



Title	Triboluminescence of Lanthanide Coordination Polymers with Face-to-Face Arranged Substituents
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Citation	Angewandte chemie-international edition, 56(25), 7171-7175 https://doi.org/10.1002/anie.201703638
Issue Date	2017-06-12
Doc URL	http://hdl.handle.net/2115/70700
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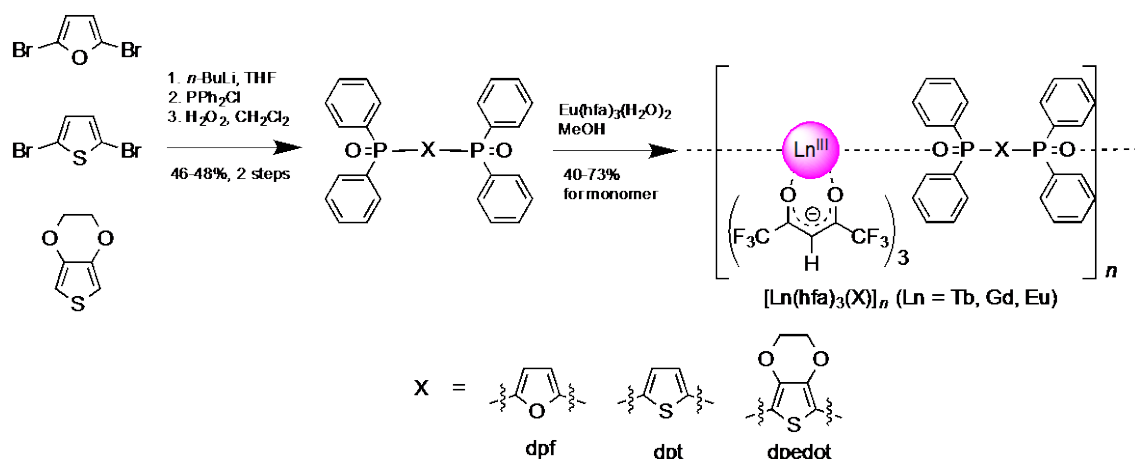


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General

Europium acetate *n*-hydrate (99.9%), terbium acetate tetrahydrate (99.9%), gadolinium acetate tetrahydrate (99.9%), 1.55 M *n*-butyllithium (*n*-BuLi) in *n*-hexane, and hydrogen peroxide were purchased from Kanto Chemical Co., Inc. 2,5-Dibromofuran, 3,4-ethylenedioxythiophene, 2,5-dibromothiophene, and chlorodiphenylphosphine (PPh₂Cl) were obtained from Tokyo Chemical Industry Co., Ltd. All other chemicals and solvents were reagent grade and were used without further purification.

¹H NMR (400 MHz) spectra were recorded on a JEOL ECS400. Chemical shifts were reported in δ ppm, referenced to an internal tetramethylsilane standard for ¹H NMR spectroscopy. Infrared spectra were recorded on a JASCO FTIR-420 spectrometer using KBr pellets. Elemental analyses were performed by an Exeter Analytical CE440. Mass spectrometry was performed by a Thermo Scientific Exactive (ESI-MS) and a JEOL JMS-700TZ (FAB-MS).



Scheme S1. Synthetic schemes of phosphine oxide ligands and Ln^{III} coordination polymers.

Preparation of [Eu(hfa)₃(H₂O)₂]₂: Europium acetate *n*-hydrate (2.0 g, 5.8 mmol) was dissolved in distilled water (30 mL). Hexafluoroacetylacetonate (4.0 g, 19 mmol) was added dropwise to the solution and let stirred for 3 h at room temperature to form pale yellow precipitates. The reaction mixture was filtered and washed with distilled water and chloroform. The resulting powder was used without further purification for the next step.

[Eu(hfa)₃(H₂O)₂]₂: Yield 4.1 g (89%). IR (KBr): 1650 (st, C=O), 1258-1145 (st, C-F) cm⁻¹. Anal. Calcd for C₁₅H₇EuF₁₈O₈: C, 22.27; H, 0.87%. Found: C, 22.12; H, 1.01%.

Preparation of 2,5-bis(diphenylphosphoryl)furan (dpf): In a degassed 3-neck round-bottomed flask (300 mL vol.), 2,5-dibromofuran (2.6 mL, 24 mmol) was dissolved in dry THF (130 mL) under argon atmosphere, then stirred until a homogeneous solution was formed at room temperature. A solution of *n*-BuLi (40 mL, 62 mmol) was added dropwise to the solution at -80°C. The addition was completed in ca. 15 min. The mixture was allowed to stir for 3 h, after which a PPh₂Cl (12 mL, 67 mmol) was added dropwise at -80°C, then the solution became cloudy. The mixture was gradually brought to room temperature, and stirred for 14 h to form clouded yellow solution. The product was extracted with dichloromethane and dried over anhydrous MgSO₄. The solvent was concentrated and dissolved in dichloromethane (100 mL) in a flask. The solution was cooled to 0°C and then 30% H₂O₂ aqueous solution (21 mL) was added to it. The reaction mixture was stirred for 3 h. The product was extracted with dichloromethane and the obtained crude powder was washed with ethyl acetate for several times to afford white powder.

dpf: Yield 5.5 g (48%). ^1H NMR (400 MHz, CD_3OD , 25°C) δ 7.61-7.67 (m, 12H, -CH), δ 7.51-7.55 (m, 8H, -CH), δ 7.27 (t, 2H, -CH) ppm. ESI-Mass (m/z): calcd for $\text{C}_{28}\text{H}_{23}\text{O}_3\text{P}_2$ $[\text{M}+\text{H}]^+$, 469.11; found, 469.11. Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{O}_3\text{P}_2$: C, 71.79; H, 4.73%. Found: C, 71.51; H, 4.67%.

Preparation of Ln^{III} coordination polymers $[\text{Ln}(\text{hfa})_3(\text{dpf})]_n$ ($\text{Ln} = \text{Tb}, \text{Gd}, \text{Eu}$): Phosphine oxide ligand, dpf (0.37 g, 0.80 mmol) and $\text{Ln}(\text{hfa})_3(\text{H}_2\text{O})_2$ ($\text{Ln} = \text{Tb}, \text{Gd}, \text{Eu}$, 0.80 mmol) were dissolved in methanol (30 mL), respectively. The solutions were mixed and refluxed for 3 h. The reaction mixture was concentrated and washed with chloroform. The solvent was evaporated and re-dissolved in 50°C methanol for recrystallization. The obtained crystals were washed with -20°C methanol.

$[\text{Tb}(\text{hfa})_3(\text{dpf})]_n$: Yield 0.65 g (65% for monomer). IR (KBr): 1657 (st, C=O), 1145 (st, P=O) cm^{-1} . ESI-Mass (m/z): calcd for $\text{C}_{38}\text{H}_{24}\text{TbF}_{12}\text{O}_7\text{P}_2$ $[\text{M}-\text{hfa}]^+$: 1041.0, found, 1041.0. Anal. Calcd for $\text{C}_{43}\text{H}_{25}\text{TbF}_{18}\text{O}_9\text{P}_2$: C, 41.37; H, 2.02%. Found: C, 41.32; H, 1.88%.

$[\text{Gd}(\text{hfa})_3(\text{dpf})]_n$: Yield 0.57 g (57% for monomer). IR (KBr): 1657 (st, C=O), 1145 (st, P=O) cm^{-1} . ESI-Mass (m/z): calcd for $\text{C}_{38}\text{H}_{24}\text{GdF}_{12}\text{O}_7\text{P}_2$ $[\text{M}-\text{hfa}]^+$: 1040.0, found, 1040.0. Anal. Calcd for $\text{C}_{43}\text{H}_{25}\text{GdF}_{18}\text{O}_9\text{P}_2$: C, 41.42; H, 2.02%. Found: C, 41.30; H, 1.87%.

$[\text{Eu}(\text{hfa})_3(\text{dpf})]_n$: Yield 0.73 g (73% for monomer). IR (KBr): 1657 (st, C=O), 1145 (st, P=O) cm^{-1} . ESI-Mass (m/z): calcd for $\text{C}_{38}\text{H}_{24}\text{EuF}_{12}\text{O}_7\text{P}_2$ $[\text{M}-\text{hfa}]^+$: 1035.0, found, 1034.7. Anal. Calcd for $\text{C}_{43}\text{H}_{25}\text{EuF}_{18}\text{O}_9\text{P}_2$: C, 41.60; H, 2.03%. Found: C, 41.62; H, 2.32%.

Preparation of $\text{Tb}^{\text{III}}/\text{Eu}^{\text{III}}$ mixed coordination polymers $[\text{Tb},\text{Eu}(\text{hfa})_3(\text{dpf})]_n$ ($\text{Tb}/\text{Eu} = 1$): $\text{Tb}(\text{hfa})_3(\text{H}_2\text{O})_2$ (0.34 g, 0.40 mmol) and $\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2$ (0.34 g, 0.40 mmol) were dissolved in methanol (30 mL). The $\text{Tb}^{\text{III}}/\text{Eu}^{\text{III}}$ -mixed solution (in total 0.80 mmol, 30 mL) was added to a methanol solution (30 mL) of dpf ligand (0.37 g, 0.80 mmol), and the mixture was refluxed for 3 h. The reaction mixture was concentrated and washed with chloroform. The solvent was evaporated and re-dissolved in 50°C methanol for recrystallization. The obtained crystals were washed with -20°C methanol.

Yield: 0.72 g (72% for monomer). IR (KBr): 1657 (st, C=O), 1145 (st, P=O) cm^{-1} . Anal. Calcd for $\text{C}_{43}\text{H}_{25}\text{Tb}_{0.5}\text{Eu}_{0.5}\text{F}_{18}\text{O}_9\text{P}_2$: C, 41.48; H, 2.02%. Found: C, 41.40; H, 1.89%.

Preparation of $\text{Tb}^{\text{III}}/\text{Eu}^{\text{III}}$ mixed coordination polymers $[\text{Tb},\text{Eu}(\text{hfa})_3(\text{dpf})]_n$ ($\text{Tb}/\text{Eu} = 10$): $\text{Tb}(\text{hfa})_3(\text{H}_2\text{O})_2$ (0.59 g, 0.73 mmol) and $\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2$ (59 mg, 0.07 mmol) were dissolved in methanol (30 mL). The $\text{Tb}^{\text{III}}/\text{Eu}^{\text{III}}$ -mixed solution (in total 0.80 mmol, 30 mL) was added to a methanol solution (30 mL) of dpf ligand (0.37 g, 0.80 mmol), and the mixture was refluxed for 3 h.

The reaction mixture was concentrated and washed with chloroform. The solvent was evaporated and re-dissolved in 50 °C methanol for recrystallization. The obtained crystals were washed with -20 °C methanol.

Yield: 0.67 g (67% for monomer). IR (KBr): 1657 (st, C=O), 1145 (st, P=O) cm^{-1} . Anal. Calcd for $\text{C}_{43}\text{H}_{25}\text{Tb}_{0.91}\text{Eu}_{0.09}\text{F}_{18}\text{O}_9\text{P}_2$: C, 41.39; H, 2.02%. Found: C, 41.36; H, 1.89%.

Preparation of 2,5-bis(diphenylphosphoryl)thiophene (dpt) and 2,5-bis(diphenylphosphoryl)ethylenedioxythiophene (dpedot) ligands:^[11]

2,5-Dibromothiophene (2 mL, 18 mmol) was dissolved in dry THF (70 mL), and a solution of *n*-BuLi (28 mL, 44 mmol) was added dropwise at -80 °C in ca. 15 min. The mixture was allowed to stir for 3 h, after which a PPh_2Cl (8.0 mL, 45 mmol) was added dropwise at -80 °C. The mixture was gradually brought to room temperature, and stirred for 14 h. The product was extracted with dichloromethane, washed with brine for three times and dried over anhydrous MgSO_4 . The solvent was concentrated and dissolved in dichloromethane (50 mL) in a flask. The solution was cooled to 0 °C and then 30% H_2O_2 aqueous solution (24 mL) was added to it. The reaction mixture was stirred for 2 h. The product was extracted with dichloromethane and obtained powder was washed with ethyl acetate for several times to afford white powder.

dpt: Yield 2.3 g (48%). ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 7.79-7.86 (m, 8H, -CH), δ 7.64-7.67 (m, 2H, -CH), δ 7.43-7.49 (m, 6H, -CH), δ 7.35-7.41 (m, 8H, -CH) ppm. ESI-Mass (m/z): calcd for $\text{C}_{28}\text{H}_{23}\text{O}_2\text{P}_2\text{S}$ [$\text{M}+\text{H}$] $^+$, 485.09; found, 485.09. Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{O}_2\text{P}_2\text{S}$: C, 69.41; H, 4.58%. Found: C, 68.90; H, 4.57%.

dpedot: Yield 4.6 g (46%). ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 7.68-7.74 (m, 8H, -CH), δ 7.51-7.55 (m, 4H, -CH), δ 7.42-7.46 (m, 8H, -CH), δ 4.12 (s, 4H, - CH_2) ppm. ESI-Mass (m/z): calcd for $\text{C}_{30}\text{H}_{25}\text{O}_4\text{P}_2\text{S}$ [$\text{M}+\text{H}$] $^+$, 543.09; found, 543.09. Anal. Calcd for $\text{C}_{30}\text{H}_{24}\text{O}_4\text{P}_2\text{S}$: C, 66.42; H, 4.46%. Found: C, 66.04; H, 4.53%.

Preparation of $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$:^[11] Phosphine oxide ligand (dpt; 1 equiv.) and $\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2$ (1 equiv.) were dissolved in methanol (30 mL), respectively. The solutions were mixed and refluxed for 3h to form white precipitates. The obtained white solid was washed with methanol.

$[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$: Yield 0.40 g (40% for monomer). IR (KBr): 1655 (st, C=O), 1143 (st, P=O) cm^{-1} . FAB-Mass (m/z): calcd for $\text{C}_{38}\text{H}_{24}\text{EuF}_{12}\text{O}_6\text{P}_2\text{S}$ [$\text{M}-\text{hfa}$] $^+$: 1051.0, found, 1050.8. Anal. Calcd for $\text{C}_{43}\text{H}_{25}\text{EuF}_{18}\text{O}_8\text{P}_2\text{S}$: C, 41.07; H, 2.00%. Found: C, 40.91; H, 2.12%.

Preparation of $[\text{Eu}(\text{hfa})_3(\text{dpedot})]_n$:^[11] Phosphine oxide ligand (dpedot; 1 equiv.) and $\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2$ (1 equiv.) were dissolved in methanol, respectively. The solutions were mixed and refluxed for 3h. The reaction mixture was concentrated and washed with chloroform. The solvent was evaporated and re-dissolved in 50°C methanol for recrystallization. The obtained crystals were washed with -20°C methanol.

$[\text{Eu}(\text{hfa})_3(\text{dpedot})]_n$: Yield 0.73 g (69% for monomer). IR (KBr): 1657 (st, C=O), 1145 (st, P=O) cm^{-1} . FAB-Mass (m/z): calcd for $\text{C}_{40}\text{H}_{26}\text{EuF}_{12}\text{O}_8\text{P}_2\text{S}$ $[\text{M}-\text{hfa}]^+$: 1109.0, found, 1109.0. Anal. Calcd for $\text{C}_{45}\text{H}_{27}\text{EuF}_{18}\text{O}_{10}\text{P}_2\text{S}$: C, 41.08; H, 2.07 %. Found: C, 40.92; H, 2.37%.

Optical Measurements: UV-Vis absorption spectra were recorded on a JASCO V-670 spectrometer. Emission and excitation spectra were recorded on a HORIBA Fluorolog-3 spectrofluorometer and corrected for the response of the detector system. 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, $\lambda = 1064$ 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. Emission lifetimes were determined from the slope of logarithmic plots of the decay profiles. The emission quantum yields excited at 380 nm (Φ_{tot}) were estimated using JASCO F-6300-H spectrometer attached with JASCO ILF-533 integrating sphere unit ($\varphi = 100$ mm). The wavelength dependence of the detector response and the beam intensity of Xe light source for each spectrum were calibrated using a standard light source. The emission quantum yields excited by Eu(III) ions (Φ_{ff}) were calculated using the following equations.^[16]

$$\Phi_{ff} = \frac{k_r}{k_r + k_{nr}} = \frac{\tau_{obs}}{\tau_{rad}} \cdot \cdot \cdot (2)$$

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

$$k_{nr} = \frac{1}{\tau_{obs}} - \frac{1}{\tau_{rad}} \cdot \cdot \cdot (4)$$

$A_{MD,0}$ is the spontaneous emission probability for ${}^5D_0 \rightarrow {}^7F_1$ transition in vacuo (14.65 s^{-1}), n is the refractive index of the medium (An average index of refraction equal to 1.5 was used.^[17]), and I_{tot}/I_{MD} is the ratio of the total area of the corrected Eu^{III} emission spectrum to the area of the ${}^5D_0 \rightarrow {}^7F_1$ band. Emission spectral shapes of $[\text{Eu}(\text{hfa})_3(\text{dpf})]_n$ were independent of their excitation spectra (Figure S1), thus the I_{tot}/I_{MD} values were constant. The TL/PL spectral measurements were performed on a Photonic Hamamatsu PMA-12 Multichannel Analyzer. The obtained spectra were corrected for the response of the detector system and normalized at maximum intensity. Generally, excitation source of TL arises from the fracture of a crystal, and excitation spectra of TL are not recorded as those of PL.

In order to measure EL spectra, incorporation of hole/electron transport units and adjustment of HOMO-LUMO energy level of the ligands in Ln^{III} coordination polymers are required.^[18] Introduction of substituents for EL devices also drastically affects on TL activity due to the

structural modification. For these reasons, EL spectra of $[\text{Ln}(\text{hfa})_3(\text{dpf})]_n$ are not available in this study.

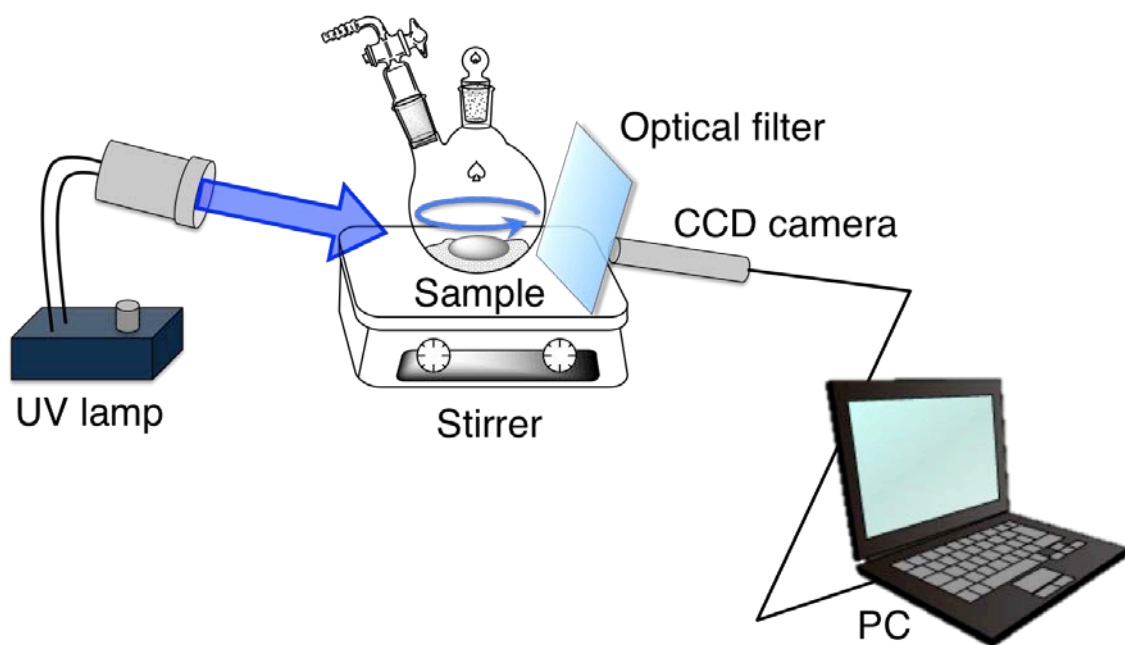


Figure S1. Experimental setups for TL and PL measurements (UV lamp: $\lambda_{\text{ex}} = 365 \text{ nm}$, Stirrer: $v_{\text{rot}} = 1500 \text{ rpm}$, Optical filter: 390 nm longpass, CCD camera: exposure time = 1000 ms, averaging = 2 times).

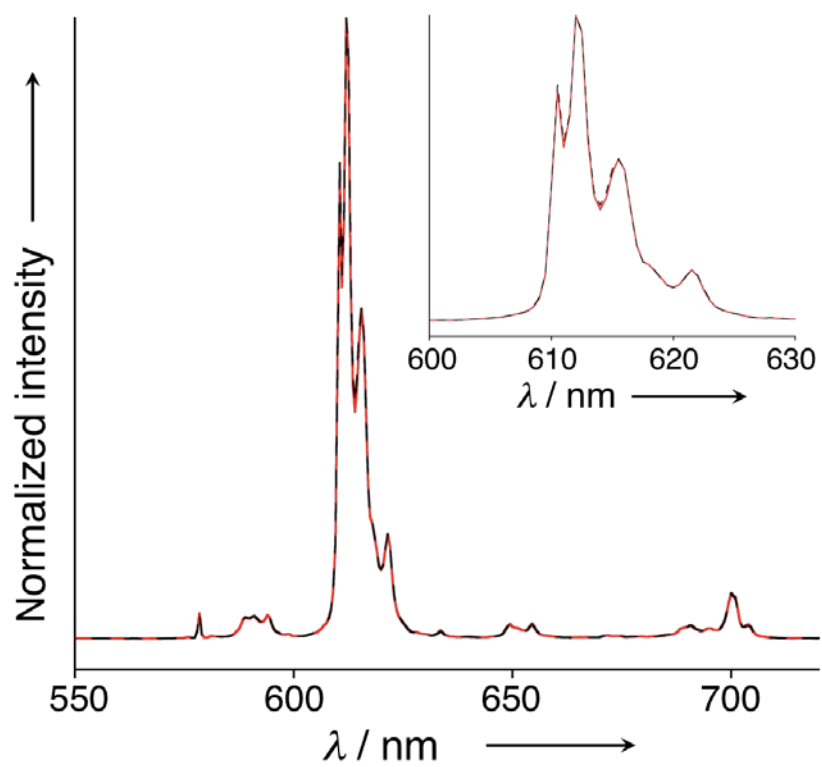


Figure S2. PL spectra of $[\text{Eu}(\text{hfa})_3(\text{dpf})]_n$ excited at 380 nm (solid red line) and at 355 nm (dashed black line) (inset shows ${}^5\text{D}_0\text{-}{}^7\text{F}_1$ band).

Crystallography: Single crystals of $[\text{Ln}(\text{hfa})_3(\text{dpf})]_n$ ($\text{Ln} = \text{Tb}, \text{Gd}, \text{Eu}$) were prepared by slow evaporation of $[\text{Ln}(\text{hfa})_3(\text{dpf})]_n/\text{methanol}$ solution. A colorless block-shaped single crystal of $[\text{Ln}(\text{hfa})_3(\text{dpf})]_n$ was mounted on a MiTiGen micromesh using Paratone-N. The measurement was performed on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Mo-K α radiation. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package. CIF data was confirmed by using the checkCIF/PLATON service.

In order to investigate the geometrical symmetry around the Eu^{III} ions, the degree of distortion against an 8-coordinated square-antiprismatic structure (8-SAP, point group: D_{4d}) and an 8-coordinated trigonal-dodecahedral structure (8-TDH, point group: D_{2d}) was evaluated on the basis of shape factor S ^[19]

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

where m , δ_i and θ_i are the number of possible edges ($m = 18$ in this study), the observed dihedral angle between planes along the i th edge and the dihedral angle for the ideal structure, respectively. The observed dihedral angles (δ_i), idealized dihedral angles for a square antiprism (θ_{SAP}) and a trigonal dodecahedron (θ_{TDH}), calculated measure shape criteria, S_{SAP} and S_{TDH} are summarized in Figure S3 and Table S1. The value of S_{SAP} is much smaller than that of S_{TDH} ($S_{\text{SAP}} = 4.98 < S_{\text{TDH}} = 12.1$), indicating that the coordination geometry is categorized to be 8-SAP.

DFT calculations: DFT calculations for bridging ligands were carried out at the B3LYP level with the basis sets 6-31G (d) using the Gaussian 09 program package.^[20] The optimized structures were adopted based on the CIF data of Eu^{III} coordination polymers.

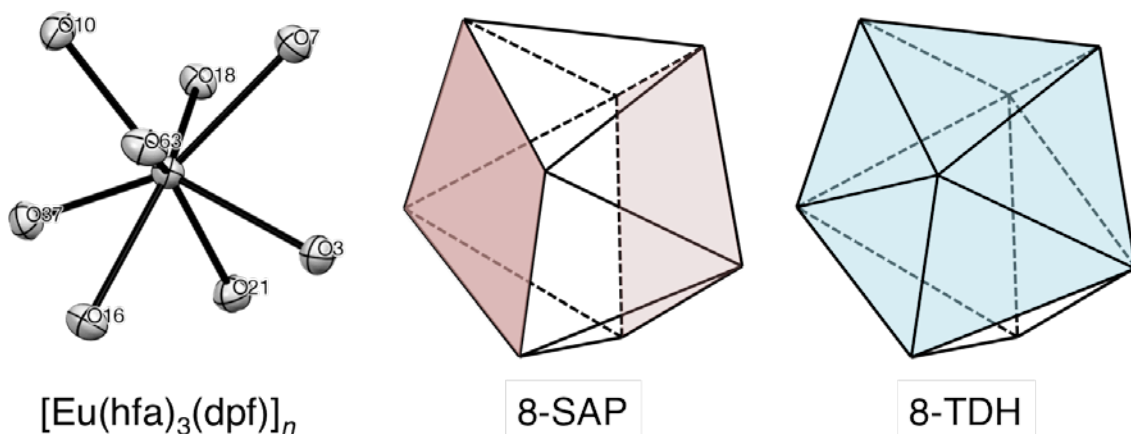


Figure S3. Coordination environments around an Eu^{III} ion of $[\text{Eu}(\text{hfa})_3(\text{dpf})]_n$.

Table S1. The observed ($\bar{\delta}_i$), idealized dihedral angles (θ_{SAP} , θ_{TDH}), and calculated S values ($S_{8\text{-SAP}}$, $S_{8\text{-TDH}}$) for $[\text{Eu}(\text{hfa})_3(\text{dpf})]_n$.

	$\bar{\delta}_i$	θ_{SAP}	SAP		θ_{TDH}	TDH		
			$\bar{\delta}_i - \theta_{\text{SAP}}$	$(\bar{\delta}_i - \theta_{\text{SAP}})^2$		$\bar{\delta}_i - \theta_{\text{TDH}}$	$(\bar{\delta}_i - \theta_{\text{TDH}})^2$	
O63-O37	12.23	0	12.23	149.57	29.86	-17.63	310.82	
O63-O10	82.10	77.1	5.00	25.00	61.48	20.62	425.18	
O63-O16	85.48	77.1	8.38	70.22	74.29	11.19	125.22	
O37-O10	77.12	77.1	0.02	0.0004	74.29	2.83	8.01	
O37-O16	84.09	77.1	6.99	48.86	61.48	22.61	511.21	
O3-O18	3.13	0	3.13	9.80	29.86	-26.73	714.49	
O3-O21	81.86	77.1	4.76	22.66	61.48	20.38	415.34	
O3-O7	77.71	77.1	0.61	0.37	74.29	3.42	11.70	
O18-O7	78.33	77.1	1.23	1.51	76.62	1.71	2.92	
O18-O21	73.55	77.1	-3.55	12.60	74.84	-1.29	1.66	
O21-O37	56.92	51.6	5.32	28.30	54.51	2.41	5.81	
O21-O16	44.33	51.6	-7.27	52.85	48.09	-3.76	14.14	
O3-O63	51.09	51.6	-0.51	0.26	47.76	3.33	11.09	
O3-O16	49.83	51.6	-1.77	3.13	54.48	-4.65	21.62	
O7-O63	53.72	51.6	2.12	4.49	52.57	1.15	1.32	
O7-O10	48.83	51.6	-2.77	7.67	52.85	-4.02	16.16	
O18-O37	54.33	51.6	2.73	7.45	47.34	6.99	48.86	
O18-O10	52.63	51.6	1.03	1.06	52.63	0	0	
			$S_{\text{SAP}} = 4.98$			$S_{\text{TDH}} = 12.12$		

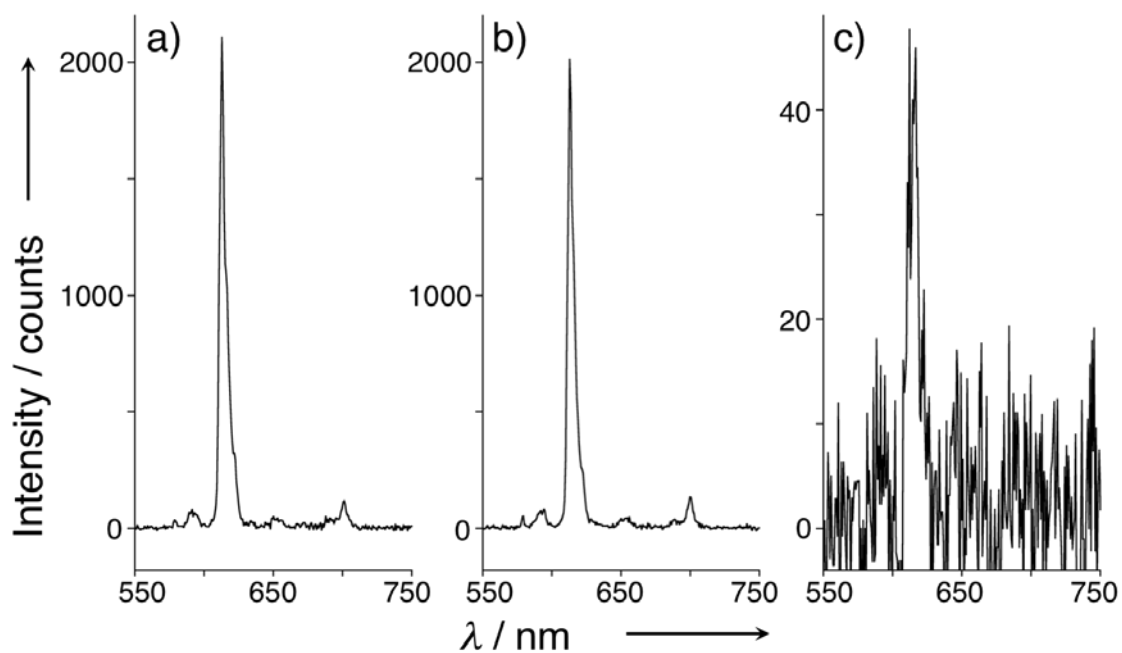


Figure S4. TL spectra of a) $[\text{Eu}(\text{hfa})_3(\text{dpf})]_n$, b) $[\text{Eu}(\text{hfa})_3(\text{dpedot})]_n$, and c) $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$.

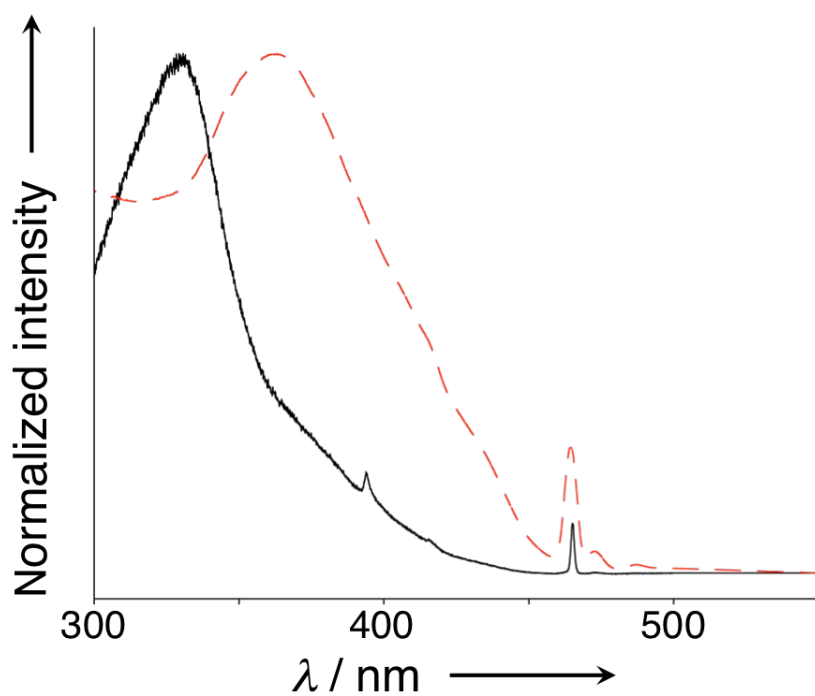


Figure S5. Excitation ($\lambda_{\text{obs}} = 613 \text{ nm}$, dashed red line) and diffuse-reflectance (solid black line) spectra of $[\text{Eu}(\text{hfa})_3(\text{dpf})]_n$ in solid state.

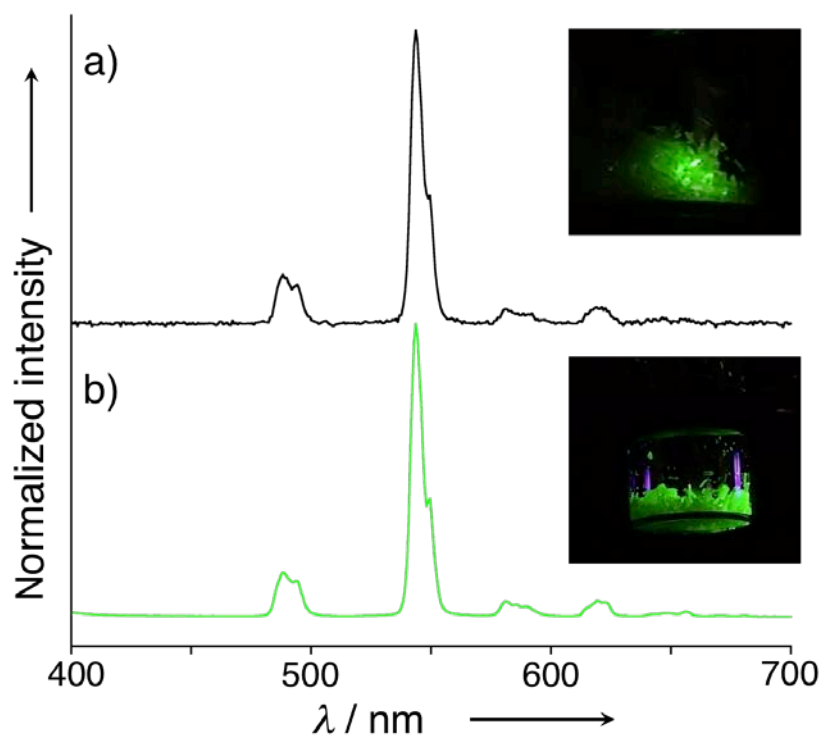


Figure S6. a) TL and b) PL spectra of $[\text{Tb}(\text{hfa})_3(\text{dpf})]_n$ ($\lambda_{\text{ex}} = 365 \text{ nm}$, inset shows pictures under grinding and UV irradiation).

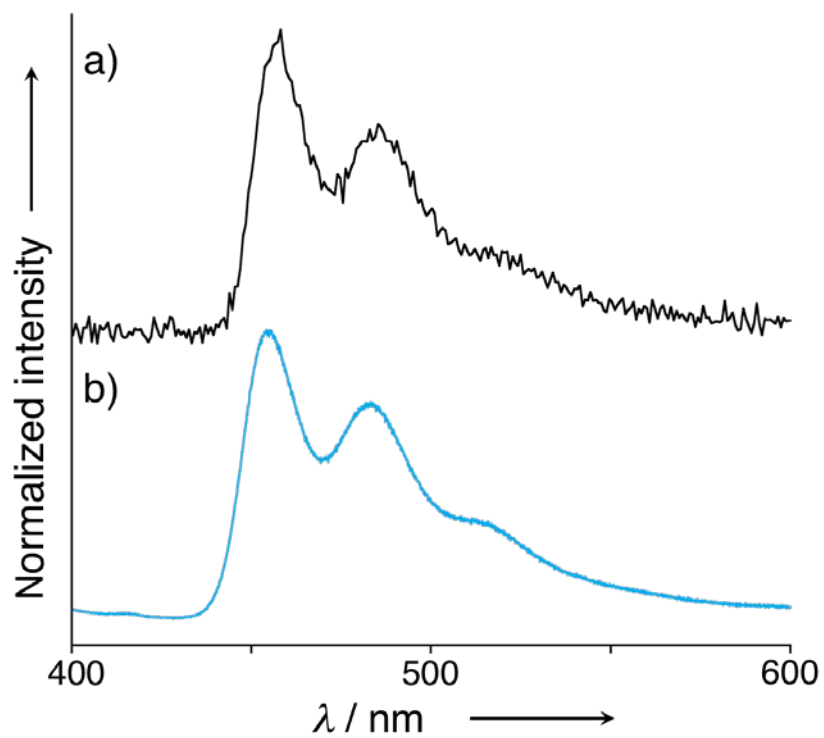


Figure S7. a) TL and b) PL spectra of $[\text{Gd}(\text{hfa})_3(\text{dpf})]_n$ ($\lambda_{\text{ex}} = 365 \text{ nm}$).

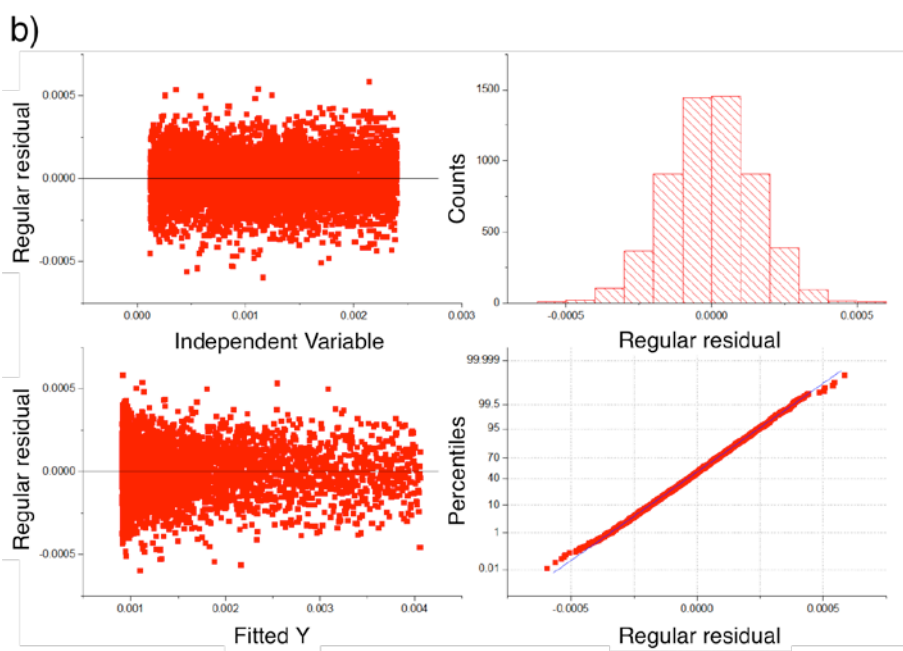
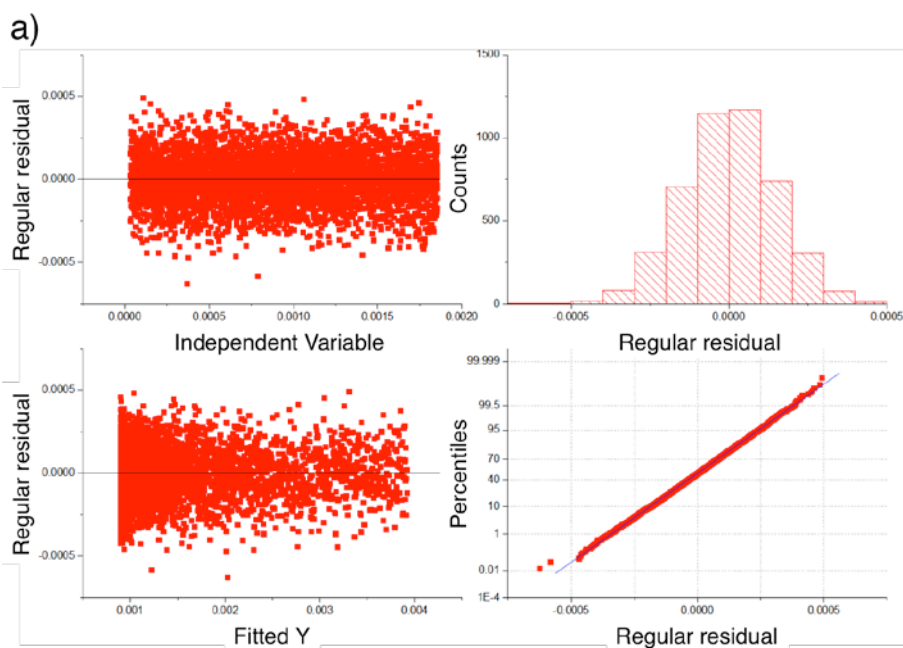


Figure S8. Fitting analyses of a) $[\text{Tb,Eu}(\text{hfa})_3(\text{dpf})]_n$ ($\text{Tb/Eu} = 1$) and b) $[\text{Tb,Eu}(\text{hfa})_3(\text{dpf})]_n$ ($\text{Tb/Eu} = 10$).

Table S2. Physical parameters of Eu^{III} coordination polymers [Eu(hfa)₃(X)]_n in solid state.

Sample	$\Phi_{\text{tot}}^{[a]}$ / %	$\Phi_{\text{ff}}^{[b]}$ / %	$\eta_{\text{sens}}^{[a]}$ / %	$\tau_{\text{obs}}^{[c]}$ / ms	$k_r^{[b]}$ / s ⁻¹	$k_{\text{nr}}^{[b]}$ / s ⁻¹	Dipole moment / D
[Eu(hfa) ₃ (dptf)] _n	64	73	88	0.72	1.0×10^3	3.8×10^2	5.80
Eu(hfa) ₃ (dptf)] _n ^[d]	60	75	80	0.75	1.0×10^3	3.3×10^2	1.17
[Eu(hfa) ₃ (dpedot)] _n ^[d]	56	85	66	0.93	9.1×10^2	1.6×10^2	4.30

[a] $\lambda_{\text{ex}} = 380$ nm. [b] Equations 2-4. [c] $\lambda_{\text{ex}} = 355$ nm. [d] Reference 11.

Table S3. Crystal data of the [Ln(hfa)₃(dpf)]_n (Ln = Tb, Gd, Eu).

	[Tb(hfa) ₃ (dpf)] _n	[Gd(hfa) ₃ (dpf)] _n	[Eu(hfa) ₃ (dpf)] _n
Chemical formula	C ₄₃ H ₂₅ F ₁₈ O ₉ P ₂ Tb	C ₄₃ H ₂₅ F ₁₈ GdO ₉ P ₂	C ₄₃ H ₂₅ EuF ₁₈ O ₉ P ₂
Formula weight	1248.51	1246.83	1241.54
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	Cc(#9)	Cc(#9)	Cc(#9)
<i>a</i> / Å	19.9974(8)	19.9832(7)	19.9767(6)
<i>b</i> / Å	14.8560(4)	14.8898(5)	14.9113(4)
<i>c</i> / Å	16.0129(6)	16.0514(5)	16.0652(5)
<i>α</i> / deg	90.000	90.000	90.000
<i>β</i> / deg	97.0396(14)	96.9250(10)	96.9906(9)
<i>γ</i> / deg	90.000	90.000	90.000
Volume / Å ³	4721.3(3)	4741.2(3)	4749.9(2)
<i>Z</i>	4	4	4
<i>d</i> _{calc} / g cm ⁻³	1.756	1.747	1.736
Temperature / °C	-150	-150	-150
<i>μ</i> (Mo Kα) / cm ⁻¹	16.868	15.938	15.085
max 2 <i>θ</i> / deg	55.0	54.8	54.9
Reflections	21629	21833	22274
Independent refle	9599	10146	9993
<i>R</i> ₁	0.0528	0.0266	0.0306
<i>wR</i> ₂	0.1426	0.0540	0.0660

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$.

Table S4. Temperature-dependent emission lifetimes of [Tb(hfa)₃(dpf)]_n in solid state.

Temperature / K	Emission lifetime / ms
100	0.69
150	0.70
200	0.70
250	0.69
300	0.60

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