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Intramolecular Energy Transfer and Co-luminescence Effect in Rare Earth Ions (La, Y, Gd and Tb) Doped with $Eu^{3+}\beta$ -diketone Complexes

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Abstract In this paper, $Eu^{3+}\beta$ -diketone Complexes with the two ligands 1-(2-naphthoyl)-3, 3, 3-trifluoroacetonate (TFNB) and 2'2-bipyridine (bpy) have been synthesized. Furthermore, we reported a systematical study of the cofluorescence effect of Eu(TFNB)₃bpy doped with inert rare earth ions (La^{3+} , Gd^{3+} and Y^{3+}) and luminescence ion Tb^{3+} . The co-luminescence effect can be found by studying the luminescence spectra of the doped complexes, which means that the existence of the other rare earth ions (La^{3+}, Y^{3+}) , Gd³⁺ and Tb³⁺) can enhance the luminescence intensity of the central Eu^{3+} , which may be due to the intramolecular energy transfer between rare earth ions and Eu^{3+} . The efficient intramolecular energy transfer in all the complexes mainly occurs between the ligand TFNB and the central Eu³⁺. Full characterization and detail studies of luminescence properties of all these synthesized materials were investigated in relation to co-fluorescence effect between the central Eu³⁺ and other inert ions. Further investigation into the luminescence properties of all the complexes show that the characteristic luminescence of the corresponding Eu³⁺ through the intramolecular energy transfers from the ligand to the central Eu³⁺. Meantime, the differences in luminescence intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition, in the ${}^{5}D_{0}$ lifetimes and in the ${}^{5}D_{0}$ luminescence quantum efficiency among all the synthesized materials confirm that the doped complex Eu_{0.5}Tb_{0.5}(TFNB)₃bpy exhibits higher

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Department of Chemistry, Tongji University, Siping Road 1239, Shanghai 200092, China ${}^{5}D_{0}$ luminescence quantum efficiency and longer lifetime than the pure Eu(TFNB)₃bpy complex and other materials.

Keywords Rare earth \cdot Co-fluorescence \cdot β -diketone complexes

Introduction

Luminescent rare earth organic complexes are of both fundamental and technical interest due to their characteristic luminescence properties, such as extremely sharp emission bands, long lifetime, and potential high internal quantum efficiency [1, 2]. In the past decades, Eu³⁺ complexes especially β-diketonates have been intensively studied due to their inherent extremely sharp emission peaks and high quantum efficiency [3, 4]. Some of the RE complexes demonstrate potential applications in efficient light-conversion molecular devices and organic light-emitting devices [5, 6]. In addition, the luminescence of rare earth ions stems from the intra-4f transitions, which in principle are forbidden transitions, resulting in relatively low emission efficiency. An effective approach to increase the luminescent efficiency is to modify the complexes with different kinds of ligands that have broad and intense absorption bands [7, 8] so that the absorbed photon energy has a large chance to transfer to the higher energy levels of rare earth ions. Another way is to mix the complexes with different sensitization ions [9, 10]. It was reported that adding certain nonfluorescing lanthanide ions, such as La³⁺, Gd³⁺ and Y^{3+} , could significantly enhance the photoluminescence intensity of the chelates of Eu³⁺. This type of fluorescence enhancement is actually an intrinsic fluorescence phenomenon referred to as the "co-fluorescence" effect [11-13], which can be found in coprecipitates, chelate suspensions, and LB films. Furthermore, in the case of Eu³⁺, immediate interaction of the ion with matrix oxygens generates an $O\rightarrow$ Eu charge transfer state (CT), which may extend into the near UV and can cause radiationless return to the ground state. These shortcomings are known to be circumvented successfully by the coordination of shielding ligands to the encapsulated rare earth ions. Bidentate aromatic organic ligands are particularly useful, as they contribute to the absorptivity and can act as "antennas" to the rare earth ion's luminescence as well. This process is well documented and proceeds along the following successive steps [14]: (1) singlet-singlet absorption of the ligand (${}^{1}S_{0}\rightarrow{}^{1}S^{*}, \pi-\pi^{*}$ in nature); (2) intersystem crossing (ISC, ${}^{1}S^{*}\rightarrow{}^{3}T$, promoted by the spin-orbit coupling due to the Eu³⁺ ion); (3) (exchange resonance driven) energy transfer ligand (${}^{3}T$) \rightarrow Eu³⁺ (${}^{5}D_{0}$).

1-(2-naphthoyl)-3, 3, 3-trifluoroacetonate (TFNB) is a kind of high absorbing chelating reagent because of the existence of β-diketones. In rare earth complexes, TFNB can absorb the photon and transfer the energy to the central metal ion effectively and give rise to very strong luminescence. In addition to that, the organic ligand TFNB also shows excellent solubility in a polymer host. To provide an insulating layer around the lanthanide complex and to reduce the probability of radiationless energy transfer from the complex to the solvent, 2'2-bipyridine (bpy) was incorporated as the synergistic agent. Under the above considerations, here, we reported a systematical study of the cofluorescence effect of Eu(TFNB)₃bpy doped with inert rare earth ions (La³⁺, Gd³⁺ and Y³⁺) and luminescence ion Tb³⁺. Full characterization and detail studies of luminescence properties of all these synthesized materials were investigated in relation to co-fluorescence effect between the central Eu^{3+} and other inert ions.

Experimental section

Chemicals

The solvent was used after desiccation with anhydrous calcium chloride. 2-acetonaphthone and ethyl trifluoroacetate were provided by Aldrich. Europium chloride (EuCl₃) ethanol solution (EtOH) was prepared by dissolving Eu_2O_3 in concentrated hydrochloric acid (HCl).

Synthetic procedures

Synthesis of organic ligand TFNB

1-(2-naphthoyl)-3,3,3-trifluoroacetonate (TFNB) was prepared using the method of Claisen condensation between 2acetonaphthone (2 mmol) and ethyl trifluoroacetate (1 mmol) in the presence of sodium ethoxide. After refluxing in anhydrous ethanol at 70 °C for 24 h, the solid was purified by recrystallization from ethanol. Anal.calcd. for $C_{14}H_9O_2F_3$: C, 63.1; H, 3.38 %. Found: C, 62.6; H, 3.29 %, m.p., 75 °C, ¹H NMR (CDCl₃): δ 6.71 (1H, s), 7.25(1H, m), 7.58(1H, m), 7.90(1H, d), 7.98(1H, d), 8.51 (1H, s), 15.25(1H, b).

Synthesis of complex Eu (TFNB)₃ bpy

A typical procedure for the preparation of the Eu³⁺ ion complex with TFNB was as follows: 1-(2-naphthoyl)-3, 3, 3trifluoroacetonate (TFNB) (1.5 mmol, 0.3993 g) and 2'2bipyridine (bpy) (0.5 mmol, 0.078 g) were first dissolved in 5 mL of ethanol solution with stirring. Then, 1 mol·L⁻¹ NaOH was dropwise added into the refluxing solution with the molar composition: TFNB: NaOH=1:1. The mixture was heated at 65 °C in a covered flask for approximately 1 h (pH=6.5). While being stirred, EuCl₃ was soaked in an appropriate amount of the above ethanol solution with the molar ratio of Eu³⁺: TFNB: bpy=1:3:1. The mixture was stirred at room temperature for 6 h, followed by filtration and extensive washing with EtOH. The resulting material Eu (TFNB)₃bpy was dried at 60 °C under vacuum overnight.

Synthesis of complex $Eu_{0.5}Ln_{0.5}(TFNB)_3bpy$ (Ln = La, Gd, Y and Tb)

The synthesis procedure for $Eu_{0.5}Ln_{0.5}(TFNB)_3$ bpy was similar to that of Eu (TFNB)₃ bpy except that the ethanol solution of EuCl₃ was replaced by the mixed solution of EuCl₃ and LnCl₃ with the molar composition: EuCl₃: LnCl₃=1:1.

Characterization-apparatus

IR spectra were measured within the 4000-400 cm⁻¹ region on a Nexus 912 AO446 FT-IR spectrophotometer.¹H NMR spectra were recorded in CDCl₃ on a Bruker AVANCE-500 spectrometer with tetramethylsilane (TMS) as internal reference. The Ultraviolet absorption spectra were carried out on an Agilent 8453 spectrophotometer. The fluorescence excitation and emission spectra were obtained with a Shimadzu RF-5301PC fluorescence spectrophotometer at room temperature. Luminescence lifetime measurements were carried out on an Edinburgh FLS920 phosphorimeter using a 450 w xenon lamp as excitation source.

Results and discussion

The IR spectral data of the ligands and coordination compounds were characterized by IR and UV absorption spectra.

FT-IR

The IR spectra for the ligands (TFNB and bpy) and all the complexes are shown in Table 1. Compared with the ligands, the coordination compounds showed the different chemical shifts in the range 4000~400 cm.⁻¹. In addition, the complexes have the same structure due to their similar IR. The IR spectra showed that the wide and strong bonds at 1,601 cm⁻¹ in free ligand TFNB, which can be assigned to the stretching mode $v_{c=0}$. Furthermore, the $v_{c=0}$ was lower than that of the normal carbonyl [15, 16] Compared with the $v_{c=0}$ bond in the free TFNB, the bond in complexes were shifted to the higher frequencies, which was probably due to the inductive effect of the fluorine atom group and the conjugated effect of bpy. These facts suggested that the ligand TFNB coordinated with RE ions through the oxygen negative ions of the enol form. The stretching band of 2,2'-bipyridine (bpy) $v_{C=N}$ was 1,456 cm⁻¹ and the stretching bands of coordination compounds were in $1,509 \sim 1,511$ cm⁻¹ region, which showed that the two nitrogen atoms in bpy coordinated with the rare earth ions.

UV absorption spectra

The UV absorption spectra of (A) TFNB (B) $Eu_{0.5}La_{0.5}$ (TFNB)₃ bpy are shown in Fig. 1. In Fig. 1a, red shift (281.2 \rightarrow 284.3 and 331.6 \rightarrow 334.5 nm) is observed, substantiating that a more extensive π - π^* conjugating system was formed due to the coordinated reaction. Comparing the absorption spectrum of $Eu_{0.5}La_{0.5}$ (TFNB)₃ bpy (C) with that of bpy, we can see a blue-shift of the major π - π^* electronic transitions (from 282 nm to 266.2 nm), indicating that the decrease of the conjugative effect as the two nitrogen atoms of bpy coordinate with RE³⁺ ions.

Photoluminescence properties

Luminescence measurements have been carried on the ternary Eu^{3+} complexes $Eu(TFNB)_3$ bpy at room temperature. The efficient ligand to the central ion energy transfer in $Eu(TFNB)_3$ bpy is investigated by energy difference

Table 1 Major IR spectra data (cm⁻¹) of ligands and the complexes

	$\nu_{\text{O-H}}$	$\nu_{C=O}$	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{C=C}$
TFNB	_	1601	1280	3057	_
Вру	3422	_	_	1453	_
Eu	3449	1611	1301	1509	1531
Eu _{0.5} La _{0.5}	3443	1613	1298	1511	1532
Eu _{0.5} Y _{0.5}	3447	1614	1300	1510	1532
Eu _{0.5} Gd _{0.5}	3446	1614	1298	1511	1531
Eu _{0.5} Tb _{0.5}	3447	1613	1299	1511	1532



Fig. 1 UV absorption spectra for TFNB (a) $Eu_{0.5}La_{0.5}$ (TFNB)₃ bpy (b)

between the triplet states of organic ligands and the resonance energy level of the central Eu³⁺ ion. According to the energy transfer and intramolecular energy mechanism [17, 18], the most important factor influencing the luminescence properties of rare earth complexes is the intramolecular energy transfer efficiency, which mainly depends on the two energy transfer processes. One is from lowest triplet level of ligands to the emissive energy level of Ln³⁺ ion (Rare earth ion) by the Dexter's resonant exchange interaction theory [19, 20]; the other is the reverse energy transition by the thermal deactivation mechanism. And the energy transfer rate constants ($k_{\rm T}$) are dependent on the energy difference ($\Delta E (T_{\rm r} - {\rm Ln}^{3+})$) between the lowest triplet level energy of ligands and the resonant emissive energy of the central Ln³⁺. Based on the

above two facts, the conclusion can be drawn that ΔE (T_r - Ln^{3+}) can have contrast influence on the two energy transfer process mentioned, and there should exist an optimal energy difference between the triplet position of ligands and the emissive energy level Eu³⁺ in the resulting material Eu(TFNB)₃bpy. If the energy difference is too big, the energy-transfer rate constant will decrease due to the diminution in the overlap between the energy donor (TFNB and bpy) and acceptor (Eu^{3+} ion). On the contrary, if the energy difference is too small, the energy can be backtransferred from the Eu^{3+} ion to the triplet state of the ligands. According to the luminescence theory of lanthanide complexes, the requirement for an efficient intramolecular energy transfer is that the energy difference between the triple state level of the ligand and the resonance energy level of the central Eu^{3+} ion be in the range 500-2,500 cm⁻¹. Thus, the energy difference $\Delta E (T_r - Eu^{3+})$ between the lowest triple state energy levels of TFNB $(19,600 \text{ cm}^{-1})$ and bpy $(22,913 \text{ cm}^{-1})$ ligands and the resonance energy levels of Eu^{3+} (⁵D₁, 19020 cm⁻¹) [24, 25] are 580 and 3,893 cm⁻¹, respectively, and it can be predicted that the triplet state energy of TFNB $(19,600 \text{ cm}^{-1})$ is more suitable for the luminescence of Eu^{3+} ion than bpy. So, it can be concluded that the efficient intramolecular energy transfer in the complex Eu (TFNB)₃bpy mainly occurs between the TFNB ligand and the Eu^{3+} ion.

Figure 2 shows the emission spectra for the pure Eu $(TFNB)_3$ bpy complex (A), $Eu_{0.5}La_{0.5}(TFNB)_3$ bpy(B), $Eu_{0.5}Y_{0.5}(TFNB)_3$ bpy(C), $Eu_{0.5}Gd_{0.5}(TFNB)_3$ bpy(D) and $Eu_{0.5}$ Tb_{0.5} (TFNB) $_3$ bpy (E). The excitation spectra of these materials were all obtained by monitoring the strongest emission wavelength of the Eu³⁺ ion at 613 nm. From the emission spectra of all the complexes, character-

istic Eu³⁺ ion emissions are observed. It can be clearly seen that mainly bands in the 450-700 nm range, which are assigned to the ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$ (J=0-4) transitions at 578 nm, 590 nm, 611 nm, 650 nm and 700 nm, respectively. The ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition is a typical electric dipole transition and strongly varies with the local symmetry of Eu³⁺ ions, while the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition corresponds to a partly allowed magnetic dipole transition, which is practically independent of the host material. In addition, among these transitions, ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition shows the strongest emission, suggesting the chemical environment around Eu³⁺ ions is in low symmetry [21, 22]. In the pure Eu(TFNB)₃bpy complex (Fig. 2a), the stark splitting reveals an ordered "stalline"re earth ion environment, rather than an amorphous one. Compared with the pure Eu(TFNB)₃bpy complex, the complexes doped with other rare earth ions (La, Y, Gd and Tb) have the higher luminescence intensities, indicating that the other rare earth ions can sensitize the central Eu³⁺. This may be ascribed to the different energy level of La^{3+} , Y³⁺ and Gd³⁺, resulted in the central Eu³⁺ obtaining more energy from the triple state level of the ligands. So we can make such a conclusion: when inert rare earth ions (La^{3+}) , Y^{3+} , and Gd^{3+}) are added to the pure complex at an appropriate ratio, the intrinsic emission peaks of Eu³⁺ are much enhanced. The mechanism of this co-luminescence enhancing effect is as follows. It is proverbial that TFNB and bpy can absorb radiant energy and then transfer it to Eu^{3+} . It can be presumed that the intramolecular energy transfer occurs and the transfer process from the energy donor to Eu³⁺ is enhanced, which agrees with the similar phenomenon in other systems [23]. As a result, the strong red luminescence was observed in the emission spectra which indicated that the effective energy transfer took place between the ligand TFNB and the chelated Eu³⁺ ions.



	Eu(TFNB) ₃ bpy	Eu _{0.5} Y _{0.5} (TFNB) ₃ bpy	Eu _{0.5} Tb _{0.5} (TFNB) ₃ bpy
$v_{00} ({\rm cm}^{-1})$	17229	17235	17235
$v_{01} (cm^{-1})$	16897	16943	16943
$v_{02} ({\rm cm}^{-1})$	16307	16334	16334
$v_{03} (cm^{-1})$	15337	15337	15332
<i>I</i> ₀₁	10.13	13.36	17.82
<i>I</i> ₀₂	101.36	128.61	169.99
I_{02}/I_{01}	10.01	9.63	9.54
τ (ms)	0.461	0.499	0.536
$1/\tau (ms^{-1})$	2.169	2.004	1.866
A _r	598	603	600
Anr	1571	1401	1266
η (%)	27.57	30.09	32.16

Furthermore, the luminescence intensities of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition for pure Eu(TFNB)₃bpy complex and the doped complex were all compared. The relative intensity of Eu_{0.5}Gd_{0.5}(TFNB)₃bpy complex is stronger than that of the other complexes. In addition, the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition can be used as a reference to compare luminescent intensities of different Eu³⁺-based materials due to its magnetic dipole nature. The relative luminescent intensities of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition (I₀₁) and the ${}^{5}D_{0} \rightarrow {}^{7}F_{2} / {}^{5}D_{0} \rightarrow {}^{7}F_{1}$



intensity ratios (red/orange ratio) for all materials are listed in Table 2.

Luminescence decay times (τ) and emission quantum efficiency (η)

The typical decay curve of the pure Eu^{3+} β -diketone complex $Eu(TFNB)_3$ bpy (A), $Eu_{0.5}Y_{0.5}$ (TFNB)₃bpy (B) and $Eu_{0.5}Tb_{0.5}$ (TFNB)₃bpy (C) were measured and they



can be described as a single exponential $(Ln(S(t)/S_0) = -k_1t = -t/\tau)$, indicating that all Eu³⁺ ions occupy the same average coordination environment (see Fig. 3). The resulting lifetime data (shown in Table 2) appears that the lifetimes of Eu_{0.5}Tb_{0.5} (TFNB)₃bpy complex are longer than that of other complexes.

According to the emission spectrum and the lifetime of the Eu³⁺ first excited level (τ , ⁵D₀), the emission quantum efficiency (η) of the ⁵D₀ Eu³⁺ excited state can be determined. Assuming that only nonradiative and radiative processes are essentially involved in the depopulation of the ⁵D₀ statea, η can be defined as follows [24]:

$$\eta = \frac{A_r}{A_r + A_{nr}} \tag{1}$$

Where A_r and A_{nr} are radiative and nonradiative transition rates, respectively. A_r can also be obtained by summing over the radiative rates A_{0J} for each ${}^5D_0 \rightarrow {}^7F_J$ (J=0-4) transitions of Eu³⁺.

$$A_r = \sum A_{0J} = A_{00} + A_{01} + A_{02} + A_{03} + A_{04}$$
(2)

The branching ratio for the ${}^{5}D_{0} \rightarrow {}^{7}F_{5, 6}$ transitions can be neglected as they are not detected experimentally, whose influence can be ignored in the depopulation of the ${}^{5}D_{0}$ excited state. Since ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ belongs to the isolated magnetic dipole transition, it is practically independent of the chemical environments around the Eu³⁺ ion, and thus can be considered as an internal reference for the whole spectrum, the experimental coefficients of spontaneous emission, A_{0J} can be calculated according to the equation [25–28].

$$A_{0J} = A_{01} (I_{0J} / I_{01}) (v_{01} / v_{0J})$$
(3)

Here, A_{0J} is the experimental coefficients of spontaneous emission. A_{01} is the Einstein's coefficient of spontaneous emission between the ⁵D₀ and ⁷F₁ energy levels. In vacuum, A_{01} as a value of 14.65 s⁻¹, when an average index of refraction *n* equal to 1.506 was considered, the value of A_{01} can be determined to be 50 s⁻¹ approximately $(A_{01}=n^3A_{01} (_{vac}))$ [29]. I_{01} and I_{0J} are the integrated intensities of the ⁵D₀ \rightarrow ⁷F₁ and ⁵D₀ \rightarrow ⁷F_J transitions (*J*= 0–4) with ν_{01} and ν_{0J} ($\nu_{0J} = 1/\lambda_J$) energy centers respectively. υ_{0J} refers to the energy barrier and can be determined from the emission bands of Eu³⁺'s ⁵D₀ \rightarrow ⁷F_J emission transitions. The emission intensity, *I*, taken as integrated intensity *S* of the ⁵D₀ \rightarrow ⁷F_{0–4} emission curves, can be defined as below:

$$I_{i-j} = h\omega_{i-j}A_{i-j}N_i \approx S_{i-j} \tag{4}$$

where *i* and *j* are the initial (${}^{5}D_{0}$) and final levels (${}^{7}F_{0-4}$), respectively, ω_{i-j} is the transition energy, A_{i-j} is the Einstein's coefficient of spontaneous emission, and N_i is

the population of the ⁵D₀ emitting level. On the basis of reference[30–34], the value of $A_{01}\approx50$ s⁻¹ and the lifetime (τ), radiative (A_r), and nonradiative (A_{nr}) transition rates are related through the following equation:

$$A_{\rm tot} = 1/\tau = A_{\rm r} + A_{\rm nr} \tag{5}$$

On the basis of the above discussion, the quantum efficiencies of the three kinds of europium complexes can be determined, as shown in Table 2. From the equation of η , it can be seen the value η mainly depends on the values of two quantum: one is lifetimes and the other is I_{02} / I_{01} . As can be clearly seen from Table 2, the quantum efficiencies of Eu_{0.5}Tb_{0.5} (TFNB)₃bpy (η =32.16%) is higher than that of pure Eu(TFNB)₃bpy and Eu_{0.5}Y_{0.5} (TFNB)₃bpy.

Conclusion

In summary, the Eu^{3+} complexes with 1-(2-naphthoyl)-3, 3, 3-trifluoroacetonate (TFNB) and 2'2-bipyridine (bpy) have been successfully prepared . In rare earth complexes, TFNB can absorb the photon and transfer the energy to the central metal ion effectively and give rise to very strong luminescence. In addition, we reported a systematical study of the co-fluorescence effect of Eu(TFNB)₃bpy doped with inert rare earth ions (La³⁺, Gd³⁺ and Y³⁺) and luminescence ion Tb³⁺. Full characterization and detail studies of luminescence properties of all these synthesized materials were investigated in relation to co-fluorescence effect between the central Eu³⁺ ion and other inert ions. Further investigation into the luminescence properties of all the complexes shows that the characteristic luminescence of the corresponding Eu³⁺ through the intramolecular energy transfers from the ligand to the central Eu³⁺ ions. Meantime, the differences in luminescence intensity of the ${}^5D_0 \rightarrow {}^7F_2$ transition, in the ${}^{5}D_{0}$ lifetimes and in the ${}^{5}D_{0}$ luminescence quantum efficiency among all the synthesized materials confirm that the doped complex Eu_{0.5}Tb_{0.5}(TFNB)₃bpy exhibits higher ⁵D₀ luminescence quantum efficiency and longer lifetime than the pure Eu(TFNB)₃bpy complex and the other materials.

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