



Title	Enhanced Luminescence of Asymmetrical Seven-Coordinate Eu-III Complexes Including LMCT Perturbation
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Abstract: Luminescent mononuclear seven-coordinate Eu^{III} complexes with monocapped-octahedral (point group: C_{3v}), monocapped-trigonalprismatic (C_{2v}), and pentagonal-bipyramidal (D_{5h}) coordination structures are reported. The complexes consist of a Eu^{III} ion, three tetramethylheptanedionates, and a phosphine oxide derivative. Controlling steric hindrance by means of introducing methyl groups into phosphine oxide ligands resulted in the formation of three types of coordination polyhedral structures. The coordination geometrical structures of the Eu^{III} complexes were evaluated by single-crystal X-ray analysis and shape-factor calculation. The radiative rate constant of the Eu^{III} complex with a monocapped-octahedral structure was larger than those with monocapped-trigonalprismatic and pentagonal-bipyramidal structures. Characteristic photophysical properties of the seven-coordinate Eu^{III} complexes are discussed with TD-DFT calculation and Arrhenius analysis of ligand-to-metal charge transfer.

Introduction

Luminescent metal complexes have been studied due to their versatile potential applications as optical materials,^[1,2] OLEDs,^[3,4] and fluorescent sensors.^[5,6] The photophysical properties of metal complexes are strongly affected by organic ligands and the coordination structure. There have been a large number of studies on control of the MLCT emission wavelengths of Ir^{III} and Ru^{II} complexes.^[7,8] The luminescence properties of Au^I and Pt^{II} complexes are dependent on the characteristic metal-metal interaction and metal-metal-to-ligand charge transfer.^[9,10] Intrinsic emission quantum yields of lanthanide (Nd^{III}, Sm^{III}, Eu^{III}, Tb^{III}, Dy^{III}, Yb^{III}, and so on) complexes are also influenced by the geometrical structures in the coordination spheres.^[11,12] We here focus on luminescent lanthanide complexes for study on the relationships between photophysical properties and coordination geometrical structures.

Luminescence of a lanthanide complex arises from 4f-

intraconfigurational transitions. The magnitude of the radiative rate constant (k_r) of 4f-4f transition is influenced by the coordination polyhedral structures. Since electric dipole transition of lanthanide complex is forbidden, a mixed parity state induced by ligand field perturbation is required to observe 4f-4f transition. A lanthanide complex has large coordination number (generally eight to twelve) and especially tends to form an eight-coordinate square-antiprismatic structure (8-SAP, D_{4d}).^[13-18] We have reported that the luminescent Eu^{III} complexes with non-centrosymmetrical coordination structures such as nine-coordinate monocapped-square-antiprism (9-SAP, C_{4v}) and eight-coordinate trigonal-dodecahedron (8-TDH, D_{2d}) showed enhanced 4f-4f transition probability based on the Laporte rule.^[19,20] Considering these photophysical findings, coordination polyhedral structures of lanthanide complexes should be strongly correlated with enhancement of luminescence efficiency.

Recently, we reported seven-coordinate Eu^{III} and Tb^{III} complexes with a monocapped-octahedral structure (7-MCO).^[21] The 7-MCO structure is categorized as C_{3v} symmetry, which is an asymmetrical structure compared with 8-SAP, 8-TDH, and 9-SAP structures. The Eu^{III} complex with a 7-MCO structure accordingly showed larger k_r value than that with a 8-SAP structure. In terms of geometrical structure, representative seven-coordinate polyhedron includes not only a 7-MCO structure but also monocapped-trigonalprismatic (7-MCTP, C_{2v}) and pentagonal-bipyramidal structures (7-PBP, D_{5h}) as shown in Figures 1a-c.^[22] Results of photophysical studies on seven-coordinate lanthanide complexes with 7-MCO, 7-MCTP, and 7-PBP structures are expected to provide a new design for highly emissive and monochromatic luminescent materials.

In this study, we synthesized three types of novel seven-coordinate Eu^{III} complexes composed of three β -diketonate ligands (tetramethylheptanedionate: tmh) and a phosphine oxide ligand (diphenyl(*p*-tolyl)phosphine oxide: L-1, tri-*p*-tolylphosphine oxide: L-2, or tri-*m*-tolylphosphine oxide: L-3) as shown in Figure 1d ([Eu(tmh)₃(L-1)]: Eu-1, [Eu(tmh)₃(L-2)]: Eu-2, and [Eu(tmh)₃(L-3)]: Eu-3). The geometrical structures of the prepared Eu^{III} complexes were characterized using single-crystal X-ray analysis and shape-measure calculation. Emission properties were evaluated using intrinsic emission quantum yield Φ_{ff} , total emission quantum yield Φ_{tot} , emission lifetime τ_{obs} , and k_r .

In our experiments, we found that the k_r value of Eu-1 with a 7-MCO (C_{3v}) was larger than those of Eu-2 with a 7-MCTP structure (C_{2v}) and Eu-3 with a 7-PBP structure (D_{5h}), although the low-symmetrical coordination geometry are expected to give rise to large k_r because of deviation from centrosymmetric geometry.^[23] According to a previous report, considering perturbation of charge-transfer state into 4f configuration, oscillator strength of 4f-4f transition is related to the energy level and dipole strength of charge-transfer transition.^[24] Recently, Hatanaka and Yabushita also reported that hypersensitive transition probability of lanthanide complexes was theoretically

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affected by the ligand-to-metal charge transfer (LMCT) state.^[25] We here discuss enhancement of the k_r value related to the characteristic LMCT state for the seven-coordinate Eu^{III} complexes. The LMCT states were evaluated using diffuse reflection spectra, TD-DFT calculations, and Arrhenius analyses of emission lifetimes. The effect on LMCT perturbation in the Eu^{III} complexes with 7-MCO, 7-MCTP, and 7-PBP is demonstrated for the first time.

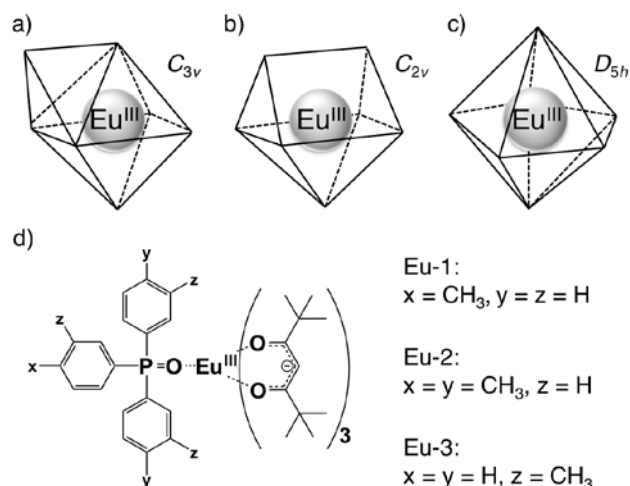


Figure 1. Seven-coordinate polyhedral structures, a) monocapped-octahedron, b) monocapped-trigonalprism, and c) pentagonal-bipyramid. d) Chemical structure of the Eu^{III} complex.

Results and Discussion

Seven-coordinate Eu^{III} complexes (Eu-1, Eu-2, and Eu-3) were synthesized by complexation of a precursor Eu^{III} complex, [Eu(tmh)₃(MeOH)₂]^[21] with three types of phosphine oxide ligand (L-1, L-2, and L-3) in methanol under reflux for 6 h. Seven-coordinate Tb^{III} complexes (Tb-1, Tb-2, and Tb-3) without LMCT band were prepared by the same method for comparison with the Eu^{III} complexes including LMCT band (see supporting information, Figure S1). A Gd^{III} complex, [Gd₂(tmh)₆], was also synthesized to estimate energy level of excited triplet state of tmh ligand. They were identified using IR and elemental analysis. Single crystals of the lanthanide complexes were prepared by recrystallization from methanol at room temperature. The crystal data for Eu^{III} complexes obtained from single-crystal X-ray analysis are summarized in Table 1. The ORTEP views of the complexes exhibit seven-coordinate structures comprised of one Eu^{III} ion, three tmh ligands and one phosphine oxide ligand (Figures 2a-c). The average bond lengths between Eu and O (β -diketonate) for Eu-1, Eu-2, and Eu-3 were 2.33, 2.33, and 2.34 Å, respectively. The bond lengths are similar to the Eu-O (phosphine oxide) bonds of Eu-1 (2.34 Å), Eu-2 (2.34 Å), and Eu-3 (2.32 Å). The Eu-O (β -diketonate) bond lengths were shorter than that for previously reported eight-coordinate Eu^{III} complex with hexafluoroacetylacetonate (hfa) and triphenylphosphine oxide

(tppo), [Eu(hfa)₃(tppo)₂] (the average bond length between Eu and O: 2.42 Å (β -diketonate) and 2.33 Å (phosphine oxide)).^[12] Calculated Mulliken charges at O atoms in diketonate ligands were slightly smaller than that in phosphine oxide ligand for all the Eu^{III} complexes. The values of Mulliken charge were summarized in Table S1.

Table 1. Crystallographic data of Eu-1, Eu-2, and Eu-3.

	Eu-1	Eu-2	Eu-3
chemical formula	C ₅₂ H ₇₄ EuO ₇ P	C ₅₄ H ₇₈ EuO ₇ P	C ₅₄ H ₇₈ EuO ₇ P
crystal system	monoclinic	orthorhombic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	11.2648(10)	16.6636(3)	13.5503(3)
<i>b</i> [Å]	21.922(2)	17.9698(3)	24.5056(6)
<i>c</i> [Å]	22.090(2)	18.5330(3)	16.7914(4)
β [deg]	104.8796(17)	–	99.7464(7)
<i>V</i> [Å ³]	5271.8(8)	5549.55(16)	5495.3(2)
<i>Z</i>	4	4	4
<i>d</i> _{calcd} [g cm ⁻³]	1.252	1.223	1.235
<i>T</i> [K]	123	123	123
μ (MoK α) [cm ⁻¹]	1.266	1.204	1.216
measured reflections	50489	73005	65353
unique reflections	12107	12685	12586
<i>R</i> ^[a]	0.0572	0.0245	0.0362
<i>wR</i> ^[b]	0.1346	0.1146	0.1024

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR = [(\sum w(|F_o| - |F_c|)^2) / \sum w(F_o^2)]^{1/2}$.

Based on the crystal structures, we calculated shape factor *S* in order to determine the coordination geometrical structures around Eu^{III} ions.^[26] The *S* value is given by

$$S = \min \sqrt{[(1/m) \sum_{i=1}^m (\delta_i - \theta_i)^2]}, \quad (1)$$

where *m* is the number of possible edges (*m* = 15 in this study), δ_i is the observed dihedral angle between planes along the *i*th edge, and θ_i is the dihedral angle of the *i*th edge for the ideal structure. The estimated *S* values of the Eu^{III} complexes are summarized in Tables S2-S4. From these calculations, we categorized the pseudo coordination polyhedral structures of Eu-1, Eu-2, and Eu-3 as 7-MCO, 7-MCTP, and 7-PBP, respectively (Figures 2d-f). The distance between Eu and O atoms is dependent on the molecular structure. In this study, the Eu-O distances for Eu-1, Eu-2, and Eu-3 were found to be 2.33-2.34 Å. The distance of Eu-O are same as an ideal geometry.

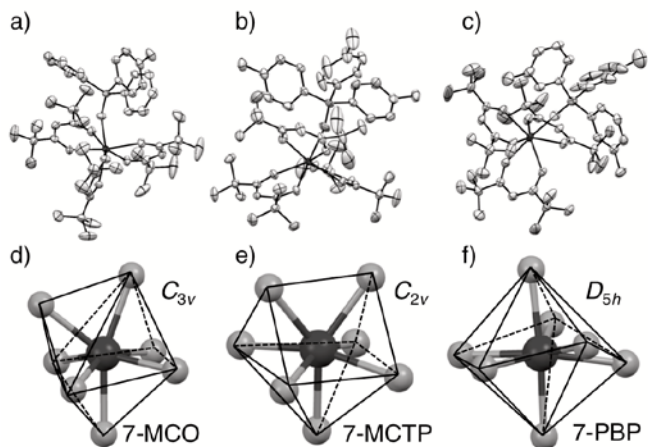


Figure 2. ORTEP drawings of a) Eu-1, b) Eu-2, and c) Eu-3. Hydrogen atoms were omitted for clarity. Thermal ellipsoids were shown at the 50% probability level. Coordination geometrical structures of d) Eu-1 (7-MCO), e) Eu-2 (7-MCTP), and f) Eu-3 (7-PBP).

Excitation and emission spectra of the Eu^{III} complexes in the solid state are shown in Figure 3a. We observed distinguishable 4f-intraconfigurational excitation bands, $^7\text{F}_0$ and $^7\text{F}_1$ to $^5\text{L}_6$, $^5\text{D}_3$, $^5\text{D}_2$, $^5\text{D}_1$, and $^5\text{D}_0$. Emission bands were observed at 578, 592, 612, 653, and 700 nm, being attributed to 4f-4f transitions of Eu^{III} ion ($^5\text{D}_0 \rightarrow ^7\text{F}_{0-4}$). The emission spectra were normalized with respect to the spectral area of magnetic dipole transitions ($^5\text{D}_0 \rightarrow ^7\text{F}_1$).^[27] The inset of Figure 3a shows the emission spectra of hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of the complexes. The characteristic Stark splittings and spectral shapes of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition are attributed to the coordination structures. The energy width of Stark splitting of $^7\text{F}_2$ sublevels for Eu-1 (430 cm^{-1}) was slightly larger than those for Eu-2 (425 cm^{-1}) and Eu-3 (417 cm^{-1}). Accurate energy values of the Stark splitting of $^5\text{D}_0 \rightarrow ^7\text{F}_{0-2}$ for the Eu^{III} complexes are given in Figure S2 and Table S5.

Time-resolved emission profiles of the Eu^{III} complexes revealed single-exponential decay with a sub-millisecond-scale lifetime as shown in Figures 3b-d. The emission lifetimes were determined from the slopes of logarithmic plots of the decay profiles. The observed emission lifetimes (τ_{obs}) were 0.50, 0.73, and 0.61 ms for Eu-1, Eu-2, and Eu-3, respectively. Emission quantum yields (Φ_{ff}) excited at 532 nm ($^5\text{D}_1 \leftarrow ^7\text{F}_3$) and total emission quantum yields (Φ_{tot}) excited at 365 nm of the Eu^{III} complexes were measured using an integrating sphere attached to a photomultiplier. We calculated k_r based on the τ_{obs} and Φ_{ff} values. The values of τ_{obs} , Φ_{ff} , Φ_{tot} , k_r , and estimated coordination geometrical structures of the Eu^{III} complexes are summarized in Table 2. The magnitudes of Φ_{tot} of the Eu^{III} complexes were less than 1%, which is due to the inefficient photosensitized energy transfer from organic ligands to Eu^{III} ion. The measured Φ_{ff} values of Eu-1, Eu-2, and Eu-3 were 82%, 85%, and 86%, respectively. These were as high as those of recently reported lanthanide complexes with efficient luminescence.^[28] The k_r value for Eu-1 was larger than those for Eu-2 and Eu-3.

Table 2. Photophysical properties and coordination geometrical structures of Eu-1, Eu-2, and Eu-3.

complex	$\tau_{\text{obs}}^{[\text{a}]}$ [ms]	$\Phi_{\text{ff}}^{[\text{b}]}$ [%]	$\Phi_{\text{tot}}^{[\text{b}]}$ [%]	$k_r^{[\text{c}]}$ [s^{-1}]	geometrical structure
Eu-1	0.50	82	0.5	1.6×10^3	7-MCO (C_{3v})
Eu-2	0.73	85	0.6	1.1×10^3	7-MCTP (C_{2v})
Eu-3	0.61	86	0.6	1.4×10^3	7-PBP (D_{5h})

[a] Emission lifetimes (τ_{obs}) were measured by excitation at 355 nm (Nd:YAG, third harmonics). [b] Emission quantum yields excited at 532 nm (Φ_{ff}) and 365 nm (Φ_{tot}) were measured using an integrating sphere unit. [c] Radiative rate constants, $k_r = \Phi_{\text{ff}} / \tau_{\text{obs}}$.

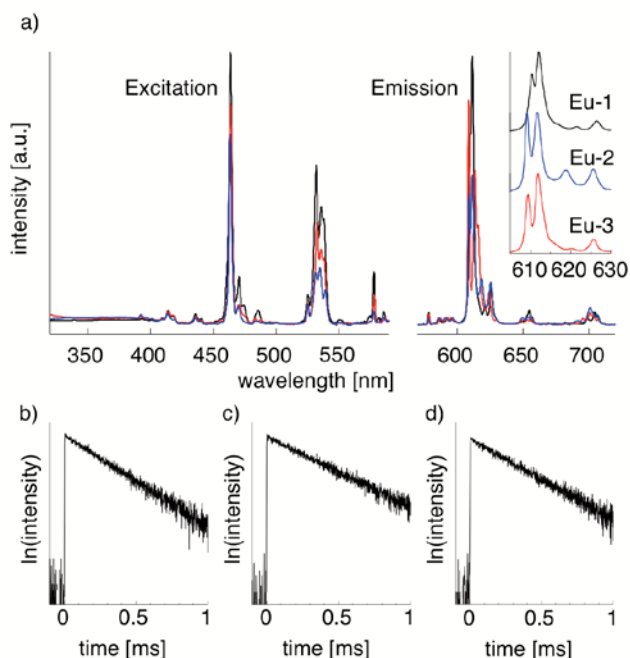


Figure 3. a) Excitation and emission spectra of Eu-1 (black line), Eu-2 (blue line), and Eu-3 (red line) in the solid state at room temperature. Excitation spectra were recorded with emission at 611 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$). Emission spectra were excited at 464 nm ($^5\text{D}_2 \leftarrow ^7\text{F}_0$). Emission decay profiles of (b) Eu-1, (c) Eu-2, and (d) Eu-3 in the solid state excited at 355 nm (Nd:YAG laser).

The radiative process is affected by the LMCT states of Eu^{III} complexes.^[24] In order to analyze the radiative process of the seven-coordinate Eu^{III} complexes, we measured diffuse reflection spectra for observation of their LMCT bands (Figure 4a). Absorption bands at around 320 nm (31250 cm^{-1}) were assigned to singlet $\pi\text{-}\pi^*$ and/or $\sigma\text{-}\pi^*$ transition of tmh ligands, which was confirmed by the absorption spectrum of $[\text{Gd}(\text{tmh})_3(\text{MeOH})_2]$ in methanol solution (see supporting information, Figure S3) and TD-DFT calculation (Tables S6-S8). We also observed absorption bands at around 370 nm (27000

cm^{-1}) for the Eu^{III} complexes. The absorption band at 370 nm for Tb^{III} complexes was not observed (Figure 4b). The other photophysical results of the Tb^{III} complexes were shown in Figure S4. Considering absorption spectra of Eu^{III} and Tb^{III} complexes, the absorption bands at around 370 nm are assumed to be LMCT band. In addition, absorption wavelength and oscillator strength of LMCT transition of Eu^{III} complexes were estimated using TD-DFT calculation. (see supporting information, Tables S6-S8). Estimated excitations of $\sigma \rightarrow 4f$ (Eu) and $\pi \rightarrow 4f$ (Eu) were clearly observed at UV region, which were categorized as LMCT absorption.

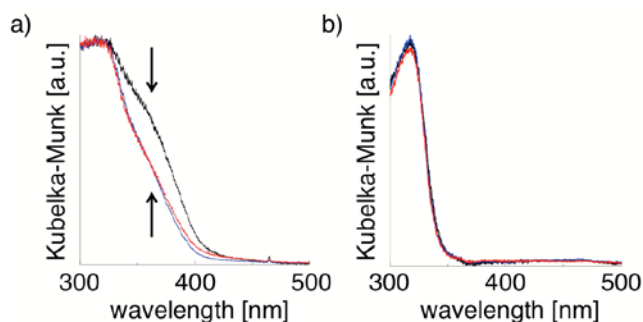


Figure 4. Diffuse reflection spectra of a) the Eu^{III} complexes and b) the Tb^{III} complexes. Eu-1 and Tb-1 (black lines), Eu-2 and Tb-2 (blue lines) and Eu-3 and Tb-3 (red lines).

A schematic energy diagram of the seven-coordinate Eu^{III} complexes is shown in Figure 5. An excited singlet state (S_1) generally undergoes intersystem crossing to a low-lying excited triplet state (T_1) due to large spin-orbit interaction of lanthanide complexes. The energy level of T_1 (410 nm, $\sim 24400 \text{ cm}^{-1}$) was also confirmed by a phosphorescence spectrum of $[\text{Gd}_2(\text{tmh})_6]$ at 100 K (see supporting information, Figure S5). The T_1 level is much higher than $^5\text{D}_0$ emitting level. The large energy gap is expected to suppress back-energy transfer from $^5\text{D}_0$ configuration to T_1 state.^[29] We herein considered that low Φ_{tot} is affected by presence of LMCT state.

Temperature-dependent emission lifetimes of Eu^{III} complexes were measured for investigation of photophysical interaction between $^5\text{D}_0$ configuration and LMCT state (Figure 6a). The emission lifetimes of Eu^{III} complexes decreased above 300 K, while we found that the emission lifetimes of Tb^{III} complexes were constant in the range of 100-350 K (see supporting information, Figure S6). The decrease in emission lifetime of Eu^{III} complexes should be due to state transition (charge transfer) from $^5\text{D}_0$ excited state to LMCT state rather than vibrational relaxation ($^5\text{D}_0 \rightarrow ^7\text{F}_0$) and back-energy transfer ($^5\text{D}_0 \rightarrow T_1$). In the temperature-dependent emission lifetime of the Eu^{III} complexes, activation energy E_a and frequency factor A were estimated from Arrhenius plot of charge-transfer rate k_{CT} from $^5\text{D}_0$ to LMCT state (Figure 6b, Table 3).

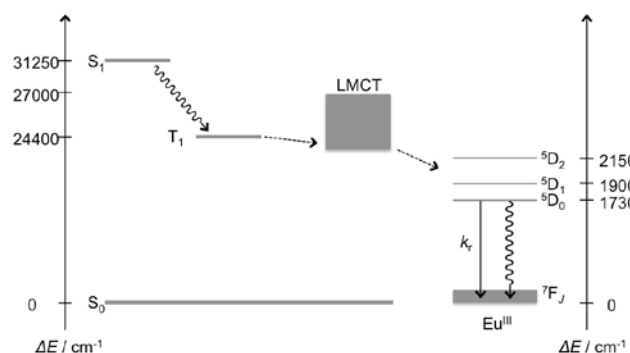


Figure 5. Schematic energy diagram of the Eu^{III} complexes

Table 3. Arrhenius parameters of charge-transfer process from $^5\text{D}_0$ configuration to LMCT state and estimated wavelength and oscillator strength of LMCT absorption edge.

complex	E_a [cm^{-1}]	A [s^{-1}]	$\lambda_{\text{CT,edge}}^{[a]}$ [nm]	$P_{\text{CT,edge}}^{[b]}$	$(E_{\text{CT}})^{-3}P_{\text{CT}}^{[c]}$ [cm^2]
Eu-1	3.5×10^3	8.0×10^8	392	0.0034	2.0×10^{-16}
Eu-2	3.3×10^3	1.3×10^8	423	0.0005	3.8×10^{-17}
Eu-3	3.9×10^3	9.8×10^8	394	0.0028	1.7×10^{-16}

[a] Wavelength and [b] oscillator strength of LMCT absorption edge obtained from TD-DFT calculation. [c] $E_{\text{CT}} = 1/\lambda_{\text{CT}}$.

The values of E_a for Eu-1, Eu-2, and Eu-3 were found to be 3.5×10^3 , 3.3×10^3 , and $3.9 \times 10^3 \text{ cm}^{-1}$, respectively. The E_a is related to the charge transfer process from $^5\text{D}_0$ to LMCT state. The E_a of Eu-2 was slightly smaller than those of Eu-1 and Eu-3. The A value of Eu-2 ($1.3 \times 10^8 \text{ s}^{-1}$) was also smaller than those of Eu-1 ($8.0 \times 10^8 \text{ s}^{-1}$) and Eu-3 ($9.8 \times 10^8 \text{ s}^{-1}$). Since A includes electronic frequency ν_{el} , the value relates to electronic coupling of $^5\text{D}_0$ configuration with LMCT state.^[30] Therefore, the degree of electronic coupling between $^5\text{D}_0$ and LMCT state for Eu-2 is smaller than those of corresponding Eu-1 and Eu-3.

According to the influence on LMCT in lanthanide complex, Henrie reported an equation for $4f-4f$ transition probability P_{ff} involving perturbation of charge-transfer transition.^[24] The equation is given by

$$P_{\text{ff}} = a^2 E_{\text{ff}} (E_{\text{CT}})^{-3} P_{\text{CT}}, \quad (2)$$

where P is oscillator strength and E is energy level. The subscripts ff and CT represent $4f-4f$ and charge-transfer transition, respectively. The a is matrix elements of odd-parity vibrations and the ligand field that mix the charge-transfer level with the $4f$ level. Note that the $(E_{\text{CT}})^{-3}P_{\text{CT}}$ term is proportional to the oscillator strength of $4f-4f$ transition. The values of E_{CT} , P_{CT} , and $(E_{\text{CT}})^{-3}P_{\text{CT}}$ of LMCT absorption edge obtained from TD-DFT calculation were also summarized in Table 3. From this calculation, we found that the value of Eu-1 was larger than those of Eu-2 and Eu-3. We here assume that the enhanced k_r of Eu-1 was influenced by the large oscillator strength of LMCT

transition. Considering the results described above, the largest k_r of Eu-1 was caused by not only low-symmetrical coordination geometry (C_{3v}) but also relatively large perturbation of LMCT state into $4f$ configuration. We propose that the enhancement of k_r would be influenced by LMCT perturbation rather than coordination polyhedral structure. In this study, the 7-MCO structure with large LMCT perturbation provided the highest k_r in the seven-coordinate Eu^{III} complexes.

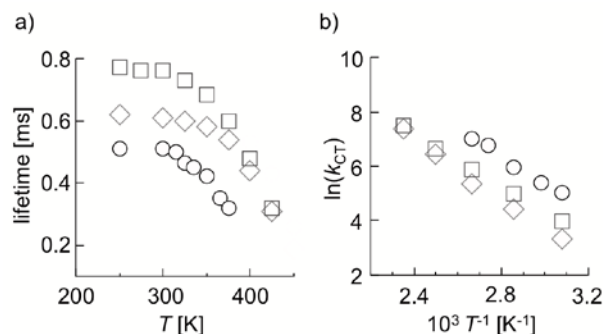


Figure 6. a) Thermal dependency of emission lifetimes of Eu-1 (circle), Eu-2 (square), and Eu-3 (rhomboid) in the solid state. b) Arrhenius plots for charge transfer rate (k_{CT}) of Eu-1 (circle), Eu-2 (square), and Eu-3 (rhomboid). $\ln(1/\tau_{\text{obs}} - 1/\tau_{300\text{K}}) = \ln(k_{CT}) = \ln A - (E_a/k_B T)$.

Conclusions

We successfully synthesized novel seven-coordinate lanthanide complexes with 7-MCO, 7-MCTP, and 7-PBP structures. The geometrical structures were dependent on the steric hindrance of phosphine oxide ligands with additional methyl groups. The radiative rate constant of Eu-1 with 7-MCO (C_{3v}) was larger than those of Eu-2 with 7-MCTP (C_{2v}) and Eu-3 with 7-PBP (D_{5h}). We consider that the enhanced radiative rate constant of Eu-1 is due to synergetic effect between the low-symmetrical coordination geometry and relatively large perturbation of the LMCT state into the $4f$ -excited state. The large perturbation was estimated by Arrhenius parameters obtained from temperature-dependent emission lifetime and TD-DFT calculation. Seven-coordinate Eu^{III} complexes in this study provided significant photophysical information for investigation of the radiative process of lanthanide complexes.

Experimental Section

Materials: Europium chloride hexahydrate (99.9%), terbium chloride pentahydrate (99.9%), and gadolinium chloride hexahydrate (99.9%) were purchased from Kanto Chemical Co., Inc. 2,2,6,6-Tetramethylheptane-3,5-dione (tmh), diphenyl(*p*-tolyl)phosphine, tri-*p*-tolylphosphine, and tri-*m*-tolylphosphine were obtained from Tokyo Kasei Organic Chemicals. Ammonia aqueous solution (28%) and H_2O_2 aqueous solution (30%) 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 with an Exeter Analytical CE440. Infrared spectra were recorded with a JASCO FT/IR-4600 spectrometer. ^1H NMR (270 and 400 MHz) spectra were recorded on a JEOL EX270 and ECS400. Chemical shifts were reported in δ ppm, which is referenced to an internal tetramethylsilane (TMS) standard.

Syntheses of diphenyl(*p*-tolyl)phosphine oxide (L-1), tri-*p*-tolylphosphine oxide (L-2), and tri-*m*-tolylphosphine oxide (L-3): Diphenyl(*p*-tolyl)phosphine (1.93 g, 7.0 mmol), tri-*p*-tolylphosphine (2.13 g, 7.0 mmol), or tri-*m*-tolylphosphine (2.13 g, 7.0 mmol) was dissolved with dichloromethane (30 mL) in a 100 mL flask. The solution was cooled using an ice bath and then H_2O_2 solution (5 mL) was added dropwise to it. The reaction mixture was stirred for 3 h. The product was extracted with dichloromethane, and the solvent was evaporated to afford a white solid of titled compounds (diphenyl(*p*-tolyl)phosphine oxide: L-1, tri-*p*-tolylphosphine oxide: L-2, and tri-*m*-tolylphosphine oxide: L-3). L-1: Yield 1.99 g (97%); ^1H NMR (270 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 7.25–7.70 (m, 14H), 2.41 (s, 3H) ppm.^[31] L-2: Yield 2.19 g (97%); ^1H NMR (270 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 7.50–7.57 (m, 6 H), 7.23–7.26 (m, 6 H), 2.40 (s, 9 H) ppm.^[31] L-3: Yield 2.18 g (97%); ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 7.54–7.57 (d, 3H), 7.28–7.39 (m, 9H), 2.35 (s, 9H) ppm.

Preparation of $[\text{Eu}(\text{tmh})_3(\text{L-1})]$ (Eu-1), $[\text{Eu}(\text{tmh})_3(\text{L-2})]$ (Eu-2), and $[\text{Eu}(\text{tmh})_3(\text{L-3})]$ (Eu-3): The precursor complex, $[\text{Eu}(\text{tmh})_3(\text{MeOH})_2]$, was synthesized as described in our previous report.^[21] Europium chloride hexahydrate (1.0 g, 2.7 mmol) was dissolved in distilled water (5 mL) in a 100 mL flask. An ethanol solution (20 mL) of tmh (1.46 g, 8.1 mmol) was added to the aqueous solution. An ammonia solution was added dropwise to the flask until pH 7. After stirring at room temperature for 6 h, the reaction mixture was poured into cold water (300 mL) in a conical flask. The produced precipitate, $[\text{Eu}_2(\text{tmh})_6]^{[32]}$ was filtered, and the resulting powder was recrystallized from methanol to afford colorless block crystals of $[\text{Eu}(\text{tmh})_3(\text{MeOH})_2]$. The precursor complex $[\text{Eu}(\text{tmh})_3(\text{MeOH})_2]$ (1.0 g, 1.4 mmol) and L-1 (0.41 g, 1.4 mmol), L-2 (0.45 g, 1.4 mmol), or L-3 (0.45 g, 1.4 mmol) were dissolved with methanol (30 mL) in a 100 mL flask. The solution was heated under reflux while stirring for 6 h. The reaction mixture was recrystallized in methanol to afford colorless crystals of titled compounds ($[\text{Eu}(\text{tmh})_3(\text{L-1})]$: Eu-1, $[\text{Eu}(\text{tmh})_3(\text{L-2})]$: Eu-2, and $[\text{Eu}(\text{tmh})_3(\text{L-3})]$: Eu-3). Eu-1: Yield 1.1 g (79%); IR (ATR) $\tilde{\nu}$ = 2861–2955 (m, C–H), 1570 (s, C=O), 1173 cm^{-1} (s, P=O); elemental analysis calcd (%) for $\text{C}_{52}\text{H}_{74}\text{EuO}_7\text{P}$: C 62.83, H 7.50; found: C 62.66, H 7.31. Eu-2: Yield 1.3 g (91%); IR (ATR) $\tilde{\nu}$ = 2860–2960 (m, C–H), 1572 (s, C=O), 1176 cm^{-1} (s, P=O); elemental analysis calcd (%) for $\text{C}_{54}\text{H}_{78}\text{EuO}_7\text{P}$: C 63.45, H 7.69; found: C 63.14, H 7.69. Eu-3: Yield 1.3 g (91%); IR (ATR) $\tilde{\nu}$ = 2860–2950 (m, C–H), 1572 (s, C=O), 1171 cm^{-1} (s, P=O); elemental analysis calcd (%) for $\text{C}_{54}\text{H}_{78}\text{EuO}_7\text{P}$: C 63.45, H 7.69; found: C 63.01, H 7.61. Tb^{III} and Gd^{III} complexes ($[\text{Tb}(\text{tmh})_3(\text{L-1})]$: Tb-1, $[\text{Tb}(\text{tmh})_3(\text{L-2})]$: Tb-2, $[\text{Tb}(\text{tmh})_3(\text{L-3})]$: Tb-3, $[\text{Gd}_2(\text{tmh})_6]$, and $[\text{Gd}_2(\text{tmh})_3(\text{MeOH})_2]$) were synthesized by the same method as described above. Tb-1: IR (ATR) $\tilde{\nu}$ = 2860–2950 (m, C–H), 1573 (s, C=O), 1174 cm^{-1} (s, P=O); elemental analysis calcd (%) for $\text{C}_{52}\text{H}_{74}\text{EuO}_7\text{PtB}$: C 62.39, H 7.45; found: C 62.52, H 7.26. Tb-2: IR (ATR) $\tilde{\nu}$ = 2860–2960 (m, C–H), 1573 (s, C=O), 1178 cm^{-1} (s, P=O); elemental analysis calcd (%) for $\text{C}_{54}\text{H}_{78}\text{O}_7\text{PtB}$: C 63.02, H 7.64; found: C 62.68, H 7.31. Tb-3: IR (ATR) $\tilde{\nu}$ = 2860–2950 (m, C–H), 1573 (s, C=O), 1173 cm^{-1} (s, P=O); elemental analysis calcd (%) for $\text{C}_{54}\text{H}_{78}\text{O}_7\text{PtB}$: C 63.02, H 7.64; found: C 62.67, H 7.27. $[\text{Gd}_2(\text{tmh})_6]$: IR (ATR) $\tilde{\nu}$ = 2860–2950 (m, C–H), 1572 (s, C=O); elemental analysis calcd (%) for $\text{C}_{66}\text{H}_{114}\text{Gd}_2\text{O}_{12}$: C 56.06, H 8.13; found: C 55.89, H 8.15.

Crystallography: Single crystals of the lanthanide complexes were mounted on micromesh (MiTeGen M3-L19-25L) using paraffin oil. All measurements were carried out using a Rigaku R-Axis RAPID imaging plate area detector with graphite monochromated MoK_α radiation. Non-

hydrogen atoms were refined anisotropically. All calculations were performed using a crystal-structure crystallographic software package. The quality of CIF data was validated by using the checkCIF/PLATON service. Crystallographic data of the Tb^{III} complexes and Gd complex were summarized in Table S9. The CIF data are presented in supporting information, and also CCDC 1507470 (Eu-1), CCDC 1507471 (Eu-2), CCDC 1507472 (Eu-3), CCDC 1515208 (Tb-1), CCDC 1515209 (Tb-2), CCDC 1515210 (Tb-3), and CCDC-1520661 ([Gd(tmh)₃(MeOH)₂]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Optical measurements: Emission and excitation spectra of the synthesized complexes were measured with a spectrofluorometer (HORIBA Fluorolog-3). Emission quantum yields were obtained using a spectrofluorometer (JASCO FP-6300) equipped with an integrating sphere unit (JASCO ILF-533). The wavelength dependency of the detector response and the beam intensity of the Xe light source for each spectrum were calibrated using a standard light source. Emission lifetimes were measured 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 $\leq$ 1.1 ns). The Nd:YAG laser response was monitored with a digital oscilloscope (Sony Tektonix, TDS3052, 500 MHz) synchronized to single-pulse excitation. Emission lifetimes were determined from the slopes of logarithmic plots of decay profiles. Emission lifetimes and emission spectra in the range of 100–400 K were measured using a cryostat (Thermal Block Company, SA-SB245T) and a temperature controller (Oxford Instruments, ITC 502S). Diffuse reflection spectra were obtained using a JASCO V-670 spectrophotometer with an ISN-723 integrating sphere unit.

Computational details: All calculations were performed with the Gaussian 09 program.^[33] The structures of three types of the seven-coordinate Eu^{III} complexes were optimized in the gas phase at the B3LYP-D3^[34,35] level. Excited-state calculations of these complexes at the optimized structures were performed by TD-DFT calculations with the LC-BLYP functional.^[36–38] The Stuttgart RECP^[39] and cc-pVDZ^[40] basis sets for Eu and the other atoms, respectively, were adopted for all calculations. The assignments of molecular orbitals were performed by the AOMix program.^[41–42] Mulliken charges of the Eu^{III} complexes were estimated by Hartree-Fock calculation with SDD(for Eu) and 3-21g(for other atoms) basis set.

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Keywords: Lanthanides • Luminescence • Charge transfer • Structure elucidation • Density functional calculations

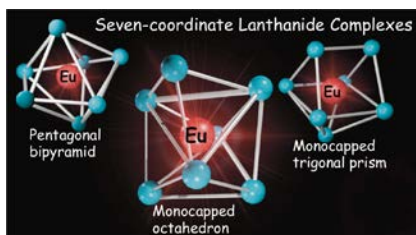
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FULL PAPER

Seven-coordinate Lanthanide

Complexes: Three types of coordination geometrical structures, monocapped-octahedron, monocapped-trigonalprism, and pentagonal-bipyramid were observed in Eu^{III} complexes constructed by β -diketonate and phosphine oxide ligands. The characteristic photophysical properties involving LMCT perturbation are discussed.



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**Enhanced Luminescence of
Asymmetrical Seven-coordinate Eu^{III}
Complexes Including LMCT
Perturbation**