

S1. Experimental section

General Methods: $^1\text{H-NMR}$ spectra were recorded in CDCl_3 on a JEOL ECS-400 (400 MHz) spectrometer; CHCl_3 ($\delta_{\text{H}} = 7.26$ ppm) was used as the internal reference. Electrospray ionization (ESI) mass spectrometry was performed using JEOL JMS-T100 LP instrument. Elemental analyses were performed using MICRO CORDER JM10. Luminescence spectra for DPA-P and $[\text{Lu}(\text{hfa})_3\text{DPA-P}]_n$ were measured using a Horiba FluoroLog®3 spectrofluorometer. Emission quantum yields for DPA-P and $[\text{Lu}(\text{hfa})_3\text{DPA-P}]_n$ were measured using a FP-6300 spectrofluorometer with an integration sphere (ILF-533). The emission lifetimes were measured by a streak camera system (Streakscope C10627, Hamamatsu). Diffuse-reflection spectra were recorded with a JASCO V-670 spectrophotometer equipped with an integrating-sphere unit (JASCO ISN-723).

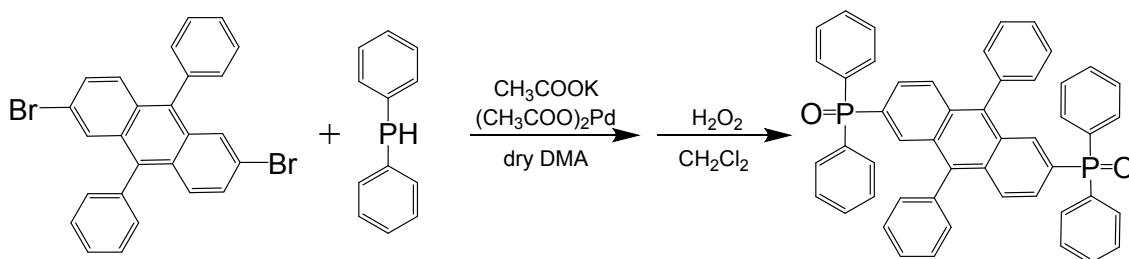
Materials: Magnesium sulfate, anhydrous (>98.0% (titration)) and chloroform- d_1 (99.8%) were purchased from Kanto Chemical Co., Inc. Potassium acetate (Guaranteed Reagent) and lutetium(III) acetate tetrahydrate (99.9 %) was purchased from Wako Pure Chemical Industries, Ltd. 2,6-Dibromo-9,10-diphenylanthracene (> 98.0%), diphenylphosphine (> 90.0 % (GC)), and palladium(II) acetate (> 98.0%) were purchased from Tokyo Chemical Industry Co., Ltd.

Preparation of [9,10-diphenyl-anthracene-2,6-diyl]bis(diphenylphosphine) oxide (DPA-P, Fig. S1, Scheme 1): A solution of potassium acetate (333 mg, 1.8 mmol) and palladium acetate (3.0 mg, 0.013 mmol) were added dropwise to a solution of 2,6-dibromo-9,10-diphenylanthracene (500 mg, 1.02 mmol) in dry DMA (15 mL). Diphenylphosphine (0.5 ml, 2.04 mmol) was then added to the solution, which was subsequently stirred for 24 h at 100°C . Then 120 mL of water was added to the solution and the obtained powder was filtrated. The product powder was dissolved in CH_2Cl_2 (100

mL) and a 30% H₂O₂ aqueous solution (2 mL) was added to the solution. The reaction mixture was stirred for 5 h. The product was extracted using CHCl₃ and washed with distilled water. The solvent was then evaporated to produce a powder. The recrystallization was performed using CH₂Cl₂/MeOH solvent (Yield: 210mg, 28%).

¹H-NMR (400 MHz, CDCl₃) δ/ppm = 7.91 (d, 2H, J = 16.0 Hz), 7.79 (dd, 2H, J = 11.6 Hz), 7.29-7.61 (m, 32H); ESI-MS: m/z calcd. for C₅₀H₃₇O₂P₂, [M+H]⁺ = 731.22; found: 731.23; elemental analysis calcd. (%) for C₅₀H₃₆O₂P₂, C 82.18, H 4.97; found: C 82.40, H 4.76.

FT-IR(ATR) = 1188 (st, P=O) cm⁻¹.



Scheme 1. Synthesis of **DPA-P** ligand.

Preparation of [Lu(hfa)₃DPA-P]_n (Fig. S1): Methanol solution (0.5 mL) containing Lu(hfa)₃(H₂O)₂ (7 mg, 0.01 mmol) and CH₂Cl₂ solution (0.5 mL) containing DPA-P (200 mg, 0.35 mmol) were prepared, respectively. The methanol solution is added to microtube, and the CH₂Cl₂ solution is added to microtube slowly. Liquid-liquid diffusion-assisted crystallization from CH₃OH (Lu(hfa)₃(H₂O)₂)/ CH₂Cl₂ (DPA-P ligand) solution gave crystals.

Elemental analysis calcd. (%) for C₆₅H₃₉F₁₈O₈P₂Lu, C 51.13, H 2.57; found: C 50.82, H 2.44. FT-IR(ATR) = 1655 (st, C=O), 1249 (st, C-F), 1169 (st, P=O) cm⁻¹.

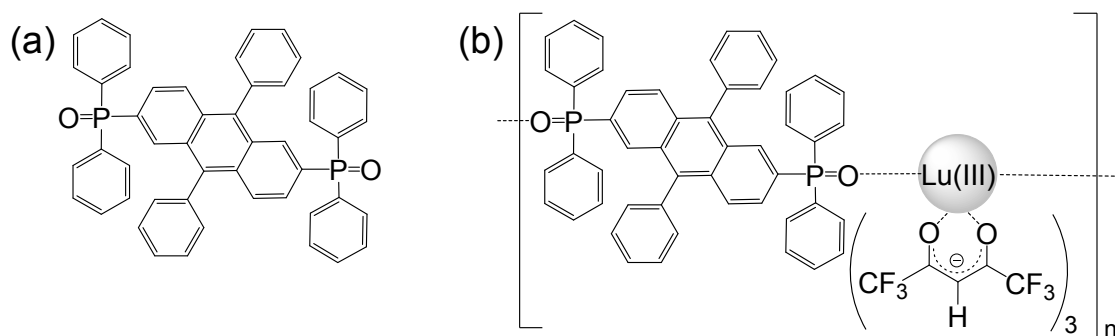


Fig. S1. Chemical structures of DPA-P (a) and $[\text{Lu}(\text{hfa})_3\text{DPA-P}]_n$ (b).

Single-Crystal X-ray Structure Determination: X-ray crystal structures and crystallographic data for DPA-P and $[\text{Lu}(\text{hfa})_3\text{DPA-P}]$ obtained by the recrystallization process using the CH_3OH ($\text{Lu}(\text{hfa})_3(\text{H}_2\text{O})_2$) / CH_2Cl_2 (DPA-P ligand) solvent system are shown in Fig. 2 and Table S1. X-ray crystal structures and crystallographic data for $[\text{Lu}(\text{hfa})_3\text{DPA-P}]$ obtained by the recrystallization process using the CHCl_3 ($\text{Lu}(\text{hfa})_3(\text{H}_2\text{O})_2$) / CH_2Cl_2 (DPA-P ligand) solvent system is shown in Fig. S5 and Table S3. Single crystals of the compounds were mounted on micromesh (MiTeGen M3-L19–25L) using paraffin oil. Measurements were made by using a Rigaku RAXIS RAPID imaging-plate area detector or XtaLAB AFC11 (RCD3) with graphite-monochromated $\text{Mo-K}\alpha$ radiation. Non-hydrogen atoms were anisotropically refined. All calculations were performed using a crystal-structure crystallographic software package. The CIF data were confirmed by the check CIF/PLATON service. CCDC-2046734 (for DPA-P), CCDC-2046736 (for $[\text{Lu}(\text{hfa})_3\text{DPA-P}]_n$ obtained by the recrystallization process using the $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ solvent system), and CCDC-2058490 (for $[\text{Lu}(\text{hfa})_3\text{DPA-P}]_n$ obtained by the recrystallization process using the $\text{CHCl}_3/\text{CH}_2\text{Cl}_2$ solvent system) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

S2. X-ray crystal data

Table. S1 Crystallographic data for DPA-P and [Lu(hfa)₃DPA-P]_n obtained by the recrystallization process using the CH₃OH/CH₂Cl₂ solvent system.

	DPA-P	[Lu(hfa) ₃ DPA-P] _n
chemical	C ₅₀ H ₃₆ O ₂ P ₂	C ₆₅ H ₃₉ F ₁₈ LuO ₈ P ₂ [+CH ₃ OH]
formula weight	730.73	1526.87
crystal system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
a / Å	10.7593(3)	18.1201(3)
b / Å	10.8776(3)	13.7081(2)
c / Å	16.3514(4)	25.8676(4)
volume / Å ³	1851.62(9)	6415.04(17)
Z	2	4
density / g cm ⁻³	1.311	1.581
Temperature / °C	-150	-150
<i>R</i>	0.0407	0.0351
<i>wR</i> ₂	0.1112	0.1282

S3. Shape measure calculation

To clarify the polyhedral structure, we calculated continuous shape measures. The continuous shape measure factor, *S*, was calculated to estimate the degree of distortion in the first coordination sphere of the coordination structure based on the crystal structure data. The *S* value is given by the following equation,

$$S = \min \frac{\sum_k^N |Q_k - P_k|^2}{\sum_k^N |Q_k - Q_0|^2} \times 100,$$

where *Q_k* represents the vertices of the actual structure, *Q₀* is the center of mass of the actual structure, *N* is the number of vertices, and *P_k* represents the vertices of the ideal structure. Based on the shape measure calculation, [Lu(hfa)₃DPA-P]_n was categorized as having SAP coordination geometry (*S* = 0.844).

Table S2. Shape measure calculation results

	SAP(D_{4d})	TDH(D_{2d})	BTP(C_{2v})
$[\text{Lu}(\text{hfa})_3\text{DPA-P}]_n$	0.844	1.529	1.588

S4. The X-ray crystal structure views of the $[\text{Lu}(\text{hfa})_3\text{DPA-P}]_n$ obtained by the recrystallization process using the $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ solvent system

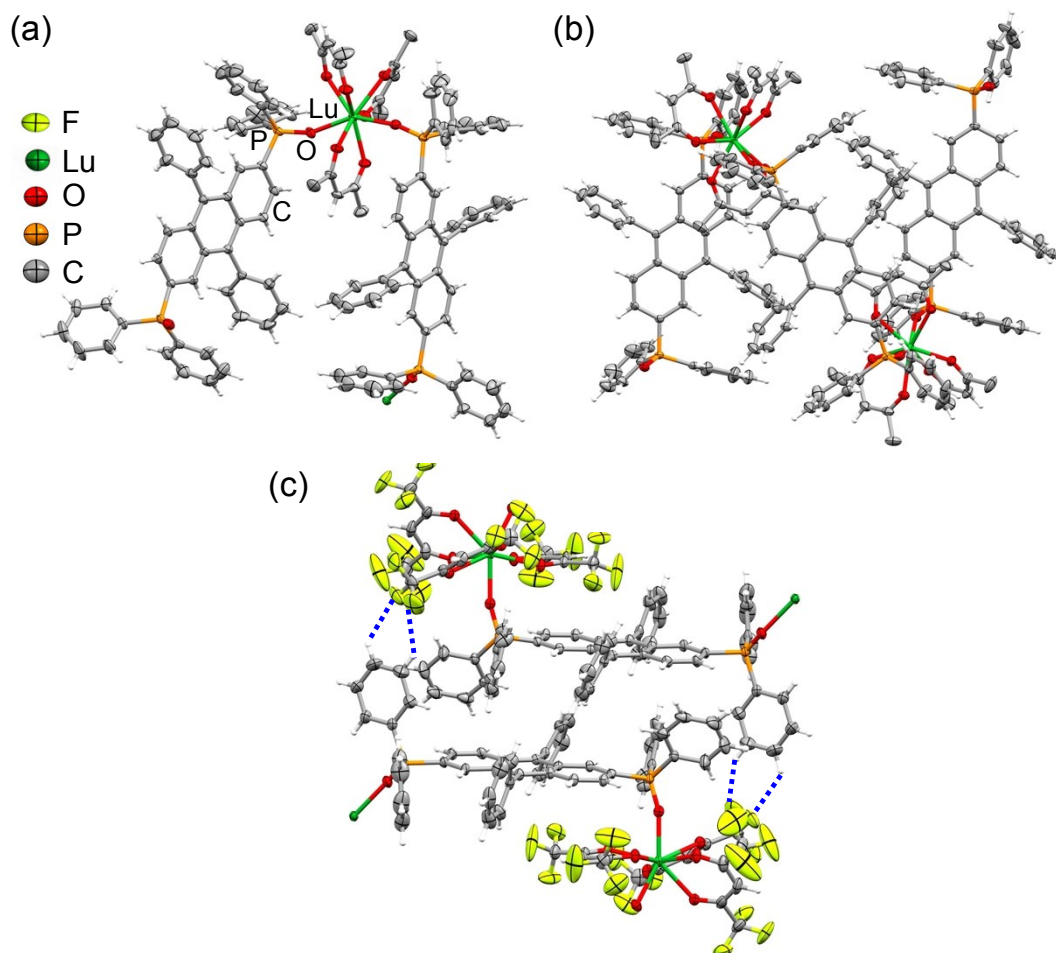


Fig. S2. The X-ray crystal structures of the $[\text{Lu}(\text{hfa})_3\text{DPA-P}]_n$ obtained by the recrystallization process using the $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ solvent system (a: $\text{Lu}(\text{hfa})_3(\text{DPA-P})_2$ without F atom, b: $\text{Lu}_2(\text{hfa})_6(\text{DPA-P})_3$ without F atom; c: Packing structure in $[\text{Lu}(\text{hfa})_3\text{DPA-P}]_n$ (Blue broken line: CH-F interaction).

S5. Emission lifetimes

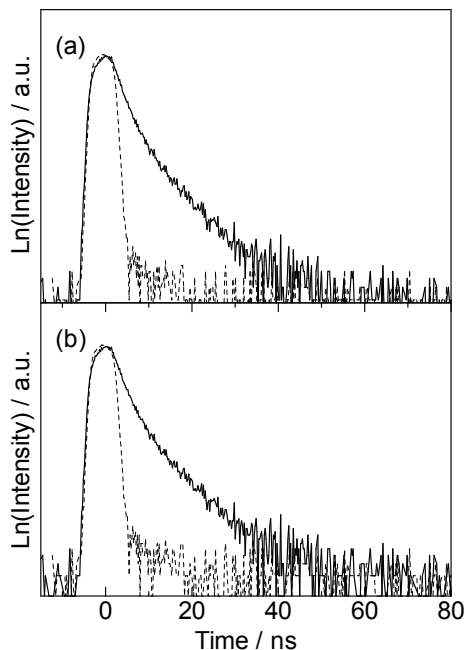


Fig. S3. Emission decay curves of DPA-P (a, solid line) and $[\text{Lu}(\text{hfa})_3\text{DPA-P}]_n$ (b, solid line) obtained by the recrystallization process using the $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ solvent system, and prompt curves (a, b, broken line).

S6. CIE (x, y) chromaticity coordinate

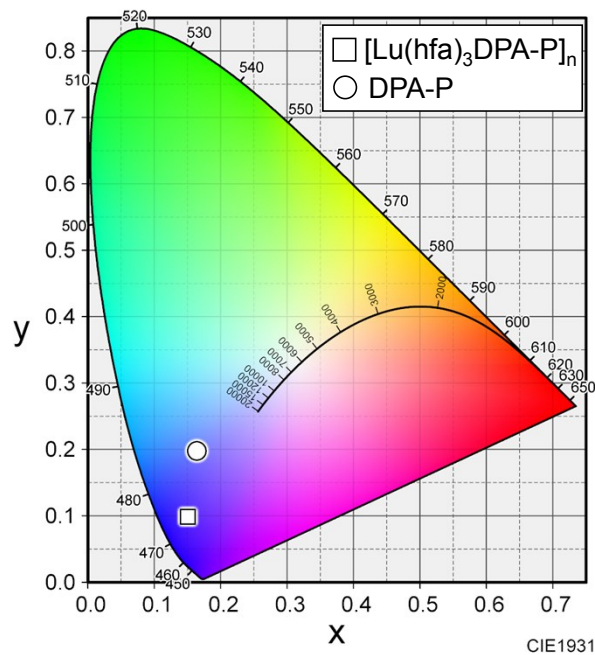


Fig. S4. CIE (x, y) chromaticity coordinates for DPA-P and $[\text{Lu}(\text{hfa})_3\text{DPA-P}]_n$ obtained by the recrystallization process using the $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ solvent system

S7. Crystal structure of [Lu(hfa)₃DPA-P]_n obtained by the recrystallization process using the CHCl₃/CH₂Cl₂ solvent system

We also prepared single crystals of [Lu(hfa)₃DPA-P]_n by recrystallization from the CHCl₃/CH₂Cl₂ solvent system (Fig S5). The crystal was identified by elemental analysis (C₆₅H₃₉F₁₈O₈P₂Lu calcd for C 51.13, H 2.57, found: C 50.87, H 2.47). The structure of the obtained crystal (Fig. S5, Table S3) is different from that of the single crystals obtained by recrystallization from the CH₃OH/CH₂Cl₂ solvent system (Fig. 2b, Table S1). The structure of the [Lu(hfa)₃DPA-P]_n crystal obtained from the CHCl₃/CH₂Cl₂ solvent system belongs to the P2₁ space group (Table S3). The CH–F interactions (< 3.0 Å) between the hfa unit and the aromatic DPA-P ligands were also observed in the [Lu(hfa)₃DPA-P]_n (Fig. S5).

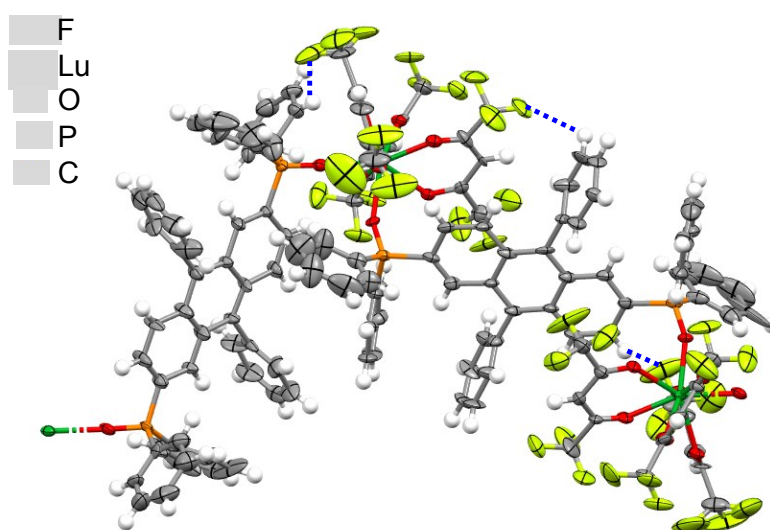


Fig. S5. X-ray crystal structure of [Lu(hfa)₃DPA-P]_n obtained by recrystallization from the CHCl₃/CH₂Cl₂ solvent system.

Table. S3 Crystallographic data for [Lu(hfa)₃DPA-P]_n obtained by the recrystallization process using the CHCl₃/CH₂Cl₂ solvent system.

	[Lu(hfa) ₃ DPA-P] _n
chemical	C ₁₃₀ H ₇₈ F ₃₆ Lu ₂ O ₁₆ P ₄ [+CHCl ₃]
formula weight	3053.75
crystal system	monoclinic
space group	<i>P</i> 2 ₁
a / Å	21.8457(5)
b / Å	15.3407(2)
c / Å	23.4512(6)
volume / Å ³	7800.4(3)
Z	2
density / g cm ⁻³	1.394
Temperature / °C	-150
<i>R</i>	0.0530
<i>wR</i> ₂	0.1417

The emission and excitation spectra are shown in Fig. S6. The FWHM is estimated to be 63 nm and is narrower than that of the DPA-P ligand (77 nm). The emission quantum yield upon excitation at 380 nm is estimated to be 30% and is higher than that of the DPA-P ligand (18%). The results also support our concept; the characteristic lanthanide fixation system improved the emission color purity and emission quantum yield.

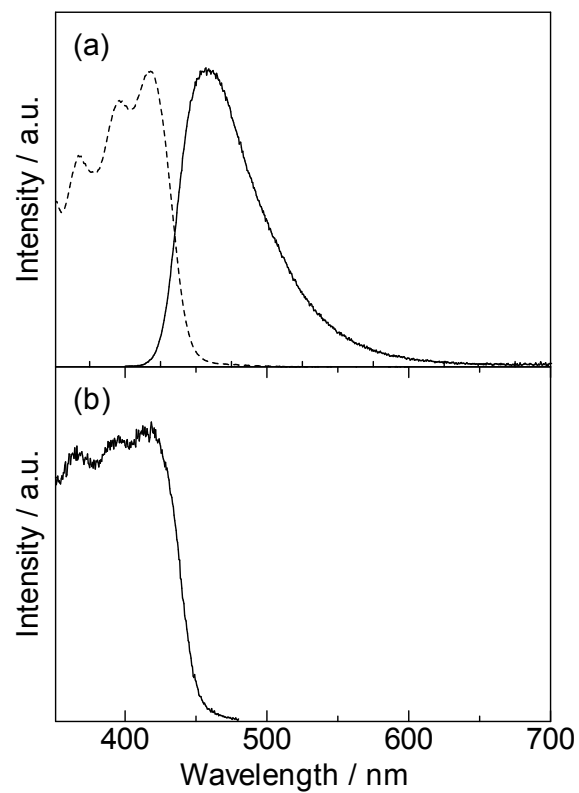


Fig. S6. (a) Absorption (broken line), emission (solid line), and (b) excitation (solid line) spectra of $[\text{Lu}(\text{hfa})_3\text{DPA-P}]_n$ in their solid states, which is obtained by the recrystallization process using the $\text{CHCl}_3/\text{CH}_2\text{Cl}_2$ solvent system. The samples were 3000-fold dilution using KBr.