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Intramolecular energy transfer mechanism between ligands in ternary rare earth complexes with aromatic carboxylic acids and 1,10-phenanthroline

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Abstract

A series of binary and ternary rare earth (Gd, Eu, Tb) complexes with aromatic acids and 1,10-phenanthroline have been synthesized. The lowest triplet state energies of ligands have been obtained by measuring the phosphorescence spectra of binary gadolinium complexes. By comparing the phosphorescence spectra of binary complexes with those of ternary ones, it is found that there exists another intramolecular energy transfer process from the aromatic acids to 1,10-phenanthroline besides the intramolecular energy transfer process between the aromatic acids and the central rare earth ions. The intramolecular energy transfer efficiencies have been calculated by determining phosphorescence lifetimes of binary and ternary gadolinium complexes. The luminescence properties of corresponding europium and terbium complexes are in agreement with the prediction based on energy transfer mechanism. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Intramolecular energy transfer mechanism; Ternary rare earth complexes; Aromatic carboxylic acids; 1,10-Phenanthroline

1. Introduction

Rare earth complexes with organic ligands, especially those containing Eu^{3+} and Tb^{3+}, often show efficient luminescence due to the strong absorption of the organic ligands and efficient energy transfer from the triplet state of ligands to rare earth ions [1]. In recent years, there has been considerable interest in the study on these complexes for their potential application as luminescent material and as a probe of chemical and biological molecules [2,3]. Many investigations have been reported on the energy match and energy transfer between the triplet state energy of β-diketones and the resonant energy level of central rare earth ions in the rare earth β-diketonates [4–6]. But little attention has been paid to the rare earth complexes with aromatic carboxylic acids [7]. The rare earth complexes of aromatic carboxylic acids have higher stability than those of β-diketones because of their infinite chain structure of chelation [8,9]. Research results indicated that the luminescence properties of rare earth complexes with organic ligands are the sensitive functions of the intramolecular energy transfer efficiencies between the triplet state energies of organic ligands and the resonant emissive energies of central rare earth ions [10–12]. The intramolecular energy transfer efficiency depends chiefly on two energy transfer processes [13]: the first is from lowest triplet level of ligands to the emissive energy level of Ln^{3+} ion by the Dexter's resonant exchange interaction [14]; the second is just an inverse energy transfer by thermal de-activation mechanism [15,16]. Both energy transfer rate constants are dependent on the energy difference between the lowest triplet level energy of ligands and the resonant emissive energy of Ln^{3+}. But in ternary complexes systems, when the second ligand is introduced, it is found that their luminescence properties change dramatically compared with the corresponding binary complexes. In order to interpret the phenomenon theoretically, one intramolecular energy transfer mechanism is put forward in the context, i.e., there may exist intramolecular energy transfer process between the two ligands (aromatic acids and heterocylic ligands). The low temperature phosphorescence spectra and lifetimes of gadolinium binary and ternary complexes with different aromatic acids and 1,10-phenanthroline (hereafter abbreviated as phen) have been measured, the energy match between the lowest triplet state energies of aromatic carboxylic acids and phen are studied and the energy transfer efficiency between the carboxylic acids and phen were determined. These results will provide relatively reliable criteria for the prediction of luminescence properties of rare earth complexes and for seeking excellent luminescent materials.

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2. Experimental details

Rare earth oxides (99.99%) were converted to their chlorides by treating with concentrated hydrochloric acid. All the acids (AR) were recrystallized before use. The binary and ternary rare earth complexes with *ortho*(*meta*, *para*) hydroxyl benzoic acid, *ortho*(*para*) aminobenzoic acid, *ortho* methoxy benzoic acid and phen were prepared according to Ref. [17–20]. Binary and ternary complexes with nicotinic acid, 3,4-furandicarboxylic acid were synthesized by using the same method as described in Ref. [21]. Rare earth complexes with *N*-phenylanthranilic acid and 1,10-phenanthroline were prepared previously [24]. The precipitate was filtered off, washed with water and ethanol, dried, and then stored over silica-gel drier. All the complexes obtained were identified by elemental analysis with a Cario-Erba 1106 elemental analyzer; IR spectra in the regions 4000–400 cm^{-1} were recorded on a Bio-Rad infrared spectrophotometer (Model FTS-7) with KBr pellet technique; TG and DTA curves were recorded on a thermal oflex DTA derivatograph at a rate of 10 K min^{-1} with the samples heating in ambient atmosphere at the sensitivities: TG—10 mg, DTA ± 50 μV.

Phosphorescence spectra and lifetimes of gadolinium complexes (5×10^{-4} mol/l ethanol and DMF mixed solution) were performed on a SPEX 1934D spectrophotometer using a 450 W xenon lamp as the excitation source at liquid nitrogen temperature. Fluorescence lifetimes of europium and terbium complexes were determined on the same instrument as above at room temperature. Fluorescence spectra were carried out on a SPEX FL-2T2 spectrofluorometer with emission and excitation slit width at 0.5 mm.

3. Results and discussion

The compositions of these prepared complexes were determined and shown in Table 1. It can be seen that most binary complexes with aromatic carboxylic acid are of the tris form $Ln(A)_3 \cdot nH_2O$ and most ternary complexes with aromatic acids and phen are of the $Ln(A)_3 \cdot phen \cdot nH_2O$ form (where A stands for aromatic carboxylic acid) [17–21].

Gadolinium complexes were selected as model complexes for the determination of the lowest triplet state energies of organic ligands due to their enhanced phosphorescence–fluorescence ratios ($\Phi_{ph}/\Phi_{fl} > 100$) compared to those of other lanthanide complexes, and the emitting level energy of Gd^{3+} is so much higher than the triplet state energies of organic ligands that it cannot be sensitized by ligands [22]. The shortest phosphorescence band in the low temperature phosphorescence spectrum may be assumed to be 0–0 transition. The lowest triplet levels were then determined and the results were summarized in Table 2. From the data of the energy difference [$\Delta E(Tr-{}^5D_j), j = 1$ or 4], it can be seen that aromatic acids and phen can all sensitize europium and terbium ions effectively, but the lowest triplet energy position

Table 1
The compositions of rare earth complexes with aromatic acids with 1,10-phenanthroline[a,b]

Binary complexes	Binary complexes	Ternary complexes	Ternary complexes
$Ln(o\text{-HBA})_3 \cdot H_2O$	$Ln(p\text{-ABA})_3 \cdot 2H_2O$	$Ln(o\text{-HBA})_3 \cdot phen \cdot 2H_2O$	$Ln(p\text{-ABA})_3 \cdot phen \cdot 2H_2O$
$Ln(p\text{-HBA})_3 \cdot 3H_2O$	$Ln(o\text{-MBA})_3 \cdot 3H_2O$	$Ln(p\text{-HBA})_3 \cdot phen$	$Ln(o\text{-MBA})_3 \cdot phen$
$Ln(N\text{-PA})_3 \cdot 4H_2O$	$Ln(NIA)_3 \cdot 2H_2O$	$Ln(N\text{-PA})_3 \cdot phen \cdot 2H_2O$	$Ln(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$
$Ln(o\text{-ABA})_3 \cdot H_2O$	$LnH(FRA)_2 \cdot 3H_2O$	$Ln(o\text{-ABA})_3 \cdot phen \cdot 2H_2O$	$LnH(FRA)_2 \cdot phen \cdot 4H_2O$

[a] Ln = Gd, Eu, Tb; *o*(*p*)HHBA = *ortho*(*para*)hydroxyl benzoic acid; *o*(*p*)HABA = *ortho*(*para*)aminobenzoic acid; *o*-HMBA = *ortho* methoxy benzoic acid; HNIA = nicotinic acid; H_2FRA = 3,4-furandicarboxylic acid, *N*-HPA = *N*-phenylanthanilic acid and phen = 1,10-phenanthroline, respectively.
[b] The detailed compositions data of the complexes can be seen in Refs. [17–21].

Table 2
The lowest triplet state energies of aromatic carboxylic acids, phen and the energy differences between them and Eu^{3+} and Tb^{3+}

Complexes	Lowest triplet state energies[a] [cm^{-1}]	$\Delta E(Tr-{}^5D_0)$ [cm^{-1}][a]	$\Delta E(Tr-{}^5D_4)$ [cm^{-1}][a]
$Gd(o\text{-HBA})_3 \cdot H_2O$	23 800	6535	3300
$Gd(p\text{-HBA})_3 \cdot 3H_2O$	23 530	6265	3030
$Gd(o\text{-ABA})_3 \cdot H_2O$	25 230	7965	4730
$Gd(p\text{-ABA})_3 \cdot 2H_2O$	24 445	7180	3945
$Gd(o\text{-MBA})_3 \cdot 4H_2O$	21 505	4240	1005
$Gd(NIA)_3 \cdot 2H_2O$	21 740	4475	1240
$GdH(FRA)_2 \cdot 3H_2O$	25 475	8210	4975
$Gd(N\text{-PA})_3 \cdot 4H_2O$	24 330	7065	3830
$Gd(phen)_2 \cdot Cl_3 \cdot 2H_2O$	22 075	4810	1575

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

of most carboxylic acid ligands except *ortho* methoxy benzoic acid and nicotinic acid are more suitable for the excited energy level of Tb^{3+}. So it can be predicted that the fluorescence intensity of Tb^{3+} complexes with these ligands would be stronger.

According to Ref. [23], the UV–visible spectra of ternary complexes of europium and terbium with salicylic acid and phen are similar to those of correspondingly binary ones with phen. Because of the different absorption peak and molecular absorbency coefficient, the energy transfer process between ligand and rare earth ions is changed. In binary complexes, salicylic acid absorbs energy and transfers it to Eu^{3+} and Tb^{3+}; while in ternary complexes, phen predominantly absorbed energy and transfer it to rare earth ions. So we can consider that in ternary complexes systems, when phen is introduced as a second ligand, it will influence luminescence intensity greatly. Because of the differences of triplet state energies between aromatic carboxylic acids and phen, there probably exist energy transfer process between some aromatic carboxylic acids and phen.

For this reason, ternary complexes of gadolinium are used as model complexes and the phosphorescence spectra of them are measured. By comparing the phosphorescence spectra of ternary complexes with those of binary ones, it is found that there exist two different phenomena. Fig. 1 shows that the phosphorescence spectra of binary and ternary gadolinium complexes with *N*-PA, *p*-ABA and phen. It can be seen that the phosphorescence spectra of ternary complex $Gd(N\text{-}PA)_3 \cdot phen \cdot 2H_2O$ and $Gd(p\text{-}ABA)_3 \cdot phen \cdot 2H_2O$ are similar to those of binary complex $Gd(phen)_2 \cdot Cl_3 \cdot 2H_2O$, while different from those of corresponding binary complex of *N*-PA, *p*-ABA, so phen is the main energy donor and predominantly sensitizes the Ln^{3+} ions' luminescence. It can be assumed that there may exist intramolecular energy migration from *N*-PA and *p*-ABA to phen. The same result can be obtained in the phosphorescence spectra of ternary and binary complexes of *ortho*(*para*) hydroxylic acid, *ortho* aminobenzoic acid, 3,4-furandicarboxylic acid and phen. On the contrary, for the gadolinium complexes with *o*-MBA, NIA and phen, there exist opposite results. Fig. 2 shows the phosphorescence spectra of their complexes. Because the lowest triplet state energies of *o*-MBA and NIA are lower than that of phen, intramolecular energy transfer from acids to phen cannot take place. In the figure, the ternary complexes $Gd(o\text{-}MBA)_3 \cdot phen$ and $Gd(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ show the same emission peak positions as that of $Gd(o\text{-}MBA)_3 \cdot 3H_2O$ and $Gd(NIA)_3 \cdot 2H_2O$, respectively. In order to verify this assumption, the low temperature phosphorescence lifetimes of complexes are determined and the intramolecular energy transfer efficiencies between aromatic carboxylic acids and phen are calculated. The data are shown in Table 2. The intramolecular energy transfer process can be described in Fig. 3. Because the low temperature phosphorescence decay curves of gadolinium complexes are all singly exponential, the decay process can be considered to be one rate dynamics equation.

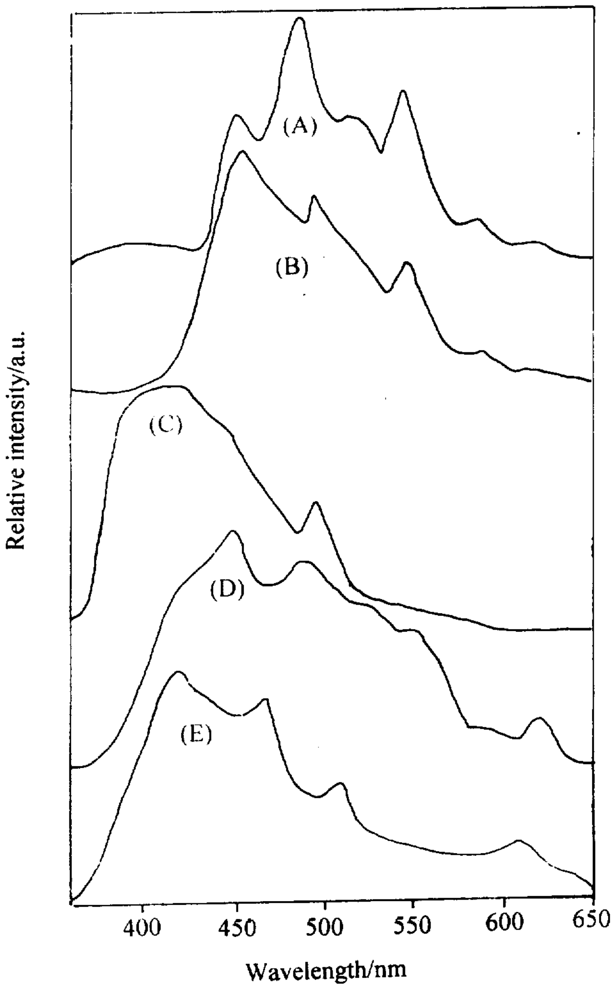

Fig. 1. The phosphorescence spectra of $Gd(phen)_2 \cdot Cl_3 \cdot 2H_2O$ ($\lambda_{ex} = 302.0$ nm) (A); $Gd(N\text{-}PA)_3 \cdot phen \cdot 2H_2O$ ($\lambda_{ex} = 307.6$ nm) (B); $Gd(N\text{-}PA)_3 \cdot 4H_2O$ ($\lambda_{ex} = 318.7$ nm) (C); $Gd(p\text{-}ABA)_3 \cdot phen \cdot 2H_2O$ ($\lambda_{ex} = 316.8$ nm) (D); and $Gd(p\text{-}ABA)_3 \cdot 2H_2O$ ($\lambda_{ex} = 334.5$ nm) (E); (5×10^{-4} mol/l ethanol and DMF mixed solution) at 77 K.

For binary complexes:

$$dC_M^*/dt = -k_1 C_M^* \quad (1)$$

For ternary complexes:

$$dC_M^*/dt = -(k_1 + k_{ET}^*) C_M^* \quad (2)$$

$$k_1 = \tau_0^{-1} \quad (3)$$

$$k_1 + k_{ET}^* = \tau_1^{-1} \quad (4)$$

So the energy transfer rate equation and the energy transfer efficiency equation can be represented as follows:

$$k_{ET}^* = \tau_0^{-1} - \tau_1^{-1} \quad (5)$$

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

where C_{M*} is the concentration of excited state of rare earth

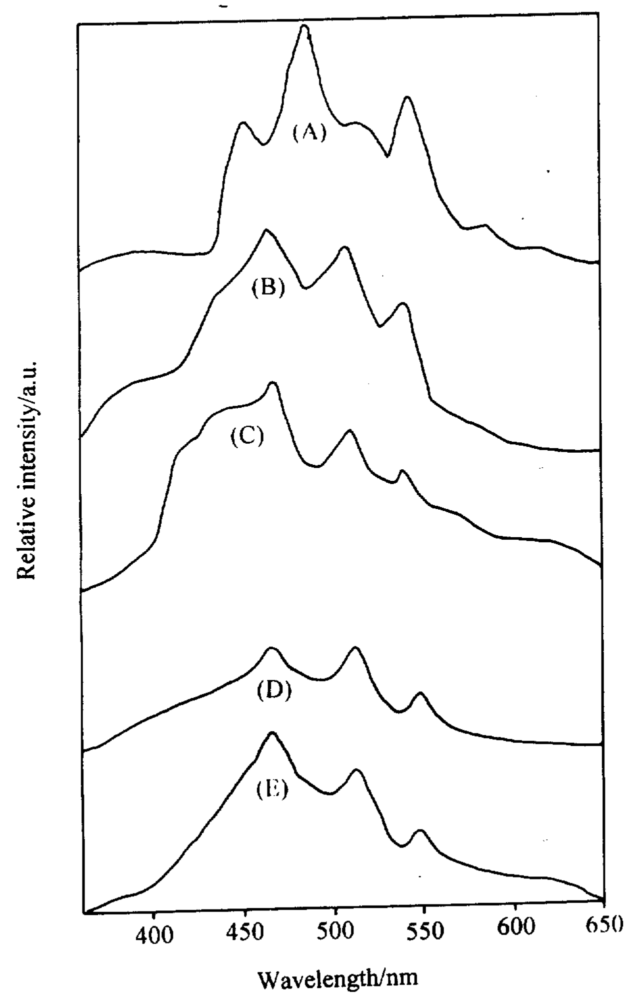

Fig. 2. The phosphorescence spectra of $Gd(phen)_2 \cdot Cl_3 \cdot 2H_2O$ (λ_{ex} = 302.0 nm) (A); $Gd(NIA)_3 \cdot 2H_2O$ (λ_{ex} = 298.8 nm) (B); and $Gd(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ (λ_{ex} = 298 nm) (C); $Gd(o\text{-}MBA)_3 \cdot H_2O$ (λ_{ex} = 288.4 nm) (D); and $Gd(o\text{-}MBA)_3 \cdot phen$ (λ_{ex} = 298.6 nm) (E); (5×10^{-4} mol/l ethanol and DMF mixed solution) at 77 K.

complexes, $k_{ET}{}^*$ is the rate constant of energy transfer from aromatic acids to phen, while k_1 is the rate constant of phosphorescence of Gd^{3+} complex with aromatic acids, τ_0 and τ_1 are phosphorescence lifetimes of binary complex and ternary complex respectively, and η_{ET} is energy transfer efficiency from aromatic acids to phen. From the data in Table 3, it can be obviously seen that intramolecular energy transfer efficiency from aromatic acids to phen is very large. So in the ternary complexes with these aromatic acids and phen, the energy match between phen and Ln^{3+} is the most important factor that influences the luminescence properties of complexes. On the contrary, the phosphorescence lifetimes of ternary complexes with HNIA, o-HMBA and phen are approximately equal to that of corresponding complexes of NIA and o-MBA. So there did not exist energy transfer from them to phen [18–21].

In accordance with the above discussion, the prerequisite of photophysics that the triplet state energies of some aromatic carboxylic acids are higher than that of phen make it possible to take place the intramolecular energy transfer process from these aromatic acids to phen. The energy from the triplet state level is transferred to the triplet of phen, and the energy of triplet state level of phen can be enhanced and further enhance the sensitization of the luminescence of europium and terbium ions. Both phosphorescence spectra and lifetimes indicate the existence of the intramolecular energy transfer process.

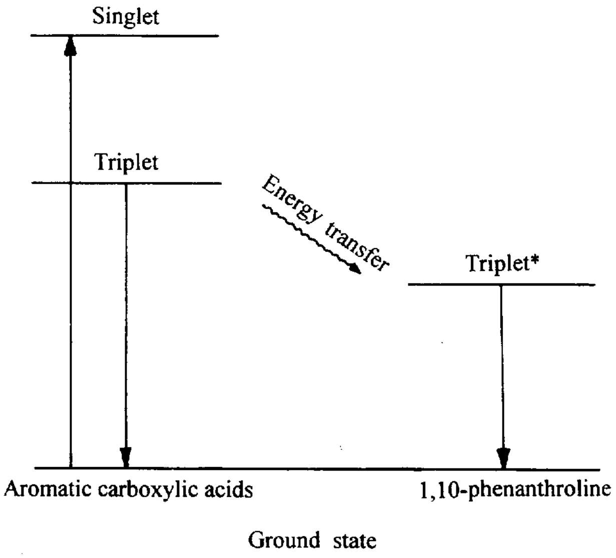

Fig. 3. The diagram of intramolecular energy transfer process from aromatic carboxylic acids to 1,10-phenanthroline.

In order to confirm the prediction from the energy difference between the triplet of ligands and the excited energy level of RE^{3+} ions, fluorescence spectrum of binary and ternary complexes of Eu^{3+} and Tb^{3+} were measured. Lumi-

Table 3
The phosphorescence lifetimes and energy transfer efficiencies from aromatic acids to phen

Complexes	Phosphorescence lifetimes[a] (s)	Energy transfer efficiencies[a] (%)
$Gd(o\text{-}HBA)_3 \cdot H_2O$	2.95	–
$Gd(o\text{-}HBA)_3 \cdot phen \cdot 2H_2O$	0.31	89
$Gd(p\text{-}HBA)_3 \cdot 3H_2O$	2.41	–
$Gd(p\text{-}HBA)_3 \cdot phen$	0.25	90
$Gd(o\text{-}ABA)_3 \cdot H_2O$	3.10	–
$Gd(o\text{-}ABA)_3 \cdot phen \cdot 2H_2O$	0.25	92
$Gd(p\text{-}ABA)_3 \cdot 2H_2O$	3.21	–
$Gd(p\text{-}ABA)_3 \cdot phen \cdot 2H_2O$	0.76	76
$Gd(o\text{-}MBA)_3 \cdot 3H_2O$	2.06	–
$Gd(o\text{-}MBA)_3 \cdot phen$	2.12	–
$Gd(NIA)_3 \cdot 2H_2O$	2.87	–
$Gd(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$	2.93	–
$Gd(N\text{-}PA)_3 \cdot 4H_2O$	3.0	–
$Gd(N\text{-}PA)_3 \cdot phen \cdot 2H_2O$	2.10	30
$GdH(FRA)_2 \cdot 3H_2O$	2.34	–
$GdH(FRA)_2 \cdot phen \cdot 4H_2O$	1.62	31

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

Table 4
The luminescence intensities of binary and ternary europium complexes

Complexes of Eu^{3+}	λ_{ex} (nm)	λ_{em} (nm)	Relative intensities (a.u.)
$Eu(o\text{-HBA})_3\cdot H_2O$	314.4	616	0.36
$Eu(o\text{-HBA})_3\cdot phen\cdot 2H_2O$	311.2	613.7, 619.5	0.87
$Eu(p\text{-HBA})_3\cdot 3H_2O$	314.7	614	0.02
$Eu(p\text{-HBA})_3\cdot phen\cdot 2H_2O$	311.4	617	28.0
$Eu(o\text{-ABA})_3\cdot H_2O$	314.4	616	1.27
$Eu(o\text{-ABA})_3\cdot phen\cdot 2H_2O$	307.2	615	4.68
$Eu(p\text{-ABA})_3\cdot H_2O$	308	618	65.6
$Eu(p\text{-ABA})_3\cdot phen\cdot 2H_2O$	308.8	617	129
$Eu(o\text{-MBA})_3\cdot 3H_2O$	308.8	620, 622	24.4
$Eu(o\text{-MBA})_3\cdot phen$	308	615, 620	21.1
$Eu(NIA)_3\cdot 2H_2O$	308.8	612.5, 620	17.3
$Eu(NIA)_3\cdot (phen)_2\cdot 3H_2O$	308	612, 620	15.2
$EuH(FRA)_2\cdot 3H_2O$	311.2	616	0.63
$EuH(FRA)_2\cdot phen\cdot 4H_2O$	314.4	613.5, 619.5	6.9

Table 5
The luminescence intensities of binary and ternary terbium complexes

Complexes of Tb^{3+}	λ_{ex} (nm)	λ_{em} (nm)	Relative intensities (a.u.)
$Tb(o\text{-HBA})_3\cdot H_2O$	304.4	541, 546	175
$Tb(o\text{-HBA})_3\cdot phen\cdot 2H_2O$	298.8	542, 549	45.8
$Tb(p\text{-HBA})_3\cdot 3H_2O$	298	540, 548	214.5
$Tb(p\text{-HBA})_3\cdot phen\cdot 2H_2O$	296.2	546	35.2
$Tb(o\text{-ABA})_3\cdot H_2O$	273.6	543, 549	95.8
$Tb(o\text{-ABA})_3\cdot phen\cdot 2H_2O$	274.4	545	30.2
$Tb(p\text{-ABA})_3\cdot H_2O$	273.6	543.6, 547.3	355
$Tb(p\text{-ABA})_3\cdot phen\cdot 2H_2O$	273.6	542, 545.5	311
$Tb(o\text{-MBA})_3\cdot 3H_2O$	275.6	543.5	0.19
$Tb(o\text{-MBA})_3\cdot phen$	274	547	0.22
$Tb(NIA)_3\cdot 2H_2O$	274.4	545.5	2.9
$Tb(NIA)_3\cdot (phen)_2\cdot 3H_2O$	273.6	545	15.7
$TbH(FRA)_2\cdot 3H_2O$	277.5	546	12.4
$TbH(FRA)_2\cdot phen\cdot 4H_2O$	274.4	543.5, 547	1.1

nescence spectra of rare earth complexes are all similar since they are the characteristic emission of rare earth center ions. Different organic ligands only change the emission intensity, the emission position change hardly. Tables 4 and 5 show the fluorescence properties of europium complexes and terbium complexes, respectively. From Table 4, it can be seen the luminescence intensities of binary Eu^{3+} complexes with nicotinic acid (and *ortho* methoxybenzoic acid) are stronger than those of ternary Eu^{3+} ones; on the contrary, the luminescence intensities of binary Eu^{3+} complexes with other aromatic carboxylic acids (*ortho*(*para*) hydroxyl benzoic (aminobenzoic) acid, 3,4-furandicarboxylic acid and *N*-phenylanthranilic acid) are weaker than those of ternary Eu^{3+} ones. From Table 5, the intensities of binary Tb^{3+} complexes with nicotinic acid (and *ortho* methylbenzoic acid) are weaker than those of ternary Tb^{3+} ones; while the intensities of binary complexes with other aromatic carboxylic acids are stronger than those of correspondingly ternary Tb^{3+} ones. All these can be well explained by the intramolecular energy transfer process between aromatic carboxylic acids and phen. The triplet state energies of $o(p)$-HHBA, $o(p)$-HABA, H_2FRA and *N*-HPA are all higher than that of phen, so there exist intramolecular energy transfer from these acids to phen, and phen becomes the main energy donor of rare earth ions in correspondingly ternary complexes systems. The luminescence properties of complexes depended on the energy match between phen and rare earth ions. The triplet state energy of phen is more suitable for the sensitization of Eu^{3+} than for Tb^{3+}, so the luminescence properties of complexes of Eu^{3+} and Tb^{3+} show the above phenomena. On the other hand, there did not exist intramolecular energy transfer process between nicotinic acid (and *ortho* methoxy benzoic acid) and phen for the triplet state energies are lower than that of phen, so the luminescence properties exhibit the contrary phenomena. This verifies the intramolecular energy transfer process between ligand and Ln^{3+} and the energy coupling mechanism.

4. Conclusions

Whether between central ions and aromatic carboxylic acid ligands or between the aromatic acid ligands and phen ligand, it is found that the intramolecular energy efficiency is a sensitive function of the relative positions of the resonance energy levels of the central rare earth ions and the lowest triplet states of the ligands. For binary complexes of rare earth with aromatic carboxylic acids, the triplet state energy state energies of *ortho* methoxy benzoic acid and nicotinic acid were suitable for the sensitization of Eu^{3+} ion. On the contrary, the other aromatic acid studied by us showed optimal energy match to the Tb^{3+}. In order to modify the luminescence properties of rare earth ions, a second ligand (phen) can be introduced and the ternary complexes obtained. When the triplet state energies of aromatic carboxylic acid are higher than that of phen, there may exist the intramolecular energy transfer from aromatic acids to phen, and then energy may be transferred from the latter to the central ions. So the luminescence properties of binary rare earth complexes can be predicted from the triplet state energies of ligands, and the luminescence properties can be changed with the addition of a second ligand. On the basis of energy match and energy transfer mechanism, excellent luminescent rare earth complexes with can be obtained molecular design. For example suitable ligands and second ligands can be selected and the excellent luminescent binary and ternary complexes can be synthesized.

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References

[1] H.S. Shou, J.P. Ye, Q. Yu, J. Lumin. 42 (1988) 29.
[2] G.F.H. De Sa, H.A. Nunes, O.L. Malta, J. Chem. Res. (S) 78 (1992) .
[3] F.S. Richardson, J. Chem. Rev. 82 (1982) 541.
[4] S. Sato, M. Wada, Bull. Chem. Soc. Jpn. 43 (1970) 1955.
[5] M. Kleinerman, S. Choi, J. Chem. Phys. 49 (90) (1968) 3901.
[6] C.R.S. Dean, T.M. Shepherd, Chem. Phys. Lett. 32 (3) (1975) 480.
[7] Y.S. Yang, M.L. Gong, Y.Y. Li, J. Alloys Comp. 207–208 (1994) 112.
[8] P.U. Guerriero, S.S. Casellato, P.A. Cigato, R. Graziani, Inorg. Chim. Acta 139 (1987) 67.
[9] J.F. Ma, Z.Z. Jin, J.Z. Ni, Polyhedron 14 (4) (1995) 563.
[10] T.A. Seiji, W.Z. Masayuki, T. Ikuzo, J. Phys. Chem. 89 (1985) 5649.
[11] Y. Haas, G. Stein, J. Phys. Chem. 75 (34) (1971) 3668.
[12] M. Kleinerman, J. Chem. Phys. 51 (6) (1969) 2370.
[13] S.L. Wu, Y.L. Wu, Y.S. Yang, J. Alloys Comp. 180 (1992) 399.
[14] D. Dexter, J. Chem. Phys. 21 (1953) 836.
[15] C.R.S. Dean, T.M. Shepherd, J. Chem. Soc., Faraday Trans. 71 (1975) 146.
[16] R.L. Hanna, R. Arza, S. Shammai, Chem. Phys. Lett. 29 (1982) 576.
[17] B. Yan, H.J. Zhang, J.Z. Ni, Chin. Chem. Lett. 8 (4) (1997) 353.
[18] B. Yan, H.J. Zhang, J.Z. Ni, Chin. J. Chem. 15 (3) (1997) 242.
[19] B. Yan, H.J. Zhang, S.B. Wang, J.Z. Ni, J. Chin. Chem. Soc. 44 (6) (1997) 567.
[20] B. Yan, H.J. Zhang, S.B. Wang, J.Z. Ni, Monatsh. Chem. 129 (2) (1997) 151.
[21] H.J. Zhang, B. Yan, S.B. Wang, J.Z. Ni, J. Photochem. Photobiol. A. Chem. 109 (1997) 223.
[22] W.F. Sager, J. Phys. Chem. 69 (1965) 1092.
[23] H.Y. Zeng, Y.S. Yang, S.H. Huang, Chin. J. Lumin. 16 (4) (1995) 549.
[24] B. Yan, H.J. Zhang, S.B. Wang, J.Z. Ni, Monath. Chem. (1998), to be published.