Hyper-stable organo-Eu\textsuperscript{III} luminophore under high temperature for photo-industrial application

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Novel organo-Eu\textsuperscript{III} luminophores, Eu(hfa)\textsubscript{x}(CPO)\textsubscript{y} and Eu(hfa)\textsubscript{x}(TCPO)\textsubscript{y} (hfa: hexafluoroacetylacetonate, CPO: 4-carboxyphenyl diphenyl phosphine oxide, TCPO: 4,4′,4″-tricarboxyphenyl phosphine oxide), were synthesized by the complexation of Eu\textsuperscript{III} ions with hfa moieties and CPO or TCPO ligands. The thermal and luminescent stabilities of the luminophores are extremely high. The decomposition temperature of Eu(hfa)\textsubscript{x}(CPO)\textsubscript{y} and Eu(hfa)\textsubscript{x}(TCPO)\textsubscript{y} were determined as 200 and 450 °C, respectively. The luminescence of Eu(hfa)\textsubscript{x}(TCPO)\textsubscript{y} under UV light irradiation was observed even at a high temperature, 400 °C. The luminescent properties of Eu(hfa)\textsubscript{x}(CPO)\textsubscript{y} and Eu(hfa)\textsubscript{x}(TCPO)\textsubscript{y} were estimated from emission spectra, quantum yields and lifetime measurements. The energy transfer efficiency from hfa moieties to Eu\textsuperscript{III} ions in Eu(hfa)\textsubscript{x}(TCPO)\textsubscript{y} was 59%. The photosensitized luminescence of hyper-stable Eu(hfa)\textsubscript{x}(TCPO)\textsubscript{y} at 400 °C is demonstrated for future photonic applications.

There has been significant interest in the development of luminescent lanthanide materials for use in devices such as fluorescent lamps\textsuperscript{1–3}, LED lights\textsuperscript{4–11} and displays\textsuperscript{10–13}. Recently, we have focused on organo lanthanide luminophores with strong luminescent properties for a future energy saving measures\textsuperscript{14}. The organo lanthanide luminophores are attached with aromatic antenna for high photon absorption efficiency. The general organic luminophores are decomposed under 200 °C unfortunately. In the case of industrial applications of organic devices using luminescent lanthanide materials, thermostability is required for effective material production process and long term durability. This manuscript describes new organo lanthanide luminophores with thermostability and strong luminescent properties using a photosensitized effect. The organo lanthanide luminophore at 400 °C is inconceivable material, which is put on a characteristics of solid ceramics and smart molecules.

There are currently various types of organo lanthanide luminophores based on characteristic ligand design that have been developed as strongly luminescent materials\textsuperscript{14–35}. A three-dimensional networks composed of organo lanthanide luminophores, which prevent stretching vibration and rotations of organic ligands, leads to a thermostable structure. Du and coworkers have synthesized a three-dimensional lanthanide compound with 1,3-benzenedicarboxylic acid for the construction of a thermostable structure\textsuperscript{36}. Hong and coworkers have demonstrated that a three-dimensional lanthanide metal-organic framework (MOF) composed of lanthanide ions (Ln\textsuperscript{III} = Nd, Sm, Eu, Gd) and tris-(4-carboxyphenyl)phosphine oxide has a high decomposition temperature (500 °C)\textsuperscript{37}. However, the benzene-typed joint ligands do not promote effective photosensitization in organo-Eu\textsuperscript{III} luminophores (η < 1%). Thermostable lanthanide luminophores with effective photosensitization are expected to open up a new field of luminescent material science. We have attempted to prepare an organo lanthanide material with high thermostability and effective photosensitized luminescence. In this study, novel organo-Eu\textsuperscript{III} luminophores with hfa moieties (hfa: hexafluoroacetylacetonato) and carboxy phosphate oxide (CPO: 4-carboxyphenyl diphenyl phosphine oxide/TCPO: 4,4′,4″-tricarboxyphenyl phosphine oxide) are reported, the structures of which are shown in Fig. 1. The hfa moieties act as photosensitization ligands in organo-Eu\textsuperscript{III} luminophores and play an important role in the suppression of non-radiative transition via vibrational relaxation due to their lower vibrational frequencies\textsuperscript{38}. Coordination of the phosphine oxide parts in CPO and TCPO as three-dimensional joint ligands provides a low-vibrational frequency for strong luminescence. The CPO and TCPO ligands are also
designed to include carboxy groups for construction of the thermostable Ln-MOF structure reported by Hong and coworkers. A mononuclear EuIII complex, Eu(hfa)₃(TPPO)₂ (TPPO: triphenylphosphine oxide) was prepared as a standard reference. The thermostability of the organo-EuIII luminophores was evaluated using thermogravimetric analysis (TGA). The luminescent properties were estimated from emission spectra, quantum yields and lifetime measurements. The bright luminescence of Eu(hfa)₃(TCPO)₂ at 400 °C was successfully observed and the energy transfer efficiency of Eu(hfa)₃(TCPO)₂ was calculated to be 47%. Thus, thermostable and effective photosensitized organo-EuIII luminophores were demonstrated for the first time.

**Results and Discussion**

**Thermostable Properties.** In previous work, EuIII luminophore with carboxy phosphine oxide have been reported. The material has no photosensitized hfa moiety. Eu(hfa)₃(TCPO)₂ and Eu(hfa)₃(CPO)₂ were synthesized by the complexation of the carboxy phosphine oxide (CPO or TCPO) with Eu(hfa)₃(H₂O)₂ in methanol under reflux. The phosphine oxide parts (P=O) and the carboxy groups (COO⁻) in CPO and TCPO ligands effectively promote the formation of polymeric structures. The significant vibrational bands at C=O and P=O groups of Eu(hfa)₃(CPO)₂ were shifted to shorter wavenumbers (1658 and 1143 cm⁻¹) (CPO ligand: 1702 and 1151 cm⁻¹). The IR bands of Eu(hfa)₃(TCPO)₂ were also observed at 1622 and 1102 cm⁻¹, which are shorter than those of the ligand (TCPO ligand: 1692 and 1115 cm⁻¹) (see Supplementary Information, Fig. S1). We successfully synthesized Eu(hfa)₃(TCPO)₂ without base condition. This chelate reaction is a new method for preparation of Eu(hfa)₃(TCPO)₂. On the other hand, Eu(hfa)₃(CPO)₂ is prepared under base-condition (addition of triethyl amine). The reaction difference might be due to moiety of the joint ligands, CPO and TCPO. The x and y in formulas in Eu(hfa)₃(CPO)₂ and Eu(hfa)₃(TCPO)₂ are defined 0 < x < 1 and 0 < y < 3. We estimated x = 0.38, y = 2.12 in Eu(hfa)₃(CPO)₂ and x = 0.03, y = 1.92 in Eu(hfa)₃(TCPO)₂ using EDX data (see Supplementary Information, Fig. S2). In order to identify the structure of Eu(hfa)₃(TCPO)₂, we tried to measure by single-crystal X-ray structure analysis. The structure was determined to be eight-coordinated structure with two water molecules and five TCPO ligands. The two TCPO ligands show bidentate bridged connection between two EuIII ions (TCPO A in Fig. 2). We also found that two TCPO ligands show bidentate (TCPO B) and monodentate (TCPO C) connection in one EuIII ion. Final TCPO ligand is attached to one EuIII ion by P=O group (TCPO D). The Eu(hfa)₃(TCPO)₂ crystal provides three dimensional network structure. This single crystal is including four methanol molecules in one unit (Fig. 2 and Table 1). These structures of the polymeric compounds were analyzed using X-ray diffraction (XRD) measurements. Figure 3 shows XRD patterns for both luminophores. Broad peaks were observed for Eu(hfa)₃(CPO)₂ at around 20° and 28° (Fig. 3a). The Eu(hfa)₃(CPO)₂ has
an amorphous structure at room temperature. In contrast, the as-prepared white powder of Eu(hfa)x(TCPO)y has noticeable peaks at 11.29°, 12.41°, 13.45°, 14.76°, 18.88°, 19.47°, 22.62°, 23.44°, 24.23°, 25.41°, 28.48°, and 30.11° (Fig. 3b), and Eu(hfa)x(TCPO)y after heat treatment (90 °C, 2 h, under reduced pressure) also has

| Chemical formula       | C22.32H17.28EuO10.6P |
|------------------------|----------------------|
| Formula weight         | 638.03               |
| Crystal system         | Triclinic            |
| Space group            | P-1(#2)              |
| a/Å                    | 10.7020(3)           |
| b/Å                    | 12.0041(3)           |
| c/Å                    | 14.5272(4)           |
| α/deg                  | 112.456(2)           |
| β/deg                  | 94.940(2)            |
| γ/deg                  | 101.867(2)           |
| Volume/Å³              | 1659.69(8)           |
| Z                       | 2                    |
| dcalc/g cm⁻³           | 1.277                |
| Temperature/°C          | −180                 |
| μ (Mo Kα)/cm⁻¹          | 19.747               |
| max 2θ/deg             | 55.0                 |
| Reflections collected  | 30169                |
| Independent reflections | 7550                 |
| R₁                      | 0.0325               |
| wR₂                     | 0.0847               |

Table 1. Crystallographic data for Eu(hfa)x(TCPO)y. [a] R₁ = \frac{\sum \left| F_o \right| - \left| F_c \right|}{\sum \left| F_o \right|}. [b] wR₂ = \frac{\sum w \left( F_o^2 - F_c^2 \right)^2}{\sum w (F_o^2)}.  

Figure 2. (a,b) ORTEP views of Eu(hfa)x(TCPO)y consisted of EuIII ions and TCPO ligands, (c) chemical structure of EuIII coordination sites.
noticeable peak at 11.32°, 11.99°, 14.05°, 15.21°, 18.22°, 18.73°, 20.21°, 20.37°, 22.29°, 22.88°, 23.23°, and 29.07° (Fig. 3c). Thus, it is considered that the triphenylphosphine oxide with three carboxy groups, the TCPO joint ligand, leads to the formation of a crystalline structure, and the structure change by heat treatment. We have checked the XRD of Eu(hfa)x(TCPO)y compared with that of Eu((CH3)2NCHO)x(TCPO)y in previous work37 (see Supplementary Information, Fig. S3). The XRD patterns of Eu(hfa)x(TCPO)y is much different from that of Eu((CH3)2NCHO)x(TCPO)y. Identification of the polymeric structure was performed using fast atom bombardment-mass spectrometry (FAB-MS) and energy dispersive X-ray spectroscopy (EDX) measurements. The fragment peaks of Eu(hfa)x(CPO)y and Eu(hfa)x(TCPO)y in the FAB-MS spectra agree with those calculated for [Eu2(hfa)3(CPO)2]+ and [Eu(hfa)2(TCPO)·5H2O]+ fragments, respectively (see Supplementary Information Fig. S4). According to the determination of element ratio, we estimated the Eu(Mα), P(Kα) and F(Kα) of Eu(hfa)x(CPO)y and Eu(hfa)x(TCPO)y for EDX measurements calibrated with Eu(hfa)3(TPPO)2 as a standard. The EDX measurements indicated the percentage of hfa moieties in Eu(hfa)x(CPO)y and Eu(hfa)x(TCPO)y were 10.8% and 0.89%, respectively. We propose that the small amount of hfa molecules attached on the crystal surface. The hfa molecules on the surface were successfully detected by ionized-fragment information using FAB-MS spectrum (Fig. S4b Eu(hfa)2TCPO·5H2O). In contrast, the EDX signals of the XRF measurement gave the average information about total element ratio of Eu(hfa)x(TCPO)y.

The thermo-stabilities of the Eu(hfa)x(CPO)y and Eu(hfa)x(TCPO)y polymeric structures were evaluated using TGA and the results are shown in Fig. 4. The TGA profile for the luminescent mononuclear EuIII complex, Eu(hfa)3(TPPO)2, was also measured as a standard reference. The decomposition temperature of Eu(hfa)x(TPPO)y was 200 °C. The weight of Eu(hfa)x(CPO)y gradually decreases from 200 °C, which may be due to the loose packing structure in amorphous Eu(hfa)x(CPO)y, to promote partial elimination of the hfa moieties. The decomposition temperature of Eu(hfa)x(TCPO)y, was 450 °C. We cannot observed the elimination of solvent from the material. This result indicates that Eu(hfa)x(TCPO)y have no solvent in the structure after heat treatment. Therefore, XRD measurements of Eu(hfa)x(TCPO)y were kept under 450 °C (see Supplementary Information, Fig. S5). The decomposition temperature of Eu(hfa)x(TCPO)y is the highest among the organo-EuIII luminophores with photosensitized hfa moieties. Thus, a luminescent organo-EuIII luminophore with extra-high thermostability was successfully synthesized.

![Figure 3. XRD patterns of (a) Eu(hfa)x(CPO)y, (b) as-prepared Eu(hfa)x(TCPO)y, and (c) Eu(hfa)x(TCPO)y under heat treatment at 90 °C.](image-url)
The luminescence images for Eu(hfa)₃(TPPO)₂, Eu(hfa)ₓ(CPO)y, and Eu(hfa)ₓ(TCPO)y heated on a hot plate under UV light irradiation (λ = 365 nm) are shown in Fig. 5. Eu(hfa)₃(TPPO)₂ exhibits red luminescence at 50 °C but does not emit photons at 250 °C due to their thermal decomposition. The red luminescence of Eu(hfa)ₓ(CPO)y faded out at around 250 °C. In contrast, bright red luminescence was successfully observed from Eu(hfa)ₓ(TCPO)y under 400 °C. (See emission spectra under control of temperature in Supplementary Information, Fig. S6a). Thus, Eu(hfa)ₓ(TCPO)y exhibits both effective photosensitized luminescence and thermostability.

**Luminescent Properties.** Excitation and emission spectra for Eu(hfa)ₓ(TPPO)₂, Eu(hfa)ₓ(CPO)y, and Eu(hfa)ₓ(TCPO)y, in the solid state detected at 613.5 nm and excited at 365 nm are shown in Fig. 6. The excitation bands of Eu(hfa)ₓ(CPO)y at around 300 nm is assigned to π–π* transition of hfa moieties. We also found characteristic excitation band at around 400 nm in Eu(hfa)ₓ(TCPO)y crystals. The emission bands were observed at around 578, 591, 613, 651, and 699 nm, which are attributed to the 4f–4f transitions of EuIII (5D₀–7F₃, J = 0, 1, 2, 3, and 4, respectively). The spectra were normalized with respect to the magnetic dipole transition intensities at 591 nm (EuIII: 5D₀–7F₁), which is known to be insensitive to the surrounding environment of the lanthanide ions. The normalized emission intensity of Eu(hfa)ₓ(TCPO)y at 613 nm is larger than that of Eu(hfa)ₓ(CPO)y. These spectral shapes of Eu(hfa)ₓ(TCPO)y and Eu(hfa)ₓ(CPO)y are different from that of crystalline Eu(hfa)₃(TPPO)₂.

Time-resolved emission profiles of Eu(hfa)ₓ(CPO)y and Eu(hfa)ₓ(TCPO)y are shown in Fig. 6b,c, respectively. The emissions from Eu(hfa)ₓ(CPO)y indicates single-exponential decays of millisecond scale. We estimated the emission lifetime of Eu(hfa)ₓ(TCPO)y using single-exponential decay. The lifetime and R² under single-exponential analysis were found to be 0.61 ms and 0.996, respectively. The lifetime is similar to that of Eu(hfa)ₓ(CPO)y. In this paper, we used the single-exponential analysis for estimation of lifetime of Eu(hfa)ₓ(TCPO)y. We consider that the luminescence of Eu(hfa)ₓ(TCPO)y comes from one-dominant EuIII species with hfa moieties on the crystal surface. The emission lifetimes of Eu(hfa)ₓ(TPPO)₂, Eu(hfa)ₓ(CPO)y, and Eu(hfa)ₓ(TCPO)y, were determined to be 0.80, 0.60 and 0.61 ms, respectively.

The 4f–4f emission quantum yields (Φ₄f–₄f) and the radiative (k_r) and non-radiative (k_nr) rate constants of these EuIII compounds were calculated using the following equations.
The radiative lifetime ($\tau_{\text{rad}}$) is defined as an ideal emission lifetime without non-radiative processes. The radiative lifetime is expressed by equation 1, where $A_{\text{MD,0}}$ is the spontaneous emission probability for the $^5D_0-^7F_1$ transition in vacuo ($14.65 \text{ s}^{-1}$), $n$ is the refractive index of the medium (an average index of refraction equal to 1.5 was employed), 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 $^5D_0-^7F_1$ band. The emission quantum yields, and the radiative and non-radiative rate constants are summarized in Table 2.

The emission quantum yield of Eu(hfa)$_x$(TCPO)$_y$ excited at 355 nm ($\Phi_{\pi\pi-\pi^*}$ transition band of hfa moieties) was also measured to calculate the energy transfer efficiency ($\eta$), which was determined as 34%. The energy transfer efficiency of Eu(hfa)$_x$(TCPO)$_y$ (decomposition temperature $= 450 ^\circ\text{C}$, $\eta = 59\%$) is larger than that of the previously reported thermostable organo-Eu$^{III}$ luminophore, [Eu(hfa)$_3$(dpbp)]$_n$ (dpbp: 4,4′-bis(diphenyl phospholyl)biphenyl, decomposition temperature $= 308 ^\circ\text{C}$, $\eta = 40\%$).

**Summary and Conclusions**

A organo-Eu$^{III}$ luminophore, Eu(hfa)$_x$(TCPO)$_y$, with effective thermostability and photosensitized luminescent property was successfully synthesized. Thermostable Eu(hfa)$_x$(TCPO)$_y$ exhibits bright red luminescence at 400°C under UV light irradiation. The luminescence of Eu(hfa)$_x$(TCPO)$_y$ is due to photosensitized energy transfer from...
hfa moieties to EuIII ions. Thermostable organo-lanthanide luminophores are expected to open up the frontier fields of photophysical science, material chemistry and industrial applications.

**Experimental Section**

**Materials.** Europium acetate \(\eta\)-hydrate (99.9%), diphenyl(\(p\)-tolyl)phosphine and tri-\(p\)-tolylphosphine were purchased from Wako Pure Chemical Industries Ltd. Hexafluoroacetylacetonate and triphenylphosphine oxide (TPPO) were obtained from Tokyo Kasei Organic Chemicals Co., Inc. Dimethyl sulfoxide-\(d_6\) (D, 99.9%) was obtained from Kanto Chemical Co., Inc. All other chemicals and solvents were reagent grade and were used without further purification.

**Apparatus.** \(^1\)H NMR (400 MHz) spectra were recorded on a JEOL ECS400. Chemical shifts were reported in \(\delta\) ppm, referenced to an internal tetramethylsilane standard for \(^1\)H NMR spectroscopy. Infrared spectra were measured using a Thermo Nicolet AVATAR 320 FT-IR spectrometer. FAB-MS spectra were recorded on a JEOL JMS-700TZ. Elemental analyses were performed on a J-Science Lab Micro Corder JM 10 and an Exeter Analytical CE440. In addition, the ratio of F to Eu was measured using Energy Dispersive X-ray Fluorescence Spectrometer EDX-8000 with (reference material: Eu(hfa)\(_3\)(TPPO)\(_2\)). XRD patterns were characterized by a RIGAKU SmartLab X-ray diffractometer with Cu K\(\alpha\) radiation, a D/teX Ultra detector, and a temperature control unit (Anton Paar, TCU-110). Thermogravimetric Analysis was performed on a Seiko Instruments Inc. EXSTAR 6000 (TG-DTA 6300) at first heating rate of 10 °C min\(^{-1}\) up to 500 °C, then cooling rate of 1 °C min\(^{-1}\) up to 100 °C, cooling rate of 10 °C min\(^{-1}\) up to 40 °C, and second heating rate of 1 °C min\(^{-1}\) up to 500 °C.

**Preparation of 4-carboxyphenyl diphenyl phosphine oxide (CPO).** CPO was synthesized by the oxidation of diphenyl(\(p\)-tolyl)phosphine with potassium permanganate, according to the procedure described in the literature\(^{42}\). Yield: 54%; \(^1\)H NMR (400 MHz, DMSO-\(d_6\), 298K): \(\delta\) 8.10—8.06 (dd, 2H), 7.78—7.72 (dd, 2H), 7.67—7.61 (m, 6H), 7.60—7.54 (dd, 4H) ppm; IR (ATR): 1658, 1592, 1540, 1498, 1411, 1254, 1144, 1118 cm\(^{-1}\); Elemental analysis calcd (%) for C\(_{15}\)H\(_7\)EuF\(_{18}\)O\(_8\): C 22.27, H 0.87; found: C 22.12, H 1.01; FAB-MS (m/z): [Eu\(_2\)(hfa)\(_3\)(CPO)\(_2\)].

**Preparation of 4′,4″-tricarboxyphenyl phosphine oxide (TCPO).** TCPO was synthesized by the oxidation of tri-\(p\)-tolylphosphine with potassium permanganate, according to the procedure described in the literature\(^{42}\). Yield: 34%; \(^1\)H NMR (400 MHz, DMSO-\(d_6\), 298K): \(\delta\) 8.12—8.08 (dd, 6H), 7.88—7.75 (dd, 6H) ppm; IR (ATR): 1692, 1395, 1246, 1162, 1102, 1016 cm\(^{-1}\); Elemental analysis calcd (%) for [C\(_{21}\)H\(_{15}\)O\(_7\)P\(_2\): C 58.89, H 4.00; found: C 58.67, H 4.08.

**Preparation of [Eu(hfa)\(_3\)](H\(_2\)O)\(_2\).** Europium acetate \(\eta\)-hydrate (5.0 g, 12 mmol) was dissolved in distilled water (20 mL). A solution of hexafluoroacetylactone 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, and the resulting powder was used without further purification for next step. Yield: 95%; IR (KBr): 1650, 1258—1145 cm\(^{-1}\); Elemental analysis calcd (%) for C\(_{19}\)H\(_{15}\)EuF\(_{18}\)O\(_8\): C 45.94, H 2.57.

**Preparation of Eu(hfa)\(_3\)(TPPO)\(_2\).** Methanol (100 mL) containing Eu(hfa)\(_3\)(H\(_2\)O)\(_2\) (4.28 g, 6 mmol) and TPPO (2.78 g, 10 mmol) was refluxed under stirring for 12 h. The reaction mixture was concentrated using a rotary evaporator. Recrystallization by addition of excess hexane solution produced crude crystal, which were washed in toluene several times. Recrystallization from hot toluene/cyclohexane gave white needle crystals. Yield: 95%; IR (ATR): 1692, 1592, 1498, 1411, 1245, 1144, 1118 cm\(^{-1}\); Elemental analysis calcd (%) for C\(_{30}\)H\(_{24}\)EuF\(_{38}\)O\(_{10}\): C 46.07, H 2.50; found: C 45.94, H 2.57.

**Preparation of Eu(hfa)\(_3\)(CPO)\(_2\).** CPO (207 mg, 0.64 mmol) and Eu(hfa)\(_3\)(H\(_2\)O)\(_2\) (720 mg, 0.89 mmol) were dispersed in methanol (30 mL), and triethylamine was added to neutralize. The dispersion was stirred for 5 h at 60 °C. The precipitate was washed with methanol several times, and dried in vacuo. Yield: 45.3 mg; IR (ATR): 1668, 1592, 1540, 1498, 1411, 1254, 1144, 1118 cm\(^{-1}\); FAB-MS (m/z): [Eu(hfa)\(_3\)(CPO)\(_2\)].

**Preparation of Eu(hfa)\(_3\)(TCPO)\(_2\).** TCPO (260 mg, 0.63 mmol) and Eu(hfa)\(_3\)(H\(_2\)O)\(_2\) (720 mg, 0.89 mmol) were dispersed in methanol (30 mL). The dispersion was stirred for 9 h at 60 °C. The white precipitate was washed with methanol several times, and dried in vacuo oven at 90 °C (see Supplementary Information, Fig. S8).

**Table 2. Photophysical properties of each complexes in the solid state.** Td is decomposition temperature. \(\Phi_{\pi−\pi}^*\) is emission quantum yield excited at 355 nm. \(\eta\) is energy transfer efficiency from hfa moieties to EuIII ions. Eu(hfa)\(_3\)(TPPO)\(_2\): see ref. 39. Eu(hfa)\(_3\)(dpbp): see ref. 40.
Yield: 294.7 mg; IR (ATR) 1624, 1548, 1398, 1382, 1185, 1145, 1116, 1050, 1018 cm⁻¹; FAB-Mass (m/z); [Eu(hfa)₂(TCPPO)-H₂O]⁺ calc'd for C₃₁H₂₇EuF₁₂O₁₆P, 1067.01; found 1067.3; EDX found (%): TCPO, 64.9; Eu, 33.8; hfa, 0.9.

Optical measurements. Emission spectra were recorded on a HORIBA Fluorolog-3 spectrofluorometer and corrected for the response of the detector system. Emission lifetimes (τ_em) 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 ≲ 1.1 ns). The Nd:YAG laser response was monitored with a digital oscilloscope (Sony Tektronix, TDS3052, 500 MHz) synchronized to the single-pulse excitation. The emission quantum yield excited at 355 nm (Φₑ) was estimated using a JASCO F-6300-H spectrometer attached with JASCO ILF-53 integrating sphere unit (ϕ = 100 mm).

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Author Contributions
A.N. performs the synthesis, measurements, and wrote the paper, A.N., T.N., Y.K., K.F., and Y.H. discussed and designed the research. T.S. and H.I. supported XRD measurements.

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