Development and Photoluminescence Properties of Dinuclear Eu(III)-β-Diketonates with a Branched Tetraphosphine Tetraoxide Ligand for Potential Use in LEDs as Red Phosphors

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SUMMARY In the field of micro-LED displays consisting of UV or Blue-LED arrays and phosphors, where the chips used are very small, particle size of phosphors must be small to suppress variation in hue for each pixel. Especially, there is a strong demand for a red phosphor with small particle sizes. However, quantum yields of inorganic phosphors decrease as particle size of phosphors gets smaller. On the other hand, in the case of organic phosphors and complexes, quantum yields don’t decrease when particle size gets smaller because each molecule has a function of absorbing and emitting light. We focus on Eu(III) complexes as candidates of red phosphors for micro-LED displays because their color purities of photoluminescence spectra are high, and have been tried to enhance photoluminescence intensity by coordinating non-ionic ligand, specifically, newly designed phosphine oxide ligands. Non-ionic ligands have generally less influential on properties of complexes compared with ionic ligands, but have a high degree of flexibility in molecular design. We found novel molecular design concept of phosphine oxide ligands to enhance photoluminescence properties of Eu(III) complexes. This time, novel dinuclear Eu(III)-β-diketonates with a branched tetraphosphine tetraoxide ligand, TDPBPO and TDPPO, were developed. They are designed to have two different phosphine oxide portions; one has aromatic substituents and the other has no aromatic substituent. TDPBPO and TDPPO ligands have functions of increasing absolute quantum yields of Eu(III)-β-diketonates. Eu(III)-β-diketonates with branched tetraphosphine tetraoxide ligands have sharp red emissions and excellent quantum yields, and are promising candidates for micro LED displays, security media, and sensing for their pure and strong photoluminescence intensity.

key words: red photoluminescence material, Eu(III)-β-diketonate, photoluminescence property, branched tetraphosphine tetraoxide ligand

1. Introduction

For display use, phosphors with large photoluminescence intensity and high color purity are required. In addition to this, in the field of micro-LED displays consisting of UV or Blue–LED arrays and phosphors, where the chips used are very small, particle size of phosphors must be small to suppress variation in hues for each pixel. There is a strong demand for a red phosphor that satisfies these conditions. In the case of inorganic phosphors, quantum yields decrease as particles size of phosphors gets smaller because they exist as fine particles in a polymer. In addition, half widths of emission spectra of inorganic phosphors are large and color purity is low.

On the other hand, in the case of organic phosphors and complexes, each molecule absorbs and emits light. Small particle size has no disadvantage in obtaining strong emission intensity. Moreover, they can be dissolved in a polymer, namely, dispersed in a polymer molecularly. We focus on Eu(III) complexes as red phosphors for display use because they have pure red color emission in addition to the above properties.

Eu(III) complexes with strong luminescence can be used in emission devices, security media, sensors, and many other applications and they are attracting much attention [1]–[8]. Ligands of Eu(III) complexes can be roughly classified as ionic or non-ionic. 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 of Eu(III) (ΦET) of Eu(III) complexes and molecular structures of β-diketonates for enhancing emission intensity reported [9], [10]. However, required photoluminescence intensity of Eu(III) complexes were not obtained only by designing β-diketonates for electronic devices use.

On the other hand, non-ionic ligands have generally less influential on properties of complexes compared with ionic ligands. However, they have a high degree of flexibility in molecular design. Phosphine oxides, which are strong Lewis bases, are promising non-ionic ligands for increasing the photoluminescence intensity of Eu(III) complexes. We found a novel molecular design concept of phosphine oxide ligands to enhance photoluminescence properties of Eu(III) complexes and reported following results.

Coordination of two different phosphine oxide structures with one Eu(III) ion together with β-diketonates is effective for increasing photoluminescence intensity and solubility [11]–[16]. Next, we found that asymmetric diphosphine dioxide ligands consisting of two different phosphine oxides connected via a methylene unit further increase absolute quantum yields and photoluminescence intensity to suppress ligand exchange [17]–[21] (Fig. 1).

Detailed investigation of the molecular structures of diphosphine dioxide ligands and the properties of Eu(III)
complexes were performed. The number of methylene unit between $P = O$ groups in a diphosphine dioxide ligand “n”, which restricts the relative positions of nearest oxygen atoms around the Eu(III) ion, influences the shape of the $^5D_0 \rightarrow ^7F_2$ transition [22]. Stark splitting is considered to be influenced by “n”. Introducing CF$_3$ groups into aromatic groups in diphosphine dioxides effectively enhances the solubility [22], [23]. Thiethyl substituted diphosphine dioxide ligand suppresses the concentration quenching of Eu(III) complexes [24]. Bulky alkyl groups in diphosphine dioxide ligand increase the half widths of the $^5D_0 \rightarrow ^7F_2$ transition of Eu(III) complexes [25]. The mutual positions of the nearest oxygen atoms around the Eu(III) ion can be strained by bulky substituents, and $\Phi_{CT}$ are enhanced.

Dinuclear Eu(III) complexes with 1,5,9,13-tetraphosphaneclohexadecane-1,5,9,13-tetraphenyl-1,5,9,13-tetraoxide (TPTO) ligand were developed [26]. The TPTO ligand plays the role of a “separator” of Eu(III) ions that prevents concentration quenching. However, these dinuclear Eu(III) complexes have molecular structures with two different phosphine oxides coordinating to one Eu(III) ion. It is expected that quantum yields of Eu(III) complexes increase much more when dinuclear Eu(III) complexes have molecular structures with two different phosphine oxides coordinating to one Eu(III) ion.

Many important results of phosphine oxide ligands for increasing luminescence intensity of Eu(III) complexes were reported and phosphine oxide ligands attracting much attention [27]–[29].

In this paper, we show the newly designed dinuclear Eu(III) complexes with a branched tetraphosphine tetraoxide and their properties.

2. Experimental Section

2.1 Synthesis of Tris(4-diphenylphosphinylbutyl) phosphine Oxide (TDPPPO)

Magnesium turnings (3.3 g, 0.136 mol) were put into a flask and suspended in THF (5.0 g) under N$_2$ atmosphere. To this was added ca. one thirtieth of a solution of 4-bromo-1-butene (18.0 g, 0.133 mol) in THF (50.0 g), and the mixture was heated at 65°C while being stirred to start the reaction. After that, the rest of the solution was added dropwise to the reaction mixture for 1 hour keeping the reaction temperature between 65°C and 70°C, and the reaction mixture was refluxed for 3 hours to make the Grignard reagent. Phosphorus oxychloride (6.4 g, 0.042 mol) were dissolved in THF (25.0 g) in another flask under N$_2$ atmosphere, and the solution was cooled to 5°C. To this was added the Grignard reagent for 1 hour keeping the reaction temperature between 5°C and 25°C, and the reaction mixture was stirred at 25°C for 2 hours. 90.4 g of water and 0.4 g of sulfuric acid were put into another flask and the coupling reaction mixture was added dropwise to this acidic solution, and the mixture was heated to 90°C to evaporate THF. To this was added Toluene (100 g) to extract reaction products. The organic layer was separated, washed with aqueous NaHCO$_3$, dried with MgSO$_4$, and concentrated in vacuo. Kugelrohr distillation (170-180°C/267 Pa) of crude products gave 6.7 g of tris(3-butenyl)phosphine oxide as a colorless liquid with a yield of 75%. Tris(3-butenyl) phosphine oxide (1.83 g, 8.62 mmol), diphenylphosphine oxide (5.23 g, 25.9 mmol), and 2,2'-azobis(isobutyronitrile) (0.71 g, 4.3 mmol) were dissolved in 20 g of toluene in a flask under N$_2$ atmosphere, and the mixture was heated at 75°C for 24 hours. After heating, the reaction mixture was concentrated in vacuo, the crude products were purified by silica gel column chromatography (15-50% of MeOH in MTBE) to give 3.64 g (4.45 mmol) of Tris(4-diphenylphosphinylbutyl)phosphine oxide (TDPPPO) as a white solid with a yield of 52%.

$^3$H NMR (600 MHz, CDCl$_3$, TMS) $\delta_H$ 7.78-7.68 (m, 12H), 7.50-7.40 (m, 18H), 2.30-2.20 (m, 6H), 1.73-1.50 (m, 18H); $^31$P NMR (162 MHz, CDCl$_3$, phosphoric acid) $\delta_P$ 47.66, 32.52; HRMS (ESI, m/z, [M + Na]$^+$) Calcd for C$_{18}$H$_{34}$NaO$_3$P$_4$ 841.287, Found 841.287 (error 0.0 ppm); IR (KBr, cm$^{-1}$) ($\nu$ = O) 1181, 1121.

2.2 Synthesis of Tris(5-diphenylphosphinylpentyl) phosphine Oxide (TDPPPO)

Tris(5-diphenylphosphinylpentyl)phosphine oxide (TDPPPO) was obtained as a white solid with a yield of 75% in the similar way as TDPPBO.

$^1$H NMR (600 MHz, CDCl$_3$, TMS) $\delta_H$ 7.75-7.65 (m, 12H), 7.52-7.40 (m, 18H), 2.28-2.18 (m, 6H), 1.75-1.40 (m, 24H); $^31$P NMR (162 MHz, CDCl$_3$, phosphoric acid) $\delta_P$ 48.42, 32.98; HRMS (ESI, m/z, [M + Na]$^+$) Calcd for C$_{32}$H$_{40}$NaO$_3$P$_4$ 883.334, Found 883.336 (error 2.2 ppm); IR (KBr, cm$^{-1}$) ($\nu$ = O) 1179, 1121.

2.3 Synthesis of Tris(4,4,5,5,6,6,6-heptafluoro-1-(2-naphthyl)-1,3-hexanedionato) Europtium(III) (Eu(III) (hfnh)$_3$)4

2-Acetylnaphthalene (25.0 g, 0.147 mol) and methyl heptafluorobutyrate (40.0 g, 0.175 mol) were dissolved in 110 g of diethyl ether under N$_2$ atmosphere. Sodium methoxide (9.9 g, 0.18 mol) was added to the solution and stirred at room temperature. After stirring for 9 hours 2nd addition of sodium methoxide (6.0 g, 0.11 mol) was done and stirred for the total of 40 hours. 30 g of water and 50 ml of 6 mol/L of HCl were put into another flask and the reaction mixture was added into the acidic water and stirred for 15 minutes.
Organic layer was separated, dried with MgSO₄ and concentrated in vacuo. Crude products were purified by silica gel column chromatography (10% ethylacetate in hexane) to give 42.2 g of 4,4,5,5,6,6,6-heptafluoro-1-(2-naphthyl)-1,3-hexanediol as a white solid with a yield of 78%.

1H-NMR (600 MHz, CDCl₃, TMS) δH 8.54 (s, IH), 7.99 (d, J = 8.1 Hz, IH), 7.95 (s, 2H), 7.91 (d, J = 8.1 Hz), 7.65 (dd, J = 7.3, 7.3 Hz, IH), 7.61 (dd, J = 7.3, 7.3 Hz, IH); IR (KBr, cm⁻¹) 3064, 1602, 1589, 1348, 1271, 1230, 1195, 1126; MS(EI) m/z = 366 (M).

4,4,5,5,6,6,6-heptafluoro-1-(2-naphthyl)-1,3-hexanediol (25.7 g, 0.070 mol) was dissolved in 150 g of methanol. 4 mol/L of NaOH aqueous solution (17.6 g, 0.070 mol) was added dropwise to the solution and stirred for 2 hours. Europium nitrate pentahydrate (10.0 g, 0.023 mol) was dissolved in 40 g of methanol in another flask and a few drops of NaOH aqueous solution was added into it to adjust pH ca. 6. After that the above reaction solution of sodium 4,4,5,5,6,6,6-heptafluoro-1-(2-naphthyl)-1,3-hexanediol was added dropwise in the europium nitrate solution over 15 minutes and stirred at ambient temperature for 1 hour. The reaction mixture was added dropwise over 1 hour into 3000 g of water and stirred for 3 hours. Resulting precipitate was filtered, and washed with distilled water several times. The wet precipitate was dried under reduced pressure to give 42.2 g of 4,4,5,5,6,6,6-heptafluoro-1-(2-naphthyl)-1,3-hexanedionato europium(III) (Eu(III)(hfnh)₆) as a white solid with a yield of 91%. IR (KBr, cm⁻¹) 3060, 1610, 1593, 1569, 1525, 1458, 1344, 1284, 1234, 1199, 1182, 1114.

2.4 Synthesis of Bis[tris(4,4,5,5,6,6,6-heptafluoro-1-(2-naphthyl)-1,3-hexanediolato) europium(III)] [Tris(4-diphenylphosphinylbutyl) phosphine Oxide] Di Europium(III) (Eu(III)₂(hfnh)₆(TDPBPO) 1)

Tris(4-diphenylphosphinylbutyl)phosphine oxide (0.41 g, 0.50 mmol) and tris(4,4,5,5,6,6,6-heptafluoro-1-(2-naphthyl)-1,3-hexanediolato) europium(III) (Eu(III)(hfnh)₃) (1.25 g, 1.00 mmol) were dissolved in 30 g of chloroform under N₂ atmosphere, and the mixture was stirred and refluxed for 4 hours. After cooled down to 30°C while stirring, the reaction mixture was concentrated under reduced pressure by evaporator and dried under reduced pressure with a vacuum pump. 1.65 g of pale yellow solid was obtained with a yield of 99%.


2.5 Synthesis of Bis[tris(4,4,5,5,6,6,6-heptafluoro-1-(2-naphthyl)-1,3-hexanediolato)][Tris(5-diphenylphosphinylpentyl)phosphine Oxide] Di Europium(III) (Eu(III)₂(hfnh)₆(TDPBPO) 2)

Eu(III)₂(hfnh)₆(TDPBPO) 2 was synthesized in the similar way as Eu(III)₂(hfnh)₆(TDPBPO) 1. Pale yellow solid was obtained with a yield of 99%.


HRMS (ESI, m/z, [M + Na]+) Calcd for C₁₄₇H₁₀₈Eu₂F₄₂NaO₁₆P₄: 3379.424. Found 3379.457 (error 9.88 ppm). IR (KBr, cm⁻¹) (P = O) 1179 and 1121 of free TDPBPO vanished. 31P NMR (162 MHz; CDCl₃; phosphoric acid, δp) −62.7 (brs), −43.3 (brs). 31P NMR (162 MHz; CDCl₃; phosphoric acid, δp) 48.42 and 32.98 of free TDPBPO vanished.

2.6 Synthesis of Bis[tris(4,4,5,5,6,6,6-heptafluoro-1-(2-naphthyl)-1,3-hexanediolato)] 1,5,9,13-Tetrathalophosphyclohexadecane-1,5,9,13-Tetraphenyl-1,5,9,13-Tetraoxide Di Europium(III) (Eu(III)₂(hfnh)₆(TPTO))

Eu(III)₂(hfnh)₆(TPTO) was synthesized according to the reference 26.

2.7 Measurement of Photoluminescence and Excitation Spectra

Each Eu(III) complex was dissolved in ethyl acetate at a concentration of 1 x 10⁻⁴ mol/L at room temperature. Photoluminescence and excitation spectra were measured at room temperature using a spectrofluorometer (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 nm and 0.6 nm for measurement of excitation spectra, respectively. 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.

2.8 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 maximum wavelength to calculate the emission lifetimes. χ² values were in
the range of $> 1.0$ and $< 1.2$.

2.9 Measurement of Absolute Quantum Yields

Total absolute quantum yields ($\Phi_{\text{TOT}}$) 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 K.K. For solid-state measurements, powder Eu(III) complex was put into a quartz cell. An integrating sphere was used in all measurements.

2.10 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.

3. Results and Discussion

3.1 A Molecular Design Concept of Branched Tetraphosphine Tetraoxide Ligands

Dinuclear Eu(III) complexes with macrocyclic TPTO ligand (1,5,9,13-tetraphosphacyclohexadecane-1,5,9,13-tetraphenyl-1,5,9,13-tetraoxide) keep relatively high quantum yields even at the large concentration in a solvent [26] (Fig. 2).

TPTO ligand has a function of “separator among Eu(III) ions” which prevents concentration quenching caused by keeping distance among Eu(III) ions. However, in dinuclear Eu(III) complexes with macrocyclic TPTO ligand, two same phosphine oxides coordinate to one Eu(III) ion because four phosphine oxide structures of macrocyclic TPTO ligand are the same. And two Eu(III) ions in a dinuclear complex are located on the similar coordination environment. Quantum yields of Eu(III) complexes are restricted by these characteristic molecular structures of a macrocyclic TPTO ligand. On the other hand, we have also reported that asymmetric diphosphine dioxide ligands enhance quantum yields of Eu(III) complexes.

We now propose the novel branched tetraphosphine tetraoxide ligands, TDPBPO and TDPPPO which form dinuclear Eu(III) complexes. They are based on the following two concepts. One is separating two Eu(III) ions as well as the macrocyclic TPTO ligand, and the other is coordinating of two different phosphine oxides to one Eu(III) ion as well as the asymmetric diphosphine dioxide ligands (Fig. 3).

Phosphine oxide structures in the center of TDPBPO and TDPPPO are aliphatic substituted ones “Phosphine Oxide I” and other phosphine oxides are both aromatic and aliphatic substituted ones “Phosphine Oxide II”. When TDPBPO or TDPPPO coordinate to Eu(III) ions, dinuclear Eu(III) complexes with different types of phosphine oxides are generated. Moreover, two Eu(III) ions in a dinuclear complex are located on the different coordination environment because one has “Phosphine Oxide I” and “Phosphine Oxide II”, and the other has two “Phosphine Oxide II” (Fig. 4).

Molecular structures of dinuclear Eu(III) complexes are shown in Fig. 5.

3.2 Identification and Purity of Branched Tetraphosphine Tetraoxide Ligands and Eu(III) Complexes

The results from $^1$H NMR and $^{31}$P NMR analyses of
tetraphosphine tetraoxide ligands, TDPBPO and TDPPPO, conform well to the expected molecular structures. The parent peaks of TDPBPO and TDPPPO were detected by HRMS analyses in the error of 0.0 ppm and 2.2 ppm, respectively. From these results, the authors concluded that molecular structure of TDPBPO and TDPPPO matched those shown in Fig. 5 and that they had high purity.

The results from elemental analyses (C and H) and ICP-AES (Eu and P) of Eu(III) complexes 1 and 2 are within acceptable error ranges (within 0.5% of theoretical values). The parent peaks of Eu(III) complexes 1 and 2 were detected by HRMS analyses in the error of 4.2 ppm and 9.8 ppm, respectively. The P = O stretching vibrations in IR spectra and the P = O signals in 31P NMR spectra of free phosphine oxide ligand TDPBPO and TDPPPO vanished. These results indicate that tetraphosphine tetraoxide compounds coordinated to a Eu(III) ion. 31P NMR spectra of coordinating phosphine oxide often broaden or vanish [30]. From these results, the authors concluded that molecular structure of novel Eu(III) complexes 1 and 2 matched those shown in Fig. 5 with high purity.

3.3 Investigation of Photoluminescence Properties of Eu(III) Complexes in Solution State

Figure 6 (a) shows the photoluminescence spectra of Eu(III) complexes 1–4 in ethyl acetate at a concentration of 1 × 10^{-3} mol/L excited at the maximum excitation wavelength of each complex (1: 393 nm, 2: 393 nm, 3: 392 nm, 4: 392 nm). (b) Excitation spectrum of each Eu(III) complex in ethyl acetate (1 × 10^{-3} mol/L) measured at the peak top of 5D0 → 7F2 transition of each emission spectrum (1: 614 nm, 2: 614 nm, 3: 613 nm, 4: 612 nm).

![Fig. 6](image)

Photoluminescence intensities of Eu(III)-β-dekentonates up to six times. This is larger than the ability of coordinating two different phosphine oxides with Eu(III)-β-diketonates, that is, up to four times [13].

Half width of Eu(III)2(hfnh)6(TPTO) 3 is almost the same as that of Eu(III)(hfnh)4 4. These results suggest that macrocyclic TPTO ligand whose four phosphine oxide structures are the same has little effects on half width.

Figure 6 (b) shows excitation spectra of europium complexes 1–4 in ethyl acetate at a concentration of 1 × 10^{-3} mol/L. The values of spectrum intensity are in the same order as the results of emission spectra. The maximum wavelengths of complexes 1 and 2 are slightly longer than those of complexes 3 and 4 (1: 393 nm, 2: 393 nm, 3: 392 nm, 4: 392 nm). The difference of maximum wavelengths can be due to the difference in coordination structure of europium complexes.

The asymmetric ratio (ratio R) is defined as the relative photoluminescence intensity of the electric dipole transition 5D0 → 7F2 to the magnetic dipole transition 5D0 → 7F1 (I(5D0 → 7F2)/I(5D0 → 7F1)). Ratio R indicates how close the local Eu(III) environment is to being centrosymmetric [31]. Ratio Rs of Eu(III) complexes 1 and 2 (1: 21.8, 2: 21.6) are larger than those of complexes 3 and 4 (3: 19.1, 4: 19.3) as shown in Table 1 indicating that local Eu(III) environment of complexes 1 and 2 are far from centrosymmetric.
Table 1  Photoluminescence properties of Eu(III) complexes in solution state.

<table>
<thead>
<tr>
<th>Eu(III) complex</th>
<th>$\tau_{\text{exp}}$ (ms)$^a$</th>
<th>$\tau_{\text{rad}}$ (ms)$^b$</th>
<th>$\Phi_{\text{ET}}$ $^e$</th>
<th>$\Phi_{\text{Ln}}$ $^a$</th>
<th>$\Phi_{\text{TOT}}$ $^e$</th>
<th>$R'$</th>
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<td>0.67</td>
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<td>0.66</td>
<td>0.88</td>
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<td>1.04</td>
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<td>0.86</td>
<td>0.57</td>
<td>21.6</td>
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<td>3</td>
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<td>1.16</td>
<td>0.58</td>
<td>0.78</td>
<td>0.45</td>
<td>19.1</td>
</tr>
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<td>0.22</td>
<td>1</td>
<td>0.23</td>
<td>19.3</td>
</tr>
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</table>

$^a$ Lifetimes measured in ethyl acetate at a concentration of $1 \times 10^{-3}$ mol/L.

$^b$ Radiative lifetimes calculated as $\tau_{\text{rad}} = 1/n^3 \text{AMD},0 \times I_{\text{MD}}/I_{\text{TOT}}$. $n = 1.372$.

$^c$ Intrinsic quantum yields calculated as $\Phi_{\text{Ln}} = \tau_{\text{exp}}/\tau_{\text{rad}}$.

$^d$ Energy transfer efficiency between the ligand and Eu(III).

$^e$ Total absolute quantum yield measured in ethyl acetate excited at the maximum excitation wavelength of each complex (1: 393 nm, 2: 393 nm, 3: 392 nm, 4: 392 nm).

$^f$ Ratio R: Asymmetric ratio calculated from the formula $J(5D_0 \rightarrow 7F_2)/J(5D_0 \rightarrow 7F_1)$ (in ethyl acetate, $1 \times 10^{-3}$ mol/L).

To elucidate the mechanism in more depth, we performed further analyses as described below. $\Phi_{\text{TOT}}$ is the product of energy transfer efficiency between the ligand and the lanthanide ($\Phi_{\text{ET}}$) and the intrinsic photoluminescence quantum yield of the lanthanide ($\Phi_{\text{Ln}}$):

$$\Phi_{\text{TOT}} = \Phi_{\text{ET}} \cdot \Phi_{\text{Ln}}$$ (1)

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

$$\Phi_{\text{Ln}} = \tau_{\text{exp}}/\tau_{\text{rad}}$$ (2)

where $\tau_{\text{rad}}$ is obtained as follows [32], [33].

$$\tau_{\text{rad}} = 1/n^3 \text{AMD},0 \times I_{\text{MD}}/I_{\text{TOT}}$$ (3)

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

Table 1 also shows the measured lifetime ($\tau_{\text{exp}}$), radiative lifetime ($\tau_{\text{rad}}$), the intrinsic quantum yield ($\Phi_{\text{Ln}}$), the energy transfer efficiency between the ligand and the lanthanide ($\Phi_{\text{ET}}$), and the total photoluminescence quantum yield ($\Phi_{\text{TOT}}$) of Eu(III) complexes in ethyl acetate at a concentration of $1 \times 10^{-3}$ mol/L.

$\tau_{\text{exp}}$ of 6-coordinate Eu(III)-$\beta$-diketonate 4 is enlarged by the coordination of each phosphine oxide ligands TDPBPO, TDPPPO, and TPTO. There is little difference between $\tau_{\text{exp}}$ of 1–3. On the other hand, $\tau_{\text{rad}}$ of complexes 1 and 2 are notably smaller than that of complex 3 followed by larger $\Phi_{\text{Ln}}$ of complexes 1 and 2. $\Phi_{\text{ET}}$ of complexes 1 and 2 are also larger than that of complex 3. From these results, it can be said that the coordination of different phosphine oxides as in the case of coordinating TDPBPO or TDPPPO ligands induce the asymmetry of the ligand fields that enlarge both $\Phi_{\text{Ln}}$ and $\Phi_{\text{ET}}$. Consequently, $\Phi_{\text{TOT}}$ of complexes 1 and 2 are larger than that of complex 3.

The comparison of Eu(III) complexes in solution and solid states will reveal the functions of TDPBPO and TDPPPO ligands. In solid states, there are no energy diffusion by solvent molecules. However, concentration quenching will occur. TDPBPO and TDPPPO ligands can suppress concentration quenching by keeping distance among Eu(III) ions. In solution state, attenuation rate of photoluminescence intensity by concentration quenching will smaller than that in solid state. However, there are energy diffusion by solvent molecules. Ligands will have strong shielding effects from solvent molecules. To elucidate these phenomena is our next studies.

3.4 Absorption Spectra of Eu(III) Complexes

Absorption spectra of Eu(III) complexes are shown in Fig. 7. Absorbance in ethyl acetate at the concentration of $1 \times 10^{-5}$ mol/L are almost the same among complexes 1–3.

Absorption spectra mainly depend on molecular structures of $\beta$-diketonates and stronger photoluminescence intensity of complexes 1 and 2 attributed to the larger quantum yields.

The maximum wavelength in excitation spectra shown in Fig. 6 (b) are much longer than the maximum absorption wavelength shown in Fig. 7. The maximum wavelength in Fig. 6 (b) and Fig. 7 were measured at the concentration of $1 \times 10^{-3}$ mol/L and $1 \times 10^{-5}$ mol/L, respectively.

As the concentrations of Eu(III) complexes increase, the intermolecular interaction among complex molecules become stronger and HOMO-LUMO gap becomes smaller. Consequently, maximum wavelength of Fig. 6 (b) is longer than that in Fig. 7.

4. Conclusions

Novel branched tetraphosphine tetraoxide ligands, TDPBPO
and TDPPPO for Eu(III) complexes were developed. They are designed to have two different phosphine oxide portions; one has aromatic substituents and the other has no aromatic substituent. We conclude that TDPPPO and TDPPPO ligands have functions of increasing absolute quantum yields of Eu(III)-β-diketonates. Eu(III)-β-diketonates with branched tetrabiphenyl-tetraoxide ligands 1 and 2 are promising candidates for micro LED displays, security media, and sensing.

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References


IWANAGA et al.: NOVEL DINUCLEAR EU(III)-DIKETONATES FOR POTENTIAL USE IN LEDS AS RED PHOSPHORS


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