the

Figure 8   The relationship between fluorescence lifetime of PBDP−Eu(TTA)$_n$ and molar ratio (n) of TTA/Eu^{3+}.

Table VIII   Relationship Between Fluorescence Lifetime and Molar Ratio of Low Molecular Weight Ligands

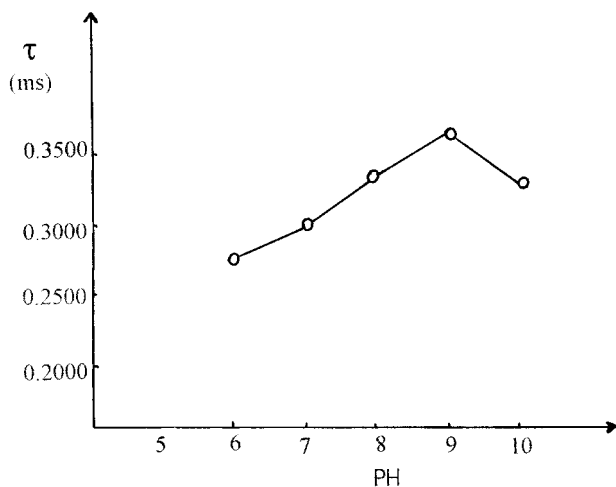|	Molar Ratio TTA(n)				
	2	3	4	5	6
MS	0.303	0.303	0.271	0.295	0.267

Figure 9 The relationship between fluorescence lifetime of PBDP–Eu(TTA)$_n$ and synthesis reaction pH.

formation of ternary complexes and Eu(III) ion basically present in only one state-complex form.

Table VII shows the fluorescence lifetime of the complex system. This lifetime is between 0.350 and 0.469 MS. There was little variation for the different polymer ligands. From the XPS results the binding energy (Eu3d5/2) of PBDAs–Eu(III)–(TTA)$_4$ is 1133.9 eV, which is much lower than that in PBDP–Eu(III)–(TTA)$_4$ (1135.72 eV).

The relationship between the fluorescence lifetime of PBDP–Eu(III)–(TTA)$_n$ and the molar ratio (n) of TTA is shown in Figure 8 and Table VIII. The lifetime (MS) change with molar ratio of TTA first increased then decreased when the molar ratio of TTA was an odd number. Its fluorescence lifetime was longer than that of an even number. In this case, probably owing to the odd number, the TTA with a polymer ligand comprised total ligands because an even number may have been arranged symmetrically around europium(III) and formed a fairly coplanar rigid structure; it benefitted the energy transfer and formed more stable complexes. Therefore, the fluorescence intensity and the lifetime of these complexes were both higher.

Figure 9 shows that the fluorescence lifetime of PBDP–Eu(III)–(TTA)$_2$ changed with the pH in the reaction. The variation law was the same as in the fluorescence intensity.

CONCLUSION

The formation of polymer ternary complexes greatly enhanced the fluorescence intensity of rare earth ions.

Various polymer ligands have different fluorescence intensity enhancement effects on rare earth ions. PBDAs is a better ligand and possesses stronger fluorescence intensity coordinated with any low molecular weight ligand.

Different low molecular weight ligands have a pronounced effect on the fluorescence of rare earth ions. TTA is the best low molecular weight ligand in our study.

Compared with Tb(III) and Sm(III), Eu(III) is the best rare earth ion to form luminescence material.

Reaction condition (pH) has an effect on fluorescence intensity and lifetime. Selecting the proper synthesis reaction conditions is an important factor in obtaining luminescence material.

Fluorescence decay and quenching studies were used to determine the type of complexes formed.

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