

Synthesis and Fluorescence Properties of the Mixed Complexes of Eu(III) with Polymer Ligand and Thenoyl Trifluoroacetone

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ABSTRACT: The mixed ligand complexes of europium(III) with poly(chloromethyl styrene)-bound 1,4,8,11-tetraazacyclotetradecane (PTACT) and thenoyl trifluoroacetone (TTA) have been synthesized and characterized by Fourier transform infrared and elemental analysis, Inductively Coupled Plasma-Atomic Emission Spectrometry, and X-ray photoelectron spectroscopy. The fluorescence properties of PTACT-Eu-TTA were studied, and it is found that the polymer-mixed ligand complexes emit strong fluorescence at room temperature. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 755–760, 1997

Key words: 1,4,8,11-tetraazacyclotetradecane; europium; polymer-mixed ligand complex; fluorescence

INTRODUCTION

Rare earth metal complexes with polymers as fluorescence materials have many important uses, so the interest of many have been stimulated by these kinds of materials.^{1,2} The studies on fluorescence properties of polymer ligand, rare earth metal, low-molecular-weight ligand ternary complex have attracted much more notice.^{3,4} The tetradentate, saturated macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane([14]aneN₄) (TACT), can form stable complexes with metal ions easily.^{5,6} Polymer-bound[14]aneN₄ synthesized by Nicolans and Wohrle was used to absorb transition metal ions.⁷ Pietraszkiewicz et al.⁸ have synthesized a substituted [14]aneN₄-Eu(III) complex, and the complex was found to be nonfluorescent in *i*-propanol or acetonitrile solution when excited at 328 or 360 nm.

To our knowledge, a study on polymer-bound [14]aneN₄ rare earth metal, mixed ligand complexes has not been found. In this article, the polymer complex (PTACT-Eu-TTA) of europium (Eu) with polymer-bound 1,4,8,11-tetraazacyclotetradecane (PTACT)

and thenoyl trifluoroacetone (TTA) has been synthesized by the method of low-molecular-weight ligand-modified polymer metal complexes, and it is found that the polymer-mixed ligand complexes emit strong fluorescence at room temperature.

EXPERIMENTAL

Materials

1,4,8,11-Tetraazacyclotetradecane was purchased from Aldrich Chemical Co. Thenoyl trifluoroacetone was the product of the Shanghai Chemical Regent Factory, Shanghai, China. The macroporous resin, which is partially chloromethylated polystyrene, was donated by the Institute of Molecular Chemistry, Nankai University, China (molar cross linked density, 2%; Cl weight content, 20.3%). Eu₂O₃ (99.99% pure) was obtained from the Yao Long Chemistry factory. All low-molecular-weight materials were analytically pure and were used without further purification.

EuCl₃ stock solution was prepared by dissolving Eu₂O₃ in concentrated hydrochloric acid and evaporating to dryness, then dissolving and diluting to in a volumetric flask with ethanol.

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Measurements

Fourier transform infrared (FTIR) spectra were recorded on an Alpha-Centauri FTIR spectrometer (KBr sheets). C, H, and N contents were determined by routine analysis using a Carbon-Erba 1106 model elementary analyzer. S and Eu contents were measured by Inductively Coupled Plasma-Atomic Emission Spectrometry analysis on an American ARL Co. 3520 model plasmascan. X-ray photoelectrospectra (XPS) were taken with England Fisonscompany ESCALAB-210 model photoelectrospectrometer [X-ray source, MgK α ; vacuum tightness, 3×10^{-10} Pa; binding energy values refer to C $_{1s}$ (284.6 eV); passing energy, 30 eV]. Fluorescence spectra measurements were carried out at room temperature using a Shimadzu RF-540 spectrofluorophotometer, and prepared fine powder samples were used throughout.

Synthesis of Polymer Mixed Ligand Complexes

Chloromethylated polystyrene (1.1 g) had been swollen in 30 mL CHCl $_3$ for 24 h and 1.1 g of

[14]aneN $_4$, 0.7 g of anhydrous K $_2$ CO $_3$, and several drops of the phase transfer catalyst (PEG-600) were added. The mixture was refluxed for 24 h with stirring. After cooling to room temperature, water was added into the mixture to dissolve the inorganic salts. The crude product was isolated by filtration and washed by water, ethanol, and chloroform for five times separately. The product was dried in vacuum, and the pale yellow polymer ligand PTACT (1.4 g) was obtained.

PTACT (0.6 g), the solution of EuCl $_3$ (0.13 mol L) in ethanol (9 mL), and triethyl orthoformate (1 mL) were added into a flask. The mixture was refluxed for 12 h with stirring. The product was filtrated and washed by ethanol for three times. After drying in vacuum, the brown red polymer metal complex PTACT-Eu was obtained.

PTACT-Eu (262.4 mg), TTA (15.6 mg), and triethyl orthoformate (1 mg) were mixed in a flask with 10 ml ethanol. The value of pH was adjusted to 7–8 by the solution of KOH in ethanol. The product was filtrated and washed by ethanol five times. After drying in vacuum at room temperature, the solid of PTACT-Eu-TTA (1) was obtained. Polymer

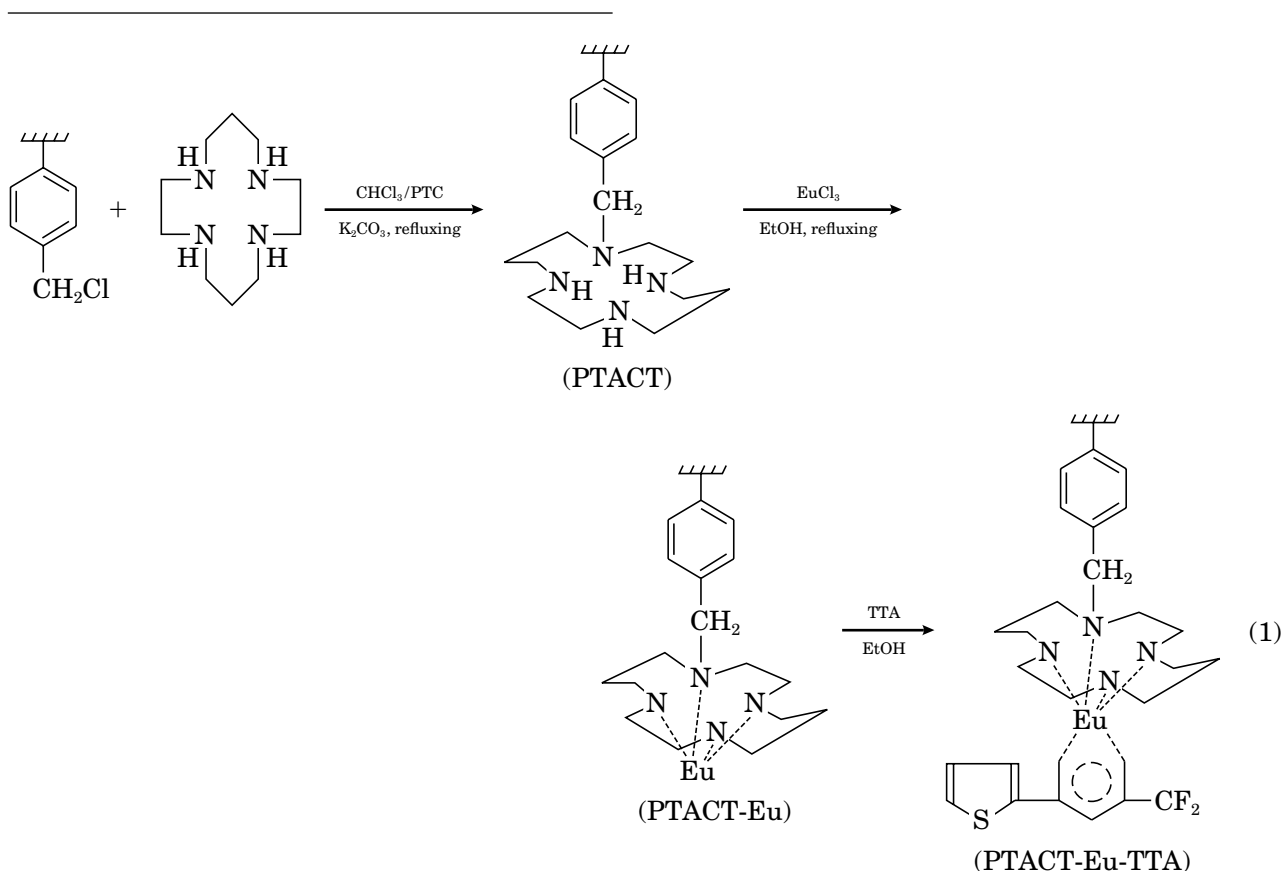


Table I IR Spectra Data of Compounds (cm⁻¹)

Compound	$\nu_{C=C}$	δ_{C-H}	ν_{C-Cl}	ν_{C-N}	ν_{N-H}	ν_{N-Eu}	ν_{O-Eu}	$\nu_{C=O}$
TTA	-	-	-	-	-	-	-	1661
PS-CH ₂ Cl	1509	824	701	-	-	-	-	-
[14]aneN ₄	-	-	-	1206	3268	-	-	-
PTACT	1509	841	701	1216	3268	-	-	-
PTACT-Eu	1510	843	702	1182	3236	337	-	-
PTACT-Eu-TTA (1)	1510	843	702	1180	3230	330	546	1650
PTACT-Eu-TTA (2)	1509	843	705	1198	3218	332	538	1615
PTACT-Eu-TTA (3)	1510	844	703	1199	3251	327	539	1614
PTACT-Eu-TTA (4)	1510	820	702	1199	3246	327	530	1614

mixed ligand complexes PTACT-Eu-TTA (2–4) were obtained by changing the amount of TTA.

RESULTS AND DISCUSSION

The synthesis route and the structure of PTACT-Eu-TTA are as follows.

Infrared Analysis

Infrared (IR) spectra data of compounds are shown in Table I. In the spectra of PTACT characteristic absorption of aromatic ring, C–N stretching vibration and N–H stretching vibration appear. The N–Eu bond absorption peak in the spectra of PTACT-Eu located at 337 cm⁻¹, the new absorption peaks in the region between 320 and 330 cm⁻¹, are due to the N–Eu stretching vibration of PTACT-Eu-TTA (1–4). These results suggest that the coordination bond was formed between the Eu³⁺ and the nitrogen atom in the polymer ligand. In the spectra of PTACT-Eu-TTA (1–4), the peaks between 530 and 550 cm⁻¹ are due to the O–Eu stretching vibration. This indicates that TTA is involved into the formation of coordination bond. The formation of the N–Eu bond and the O–Eu bond indicates that the polymer

mixed ligand complexes PTACT-Eu-TTA were formed. In the IR spectra of the complexes, the stretching frequencies of C–N bond and $\nu_{C=O}$ were shifted because Eu³⁺ is involved in bonding to the nitrogen atom and the oxygen atom; and intensities of ν_{N-H} decreased, which shows that the polymer ligands were not completely complexed with Eu³⁺.

Elemental Analysis

Elemental analysis data of polymer ligand and its metal complexes are shown in Table II. The weight content of nitrogen in PTACT indicates that there is 0.161 molar tetranitrogen ring in every 100 g polymer ligand. The content of functional group in the polymer ligand is 31%, which was investigated by the analyzing element, cross-linked density of the resin and the content of chloride in the resin used in this experiment. The molar ratio of S : Eu is not more than 0.4 because of the hindrance of the polymer skeleton.

XPS Analysis

Table 3 gives XPS data of several compounds. N_{1s} peaks of PTACT, PTACT-Eu, and PTACT-Eu-TTA (1) were fitted by the computer fitting pro-

Table II Elemental Analysis Data of Polymer Ligand and Complexes (wt %)

Compound	N	Eu	S	S : Eu (Molar Ratio)
PTACT	9.01	-	-	-
PTACT-Eu	8.98	8.15	-	-
PTACT-Eu-TTA (1)	8.82	5.52	0.31	0.27
PTACT-Eu-TTA (2)	8.40	2.87	0.18	0.30
PTACT-Eu-TTA (3)	7.92	2.04	0.13	0.32
PTACT-Eu-TTA (4)	7.15	2.60	0.20	0.37

Table III XPS Data of Compounds

Compound	Binding Energy (eV)						
	N _{1s}			ΔE (eV)			
	Eu _{4d_{3/2}}	N _{1s} ¹	N _{1s} ²	O _{1s}	Eu _{4d_{3/2}}	N _{1s} ²	O _{1s}
TTA	-	-	-	530.9	-	-	-
EuCl ₃	137.6	-	-	-	-	-	-
PTACT	-	399.1		-	-	-	-
PTACT-Eu	136.7	399.0	401.2	-	-0.9	+2.1	-
PTACT-Eu-TTA (1)	136.5	399.0	401.1	531.9	-1.1	+2.0	+1.0

gram respectively. The fitting shows that N_{1s} peaks of PTACT-Eu and PTACT-Eu-TTA (1) contain two peaks named N_{1s}¹ and N_{1s}², respectively. Otherwise, N_{1s} peak of PTACT is a single peak. The binding energy value of N_{1s}¹ and Eu_{4d_{3/2}} is shown in Table III. N_{1s}² binding energy in PTACT-Eu and PTACT-Eu-TTA (1) is increased by 2.1 and 2.0 eV, compared with the N_{1s} binding energy in PTACT. This result shows that N_{1s}² is involved in bonding to Eu³⁺. The Eu_{4d_{3/2}} binding energy in PTACT-Eu and PTACT-Eu-TTA (1) decreased by 0.9 and 1.1 eV, respectively, because the charge was transferred from the nitrogen atom to Eu³⁺ when Eu³⁺ was coordinated with polymer ligand. The O_{1s} binding energy of PTACT-Eu-TTA (1) is increased by 1.0 eV compared with that of TTA; that is to say, the oxygen atom in TTA is involved in bonding to Eu³⁺. TTA coordinated with Eu³⁺ by its enolic form under the experimental conditions described above.⁴ According to the analysis described above, the structures of polymer mixed ligand complexes are as the synthesis route and the structure of PTACT-Eu-TTA.

Fluorescence Properties of Complexes

The excitation and emission wavelengths, as well as the fluorescence intensity, were measured on dried and finely powdered samples at room temperature. The results are shown in Table IV. Eu³⁺-containing complexes was perturbed by the ligand to emit fluorescence light, which is from the 4*f** → 4*f* transition. The *f** → *f* transition of the rare earth ion is forbidden unless the rare earth ion is perturbed by the ligands around the ion. Fluorescence properties of rare earth metal complexes at solid state is related to the transmission course of exchanging energy.⁹ The energy that is from the π* → π transition of the exciting ligands around Eu³⁺ was transmitted to Eu³⁺. The Eu³⁺ in the polymer-mixed ligand complexes emitted fluorescence light after accepting the energy. The complex PTACT-Eu has no fluorescence because of no π* → π transition in the complex. The fluorescence intensity of polymer mixed ligand complexes (1)–(4) increase with the increase in the S/Eu value in the mixed complexes

Table IV Relationship Between Fluorescence Emission Intensity and the S-Eu Value

Complexes	Excitation (nm)	Emission (nm)	Slit (Ex/Em)	Intensity	S : Eu (Molar Ratio)
PTACT-Eu		no		0	0
PTACT-Eu-TTA (1)	352.1	592.6	10/10	5.3	0.27
		614.1		20.3	
PTACT-Eu-TTA (2)	366.0	593.0	10/10	5.8	0.30
		614.3		31.4	
PTACT-Eu-TTA (3)	366.4	593.0	10/10	6.5	0.31
		614.1		37.3	
PTACT-Eu-TTA (4)	371.5	593.1	10/10	10.5	0.37
		614.3		63.5	

Parameter: Ordinate Scale (FI) × 1; low sensitivity.

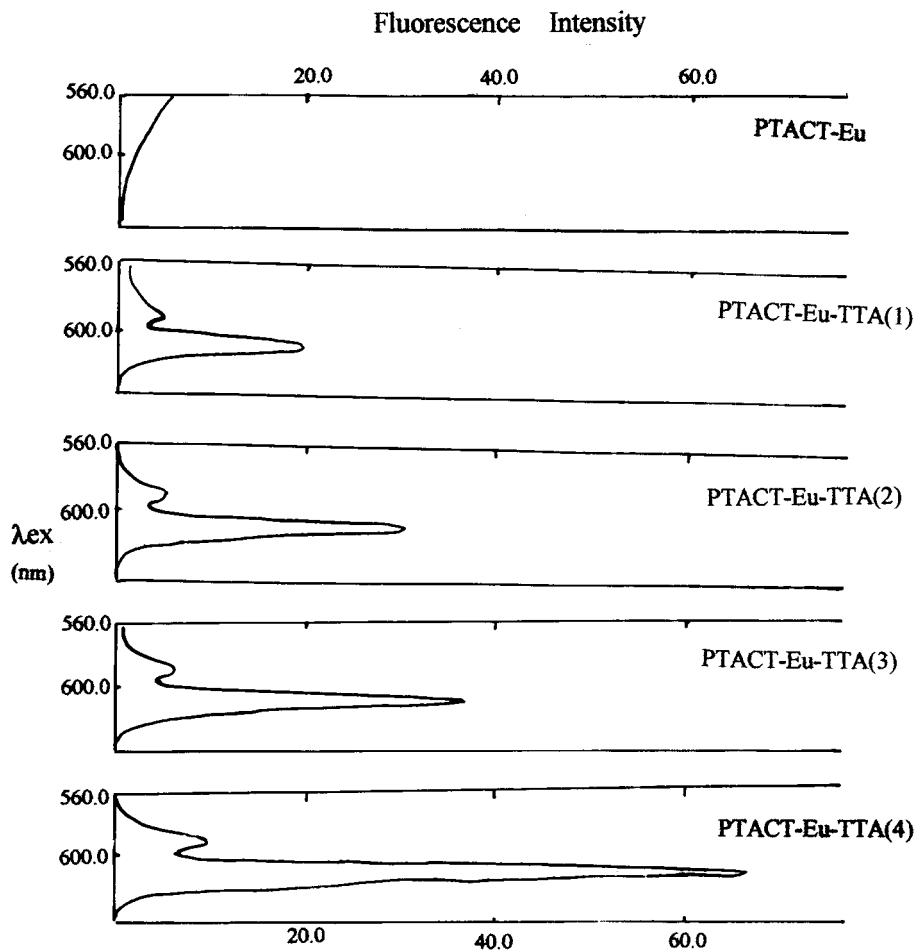


Figure 1 Fluorescence spectra of complexes (Ordinate scale $\times 1$, Low Sensitivity)

(Table IV). This is related to the energy transfer from TTA to Eu^{3+} . TTA coordinated to Eu^{3+} is good for energy transfer because of the $\pi^* \rightarrow \pi$ transition of TTA. On the other hand, fluorescence intensity is related to the rigid planar structure of complexes. [14]aneN₄ is nonplanar molecule. Fluorescence intensity of the mixed ligand complexes was decreased by the thermal vibration of [14]aneN₄. The degree of thermal vibration is decreased by the formation of polymer-mixed ligand complexes, which enhances the fluorescence intensity of the mixed ligand complexes. The fluorescence spectra are shown in Figure 1.

The fluorescence light of Eu^{3+} was assigned to the transition from the $5D_0$ level to the levels of $7F_j$ ($j = 1, 2$). The emission peak at 593 nm (Table IV) corresponds to the $5D_0 \rightarrow 7F_2$ transition of Eu^{3+} , which is a magnetic dipole transition insensitive to the crystalline field, and the fluorescent intensity at 593 nm is laid to the influence of TTA. The emission peak at around 614 nm (Table IV)

corresponds to the $5D_0 \rightarrow 7F_2$ transition of Eu^{3+} , which is the electric dipole transition sensitive to the crystalline field,¹⁰ and its fluorescent intensity was influenced clearly by TTA.

CONCLUSIONS

Polymer-mixed ligand complexes PTACT-Eu-TTA were synthesized and characterized, and their fluorescence properties were studied. The results indicate that the fluorescence intensity was varied with the S : Eu (molar ratio) value in the polymer-mixed ligand complexes.

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REFERENCES

1. E. Banks, Y. Okamoto, and Y. Ueba, *J. Appl. Polym. Sci.*, **25**, 2007 (1980).

2. Y. Okamoto, Y. Ueba, N. F. Dzhanibekov, and E. Banks, *Macromolecules*, **14**, 17 (1981).
3. S. H. Jian, S. J. Guo, P. Wang, and Y. P. Wang, *Xi'an International Symposium on Function and Fine Polymers (Preprints)*, Xian, China 1988, p. 165.
4. Y. P. Wang, Z. Q. Lei, H. Y. Feng, J. T. Bao, and Y. B. Wang, *J. Appl. Polym. Sci.*, **45**, 1641 (1992).
5. B. S. Nakani, J. B. Welsh, and R. D. Hancock, *Inorg. Chem.*, **22**, 2956 (1983).
6. M. R. Spirlet, J. Rebizant, J. F. Desreux, and M. F. Loncin, *Inorg. Chem.*, **23**, 359 (1984).
7. V. Nicolans and D. Wohrle, *Die Angew. Makromol. Chem.*, **198**, 179 (1992).
8. M. Pietraszkiewicz, J. Karpiuk, R. Bilewicz, and S. P. Kaspriyk, *J. Coord. Chem.*, **21**, 75 (1990).
9. D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).
10. A. F. Kirby and F. S. Richardson, *J. Phys. Chem.*, **87**, 2544 (1983).