S1. Experimental section

General Methods: $^1$H-NMR spectra were recorded in CDCl$_3$ on a JEOL ECS-400 (400 MHz) spectrometer; CHCl$_3$ ($\delta_H = 7.26$ 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 [Lu(hfa)$_3$DPA-P]$_n$ were measured using a Horiba FluoroLog®3 spectrofluorometer. Emission quantum yields for DPA-P and [Lu(hfa)$_3$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$_2$Cl$_2$ (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.](image-url)

**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 [Lu(hfa)₃DPA-P]ₙ (b).

**Single-Crystal X-ray Structure Determination:** X-ray crystal structures and crystallographic data for DPA-P and [Lu(hfa)₃DPA-P] obtained by the recrystallization process using the CH₃OH (Lu(hfa)₃(H₂O)₂) / CH₂Cl₂ (DPA-P ligand) solvent system are shown in Fig. 2 and Table S1. X-ray crystal structures and crystallographic data for [Lu(hfa)₃DPA-P] obtained by the recrystallization process using the CHCl₃ (Lu(hfa)₃(H₂O)₂) / CH₂Cl₂ (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 Mo-Kα 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 [Lu(hfa)₃DPA-P]ₙ obtained by the recrystallization process using the CH₃OH/CH₂Cl₂ solvent system), and CCDC-2058490 (for [Lu(hfa)₃DPA-P]ₙ obtained by the recrystallization process using the CHCl₃/CH₂Cl₂ 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)₃DPA-P]ₙ |
|------------------|----------------------------|-----------------|
| chemical         | C₅₀H₃₆O₂P₂                 | C₁₆₅H₅₉F₁₈LuO₈P₂ [CH₃OH]            |
| formula weight   | 730.73                     | 1526.87         |
| crystal system   | monoclinic                 | monoclinic      |
| space group      | P 2/n                      | P 2/i/c         |
| 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 / Å³      | 1851.62(9)                 | 6415.04(17)     |
| Z                | 2                          | 4               |
| density / g cm⁻³ | 1.311                      | 1.581           |
| Temperature / °C | -150                       | -150            |
| R                | 0.0407                     | 0.0351          |
| wR₂              | 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,

\[
S = \min \frac{\sum_i \left| Q_i - P_i \right|^2}{\sum_i \left| Q_i - \bar{Q} \right|^2} \times 100,
\]

where \(Q_i\) represents the vertices of the actual structure, \(Q_0\) is the center of mass of the actual structure, \(N\) is the number of vertices, and \(P_i\) 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($C_{2v}$) |
|-------|---------------|---------------|---------------|
| [Lu(hfa)$_3$DPA-P]$_n$ | 0.844 | 1.529 | 1.588 |

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

Fig. S2. The X-ray crystal structures of the [Lu(hfa)$_3$DPA-P]$_n$ obtained by the recrystallization process using the CH$_3$OH/CH$_2$Cl$_2$ solvent system (a: Lu(hfa)$_3$(DPA-P)$_2$ without F atom, b: Lu$_2$(hfa)$_6$(DPA-P)$_3$ without F atom; c: Packing structure in [Lu(hfa)$_3$DPA-P]$_n$ (Blue broken line: CH-F interaction).
S5. Emission lifetimes

Fig. S3. Emission decay curves of DPA-P (a, solid line) and [Lu(hfa)₃DPA-P]ₙ (b, solid line) obtained by the recrystallization process using the CH₃OH/CH₂Cl₂ 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 [Lu(hfa)₃DPA-P]ₙ obtained by the recrystallization process using the CH₃OH/CH₂Cl₂ solvent system
S7. Crystal structure of [Lu(hfa)$_3$DPA-P]$_n$ obtained by the recrystallization process using the CHCl$_3$/CH$_2$Cl$_2$ solvent system

We also prepared single crystals of [Lu(hfa)$_3$DPA-P]$_n$ by recrystallization from the CHCl$_3$/CH$_2$Cl$_2$ solvent system (Fig S5). The crystal was identified by elemental analysis (C$_{65}$H$_{39}$F$_{18}$O$_8$P$_2$Lu 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 CH$_3$OH/CH$_2$Cl$_2$ solvent system (Fig. 2b, Table S1). The structure of the [Lu(hfa)$_3$DPA-P]$_n$ crystal obtained from the CHCl$_3$/CH$_2$Cl$_2$ solvent system belongs to the P2$_1$ 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)$_3$DPA-P]$_n$ (Fig. S5).

Fig. S5. X-ray crystal structure of [Lu(hfa)$_3$DPA-P]$_n$ obtained by recrystallization from the CHCl$_3$/CH$_2$Cl$_2$ solvent system.
Crystallographic data for $[\text{Lu(hfa)}_3\text{DPA-P}]_n$ obtained by the recrystallization process using the CHCl$_3$/CH$_2$Cl$_2$ solvent system.

| Property                  | Value                      |
|---------------------------|----------------------------|
| Chemical formula          | $\text{C}_{130}\text{H}_{78}\text{F}_{36}\text{Lu}_2\text{O}_{16}\text{P}_4$ [$^\ast\text{CHCl}_3$] |
| Formula weight            | 3053.75                    |
| Crystal system            | monoclinic                 |
| Space group               | $P\ 2_1$                   |
| $a$ / 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          | $-150$                     |
| $R$                       | 0.0530                     |
| $wR_2$                    | 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 [Lu(hfa)₃DPA-P]₆ in their solid states, which is obtained by the recrystallization process using the CHCl₃/CH₂Cl₂ solvent system. The samples were 3000-fold dilution using KBr.