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Intra-Complex Energy Transfer of Europium(III) Complexes Containing Anthracene and Phenanthrene Moieties

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Laser excitation and luminescence studies were carried out for an ethanol solution of tris(hexafluoroacetylacetonato)europium(III), $Eu(hfac)_3(H_2O)_2$ (**1**), and *n*-hexane solutions of tris(hexafluoroacetylacetonato)europium(III) bis(9-diisopropylphosphorylanthracene), $Eu(hfac)_3(DiPAnO)_2$ (**2**), and tris(hexafluoroacetylacetonato)europium(III) bis(2-diisopropylphosphorylphenanthrene), $Eu(hfac)_3(DiPPheO)_2$ (**3**). The absorption spectra of **2** and **3** in *n*-hexane are interpreted by assuming that the central Eu(III) ion weakly interacts with the DiPAnO and DiPPheO moieties. The emission spectroscopic studies revealed that (1) $Eu(hfac)_3(DiPAnO)_2$ emitts only fluorescence from the DiPAnO moiety and (2) $Eu(hfac)_3(DiPPheO)_2$ gives luminescence from the central Eu(III) ion, and (3) $Eu(hfa)_3(H_2O)_2$ and $Eu(hfac)_3(DiPPheO)_2$ afford emission from both the $^5D_1$ and $^5D_0$ states of the Eu(III) ion upon 355 nm laser excitation. The intracomplex energy transfer processes are presented on the basis of absorption, emission and laser excitation studies.

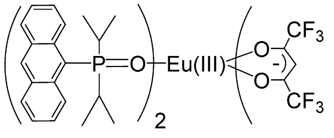
Introduction

Luminescence from Eu(III) complexes has been the subject of extensive studies owing to their importance in the application to light-emitting devices and luminescence probes of biomolecules.[1−8] The Eu(III) complexes exhibit several characteristics: (1) the Eu(III) ion in the complexes gives a series of line-like emission, (2) the lifetimes of Eu luminescence from some Eu(III) complexes in solutions are as long as ms at room temperature because of their Laporte forbidden nature (f−f transition), and (3) luminescence from the Eu(III) ion is readily quenched by water molecules coordinated.[9,10]

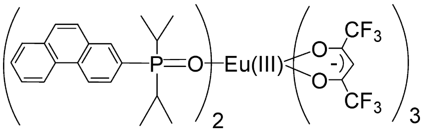
When the Eu(III) complexes having organic ligands with π orbitals are exposed to light, the ligand principally absorbs light because of the fact that the optical transition of the Eu(III) ion is very weak in comparison with that of the $\pi-\pi$ transition of the ligand. The light-absorbed ligand transfers the electronic energy to the central Eu(III) ion to give red luminescence. Since an earlier paper reported in 1942,[11] a number of studies have been carried out to elucidate the energy transfer mechanisms.[12−17] The steady state luminescence from Eu(III) complexes has been interpreted in terms of electronic energy transfer from the excited triplet state of the ligand to the central Eu(III) ion.[18−20] Luminescence of the excited Eu(III) ion has been confirmed to originate from the $^5D_1$ and $^5D_0$ states.[21]

In 1975,[21] studies on laser-excited luminescence from several Eu(III) complexes have been carried out. The complexes are divided into two categories: (1) the lowest excited triplet state of the ligand lies higher in energy than the $^5D_1$ state and (2) that lies between the $^5D_1$ and $^5D_0$ states. The complexes of the category (1) give emission from both the $^5D_1$ and $^5D_0$ states by laser excitation. However, those of category (2) afford emission only from the $^5D_0$ state.

CHART 1: Chemical Structures of Complexes 2 and 3



$Eu(hfac)_3(DiPAnO)_2$ **2**



$Eu(hfac)_3(DiPPheO)_2$ **3**

In the present work, we synthesized tris(hexafluoroacetylacetonato)europium(III) bis(9-diisopropylphosphorylanthracene), $Eu(hfac)_3(DiPAnO)_2$ (**2**) (DiPAnO = 9-diisopropylphosphorylanthracene), and tris(hexafluoroacetylacetonato)europium(III) bis(2-diisopropylphosphorylphenanthrene), $Eu(hfa)_3(DiPPheO)_2$ (**3**) (DiPPheO = 2-diisopropylphosphorylphenanthrene) (Chart 1). Emission from an ethanol solution of tris(hexafluoroacetylacetonato)europium(III), $Eu(hfa)_3(H_2O)_2$, and *n*-hexane solutions of $Eu(hfa)_3(DiPAnO)_2$ and $Eu(hfa)_3(DiPPheO)_2$ is investigated to understand the role of the hfac, DiPAnO, and DiPPheO moieties in the energy transfer from the excited ligands to the central Eu(III) ion, particularly focusing our attention to the excited energy levels of these moieties.

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of Ar, unless otherwise indicated. Solvents used for spectroscopic measurements were distilled prior to use. ^1H NMR and ^{31}P NMR were recorded on a JEOL EX-400 and a JEOL EX-500 spectrometer, respectively.

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Absorption and steady state emission spectra were recorded by a Shimadzu UV-3100 spectrophotometer and a RF-5300 fluorometer, respectively. The light-intensity distribution of a xenon lamp has been corrected with the use of Rhodamine B in ethyleneglycol and the wavelength-dependent characteristics of photomultiplier have been calibrated in the wavelength range 300−850 nm by using a secondary standard lamp. Dissolved dioxygen in sample solutions for luminescence studies was removed by repeated freeze−pump−thaw cycles. The fluorescence quantum yields were determined by a standard method: an ethanol solution of anthracene ($\Phi_F = 0.27$) was used as a reference.[22] HRMS spectra were recorded on a JEOL JMS-700 mass spectrometer. Laser excitation studies were carried out with the use of a Nd:YAG laser (Sure Light 400 from Hoya Continuam Ltd.) equipped with second, third, and forth harmonic generators. Excitation light for lifetime measurements of phosphorescence was third harmonics (355 nm): the duration and the energy of the laser pulse are 5 ns and 30 mJ/pulse, respectively. The monitoring system for the decay of phosphorescence as well as transient absorption spectra has already been reported elsewhere.[23]

Materials. Hexafluoroacetylacetone, $EuCl_3 \cdot 6H_2O$, diisopropylchlorophosphine, and 9-bromoanthracene were purchased and used as received. Tris(hexafluoroacetylacetonato)europium(III) ($Eu(hfa)_3(H_2O)_2$, **1**) and 2-bromophenanthrene were synthesized according to literatures.[24,25]

Preparation of 9-Diisopropylphosphorylanthracene (DiPAnO). This compound was synthesized according to the literature.[26] Yield: 272 mg of pale yellow solid (68%) based on 9-bromoanthracene (300 mg). Analytically pure material was obtained by a flash chromatography packed with silica gel 60N and eluted with CH_2Cl_2−methanol (9:1). ^{1}H NMR (400 MHz,$CDCl_3$): δ = 9.21 (br, 2H, $H_{1,8}$), 8.59 (s, 1H, H_{10}), 8.02 (d, J(H,H) = 8.40 Hz, 2H, $H_{4,5}$), 7.56−7.46 (m, 4H, $H_{2,3,6,7}$), 2.83−2.73 (m, 2H, $H_{methine}$), 1.51(dd, J(H,P) = 14.8 Hz, J(H,H) = 7.10 Hz, 6H, H_{methyl}), 0.94 (dd, J(H,P) = 16.5 Hz, J(H,H) = 7.33 Hz, 6H, H_{methyl}). ^{31}P{^{1}H} NMR (400 MHz,$CDCl_3$): δ = 58.7 (s). HRMS (FAB, mNBA) (m/z) calcd for $C_{20}H_{23}OP$ 310.1487, found 310.1477. Anal. Calcd for $C_{20}H_{23}OP$: C, 77.40; H, 7.47; P, 9.98. Found: C, 77.54; H, 7.70; P, 9.92.

Preparation of 2-Diisopropylphosphorylphenanthrene (DiPPheO). 2-Diisopropylphosphorylphenanthrene was obtained using the same method as previously reported.[27,28] To a solution of 2-bromophenanthrene[25] (300 mg, 1.17 mmol) in THF (50 mL) cooled below −50 °C was added n-BuLi (1.20 mL, 1.56 M in n-hexane) via microsyringe. After 10 min, neat diisopropylchlorophosphine, $P(iPr)_2Cl$ (0.19 mL, 1.17 mmol), was added via microsyringe. The reaction mixture was allowed to warm to room temperature after stirring for 30 min at −50 °C. The crude compound was purified through a flash chromatography packed with silica gel 60N and eluted with CH_2Cl_2−hexane (1:3) affording the analytically pure 2-Diisopropylphosphinophenanthrene (338 mg, 75%). H_2O_2 (30%, 0.2 mL, 1.89 mmol) and water (5 mL) was slowly added to a 30 mL THF solution of 2-diisopropylphosphinophenanthrene (338 mg) and stirred for 4 h. After evaporation of THF, the aqueous residue was extracted with $CHCl_3$ (3 × 30 mL). The combined organic solutions were dried over Na_2SO_4. The solvent was removed under vacuum. The crude compound was purified through a flash chromatography packed with silica gel 60N and eluted with CH_2Cl_2−methanol (9:1) affording the analytically pure compound DiPPheO (183 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, J(H,H) = 8.56 Hz, 1H, H_5), 8.71 (d, J(H,H) = 8.04 Hz, 1H, H_4), 8.35 (d, J(H,H) = 10.96 Hz, 1H, H_8), 7.92−7.63 (m, 6H, $H_{1,3,6,7,9,10}$), 2.48−2.40 (m, 2H, $H_{methine}$), 1.25 (dd, J(H,P) = 16.5 Hz, J(H,H) = 7.33 Hz, 6H, H_{methyl}), 1.11 (dd, J(H,P) = 16.0 Hz, J(H,H) = 7.25 Hz, 6H, H_{methyl}). ^{31}P{^{1}H} NMR (162 MHz,$CDCl_3$): δ = 51.3 (s). HRMS (FAB, mNBA) (m/z) calcd for $C_{20}H_{23}OP$ 310.1487, found 310.1493. Anal. Calcd for $C_{20}H_{23}OP$: C, 77.40; H, 7.47; P, 9.98. Found: C, 77.36; H, 7.40; P, 9.86.

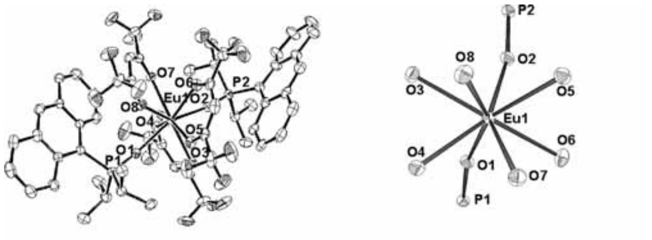
TABLE 1: Cryatallographic Data for 2 and 3

	2	3
formula	$C_{55}H_{49}EuF_{18}O_8P_2$	$C_{55}H_{49}EuF_{18}O_8P_2$
formula weight	1393.87	1393.87
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a/Å	15.8040(16)	12.9551(8)
b/Å	20.343(2)	15.8320(10)
c/Å	18.9226(19)	16.3342(9)
α/deg		71.639(4)
β/deg	96.2858(18)	70.877(4)
γ/deg		73.768(4)
V/Å^3	6047.2(10)	2945.6(3)
Z	4	2
d_{calcd}/g cm^{-3}	1.531	1.571
T/K	90.0(1)	90.0(1)
radiation	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
μ/cm^{-1}	1.193	1.224
diffractometer	Rigaku AFC-8	Rigaku AFC-8
max 2θ/deg	55	60
no. of reflns collcd	58078	48822
no. of indep reflns	13752 (R_{int} = 0.054)	17118 (R_{int} = 0.040)
no. of param refined	758	758
$R1$, $wR2$ ($I > 2\sigma I$)	0.0589, 0.1779	0.0480, 0.1244
S	1.113	1.074

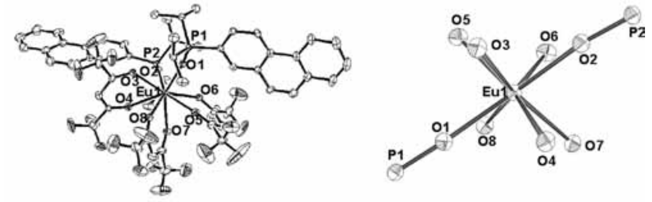
Preparation of Tris(hexafluoroacetylacetonato)europium(III) Bis(9-diisopropylphosphorylanthracene) ($Eu(hfa)_3(DiPAnO)_2$, 2). Complex **2** was obtained using the similar method as previously reported.[24] The methanol solution (20 mL) of DiPAnO (183 mg, 0.590 mmol) and $Eu(hfa)_3(H_2O)_2$ (231 mg, 0.295 mmol) was refluxed under stirring for 8 h. The reaction mixture was dried using a rotary evaporator. Recrystallization of the crude product from the mixture solvent n-hexane/acetone afforded analytical pure $Eu(hfa)_3(DiPAnO)_2$ as yellow crystals (226 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (br s), 8.27 (br m), 5.97 (br s), 1.96 (br), 1.98 (br m), 0.91−0.83 (br m). Anal. Calcd for $C_{55}H_{49}F_{18}O_8P_2Eu$: C, 47.39; H, 3.54. Found: C, 47.86; H, 3.95.

Preparation of Tris(hexafluoroacetylacetonato)europium(III) bis(2-diisopropylphosphorylphenanthrene) ($Eu(hfa)_3(DiPPheO)_2$, 3). This compound ($Eu(hfa)_3(DiPPheO)_2$) was prepared similarly to $Eu(hfa)_3(DiPAnO)_2$. Analytically pure material was obtained by recrystallization from methanol. Yield: 190 mg of pale yellow solid (46%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (d, J(H, H) = 11.0 Hz, 1H), 8.55−8.50 (m, 2H), 8.03−7.57 (m, 6H), 6.65 (br, 3H), 2.12 (dd, J(H,P) = 15.4 Hz, J(H,H) = 6.60 Hz, 6H, H_{methyl}), 1.89−1.67 (m, 2H, $H_{methine}$), 0.93 (dd, J(H,P) = 16.5 Hz, J(H,H) = 7.12 Hz, 6H, H_{methyl}). Anal. Calcd for $C_{55}H_{49}F_{18}O_8P_2Eu$: C, 47.39; H, 3.54. Found: C, 47.39; H, 3.78.

Crystal Structure Determination. The crystallographic data and the results of the structure refinements are summarized in Table 1. In the reduction of data, Lorentz and polarization corrections and empirical absorption corrections were made.[29] The structures were solved by the direct method (SIR2004).[30] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed at calculated positions.



(a) Eu(hfac)$_3$(DiPAnO)$_2$ **2**



(b) Eu(hfac)$_3$(DiPPheO)$_2$ **3**

Figure 1. ORTEP drawings of **2** and **3**: (left) whole structure; (right) coordination sites.

TABLE 2: Selected Bond Distances (Å) for 2 and 3

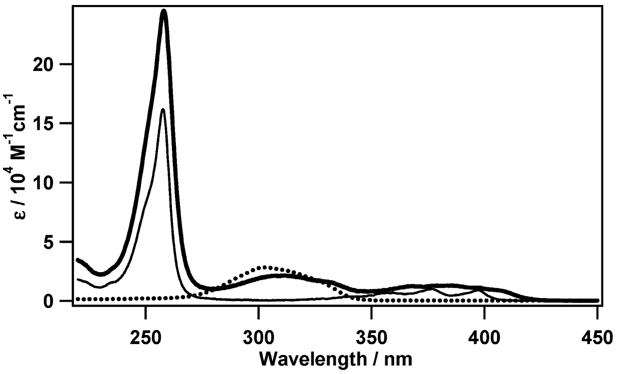
	2	3
Eu1−O1(P=O)	2.361(3)	2.299(2)
Eu1−O2(P=O)	2.328(3)	2.304(2)
average (Eu − O1∼2)	2.345	2.302
Eu1−O3	2.427(3)	2.441(3)
Eu1−O4	2.413(3)	2.454(2)
Eu1−O5	2.375(3)	2.428(3)
Eu1−O6	2.427(4)	2.435(3)
Eu1−O7	2.414(3)	2.407(2)
Eu1−O8	2.408(3)	2.380(2)
average (Eu − O3∼8)	2.411	2.424

CCDC reference numbers are 733848 for **2** and 733849 for **3**, respectively.

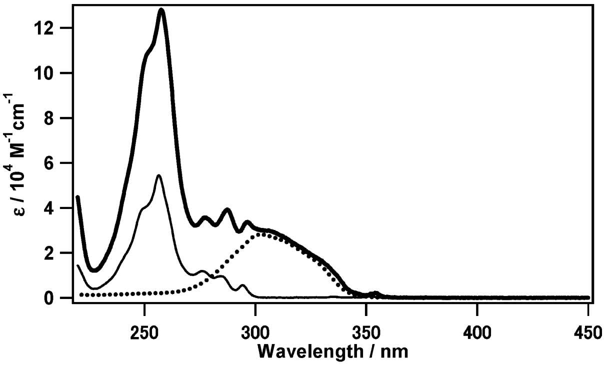
Results

Molecular Structure of Eu(III) Complexes. Figure 1 shows the molecular structures of Eu(hfac)$_3$(DiPAnO)$_2$ (**2**) and Eu(hfac)$_3$(DiPPheO)$_2$ (**3**) determined by the X-ray structure analysis. Selected bond distances are listed in Table 2. Both Eu(III) ions adopt distorted antisymmetrical square-antiprism structures. Complex **2** has two DiPAnO with a hfac ligand between them, and complex **3**, two DiPPheO coordinated to Eu(III) side by side. The difference in theie structures is presumably due to the steric effects of the ligands: the local structure of DiPAnO around the P atom is crowded more than that of DiPPheO, and thus, the two DiPAnO are unable to locate side by side in **2**. The bond lengths between Eu and O(O=P) are 2.345 Å for complex **2**, and 2.302 Å for complex **3**. Other bond lengths between Eu and O(hfac) are very similar to each other (Table 2).

Absorption Spectra of Eu Complexes. Figure 2a shows the absorption spectra of complex **2** and DiPAnO in *n*-hexane and complex **1** in ethanol. Complex **1** in ethanol has a broad absorption peak at 308 nm, which is ascribed to the hfa moiety in the complex. DiPAnO in *n*-hexane exhibits two absorption peaks at ca. 370 and ca. 260 nm. The 0−0 band of DiPAnO in the first absorption band in hexane is red-shifted by 1390 cm^{-1} in comparison with that of anthracene. The absorption spectrum of complex **2** is qualitatively explained as a sum of the spectra of 1 mol of complex **1** and 2 mol of DiPAnO. The first absorption band of Eu(hfac)$_3$(DiPAO)$_2$ around 350−400 nm and the second one at ca. 260 nm are much broader than those of DiPAnO, suggesting that the π-electron system of the DiPAnO moiety in complex **2** is weakly affected by the central Eu(III) ion.



(a) **1** (dashed), DiPAnO (full) and **2** (bold)



(b) **1** (dashed), DiPPheO (full) and **3** (bold)

Figure 2. Absorption spectra: (a) **1** in ethanol, DiPAnO and **2** in *n*-hexane; (b) **1** in ethanol, DiPPheO and **3** in *n*-hexane.

TABLE 3: Electronic Absorption Data for 1, 2, and 3

	$\lambda_{\max}$, nm (ε, 10^4 M^{-1} cm^{-1})
Eu(hfac)$_3$(H$_2$O)$_2$, **1**[a]	308 (2.8)
Eu(hfac)$_3$(DiPAnO)$_2$, **2**[b]	258 (25), 312 (2.1), 384 (1.3)
DiPAO[b]	258 (16), 357 (0.7), 377 (1.0), 397 (0.9)
Eu(hfac)$_3$(DiPPheO)$_2$, **3**[b]	258 (13), 278 (3.6), 287 (4.0), 297 (3.4), 354 (0.2)
DiPPheO[b]	257 (5.4), 276 (1.2), 285 (1.0), 295 (0.6), 335 (0.05), 351 (0.06)

[a] Measurement was carried out in ethanol. [b] Measurements were carried out in *n*-hexane.

Figure 2b shows the absorption spectra of complex **3** and DiPPheO in *n*-hexane and complex **1** in ethanol. The spectrum of DiPPheO has three absorption bands at ca. 360, ca. 290, and ca. 260 nm. The 0−0 band of DiPPheO in the first absorption band in hexane is red-shifted by 730 cm^{-1} in comparison with that of phenenthrene. Complex **3** gives the absorption spectrum almost identical with the sum of the spectra of 1 mol of Eu(hfac)$_3$(H$_2$O)$_2$ plus 2 mol of DiPPhO in the wavelength region $\lambda > 270$ nm. Presumably, the DiPPheO moiety in complex **3** interacts with the Eu(III) ion more weakly than the DiPAnO moiety in complex **2**. In Table 3 are listed the absorption peaks and the molar absorption coefficients of the molecules studied.

Emission Spectra of Eu Complexes. Steady state emission spectra of Eu(hfac)$_3$(H$_2$O)$_2$ (**1**) in various solvents have been reported.[31−34] The spectrum measured in ethanol has a strong peak around 615 nm together with weak ones at 536, 578, 591,

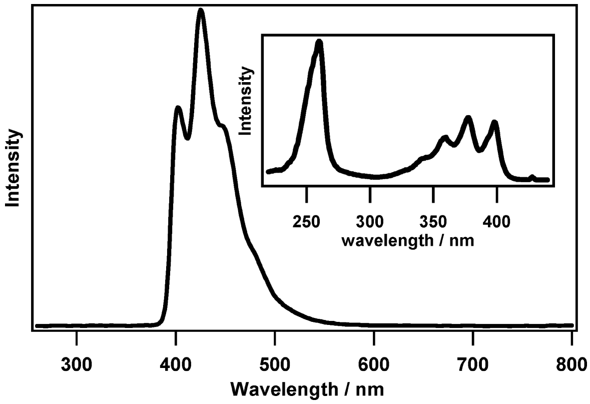


Figure 3. Emission spectrum of **2** in *n*-hexane (λ_{exc} = 355 nm). The inset shows the excitation spectrum of **2** in *n*-hexane (λ_{em} = 425 nm).

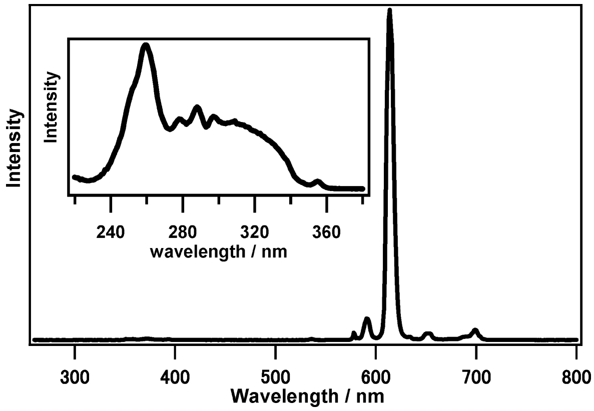


Figure 4. Emission spectrum of **3** in *n*-hexane (λ_{exc} = 355 nm). The inset shows the excitation spectrum of **3** in *n*-hexane (λ_{em} = 614 nm).

650, and 698 nm. Figure 3 shows the emission spectrum of Eu(hfac)$_3$(DiPAnO)$_2$ (**2**) in *n*-hexane observed with the excitation at 355 nm. The fluorescence spectrum having peaks at 402, 425, and 448 nm is in good accord with that of DiPAnO in hexane and no emission from the central Eu(III) ion was observed. The excitation spectrum inserted in Figure 3 reveals that the blue fluorescence from complex **2** is detected when the DiPAnO moiety is illuminated. It is noteworthy that neither the fluorescence from the DiPAnO moiety nor the emission from the Eu(III) ion is detected when the absorption band of the hfac moiety in complex **2** is excited.

From the fluorescence spectrum of DiPAnO, the energy of the excited singlet state is determined as 2.49 × 10^4 cm^{-1}. The quantum yields of fluorescence, Φ_f, measured for DiPAnO and complex **2** in *n*-hexane are respectively obtained as Φ_f =0.85 ± 0.05 and Φ_f = 0.42 ± 0.04, independent of the excitation wavelengths, 266 and 355 nm. This result suggests that the electronic interaction between the DiPAnO moieties and the Eu(III) ion results in the smaller fluorescence yield of complex **2** than DiPAnO. For determination of the triplet energy of DiPAnO in *n*-hexane, phosphorescence measurements were performed at 77 K. However, no phosphorescence was detected. We, thus, merely assumed that the triplet energy of DiPAnO is close to that of anthracene (ca. 14 900 cm^{-1} (670 nm)).[35]

Figure 4 shows the emission spectrum observed for comlex **3** in *n*-hexane measured with the excitation light at 355 nm. The line-like spectrum is in good agreement with that observed for complex **1**: the strong emission peak is located at 615 nm. Differently from complex **2**, the DiPhheO moiety scarcely gives fluorescence even when the absorption bands due to the DiPPheO moiety were excited in the wavelength region, 250−350 nm. As shown in the excitation spectrum inserted in Figure 4, both the DiPPheO and hfac moieties in complex **3** afford the red emission from the central Eu(III) ion.

The excitation-wavelength dependence of the emission yields from the central Eu(III) ion were examined by the measurement of the relative emission intensities at the excitation wavelengths, 266 and 355 nm. Here, we used *n*-hexane solution of DiPAnO as a standard solution, which has prepared to have the absorbance identical with that of complex **3** at the excitation wavelengths. The emission intensity, I_p, at 615 nm from the central Eu(III) ion is expressed as

$$I_p = C\Phi_p I_{abs}(\lambda) \tag{1}$$

where C, Φ_p, and $I_{abs}(\lambda)$ are the constant, emission yield, and the number of photons absorbed by complex **2** at the excitation wavelength, λ, respectively. Similarly, the standard hexane solution of DiPAO gives the fluorescence intensity I_s,

$$I_s = C\Phi_s I_{abs}(\lambda) \tag{2}$$

The fluorescence quantum yield, Φ_s, was determined as 0.85 at the excitation wavelength, 266 and 355 nm. From eqs 1 and 2, we obtain

$$I_p/I_s = (\Phi_s/\Phi_p) \tag{3}$$

Since the relative values, obtained I_p/I_s, at 266 and 355 nm excitation wavelengths were found to be very close each other, the emission yield (Φ_p) from the Eu(III) ion in complex **3** is considered to be almost independent of the excitation wavelengths.

The phosphorescence spectrum of DiPPheO in hexane was measured at 77 K. The 0−0 band was found to be located at 463 nm (21 600 cm^{-1}). The triplet energy level of DiPPheO is, therefore, 139 cm^{-1} lower than that (460 nm) of phenanthrene. The 0−0 bands of fluorescence from phenanthrene and DiPPheO are located at 2.890 × 10^4 cm^{-1} (346 nm) and 2.817 × 10^4 cm^{-1} (355 nm), respectively. The difference (730 cm^{-1}) in the 0−0 bands of fluorescence is much larger than that (139 cm^{-1}) of phosphorescence between phenanthrene and DiPPheO. The fluorescence quantum yield of DiPPheO in *n*-hexane was determined as 0.33 ± 0.03.

Laser Excitation: Eu(hfa)$_3$(H$_2$O)$_2$ (1) in Ethanol. The 355 nm laser excitation studies were carried out for understanding the origin of emission from complexes **1**−**3**. When the ethanol solution of complex **1** was subjected to the 355 nm laser pulse, a strong red emission from the excited Eu(III) ion was observed. We have monitored emission at 536, 556, 585, 591, 615, 650, and 698 nm. The former three emission peaks disappear within 20 μs after the pulse. The latter four live long over a few hundred microseconds. Figure 5 shows the digital oscilloscope traces monitored at 536 and 615 nm as examples.

The decay of the emission intensity, $I_f(\lambda)$, at 536, 556, and 585 nm follows first-order kinetics with the rate constant, k_d = (8.5 ± 0.5) × 10^5 s^{-1}. On the other hand, the emission intensities of the latter four, 591, 615, 650, and 698 nm, exhibit a rapid rise within a laser pulse duration (20 ns) followed by a slow increase that levels off around 20 μs, and then, decays over several hundred microseconds after the pulse. With the use of

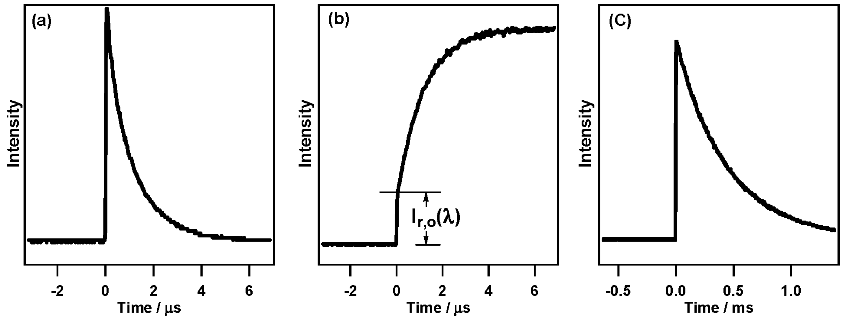


Figure 5. Emission decays profiles of **1** in ethanol: (a) at 536 nm; (b) and (c) at 615 nm.

TABLE 4: Rate Constants for Rise and Decay of Emission from 1[a]

wavelength, nm	rate constants for rise, s^{-1}	rate constants for decay, s^{-1}
536		8.6×10^5
556		8.9×10^5
585		8.0×10^5
591	8.0×10^5	2.2×10^3
615	8.5×10^5	2.3×10^3
650	*b*	2.3×10^3
698	8.0×10^5	2.2×10^3
824	9.0×10^5	2.2×10^3

[a] Experimental errors of the rate constants are within ±10%. [b] The signal intensity is too small to measure the rate for the rise of emission.

the rate constant, k_r, for the rise of emission, the initial increase in the emission intensity, $I_r(\lambda)$, is given by

$$I_r(\lambda)=I_{r,0}(\lambda) + (I_{r,\infty}(\lambda) - I_{r,0}(\lambda))(1 - \exp(-k_r t)) \quad (4)$$

Here $I_{r,0}(\lambda)$ and $I_{r,\infty}$ denote the emission intensity at $t = 0$ and at ca. 20 μs after the pulse, respectively. The value of k_r is obtained as $(8.7 \pm 0.2) \times 10^5$ s^{-1} for emission at the four wavelengths, 591, 615, 650, and 698 nm. The ratio, $I_{r,0}(\lambda)/I_{r,\infty}(\lambda)$, was obtained as 0.88.

After 20 μs, the decay of the emission intensities, $I_s(\lambda)$, at 591, 615, and 698 nm strictly follows first-order kinetics with the rate constant, $k_s = (2.2 \pm 0.1) \times 10^3$ s^{-1}.

Table 4 lists the rate constants at several wavelengths of emission. Since the rate constants for the decay at 536, 585, and 556 nm are almost identical, the emission observed at the three wavelengths is concluded to originate from the same excited state of the central Eu(III) ion. As will be discussed later, the excited state is ascribed to $^5D_1$.

The rate constants, k_r, for the rise of emission at 591, 615, 650, and 698 nm are in good agreement with those for the decay of emission from the $^5D_1$ state, indicating that the excited state that gives emission mostly comes from $^5D_1$. According to earlier studies,[30,33] the $^5D_0$ excited state is known to afford the 591, 615, 650, and 698 nm emission.

Figure 6 shows the steady state emission spectrum and the histogram of the emission intensities observed for a hexane solution of $Eu(hfac)_3(H_2O)_2$ (**1**) measured at 50 ns and 20 μs after the pulse, represented as a function of wavelength. The distribution of the emission intensity taken at 50 ns markedly differs from that at 20 μs. Laser excited emission observed at 50 ns comes from both the $^5D_1$ and $^5D_0$ excited states, each of which are initially populated within a pulse duration. The $^5D_0$ excited state is a source of emission detected at 20 μs after the laser pulse.

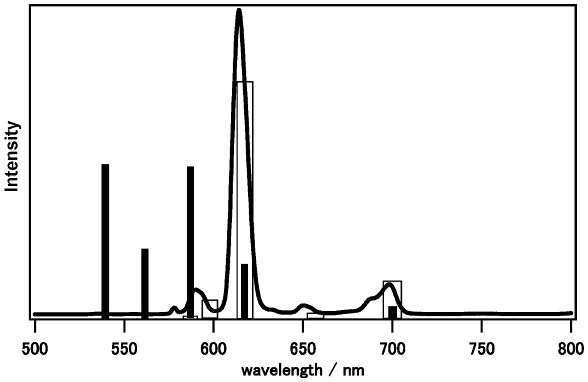


Figure 6. Steady state emission spectrum (black) and histogram of emission intensities observed for **1** in ethanol measured at 50 ns (black bar) and 20 μs (outline bar) after the pulse.

Laser Excitation: DiPAO and $Eu(hfa)_3(DiPAO)_2$ (2) in *n*-Hexane. With the use of the laser excitation of DiPAnO in hexane, a weak T−T absorption spectrum was found to have a peak at ca. 430 nm. The peak wavelength is in accord with that of the triplet anthracene.[35] The triplet DiPAnO decays according to first-order kinetics with a rate constant 6.1×10^5 s^{-1}.

The laser irradiation of complex **2** in *n*-hexane gives blue emission solely ascribable to the DiPAnO moiety. Red emission from the central Eu(III) ion could not be detected. The transient observed after the pulse is the triplet of complex **2** with an absorption peak at 430 nm. Since the spectrum resembles that of DiPAnO, the triplet energy of complex **2** is considered to be principally located at the DiPAnO moiety of complex **2**. The T−T absorption spectrum decays with the first order rate constant, 6.2×10^5 s^{-1}, and readily quenched by oxygen.

Laser Excitation: DiPPheO and $Eu(hfa)_3(DiPPheO)_2$ (3) in *n*-Hexane. A *n*-hexane solution of DiPPheO gives the T−T absorptrion spectrum with a peak at 485 nm. The first-order rate constant for the decay of the triplet state is obtained as 6.0×10^4 s^{-1}. It is noted that the phenanthrene triplet state has a strong absorption peak around 490 nm.[36]

The 355 nm laser excitation of $Eu(hfac)_3(DiPPheO)_2$ (**3**) in *n*-hexane has been carried out to investigate the excited state nature of complex **3**. The emission spectra detected after the laser pulse are very similar to those observed for an ethanol solution of $Eu(hfac)_3(H_2O)_2$ (**1**). The emission peaks at 536, 556, and 585 nm taken at 50 ns after the pulse follow first-order kinetics with the rate constant $(7.2 \pm 0.3) \times 10^5$ s^{-1}. The emission intensities at 591, 615, 650, and 698 nm were found to initially increase and eventually disappear with time after the pulse. The rate constants for the increase and the decay are $(7.4 \pm 0.2) \times 10^5$ and $(1.2 \pm 0.1) \times 10^3$ s^{-1}, respectively. The former value is in good agreement with the emission decay rate constant measured at 536, 556, and 585 nm. The ratio, $I_{r,0}(\lambda)/$

$I_{r,\infty}(\lambda)$, was determined as 0.81 from the rise curve of emission at 615 nm. The histogram of the emission intensities measured by laser excitation and the emission spectrum taken with conventional fluorometer are given in the Supporting Information (Figure S-1).

The transient absorption spectra of complex **3** in degassed hexane are hardly detected. Presumably, in contrast to Eu(hfac)$_3$(DiPAnO)$_2$ (**2**), the lifetime of the triplet DiPPheO moiety in complex **3** is too short to be detected by the present laser excitation study.

Discussion

Emission from Eu(III) of Eu(hfac)$_3$(H$_2$O)$_2$ (1) and Eu(hfac)$_3$(DiPPheO)$_2$ (2). The 355 nm laser excitation of complex **1** in ethanol affords two kinds of emission: one has the peak intensities around 536, 556, 585 nm with the decay rate constant $(8.5 \pm 0.5) \times 10^5$ s^{-1}, and another, around 591, 615, 650, and 698 nm with the decay rate constant $(2.2 \pm 0.1) \times 10^3$ s^{-1}. Thus, the emission spectrum is time-dependent: the intensity distribution of emission, represented as a function of wavelength, observed at 50 ns after the pulse is significantly different from that at 20 μs.

When the two kinds of emission with different lifetimes are observed with laser excitation, the whole emission spectrum, $f(\lambda)$, is expressed as

$$f(\lambda) \int_0^\infty \mathrm{d}t\, f_1(t) = + \int_0^\infty \mathrm{d}t\, f_2(t) \qquad (5)$$

Here $f_1(t)$ and $f_2(t)$ are, respectively, the time functions of the emission intensities from the D$_1$ and the D$_0$ state after the pulse. The spectrum, $f(\lambda)$, is identical with that measured by the conventional fluorometer.

In the present study, $k_s \ll k_d$, and therefore $f_1(t)$ and $f_2(t)$ are formulated as the single exponential function of time. Equation 5 is simply written as

$$f(\lambda)=I_{d,0}(\lambda)(1/k_d) + I_{r,\infty}(\lambda)(1/k_s) \qquad (6)$$

where $I_{d,0}(\lambda)$ denotes the emission intensity from the D$_1$ state at 50 ns after laser excitation.

Because of the facts that (1) $I_{d,0}(\lambda) \approx I_{r,\infty}(\lambda)$ as represented in Figure 6 and (2) the value of k_s is ca. 3 order of magnitude smaller than that of k_d, the whole spectrum, $f(\lambda)$, approximately resembles the spectrum, $I_{r,\infty}(\lambda)$. In fact, we found that the histogram of the emission intensities at several wavelengths taken at 20 μs after the pulse resembles the emission spectrum measured with a conventional fluorometer.

Assignment of the Emission Band Observed for Eu(hfac)$_3$(H$_2$O)$_2$ (1) and Eu(hfac)$_3$(DiPPheO)$_2$ (3). Rare earth trivalent ions have been known to give the sharp lined absorption and emission spectra of the 4f^n configurations.[30,37−42] The energy level assignments of Eu(III) have been made on the basis of absorption and emission spectroscopy combined with the theoretical calculations.[41] From the energy levels reported for Eu(III) ion in Eu(C$_2$H$_5$SO$_4$)$_3$·9H$_2$O,[41] the transition energies between D and F states can be calculated. In Table 5 are listed the transition wavelengths of Eu(III) and emission peak wavelengths obtained for complex **1** in ethanol with the conventional fluorometer and laser excitation.

TABLE 5: Wavelengths for Optical Transitions of 1

transitions[a]	λ(calc),[b] nm	λ(laser),[c] nm	λ(fluorometer),[d] nm
$^5D_1-^7F_0$	525.82		
$^5D_1-^7F_1$	536.25	536	536 (v.w.)
$^5D_1-^7F_2$	556.79	556	556 (v.w.)
$^5D_1-^7F_3$	584.39	585	
$^5D_1-^7F_4$	619.35		
$^5D_1-^7F_5$	663.04		
$^5D_1-^7F_6$	711.54		
$^5D_0-^7F_0$	579.24		578 (v.w.)
$^5D_0-^7F_1$	591.93	591	591 (m)
$^5D_0-^7F_2$	617.06	615	615 (s)
$^5D_0-^7F_3$	651.13	650	650 (m)
$^5D_0-^7F_4$	694.84	698	698 (m)
$^5D_0-^7F_5$	750.30		749 (v.w.)
$^5D_0-^7F_6$	813.01		>800

[a] Transition of the Eu(III) ion. [b] Transition wavelengths calculated from the energy levels of the Eu(III) ion in Eu(EtSO$_4$)$_3$·9H$_2$O.[40] [c] Emission wavelengths observed with laser excitation of Eu(hfac)$_3$(H$_2$O)$_2$ in ethanol. [d] Emission wavelengths observed for Eu(hfac)$_3$(H$_2$O)$_2$ in ethanol with the conventional fluorometer.

The emission spectra of Eu(hfac)$_3$(DiPPheO)$_2$ (**3**) in hexane measured by the conventional fluorometer and the histogram of emission intensities at several wavelengths observed with laser excitation are very similar to those observed for complex **1** in ethanol. Thus, the DiPPheO moieties in complex **3** are concluded to give a minimum effect on the energy levels of the central Eu(III) ion. The assignment of the emission bands of complex **3** is almost identical with that of complex **1**.

Intramolecular Energy Transfer. Light absorption of Eu(III) complexes initially takes place at the ligand to give the ligand excited state, L$_E$, followed by energy transfer from L$_E$ to the Eu(III) ion. The excited state nature of L$_E$, the singlet or the triplet state, is a subject of arguments to explain the intracomplex energy transfer mechanism.[17,19,43] A number of studies on emission from the Eu(III) complexes point out that the triplet state of the ligand principally plays an important role in the intracomplex energy transfer.[13,15,44]

As observed for the rise curve monitored at 615 nm, the intensity of emission, $I_{r,0}(\lambda)$, from the $^5D_0$ state detected immediately after a pulse increases with time and gives a maximum intensity, $I_{r,\infty}(\lambda)$, at ca. 20 μs. Therefore, the $^5D_0$ state is concluded to be populated by the two processes: one is the process, which terminates within a laser pulse duration, and the other, the process, via the $^5D_1$ state. Probably, the ligand excited state transfers the electronic energy to either the $^5D_1$ and $^5D_0$ state of the Eu(III) ion within a pulse duration. Because $I_{r,0}(\lambda)/I_{r,\infty}(\lambda)$ is obtained as 0.88 for the emission intensities from the $^5D_0$ state of the Eu(III) ion in Eu(hfac)$_3$(H$_2$O)$_2$ (**1**), the major part, ca. 90%, of the $^5D_0$ state is concluded to be populated via. the $^5D_1$ state. The remaining part, 10%, of the $^5D_0$ state is populated by a direct energy transfer from the ligand excited state. A similar value, $I_{r,0}(\lambda)/I_{r,\infty}(\lambda) = 0.81$, was obtained for a hexane solution of Eu(hfac)$_3$(DiPPheO)$_2$ **3**.

Contrary to the present work, a previous paper reports that laser excitation of complex **1** in ethanol gives $I_{r,0}(\lambda)/I_{r,\infty}(\lambda) = 0$, suggesting that the $^5D_0$ state is solely populated via the $^5D_1$.[44] However, studies on laser excited luminescence from tris(β-diketonato)europium(III) complexes have shown that the value of $I_{r,0}(\lambda)/I_{r,\infty}(\lambda)$ at 77 K ranges from 0.1 to 0.8 and is highly dependent on both the triplet energy of ligands and the nature of the solvent.[21] As mentioned below, the triplet energy of hfac is higher than that of $^5D_1$, leading to the conclusion that laser excitation of complex **1** can populate the two states, $^5D_1$ and $^5D_0$ by energy transfer from the triplet ligand.

Eu(hfac)$_3$(H$_2$O)$_2$ in ethanol exhibits strong red emission from the Eu(III) ion. The ligand hfac gives no fluorescence. Phosphorescence from the hfac ligand has been detected with the use of the Gd(III) ion, which enhances the S−T transition by heavy atom effects: the triplet state energy of hfac is estimated as 2.22×10^4 cm^{-1} (450 nm).[46] The assumption that the intracomplex energy transfer occurs from the ligand triplet state to the central Eu^{III} ion leads to the conclusion that the possible energy-acceptor level of the Eu(III) ion is $^5D_2$ (2.15×10^4 cm^{-1}), $^5D_1$ (1.9×10^4 cm^{-1}), and $^5D_0$ (1.727×10^4 cm^{-1}). We, however, could not detect emission from the $^5D_2$ state. The major acceptor levels are suggested to be $^5D_1$ and $^5D_0$.

The kinetic behavior of the Eu(III) emission from complex **3** resembles that from complex **1**. The ligand in the excited state initially undergoes intracomplex energy transfer to the central Eu(III) ion and eventually gives the emission from the Eu(III) ion. Complex **3** contains two kinds of ligands, hfac and DiPPheO. The emission observed for complex **3** is solely ascribed to the excited Eu(III) ion. No fluorescence was observed from the DiPPheO moiety. Since the excitation spectrum of the Eu(III) emission at 615 nm agrees well with the absorption spectrum of complex **3**, we conclude that the light energy absorbed by either the hfac and DiPPheO moieties is converted to the emission from the central Eu(III) ion.

The triplet energies of DiPPheO and hfac are determined as 2.16×10^4 and 2.22×10^4 cm^{-1},[46] respectively. Because of a small difference (600 cm^{-1}) in the triplet energy between hfac and DiPPheO, it is likely that the following thermal equilibrium exists:

$$\mathrm{Eu[(hfac)_3(^*T_1)][(DiPPheO)_2]} \rightleftarrows \mathrm{Eu[(hfac)_3][(DiPPheO)_2(^*T_1)]}$$

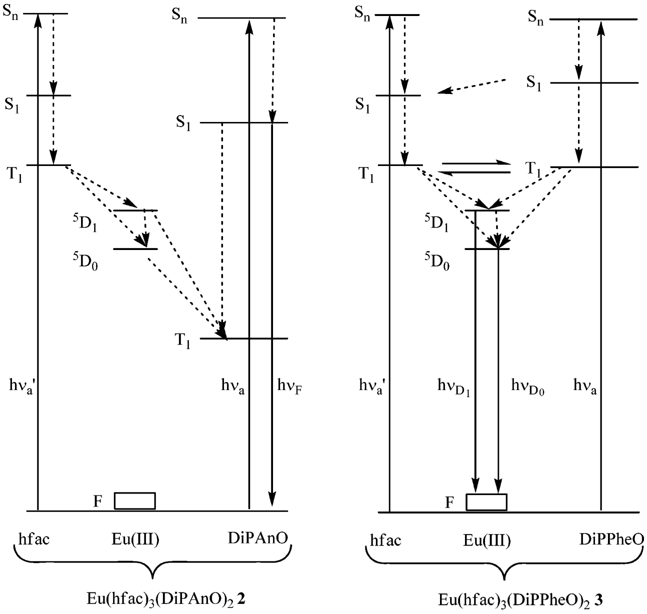
Eu[(hfac)$_3$(*T$_1$)][(DiPPheO)$_2$], in which one of three hfac moieties is in the triplet state, thermally equilibrates with Eu[(hfac)$_3$][(DiPPheO)$_2$(*T$_1$)], in which one of the two DiPPheO moieties is in the triplet state. It is assumed that the DiPPheO and hfac moieties absorb light to form the equilibrium mentioned above and effectively transfer the electronic energy to the central Eu(III) ion.

Fluorescence is hardly detected with excitation of the DiPPheO moiety in complex **3**. The energy of the excited singlet state of the hfac moiety, E(S$_1$,hfac), is estimated from the long wavelength edge of the absorption band of Eu(hfac)$_3$(H$_2$O)$_2$: $E(\mathrm{S_1,hfac}) < 2.86 \times 10^4$ cm^{-1}. Incidentally, the energy of the excited singlet state of DiPPheO, E(S$_1$,DiPPheO), has been determined as $E(\mathrm{S_1,DiPPheO}) = 2.82 \times 10^4$ cm^{-1}. We assume $E(\mathrm{S_1,DiPPheO}) > E(\mathrm{S_1,hfac})$, and thus, the DiPPheO moiety in the excited singlet state readily undergoes energy transfer to the hfac moieties, leading to the internal quenching of fluorescence. In Scheme 1, a simple diagram for intracomplex energy transfer processes of Eu(hfac)$_3$(DiPPheO)$_2$ and Eu(hfac)$_3$(DiPAnO)$_2$ is represented.

Photophysics of complex **2** in *n*-hexane markedly differs from that of complex **3**. We found that (1) no emission from Eu(III) is detected when the absorption bands of both ligand moieties, DiPAnO and hfac, are excited, (2) fluorescence from the DiPAnO moiety is detected only when the absorption bands ascribed to the DiPAnO moiety are excited, and (3) the T−T absorption intensity of the DiPAnO moiety observed for complex **2** was much larger than that of DiPAnO itself as measured by laser excitation.

Finding 1 implies that the excited Eu(III) ion, which is produced by excitation of complex **2**, is internally quenched by the DiPAnO moieties, presumably owing to the intracomplex triplet energy transfer: the $^0D_5$ and/or $^1D_5$ states effectively transfer the electronic energy to the DiPAnO moiety to yield the triplet state. As mentioned above, the triplet energy of DiPAnO is assumed to be at most ca. 1.49×10^4 cm^{-1}. This value is smaller than those of the energy levels of the $^0D_5$ (1.73×10^4) and $^5D_1$ (1.9×10^4 cm^{-1}) states.

SCHEME 1: Diagram of Simplified Intra-Complex Energy Transfer Processes of Eu(hfac)$_3$(DiPAnO)$_2$ (2) and Eu(hfac)$_3$(DiPPheO)$_2$ (3)



Finding 2 suggests that excited singlet state of the hfac moieties hardly transfers the electronic energy to the DiPAnO moiety. Though the excited singlet state of the hfac moiety is higher in energy than DiPAO, the rate for intersystem crossing of the hfac moiety is assumed to be much faster than that of the energy transfer process. Excitation of the absorption band of the DiPAnO moiety leads to the formation of the excited singlet state. From the absorption spectra in Figure 2a, the energy of the excited singlet state of DiPAnO, 2.49×10^4 cm^{-1}, is suggested to be smaller than that of the hfac moiety. Thus, the excited singlet state of DiPAnO decays without electronic interference from the hfac moiety. Taking account of the fact that the quantum yield of fluorescence from the DiPAnO moiety of complex **2** is ca. half that from DiPAnO, we consider that the Eu(III) ion enhances the S−T transition of the DiPAnO moiety in the excited singlet state by the heavy atom effects resulting in the reduction of the fluorescence yield. Finding 3 qualitatively supports this assumption.

Conclusion

Laser excitation and luminescence studies of complexes **1**−**3** have revealed that (1) complex **2** emitts only fluorescence from the DiPAnO moiety, (2) complex **3** gives luminescence from the central Eu(III) ion, and (3) complexes **1** and **3** afford emission from both the $^5D_1$ and $^5D_0$ states of the Eu(III) ion upon 355 nm laser excitation. These observations have been interpreted by the intracomplex energy transfer processes consisting of the Eu(III) ion, hfac, and phosphine oxide ligands.

Supporting Information Available: Steady state emission spectrum and histogram of emission intensities observed for complex **3** and X-ray crystallographic data of complexes **2** and

3. This material is available free of charge via the Internet at http://pubs.acs.org.

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