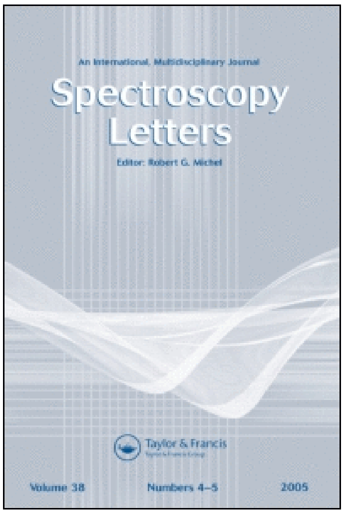

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Spectroscopic Study of Luminescence and Energy Transfer of Binary and Ternary Complexes of Rare Earth with Aromatic Carboxylic Acids and 1,10-Phenanthroline

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SPECTROSCOPIC STUDY OF LUMINESCENCE AND ENERGY TRANSFER OF BINARY AND TERNARY COMPLEXES OF RARE EARTH WITH AROMATIC CARBOXYLIC ACIDS AND 1,10-PHENANTHROLINE

Key Words: Spectroscopy, Luminescence, Energy transfer, Rare earth complexes, Aromatic carboxylic acid, 1,10-phenanthroline

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ABSTRACT

A series of rare earth (Gd, Eu, Tb) complexes with different substituent group carboxylic acids (ortho-hydroxylbenzioc acid, ortho-aminobenzoic acid and ortho-methoxy benzoic acid) and 1,10-phenanthroline were synthesized. The spectroscopic studies of the photophysical properties such as luminescence properties, energy match and intramolecular energy transfer were carried out. The lowest triplet state energies of ligands and the intramolecular energy transfer efficiencies were determined with the measurement of low phosphorescence spectra and lifetimes of Gd complexes.

INTRODUCTION

Rare earth complexes with carboxylic acids may be used as a structural and functional probe of biological macromolecule systems [1, 2]. On the other hand, it is a

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potential luminescent material for further application. So there has been a growing interest in the studies of the luminescence of rare earth complexes with aromatic carboxylic acids. But a lot of research were reported on the luminescence properties from energy match between the triplet state energy of β-Diketones ligands and the resonance energy level of central ion in rare earth chelates [3, 4], little attention has been paid to the rare earth complexes with aromatic carboxylic acids [5]. In this paper, phosphorescence spectra and lifetimes of gadolinium complexes were measured and the triplet state energy of ligands were determined, the intramolecular energy transfer efficiencies between aromatic carboxylic acids and 1,10-phenanthroline in ternary complexes were calculated. From the results, luminescence properties and energy transfer mechanism were discussed in details. The study will provide fundamental experimental data for predicting luminescence properties of rare earth complexes and seeking for new luminescent materials.

2. EXPERIMENTAL

The rare earth binary complexes with three kinds of ortho-substituent benzoic acids were prepared according to the report in ref [6, 7, 8]. The binary complexes of rare earth with 1,10-phenanthroline were prepared as the same method in ref [9]. The rare earth ternary complexes were synthesized as follows: An alcohol solution of rare earth chloride was added to an alcoholic solution of aromatic carboxylic acid by stirring with the molar ratio of the acid to RE^{3+} 3:1, whose pH value was adjusted to 6-7 by adding aqueous sodium hydroxide. Then the 1,10-phenanthroline in ethanol solution was added to the reaction mixture in the molar ratio of it to RE^{3+} ion 1:1. The precipitate was filtered off, washed with water and ethanol , and dried first at room temperature , then was stored over silica-gel drier.

To determine the composition of these complexes, elemental analysis was carried out on a CARIO-ERBA 1106 elemental analyzer . The luminescence spectra were measured on a SPEX FL-2T2 spectrofluorometer with excitation and emission slit at 0.5 mm. The low temperature phosphorescence spectra and lifetimes were carried out on the same instrument (at 77 K) as above (5×10^{-4} mol/L Chloroform solution).

3. RESULTS AND DISCUSSIONS

On the basis of elemental analysis, the composition data of the prepared complexes were shown in TABLE 1. where RE=Gd, Eu, Tb; *o*-HHBA (HABA and HMBA) =ortho hydroxyl benzoic (aminobenzoic and methoxybenzoic) acid and phen=1,10-phenanthroline, respectively.

Low temperature phosphorescence spectra of Gd^{3+} binary complexes with aromatic carboxylic acids and phen were measured. The shortest wavelength of emission bands was assumed to be 0-0 transition [3] . So the lowest triplet state energies of ligands ,the energy differences between the lowest triplet state energies and the resonance energy level of central Eu^{3+} and Tb^{3+} ions ($\Delta E(Tr\text{-}^5D_J$, J=0 or 4) were calculated . The data was shown in TABLE 2.

Intramolecular energy transfer efficiency chiefly depends on two energy transfer process [10]: one is from the lowest triplet state level of ligand to the resonance level of RE^{3+} by resonant exchange interaction [11], and the other is just an inverse energy transfer by thermal deactivation mechanism [12].Both energy transfer rate constant depend on the energy difference $\Delta E(Tr\text{-}^5D_J)$ between the triplet level energy of the ligands and the emitting level energy of Eu^{3+} and Tb^{3+}. The detailed discussion was shown as below:

For the resonant exchange interaction:

$$k_{ET}=P\mathrm{da}\bullet(-2R\mathrm{da}/L) \qquad (1)$$

$$P\mathrm{da}=(2\pi Z^2/R)\bullet\int F\mathrm{d}(E)\,E\mathrm{a}(E)\mathrm{d}(E) \qquad (2)$$

For the thermal deactivation mechanism:

$$k(T)=A\exp(-Ea/RT) \qquad (3)$$

where k_{ET} and $k(T)$ are the rate constant of resonant exchange interaction and thermal de-excitation respectively; *P*da is the transition probability from energy donor (carboxylic acid ligand) to energy acceptor (RE^{3+}); *R*da is the intermolecular distance between donor and acceptor and *L* is Vander Waals radius, both of them are considered to be equal to constant for intramolecular energy migration process); *F*d(E) and *E*a(E) are the experimental luminescence spectrum of energy donor (sensitizer) and the experimental absorption spectrum of energy acceptor (activator) respectively; The term of $2\pi Z^2/R$ is a constant related to the mutual orbital distance; *E*a(E) in equation (2) is the

TABLE 1. The Compositions of Rare Earth Complexes with Aromatic Carboxylic Acids and 1,10-Phenanthroline

Complexes	Found (%)				(Calculated) (%)			
	C	H	N	RE	C	H	N	RE
Gd(*o*-HBA)$_3$·H$_2$O	42.57	2.56	------	26.01	42.96	2.92	------	26.14
Gd(*o*-HBA)$_3$·phen·2H$_2$O	50.58	3.21	3.43	19.87	50.47	3.44	3.57	20.04
Eu(*o*-HBA)$_3$·H$_2$O	43.47	2.59	------	26.59	43.35	2.90	------	26.81
Eu(*o*-HBA)$_3$·phen·2H$_2$O	50.41	3.22	3.40	19.77	50.81	3.46	3.59	19.50
Tb(*o*-HBA)$_3$·H$_2$O	43.02	2.57	------	27.19	42.84	2.90	------	27.02
Tb(*o*-HBA)$_3$·phen·2H$_2$O	50.23	3.19	3.41	20.10	50.36	3.44	3.56	20.21
Gd(*o*-ABA)$_3$·H$_2$O	42.28	3.36	6.95	26.81	43.18	3.43	6.95	26.87
Gd(*o*-ABA)$_3$·phen·2H$_2$O	50.31	3.68	8.66	20.37	50.65	4.09	8.95	20.11
Eu(*o*-ABA)$_3$·H$_2$O	43.26	3.41	7.10	26.37	43.59	3.46	7.26	26.28
Eu(*o*-ABA)$_3$·phen·2H$_2$O	51.48	3.87	8.92	19.89	50.99	4.12	9.01	19.57
Tb(*o*-ABA)$_3$·H$_2$O	42.87	3.33	7.06	27.22	43.05	3.42	7.18	27.15
Tb(*o*-ABA)$_3$·phen·2H$_2$O	49.31	3.84	8.66	20.41	50.54	4.08	8.93	20.28
Gd(*o*-MBA)$_3$·3H$_2$O	43.09	3.69	------	23.27	42.97	4.03	------	23.46
Gd(*o*-MBA)$_3$·phen	54.37	3.27	3.38	19.89	54.25	3.64	3.52	19.75
Eu(*o*-MBA)$_3$·3H$_2$O	43.18	3.80	------	23.06	43.31	4.06	------	22.85
Eu(*o*-MBA)$_3$·phen	54.77	3.25	3.37	19.53	54.62	3.67	3.54	19.21
Tb(*o*-MBA)$_3$·3H$_2$O	43.02	3.77	------	23.41	42.86	4.02	------	23.65
Tb(*o*-MBA)$_3$·phen	54.33	3.29	3.59	19.73	54.14	3.63	3.51	19.92
Gd(phen)$_2$·Cl$_3$·2H$_2$O	43.30	2.94	8.20	23.97	43.65	3.03	8.49	23.84
Eu(phen)$_2$·Cl$_3$·2H$_2$O	43.76	2.92	8.23	23.65	44.01	3.06	8.56	23.22
Tb(phen)$_2$·Cl$_3$·2H$_2$O	43.80	2.89	8.19	24.31	43.54	3.02	8.47	24.03

TABLE 2. The Lowest Triplet State Energies and the Energy Differences $\Delta E(\mathrm{Tr}\text{-}{}^5D_J)$

Complexes	Lowest triplet state energies (cm^{-1})	$\Delta E(\mathrm{Tr}\text{-}{}^5D_0)$ (cm^{-1})	$\Delta E(\mathrm{Tr}\text{-}{}^5D_4)$ (cm^{-1})
Gd(*o*-HBA)$_3$·H$_2$O	23800	6536	3300
Gd(*o*-ABA)$_3$·H$_2$O	25229	7965	4729
Gd(*o*-MBA)$_3$·3H$_2$O	21505	4241	1005
Gd(phen)$_2$·Cl$_3$·2H$_2$O	22075	4811	1575

activation energy of the inverse energy transfer and may be equal to $\Delta E(\mathrm{Tr}\text{-}{}^5D_J)$. From equation (1), it can be seen that the overlap between the luminescence spectrum of ligands and the absorption spectrum of central RE^{3+} increased with the decreasing of $\Delta E(\mathrm{Tr}\text{-}{}^5D_J)$, namely k_{ET} increased with the decreasing of the energy difference. On the other hand, from equation (3), the conclusion can be drawn that $k(T)$ also show the same change tendency as k_{ET} with the decreasing of $\Delta E(\mathrm{Tr}\text{-}{}^5D_J)$. So it can be deduced that

$\Delta E(T)$ should be neither too large nor too small, there would be a optimal value. On the basis of the discussion, three carboxylic acids will sensitize Tb^{3+} more than Eu^{3+} efficiently due to the suitable energy difference between them and Tb^{3+}, while the energy match between phen and Eu^{3+} is better, so when phen is the predominate energy donor, it will sensitize Eu^{3+} more effectively.

Fig. 1 shows the phosphorescence spectra of $Gd(o\text{-}HBA)_3{\cdot}H_2O$, $Gd(phen)_2Cl_3{\cdot}2H_2O$ and $Gd(o\text{-}HBA)_3{\cdot}phen{\cdot}2H_2O$. It can be obviously seen that the phosphorescence spectrum of $Gd(o\text{-}HBA)_3{\cdot}phen{\cdot}2H_2O$ is similar to that of $Gd(phen)_2Cl_3 2H_2O$. The result suggested that phen is the main luminescent sensitizer in the ternary rare earth complexes and it is possible for energy migration between carboxylic acid and phen. The same result may be seen in the phosphorescence spectra of complexes with *o*-ABA and phen (Fig. 2). Fig. 3 shows the phosphorescence spectra of $Gd(phen)_2{\cdot}Cl_3{\cdot}2H_2O$, $Gd(o\text{-}MBA)_3{\cdot}3H_2O$ and $Gd(o\text{-}MBA)_3{\cdot}phen$, the result turned out the contrary to the former. $Gd(o\text{-}MBA)_3{\cdot}phen$ shows the same phosphorescence emission band position as that of $Gd(o\text{-}MBA)_3{\cdot}3H_2O$, the phenomenon indicate the intramolecular energy transfer process can't take place between *o*-HMBA and phen because that the low triplet state energy of *o*-HMBA is higher than that of phen.

In order to further interpret the opinion, low temperature phosphorescence lifetimes of Gd^{3+} complexes were determined, the results were summarized in TABLE 3. From the data in TABLE 3, the phosphorescence lifetimes of three ternary complexes were obviously all abated compared with the corresponding binary complexes with carboxylic acids.

Therefore, it can be deduced that energy transfer between acids and phen take place definitely. Here the intramolecular energy transfer process can be shown in Fig. 4.

The energy transfer rate and energy efficiency can be expressed as below

$$k^*_{ET}=\tau_1^{-1}-\tau_0^{-1} \qquad (4)$$

$$\eta_{ET}=k^*_{ET}\,(k^*_{ET}+k_1)^{-1} \qquad (5)$$

where k^*_{ET} and η_{ET} are the energy transfer rate constant and efficiency from carboxylic acids to phen respectively, τ_1 and τ_0 are the phosphorescence lifetimes of Gd^{3+} ternary complexes and correspondingly binary carboxylic acid complexes respectively and k_1 is phosphorescence rate constant. The data were also shown in TABLE 3.

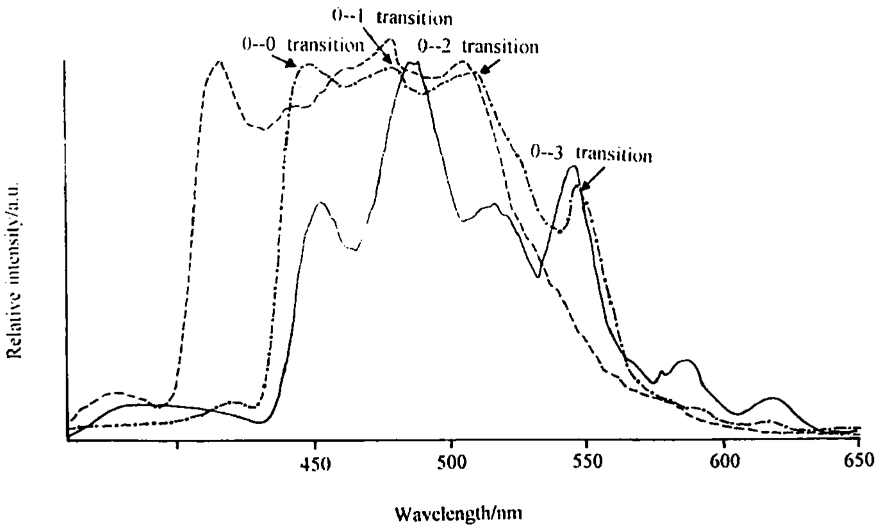

FIG. 1 The low temperature phosphorescence spectra of Gd(phen)$_2$·Cl$_3$·2H$_2$O (—) (λex=302.0 nm), Gd(*o*-HBA)$_3$·H$_2$O (—) (λex=318.7 nm) and Gd(*o*-HBA)$_3$·phen·2H$_2$O (—-) (λex=303.4 nm). (5×10^{-4} mol/l chloroform solution)

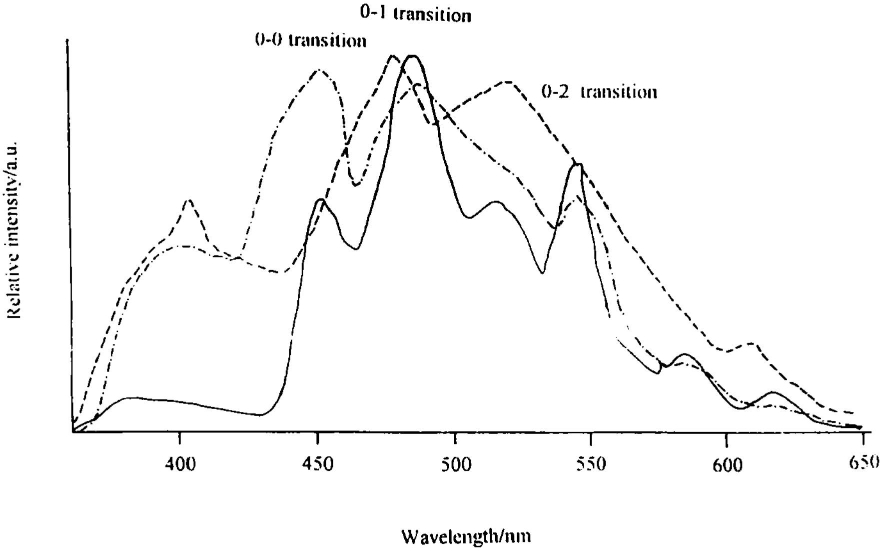

FIG. 2 The low temperature phosphorescence spectra of Gd(phen)$_2$·Cl$_3$·2H$_2$O (—)(λex=302.0 nm), Gd(*o*-ABA)$_3$·2H$_2$O (—) (λex=327.6 nm) and Gd(*o*-ABA)$_3$·phen·2H$_2$O (—-) (λex=307.4 nm). (5×10^{-4} mol/l chloroform solution)

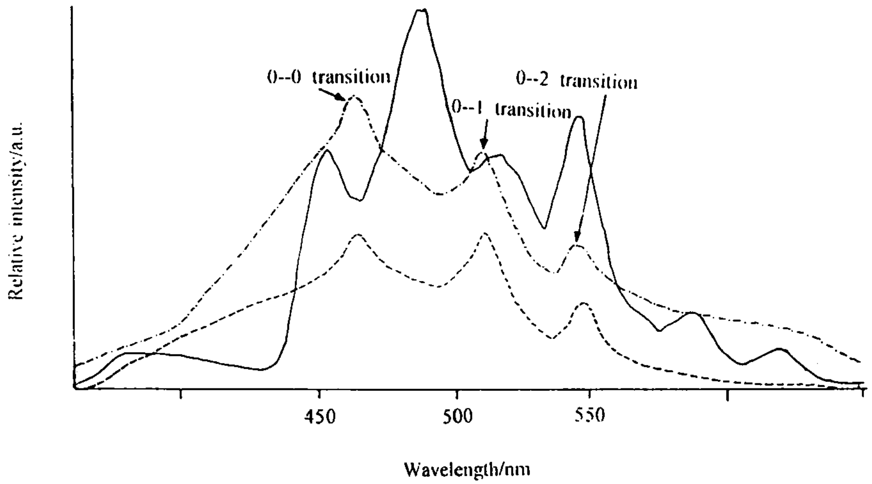

FIG. 3 The low temperature phosphorescence spetra of Gd(phen)$_2$·Cl$_3$·2H$_2$O (—)(λex=302.0 nm),Gd(*o*-MBA)$_3$·3H$_2$O (—)(λex=288.4 nm), and Gd(*o*-MBA)$_3$·phen (-—)(λex=298.6 nm).(5×10^{-4} mol/l chloroform solution)

TABLE 3. Phosphorescence Lifetimes of Gd^{3+} Complexes and the Energy Transfer Efficiencies between Aromatic Carboxylic Acids and 1,10-Phenanthroline

Complexes	Phosphorescence lifetimes (τ) (s) a)	Energy transfer efficiencies (%)
Gd(*o*-HBA)$_3$·H$_2$O	2.95	-------------
Gd(*o*-HBA)$_3$·phen·2H$_2$O	0.30	89.7
Gd(*o*-ABA)$_3$·H$_2$O	3.10	-------------
Gd(*o*-ABA)$_3$·phen·2H$_2$O	0.25	92.0
Gd(*o*-MBA)$_3$·3H$_2$O	2.06	-------------
Gd(*o*-MBA)$_3$·phen	2.12	-------------

a): the experimental errors ±10% on phosphorescence lifetimes

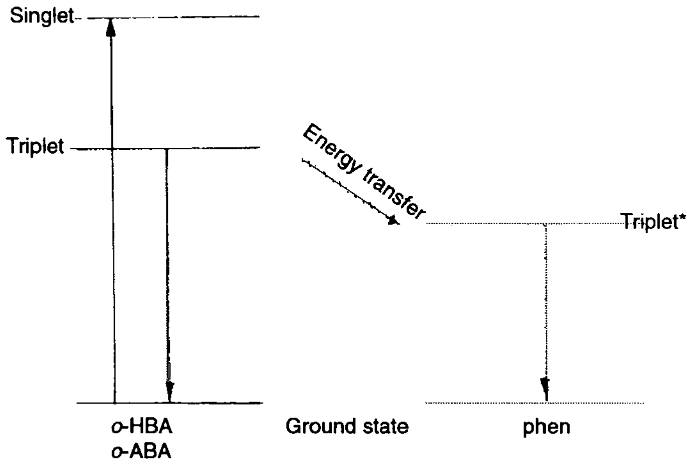

FIG. 4 The intramolecular energy transfer process from aromatic carboxylic acids to 1,10-phenanthroline

According to the value of η_{ET}, the energy transfer between *o*-HBA (or *o*-ABA) and phen is very large even that in ternary systems, the second ligand, phen is the chief energy donor. On the contrary, there can't exist intramolecular energy migration from *o*-MBA to phen and so the phosphorescence lifetime of ternary complex is roughly same as the corresponding complexes of *o*-MBA.

So as to demonstrate the above prediction, the fluorescence spectra of Eu^{3+} and Tb^{3+} were measured. Fig. 5 and Fig. 6 show the fluorescence spectrum of Eu(*o*-HBA)$_3$·phen·2H$_2$O and Tb(*o*-HBA)$_3$·phen·2H$_2$O respectively.

In Fig. 5, the emission of Eu(*o*-HBA)$_3$·phen·2H$_2$O at 579.5 nm, 591.5 nm, 613.7 (619) nm, 650 nm and 700 nm were 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; In Fig. 6, the emission of Tb(*o*-HBA)$_3$·phen·2H$_2$O at 486 nm, 542 (549) nm, 583 nm and 614.5 (620.9) nm were originated from $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$ transitions separately. Among these transitions, $^5D_0 \rightarrow ^7F_2$ transition of Eu(*o*-HBA)$_3$·phen·2H$_2$O and $^5D_4 \rightarrow ^7F_5$ transition of Tb(*o*-HBA)$_3$·phen·2H$_2$O is the strongest emission. TABLE 4 gives the relative luminescence intensities of the strongest emission of Eu^{3+} and Tb^{3+} complexes.

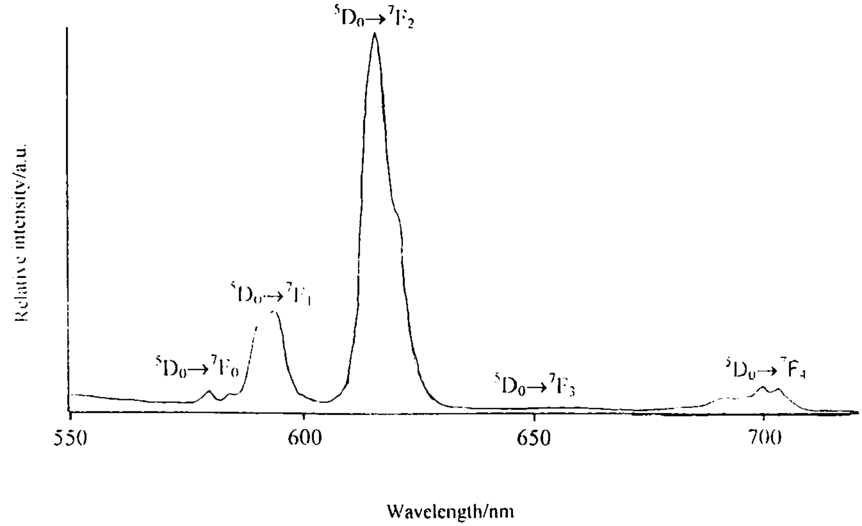

FIG. 5 The luminescence spectrum of Eu(*o*-HBA)$_3$·phen·2H$_2$O (solid sample)

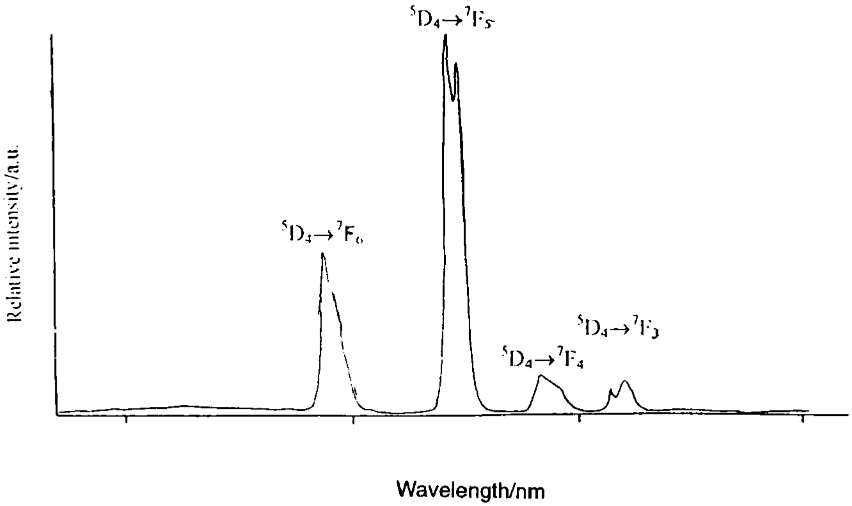

FIG. 6 The luminescence spectrum of Tb(*o*-HBA)$_3$·phen·2H$_2$O (solid sample)

TABLE 4. The Luminescence Properties of Eu^{3+} and Tb^{3+} Complexes

Complexes	λex (nm)	λem (nm)	Relative intensities (a.u.)
Eu(*o*-HBA)$_3$·H_2O	314.4	616	0.36
Eu(*o*-HBA)$_3$·phen·$2H_2O$	311.2	613.7, 619.5	0.87
Eu(*o*-ABA)$_3$·H_2O	314.4	616	1.27
Eu(*o*-ABA)$_3$·phen·$2H_2O$	307.2	615	4.68
Eu(*o*-MBA)$_3$·$3H_2O$	308.8	620, 622	24.4
Eu(*o*-MBA)$_3$·phen	308	615, 620	21.1
Eu(phen)$_2$·Cl_3·$2H_2O$	308	614, 620	47.8
Tb(*o*-HBA)$_3$·H_2O	304.4	541, 546	175
Tb(*o*-HBA)$_3$·phen·H_2O	298.8	542, 549	45.8
Tb(*o*-ABA)$_3$·H_2O	273.6	543, 549	30.2
Tb(*o*-ABA)$_3$·phen·$2H_2O$	274.4	545	95.8
Tb(*o*-MBA)$_3$·$3H_2O$	275.6	543.5	0.19
Tb(*o*-MBA)$_3$· phen	274	547	0.22
Tb(phen)$_2$·Cl_3·$2H_2O$	273.6	546	19.6

The reported luminescence intensity values were obtained by integration of each luminescence spectrum for the entire peak. As the data indicated, the luminescence intensities of Eu^{3+} and Tb^{3+} ternary complexes with *o*-MBA and phen are near to the luminescence intensities of Eu^{3+} and Tb^{3+} binary complexes with *o*-MBA, which can be well interpreted that the triplet state energy of *o*-MBA is close to that of phen and intramolecular energy migration is forbidden. Nevertheless, on account of the intramolecular energy transfer from *o*-HBA (or *o*-ABA) to phen, in their ternary complex systems, phen becomes the chief luminescence sensitizer, so the ternary complexes of Eu^{3+} with *o*-HBA (or *o*-ABA) and phen show the stronger emission than their corresponding binary complexes of Eu^{3+} with acids, and in the light of energy match principle, the luminescence properties of binary complexes of Eu^{3+} with *o*-MBA are superior to that of Eu^{3+} with the other carboxylic acids, while it is contrast for Tb^{3+} complexes, which are in good agreement with above results discussed.

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