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Photosensitized luminescence of highly thermostable mononuclear Eu (III) complexes with π -expanded β -diketonate ligands

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Abstract

Thermostable mononuclear Eu(III) complexes with a π -expanded system, [Eu(btfa)₃(DPEPO)] and [Eu(ntfa)₃ (DPEPO)] (DPEPO: bis[2-(diphenylphosphino)phenyl] ether oxide, btfa: benzoyltrifluoroacetonate, ntfa: 3-(2-naphthoyl)-1,1,1-trifluoroacetonate), are reported. Decomposition temperature (dp) of [Eu(btfa)₃(DPEPO)] and that of [Eu(ntfa)₃(DPEPO)] are estimated to be 320°C and 318°C, respectively. These values are higher than that of the previous [Eu(hfa)₃(DPEPO)] (hfa: hexafluoroacetylacetonate, dp = 228°C). The photosensitized emission quantum yield $\Phi_{\pi-\pi^*}$ and photosensitized energy transfer efficiency η_{sens} of [Eu(ntfa)₃(DPEPO)] ($\Phi_{\pi-\pi^*} = 45\%$, $\eta_{sens} = 77\%$) are larger than those of [Eu(btfa)₃(DPEPO)] ($\Phi_{\pi-\pi^*} = 38\%$, $\eta_{sens} = 55\%$). The thermostable Eu(III) complex with a π -expanded system is expected to be useful for fabrication of LED devices.

1. Introduction

Lanthanide complexes have attracted considerable attention due to their highly efficient luminescence for use in lighting, displays and lasers.¹⁻⁵ A lanthanide complex provides highly monochromatic and clear emission with small full width at half maximum (fwhm) of less than 15 nm in the visible region. Photosensitized luminescence of lanthanide complexes with characteristic organic ligands has been reported.⁶⁻¹⁵ Moudam and Miyata reported that Eu(III) and Sm(III) complexes with DPEPO (DPEPO: DPEPO: Bis[2-(diphenylphosphino)phenyl] ether oxide) show strong red luminescence and deep-red luminescence, respectively.^{6, 7} Nakanishi and coworkers reported brilliant green luminescence of nine Tb(III) clusters.⁸ Blue luminescence of Tm(III) metallopolymer with a Pybox (pyridine-bis(oxazoline)) ligand was also observed.⁹ Bünzli summarized the design of highly luminescent lanthanide complexes and discussed all aspects needing optimization.¹⁶ Luminescent lanthanide complexes have been extensively studied in the fields of photophysical, coordination and material chemistry.

For recent lanthanide complexes, monochromatic emission excited by ultraviolet light-emitting diodes (UV-LEDs) has been investigated. Various types of red, green and blue luminescent lanthanide complexes based on UV-LED excitation have been investigated as wavelength conversion materials for fabrication of a white luminescent LED.¹⁷⁻¹⁹ For fabrication of such an LED, a GaN chip should be covered with silicone resin in which a wavelength conversion material is despersed.² Densities of typical silicone resins ($\rho \approx 1.20$ g cm⁻³) are similar to those of lanthanide complexes ($\rho = 1.28-1.69$ g cm⁻³), which show good solubility in organic solvents and polymers, though an inorganic phosphor such as YAG ($\rho \approx 4.8$ g cm⁻³) is not homogeneously dispersed in silicone resins.^{7, 20, 21} From an industrial view point, a lanthanide complex is an ideal wavelength conversion material for LED devices.

A thermostable wavelength convertor such as a lanthanide complex is required for reflow soldering process (260°C) in fabrication of LED devices. We recently reported a luminescent lanthanide coordination polymer with high thermostability.²¹ The use of thermostable lanthanide coordination polymers composed of phosphine oxide and β-diketonate ligands, however, leads to the formation of insoluble compounds in organic media. A thermostable and resin-soluble lanthanide complex with photosensitized luminescence should be useful for fabrication of LED devices. In order to achieve thermostability, we focused on the introduction of π -expanded systems to β-diketonate ligands. Versatility of β-diketonate and its derivatives was reviewed in the recent work.²² Honjo reported that binding constants of lanthanide complexes with benzoylacetonate and β -naphthoylacetonate ligands are larger than that with an acetylacetonate ligand.²³ The β -diketonate ligands with π -expanded systems lead to also increase of boiling points related to the decomposition temperatures (dp) of lanthanide complexes.

In this study, Eu(III) complexes attached with Bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) and β-diketonate containing phenyl and napthyl groups, [Eu(btfa)₃(DPEPO)] (btfa: benzovltrifluoroacetonate) and [Eu(ntfa)₃(DPEPO)] (ntfa: 3-(2-naphthoyl)-1,1,1-trifluoroacetonate)) were prepared (Figure 1). The phosphine oxide ligand DPEPO promotes the formation of an asymmetric coordination geometry of a lanthanide complex related to enhancement of the emission quantum yields and the radiative rate constant $k_{\rm r}$.⁷ The dp values of [Eu(btfa)₃(DPEPO)] and [Eu(ntfa)₃(DPEPO)] are estimated to be 320°C and 318°C, respectively. These values are higher than that of the previous strong luminescent [Eu(hfa)₃(DPEPO)] (hfa: hexafluoro acetylacetonate, dp = 228°C). The photosensitized emission quantum yield $\Phi_{\pi-\pi^*}$ and photosensitized energy transfer efficiency η_{sens} of [Eu(ntfa)₃(DPEPO)] ($\Phi_{\pi-\pi^*} = 45\%$, $\eta_{\text{sens}} =$ 77%) are larger than those of [Eu(btfa)₃(DPEPO)] ($\Phi_{\pi-\pi^*} = 38\%$, $\eta_{\text{sens}} = 55\%$). High thermostability and good luminescence properties of mononuclear Eu(III) complexes with π -expanded systems in β -diketonate ligands are demonstrated.



Figure 1. Chemical structures of a) [Eu(hfa)₃(DPEPO)], b) [Eu(btfa)₃(DPEPO)] and c) [Eu(ntfa)₃(DPEPO)].

2. Experimental

Materials. Bis[2-(diphenylphosphino)phenyl]ether and 1,1,1,5,5,5-Hexafluoro-2,4-pentane dione and 3-(2-naphthoyl) -1,1,1-trifluoroacetone were obtained from Tokyo Chemical Industry Co., Ltd. Europium chloride hexahydrate was purchased from Kanto Chemical Co., Inc. 4,4,4-trifluoro -1-phenyl-1,3-butanedione were obtained from Aldrich Chemical Company Inc. Europium(III) acetate n-hydrate and H_2O_2 aqueous solution (30%), Ammonia aqueous solution (28%) were purchased from Wako Pure Chemical Industries Ltd. All other chemicals and solvents were reagent grade and were used without further purification.

Apparatus. Elemental analyses were performed on a J-Science Lab JM 10 Micro Corder and an Exeter Analytical CE440. ¹H-NMR (400 MHz) spectra were recorded on a JEOL ECS400. Infrared spectra were recorded with a JASCO FTIR-4600 spectrometer. Thermogravimetric Analysis (TGA) was performed by a Seiko Instruments Inc. EXSTAR 6000 TG/DTA 6300.

Preparation of [Eu(hfa)₃(DPEPO)]. DPEPO (bis[2-(diphenylphosphory)phenyl]ether) was prepared by the same method previous report.⁷ Europium acetate n-hydrate (5.0 g, 13 mmol) was dissolved in 60mL of distilled water. A solution of 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione (8.1 g, 39 mmol) was added dropwise to the solution. The reaction mixture produced a precipitation of white yellow powder after stirring for 3 h at room temperature. The reaction mixture was filtered. Reprecipitation from water and methanol gave a white powder.

Prepared DPEPO (1.4 g, 2.8 mmol) and the $[Eu(hfa)_3 (H_2O)_2]$ (2.4 g, 3.0 mmol) was dissolved in 40 ml of methanol. The solution was heated at reflux while stirring for 7 h. The residue was washed with chloroform several times. The insoluble material was removed by filtration, and the filtrate was concentrated. The obtained powder was dissolved in 10 mL of hot methanol solution (50°C), and then permitted to stand at room temperature. Recrystallization from methanol gave colorless block crystals of the title complex.

[Eu(hfa)₃(DPEPO)]: Yield: 2.0g (50%); ¹H NMR (400 MHz, C₃D₆O, 20°C): δ = 8.65 (dd, 4H; Ar), 8.4 (dd, 4H; Ar), 7.9 (t, 2H; Ar), 7.75 (s, 4H; Ar), 7.6 (t, 2H; Ar), 7.4-7.5 (m, 6H; Ar), 7.1 (m, 4H; Ar), 6.85 (m, 2H; Ar), 5.2 ppm (s, 3H; β-diketone-H). IR (KBr): 1655 (st, C=O), 1255 (st, C=F), 1242 (st, P=O) cm⁻¹. Elemental analysis calcd (%) for C₅₁H₃₁EuF₁₈O₉P₂: C, 45.59; H, 2.33. Found: C, 45.61; H, 2.59.

Preparation of [Eu(btfa)₃(DPEPO)]. Europium chloride hexahydrate (2.2 g, 6.0 mmol) was dissolved in distilled 5 mL

of water and 40 mL of methanol. A solution of 4,4,4-Trifluoro-1-phenyl-1,3-butanedione (4.0 g, 19 mmol) was added to the solution. An ammonia solution was added dropwise to the solution until it approximately reached pH 7. After stirring at room temperature for 4 h, the reaction mixture was poured into water. The mixture solution stirred 1day to obtain white precipitate. The precipitate was filtered, washed with hexane several times, and dried in vacuo.

Prepared DPEPO (0.57 g, 1.0 mmol) and the $[Eu(btfa)_3 (H_2O)_2]$ (0.83 g, 1.0 mmol) were dissolved in 30 mL of methanol. The solution was heated at reflux while stirring for 8 h. The reaction mixture was cooled at room temperature. The produced precipitate was filtered, washed with cool methanol and dried in vacuo. The white powder was produced.

[Eu(btfa)₃(DPEPO)]. Yield: 1.1 g (83%); ¹H NMR (400 MHz, C₃D₆O, 20°C): δ = 8.95 (dd, 4H; Ar), 8.45 (dd, 4H; Ar), 7.75 (m, 8H; Ar), 7.55 (s, 4H; Ar), 7.45 (t, 2H; Ar), 7.3 (t, 2H; Ar), 7.05 (s, 4H; Ar), 7.0 (t, 3H; Ar), 6.9 (t, 6H; Ar), 6.85 (d, 6H; Ar), 4.83 ppm (s, 3H; β-diketone-H). IR (KBr): 1616 (st, C=O), 1290 (st, C–F), 1171 (st, P=O) cm⁻¹. Elemental analysis calcd (%) for C₆₆H₄₆EuF₉O₉P₂: C, 57.95; H, 3.39. Found: C, 57.98; H, 3.28.

Preparation of [Eu(ntfa)₃(DPEPO)]. Europium chloride hexahydrate (1.7 g, 4.5 mmol) was dissolved in distilled 5 mL of water and 40 mL of methanol. A solution of 4,4,4-Trifluoro-1-(2-naphthyl)-1,3-butanedione (3.6 g, 13.5 mmol) was added to the solution. An ammonia solution was added dropwise to the solution until it approximately reached pH 7. After stirring at room temperature for 4 h, the reaction mixture was poured into water. The mixture was solution stirred 1 day to obtain brown precipitates. The precipitates were filtered, washed with hexane several times, and dried in vacuo. The cream powder was obtained.

[Eu(ntfa)₃(H₂O)₂]. Yield: 3.4 g (77%); ¹H NMR (400 MHz, CD₃OD, 20°C): δ =7.88-7.82 (m, 3H; Ar), 7.67-7.60 (d, 3H; Ar), 7.52-7.30 (m, 15H; Ar) ppm. IR (KBr): 3648 (st, O-H), 1607 (st, C=O), 1288 (st, C-F) cm⁻¹. Elemental analysis calcd (%) for C₄₂H₂₈EuF₉O₈: C, 51.29; H, 2.87. Found: C, 51.73; H, 2.96.

Prepared DPEPO (0.57 g 1.0 mmol) and $[Eu(ntfa)_3 (H_2O)_2]$ (0.98 g 1.0 mmol) were dissolved in 30 ml methanol. The solution was heated at reflux while stirring for 8 h. The reaction mixture was cooled at room temperature. The produced precipitate was filtered, washed with cool methanol and dried in vacuo. The brown powder was obtained.

[Eu(ntfa)₃(DPEPO)]. Yield: 0.89 g (59%); ¹H NMR (400 MHz, C₃D₆O, 20°C): δ =9.05 (t, 4H; Ar), 8.6 (t, 4H; Ar), 7.8 (m, 3H; Ar), 7.65 (m, 8H; Ar), 7.55 (t, 7H; Ar), 7.32-7.44 (m, 14H; Ar), 7.25 (t, 2H; Ar), 7.1-7.2 (m, 7H; Ar), 5.27 ppm (s, 3H; β-diketone-H). IR (KBr): 1617 (st, C=O), 1294 (st, C–F), 1133 (st, P=O) cm⁻¹. Elemental analysis calcd (%) for C₇₈H₅₂EuF₉O₉P₂: C, 61.71; H, 3.45. Found: C, 61.69; H, 3.34.

Optical Measurements. UV–vis absorption spectra of the Eu(III) complexes were recorded on a JASCO V-670 spectrometer. Those of emission and excitation spectra were measured with a HORIBA Fluorolog-3 spectrofluorometer and corrected for the response of the detector system. The photosensitized emission quantum yields were obtained by using a JASCO F-6300-H spectrometer attached to a JASCO ILF-533 integrating sphere unit ($\varphi = 100$ mm). The wavelength dependence of the detector response and the beam intensity of

Xe light source for each spectrum were calibrated by using a standard light source. Emission lifetimes (τ_{obs}) were measured by using the third harmonics (355 nm) of a Q-switched Nd:YAG laser (Spectra Physics, INDI-50, fwhm = 5 ns, λ = 1064 nm) and a photomultiplier (Hamamatsu Photonics, R5108, response time = 1.1 ns). The Nd:YAG laser response was monitored with a digital oscilloscope (Sony Tektonix, TDS3052, 500 MHz) synchronized to the single-pulse excitation. Emission lifetimes were determined from the slope of logarithmic plots of the decay profiles.

Density Functional Theory Calculations. DFT geometry optimizations and molecular orbital (MO) calculations of simplified clusters were performed with Gaussian 09, revision D.01, employing the B3LYP hybrid functional consisting of the three-parameter Becke exchange functional and the correlation functional of Lee, Yang, and Parr. The 6-31G(d) basis set was used for all atoms.^{24, 25}

3. Results and Discussion

[Eu(btfa)₃(DPEPO)] and [Eu(ntfa)₃(DPEPO)] were prepared by chelation of [Eu(btfa)₃(H₂O)₂] and [Eu(ntfa)₃ (H₂O)₂], respectively, with DPEPO in methanol under reflux. Their identifications were performed using NMR, IR and elemental analyses. Thermogravimetric analysis (TGA) curves of Eu(III) complexes are shown in Figure 2. The dp values of [Eu(hfa)₃(DPEPO)], [Eu(btfa)₃(DPEPO)] and [Eu(ntfa)₃ (DPEPO)] were found to be 228°C, 320°C and 318°C, respectively. The dp values of [Eu(btfa)₃(DPEPO)] and [Eu(ntfa)₃(DPEPO)] with π -expanded systems were higher than that of $[Eu(hfa)_3(DPEPO)]$ without a π -expanded system. Eu(III) complexes with high dp values ($> 300^{\circ}$ C) is suitable for a reflow soldering process (260°C) in fabrication of LED devices. The dp of an Eu(III) complex is dependent on its coordination ability.



Figure 2. Thermogravimetric analysis (TGA) curves of a) [Eu(hfa)₃(DPEPO)], b) [Eu(btfa)₃(DPEPO)] and c) [Eu(ntfa)₃ (DPEPO)] in an argon flow atmosphere (100 ml min⁻¹) at a heating rate of 5° C min⁻¹.

In order to evaluate the coordination abilities of β -diketonate ligands, Mulliken charges of their oxygen atoms were estimated by DFT calculation (B3LYP 6-31G (d)) performed on simplified models of an Eu(III) complex, a

β-diketonate ligand bonded to a lithium ion.⁸ Calculated Mulliken charges are summarized in Table 1. The negative charge of densities in btfa and ntfa (-0.6395 and -0.6363, respectively) are larger than that in hfa (-0.6015). We consider that the coordination abilities of ntfa and btfa ligands are superior to that of an hfa ligand. The boiling point (bp) of btfa with π-expanded system (bp = 224° C) is much higher than that of hfa (bp = 70° C). We speculate that β-diketonate ligands with π-expanded systems caused an increase of decomposition temperatures in Eu(III) complexes.

Absorption spectra of Eu(III) complexes in acetone $(1.0 \times 10^{-3} \text{ M})$ are shown in Figure 3. The absorption band-edges of π - π * transition at around 400 nm show effective red shifts depending on expansion of the π -conjugated system in β -diketonate ligands. The wavelengths of the band edges in [Eu(hfa)₃(DPEPO)], [Eu(btfa)₃(DPEPO)] and [Eu(ntfa)₃(DPEPO)] were found to be 361, 380 and 394 nm, respectively.



[Eu(ntfa)₃(DPEPO)] is a candidate for an effective luminophore under UV-LED irradiattion at 390 nm.

Figure 3. Absorption spectra of a) $[Eu(hfa)_3(DPEPO)]$, b) $[Eu(btfa)_3(DPEPO)]$ and c) $[Eu(ntfa)_3(DPEPO)]$ in 1.0×10^{-3} M acetone at room temperature. Absorption edges were estimated by drawing tangents of the spectra.

Emission spectra of Eu(III) complexes are shown in Figure 4. The emission spectra at around 578, 592, 613, 650, and 698 nm were attributed to the 4f-4f transitions of Eu(III) $({}^{5}D_{0}-{}^{7}F_{J}$: J = 0, 1, 2, 3, and 4, respectively). The spectra were normalized with respect to the magnetic dipole transition intensity at 592 nm (Eu: ${}^{5}D_{0}-{}^{7}F_{1}$), which is known to be insensitive to the environment surrounding lanthanide ions. The relative spectral integration at ${}^{5}D_{0}-{}^{7}F_{2}$ is generally dependent on the coordination geometry around Eu(III) ions. The relative spectral integration values of [Eu(hfa)₃(DPEPO)], [Eu(btfa)₃(DPEPO)] and [Eu(ntfa)₃(DPEPO)] are 18.9, 20.4 and 21.9, respectively. The differences of relative spectral integration values are caused by introduction of asymmetric geometry linked to enhancement of the electric dipole transition (⁵D₀-⁷F₂). Expansion of the π -conjugated system in β-diketonate ligands leads to asymmetric coordination geometry of the their Eu(III) complexes.

Table 1. Carbonyl bond lengths for β-diketonate ligands

| | Mulliken Charge | Carbonyl bond length (Å) | | |
|---------------------------------|-----------------|--------------------------|--------|------------|
| | X side | Bond 1 | Bond 2 | Δd |
| [Eu(hfa) ₃ (DPEPO)] | -0.6015 | 1.2632 | 1.2632 | 0 |
| [Eu(btfa) ₃ (DPEPO)] | -0.6395 | 1.2704 | 1.2734 | 0.0030 |
| [Eu(ntfa) ₃ (DPEPO)] | -0.6363 | 1.2704 | 1.2739 | 0.0035 |

The time-resolved emission profiles of Eu(III) complexes in acetone revealed single exponential decays with millisecond-scale lifetimes. The emission lifetimes were determined from the slopes in logarithmic plots of the profiles (Figure 5). A decrease in emission lifetime was related to expansion of the π -conjugated system. The intrinsic emission quantum yield $\Phi_{4f.4f.}$ radiative rate constant k_r and non-radiative rate constant k_{nr} were estimated by using the following equations:

$$\Phi_{4f-4f} = \frac{k_r}{k_r + k_{nr}} = \frac{\tau_{obs}}{\tau_{rad}}$$
(1)

$$k_{\rm r} = A_{\rm MD,0} n^3 \left(\frac{I_{\rm tot}}{I_{\rm MD}}\right) = \frac{1}{\tau_{\rm rad}}$$
(2)

$$k_{\rm nr} = \frac{1}{\tau_{\rm obs}} - \frac{1}{\tau_{\rm rad}} \quad , \tag{3}$$

where $A_{\text{MD},0}$ is the spontaneous emission probability for the ${}^{5}\text{D}_{0}{}^{-7}\text{F}_{1}$ transition in vacuo (14.65 s⁻¹), *n* is the refractive index of acetone (1.365), and ($I_{\text{tot}}/I_{\text{MD}}$) is the ratio of the total area of the corrected Eu(III) emission spectrum to the area of the ${}^{5}\text{D}_{0}{}^{-7}\text{F}_{1}$ band. The photosensitized quantum yields $\Phi_{\pi-\pi^{*}}$ were measured using an emission spectrometer with an integrated sphere unit ($\varphi = 100$ mm). The photosensitized energy transfer efficiency η_{sens} was calculated by

$$\eta_{\text{sens}} = \frac{\phi_{\pi-\pi^*}}{\phi_{4f-4f}} \quad . \tag{4}$$



Figure 4. Emission spectra of a) [Eu(hfa)₃(DPEPO)] (5.0 $\times 10^{-3}$ M), b) [Eu(btfa)₃(DPEPO)] (1.0 $\times 10^{-3}$ M) and c) [Eu(ntfa)₃(DPEPO)] (1.0 $\times 10^{-4}$ M) in acetone at room temperature. Emission spectra were normalized at the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition.

The photophysical properties of $[Eu(hfa)_3(DPEPO)]$, $[Eu(btfa)_3(DPEPO)]$ and $[Eu(ntfa)_3(DPEPO)]$ are summarized in Table 2. Expansion of the π -conjugated system contributes to



an increase in the value of k_r . The increase of k_r is related to the coordination geometry of the Eu(III) complex. We here focused on the bond length of coordination sites ($d_{C=O}$) in each β -diketonate ligand. Selected bond lengths ($d_{C=O}$) that were estimated by DFT calculation (B3LYP 6-31G (d)) are shown in Table 1. The difference in length (Δ d) between bonds 1 and 2 in β -diketonate ligands increased with expansion of the π -conjugated system. Asymmetric coordination sites with large Δ d values promote a large k_r value.



Figure 5. Emission decay profiles of a) [Eu(hfa)₃(DPEPO)] (5.0×10^{-3} M), b) [Eu(btfa)₃(DPEPO)] (1.0×10^{-3} M) and c) [Eu(ntfa)₃(DPEPO)] (1.0×10^{-4} M) in acetone at room temperature.

We also found that expansion of the π -conjugated system leads to an increase of the k_{nr} value. Generally, the k_{nr} value is linked to vibrational relaxation of organic ligands and energy back transfer from the ${}^{5}D_{0}$ state of Eu(III) ions to the lowest triplet energy state (T_1) of the ligand. The T_1 level and the energy gap between the triplet states of Gd complexes and emitting level of Eu(III) ion with hfa, btfa and ntfa ligands are summarized in Table 2. The energy gap (EG) between the triplet states of Gd complexes and emitting level of Eu(III) ions with hfa, btfa and ntfa ligands are estimated to be 4900, 4100 and 2300 cm⁻¹, respectively (Gd complex being a standard compound for estimation of T_1 energy level of the ligand).²⁶⁻²⁸ These energy gaps were larger than 2000 cm⁻¹, which is the critical energy for prevention of energy back transfer.²⁹ We consider that energy back transfer from Eu(III) ions to T1 of ligands is not generated. Note that the number of C-H bonds in the π -conjugated system directly affects the vibrational relaxation of an excited Eu(III) complex. The numbers of C-H bonds in hfa, btfa and ntfa were found to be one, six and eight, respectively, as shown in Figure 6. We suppose that the π -expanded system in a β -diketonate ligand is related to magnitude of the vibrational relaxation in an Eu(III) complex.

Table 2. Photophysical properties of Eu(III) complexes in acetone^a

| | $\varPhi_{\pi\text{-}\pi^*}$ | $arPsi_{ m 4f-4f}$ | $\eta_{\rm sens}$ | $	au_{ m obs}$ | $k_{ m r}$ | k _{nr} | T_1 | EG |
|---------------------------------|------------------------------|--------------------|-------------------|-------------------|---------------------|---------------------|-----------------|-------------------------------|
| | (%) ^b | (%) ^c | (%) ^d | (ms) ^e | $(s^{-1})^{e}$ | $(s^{-1})^{e}$ | $(cm^{-1})^{f}$ | $(\text{cm}^{-1})^{\text{f}}$ |
| [Eu(hfa) ₃ (DPEPO)] | 57 | 71 | 79 | 1.0 | 7.0×10^{2} | 2.8×10^2 | 22200 | 4900 |
| [Eu(btfa) ₃ (DPEPO)] | 38 | 69 | 55 | 0.91 | 7.6×10^{2} | 3.4×10^{2} | 21400 | 4100 |
| [Eu(ntfa) ₃ (DPEPO)] | 45 | 58 | 77 | 0.71 | 8.2×10^2 | 5.9×10^2 | 19600 | 2300 |

a) Concentrations of [Eu(hfa)₃(DPEPO)] (5.0×10^{-3} M), [Eu(btfa)₃(DPEPO)] (1.0×10^{-3} M) and [Eu(ntfa)₃(DPEPO)] (1.0×10^{-4} M). b) Photosensitized emission quantum yield (excited at 380 nm). c) $\Phi_{4f-4f} = k_r / (k_r + k_{nr})$ (excited at 380 nm). d) From calculation using Equation (4). e) Emission lifetimes (τ_{obs}) of the Eu(III) complexes were measured by excitation at 355 nm (Nd:YAG 3 ω). From calculations using Equations (1) – (3). f) See references 26-28.

Photosensitized energy transfer efficiency η_{sens} of [Eu(ntfa)₃(DPEPO)] ($\eta_{sens} = 77\%$) is larger than that of [Eu(btfa)₃(DPEPO)] ($\eta_{sens} = 55\%$). The value of η_{sens} is also influenced by the energy levels of T_1 in a β -diketonate ligand with the π -expanded system. According to the literature, an Eu(III) ion is able to accept energy with ${}^{5}D_{0}$ (17227 cm⁻¹), ${}^{5}D_{1}$ (19028 cm⁻¹), and ${}^{5}D_{2}$ (21519 cm⁻¹).³⁰ An energy diagram of ${}^{5}D_{I}$ (J = 0, 1 and 2) and T₁ levels of the ligands are shown in Figure 7. Efficient energy transfer is generated by location of T_1 levels on upper 5D_J . On the other hand, location under 5D_J does not promote efficient energy transfer. The ntfa and hfa ligands are suitable for accepting energy with ${}^{5}D_{1}$ and ${}^{5}D_{2}$, respectively. Based on the energy transfer process, high energy transfer efficiencies of [Eu(ntfa)₃(DPEPO)] ($\eta_{sens} = 77\%$) and [Eu(hfa)₃(DPEPO)] ($\eta_{sens} = 79\%$) are achieved. Taking these structural and photophysical findings into consideration, [Eu(ntfa)₃(DPEPO)] shows excellent thermo-stability and energy transfer efficiency.



Figure 6. C-H bonds in the π -conjugated systems of a) [Eu(hfa)₃(DPEPO)], b) [Eu(btfa)₃(DPEPO)] and c) [Eu(ntfa)₃(DPEPO)].



Figure 7. Energy diagram of Eu ions at the levels of ${}^{5}D_{J}$ (J = 0, 1 and 2) and T₁ levels of hfa, btfa and ntfa ligands.

4. Conclusion

A lanthanide complex with highly thermostability and high photosensitized emission quantum yield $\Phi_{\pi-\pi^*}$ is expected to be an effective luminophore for LED devices. In this study, [Eu(ntfa)₃(DPEPO)] showed a large decomposition temperature (dp = 318°C) and high photosensitized energy transfer efficiency ($\eta_{\text{sens}} = 77\%$). Suitable expansion of the π -conjugated system promotes high thermostability. This study has shown a possible wavelength conversion material for LED devices.

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Graphical Abstract

<Title>

Photosensitized luminescence of highly thermostable mononuclear Eu (III) complexes with π-expanded β-diketonate ligands

<Authors' names>

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<Summary>

Thermostable mononuclear Eu(III) complexes with a π -expanded system, [Eu(btfa)₃(DPEPO)] and [Eu(ntfa)₃(DPEPO)], are reported (decomposition temperatures = 320°C and 318°C). The photosensitized emission quantum yield $\Phi_{\pi-\pi^*}$ and photosensitized energy transfer efficiency η_{sens} of [Eu(ntfa)₃(DPEPO)] ($\Phi_{\pi-\pi^*} = 45\%$, $\eta_{\text{sens}} = 77\%$) are larger than those of [Eu(btfa)₃(DPEPO)] ($\Phi_{\pi-\pi^*} = 38\%$, $\eta_{\text{sens}} = 55\%$). [Eu(ntfa)₃(DPEPO)] shows excellent thermostability and high η_{sens} .

<Diagram>

