# 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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# ABSTRACT

Novel dinuclear Eu(III)- $\beta$ -diketonates with a branched tetraphosphine tetraoxide ligand, TDPBPO and TDPPPO, were developed. They have sharp red emissions and excellent quantum yields, and are promising candidates for LED devices, security media, and sensing for their pure and bright photoluminescence.

### 1 Introduction

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. Ligands of Eu(III) complexes can be roughly classified as ionic or non-ionic. Ionic ligands such as  $\beta$ diketonates neutralize the charge of the Eu(III) ion. Substituents of  $\beta$ -diketonates greatly increase the intramolecular energy transfer efficiencies from the lowest triplet state of the ligands to the <sup>5</sup>D<sub>1</sub> level of the of Eu(III) ( $\Phi_{\text{ET}}$ ) of Eu(III) complexes [1]. Phosphine oxides, which are strong Lewis bases, are known to be effective nonionic ligands for increasing the photoluminescence intensity of Eu(III) complexes.

We have previously reported that the coordination of two different phosphine oxide structures with one Eu(III) ion together with  $\beta$ -diketonates is effective for increasing absolute quantum yields ( $\Phi_{TOT}$ ) and photoluminescence intensity [2-4].

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 [5,6]. Next, detailed investigation of the molecular structures of diphosphine dioxide ligands and the properties of Eu(III) complexes was 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  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition [7]. Stark splitting is considered to be influenced by "n". Introducing CF<sub>3</sub> groups into aromatic groups in diphosphine dioxides effectively enhances the

solubility [8,9]. Thienyl substituted diphosphine dioxide ligand suppresses the concentration quenching of Eu(III) complexes [9]. Bulky alkyl groups in diphosphine dioxide ligand increase the half widths of the  ${}^5D_0 \rightarrow {}^7F_2$  transition of Eu(III) complexes [10]. The mutual positions of the nearest oxygen atoms around the Eu(III) ion can be strained by bulky substituents, and  $\Phi_{\text{ET}}$  are enhanced.

Eu(III) complexes with Dinuclear 1,5,9,13tetraphosphacyclohexadecane-1,5,9,13-tetraphenyl-1,5,9,13-tetraoxide (TPTO) ligand were developed [11] The TPTO ligand plays the role of a "separator" of Eu(III) ions that prevents concentration quenching. However, these dinuclear Eu(III) complexes do not have the molecular structure with two different phosphine oxides coordinating to one Eu(III) ion. It is expected that guantum yields of Eu(III) complexes increase much more when dinuclear Eu(III) complexes have molecular structure with two different phosphine oxides coordinating to one Eu(III) ion.

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

#### 2. Experiment

# 2.1. Measurement of Photoluminescence and Excitation Spectra.

Each Eu(III) complex was dissolved in ethyl acetate at a concentration of  $1 \times 10^{-3}$  mol/L at room temperature. Photoluminescence and excitation spectra were measured at room temperature using а 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, 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.

# 2.2. 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.  $\chi^2$  values were in the range of > 1.0 and < 1.2.

### 2.3. Measurement of Absolute Quantum Yields

Total absolute quantum yields ( $\Phi_{TOT}$ ) 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 1×10<sup>-3</sup> mol/L using a PMA-12 C10027-01, Hamamatsu Photonics K.K.

# 2.4. 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-1,5,9,13tetraphenyl-1,5,9,13-tetraoxide) keep relatively high quantum yields even at the large concentration in a solvent [11]. 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 (Figure 1). 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 (Figure 2) because one has "Phosphine Oxide I" and "Phosphine Oxide II", and the other has two "Phosphine Oxide II".



Figure 1. Molecular structures of branched tetraphosphine tetraoxide ligands for Eu(III) complexes.

The molecular structure of novel Eu(III) complexes **1** and **2** with TDPBPO or TDPPPO ligand are shown in Figure 2.



Figure 2. Molecular structures of dinuclear Eu(III)- $\beta$ diketonates 1 and 2 with branched tetraphosphine tetraoxide ligands, and 3 with macrocyclic tetraphosphine tetraoxide ligand.

# 3.2. Investigation of Photoluminescence Properties of Eu(III) Complexes in Solution State.

Figure 3 (a) shows the photoluminescence spectra of Eu(III)<sub>2</sub>(hfnh)<sub>6</sub>(TDPBPO) **1**, Eu(III)<sub>2</sub>(hfnh)<sub>6</sub>(TDPPPO) **2**, Eu(III)<sub>2</sub>(hfnh)<sub>6</sub>(TPTO) **3**, and Eu(III)(hfnh)<sub>3</sub> **4** in ethyl acetate at a concentration of  $1 \times 10^{-3}$  mol/L. Photoluminescence intensity of Eu(III) complexes **1** and **2** are larger than those of complexes **3** and **4** and half widths of  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition of complexes **1** and **2** are also larger than those of complexes **3** and **4**. These results indicate that branched tetraphosphine tetraoxide ligands, TDPBPO and TDPPPO, have a function of symmetry reduction of ligand field and enlarge photoluminescence intensity.



Figure 3. (a) Photoluminescence spectra of Eu(III) complexes 1~4 in ethyl acetate at a concentration of 1 × 10<sup>-3</sup> mol/L measured at intervals of 1 nm. Excitation and emission slit widths were set to 0.5 nm. Scanning rate of 600nm/min. was set. They are 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<sup>-3</sup> mol/L) measured at intervals of 1 nm. Excitation and emission slit widths were set to 0.7 nm and 0.6 nm, respectively. Scanning rate of 600 nm/min. was set. They are measured at the peak top of  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition of each emission spectrum (1: 614 nm, 2: 614 nm, 3: 613 nm, 4: 612 nm).

On the other hand, half width of  $Eu(III)_2(hfnh)_6(TPTO)$  **3** is almost the same as that of  $Eu(III)(hfnh)_3$  **4**. These results suggest that macrocyclic TPTO ligand whose four phosphine oxide structures are the same has little effects on half width.

Figure 3(b) shows excitation spectra of europium complexes  $1 \sim 4$  in ethyl acetate at a concentration of  $1 \times 10^{-3}$  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  ${}^5D_0 \rightarrow {}^7F_2$  to the magnetic dipole transition  ${}^5D_0 \rightarrow {}^7F_1$  (I( ${}^5D_0 \rightarrow {}^7F_2$ )/I( ${}^5D_0 \rightarrow {}^7F_1$ )). Ratio R indicates how close the local Eu(III) environment is to being centrosymmetric. 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)
Comp	lexe	es in Solution State			

Eu(III) complex	$ au_{exp}$ (ms) <sup>a</sup>	$(ms)^{b}$	$\Phi_{Ln}{}^c$	$\Phi_{\text{ET}}{}^{d}$	$\Phi_{\text{TOT}}^{e}$	$\mathbf{R}^{\mathrm{f}}$			
1	0.67	1.03	0.66	0.88	0.58	21.8			
2	0.68	1.04	0.66	0.86	0.57	21.6			
3	0.68	1.16	0.58	0.78	0.45	19.1			
4	0.25	1.13	0.22	1	0.23	19.3			
a Lifetimes measured in ethyl acetate at a concentration									
of	1	×		10 <sup>-3</sup>	n	nol/L.			

b Radiative lifetimes calculated as 1/n<sup>3</sup>A<sub>MD,0</sub>×I<sub>MD</sub>/I<sub>TOT</sub>. n = 1.372

c Intrinsic quantum yields calculated as  $\Phi_{Ln} = \tau_{exp} / \tau_{rad.}$ d Energy transfer efficiency between the ligand and Eu(III).

τrad

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  $I({}^{5}D_{0} \rightarrow {}^{7}F_{2}) / I({}^{5}D_{0} \rightarrow {}^{7}F_{1})$  (in ethyl acetate, 1×10<sup>-3</sup> mol/L).

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

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

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

$$\Phi_{\rm Ln} = \tau_{\rm exp} / \tau_{\rm rad} \tag{2}$$

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

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

where,  $A_{MD,0}$  is the spontaneous emission probability for the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition in vacuo (14.65 s<sup>-1</sup>),  $I_{MD}/I_{TOT}$ is the ratio between the integrated intensity of the  ${}^{5}D_{0} \rightarrow$  ${}^{7}F_{1}$  transition ( $I_{MD}$ ) and the total integrated emission intensity  ${}^{5}D_{0} \rightarrow {}^{7}F_{j}$  (J = 0–6) ( $I_{TOT}$ ), and n is the refractive index of the medium (in ethyl acetate: n = 1.372. Table 1 also shows the measured lifetime ( $\tau_{exp}$ ), the radiative lifetime ( $\tau_{rad}$ ), the intrinsic quantum yield ( $\Phi_{Ln}$ ), the energy transfer efficiency between the ligand and the lanthanide ( $\Phi_{ET}$ ), and the total photoluminescence quantum yield ( $\Phi_{TOT}$ ) of Eu(III) complexes in ethyl acetate at a concentration of 1×10<sup>-3</sup> mol/L.

 $τ_{exp}$  of 6-coordinate Eu(III)-β-diketonate **4** (0.25 ms) is enlarged by the coordination of each phosphine oxide ligands TDPBPO, TDPPPO, and TPTO (**1** (TDPBPO): 0.67 ms, **2** (TDPPPO): 0.68 ms, **3** (TPTO): 0.68 ms). There is little difference between  $τ_{exp}$  of **1~3**. On the other hand,  $τ_{rad}$  of complexes **1** and **2** are notably smaller than that of complex **3** followed by larger Φ<sub>Ln</sub> of complexes **1** and **2** (**1**: 0.66, **2**: 0.66, **3**: 0.58). Φ<sub>ET</sub> of complexes **1** and **2** (**1**: 0.88, **2**: 0.86) are also larger than that of complex **3** (0.78). From these results, it can be said that the coordinating TDPBPO or TDPPPO ligands induce the asymmetry of the ligand fields that enlarge both Φ<sub>Ln</sub> and Φ<sub>ET</sub>. Consequently, Φ<sub>TOT</sub> of complexes **1** and **2** are larger than that of complex **3** (**1**: 0.58, **2**: 0.57, **3**: 0.45).

**3.3.** Absorption Spectra of Eu(III) Complexes Absorption spectra of Eu(III) complexes are shown in Figure 4.



Figure 4. Absorption spectra of eight- fold Eu(III) complexes 1~3.

Absorbance in ethyl acetate at the concentration of  $1 \times 10^{-3}$  mol/L are almost the same among complexes  $1 \sim 3$ . 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.

#### 4. Conclusion

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 TDPBPO and TDPPPO ligands have functions of increasing absolute quantum yields of Eu(III)- $\beta$ -diketonates. Eu(III)- $\beta$ -diketonates **1** and **2** with branched tetraphosphine tetraoxide ligands are promising

candidates for future emission devices, security media, and sensing.

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