

Supporting Information

Dynamic Molecular Triplet Excitons Tune Lanthanide Emission Lifetime

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1 Methods

1.1 Materials

Lutetium chloride hexahydrate (99.99%) was purchased from Aldrich Co., Ltd. Europium nitrate hexahydrate (99.95%), terbium chloride hexahydrate (99.95%), *n*-butyllithium in *n*-hexane (1.6 mol/L), and chloroform-*d* (99.8%) were obtained from Kanto Chemical Co., Inc. Tetrahydrofuran, super dehydrated, stabilizer free (for organic synthesis), hydrogen peroxide (30%), anhydrous sodium sulfate, methanol-*d*₄, and chloroform (for spectrochemical analysis) were obtained from Wako Pure Chemical Industries, Ltd. Chlorodiphenylphosphine (>97.0%), chlorodicyclohexylphosphine (>97.0%), 2,2,6,6-tetramethyl-3,5-heptanedione (>97.0%), and 2,7-dibromophenanthrene (>98.0%) were purchased from Tokyo Chemical Industry Co., Ltd.

1.2 General methods

¹H-NMR, ¹³C-NMR, and ³¹P-NMR spectra were recorded in chloroform-*d* or methanol-*d*₄ using a JEOL ECS-400 spectrometer (¹H: 400 MHz, ¹³C: 100 MHz, ³¹P: 162 MHz). Tetramethylsilane (TMS, $\delta_{\text{H}} = 0$ ppm for ¹H-NMR, $\delta_{\text{C}} = 0$ ppm for ¹³C-NMR) and H₃PO₄ ($\delta_{\text{P}} = 0$ ppm for ³¹P-NMR) were used as internal standards. Elemental analyses were performed using MICRO CORDER JM10. Electrospray ionization (ESI) mass spectrometry was conducted on a JEOL JMS-T100 LP instrument. Absorption spectra of dp⁺ and dc⁺ were measured using a JASCO V-670 spectrometer. Fourier transform infrared (FT-IR) spectra were measured using a JASCO FT/IR-4600 instrument. Diffuse-reflectance spectra of Lu₂-dp⁺ and Eu₂-dp⁺, diluted 100-fold in KBr, were recorded using a JASCO V-670 spectrometer equipped with an integrating sphere (JASCO ISN-723). Emission spectra ($\lambda_{\text{ex}} = 356$ nm), excitation spectra ($\lambda_{\text{em}} = 548$ and 612 nm, diluted 10,000-fold in KBr), and emission decay curves ($\lambda_{\text{ex}} = 356$ nm, $\lambda_{\text{em}} = 548, 608, \text{ and } 612$ nm) were obtained using a Horiba FluoroLog[®]3 spectrofluorometer. Emission quantum yields ($\lambda_{\text{ex}} = 356$ nm) of the mixed lanthanide crystals were measured using FP-6300 spectrofluorometer with an integration sphere (ILF-533). Powder X-ray diffraction (PXRD) was performed on a Rigaku SmartLab using MoK α radiation ($\lambda = 0.71073$ Å). The ratios of Eu³⁺ (or Tb³⁺) in the mixed lanthanide crystals were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Agilent 5900). Emission photographs were taken using a PENTAX K-70.

1.3 Preparation of 2,7-bis(diphenylphosphoryl)phenanthrene (dpph)

The dpph ligand was synthesized by the same method in the previous report.^[25]

Yield: 38.2%, 0.198 g, 3.42 mmol. ¹H NMR (400 MHz, chloroform-*d*, **Figure S1**) δ /ppm = 8.75 (dd, J = 8.8 Hz, 2.4 Hz, 2H), 8.31 (dd, J = 13.4 Hz, 1.0 Hz, 2H), 7.88 (t, J = 9 Hz, 2H), 7.79-7.47 (m, 22H). ³¹P-NMR (162 MHz, chloroform-*d*, **Figure S2**) δ /ppm = 28.8 (s). ESI-MS: m/z calcd. for $[\text{C}_{38}\text{H}_{29}\text{O}_2\text{P}_2]^+ = 579.16$; found: 579.16.

1.4 Preparation of 2,7-bis(dicyclohexylphosphoryl)phenanthrene (dcph)

n-Butyllithium (4.9 mL, 7.9 mmol) was added dropwise to a solution of 2,7-dibromophenanthrene (1.20 g, 3.58 mmol) in dry tetrahydrofuran (20 mL) at $-80\text{ }^\circ\text{C}$ under Ar atmosphere. After 0.5 h, chlorodicyclohexylphosphine (1.8 mL, 8.2 mmol) was added to the solution and stirred for 1.0 h at $-80\text{ }^\circ\text{C}$ under Ar atmosphere and then stirred for 2.5 h at room temperature. A 30% hydrogen peroxide aqueous solution (5 mL) was added to the solution and stirred for 2 h at $0\text{ }^\circ\text{C}$. The product was extracted by dichloromethane and distilled water, and then the organic layer was dried over anhydrous Na_2SO_4 . The crude product was purified by silica gel column chromatography (ethyl acetate:methanol = 9:1).

Yield: 70.6%, 1.52 g, 2.52 mmol. ¹H NMR (400 MHz, methanol-*d*₄, **Figure S3**) δ /ppm = 8.99 (dd, J = 8.7 Hz, 2.3 Hz, 2H), 8.36 (d, J = 11.0 Hz, 2H), 8.00 (s, 2H), 7.95 (td, J = 8.5 Hz, 1.2 Hz, 2H), 2.42-2.24 (m, 4H), 2.16-2.02 (m, 4H), 1.90-1.61 (m, 16H), 1.49-1.18 (m, 16H), 1.18-1.04 (m, 4H). ³¹P-NMR (162 MHz, chloroform-*d*, **Figure S4**) δ /ppm = 45.3 (s). ESI-MS: m/z calcd. for $[\text{C}_{38}\text{H}_{53}\text{O}_2\text{P}_2]^+ = 603.35$; found: 603.35.

1.5 Preparation of [Lu(tmh)₃]

Lutetium chloride hexahydrate (2.01 g, 5.16 mmol) was dissolved in water (4 mL) and ethanol (2 mL). 2,2,6,6-Tetramethyl-3,5-heptanedione (tmh; 2.85 g, 15.5 mmol) was added dropwise to the solution, and then an ammonia solution was added dropwise until pH reached 9. After stirring for 1.5 h, water (200 mL) was added to the solution. After stirring for 18 h, the resulting white precipitate was collected by filtration. The obtained

powder was dried by heating at 373 K.

Yield: 76.2%, 2.85 g, 3.93 mmol. Elemental analysis calcd. (%) for $C_{33}H_{57}LuO_6$, C 54.69, H 7.93; found: C 54.45, H 7.90; ESI-MS: m/z calcd. for $[C_{33}H_{58}LuO_6]^+ = 725.36$; found: 725.36.

1.6 Preparation of $[Ln_2(tmh)_6]$ ($Ln^{3+} = Eu^{3+}$ or Tb^{3+})

Europium nitrate hexahydrate (1.01 g, 2.26 mmol) or terbium chloride hexahydrate (1.01 g, 2.70 mmol) was dissolved in water (4 mL) and ethanol (2 mL). 2,2,6,6-Tetramethyl-3,5-heptanedione (tmh; 1.24 g, 6.71 mmol for $[Eu_2(tmh)_6]$ or 1.51 g, 8.21 mmol for $[Tb_2(tmh)_6]$) was added dropwise to the solution, and then an ammonia solution was added dropwise until pH reached 9. After stirring for 1.5 h, water (250 mL for $[Eu_2(tmh)_6]$ or 200 mL for $[Tb_2(tmh)_6]$) was added to the solution. After stirring for 19 h (for $[Eu_2(tmh)_6]$) or 8 h (for $[Tb_2(tmh)_6]$), the reaction solution was filtered to obtain white powder. The white powder was recrystallized in methanol.

$[Eu_2(tmh)_6]$

Yield: 27.4%, 0.870 g, 0.620 mmol. Elemental analysis calcd. (%) for $C_{66}H_{114}Eu_2O_{12}$, C 56.48, H 8.19; found: C 56.28, H 8.19; ESI-MS: m/z calcd. for $[C_{55}H_{95}Eu_2O_{10}]^+ = 1219.53$; found: 1219.54.

$[Tb_2(tmh)_6]$

Yield: 40.1%, 1.53 g, 1.08 mmol. Elemental analysis calcd. (%) for $C_{66}H_{114}O_{12}Tb_2$, C 55.93, H 8.11; found: C 55.73, H 8.10; ESI-MS: m/z calcd. for $[C_{66}H_{114}NaO_{12}Tb_2]^+ = 1439.67$; found: 1439.55.

1.7 Preparation of $[Lu_2(tmh)_6dpph]$ (Lu_2 -dpph)

$[Lu_2(tmh)_6dpph]$ was prepared by the same procedure in the previous report.^[25]

Elemental analysis calcd. (%) for $C_{104}H_{142}Lu_2O_{14}P_2$, C 61.59, H 7.06; found: C 61.19, H 7.06; ESI-MS: m/z calcd. for $[C_{82}H_{104}Lu_2O_{10}P_2]^{2+} = 830.29$; found: 830.28.

1.8 Preparation of [Eu₂(tmh)₆dp₃h] (Eu₂-dp₃h)

The dp₃h ligand (50.5 mg, 0.09 mmol) and [Eu₂(tmh)₆] (121.3 mg, 0.086 mmol) were dissolved in methanol (7 mL). The solution was refluxed for 2 h. The mixture was filtered and then recrystallized in methanol at 25 °C (Yield: 30.5%, 52.8 mg, 0.027 mmol).

Elemental analysis calcd. (%) for C₁₀₄H₁₄₂Eu₂O₁₄P₂, C 63.02, H 7.22; found: C 62.82, H 7.18; ESI-MS: *m/z* calcd. for [C₈₂H₁₀₄Eu₂O₁₀P₂]²⁺ = 807.27; found: 807.29.

1.9 Preparation of [Tb₂(tmh)₆dp₃h] (Tb₂-dp₃h)

[Tb₂(tmh)₆dp₃h] was prepared by the same procedure in the previous report.^[25]

Elemental analysis calcd. (%) for C₁₀₄H₁₄₂O₁₄P₂Tb₂, C 62.58, H 7.17; found: C 62.25, H 7.14; ESI-MS: *m/z* calcd. for [C₈₂H₁₀₄O₁₀P₂Tb₂]²⁺ = 814.28; found: 814.29.

1.10 Preparation of [Eu_xLu_{2-x}(tmh)₆dp₃h] (Eu_xLu_{2-x}-dp₃h, x = 0.010, 0.028, or 0.084)

[Eu_{0.010}Lu_{1.990}(tmh)₆dp₃h]: The dp₃h ligand (50.8 mg, 8.78 × 10⁻² mmol), [Lu(tmh)₃] (123.31 mg, 0.16875 mmol), and [Eu₂(tmh)₆] (1.20 mg, 8.55 × 10⁻⁴ mmol) were dissolved in methanol (7 mL). The solution was refluxed for 4 h at 70 °C. The mixture was filtered and then recrystallized in methanol at 25 °C (Yield: 54.1%, 96.3 mg, 4.75 × 10⁻² mmol). The chemical compositions of Lu³⁺ and Eu³⁺ were determined by ICP-AES (Eu³⁺/(Eu³⁺+Lu³⁺) = 0.51%).

Elemental analysis calcd. (%) for C₁₀₄H₁₄₂Eu_{0.010}Lu_{1.990}O₁₄P₂, C 61.60, H 7.06; found: C 61.48, H 7.04.

[Eu_{0.028}Lu_{1.972}(tmh)₆dp₃h]: The dp₃h ligand (50.4 mg, 8.71 × 10⁻² mmol), [Lu(tmh)₃] (118.17 mg, 0.16304 mmol), and [Eu₂(tmh)₆] (6.02 mg, 4.29 × 10⁻³ mmol) were dissolved in methanol (7 mL). The solution was refluxed for 3.5 h at 70 °C. The mixture was filtered and then recrystallized in methanol at 25 °C (Yield: 55.6%, 98.1 mg, 4.84 × 10⁻² mmol). The chemical compositions of Lu³⁺ and Eu³⁺ were determined by ICP-AES (Eu³⁺/(Eu³⁺+Lu³⁺) = 1.4%).

Elemental analysis calcd. (%) for $C_{104}H_{142}Eu_{0.028}Lu_{1.972}O_{14}P_2$, C 61.61, H 7.06; found: C 61.72, H 7.05.

[Eu_{0.084}Lu_{1.916}(tmh)₆dpph]: The dpph ligand (50.4 mg, 8.71×10^{-2} mmol), [Lu(tmh)₃] (112.77 mg, 0.15559 mmol), and [Eu₂(tmh)₆] (12.19 mg, 8.69×10^{-3} mmol) were dissolved in methanol (7 mL). The solution was refluxed for 3 h at 70 °C. The mixture was filtered and then recrystallized in methanol at 25 °C (Yield: 47.3%, 83.4 mg, 4.12×10^{-2} mmol). The chemical compositions of Lu³⁺ and Eu³⁺ were determined by ICP-AES (Eu³⁺/(Eu³⁺+Lu³⁺) = 4.2%).

Elemental analysis calcd. (%) for $C_{104}H_{142}Eu_{0.084}Lu_{1.916}O_{14}P_2$, C 61.65, H 7.06; found: C 61.71, H 7.05.

1.11 Preparation of [Tb_xLu_{2-x}(tmh)₆dpph] (Tb_xLu_{2-x}-dpph, x = 0.013, 0.060, or 0.14)

[Tb_{0.013}Lu_{1.987}(tmh)₆dpph]: The dpph ligand (50.9 mg, 8.80×10^{-2} mmol), [Lu(tmh)₃] (124.01 mg, 0.17110 mmol), and [Tb₂(tmh)₆] (1.23 mg, 8.68×10^{-4} mmol) were dissolved in methanol (7 mL). The solution was refluxed for 3 h at 70 °C. The mixture was filtered and then recrystallized in methanol at 25 °C (Yield: 47.0%, 83.8 mg, 4.13×10^{-2} mmol). The chemical compositions of Lu³⁺ and Tb³⁺ were determined by ICP-AES (Tb³⁺/(Tb³⁺+Lu³⁺) = 0.66%).

Elemental analysis calcd. (%) for $C_{104}H_{142}Lu_{1.987}O_{14}P_2Tb_{0.013}$, C 61.60, H 7.06; found: C 61.53, H 7.03.

[Tb_{0.060}Lu_{1.940}(tmh)₆dpph]: The dpph ligand (50.6 mg, 8.75×10^{-2} mmol), [Lu(tmh)₃] (119.00 mg, 0.16419 mmol), and [Tb₂(tmh)₆] (6.02 mg, 4.31×10^{-3} mmol) were dissolved in methanol (7 mL). The solution was refluxed for 2.5 h at 70 °C. The mixture was filtered and then recrystallized in methanol at 25 °C (Yield: 54.4%, 96.5 mg, 4.76×10^{-2} mmol). The chemical compositions of Lu³⁺ and Tb³⁺ were determined by ICP-AES (Tb³⁺/(Tb³⁺+Lu³⁺) = 3.0%).

Elemental analysis calcd. (%) for $C_{104}H_{142}Lu_{1.940}O_{14}P_2Tb_{0.060}$, C 61.62, H 7.06; found: C 61.73, H 7.06.

[Tb_{0.140}Lu_{1.860}(tmh)₆dpph]: The dpph ligand (50.0 mg, 8.64×10^{-2} mmol), [Lu(tmh)₃] (112.72 mg, 0.15552 mmol), and [Tb₂(tmh)₆] (12.19 mg, 8.64×10^{-3} mmol) were dissolved in methanol (7 mL). The solution was

refluxed for 2.5 h at 70 °C. The mixture was filtered and then recrystallized in methanol at 25 °C (Yield: 51.9%, 90.8 mg, 4.48×10^{-2} mmol). The chemical compositions of Lu^{3+} and Tb^{3+} were determined by ICP-AES ($\text{Tb}^{3+}/(\text{Tb}^{3+}+\text{Lu}^{3+}) = 6.9\%$).

Elemental analysis calcd. (%) for $\text{C}_{104}\text{H}_{142}\text{Lu}_{1.860}\text{O}_{14}\text{P}_2\text{Tb}_{0.140}$, C 61.69, H 7.07; found: C 61.81, H 7.06.

1.12 Preparation of $[\text{Eu}_2(\text{tmh})_6\text{dcph}]$ ($\text{Eu}_2\text{-dcph}$)

The dcph ligand (30.9 mg, 5.13×10^{-2} mmol) and $[\text{Eu}_2(\text{tmh})_6]$ (70.9 mg, 5.05×10^{-2} mmol) were dissolved in methanol (5 mL). The solution was refluxed for 2 h at 70 °C. The mixture was filtered and then recrystallized in methanol at 25 °C (Yield: 33.5%, 34.5 mg, 1.72×10^{-2} mmol).

Elemental analysis calcd. (%) for $\text{C}_{104}\text{H}_{166}\text{Eu}_2\text{O}_{14}\text{P}_2$, C 62.26, H 8.34; found: C 61.29, H 8.31; ESI-MS: m/z calcd. for $[\text{C}_{82}\text{H}_{128}\text{Eu}_2\text{O}_{10}\text{P}_2]^{2+} = 819.37$; found: 819.43.

1.13 Preparation of $[\text{Tb}_2(\text{tmh})_6\text{dcph}]$ ($\text{Tb}_2\text{-dcph}$)

The dcph ligand (30.0 mg, 4.98×10^{-2} mmol) and $[\text{Tb}_2(\text{tmh})_6]$ (71.1 mg, 5.02×10^{-2} mmol) were dissolved in methanol (5 mL). The solution was refluxed for 2 h at 70 °C. The mixture was filtered and then recrystallized in methanol at 25 °C (Yield: 30.5%, 30.8 mg, 1.52×10^{-2} mmol).

Elemental analysis calcd. (%) for $\text{C}_{104}\text{H}_{166}\text{Tb}_2\text{O}_{14}\text{P}_2$, C 61.83, H 8.28; found: C 60.95, H 8.28; ESI-MS: m/z calcd. for $[\text{C}_{82}\text{H}_{128}\text{O}_{10}\text{P}_2\text{Tb}_2]^{2+} = 826.37$; found: 826.37.

1.14 Preparation of $[\text{Lu}_2(\text{tmh})_6\text{dcph}]$ ($\text{Lu}_2\text{-dcph}$)

The dcph ligand (50.5 mg, 8.38×10^{-2} mmol) and $[\text{Lu}(\text{tmh})_3]$ (120 mg, 1.66×10^{-1} mmol) were dissolved in methanol (7 mL). The solution was refluxed for 5 h at 70 °C. The mixture was filtered and then recrystallized in methanol at 25 °C (Yield: 29.4%, 85.9 mg, 4.19×10^{-2} mmol).

Elemental analysis calcd. (%) for $\text{C}_{104}\text{H}_{166}\text{Lu}_2\text{O}_{14}\text{P}_2$, C 60.86, H 8.15; found: C 60.64, H 8.20; ESI-MS: m/z calcd. for $[\text{C}_{104}\text{H}_{167}\text{Lu}_2\text{O}_{14}\text{P}_2]^+ = 2053.07$; found: 2053.11.

1.15 Preparation of [Eu_{0.005}Lu_{1.995}(tmh)₆dcph] (Eu_{0.005}Lu_{1.995}-dcph)

The dcph ligand (50.8 mg, 8.43×10^{-2} mmol), [Lu(tmh)₃] (119.3 mg, 0.16460 mmol), and [Eu₂(tmh)₆] (1.18 mg, 8.41×10^{-4} mmol) were dissolved in methanol (7 mL). The solution was refluxed for 10.5 h at 70 °C. The mixture was filtered and then recrystallized in methanol at 25 °C (Yield: 41.5%, 71.0 mg, 3.50×10^{-2} mmol). The chemical compositions of Lu³⁺ and Eu³⁺ were determined by ICP-AES ($\text{Eu}^{3+}/(\text{Eu}^{3+}+\text{Lu}^{3+}) = 0.26\%$). Elemental analysis calcd. (%) for C₁₀₄H₁₆₆Eu_{0.005}Lu_{1.995}O₁₄P₂, C 60.87, H 8.15; found: C 60.69, H 8.18.

1.16 Preparation of [Tb_{0.011}Lu_{1.989}(tmh)₆dcph] (Tb_{0.011}Lu_{1.989}-dcph)

The dcph ligand (50.9 mg, 8.44×10^{-2} mmol), [Lu(tmh)₃] (119.1 mg, 0.16433 mmol), and [Tb₂(tmh)₆] (1.17 mg, 8.25×10^{-4} mmol) were dissolved in methanol (7 mL). The solution was refluxed for 5 h at 70 °C. The mixture was filtered and then recrystallized in methanol at 25 °C (Yield: 41.5%, 73.0 mg, 3.50×10^{-2} mmol). The chemical compositions of Lu³⁺ and Tb³⁺ were determined by ICP-AES ($\text{Tb}^{3+}/(\text{Tb}^{3+}+\text{Lu}^{3+}) = 0.54\%$). Elemental analysis calcd. (%) for C₁₀₄H₁₆₆Lu_{1.989}O₁₄P₂Tb_{0.011}, C 60.87, H 8.15; found: C 60.71, H 8.18.

1.17 Single-crystal X-ray determination

Single crystals of [Ln₂(tmh)₆dp_h] (Ln³⁺ = Eu³⁺, Tb³⁺, and Lu³⁺) were obtained by recrystallization from methanol. Single-crystal X-ray structural analyses were carried out using a Rigaku XtaLAB Synergy-R/DW equipped with a Hypix-6000HE detector (MoK_α radiation, $\lambda = 0.71703$ Å). The structure was solved using direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically using the SHELX system.^[41] Hydrogen atoms were refined using the riding model. All calculations were performed using the Olex2 crystallographic software package except for the refinement, which was performed using SHELXL.^[42] The CIF data were confirmed by the checkCIF/PLATON service. CCDC-2426790 (for [Eu₂(tmh)₆dp_h]), CCDC-2128735 (for [Tb₂(tmh)₆dp_h]), CCDC-2128731 (for [Lu₂(tmh)₆dp_h]), CCDC-2426793 (for [Lu₂(tmh)₆dcph]), and CCDC-2478483 (for [Gd₂(tmh)₆dp_h]). The crystallographic data are summarized in Table S1.

1.18 Calculation method of photophysical parameters of Eu complex^[43]

The photophysical parameters, radiative rate constant (k_r), non-radiative rate constant (k_{nr}), and intrinsic emission quantum yield (Φ_{ff}) were estimated using the following equations.

$$k_r = \frac{1}{\tau_{rad}} = A_{MD,0} n^3 \frac{I_{tot}}{I_{MD}} \quad (S1)$$

$$\phi_{ff} = \frac{k_r}{k_r + k_{nr}} = \frac{\tau_{obs}}{\tau_{rad}} \quad (S2)$$

$$k_{nr} = \frac{1}{\tau_{obs}} - \frac{1}{\tau_{rad}} \quad (S3)$$

where τ_{obs} , τ_{rad} , $A_{MD,0}$, n , and I_{tot}/I_{MD} are the observed and radiative emission lifetimes, spontaneous emission probability for $^5D_0 \rightarrow ^7F_1$ transition in degassed condition (14.65 s^{-1}), refractive index of the medium ($n = 1.5$), and ratio of the total area of $^5D_0 \rightarrow ^7F_J$ ($J = 0, 1, 2, 3, 4$) bands of Eu(III) emission spectrum to the area of the $^5D_0 \rightarrow ^7F_1$ band, respectively.^[43]

1.19 NMR spectra of dpph and dcph

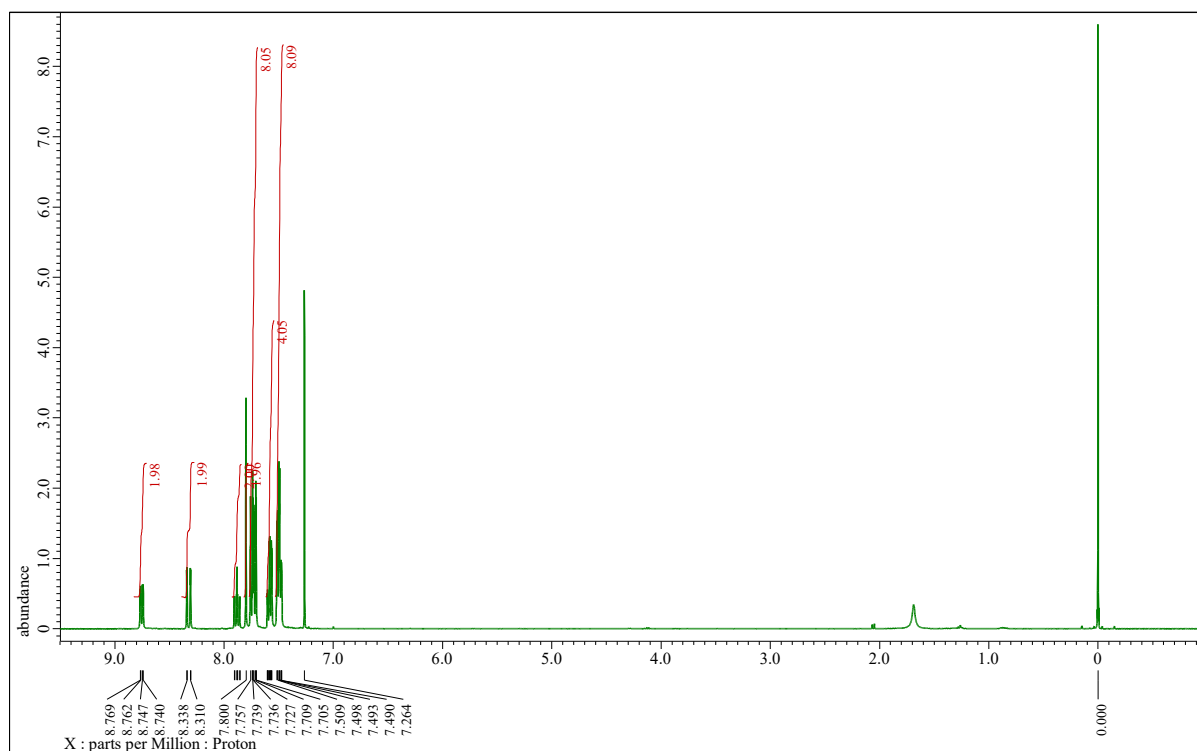


Figure S1. ^1H -NMR spectrum of dpph in chloroform-*d*.

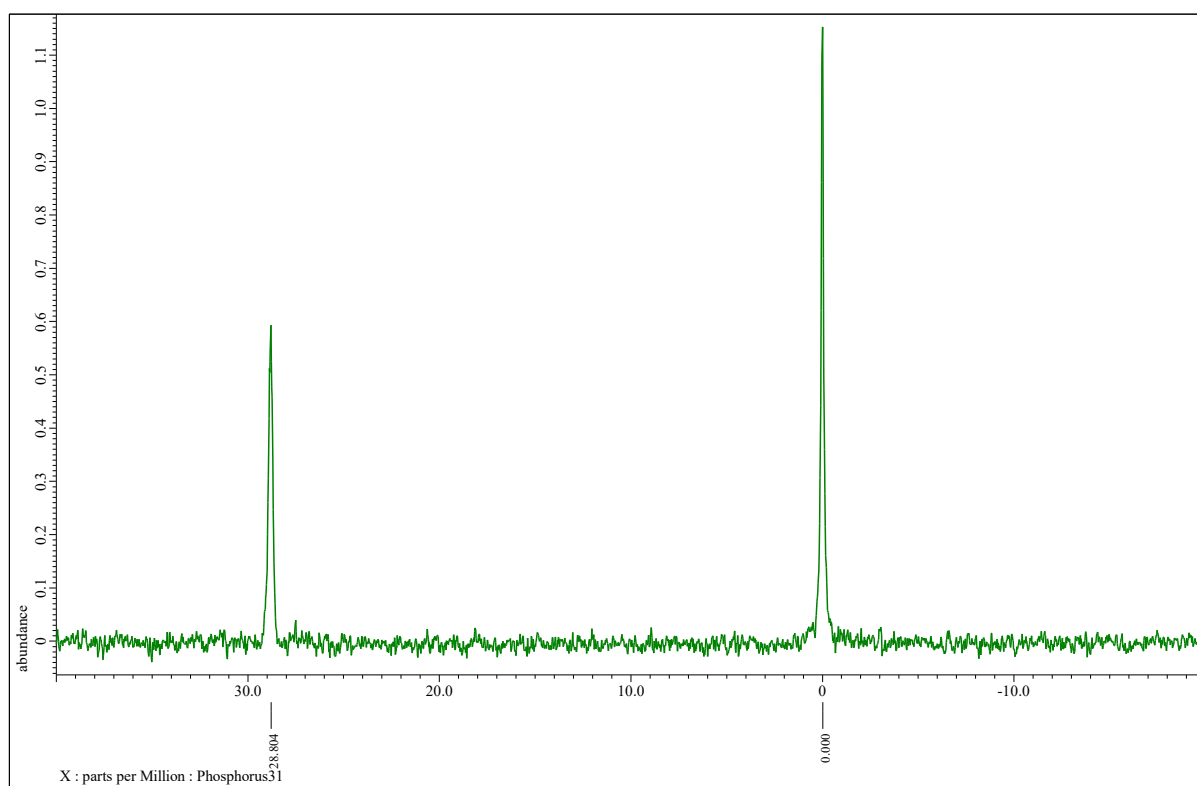


Figure S2. ^{31}P -NMR spectrum of dpph in chloroform-*d*.

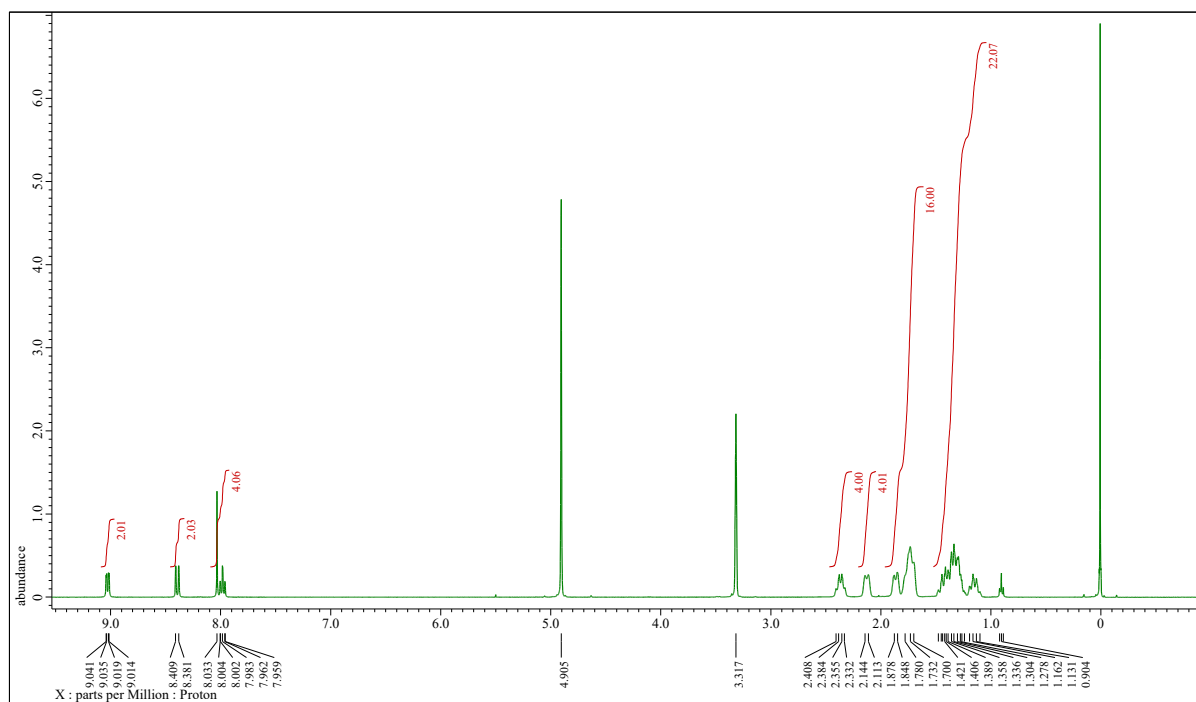


Figure S3. ^1H -NMR spectrum of dcph in methanol- d_4 .

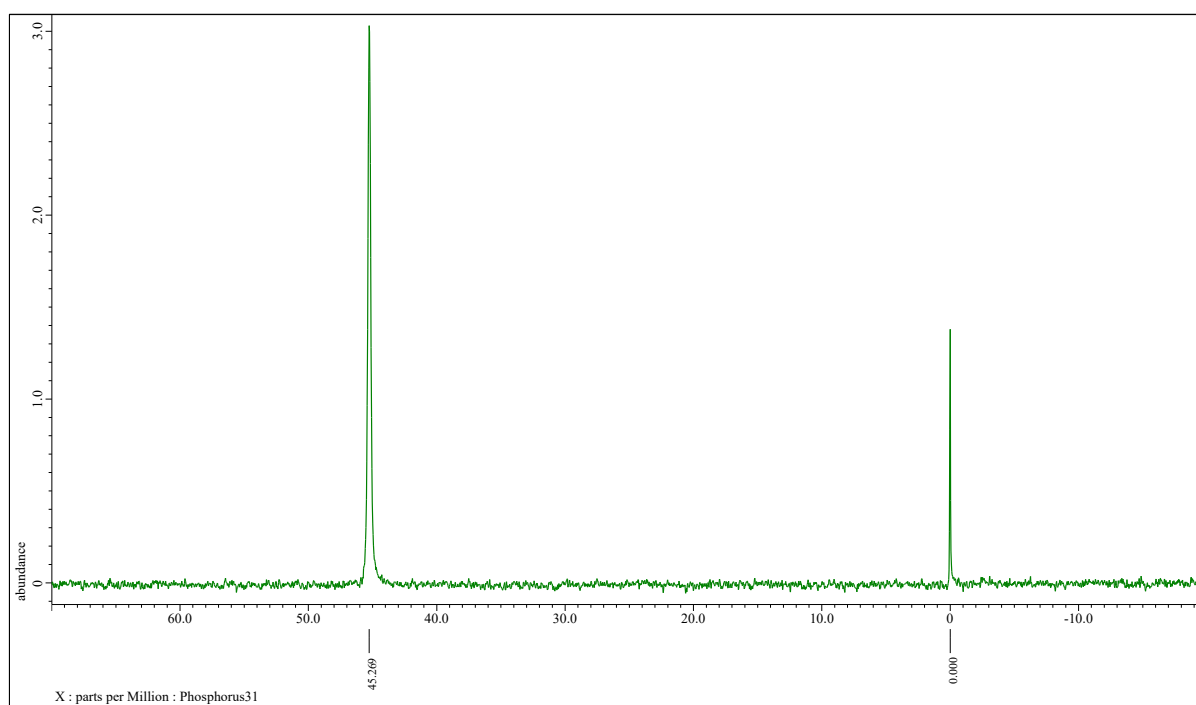


Figure S4. ^{31}P -NMR spectrum of dcph in chloroform- d .

1.20 Infrared spectra of lanthanide complexes

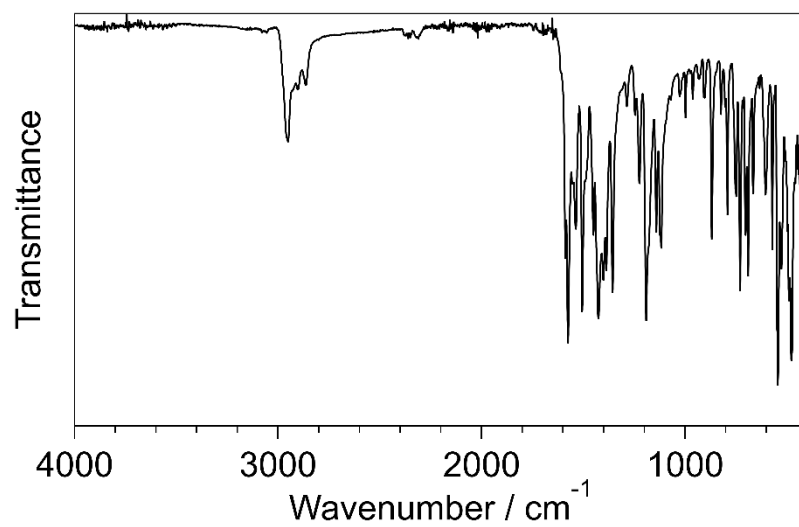


Figure S5. FT-IR spectrum of $\text{Lu}_2\text{-dpph}$.

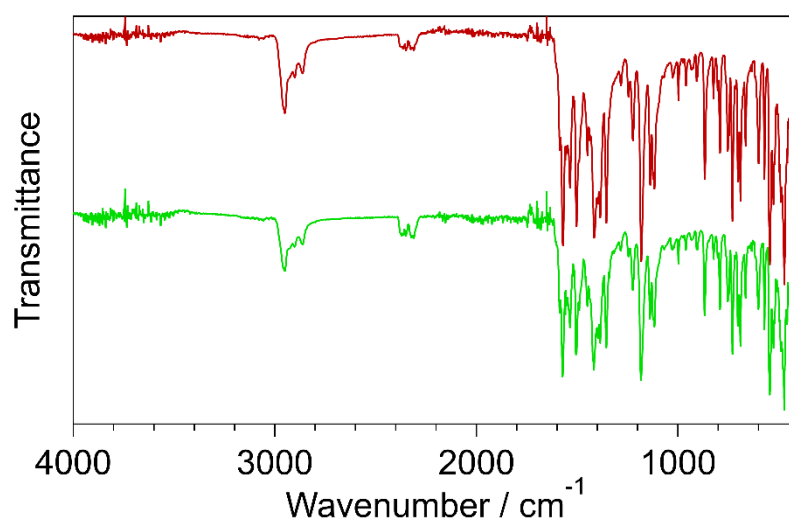


Figure S6. FT-IR spectra of $\text{Eu}_2\text{-dpph}$ (red line) and $\text{Tb}_2\text{-dpph}$ (green line).

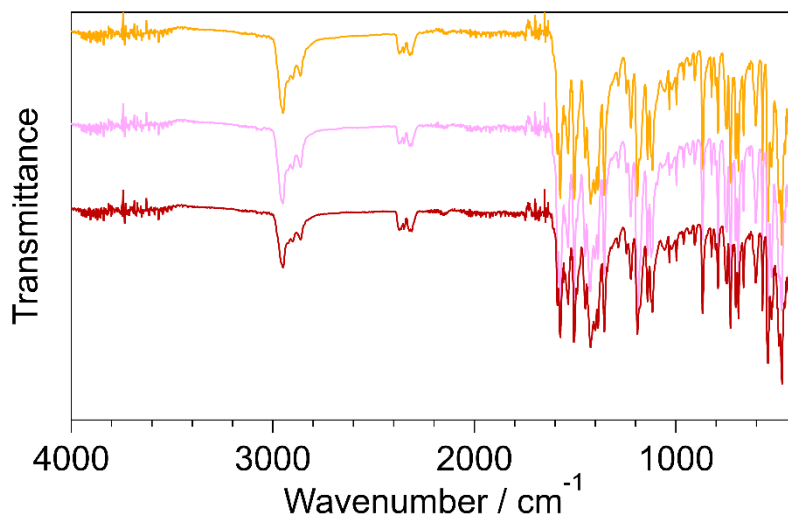


Figure S7. FT-IR spectra of **Eu_{0.010}Lu_{1.990}-dpph** (orange line), **Eu_{0.028}Lu_{1.972}-dpph** (pink line), **Eu_{0.084}Lu_{1.916}-dpph** (red line).

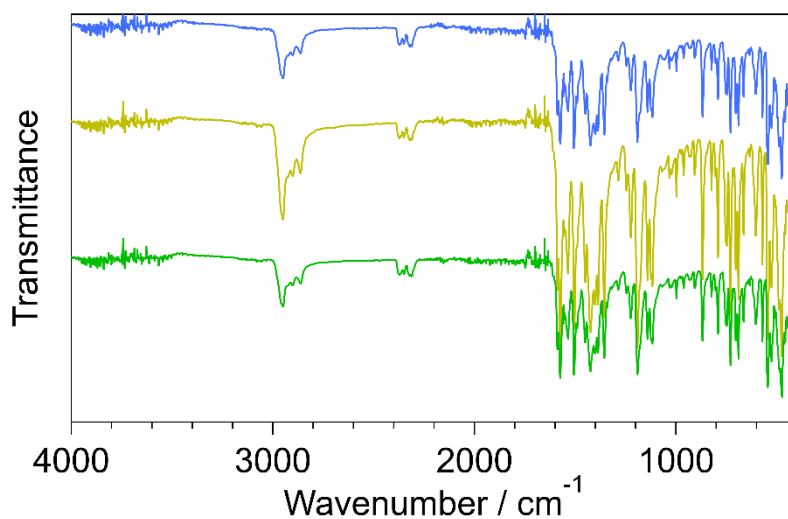


Figure S8. FT-IR spectra of **Tb_{0.013}Lu_{1.987}-dpph** (blue line), **Tb_{0.060}Lu_{1.940}-dpph** (yellow line), and **Tb_{0.140}Lu_{1.860}-dpph** (green line).

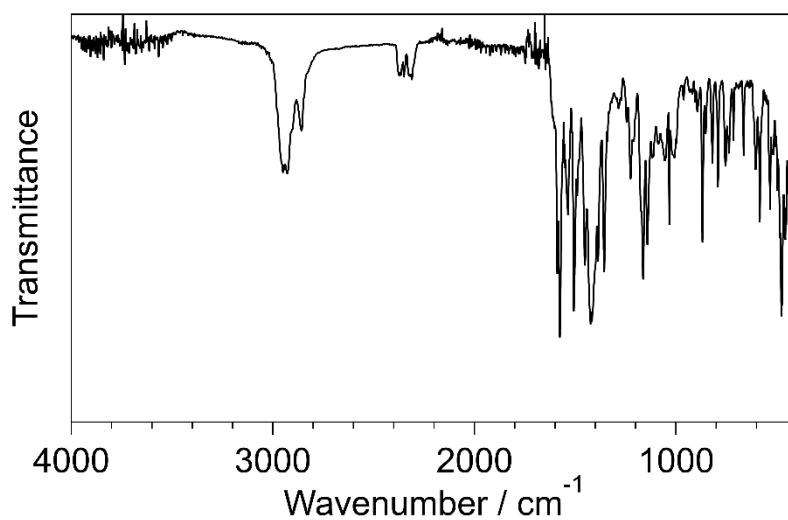


Figure S9. FT-IR spectrum of $\text{Lu}_2\text{-dcph}$.

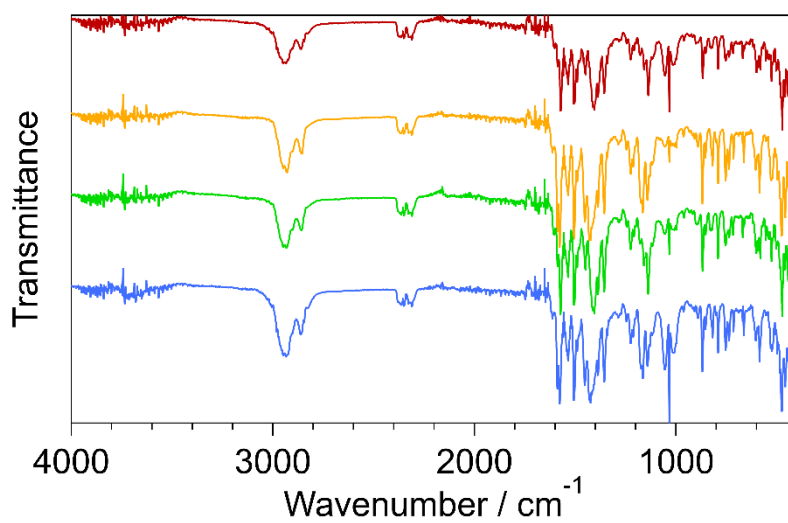


Figure S10. FT-IR spectra of $\text{Eu}_2\text{-dcph}$ (red line), $\text{Eu}_{0.005}\text{Lu}_{1.995}\text{-dcph}$ (orange line), $\text{Tb}_2\text{-dcph}$ (green line), and $\text{Tb}_{0.011}\text{Lu}_{1.989}\text{-dcph}$ (blue line).

2 Crystal structure analysis and photophysical properties

Supplementary Note 1: Comparison of other non-luminescent lanthanide ions

In the present mixed lanthanide system, La^{3+} and Gd^{3+} ions are also potential candidates owing to their high lowest excited state levels. To consider the optimal lanthanide ions, we attempted to synthesize the $[\text{La}_2(\text{tmh})_6\text{dpph}]$ and $[\text{Gd}_2(\text{tmh})_6\text{dpph}]$ complexes using the same scheme as that for $[\text{Lu}_2(\text{tmh})_6\text{dpph}]$. Single crystals of the Gd^{3+} complex were obtained by recrystallization in a methanol solution. By contrast, the La^{3+} complex did not crystallize under the identical conditions as those used the Lu^{3+} and Gd^{3+} complexes.

Single-crystal X-ray diffraction analysis revealed that the Gd^{3+} complex formed a dinuclear structure (**Figure S11**, crystallographic data are listed in **Table S1**), which is similar structure to that of $[\text{Lu}_2(\text{tmh})_6\text{dpph}]$. An emission band was observed at approximately 550 nm in the emission spectrum of $[\text{Gd}_2(\text{tmh})_6\text{dpph}]$ (**Figure S12**), which is assigned to phosphorescence from the dpph ligand. The emission decay curve of $[\text{Gd}_2(\text{tmh})_6\text{dpph}]$ was fitted with a triple-exponential function (**Figure S13**). The average emission lifetime of $[\text{Gd}_2(\text{tmh})_6\text{dpph}]$ was estimated as 36.3 ms ($\tau_1 = 26.3$ ms (79.9%), $\tau_2 = 67.0$ ms (20.0%), $\tau_3 = 1340$ ms (0.01%)), which is shorter than that of $[\text{Lu}_2(\text{tmh})_6\text{dpph}]$ (47 ms). Based on these results, $[\text{Lu}_2(\text{tmh})_6\text{dpph}]$ was selected as the host crystal for effective delayed emission from Eu^{3+} and Tb^{3+} .

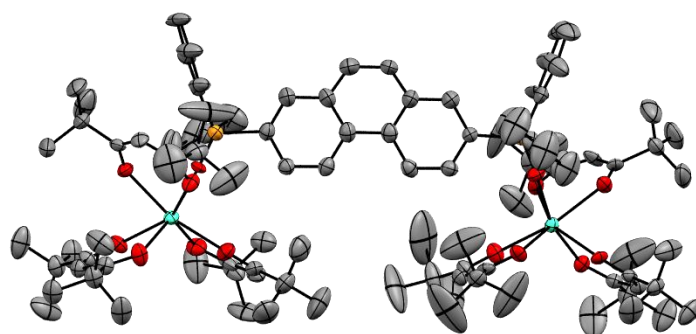


Figure S11. ORTEP drawings of $[\text{Gd}_2(\text{tmh})_6\text{dpph}]$ (50% probability ellipsoids). Gray spheres represent carbon; red spheres, oxygen; orange spheres, phosphorus; light green spheres, gadolinium. Hydrogen atoms are omitted for clarity.

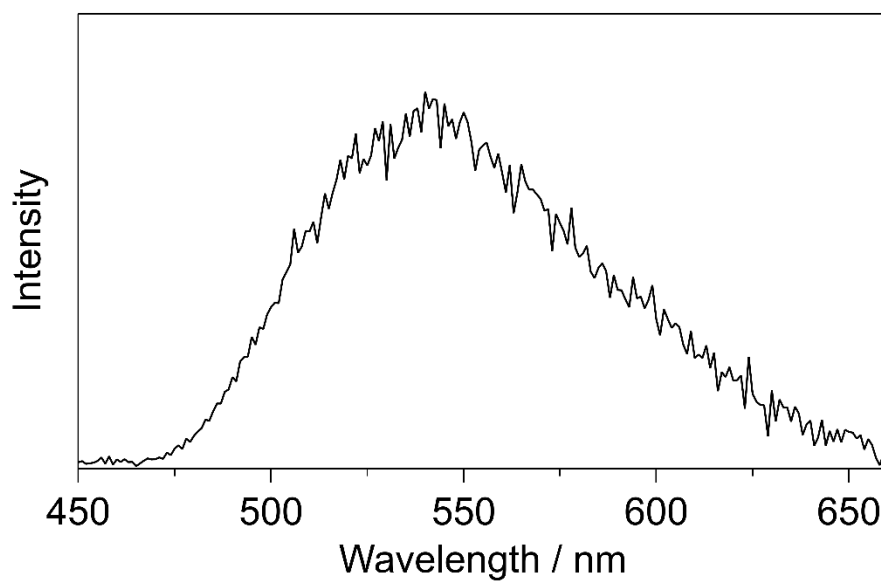


Figure S12. Emission spectrum of $[\text{Gd}_2(\text{tmh})_6\text{dpPh}]$ ($\lambda_{\text{ex}} = 405$ nm, 30 ms delay, 100 K, degassed condition).

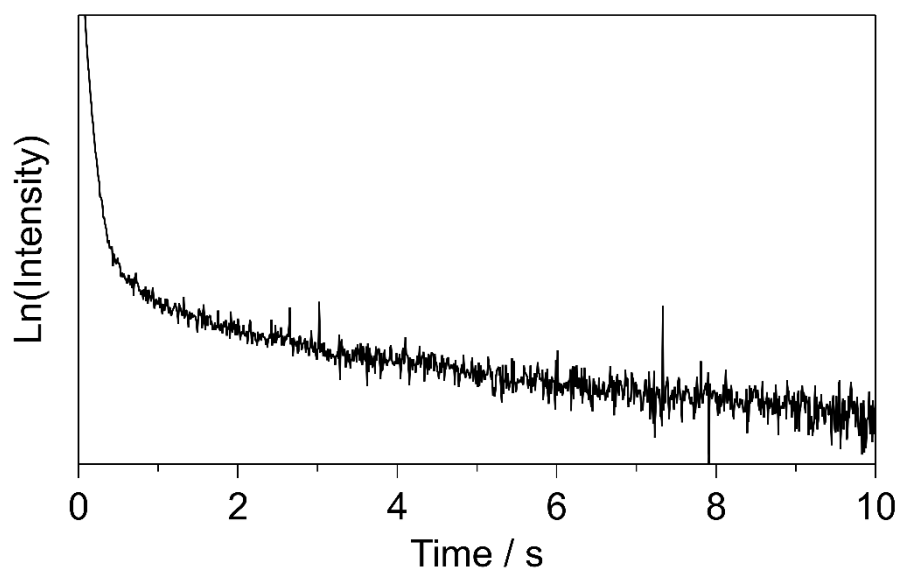


Figure S13. Emission decay curve of $[\text{Gd}_2(\text{tmh})_6\text{dpPh}]$ under degassed condition ($\lambda_{\text{ex}} = 380$ nm, $\lambda_{\text{em}} = 530$ nm, delay time: 80 ms, 293 K).

Table S1. Crystallographic parameters for [Ln₂(tmh)₆dpph] (Ln³⁺ = Eu³⁺, Tb³⁺, Gd³⁺ and Lu³⁺).

	[Eu ₂ (tmh) ₆ dpph]	[Gd ₂ (tmh) ₆ dpph]	[Tb ₂ (tmh) ₆ dpph] ^[25]	[Lu ₂ (tmh) ₆ dpph]
Chemical formula	C ₁₀₄ H ₁₄₂ Eu ₂ O ₁₄ P ₂	C ₁₀₄ H ₁₄₂ Gd ₂ O ₁₄ P ₂	C ₁₀₄ H ₁₄₂ O ₁₄ P ₂ Tb ₂	C ₁₀₄ H ₁₄₂ O ₁₄ P ₂ Lu ₂
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1	P-1
<i>a</i> / Å	20.4908(3)	20.5881(4)	20.6292(3)	20.6743(3)
<i>b</i> / Å	21.7700(3)	21.7908(5)	21.8080(3)	21.7193(3)
<i>c</i> / Å	23.8309(3)	23.8658(5)	23.8231(3)	23.5751(3)
Volume / Å ³	10514.5(3)	10594.2(4)	10599.8(3)	10467.7(3)
<i>Z</i>	4	4	4	4
Density / g cm ⁻³	1.252	1.249	1.251	1.287
Temperature / °C	−150	−150	−150	−150
<i>R</i>	0.0735	0.0840	0.0609	0.0814
<i>wR</i> ₂	0.2123	0.2090	0.1696	0.2171

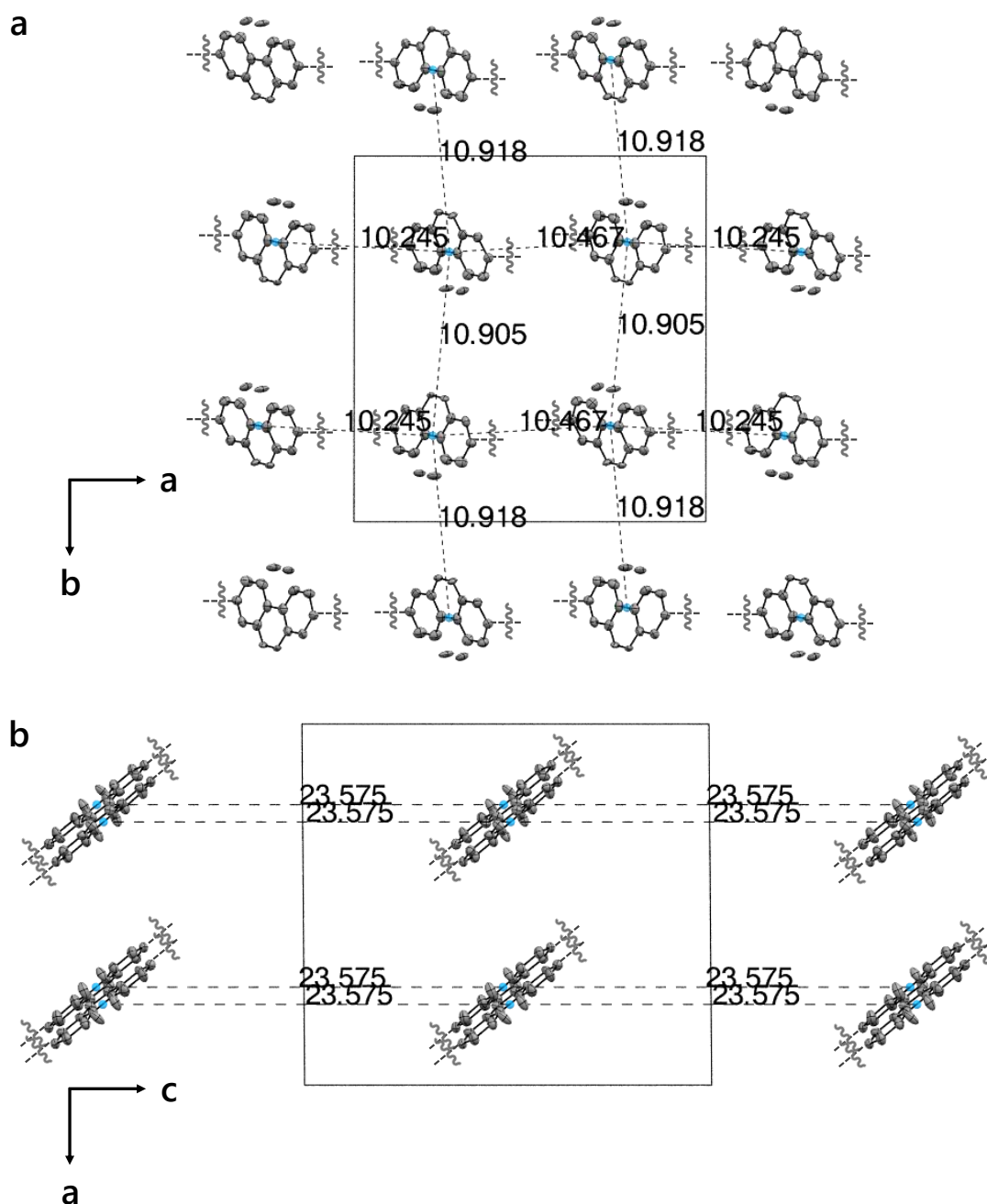


Figure S14. X-ray crystal structure of **Lu₂-dpph** viewed along the **a)** c-axis and **b)** b-axis (50% probability ellipsoids). Except for phenanthrene units, all other atoms are omitted for clarity. The unbonded carbon atoms denote a two-site disorder of the phenanthrene units. Blue spheres represent centroid of 14 carbon atoms.

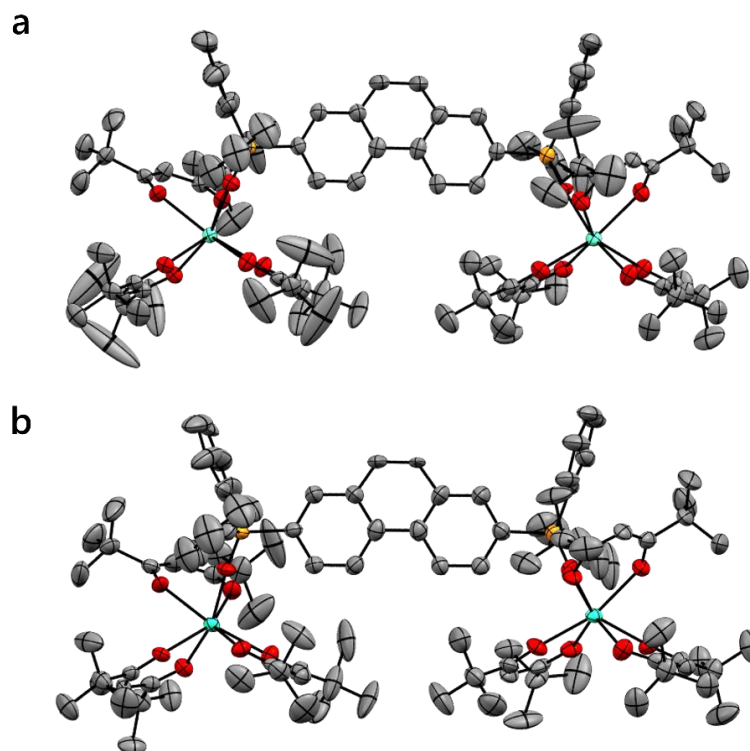


Figure S15. ORTEP drawings of a) **Eu₂-dpph** and b) **Tb₂-dpph**^[25] (50% probability ellipsoids). Gray spheres represent carbon; red spheres, oxygen; orange spheres, phosphorus; light green spheres, europium or terbium. Hydrogen atoms are omitted for clarity.

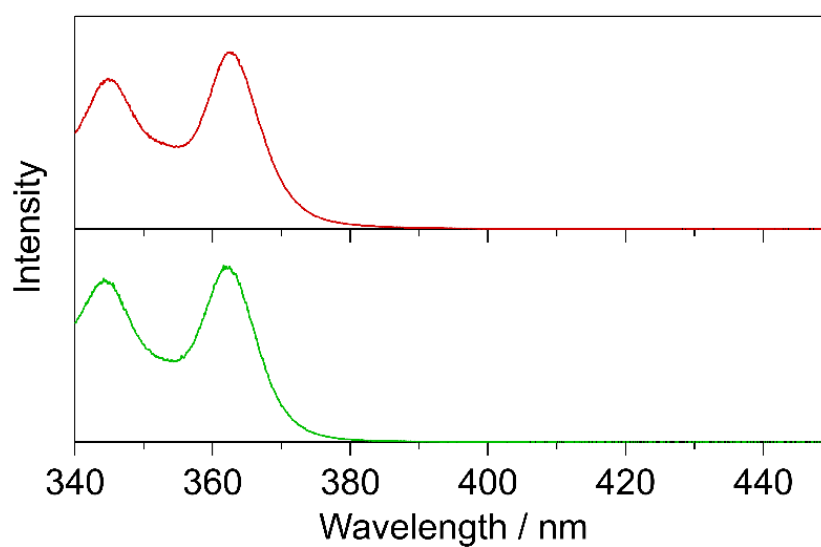


Figure S16. Excitation spectra of **Eu₂-dpph** (red line, $\lambda_{em} = 612$ nm) and **Tb₂-dpph** (green line, $\lambda_{em} = 548$ nm) under degassed condition at 293 K.

Supplementary Note 2: Excited state dynamics of Eu₂-dpph and Tb₂-dpph

The photophysical properties of **Eu₂-dpph** and **Tb₂-dpph** are summarized in Table S2. For **Eu₂-dpph**, intrinsic emission quantum yield (Φ_{ff}) and emission quantum yield by ligand excitation (Φ_{tot}) of **Eu₂-dpph** were estimated to be 55.5 and 9.8%, respectively. The calculated photosensitized energy transfer efficiency ($\eta_{\text{sens}} = 17.8\%$) is inefficient, indicating the presence of quenching state in photosensitization process. To reveal the quenching state, diffuse-reflectance spectra of **Eu₂-dpph** and **Lu₂-dpph** were measured (Figure S17). Absorption bands were observed at 364 and 346 nm, which are assigned to 0-0 and 0-1 π - π^* transitions of dpph ligand, respectively. For **Eu₂-dpph**, an additional absorption band arising from 400 nm is also observed. Eu³⁺ has a lower reduction potential compared to Lu³⁺ (Eu³⁺/Eu²⁺ = −0.35 V vs NHE; Lu³⁺/Lu²⁺ = −2.7 V vs NHE^[44]), resulting in a ligand-to-metal charge transfer (LMCT) states with lower energy than dpph singlet state. Thus, ineffective energy transfer efficiency in **Eu₂-dpph** is attributed to energy transfer quenching from dpph singlet state.^[37-40]

Table S2 Photophysical properties of **Eu₂-dpph** and **Tb₂-dpph**.

	$\Phi_{\text{tot}}^{[a]} / \%$	$\Phi_{\text{ff}}^{[b]} / \%$	$\eta_{\text{sens}} / \%$	$\tau^{[c]} / \text{ms}$
Eu₂-dpph	9.8	55.5	17.8	0.55
Tb₂-dpph	67.9	---	---	0.83

[a] $\lambda_{\text{ex}} = 375 \text{ nm}$, crystalline state, N₂ atmosphere, 293 K. [b] Φ_{ff} was calculated from equation

S1-S3^[43]. [c] $\lambda_{\text{ex}} = 356 \text{ nm}$, $\lambda_{\text{em}} = 612 \text{ nm}$ (for **Eu₂-dpph**) or 548 nm (for **Tb₂-dpph**), 293 K.

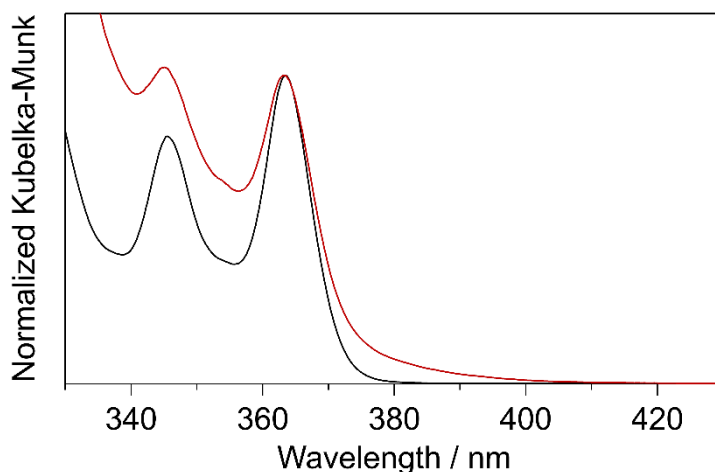


Figure S17. Diffuse-reflectance spectra of **Eu₂-dpph** (red) and **Lu₂-dpph** (black).

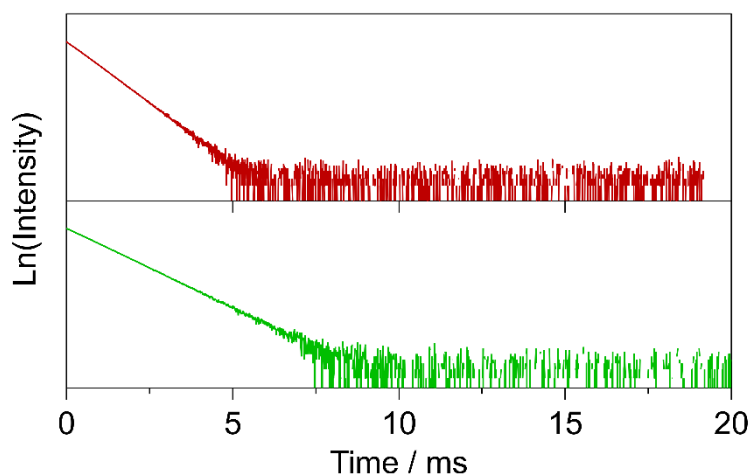


Figure S18. Emission decay curves of **Eu₂-dpph** (red line, $\lambda_{\text{ex}} = 510$ nm, $\lambda_{\text{em}} = 612$ nm, crystalline state) and **Tb₂-dpph** (green line, $\lambda_{\text{ex}} = 495$ nm, $\lambda_{\text{em}} = 548$ nm, crystalline state) by direct Eu^{3+} or Tb^{3+} excitation at 293 K under degassed condition.

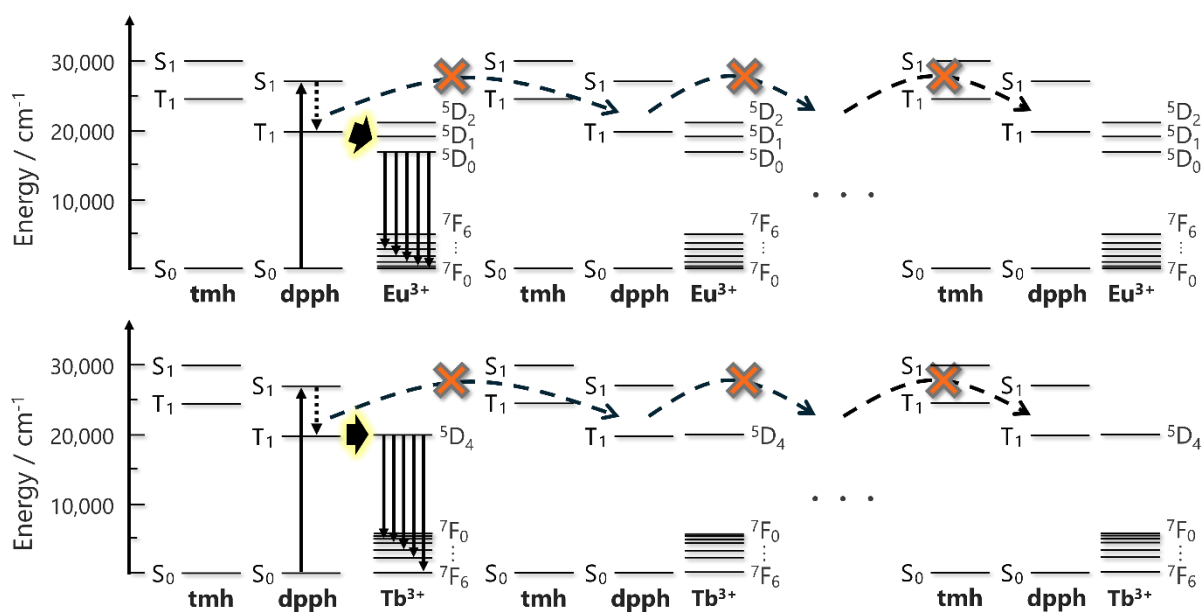


Figure S19. Energy diagrams of **Eu₂-dpph** (upper) and **Tb₂-dpph** (lower). Emission lifetimes of **Eu₂-dpph** and **Tb₂-dpph** by dpph excitation were almost consistent with those by Eu^{3+} or Tb^{3+} excitation. This result indicates the inexistence of intermolecular energy transfer.

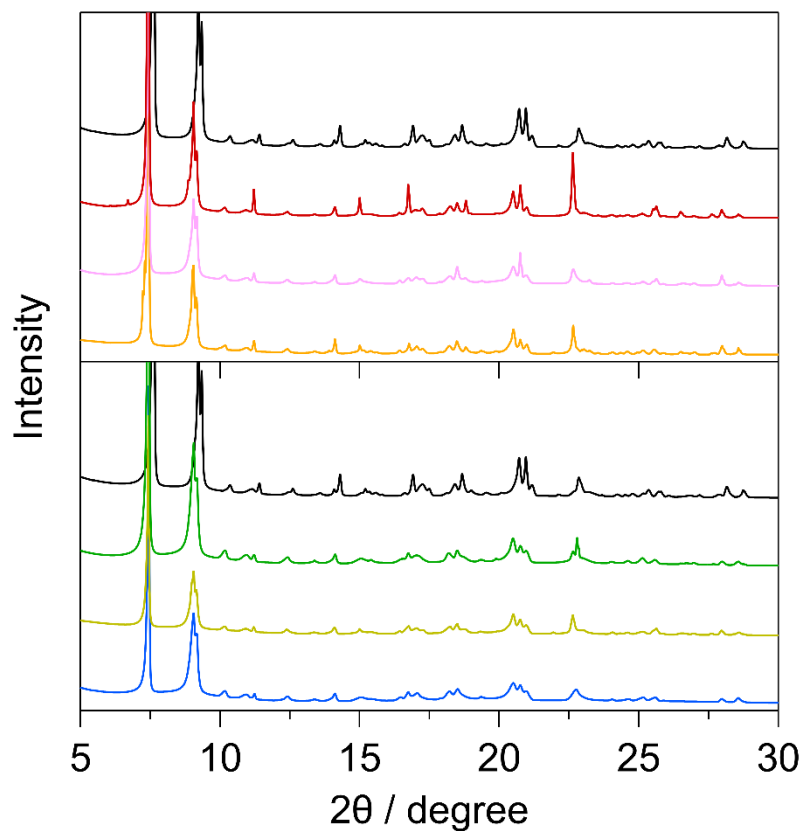


Figure S20. Powder X-ray diffraction patterns of **Lu₂-dpph** (black line), **Eu_{0.084}Lu_{1.916}-dpph** (red line), **Eu_{0.028}Lu_{1.972}-dpph** (pink line), **Eu_{0.010}Lu_{1.990}-dpph** (orange line), **Tb_{0.140}Lu_{1.860}-dpph** (green line), **Tb_{0.060}Lu_{1.940}-dpph** (yellow line), and **Tb_{0.013}Lu_{1.987}-dpph** (blue line).

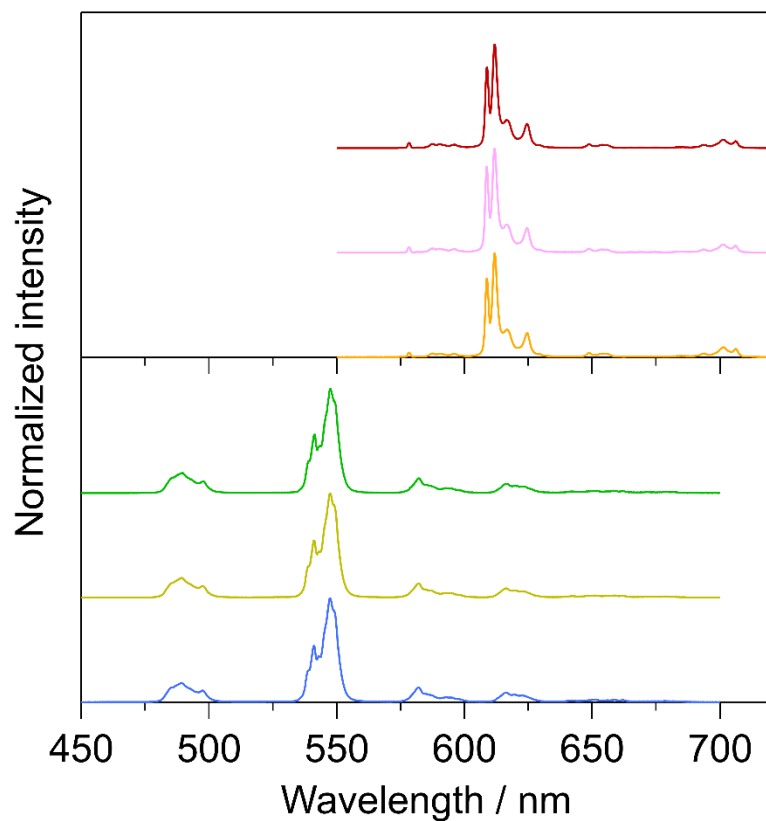


Figure S21. Emission spectra ($\lambda_{\text{ex}} = 356$ nm, crystalline state, 293 K, under degassed condition) of **Eu_{0.084}Lu_{1.916}-dpph** (red line), **Eu_{0.028}Lu_{1.972}-dpph** (pink line), **Eu_{0.010}Lu_{1.990}-dpph** (orange line), **Tb_{0.140}Lu_{1.860}-dpph** (green line), **Tb_{0.060}Lu_{1.940}-dpph** (yellow line), and **Tb_{0.013}Lu_{1.987}-dpph** (blue line).

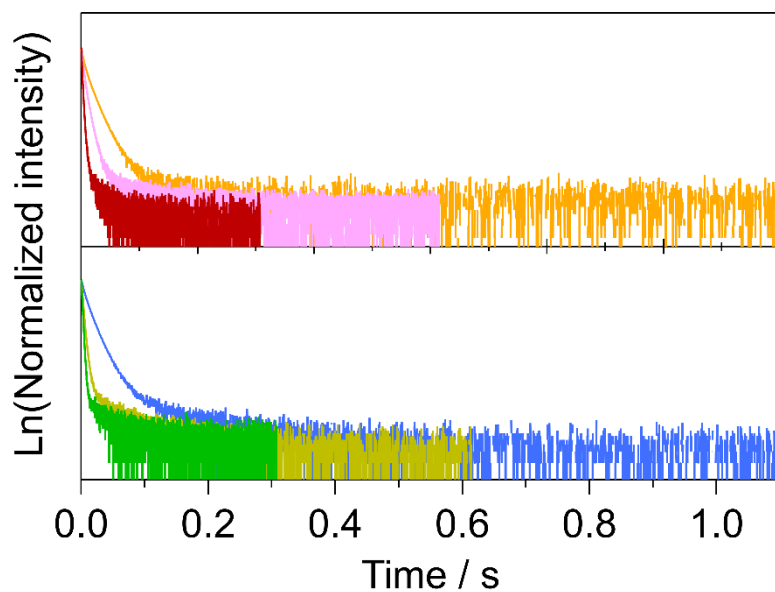


Figure S22. Emission decay curves ($\lambda_{\text{ex}} = 356$ nm, crystalline state, 293 K, under degassed condition) of **Eu_{0.084}Lu_{1.916}-dpph** ($\lambda_{\text{em}} = 612$ nm, red line), **Eu_{0.028}Lu_{1.972}-dpph** ($\lambda_{\text{em}} = 612$ nm, pink line), **Eu_{0.010}Lu_{1.990}-dpph** ($\lambda_{\text{em}} = 612$ nm, orange line), **Tb_{0.140}Lu_{1.860}-dpph** ($\lambda_{\text{em}} = 548$ nm, green line), **Tb_{0.060}Lu_{1.940}-dpph** ($\lambda_{\text{em}} = 548$ nm, yellow line), and **Tb_{0.013}Lu_{1.987}-dpph** ($\lambda_{\text{em}} = 548$ nm, blue line).

Table S3 Fitting results for emission decay curves of mixed lanthanide crystals.

	$\tau_{\text{avg}} / \text{ms}$	τ_1 / ms	τ_2 / ms	τ_3 / ms
Eu₂-dpph	0.55	---	---	---
Eu_{0.084}Lu_{1.916}-dpph	1.22	0.99 (81.2%)	2.14 (18.8%)	25.5 (0.7%)
Eu_{0.028}Lu_{1.972}-dpph	3.54	1.88 (47.4%)	4.80 (51.6%)	16.8 (1.0%)
Eu_{0.010}Lu_{1.990}-dpph	7.42	2.56 (33.8%)	8.02 (52.8%)	17.3 (13.4%)
Eu_{0.005}Lu_{1.995}-dcph	148	20.7 (21.9%)	104 (30.8%)	235 (47.2%)
Tb₂-dpph	0.83	---	---	---
Tb_{0.140}Lu_{1.860}-dpph	1.31	1.27 (99.6%)	6.02 (0.33%)	13.2 (0.04%)
Tb_{0.060}Lu_{1.940}-dpph	2.14	1.88 (89.7%)	3.88 (10.2%)	5.77 (0.1%)
Tb_{0.013}Lu_{1.987}-dpph	7.80	3.76 (39.1%)	9.78 (59.1%)	30.4 (1.8%)
Tb_{0.011}Lu_{1.989}-dcph	152	27.1 (29.4%)	172 (66.3%)	700 (4.3%)

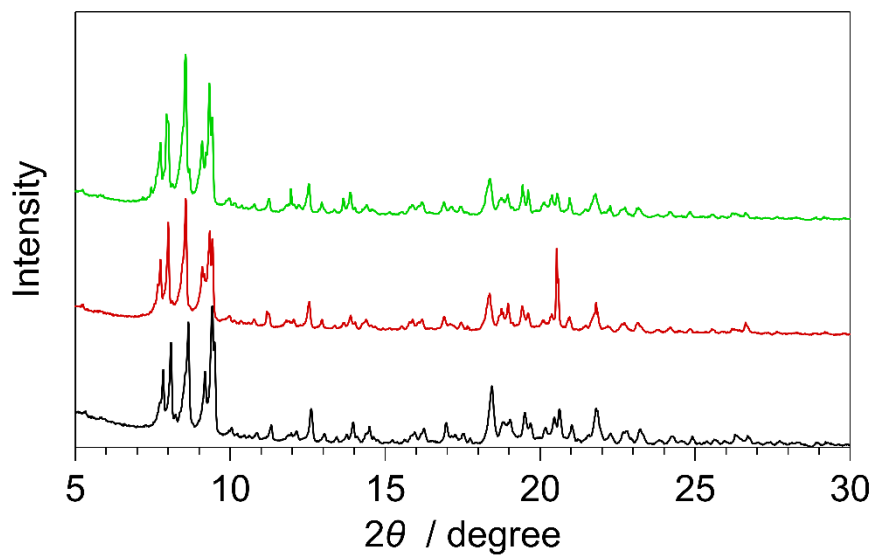


Figure S23. Powder X-ray diffraction patterns of **$\text{Lu}_2\text{-dcph}$** (black line), **$\text{Eu}_{0.005}\text{Lu}_{1.995}\text{-dcph}$** (red line), and **$\text{Tb}_{0.011}\text{Lu}_{1.989}\text{-dpph}$** (green line).

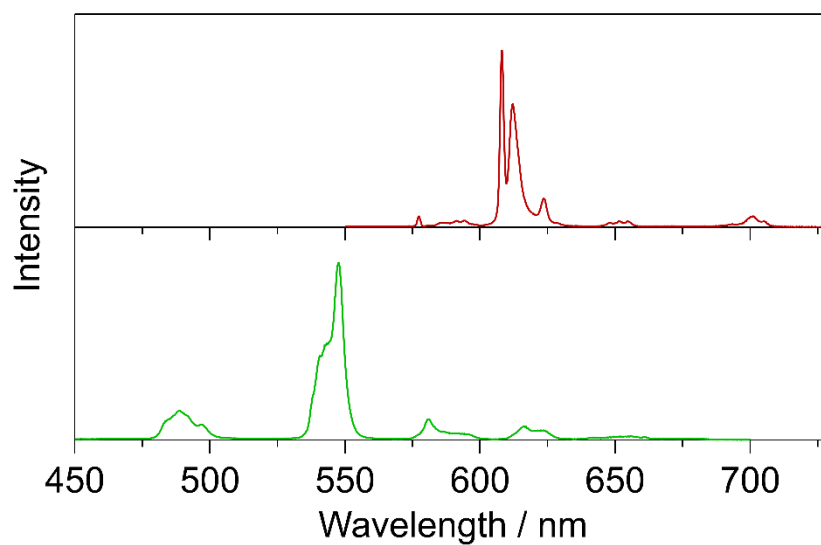


Figure S24. Emission spectra ($\lambda_{\text{ex}} = 356$ nm, crystalline state, 293 K, under degassed condition) of **$\text{Eu}_{0.005}\text{Lu}_{1.995}\text{-dcph}$** (red line) and **$\text{Tb}_{0.011}\text{Lu}_{1.989}\text{-dcph}$** (green line).

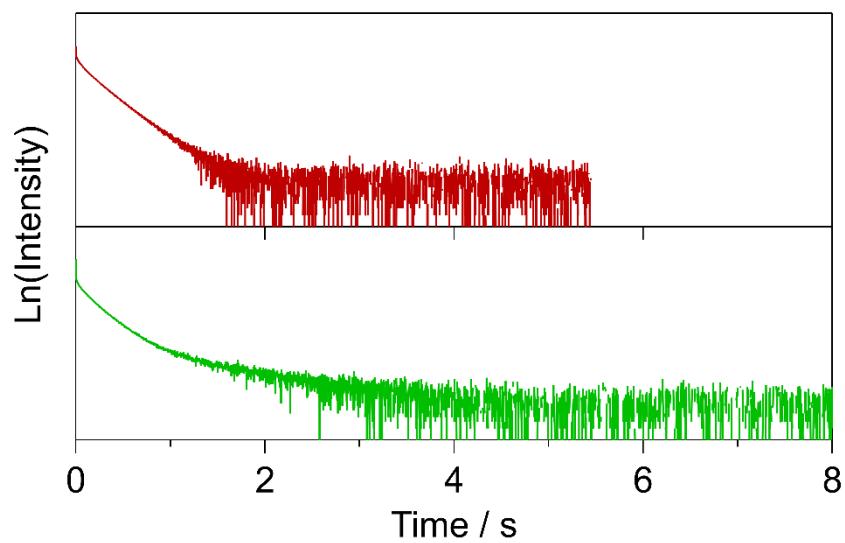


Figure S25. Emission decay curves ($\lambda_{\text{ex}} = 356$ nm, crystalline state, 293 K, under degassed condition) of **Eu_{0.005}Lu_{1.995}-dcph** ($\lambda_{\text{em}} = 608$ nm, red line) and **Tb_{0.011}Lu_{1.989}-dcph** ($\lambda_{\text{em}} = 548$ nm, green line).

Supplementary Note 3: Evaluation of emission lifetime for Lu₂-dcph

To evaluate the emission lifetime for [Lu₂(tmh)₆dcph] (where **Lu₂-dcph**), **Lu₂-dcph** was synthesized and single-crystal X-ray diffraction measurement was performed. **Lu₂-dcph** is seven-coordinated dinuclear structure, in which two [Lu(tmh)₃] units are connected by dcph ligand (**Figure S26**, crystallographic parameters are shown in **Table S4**). One phenanthrene unit in Lu complex is surrounded by two adjacent phenanthrene units at distance of 1.14 nm (**Figure S27**).

The emission spectrum of **Lu₂-dcph** crystal exhibited broad emission bands at around 550 nm (**Figure S28**), which originated from the π - π^* transition of dcph ligand. The T₁ level of dcph ligand was estimated to be 20,000 cm⁻¹ based on the emission spectrum deconvolution using Gaussian functions. The emission decay curve of **Lu₂-dcph** (**Figure S29**) was fitted using triple-exponential functions and the emission lifetime was estimated to be 246 ms ($\tau_1 = 54.3$ ms (67.5%), $\tau_2 = 273$ ms (17.1%), $\tau_3 = 1057$ ms (15.4%)).

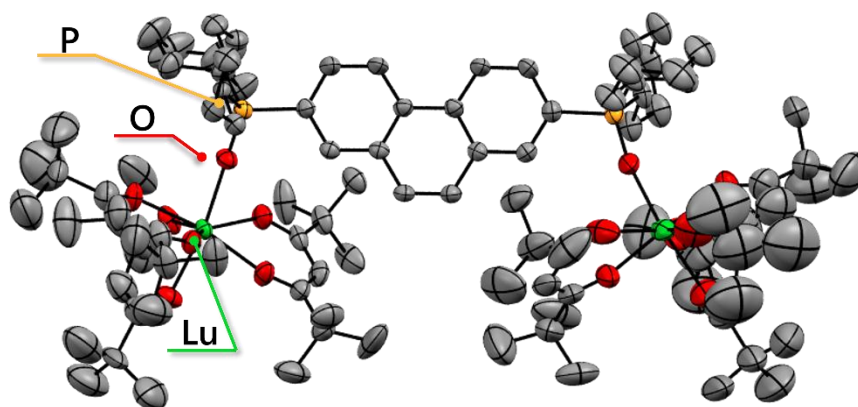


Figure S26. ORTEP drawing of **Lu₂-dcph** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Gray spheres represent carbon; red spheres, oxygen; orange spheres, phosphorus; green spheres, lutetium.

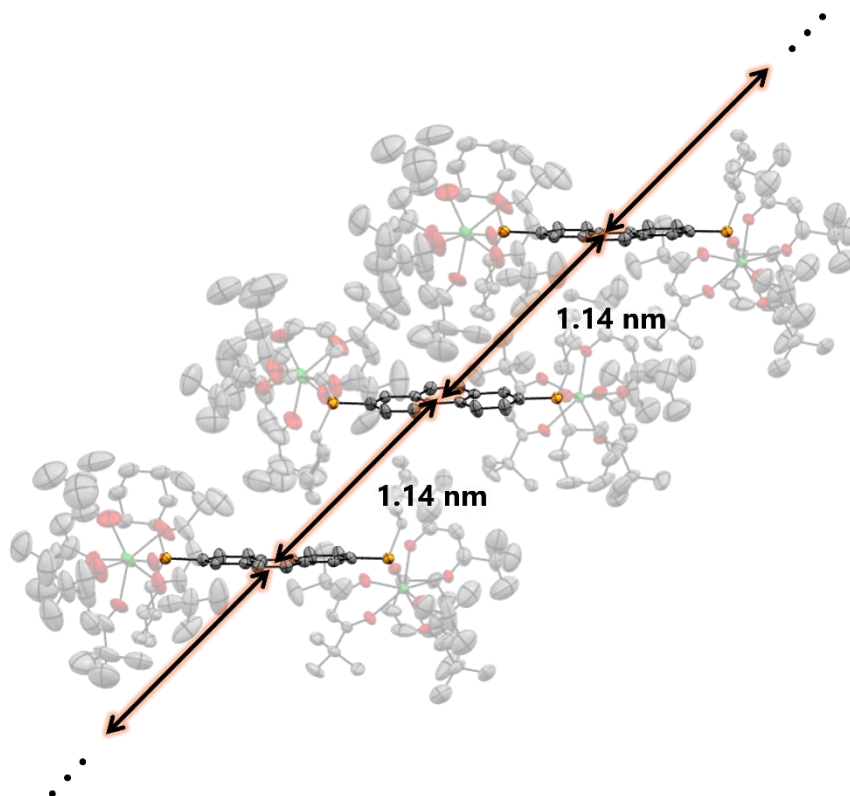


Figure S27. X-ray crystal structure of **Lu₂-dcph** viewed from b-axis (50% probability ellipsoids). The distances were calculated based on the centroids of phenanthrene units.

Table S4. Crystallographic parameters for [Lu₂(tmh)₆dcph]

	[Lu ₂ (tmh) ₆ dcph]
Chemical formula	C ₁₀₄ H ₁₆₆ O ₁₄ P ₂ Lu ₂
Crystal system	Monoclinic
Space group	P2 ₁ /c
<i>a</i> / Å	29.9349(8)
<i>b</i> / Å	24.2487(6)
<i>c</i> / Å	22.7643(5)
Volume / Å ³	16498.5(7)
<i>Z</i>	6
Density / g cm ⁻³	1.239
Temperature / °C	−150
<i>R</i>	0.0671
<i>wR</i> ₂	0.1866

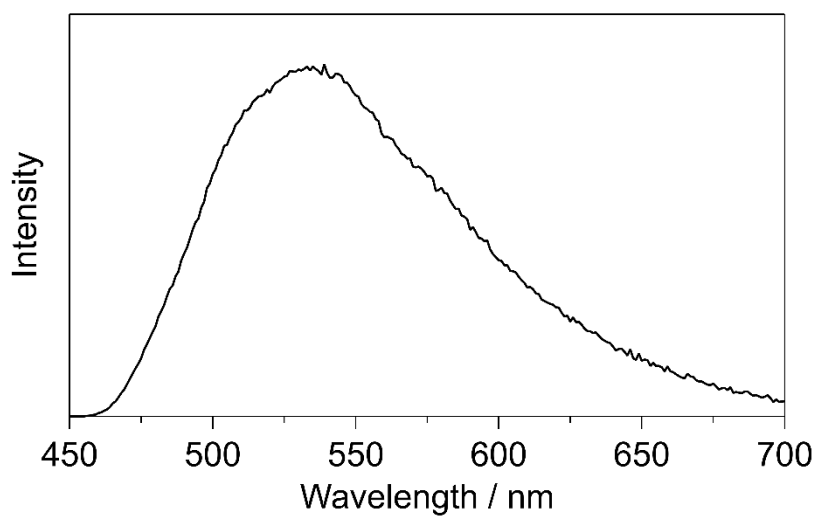


Figure S28. Emission spectrum ($\lambda_{\text{ex}} = 400$ nm, delay time: 80 ms, crystalline state, 100 K, under degassed condition) of **Lu₂-dcph**.

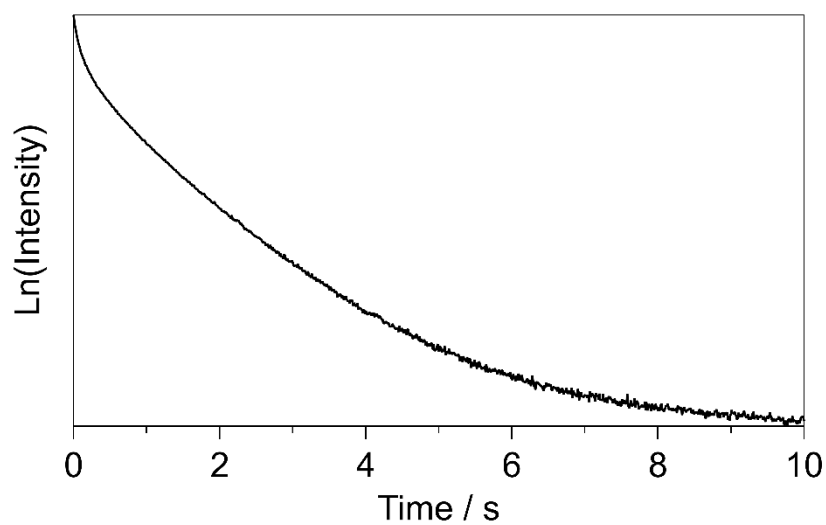


Figure S29. Emission decay curve ($\lambda_{\text{ex}} = 400$ nm, $\lambda_{\text{em}} = 530$ nm, crystalline state, 298 K, under degassed condition) of **Lu₂-dcph**.

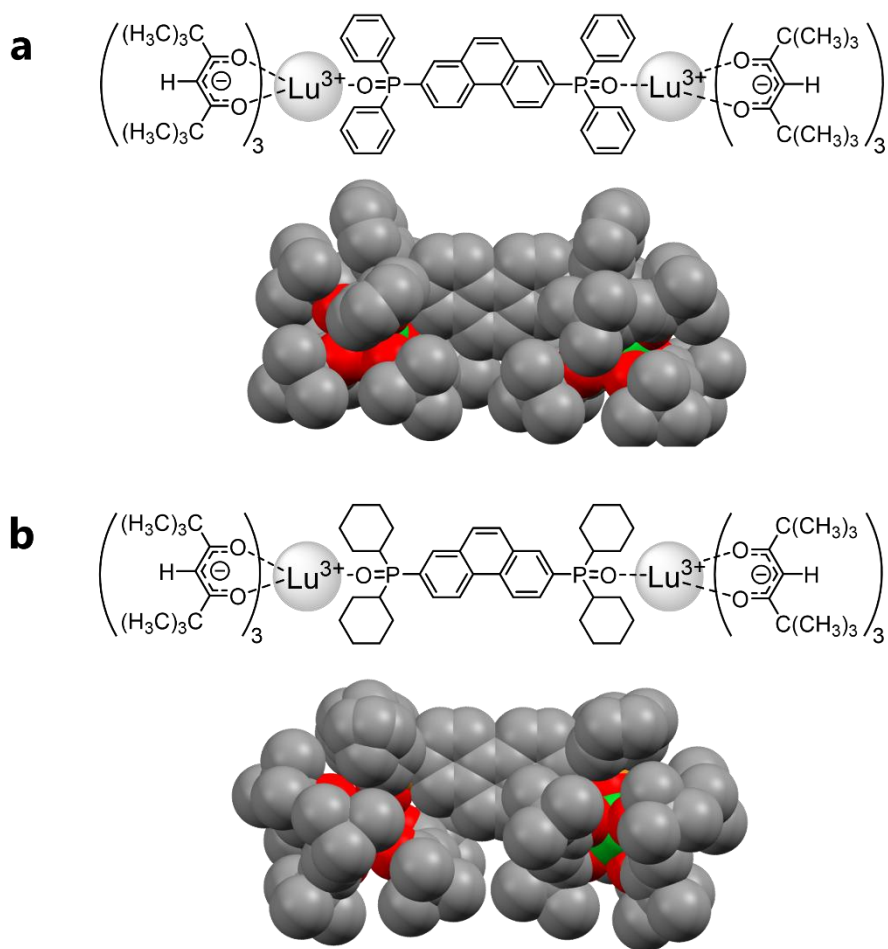


Figure S30. Space-fill drawing models of a) **Lu₂-dpph** and b) **Lu₂-dcph**.

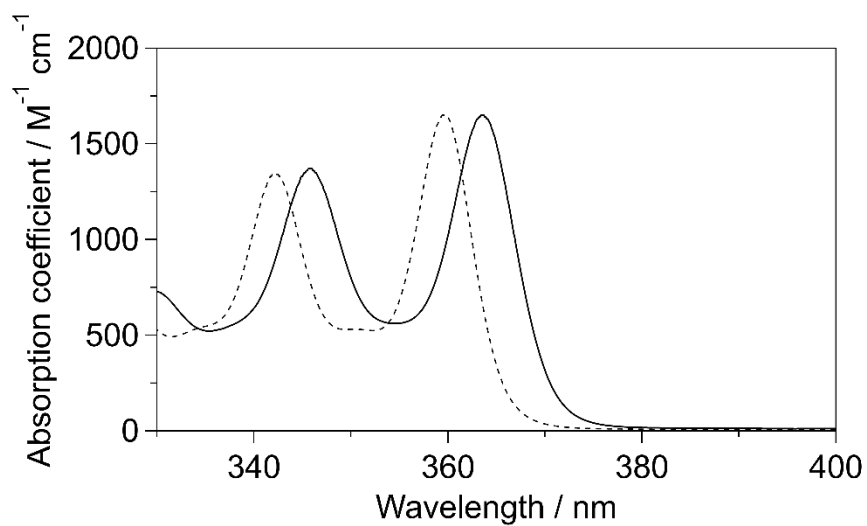


Figure S31. Absorption spectra of dpph (solid line, 0.8 mM) and dcph (dashed line, 0.8 mM). Absorption coefficients at 356 nm of dpph and dcph were determined to be 575 and 872 M⁻¹ cm⁻¹, respectively.

Supplementary Note 4: Photophysical properties of Eu₂-dcph and Tb₂-dcph

For the evaluation of photophysical properties for **Eu_{0.005}Lu_{1.995}-dcph** and **Tb_{0.011}Lu_{1.989}-dcph**, pure lanthanide crystals ([Eu₂(tmh)₆dcph]: **Eu₂-dcph** and [Tb₂(tmh)₆dcph]: **Tb₂-dcph**) were synthesized and identified by the same procedure of (**Eu₂-dpph** and **Tb₂-dpph**). **Eu₂-dpph** exhibits emission bands at 578, 594, 608, 655, 701 nm (**Figure S32**), which are assigned to ⁵D₀ → ⁷F_J (*J* = 0, 1, 2, 3, and 4, respectively). For **Tb₂-dpph**, emission bands at 489, 548, 581, 616, and 655 nm were observed (**Figure S33**), assigned to ⁵D₄ → ⁷F_J (*J* = 6, 5, 4, 3, and 2, respectively). The emission spectra shapes of **Eu₂-dcph** and **Tb₂-dcph** are similar to those of **Eu_{0.005}Lu_{1.995}-dcph** and **Tb_{0.011}Lu_{1.989}-dcph**, respectively, indicating similar coordination environment between pure lanthanide crystals and mixed lanthanide crystals.

The photophysical properties of **Eu₂-dcph** and **Tb₂-dcph** are summarized in **Table S5**. From the emission decay analyses of **Eu₂-dcph** and **Tb₂-dcph** (**Figure S34**), the emission lifetimes were estimated to be 0.46 and 0.63 ms, respectively. The emission quantum yields for **Eu₂-dcph** and **Tb₂-dcph** were estimated to be 5.2 and 63%, respectively. The *I_B* values were evaluated to be 45.3 (**Eu₂-dcph**) and 549 (**Tb₂-dcph**) M⁻¹ cm⁻¹. From these results, effective photosensitized emission is considered to occur in **Eu_{0.005}Lu_{1.995}-dcph** and **Tb_{0.011}Lu_{1.989}-dcph**.

Table S5 Photophysical properties of **Eu₂-dcph** and **Tb₂-dcph**.

	$\tau^{[a]}$ / ms	$\Phi_{\text{tot}}^{[b]}$ / %	$I_{\text{B}}^{[c]}$ / M ⁻¹ cm ⁻¹
Eu₂-dcph	0.46	5.2	45.3
Tb₂-dcph	0.63	63.0	549

[a] λ_{ex} = 360 nm, λ_{em} = 612 nm (for **Eu₂-dpph**) or 548 nm (for **Tb₂-dpph**). [b] λ_{ex} = 356

nm, N₂ flow. [c] λ_{ex} = 356 nm.

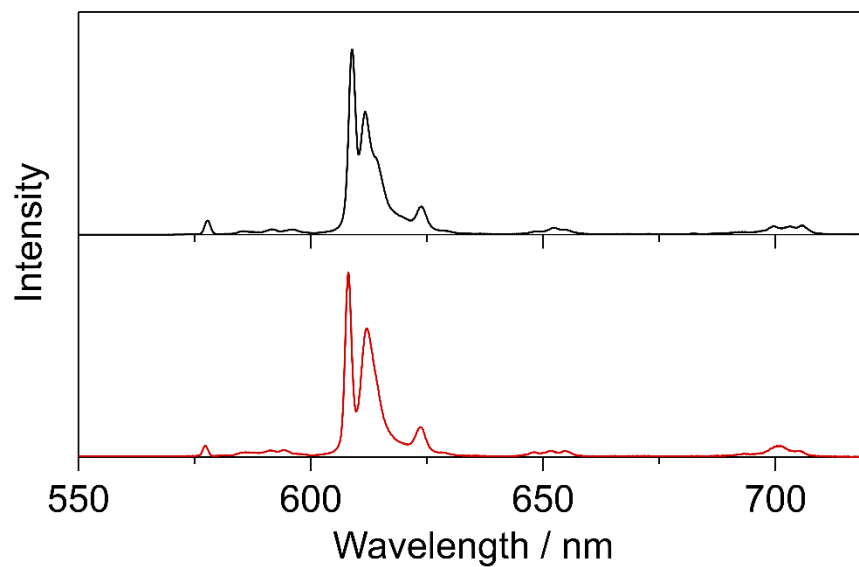


Figure S32. Emission spectra ($\lambda_{\text{ex}} = 356$ nm, 298 K, crystalline state, under degassed condition) of **Eu₂-dcph** (upper) and **Eu_{0.005}Lu_{1.995}-dcph** (lower).

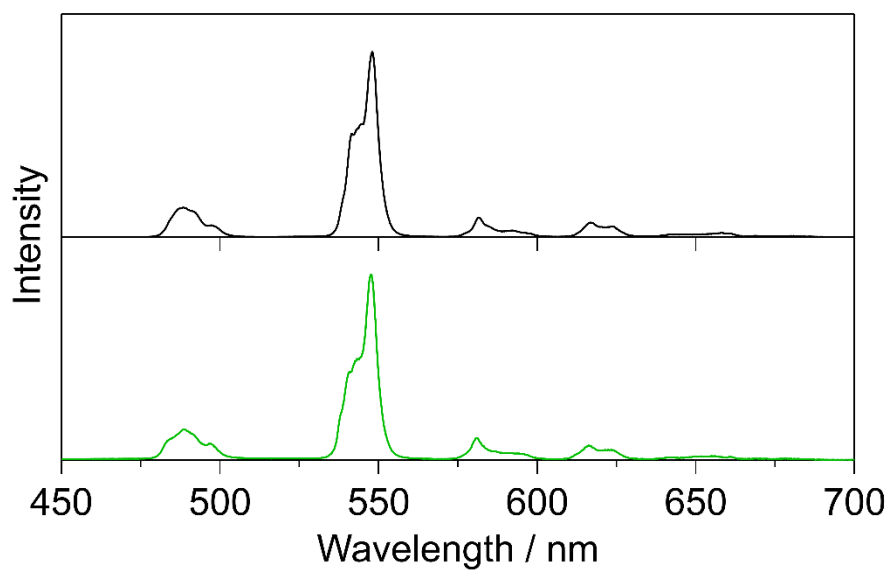


Figure S33. Emission spectra ($\lambda_{\text{ex}} = 356$ nm, 298 K, crystalline state, under degassed condition) of **Tb₂-dcph** (upper) and **Tb_{0.011}Lu_{1.989}-dcph** (lower).

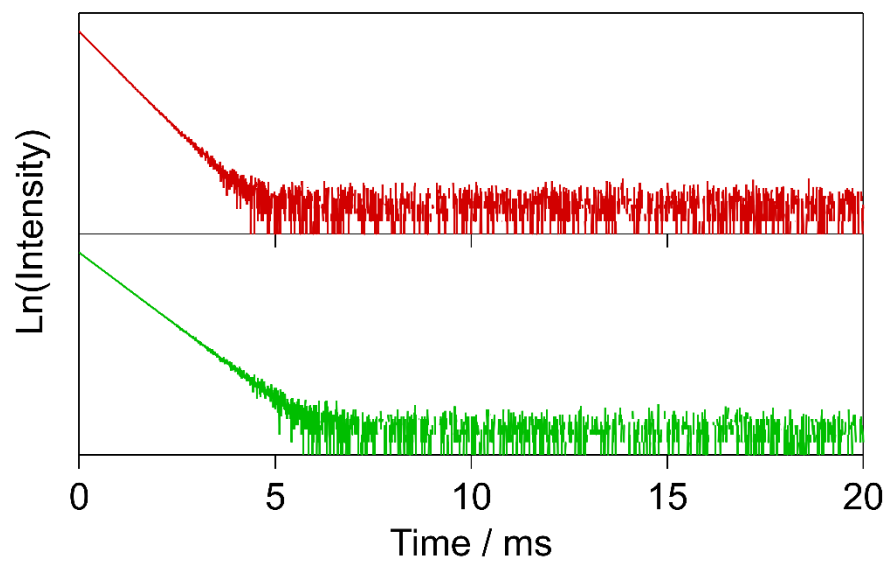


Figure S34. Emission decay curves ($\lambda_{\text{ex}} = 360$ nm, 298 K, crystalline state, under degassed condition) of **Eu₂-dcph** (upper, $\lambda_{\text{em}} = 608$ nm) and **Tb₂-dcph** (lower, $\lambda_{\text{em}} = 548$ nm).

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