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The conformational arrangement effect of luminescent Eu(III) coordination polymers with phenylene diamide units on structural and photophysical properties

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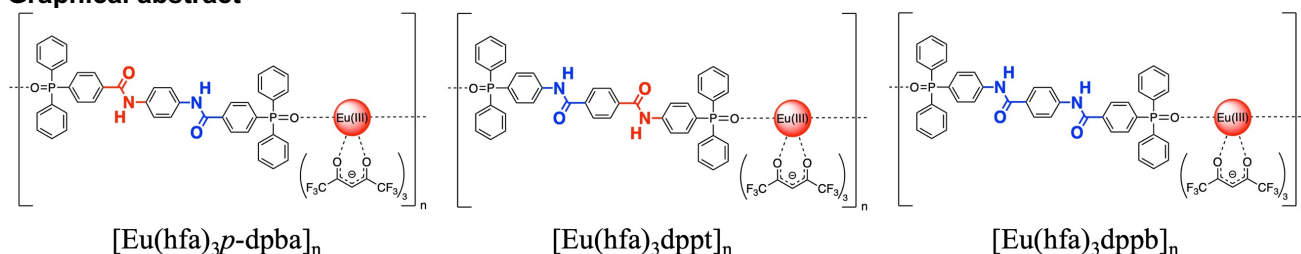
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Abstract

Luminescent Eu(III) coordination polymers with phosphine oxide linker ligands containing phenylenediamide units, [Eu(hfa)₃-*p*-dpba]_n, [Eu(hfa)₃dppt]_n, and [Eu(hfa)₃dppb]_n (hfa: hexafluoroacetylacetonate, *p*-dpba: (*N,N'*-(1,4-phenylene)bis(4-(diphenylphosphoryl)benzamide), dppt: *N,N'*-(1,4-bis(4-(diphenylphosphoryl)phenyl)terephthalamide), dppb: 4-(diphenylphosphoryl)-*N'*-(4-(4-(diphenylphosphoryl)phenyl)carbamoyl)phenyl)benzamide)), were reported. The structural and photophysical properties of the Eu(III) coordination polymers were evaluated. The phase transition temperatures of [Eu(hfa)₃-*p*-dpba]_n, [Eu(hfa)₃dppt]_n, and [Eu(hfa)₃dppb]_n were determined to be 153, 148, and 79 °C, respectively. The overall emission quantum yield (Φ_{em}) and photosensitized efficiency (η_{sens}) excitation of [Eu(hfa)₃dppt]_n ($\Phi_{\text{em}}^* = 19\%$, $\eta_{\text{sens}} = 43\%$) and [Eu(hfa)₃dppb]_n ($\Phi_{\text{em}}^* = 19\%$, $\eta_{\text{sens}} = 37\%$) under 370 nm excitation were found to be larger than those of [Eu(hfa)₃-*p*-dpba]_n ($\Phi_{\text{em}}^* = 4.4\%$, $\eta_{\text{sens}} = 6.8\%$). We demonstrated the systematic evaluation of amide units on their structural and photophysical properties.

Keywords: luminescent, lanthanide, coordination polymer

Graphical abstract



1. Introduction

Lanthanide coordination polymers, which are composed of lanthanide ions and organic linker ligands, have attracted considerable attention in the fields of coordination, photophysical, and materials chemistry.¹⁻⁶ Lanthanide coordination polymers have been widely applied for luminescent materials such as lighting, display and sensing applications due to their characteristic photophysical properties with narrow emission bands (full width at half maximum, FWHM < 10 nm) and long emission lifetimes ($\tau > 1 \mu\text{s}$) based on the 4f–4f transitions.⁷⁻¹¹ Bünzli presented lanthanide coordination polymers composed of lanthanide ions and 1,4-disubstituted benzenes.¹² Carlos demonstrated Eu/Tb mixed coordination polymer with 1,4-benzendicarboxylate as a thermometer.¹³ Recently, various types of lanthanide coordination polymers have been reported.¹⁴⁻²⁰

The structural and photophysical properties of lanthanide coordination polymers were depended on the molecular structure of the linker ligands.²¹⁻²³ The effect of the aromatic substitution orientation on the structural and photophysical properties of Eu(III) coordination polymers has been reported.²⁴ Herein, we focused on the amide unit for the characteristic conformation of lanthanide coordination polymer. Zhu demonstrated that the introduction of strong intermolecular hydrogen bonds by the amide unit in isomeric polyimideamides affected the tensile strengths and tensile moduli.²⁵ Kumar reported that the orientation of the amide units influenced the morphology of the discotic tripeptides.²⁶ The conformational arrangement of the amide units plays an important role in controlling of the assemble structures.^{27,28}

In this study, the molecular conformational arrangement of amide units with the same molecular formula as the luminescent Eu(III) coordination polymers was prepared. Three types of Eu(III) coordination polymers with systematically changed amide bond directions were synthesized. Eu(III) coordination polymer with phosphine oxide linker ligands containing phenyldiamide unit, $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$ (hfa: hexafluoroacetylacetonate, p-dpba: *N,N*-(1,4-phenylene)bis(4-(diphenylphosphoryl)benzamide); Fig. 1a) have been reported.²⁹ The single crystal X-ray analysis revealed that the hydrogen bonds between amide and carbonyl oxygens in $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$ were formed. Novel coordination polymers with systematically altered amide bonds, $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$ and $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$ were additionally synthesized (Fig. 1b and c; dppt: *N,N'*-4-bis(4-(diphenylphosphoryl)phenyl)terephthalamide, dppb: 4-(diphenylphosphoryl)-*N*-(4-((4-(diphenylphosphoryl)phenyl)carbamoyl)phenyl)benzamide. The structural properties were characterized using

differential scanning calorimetry (DSC) and powder X-ray diffraction (PXRD). The photophysical properties were analyzed by their emission spectra, quantum yields, and emission lifetimes. The effect of molecular conformational arrangement on structural and photophysical properties was demonstrated.

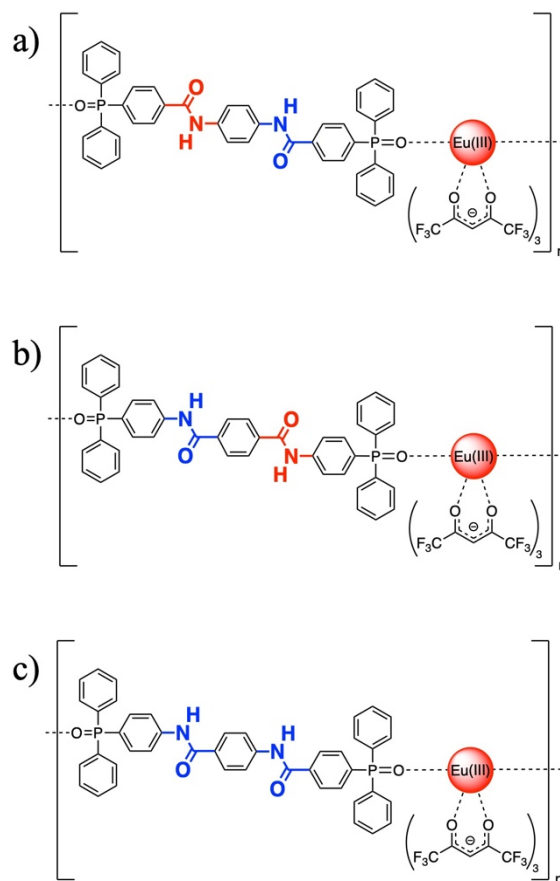


Fig. 1. Molecular structures of a) $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$, b) $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$, and c) $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$.

2. Experimental

Materials. Europium acetate *n*-hydrate (99.9%) was obtained from FUJIFILM Wako Pure Chemical Corporation. All other reagents were of reagent grade and were used without further purification.

Apparatus. ^1H , ^{13}C , and ^{31}P NMR spectra were recorded using a JEOL ECS400 and ECZ400S. Tetramethylsilane ($\delta_{\text{H}} = 0.00 \text{ ppm}$) and phosphoric acid ($\delta_{\text{P}} = 0.00 \text{ ppm}$) were used as references for ^1H and ^{31}P NMR, respectively. Electrospray ionization-mass (ESI-MS) spectra were recorded using a JEOL JMS-T100LP instrument. Elemental analyses were performed on an Exeter Analytical CE440. Powder X-ray diffraction was performed on a Rigaku SmartLab (CuK α radiation, $\lambda = 1.5418 \text{ \AA}$).

Optical measurements. The excitation and emission spectra under air condition were measured using a HORIBA Fluorolog-3 spectrofluorometer. The 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 using a digital oscilloscope (TDS3052, 500 MHz, Sony Tektronix) synchronized with a single-pulse excitation. The emission lifetimes were determined from the slopes of the logarithmic plots of the decay profiles. The emission quantum yields (Φ_{em}) were estimated using a JASCO F-6300-H spectrometer attached to a JASCO ILF-533 integrating sphere unit ($\Phi = 100$ mm).

Computational details. All quantum chemical calculations were performed using the density functional theory (DFT) using the Gaussian 16 package.³⁰ The excited states were investigated using time-dependent (TD)-DFT with the long-range corrected LC-BLYP functional.³¹

Preparation of 4-(diphenylphosphinyl)benzenamine
4-(diphenylphosphinyl)benzenamine was synthesized according to a previously reported procedure.²⁹

Preparation of *N*¹, *N*⁴-bis(4-(diphenylphosphoryl)phenyl)terephthalamide (dppt)

4-(diphenylphosphinyl)benzenamine (293.3 mg, 1.0 mmol) was dissolved in dichloromethane (10 mL). Terephthaloyl chloride (101.5 mg, 0.5 mmol) and triethylamine (1 mL) were added successively at 0°C. After stirring for 2 h at room temperature, the precipitate was filtered and purified by recrystallization from dichloromethane and MeOH to give *N*¹, *N*⁴-bis(4-(diphenylphosphoryl)phenyl)terephthalamide (81.7 mg, 0.114 mmol, 22.8%): ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.66 (s, 2H), 8.14-8.09 (m, 4H), 7.99 (m, 4H), 7.66-7.54 (m, 24H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 165.4, 142.4, 137.4, 133.5, 132.5, 132.1, 131.5, 131.4, 128.9, 128.8, 128.1, 127.9, 127.6, 126.6, 120.2, 120.1 ppm. ³¹P NMR (162 MHz, DMSO-*d*₆) δ 26.0 ppm. MS(ESI) found: *m/z* 739.19 Calcd. for C₄₄H₃₄N₂NaO₄P₂: [M+Na]⁺, 739.19.

Preparation of 4-(diphenylphosphoryl)benzoic acid
4-(diphenylphosphoryl)benzoic acid was synthesized according to a previously reported procedure.³²

Preparation of methyl 4-(4-(diphenylphosphoryl)benzamido)benzoate

4-(diphenylphosphoryl)benzoic acid (322.3 mg, 1.0 mmol) was dissolved in thionyl chloride (1 mL) and stirred for 30 min at room temperature. The solvent was removed in vacuo. The residue was dissolved in dichloromethane (10 mL). Methyl 4-aminobenzoate (151.2 mg, 1.0 mmol) and triethylamine (1 mL) were added successively at 0°C. After stirring for 2 h at room

temperature, the reaction mixture was washed with 2% hydrochloric acid, aqueous 5% sodium hydrogen carbonate and distilled water. The organic layer was dried over sodium sulfate and evaporated. The residue was dissolved and purified by recrystallization from dichloromethane and MeOH to give methyl 4-(4-(diphenylphosphoryl)benzamido)benzoate (249.1 mg, 0.547 mmol, 54.7%): ¹H NMR (400 MHz, CDCl₃) δ 10.27 (1H, s), 8.04-7.97 (6H, m), 7.59-7.41 (12H, m), 3.91 (3H, s) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 166.3, 143.5, 139.3, 135.7, 134.7, 132.6, 132.6, 132.4, 132.3, 132.1, 132.0, 131.0, 130.7, 129.0, 128.9, 128.2, 128.1, 125.6, 119.8, 52.1 ppm. ³¹P NMR (162 MHz, CDCl₃) δ 29.5 ppm. MS(ESI) found: *m/z* 478.12. Calcd. for C₂₇H₂₂NNaO₄P: [M+Na]⁺, 478.12.

Preparation of 4-(4-(diphenylphosphoryl)benzamido)benzoic acid

Methyl 4-(4-(diphenylphosphoryl)benzamido)benzoate (455.5 mg, 1.0 mmol) and sodium hydroxide (40.0 mg, 1.0 mmol) was added in ethanol (10 mL) and water (10 mL). The reaction mixture was refluxed overnight. The reaction solution was cooled to room temperature. Hydrogen chloride (1 mL) and water (9 mL) were added successively. The white precipitate was filtered and washed with distilled water to give 4-(4-(diphenylphosphoryl)benzamido)benzoic acid (194.7 mg, 0.441 mmol, 44.1%): ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.69 (s, 1H), 8.08-8.05 (m, 2H), 7.96-7.88 (m, 4H), 7.82-7.77 (m, 2H), 7.68-7.56 (m, 10H) ppm. ¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.0, 165.5, 143.1, 138.0, 136.7, 135.7, 132.7, 132.6, 132.4, 132.0, 131.8, 131.7, 131.7, 131.6, 130.4, 129.5, 129.4, 129.1, 128.9, 128.2, 128.0, 125.9, 119.6 ppm. ³¹P NMR (162 MHz, DMSO-*d*₆) δ 26.9 ppm. MS(ESI) found: *m/z* 464.10. Calcd. for C₂₆H₂₀NNaO₄P: [M+Na]⁺, 464.10.

Preparation of 4-(diphenylphosphoryl)-*N*-(4-(4-(diphenylphosphoryl)phenyl)carbamoyl)phenyl)benzamide (dppb)

4-(4-(diphenylphosphoryl)benzamido)benzoic acid (441.4 mg, 1.0 mmol) was dissolved in thionyl chloride (1 mL) and stirred for 30 min at room temperature. The solvent was removed in vacuo. The residue was dissolved in dichloromethane (10 mL), and 4-(diphenylphosphinyl)benzenamine (293.3 mg, 1.0 mmol) and triethylamine (1 mL) were added successively at 0°C. After stirring for 2 h at room temperature, the reaction mixture was washed with 2% hydrochloric acid, aqueous 5% sodium hydrogen carbonate and distilled water. The organic layer was dried over sodium sulfate and evaporated. The residue was dissolved and purified by recrystallization from dichloromethane and MeOH to give 4-(diphenylphosphoryl)-*N*-(4-(4-(diphenylphosphoryl)phenyl)carbamoyl)phenyl)benzamide (391.7 mg, 0.547 mmol, 54.7%): ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.65 (s, 1H), 10.43 (s, 1H), 8.08 (m, 2H), 8.01-7.91 (m, 6H), 7.80 (m, 2H), 7.68-7.53 (m, 22H) ppm. ¹³C NMR (100 MHz,

1 DMSO- d_6) δ 165.3, 142.7, 142.2, 133.5, 132.7, 132.5,
 2 132.4, 132.3, 132.0, 131.7, 131.7, 131.6, 131.6, 131.5,
 3 131.5, 131.4, 129.5, 129.0, 128.8, 128.8, 128.7, 128.7,
 4 128.0, 127.9, 127.1, 120.0, 119.8, 119.5 ppm. ^{31}P NMR
 5 (162 MHz, DMSO- d_6) δ 26.1, 26.0 ppm. MS(ESI) found:
 6 m/z 739.19 Calcd. for $\text{C}_{44}\text{H}_{34}\text{N}_2\text{NaO}_4\text{P}_2$: $[\text{M}+\text{Na}]^+$, 739.19.

8 Preparation of $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$

9 $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$ was synthesized according to the
 10 previously reported procedures.³³

12 Preparation of $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$

13 $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$ (80.9 mg, 0.1 mmol) was added to
 14 dichloromethane (5 mL) and MeOH (5 mL) mixture
 15 solution of **dppt** (71.6 mg, 0.1 mmol), and the mixture
 16 was stirred for 1 h. The recrystallization from
 17 dichloromethane yielded $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$ (31.9 mg, 21.4
 18 μmol , 21.4%) as a white powder: MS(ESI) found: m/z
 19 1283.10. Calcd. for $\text{C}_{54}\text{H}_{36}\text{EuF}_{12}\text{N}_2\text{O}_8\text{P}_2$: $[\text{M}-\text{hfa}]^+$,
 20 1283.10; found: m/z 2773.14. Calcd. for
 21 $\text{C}_{113}\text{H}_{73}\text{Eu}_2\text{F}_{30}\text{N}_4\text{O}_{18}\text{P}_4$ $[\text{M}_2-\text{hfa}]^+$, 2773.18; found: m/z
 22 4263.21. Calcd. for $\text{C}_{172}\text{H}_{110}\text{Eu}_3\text{F}_{48}\text{N}_6\text{O}_{28}\text{P}_6$ $[\text{M}_3-\text{hfa}]^+$,
 23 4263.27. Elemental analysis: found (%): C 48.68, H 2.64,
 24 N 2.18. Calcd. for $\text{C}_{59}\text{H}_{37}\text{EuF}_{18}\text{N}_2\text{O}_{10}\text{P}_2$: C 47.57, H 2.50,
 25 N 1.88.

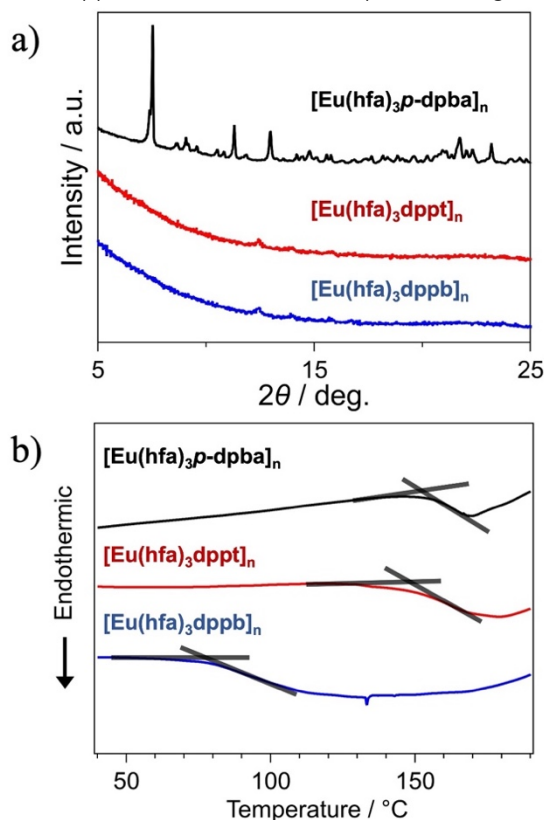
27 Preparation of $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$

28 $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$ (80.9 mg, 0.1 mmol) was added to a
 29 dichloromethane (5 mL) and MeOH (5 mL) mixture
 30 solution of **dppb** (71.6 mg, 0.1 mmol), and the mixture
 31 was stirred for 1 h. The recrystallization from
 32 dichloromethane gave $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$ (29.3 mg, 19.7
 33 μmol , 19.7%) as a white powder: MS(ESI) found: m/z
 34 1283.11. Calcd. for $\text{C}_{54}\text{H}_{36}\text{EuF}_{12}\text{N}_2\text{O}_8\text{P}_2$: $[\text{M}-\text{hfa}]^+$,
 35 1283.10; found: m/z 2773.23. Calcd. for
 36 $\text{C}_{113}\text{H}_{73}\text{Eu}_2\text{F}_{30}\text{N}_4\text{O}_{18}\text{P}_4$ $[\text{M}_2-\text{hfa}]^+$, 2773.18; found: m/z
 37 4263.30. Calcd. for $\text{C}_{172}\text{H}_{110}\text{Eu}_3\text{F}_{48}\text{N}_6\text{O}_{28}\text{P}_6$ $[\text{M}_3-\text{hfa}]^+$,
 38 4263.27. Elemental analysis: found (%): C 47.03, H 2.67,
 39 N 1.57. Calcd. for $\text{C}_{59}\text{H}_{37}\text{EuF}_{18}\text{N}_2\text{O}_{10}\text{P}_2$: C 47.57, H 2.50,
 40 N 1.88.

42 3. Results and discussion

43 **Structural properties.** The Eu(III) coordination polymers,
 44 $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$, $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$, and $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$
 45 were synthesized by the complexation of the
 46 corresponding linker ligands with precursor complex,
 47 $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$, in a mixed solution of methanol and
 48 dichloromethane. TG measurements were conducted
 49 in a nitrogen atmosphere to evaluate the
 50 thermophysical properties of the Eu(III) coordination
 51 polymers. The decomposition temperatures of
 52 $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$, $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$, and $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$
 53 were estimated to be around 250 °C (Fig. S1). The
 54 PXRD patterns of the linker ligands and Eu(III)
 55 coordination polymers are shown in Fig. S2 and Fig. 2a,
 56 respectively. The linker ligands and $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$
 57 showed sharp PXRD pattern. The diffraction patterns of
 58 $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$ and $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$ were not matched
 59 with those of **dppt** and **dppb** ligands (Fig. S3). The

60 Eu(III) coordination polymers exhibited a baseline shift
 61 associated with the phase transition (Fig. 2b). The
 62 phase transition temperatures of $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$,
 63 $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$, and $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$ were calculated to
 64 be 153, 148 and 79 °C, respectively. However, the
 65 ligands did not exhibit characteristic phase transition
 66 behavior (Fig. S4). From these results, the Eu(III)
 67 coordination polymers exhibited phase transition
 68 behavior. The transition behavior at low temperature of
 69 $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$ might be attributed to low crystallinity
 70 based various arrangement patterns in the polymer
 71 chain (Fig. S5). The basic structure of $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$
 72 has been reported.²⁹ We measured the IR spectra of
 73 three Eu(III) coordination polymers for check the basic
 74 structures of $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$ and $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$. The
 75 significant vibrational bands at C=O groups were
 76 observed around at 1650 and around 1680 cm^{-1} (Fig S6).
 77 The vibrational signal at 1650 cm^{-1} is assigned to
 78 coordinated C=O...Eu groups in hfa ligands, which is
 79 similar to those of previous Eu(III) complexes and Eu(III)
 80 coordination polymers.³⁴ The broad band at around
 81 1680 cm^{-1} might be caused by amido (NHCO) units. The
 82 broad band of solid $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$ is also similar to
 83 those of solid $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$ and $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$. The
 84 detail basic structures of $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$ and
 85 $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$ are not clear at the present stage.



86 **Fig. 2.** a) PXRD patterns and b) DSC thermograms of
 87 $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$ (black), $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$ (red), and
 88 $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$ (blue).
 89
 90

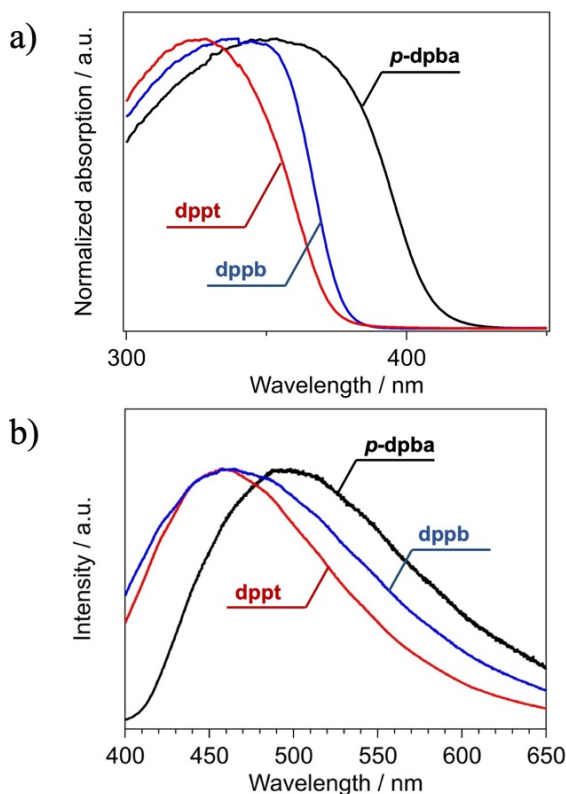


Fig. 3. a) Diffuse reflectance and b) emission spectra ($\lambda_{\text{ex}} = 330 \text{ nm}$) of **p-dpba** (black), **dppt** (red), and **dppb** (blue).

Photophysical properties. The diffuse reflectance spectra of the ligands by diluting them 10-folds in KBr are shown in Fig. 3a. The absorption spectra exhibited a broad band at approximately 350 nm. The absorption edge of **dppt** and **dppb** (ca. 380 nm) were shorter than that of the **p-dpba** (ca. 420 nm). From these results, the -CO-(Ph)-CO- substituents of **p-dpba** induced intramolecular ligand-to-ligand charge transfer (LLCT) quenching state based on the calculation (Fig. S7a). The absorption spectra of the ligands in DMSO were measured to estimate their light-harvesting abilities (Fig. S8). The absorption coefficient maximum (ϵ_{max}) of **p-dpba**, **dppt**, and **dppb**, were calculated to be 40200, 44400, and 38000 $\text{M}^{-1} \text{cm}^{-1}$, respectively. The wavelength at absorption edge of **dppt** and **dppb** were shorter than that of the **p-dpba**. The emission spectra of the ligands are shown in Fig. 3b. The emission peak

of **p-dpba** (495 nm) was longer than those of **dppt** (457 nm) and **dppb** (464 nm). To estimate the triplet (T_1) state, we measured the phosphorescence spectra of the ligands (Fig. S9). The T_1 levels of **p-dpba**, **dppt**, and **dppb** ($> 20,000 \text{ cm}^{-1}$) were higher than those of previous organic ligands with induction of back energy transfer from Eu(III) to ligands.³⁵

The excitation spectra of **[Eu(hfa)₃p-dpba]_n**, **[Eu(hfa)₃dppt]_n**, and **[Eu(hfa)₃dppb]_n** are shown in Fig. S10. The excitation bands observed at 300-350 nm and 350-420 nm correspond to the π - π^* transition of the hfa ligand and the absorption bands of the linker ligand, respectively. The excitation bands monitored at 612 nm showed characteristic bands at 300-350 nm (Fig. S10b). The results demonstrated that the emission of Eu(III) is mainly came from the hfa ligands.

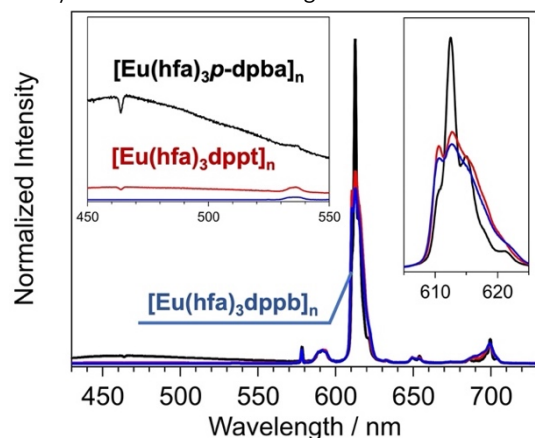


Fig. 4. Emission spectra of **[Eu(hfa)₃p-dpba]_n** (black), **[Eu(hfa)₃dppt]_n** (red), and **[Eu(hfa)₃dppb]_n** (blue). ($\lambda_{\text{ex}} = 370 \text{ nm}$)

The emission spectra of the three Eu(III) coordination polymers are shown in Fig. 4. The sharp emission bands were detected around 578, 592, 613, 650, and 698 transitions of the Eu(III) ($^5D_0 \rightarrow ^7F_J$; $J = 0, 1, 2, 3$, and 4), respectively.³⁶ The spectra were normalized with respect to the magnetic dipole transition (MD) intensities at around 592 nm ($^5D_0 \rightarrow ^7F_1$), which are insensitive to the surrounding environment of the Eu(III). The emission band at approximately 613 nm was strongly dependent on the coordination geometry. The splitting bands of the $^5D_0 \rightarrow ^7F_2$ transition in **[Eu(hfa)₃p-dpba]_n** were the almost same as that in **[Eu(hfa)₃dppt]_n** and **[Eu(hfa)₃dppb]_n**. (Fig. 4, inset). The splitting bands of the $^5D_0 \rightarrow ^7F_2$ transition were affected by the surrounding environment at Eu(III) ion. On the

Table 1. Photophysical properties of **[Eu(hfa)₃p-dpba]_n**, **[Eu(hfa)₃dppt]_n**, and **[Eu(hfa)₃dppb]_n**.

	$\tau_{\text{obs}} / \text{ms}^{\text{a}}$	Φ_{ir} / %	$k_{\text{r}} / \text{s}^{-1}$	$k_{\text{nr}} / \text{s}^{-1}$	$\Phi_{\text{ir}}^*, 330 \text{ nm}$ / %	$\eta_{\text{sens}}, 330 \text{ nm}$ / %	$\Phi_{\text{ir}}^*, 370 \text{ nm}$ / %	$\eta_{\text{sens}}, 370 \text{ nm}$ / %
[Eu(hfa)₃p-dpba]_n	0.74	64	8.7×10^2	4.8×10^2	22	34	4.4	6.8
[Eu(hfa)₃dppt]_n	0.55	44	8.0×10^2	1.0×10^3	26	59	19	43
[Eu(hfa)₃dppb]_n	0.63	52	8.2×10^2	7.6×10^2	27	52	19	37

a) $\lambda_{\text{ex}} = 355 \text{ nm}$, $\lambda_{\text{em}} = 610 \text{ nm}$.

other hand, their oscillator strength of $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$ was different from those in $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$ and $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$. $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$ and $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$ exhibited broad emission bands at 461 nm and 465 nm, respectively. The observed emission bands correspond to the emission of linker ligands (Fig. 3b). In particular, the broad emission band of $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$ was blue-shifted (34 nm) from that of p-dpba . This shift was originated from the differences of aggregation structure between $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$ and p-dpba . The effect of solvent polarity could not be evaluated because the $\text{Eu}(\text{III})$ coordination polymers were insoluble.

The emission lifetimes were determined from the slope of the logarithmic decay profile. The overall emission quantum yields ($\Phi_{\pi\pi^*}$) were also measured. These photophysical parameters are listed in Table 1. Based on the emission lifetimes and spectra, the 4f-4f emission quantum yield (Φ_{ff}), radiative rate constant (k_r), non-radiative rate constant (k_{nr}), photosensitization efficiency (η_{sens}) were calculated using the equations (1)-(4).

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

$$k_{\text{nr}} = \frac{1}{\tau_{\text{obs}}} - \frac{1}{\tau_{\text{rad}}} \quad (2)$$

$$\Phi_{\text{ff}} = \frac{k_r}{k_r + k_{\text{nr}}} \quad (3)$$

$$\Phi_{\pi\pi^*} = \eta_{\text{sens}} \Phi_{\text{ff}} \quad (4)$$

No significant difference was observed in the k_r values in the three $\text{Eu}(\text{III})$ coordination polymers. On the other hand, the k_{nr} values of the $\text{Eu}(\text{III})$ coordination polymers were dependent on the molecular conformational arrangement of the amide units. The overall emission quantum yields ($\Phi_{\pi\pi^*}$) for $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$, $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$, and $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$ excited at 370 nm were estimated to be 4.4 %, 19 % and 19 %, respectively. The -CO-(Ph)-CO- substituents of p-dpba induced intramolecular ligand-to-ligand charge transfer (LLCT) quenching, resulting in the low overall emission quantum yields ($\Phi_{\pi\pi^*}$) of $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$. Notably, previous $\text{Eu}(\text{III})$ coordination polymers with hfa and bidentate phosphine oxide ligands exhibit relatively high $\Phi_{\pi\pi^*}$ (50%-70%) upon the excitation of hfa ligand.^{37,38} This high $\Phi_{\pi\pi^*}$ is attributed to effective energy transfer from hfa, while the contribution of bidentate phosphine oxide ligands to energy transfer is negligible due to their very weak absorption in the UV region.

We considered the amide unit-functionalized phosphine oxide ligand attributed to the low $\Phi_{\pi\pi^*}$ and low η_{sens} for $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$, $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$, and $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$. The absorption coefficients at 370 nm excitation (ϵ_{370}) of p-dpba , dppt , and dppb were estimated to be 6400, 40, and 40 $\text{M}^{-1} \text{cm}^{-1}$, respectively. The ϵ_{370} of p-dpba was 90 times larger than that of hfa unit ($\epsilon_{370} = 70 \text{ M}^{-1} \text{cm}^{-1}$). The higher absorption coefficient of p-dpba and ineffective energy transfer via phosphine oxide ligand with amide unit are considered

to decrease the $\Phi_{\pi\pi^*}$ and low η_{sens} based on hfa excitation. The overall emission quantum yields ($\Phi_{\pi\pi^*}$) for $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$, $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$, and $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$ excited at 330 nm were found to be 22 %, 26 % and 27 %, respectively. The quantum yields at 330 nm excitation were larger than those at 370 nm excitation. According to the excitation spectra, we think that the hfa ligand excitation is more effective for $\text{Eu}(\text{III})$ emission. The absorption coefficients at 330 nm excitation (ϵ_{330}) of p-dpba , dppt , dppb , and hfa were estimated to be 36600, 10600, 15600, and 15200 $\text{M}^{-1} \text{cm}^{-1}$, respectively. These results indicated that the modulation of the light absorption of phosphine oxide with amide unit is a key factor for controlling overall emission quantum yields of $\text{Eu}(\text{III})$ coordination polymers.

4. Conclusion

Novel $\text{Eu}(\text{III})$ coordination polymers with systematically changed amide units were synthesized. The structural and photophysical properties of these $\text{Eu}(\text{III})$ coordination polymers were found to be dependent on the molecular conformational arrangement of the amide units. The overall emission quantum yields of $[\text{Eu}(\text{hfa})_3\text{dppt}]_n$ and $[\text{Eu}(\text{hfa})_3\text{dppb}]_n$ were larger than that of $[\text{Eu}(\text{hfa})_3\text{p-dpba}]_n$. The structural and photophysical properties of these $\text{Eu}(\text{III})$ coordination polymers were dependent on the electronic structures of the amide units. The relationship between the steric structure and the photophysical properties of $\text{Eu}(\text{III})$ coordination polymers has the potential to open up new research fields in coordination and photophysical photochemistry.

Supplementary data

Supplementary material is available at *Bulletin of the Chemical Society of Japan*.

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