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Enhanced luminescence and energy transfer of Eu(III) by Tb(III) in chelates in micelle solutions

Wenlian Li, Weili Li, Gui Yu, Qingrong Wang and Yongjie Jin
Changchun Institute of Physics, Academia Sinica, 1-Yan An Street, Changchun 130021 (China)

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Abstract

Fluorescence enhancement of Eu(III) by Tb(III) in TTA–Phen or BFA–Phen micelle solution was observed. From fluorescence absorption, excitation spectra and the decay time of Eu(III) emission in the complex solution systems, it can be demonstrated that the enhancement effect was the result of two mechanisms, one of which was the 'wrapping effect' of Tb complexes for Eu complexes and the other was intermolecular energy transfer from Tb complexes to Eu(III) ions.

1. Introduction

There have been several reports involving the sensitized emission of Eu(III) and Tb(III) β-dichetone chelates [1–3] since Weissman first described energy transfer from salicylaldehyde and β-dichetone ligand to Eu(III) ion [4]. The studies demonstrated that the sensitized emission of Eu(III) by Tb(III) in chelates arises from an intramolecular energy transfer which takes place at a triplet state of the chelating ligand. Recently, two interesting applications have been paid considerable attention. Firstly, lanthanide ions have been used as sensitive probes in their bimolecular complexes [5, 6]. Secondly, sensitized Eu(III) chelates were used for fluoroimmunoassays in clinical diagnostics [7, 8]. The applications have further promoted numerous fundamental studies of fluorescence properties in solutions of Eu or Tb complexes. Yang and coworkers [13, 14] have also observed fluorescence enhancement of Sm(III) by adding Ln(Ln$\equiv$Gd, Y), a phenomenon which they called 'co-luminescence'. The interpretation of the mechanism, however, has been not confirmed clearly. In this work we continue the investigation of enhanced fluorescence of the Eu β-dichetone complex system, though here we add Tb(III) rather than Y(III) or Gd(III). In our experiment TTA (thenoyltrifluoroacetone) and BFA (benzoyltrifluoroacetone) were used as the chelating reagents, and Phen (phenanthroline) was used as the neutral ligand for the two Eu–Tb complexes in micelle solutions.

2. Experimental details

2.1. Reagents and procedures

All the stock solutions of Eu(III), Tb(III) and Ln(III) ions were obtained by dissolving 99.95% of corresponding oxides in a minimum amount of lN HCl, the solutions were the heated to evaporate out extra HCl and then diluted to the desired volume using deionized water. The concentrations of the stock solutions were as follows: Eu(III), 1×10^{-3} M; Tb(III), 5×10^{-3} M; Ln(III) (Ln$\equiv$Y, La, Gd and Lu); 2×10^{-3} M. TTA, BFA and Phen were of analytical grade and their standard solutions were prepared by diluting corresponding stock solutions (1×10^{-3} M). The stock solutions of TTA, BFA and Phen were prepared by dissolving the appropriate amount of each compound in a mixed solvent of deionized water with 10% Triton X-100 solution at 40–60 °C. The stock solution of Triton X-100 was prepared by dissolving the appropriate volume of the biochemical reagent in deionized water, and the concentration was 1 vol.%. The standard buffer solution was prepared by dissolving 4 g of hexamethylenetetramine (analytical grade) in 100 ml of deionized water.

To a 10 ml test tube, the standard solution of Eu(III) and/or Tb (III) ion, β-dichetone, Phen, Triton X-100 and the buffer were successively added. The pH values of all the solutions were adjusted to 7 with HCl and/or NaOH solution. All the micelle solutions were shaken rigorously until clearly transparent and left for 30 min before taking measurements. The measuring solutions contained 1×10^{-7} M Eu(III), 0.025 vol.% Triton X-100, 1×10^{-4} M Phen, TTA (for the TTA system) or

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BFA (for the BFA system), and the concentration of the Tb(III) was changed from 10^{-6} to 10^{-5} M.

2.2. *Apparatus*

The excitation and emission spectra were obtained by a Shimadzu RF-520 spectrofluorimeter at room temperature. Absorption spectra were determined on a Shimadzu model UV-3000 dual-wavelength/double-beam recording spectrophotometer. The decay time was measured using a Spex 1403 double-grating spectrometer and an R928 photomultiplier tube; the sample was excited by an N_2 laser at 337.1 nm. The time constant can be determined from the decay curve obtained by a PARC 162 Boxcar and processed by a microprocessor. The fluorescence quantum yields of the complexes were determined by comparison with that of $1{\cdot}\times 10^{-5}$ M quinine–bisulphate–0.1 N H_2SO_4 solution ($\phi = 0.55$) [15].

3. Results and discussion

The excitation and emission spectra for Eu–TTA–Phen and Eu–BFA–Phen in micelle solutions are shown in Fig. 1. Figure 2 shows the absorption spectra of the two systems. From Fig. 1 and 2 it can be seen that the excitation spectra corresponded to their absorption spectra, and 'red-shifting' of the absorption band of the β-dichetone solution was observed when the Eu(III) ions were added into the β-dichetone micelle solution. The 'red-shifting' is probably the result of complex formation between the Eu(III) and the ligand; the conjugation of the structure is much stronger for the Eu complex than for the free ligand. The stable, conjugated structure can decrease the energy difference between S_1 and S_0. The absorption band (28.9×10^3 cm^{-1}) of the Eu–TTA system and that (30.8×10^3 cm^{-1}) of the Eu–BFA system originate from the electron transition of chelating rings and a large conjugated complex system [16]. Therefore, it was concluded that stable Eu–TTA–Phen and Tb–TTA–Phen complexes should exist in their respective micelle solutions, and a polynuclear complex can be seldom formed.

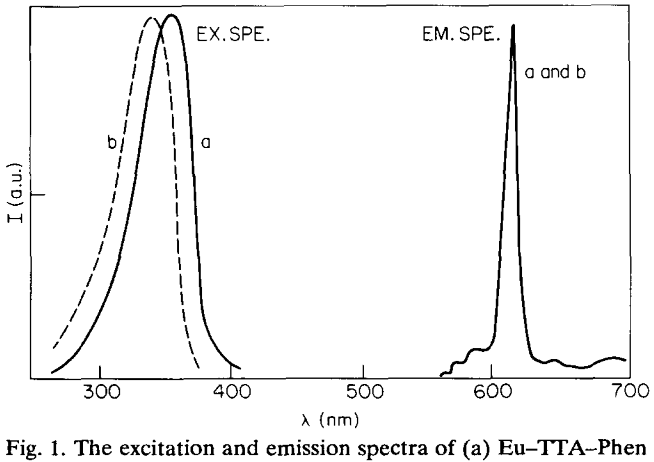

Fig. 1. The excitation and emission spectra of (a) Eu–TTA–Phen and (b) Eu–BFA–Phen in micelle solutions. Eu(III) 1×10^{-7} M; Tb(III), 1×10^{-5} M.

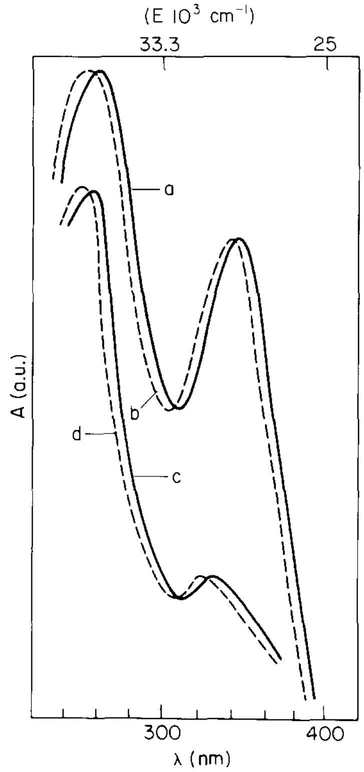

Fig. 2. Absorption spectra of (a) Eu–TTA–Phen, (b) TTA–Phen, (c) Eu–BFA–Phen, and (d) BFA–Phen in micelle solutions. Eu(III) 1×10^{-7} M.

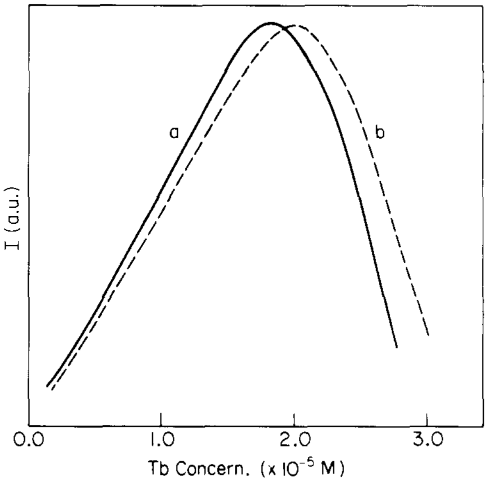

Fig. 3. The dependence of the emission intensities of Eu(III) ions on Tb(III) concentrations of (a) Eu–TTA–BFA and (b) Eu–BFA–Phen in micelle solutions. Eu(III) 1×10^{-7} M.

Figure 3 shows the effect of the Tb(III) ion concentration on the emission intensity of Eu(III) complexed with TTA–Phen and BFA–Phen in a micelle solution. From Fig. 3 it can be observed that the addition of Tb(III) increases the luminescence intensity of Eu(III), and there is a maximum in each of the curves. Table 1 displays the fluorescence properties of the Eu(III)–Tb(III)–TTA–Phen and Eu(III)–Tb(III)–BFA–Phen systems; those of complex systems are also collected in the table for comparison. The enhanced emission is probably related to the increasing quantum efficiency of Eu(III) fluorescence on the addition of Tb(III) (or Ln). In comparison with the Eu system, the Eu–Tb system has a much higher absorption intensity and longer decay time (see Table 1). On the other hand, the fluorescence intensities are much stronger for the TTA system than for the BFA system.

The fluorescence enhancement effect for Eu(III) in chelate micelle solution by adding Ln(III) ions has been discussed by other authors [12]. Because of the differences between Tb(III) and Ln(III) (Ln≡Y, La, Gd and Lu) in their 4f electron configurations, the effect of Tb(III) ions on Eu(III) fluorescence properties differs from that of the Ln(III) ions. The mechanism of enhancement of the Eu(III) emission can be explained as follows. First, the Tb complexes act presumably as an 'insulating sheath' reducing the radiationless energy loss from Eu(III) emission, which is similar to the effect of Ln(III) ions on Eu(III) emission as described in ref. 12. The addition of Tb(III) prolongs the $^5D_0$ decay time of Eu(III) emission up to 57% for the TTA system and 6.6% for the BFA system. The increase in the decay time indicates that radiationless deactivation from the $^5D_0$ level of Eu(III) to the O–H vibrational levels of H_2O molecules is markedly reduced. It is noticed that the Tb(III) concentrations are much higher than the Eu(III) concentrations in the two complex systems, and that the Eu(III) ions and Tb(III) ions are bound in a small volume. The Tb complex is close to the Eu complex, and can prevent the Eu(III) ion complex with β-dichetone from interacting with the aqueous environment. This is because the solution environment surrounding the Eu(III) ions is changed from an unorderly arrangement of free ligands to an orderly arrangement of Tb complexes. This is supported by the fact that no enhancement is observed in pure aqueous solution or in ethanol solution for the two Eu–Tb systems.

TABLE 1. Fluorescence properties of Eu–Tb–TTA–Phen and Eu–Tb–BFA–Phen in micelle solutions

Complex	$\log(I/I_0)$[a]	A/A_0[b]	ϕ/ϕ_0[c]	$\tau(\mu s)$[d]
Eu–TTA–Phen system				
Eu–TTA–Phen	0.00	1.00	1.00	322
Eu–Tb–TTA–Phen	1.93	2.08	44.5	507
Eu–La–TTA–Phen	1.86	1.97	29.5	539
Eu–Y–TTA–Phen	1.61	2.21	13.1	
Eu–Tb–BFA–Phen system				
Eu–BFA–Phen	0.00	1.00	1.00	563
Eu–Tb–BFA–Phen	1.14	1.14	12.1	600
Eu–Lu–BFA–Phen	0.50	1.10	2.83	609
Eu–Gd–BFA–Phen	0.92	1.06	7.98	645

[a] I_0 and I are the emission intensities of the Eu complex and the Tb or Ln complex respectively.

[b] A_0 and A are the absorbances of the Eu complex and the Tb or Ln complex respectively.

[c] ϕ and ϕ_0 are the quantum yields of the Eu complex, and the Tb or Ln complex respectively.

[d] Decay time of the $^5D_0$ level of the Eu(III) ions in the complexes.

Secondly, there would be an energy transfer from the Tb complex to the Eu(III) ions in the two complex systems. The fluorescence of Tb(III) ions in the system without Eu(III) ions can also be measured but the intensities are very weak. The $^5D_0$ level of Eu(III) ions and the $^5D_4$ level of Tb(III) ions in chelates are both 17.8×10^3 cm^{-1}, and the lowest excited triplets T_1 of TTA and BFA are at 20.6×10^3 cm^{-1} and 21×10^3 cm^{-1} in the two complex systems respectively. Thus the energy transfer between the T_1 and $^5D_0$ levels of Eu(III) would be more efficient than that between the T_1 and $^5D_4$ levels of Tb(III) [18–20], because the energy mismatch between the T_1 and $^5D_4$ levels of Tb(III) is too small to prevent a thermal deactivation process [17]. In the following, we will explain why the energy transfer from Tb complexes to Eu(III) can take place efficiently.

From Table 1 it is noticed that the absorptions were much higher for Eu–Tb complexes than for Eu complexes. It is shown that the increasing absorbance would be related to the large conjugated system which is due to complex formation between the Tb(III) and the TTA (or BFA) around the Eu(III) ions. Therefore, the energies absorbed by the Tb complexes should be transferred to the central Eu(III) ion. It seems that the transfer occurs through the lowest excited triplet T_1. On the other hand, a number of the molecules in the Tb complex must encounter the Eu(III) ions in the small volume. In the two micelle solutions, the Tb and Eu complexes are bound together by the surfactance, and the average distance between the Tb and Eu complexes should be short. According to Dexter's theory [21], the calculated average distance between the Tb and Eu complexes in the micelle solution is about 12 Å. The probability P_{SA} of transfer from S (sensitizer) to A (activator) is given by the expression [21]

$$P_{SA}=(27/r_{SA})^6\tau_S^{-1}$$

In the equation, the r_{SA} must be expressed in angstroms, τ_S is the decay time of S in the absence of A, and the effect of τ_S is much less than that of $(27/r_{SA})^6$ on P_{SA}. If $r_{SA}=27$ Å, r_{SA} is called the critical distance and is denoted by symbol $r_{SA}{}^0$. When $r_{SA}<r_{SA}{}^0$, energy transfer

dominates and is more important the smaller the value of r_{SA}. Therefore, the energy transfer from Tb complexes to Eu(III) ions should have a high probability. The transfer process is shown in Fig. 4.

Now let us compare the difference in the Eu(III) emission by adding Tb(III) ions. The Eu(III) emission enhancement in the former case is much larger than that in the latter (see Table 1). In the two Eu–Tb complexes, Eu(III) ions compete with the Tb(III) ions to obtain energy from the ligands. The emission intensity of Tb(III) in the BFA system is stronger than in the TTA system because the $^5D_4$ level of Tb(III) matches the T_1 level of the BFA ligand. Therefore, less energy of the BFA ligand is transferred to the $^5D_0$ level of the Eu(III) ions in the BFA system, and the enhancement of the Eu(III) fluorescence is weaker than in the TTA system.

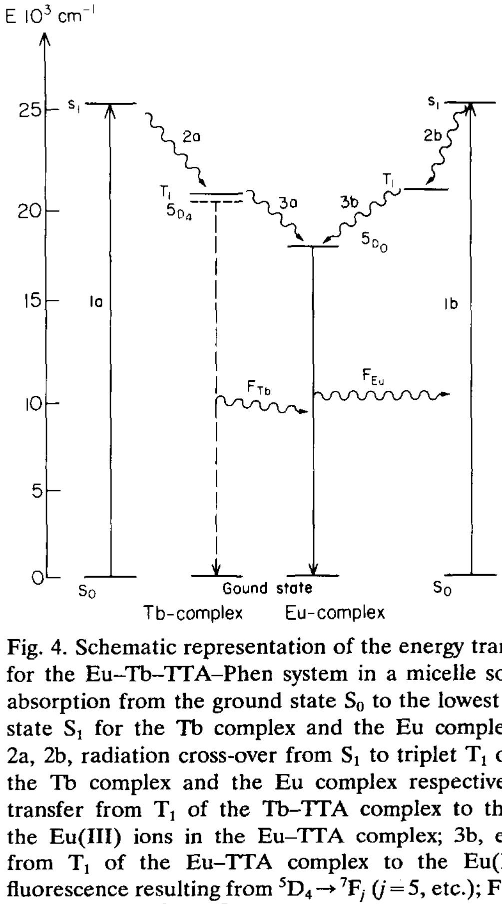

Fig. 4. Schematic representation of the energy transfer processes for the Eu–Tb–TTA–Phen system in a micelle solution: 1a, 1b, absorption from the ground state S_0 to the lowest excited singlet state S_1 for the Tb complex and the Eu complex respectively; 2a, 2b, radiation cross-over from S_1 to triplet T_1 of the TTA for the Tb complex and the Eu complex respectively; 3a, energy transfer from T_1 of the Tb–TTA complex to the $^5D_0$ level of the Eu(III) ions in the Eu–TTA complex; 3b, energy transfer from T_1 of the Eu–TTA complex to the Eu(III) ions; F_{Tb}, fluorescence resulting from $^5D_4 \rightarrow {}^7F_j$ ($j=5$, etc.); F_{Eu} fluorescence resulting from $^5D_0 \rightarrow {}^7F_j$ ($j=2$, 1).

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