



HOKKAIDO UNIVERSITY

Title	Study on Luminescent Lanthanide Coordination Polymers with Amide-based Linker Ligands
Author(s)	林, 穰
Degree Grantor	北海道大学
Degree Name	博士(工学)
Dissertation Number	甲第16384号
Issue Date	2025-03-25
DOI	https://doi.org/10.14943/doctoral.k16384
Doc URL	https://hdl.handle.net/2115/97639
Type	doctoral thesis
File Information	HAYASHI_Joe.pdf



Study on Luminescent Lanthanide Coordination Polymers with Amide- based Linker Ligands

アミド誘導体を架橋配位子とする
発光性希土類配位高分子に関する研究

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Chapter 1

General Introduction

1.1 Introduction

Humans began using light as early as the Stone Age, and its uses expanded as ancient civilizations developed. After the Industrial Revolution, advances in chemistry and electricity provided the basis and tools for the invention of many light-related devices, from photography to chemical and electric lighting. In the 20th century, the wave and quantum paradigm and research into the interaction of light with matter at the subatomic level provided the knowledge for the wider use of light in various fields, leading to today's light-based science and technologies.

The science and technology of light is one of the most extensive and most practical areas of science. Light-based technologies are applied in many areas, including display, fiber-optic communications, and lasers (**Figure 1.1**).^[1-3] In particular, display technologies have become indispensable in today's life, with a wide range of applications including smartphones, computers, projectors and VR/AR devices.^[4] Light-Emitting Diode (LED) and OLED-based display systems need to achieve high color saturation, high brightness and low power consumption for use as pixel-based resolution, and miniaturisation of LEDs is a challenge.^[5] OLED, mini-LEDs (mLEDs) and micro-LEDs (μ LEDs) displays have attracted attention as LED display technologies to overcome this challenge.^[6-8] In the research field, lasers are widely used such as femtosecond lasers, confocal laser scanning microscope (CLSM), Raman Spectrometer, X-ray free electron laser, optical tweezer, super-resolution fluorescence microscopy (STORM), terahertz spectroscopy equipment.^[3,9-14] The laser technologies have become a very useful tool in a wide range of research areas, including biological and medical science.^[15]

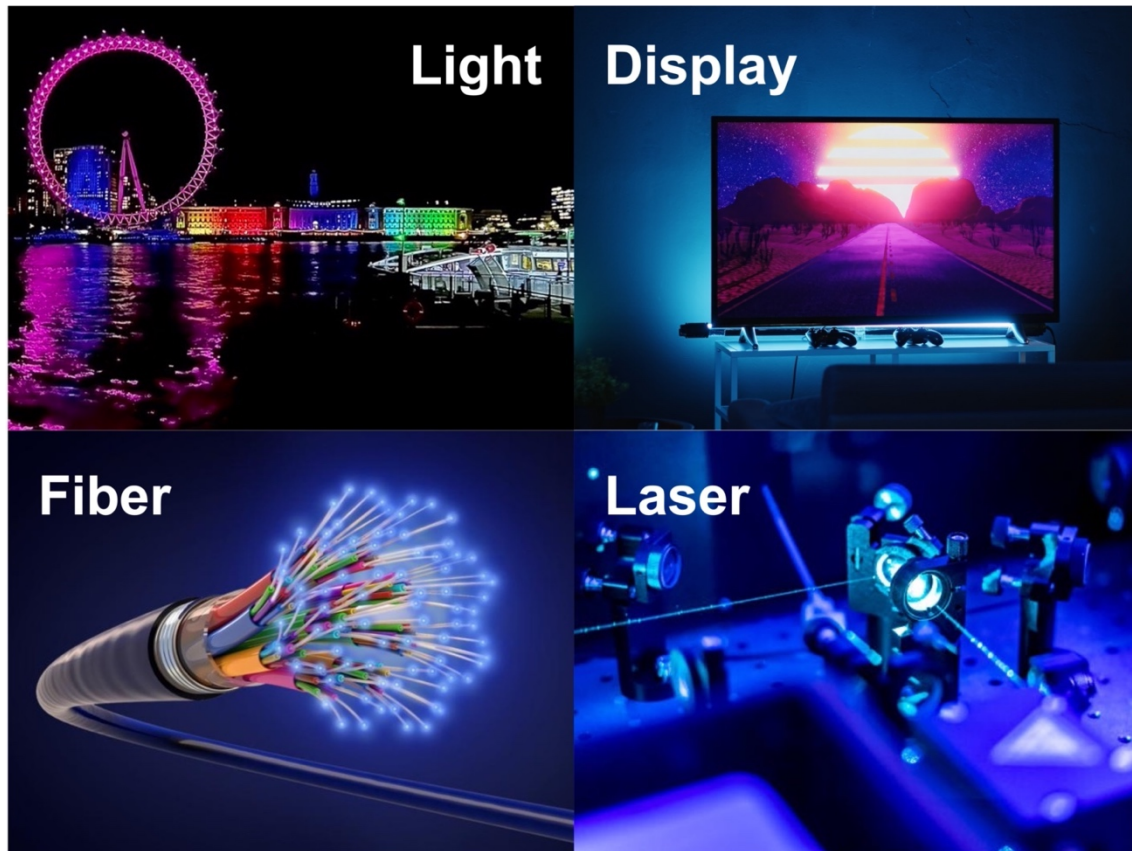


Figure 1.1 Examples of application of light. Images taken from reference ^[16] (top right), ^[17] (bottom left), and ^[18] (bottom right).

1.2 Lanthanides

The lanthanide series contains fifteen elements with atomic number from 57 (La) to atomic number 71 (Lu). They are placed at the bottom of the periodic table (**Figure 1.2**). The rare earth elements consist of lanthanide elements plus scandium (atomic number 21) and yttrium (atomic number 39) because of their similar chemical properties. Contrary to the classification name 'rare earths', they are relatively abundant in the Earth's crust. In total, it is estimated that up to 242 ppm of rare earths are present in the Earth's crust, more than the amount of carbon (200 ppm).^[19] The lanthanides and actinides, atomic number from 89 to atomic number 103, were classified as the “f-block elements”. This classification was because electron gradually fills seven 4f-orbitals for lanthanides (5f-orbitals for actinides) with increasing atomic number.

The Periodic Table

Rare-earths

Sc 21

Y 39

Actinides

Lanthanides

La 57 Ce 58 Pr 59 Nd 60 Pm 61 Sm 62 Eu 63 Gd 64 Tb 65 Dy 66 Ho 67 Tm 68 Er 69 Yb 70 Lu 71

Figure 1.2 Rare-earths (shaded in yellow and blue), lanthanides (blue), and actinides (orange) in the periodic table. The numbers are the atomic numbers.

The filling of the seven 4f orbitals of the lanthanides generates several unique chemical properties, including similar ionic radii, reduction potentials, oxidation states and electronegativity (**Figure 1.3a**). These chemical properties are similar throughout the lanthanide series because the 4f orbitals are shielded by the outer 5s and 5p orbitals and are less affected by the environment (**Figure 1.3b**). Lanthanides applied for many technologies such as lasers, catalysis, magnets, security inks, and bio imaging.^[20-26]

The electron configuration of lanthanides is shown in **Table 1.1**. The seven 4f orbital can accommodate a maximum of fourteen electrons.^[27] In the zerovalent state, the configuration of lanthanides ($[\text{Xe}]4f^x5d^y6s^2$) involves with two electrons in the 6s orbital and zero or one electron in the 5d orbital. The electrons in 4f orbital are partially and irregularly added from lanthanum (La: $[\text{Xe}]4f^05d^16s^2$) to lutetium (Lu: $[\text{Xe}]4f^{14}5d^16s^2$).^[28] The lanthanide elements generally exist as their trivalent state. In the trivalent state, lanthanide (Ln(III)) loses three electrons: two from the 6s-orbital and one from either the 4f orbital or 5d orbital. This results in a Ln(III) ion with 4f-orbitals that is not completely filled except lanthanum (La) and lutetium (Lu). The 4f electrons in the trivalent ions are gradually added from $[\text{Xe}]4f^0$ (lanthanum) to $[\text{Xe}]4f^{14}$ (lutetium). Lanthanides are usually in the trivalent state, but they can also exist in the divalent and tetravalent states. For example, europium (Eu) and ytterbium (Yb) are stable in the divalent state because Eu(II) and Yb(II) are the same electron configuration as the trivalent state of gadolinium (Gd) and Lu, respectively. Similarly, cerium (Ce) and terbium (Tb) are stable in the quadrivalent state because Ce(IV) and Tb(IV) are the same electron configuration as the trivalent state of La and Gd, respectively. The ionic radii of lanthanides gradually decrease the range of between 0.977 (lutetium) and 1.16 Å (lanthanum). This phenomenon (lanthanide contraction) is due to the low shielding effect of the 4f electrons, which cannot sufficiently shield the increasing positive charge of the nucleus, and the

valence electrons in the outer orbitals are subject to a strong nuclear attraction. The monotonic decrease in ionic radius contributes to the similarity of chemical properties.

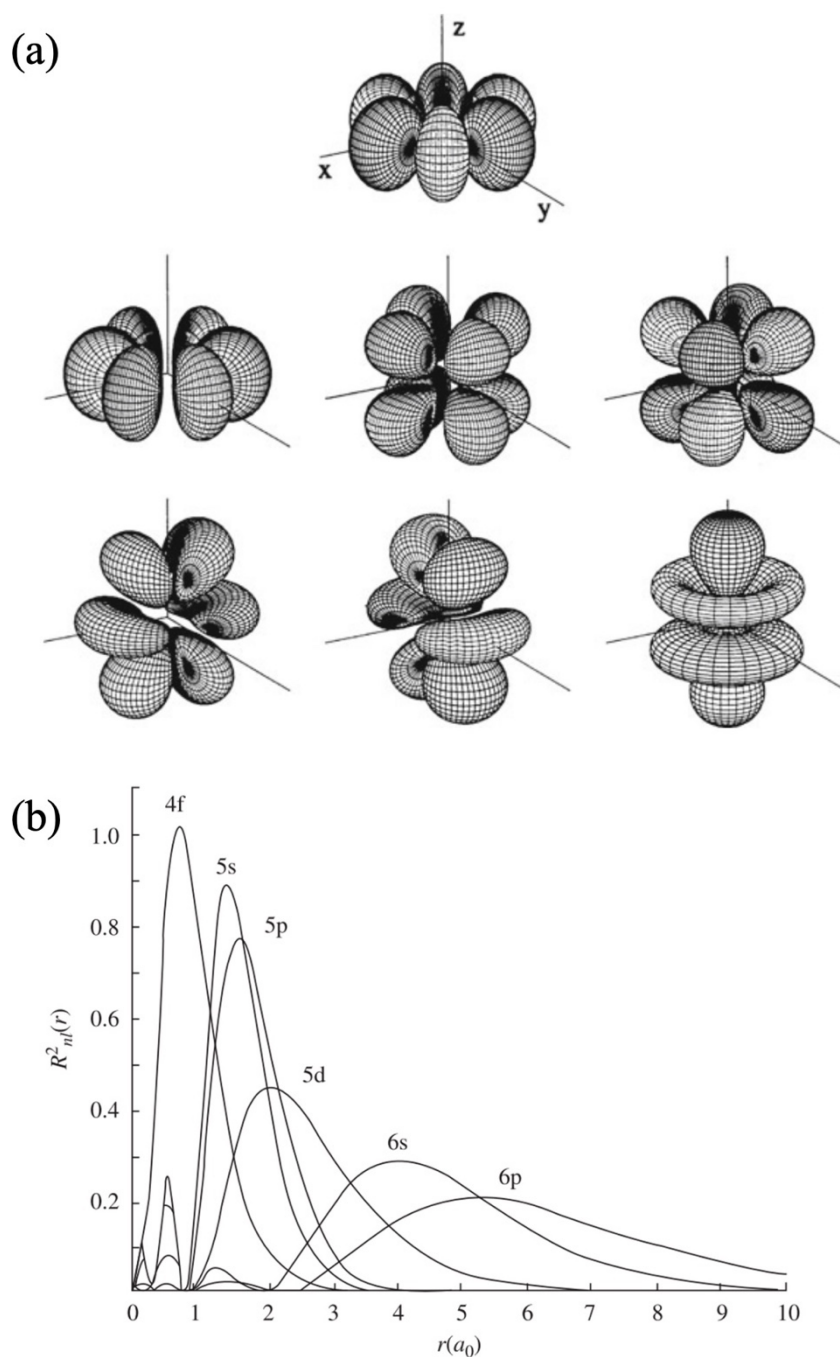


Figure 1.3 (a) Depiction of the real wavefunctions of 4f-orbitals reprinted from reference [29]. (b) Radial part of the wavefunction of the orbitals reprinted from reference [30].

Table 1.1 Electronic configurations of lanthanides.

Atomic number	Element	Electronic configuration		Atom radii / Å ^{a)}
		Atom	Trivalent ion	
57	La	[Xe]5d ¹ 6s ²	[Xe]	1.16
58	Ce	[Xe]4f ¹ 5d ¹ 6s ²	[Xe]4f ¹	1.14
59	Pr	[Xe]4f ³ 6s ²	[Xe]4f ²	1.13
60	Nd	[Xe]4f ⁴ 6s ²	[Xe]4f ³	1.11
61	Pm	[Xe]4f ⁵ 6s ²	[Xe]4f ⁴	1.10
62	Sm	[Xe]4f ⁶ 6s ²	[Xe]4f ⁵	1.08
63	Eu	[Xe]4f ⁷ 6s ²	[Xe]4f ⁶	1.07
64	Gd	[Xe]4f ⁷ 5d ¹ 6s ²	[Xe]4f ⁷	1.05
65	Tb	[Xe]4f ⁹ 6s ²	[Xe]4f ⁸	1.04
66	Dy	[Xe]4f ¹⁰ 6s ²	[Xe]4f ⁹	1.03
67	Ho	[Xe]4f ¹¹ 6s ²	[Xe]4f ¹⁰	1.02
68	Er	[Xe]4f ¹² 6s ²	[Xe]4f ¹¹	1.00
69	Tm	[Xe]4f ¹³ 6s ²	[Xe]4f ¹²	0.99
70	Yb	[Xe]4f ¹⁴ 6s ²	[Xe]4f ¹³	0.99
71	Lu	[Xe]4f ¹⁴ 5d ¹ 6s ²	[Xe]4f ¹⁴	0.98

a) Shannon radii of 8-coordinate Ln(III) ion.

Ln(III) ions exhibit characteristic luminescence properties derived from the 4f orbital, including spectrally sharp absorption and emission bands, long emission lifetimes and small absorption coefficients (**Figure 1.4**).

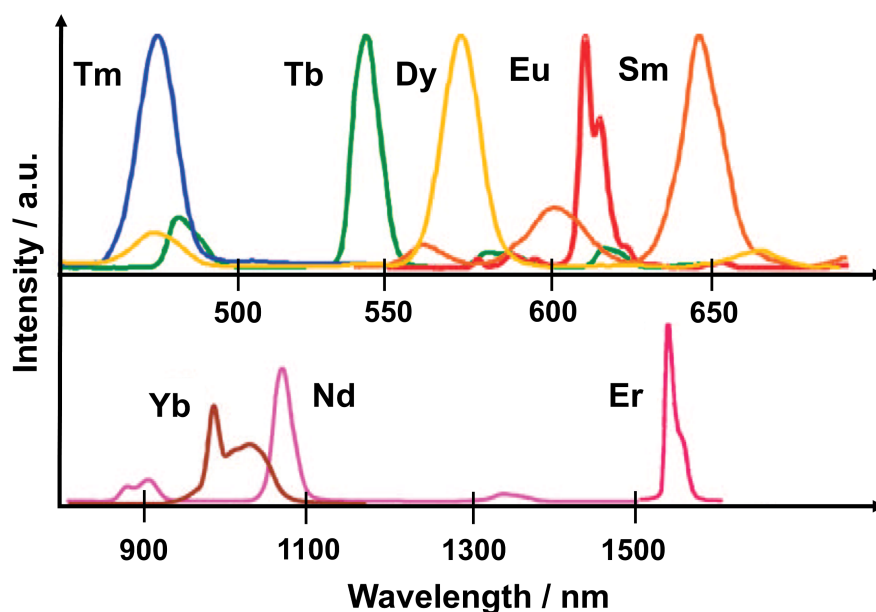


Figure 1.4 The emission spectra of some Ln(III) complexes adapted from reference ^[31].

The energy levels of the 4f orbitals in Ln(III) are determined by several perturbations including electron repulsion, spin-orbit coupling, the crystal-field perturbation, and the Zeeman effect (**Figure 1.5**). The electron repulsion is the electrostatic interaction between electrons in the different 4f orbitals. The spin-orbit coupling results from the interaction between the spin magnetic moment of the 4f electrons and the magnetic field created by the 4f electrons moving around the nucleus. The crystal field effect is caused by the interaction between the 4f electrons and the electrons of the ligand. The Zeeman effect is the splitting of energy levels by an external magnetic field. Among these perturbations, the crystal-field and Zeeman effect are minor perturbations due to the shielded character

of 4f orbitals. The split energy level can be labeled by the Russell-Saunders term symbol ($^{2S+1}L_J$). The numbers of S , L , and J indicate the total spin quantum number, total orbital quantum number, and total angular quantum number, respectively. The energy level diagram of Ln(III) is known as the “Dieke diagram” (**Figure 1.6**).^[32] The energy levels of the 4f orbitals of Ln(III) ions are unique to each element and hardly change with the crystal field, resulting in very accurate emission and absorption wavelengths with little variation (**Table 1.2**). This intrinsic energy level is advantageous for the design of luminescent materials. It makes it easy to predict the emission wavelength.

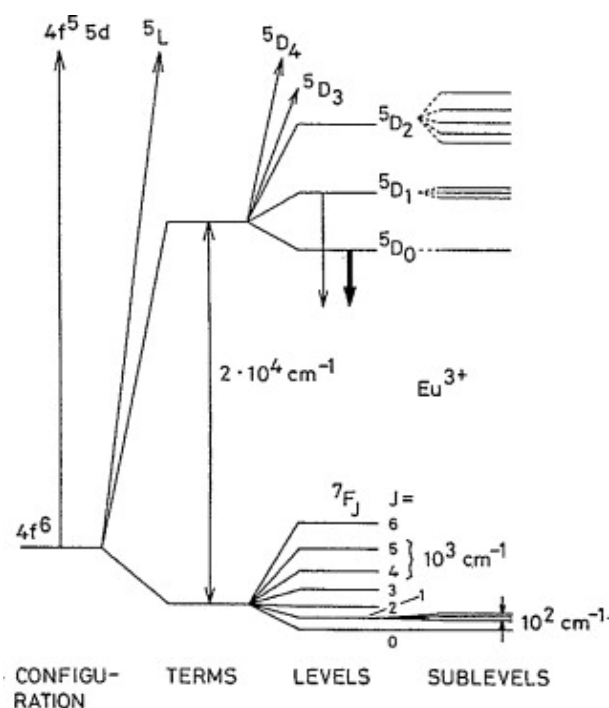


Figure 1.5 Partial energy diagram of Eu(III) showing the relative magnitude of the interelectronic repulsion (terms), spin–orbit coupling (levels), and crystal-field effects (sublevels).^[33]

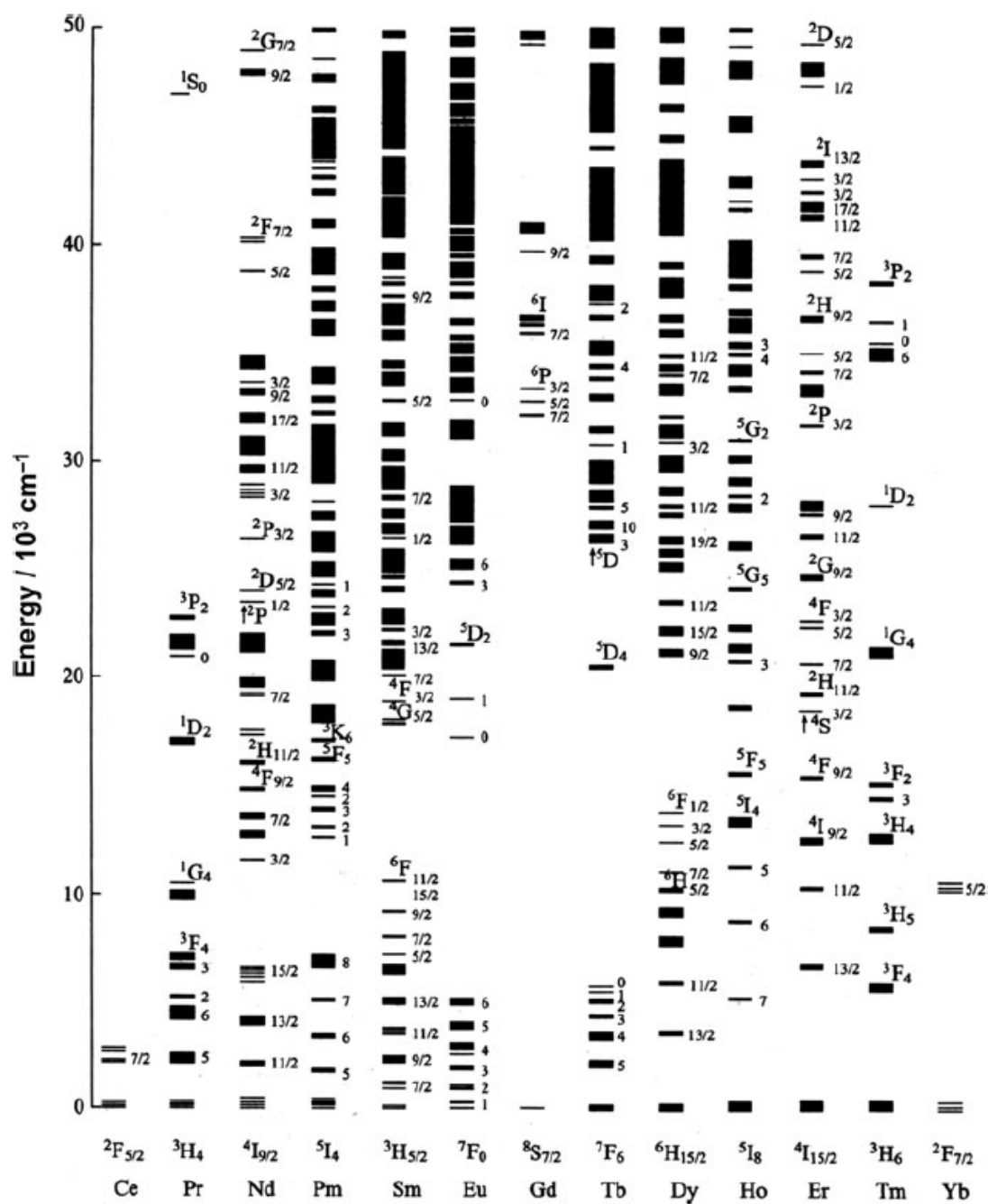


Figure 1.6 Dieke diagram of lanthanide ions reprinted from reference [29].

Table 1.2 Most common emissive 4f-4f transitions of Ln(III) ions. ^[34]

Element	Transition	Wavelength / nm
Pr	$^1D_2 \rightarrow ^3F_4$	1000
	$^1D_2 \rightarrow ^1G_4$	1440
	$^1D_2 \rightarrow ^3H_J (J = 4, 5)$	600, 690
	$^3P_0 \rightarrow ^3H_J (J = 4 - 6)$	490, 545, 615, 640
	$^3P_0 \rightarrow ^3F_J (J = 2 - 4)$	700, 725
Nd	$^4F_{3/2} \rightarrow ^4I_J (J = 9/2 - 13/2)$	900, 1060, 1350
Sm	$^4G_{5/2} \rightarrow ^6H_J (J = 9/2 - 13/2)$	560, 595, 640, 700, 775
	$^4G_{5/2} \rightarrow ^6F_J (J = 1/2 - 9/2)$	870, 887, 926, 1010, 1150
Eu	$^5D_0 \rightarrow ^7F_J (J = 0 - 6)$	580, 590, 615, 650, 720, 750, 820
Gd	$^6P_{7/2} \rightarrow ^8S_{7/2}$	315
Tb	$^5D_4 \rightarrow ^7F_J (J = 6 - 0)$	490, 540, 580, 620, 650, 660, 675
Dy	$^4F_{9/2} \rightarrow ^6H_J (J = 15/2 - 9/2)$	475, 570, 660, 750
	$^4I_{15/2} \rightarrow ^6H_J (J = 15/2 - 9/2)$	455, 540, 615, 695
Ho	$^5S_2 \rightarrow ^5I_J (J = 8, 7)$	545, 750
	$^7F_5 \rightarrow ^5I_J (J = 8, 7)$	650, 965
Er	$^4S_{3/2} \rightarrow ^4I_J (J = 15/2 - 13/2)$	545, 850
	$^4F_{9/2} \rightarrow ^4I_{15/2}$	660
Tm	$^1D_2 \rightarrow ^3F_4, ^3H_4, ^3F_J (J = 3, 2)$	450, 650, 740, 775
	$^1G_4 \rightarrow ^3H_6, ^3F_4, ^3H_5$	470, 650, 770
	$^3H_4 \rightarrow ^3H_6$	800
Yb	$^2F_{5/2} \rightarrow ^2F_{7/2}$	980

The two 4f states do not show any intrinsic change in the potential curve, as the 4f orbitals do not contribute to the coupling due to shielding effects. As a result, the absorption and emission between the two 4f states is extremely sharp (**Figure 1.7**).

Electronic transitions of Ln(III) ions are often weak because 4f-4f transitions are Laporte forbidden. Because of forbidden properties, the transitions cannot occur in a fully symmetrical crystal field. However, in the most cases, both absorption and emission can be measured rather weakly because of the partial mixing of the 5d orbitals via asymmetrical crystal field. [35,36]

Emission lifetimes of Ln(III) ions are typically long: in the order of microseconds to milliseconds. Emission lifetime (τ_{obs}) is given by the following equation.

$$\tau_{\text{obs}} = \frac{1}{k_r + k_{nr}} \quad (1)$$

where k_r and k_{nr} are radiative and non-radiative rate constants, respectively. A small offset between the ground and excited states because of the shielded 4f-orbitals of Ln(III) ions leads to less state overlap, resulting in the small non-radiative rate constants ($k_{nr} \approx 10^2 - 10^3 \text{ s}^{-1}$). On the other hand, the radiative rate constant is rather low ($k_r \approx 10^2 - 10^3 \text{ s}^{-1}$) because of the Laporte forbidden 4f-transition in Ln(III). These two factors contribute to the long lifetimes of Ln(III) ions using Equation (1).

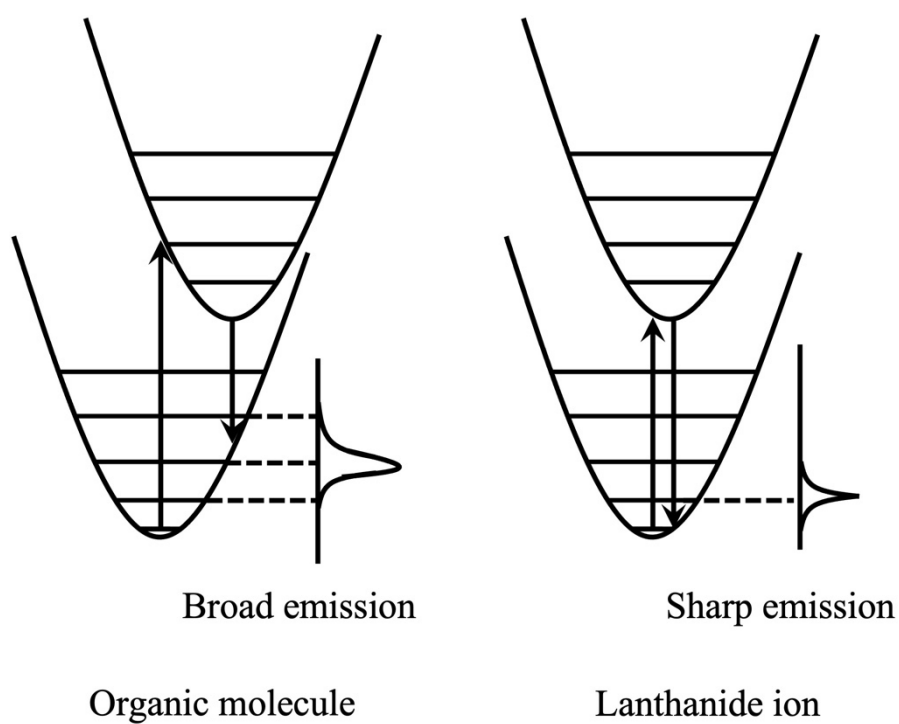


Figure 1.7 Potential curve shifts and emission phenomena of organic molecules and Ln(III) ions.

1.3 Lanthanide complexes

As previously reported, the absorption coefficient (ϵ) of lanthanide ions is very small ($\epsilon < 10 \text{ M}^{-1} \text{ cm}^{-1}$). This weak absorption leads to the weak luminescence intensity.^[37] In 1942, Weissman discovered the method to overcome the weak absorption and luminescence, so-called “antenna effect”. They demonstrated that Eu(III) complexes showed the intense luminescence via the photosensitization by the organic ligand. Generally, β -diketonate, phosphine oxide, pyridine and carboxylate were used for the achievement of strong luminescence.^[38,39]

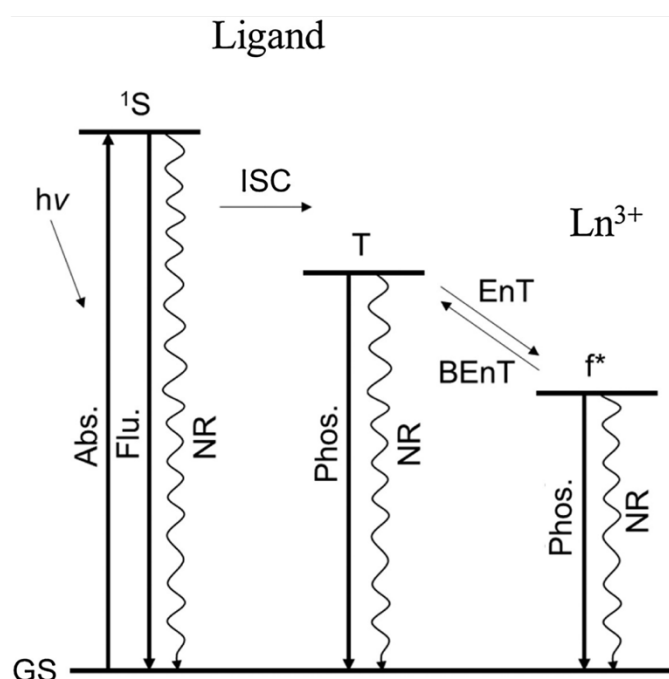


Figure 1.8 Energy diagram of lanthanide complexes.

The energy diagram in the luminescence of the lanthanide complex is shown in **Figure 1.8**. First, the absorption of light induces an excitation of organic ligand from the ground singlet state (S_0) to the excited singlet state (S_1). Next, the intersystem crossing (ISC)

from S_1 to the excited triplet state (T_1) was performed. This process is promoted by the strong spin-orbit coupling of Ln(III) ion (heavy atom effect). Subsequently, the energy transfer (EnT) from T_1 of organic ligand to the excited state of lanthanide ions occurs. Finally, the lanthanide ion exhibits a characteristic strong luminescence.

In this diagram, With this mechanism, quantum yield of Ln(III) complexes by ligand excitation ($\Phi_{\pi\pi^*}$) can be calculated from the following equation.

$$\Phi_{\pi\pi^*} = \eta_{\text{sens}} \Phi_{\text{ff}} \quad (2)$$

Where η_{sens} is energy transfer efficiency of the Ln(III) ion by the organic ligands. Φ_{ff} is the quantum yield of Ln(III) complexes by direct excitation of Ln(III) ion. Φ_{ff} is given by the following equations.

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

The radiative (k_r) and non-radiative (k_{nr}) rate constants can be calculated as well.

$$k_r = \frac{1}{\tau_{\text{rad}}} \quad (4)$$

$$k_{\text{nr}} = \frac{1}{\tau_{\text{obs}}} - \frac{1}{\tau_{\text{rad}}} \quad (5)$$

Where emission lifetime τ_{obs} and intrinsic emission lifetime τ_{rad} .

In the case of Eu(III) complexes, the k_r value can be estimated by the following calculation because the $^5D_0 \rightarrow ^7F_1$ transition of Eu(III) complexes is a magnetic dipole transition allowed and electric dipole transition forbidden. ^[40]

$$k_r = A_{\text{MD},0} n^3 \frac{I_{\text{tot}}}{I_{\text{MD}}} \quad (6)$$

Where $A_{\text{MD},0}$, n , and $I_{\text{tot}}/I_{\text{MD}}$ are the spontaneous emission probability of the $^5D_0 \rightarrow ^7F_1$ transition in vacuum (14.65 s^{-1}), the refractive index ($n=1.5$ is used for solid sample), the ratio of the total area of the corrected Eu(III) emission spectrum to the area of the $^5D_0 \rightarrow ^7F_1$ band, respectively.

1.4 Lanthanide coordination polymers

Among various lanthanide complexes, lanthanide coordination polymers have attracted great interest in the recent years due to their potential applications in many fields such as molecular magnetism, chemical sensing, and luminescent materials.^[41-43] They are constructed of linker ligands and Ln(III) ions. The polymer structure form 1D, 2D, and 3D type networks depending on the molecular structure of linker ligands.^[44]

In 1991, Yamase described first Eu(III) coordination polymer.^[45] Various lanthanide coordination polymers have been gradually increasing reported.^[46-49] Bünzli presented lanthanide coordination polymers composed of lanthanide ions and 1,4-disubstituted benzenes.^[50] Carlos exhibited Eu(III) coordination polymer with phenanthroline units.^[51] Hasegawa have reported luminescent lanthanide coordination polymers with bidentate phosphine oxide linker ligands and β -diketonate ligands.^[52,53] The low frequency vibration structure of phosphine oxide (P=O: 1125 cm^{-1}) and β -diketonate (C-F: 1200 cm^{-1} , C=O: 1650 cm^{-1}) provides effective suppression of the non-radiative relaxation. The molecular structure of bidentate phosphine oxide linker ligands affect the photophysical properties of Ln(III) coordination polymers.

On the basis of such a background, morphological and steric control of lanthanide coordination polymer by leads to further understanding and development of photochemistry and coordination chemistry.

1.5 Lanthanide coordination polymers with amide-type ligands

Among various linker ligands, amide-type ligands have attracted attention due to their structural flexibility and potential binding sites.^[54-56] Recently, lanthanide coordination polymers with amide type ligand with salicylamide moieties have been developed as a new type of multifunctional materials.^[57-59] Song have been demonstrated that Eu(III) coordination polymers with salicylamide ligands constructed two-dimensional (2D) networks.^[60] PMMA films doped with Eu(III) coordination polymer exhibited luminescent recognition of Zn(II) in aqueous solution. Wang reported 2D typed Eu-MOF bridged by a dicarboxylic acid ligand with amide groups.^[61] The Eu-MOF has the ability to detect benzaldehyde and Fe(III) ion. Precise molecular design using amide typed ligands is effective approach for novel photofunctional materials.

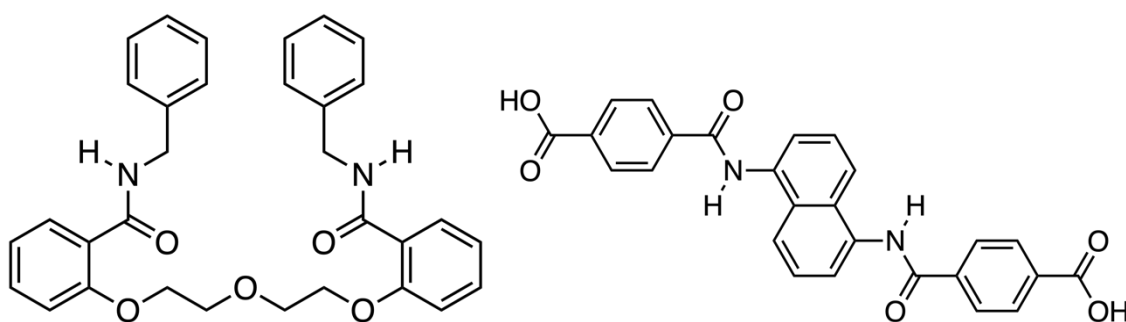


Figure 1.9 Molecular structures of previously reported amide-type ligands in lanthanide coordination polymers. Adapted from reference ^[60] (left) and ^[61] (right).

1.6 Objective

The molecular design of the organic ligand is crucial in determining the assemble structure of the lanthanide coordination polymer. The precisely control of morphology and molecular structure expects to be applied to next-generation optical materials.

In this study, the author focuses on the amide-type ligands for the morphological and steric control of Ln(III) coordination compounds. The C=O and N–H groups of amide bonds induce hydrogen bonding interactions and act as donors and acceptors of hydrogen bonding. The hydrogen bonding promotes dynamic decomposition and rearrangement by external stimuli such as heat, light, and pressure.^[62-64] Amide bonds are both rigid and flexible due to the partial double bond property of the C-N bond. This characteristic bonding property provide various stacking higher-order structures such as capsule, sheet, and helix.^[65-67] The morphological control based on the hydrogen bonding via amide linker ligands and the steric control approaches provide an effective approach for producing novel functional materials.

1.7 Outline

This thesis consists of five chapters.

In **Chapter 1**, the overviews of the lanthanide chemistry and luminescent lanthanide complexes are provided, and the objective of this study is described.

In **Chapter 2**, Eu(III) coordination polymer with flexible substituents in the linker ligands is demonstrated for expressing new material properties. The amide unit in linker ligands provided characteristic phase transition behavior upon heat treatment. The flexibility of ethylenediamine unit in linker ligand and the hydrogen bonding network in the Eu(III) coordination polymer provide glass forming ability.

In **Chapter 3**, the author focuses on the molecular conformational arrangement of linker ligands with the same molecular formula. A series of Eu(III) coordination polymers with systematically changed amide bond directions was prepared. The effect of this change in molecular conformation on structural and photophysical properties was evaluated.

In **Chapter 4**, the lanthanide coordination polymers with CO₂ adsorption properties are demonstrated. The lanthanide coordination polymers constructed cylindrical structure. The inner surfaces of the cylindrical channels were covered with the fluorine atoms of the hfa ligands. The emission intensity ratio between Eu(III) and Tb(III) in Eu(III)/Tb(III) mixed coordination polymer is affected by the CO₂ gas adsorption behavior.

In **Chapter 5**, summary and outlook of the research are described.

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Chapter 2

***Eu(III) Coordination Polymer with
Alkylamide Moiety for Transparent
Luminescent Material***

2.1 Introduction

Lanthanide coordination polymers have attracted much attention for characteristic luminescent materials such as sensing, displays, and bioimaging applications because of their 4f-4f transitions with narrow emission bands (Full Width at Half Maximum, FWHM < 10 nm) and long emission lifetimes ($\tau > 1 \mu\text{s}$).^[1-4] Recently, Hasegawa have demonstrated bright luminescent lanthanide coordination polymers, which are composed of lanthanide ions and phosphine oxide linker ligands.^[5] The structural molecular designs of phosphine oxide ligand in lanthanide coordination polymers plays an essential role in controlling photophysical properties.^[6,7]

In this chapter, the author selected amide-based linker ligand to novel functional luminescent materials. The hydrogen bonding networks in polyamide compounds are intrinsically important in the development of functional materials. Polyamide compounds have been reported as functional materials with thermoresponse and self-repair due to the rearrangement of the hydrogen bonding network by external stimuli including temperature and acidity.^[8-11] The author considered luminescent lanthanide coordination polymers with amide-based linker ligand to form hydrogen bonding network.

Based on this strategy, the author prepared Eu(III) coordination polymers, $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ and $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$, composed of Eu(III) ion, hexafluoroacetylacetonate (**hfa**), and phosphine oxide linker ligand with amide groups, **dpba** (*N, N'*-(ethane-1,2-diyl)bis(4-(diphenylphosphoryl)benzamide)) or **p-dpba** (*N, N'*-(1,4-phenylene)bis(4-(diphenylphosphoryl)benzamide)) (**Figure 2.1 a and b**). The **dpba** and **p-dpba** ligands contained ethylenediamide and *p*-phenylnediamie unit, respectively. The thermal properties were characterized by thermogravimetric (TG) and differential scanning calorimetry (DSC). The structural properties were evaluated by the X-ray diffraction (XRD). The photophysical properties were estimated using emission spectra, emission quantum yields, and emission lifetimes. The author also prepared a Eu(III)

coordination polymer with an alkyl-bridged linker ligand, **dph** (1,6-bis(diphenylphosphoryl)hexane), as a reference sample (**Figure 2.1 c**, $[\text{Eu}(\text{hfa})_3(\text{dph})]_n$).

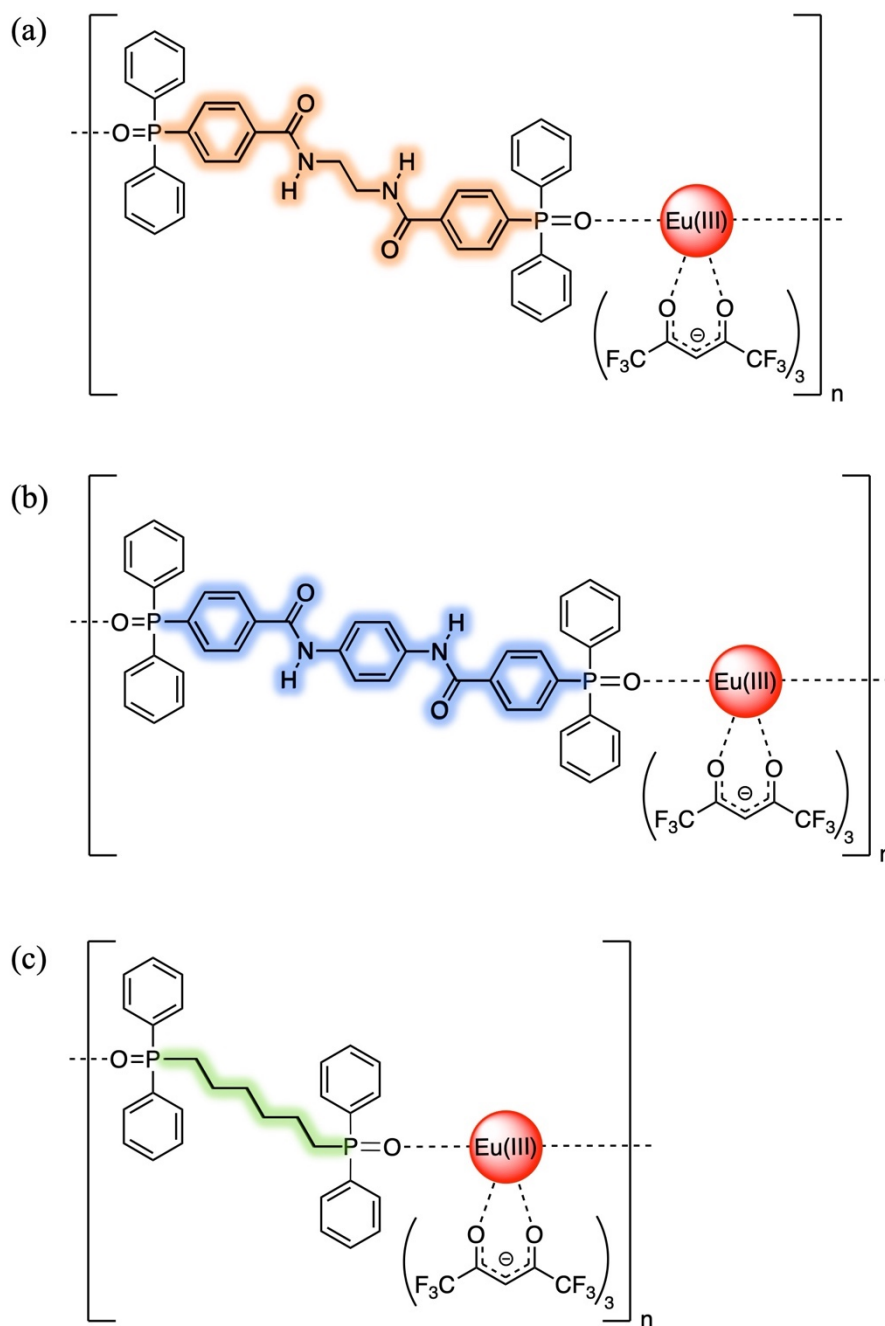


Figure 2.1 Molecular structures of (a) $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$, (b) $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$, and (c) $[\text{Eu}(\text{hfa})_3(\text{dph})]_n$.

2.2 Methods

2.2.1 Materials and apparatus

Diphenyl(*p*-tolyl)phosphine and europium(III) acetate *n*-hydrate (99.9%) were purchased from FUJIFILM Wako Pure Chemical Corporation. 1,6-Bis(diphenylphosphino)hexane, ethylenediamine, and *p*-phenylenediamine, were purchased from Tokyo Chemical Industry Co., Ltd. The other chemicals as reagent grade were used without further purification. ESI-MS spectra were recorded using a JEOL JMS-T100LP. ¹H NMR (400 MHz), ¹³C NMR (100 MHz), and ³¹P NMR (162 MHz) spectra were recorded on a JEOL ECS400 or JEOL ECZ400S. Tetramethylsilane ($\delta_{\text{H}} = 0.00$ ppm) was used as a reference for ¹H NMR. Thermogravimetric analyses were performed using on a Hitachi High-Tech TG/DTA 6300 instrument analyzer or TG-DTA8122/S under a nitrogen atmosphere at a heating rate of 5 °C min⁻¹. Differential scanning calorimetry were performed on a Hitachi High-Tech DSC 7020 under a nitrogen atmosphere at a heating and cooling rate of 5 °C min⁻¹. Powder X-ray diffraction was performed on a Rigaku SmartLab (CuK α radiation, $\lambda = 1.5418$ Å). The surface images were observed using JEOL JSM-6500F scanning electron microscopy. Heat treatment was performed with AS ONE hot plate ND-1A. Emission spectra and lifetimes were recorded on a HORIBA Fluorolog-3 spectrofluorometer. Emission lifetimes were determined from the slope of logarithmic plots of the decay profiles. The CD spectra were recorded on a JASCO J-1500 spectro-polarimeter.

2.2.2 Crystallography

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, $\lambda = 0.71073$ Å). The structure was resolved using direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically using the SHELX system. ^[12] Hydrogen atoms were refined using the riding model. All calculations were performed using the Olex2 crystallographic software package except for refinement, which was performed using SHELXL. ^[13] The CIF data were confirmed by the checkCIF/PLATON service. CCDC-2379686 for **[Eu(hfa)₃(*p*-dpba)]_n** contain the supplementary crystallographic data for this chapter.

2.2.3 Syntheses

Preparation of 4-(diphenylphosphoryl)benzoic acid

4-(Diphenylphosphoryl)benzoic acid was synthesized from commercially available diphenyl(*p*-tolyl)phosphine according to the reported procedures. ^[14]

Preparation of *N,N'*-(ethane-1,2-diyl)bis(4-(diphenylphosphoryl)benzamide) (**dpba**)

4-(Diphenylphosphoryl)benzoic acid (966.9 mg, 3.0 mmol) was dissolved in thionyl chloride (3 mL), and the mixture was stirred for 30 min at room temperature. Thionyl chloride was removed in vacuo. The residue was dissolved in CH₂Cl₂ (10 mL), and successively added ethylenediamine (0.4 mL, 6.0 mmol) and triethylamine (0.8 mL, 6.0 mmol). After stirring for 2 h at room temperature, the reaction mixture was washed with 2% HCl, aqueous 5% NaHCO₃, and distilled water. The organic layer was dried over Na₂SO₄ and evaporated. The residue was purified by silica gel column chromatography (10% MeOH–CH₂Cl₂) to give **dpba** (482.0 mg, 0.721 mmol, 48%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.48 (2H, s), 7.82 (4H, dd, *J* = 2, 8 Hz), 7.55–7.37 (24H, m),

3.70 ppm (4H, s). ^{31}P NMR (162 MHz, CDCl_3) δ 29.7 ppm. MS(ESI) found: m/z 691.19. Calcd. for $\text{C}_{40}\text{H}_{34}\text{N}_2\text{NaO}_4\text{P}_2$: $[\text{M}+\text{Na}]^+$, 691.19.

Preparation of *N,N'*-(1,4-phenylene)bis(4-(diphenylphosphoryl)benzamide (*p*-dpba))

4-(Diphenylphosphoryl)benzoic acid (322.3 mg, 1.0 mmol) was dissolved in thionyl chloride (1 mL), and the mixture was stirred for 30 min at room temperature. Thionyl chloride was removed in vacuo. The residue was dissolved in dichloromethane (10 mL), and successively added *p*-phenylenediamine (54.07 mg, 0.5 mmol) and triethylamine (1 mL) at 0°C. After stirring for 2 h at room temperature, the precipitate was filtered and purified by recrystallization from CH_2Cl_2 and MeOH to give *p*-dpba (158.4 mg, 0.221 mmol, 44%): ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 10.37 (2H, s), 8.07 (4H, d), 7.80-7.56 (34H, m) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 164.7, 138.2, 136.3, 135.3, 134.9, 132.8, 132.2, 131.7, 131.6, 131.5, 131.4, 128.9, 128.8, 127.8, 127.7, 120.7 ppm. ^{31}P NMR (162 MHz, $\text{DMSO}-d_6$) δ 25.8 ppm. MS(ESI) found: 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.

Preparation of 1,6-bis(diphenylphosphoryl)hexane (dph)

1,6-Bis(diphenylphosphoryl)hexane) was synthesized from commercially available 1,6-bis(diphenylphosphino)hexane according to the reported procedures. ^[15]

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

$[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$ was synthesized from commercially available europium(III) acetate *n*-hydrate according to the reported procedures. ^[16]

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

Dpba (66.9 mg, 0.1 mmol) and $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$ (80.9 mg, 0.1 mmol) were dissolved in CHCl_3 (10 mL). After the reaction mixture was stirred for 3 h at room temperature, the solvent was evaporated to give $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ (364.8 mg, 25.3 μmol , 25%) as white powder. MS(ESI) found: m/z 1235.09. Calcd. for $\text{C}_{50}\text{H}_{36}\text{EuF}_{12}\text{N}_2\text{O}_8\text{P}_2$ $[\text{M}-\text{hfa}]^+$, 1235.10.

found: m/z 2677.19. Calcd. for $C_{105}H_{73}Eu_2F_{30}N_4O_{18}P_4$ $[M_2\text{-hfa}]^+$, 2677.18; found: m/z 4119.18. Calcd. for $C_{160}H_{110}Eu_3F_{48}N_6O_{28}P_6$ $[M_3\text{-hfa}]^+$, 4119.27.

Preparation of $[Eu(hfa)_3(p\text{-dpba})]_n$

$[Eu(hfa)_3(H_2O)_2]$ (80.9 mg, 0.1 mmol) was added to a dichloromethane (5 mL) and MeOH (5 mL) mixture solution of ***p*-dpba** (71.6 mg, 0.1 mmol), and the mixture was stirred for 1 h. The recrystallization from dichloromethane and gave $[Eu(hfa)_3(p\text{-dpba})]_n$ (39.0 mg, 26.2 μmol , 26%) as a white powder: MS(ESI) found: m/z 1283.11. Calcd. for $C_{54}H_{36}EuF_{12}N_2O_8P_2$: $[M\text{-hfa}]^+$, 1283.10; found: m/z 2773.20. Calcd. for $C_{113}H_{73}Eu_2F_{30}N_4O_{18}P_4$ $[M_2\text{-hfa}]^+$, 2773.18; found: m/z 4263.20. Calcd. for $C_{172}H_{110}Eu_3F_{48}N_6O_{28}P_6$ $[M_3\text{-hfa}]^+$, 4263.27.

Preparation of $[Eu(hfa)_3(dph)]_n$

Dph (48.7 mg, 0.1 mmol) and $[Eu(hfa)_3(H_2O)_2]$ (80.9 mg, 0.1 mmol) were dissolved in $CHCl_3$ (10 mL). After the reaction mixture was stirred for 3 h at room temperature, the solvent was evaporated to give $[Eu(hfa)_3(dph)]_n$ (274.6 mg, 21.8 μmol , 22%) as white powder. MS(ESI) found: m/z 1283.06. Calcd. for $C_{45}H_{35}EuF_{18}NaO_8P_2$: $[M+Na]^+$, 1283.06; found: m/z 2313.17. Calcd. for $C_{85}H_{69}Eu_2F_{30}O_{14}P_4$: $[M_2\text{-hfa}]^+$, 2313.16.

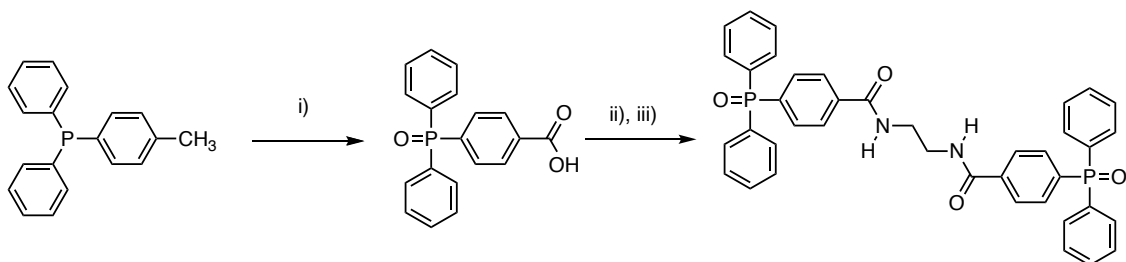


Figure 2.2 Synthetic scheme of **dpba**: i) KMnO_4 , NaOH aq., 90°C ; ii) SOCl_2 ; iii) ethylenediamine, Et_3N , CH_2Cl_2 , 0°C .

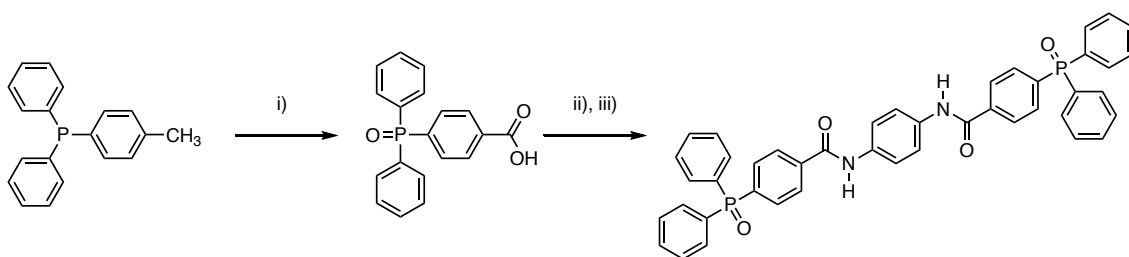


Figure 2.3 Synthetic scheme of ***p*-dpba**: i) KMnO_4 , NaOH aq., 90°C ; ii) SOCl_2 ; iii) *p*-phenylenediamine, Et_3N , CH_2Cl_2 , 0°C .

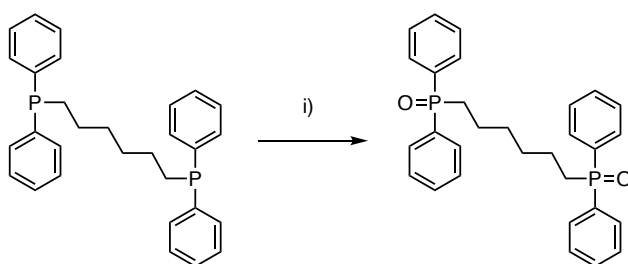


Figure 2.4 Synthetic scheme of **dpb**: i) 30% H_2O_2 aq., CH_2Cl_2 , 0°C .

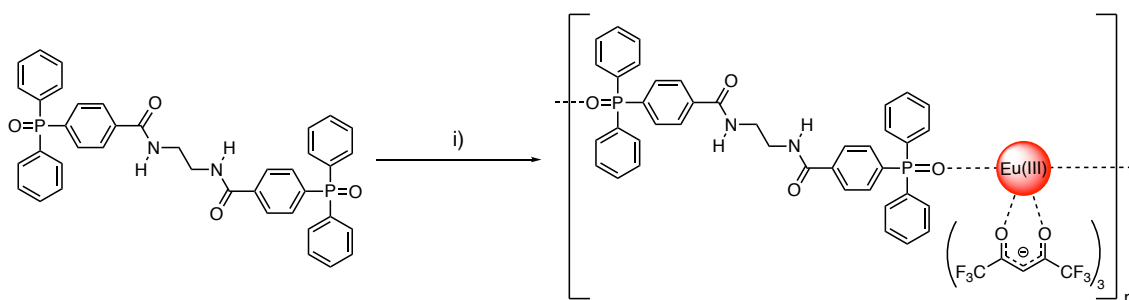


Figure 2.5 Synthetic scheme of $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$: i) $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$, CHCl_3 .

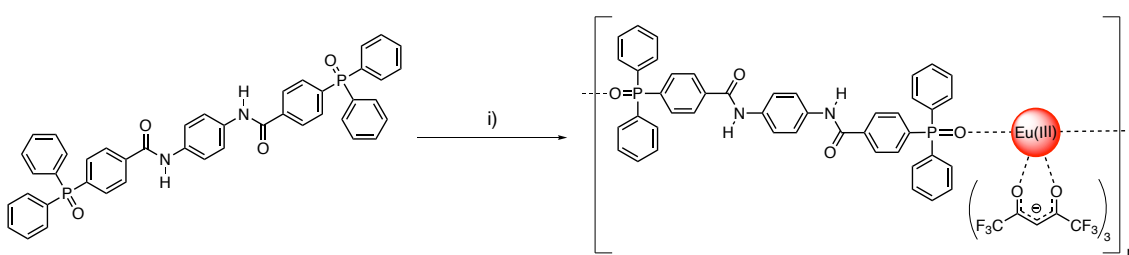


Figure 2.6 Synthetic scheme of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$: i) $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$, CH_2Cl_2 , MeOH .

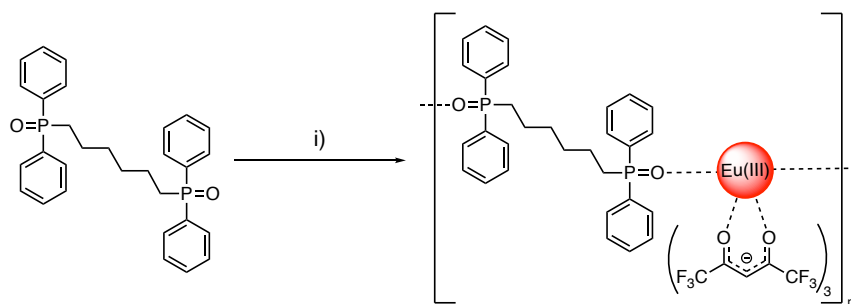


Figure 2.7 Synthetic scheme of $[\text{Eu}(\text{hfa})_3(\text{dph})]_n$: i) $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$, CHCl_3 .

2.3 Results and discussion

2.3.1 Structural characterizations

Eu(III) coordination polymers were synthesized by the complexation of the corresponding phosphine oxide ligand with precursor complex, $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$, in chloroform at room temperature. The crystal structure of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ is shown in **Figure 2.8a**. The Eu(III) ions of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ were also coordinated to eight oxygen atoms from three **hfa** ligands and two **p-dpba** ligands. The geometrical symmetry around the Eu(III) ions was determined to be an 8-coordinated square-antiprismatic structure (point group = D_{4d}). The intermolecular hydrogen bonding network of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ was observed (**Figure 2.8b**). As shown in **Figure 2.8c**, the two binding pattern of the hydrogen bonding network were confirmed. The first pattern is between the amide bonds, and the second pattern is through the methanol molecule. The two phosphine oxide groups in the **p-dpba** ligand were attached to different Eu(III) ions to form stacking structure (**Figure 2.8d**). Their thermal properties were evaluated using TG and DSC measurements. The decomposition temperatures of $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$, $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$, and $[\text{Eu}(\text{hfa})_3(\text{dph})]_n$ were estimated to be approximately 250°C (**Figure 2.9**). In the DSC measurements, baseline shifts corresponding to the phase-transition of $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ and $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ were observed, although $[\text{Eu}(\text{hfa})_3(\text{dph})]_n$ showed no phase transition behavior (**Figure 2.10**). PXRD patterns of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ at various temperatures are shown in **Figure 2.11**. The characteristic peak change in the PXRD patterns of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ was observed at the range from 25°C to 200°C, which were related to the elimination of methanol molecule or phase-transition behavior of Eu(III) coordination polymer.

To analyze the phase transition behavior, heat treatment was performed at 200°C for 15 min. The surface images of $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ without and with heat treatment were

observed using scanning electron microscopy. $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ without heat treatment provided harsh surface, while smooth surface was observed after heat treatment (**Figure 2.12**). On the other hand, needle crystal was observed using the surface image of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ with heat treatment (**Figure 2.13**). From these results, the transformation of hydrogen bonding network may be driven by the phase transition behavior. Compared to $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ and $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$, the structural flexibility of linker ligand induces to the glass-forming ability.

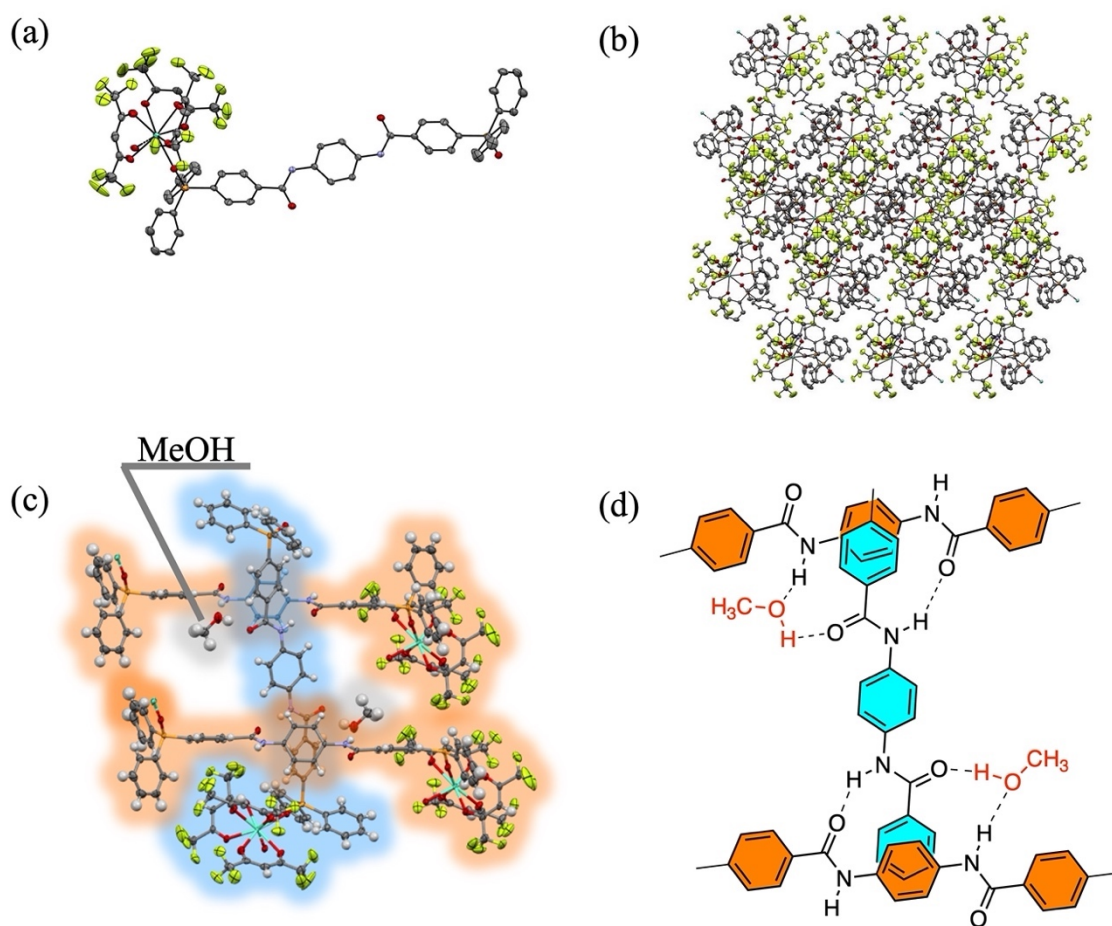


Figure 2.8 (a) ORTEP drawings (ellipsoids set at 50 % probability, hydrogen atoms were omitted for clarity) of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$. (b) Views of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ along c axis. (c) (d) Illustration of intramolecular hydrogen bonding network.

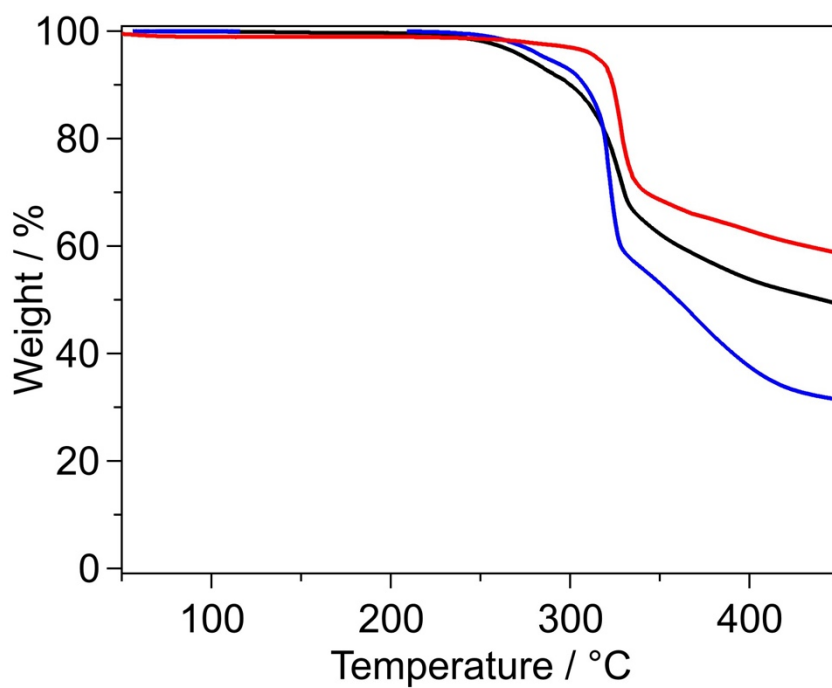


Figure 2.9 TG thermograms of $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ (black), $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ (red), and $[\text{Eu}(\text{hfa})_3(\text{dph})]_n$ (blue). (Heat rate : 5°C min^{-1} , N_2 flow)

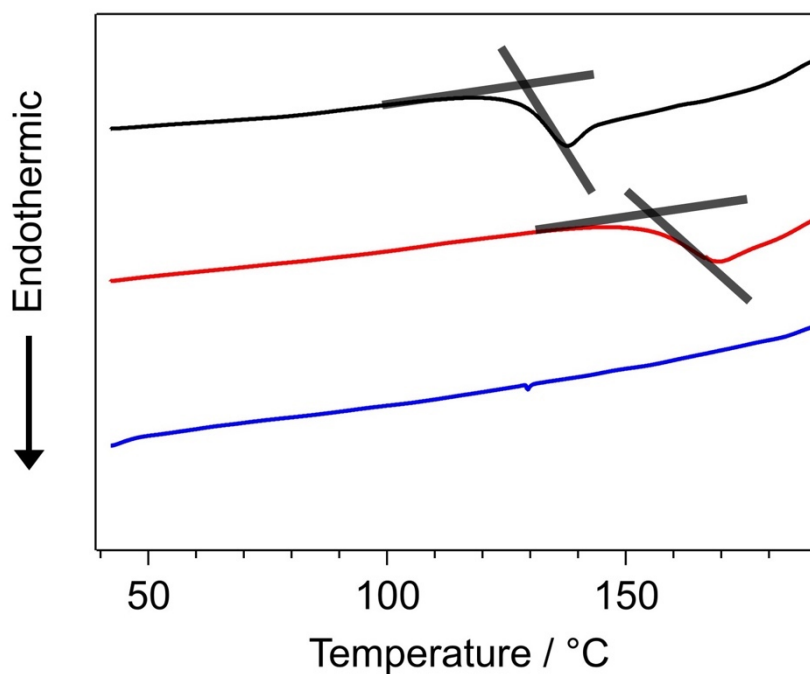


Figure 2.10 DSC thermograms of $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ (black), $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ (red), and $[\text{Eu}(\text{hfa})_3(\text{dph})]_n$ (blue). (Heat rate : 5°C min^{-1} , N_2 flow)

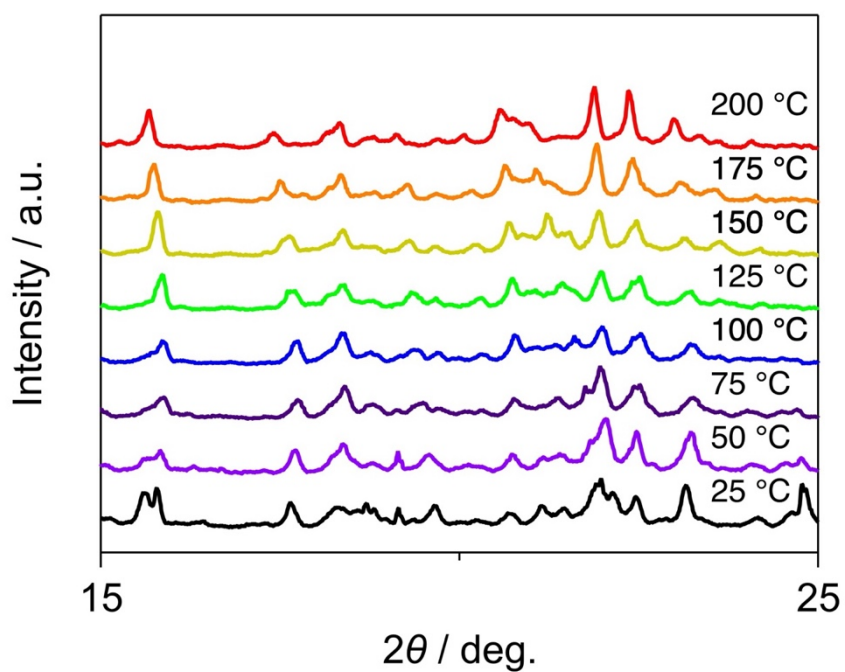


Figure 2.11 PXRD patterns of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ in the temperature range of 25-200 °C.

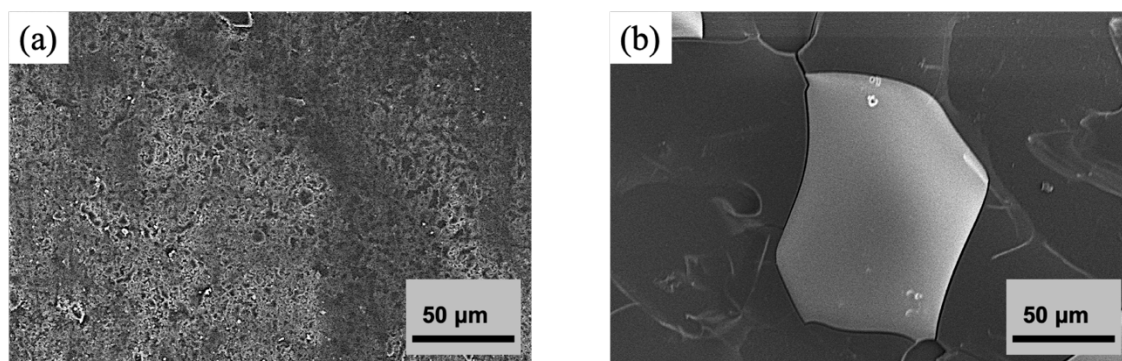


Figure 2.12 SEM images of $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ (a) without heat treatment and (b) with heat treatment.

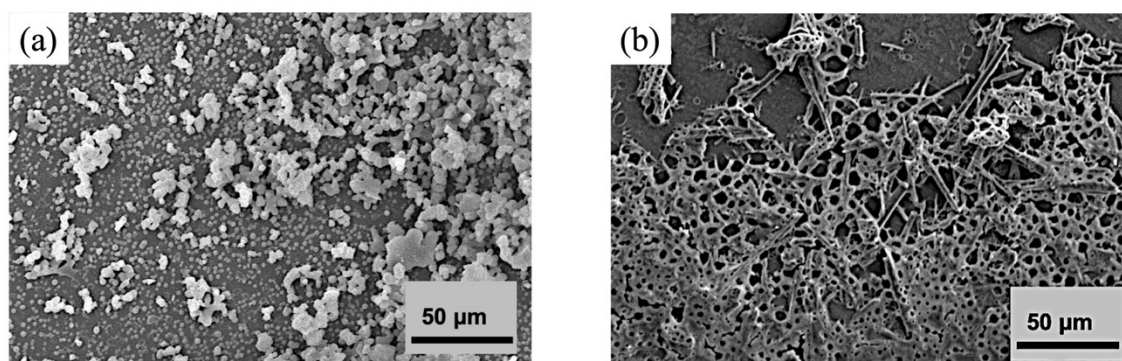


Figure 2.13 SEM images of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ (a) without heat treatment and (b) with heat treatment.

2.3.2 Luminescence properties

The emission spectra of $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ without and with heat treatment are shown in **Figure 2.14**. The sharp emission bands at around 578, 592, 613, 650, and 698 nm were observed and assigned to the 4f-4f transitions of the Eu(III) ($^5\text{D}_0 \rightarrow ^7\text{F}_J$: $J = 0, 1, 2, 3$, and 4).^[17] The spectra were normalized with respect to the magnetic dipole transition intensities (MD) at around 592 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), which are insensitive to the surrounding environment of the Eu(III). The emission bands at around 613 nm are strongly dependent on the coordination geometry. The spectral shape of emission band at around 613 nm of $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ with heat treatment is the same as that without heat treatment. These behaviors were also observed for $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$. The emission lifetimes were determined from the slope of the logarithmic decay profile. The overall emission quantum yields ($\Phi_{\pi\pi^*}$) were also measured. Based on the emission lifetimes and spectra, the 4f-4f emission quantum yield (Φ_{ff}), radiative rate constant (k_r), and non-radiative rate constant (k_{nr}) were estimated using equations (1)-(6) (**Table 2.1**).

The Φ_{ff} values of $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ and $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ without and with heat treatment were estimated to be 67% and 68%, respectively. The Φ_{ff} value of $[\text{Eu}(\text{hfa})_3(\text{dph})]_n$ were the same as those of amide-bridged $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ and $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$. These values are similar to those of previously reported bright luminescent Eu(III) coordination polymer, $[\text{Eu}(\text{hfa})_3(\text{bdpc})]_n$ (bdpc: 6,12-bis(diphenylphosphoryl)chrysene).^[4] Additionally, the k_r and k_{nr} of $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ with heat treatment were agreed well with those of $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ without heat treatment. These results indicated that the phase transition behavior was not caused by the change of the coordination geometry of $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$. These behaviors were also observed for $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$. The LD spectrum for $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ exhibited a broad band at 320 nm, which was attributed to $\pi\text{-}\pi^*$ transitions of hfa ligands, and the

signal strengths were very weak (**Figure 2.15**). This result exhibited that the **[Eu(hfa)₃(dpba)]_n** amorphous film showed no-effective orientation.

Table 2.1 Photophysical properties of **[Eu(hfa)₃(dpba)]_n** and **[Eu(hfa)₃(*p*-dpba)]_n** without and with heat treatment, **[Eu(hfa)₃(dph)]_n**, and **[Eu(hfa)₃(bdpc)]_n**.

Compound	k_r / s^{-1}	k_{nr} / s^{-1}	$\tau_{obs} / ms^{[a]}$	$\Phi_{ff} / \%$	$\Phi_{\pi\pi^*} / \%$
[Eu(hfa)₃(dpba)]_n without heat treatment	9.2×10^2	4.5×10^2	0.73	67	47
[Eu(hfa)₃(dpba)]_n with heat treatment	9.6×10^2	4.5×10^2	0.71	68	47
[Eu(hfa)₃(<i>p</i>-dpba)]_n without heat treatment	8.7×10^2	5.4×10^2	0.71	62	4.4
[Eu(hfa)₃(<i>p</i>-dpba)]_n with heat treatment	8.7×10^2	5.4×10^2	0.71	62	4.4
[Eu(hfa)₃(dph)]_n	9.2×10^2	3.7×10^2	0.77	71	50
[Eu(hfa)₃(bdpc)]_n^[4]	9.0×10^2	4.0×10^2	0.77	69	36

[a] $\lambda_{ex} = 350$ nm, $\lambda_{em} = 613$ nm.

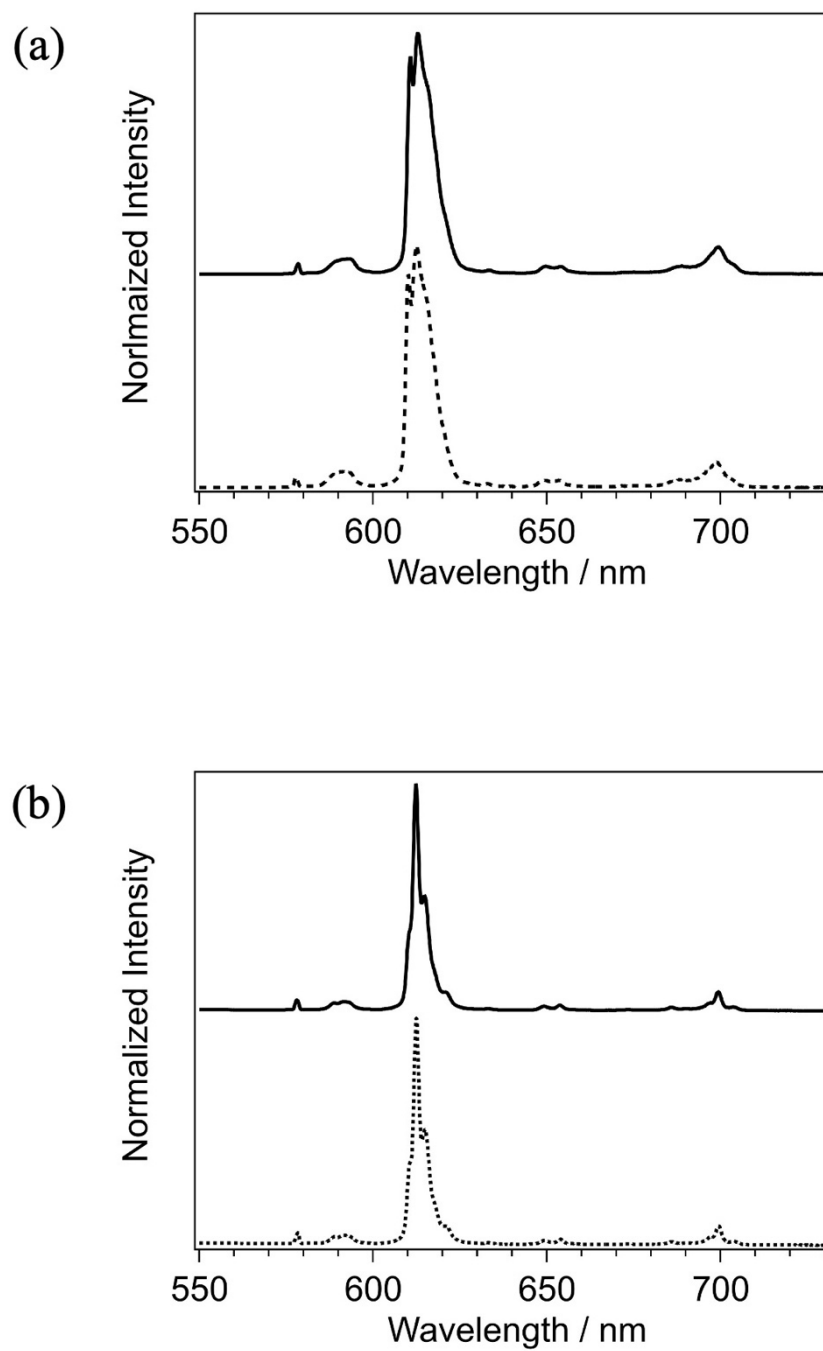


Figure 2.14 Emission spectra ($\lambda_{\text{ex}} = 370$ nm) of (a) $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ and (b) $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ without heat treatment (solid line) and with heat treatment (dash line).

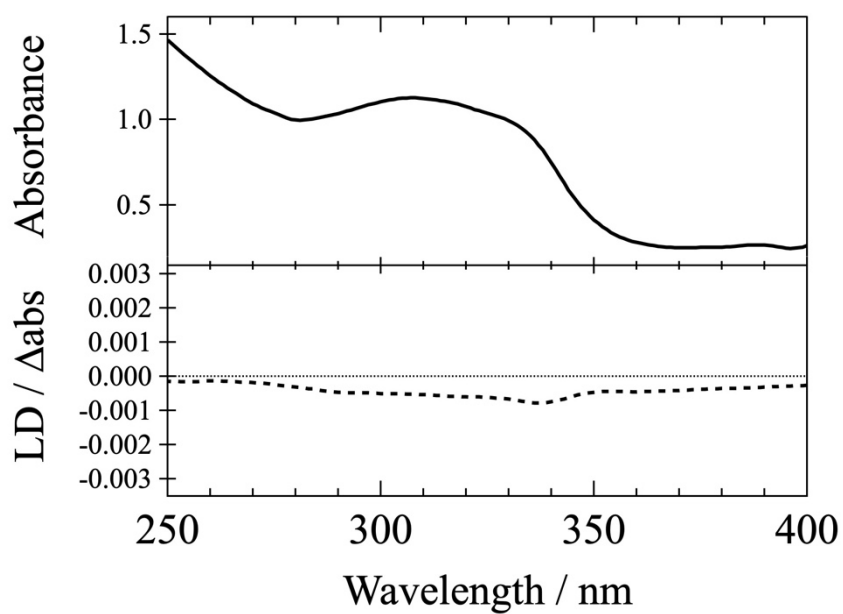


Figure 2.15 Absorption (Solid line) and LD spectra (dash line) of $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ with heat treatment in solid state.

2.4 Conclusion

Novel Eu(III) coordination polymers were synthesized. The structural analysis confirmed that the formation of the intramolecular hydrogen bonding into polymer chains. DSC measurements exhibited that $[\text{Eu}(\text{hfa})_3(\text{dpba})]_n$ and $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ showed phase transition behavior. The smooth surface of the Eu(III) coordination polymer after heat treatment was observed. The photophysical properties were not changed after heat treatment. The hydrogen bonding network and flexible structure of amide unit linker ligand provided glass-forming ability. This transparent luminescent lanthanide coordination polymer provides novel insights in the fields of coordination chemistry, material science, and solid-state photophysical chemistry.

2.5 References

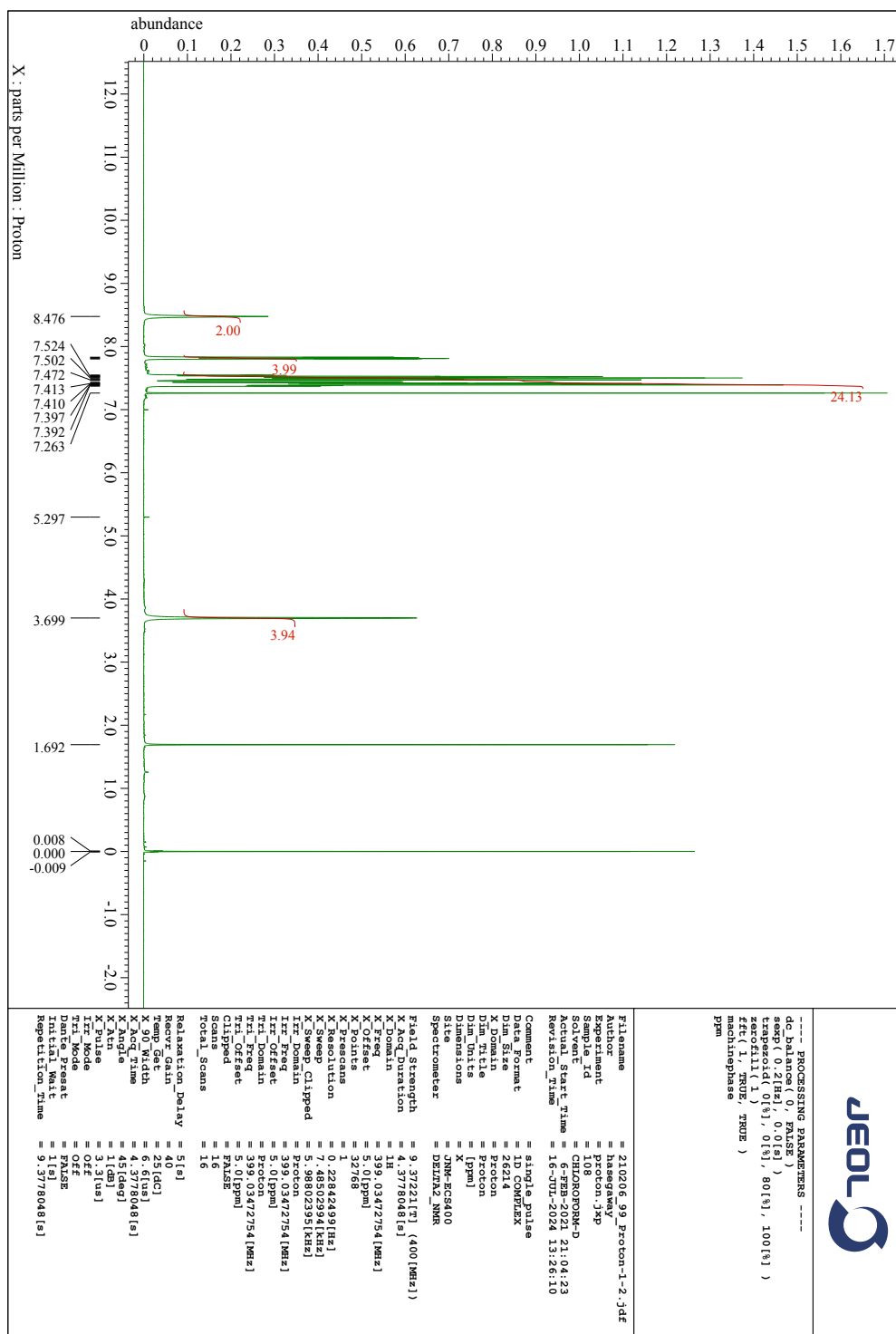
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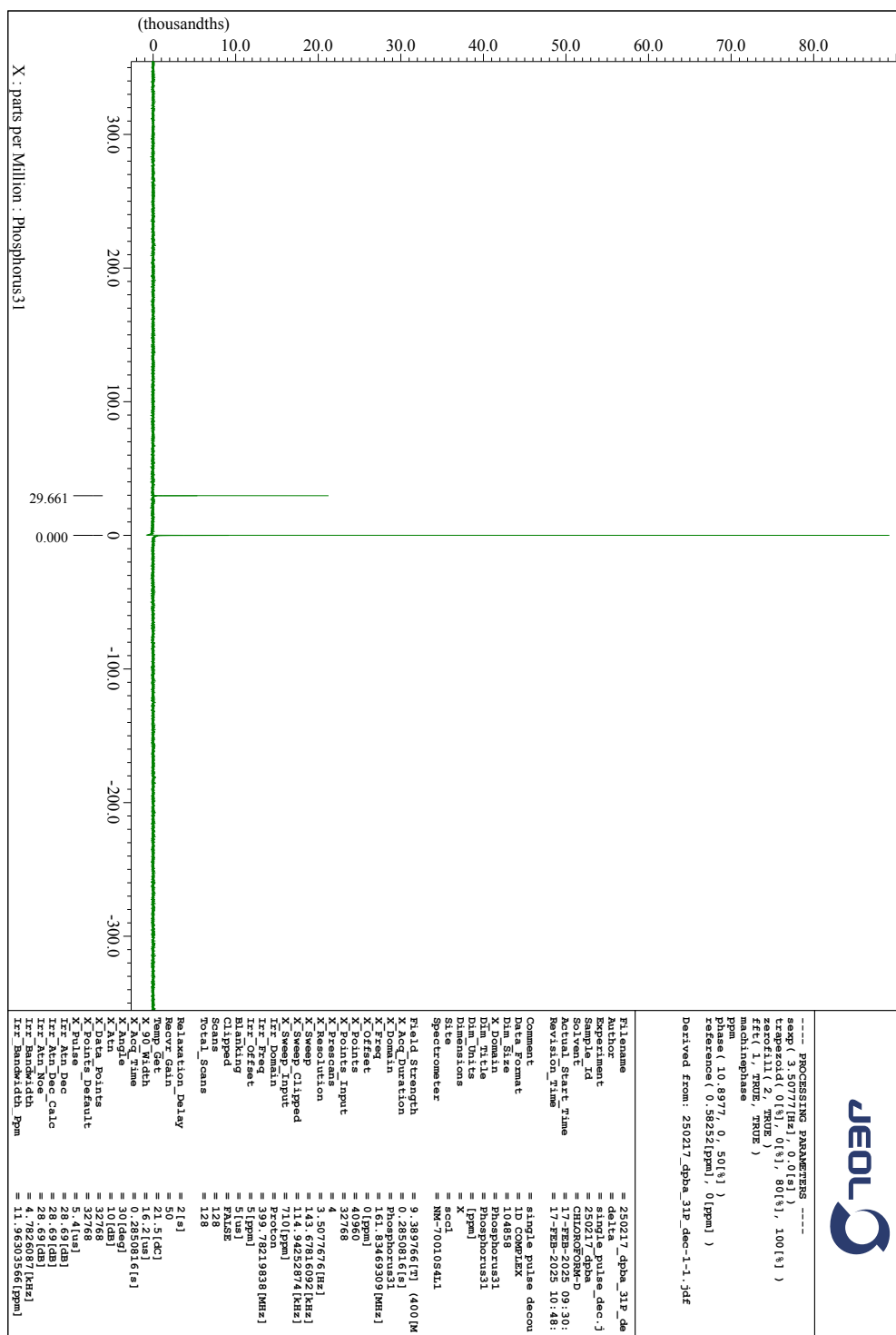
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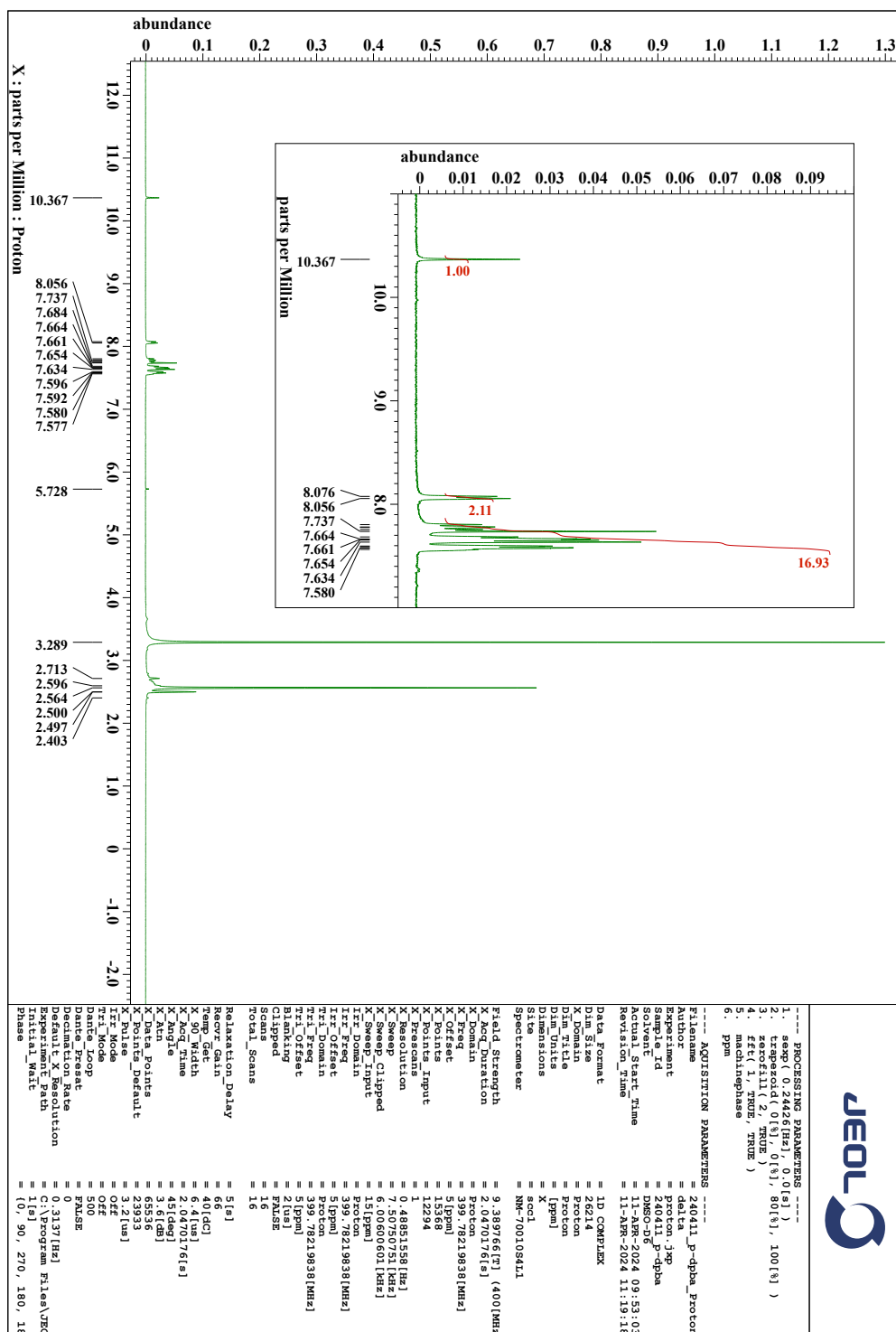
2.6 Appendix

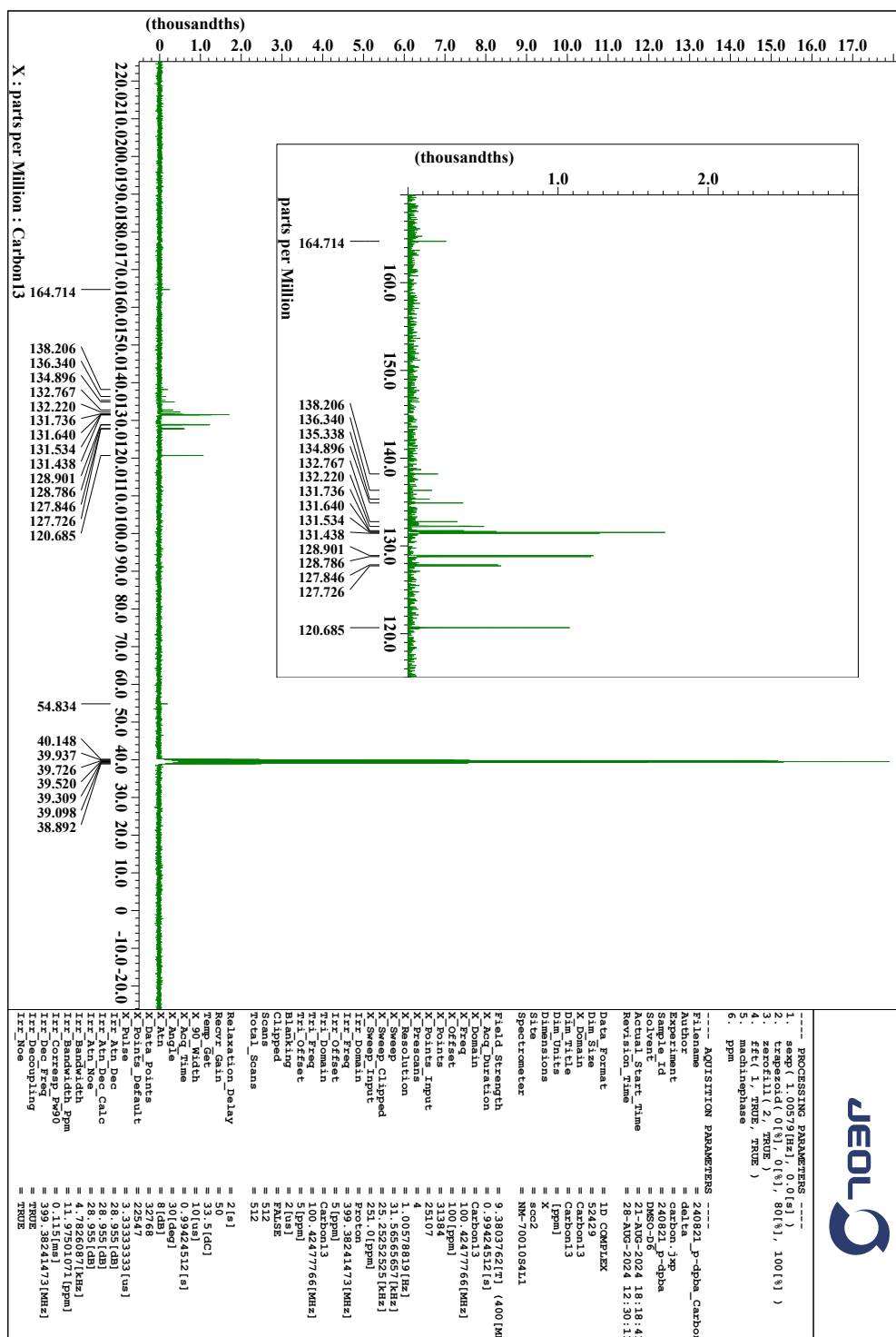
Table 2.2 Crystallographic data of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$.

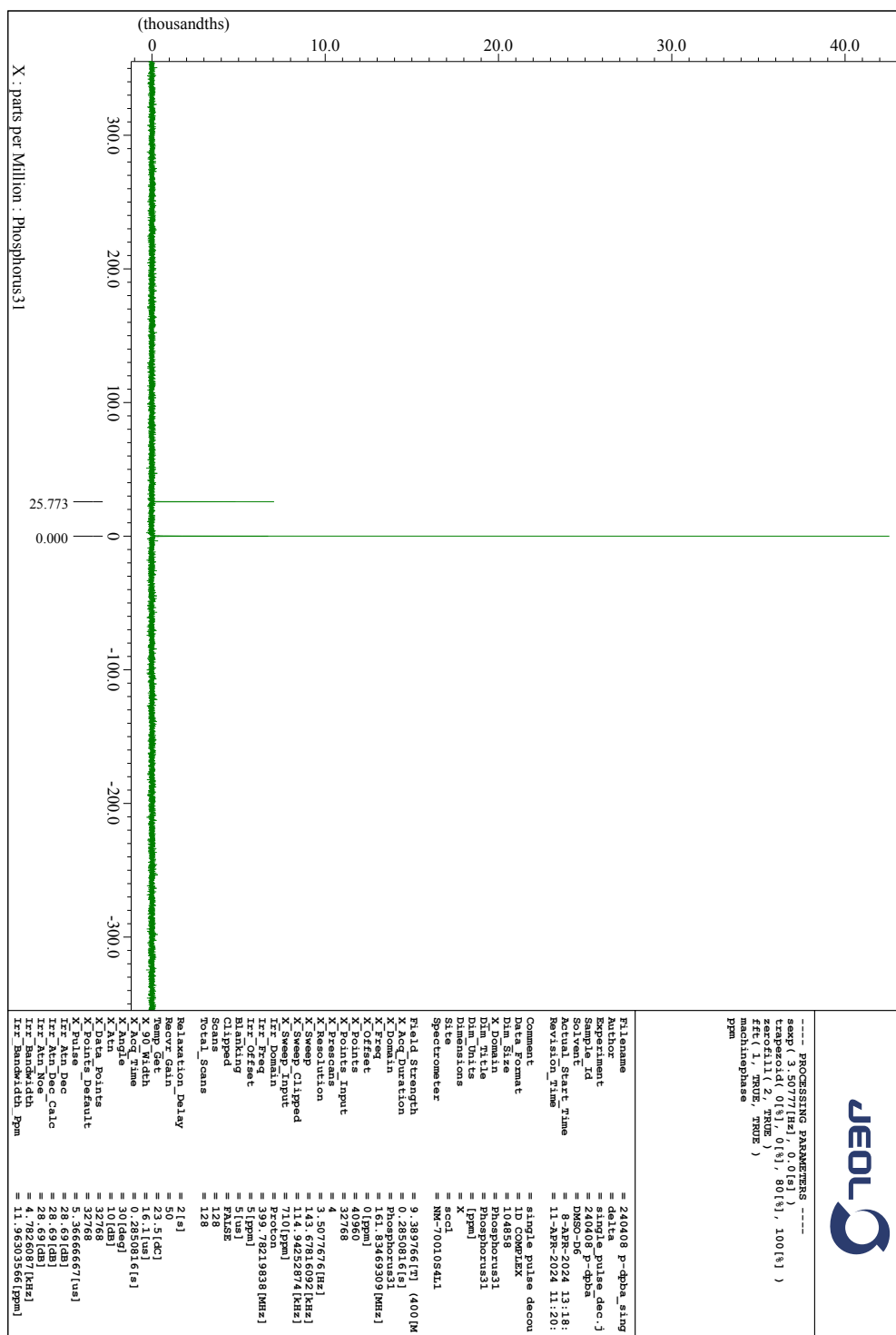
Compound	$[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$
Crystal system	triclinic
Space group	P-1
$a / \text{\AA}$	11.4194(2)
$b / \text{\AA}$	13.0025(2)
$c / \text{\AA}$	23.4183(4)
$\alpha / \text{deg.}$	79.3790(10)
$\beta / \text{deg.}$	87.3620(10)
$\gamma / \text{deg.}$	66.135(2)
Volume / $\text{\AA}^3$	3123.82(10)
Z	2
$d_{\text{calc}} / \text{g cm}^{-3}$	1.618
Temperature / K	123
Radiation	Mo $K\alpha$ ($\lambda = 0.71073$)
R_1	0.0669
wR_2	0.1238

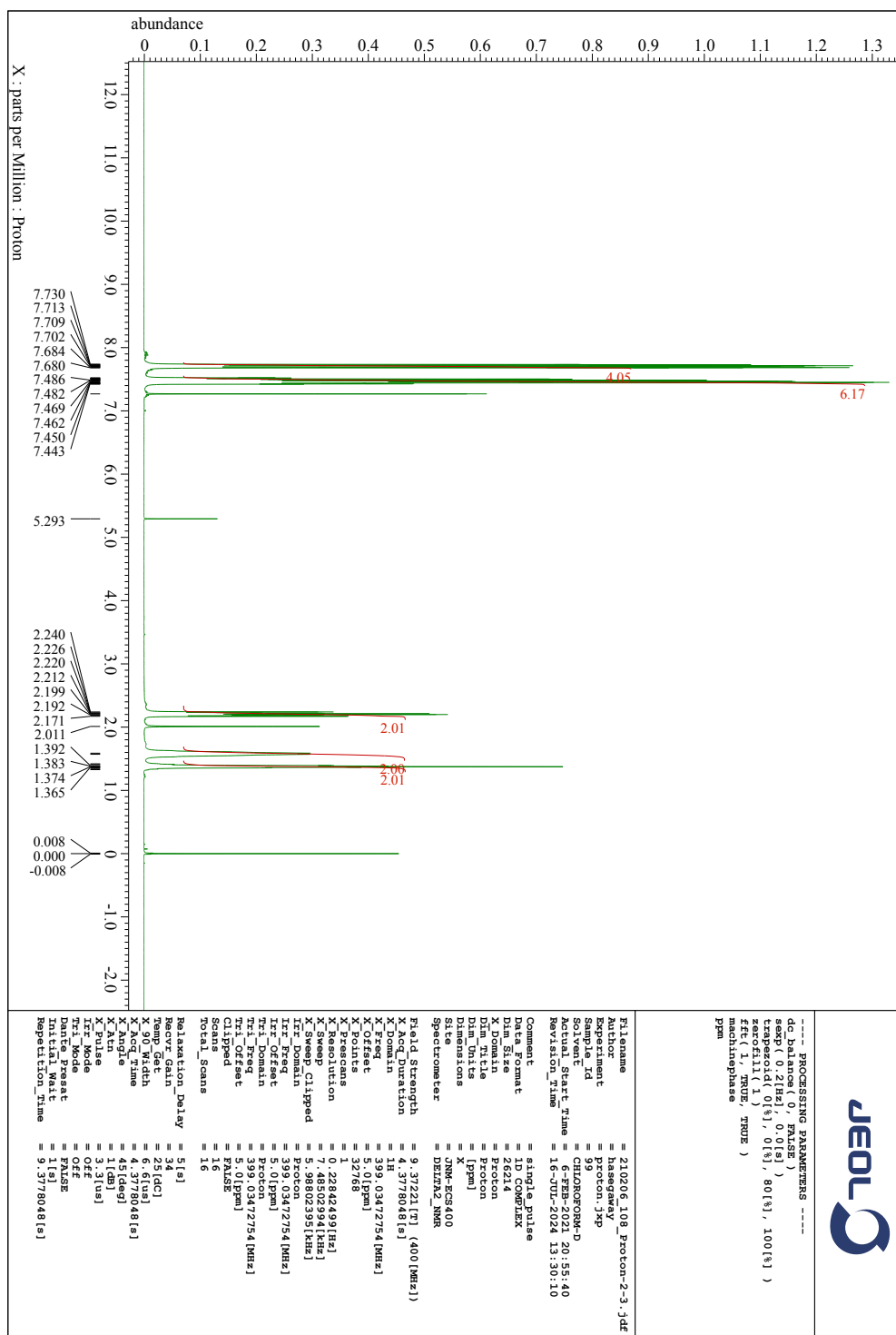
Figure 2.16 ^1H NMR spectra of dpba.

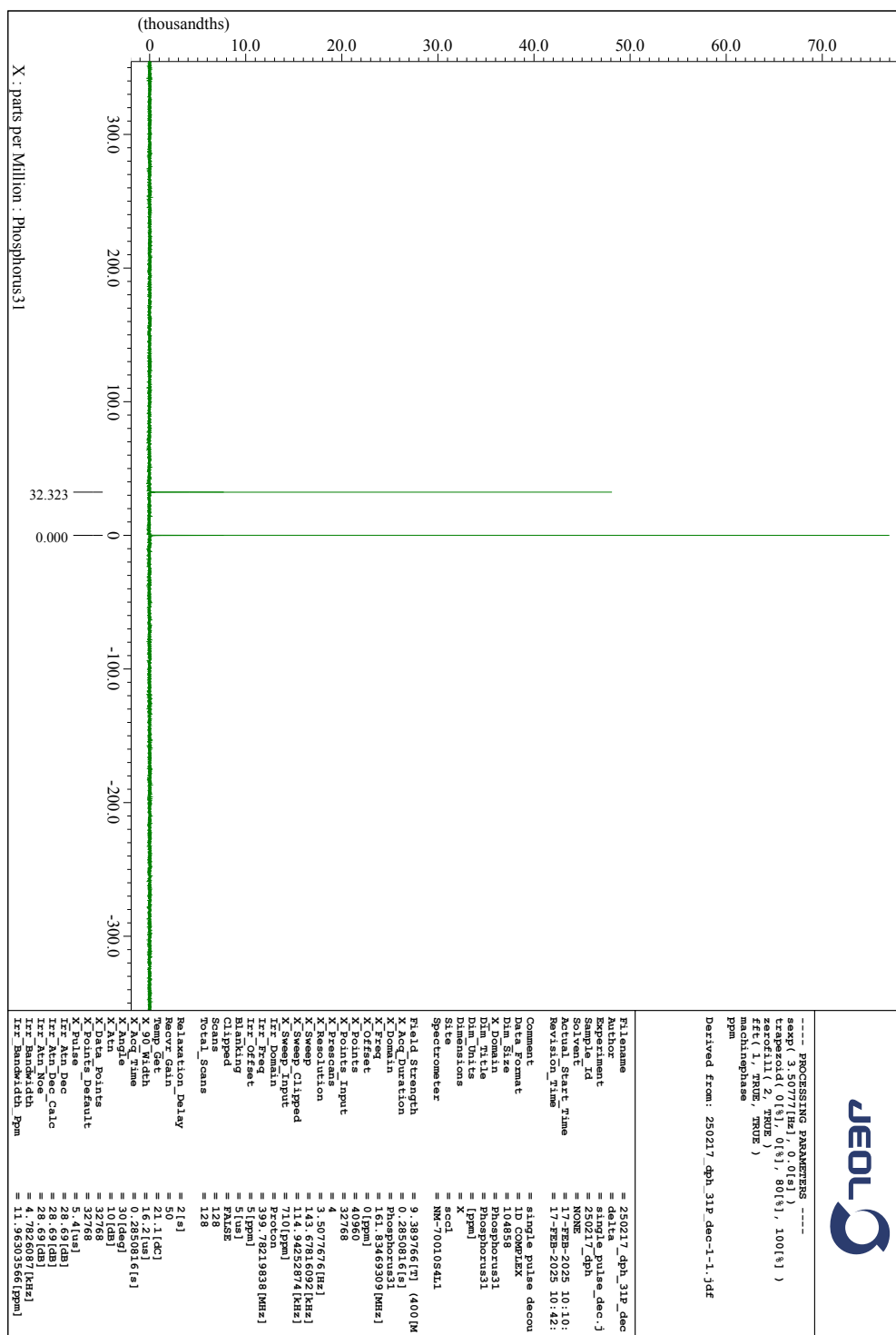
Figure 2.17 ^{31}P NMR spectra of dpba.

Figure 2.18 ^1H NMR spectra of *p*-dpba.

Figure 2.19 ^{13}C NMR spectra of *p*-dpba.

Figure 2.20 ^{31}P NMR spectra of *p*-dpba.

Figure 2.21 ^1H NMR spectra of dph.

Figure 2.22 ^{31}P NMR spectra of dph.

Chapter 3

***A Systematic Structural Control of the
Phenylenediamide Moiety in the Linker
Ligands of Eu(III) Coordination Polymers***

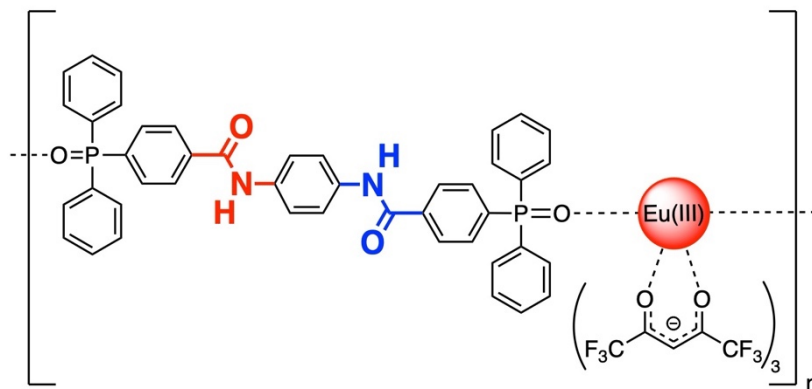
3.1 Introduction

In **Chapter 2**, the author presented a discussion on the morphology control of luminescent Eu(III) coordination polymers. The formation of hydrogen bonding networks and the incorporation of flexible structures were found to exert a significant effect on the glass formability of lanthanide coordination polymers. The structural and physicochemical properties of lanthanide coordination polymers depend on the molecular structure of the linker ligands. ^[1-3] Hasegawa reported the effects of ortho-, meta- and para- position of aromatic substituents on the structure and emission properties of Eu(III) coordination polymers. ^[4] Here, the author focused on the direction of amide bonds as a systematic change in molecular structure. Zhu demonstrated that the introduction of strong intermolecular hydrogen bonds by amide unit in isomeric polyimideamides affected the tensile strengths and tensile moduli. ^[5] Kumar reported the discotic tripeptides with various amide bond orientations. ^[6] The orientation of amide bonds effects on aggregation and photophysical properties. ^[7,8]

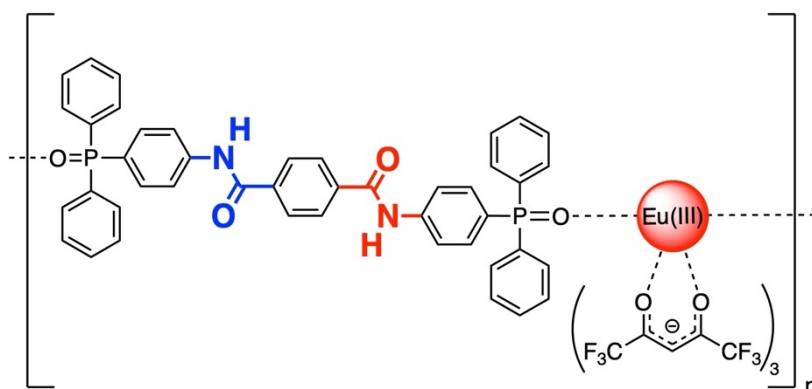
In this chapter, the molecular conformational arrangement of amide units with the same molecular formula in luminescent Eu(III) coordination polymers were prepared. Three Eu(III) coordination polymers with systematic-changed amide bond directions was prepared. $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ was chosen as one of the systematic molecular structures (**Figure 2.1b** or **Figure 3.1a**). Two other ligands with systematically altered amide bonds, **dppt** and **dppb**, were synthesized. (**Figure 3.1 b** and **c**, **dppt**: N^1, N^4 -bis(4-(diphenylphosphoryl)phenyl)terephthalamide, **dppb**: 4-(diphenylphosphoryl)- N -(4-((4-(diphenylphosphoryl)phenyl)carbamoyl)phenyl)benzamide)). The effect of molecular conformation on structural and photophysical properties was evaluated. Thermal properties were characterized by thermogravimetry (TG) and differential scanning

calorimetry (DSC). Luminescence properties were analyzed by emission quantum yield and lifetime, related with radiative and non-radiative rate constants.

(a) $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ (Chapter 2)



(b) $[\text{Eu}(\text{hfa})_3(\text{dppt})]_n$ (New)



(c) $[\text{Eu}(\text{hfa})_3(\text{dppb})]_n$ (New)

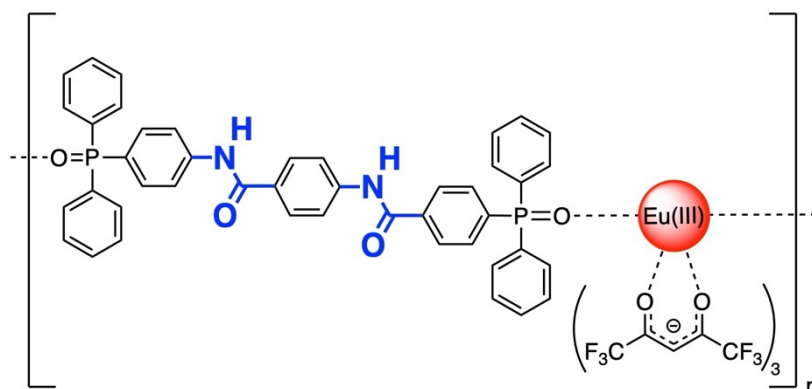


Figure 3.1 Molecular structures of (a) $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$, (b) $[\text{Eu}(\text{hfa})_3(\text{dppt})]_n$, and (c) $[\text{Eu}(\text{hfa})_3(\text{dppb})]_n$.

3.2 Methods

3.2.1 Materials and apparatus

Diphenyl(*p*-tolyl)phosphine and europium(III) acetate *n*-hydrate were purchased from FUJIFILM Wako Pure Chemical Corporation. The other chemicals were of reagent grade and used without further purification. ESI-MS spectra were measured using a JEOL JMS-T100LP. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{31}P NMR (162 MHz) spectra were recorded on a JEOL ECS400. ^1H chemical shifts were determined with tetramethylsilane as an internal standard ($\delta = 0$ ppm). ^{31}P chemical shifts were determined with 85% H_3PO_4 as an external standard ($\delta = 0$ ppm). 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 ($\text{CuK}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$).

The emission and excitation spectra were recorded on a HORIBA Fluorolog-3 spectrofluorometer and corrected for the response of the detector system. 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, $\lambda = 1064 \text{ nm}$) and a photomultiplier (Hamamatsu Photonics, R5108, response time $\leq 1.1 \text{ ns}$). The Nd:YAG laser response was monitored with a digital oscilloscope (Sony Tektronix, TDS3052, 500 MHz) synchronized to the single-pulse excitation. The emission lifetimes were determined from the slope of logarithmic plots of the decay profiles. The emission quantum yields excited at 370 nm (Φ_{tot}) were estimated using a JASCO FP-6300 spectrometer attached with a JASCO ILF-533 integrating sphere unit ($\varphi = 100 \text{ mm}$).

3.2.2 Syntheses

Preparation of 4-(diphenylphosphinyl)benzenamine

Potassium acetate (176.7 mg, 1.8 mmol), 4-iodoaniline (328.5 mg, 1.5 mmol), and palladium(II) acetate (0.34 mg, 1.5 μ mol) were dissolved in DMA (10 ml) at room temperature under Ar atmosphere. After diphenyl phosphine (0.29 ml, 1.5 mmol) was added to the solution, the solution was stirred at 130°C for 3 h. The reaction mixture was cooled to room temperature and the solvent was evaporated in vacuo. The residue was dissolved in CH₂Cl₂ and washed with aqueous 5% NaHCO₃ and distilled water. The organic layer was concentrated in vacuo. The residue was dissolved in CH₂Cl₂ (10 ml) and added aqueous 30% H₂O₂ (1 ml) at 0°C. After stirring for 1 h, the reaction mixture was washed with distilled water. The organic layer was dried over Na₂SO₄ and evaporated to give 4-(diphenylphosphinyl)benzenamine (154.3 mg, 0.526 mmol, 35.0%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.69–7.64 (4H, m), 7.54–7.50 (2H, m), 7.46–7.36 (6H, m), 6.69–6.66 (2H, m), 4.09 (2H, s) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 149.9, 149.9, 133.8, 133.7, 132.8, 132.1, 132.0, 131.6, 131.6, 128.4, 128.3, 120.3, 119.2, 114.3, 114.2 ppm. ³¹P NMR (162 MHz, CDCl₃) δ 29.7 ppm. MS(ESI) found: m/z 316.09. Calcd. for C₁₈H₁₆NNaOP: [M+Na]⁺, 316.09.

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), and successively added terephthaloyl chloride (54.07 mg, 0.5 mmol) and triethylamine (1 mL) 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 **dppt** (81.7 mg, 0.114 mmol, 22.8%). ¹H NMR (400 MHz, DMSO-d₆) δ

10.66 (s, 2H), 8.14-8.09 (m, 4H), 7.99 (m, 4H), 7.66-7.54 (m, 24H). ^{13}C 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. ^{31}P NMR (162 MHz, DMSO- d_6) δ 26.0 ppm. MS(ESI) found: 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.

Preparation of 4-(diphenylphosphoryl)benzoic acid

4-(diphenylphosphoryl)benzoic acid was synthesized according to the previously reported in previous chapter.

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), and successively added methyl 4-aminobenzoate phenylenediamine (151.2 mg, 1.0 mmol) and triethylamine (1.0 mL) 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, 55%). ^1H NMR (400 MHz, CDCl_3) δ 10.27 (1H, s), 8.04-7.97 (6H, m), 7.59-7.41 (12H, m), 3.91 (3H, s) ppm. ^{13}C NMR (101 MHz, CDCl_3) 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. ^{31}P NMR (162 MHz, CDCl_3) δ 29.5 ppm. MS(ESI) found: m/z 478.12. Calcd. for $\text{C}_{27}\text{H}_{22}\text{NNaO}_4\text{P}$: $[\text{M}+\text{Na}]^+$, 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, and successively added hydrogen chloride (1 mL) and water (9 mL). 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%). ^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. ^{13}C 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. ^{31}P NMR (162 MHz, DMSO- d_6) δ 26.9 ppm. MS(ESI) found: m/z 464.10. Calcd. for $\text{C}_{26}\text{H}_{20}\text{NNaO}_4\text{P}$: $[\text{M}+\text{Na}]^+$, 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 successively added 4-(diphenylphosphinyl)benzenamine (293.3 mg, 1.0 mmol) and triethylamine (1 mL) 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 **dppb** (249.1 mg, 0.547 mmol, 55%). ^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. ^{13}C NMR (100 MHz, DMSO- d_6) δ 165.3, 142.7, 142.2, 133.5, 132.7, 132.5, 132.4, 132.3, 132.0, 131.7, 131.7, 131.6, 131.6, 131.5, 131.5, 131.4, 129.5, 129.0, 128.8, 128.8, 128.7, 128.7, 128.0, 127.9, 127.1, 120.0, 119.8, 119.5 ppm. ^{31}P NMR (162 MHz, DMSO- d_6) δ 26.1, 26.0 ppm. MS(ESI) found: 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.

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

$[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$ was synthesized according to the previously reported in previous chapter.

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

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

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

$[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$ (80.9 mg, 0.1 mmol) was added to a dichloromethane (5 mL) and MeOH (5 mL) mixture solution of **dppb** (71.6 mg, 0.1 mmol), and the mixture was stirred for 1 h. The recrystallization from dichloromethane and gave $[\text{Eu}(\text{hfa})_3(\text{dppb})]_n$ (29.3 mg, 19.7 μmol , 19.7%) as a white powder: MS(ESI) found: m/z 1283.11. Calcd. for

$\text{C}_{54}\text{H}_{36}\text{EuF}_{12}\text{N}_2\text{O}_8\text{P}_2$: $[\text{M-hfa}]^+$, 1283.10.; found: m/z 2773.23. Calcd. for $\text{C}_{113}\text{H}_{73}\text{Eu}_2\text{F}_{30}\text{N}_4\text{O}_{18}\text{P}_4$ $[\text{M}_2\text{-hfa}]^+$, 2773.18; found: m/z 4263.30. Calcd. for $\text{C}_{172}\text{H}_{110}\text{Eu}_3\text{F}_{48}\text{N}_6\text{O}_{28}\text{P}_6$ $[\text{M}_3\text{-hfa}]^+$, 4263.27. Elemental analysis: found (%): C 47.03, H 2.67, 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, N 1.88.

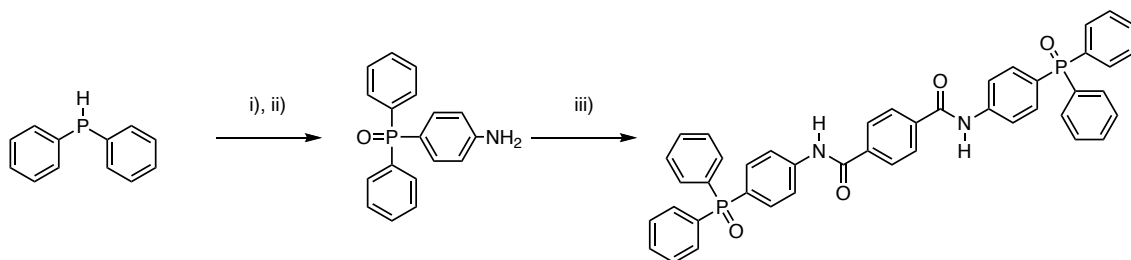


Figure 3.2 Synthetic scheme of **dppt**: i) 4-iodoaniline, KOAc, Pd(OAc)₂, DMA, 130°C; ii) 30% H₂O₂ aq., CH₂Cl₂, 0°C; iii) Terephthaloyl chloride, Et₃N, CH₂Cl₂, 0°C.

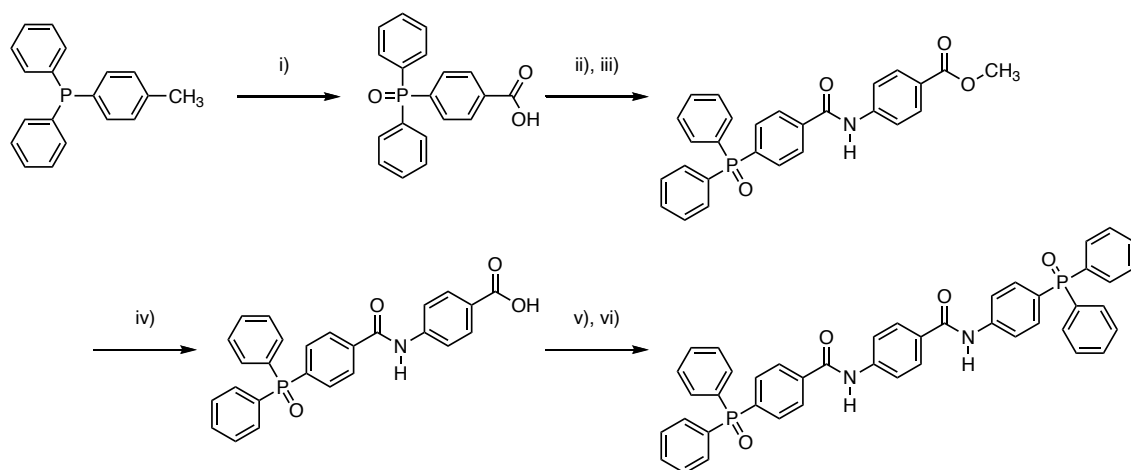


Figure 3.3 Synthetic scheme of **dppb**: i) KMnO₄, NaOH aq., 90°C; ii) SOCl₂; iii) Methyl 4-aminobenzoate, Et₃N, CH₂Cl₂, 0°C; iv) NaOH aq., EtOH, reflux; v) SOCl₂; vi) 4-(diphenylphosphinyl)benzenamine, Et₃N, CH₂Cl₂, 0°C.

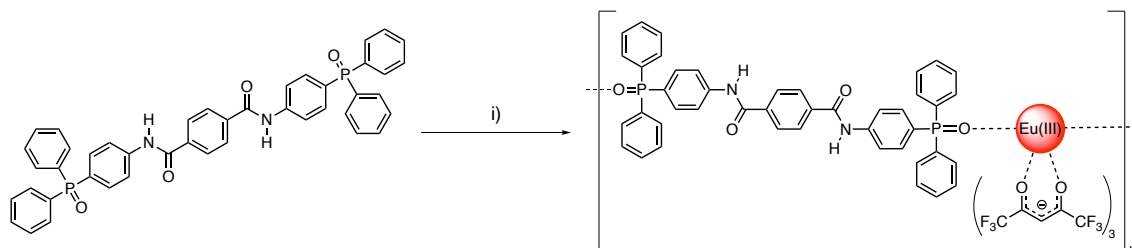


Figure 3.4 Synthetic scheme of $[\text{Eu}(\text{hfa})_3(\text{dppt})]_n$: i) CH_2Cl_2 , MeOH .

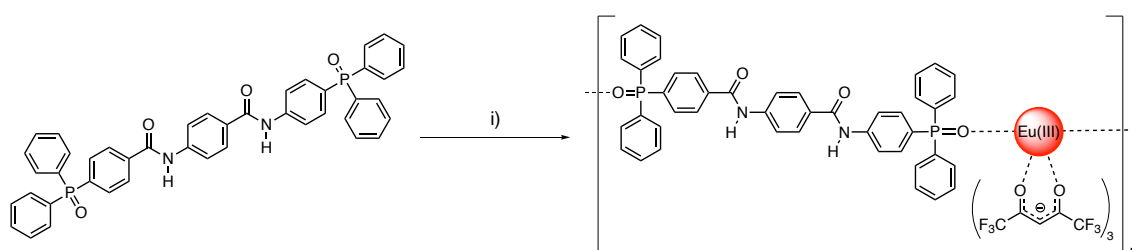


Figure 3.5 Synthetic scheme of $[\text{Eu}(\text{hfa})_3(\text{dppb})]_n$: i) CH_2Cl_2 , MeOH .

3.3 Results and discussion

3.3.1 Structural properties

The Eu(III) coordination polymers, $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$, $[\text{Eu}(\text{hfa})_3(\text{dppt})]_n$ and $[\text{Eu}(\text{hfa})_3(\text{dppb})]_n$ were synthesized by the complexation of the corresponding linker ligands with precursor complex, $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$, in a mixed solution of dichloromethane and methanol. TG measurements were conducted in a nitrogen atmosphere to evaluate the thermophysical properties of the Eu(III) coordination polymers. The decomposition temperatures of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$, $[\text{Eu}(\text{hfa})_3(\text{dppt})]_n$ and $[\text{Eu}(\text{hfa})_3(\text{dppb})]_n$, were estimated to be around 250 °C (**Figure 3.6**). The PXRD patterns of linker ligands and Eu(III) coordination polymers showed in **Figure 3.7** and **Figure 3.8**, respectively. The linker ligands and $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ showed sharp PXRD pattern, while $[\text{Eu}(\text{hfa})_3(\text{dppt})]_n$ and $[\text{Eu}(\text{hfa})_3(\text{dppb})]$ did not exhibit sharp diffraction patterns. The diffraction patterns of $[\text{Eu}(\text{hfa})_3(\text{dppt})]_n$ and $[\text{Eu}(\text{hfa})_3(\text{dppb})]_n$ were not matched those of **dppt** and **dppb** ligands (**Figure 3.9**). The Eu(III) coordination polymers exhibited a baseline shift associated with the phase transition (**Figure 3.10**). The phase transition temperatures of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$, $[\text{Eu}(\text{hfa})_3(\text{dppt})]_n$ and $[\text{Eu}(\text{hfa})_3(\text{dppb})]_n$ were calculated to be 153, 148 and 79 °C, respectively. However, the ligands did not exhibit characteristic phase transition behavior (**Figure 3.11**). From these results, the Eu(III) coordination polymers exhibited phase transition behavior. The transition behavior at low temperature of $[\text{Eu}(\text{hfa})_3(\text{dppb})]$ might be due to low crystallinity based on several arrangements of the ligand coordination in the polymer chain (**Figure 3.12**).

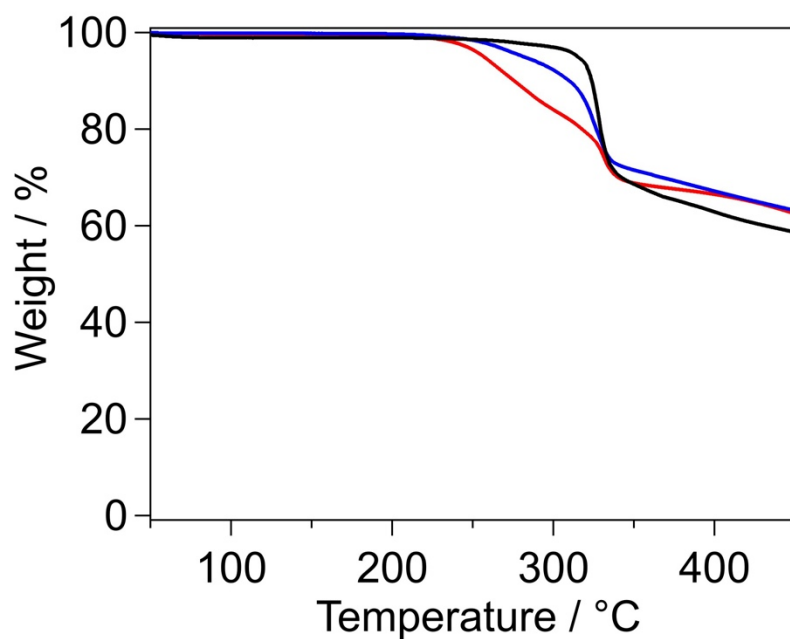


Figure 3.6 TG thermograms of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ (black), $[\text{Eu}(\text{hfa})_3(\text{dppt})]_n$ (red), and $[\text{Eu}(\text{hfa})_3(\text{dppb})]_n$ (blue).

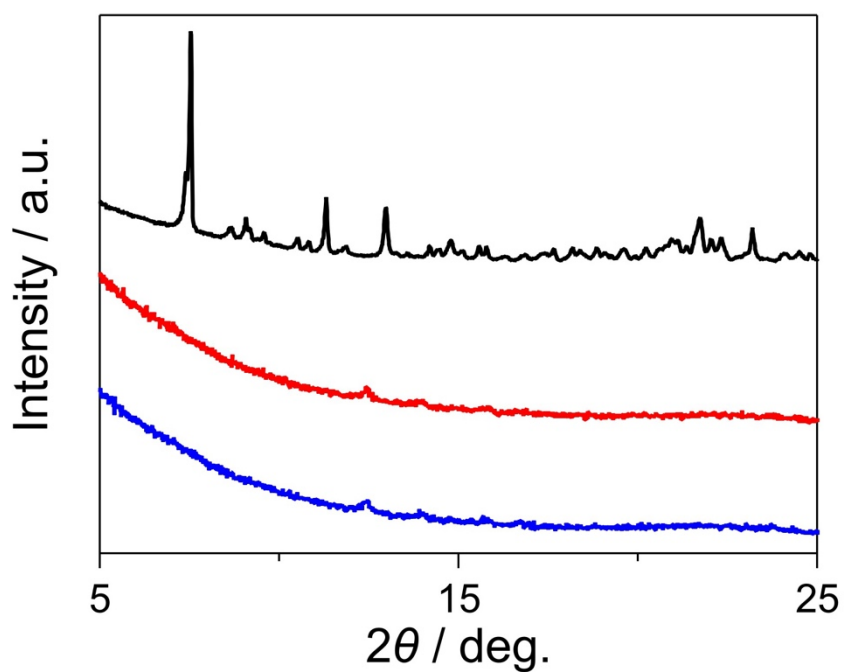


Figure 3.7 PXRD patterns of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ (black), $[\text{Eu}(\text{hfa})_3(\text{dppt})]_n$ (red), and $[\text{Eu}(\text{hfa})_3(\text{dppb})]_n$ (blue).

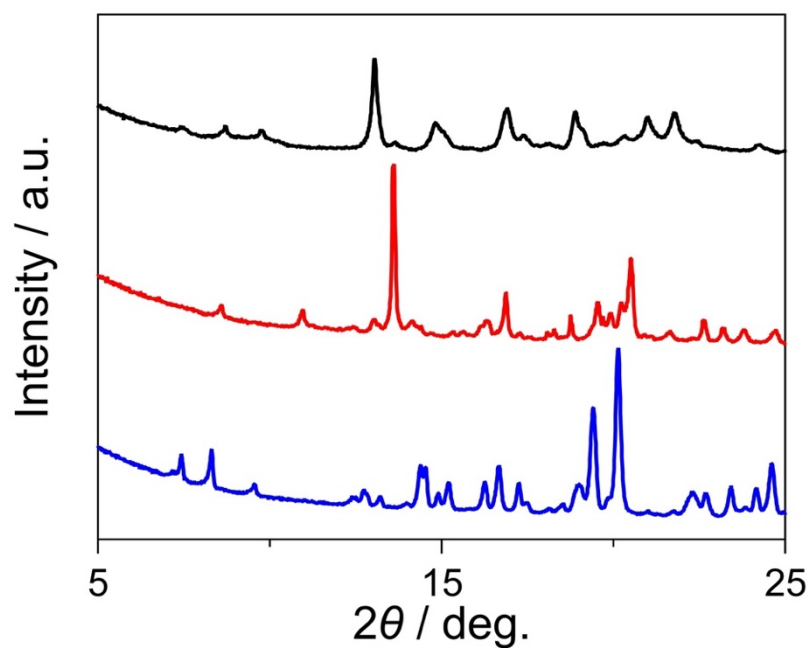


Figure 3.8 PXRD patterns of *p*-dpba (black), dppt (red), and dppb (blue)

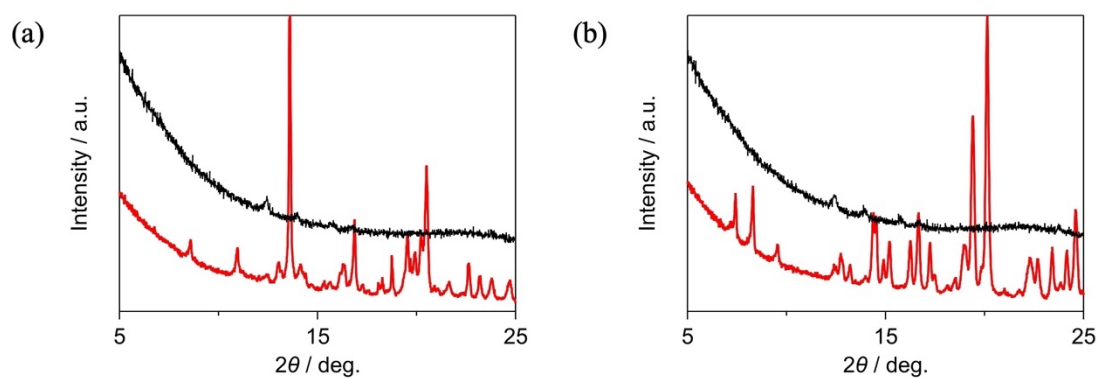


Figure 3.9 PXRD patterns of Eu-dppt (a, black), dppt (a, red), Eu-dppb (b, black) and dppb (b, red).

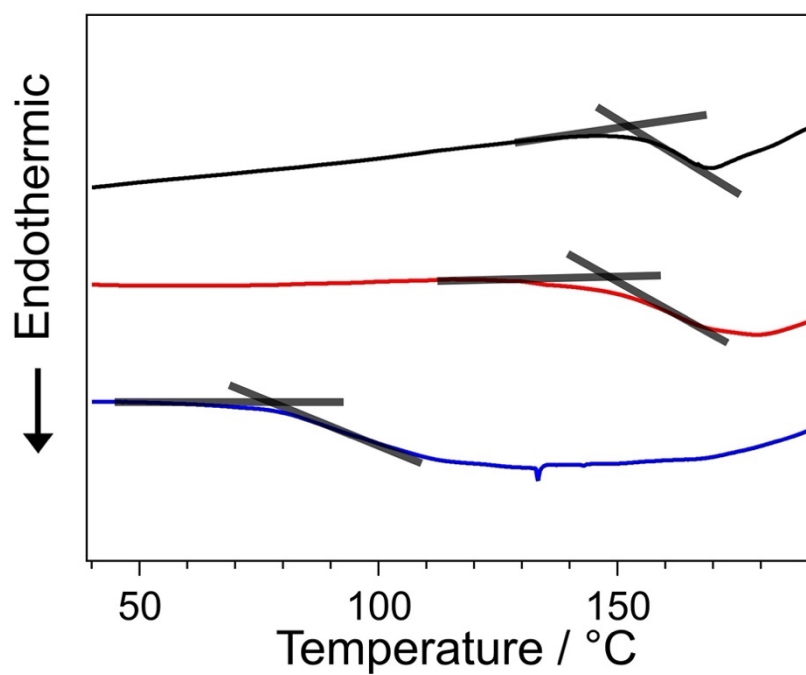


Figure 3.10 DSC thermograms of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ (black), $[\text{Eu}(\text{hfa})_3(\text{dppt})]_n$ (red), and $[\text{Eu}(\text{hfa})_3(\text{dppb})]_n$ (blue) (Heating rate : 5°C min^{-1} , N_2 flow).

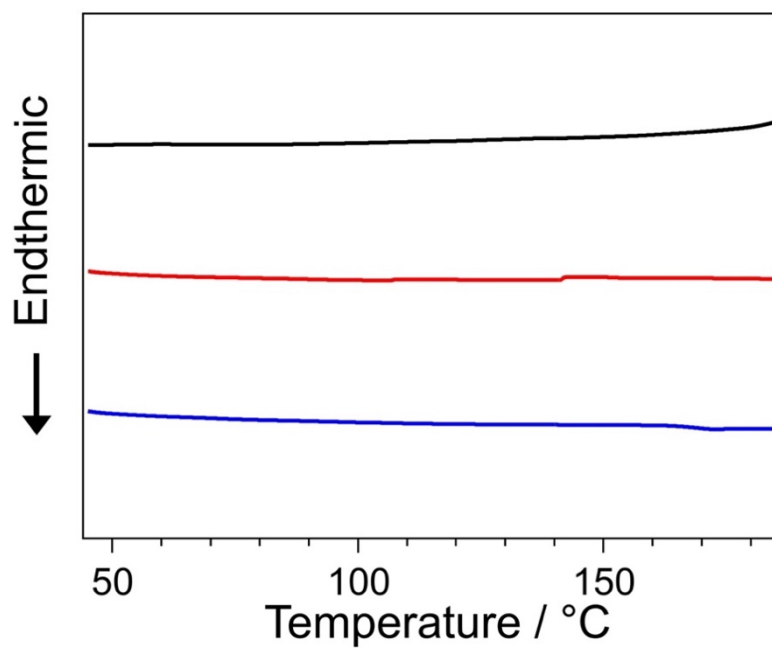


Figure 3.11 DSC thermograms of *p*-dpba (black), dppt (red), and dppb (blue).

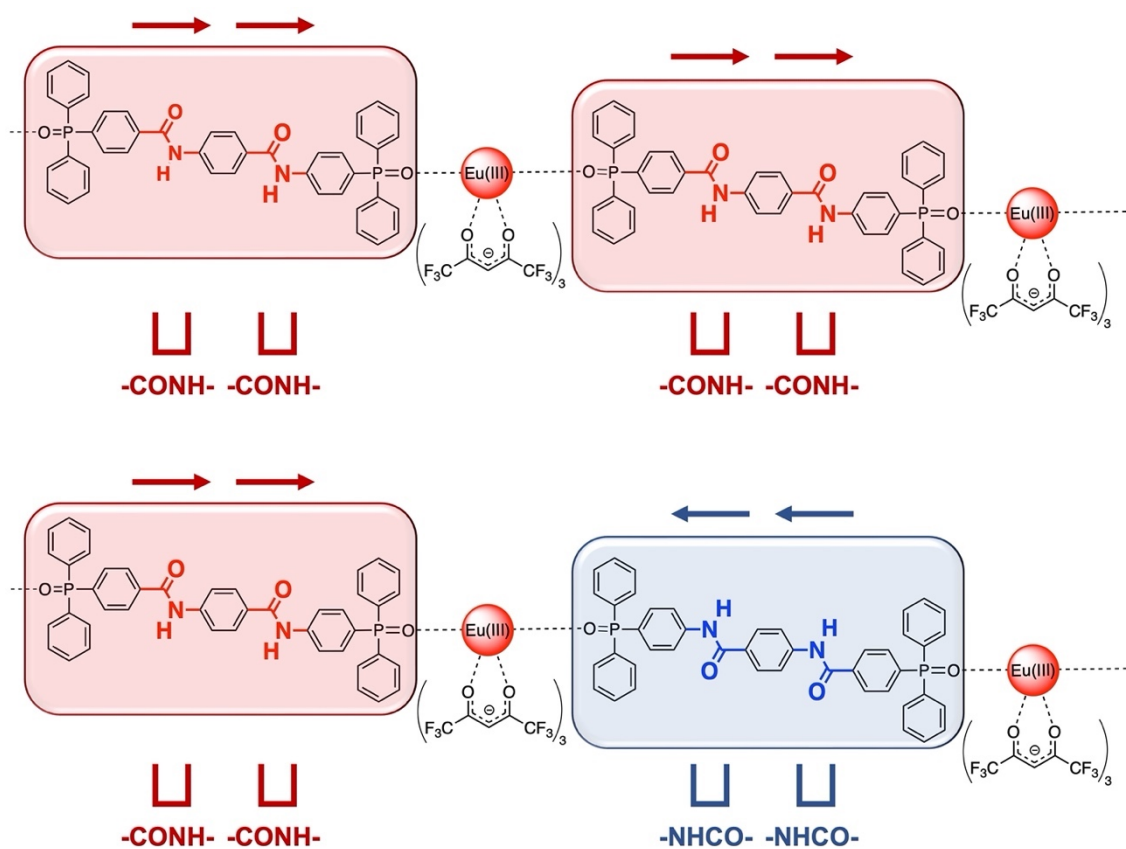


Figure 3.12 Monomer arrangement patterns of $[\text{Eu}(\text{hfa})_3(\text{dppb})]_n$.

3.3.2 Photophysical properties

The diffuse reflectance spectra of the ligands by diluting them 10-folds in KBr are shown in **Figure 3.13**. 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). The absorption spectra of the ligands in DMSO were measured to estimate their light-harvesting abilities (**Figure 3.14**). The absorption coefficient maximum ($\epsilon_{\max}$) of *p*-dpba, **dppt**, and **dppb**, were calculated to be 40200, 44400, and 38000 M⁻¹ cm⁻¹, respectively. The absorption edge of **dppt** and **dppb** were shorter than that of the *p*-dpba. The emission spectra of the ligands are shown in **Figure 3.15**. The emission peak of *p*-dpba (495 nm) was longer than those of **dppt** (457 nm) and **dppb** (464 nm). To estimate the triplet (T₁) state, we measured the phosphorescence spectra of the ligands (**Figure 3.16**). The T₁ levels of *p*-dpba, **dppt**, and **dppb** (> 20,000 cm⁻¹) were higher than those of previous organic ligands with induction of back energy transfer from Eu(III) to ligands.^[9]

The emission spectra of three Eu(III) coordination polymers are shown in **Figure 3.17**. The sharp emission bands at around 578, 592, 613, 650, and 698 nm were observed and assigned to the 4f-4f transitions of the Eu(III) ($^5D_0 \rightarrow ^7F_J$; $J = 0, 1, 2, 3$, and 4), respectively.^[10] The spectra were normalized with respect to the magnetic dipole transition intensities (MD) at around 592 nm ($^5D_0 \rightarrow ^7F_1$), which are insensitive to the surrounding environment of the Eu(III). The emission bands at around 613 nm are strongly dependent on the coordination geometry. The Stark splitting of the $^5D_0 \rightarrow ^7F_2$ transition in **[Eu(hfa)₃(dppt)]_n** is the almost same as that in **[Eu(hfa)₃(dppb)]_n**. However, the Stark splitting of **[Eu(hfa)₃(*p*-dpba)]_n** was different from those of **[Eu(hfa)₃(dppt)]_n** and **[Eu(hfa)₃(dppb)]_n**. **[Eu(hfa)₃(*p*-dpba)]_n** and **[Eu(hfa)₃(dppt)]_n** exhibited broad

emission bands at 461 nm and 465 nm, respectively. The observed emission bands correspond to the emission of linker ligands. 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 excitation spectra of $[\text{Eu}(\text{hfa})_3(\text{p-dpba})]_n$ are shown in **Figure 3.18**. The excitation bands observed at 300-350 nm and 350-400 nm correspond to the $\pi\text{-}\pi^*$ transition of the **hfa** ligand and the absorption bands of the p-dpba ligand, respectively. The results demonstrate that the energy transfer pathway is mainly occurred from the hfa ligands.

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 3.1**. 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}), and photosensitization efficiency (η_{sens}) were estimated using equations (1)-(6). No significant difference was observed in the k_r values in the three Eu(III) coordination polymers. On the other hand, the k_{nr} values of the Eu(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 by 370 nm were estimated to be 4.4 %, 4.4 %, and 19 %. Notably, previous Eu(III) coordination polymers with hfa and bidentate phosphine oxide ligands exhibit relatively high $\Phi_{\pi\pi^*}$ (50%-70%) upon the excitation of hfa ligand.^[10,11] 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 $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$, $[\text{Eu}(\text{hfa})_3(\text{dppt})]_n$ 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 50 times larger than that of hfa unit ($\epsilon_{370} = 120 \text{ M}^{-1} \text{cm}^{-1}$). 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. 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 Eu(III) coordination polymers.

Table 3.1 Photophysical properties of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$, $[\text{Eu}(\text{hfa})_3(\text{dppt})]_n$, and $[\text{Eu}(\text{hfa})_3(\text{dppb})]_n$.

	$\tau_{\text{obs}} / \text{ms}^{\text{a}}$	$\Phi_{\text{ff}} / \%$	$k_{\text{r}} / \text{s}^{-1}$	$k_{\text{nr}} / \text{s}^{-1}$	$\Phi_{\pi\pi^*} / \%^{\text{b}}$	$\eta_{\text{sens}} / \%$
$[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$	0.74	64	8.7×10^2	4.8×10^2	4.4	6.8
$[\text{Eu}(\text{hfa})_3(\text{dppt})]_n$	0.55	44	8.0×10^2	1.0×10^3	19	43
$[\text{Eu}(\text{hfa})_3(\text{dppb})]_n$	0.63	52	8.2×10^2	7.6×10^2	19	37

(a) $\lambda_{\text{ex}} = 355 \text{ nm}$, $\lambda_{\text{em}} = 610 \text{ nm}$, (b) $\lambda_{\text{ex}} = 370 \text{ nm}$.

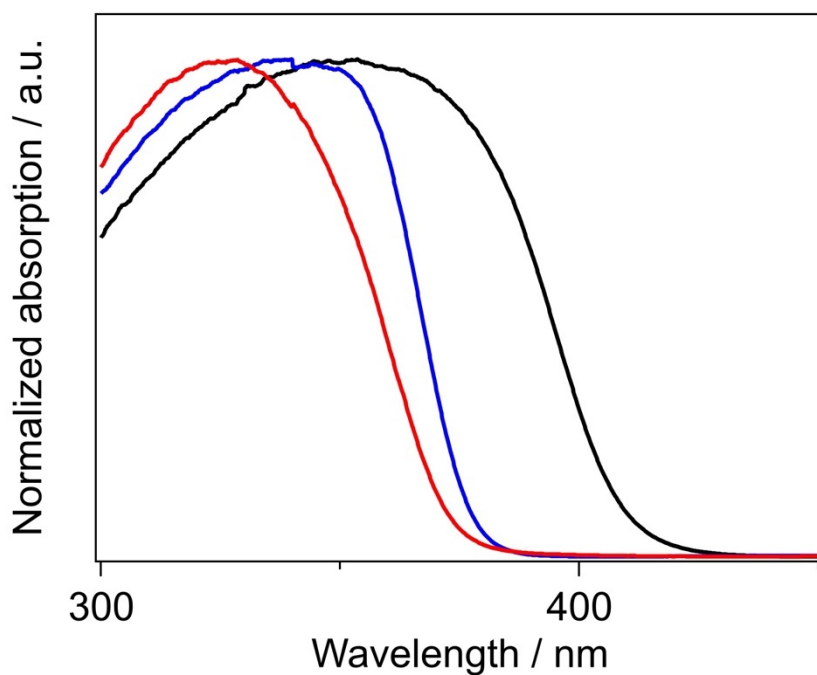


Figure 3.13 Diffuse reflectance spectra of **p-dpba** (black), **dppt** (red), and **dppb** (blue).

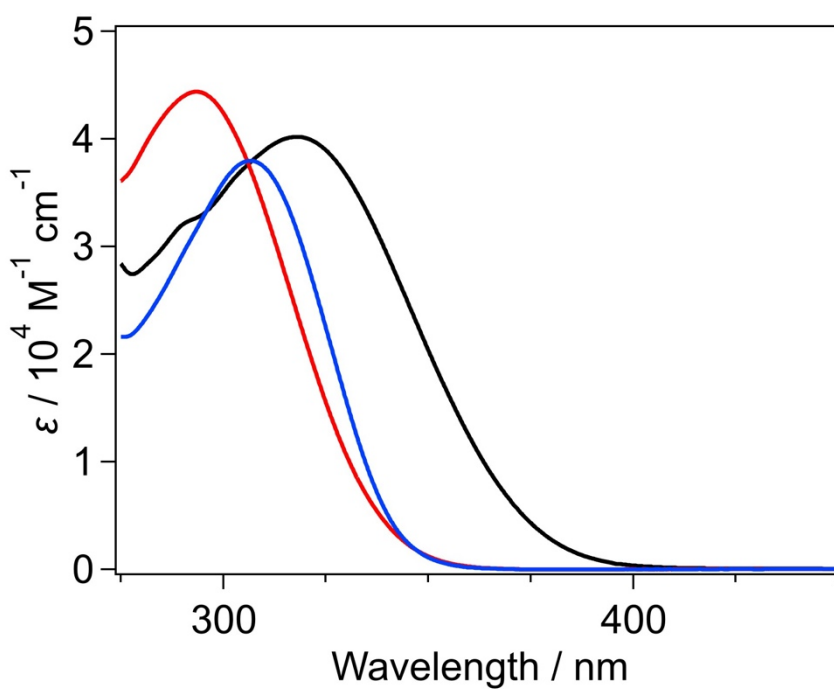


Figure 3.14 Absorption spectra of **p-dpba** (black), **dppt** (red), and **dppb** (blue).

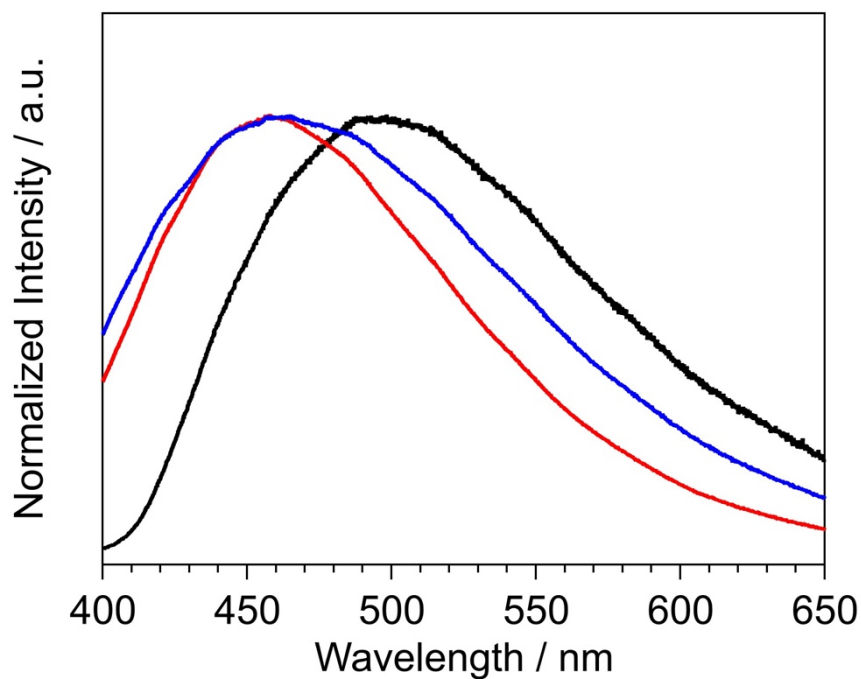


Figure 3.15 Emission spectra of *p*-dpba (black), dppt (red) and dppb (blue). ($\lambda_{\text{ex}} = 330$ nm)

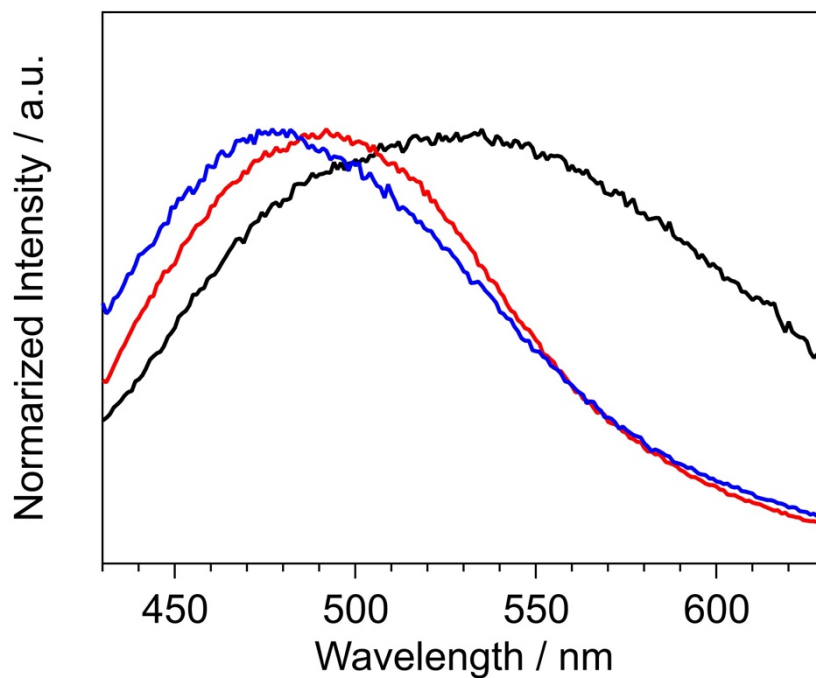


Figure 3.16 Phosphorescence spectra of *p*-dpba (black), dppt (red) and dppb (blue). ($\lambda_{\text{ex}} = 370$ nm, 90K, degassed, 10 ms delay)

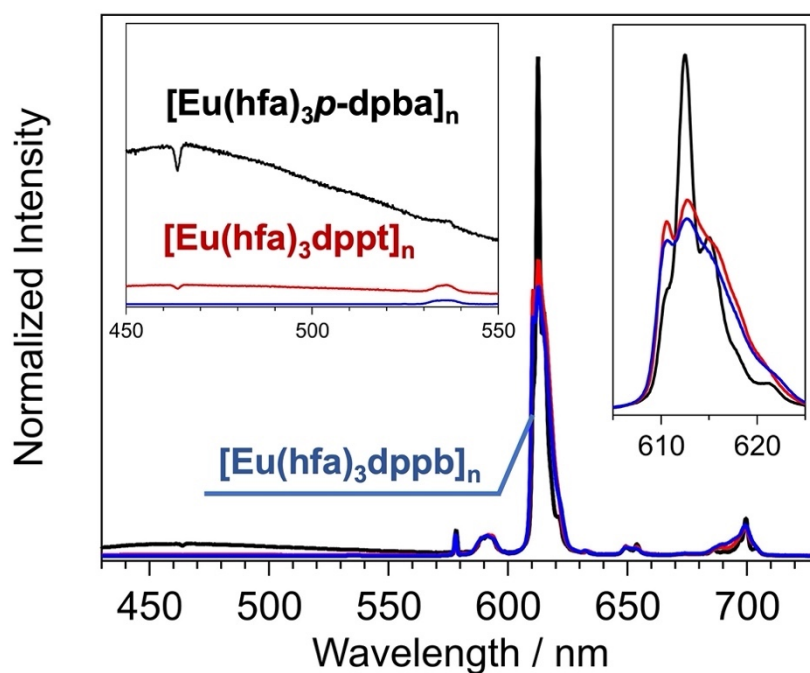


Figure 3.17 Emission spectra ($\lambda_{\text{ex}} = 370$ nm) of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ (black), $[\text{Eu}(\text{hfa})_3(\text{dppt})]_n$ (red) and $[\text{Eu}(\text{hfa})_3(\text{dppb})]_n$ (blue).

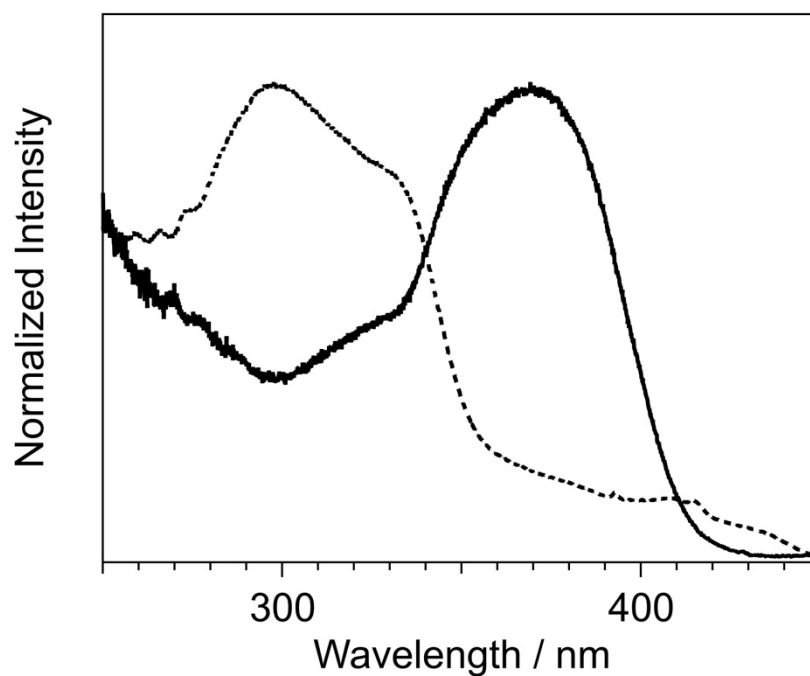


Figure 3.18 Excitation spectra of $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$. (Solid line: $\lambda_{\text{em}} = 500$ nm, dash line: $\lambda_{\text{em}} = 612$ nm).

3.4 Conclusion

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

3.5 References

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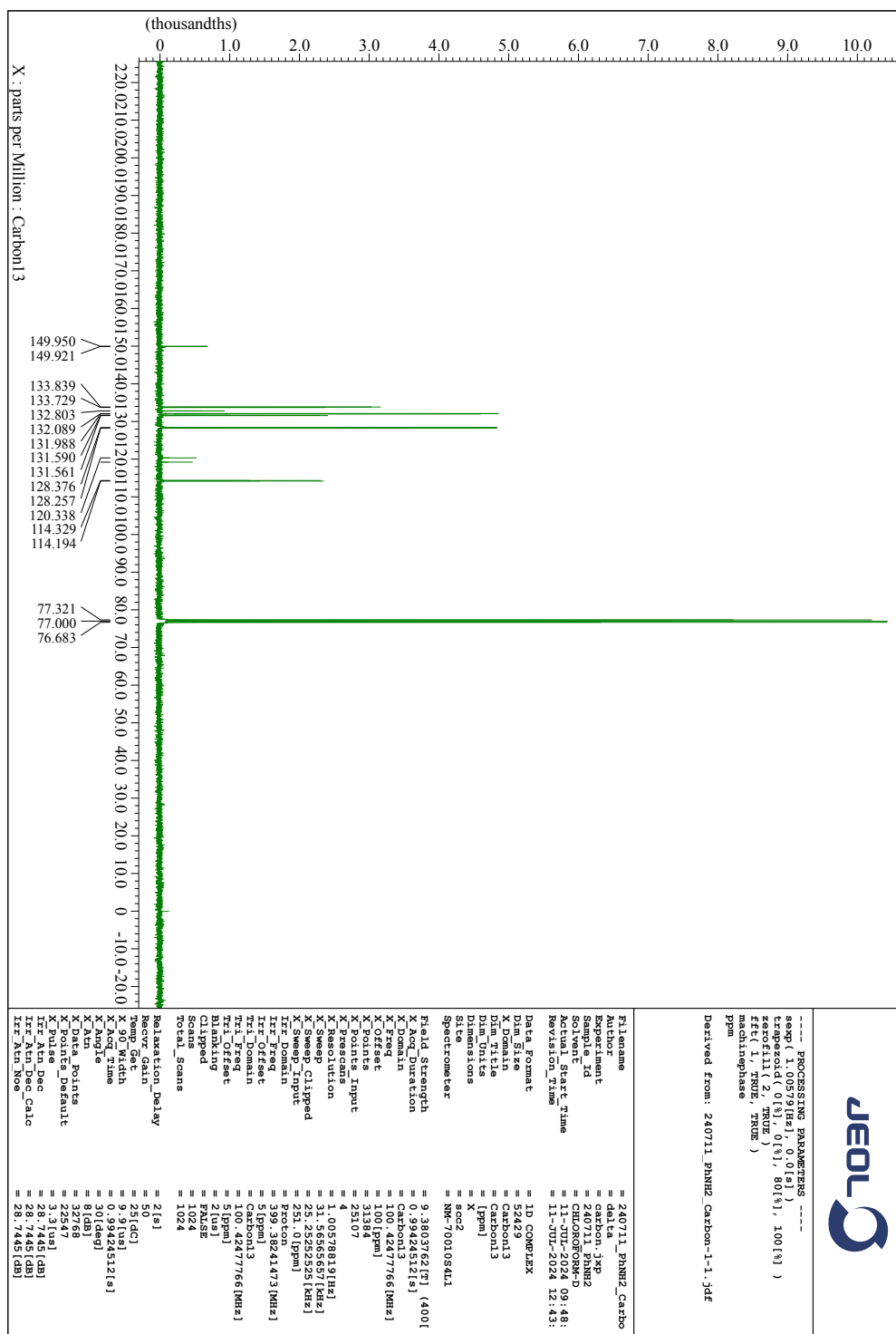
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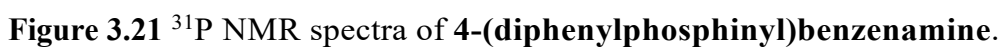
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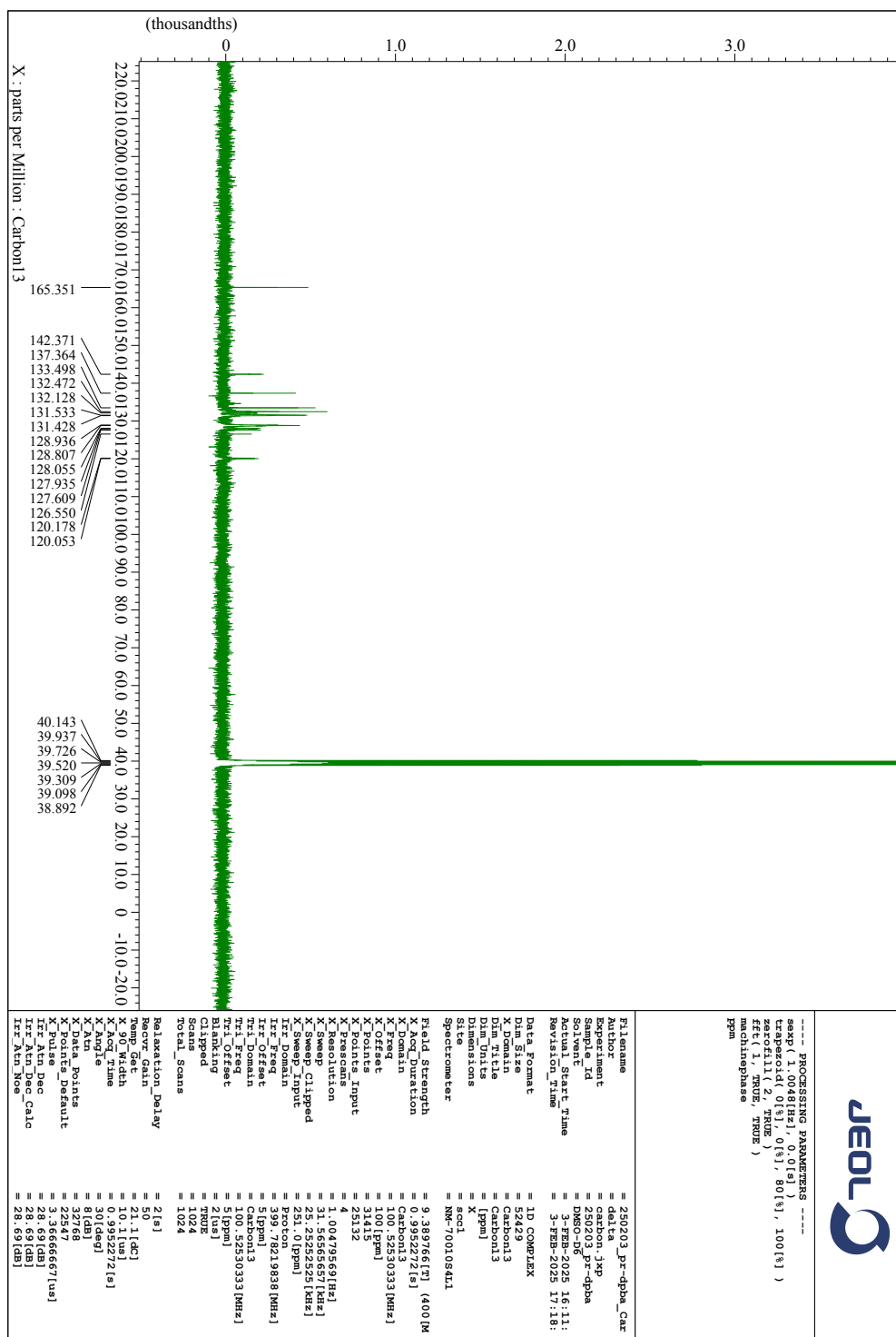
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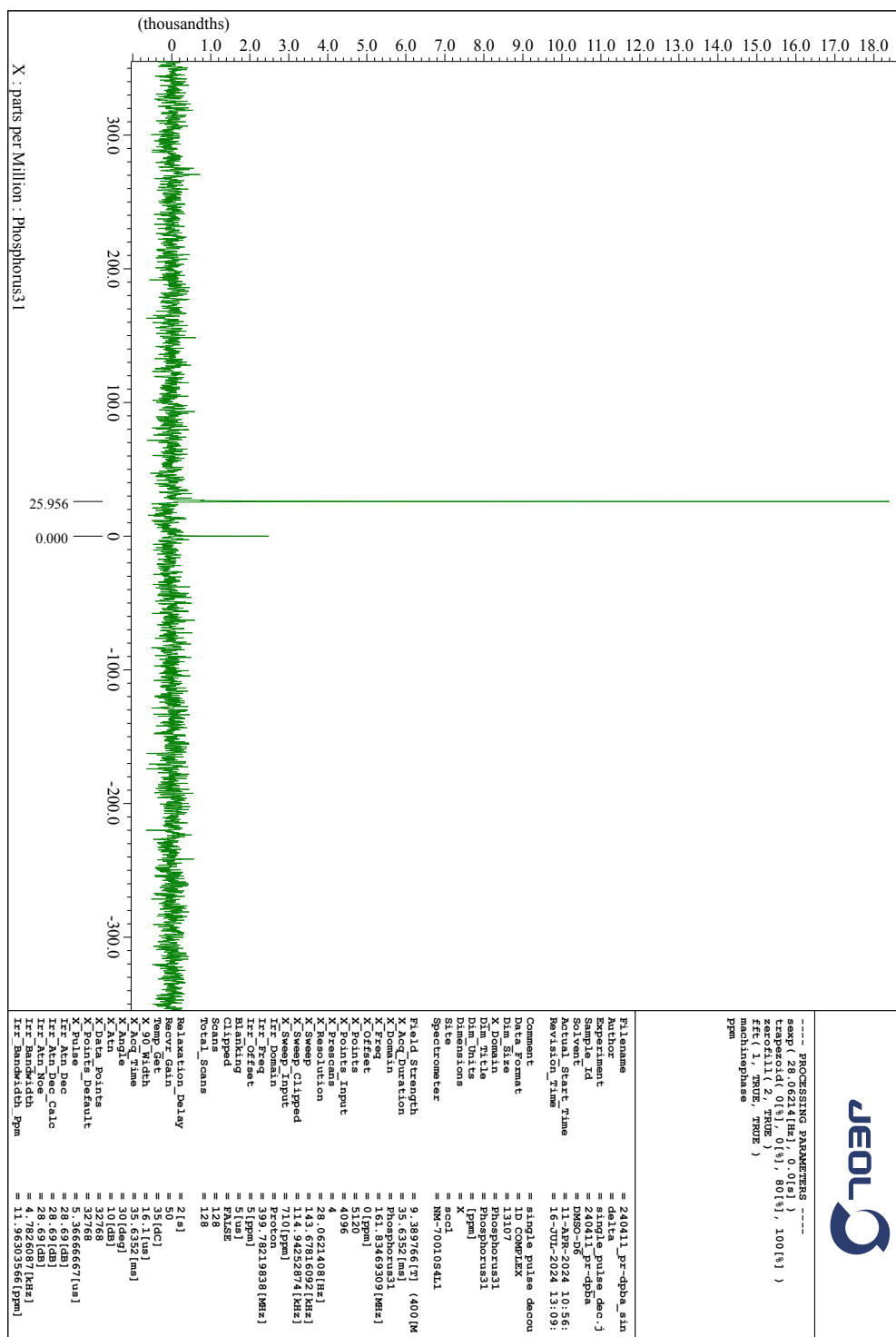
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Figure 3.20 ^{13}C NMR spectra of 4-(diphenylphosphinyl)benzenamine.





Figure 3.23 ^{13}C NMR spectra of dppt.

Figure 3.24 ^{31}P NMR spectra of dppt.

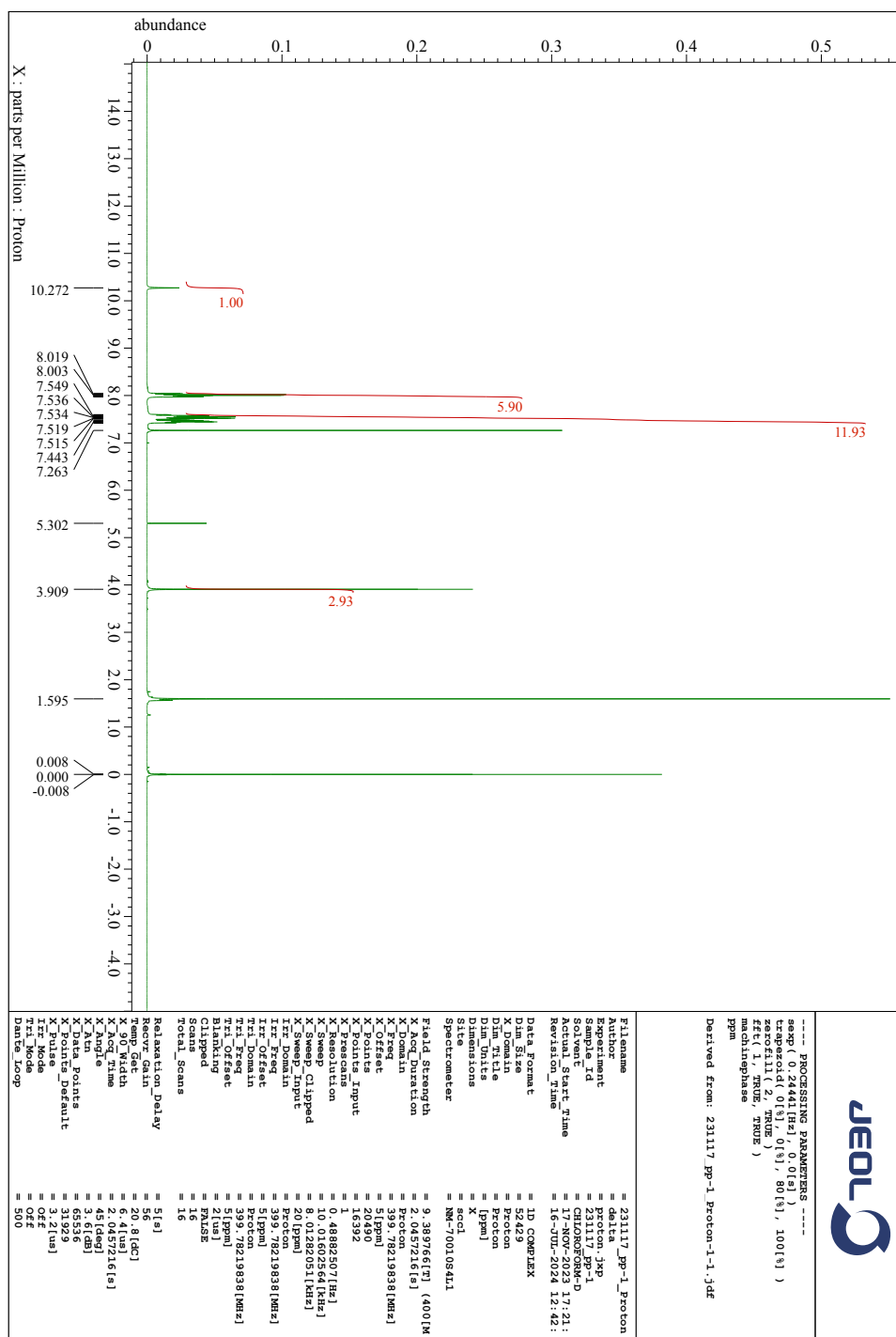


Figure 3.25 ^1H NMR spectra of Methyl 4-(4-(diphenylphosphoryl)benzamidyl)benzoate.

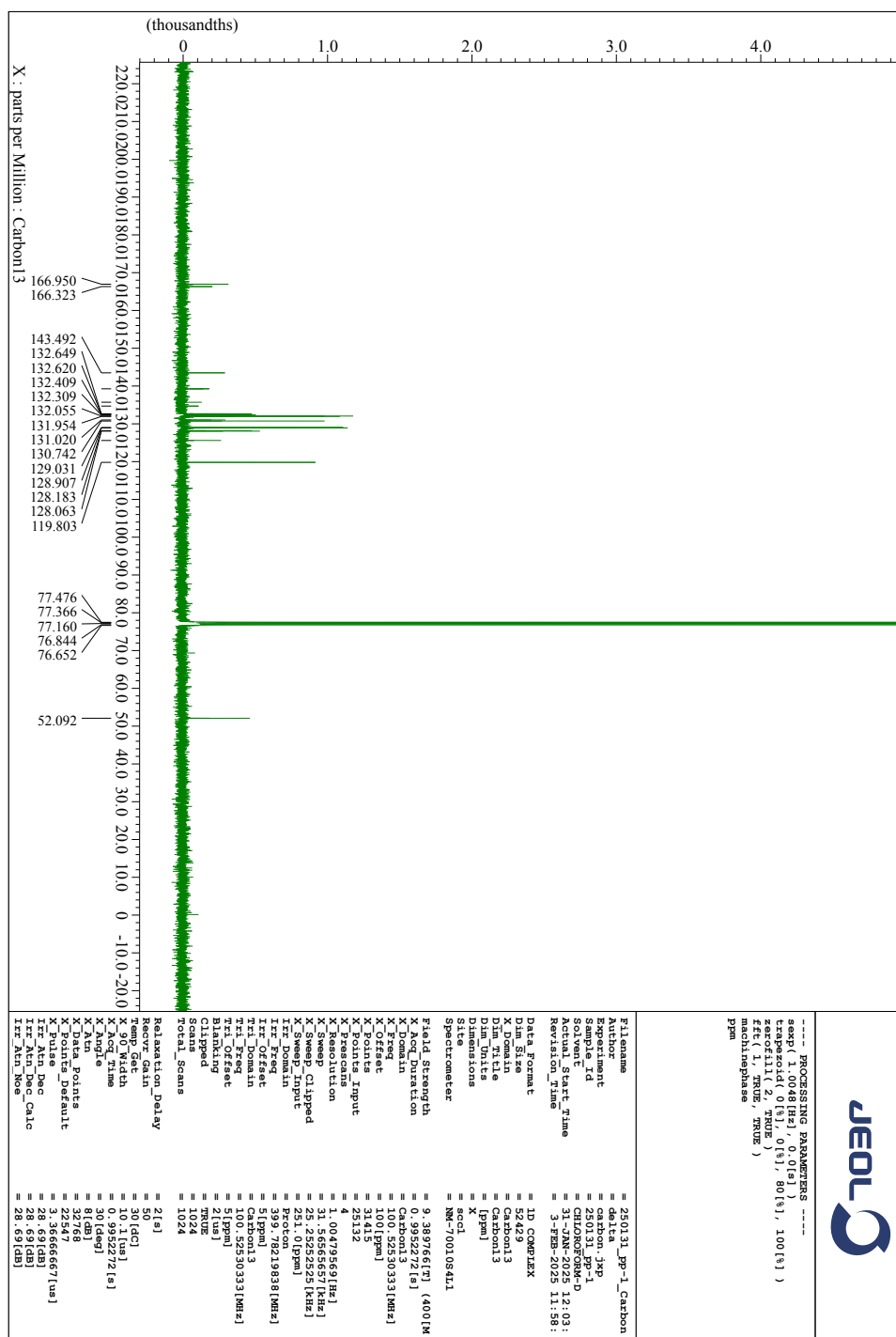
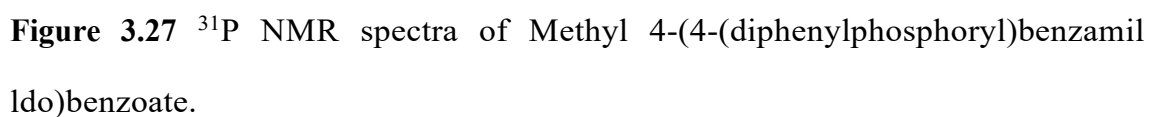


Figure 3.26 ^{13}C NMR spectra of Methyl 4-(4-(diphenylphosphoryl)benzamidido)benzoate.



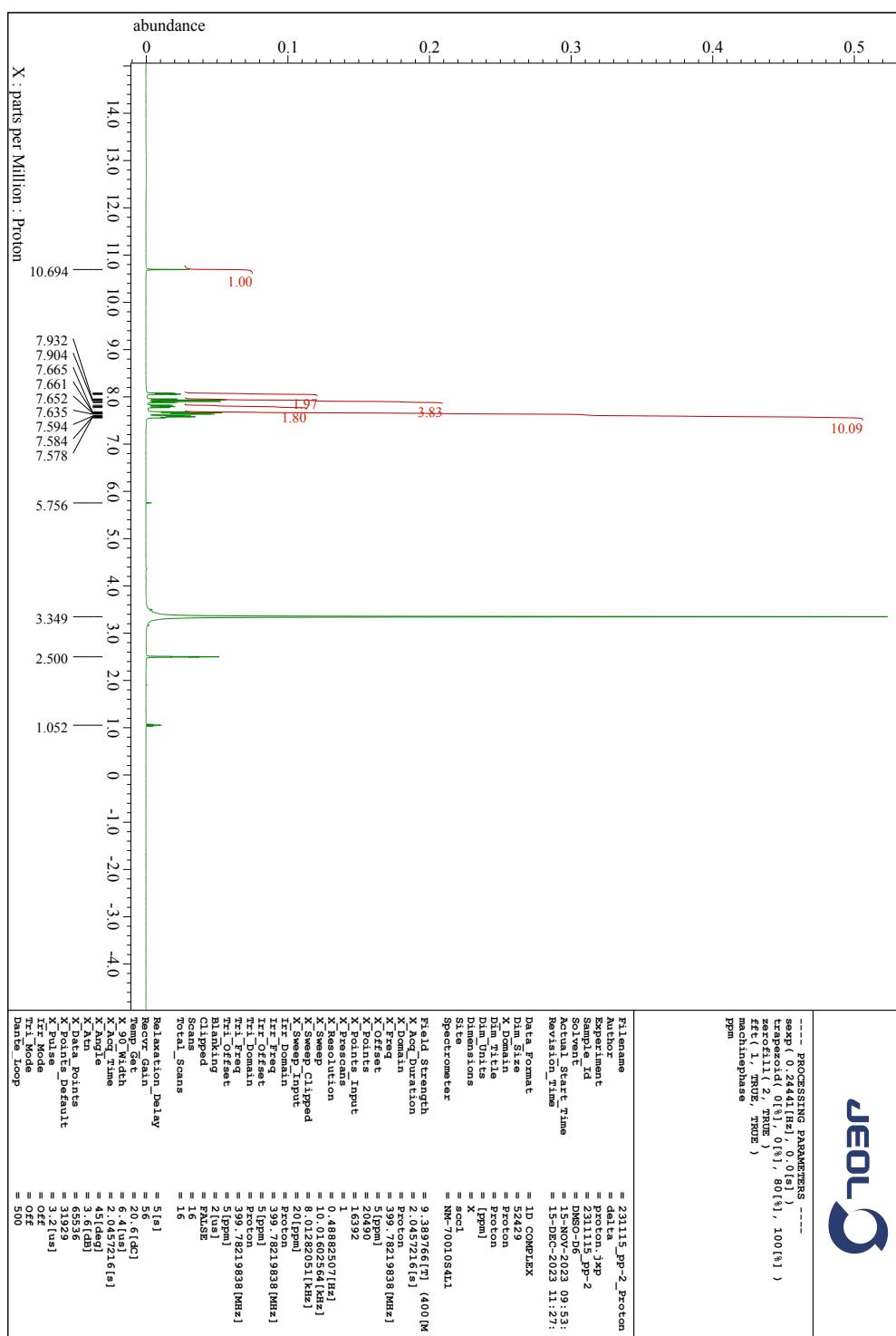
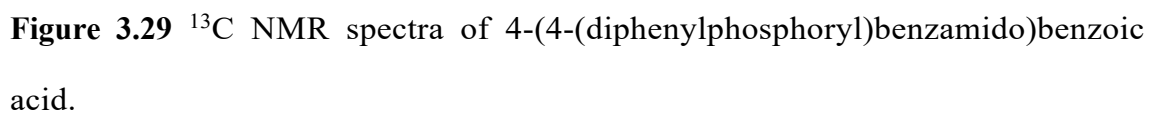
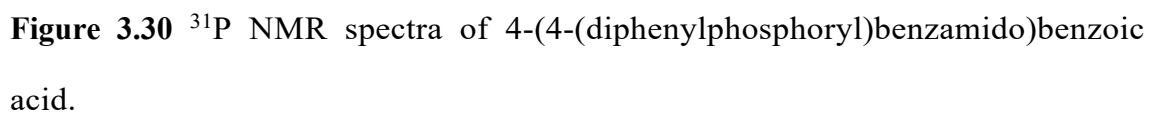


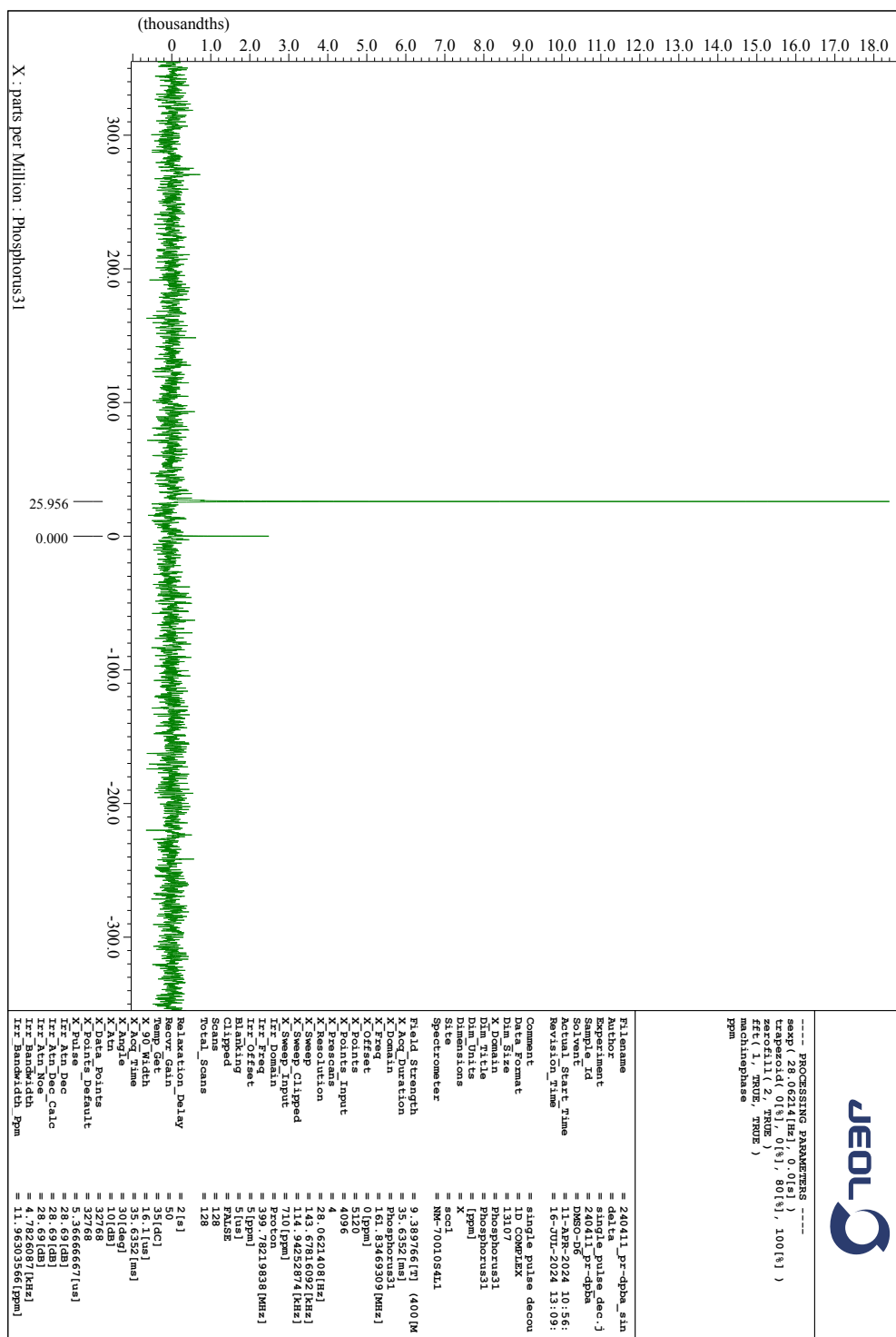
Figure 3.28 ^1H NMR spectra of 4-(4-(diphenylphosphoryl)benzamido)benzoic acid.









Figure 3.33 ^{31}P NMR spectra of dppb.

Chapter 4

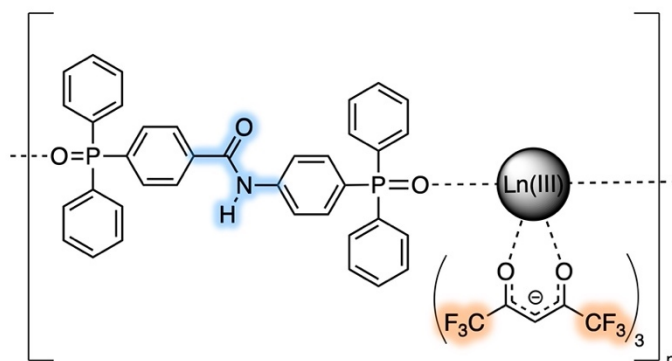
***Steric Control of Lanthanide Coordination
Polymer with Monoamide Moiety for CO₂
Adsorption Material***

4.1 Introduction

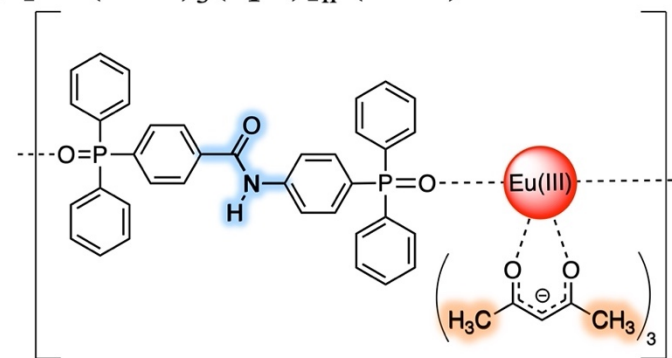
In **Chapter 3**, the author discussed on the systematic structural control of luminescent Eu(III) coordination polymers. The structural and physicochemical properties of lanthanide coordination polymers depend on the molecular structure of the linker ligands. Here, the author focused on a helical cylindrical structure with an inner channel for the application to gas adsorption. A flexible V-shaped amide spacer is effective method for the successful construction of helical structure. ^[1-4] Amide linker ligand **dpa** (4-(diphenylphosphoryl)-*N*-(4-(diphenylphosphoryl)phenyl)benzamide) was selected for the cylindrical structure. Additionally, to create strong binding interactions with the electropositive carbon atom of the CO₂ molecule, **hfa** ligand (hexafluoroacetylacetonate) accompanied by electronegative fluorine atoms was chosen. ^[5,6] The Eu(III) and Tb(III) ions exhibited 4f-4f transition-based red and green emissions, respectively. Hasegawa previously reported a ratiometric temperature sensor using Eu(III)/Tb(III)-mixed coordination polymers. ^[7] Dual-emission lanthanide coordination polymers are a promising strategy for develop effective ratiometric sensors. Therefore, luminescent porous Eu(III)/Tb(III)-mixed coordination polymers was to visualize CO₂ gas detection (**Figure 4.1 a**). The structural design of the coordination polymers i) produces a highly ordered helical structure, ii) positions the fluorinated units on the inner surface of the helical cylinder, facilitating CO₂ storage, and iii) enables ratiometric detection by monitoring the Eu(III)/Tb(III) emission intensity. In addition, a Gd(III) coordination polymer was prepared to estimate the excited triplet lifetime of the **hfa** ligands under CO₂ gas condition. A For reference, the author has prepared two lanthanide coordination polymers, [Eu(**acac**)₃(**dpa**)]_n and [Eu(**hfa**)₃(*p*-**dpba**)]_n (**Figure 4.1 b and c**; **acac**: acetylacetonate). [Eu(**acac**)₃(**dpa**)]_n has replaced the **hfa** ligand of [Eu(**hfa**)₃(**dpa**)]_n with non-fluorinated **acac** ligand. [Eu(**hfa**)₃(*p*-**dpba**)]_n. has two amide units in the phosphine oxide linker ligand, *p*-**dpba**. This study demonstrates a luminescence changeable CO₂-

storage cylinder composed of a triple-stranded helical Eu(III)/Tb(III) coordination polymer, $[\text{Eu}_{0.1}\text{Tb}_{0.9}(\text{hfa})_3(\text{dpa})]_n$.

(a) $[\text{Ln}(\text{hfa})_3(\text{dpa})]_n$ (New)



(b) $[\text{Eu}(\text{acac})_3(\text{dpa})]_n$ (New)



(c) $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ (Chapter 2, 3)

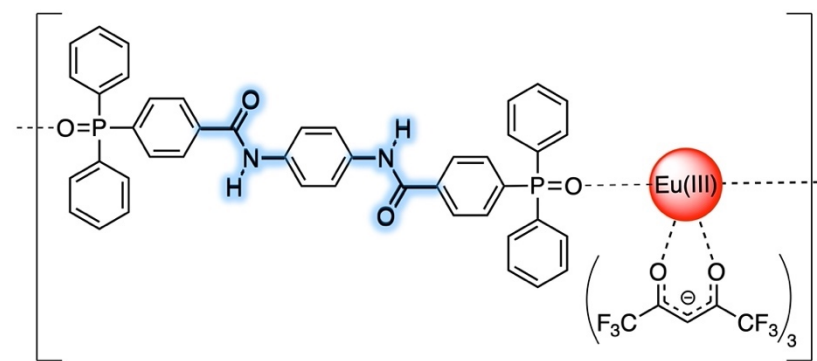


Figure 4.1 Molecular structures of (a) $[\text{Ln}(\text{hfa})_3(\text{dpa})]_n$ ($\text{Ln} = \text{Eu}, \text{Tb}, \text{or Gd}$), (b) $[\text{Eu}(\text{acac})_3(\text{dpa})]_n$, and (c) $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$.

4.2 Methods

4.2.1 Materials and apparatus

Europium(III) acetate n-hydrate (99.9%), terbium(III) acetate tetrahydrate (99.9%), and gadolinium(III) acetate tetrahydrate (99.9%) were purchased from FUJIFILM Wako Pure Chemical Corporation. 4-Iodoaniline, diphenyl phosphine, and hexafluoroacetylacetone were purchased from Tokyo Chemical Industry Co., Ltd. All other reagents were of reagent grade and used without further purification. Elemental analyses were performed on an Exeter Analytical CE440. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{31}P NMR (162 MHz) spectra were recorded on a JEOL ECS400. ^1H chemical shifts were determined with tetramethylsilane as an internal standard ($\delta = 0$ ppm). ^{31}P chemical shifts were determined with 85% H_3PO_4 as an external standard ($\delta = 0$ ppm). Thermogravimetric analyses were performed using on a Rigaku TG-DTA8122/S under a nitrogen atmosphere at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$. DSC was performed on a Hitachi High-Tech DSC 7020 under a nitrogen atmosphere at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$. Powder X-ray diffraction was performed on a Rigaku SmartLab using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$).

Emission and excitation spectra were recorded on a HORIBA Fluorolog-3 spectrofluorometer and corrected for the response of the detector system. Emission decay profiles were measured using the third harmonics (355 nm) of a Q-switched Nd:YAG laser (Spectra Physics, INDI-50, FWHM = 5 ns, $\lambda = 1064\text{ nm}$) and a photomultiplier (Hamamatsu Photonics, R5108, response time $\leq 1.1\text{ ns}$). 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.

4.2.2 Crystallography

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, $\lambda = 0.71073$ Å). The structure was resolved using direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically using the SHELX system. [8] Hydrogen atoms were refined using the riding model. All calculations were performed using the Olex2 crystallographic software package except for refinement, which was performed using SHELXL. [9] The CIF data were confirmed by the checkCIF/PLATON service. CCDC-2370098 for **[Eu(hfa)₃(dpa)]_n** contain the supplementary crystallographic data for this chapter.

4.2.3 Syntheses

Preparation of 4-(diphenylphosphinyl)benzenamine

4-(diphenylphosphinyl)benzenamine was synthesized according to the previously reported in previous chapter.

Preparation of 4-(diphenylphosphoryl)benzoic acid

4-(diphenylphosphoryl)benzoic acid was synthesized according to the previously reported in previous chapter.

Preparation of 4-(diphenylphosphoryl)-N-(4-(diphenylphosphoryl)phenyl)benzamide (dpa)

Thionyl chloride (1.0 mL) was added to 4-(diphenylphosphoryl)benzoic acid (322.3 mg, 1.0 mmol) at room temperature and stirred for 30 min at room temperature. The solvent was removed in vacuo. The resulting residue was dissolved in CH₂Cl₂ (10 mL), and successively added 4-(diphenylphosphinyl)benzenamine (293.3 mg, 1.0 mmol) and triethylamine (0.3 mL). After stirring for 2 h at room temperature, the reaction mixture

was washed with aqueous 2% HCl, aqueous 5% NaHCO₃, and distilled water. The organic layer was dried over Na₂SO₄ and evaporated. The residue was purified by silica gel column chromatography (5% MeOH–CH₂Cl₂) to give **dpa** (299.0 mg, 0.500 mmol, 50%) as white solid. ¹H NMR (400 MHz, CDCl₃) δ 10.89 (1H, s), 8.03–8.00 (4H, m), 7.67–7.40 (24H, m) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 142.6, 138.7, 135.5, 134.5, 132.9, 132.8, 132.7, 132.3, 132.3, 132.0, 132.0, 131.9, 131.9, 131.8, 131.8, 131.7, 130.8, 128.7, 128.6, 128.5, 128.4, 128.1, 128.0, 127.1, 126.0, 120.4, 120.3 ppm. ³¹P NMR (162 MHz, CDCl₃) δ 29.5, 29.2 ppm. MS(ESI) found: *m/z* 620.15. Calcd. for C₃₇H₂₉NNaO₃P₂: [M+Na]⁺, 620.15.

Preparation of [Eu(hfa)₃(H₂O)₂]

[Eu(hfa)₃(H₂O)₂] was synthesized according to the previously reported in previous chapter.

Preparation of [Ln(hfa)₃(H₂O)₂] (Ln = Tb or Gd)

[Ln(hfa)₃(H₂O)₂] was synthesized according to the previously reported procedures. [10,11]

Preparation of [Ln(hfa)₃(dpa)]_n (Ln = Eu, Tb, or Gd)

[Ln(hfa)₃(H₂O)₂] (0.1 mmol) was added to a MeOH (10 mL) solution of **dpa** (59.8 mg, 0.1 mmol), and the mixture was refluxed for 1 h. The recrystallization from acetonitrile and MeOH gave [Ln(hfa)₃(dpa)]_n as a white powder.

[Eu(hfa)₃(dpa)]_n: yield 46%. MS(ESI) found: *m/z* 1394.04. Calcd. for C₅₂H₃₂EuF₁₈NNaO₉P₂: [M+Na]⁺, 1394.04. Elemental analysis: found (%): C 45.47, H 2.30, N 1.15. Calcd. for C₅₂H₃₂EuF₁₈NO₉P₂: C 45.57, H 2.35, N 1.02.

[Tb(hfa)₃(dpa)]_n: yield 44%. MS(ESI) found: *m/z* 1400.05. Calcd. for C₅₂H₃₂F₁₈NNaO₉P₂Tb: [M+Na]⁺, 1400.04. Elemental analysis: found (%): C 45.29, H 2.37, N 1.10. Calcd. for C₅₂H₃₂F₁₈NNaO₉P₂Tb: C 45.34, H 2.34, N 1.02.

[Gd(hfa)₃(dpa)]_n: yield 46%. MS(ESI) found: m/z 1399.04. Calcd. for $C_{52}H_{32}F_{18}GdNNaO_9P_2$: $[M+Na]^+$, 1399.09. Elemental analysis: found (%): C 45.67, H 2.38, N 1.12. Calcd. for $C_{52}H_{32}F_{18}GdNO_9P_2$: C 45.39, H 2.34, N, 1.02.

Preparation of [Eu_{0.1}Tb_{0.9}(hfa)₃(dpa)]_n

[Eu(hfa)₃(H₂O)₂] (8.09 mg, 0.01 mmol) and [Tb(hfa)₃(H₂O)₂] (53.9 mg, 0.09 mmol) was added to a MeOH (10 mL) solution of dpa (59.8 mg, 0.1 mmol), and the mixture was refluxed for 1 h. The recrystallization from acetonitrile and MeOH gave **[Eu_{0.1}Tb_{0.9}(hfa)₃(dpa)]_n** (57.7 mg, 41.9 μ mol, 42%) as a white powder: Elemental analysis: found (%): C 45.51, H 2.50, N, 1.26. Calcd. for $C_{52}H_{32}Eu_{0.1}F_{18}NO_9P_2Tb_{0.9}$: C 45.36, H 2.34, N 1.02.

Preparation of [Eu(acac)₃(dpa)]_n

[Eu(acac)₃·nH₂O] (44.2 mg, 0.1 mmol) was added to a MeOH (10 mL) mixture solution of dpa (59.8 mg, 0.1 mmol), and the mixture was refluxed for 1 h. The reaction mixture was evaporated to give **[Eu(acac)₃(dpa)]_n** (31.8 mg, 30.4 μ mol, 30%) as a white powder: MS(ESI) found: m/z 1070.20. Calcd. for $C_{52}H_{50}EuNNaO_9P_2$: $[M+Na]^+$, 1070.20.

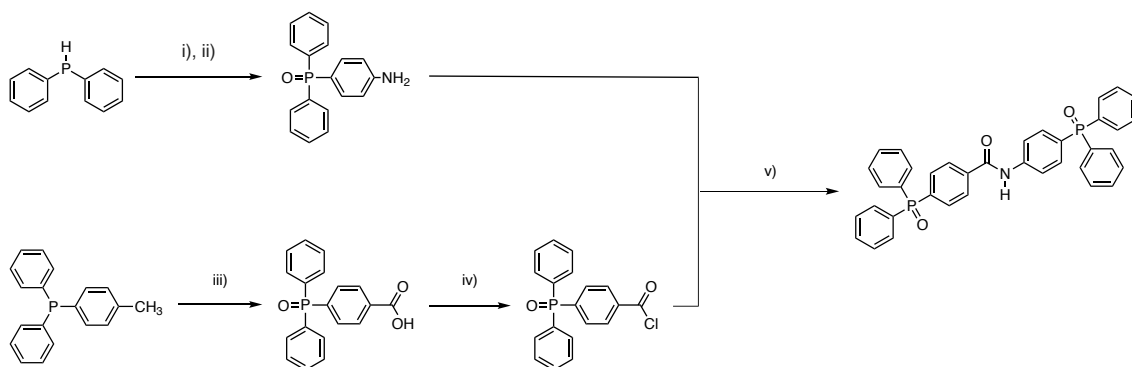


Figure 4.2 Synthetic scheme of **dpa**: i) 4-iodoaniline, KOAc, Pd(OAc)₂, DMA, 130°C; ii) 30% H₂O₂ aq., CH₂Cl₂, 0°C; iii) KMnO₄, NaOH aq., 90°C; iv) SOCl₂; v) Et₃N, CH₂Cl₂, 0°C.

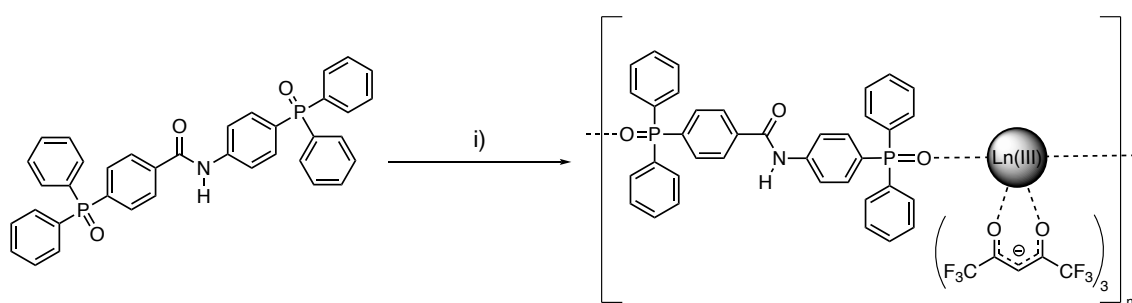


Figure 4.3 Synthetic scheme of **[Ln(hfa)₃(dpa)]_n** (Ln=Eu, Tb, Gd, or Eu_{0.1}Tb_{0.9}): i) [Ln(hfa)₃(H₂O)₂] (Ln=Eu, Tb, or Gd), MeOH, reflux.

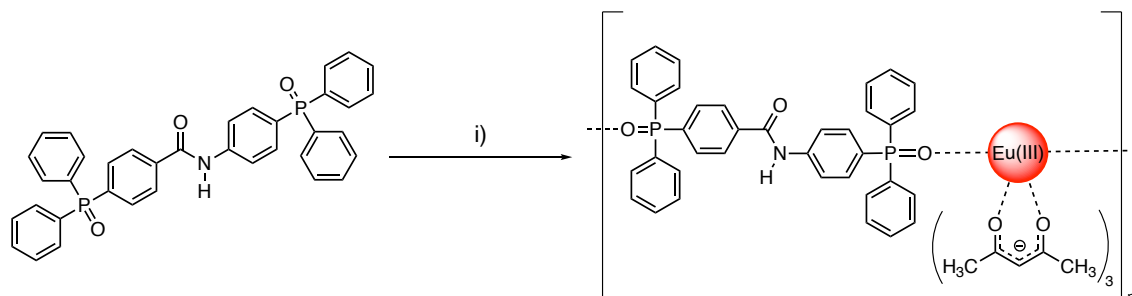


Figure 4.4 Synthetic scheme of **[Eu(acac)₃(dpa)]_n**: i) [Eu(acac)₃·nH₂O], MeOH, reflux.

4.3 Results and discussion

4.3.1 Structural characterizations

The lanthanide coordination polymers, $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$, $[\text{Tb}(\text{hfa})_3(\text{dpa})]_n$, $[\text{Gd}(\text{hfa})_3(\text{dpa})]_n$, and $[\text{Eu}_{0.1}\text{Tb}_{0.9}(\text{hfa})_3(\text{dpa})]_n$ were obtained by the reaction of **dpa** with precursor complexes, $[\text{Ln}(\text{hfa})_3(\text{H}_2\text{O})_2]$ ($\text{Ln} = \text{Eu}, \text{Tb}, \text{or Gd}$), in methanol under reflux condition. Single crystals of lanthanide coordination polymers were obtained by the recrystallization from a methanol/acetonitrile mixture solution. The crystallographic data of $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$ were summarized in **Figure 4.5a** and **Table 4.1**. The Eu(III) ions were coordinated to eight oxygen atoms from three **hfa** ligands and two **dpa** ligands. Based on their crystal data, the continuous shape measure (CShM) calculations using SHAPE was performed to determine the geometrical structures around the Eu(III) ions in the first coordination sphere.^[12,13] The CShM factor (S_{CShM}) expresses the degree of deviation from the ideal coordination structure and is determined using the following equation.

$$S_{\text{CShM}} = \min \frac{\sum_k^N |Q_k - P_k|^2}{\sum_k^N |Q_k - Q_0|^2} \times 100 \quad (7)$$

where N , Q_k , Q_0 , and P_k are the number of vertices, vertices of the actual structure, position vectors of the geometrical center, and vertices of the ideal structure, respectively. The geometrical symmetry around the Eu(III) ions was determined to be an 8-coordinated square-antiprismatic structure (point group = D_{4d}). The two phosphine oxide groups in the **dpa** ligand were attached to different Eu(III) ions to form a triple-stranded helical structure. The triple-stranded helical structure was formed by three polymer chains. The helical structure provided cylindrical channels along the c-axis (**Figure 4.5b**). The inner surfaces of the channels were covered with the fluorine atoms of the **hfa** units. The

diameter of the channel was estimated to be 9.1 Å, which was larger than that of the CO₂ molecule (3.4 Å). The Eu-Eu distance between the cylindrical channels ($d_{\text{Eu-Eu}}$) and the pitch of the helical chains were 9.8 and 35.1 Å, respectively. Their right-handed and left-handed helical chains were arranged, alternately (**Figure 4.5c**). The powder X-ray diffraction (PXRD) pattern of $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$ matched with the simulate pattern of the single-crystal structure (**Figure 4.6a**). The PXRD patterns of $[\text{Tb}(\text{hfa})_3(\text{dpa})]_n$, $[\text{Gd}(\text{hfa})_3(\text{dpa})]_n$, and $[\text{Eu}_{0.1}\text{Tb}_{0.9}(\text{hfa})_3(\text{dpa})]_n$ were similar to those of $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$ (**Figure 4.6a**). The PXRD patterns of $[\text{Eu}(\text{acac})_3(\text{dpa})]_n$ showed characteristic peaks (**Figure 4.6b**). The decomposition temperature of $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$ was found to be around 320 °C from the TGA profile (**Figure 4.7**).

The gas adsorption capacity of $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$ was estimated from the adsorption isotherms at 298 K (**Figure 4.8**). The CO₂ adsorption measurements showed reversibility of gas adsorption and desorption behaviour, whereas no adsorption and desorption behaviour were observed for N₂. However, the CO₂ gas adsorption and desorption behaviors were not observed for $[\text{Eu}(\text{hfa})_3(p\text{-dpba})]_n$ and $[\text{Eu}(\text{acac})_3(\text{dpa})]_n$ (**Figure 4.9**). The selectivity of CO₂ adsorption is due to its quadrupole moment, which results in a stronger interaction with the CF₃ groups on the inner surface of the cylindrical channels.

[14]

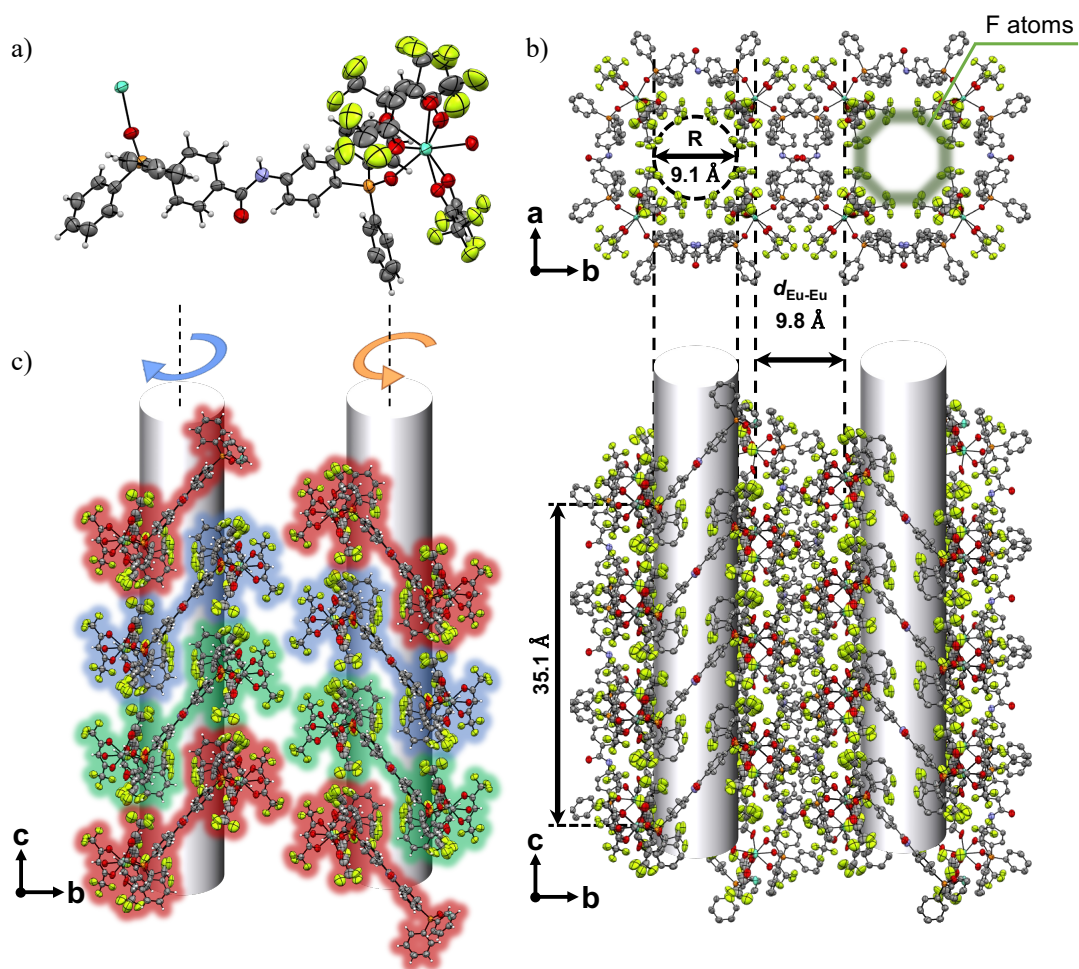


Figure 4.5 a) ORTEP drawings (ellipsoids set at 50 % probability, hydrogen atoms were omitted for clarity) of $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$. b) Views of $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$ along *a* and *c* axis. c) View of the left- and right-handed helical chains in $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$.

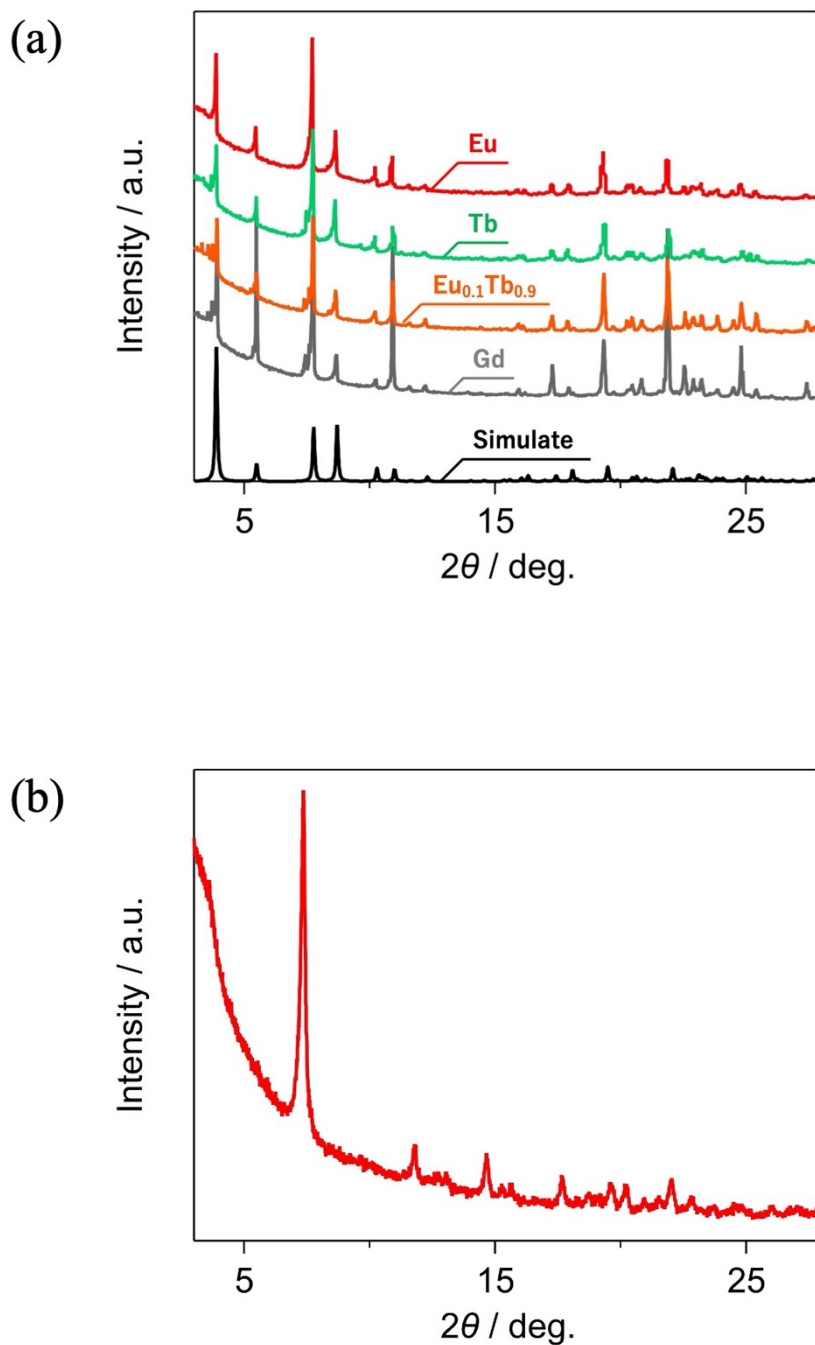


Figure 4.6 (a) Measured PXRD patterns of $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$ (red), $[\text{Tb}(\text{hfa})_3(\text{dpa})]_n$ (green), $[\text{Eu}_{0.1}\text{Tb}_{0.9}(\text{hfa})_3(\text{dpa})]_n$ (orange), $[\text{Gd}(\text{hfa})_3(\text{dpa})]_n$ (gray), and simulated pattern of $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$ from CIF file (black). (b) Measured PXRD patterns of $[\text{Eu}(\text{acac})_3(\text{dpa})]_n$.

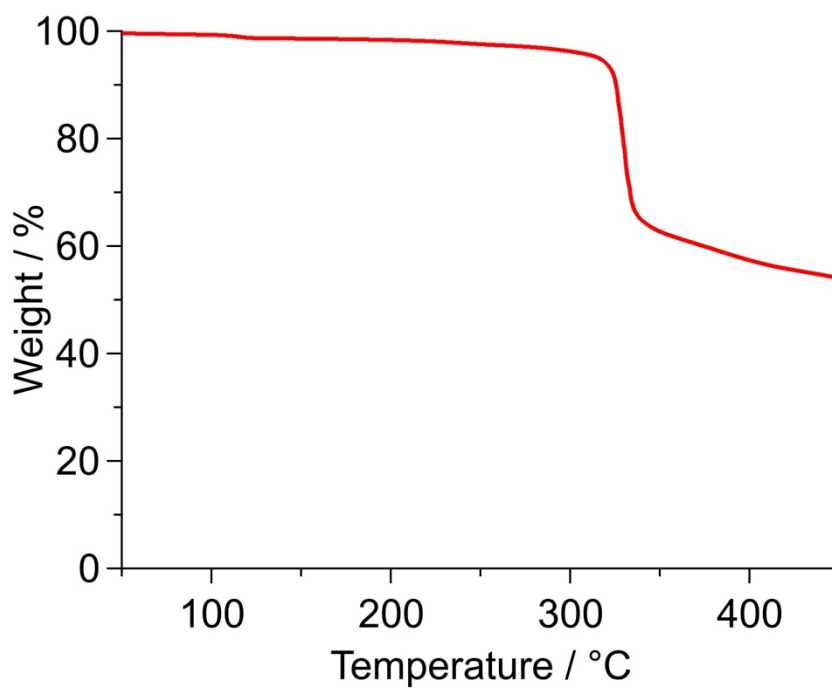


Figure 4.7 TG curve of $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$.

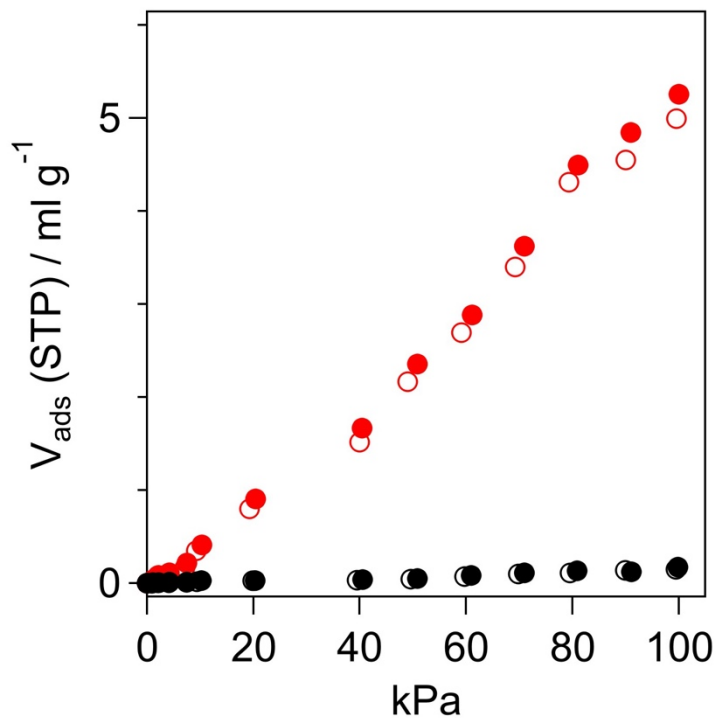


Figure 4.8 CO₂ (red) and N₂ (black) adsorption (solid symbols) and desorption (open symbols) isotherms of $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$ at 298 K.

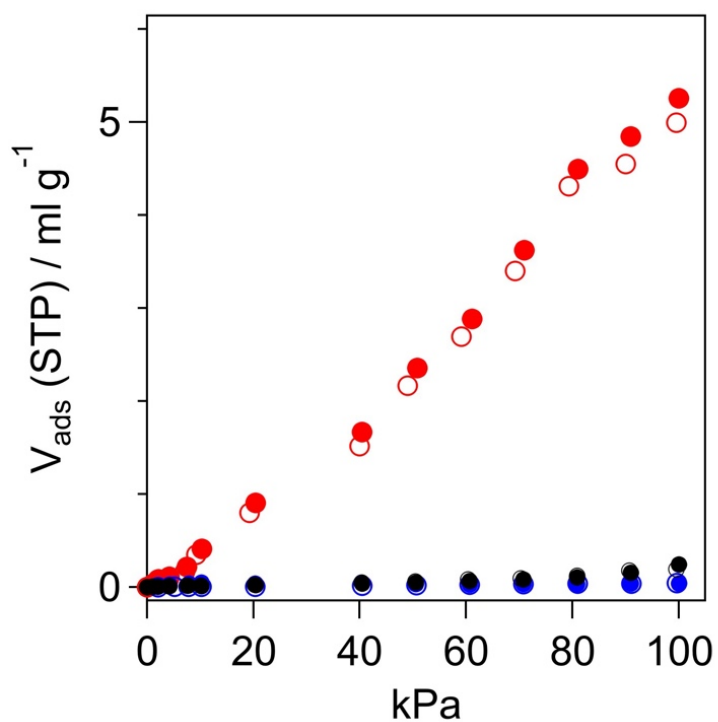


Figure 4.9 CO₂ adsorption (solid symbols) and desorption (open symbols) isotherms of [Eu(hfa)₃(dpa)]_n (red), [Eu(hfa)₃(*p*-dpba)]_n (blue) and [Eu(acac)₃(dpa)]_n (black) at 298 K.

4.3.2 Photophysical properties

The emission bands at 578, 590, 610, 652, and 700 nm are assigned to be $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$, and $^5D_0 \rightarrow ^7F_4$ transitions of Eu(III), respectively (**Figure 4.10a**).^[15] The excitation bands observed in the UV region were attributed to the $\pi-\pi^*$ transition of **hfa** ligand. The shape emission spectra of $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$ are also measured under CO₂ and N₂ conditions (**Figure 4.11a**). The emission lifetimes (τ_{obs}) were determined from the slope of the logarithmic decay profile. The τ_{obs} under CO₂ condition was estimated to be 0.81 ms, which is the same as that under N₂ gas (**Table 4.1**). Photophysical parameters were calculated based on the emission spectra and lifetime (**Table 4.2**). The overall emission quantum yield (excited at $\pi-\pi^*$ transition band of **hfa** ligands, $\Phi_{\pi\pi^*}$) under each condition was around 61% (**Table 4.1**). $[\text{Tb}(\text{hfa})_3(\text{dpa})]_n$ also showed excitation bands in the UV region and emission bands at 490, 540, 580, 620, and 650 nm, corresponding to $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_3$, and $^5D_4 \rightarrow ^7F_2$ transitions of Tb(III), respectively (**Figure 4.10b**). The similar shape of $[\text{Tb}(\text{hfa})_3(\text{dpa})]_n$ emission spectra are also measured under CO₂ and N₂ conditions (**Figure 4.11b**). The emission quantum yield of $[\text{Tb}(\text{hfa})_3(\text{dpa})]_n$ was 9.5% (under CO₂) or 11.6% (under N₂) (**Table 4.1**). The τ_{obs} was estimated to be 0.13 ms (under CO₂) or 0.14 ms (under N₂) (**Table 4.1**).

The gas adsorption and desorption measurement of $[\text{Eu}_{0.1}\text{Tb}_{0.9}(\text{hfa})_3(\text{dpa})]_n$ was performed at 298 K (**Figure 4.12**). In the CO₂ adsorption measurements, a characteristic linear plot of the gas adsorption isotherm was observed. On the other hand, the N₂ gas adsorption behavior was not observed. The emission spectra of $[\text{Eu}_{0.1}\text{Tb}_{0.9}(\text{hfa})_3(\text{dpa})]_n$ under CO₂ and N₂ condition were measured (**Figure 4.13**). The emission intensity ratio between 542 nm (Tb(III)) and 612 nm (Eu(III)), denoted as $I_{\text{Eu}} / I_{\text{Tb}}$, depends on the gas condition. The calculated $I_{\text{Eu}} / I_{\text{Tb}}$ values were calculated to be 1.9 (under CO₂) and 1.8 (under N₂), respectively (**Table 4.1**). The recycling emission spectra between CO₂ and

N₂ were investigated for [Eu_{0.1}Tb_{0.9}(hfa)₃dpa]_n (Figure 4.13, inset). The coordination polymer exhibited reversible intensity ratio between Eu(III) and Tb(III). The reduction in $I_{\text{Eu}} / I_{\text{Tb}}$ values from CO₂ to CO₂/N₂ ratio of 1:9 was about 15% of that from CO₂ to N₂ (Table 4.3). Figure 4.14 showed the photographs of the luminescence of [Eu_{0.1}Tb_{0.9}(hfa)₃(dpa)]_n under UV light irradiation in N₂ and CO₂ conditions. The drastic change of emission color between N₂ and CO₂ conditions cannot be observed. The CO₂ gas caused the decrease of $I_{\text{Eu}} / I_{\text{Tb}}$ value. CO₂ gas adsorption promoted a lifetime change in the excited triplet state of the photosensitized hfa ligand. Previously, Kitagawa reported that the excited-state equilibrium between the ⁵D₄ (Tb(III)) and T₁ (hfa) states affected the change in emission lifetime.^[16] From the viewpoint of the emission lifetime in the excited triplet state, the emission lifetimes of [Gd(hfa)₃(dpa)]_n under CO₂ and N₂ conditions were measured (Table 4.4). The emission lifetime (τ_{obs}) in the CO₂ condition (0.36 ms) was shorter than that in the N₂ condition (0.38 ms).

The τ_{obs} of [Eu_{0.1}Tb_{0.9}(hfa)₃(dpa)]_n was estimated to be 0.13 ms (under CO₂) or 0.16 ms (under N₂) (Table 4.1). The τ_{obs} under degas condition were measured to be 0.15 ms. The pressure sensitivity was calculated to be 0.20 $\mu\text{s kPa}^{-1}$. This value is almost same as previously reported optical membrane sensor with Ru(II) (0.23 $\mu\text{s kPa}^{-1}$). The lifetime of [Eu_{0.1}Tb_{0.9}(hfa)₃(dpa)]_n is similar to that of previous optical Ru(II) membrane sensor.^[17]

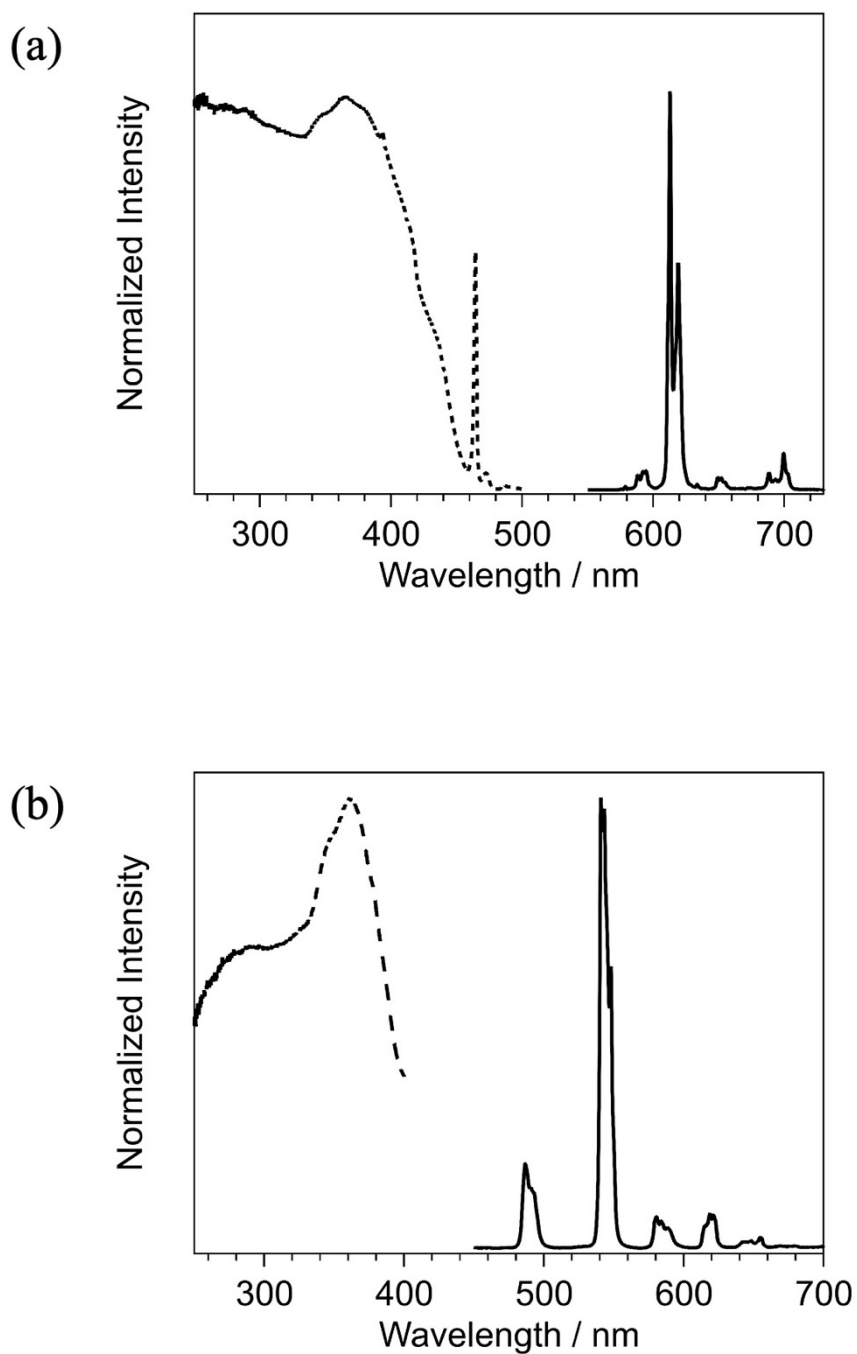


Figure 4.10 (a) Normalized emission (solid line, $\lambda_{\text{ex}} = 370$ nm) and excitation (dashed line, $\lambda_{\text{em}} = 616$ nm) spectra of $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$. (b) Normalized emission (solid line, $\lambda_{\text{ex}} = 370$ nm) and excitation (dashed line, $\lambda_{\text{em}} = 544$ nm) spectra of $[\text{Tb}(\text{hfa})_3(\text{dpa})]_n$.

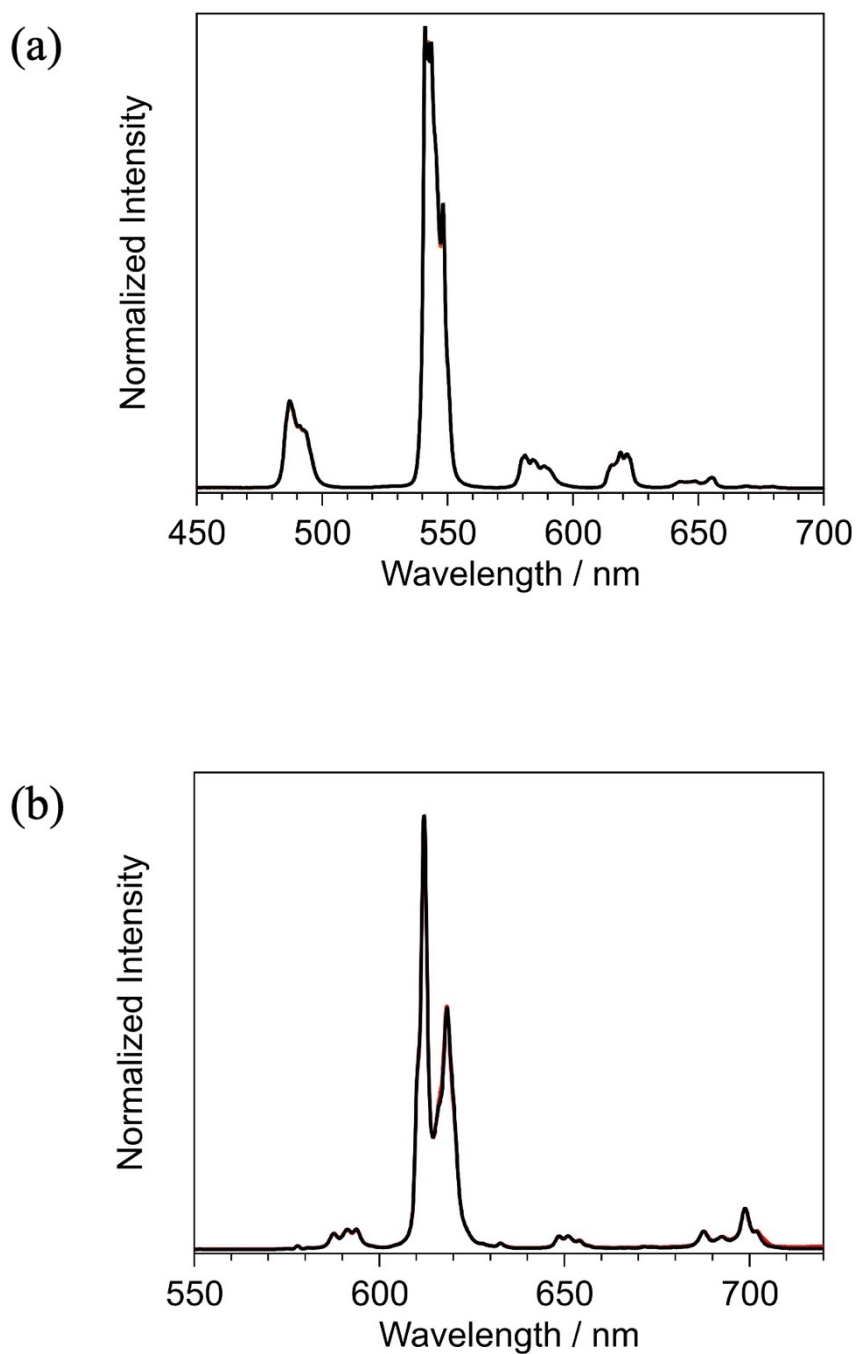


Figure 4.11 Normalized emission spectra ($\lambda_{\text{ex}} = 370$ nm) of (a) $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$ and (b) $[\text{Tb}(\text{hfa})_3(\text{dpa})]_n$ under CO₂ (red) and N₂ (black) condition.

Table 4.1 Photophysical parameters of lanthanide coordination polymers.

Compound	Gas	$\tau_{\text{obs}} / \text{ms}$	$\Phi_{\pi\pi^*} / \%$ ^[c]	$I_{\text{Eu}} / I_{\text{Tb}}$ ^[c]
[Eu(hfa)₃(dpa)]_n	CO ₂	0.81 ^[a]	61.3	--
	N ₂	0.81 ^[a]	61.1	--
[Tb(hfa)₃(dpa)]_n	CO ₂	0.13 ^[b]	9.5	--
	N ₂	0.14 ^[b]	11.6	--
[Eu_{0.1}Tb_{0.9}(hfa)₃(dpa)]_n	CO ₂	0.13 ^[b]	20.8	1.9
	N ₂	0.16 ^[b]	24.6	1.8

[a] $\lambda_{\text{ex}} = 355 \text{ nm}$, $\lambda_{\text{em}} = 610 \text{ nm}$. [b] $\lambda_{\text{ex}} = 355 \text{ nm}$, $\lambda_{\text{em}} = 540 \text{ nm}$, [c] $\lambda_{\text{ex}} = 370 \text{ nm}$.

Table 4.2 Photophysical parameters of **[Eu(hfa)₃(dpa)]_n**.

Compound	Gas	$\tau_{\text{obs}} / \text{ms}$ ^[a]	$k_{\text{r}} / \text{s}^{-1}$	$k_{\text{nr}} / \text{s}^{-1}$
[Eu(hfa)₃(dpa)]_n	CO ₂	0.81	9.2×10^2	3.2×10^3
	N ₂	0.81	9.2×10^2	3.1×10^3

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

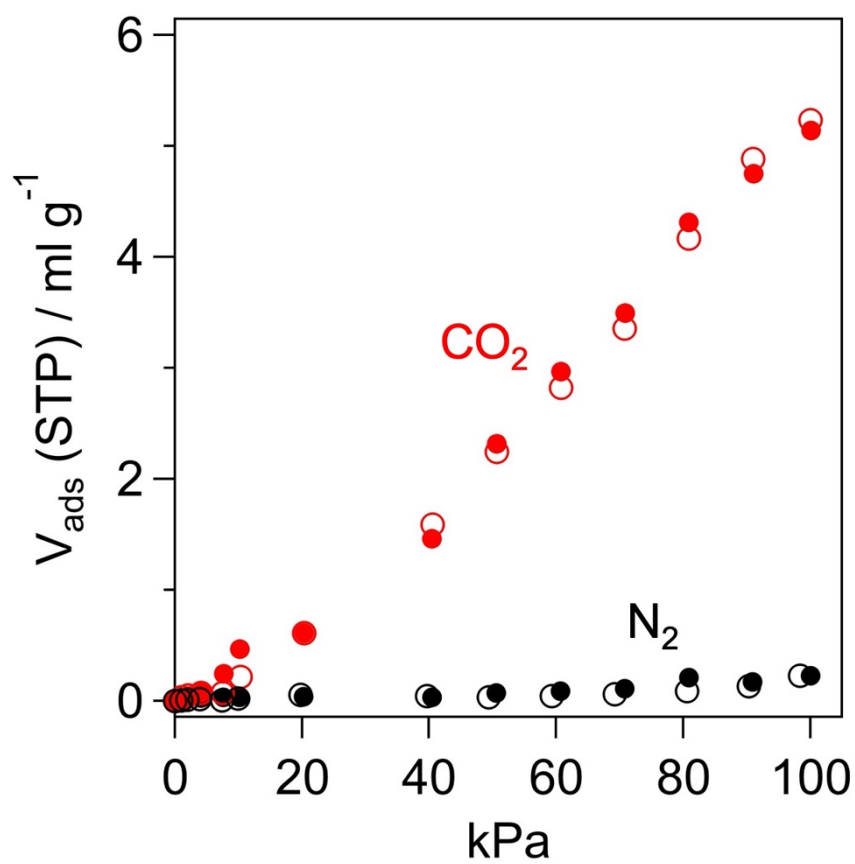


Figure 4.12 CO_2 (red) and N_2 (black) adsorption (solid symbols) and desorption (open symbols) isotherms of $[\text{Eu}_{0.1}\text{Tb}_{0.9}(\text{hfa})_3(\text{dpa})]_n$ at 298 K.

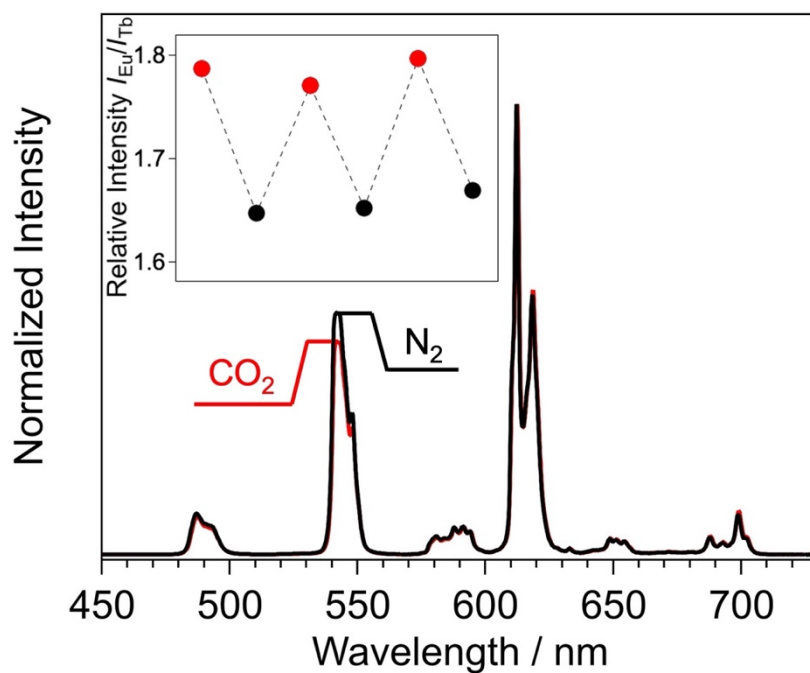


Figure 4.13 Normalized emission spectra of $[\text{Eu}_{0.1}\text{Tb}_{0.9}(\text{hfa})_3(\text{dpa})]_n$ under CO_2 (red) and N_2 (black) conditions ($\lambda_{\text{ex}} = 370 \text{ nm}$). Recycle measurement of emission intensity ratio between Eu(III) and Tb(III) in $[\text{Eu}_{0.1}\text{Tb}_{0.9}(\text{hfa})_3(\text{dpa})]_n$ (inset). The emission intensity ratios of $I_{\text{Eu}}/I_{\text{Tb}}$ are depended on the anisotropy of the mixed-crystals, which are different from data in Table 4.1.

Table 4.3 $I_{\text{Eu}} / I_{\text{Tb}}$ value of $[\text{Eu}_{0.1}\text{Tb}_{0.9}(\text{hfa})_3(\text{dpa})]_n$ under CO_2 , N_2 , $\text{CO}_2\text{-N}_2$ (1:9) conditions.

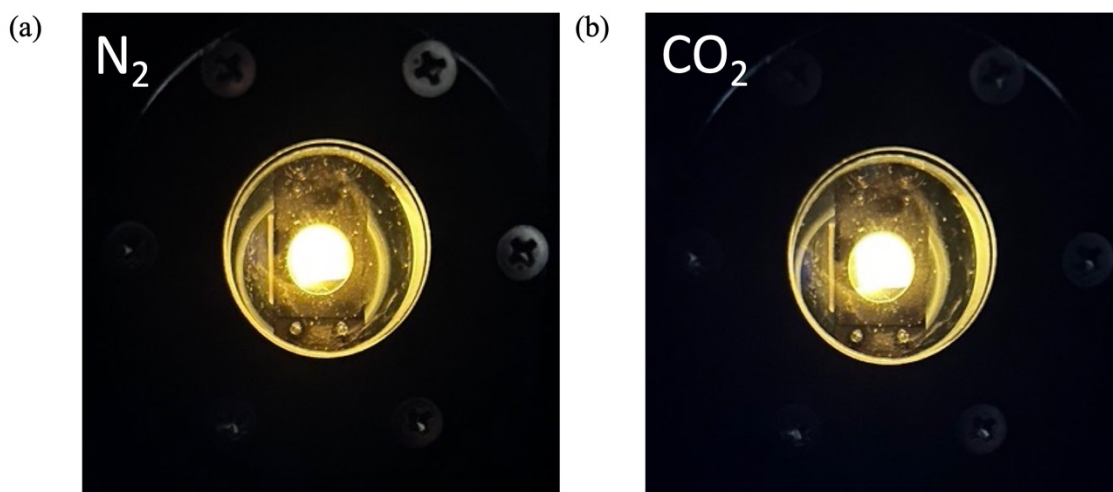
Compound	Gas	$I_{\text{Eu}} / I_{\text{Tb}}$
$[\text{Eu}_{0.1}\text{Tb}_{0.9}(\text{hfa})_3(\text{dpa})]_n$	CO_2	1.99
	$\text{CO}_2 : \text{N}_2 = 1 : 9$	1.97
	N_2	1.86

$\lambda_{\text{ex}} = 370$ nm. The emission intensity ratios of $I_{\text{Eu}}/I_{\text{Tb}}$ are depended on the anisotropy of the mixed-crystals, which are different from data in Table 4.1.

Table 4.4 Emission lifetime of $[\text{Gd}(\text{hfa})_3(\text{dpa})]_n$ under CO_2 and N_2 condition.

Compound	CO_2	N_2
$[\text{Gd}(\text{hfa})_3(\text{dpa})]_n$	0.380 ± 0.006 ms	0.365 ± 0.003 ms

$\lambda_{\text{ex}} = 355$ nm, $\lambda_{\text{em}} = 540$ nm.

**Figure 4.14** Photographs of the emission of $[\text{Eu}_{0.1}\text{Tb}_{0.9}(\text{hfa})_3(\text{dpa})]_n$ under (a) N_2 and (b) CO_2 condition ($\lambda_{\text{ex}}=370$ nm).

4.4 Conclusion

Novel lanthanide coordination polymers, $[\text{Ln}(\text{hfa})_3(\text{dpa})]_n$ ($\text{Ln} = \text{Eu}, \text{Tb}, \text{Gd}, \text{ or } \text{Eu}_{0.1}\text{Tb}_{0.9}$) were successfully synthesized. These coordination polymers constructed cylindrical structure with inner channel. The novel coordination polymers showed the CO_2 gas adsorption behavior. The photophysical properties of $[\text{Tb}(\text{hfa})_3(\text{dpa})]_n$ between CO_2 and N_2 condition were significantly changed, while that of $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$ were not. The fluorine atoms of the **hfa** unit on the inner surface of the cylinder promote CO_2 gas adsorption properties. The emission intensity ratio between Tb(III) and Eu(III) was changed by the gas adsorption behavior. The visualization of gas adsorption behavior is expected to be applied to next-generation optical materials.

4.5 References

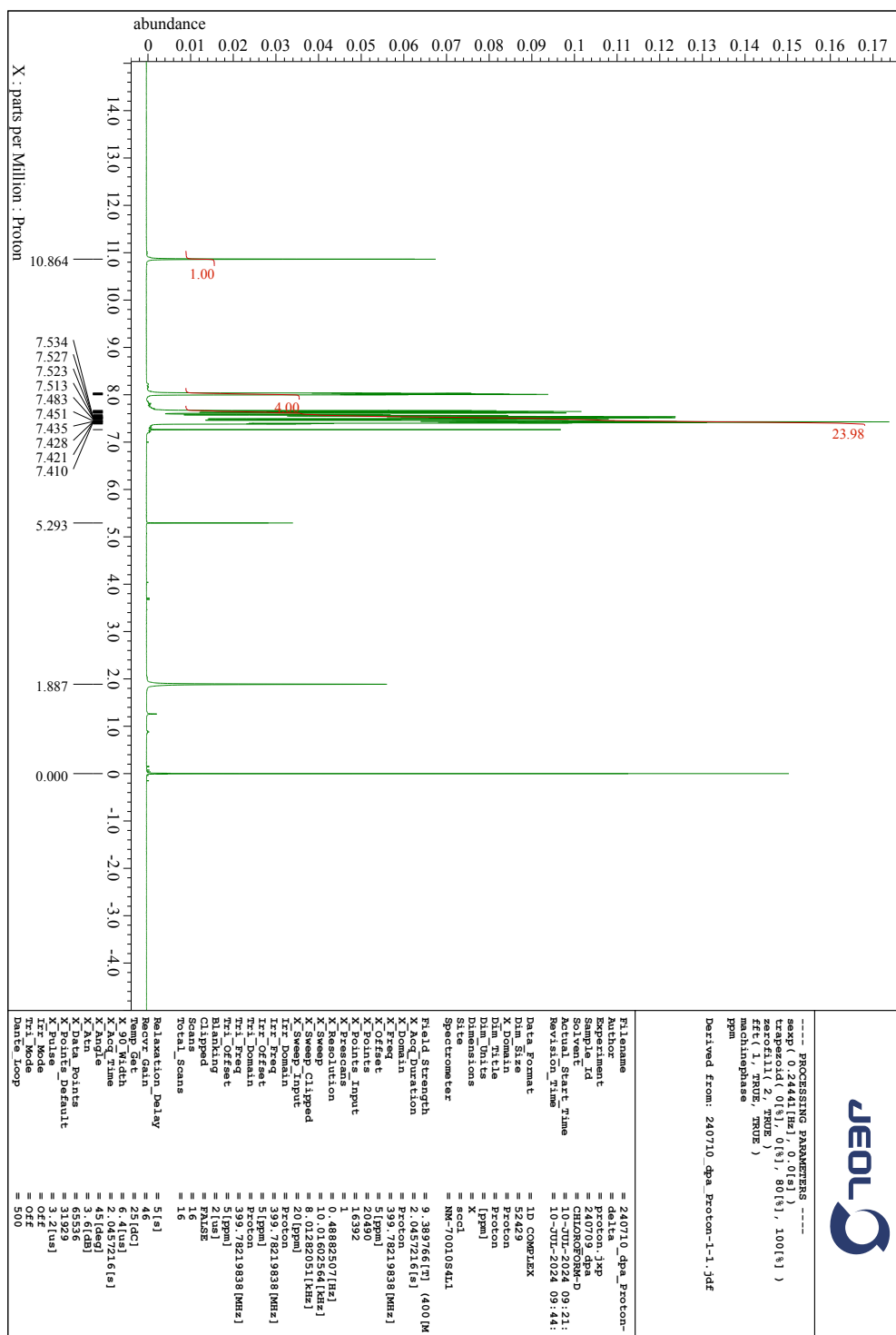
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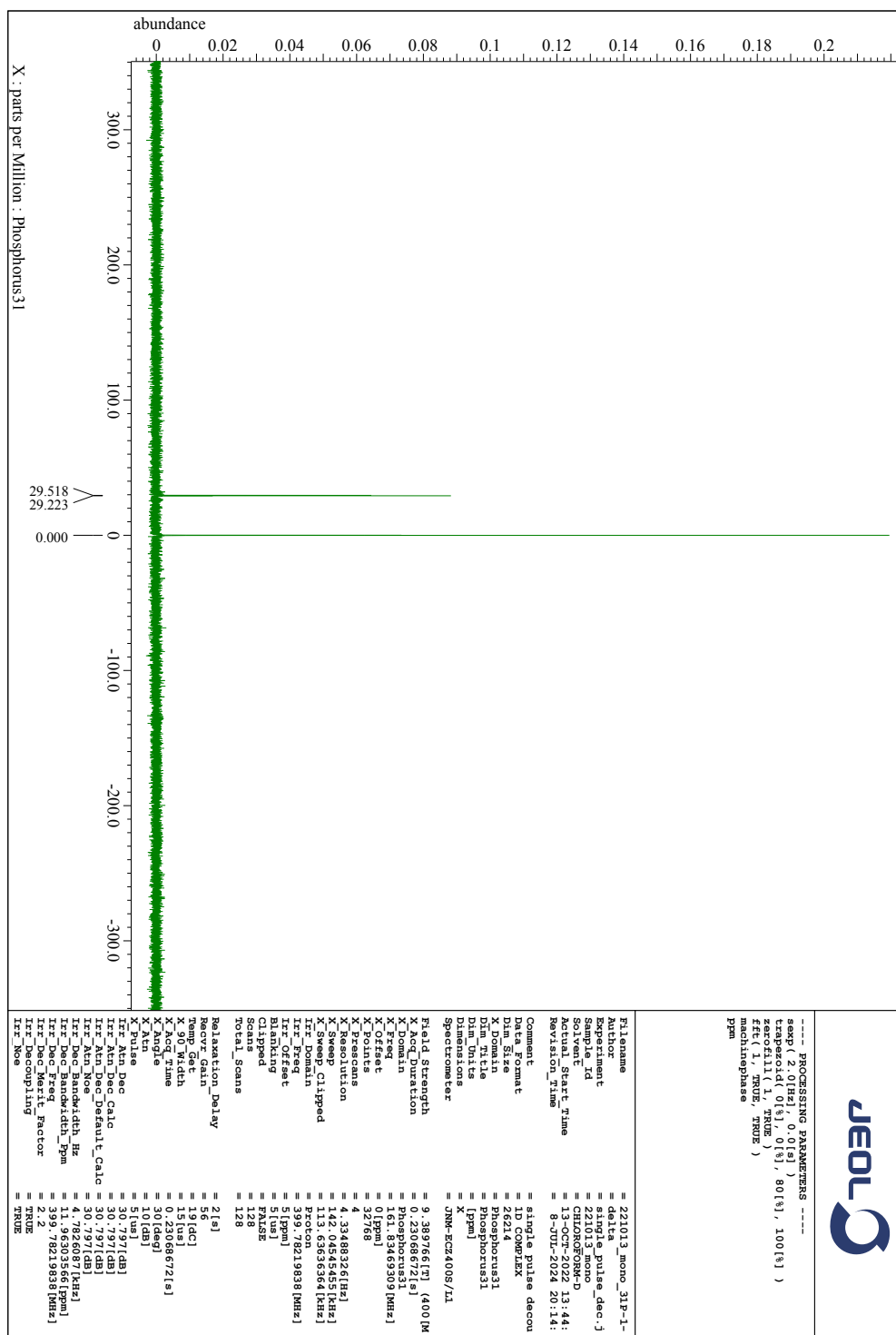
4.6 Appendix

Table 4.5 Crystallographic data of $[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$.

Compound	$[\text{Eu}(\text{hfa})_3(\text{dpa})]_n$
Crystal system	tetragonal
Space group	$I4_1/acd$
$a / \text{\AA}$	45.5365(7)
$b / \text{\AA}$	45.5365(7)
$c / \text{\AA}$	11.7266(3)
$\alpha / \text{deg.}$	90
$\beta / \text{deg.}$	90
$\gamma / \text{deg.}$	90
Volume / $\text{\AA}^3$	24316.0(10)
Z	32
$d_{\text{calc}} / \text{g cm}^{-3}$	1.498
Radiation	Mo $K\alpha$ ($\lambda = 0.71073$)
R_1	0.0529
wR_2	0.1224

Figure 4.15 ^1H NMR spectra of dpa.



Figure 4.17 ^{31}P NMR spectra of dpa.

Chapter 5

Summary

5.1 Summary and outlook

In **Chapter 1**, overviews of the lanthanide chemistry and luminescent lanthanide complexes are provided.

In **Chapter 2**, an Eu(III) coordination polymer with glass-forming ability was reported. The structural flexibility was enhanced by the introduction of an ethynyl group to the phosphine oxide ligand. The combination of structural flexibility and the formation of a hydrogen bonding network resulted in the glass-forming ability observed upon heat treatment. The photophysical properties were maintained after heat treatment.

In **Chapter 3**, the author investigated the molecular conformational arrangement of linker ligands with the same molecular formula. Three different Eu(III) coordination polymers with systematically varied amide bonds were prepared. The effect of molecular conformation on the structural and photophysical properties was evaluated.

In **Chapter 4**, the author demonstrated a gas adsorption and detection system based on Ln(III) coordination polymers. A cylindrical structure with an inner channel was constructed with the objective of adsorbing gas molecules. The inner channel surface was covered with fluorine atoms in the CF₃ moiety, which facilitated the adsorption of CO₂ molecules. Moreover, the luminescence intensity ratio of Eu(III) to Tb(III) in the Eu(III)/Tb(III) mixed coordination polymer exhibited a change in the presence of CO₂ and N₂ gases. These lanthanide coordination polymers are promising materials for visualising CO₂ adsorption.

The novel linker ligand designs presented in this paper offer a promising outlook for the further development of gas-adsorbed luminescent application materials and transparent luminescent materials. These materials are attractive as a prospective next generation of functional luminescent materials.

5.2 List of Publications

For thesis

- [1] Joe Hayashi, Sunao Shoji, Yuichi Kitagawa, Koji Fushimi, and Yasuchika Hasegawa “Amide-bridged Eu(III) coordination polymer for stable luminescent glass material”, *Materials letters*, 2021, 297, 130012. (Chapter 2)
- [2] Joe Hayashi, Sunao Shoji, Yuichi Kitagawa, and Yasuchika Hasegawa “Amorphous lanthanide complexes for organic luminescent materials”, *Coordination Chemistry Reviews*, 2022, 467, 214607. (Chapter 2)
- [3] Joe Hayashi, Shinichiro Iwamura, Yuta Nakasaka, Mengfei Wang, Sunao Shoji, Yuichi Kitagawa, Koji Fushimi, Shin R. Mukai and Yasuchika Hasegawa “Luminescence changeable CO₂-storage cylinder: Triple-stranded helical Eu(III)/Tb(III) fluorinated MOFs with amide linkers”, *Chemistry – A European Journal*, 2024, e202403224. (Chapter 4)
- [4] Joe Hayashi, Mengfei Wang, Yuichi Kitagawa, and Yasuchika Hasegawa “A systematic approach to controlling the molecular structure of the phenyleneamide moiety of the linker ligand in Eu(III) coordination polymers.”, manuscript in preparation. (Chapter 3)

Other Publications

- [1] Yasuchika Hasegawa, Natsumi Sato, Joe Hayashi, Yuichi Kitagawa, and Koji Fushimi “Thermo-Sensitive Eu^{III} Coordination Polymers with Amorphous Networks”, *ChemistrySelect*, 2021, 6, 2812-2816.

5.3 List of Presentations

- [1] ○Joe Hayashi, Sunao Shoji, Yuichi Kitagawa, Koji Fushimi, Tomohiro Seki, Hajime Ito, and Yasuchika Hasegawa, “Synthesis and photophysical properties of Eu(III) coordination polymers with amide groups”, 日本化学会第 100 春季年会, 1G4-37, 東京理科大学, 2020.3.22 (COVID-19 により中止、要旨集の発行をもって発表は成立)
- [2] ○林穰, 庄司淳, 北川裕一, 伏見公志, 長谷川靖哉, 「自己会合能を有する Eu(III)配位高分子の光物性」, 第 69 回 高分子討論会, PC0811, オンライン, 2020.9.18 (Poster Presentation).
- [3] ○Joe Hayashi, Sunao Shoji, Yuichi Kitagawa, Koji Fushimi, and Yasuchika Hasegawa, “Photophysical properties of a Eu(III) coordination polymer including amide groups”, 3rd G'Lowing Polymer Symposium in KANTO, B21, オンライン, 2020.11.28 (Oral Presentation).
- [4] ○林穰, 庄司淳, 北川裕一, 伏見公志, 長谷川靖哉, 「ガラス形成能を有する Eu(III)配位高分子の合成と光物性」, 第 55 回北海道支部研究発表会, O09, オンライン, 2021.1.28 (Oral Presentation).
- [5] ○林穰, 庄司淳, 北川裕一, 伏見公志, 長谷川靖哉, 「アミド基を有する Eu(III)配位高分子の合成と光物性」, 第 37 回希土類討論会, 2-08, オンライン, 2021.5.20 (Oral Presentation).
- [6] ○Joe Hayashi, Sunao Shoji, Yuichi Kitagawa, Koji Fushimi, and Yasuchika Hasegawa, “ Synthesis and photophysical properties of amide-bridged Eu(III) coordination polymers”, SNCPP21, P-09, オンライン, 2021.6.12 (Oral Presentation).
- [7] ○林穰, 庄司淳, 北川裕一, 伏見公志, 長谷川靖哉, 「アミド基を有する発光性 Eu(III)配位高分子のガラス状態形成」, 第 70 回 高分子討論会, 3D08, 北海道大学, 2021.9.8 (Oral Presentation).
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[9] ○Joe Hayashi, Sunao Shoji, Yuichi Kitagawa, Koji Fushimi, and Yasuchika Hasegawa, “Synthesis and photophysical properties of Eu(III) coordination polymers including amide groups”, 第 72 回 錯体化学討論会, 1PF-45, 九州大学, 2022.9.26 (Poster Presentation).

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[12] ○Joe Hayashi, Wang Mengfei, Yuichi Kitagawa, and Yasuchika Hasegawa, “Gas detection of Eu (III) /Tb (III) coordination polymers with triple-stranded helical structure”, 第 74 回 錯体化学討論会, 3Fb-01, 岐阜大学, 2024.9.20 (Oral Presentation).

5.4 Award

[1] 「学生講演賞」 第 40 回希土類討論会.

5.5 Patent

[1] 長谷川靖哉, 林穰, 北川裕一, 庄司淳, 伏見公志 「アモルファス希土類配位高分子」 (特願 2021-074135)

5.6 Acknowledgments

I would like to my sincere gratitude to Prof. Yasuchika Hasegawa, Laboratory of Advanced Materials Chemistry (AMC Lab) in Hokkaido University, as my main supervisor for his continuous support and kind instruction of this study.

I wish to thank my gratitude to Assoc. Prof. Yuichi Kitagawa in AMC Lab for their kind suggestions and advice for this study.

I would also like to thank my gratitude to Prof. Kazuki Sada, Prof. Shin Mukai, and Assoc. Prof. Koji Fushimi in Hokkaido University for his helpful advice as my sub supervisor.

I wish to thank my gratitude to Dr. Sunao Shoji in Nara Women's University and Dr. Mengfei Wang in AMC Lab for their kind support of this study.

I also like to show my gratitude, Prof. Clémence Allain in ENS Paris-Saclay for accepting for joining the research as an internship student.

I would like to thank the members of AMC Lab for supporting my daily work and sharing precious time.

I also appreciate the financial support of the Japan Society for the Promotion of Science (JSPS) with their Research Fellowship for Young Scientists program.

Finally, I am particularly thankful to my family for their continuous support and understanding of my student life.

March 2025

Sapporo, Japan

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