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# Intramolecular Energy Transfer in Europium Chelates Due to Excitation of the Triplet State

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The purpose of this paper is to clarify whether intramolecular energy transfer in europium chelates occurs *via* the triplet state of the ligand. It is attempted to excite the triplet state of europium dibenzoylmethide (EuD) by utilizing intermolecular triplet-triplet energy transfer from lanthanum dibenzoylmethide (LaD). In mixed solutions of EuD and LaD, the intensity and decay time of the ligand phosphorescence of LaD decreases with increasing molar fraction of EuD at liquid nitrogen temperature. Nearly in proportion to this, the intensity of the europium emission of EuD is enhanced, veryfying the occurrence of energy transfer from LaD to EuD. This fact is taken as clear evidence that intramolecular energy transfer takes place *via* the triplet state.

Chelates of trivalent europium and some other rare earth ions emit luminescence of line spectrum characteristic of central rare earth ions due to $f$–$f$ transitions. This luminescence is mainly caused by absorption by the ligand accompanied by subsequent intramolecular energy transfer to the central ions. Recently, these chelates have attracted great attention, since several investigators have suggested[1,2] the possibility of their use as laser materials, and succeeded[3-5] in achieving laser action with europium(III) $\beta$-diketonates. As for laser materials, one has to find chelates in which intramoecular energy transfer occurs efficiently. It is important, for this purpose, to clarify the mechanism of this intramolecular energy transfer.

Crosby *et al.*[6] investigated intramolecular energy transfer in chelates of various trivalent rare earth ions. They found that if the lowest triplet level of the ligand is located below the emitting levels of the chelated rare earth ions, luminescence attributed to the rare earth ions is not observed even if the singlet excited level of the ligand is located above them. Based on this fact, they suggested that intramolecular energy transfer takes place *via* the lowest triplet state of the ligand. El-Sayed and Bhaumik[7] reported that it is possible to enhance the luminescence of the chelated europium ion by intermolecular triplet-triplet energy transfer from benzophenone as energy donor. In this case, however, it is considered that the energy donor is further coordinated to the hexa-coordinated europium ion studied by them. If it is the case, the enhancement of the europium emission due to the addition of the energy donor would be attributed to the direct intramolecular energy transfer from the energy donor. Furthermore, Bhaumik and El-Sayed[8] showed that some aromatic compounds whose triplet levels are located between the emitting level of europium ion and the triplet level of the ligand of europium chelates quench the emission due to the europium ion. We have also showed[9] that the emission intensity of the chelated rare earth ion decreases if the triplet state of the ligand is quenched by the heavy-atom effect.

These observations all suggest that intramolecular energy transfer takes place *via* the triplet state of the ligand. However, clear evidence has not yet been reported, since it is difficult to excite the chelates directly from the ground state to the triplet state by optical absorption because of the very small probability of the singlet-triplet transition.

The purpose of this paper is to clarify whether energy transfer from the ligand to the europium ion takes place *via* the triplet state of the ligand. In this work, excitation of europium chelate to the triplet state is attempted by utilizing a phenomenon

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9) S. Shionoya, Y. Matsuda, M. Morita and S. Makishima, a contributed paper at Internatl. Conf. Luminescence, Budapest, 1966, p. 9—84, in press in Proc.

of intermolecular triplet-triplet energy transfer.

Europium dibenzoylmethide (EuD) was used as energy acceptor, because it shows intramolecular energy transfer of relatively high efficiency. Also, it is easily prepared and purified.[1] As energy donor, lanthanum dibenzoylmethide (LaD) was chosen, and the effect of its addition on the intensity of the europium emission of EuD investigated. Dibenzoylmethides of lanthanum, gadolinium, lutetium and samarium exhibit phosphorescence attributed to the transition from the ligand triplet state to the ground state. There is no significant differences in their phosphorescence.[1] This suggests that the energy level of the triplet state is independent of the species of coordinated rare earth ion. It is expected that if EuD is mixed with some other rare earth dibenzoylmethide showing ligand phosphorescence, intermolecular energy transfer takes place from the triplet state of the latter chelate to the triplet state of the former, since there is sufficient energy mathcing between the triplet states of the two chelates. We found that LaD has the longest lifetime of ligand phosphorescence among the various rare earth dibenzoylmethides. Therefore, LaD was chosen as energy donor.

## Experimental Methods

**Samples.** EuD and LaD were prepared by the ordinary piperidine method at first, and then kept in vacuum at 150°C for 24—30 hr. In the optical measurements, these chelates were dissolved in either ethanol or ethanol-methanol (3 : 1). These solutions become rigid glasses when cooled to liquid nitrogen temperature.

**Emission Spectra.** A high pressure mercury arc lamp connected with a Bausch & Lomb grating monochromator was used as the exciting light source. A Kipp & Zonen double monochromator with flint prisms was used for spectral measurement. Emission spectra were obtained for the alcohol solutions of LaD and EuD of concentrations $10^{-4}$—$10^{-3}$ M.

**Excitation Spectra.** A 500 W xenon arc lamp and a 500W tungsten lamp combined with the Kipp & Zonen double monochromator with quartz and flint prisms, respectively, were used for the excitation sources. Emission from the samples was filtered by color and interference filters. For EuD, measurement was made for the strongest emission line of 612 m$\mu$, due to the transition $^5D_0 \rightarrow {}^7F_2$ of the trivalent europium ion. For LaD, the excitation spectrum was measured for ligand phosphorescence at a wavelength of 490 m$\mu$, and ligand fluorescence at 425 m$\mu$.

**Emission Lifetime.** An Edgerton FX-3 1 joule and a Miyata 20 joule xenon flash lamp with durations of 2$\mu$ sec and 20$\mu$ sec, respectively, were used as excitation sources with ultraviolet pass glass filters and a 365 m$\mu$ interference filter. The output of the photomultiplier, RCA 931A, was fed to a synchroscope, and the decay curve photographed. The concentrations of the solutions were $10^{-3}$—$10^{-5}$ M for the pure solutions of EuD and LaD, and $2 \times 10^{-4}$ M for the mixed solutions of LaD and EuD.

**Time-Resolved Emission Spectra.** An Edgerton FX-3 xenon flash lamp was used as the exciting light source with ultraviolet pass filters and a 365 m$\mu$ interference filter. This lamp was operated at a frequency of 10 cps. High pulse voltage with a 2 $\mu$ sec width was applied to the photomultiplier tube, RCA 931 A, with the delay time changing from zero to 1 msec for the light flash.

## Results and Discussion

The emission spectra of LaD and EuD in ethanol solution at liquid nitrogen temperature are given in Fig. 1. EuD exhibits only sharp emission lines due to the $f$–$f$ transition of trivalent europium ion. The strongest line is the one for the transition $^5D_0$

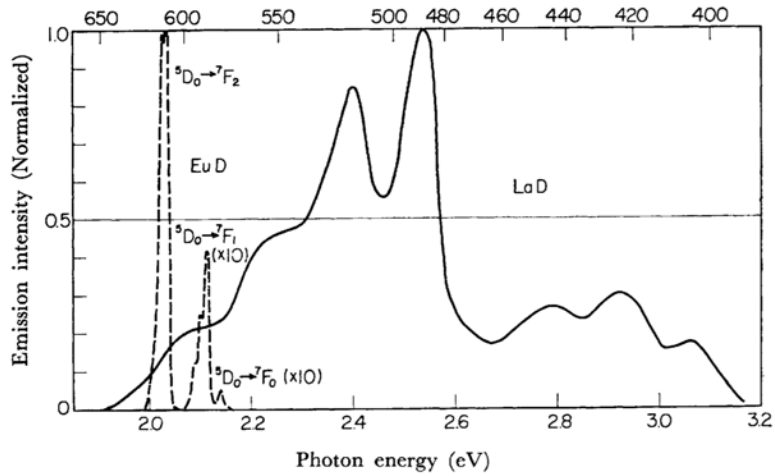


Fig. 1. Emission spectra of EuD and LaD in alcohol solutions at liquid nitrogen temperature. The intensities of EuD emission lines due to the transitions of $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ are magnified ten times.

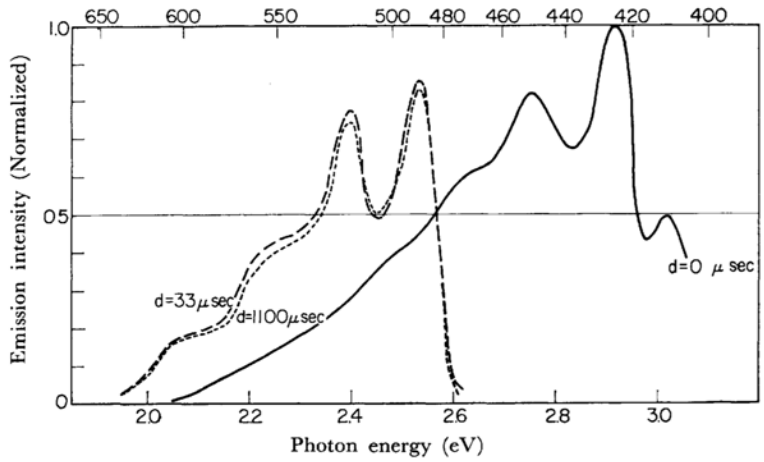


Fig. 2. Time-resolved emission spectra of LaD in alcohol solution at liquid nitrogen temperature. The delay time after the flash of exciting light is given by $d$. The relative intensities of emission bands for $d=33$ and 1100 $\mu$sec are magnified ten times.

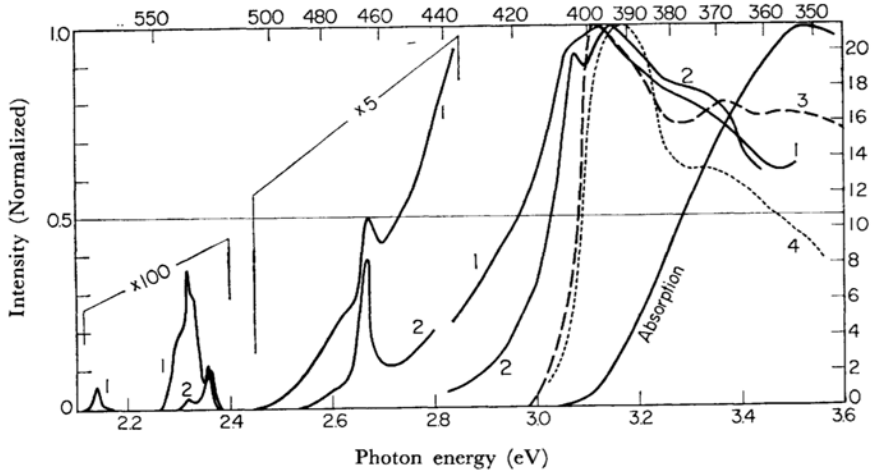


Fig. 3. Excitation spectra of EuD and LaD solutions at room and liquid nitrogen temperatures. No. 1: for europium emission of EuD at room temperature. 2: for europium emission at liquid nitrogen temperature. 3: for ligand phosphorescence of LaD at liquid nitrogen temperature. 4: for ligand fluorescence of LaD at liquid nitrogen temperature. The intensities of excitation bands in the region of 2.4—2.8 eV and 2.1—2.4 eV are magnified five and one hundred times, respectively. The absorption spectrum of EuD at room temperature is given for reference.

$\rightarrow {}^7F_2$. The emission spectrum of LaD consists of broad emission bands attributed to fluorescence and phosphorescence of the ligand. LaD exhibits no emission at room temperature. This is thought to be due to the collision of molecules in solution. At liquid nitrogen temperature, on the other hand, the sample is a rigid glass and no collisions take place; thus phosphorescence appears. EuD shows the emission both at room and liquid nitrogen temperatures although the emission intensity is much weaker at room temperature than at liquid nitrogen temperature.

The time-resolved emission spectra of LaD in ethanol solution at liquid nitrogen temperature are shown in Fig. 2. The higher energy bands in the spectra at 2.6 to 3.0 eV show very rapid decay, while the lower energy bands at 2.0 to 2.6 eV decay slowly. Thus the former is regarded as fluorescence due to the singlet-singlet transition and the later as phosphorescence due to the triplet-singlet transition.

The excitation spectra for europium emission due to the transition ${}^5D_0 \rightarrow {}^7F_2$ in EuD and also those for the ligand fluorescence and phosphorescence of LaD are shown in Fig. 3. The low energy edge of the excitation bands for the fluorescence and phosphorescence of LaD are located at nearly the same wavelength, 410 m$\mu$. Comparing Fig. 3

with Figs. 1 and 2, it is obvious that the probability of excitation of the triplet state of the ligand due to direct optical absorption from the ground state is extremely small. As for europium emission, narrow excitation bands are found at 402 m$\mu$, 464 m$\mu$, 530 m$\mu$ and 580 m$\mu$, in addition to the excitation band due to absorption by the ligand. These bands are attributed to transitions in the chelated europium ion, $^7F_{0,1} \rightarrow {}^5D_3$, $^7F_{0,1} \rightarrow {}^5D_2$, $^7F_{0,1} \rightarrow {}^5D_1$ and $^7F_{0,1} \rightarrow {}^5D_0$, respectively.

The decay curves of europium emission from EuD and of phosphorescence from LaD were measured at liquid nitrogen temperature. The decay time of the fluorescence from LaD could not be measured. The decay of the europium emission was exponential with a decay time of 0.394 msec. The phosphorescence from LaD also showed exponential decay with a decay time of 31.9 msec. This was found to be the longest decay time found among the various rare earth dibenzoylmethides.

The phosphorescence lifetime of LaD was measured in mixed solutions of LaD and EuD at liquid nitrogen temperature, in order to investigate whether energy transfer takes place from LaD to EuD. The total concentration, $C_{LaD}+C_{EuD}$, was kept at $2\times10^{-4}$ M, while the ratio of $C_{LaD}$ to $C_{EuD}$ was changed. The result is shown in Fig. 4 as a function of the molar fraction of EuD ($X_{EuD}$). The lifetime is nearly constant in the region of $X_{EuD}$ from 0 to 0.5, but in the region of $X_{EuD}$ greater than 0.5, it decreases rapidly, becoming one fourth of the initial value at $X_{EuD}=0.9$. This fact indicates that the triplet state of LaD is quenched by the existence of EuD in the mixed solution.

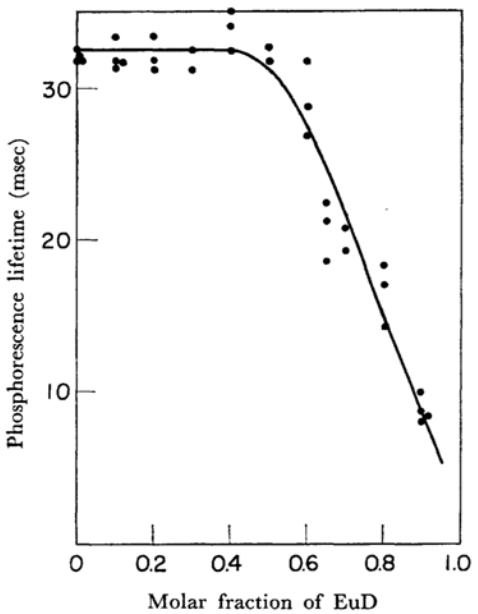


Fig. 4. The phosphorescence lifetime of LaD in mixed solutions of EuD and LaD at liquid nitrogen temperature.

The relative change of the europium emission intensity with the EuD molar fraction in the series of mixed solutions of EuD and LaD was measured with 546 m$\mu$ light excitation through the absorption of europium ion, and also with 365 m$\mu$ light excitation through the absorption by the ligand. The results at room temperature are given in Fig. 5. The intensities are normalized to unity at $X_{EuD}=1$ for both cases. It is seen that the europium emission intensity is exactly proportional to the EuD molar fraction.

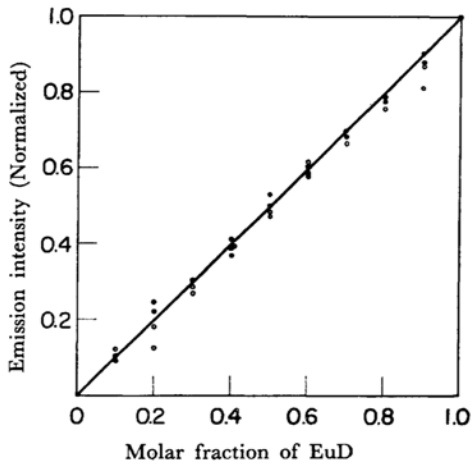


Fig. 5. The relative emission intensities of EuD in mixed solutions of EuD and LaD at room temperature. The mark ○ denotes the intensity obtained with direct excitation of europium ion (546 m$\mu$), and ● indicates the intensity obtained with excitation of the ligand (365 m$\mu$).

The absorbance of 546 m$\mu$ light by EuD is very small, and the optical density for a 1 cm thick layer of the solution with an EuD concentration of nearly $5\times10^{-1}$ M is much smaller than 0.1. Therefore, the number of photons absorbed by the sample solution, $n$, is proportional to $C_{EuD}$, since

$$n = aI_0\{\exp(-\alpha C_{EuD}d)^{-1}\} \simeq a'I_0C_{EuD},$$

where $I_0$ is the intensity of light, $\alpha$ the absorption coefficient, and $a$ and $a'$ constants. If quenching of the emission from the chelated europium ion due to direct interaction between the europium ions does not occur, its emission intensity with 546 m$\mu$ excitation in the mixed solution, denoted by $I_{Eu}(546)$, should be

$$I_{Eu}(546) = \eta n = \eta a'IC_{EuD},$$

where $\eta$ is the efficiency of the inner transition of europium ion. Figure 5 shows that this is actually the case.

For excitation with 365 m$\mu$ light, the absorption coefficient, $\alpha$, of the ligand of EuD and LaD is nearly $2.0\times10^4$ $l$/mol cm. Therefore, light is

absorbed mostly in the vicinity of the front surface of the sample solution in the case of a concentration of $C_{LaD}+C_{EuD}=5\times10^{-3}$ M. The number of photons absorbed by EuD, $n'$, is given by

$$n' = n_0 X_{EuD} = a' I_0' X_{EuD},$$

where $n_0$ is the number of photons absorbed by the mixed solution sample and $I_0'$ the intensity of light. If intermolecular energy transfer from LaD to EuD is negligible, the europium emission intensity should be

$$I_{Eu}(365) = \eta' n' = \eta' a' I_0' X_{EuD},$$

where $\eta'$ is the product of the efficiency of the intramolecular energy transfer and that of the emitting tansition of EuD. This agrees well with the experimental result given in Fig. 5. At room temperature, the phosphorescence of LaD, even in a solution of LaD only, is perfectly quenched, as mentioned above, because of the collision of molecules. This indicates that the lifetime of the triplet state of LaD is very short. Therefore, energy transfer from LaD to EuD at room temperature might be resonably neglected.

At liquid nitrogen temperature, since LaD shows phosphorescence, intermolecular energy transfer from LaD to EuD is expected to occur. In this case, it was difficult to measure directly the relative change of the europium emission intensity with EuD molar fraction in the mixed solutions. For this reason, the relative intensity was estimated from the excitation spectra in the following way. As mentioned above, at room temperature the concentration quenching of the europium emission due to interaction between chelated europium ions does not take place at the concentrations studied. This would also be the case at liquid nitrogen temperature. Then the relative change of the europium emission intensity with EuD molar fraction under 365 m$\mu$ light excitation, $I_{Eu}$ (365), can be estimated by comparing the intensity of the excitation band due to ligand absorption with that of the excitation band due to europium absorption in the excitation spectrum for europium esmission. Namely,

$$I_{Eu}(365) = X_{EuD}\frac{J_{Eu}(365)}{J_{Eu}(568)\{\text{or } J_{Eu}(464)\}},$$

where $J_{Eu}(456)$ and $J_{Eu}(528)$ are the areas of the excitation bands at 456 and 528 m$\mu$ due to europium absorption, respectively, and $J_{Eu}(365)$ is the area of the excitation band due to ligand absorption between 360 and 380 m$\mu$. The result is given in Fig. 6(a). The values are normalized to unity at $X_{EuD}=1.0$. If intermolecular energy transfer from LaD to EuD does not occur, $I_{Eu}(365)$ should be proportional to $X_{EuD}$. In the figure, it is seen that the curve of the intensity of the europium emission is located above the 45° line. This fact indicates that intermolecular energy transfer takes place from LaD to EuD, thus giving rise to an enhancement of the europium emission.

The relative change of the intensity of phosphorescence from LaD with EuD molar fraction in the mixed solutions was measured in a way similar to the case of europium emission. The relative intensity of the phosphorescence with 365 m$\mu$ excitation, $I_{ph}(365)$, is given by

$$I_{ph}(365) = X_{EuD}\frac{J_{ph}(365)}{J_{Eu}(464 \text{ or } 528)},$$

where $J_{ph}(365)$ is the area of the excitation band from 360 to 380 m$\mu$ for ligand phosphorescence. The result is given in Fig. 6(b). The values are normalized to 0.9 at $X_{EuD}=0.1$. If intermolecular energy transfer does not occur, $I_{ph}(365)$ should be proportional to the molar fraction of LaD. It is seen that the curve of phosphorescence intensity is located below the 45° line. As shown in Fig. 4,

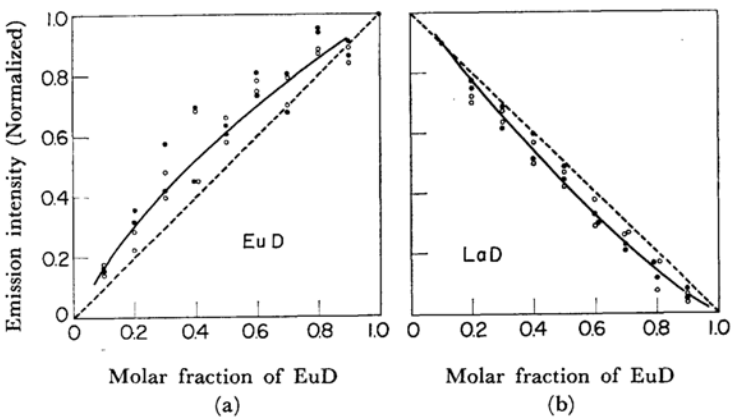


Fig. 6. The relative intensities of (a) europium emission of EuD and (b) ligand phosphorescence of LaD in mixed solutions of EuD and LaD with excitation of the ligand at liquid nitrogen temperature. The mark ● and ○ denote, respectively, that in the measurement the area of the excitation band at 528 and 464 m$\mu$ due to europium absorption is referred to.

the decay time of the phosphorescence of LaD is decreased in mixed solutions with higher EuD concentrations. These facts clearly indicate that ligand phosphorescence is quenched by the existence of EuD in solutions because of energy transfer at liquid nitrogen temperature.

Comparing Fig. 6(a) and 6(b), it is seen that enhancement of the europium emission is nearly proportional to the quenching of the phosphorescence of LaD. Therefore, it is quite obvious that intermolecular energy transfer occurs efficiently from the triplet state of LaD to the chelated europium ion in EuD. The possibility that this energy transfer occurs directly from the triplet state of LaD to the excited state of the europium ion in EuD can be rejected, since it was confirmed that in the mixed ethanol solution of europium free ion and free ligand, *i. e.*, dibenzoylmethane, energy transfer from the latter to the former is not observed.

It is, therefore, undoubted that energy transfer takes place from the triplet state of LaD to the triplet state of EuD, and further to the chelated europium ion. Then, in final conclusion, one can say that this fact is clear evidence that intramolecular energy transfer in europium chelates occurs *via* the triplet state of the ligand.

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