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Photophysical Properties of Some Binary and Ternary Complexes of Rare Earth Ions with Aminobenzoic Acids and 1,10-Phenanthroline

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Summary. Photophysical properties (*e.g.* luminescence and energy transfer) of binary and ternary complexes of Gd^{3+}, Eu^{3+}, and Tb^{3+} with aminobenzoic acids and 1,10-phenanthroline were studied in connection with their spectroscopic characterization. Intramolecular energy transfer between center ions and ligands as well as between ligands is discussed in detail.

Keywords. Complexes of Gd^{3+}, Eu^{3+}, and Tb^{3+}; Photophysical properties; Aminobenzoic acids; 1,10-Phenanthroline.

Photophysikalische Eigenschaften einiger binärer und ternärer Komplexe von Seltenerdionen mit Aminobenzoesäuren und 1,10-Phenanthrolin

Zusammenfassung. Die photophysikalischen Eigenschaften (z.B. Lumineszenz und Energieübertragung) von binären und ternären Komplexen von Gd^{3+}, Eu^{3+}, und Tb^{3+} mit Aminobenzoesäuren und 1,10-Phenanthrolin wurden im Zusammenhang mit ihrer spektroskopischen Charakterisierung bestimmt. Der intramolekulare Energietransfer zwischen Zentralionen und Liganden bzw. zwischen Liganden wird detailliert erörtert.

Introduction

In recent years there has been a growing interest in the potential application of europium and terbium coordination compounds as luminescent material and liminescent probes for a variety of chemical and biological studies [1, 2]. Investigations focused mainly on luminescence properties, energy match, and energy transfer of rare earth chelates with β-diketones [3–5]. However, little attention has been paid to luminescent lanthanide complexes with carboxylic acids. Compared to the rare earth chelates with β-diketones, the complexes with aromatic carboxylic acids offer the advantage of stable luminescent properties owing to their infinite chain structure. In this paper, binary and ternary complexes of gadolinium are used as model complexes. The triplet state position of *ortho* and *para* aminobenzoic acid and 1,10-phenanthroline were determined. From the assumption of energy matching, the luminescence properties of the corresponding complexes of europium and terbium were studied. The intramolecular energy migration process between aminobenzoic acids and Ln^{3+} and from aminobenzoic acids to 1,10-phenanthroline are discussed in detail. The results provide a criterion for the prediction of luminescence properties of rare earth complexes.

Results and Discussion

The compositions of the complexes were established on the basis of the elemental analysis data (Table 1).

Gd^{3+} complexes were selected as model complexes for the determination of the triplet state energies of the organic ligands owing to their high phosphorescence-fluorescence ratios compared to those of other Ln^{3+} complexes. The phosphorescence spectra of $Gd(o\text{-}ABA)_3 \cdot H_2O$, $Gd(p\text{-}ABA)_3 \cdot 2H_2O$, and $Gd(phen)_2 \cdot Cl_3 \cdot 2H_2O$ were measured at 77 K in ethanolic solution. The lowest triplet state energy was determined by assuming the shortest phosphorescence band wavelength to be the 0–0 transition. The energy differences between the triplet state of the ligands and the resonance energy levels of Eu^{3+} ($^5D_0$) and Tb^{3+} ($^5D_4$) ions were calculated. The results are summarized in Table 2. From the data of the energy difference ($\Delta E = (Tr\text{-}^5D_j)$, $j = 1$ or 4) it can be seen that both *o-ABA* and *p-ABA* can sensitize europium and terbium ions effectively, but the lowest triplet state energy positions of the carboxylic acid ligands are more suitable for the excited energy level of Tb^{3+}; it can therefore be predicted that the fluorescence intensity of Tb^{3+} complexes would be stronger. According to the general luminéscence principle of rare earth complexes with organic ligands, the intramolecular energy transfer efficiency depends chiefly on two energy transfer processes: from the lowest triplet state level of ligands to the emissive energy level of Ln^{3+} (*Dexter*'s resonant

Table 1. Elemental analyses (*o-ABA* = *o*-aminobenzoic acid, *p-ABA* = *p*-aminobenzoic acid, *phen* = 1,10-phenanthroline; *RE* = rare earth ion)

	Found (%)				Calculated (%)			
	C	H	N	*RE*	C	H	N	*RE*
$Gd(o\text{-}ABA)_3 \cdot H_2O$	42.28	3.36	6.95	26.81	42.18	3.43	6.95	26.87
$Ev(o\text{-}ABA)_3 \cdot H_2O$	43.26	3.41	7.10	26.37	43.59	3.46	7.26	26.28
$Tb(o\text{-}ABA)_3 \cdot H_2O$	42.87	3.33	7.06	27.22	43.05	3.42	7.18	27.15
$Gd(p\text{-}ABA)_3 \cdot 2H_2O$	42.36	3.44	6.68	26.31	41.90	3.33	6.98	26.14
$Eu(p\text{-}ABA)_3 \cdot 2H_2O$	42.27	3.22	6.80	25.63	42.55	3.35	7.04	25.48
$Tb(p\text{-}ABA)_3 \cdot 2H_2O$	41.80	3.17	7.10	26.29	41.77	3.31	6.96	26.34
$Gd(phen)_2 \cdot Cl_3 \cdot 2H_2O$	43.30	2.94	8.20	23.97	43.65	3.03	8.49	23.84
$Eu(phen)_2 \cdot Cl_3 \cdot 2H_2O$	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
$Gd(o\text{-}ABA)_3 \cdot phen \cdot 2H_2O$	50.31	3.68	8.66	20.37	50.65	4.09	8.95	20.11
$Eu(o\text{-}ABA)_3 \cdot phen \cdot 2H_2O$	51.48	3.87	8.92	19.89	50.99	4.12	9.01	19.57
$Tb(o\text{-}ABA)_3 \cdot phen \cdot 2H_2O$	49.31	3.84	8.66	20.41	50.54	4.08	8.93	20.28
$Gd(p\text{-}ABA)_3 \cdot phen \cdot 2H_2O$	50.36	3.73	8.63	20.34	50.65	4.09	8.95	20.11
$Eu(p\text{-}ABA)_3 \cdot phen \cdot 2H_2O$	51.09	3.94	8.92	19.76	50.99	4.12	9.01	19.57
$Tb(p\text{-}ABA)_3 \cdot phen \cdot 2H_2O$	50.10	3.56	8.50	20.19	50.54	4.08	8.93	20.28

Table 2. Lowest triplet state energies of Gd^{3+} complexes and the corresponding $\Delta E(Tr - {}^5D_j)$

	Lowest triplet state energy (cm^{-1})	$\Delta E(Tr - {}^5D_0)$ (cm^{-1})	$\Delta E(Tr - {}^5D_4)$ (cm^{-1})
$Gd(o\text{-}ABA)_3 \cdot H_2O$	25229	7965	4729
$Gd(p\text{-}ABA)_3 \cdot 2H_2O$	24444	7180	3944
$Gd(phen)_2 \cdot Cl_3 \cdot 2H_2O$	22075	4811	1575

exchange interaction [8]) and from an inverse energy transfer by thermal deactivation. Both energy transfer rate constants depend on the energy difference between the lowest triplet state level energy of ligands and the resonant emissive energy of Ln^{3+}.

The intramolecular energy transfer in rare earth complexes conforms to *Dexter*'s exchange energy transfer theory [9]:

$$k_{ET} = P_{da} \cdot \exp(-2R_{da}/L) \tag{1}$$

(k_{ET}: rate constant of energy transfer; R_{da}: intramolecular distance between energy donor atom and acceptor atom; L: *van der Waals* radius; P_{da}: transition probability of the resonant exchange interaction). P_{da} can be represent as follows:

$$P_{da} = (2\pi Z^2/\mathrm{R}) \int F_d(E) \cdot E_a(E) dE. \tag{2}$$

The integral in this equation represents the overlap between the luminescence spectrum of the ligands and the absorption spectrum of Ln^{3+}. $F_d(E)$ and $E_a(E)$ are the luminescence spectrum of the donor (ligand) and the absorption spectrum of the acceptor (Ln^{3+}), respectively. $2\pi Z^2/\mathrm{R}$ is a constant relating to the mutual distance between Ln^{3+} and the coordinated atom. R_{da} and L are both considered to be constant for intramolecular energy transfer processes; therefore,

$$k_{ET} = (2\pi Z^2/\mathrm{R}) \cdot \int F_d(E) \cdot E_a(E) dE \cdot \exp(-2R_{da}/L) \tag{3}$$

From Eq. (3), k_{ET} increases with decreasing ΔE between the triplet state energy of ligands and the resonance emission energy of Eu^{3+} and Tb^{3+}. Thus, ligands with larger energy differences cannot sensitize rare earth ions effectively. On the other hand, there exists an inverse energy transfer process which affects luminescence intensity [10]:

$$k(T) = A\exp(-\Delta E(Tr - Ln^{3+})/\mathrm{R}T) \tag{4}$$

$k(T)$: rate constant of inverse energy transfer process (thermal deactivation process); A: preexponential factor.

It can be seen that in inverse energy transfer processes the activation energy is approximately equal to $\Delta E(Tr - Ln^{3+})$; a decreasing energy difference can therefore increase $k(T)$. The conclusion can be drawn that $\Delta E(Tr - Ln^{3+})$ can have an opposite influence on the two energy transfer processes mentioned, and it can be assumed that there exists an optimal value.

The luminescence properties of ternary complexes of rare earth ions with carboxylic acids and *phen* differ dramatically from those of the binary ones [11]. *Phen* will influence the luminescence intensity greatly if there exists an energy transfer between the ligands. Figures 1 and 2 show the phosphorescence spectra of $\mathrm{Gd}(p\text{-}ABA)_3 \cdot 2\mathrm{H_2O}$, $\mathrm{Gd}(p\text{-}ABA)_3 \cdot phen \cdot 2\mathrm{H_2O}$, $\mathrm{Gd}(phen)_2 \cdot \mathrm{Cl_3} \cdot 2\mathrm{H_2O}$, $\mathrm{Gd}(o\text{-}ABA)_3 \cdot \mathrm{H_2O}$, $\mathrm{Gd}(o\text{-}ABA)_3 \cdot phen \cdot 2\mathrm{H_2O}$, and $\mathrm{Gd}(phen)_2 \cdot \mathrm{Cl_3} \cdot 2\mathrm{H_2O}$, respectively. It can be seen that the phosphorescence spectrum of the ternary complex $\mathrm{Gd}(p\text{-}ABA)_3 \cdot phen \cdot 2\mathrm{H_2O}$ is similar to that of the binary complex $\mathrm{Gd}(phen)_2 \cdot \mathrm{Cl_3} \cdot 2\mathrm{H_2O}$, but not to that of the corresponding binary complex of *p-ABA*. Obviously, in Gd^{3+} ternary complexes, *phen* is the main energy donor and predominantly sensitizes the Ln^{3+} ion luminescence. Besides, there exists an intramolecular energy migration from *p-ABA* to *phen*. In order to verify this assumption, the low temperature phosphorescence lifetimes of complexes were determined, and the intramolecular energy transfer efficiencies between aromatic carboxylic acids and phen were calculated. The data are shown in Table 3. The intramolecular energy transfer process can be described as shown in Fig. 3 [12].

Table 3. Phosphorescence lifetimes of Gd^{3+} complexes and energy transfer efficiencies from *ortho* (*para*) aminobenzoic acid to *phen*

	Phosphorescence lifetimes τ(s)	Energy transfer efficiencies (%)
$\mathrm{Gd}(o\text{-}ABA)_3 \cdot \mathrm{H_2O}$	3.10	–
$\mathrm{Gd}(o\text{-}ABA)_3 \cdot phen \cdot 2\mathrm{H_2O}$	0.247	92.03
$\mathrm{Gd}(p\text{-}ABA)_3 \cdot 2\mathrm{H_2O}$	3.18	–
$\mathrm{Gd}(p\text{-}ABA)_3 \cdot phen \cdot 2\mathrm{H_2O}$	0.762	76.04

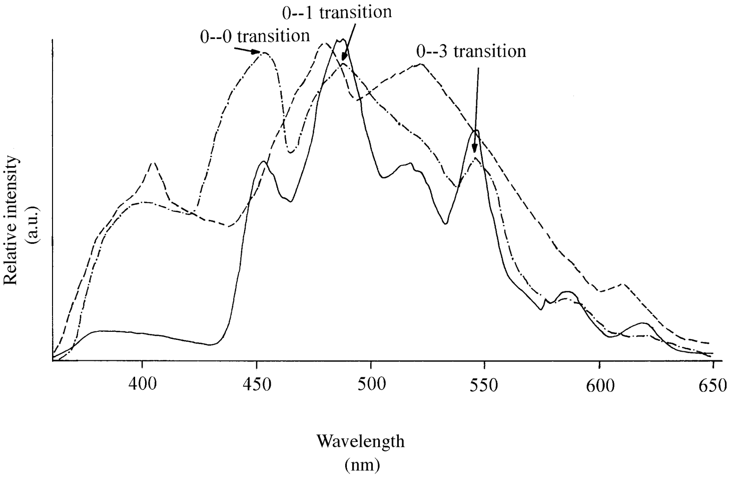

Fig. 1. Low temperature phosphorescence spectra of $\mathrm{Gd}(phen)_2 \cdot \mathrm{Cl_3} \cdot 2\mathrm{H_2O}$ (–, $\lambda_{\mathrm{ex}} = 302.0\,\mathrm{nm}$), $\mathrm{Gd}(p\text{-}ABA)_3 \cdot 2\mathrm{H_2O}$ (–, $\lambda_{\mathrm{ex}} = 334.5\,\mathrm{nm}$), and $\mathrm{Gd}(p\text{-}ABA)_3 \cdot phen \cdot 2\mathrm{H_2O}$ (–, $\lambda_{\mathrm{ex}} = 316.8\,\mathrm{nm}$) in $5 \times 10^{-4}\,M$ ethanol/*DMF* at 77 K

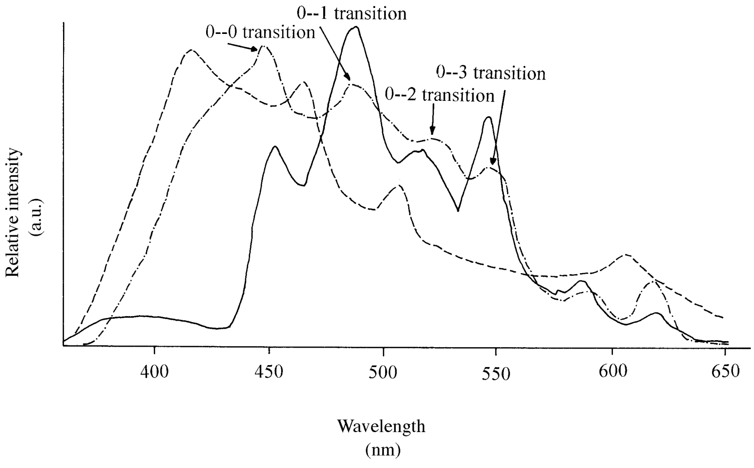

Fig. 2. Low temperature phosphorescence spectra of Gd(*phen*)$_2 \cdot Cl_3 \cdot 2H_2O$ (—, $\lambda_{ex} = 302.0$ nm), Gd(*o-ABA*)$_3 \cdot H_2O$ (– –, $\lambda_{ex} = 327.6$ nm), and Gd(*o-ABA*)$_3 \cdot$ *phen* $\cdot 2H_2O$ (- · · -, $\lambda_{ex} = 307.4$ nm) in 5×10^{-4} *M* ethanol/*DMF* at 77 K

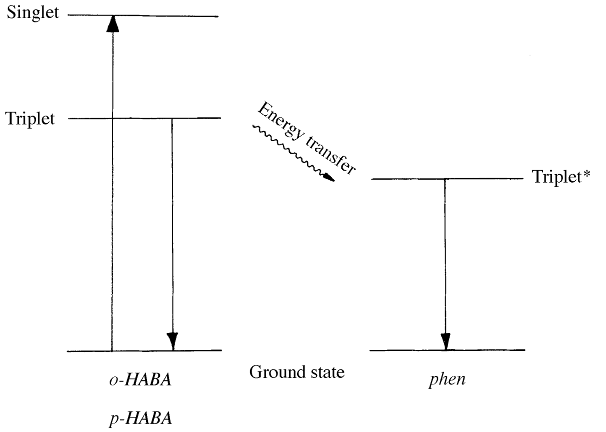

Fig. 3. Intramolecular energy transfer process from aminobenzoic acids to 1,10-phenanthroline

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

$$k^*_{ET} = \tau_0^{-1} - \tau_1^{-1} \tag{5}$$

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

(k^*_{ET}: rate constant of energy transfer from *o-ABA* and *p-ABA* to *phen*; k_1: rate constant of phosphorescence of the Gd^{3+} complex with *o*(*p*)*-ABA*; τ_0, τ_1: phosphorescence lifetimes of the binary and ternary complex, respectively; η_{ET}: energy transfer efficiency from *o*(*p*)*-ABA* to *phen*). It can be seen that the intramolecular energy transfer efficiency from *o*(*p*)-aminobenzoic acids to *phen* is very large. In the ternary complexes, the energy match between *phen* and Ln^{3+} is the main factor determining the luminescence properties of the complexes.

In order to confirm the prediction from the energy difference between the triplet state of ligands and the excited energy level of rare earth ions, fluorescence spectra of binary and ternary complexes of Eu^{3+} and Tb^{3+} were measured. Luminescence spectra of rare earth complexes are all similar owing to the fact that they are the characterized by the emission of the center ions. Organic ligands change only the emission intensity, but hardly the emission position. Figures 4 and 5 show the fluorescence spectra of $Eu(p\text{-}ABA)_3 \cdot phen \cdot 2H_2O$ and $Tb(p\text{-}ABA)_3 \cdot phen \cdot 2H_2O$. In Fig. 4, the emissions of $Eu(p\text{-}ABA)_3 \cdot phen \cdot 2H_2O$ at 580, 591(594), 617, 651, and 696 nm originate from the transitions ${}^5D_0 \rightarrow {}^7F_0$, ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_2$, ${}^5D_0 \rightarrow {}^7F_3$, and ${}^5D_0 \rightarrow {}^7F_4$, respectively. Among these transitions, ${}^5D_0 \rightarrow {}^7F_2$ is the strongest one. In Fig. 5, the emissions of $Tb(p\text{-}ABA)_3 \cdot phen \cdot 2H_2O$ at 491, 541.8 (545.5), 583.6, and 621.4 nm originate from ${}^5D_4 \rightarrow {}^7F_6$, ${}^5D_4 \rightarrow {}^7F_5$, ${}^5D_4 \rightarrow {}^7F_4$, and ${}^5D_4 \rightarrow {}^7F_3$, respectively, ${}^5D_4 \rightarrow {}^7F_5$ being the strongest transition. Table 4 presents the relative luminescence intensities of Eu^{3+} complexes originating from the ${}^5D_0 \rightarrow {}^7F_2$ transition and those of the Tb^{3+} complexes originating from the ${}^5D_4 \rightarrow {}^7F_5$ transition. The data of Table 4 indicate that the emission intensities of Tb^{3+} complexes are stronger than those of Eu^{3+} compounds

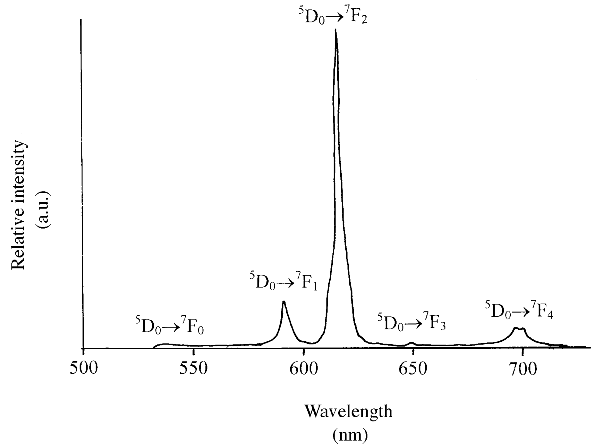

Fig. 4. Luminescence spectrum of $Eu(p\text{-}ABA)_3 \cdot phen \cdot 2H_2O$ (solid sample)

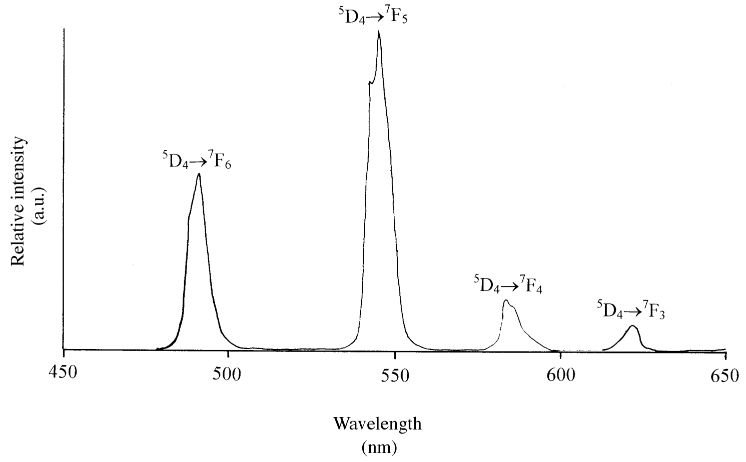

Fig. 5. Luminescence spectrum of $Tb(p\text{-}ABA)_3 \cdot phen \cdot 2H_2O$ (solid sample)

Table 4. Luminescence intensities of Eu^{3+} and Tb^{3+} complexes

Headers:	λ_{em} (nm)	λ_{ex} (nm)	Relative intensities (a.u.)
$Eu(o\text{-}ABA)_3 \cdot H_2O$	616	314.4	1.27
$Eu(p\text{-}ABA)_3 \cdot 2H_2O$	618	308	6.56
$Eu(o\text{-}ABA)_3 \cdot phen \cdot 2H_2O$	615	307.2	4.68
$Eu(p\text{-}ABA) \cdot phen \cdot 2H_2O$	617	308.8	129
$Eu(phen)_2 \cdot Cl_3 \cdot 2H_2O$	614, 620	308	61.9
$Tb(o\text{-}ABA)_3 \cdot H_2O$	543, 549	274.4	30.2
$Tb(p\text{-}ABA)_3 \cdot 2H_2O$	543.6, 547.3	273.6	35.5
$Tb(o\text{-}ABA)_3 \cdot phen \cdot 2H_2O$	545	273.6	95.8
$Tb(p\text{-}ABA)_3 \cdot phen \cdot 2H_2O$	542, 545.5	273.6	311
$Tb(phen)_2 \cdot Cl_3 \cdot 2H_2O$	546	274.4	109

Table 5. Luminescence lifetimes and quantum efficiencies of Eu^{3+} and Tb^{3+} complexes

	Luminescence lifetimes (μs)	Quantum efficiencies (a.u.)[a]
$Eu(p\text{-}ABA)_3 \cdot 2H_2O$	219.9	–[b]
$Eu(p\text{-}ABA)_3 \cdot phen \cdot 2H_2O$	955.2	51.8
$Eu(phen)_2 \cdot Cl_3 \cdot 2H_2O$	837.8	33
$Tb(p\text{-}ABA)_3 \cdot 2H_2O$	790.0	6.2
$Tb(p\text{-}ABA)_3 \cdot phen \cdot 2H_2O$	1300	50
$Tb(phen)_2 \cdot Cl_3 \cdot 2H_2O$	1374	9.4

[a] The quantum efficiencies of Eu^{3+} complexes were measured against $HQEu(TTA)_4$ as reference (100%; *HTTA* = 1-(2-thenoyl)-3,3,3-trifluoracetone, *Q* = pyrrolidine), the quantum efficiencies of Tb^{3+} complexes were measured against $Tb(acac)_3 \cdot phen$ as reference (100%; H*acac* = acetylacetone, *phen* = 1,10-phenanthroline); [b]The quantum efficiency of $Eu(p\text{-}ABA)_3 \cdot 2H_2O$ is too low to be determined

because of the favorable energy difference between the triplet state energy of ligands and Tb^{3+} ions. The results also show that the luminescence intensities of ternary complexes are higher than those of binary complexes of Tb^{3+}, whereas it is opposite for Eu^{3+} complexes. This can be well explained by intramolecular energy transfer process taking place from *o-ABA* and *p-ABA* to *phen*. Thus, *phen* is the dominating energy donor, and the difference in energy, yields the mismatch between the lowest triplet state of *phen* and the first excited europium state. In order to further demonstrate this distinctly, we measured the luminescence lifetimes and quantum efficiencies of Eu^{3+} and Tb^{3+} complexes with *p*-aminobenzoic acid and 1,10-phenanthroline. The results are summarized in Table 5. The quantum efficiencies and luminescence lifetimes of ternary complexes are higher than those of the corresponding binary complexes, testifying that an intramolecular energy transfer between ligands can take place. The luminescence lifetimes and quantum efficiencies of Tb^{3+} complexes are larger than those of Eu^{3+} complexes, verifying the intramolecular energy transfer process between ligand and Ln^{3+} and the energy coupling mechanism. The results also indicate that the luminescence quantum efficiencies of Eu(*p-ABA*)$_3 \cdot$ *phen* $\cdot$ 2H$_2$O and Tb(*p-ABA*)$_3 \cdot$ *phen* $\cdot$ 2H$_2$O are the largest in the corresponding Eu^{3+} and Tb^{3+} complexes.

Experimental

Preparation of rare earth complexes

Lanthanide oxide (99.99%) was converted to its chloride by treatment with concentrated hydrochloric acid. The lanthanide complexes with *ortho* or *para* aminobenzoic acid were prepared according to Ref. [6] by homogeneous precipitation. Binary complexes with 1,10-phenanthroline were synthesized by the method described in Ref. [7]. Ternary complexes of rare earths with aminobenzoic acid and 1,10-phenanthroline were synthesized as follows: An aqueous solution of rare earth chloride was added to a mixed alcoholic solution of aminobenzoic acid and 1,10-phenanthroline whose *pH* value was adjusted to 6.0–7.0 by adding aqueous sodium hydrate with stirring (molar ratio of LnCl$_3 \cdot 6$H$_2$O:aminobenzoic acid:1,10-phenanthroline: 1:3:1). The precipitate was filtered off, washed with water and ethanol, dried, and stored over silica gel.

Measurements

Elemental analyses (C, H, N) were carried out with a Carlo-Erba 1106 elemental analyzer. The content of rare earth ions was determined by titration with *EDTA* using xylenol orange as indicatior and hexamethylenetetramine as buffer. Phosphorescence spectra and phosphorescence lifetimes of gadolinium complexes were measured with a SPEX 1934D spectrophotometer using a 450 W xenon lamp as excitation source at liquid nitrogen temperature in mixed $5 \times 10^{-4}\,M$ solutions (absolute ethanol: $DMF = 2{:}8$). Fluorescence lifetimes were obtained with the same spectrophotometer at room temperature. Fluorescence spectra were recorded on a SPEX FL-2T2 spectrofluorometer (excitation and emission slit width: 0.5 nm). The luminescence quantum efficiencies were determined with a MPF-4 spectrophotofluorimeter.

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