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The photophysical properties of binary and ternary complexes of rare earths with conjugated carboxylic acids and 1,10-phenanthroline

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Abstract

Results of photophysical properties of the complexes of Gd^{3+}, Eu^{3+} and Tb^{3+} with conjugated carboxylic acids (3,4-funandicarboxylic acid and nicotinic acid) and 1,10-phenanthroline are reported. Whether between central ions and ligands or between the two ligands, it is found that the intramolecular energy efficiency is a sensitive function of the relative positions of the resonance energy levels of the central ions and the lowest triplet states of the ligands. Couplings of rare earth ions to the ligands are discussed in detail. © 1997 Elsevier Science S.A.

Keywords: Photophysical properties; Intramolecular energy transfer; Conjugated carboxylic acids; Rare earth complexes

1. Introduction

Rare earth complexes with aromatic acids have excellent luminescence properties and have extensive interest for chemists [1,2]. In recent years, there have appeared some reports on rare earth complexes with conjugated carboxylic acids which contain aromatic heterocycles [3–5], but little attention has been paid to the energy coupling between the lowest triplet state energies of carboxylic acid ligands and the resonant emissive energy of rare earth ions [6]. However, a theory on the luminescence and energy transfer of rare earth chelates with organic ligands has been accepted, and it has been discovered that the triplet position of organic ligands is one of the most important factors which restrict the luminescence intensities in the course of studies on the luminescence of rare earth complexes with β-diketones [7–9]. In the present work, two kinds of conjugate carboxylic acid (3,4-furandicarboxylic acid and nicotinic acid, which have a furan-cycle and pydine-cycle respectively) were used as ligands; their complexes with rare earth ions and 1,10-phenanthroline were synthesized. The photophysical properties (luminescence and intramolecular energy transfer between carboxylic acid and rare earth central ion and from carboxylic acid to 1,10-phenanthroline) are discussed. The results will provide a criterion to predict luminescence properties of rare earth complexes with organic ligands and from it to develop new luminescent materials.

2. Experimental details

2.1. The synthesis of rare earth complexes

Rare earth binary complexes with 3,4-furandicarboxylic acid and nicotinic acid were prepared according to Refs. [10,11]. The Gd^{3+} complex with 1,10-phenanthroline was synthesized as described in Ref. [12]. The rare earth ternary complexes with nicotinic acid and 1,10-phenanthroline were prepared as described in Ref. [13]. The ternary complexes with 3,4-furandicarboxylic acid and 1,10-phenanthroline were synthesized as follows. Excess 3,4-furandicarboxylic acid (about 3 mmol) and excess 1,10-phenanthroline (over 1 mmol) were soluted by absolute ethanol and mixed together, the pH value of the mixture was adjusted to 6.3 by adding aqueous sodium hydroxide with stirring. Then an alcoholic solution of rare earth chloride (1 mmol) was added to the mixed alcoholic solution above. After heating and stirring for 3 h, the precipitate was filtered off, washed with water and ethanol, dried first at room temperature, and was stored over silica-gel drier.

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Table 1
The composition of rare earth complexes by elemental analysis

Complex [a]	Found (%)				Calculated (%)			
	C	H	N	RE	C	H	N	RE
$Gd(NIA)_3 \cdot 2H_2O$	39.21	2.56	7.23	27.46	38.60	3.46	7.51	28.10
$Gd(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$	53.52	3.46	10.21	17.10	53.76	3.63	10.45	16.77
$Eu(NIA)_3 \cdot 2H_2O$	38.75	2.63	7.40	27.64	38.97	2.87	7.58	28.31
$Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$	54.48	3.34	10.24	16.94	54.06	3.65	10.51	16.30
$Tb(NIA)_3 \cdot 2H_2O$	39.27	2.67	7.15	28.05	53.66	2.85	7.48	27.42
$Tb(NJA)_3 \cdot (phen)_2 \cdot 3H_2O$	54.08	3.21	10.57	17.09	53.66	3.62	10.43	16.93
$GdH(FRA)_2 \cdot 3H_2O$	27.03	2.03	–	29.87	27.66	2.11	–	30.20
$GdH(FRA)_2 \cdot phen \cdot 4H_2O$	39.84	2.58	4.16	21.74	40.09	2.92	4.16	21.80
$EuH(FRA)_2 \cdot 3H_2O$	27.99	1.96	–	29.92	27.75	2.14	–	29.50
$EuH(FRA)_2 \cdot phen \cdot 4H_2O$	40.17	2.64	4.14	21.80	40.39	2.94	3.93	21.23
$TbH(FRA)_2 \cdot 3H_2O$	27.82	2.04	–	30.04	27.58	2.04	–	30.44
$TbH(FRA)_2 \cdot phen \cdot 4H_2O$	39.47	2.49	4.09	22.61	39.99	2.92	3.89	22.17
$Gd(phen)_2 \cdot Cl_3 \cdot 2H_2O$	43.30	3.44	8.20	23.97	43.62	3.63	8.48	23.78
$Eu(phen)_2 \cdot Cl_3 \cdot 2H_2O$	43.76	2.92	8.23	23.65	44.01	3.06	8.56	23.22
$Tb(phen)_2 \cdot Cl_3 \cdot 2H_2O$	43.80	2.89	8.19	24.31	43.54	3.02	8.47	24.03

[a] HNIA nicotinic acid, H_2FRA 3,4-furandicarboxylic acid, phen 1,10-phenanthroline.

2.2. Measurement of the compositions and properties of rare earth complexes

The elemental contents of these complexes were measured with a CARIO-ERBA 1106 elemental analyzer. The fluorescence spectra were obtained on a SPEX FL-2T2 spectrofluorometer with excitation and emission slit at 0.6 mm. The fluorescence lifetimes were measured on a SPEX 1934D spectrophotometer using a 450 W xenon lamp as the excitation source. The phosphorescence spectra and lifetime measurements at 77 K were carried out on rigid-glass samples in a 12 mm square quartz cube in a glass Dewar with quartz windows with the same instrument as above. The luminescence quantum efficiencies of solid europium and terbium complexes were determined on an MPF-4 spectrophotofluorimeter.

3. Results and discussion

The compositions of these prepared complexes were confirmed by elemental analysis, the results are summarized in Table 1.

In order to elucidate the energy transfer mechanism of rare earth complexes and predict their luminescence properties, Gd^{3+} complexes with the two conjugated carboxylic acids and phen were used as model complexes to determine the lowest triplet state energies of the two conjugated carboxylic acids and 1,10-phenanthroline owing to the high phosphorescence-to-fluorescence ratio of Gd^{3+}. The low temperature phosphorescence spectra of binary complexes of each ligand were measured and the shortest wavelength of the emission band was assumed to be a 0–0 transition. So the lowest triplet state energies of ligands and the energy differences ($\Delta E(\text{Tr-}^5D_j)$ $j=0$ or 4; for Eu^{3+} $^5D_0 = 17\,264$ cm^{-1}, for Tb^{3+} $^5D_4 = 20\,500$ cm^{-1}) between them and the emitting levels of Eu^{3+} and Tb^{3+} were determined; the data are shown in Table 2.

According to Sato's results [8], the intramolecular energy migration efficiency from organic ligands to the central Ln^{3+} is the most important factor influencing the luminescence properties of rare earth complexes. The intramolecular energy transfer efficiency depends mainly on two energy transfer processes [14]. One is from the lowest triplet state energy of

Table 2
The lowest triplet state energies of Gd^{3+} complexes with HNIA, H_2FRA and phen, the energy difference ($\Delta E(\text{Tr-}^5D_j)$ $j=0$ or 4), phosphorescence lifetimes of Gd^{3+} complexes and the energy transfer efficiencies from HNIA, H_2FRA to phen

Complex	Lowest triplet state energy (cm^{-1}) [a]	$\Delta E(\text{Tr-}^5D_0)$ (cm^{-1}) [a]	$\Delta E(\text{Tr-}^5D_4)$ (cm^{-1}) [a]	Phosphorescence lifetime τ (s) [b]	Energy transfer efficiency (%) [b]
$Gd(NIA)_3 \cdot 2H_2O$	21739 ± 21	4475 ± 21	1239 ± 21	2.9 (τ_D)	–
$Gd(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$	–	–	–	2.9 (τ_T)	–
$GdH(FRA)_2 \cdot 3H_2O$	25475 ± 15	8211 ± 15	4975 ± 15	2.3 (τ_D)	–
$GdH(FRA)_2 \cdot phen \cdot 4H_2O$	–	–	–	1.6 (τ_T)	31
$Gd(phen)_2 \cdot Cl_3 \cdot 2H_2O$	22075 ± 24	4811 ± 24	1575 ± 24	–	–

[a] The magnitude of experimental uncertainty was ±0.5 nm (SPEX spectrophotometer), the data of lowest triplet $\Delta E(\text{Tr-}^5D_1)$ and $\Delta E(\text{Tr-}^5D_4)$ were calculated with the wavelength of phosphorescence spectra.

[b] The experimental errors are ±10% on phosphorescence lifetimes and so the calculating errors are ±10% on energy transfer efficiencies.

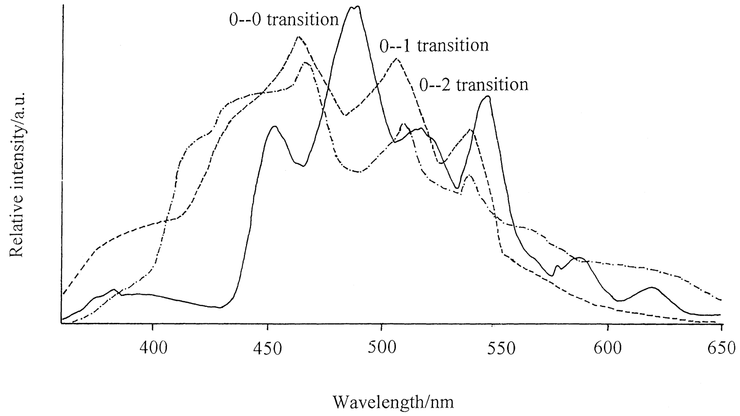

Fig. 1. The low temperature phosphorescence spectra of $Gd(phen)_2 \cdot Cl_3 \cdot 2H_2O$ (———, $\lambda_{ex} = 302.0$ nm), $Gd(NIA)_3 \cdot 2H_2O$ (- - -, $\lambda_{ex} = 298.8$ nm) and $Gd(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ (– · –, $\lambda_{ex} = 298$ nm). 5×10^{-4} mol l^{-1} ethanol and DMF mixed solution, 77 K.

organic ligands to the resonant energy level by Dexter's resonant exchange interaction theory [15]:

$$k_{ET} = KP_{da} \exp(-R_{da}/L) \quad (1)$$

$$P_{da} = (2\pi Z^2/R) \int F_d(E) E_a(E) \, dE \quad (2)$$

$$K_{ET} = KP_{da} \exp(-2R_{da}/L) = K \int F_d(E) E_a(E) \, dE \quad (3)$$

The other is the inverse energy transition by the thermal deactivation mechanism [16]:

$$k(T) = A \exp(-\Delta E/RT) \quad (4)$$

where k_{ET} is the rate constant of the intermolecular energy transfer and P_{da} is the transition probability of the resonant exchange interaction. $2\pi Z^2/R$ is constant relating to the specific mutual distance between the central Ln^{3+} ion and its coordinated atoms (O or N). $F_d(E)$ and $E_a(E)$ are the experimental luminescence spectrum of energy donor (ligands) and the experimental absorption spectrum of energy acceptor (Ln^{3+}) respectively, so both of them represent the overlap of the luminescence spectrum of ligands and the absorption spectrum of Ln^{3+}. R_{da} is the intermolecular distance between donor atoms and acceptor atom, and L is the van der Waals radius. Both R_{da} and L may be considered to be constant in intramolecular energy transfer processes, so k_{ET} is proportional to the overlap of $F_d(E)$ and $E_a(E)$. With the decrease in the energy difference between the triplet state energy of conjugated carboxylic acid and Ln^{3+}, the overlap of $F_d(E)$ and $E_a(E)$ is increased. So from the above equation, it can be concluded that with the decreasing overlap between the luminescence spectrum of organic ligands and the absorption spectrum of Ln^{3+}, that is to say with the decreasing energy difference between the triplet state energy and the emissive energy of Ln^{3+}, the intramolecular energy rate constant k_{ET} will be increased. In Table 2, the energy difference between the triplet state energies and the emitting energies of Tb^{3+} are smaller than that of Eu^{3+}. So it can be predicted that the two conjugated carboxylic acids will sensitize Tb^{3+} more effectively than Eu^{3+}. On the other hand, the activation energy ΔE in Eq. (4) is equal to the energy difference $\Delta E(\text{Tr-Ln}^{3+})$, while from the formula, the inverse energy transfer rate constant $k(T)$ increased with decreasing $\Delta E(\text{Tr-Ln}^{3+})$. As discussed above, there should exist an optimal energy difference between the triplet position of organic acid and the emissive energy level of Ln^{3+}, the larger and the smaller $\Delta E(\text{Tr-Ln}^{3+})$ will decrease the luminescence properties of rare earth complexes.

Fig. 1 shows the phosphorescence spectra of $Gd(NIA)_3 \cdot 2H_2O$, $Gd(NIA)_3 \cdot (phen)_2 \cdot 2H_2O$ and $Gd(phen)_2 \cdot Cl_3 \cdot 2H_2O$. The phosphorescence emission of $Gd(NIA)_3 \cdot (phen)_2 \cdot 2H_2O$ shows the same emission band as that of $Gd(NIA)_3 \cdot 2H_2O$; this result indicates that the intramolecular energy transfer between HNIA and phen could not take place because HNIA has a lower triplet level energy than that of phen. Fig. 2 shows the phosphorescence spectra of $GdH(FRA)_2 \cdot 3H_2O$, $GdH(FRA)_2 \cdot phen \cdot 4H_2O$ and $Gd(phen)_2 \cdot Cl_3 \cdot 2H_2O$. It can be seen that the phosphorescence spectrum of ternary complexes $GdH(FRA)_2 \cdot phen \cdot 4H_2O$ is similar to that of binary $Gd(phen)_2 \cdot Cl_3 \cdot 2H_2O$, which indicates that in ternary complexes with conjugated carboxylic acids and 1,10-phenanthroline, the predominant energy donor is phen, and there might exist an intramolecular energy transfer process from H_2FRA to phen because the triplet state energy of H_2FRA is higher than that of phen. In order to verify further these deductions, the phosphorescence lifetimes of Gd^{3+} complexes were measured. Fig. 3 is the diagram of the intramolecular energy transfer between acids and phen [17]. According to the mechanism, the energy transfer rate and efficiency equation can be represented as follows:

$$k^*_{ET} = \tau_T^{-1} - \tau_D^{-1} \quad (5)$$

$$\eta_{ET} = k^*_{ET}(K^*_{ET} + k_1)^{-1} \quad (6)$$

Where k^*_{ET} and k_1 are the intramolecular energy transfer rate constant from conjugated carboxylic acid to phen and the phosphorescence rate constant of gadolinium binary complexes with HNIA and H_2FRA separately; τ_T and τ_D are the phosphorescence lifetimes of the Gd^{3+} ternary complex and its corresponding binary complex with acids respectively. η_{ET}

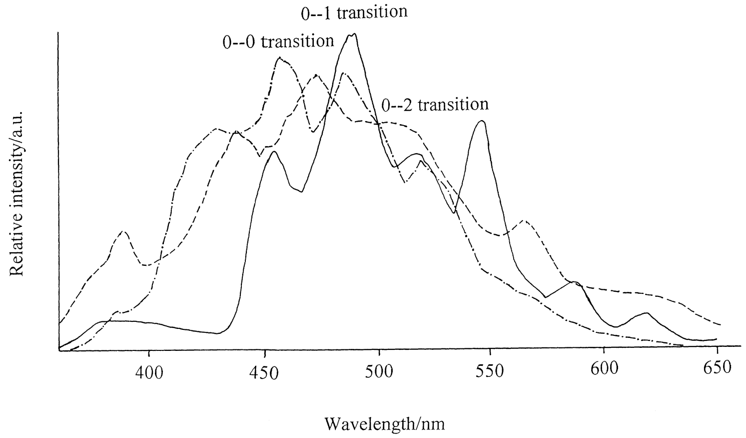

Fig. 2. The low temperature phosphorescence spectra of $Gd(phen)_2 \cdot Cl_3 \cdot 2H_2O$ (———, $\lambda_{ex} = 302.0$ nm), $GdH(FRA)_2 \cdot 3H_2O$ (- - -, $\lambda_{ex} = 317.6$ nm) and $GdH(FRA)_2 \cdot phen \cdot 4H_2O$ (– · –, $\lambda_{ex} = 304.4$ nm). 5×10^{-4} mol l^{-1} ethanol and DMF mixed solution, 77 K.

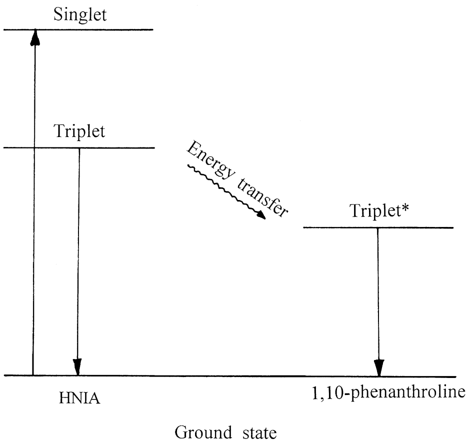

Fig. 3. The intramolecular energy transfer process from nicotinic acid and 3,4-furandicarboxylic acid to 1,10-phenanthroline.

is the energy transfer efficiency. By means of the two equations, η_{ET} can be calculated. The data for τ_T, τ_D and η_{ET} are summarized in Table 2. As the data indicate, the phosphorescence lifetime of the ternary complex with HNIA and phen is near to that of the binary complex with HNIA, and HNIA does not transfer energy to phen; the energy efficiency between H_2FRA and phen is not so large that it can be predicted that the corresponding ternary complexes of Eu^{3+} and Tb^{3+} would not change much compared with the binary complexes of Eu^{3+} and Tb^{3+}.

1,10-phenanthroline is a heterocylic molecule containing two nitrogen atoms, and the conjugated π bond of phen is larger than that of conjugated aromatic carboxylic acids, so it is suitable for energy transfer using phen as additional ligand. Besides this, the triplet state energy of phen is lower than that of aromatic carboxylic acids, except for nicotinic acid etc., and its triplet state energy is more suitable for the luminescence of Eu^{3+} than for Tb^{3+} Thus in ternary complexes of rare earths of carboxylic acids and phen, on account of the intramolecular energy transfer process between carboxylic acids (such as H_2FRA) and phen, phen may become the main energy donor and its energy coupling with RE^{3+} restricts the luminescence properties of complexes. Therefore, the luminescence intensities of europium ternary complexes may be stronger than those of europium binary complexes and the luminescence intensities of terbium ternary complexes may be weaker than those of terbium binary complexes. For this reason, phen is used as the additional ligand and introduced into rare earth complex systems, which is a kind of molecular design.

In order to prove the validity and reliability of the energy match and energy transfer theory, the luminescence spectra of europium and terbium complexes were measured, Fig. 4 and Fig. 5 show the fluorescence spectra of $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ and $Tb(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ respectively. From Fig. 4, the emission of $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ at 580 nm, 593 nm, 612 (620) nm, 650 nm and 701 nm originated from ${}^5D_0 \rightarrow {}^7F_0$, ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_2$, ${}^5D_0 \rightarrow {}^7F_3$ and ${}^5D_0 \rightarrow {}^7F_4$ transitions separately, and among these transitions, ${}^5D_0 \rightarrow {}^7F_2$ is the strongest. From Fig. 5, the emission of $Tb(NIA)_3 \cdot (phen)_2 \cdot 2H_2O$ at 488.5 nm, 545 nm, 585.5 nm and 620 nm originated from the ${}^5D_4 \rightarrow {}^7F_6$, ${}^5D_4 \rightarrow {}^7F_5$, ${}^5D_4 \rightarrow {}^7F_4$ and ${}^5D_4 \rightarrow {}^7F_3$ transitions separately, and the ${}^5D_4 \rightarrow {}^7F_5$ transition is the strongest emission. Table 3 shows the relative intensities of the strongest emissions of Eu^{3+} and Tb^{3+} complexes. As the data indicate, the ternary complexes with HNIA and phen show emission intensities close to those of their corresponding binary complexes with HNIA since the triplet state energy of HNIA is near to that of phen. Nevertheless, on account of the intramolecular energy transfer from H_2FRA to phen, in the ternary complex systems, phen becomes the chief luminescence sensitizer, so the ternary complexes of Eu^{3+} with H_2FRA and phen show stronger emission than the corresponding binary complexes of Eu^{3+} with acids. In the light of the energy match principle, the luminescence properties of the binary complex of Eu^{3+} with HNIA is superior to that of Eu^{3+} with H_2FRA, while it is in contrast for Tb^{3+} complexes. In order to illustrate further the result, the luminescence lifetimes and relative luminescence quantum efficiencies are given in Table 4. The data also draw the same conclusion that the luminescence lifetime and quantum efficiencies of Eu^{3+} binary complexes are much higher

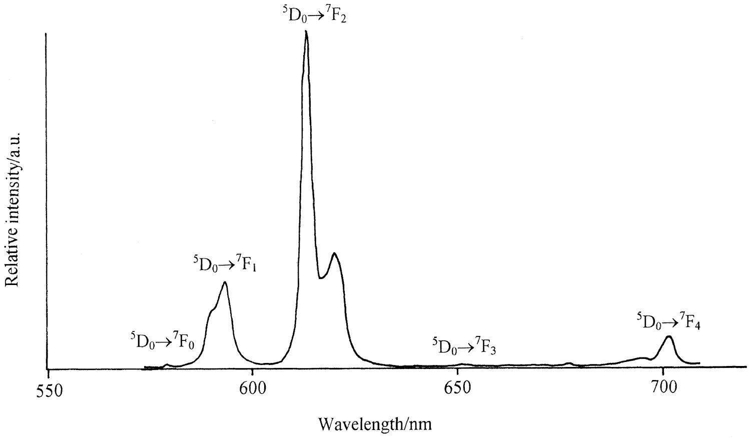

Fig. 4. The luminescence spectrum of Eu(NIA)$_3$·(phen)$_2$·3H$_2$O (solid sample).

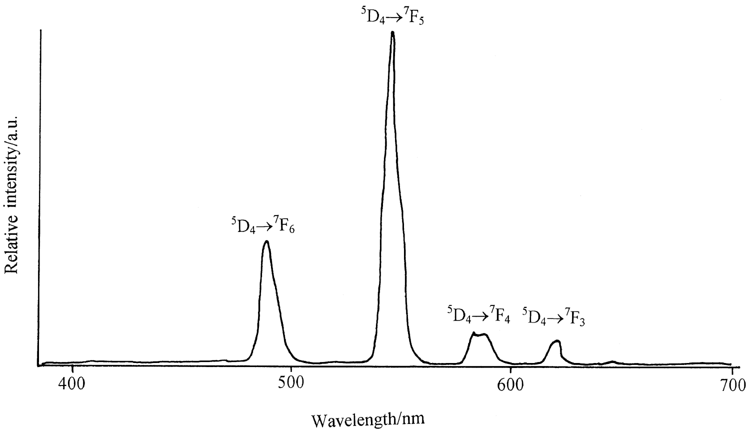

Fig. 5. The luminescence spectrum of Tb(NIA)$_3$·(phen)$_2$·3H$_2$O (solid sample).

Table 3
The luminescence intensities of Eu^{3+} and Tb^{3+} complexes ($^5D_0 \rightarrow {}^7F_2$ and $^5D_4 \rightarrow {}^7F_4$)

Complex	λ_{em} (nm)	λ_{ex} (nm)	Relative intensity (a.u.) [a]
Eu(NIA)$_3$·2H$_2$O	308.8	612.5, 620	29.7
Eu(NIA)$_3$·(phen)$_2$·3H$_2$O	308	612, 620	26.9
EuH(FRA)$_2$·3H$_2$O	311.2	616	1.3
EuH(FRA)$_2$·phen·4H$_2$O	314.4	613.5, 619.5	14.7
Eu(phen)$_2$·Cl$_3$·2H$_2$O	307.2	614, 620	47.9
Tb(NIA)$_3$·2H$_2$O	274.4	545.5	6.8
Tb(NIA)$_3$·(phen)$_2$·3H$_2$O	273.6	545	23.8
TbH(FRA)$_2$·3H$_2$O	277.5	546	20.7
TbH(FRA)$_2$·phen·4H$_2$O	274.4	543.5, 547	1.9
Tb(phen)$_2$·Cl$_3$·2H$_2$O	274.4	546	19.6

[a] Relative intensity is obtained from the integral area of the experimental luminescence spectrum, the experimental errors is ±5%.

than those of Tb^{3+} complexes, which is in good agreement with the results discussed above.

From the above discussion, it can be concluded that there exist two types of intramolecular energy transfer processes in the ternary complex systems of rare earths with conjugated carboxylic acids and 1,10-phenanthroline. One intramolecular energy transfer is from ligands (conjugated carboxylic acids) to the central rare earth ions (Eu^{3+} and Tb^{3+}) (LMET), which depends on the energy match between the lowest triplet energies and the resonant emitting levels of lanthanide ions. The other is the intramolecular energy transfer process between ligands (from conjugated carboxylic acids to 1,10-phenanthroline) (LLET), whose essential prerequisite is that the lowest triplet state energy of conjugated carboxylic acid is higher than that of 1,10-phenanthroline. In binary complexes, there exists only one intramolecular energy process, i.e. LMET. The distinction between the two intramolecular energy transfer processes is that LMET is the energy transfer from the triplet state energy of conjugated carboxylic acids to the resonant emitting level of RE^{3+} (sin-

Table 4
The luminescence lifetimes and luminescence quantum efficiencies of Eu^{3+} and Tb^{3+} complexes with nicotinic acid and 1,10-phenanthroline

Complex	Luminescence lifetime (10^{-6} s) [a]	Quantum efficiency [a,b]
$Eu(NIA)_3 \cdot 2H_2O$	737	0.086
$Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$	759	0.11
$Eu(phen)_2 \cdot Cl_3 \cdot 2H_2O$	838	0.33
$Tb(NIA)_3 \cdot 2H_2O$	820	0.038
$Tb(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$	1820	0.072
$Tb(phen)_2 \cdot Cl_3 \cdot 2H_2O$	1374	0.094

[a] The experimental error is ±10% on luminescence lifetimes and quantum efficiencies.
[b] The quantum efficiency of Eu^{3+} complexes is measured with $HQEu(TTA)_4$ as reference 1.00, HTTA ≡ 1-(2-thenoyl)-3,3,3-trifluoracetone, HQ ≡ pyrrolidine. The quantum efficiency of Tb^{3+} complexes is measured with $Tb(AcAc)_3 \cdot$ phen as reference 1.00, HAcAc ≡ acetylacetone, phen ≡ 1,10-phenanthroline.

glet state energy), while LLET is the energy transfer from the triplet state energy of conjugated carboxylic acids to the triplet state energy of 1,10-phenanthroline.

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