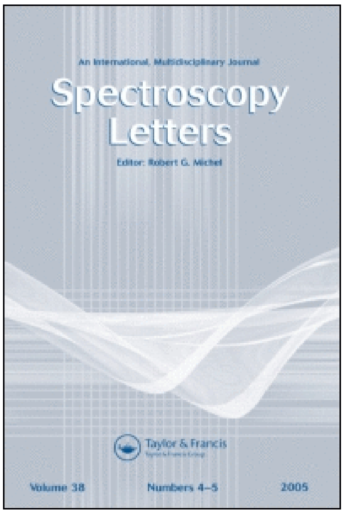

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Spectral Study of the Co-luminescence Effect of Lanthanide Ternary Complexes with Benzoic Acid and Phenanthroline

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Spectral Study of the Co-luminescence Effect of Lanthanide Ternary Complexes with Benzoic Acid and Phenanthroline

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ABSTRACT

The photoacoustic (PAS) spectra and luminescence spectra of $Eu(Hba)_3$ Phen and coprecipitates $Eu_{0.6}Ln_{0.4}(Hba)_3$ Phen complexes (Ln^{3+}: Y^{3+}, Nd^{3+}; Hba: benzoic acid; Phen: phenanthroline) have been measured, and the co-luminescence effect of the coprecipitates are reported. The PAS intensities of the central lanthanide ions are interpreted in terms of the probability of nonradiative transitions. It is found that the PAS intensity of the ligand bears a relationship with the energy transfer processes. The PAS intensity in the region of ligand absorption increases in the order of $Eu_{0.6}Nd_{0.4}(Hba)_3$ Phen > $Eu(Hba)_3$ Phen > $Eu_{0.6}Y_{0.4}(Hba)_3$ Phen, which indicates that addition of the second lanthanide ions in each case changes the relaxation processes of the complexes. The energy transfer

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and relaxation processes are discussed in combination with the luminescence spectra.

Key Words: Photoacoustic spectroscopy; Lanthanide complex; Co-luminescence effect; Energy transfer process.

INTRODUCTION

In recent years, lanthanide complexes with aromatic carboxylic acids are frequently used as structural and functional probes in systems of biological importance.[1,2] On the other hand, they are potential luminescence materials for further application for which there has been a growing interest in studies of the luminescence properties of such complexes.[3]

In a study of the Eu^{3+} (Sm^{3+}) complexes in solution, a fluorescence enhancement or co-luminescence effect was observed when La^{3+}, Gd^{3+}, Tb^{3+}, Lu^{3+}, or Y^{3+} was added.[4,5] The co-luminescence effect can be found in complex suspensions and in the micellar environment.[6,7] In an actual solution, there is no co-luminescence enhancement because the long distance between the complexes makes intermolecular energy transfer impossible.

In solids, especially in coprecipitates, the distance between the complexes can be short enough to incur an intermolecular energy transfer. It is necessary to study the co-luminescence effect of those compounds in the solid state. Such a study can be helpful for a better understanding of the co-luminescence phenomenon, and of the design of highly efficient lanthanide complexes.

Absorption and fluorescence techniques have been widely used in studies of lanthanide complexes. However, absorption spectroscopy has limits for use in the solid state because of the nontransparent or scattering properties of the solid samples. Photoacoustic (PAS) spectroscopy is a relatively new technique for studies of the chemical and physical properties of many kinds of samples, including samples that are crystalline, powder or gel.[8,9] PAS is appropriate for the study of solid lanthanide complexes according to the recent work.[10,11]

In our previous work, fluorescence enhancement and quenching phenomena have been found for the coprecipitates of lanthanide β-diketone complexes.[11] Similar to lanthanide β-diketone complexes, lanthanide complexes with aromatic carboxylic acids and phenanthroline exhibit excellent luminescence properties. In this work, $Eu(Hba)_3$ Phen and coprecipitates $Eu_{0.6}Ln_{0.4}(Hba)_3$ Phen complexes (Ln: Y^{3+}, Nd^{3+}) have been prepared and co-luminescence phenomena of the coprecipitates are reported.

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EXPERIMENTAL

Preparation of the Solid Complexes

$Eu(Hba)_3$ Phen was prepared as follows. Benzoic acid was solved in 95% ethanol solution and the pH value was adjusted to 7.2 by sodium hydroxide. Then phenanthroline was added to the above solution. The ethanolic mixture was added to a hot aqueous solution of europium chloride dropwise while stirring. The molar ratio of benzoic acid : phenanthroline : europium chloride was 3 : 1 : 1. The reaction mixture was stirred on a water bath at 50°C for 2 hr and allowed to cool. The product was collected by filtration, washed with water and ethanol, and dried under vacuum.

$Eu_{0.6}Ln_{0.4}(Hba)_3$ Phen (Ln^{3+}: Y^{3+} or Nd^{3+}) was prepared according to the procedure described above except that the ethanol solution containing benzoic acid and phenanthroline was added to the aqueous solution containing stoichiometric $EuCl_3$ $6H_2O$ and $LnCl_3$ $6H_2O$ (Ln^{3+}: Y^{3+} or Nd^{3+}).

Elemental analyses were performed and were consistent with the expected formulae.

Spectroscopic Measurements

Infrared spectra were measured as KBr pellets on a Nicolet IR-170SX spectrometer. For the IR spectra of the complexes, the absorption bands of characteristic asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of carboxyl group shift to lower frequencies compared with those of sodium benzoate. The different between ν_{as} and ν_s ranges from 120 to 125 cm^{-1} for the complexes, which is less than that of sodium benzoate ($\Delta\nu = 137\,cm^{-1}$). Both of the absorption bands (ν_{as} and ν_s) show splitting. It is suggested that the carboxyl groups coordinate with lanthanide ions in both chelating and bridging structures[12,13] and the complexes have a structure of a polynuclear form.

X-ray powder diffraction measurements were recorded on a D/max-RA diffractometer using Cu Kα radiation. The x-ray powder diffraction patterns for the $Eu_{0.6}Ln_{0.4}(Hba)_3$ Phen (Ln: Y^{3+}, Nd^{3+}) coprecipitates are consistent with that of $Eu(Hba)_3$ Phen. The coprecipitates crystallize in triclinic, $P1$ space group with similar cell parameters to those of $Eu(Hba)_3$ Phen, which indicates that the two types of complex have the same structure.

The PAS spectra were measured on a single-beam spectrometer constructed in our laboratory.[14] A 500 w xenon lamp, a monochromator and a PAS cell fitted with an electret microphone were used. The chopper frequency was 33 Hz. The output signal of the microphone was amplified by a preamplifier and then fed to a lock-in amplifier with a reference signal from the chopper. The final signal was normalized for changes in lamp intensity using a carbon-black reference. All the PAS spectra were recorded to the room temperature in the range of 300–800 nm.

Luminescence spectra were recorded with a Hitachi 850 fluorescence spectrophotometer.

RESULTS AND DISCUSSION

Photoacoustic and Luminescence Spectra

The PAS spectra of the complexes in the range of 300–800 nm are shown in Fig. 1. The PAS signal is obtained by detecting the heat generated through nonradiative transitions of the sample after absorbing a periodically varying incident light. The PAS signal (P) can be written as:[15]

$$P = KA_{\mathrm{abs}\gamma} \tag{1}$$

where A_{abs} is the absorbance of the sample, γ is the probability of nonradiative transitions after excitation, and K is a coefficient which is determined by the thermal properties of the sample and by the spectrometer. PAS absorption at 305 nm is assigned to the π–π^* transition of Hba and the broad absorption in the region of 340 nm results from the π–π^* absorption of Phen.

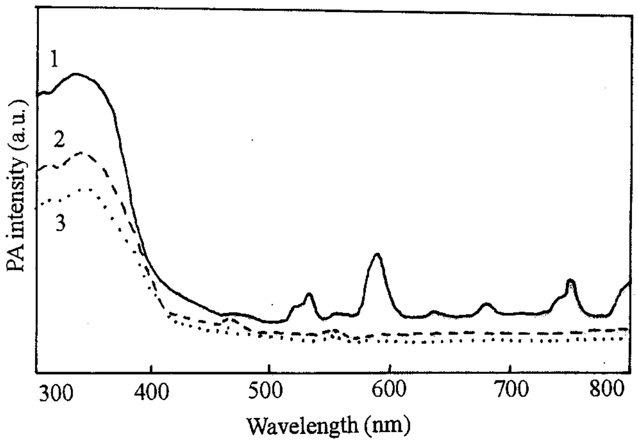

Figure 1. The PAS spectra of the complexes: (1) $Eu_{0.6}Nd_{0.4}(Hba)_3$ Phen; (2) $Eu(Hba)_3$ Phen; and (3) $Eu_{0.6}Y_{0.4}(Hba)_3$ Phen.

It is known that after excitation there are two kinds of relaxation processes: radiative and nonradiative processes. As the PAS spectrum only corresponds to the nonradiative relaxation processes, the PAS signals of energy levels that have strong fluorescence properties are quite weak or nonexistent.[16]

In the UV-VIS region, Y^{3+} ion has no absorption. The absorption of different energy levels of Nd^{3+} is clearly shown in the PAS spectrum. Since the luminescence of Nd^{3+} is weak and the numerous closely packed energy levels of Nd^{3+} are often intermixed, the Nd^{3+} ion has a high probability to relax by nonradiative relaxation processes. While for Eu^{3+}, the relaxation of $^5D_0$ cannot be monitored by PAS, and the PAS signals of $^5D_1$, $^5D_2$ at 469 and 541 nm are also quite weak. Among the energy levels of Eu^{3+} ion, the longest-lived energy level is $^5D_0$, and it is also a strong fluorescence level. The electron in the excited level $^5D_0$ has a high probability to take a radiative relaxation process. When the electrons are excited to $^5D_1$, $^5D_2$ levels, usually they will relax to $^5D_0$ by a nonradiative process, and then relax by radiative process (luminescence) to the ground multiplet of Eu^{3+} (^7F) as can be seen in Fig. 2. The relaxation processes of $^5D_2$, $^5D_1$, and $^5D_0$ are mostly through the radiative processes. All the PAS absorptions are assigned based on the lanthanide spectra as summarized by Dieke and Crosswhite[17] in Table 1.

In the region of ligand absorption, the PAS intensity changes significantly for the title complexes. As we know, the PAS intensity of the ligand is the sum of the nonradiative relaxation of the ligand, the energy transfer, and the following nonradiative relaxation of the central Ln^{3+} ion.[18,19] The PAS intensity of $Eu_{0.6}Nd_{0.4}(Hba)_3$ Phen is stronger than that of $Eu(Hba)_3$ Phen,

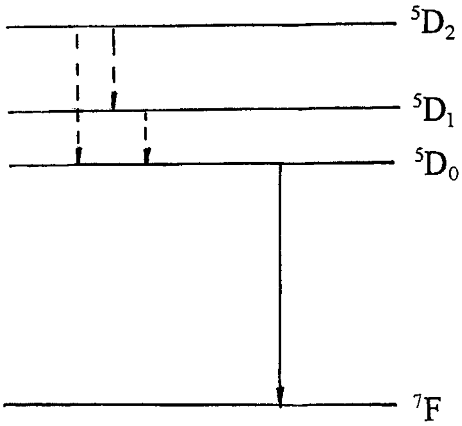

Figure 2. Model for the relaxation processes of Eu^{3+}: radiative and nonradiative.

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Table 1. PAS band assignments of the title complexes (nm). (Ground states: $^7F_0$ for Eu^{3+}, $^4I_{9/2}$ for Nd^{3+}).

$Eu(Hba)_3$	Phen	$Eu_{0.6}Nd_{0.4}(Hba)_3$	Phen
$\pi-\pi^*$	305	$\pi-\pi^*$	305
$\pi-\pi^*$	340	$\pi-\pi^*$	340
$^5D_2$	469	$^5D_2$	469
$^5D_1$	541	$^5D_1$	541
		$^2G_{9/2}$	520
		$^4G_{7/2}$	531
		$^4G_{5/2} + {}^2G_{7/2}$	587
		$^4F_{9/2}$	681
		$^4S_{3/2}$	740
		$^4F_{7/2}$	748
		$^4F_{5/2}$	799

while the PAS intensity of $Eu_{0.6}Y_{0.4}(Hba)_3$ Phen is weaker than that of $Eu(Hba)_3$ Phen in the region of ligand absorption as can be seen in Fig. 1. Since the absorption of the ligand depends slightly on the central lanthanide ions. It can be inferred that the probability of nonradiative transitions γ increases in the order of $Eu_{0.6}Nd_{0.4}(Hba)_3$ Phen > $Eu(Hba)_3$ Phen > $Eu_{0.6}Y_{0.4}(Hba)_3$ Phen. Addition of the second lanthanide ions change the relaxation process of the complexes. The changes can be reflected in the luminescence spectra.

The luminescence spectra of the complexes are shown in Fig. 3. In the emission spectra, the narrow bands at 591 and 612 nm are attributed to the characteristic emissions of $Eu^{3+}(^5D_0 \rightarrow {}^7F_1$ and $^7F_2)$. When the excitation wavelength is fixed in the region of the ligand absorption, the existence of characteristic emissions of Eu^{3+} demonstrates energy transfer processes from the ligand to Eu^{3+} for the complexes. This is confirmed by the excitation spectra. For the complexes, the addition of Nd^{3+} weakens the luminescence of Eu^{3+}, while the addition of Y^{3+} enhances the luminescence of Eu^{3+}. This result is coincident with the PAS spectra. As the probability of radiative transition increases, the PAS intensity exhibits a corresponding decrease.[16]

Relaxation Processes of the Complexes

It is generally accepted that the intramolecular energy transfer from the ligand to lanthanide ion occurs from the lowest triplet state energy level of the ligand to the resonance energy level of lanthanide ion, to which is attributed the excellent luminescence properties of lanthanide chelates.[20,21] For the complexes, the excited singlet states of the ligands undergo nonradiative

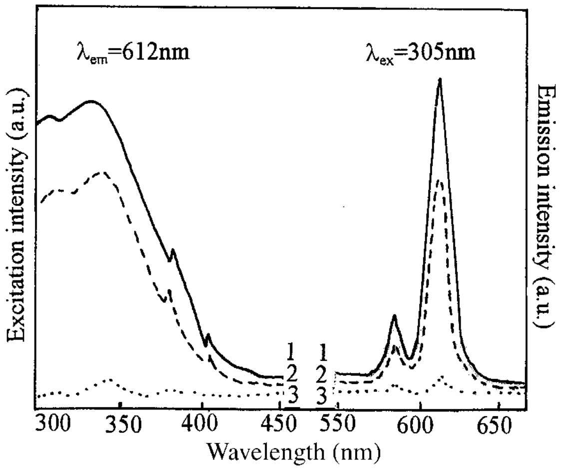

Figure 3. Excitation and emission spectra of the complexes: (1) $Eu_{0.6}Y_{0.4}(Hba)_3$ Phen; (2) $Eu(Hba)_3$ Phen; and (3) $Eu_{0.6}Nd_{0.4}(Hba)_3$ Phen.

transitions to the triplet states whose energy levels T_{Hba} (the triplet state of Hba) and T_{Phen} (the triplet state of Phen) are at 24,800 and 22,100 cm^{-1}, respectively.[22,23] The intramolecular energy transfer from the triplet states to the central Eu^{3+} ions results in the characteristic line-type emission of Eu^{3+}. Since the triplet state of Phen is closer to the resonance energy levels of Eu^{3+} than that of Hba, the energy transfer is more efficient from Phen to Eu^{3+}.[24]

The intramolecular energy transfer can explain the characteristic emission of Eu^{3+} ion in the fluorescence spectra. However, it cannot explain the change of luminescence intensity of Eu^{3+} with addition of the second lanthanide ions. For the system studied, $Eu_{0.6}Ln_{0.4}(Hba)_3$ Phen are prepared by coprecipitation. The short distance between molecules (lesser than 1 nm) in the coprecipitates makes the intermolecular energy transfer possible.[25,26] The single crystal structure has been reported for $Eu(Hba)_3$ Phen, which is composed of a dinuclear molecule.[27] It can be inferred that the possible species in the coprecipitates are a dinuclear complex with unlike lanthanide ions and two kinds of dinuclear complexes including like lanthanide ions, according to the results of x-ray diffraction and IR spectra.

Y^{3+} has no low-lying energy levels and the energy absorbed by its molecules cannot be dissipated through the central Y^{3+} ions. The excited energy on yttrium molecules may transfer to the nearby europium molecules in the $Eu_{0.6}Y_{0.4}(Hba)_3$ Phen coprecipitate. The luminescence of Eu^{3+} is enhanced by intermolecular energy transfer processes. For $Eu_{0.6}Nd_{0.4}(Hba)_3$ Phen, numerous closely packed excited states of the Nd^{3+} ion provide paths

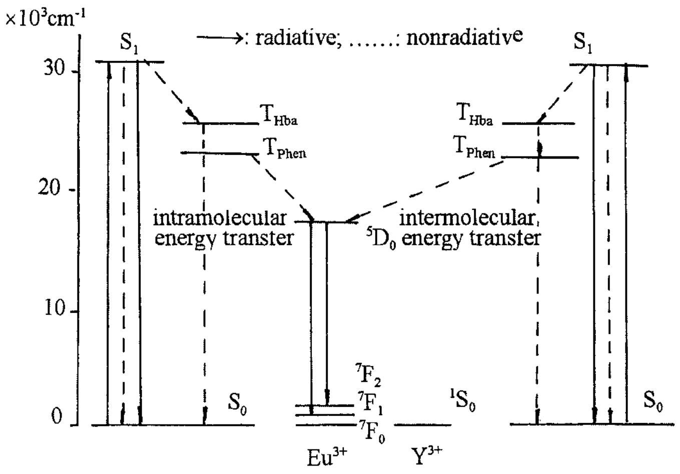

Figure 4. Model for relaxation and energy transfer processes of $Eu_{0.6}Y_{0.4}(Hba)_3$ Phen.

for efficient quenching of the excited states of the complex. A large part of the excited energy of europium molecules is transferred to Nd^{3+}, which results in a weakening of the luminescence of Eu^{3+}. The energy transfer and relaxation processes are illustrated in Fig. 4, which may involve both Dexter and Forster's mechanisms according to Refs.[28,29].

Experimental results show that fluorescence enhancement and quenching phenomena cannot be found in the mixtures of $Eu(Hba)_3$ Phen and $Ln(Hba)_3$ Phen (Ln^{3+}: Y^{3+}, Nd^{3+}) in any proportion. As the mixture is obtained in a mechanical way, the distance between the molecules is too far to incur an intermolecular energy transfer.

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