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Author(s)	Yanagisawa, Kei; Nakanishi, Takayuki; Kitagawa, Yuichi et al.
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Seven-Coordinate Luminophores: Brilliant Luminescence of Lanthanide Complexes with C_{3v} Geometrical Structures

Kei Yanagisawa,^[b] Takayuki Nakanishi,^[a] Yuichi Kitagawa,^[a] Tomohiro Seki,^[a] Tomoko Akama,^[c] Masato Kobayashi,^[c] Tetsuya Taketsugu,^[c] Hajime Ito,^[a] Koji Fushimi,^[a] Yasuchika Hasegawa^{*[a]}

Abstract: Enhanced Luminescence properties of mononuclear lanthanide complexes with asymmetric seven-coordination structure are reported for the first time. The lanthanide complexes are composed of a lanthanide ion (Eu^{III} or Tb^{III}), three tetramethyl heptanedionatos and one triphenyl phosphine oxide. The coordination geometries of the lanthanide complexes are evaluated using single crystal X-ray analyses and shape-measurement calculations. The complexes are categorized to be seven-coordinate monocapped octahedral structure (point group: C_{3v}). The seven-coordinate lanthanide complexes show high intrinsic emission quantum yields, extra-large radiative rate constants and unexpected small non-radiative rate constants. The brilliant luminescence properties are elucidated in terms of the asymmetric coordination geometry and small vibrational quanta related to the thermal relaxation.

Introduction

Luminescent metal complexes have attracted considerable attention in the fields of inorganic chemistry, photophysics and materials science for photofunctional molecules for applications such as photocatalysts, display materials and a bio-imaging.^[1–3] A typical luminescent metal complex is composed of one metal ion and characteristic organic ligands in a three-dimensional structure. The three-dimensional geometries of coordination structures dominate their photochemical and photophysical properties. The coordination numbers of the metal complex are generally known to be even numbers (two, four and six for transition metal complexes, eight and ten for lanthanide complexes). Metal complexes with odd coordination numbers, in particular seven-coordination structures, have rarely been reported. Ahmed and Iftikhar predicted that asymmetric seven-coordinate lanthanide complexes have the potential to be strong luminescent materials.^[4] Eliseeva and co-workers have also reported the dinuclear lanthanide complexes with six oxygen atoms and one nitrogen atom.^[5] While seven-coordination may influence the orbit splitting of metals, multinuclear complexes have a difficulty for analyzing the physicochemical property in

detail. Zuo and co-workers studied on seven-coordinate lanthanide porphyrinate and phthalocyaninate complexes with tripodal phosphine oxide ligand for single-molecule magnet.^[6] The seven-coordination would be due to the steric hindrance of macrocyclic molecules. Based on such background, an investigation of a simple mononuclear lanthanide complex surrounded by seven oxygen atoms is expected lead to further understanding and development of coordination chemistry and photophysical science.

Lanthanide complexes with characteristic narrow emission bands and long emission lifetimes based on the $4f-4f$ transitions have been regarded as attractive luminescent materials for applications such as lasers, electroluminescence devices and bio-probes.^[7–9] Various types of luminescent lanthanide complexes have been reported to date.^[10–21] Lanthanide complexes with asymmetric coordination structures exhibit high emission quantum yields (Φ_{f}) and large radiative rate constants (k_{r}).^[22,23] Lanthanide complexes generally provide eight-coordinate square anti-prism structures that are categorized as D_{4d} in point group theory (8-SAP, Figure 1a). Recently, Hasegawa and co-workers have synthesized more asymmetric lanthanide complexes with eight-coordinate trigonal dodecahedron (8-TDH: D_{2d} , Figure 1b) and nine-coordinate monocapped square anti-prism (9-SAP: C_{4v} , Figure 1c) structures. k_{r} for the lanthanide complexes with 8-TDH and 9-SAP structures are larger than those of typical 8-SAP structures, based on the Laporte rule related to the transition probability.^[24,25] The ideal asymmetric lanthanide complex with a seven-coordination structure would construct a unique monocapped octahedron (7-MCO: C_{3v} , Figure 1d) or monocapped trigonal prism (7-MCTP: C_{2v} , Figure 1e), which would promote the enlargement of k_{r} and Φ_{f} .

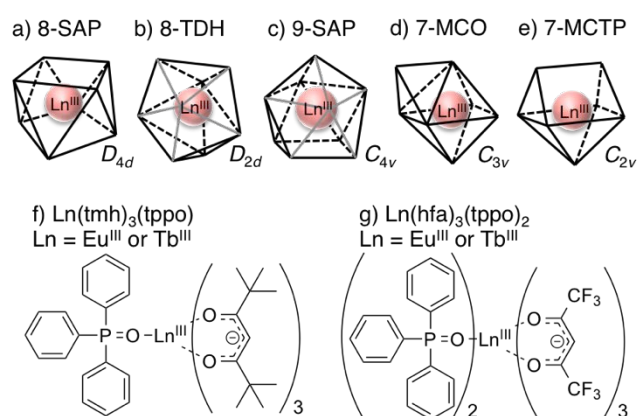


Figure 1. Ideal coordination geometrical structures of a) eight-coordinate square anti-prism, b) eight-coordinate trigonal dodecahedron, c) nine-coordinate monocapped square anti-prism, d) seven-coordinate monocapped octahedron and e) seven-coordinate monocapped trigonal prism. Chemical structures of f) $\text{Ln}(\text{tmh})_3(\text{tppo})$ with seven-coordination structure and g) $\text{Ln}(\text{hfa})_3(\text{tppo})_2$ with eight-coordinate structure.

[a] Dr. T. Nakanishi, Dr. Y. Kitagawa, Dr. T. Seki, Dr. Prof. H. Ito, Dr. Prof. K. Fushimi, Dr. Prof. Y. Hasegawa
Faculty of Engineering, Hokkaido University
Kita-13 Jo, Nishi-8 Chome, Sapporo, Hokkaido 060-8628 (Japan)
E-mail: hasegaway@eng.hokudai.ac.jp

[b] K. Yanagisawa
Graduate School of Chemical Sciences and Engineering,
Hokkaido University, Kita-13 Jo, Nishi-8 Chome, Sapporo, Hokkaido 060-8628 (Japan)

[c] Dr. T. Akama, Dr. Prof. M. Kobayashi, Dr. Prof. T. Taketsugu
Faculty of Science, Hokkaido University, Kita-10 Jo, Nishi-8 Chome, Sapporo, Hokkaido 060-0810 (Japan)
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In this study, we have attempted to synthesize mononuclear luminescent lanthanide complexes (Eu^{III} and Tb^{III} complexes) with characteristic seven-coordination structures. Three bidentate β -diketonato ligands with large steric hindrance, tetramethylheptanedionato (tmh; six-coordination) and monodentate triphenyl phosphine oxide (tpo; one-coordination) were introduced to construct the seven-coordination structure shown in Figure 1f. The geometrical structures of the prepared lanthanide complexes were characterized using single-crystal X-ray analyses and shape-measurement calculations. Based on the structural analyses, the formation of an ideal seven-coordination structure was successfully categorized as the C_{3v} group. The emission properties were evaluated using the **intrinsic emission quantum yields**, emission lifetimes, k_r and k_{nr} (non-radiative rate constant). The seven-coordinate lanthanide complexes exhibited an extra large k_r and an unexpectedly small k_{nr} , although *t*Bu groups in the tmh ligand promote non-radiative transitions via the vibrational frequency of C-H bonds.^[26] The small k_{nr} was explained using the spectral overlap between 4f-4f transitions of lanthanide ions and the harmonic overtones of the vibration frequencies of the organic ligands. This study provides significant results that are directly related to molecular science, photophysical chemistry and photonic device applications.

Results and Discussion

The seven-coordination lanthanide complexes were synthesized by the reaction of precursor Ln(tmh)₃(MeOH)₂ with tpo in methanol under reflux (Supporting information). Single crystals of the Ln(tmh)₃(tpo) were prepared by recrystallization from methanol solutions at room temperature. The crystal data obtained from single-crystal X-ray analyses is summarized in Table S1. The ORTEP views of Eu(tmh)₃(tpo) and Tb(tmh)₃(tpo) showed seven-coordinate structures, which were comprised of three tmh and one tpo ligands (Figure 2). The bond length between Eu and O atoms for Eu(tmh)₃(tpo) (average length_{Eu-O} = 2.338 Å) was shorter than that for previous reported Eu(hfa)₃(tpo)₂^[23] (average length_{Eu-O} = 2.415 Å, hfa: hexafluoroacetylacetonato, Figure 1g). We consider that Eu(tmh)₃(tpo) shows a tighter packing structure. In contrast, the carbonyl bond for Eu(tmh)₃(tpo) (average length_{C=O} = 1.27 Å) was longer than that for Eu(hfa)₃(tpo)₂ (average length_{C=O} = 1.25 Å). The longer C=O bond in tmh might be caused by electron-donation effect on *t*Bu group.

Based on the crystal data, the coordination geometry was calculated using the shape factor *S*, to estimate the degree of distortion of the coordination structure in the first coordination sphere.^[27] The *S* value is given by

$$S = \min \sqrt{\left(\frac{1}{m}\right) \sum_{i=1}^m (\delta_i - \theta_i)^2}, \quad (1)$$

where *m*, δ_i and θ_i are the number of possible edges (*m* = 15 in this study^[28]), the observed dihedral angle between planes along the *i*th edge and the dihedral angle for the ideal structure,

respectively. The estimated *S* values of lanthanide complexes were summarized in Tables S2 and S3. For Eu(tmh)₃(tpo), the *S* value calculated for a seven-coordinate monocapped octahedral structure (7-MCO, point group: C_{3v} , $S_{C_{3v}}$ = 7.6) was smaller than that for the seven-coordinate monocapped trigonal prismatic structure (7-MCTP, point group: C_{2v} , $S_{C_{2v}}$ = 13.8), which suggests that the coordination structure is closer to 7-MCO rather than 7-MCTP. As a result, the coordination geometry of Eu(tmh)₃(tpo) was determined to be distorted 7-MCO. Tb(tmh)₃(tpo) was also estimated as 7-MCO using a similar calculation ($S_{C_{3v}}$ = 8.8, $S_{C_{2v}}$ = 14.1). The characteristic structures of the lanthanide complexes are expected to provide larger k_r and higher Φ_{ff} .

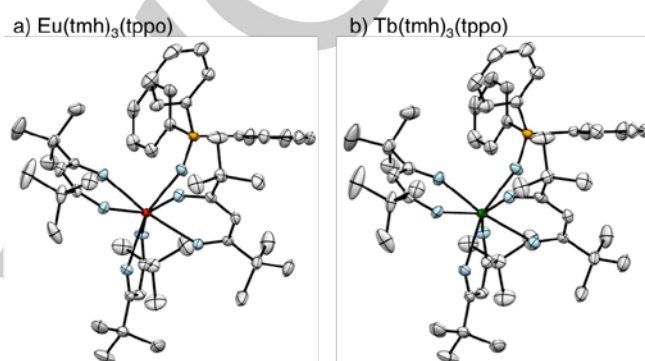


Figure 2. ORTEP drawings of a) Eu(tmh)₃(tpo) and b) Tb(tmh)₃(tpo). Hydrogen atoms were omitted for clarity. Thermal ellipsoids were shown at the 50% probability level.

Figure 3a shows the emission spectra of Eu(tmh)₃(tpo) and Eu(hfa)₃(tpo)₂ in the solid state. The spectra were normalized with respect to the magnetic dipole transition intensities at around 590 nm (⁵D₀-⁷F₁), which are insensitive to the surrounding environment of the lanthanide ions.^[29] The emission bands at around 615 nm were due to the hypersensitive transitions, which are strongly dependent on the coordination geometry.^[30] The Stark splitting structure of the electric dipole transition bands for Eu(tmh)₃(tpo) was critically

Table 1. Photophysical properties and point groups of the lanthanide complexes.

complex	$\tau_{\text{obs}}^{[a]}$ ms	$k_r^{[b]}$ /s ⁻¹	$k_{nr}^{[c]}$ /s ⁻¹	$\Phi_{ff}^{[d]}$ /%	point group
Eu(tmh) ₃ (tpo)	0.76	1.05×10^3	2.61×10^2	80	C_{3v}
Eu(hfa) ₃ (tpo) ₂	0.87	8.63×10^2	2.86×10^2	75	D_{4d}
Tb(tmh) ₃ (tpo)	0.84	1.04×10^3	1.49×10^2	88	C_{3v}
Tb(hfa) ₃ (tpo) ₂	0.12	1.02×10^3	7.31×10^3	12	D_{4d}

[a] Emission lifetimes (τ_{obs}) measured by excitation at 355 nm (Nd: YAG, third harmonics), [b] radiative rate constants (k_r) for Eu^{III} complexes estimated from $\frac{1}{\tau_{\text{obs}}} = A_{\text{MD}} n^3 \left(\frac{f_{\text{tot}}}{\tau_{\text{rad}}}\right)$ ^[31,32], [c] non-radiative rate constants $k_{nr} = \frac{1}{\tau_{\text{obs}}} - \frac{1}{\tau_{\text{rad}}}$ and [d] **The intrinsic emission yields** $\Phi_{ff} = \frac{k_r}{k_r + k_{nr}} = \frac{\tau_{\text{obs}}}{\tau_{\text{rad}}}$. The k_r of Tb complexes were calculated under the assumption that the emission lifetimes at 77 K were the radiative emission lifetime (τ_{rad}).^[33]

different from that for $\text{Eu}(\text{hfa})_3(\text{tppo})_2$. The relative spectral integration for $\text{Eu}(\text{tmh})_3(\text{tppo})$ was 1.7 times larger than that for the corresponding $\text{Eu}(\text{hfa})_3(\text{tppo})_2$. The large spectral integration for $\text{Eu}(\text{tmh})_3(\text{tppo})$ is based on the asymmetric coordination structure in solid state. The observation of intense $\text{Eu}({}^5\text{D}_0\text{--}{}^7\text{F}_2)$ transition (with respect to $\text{Eu}({}^5\text{D}_0\text{--}{}^7\text{F}_1)$) is the signature of the lack of center of inversion. Both 7-MCO and 8-SAP structures have no inversion center.

We also measured the emission spectrum of $\text{Eu}(\text{tmh})_3(\text{tppo})$ in methanol. The spectral shape is different from that in the solid state. The coordination structure of $\text{Eu}(\text{tmh})_3(\text{tppo})$ in methanol might be not the same as seven-coordinate C_{3v} structure. (The emission spectrum and the emission lifetime decay are shown in Figure S1 and S2, respectively. The luminescence properties of $\text{Eu}(\text{tmh})_3(\text{tppo})$ in methanol are summarized in Table S5.) The radiative rate constant of $\text{Eu}(\text{tmh})_3(\text{tppo})$ ($k_r = 0.7 \times 10^3$) is slightly larger than that of $\text{Eu}(\text{hfa})_3(\text{tppo})_2$ ($k_r = 0.5 \times 10^3$) in solution.^[25] The spectral shape of $\text{Eu}(\text{tmh})_3(\text{tppo})$ is also different from that of $\text{Eu}(\text{hfa})_3(\text{tppo})_2$ in solution. We consider that the geometrical structure of $\text{Eu}(\text{tmh})_3(\text{tppo})$ in solution might be pseudo-eight-coordinate structure.

The emission lifetime decay profiles of the Eu^{III} complexes are shown in Figure 3b. The emission lifetime (τ_{obs}) for $\text{Eu}(\text{tmh})_3(\text{tppo})$ is slightly shorter than that for $\text{Eu}(\text{hfa})_3(\text{tppo})_2$. Their τ_{obs} , k_r , k_{nr} , Φ_{f} and the point groups were summarized in Table 1. $\text{Eu}(\text{tmh})_3(\text{tppo})$ exhibited a high Φ_{f} of 80% due to the extra-large k_r ($1.05 \times 10^3 \text{ s}^{-1}$) and relatively small k_{nr} ($2.61 \times 10^2 \text{ s}^{-1}$). The Φ_{f} is as high as previous reported poly-enolates with Eu^{III} systems^[34–36].

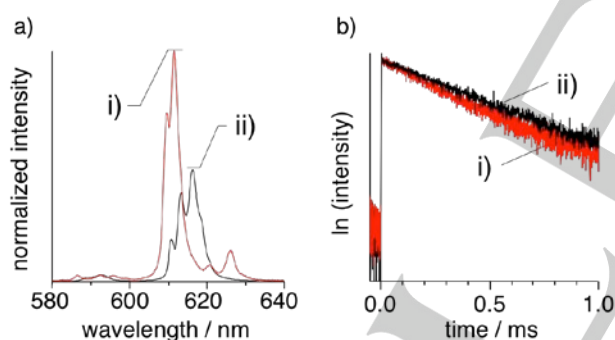


Figure 3. a) Emission spectra of i) $\text{Eu}(\text{tmh})_3(\text{tppo})$ and ii) $\text{Eu}(\text{hfa})_3(\text{tppo})_2$ in the solid state at room temperature exited at 350 nm. The spectra were normalized with respect to the magnetic dipole transition (${}^5\text{D}_0\text{--}{}^7\text{F}_1$). b) Emission lifetime decays of i) $\text{Eu}(\text{tmh})_3(\text{tppo})$ and ii) $\text{Eu}(\text{hfa})_3(\text{tppo})_2$ in the solid state at room temperature exited at 355 nm (third harmonics of a Q-switched Nd-YAG laser: fwhm = 5 ns, λ = 1064 nm).

The emission spectra and emission lifetime decays of Tb^{III} complexes are shown in Figure 4. The stark splitting of the spectrum of $\text{Tb}(\text{tmh})_3(\text{tppo})$ was also clearly distinguishable from that of $\text{Tb}(\text{hfa})_3(\text{tppo})_2$. The k_r and Φ_{f} of Tb^{III} complexes were calculated under the assumption that the emission lifetimes at 77 K (Figure 4b and 4c) were the radiative emission lifetime (τ_{rad}).^[33] $\text{Tb}(\text{tmh})_3(\text{tppo})$ also exhibited a high Φ_{f} of 88%, a large k_r ($1.04 \times 10^3 \text{ s}^{-1}$) and a small k_{nr} ($1.49 \times 10^2 \text{ s}^{-1}$). Hasegawa et al.

have reported that the energy gaps between the emitting level of the terbium ion and the excited triplet state of the hfa ligand in $\text{Tb}(\text{hfa})_3(\text{tppo})_2$ were 1700 cm^{-1} .^[37] The back energy transfer from lanthanide ion to the ligands is enhanced when the energy gap is less than 1850 cm^{-1} .^[38] Therefore, the combination of Tb^{III} with hfa ligand is expected to enhance back energy transfer, resulting in low intrinsic emission quantum yield at room temperature.

In order to determine the energy of the triplet state of tmh ligand, the emission spectrum of the $\text{Gd}(\text{tmh})_3(\text{tppo})$ was measured. Figure 5 presented broad peak with maxima at around 410 nm (24390 cm^{-1}), which would be the phosphorescence of tmh ligand. Since the energy gap of Tb^{III} and the triplet state energy of the ligand is about 3500 cm^{-1} , the back energy transfer would be suppressed substantially, resulting in the small k_{nr} of $\text{Tb}(\text{tmh})_3(\text{tppo})$.

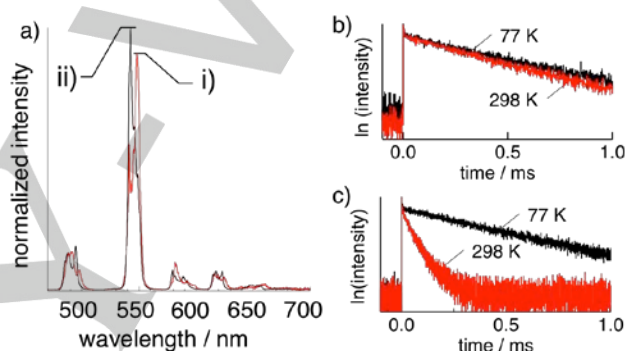


Figure 4. a) Emission spectra of i) $\text{Tb}(\text{tmh})_3(\text{tppo})$ and ii) $\text{Tb}(\text{hfa})_3(\text{tppo})_2$ in the solid state at room temperature exited at 350 nm. The spectra were normalized with respect to the spectral integration area at ${}^5\text{D}_4\text{--}{}^7\text{F}_6$ transitions. b) Emission lifetime decays of b) $\text{Tb}(\text{tmh})_3(\text{tppo})$ and c) $\text{Tb}(\text{hfa})_3(\text{tppo})_2$ in the solid state at 77 K and 298 K exited at 355 nm.

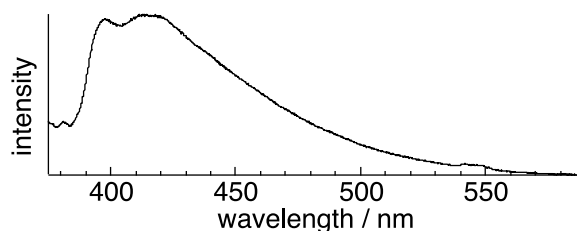


Figure 5. Emission spectrum of $\text{Gd}(\text{tmh})_3(\text{tppo})$ in the solid state at 77 K, which presents the phosphorescence of organic ligands.

The $\text{Ln}(\text{tmh})_3(\text{tppo})$ exhibited small k_{nr} values, although the *t*Bu groups in the complexes are composed of high-vibrational frequency C-H bonds (2950 cm^{-1}).^[25] High-vibrational C-H bonds generally promote effective thermal relaxation from the excited state of lanthanide complexes.^[39] We have suggested that introducing low-vibrational frequency group such as C-F (1200 cm^{-1}) instead of C-H was available for suppression of the thermal quenching like $\text{Eu}(\text{hfa})_3(\text{tppo})_2$. In order to analyze the effect of the vibrational frequency of the ligands, the spectral

overlap between the energy gap of 4*f*-4*f* transitions and the vibrational harmonics was estimated from IR measurements and calculations. Pecoraro et al. reported that one of the important parameters to suppress vibrational relaxation was the distance between the lanthanide ion and the highly oscillated functional groups.^[40] We have focused on the carbonyl group, which is the closest group to the lanthanide ion. The IR spectra of carbonyl groups for Eu(tmh)₃(tppo) and Eu(hfa)₃(tppo)₂ are shown in Figure 6a. The vibrational frequency of carbonyl groups for Eu(tmh)₃(tppo) ($\tilde{\nu}_{C=O} = 1573 \text{ cm}^{-1}$) was smaller than that for Eu(hfa)₃(tppo)₂ ($\tilde{\nu}_{C=O} = 1654 \text{ cm}^{-1}$).

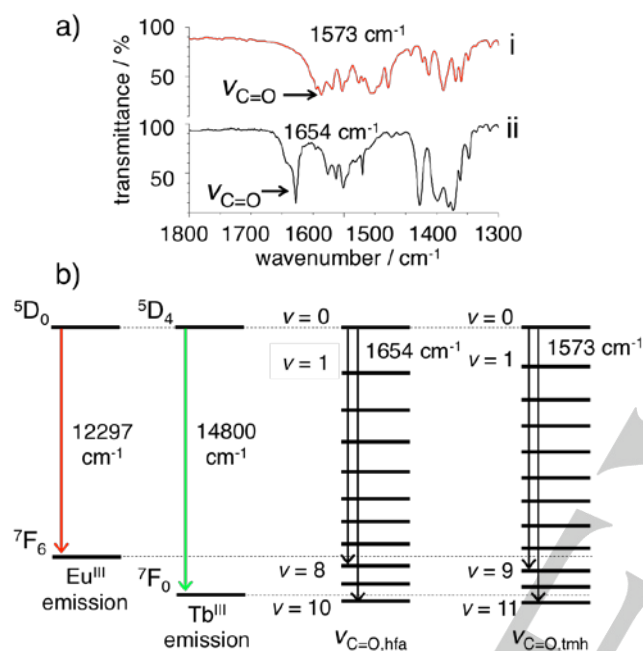


Figure 6. a) IR spectra of i) Eu(tmh)₃(tppo) and ii) Eu(hfa)₃(tppo)₂. The vibrational wavenumber of carbonyl stretching frequency were marked (1573 cm⁻¹: Eu(tmh)₃(tppo) and 1654 cm⁻¹: Eu(hfa)₃(tppo)₂). b) Schematic diagram of energy of Eu^{III}, Tb^{III} and vibrational harmonic overtones of carbonyl groups in tmh and hfa ligands.

The vibrational frequencies of coordinated carbonyl groups in the Eu^{III} complexes were also estimated from density functional theory (DFT) calculations at the B3LYP-D3 level with the Stuttgart RECP basis set for Eu and cc-pVDZ for the other atoms. The results indicated that the vibrational frequency of the carbonyl stretching for Eu(tmh)₃(tppo) and Eu(hfa)₃(tppo)₂ were 1548-1554 and 1633 cm⁻¹, respectively (see Table S4, supporting information). The vibrational frequencies of the coordination sites were supported by DFT calculations with the lanthanide ions. The vibrational transition probability is proportional to the Franck-Condon factor, i.e., the overlap integrals between the energy gap of 4*f*-4*f* transitions and the vibrational harmonics of organic ligands. The Franck-Condon factor decreases with an increase in vibrational quanta ν , which is the harmonic number matched with the energy gap of the

lanthanide ion.^[41] The energy gaps of Eu^{III} (⁵D₀-⁷F₆) and Tb^{III} (⁵D₄-⁷F₀) have been reported to be 12297 and 14800 cm⁻¹, respectively.^[42] The ν was estimated by the following equation including anharmonic constant ($x_e = 6.5 \times 10^{-3}$).^[43]

$$\Delta G_{\nu+\frac{1}{2}} = \tilde{\nu} - 2(\nu+1)x_e\tilde{\nu} + \dots, \quad (2)$$

where G , $\tilde{\nu}$ are vibrational energy and vibrational frequency, respectively. ν for Eu(tmh)₃(tppo) and Eu(hfa)₃(tppo)₂ were calculated to be 9 and 8, respectively (Figure 4b). The Franck-Condon factor estimated for Eu(hfa)₃(tppo)₂ (8-SAP: D_{4d}) is nine times larger than that for Eu(tmh)₃(tppo) (7-MCO: C_{3v}). The Franck-Condon factor for Tb(tmh)₃(tppo) ($\nu = 11$) was also estimated to be eleven times larger than that for Tb(tmh)₃(tppo)₂ ($\nu = 10$). From these calculations, it was concluded that the vibrational relaxation in Ln(tmh)₃(tppo) would be effectively suppressed because of the small vibrational quanta of the carbonyl groups, which would result in a small k_{nr} constant.

Conclusions

In summary, we have successfully synthesized novel lanthanide complexes with characteristic seven-coordinate geometrical structures. This is the first reported mononuclear luminescent complex surrounded by seven oxygen atoms. The ideal seven-coordinate structure is useful for comparison with the previous eight-coordinate structure as a strong luminescent material. The lanthanide complexes exhibited extra large radiative rate constants due to their asymmetric coordination geometries. It was experimentally revealed that the asymmetric seven-coordinate geometry enhances the luminescence properties by the large k_r and small k_{nr} constants. We have also proposed that the vibrational frequency of carbonyl groups is effective for thermal relaxation, and IR spectra calculations of the carbonyl groups for Eu^{III} complexes supported the experimental results. The photophysical results reported here should contribute to the design of lanthanide complexes with remarkable luminescence properties.

Werts and co-workers have shown the chemical structure of seven-coordinate Mk-EuFOD complex (FOD: 1,1,1,2,2-pentafluoro-6,6-dimethylheptane-3,5-dione, Mk: Michler's ketone, bis(4-(dimethylamino)phenyl)methanone) without single-crystal X-ray analysis. In contrast, We insisted on the importance of direct seven-coordinate crystal structure and their photophysical property based on the X-ray analysis of Ln(tmh)₃(tppo). Various type of lanthanide complexes with photosensitized ligand have been reported.^[44-48] Tb(tmh)₃(tppo) exhibited excitation peak in UV region (Figure S3). Luminescent seven-coordinate Eu^{III} complex excited at around 450 nm (visible region) may be ideal phosphor for applications such as LEDs, biomarkers, and chemical sensing devices. Recently, Marta and co-workers reported similar system of lanthanide complex.^[49] We hope all seven-coordinate complexes would give large k_r . In the future, other seven-coordinate complexes could be synthesized and the photophysical properties will be revealed. Seven-coordinate lanthanide complexes have the potential to break

new ground in the fields of photophysical, coordination and materials chemistry.

Experimental Section

Materials:

Europium chloride hexahydrate (99.9%), terbium chloride pentahydrate (99.9%) were purchased from Kanto Chemical Co., Inc. 2,2,6,6-tetramethylheptane-3,5-dione and triphenyl phosphine oxide were obtained from Tokyo Kasei Organic Chemicals. Europium acetate monohydrate (99.9%), terbium acetate tetrahydrate (99.9%) and ammonia 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:

Infrared spectra were recorded with a JASCO FTIR-420 spectrometer. Elemental analyses were performed with an Exeter Analytical CE440. Mass spectra were measured using Thermo Scientific Exactive.

Preparation of Ln(tmh)₃(MeOH):

Europium chloride hexahydrate (1.0 g, 2.7 mmol) or Terbium chloride pentahydrate (1.0 g, 2.4 mmol) was dissolved in distilled water (5 mL) in a 100 mL flask. A solution of 2,2,6,6-tetramethylheptane-3,5-dione: tmh (1.46 g, 8.1 mmol for Eu^{III} complex or 1.32 g, 7.2 mmol for Tb^{III} complex) was added to the solution with ethanol (20 mL). Ammonia solution was added dropwise to the solution until pH 7, approximately. After stirring for 3 h at room temperature, the reaction mixture was reprecipitated by cold water. The produced precipitation was filtered, and resulting powder was recrystallized from methanol to afford colorless block crystals of the titled compound. Yield: 2.07 g (99%).

Preparation of Ln(tmh)₃(tppo):

Triphenyl phosphine oxide (0.4 g, 1.4 mmol) and Ln(tmh)₃(MeOH)₂ (1.0 g, 1.4 mmol) were dissolved in methanol (30 mL). The solution was heated at reflux while stirring for 12 h. The reaction mixture was recrystallized in methanol. Recrystallization gave colorless rod-shaped crystals of the lanthanide complexes. Yield: 1.1 g (84%); IR (KBr) : $\tilde{\nu}$ = 1573 (st, C=O), 1138 cm⁻¹ (st, P=O); ESI-MS: *m/z*: calcd for C₅₁H₇₂EuO₇P [M+H]⁺: 981.42; found: 981.41, calcd for C₅₁H₇₂O₇PTb [M+H]⁺: 987.42; found: 987.43; elemental analysis calcd (%) for C₅₁H₇₂EuO₇P: C 62.50, H 7.41; found: C 62.56, H 7.32; calcd (%) for C₅₁H₇₂O₇PTb: C 62.06, H 7.35; found: C 62.11, H 7.31.

Crystallography:

Colorless single crystals of the lanthanide complexes were mounted on a MiTeGen micromesh using paraffin oil. All measurements were made using a Rigaku RAXIS RAPID imaging plate area detector with graphite – monochromated MoK α radiation. Non-hydrogen atoms were refined anisotropically. All calculation was performed using the crystal-structure crystallographic software package. CIF data was confirmed by using the checkCIF/PLATON service. CCDC-1400251 for Eu(tmh)₃(tppo) and CCDC-1400286 for Tb(tmh)₃(tppo) 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 lanthanide complexes were measured with a HORIBA Fluorolog-3 spectrofluorometer and corrected for the response of the detector system. The emission quantum yields were obtained using JASCO F-6300-H spectrometer attached with JASCO ILF-53 integrating sphere unit. The wavelength dependence 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 (τ_{obs}) 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 the single-pulse excitation. Emission lifetimes were determined from the slope of logarithmic plots of the decay profiles.

Computational details:

All calculations were performed with the GAUSSIAN 09 program.^[50] The structure of the seven- and eight-coordinate Eu^{III} complexes, Eu(tmh)₃(tppo) and Eu(hfa)₃(tppo)₂, were optimized in the gas phase at the B3LYP-D3^[51,52] level with the Stuttgart RECP^[53] and cc-pVDZ^[54] basis sets for Eu and the other atoms, respectively. Then, the normal mode analysis of each molecule at the optimized structure was executed at the same level to obtain vibrational frequencies and IR intensities. The vibrational frequencies were corrected with the scaling factor of 0.9614, which was reported as the optimal value for the B3LYP functional.^[55]

Acknowledgements

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Keywords: lanthanides • luminescence • O ligands • structural analysis • DFT calculation

- [1] T. Stoll, M. Gennari, J. Fortage, C. E. Castillo, M. Rebarz, M. Sliwa, M.-N. Collomb, *Angew. Chem. Int. Ed.* **2014**, 53, 1654-1658.
- [2] K. M.-C. Wong, M. M.-Y. Chan, V. W.-W. Yam, *Adv. Mater.* **2014**, 26, 5558-5568.
- [3] C. Li, M. Yu, Y. Sun, Y. Wu, C. Huang, F. Li, *J. Am. Chem. Soc.* **2011**, 133, 11231-11239.
- [4] Z. Ahmed, K. Iftikhar, *J. Phys. Chem. A* **2013**, 117, 11183-11201.
- [5] S. V. Eliseeva, O. X. Kotova, F. Gumy, S. N. Semenov, V. G. Kessler, L. S. Lepnev, J.-C. G. Bünzli, N. P. Kuzmina, *J. Phys. Chem. A* **2008**, 112, 3614-3626.
- [6] a) F. Gao, M.-X. Yao, Y.-Y. Li, Y. Song, J.-L. Zuo, *Inorg. Chem.* **2013**, 52, 6407-6416; b) F. Gao, L. Cui, W. Liu, L. Hu, Y.-W. Zhong, Y.-Z. Li, J.-L. Zuo, *Inorg. Chem.* **2013**, 52, 11164-11172.
- [7] K. Kuriki, Y. Koike, Y. Okamoto, *Chem. Rev.* **2002**, 102, 2347-2356.
- [8] X.-L. Zheng, Y. Liu, M. Pan, X.-Q. Lu, J.-Y. Zhang, C.-Y. Zhao, Y.-X. Tong, C.-Y. Su, *Angew. Chem. Int. Ed.* **2007**, 46, 7399-7403.
- [9] B. McMahon, P. Mauer, C. P. McCoy, T. C. Lee, T. Gunnlaugsson, *J. Am. Chem. Soc.* **2009**, 131, 17542-17543.

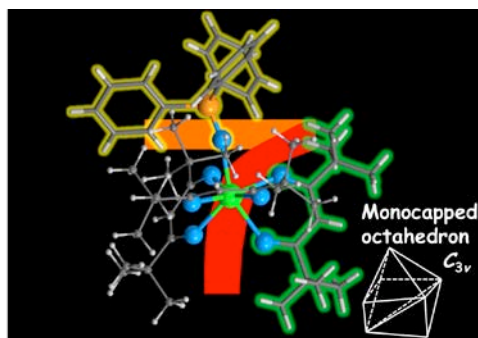
- [10] A. de Battencourt-Dias, P. S. Barber, S. Bauer, *J. Am. Chem. Soc.* **2012**, *134*, 6987-6994.
- [11] K. Goossens, D. W. Bruce, R. V. Deun, K. Binnemans, T. Cardinaels, *Dalton Trans.* **2012**, *41*, 13271-13273.
- [12] S. J. Bulter, B. K. McMahon, R. Pal, D. Parker, J. W. Walton, *Chem. Eur. J.* **2013**, *19*, 9511-9517.
- [13] O. Kotova, J. A. Kitchen, C. Lincheneau, R. D. Peacock, T. Gunnlaugsson, *Chem. Eur. J.* **2013**, *19*, 16181-16186.
- [14] E. R. Trivedi, S. V. Eliseeva, J. Jankolovits, M. M. Olmstead, S. Petoud, V. L. Pecoraro, *J. Am. Chem. Soc.* **2014**, *136*, 1526-1534.
- [15] A. Foucault-Collet, C. M. Shade, I. Nazarenko, S. Petoud, S. V. Eliseeva, *Angew. Chem. Int. Ed.* **2014**, *53*, 2927-2930.
- [16] J. I. Pacold, D. S. Tatum, G. T. Seidler, K. N. Raymond, X. Zhang, A. B. Strickrath, D. R. Mortensen, *J. Am. Chem. Soc.* **2014**, *136*, 4186-4191.
- [17] X.-S. Ke, B.-Y. Yang, X. Cheng, S. L.-F. Chan, J.-L. Zhang, *Chem. Eur. J.* **2014**, *20*, 4324-4333.
- [18] A. F. Martins, S. V. Eliseeva, H. F. Carvalho, J. M. C. Teixeira, C. T. B. Paula, P. Herann, C. Platas-Iglesias, S. Petoud, E. Toth, C. G. C. Geraldes, *Chem. Eur. J.* **2014**, *20*, 14834-14845.
- [19] Z. Liao, M. Tropicano, K. Mantulinikovs, S. Faulkner, T. Vosch, T. J. Sørensen, *Chem. Commun.* **2015**, *51*, 2372-2375.
- [20] H. Ito, S. Shinoda, *Chem. Commun.* **2015**, *21*, 3882-3885.
- [21] D. Ananias, F. A. A. Paz, D. S. Yufit, L. D. Carlos, J. Rocha, *J. Am. Chem. Soc.* **2015**, *137*, 3051-3058.
- [22] N. B. D. Lima, S. M. C. Goncalves, S. A. Junior, A. M. Simas, *Sci. Rep.* **2013**, *3*, 2395-2402.
- [23] Y. Hasegawa, M. Yamamuro, Y. Wada, N. Kanehisa, Y. Kai, S. Yanagida, *J. Phys. Chem. A* **2003**, *107*, 1697-1702.
- [24] K. Miyata, T. Nakagawa, R. Kawakami, Y. Kita, K. Sugimoto, T. Nakashima, T. Harada, T. Kawai, Y. Hasegawa, *Chem. Eur. J.* **2011**, *17*, 521-528.
- [25] K. Miyata, Y. Hasegawa, Y. Kuramochi, T. Nakagawa, T. Yokoo, T. Kawai, *Eur. J. Inorg. Chem.* **2009**, *32*, 4777-4785.
- [26] Y. Hasegawa, Y. Kimura, K. Murakoshi, Y. Wada, J.-H. Kim, N. Nakashima, T. Yamanaka, S. Yanagida, *J. Phys. Chem.* **1996**, *100*, 10201-10205.
- [27] J. D. Xu, E. Radkov, M. Ziegler, K. N. Raymond, *Inorg. Chem.* **2000**, *39*, 4156-4164.
- [28] I. Baxter, S. R. Drake, M. B. Hursthouse, K. M. A. Malik, J. McAleese, D. J. Otway, J. C. Plakatouras, *Inorg. Chem.* **1995**, *34*, 1384-1394.
- [29] C. Görrler-Walrand, L. Fluyt, A. Ceulemans, W. T. Carnall, *J. Chem. Phys.* **1991**, *95*, 3099-3106.
- [30] K. Nakamura, Y. Hasegawa, Y. Wada, S. Yanagida, *Chem. Phys. Lett.* **2004**, *398*, 500-504.
- [31] L. Prodi, M. Maestri, R. Ziessel, V. Balzani, *Inorg. Chem.* **1991**, *30*, 3798-3802.
- [32] M. H. V. Werts, R. T. F. Jukes, J. W. Verhoeven, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1542-1548.
- [33] R. Pavithran, N. S. S. Kumar, S. Biju, M. L. P. Reddy, S. A. Junior, R. O. Freire, *Inorg. Chem.* **2006**, *45*, 2184-2192.
- [34] R. O. Freire, R. Q. Albuquerque, S. A. Junior, G. B. Rocha, M. E. Mesquita, *Chem. Phys. Lett.* **2005**, *405*, 123-126.
- [35] J. D. L. Dutra, I. F. Gimenez, N. B. da Costa Junior, O. Freire, J. Photochem. Photobiol. A: Chem. **2011**, *217*, 389-394.
- [36] S. Biju, R. O. Freire, Y. K. Eom, R. Scopelliti, J.-C. G. Bünzli, H. K. Kim, *Inorg. Chem.* **2014**, *53*, 8407-8417.
- [37] K. Miyata, Y. Konno, T. Nakanishi, A. Kobayashi, M. Kato, K. Fushimi, Y. Hasegawa, *Angew. Chem. Int. Ed.* **2013**, *52*, 6413-6416.
- [38] S. Sato, M. Wada, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1955.
- [39] Y. Haas, G. Stein, E. Wurzberg, *J. Chem. Phys.* **1974**, *60*, 258-263.
- [40] J. Jankolovits, C. M. Andolina, J. W. Kampf, K. N. Raymond, V. L. Pecoraro, *Angew. Chem. Int. Ed.* **2011**, *50*, 9660-9664.
- [41] Y. Hasegawa, K. Murakoshi, Y. Wada, S. Yanagida, J.-H. Kim, N. Nakashima, T. Yamanaka, *Chem. Phys. Lett.* **1996**, *248*, 8-12.
- [42] W. T. Carnall, P. R. Fields, K. Rajnak, *J. Chem. Phys.* **1968**, *49*, 4450-4455.
- [43] H. W. Siesler, Y. Ozaki, S. Kawata, H. M. Heise, *Near-Infrared Spectroscopy: Principles, Instruments, Applications*, **2008**, John Wiley & Sons, p. 16.
- [44] M. D. McGehee, T. Bergstedt, C. Zhang, A. P. Saab, M. B. O'Regan, G. C. Bazan, V. I. Srdanov, A. J. Heeger, *Adv. Mater.* **1999**, *11*, 1349-1354.
- [45] A. Dogariu, R. Gupta, A. J. Heeger, H. Wang, *Synth. Met.* **1999**, *100*, 95-100.
- [46] T.S. Kang, B.S. Harrison, M. Bouguettaya, T.J. Foley, J.M. Boncella, K.S. Schanze, J.R. Reynolds, *Adv. Funct. Mater.* **2003**, *13*, 205-210.
- [47] V. Divya, R. O. Freire, M. L. P. Reddy, *Dalton Trans.* **2011**, *40*, 3257-3268.
- [48] P. Martin-Ramos, I. R. Martin, F. Lohoz, S. Hernandez-Navarro, P. S. Pereira da Silva, I. Hernandez, V. Lavin, M. Ramos Silva, *J. Alloys Compd.* **2015**, *619*, 553-559.
- [49] Y. C. Miranda, L. L. A. L. Pereira, J. H. P. Barbosa, H. F. Brito, M. C. F. C. Felinto, O. L. Malta, W. M. Faustino, E. E. S. Teotonio, *Eur. J. Inorg. Chem.* **2015**, *18*, 3019-3027.
- [50] Gaussian 09, Revision D.01, M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, 2009.
- [51] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.
- [52] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
- [53] M. Dolg, H. Stoll, H. Preuss, and R. M. Pitzer, *J. Phys. Chem.* **1993**, *97*, 5852.
- [54] T. H. Dunning, Jr., *J. Chem. Phys.* **1989**, *90*, 1007; D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **1993**, *98*, 1358.
- [55] A. P. Scott and L. Radom, *J. Phys. Chem.* **1996**, *100*, 16502.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

This work reported that lanthanide complexes with seven-coordination showed brilliant luminescence properties due to the asymmetric geometrical structure. The complexes exhibited extra-large radiative rate constants and unexpected small non-radiative rate constants.



*Kei Yanagisawa, Takayuki Nakanishi, Yuichi Kitagawa, Tomohiro Seki, Tomoko Akama, Masato Kobayashi, Tetsuya Taketsugu, Hajime Ito, Koji Fushimi, Yasuchika Hasegawa**

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Seven-Coordinate Luminophores: Brilliant Luminescence of Lanthanide Complexes with Asymmetric C_{3v} Structures