Enhanced Luminescence of Asymmetrical Seven-coordinate Eu\textsuperscript{III} Complexes Including LMCT Perturbation

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Abstract: Luminescent mononuclear seven-coordinate Eu\textsuperscript{III} complexes with monocapped-octahedral (point group: C\textsubscript{4}v), monocapped- trigonalprismatic (C\textsubscript{3}v), and pentagonal-bipiramidal (D\textsubscript{5h}) coordination structures are reported. The complexes consist of a Eu\textsuperscript{III} ion, three tetramethylheptanedionates, and a phosphine oxide derivative. Controlling steric hindrance by means of introducing methyl groups into phosphate oxide ligands resulted in the formation of three types of coordination polyhedral structures. The coordination geometrical structures of the Eu\textsuperscript{III} complexes were evaluated by single-crystal X-ray analysis and shape-factor calculation. The radiative rate constant of the Eu\textsuperscript{III} complex with a monocapped-octahedral structure was larger than those with monocapped-trigonalprismatic and pentagonal-bipiramidal structures. Characteristic photophysical properties of the seven-coordinate Eu\textsuperscript{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\textsuperscript{[1-2]} OLEDs\textsuperscript{[3,4]} and fluorescent sensors.\textsuperscript{[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\textsuperscript{III} and Ru\textsuperscript{II} complexes.\textsuperscript{[7,8]} The luminescence properties of Au\textsuperscript{I} and Pt\textsuperscript{II} complexes are dependent on the characteristic metal-metal interaction and metal-metal-to-ligand charge transfer.\textsuperscript{[9,10]} Intrinsic emission quantum yields of lanthanide (Nd\textsuperscript{III}, Sm\textsuperscript{III}, Eu\textsuperscript{III}, Tb\textsuperscript{III}, Dy\textsuperscript{III}, Yb\textsuperscript{III}, and so on) complexes are also influenced by the geometrical structures in the coordination spheres.\textsuperscript{[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-4f intraconfigurational transitions. The magnitude of the radiative rate constant (k\textsubscript{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\textsubscript{4h})\textsuperscript{[13-18]} We have reported that the luminescent Eu\textsuperscript{III} complexes with non-centrosymmetrical coordination structures such as nine-coordinate monocapped-square-antiprism (9-SAP, C\textsubscript{2}v) and eight-coordinate trigonal-dodecahedron (8-TDH, D\textsubscript{5h}) showed enhanced 4f-4f transition probability based on the Laporte rule.\textsuperscript{[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\textsuperscript{III} and Tb\textsuperscript{III} complexes with a monacapped-octahedral structure (7-MCO).\textsuperscript{[21]} The 7-MCO structure is categorized as C\textsubscript{2}v symmetry, which is an asymmetrical structure compared with 8-SAP, 8-TDH, and 9-SAP structures. The Eu\textsuperscript{III} complex with a 7-MCO structure accordingly showed larger k\textsubscript{r} value than that with a 8-SAP structure. In terms of geometrical structure, representative seven-coordination polyhedron includes not only a 7-MCO structure but also monocapped-trigonalprismatic (7-MTCP, C\textsubscript{3}v) and pentagonal-bipiramidal structures (7-PBP, D\textsubscript{3h}) as shown in Figures 1a-c.\textsuperscript{[22]} Results of photophysical studies on seven-coordinate lanthanide complexes with 7-MCO, 7-MTCP, 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\textsuperscript{III} complexes composed of three \(\beta\)-diketonate ligands (tetrakis(dihydroxyethyl)pentanetionate: 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 (\([\text{Eu(tmh)}\textsubscript{3}(L-1)]\); Eu-1, \([\text{Eu(tmh)}\textsubscript{3}(L-2)]\); Eu-2, and \([\text{Eu(tmh)}\textsubscript{3}(L-3)]\); Eu-3). The geometrical structures of the prepared Eu\textsuperscript{III} complexes were characterized using single-crystal X-ray analysis and shape-measure calculation. Emission properties were evaluated using intrinsic emission quantum yield \(\Phi\text{r}\), total emission quantum yield \(\Phi\text{m}\), emission lifetime \(\tau\text{EM}\), and \(k\text{r}\).

In our experiments, we found that the \(k\text{r}\) value of Eu-1 with a 7-MCO (C\textsubscript{3}v) was larger than those of Eu-2 with a 7-MTCP structure (C\textsubscript{3}v) and Eu-3 with a 7-PBP structure (D\textsubscript{3h}), although the low-symmetrical coordination geometry are expected to give rise to large \(k\text{r}\) because of deviation from centrosymmetric geometry.\textsuperscript{[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.\textsuperscript{[24]} Recently, Hatanaka and Yabushita also reported that hypersensitive transition probability of lanthanide complexes was theoretically
affected by the ligand-to-metal charge transfer (LMCT) state.\textsuperscript{[25]} We here discuss enhancement of the $k_e$ value related to the characteristic LMCT state for the seven-coordinate Eu\textsuperscript{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\textsuperscript{III} complexes was demonstrated for the first time.

<table>
<thead>
<tr>
<th>Eu-1</th>
<th>Eu-2</th>
<th>Eu-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>chemical formula</td>
<td>$\text{C}_2\text{H}_7\text{EuO}_3\text{P}$</td>
<td>$\text{C}_2\text{H}_7\text{EuO}_3\text{P}$</td>
</tr>
<tr>
<td>crystal system</td>
<td>monoclinic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>space group</td>
<td>$P 2_1/n$</td>
<td>$P 2_12_12$</td>
</tr>
<tr>
<td>$a$ [Å]</td>
<td>11.2648(10)</td>
<td>16.6363(3)</td>
</tr>
<tr>
<td>$b$ [Å]</td>
<td>21.922(2)</td>
<td>17.9698(3)</td>
</tr>
<tr>
<td>$c$ [Å]</td>
<td>22.090(2)</td>
<td>18.5330(3)</td>
</tr>
<tr>
<td>$\beta$ [deg]</td>
<td>104.8796(17)</td>
<td>–</td>
</tr>
<tr>
<td>$V$ [Å$^3$]</td>
<td>5271.8(8)</td>
<td>5549.55(16)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$d_{calc}$ [g cm$^{-1}$]</td>
<td>1.252</td>
<td>1.223</td>
</tr>
<tr>
<td>$\mu$ (MoK$\alpha$) [cm$^{-1}$]</td>
<td>1.266</td>
<td>1.204</td>
</tr>
<tr>
<td>measured reflections</td>
<td>50489</td>
<td>73005</td>
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<tr>
<td>unique reflections</td>
<td>12107</td>
<td>12685</td>
</tr>
<tr>
<td>$R_{cr}^{[1]}$</td>
<td>0.0572</td>
<td>0.0245</td>
</tr>
<tr>
<td>$wR^{[2]}$</td>
<td>0.1346</td>
<td>0.1146</td>
</tr>
</tbody>
</table>

\[ R = \Sigma |F_0| - |F_c| / \Sigma |F_0|, \quad wR = \left[ \Sigma w(F_0^2 - F_c^2)^2 / \Sigma wF_0^2 \right]^{1/2}. \]

Based on the crystal structures, we calculated shape factor $S$ in order to determine the coordination geometrical structures around Eu\textsuperscript{III} ions.\textsuperscript{[25]} The $S$ value is given by

\[ S = \min \{ (1/m)\Sigma_1^m (\delta - \theta)^2 \}, \quad (1) \]

where $m$ is the number of possible edges ($m = 15$ in this study), $\delta$ is the observed dihedral angle between planes along the $i$th edge, and $\theta$ is the dihedral angle of the $i$th edge for the ideal structure. The estimated $S$ values of the Eu\textsuperscript{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.
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, 7F2 and 7F1 to 5D0, 5D2, 5D1, and 5D0. Emission bands were observed at 578, 592, 612, 653, and 700 nm, being attributed to 4f-4f transitions of Eu III ion (5D0 → 7F2). The emission spectra were normalized with respect to the spectral area of magnetic dipole transitions (5D0 → 7F1). The inset of Figure 3a shows the emission spectra of hypersensitive 5D0 → 7F2 transition of the complexes. The characteristic Stark splittings and spectral shapes of 5D0 → 7F2 transition are attributed to the coordination structures. The energy width of Stark splitting of 7F2 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 5D0 → 7F0-2 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 (τobs) were 0.50, 0.73, and 0.61 ms for Eu-1, Eu-2, and Eu-3, respectively. Emission quantum yields (Φff) excited at 532 nm (5D1 ← 7F0) and total emission quantum yields (Φtot) excited at 365 nm were measured using an integrating sphere unit. Radiative rate constants, kr = Φff/τobs.

The radiative process is affected by the LMCT states of the Eu III complexes. 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 π-π* and/or σ-π* transition of tmh ligands, which was confirmed by the absorption spectrum of [Gd(tmh)3(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).
The absorption band at 370 nm for TbIII complexes was not observed (Figure 4b). The other photophysical results of the TbIII complexes were shown in Figure S4. Considering absorption spectra of EuIII and TbIII complexes, the absorption bands around 370 nm are assumed to be LMCT band. In addition, absorption wavelength and oscillator strength of LMCT transition of EuIII complexes were estimated using TD-DFT calculation. (see supporting information, Tables S6-S8). Estimated excitations of σ→4f (Eu) and τ→4f (Eu) were clearly observed at UV region, which were categorized as LMCT absorption.

A schematic energy diagram of the seven-coordinate EuIII complexes is shown in Figure 5. An excited singlet state (S1) generally undergoes intersystem crossing to a low-lying excited triplet state (T1) due to large spin-orbit interaction of lanthanide complexes. The energy level of T1 (410 nm, ~24400 cm⁻¹) was also confirmed by a phosphorescence spectrum of [Gd2(tmh)₆] at 100 K (see supporting information, Figure S5). The T1 level is much higher than 5D0 emitting level. The large energy gap is expected to suppress back-energy transfer from 5D0 to LMCT state.[29] Therefore, the degree of back-energy transfer from 5D0 configuration to T1 state.[29] We herein considered that low Φel is affected by presence of LMCT state.

Temperature-dependent emission lifetimes of EuIII complexes were measured for investigation of photophysical interaction between 5D0 configuration and LMCT state (Figure 6a). The emission lifetimes of EuIII complexes decreased above 300 K, while we found that the emission lifetimes of EuIII complexes were constant in the range of 100-350 K (see supporting information, Figure S6). The decrease in emission lifetime of EuIII complexes should be due to state transition (charge transfer) from 5D0 excited state to LMCT state rather than vibrational relaxation (5D0→T₁) and back-energy transfer (5D0→T₁). In the temperature-dependent emission lifetime of the EuIII complexes, activation energy Eₐ and frequency factor A were estimated from Arrhenius plot of charge-transfer rate kₜ from 5D0 to LMCT state (Figure 6b, Table 3).

![Figure 4](47x291 to 291x617) Diffuse reflection spectra of a) the EuIII complexes and b) the TbIII complexes. Eu-1 and Tb-1 (black lines), Eu-2 and Tb-2 (blue lines) and Eu-3 and Tb-3 (red lines).

![Figure 5](305x626 to 548x758) Schematic energy diagram of the EuIII complexes

Table 3. Arrhenius parameters of charge-transfer process from 5D0 configuration to LMCT state and estimated wavelength and oscillator strength of LMCT absorption edge.

<table>
<thead>
<tr>
<th>complex</th>
<th>Eₐ [cm⁻¹]</th>
<th>A [s⁻¹]</th>
<th>λₕ [(CT)] [nm]</th>
<th>Pₜ [(CT)] [cm³/s]</th>
<th>(Eₐ)²Pₜ [cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu-1</td>
<td>3.5×10³</td>
<td>8.0×10⁴</td>
<td>392</td>
<td>0.0034</td>
<td>2.0×10⁻⁹</td>
</tr>
<tr>
<td>Eu-2</td>
<td>3.3×10³</td>
<td>1.3×10⁴</td>
<td>423</td>
<td>0.0005</td>
<td>3.8×10⁻¹⁰</td>
</tr>
<tr>
<td>Eu-3</td>
<td>3.9×10³</td>
<td>9.8×10⁴</td>
<td>394</td>
<td>0.0028</td>
<td>1.7×10⁻¹⁰</td>
</tr>
</tbody>
</table>


The values of Eₐ for Eu-1, Eu-2, and Eu-3 were found to be 3.5×10³, 3.3×10³, and 3.9×10³ cm⁻¹, respectively. The Eₐ is related to the charge transfer process from 5D0 to LMCT state. The Eₐ of Eu-2 was slightly smaller than those of Eu-1 and Eu-3. The A value of Eu-2 (1.3×10⁸ s⁻¹) was also smaller than those of Eu-1 (8.0×10⁸ s⁻¹) and Eu-3 (9.8×10⁸ s⁻¹). Since A includes electronic frequency νₑ, the value relates to electronic coupling of 5D₀ configuration with LMCT state.[30] Therefore, the degree of electronic coupling between 5D₀ 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 Pₜ involving perturbation of charge-transfer transition.[24] The equation is given by

$$Pₜ = a^2Eₐ(Eₐ)^{-1}P_{CT},$$

where Pₜ is oscillator strength and Eₐ 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 (Eₐ)²Pₜ term is proportional to the oscillator strength of 4f-4f transition. The values of Eₐ, Pₜ, and (Eₐ)²Pₜ 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 kₜ of Eu-1 was influenced by the large oscillator strength of LMCT absorption.
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 EuIII 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). $\ln(1/\tau_{obs})/T = \ln(k_{ct}) = \ln(A/Ey/kT)$.

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 ($C_{3v}$) 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 EuIII 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 hexahydrate (99.9%), and gadolinium chloride hexahydrate (99.9%) were purchased from Kanto Chemical Co., Inc. 2,2,6,6-Tetramethylheptane-3,5-dion (tmh), diphenyl(p-tolyl)phosphate, tri-p-tolyphosphine, and tri-m-tolyphosphine were obtained from Tokyo Kasei Organic Chemicals. Ammonia aqueous solution (28%) and H$_2$O$_2$ 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. $^1$H NMR (270 and 400 MHz) spectra were recorded on a JEOL EX270 and ECS400. Chemical shifts were reported in $\delta$ ppm, which is referenced to an internal tetramethylsilane (TMS) standard.

Syntheses of diphenyl(p-tolyl)phosphine oxide (L-1), tri-p-tolyphosphine oxide (L-2), and tri-m-tolyphosphine oxide (L-3): Diphenyl(p-tolyl)phosphine (1.93 g, 7.0 mmol), tri-p-tolyphosphine (2.13 g, 7.0 mmol), or tri-m-tolyphosphine (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$_2$O$_2$ 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-tolyphosphine oxide: L-2, and tri-m-tolyphosphine oxide: L-3): 7-MCO: Eu-1, Eu-2, and Eu-3. Eu-1: Yield 1.1 g (79%); $^1$H NMR (ATR) $\nu$=2861-2955 (m, C-H), 1570 (s, C=O), 1174 cm$^{-1}$ (s, P=O); elemental analysis calcd (%) for C$\text{62.68}$, H $\text{7.26}$: found C $\text{62.52}$, H $\text{7.26}$. Tb-1: IR (ATR) $\nu$=2860-2960, 1573 (s, C=O), 1175 cm$^{-1}$ (s, P=O); elemental analysis calcd (%) for C$\text{62.52}$, H $\text{7.26}$: found C $\text{62.68}$, H $\text{7.26}$. Gd-1: IR (ATR) $\nu$=2860-2960, 1573 (s, C=O), 1175 cm$^{-1}$ (s, P=O); elemental analysis calcd (%) for C$\text{62.68}$, H $\text{7.26}$: found C $\text{62.52}$, H $\text{7.26}$. Nb-1, Nb-2, and Nb-3: Nb-1: Yield 1.1 g (97%); 1H NMR (270 MHz, CDCl$_3$, 25 $^\circ$C): $\delta$=7.54-7.57 (d, 3H), 7.28-7.39 (m, 9H), 2.35 (s, 9H) ppm. Nb-2: Yield 2.19 g (97%); 1H NMR (270 MHz, CDCl$_3$, 25 $^\circ$C): $\delta$=7.50-7.57 (m, 6 H), 7.23-7.26 (m, 6 H), 2.40 (s, 9 H) ppm. Nb-3: Yield 2.18 g (97%); $^1$H NMR (400 MHz, CDCl$_3$, 25 $^\circ$C): $\delta$=7.54-7.75 (d, 3H), 7.28-7.39 (m, 9H), 2.35 (s, 9H) ppm.

Preparation of [Eu(tmh)$_3$(L-1)] (Eu-1), [Eu(tmh)$_3$(L-2)] (Eu-2), and [Eu(tmh)$_3$(L-3)] (Eu-3): The precursor complex, [Eu(tmh)$_3$(MeOH)$_2$], was synthesized as described in our previous report.$^{21}$ Europium chloride hexahydrate (1.0 g, 2.7 mmol), 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) was 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 ([Eu(tmh)$_3$(MeOH)$_2$]). The precursor complex [Eu(tmh)$_3$(MeOH)$_2$] (1.0 g, 1.4 mmol) and L-1 (0.41 g, 1.4 mmol) were dissolved with dichloromethane, and the solvent was evaporated to afford a white solid of titled compounds (Eu-1, [Eu(tmh)$_3$(L-1)]: Eu-1, [Eu(tmh)$_3$(L-2)]: Eu-2, and [Eu(tmh)$_3$(L-3)]: Eu-3). Eu-1: Yield 1.1 g (79%); IR (ATR) $\nu$=2861-2955 (m, C-H), 1570 (s, C=O), 1173 cm$^{-1}$ (s, P=O); elemental analysis calcd (%) for C$\text{62.66}$, H $\text{7.31}$: found C $\text{62.52}$, H $\text{7.26}$. Tb-1: IR (ATR) $\nu$=2860-2960, 1573 (s, C=O), 1176 cm$^{-1}$ (s, P=O); elemental analysis calcd (%) for C$\text{62.39}$, H $\text{7.45}$: found C $\text{62.52}$, H $\text{7.26}$. Tb-2: IR (ATR) $\nu$=2860-2960, 1573 (s, C=O), 1177 cm$^{-1}$ (s, P=O); elemental analysis calcd (%) for C$\text{62.83}$, H $\text{7.50}$: found C $\text{62.68}$, H $\text{7.31}$. Tb-3: IR (ATR) $\nu$=2860-2960 (m, C-H), 1572 (s, C=O), 1175 cm$^{-1}$ (s, P=O); elemental analysis calcd (%) for C$\text{62.17}$, H $\text{7.64}$: found C $\text{62.83}$, H $\text{7.31}$. Gd-1: IR (ATR) $\nu$=2860-2960 (m, C-H), 1573 (s, C=O), 1175 cm$^{-1}$ (s, P=O); elemental analysis calcd (%) for C$\text{56.06}$, H $\text{8.13}$: found C $\text{55.89}$, H $\text{8.15}$.

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$\alpha$ 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(tmm)6(MeOH)4]) 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 spectrophotometer (HORIBA Fluorolog-3). Emission quantum yields were obtained using a spectrophotometer (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 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 EuIII complexes were calculated using the AOMix program. [41-42] Mulliken charges of the EuIII 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


Seven-coordinate Lanthanide Complexes: Three types of coordination geometrical structures, monocapped-octahedron, monocapped-trigonal prism, and pentagonal-bipyramid were observed in EuIII complexes constructed by β-diketonate and phosphine oxide ligands. The characteristic photophysical properties involving LMCT perturbation are discussed.