Quantum Yield and Photoluminescence Intensity Enhancement Effects of a Diphosphine Dioxide Ligand on a 6-Coordinate Eu(III)-β-Diketonate Complex with Low Luminescence

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ABSTRACT: Tris[6,6,7,8,8-heptafluoro-1-[2-(9,9-dimethylfluorenyl)]-1,3-octanedionate] europium(III) (Eu(III)(hfod), 1) was synthesized, which was designed to have low luminescence and a large absorption coefficient in order to elucidate the coordination effects of phosphate oxide ligands. The quantum yield (Φ_TOT) and photoluminescence intensity of complex 1 were dramatically enhanced by coordinating a diphenyl-4-(dibutylphosphinyl)butyl phosphate oxide (DPDB) ligand, thanks to the increased intrinsic photoluminescence quantum yield of the lanthanide (Φ_Ln) and the increased energy transfer efficiency (Φ_ET) in the solution and solid states. In the solid state, there was no energy dissipation by solvent molecules. This excluded the steric shielding effects of the DPDB ligand and allowed the effects of the ligand field environment to be extracted. Φ_Ln and Φ_ET of complex 2 were much larger in the solid state than those in the solution state, resulting in larger Φ_TOT (solution state: Φ_Ln 0.50, Φ_ET 0.42, and Φ_TOT 0.21 and solid state: Φ_Ln 0.74, Φ_ET 0.47, and Φ_TOT 0.35). Larger asymmetry ratios (ratio R) of Eu(III)(hfod)(DPDB) 2 than those of complex 1 in the solution and solid states indicate that the ligand field of the Eu(III) ion becomes more asymmetric by coordination of the DPDB ligand. Density functional theory calculations showed that Φ_Ln and Φ_ET increased when the ligand field around the Eu(III) ion became more asymmetric. Based on these results, we propose a hypothesis on the enhancement of the photoluminescence intensity of 6-coordinated Eu(III)-β-diketonate by a DPDB ligand. When a DPDB ligand coordinates to a Eu(III) ion, the positions of the nearest oxygen atoms around the Eu(III) ion are shifted by steric repulsion and the relative positions of the nearest oxygen atoms are distorted. The distorted coordination environment induces asymmetry in the ligand field, increasing Φ_Ln and Φ_ET. Φ_TOT is enhanced by the DPDB ligand because it is the product of Φ_Ln and Φ_ET. Photoluminescence intensity increases because of the enhanced Φ_TOT.

INTRODUCTION

Lanthanide complexes are used in a wide range of scientific and industrial applications. Eu(III) complexes with strong luminescence, in particular, have attracted much attention, as they can be used in emission devices,1–4 secure media,5 sensors,6,7 and many other applications. Ligands of Eu(III) complexes can be roughly classified as ionic or nonionic. Ionic ligands such as β-diketonates neutralize the charge of the Eu(III) ion. Substituents of β-diketonates greatly increase the intramolecular energy transfer efficiencies from the lowest triplet state of the ligands to the 5D1 level of the Eu(III)(Φ_ET) of Eu(III) complexes. The relation between quantum yield and the energy difference between the ligand triplet state and 5D1 level of the Eu(III) ion was investigated.8 Quantum yield decreases as the energy difference increases. Latva and co-workers investigated the dependence of the quantum yields of Eu(III) complexes on the triplet state energies of the ligands by analyzing many Eu(III) complexes and concluded that the energy of the lowest triplet state has a major influence on the quantum yield of a complex.9 The optimal triplet energy level of ligands of Eu(III) complexes for increasing Φ_ET is reported to be in the range of 21,740–19,532 cm−1.10 Φ_ET strongly depends on the intersystem crossing rate relative to nonradiative singlet-state decay.11 From the viewpoint of molecular structures of ligands, bulky perfluoroalkyl groups enhance quantum yields.12 Photoluminescence intensity is known to be enhanced by coordinating nonionic ligands in addition to β-diketonates. Phosphine oxides, which are strong Lewis bases, are known to be effective nonionic ligands for increasing the photoluminescence intensity of Eu(III) complexes.13–15

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We have previously reported that the coordination of two different phosphine oxide structures to one Eu(III) ion together with β-diketonates is effective for increasing total absolute quantum yield (Φ_{TOT}) and photoluminescence intensity. Simas and co-workers also reported that the coordination of various nonionic ligands to the Eu(III) ion is effective for increasing the quantum yields of Eu(III) complexes. They investigated radiative decay rates to explain the effects of coordinating different nonionic ligands.

We found that an asymmetric diphosphine dioxide ligand consisting of two different phosphine oxide structures connected via a methylene unit further increases Φ_{TOT} and photoluminescence intensity. Next, a detailed investigation of the molecular structures of diphosphine dioxide ligands and the properties of Eu(III) complexes was performed. The number of methylene units between P=O groups in a diphosphine dioxide ligand “n”, which restricts the relative positions of the nearest oxygen atoms around the Eu(III) ion of P=O groups, influences the shape of the 5D_{0} → 7F_{2} transition. Stark splitting is influenced by “n”. Substitution of CF3 groups in phenyl groups of diphosphine dioxides effectively enhances the solubility. Thiényl-substituted diphosphine dioxide ligands serve to suppress the concentration quenching of Eu(III) complexes. Bulky alkyl groups in a diphosphine dioxide ligand increase the half widths of the 5D_{0} → 7F_{2} transition of Eu(III) complexes. The mutual positions of the nearest oxygen atoms around the Eu(III) ion can be strained by bulky substituents, which enhances ET. On the other hand, the photoluminescence of Eu(III)-diketonate complexes is drastically and rapidly quenched by coexisting 2,2-dichlorovinyl dimethyl phosphate (organophosphorus pesticide, popular name dichlorvos) through reducising Φ_{ET}. These results indicate that the Φ_{ET} of Eu(III)-β-diketonate depends not only on the energy difference between the ligand triplet state of β-diketonates and the D_{1} level of the Eu(III) ion but also on the molecular structures of the phosphine oxide ligands. This paper seeks to examine the effects of a diphosphine dioxide ligand on the photoluminescence properties of Eu(III)-β-diketonates.

**RESULTS AND DISCUSSION**

**Molecular Design Concept of a Eu(III)-β-Diketonate with Low Luminescence and a Large Molar Absorption Coefficient.** We designed tris{6,6,7,7,8,8,8-heptafluoro-1-[2-(9,9-dimethylfluorenlyl)]-1,3-octanodionate}europium(III) (Eu(III)(hfod)3) 1, which is a 6-coordinate Eu(III)-β-diketonate complex with low luminescence and a large molar absorption coefficient (Figure 1). 9,9-dimethylfluorenyl groups are bulky aromatic substituents with large absorption coefficients, which are designed to be strongly sterically affected by coordination of phosphine oxide ligands. Partially fluorinated alkyl groups in β-diketonates (CH2CH2CF2CF2CF3) are also designed to be bulky for the purpose of being easily sterically affected by coordination of phosphine oxide ligands. They are electron-donating substituents, which decrease Φ_{ET} by increasing the energy difference between the ligand triplet state of β-diketonates and the D_{1} level of the Eu(III) ion.

**Identification and Purity of Eu(III) Complexes.** Tris{6,6,7,7,8,8,8-heptafluoro-1-[2-(9,9-dimethylfluorenlyl)]-1,3-octanodionate}europium(III) (Eu(III)(hfod)3) 1 and Tris{6,6,7,7,8,8,8-heptafluoro-1-[2-(9,9-dimethylfluorenlyl)]-1,3-octanodionate}(diphenyl-4-(dibutylphosphinyl)butyl phosphine oxide] europium(III) (Eu(III)(hfod)((DPDB) 2 were prepared according to our patent. The brief descriptions and synthetic scheme of the ligand and complexes are shown in the Supporting Information (Scheme S1). The molecular structures and purity of Eu(III) complexes 1 and 2 were determined by elemental analysis, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), 31P NMR spectroscopy, and ESI-MS. The results of elemental analysis (C and H) and ICP-AES (Eu and P) of Eu(III) complexes 1 and 2 were within acceptable error ranges (within 0.5% of theoretical values). Indeed, water molecules are easy to coordinate with a Eu(III) ion. However, we found no coordination of water molecules by TPD-MS (temperature-programmed desorption mass spectrometry) analysis. This result is presumed to be due to the very bulky and hydrophobic substituents of β-diketonates of complex 1. Parent peaks of Eu(III) complexes 1 and 2 were detected by HRMS analysis at errors of 0.3 and 1.1 ppm, respectively. As for complex 2, the P=O signals in 31P NMR spectra of free diphenyl-4-(dibutylphosphinyl)butyl phosphine oxide (DPDB) (48.79 and 32.24 ppm) disappeared. These results indicate that a DPDB coordinated with Eu(III) because the 31P NMR spectra of coordinated phosphine oxide often broaden or disappear. From these results, we concluded that the molecular structures of novel Eu(III) complexes 1 and 2 matched those shown in Figure 1 and that they were of high purity.

**Photoluminescence Properties of Eu(III) Complexes in the Solution State.** Figure 2a shows photoluminescence spectra of Eu(III)(hfod)3 1, Eu(III)(hfod)(3) 1 + 2 equiv of triphenylphosphine oxide (TPPO), Eu(III)(hfod)(3) 1 + 1 equiv of triphenylphosphine oxide (TPPO) + 1 equiv of tributylphosphine oxide (TBPO), and Eu(III)(hfod)(3)(DPDB) 2 in ethyl acetate at a concentration of 1 × 10^{-3} mol/L. Eu(III)(hfod)(3) 1 has a large molar absorption coefficient (ε = 86,000). Despite this, it has low photoluminescence intensity. This meets the molecular design concept of complex 1 for decreasing Φ_{ET} by partially fluorinated alkyl groups. Coordination of TPPO enhances photoluminescence intensity, and coordination of two different phosphine oxides, TPPO and TBPO, further enhances the photoluminescence intensity. Coordination of asymmetric diphosphine dioxide (DPDB) further increases photoluminescence intensity and half widths of the 5D_{0} → 7F_{2} transition (1: 6 nm; 2: 8 nm). The larger half width of Eu(III)(hfod)(3)(DPDB) 2 indicates the lower symmetry of the ligand field. Excitation spectra of these Eu(III) complexes are shown in Figure 2b. The order of

![Figure 1. Molecular structures of Eu(III)-β-diketonate complexes used in this study.](image)
intensity in the excitation spectra is the same as that in the photoluminescence spectra.

Figure 3a shows the action spectra (excitation wavelength vs $\Phi_{TOT}$) of each Eu(III) complex in ethyl acetate at a concentration of $1 \times 10^{-3}$ mol/L. The order of $\Phi_{TOT}$ of Eu(III) complexes is the same as the order of photoluminescence intensity (Figure 2a) in ethyl acetate around 400 nm, which is near the maximum wavelength of the excitation spectra.

$\Phi_{TOT}$ for complex 2 in the solid state (Figure 3b) is higher than in the solution state because it has no energy dissipation because of solvent molecules.

To elucidate the $\Phi_{TOT}$ enhancement mechanism, we performed further analysis as described below. $\Phi_{TOT}$ is the product of intrinsic photoluminescence quantum yield of the lanthanide ($\Phi_{Ln}$) and $\Phi_{ET}$

$$\Phi_{TOT} = \Phi_{Ln} \cdot \Phi_{ET}$$

$\Phi_{Ln}$ is defined as the ratio of the experimental lifetime $\tau_{obs}$ and the radiative lifetime $\tau_{rad}$

$$\Phi_{Ln} = \frac{\tau_{obs}}{\tau_{rad}}$$

where $\tau_{rad}$ is obtained as follows:

$$\tau_{rad} = \frac{n^3 A_{MD,0} \times I_{MD}}{I_{TOT}}$$

where $A_{MD,0}$ is the spontaneous emission probability for the $^5D_0 \rightarrow ^7F_1$ transition in vacuo (14.65 s$^{-1}$), $I_{MD}/I_{TOT}$ is the ratio between the integrated intensity of the $^5D_0 \rightarrow ^7F_1$ transition ($I_{MD}$) and the total integrated emission intensity $^5D_0 \rightarrow ^7F_J$ ($J = 0$–6) ($I_{TOT}$), and $n$ is the refractive index of the medium ($n$ = 1.372 in ethyl acetate).

Table 1 shows the $\tau_{obs}$, $\tau_{rad}$, $\Phi_{Ln}$, $\Phi_{ET}$, $\Phi_{TOT}$, and asymmetric ratio (ratio R) of Eu(III) complexes in ethyl acetate at a concentration of $1 \times 10^{-3}$ mol/L. The ratio R is defined as the relative photoluminescence intensity of the electric dipole transition $^5D_0 \rightarrow ^7F_2$ to the magnetic dipole transition $^5D_0 \rightarrow ^7F_1$ ($I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)$). This ratio indicates how close the local Eu(III) environment is to being centrosymmetric.

$\Phi_{Ln}$ of Eu(III)(hfod)$_3$ increases when phosphine oxide ligands (TPPO, TBPO, and DPDB) coordinate to the Eu(III) ion because $\tau_{obs}$ increases and $\tau_{rad}$ decreases. The values of $\Phi_{Ln}$ descend in the order 2 (0.50), 1 + 1 equiv of TPPO and TBPO (0.35), 1 + 2 equiv of TPPO (0.24), and 1 (0.08). Values of $\tau_{obs}$ are 2 (0.49 ms), 1 + 1 equiv of TPPO and TBPO (0.36), 1 + 2 equiv of TPPO (0.24), and 1 (0.11). $\tau_{obs}$ increases because energy dissipation by solvent molecules is suppressed by the

Figure 2. (a) Photoluminescence spectra and (b) excitation spectra of Eu(III)-β-diketonate measured in ethyl acetate at a concentration of $1 \times 10^{-3}$ mol/L. (a) Excited at the maximum excitation wavelength of excitation spectra (1: 402 nm, 1 + TPPO: 402 nm, 1 + TPPO + TBPO: 402 nm, and 2: 403 nm). (b) Observed at the maximum wavelength of emission spectra (1: 612 nm, 1 + TPPO: 613 nm, 1 + TPPO + TBPO: 613 nm, and 2: 614 nm).

Figure 3. (a) Action spectra (excitation wavelength vs $\Phi_{TOT}$) of each Eu(III) complex in ethyl acetate at a concentration of $1 \times 10^{-3}$ mol/L. (b) Action spectra of Eu(III) complexes in the solid state.
Table 1. Photoluminescence Properties of Eu(III) Complexes in the Solution State Excited by the Peak Wavelength of Excitation Light 

| Eu(III) complex | \( \tau_{obs}^{a} \) | \( \tau_{rad}^{b} \) | \( \Phi_L^{a} \) | \( \Phi_{ET}^{c} \) | \( \Phi_{TOT}^{d} \) | \( R^{f} \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1               | 0.11            | 1.4             | 0.080           | 0.24            | 0.019           | 14.3            |
| 1 + 2 equiv of TPPO | 0.24            | 0.99            | 0.24            | 0.55            | 0.13            | 22.6            |
| 1 + 1 equiv of TPPO and TBPO | 0.36            | 1.02            | 0.35            | 0.59            | 0.21            | 21.7            |
| 2               | 0.49            | 0.99            | 0.50            | 0.42            | 0.21            | 22.1            |

*Life times measured in ethyl acetate (ms) at a concentration of 1 × 10^{-3} mol/L excited at 370 nm light.*

*Radiative lifetimes (ms) calculated as \( \tau_{rad} = 1/\hbar A_{LD} \times \hbar \omega / \Delta E \). *Intrinsic quantum yields calculated as \( \Phi_L = \tau_{obs} / \tau_{rad} * Energy transfer efficiency between the ligand and Eu(III). *Total absolute quantum yield measured in ethyl acetate. *Asymmetry ratio (ratio \( R \)) calculated from the formula \( I(\Delta D_{0} \rightarrow \gamma F_{j}) / I(\Delta D_{0} \rightarrow \gamma F_{i}) \) (in ethyl acetate, 1 × 10^{-3} mol/L).

shielding effect of phosphine oxide ligands. \( \tau_{obs} \) of complex 2 is the largest because the shielding effects of the DPDB ligand are thought to be the largest because of the chelate effect. On the other hand, \( \tau_{rad} \) decreases when phosphine oxide ligands are coordinated probably because of strong \( J \)-mixing effects and does not depend on differences in phosphine oxides (1: 1.4 ms; 1 + 2 equiv of TPPO: 0.99 ms; 1 + 1 equiv of TPPO and TBPO: 1.02 ms; and 2: 0.99 ms).

The ratio \( R \) of Eu(III)(hfod) \( \gamma \) increases when phosphine oxide ligands coordinate to the Eu(III) ion (1: 14.3; 1 + 2 equiv of TPPO: 22.6; 1 + 1 equiv of TPPO and TBPO: 21.7; and 2: 22.1) because the nearest oxygen atoms in chemical environments (P=Q) that differ from those of \( \beta \)-diketonates additionally coordinate to the Eu(III) ion. The degree of increase in the ratio \( R \) does not depend on differences in phosphine oxides just as the degree of decrease in \( \tau_{rad} \) does not depend on them.

\( \Phi_{ET} \) also increases by coordination of phosphine oxide ligands (1: 0.24; 1 + 2 equiv of TPPO: 0.55; 1 + 1 equiv of TPPO and TBPO: 0.59; and 2: 0.42). However, it is difficult to explain these results because all the Eu(III) complexes listed in Table 1 have the same \( \beta \)-diketonates. It is known that substituents of \( \beta \)-diketonates have a great effect on the \( \Phi_{ET} \) of Eu(III) complexes. A strong correlation between \( \Phi_{ET} \) and the energy difference between the ligand triplet state and \( 5D_{1} \) level of the Eu(III) ion has been reported.

\( \Phi_{L} \) of complex 1 + 2TPPO (0.24) is much smaller than that of complex 2 (0.50). The diphosphine dioxide ligand of complex 2 (DPDB) is strongly coordinated to the Eu(III) ion because of the chelate effect and energy dissipation effects of solvent molecules more strongly suppressed by shielding effects of DPDB. On the other hand, ligand exchange occurs when TPPO coordinates to a Eu(III) ion. Shielding effects of TPPO is small and \( \tau_{obs} \) of complex 1 + 2TPPO (0.24) is much smaller than that of complex 2 (0.49). These results lead to the smaller total quantum yield of complex 1 + 2TPPO compared to that of complex 2 despite the fact that complex 1 + 2TPPO has a larger asymmetric ratio and energy transfer efficiency than complex 2.

Photoluminescence Properties of Eu(III) Complexes in the Solid State. To elucidate the effects of phosphine oxide ligands more clearly, we investigated the photoluminescence properties of complexes 1 and 2 in the solid state, in which there is no energy dissipation by solvent molecules. In the solid state, the steric shielding effect of the DPDB ligand is excluded and the effects of the environment of ligand fields can be extracted. Table 2 shows the photoluminescence properties of Eu(III)(hfod) \( \gamma \) and Eu(III)-(hfod)(DPDB) \( \gamma \) in the solid state excited by ultraviolet rays.

| Eu(III) complex | \( \tau_{obs}^{a} \) | \( \tau_{rad}^{b} \) | \( \Phi_L^{a} \) | \( \Phi_{ET}^{c} \) | \( \Phi_{TOT}^{d} \) | \( R^{f} \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1               | 0.33            | 1.4             | 0.25            | 0.057           | 0.014           | 7.5             |
| 2               | 0.58            | 0.79            | 0.74            | 0.47            | 0.35            | 18.2            |

*Life times measured in the solid state excited at 370 nm light.*

*Radiative lifetimes (ms) calculated as \( \tau_{rad} = 1/\hbar A_{LD} \times \hbar \omega / \Delta E \). *Intrinsic quantum yields calculated as \( \Phi_L = \tau_{obs} / \tau_{rad} * Energy transfer efficiency between the ligand and Eu(III). *Total absolute quantum yield measured in the solid state. *Asymmetry ratio \( R \) calculated from the formula \( I(\Delta D_{0} \rightarrow \gamma F_{j}) / I(\Delta D_{0} \rightarrow \gamma F_{i}) \).

When the photoluminescence properties of complexes 1 and 2 in the solid state are compared, the \( \Phi_{ET} \) of complex 2 is much larger than that of complex 1 because of the effects of the environment of the ligand field by the DPDB ligand (1: 0.25 and 2: 0.74). \( \Phi_{ET} \) of complex 2 is larger because \( \tau_{obs} \) of complex 2 is larger (1: 0.33 ms and 2: 0.58 ms) and \( \tau_{rad} \) of complex 2 is smaller (1.4 ms and 2: 0.79 ms). It is notable that \( \Phi_{ET} \) of complex 2 (0.47) is much larger than that of complex 1 (0.057). \( \Phi_{ET} \) of complex 2 is also larger than that of complex 1 in the solution state, as shown in Table 1 (1: 0.24 and 2: 0.42), but it is more drastically enlarged in the solid state.

Comparison of Photoluminescence Properties in Solution and Solid States. Photoluminescence properties in solution and solid states are compared for each complex. Comparison of the properties in solution and solid states reveals the mechanism of the coordination effects of the DPDB ligand. \( \Phi_{ET} \) of complexes 1 and 2 in the solid state is much larger than in the solution state (in the solution state: 1 (0.08) and 2 (0.50); in the solid state: 1 (0.25) and 2 (0.74)). \( \tau_{obs} \) of complex 1 in the solid state (1: 0.33 ms and 2: 0.58 ms) is much larger than in the solution state (1: 0.11 ms and 2: 0.49 ms). This is because there is no energy dissipation by solvent molecules in the solid state and the value of \( \tau_{obs} \) is maintained. \( \tau_{rad} \) of complex 2 in the solid state (0.79 ms) is smaller than that in the solution state (0.99 ms). \( \tau_{rad} \) is proportional to the ratio of the intensities of magnetic transitions \( I_{MD}/I_{TOT} \) with smaller \( \tau_{rad} \) meaning smaller \( I_{MD}/I_{TOT} \) in the solid state. This should be specially mentioned because these results indicate that the ligand field can be more asymmetric in the solid state than in the solution state. Strong steric repulsion between bulky substituents of \( \beta \)-diketonates and the DPDB ligand could be the cause of this phenomenon. On the other hand, \( \tau_{rad} \) of complex 1 is the same in solution and solid states (1.4 ms). This means that \( I_{MD}/I_{TOT} \) does not change between the spectra in solution and solid states. It can be said that complex 2 in the solid state has an asymmetric ligand field caused by the DBDP ligand and that it has a smaller \( \tau_{rad} \) even in the solid state.

The difference in \( \tau_{obs} \) of complex 2 between solution and solid states is smaller than in the case of complex 1 because \( \tau_{obs} \) of complex 2 in the solution state (0.49 ms) is much larger than that of complex 1 (0.11 ms) because of the solvent molecule shielding effects of the DPDB.

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The behavior of $\Phi_{ET}$ greatly differs between complexes 1 and 2. $\Phi_{ET}$ of 1 in the solid state (=0.057) is much smaller than in the solution state (=0.24) despite the lack of the energy dissipation effect by solvent molecules in the solid state. The ratio $R$ of Eu(III)(hfod)$_3$ 1 in the solid state is much smaller than in the solution state (solution: 14.3 and solid: 7.5), indicating that the local Eu(III) environment of 1 in the solid state is much more centrosymmetric than in the solution state in the case of complex 1. It is shown that complex 1 has no coordination with water molecules and there is no quenching effect by water molecules. These results show that the small $\Phi_{ET}$ of 1 in the solid state is due to the more centrosymmetric ligand field. In conclusion, there is no noticeable difference between $\Phi_{Tot}$ in solid and solution states in complex 1 because the $\Phi_{In}$ enhancement effect is canceled out by a smaller $\Phi_{ET}$ in the solid state (solution: 0.019 and solid: 0.014).

On the other hand, $\Phi_{ET}$ of complex 2 in the solid state (0.47) is larger than in the solution state (0.42) unlike in the case of complex 1. There is also a small difference in the ratio $R$ of complex 2 between solution and solid states (solution: 22.1 and solid: 18.2). On the other hand, the optimal triplet energy level of ligands of Eu(III) complexes for increasing $\Phi_{ET}$ is reported to be in the range of 21,740−19,532 cm$^{-1}$. For the complexes 1, 1 + 2TPPO, 1 + TPPO + TBPO, and 2, the calculated triplet energy levels are 22,938, 22,314, 22,204, and 22,099 cm$^{-1}$, respectively. Considering that the calculated excitation energy in vacuum is usually larger than that in solution, these triplet energy levels are considered to be optimal and the difference among these triplet energy levels is small. It is difficult to explain the difference in behaviors of $\Phi_{ET}$ between complexes 1 and 2 by triplet energy levels of ligands.

These results suggest that the local Eu(III) environment of complex 2 does not become symmetric even in the solid state by the effects of the DPDB ligand. The energy dissipation effects of solvent molecules in the solid state cannot cause a larger $\Phi_{ET}$ in the solid state. Larger $\Phi_{ET}$ in the solid state than in the solution state has also been reported for other Eu(III)-$\beta$-diketonate complexes with asymmetric diphosphine dioxide ligands. In conclusion, both $\Phi_{In}$ and $\Phi_{ET}$ of complex 2 in solid state are much larger than in the solution state, resulting in larger $\Phi_{Tot}$ in the solid state compared with that in the solution state (solution: $\Phi_{In}$ 0.50, $\Phi_{ET}$ 0.42, and $\Phi_{Tot}$ 0.21 and solid: $\Phi_{In}$ 0.74, $\Phi_{ET}$ 0.47, and $\Phi_{Tot}$: 0.35).

From the results of the photoluminescence properties mentioned earlier, it can be said that both $\Phi_{In}$ and $\Phi_{ET}$ of complex 1 with low luminescence are drastically enlarged by coordinating a DPDB ligand, which results in strong photoluminescence intensity. The DPDB ligand has the function of maintaining the asymmetry of the ligand field even in the solid state. This trend is thought to be emphasized by the marked steric repulsion between the DPDB ligand and bulky substituents of $\beta$-$\delta$-diketones that induce distortion in the relative positions of the nearest oxygen atoms. Many types of asymmetric diphosphine dioxide compounds were reported and they can be used as ligands for lanthanide complexes.

Excitation Wavelength Dependency of Photoluminescence Properties. Figure 4a shows the photoluminescence spectra of Eu(III)(hfod)$_3$ 1 and Eu(III)(hfod)$_3$(DPDB)$_2$ 2 in the solid state normalized to the $^5D_0 \rightarrow ^7F_1$ transition.

The half width of the $^5D_0 \rightarrow ^7F_1$ transition of complex 2 excited at 392 and 464 nm is much larger than that of complex 1 [1: 5 nm and 2: 8 nm (excited at 392 and 464 nm)] as is the case in the solution state (Figure 2a). The larger half widths of Eu(III)(hfod)$_3$(DPDB)$_2$ 2 mean that the symmetry of the ligand field is lower than that of complex 1 because of the effects of coordinating a DPDB ligand. These results agree well with the results of the larger ratios ($R$) of complex 2 than those of complex 1 in both solution and solid states (Tables 1 and 2).

The photoluminescence spectra of complex 2 depend on the excitation wavelength. The photoluminescence spectrum due to direct absorption by the Eu(III) ion (464 nm: $^7F_0 \rightarrow ^5D_2$) differs from that due to ligand absorption (392 nm). The ratio $R$ of the spectrum excited by ligand absorption is much larger than that by direct absorption. In the case of direct absorption, Eu(III) in $^7F_0$ is excited to $^5D_2$, then relaxes to $^5D_0$ and then relaxes to $^3F_1$ (magnetic dipole transition) or $^3F_2$ (electric dipole transition). On the other hand, in the case of ligand absorption, excitation energy transfers from the ligand to the Eu(III), and Eu(III) is excited to one of the following states: $^5D_0$, $^5D_1$, and $^5D_2$. Eu(III) then relaxes to $^5D_0$ and then relaxes to $^3F_1$ (magnetic dipole transition) or $^3F_2$ (electric dipole transition). We consider that the stay at $^3D_0$ or $^3D_1$ may affect...
the allocation between the magnetic dipole transition (5D2 \rightarrow 7F_j) and the electric dipole transition (5D0 \rightarrow 7F_j) because of J-mixing effects.

Figure 4b shows the excitation spectra of complexes 1 and 2 in the solid state. In the case of complex 2, the peak at 464 nm at the wavelength of direct absorption by the Eu(III) ion is conspicuous, thanks to the notable asymmetry of ligand fields induced by the DPDB ligand.

The DPDB ligand has great effects on the intensity of the forbidden 5D0 \rightarrow 7F_0 transition. The 5D0 \rightarrow 7F_0 transition of Eu(III)(hfac)_2(DPDB) 2 in both solution and solid states is notably larger than others (Figures 2a, 4a). Additionally, the 7F_0 \rightarrow 5D_2 transition in excitation spectra also remarkably appears (Figure 4b). From these results, we conclude that ligand fields are conspicuously asymmetric by the DPDB ligand and quantum yields are enlarged and simultaneously, 7F_0 transition is activated.

DFT Calculation of Eu(III) Complexes. Figure 5 shows a schematic illustration of the mechanism of photoexcitation, intersystem crossing (ISC), energy transfer, and light emission for the Eu(III) complexes. To analyze the experimental results, we performed density functional theory (DFT) calculations, the details of which are given in S11 (Supporting Information).

The calculated absorption spectra are shown in S12 (Supporting Information). The obtained absorption coefficients are thought to be large enough for all complexes that \( \Phi_{\text{ET}} \) and \( \Phi_{\text{ISC}} \) do not depend on the absorption coefficient. The calculated absorption spectra for free ligands show that the band at 464 nm observed in excitation spectra does not belong to a particular ligand. The band at 464 nm observed in excitation spectra belongs to the 7F_0 \rightarrow 5D_2 transition of a Eu(III) ion (Figure 4b).

It has been reported that energy transfer from both the singlet excited state and triplet excited state of the ligand to Eu(III) can occur. However, the reported rate of energy transfer from the triplet excited state is much larger than from the singlet excited state, and ISC usually proceeds faster than fluorescence. Therefore, we assume that the singlet excited state S1 of the ligand mainly relaxes to T1 through ISC.

The ET rate can be written as

\[
k_{\text{ET}} = \frac{2\pi}{h} |H_{I\text{-FF}}|^2 \left( \frac{1}{4\pi\kappa_0 T I} \right) e^{-\left(\lambda + \Delta G\right)^2 / 4k_0 T}
\]

Equation 4 is valid in both the Dexter and Forster limits of energy transfer. From DFT calculations, we obtained the prefactor in eq 4, which is the value in eq 4 that multiplies \( |H_{I\text{-FF}}|^2 \). The calculation details are given in S13 (Supporting Information). The obtained prefactors are shown in Table 3.

Table 3. Energy Transfer Rate Prefactor and the Norm of the Effective Dipole Moment of the Ligand Field for Each Eu(III) Complex

| Eu(III) complex | \( |H_{I\text{-FF}}|^2 \) [(eV)\(^{-2}\) s\(^{-1}\)] | \( \mu^\text{ff} \) (Debye) |
|-----------------|-----------------|-----------------|
| 1               | 4.6e+16         | 2.4e+16         |
| 1 + 2 eq. of TPPO | 4.8e+16         | 3.8e+16         |
| 1 + 1 eq. of TPPO and TBP | 1.2e+17      | 2.8e+16         |
| 2               | 8.4e+17         | 4.4e+17         |

*a*Details of the calculation of the energy transfer rate prefactor are given in S3. *b*Details of the norm of the effective dipole moment of the ligand field are given in S4.

The prefactors reported previously are of the order of 10\(^{16}\) (ev)\(^{-2}\) s\(^{-1}\). We therefore think that the prefactors are large enough for all complexes. Next, we consider \( |H_{I\text{-FF}}|^2 \). A theory of intramolecular energy transfer rates in lanthanide complexes has been developed by Malta and co-workers. According to this theory, \( |H_{I\text{-FF}}|^2 \) depends on the Judd-Ofelt intensity parameters. As the site of Eu(III) becomes more asymmetric, the energy transfer rate becomes larger. We therefore define \( \mu^\text{ff} \), which is the norm of the effective dipole moment of the ligand field, using the DFT-optimized geometry. The definition of \( \mu^\text{ff} \) is given in S14 (Supporting Information). As \( \mu^\text{ff} \) becomes larger, the ligand field becomes more asymmetric and larger.

The value of \( \mu^\text{ff} \) for each complex in both state [T1, 7F] and state [S0, 5D0] is shown in Table 3. We consider the case where energy transfer occurs at the geometry of [T1, 7F]. We then find that the order of the averaged value of \( \mu^\text{ff} \) for [T1, 7F] and [S0, 5D0] is larger in Eu(III) complexes with the phosphine oxide ligands (1 + 2TPPO, 1 + TPPO + TBP, and 2) than in 1, which is in agreement with the order of \( \Phi_{\text{ET}} \). Hence, we assume that \( \Phi_{\text{ET}} \) of the Eu(III) complexes in this study strongly depends on the asymmetry of the ligand field. In order to validate this assumption, \( |H_{I\text{-FF}}|^2 \) needs to be calculated and this is left as a future research topic. As already mentioned, triplet energy levels for the complexes 1, 1 + 2TPPO, 1 + TPPO + TBP, and 2 are considered to be optimal. The value \( r - \langle r \rangle \), which is the deviation of the bond length Eu−O from the averaged value, is shown in Tables S2−S9 (Supporting Information). For \( r - \langle r \rangle \) of charged oxygen in the triplet state in Complex 2 (Table S8), some deviations are quite large. Hence, the asymmetry of the ligand field of complex 2 in the triplet state is considered to be very large. Next, we mention the nature of the triplet states. The spin density distribution of [T1, 7F] for all complexes shown in Figures S3−S6 (Supporting Information) is localized on one \( \beta \)-diketonate. There are no contributions from the phosphine oxide ligands. Finally, we consider the emission which occurs at the geometry of [S0, 5D0]. We also find that the order of the magnitude of \( \mu^\text{ff} \) in [S0, 5D0] is \( 1 < 1 + 2TPPO < 1 + TPPO + TBP < 2 \),
which is in agreement with the order of $\Phi_{la}$ in Table 1. We therefore assume that $\Phi_{la}$ of the Eu(III) complexes in this study depends on the symmetry of the ligand field. This assumption needs to be validated by the calculation of the emission rate. Density functional theory (DFT) calculations successfully show that $\Phi_{ET}$ increases when Eu(III) becomes more asymmetric.

Hypothesis about Photoluminescence Intensity Enhancement Effects of 6-Coordinated Eu(III)-β-Diketone by the DPDB Ligand. We propose a hypothesis about the photoluminescence intensity enhancement effects of 6-coordinated Eu(III)-β-diketone by the DPDB ligand. When a DPDB ligand coordinates to the Eu(III) ion of a 6-coordinated Eu(III)-β-diketone, the positions of the nearest oxygen atoms around the Eu(III) ion are shifted by steric repulsion and the relative positions of the nearest oxygen atoms become distorted. Remarkable steric repulsion between bulky substituents of β-diketones and the DPDB ligand can promote the distortion effectively, and the ligand field around the Eu(III) ion becomes more asymmetric. This indicates that asymmetry of the ligand field enhances $\Phi_{la}$ and $\Phi_{ET}$ found by DFT calculations. $\Phi_{TOT}$ is enhanced because it is a product of $\Phi_{la}$ and $\Phi_{ET}$. Consequently, the photoluminescence intensity of Eu(III)-β-diketone is drastically enhanced by a DPDB ligand.

CONCLUSIONS

We synthesized Eu(III)(hfod)$_3$ 1 that is designed to have low luminescence and a large absorption coefficient in order to elucidate the coordination effects of phosphine oxide ligands. $\Phi_{TOT}$ and the photoluminescence intensity of complex 1 are dramatically enhanced by coordinating a DPDB ligand [generating Eu(III)(hfod)$_3$(DPDB) 2], thanks to the increased $\Phi_{la}$ and $\Phi_{ET}$ in both solution and solid states. In the solid state, there is no energy dissipation by solvent molecules. This excludes the steric shielding effects of the DPDB ligand, allowing the effects of the environment of ligand fields to be extracted in the solid state. Both $\Phi_{la}$ and $\Phi_{ET}$ of complex 2 are much larger than those in the solution state, resulting in a larger $\Phi_{TOT}$ in the solid state (solution state: $\Phi_{la}$ 0.50, $\Phi_{ET}$ 0.42, and $\Phi_{TOT}$ 0.21 and solid state: $\Phi_{la}$ 0.74, $\Phi_{ET}$ 0.47, and $\Phi_{TOT}$ 0.35).

The larger asymmetry ratios (ratio $R$) of complex 2 than those of complex 1 in solution and solid states indicate that the ligand field of the Eu(III) ion becomes more asymmetric by coordination of the DPDB ligand. DFT calculations show that $\Phi_{la}$ and $\Phi_{ET}$ increase when the ligand field around the Eu(III) ion becomes more asymmetric.

Based on these results, we propose a hypothesis about the enhancement of the photoluminescence intensity of 6-coordinated Eu(III)-β-diketone by a DPDB ligand. When a DPDB ligand coordinates to the Eu(III) ion of a 6-coordinated Eu(III)-β-diketone, the positions of the nearest oxygen atoms around the Eu(III) ion of β-diketones are shifted by steric repulsion and the relative positions of the nearest oxygen atoms become distorted. The asymmetry of the ligand field is induced by the distorted coordination environment, which enlarges $\Phi_{la}$ and $\Phi_{ET}$. $\Phi_{TOT}$ is enhanced by the DPDB ligand because it is the product of $\Phi_{la}$ and $\Phi_{ET}$. Photoluminescence intensity is enlarged by the effects of enhanced $\Phi_{TOT}$. We conclude that the mechanism by which diphosphine dioxide ligands increase $\Phi_{TOT}$ and the photoluminescence intensity of Eu(III)-β-diketones is that they generate a distorted coordination environment.

EXPERIMENTAL SECTION

Materials. Tris[6,6,7,7,8,8,8-heptafluoro-1-[2-(9,9-dimethylfluoren-1-yl)-1,3-octanedionate](triphenyl Phosphine Oxide) Europium(III) (Eu(III)(hfod)$_3$(DPDB) 2). Anal. Calcd for C$_9$H$_8$EuF$_2$I$_{10}$O$_6$: C, 54.60; H, 4.66. Found: C, 57.7; H, 4.80. Eu and P content by ICP-AES: Calcd for: C$_9$H$_8$EuF$_2$I$_{10}$O$_6$: Eu, 9.93. Found: Eu, 9.83. HRMS (ESI, $m/z$, [M + H]$^+$): calcd for C$_9$H$_8$EuF$_2$I$_{10}$O$_6$: 1531.288; found, 1531.287 (error 0.3 ppm). Pale yellow solid.

$\Phi_{ETS}$ found by ICP-AES: Calcd for: C$_9$H$_8$EuF$_2$I$_{10}$O$_6$: Eu, 9.93. Found: Eu, 9.83. HRMS (ESI, $m/z$, [M + Na]$^+$): calcd for C$_9$H$_8$EuF$_2$I$_{10}$NaO$_2$: 1971.489; found, 1971.491 (error 1.1 ppm). $^3$P NMR δ$_p$ (400 MHz; CDCl$_3$, phosphoric acid) 48.79 and 32.49 of free diphosphine dioxide disappeared. Pale yellow solid.

Tris[6,6,7,7,8,8,8-heptafluoro-1-[2-(9,9-dimethylfluoren-1-yl)-1,3-octanedionate](triphosphine oxide)(triphenyl phosphine oxide) europium(III) (Eu(III)(hfod)$_3$(TPPO)$_2$). Eu(III)(hfod)$_3$ and 2 M equiv of TPPO coexist in a solution. Generation of Eu(III)(hfod)$_3$(TPPO)$_2$ was confirmed by the disappearance of the $^3$P NMR spectrum of free triphenyl phosphate oxide (29.6 ppm).

Tris[6,6,7,7,8,8,8-heptafluoro-1-[2-(9,9-dimethylfluoren-1-yl)-1,3-octanedionate](triphenyl phosphine oxide)(triphenyl phosphine oxide) europium(III) (Eu(III)(hfod)$_3$(TPPO) 2). Eu(III)(hfod)$_3$ and 1 M equiv of TPPO and TBPO coexist in a solution. Generation of Eu(III)(hfod)$_3$(TPPO) 2 was confirmed by the disappearance of $^3$P NMR spectrum of free triphenyl phosphate oxide and tributylphosphine oxide (29.6 and 49.1 ppm, respectively).

Measurement of Photoluminescence and Excitation Spectra. Each Eu(III) complex was dissolved in ethyl acetate at a concentration of 1 × 10$^{-5}$ mol/L at room temperature. Photoluminescence and excitation spectra were measured at room temperature using a spectrophotofluorometer (Fluoromax 4, Horiba Jobin Yvon Inc.). Excitation and emission slit widths were set to 0.5 nm for measurement of emission spectra and to 0.7 and 0.6 nm, respectively, for measurement of excitation spectra. Photoluminescence and excitation spectra were measured at intervals of 1 nm using a scanning rate of 600 nm/min. Dark offset and corrections were applied to both emission and excitation sites. In the measurements of photoluminescence spectra, each solution of Eu(III) complexes was excited at the maximum excitation wavelength of excitation spectra. Excitation spectra were measured at the maximum wavelength of emission spectra. Solid-state emission and excitation spectra were measured using the same slit width as that for the measurement of solution-state spectra using an ND10 filter.

Measurement of Emission Lifetimes. Emission lifetimes were measured as follows. Each solution of Eu(III) complexes was placed in a sealed cell and measured using a Fluoromax 4. The excitation wavelength was set to 370 nm. Single-exponential functions were used to fit the relative decay curves monitored at the maximum wavelength to calculate the emission lifetimes. $\chi^2$ values were in the range of >1.0 and <1.2.
Measurement of Total Absolute Quantum Yields.

Total absolute quantum yields ($\Phi_{\text{abs}}$) were measured as follows. Each solution of Eu(III) complexes was placed in a sealed cell and measured in ethyl acetate at a concentration of $1 \times 10^{-3}$ mol/L using a PMA-12 C10027-01, Hamamatsu Photonics KsK. For solid-state measurements, the powder Eu(III) complex was put into a quartz cell. An integrating sphere was used in all measurements.

Measurement of Absorption Spectra. Absorption spectra of Eu(III) complexes were measured using a spectrophotometer (V-670, JASCO) in ethyl acetate at a concentration of $1 \times 10^{-5}$ mol/L. Measurements were performed at intervals of 0.1 nm, the UV/Vis band width was set to 2.0 nm, and a scanning rate of 100 nm/min was used.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04826.

Details of DFT calculations. Absorption spectra obtained by TDDFT calculation. Calculation of $\lambda$, $\Delta G$, and the prefactor of the ET rate. Norm of the effective dipole moment of the ligand field. Brief descriptions and synthetic scheme of the ligand and complexes (PDF)

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**Notes**

The authors declare no competing financial interest.

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