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Study on Circularly Polarized Luminescence and Electronic Structure of Chiral Lanthanide Complexes

キラル希土類錯体の円偏光発光と
電子構造に関する研究

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Chapter 1

GENERAL INTRODUCTION

1.1 Lanthanides

1.1.1 Lanthanides

Lanthanides have attracted attention in the fields of light-emitting materials, magnetic materials, and medical field due to their unique chemical and physical properties.^[1–6] Lanthanides are a group of elements consisting of fifteen elements from La (atomic number 57) to Lu (atomic number 71) in the periodic table (**Figure 1.1**). They are called rare-earths together with Sc and Y because of their chemical similarities. Among the lanthanides, fourteen elements from Ce to Lu have electrons in the f-orbital and show different characteristics from organic molecules and transition metal complexes. The electronic configurations of lanthanides are summarized in **Table 1.1**. Lanthanides are generally stable in the trivalent state, but some elements are also stable in the divalent or tetravalent state. For example, Eu and Yb are stable because their 4f orbitals are half-filled (Eu(II): [Xe]4f⁷) and closed (Yb(II): [Xe]4f¹⁴) shell in the divalent state. Ce and Tb are also stable in the tetravalent state due to empty (Ce(IV): [Xe]) and half-filled (Tb(IV): [Xe]4f⁷) of the 4f orbitals.

The diagram illustrates the periodic table with the Lanthanide and Actinide series highlighted. The Lanthanide series (La to Lu) is shown as a separate row below the main table, connected by lines to their respective positions in the 4f block of the main table. The Actinide series (Ac to Lr) is shown as a separate row below the Lanthanides, connected by lines to their respective positions in the 5f block of the main table. The Lanthanides are labeled 'Lanthanides' and the Actinides are labeled 'Actinides'.

Figure 1.1 Lanthanides and rare-earths in the periodic table.

Table 1.1 Electronic configurations of lanthanides.

Atomic number	Element	Electronic configuration	
		Atom	Trivalent ion
57	La	[Xe]5d ¹ 6s ²	[Xe]
58	Ce	[Xe]4f ¹ 5d ¹ 6s ²	[Xe]4f ¹
59	Pr	[Xe]4f ³ 6s ²	[Xe]4f ²
60	Nd	[Xe]4f ⁴ 6s ²	[Xe]4f ³
61	Pm	[Xe]4f ⁵ 6s ²	[Xe]4f ⁴
62	Sm	[Xe]4f ⁶ 6s ²	[Xe]4f ⁵
63	Eu	[Xe]4f ⁷ 6s ²	[Xe]4f ⁶
64	Gd	[Xe]4f ⁷ 5d ¹ 6s ²	[Xe]4f ⁷
65	Tb	[Xe]4f ⁹ 6s ²	[Xe]4f ⁸
66	Dy	[Xe]4f ¹⁰ 6s ²	[Xe]4f ⁹
67	Ho	[Xe]4f ¹¹ 6s ²	[Xe]4f ¹⁰
68	Er	[Xe]4f ¹² 6s ²	[Xe]4f ¹¹
69	Tm	[Xe]4f ¹³ 6s ²	[Xe]4f ¹²
70	Yb	[Xe]4f ¹⁴ 6s ²	[Xe]4f ¹³
71	Lu	[Xe]4f ¹⁴ 5d ¹ 6s ²	[Xe]4f ¹⁴

The radial distribution function of the orbitals is shown in **Figure 1.2**.^[7] Since the 4f orbitals are distributed closer to the nucleus, they are shielded by the outer 5s and 5p orbitals. Therefore, the 4f orbitals tend to be less involved in bonding with neighboring atoms and their chemical and physical properties are relatively insensitive to the surrounding environment. As a result, the energy levels of the 4f orbitals in lanthanides are shown in Dieke diagram (**Figure 1.3**).^[8] The energy levels are described by a Russell-Saunders term symbol. (^{2S+1}L_J) where *S*, *L*, and *J* are the total spin quantum number, total orbital quantum number, and total angular momentum quantum number, respectively.

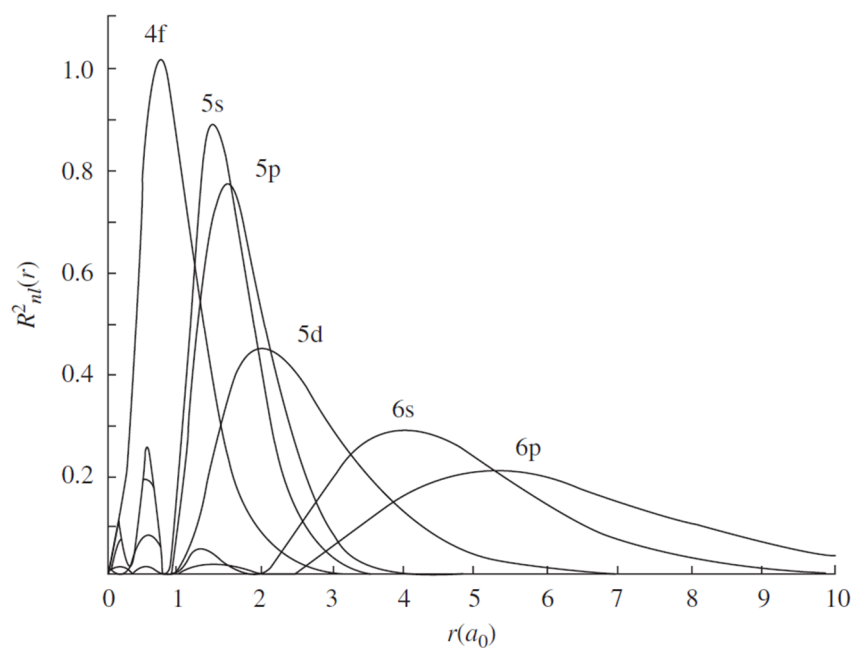


Figure 1.2 Radial part of the wavefunction of the orbitals reprinted from reference.^[7]

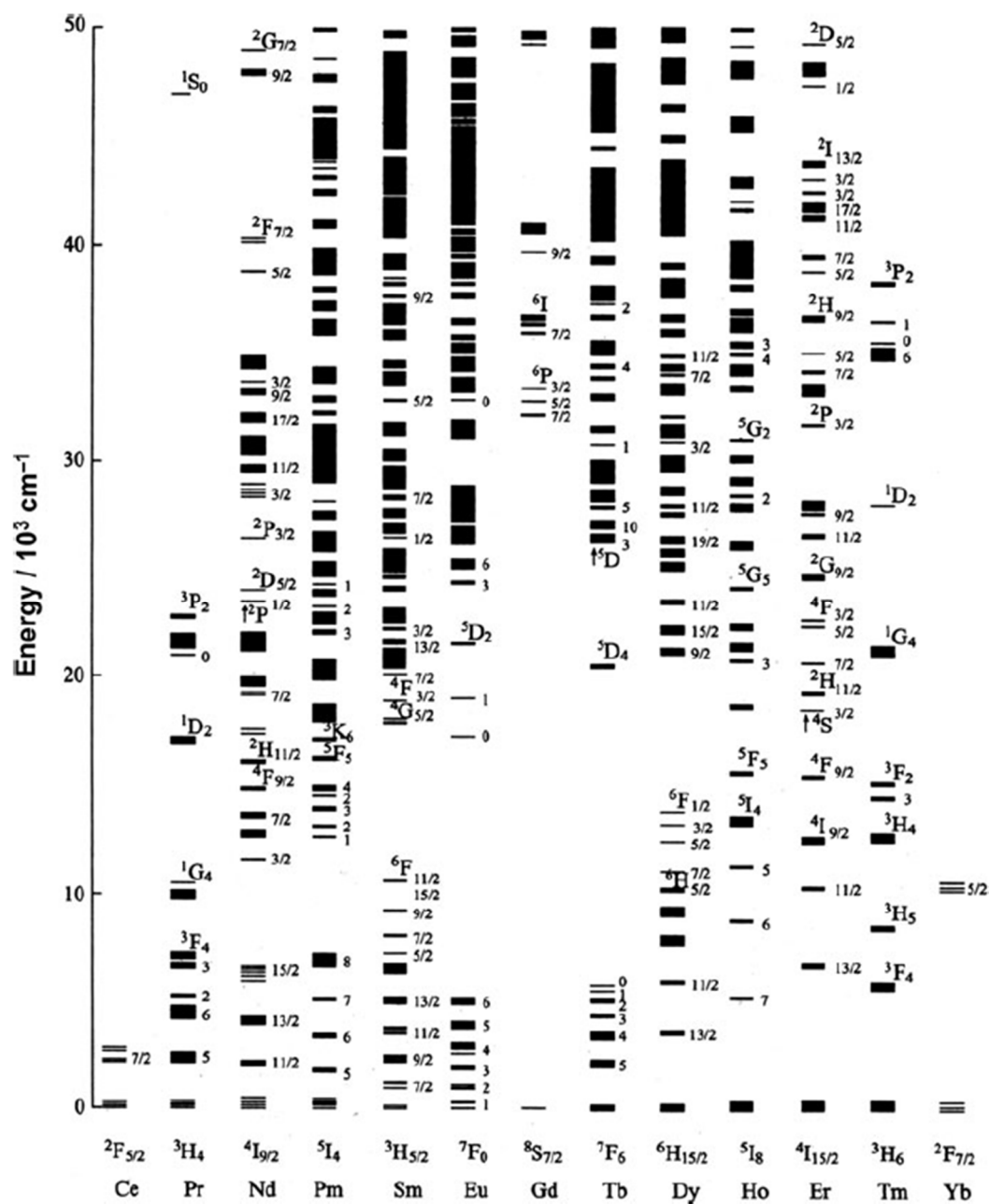


Figure 1.3 Dieke diagram of lanthanide ions reprinted from reference.[8]

1.1.2 Luminescence properties of lanthanide compounds

Lanthanide ions react with hard Lewis bases such as O, N, and F to form oxides, fluoride, complexes, and clusters. Among them, lanthanide complexes composed of lanthanide ions and organic ligands show long-lived luminescence with high color purity originating from the 4f-4f transition, and are expected to be applied as luminescent materials.^[1-6]

As mentioned above, electrons in the 4f orbitals of lanthanides are shielded and are less sensitive to external environment. Therefore, the structural change between the ground and excited states is minimal, leading to the slight difference in the shape and nuclear coordinate of the potential energy curve (**Figure 1.4**). While organic molecules are known to exhibit broad luminescence as a result of the large shift in nuclear coordinates before and after excitation, lanthanide emission is typically characterized by a narrow full width at half maximum. The emission is specific to the kind of lanthanide ions corresponding to the energy difference between the ground and excited state of the

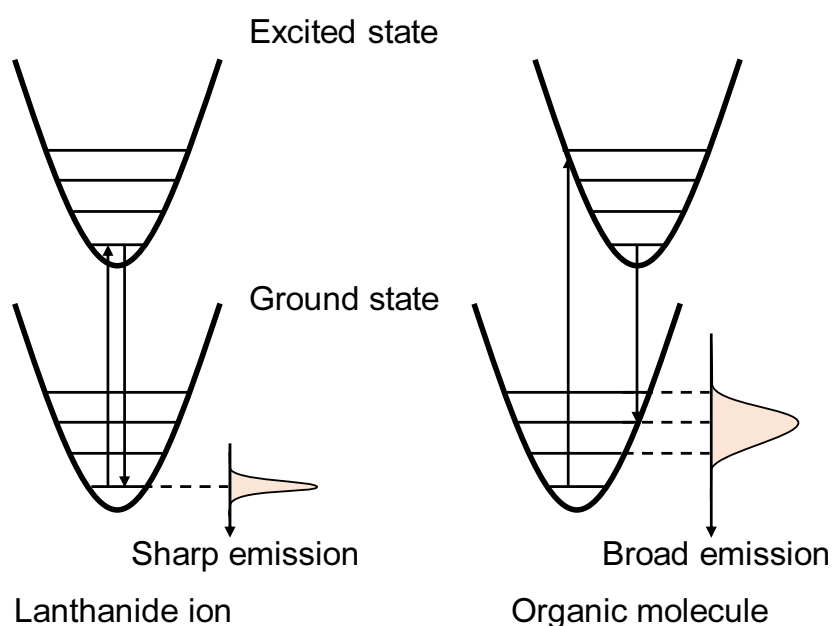


Figure 1.4 Potential energy curve of lanthanide and organic molecule.

Dieke diagram shown in **Figure 1.3**. The emission wavelengths vary from near-infrared to visible light. For example, Eu(III) shows red emission around 610 nm, Tb(III) shows green emission around 540 nm, and Yb(III) shows near-infrared emission around 980 nm (**Figure 1.5**).^[5]

However, the 4f-4f transition is parity forbidden, resulting in a very small absorption coefficient for lanthanide ions ($\epsilon < 10 \text{ M}^{-1} \text{ cm}^{-1}$), which limits their ability to absorb excitation light sufficiently. Therefore, strong luminescence is achieved by utilizing the absorption of organic ligands, whose absorption coefficient is much higher ($\epsilon \sim 10^4 - 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) than that of lanthanide ions. The transferring the excitation energy to the lanthanide ion, strong luminescence of lanthanide ion can be achieved (antenna effect). Therefore, the light absorption ability of the organic ligand and the efficiency of energy transfer from the ligand to the lanthanide ion are important for the achievement of strong luminescence.

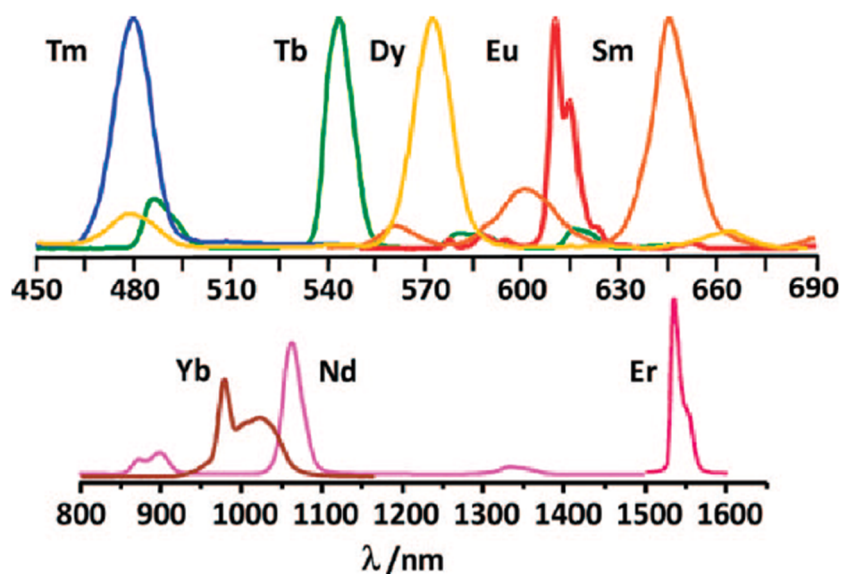


Figure 1.5 Emission spectra of lanthanide complexes reprinted from the reference.^[5]

The energy diagram in the luminescence of the lanthanide complex is shown in **Figure 1.6**. First, the ligand is excited from the ground singlet state (S_0) to the excited singlet state (S_1). Thereafter, the ligand undergoes intersystem crossing (ISC) from S_1 to the excited triplet state (T_1). The energy transfer (EnT) from T_1 to the excited state of lanthanide ions occurs, and emission occurs during the transition from the excited states to the ground state of lanthanide ions. The energy of the lowest excited level (5D_0) of Eu(III) is about $17,200\text{ cm}^{-1}$, and the energy of T_1 should be higher than that. However, if the energy of T_1 is close to the energy of 5D_0 , there is a back energy transfer (BEnT) process that returns energy from 5D_0 to T_1 . Therefore, the BEnT process must be suppressed for efficient energy transfer, and the energy level of T_1 has a significant impact on the luminescence efficiency. Recently, it has become clear that not only the energy level of T_1 but also the lifetime of T_1 state is important for the energy transfer efficiency.^[9] In the systems where the energy level of T_1 is close to the excited level of the lanthanide ions, the BEnT process occurs. If the lifetime of T_1 state is longer than that of lanthanide ions, the forward energy transfer (T_1 to lanthanide ions) occurs again before

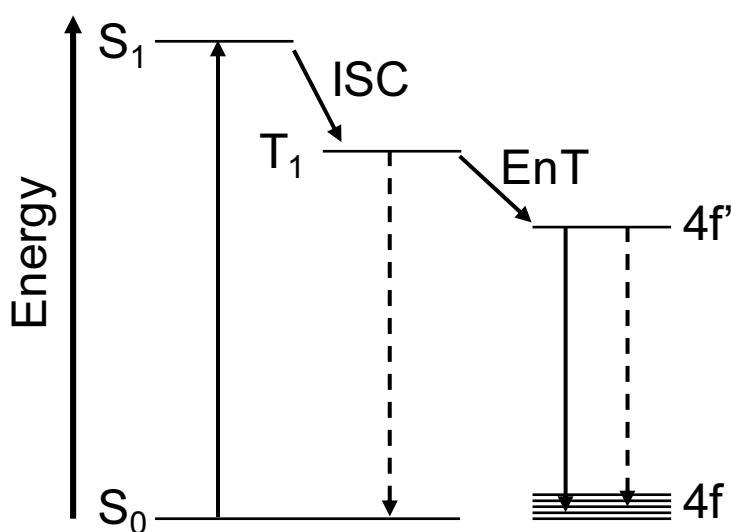


Figure 1.6 Energy diagram of lanthanide complexes.

the quenching from the T_1 state. This phenomenon is called excited-state equilibrium, resulting in high energy transfer efficiency.

In order to achieve strong luminescence of lanthanide complexes, the balance of the radiative rate constant (k_r) and the non-radiative rate constant (k_{nr}) is also important. Higher k_r than that of k_{nr} are required to increase the emission quantum yields. The k_r is strongly affected by the symmetry around the lanthanide ion. Miyata et al. reported that k_r increases in lanthanide complexes with eight-coordinate trigonal dodecahedron structure (8-TDH) compared to the eight-coordinate square antiprism structure (8-SAP) structure.^[10] Decreasing symmetry in lanthanide complexes with nine-coordinate mono-capped square-antiprismatic structure (9-SAP) and seven-coordinate mono-capped octahedron structure (7-MCO) also enhances the k_r value.^[11,12] The k_{nr} is greatly affected by the vibrational relaxation of organic ligands. To reduce the k_{nr} , its vibration must be suppressed. Surrounding the lanthanide ions with low vibrational ligands is the useful way to decrease the k_{nr} value. For example, ligands with C-F ($1,200\text{ cm}^{-1}$) and P=O ($1,120\text{ cm}^{-1}$) bonds instead of O-H ($3,600\text{ cm}^{-1}$) and C-H ($2,900\text{ cm}^{-1}$) bonds are suitable for suppressing vibration-induced deactivation.^[13]

Since the $^5D_0 \rightarrow ^7F_1$ transition of Eu(III) complexes is a magnetic dipole transition allowed and electric dipole transition forbidden, the k_r value can be estimated by calculation using the intensity ratio of emission spectrum (Equation (1.1)).^[14]

$$k_r = \frac{1}{\tau_{\text{rad}}} = A_{\text{MD},0} n^3 \frac{I_{\text{tot}}}{I_{\text{MD}}} \quad (1.1)$$

In this equation, $A_{\text{MD},0}$, 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 intensity ratio of the total ($^5D_0 \rightarrow ^7F_{0-6}$) and $^5D_0 \rightarrow ^7F_1$ transition in the emission spectra, respectively. The k_{nr} , the radiative emission lifetime (τ_{rad}), the emission quantum yield of the 4f-4f transition (internal quantum yield: $\Phi_{\text{f-f}}$), and energy transfer efficiency

(η_{sens}) can also be calculated using k_r , observed emission lifetime (τ_{obs}), and emission quantum yield of ligand excitation (Φ_{tot}) by Equation (1.2)-(1.4).

$$\Phi_{\text{f-f}} = \frac{k_r}{k_r + k_{\text{nr}}} = \frac{\tau_{\text{obs}}}{\tau_{\text{rad}}} \quad (1.2)$$

$$k_{\text{nr}} = \frac{1}{\tau_{\text{obs}}} - \frac{1}{\tau_{\text{rad}}} \quad (1.3)$$

$$\eta_{\text{sens}} = \frac{\Phi_{\text{tot}}}{\Phi_{\text{f-f}}} \quad (1.4)$$

1.2 Circularly polarized luminescence

1.2.1 Electromagnetic waves

An electromagnetic wave is a transverse wave generated by the oscillation of electric and magnetic field. The oscillation of the electric and magnetic fields is always perpendicular to their direction of travel, and the phases are always equal (**Figure 1.7**). The properties of electromagnetic waves differ significantly depending on their wavelength. Among electromagnetic waves, ultraviolet light is distinguished as having a wavelength of 1 nm to 380 nm, visible light as 380 nm to 780 nm, and infrared light as 780 nm to 1 mm, and electromagnetic waves in this wavelength range are often called "light". Electromagnetic waves with shorter wavelengths (higher energy) than ultraviolet light include X-rays and γ -rays, which have a high penetrability into materials. In chemistry, they are used for structural analysis and elemental identification, whereas in medicine, they are used for cancer treatment and computed tomography (CT) scans. On the other hand, electromagnetic waves with longer wavelengths (lower energy) than infrared light are called radio waves. Although they have less energy, they can interact

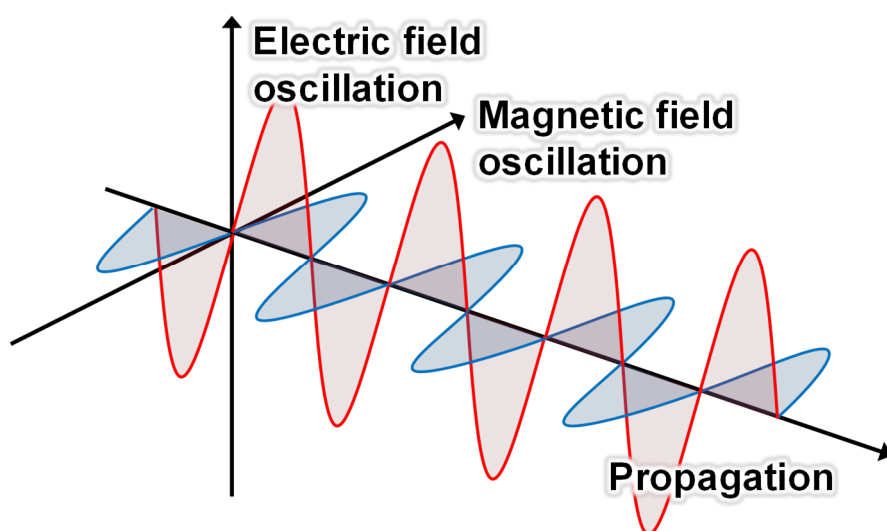


Figure 1.7 The oscillation of electromagnetic wave.

with substances, depending on their energy bands. It is used chemically in nuclear magnetic resonance (NMR) for example. They are also commonly used in communications, radars, and other applications.

As the direction of the oscillation of the electric and magnetic fields of light (electromagnetic waves) are always orthogonal, the direction of the magnetic field is determined at the same time that the direction of the electric field is determined. Therefore, when considering the direction of oscillation of electromagnetic waves, only the direction of the oscillation of the electric field is considered in most cases. Considering light of a single wavelength (wavenumber), the electric field vector $\mathbf{E}$ varies sinusoidally with position in the traveling direction (z direction) and time t (**Figure 1.7**). The magnitude of the electric field vector at position z and time t , $|\mathbf{E}(z,t)|$, is expressed by Equation (1.5),

$$|\mathbf{E}(z,t)| = A \cos(kz - \omega t + \delta) \quad (1.5)$$

where A , k , ω and δ are the amplitude, the wavenumber, the angular frequency, and the initial phase at $z=0$ and $t=0$, respectively.

Natural light such as direct sunlight is a mixture of electric fields of various wavelengths, phases, and oscillation directions. Since natural light has a uniform oscillation direction in all directions, the oscillation direction of the synthesized electric field vector is not biased in any particular direction. Such a state of light is called unpolarized light. On the other hand, when the direction of oscillation of the synthesized electric field vector is biased in a certain direction, the light is called polarized light.

1.2.2 Polarized light

When the electric field of an electromagnetic wave is observed from the z direction, the electric field vector oscillates on the xy plane (**Figure 1.8**) and can be decomposed into an x component (**Figure 1.8**: blue arrow) and a y component (**Figure 1.8**: green arrow). The x -component E_x and y -component E_y of the electric field vector E are expressed by equation (1.6) and (1.7), respectively.

$$E_x = A_x \cos(kz - \omega t + \delta_x) \quad (1.6)$$

$$E_y = A_y \cos(kz - \omega t + \delta_y) \quad (1.7)$$

Equation (1.8) holds when the phase of the x -component coincides with that of the y -component ($\delta_x = \delta_y$).

$$\frac{E_x}{E_y} = \frac{A_x}{A_y} = \tan \alpha \quad (1.8)$$

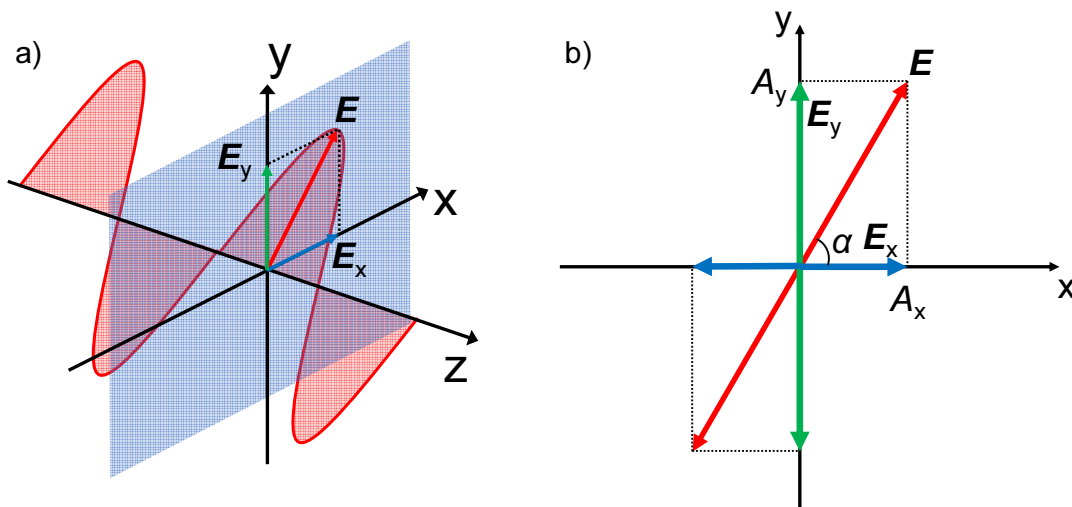


Figure 1.8 The oscillation of electric field of linearly polarized light.

This indicates that the electric field vector E is always oscillating tilted by an angle α , and this light is called linearly polarized light. On the other hand, when the amplitude of the x and y components are equal ($A_x=A_y$) and the phase difference is $\pm\pi/2$ ($\delta_y-\delta_x=\pm\pi/2$), equations (1.6) and (1.7) are written as equations (1.9) and (1.10) respectively.

$$E_x = A \cos(kz - \omega t) \quad (1.9)$$

$$\begin{aligned} E_y &= A \cos\left(kz - \omega t \pm \frac{\pi}{2}\right) \\ &= \mp A \sin(kz - \omega t) \end{aligned} \quad (1.10)$$

From equations (1.9) and (1.10), equation (1.11) is derived.

$$E_x^2 + E_y^2 = A^2 \quad (1.11)$$

Equation (1.11) is the equation of a circle of radius A . This means that the electric field vector lies on the circumference of a circle of radius A , and the electric field vector rotates on the circumference in one direction. This is called circularly polarized light (**Figure 1.9**). There are two types of circularly polarized light. In general, circularly polarized light in which the electric field vector rotates to the right when viewed from the z direction is called right-circularly polarized light, and circularly polarized light in which it rotates to the left is called left-circularly polarized light. Based on this definition, when the phase

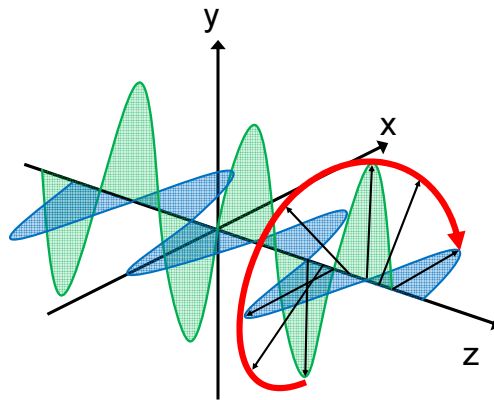


Figure 1.9 The oscillation of electric field of circularly polarized light.

of the y component is more advanced than that of the x component ($\delta_y - \delta_x = \pi/2$), the light is right circularly polarized, and when the phase of the x component is more advanced than that of the y component ($\delta_y - \delta_x = -\pi/2$), the light is left circularly polarized.

Circularly polarized light is obtained by adding a phase difference between the x - and y -component light. Generally, a waveplate is used to phase-differ the light. Waveplates are made of birefringent materials. Birefringence is a phenomenon in which the refractive index of light passing through a material differs on each vibrating surface. Since the refractive index depends on the polarization of the oscillating direction of the electric field of the light passing through the material, birefringence is caused by using a material whose polarization differs according to the direction. There are various types of waveplates, but the most commonly used are quarter waveplates and half waveplates. Quarter waveplates provide a phase difference of $\pi/2$ with respect to the direction of oscillation of the electric field vector of the incident light, so circular polarization is obtained by incident linearly polarized light at 45° angle to the quarter waveplate. The circularly polarized light can also be changed to linearly polarized light by incident circularly polarized light. On the other hand, the half wave plate provides a phase difference of π to the direction of oscillation of the electric field vector of the incident light, so that the direction of rotation can be reversed when circularly polarized light is incident. When the phases of the x and y components are other than 0 , $\pm\pi/2$, and $\pm\pi$, equations (1.9) and (1.10) can be transformed as follows.

$$\frac{E_x}{A_x} = \cos(kz - \omega t) \quad (1.12)$$

$$\frac{E_y}{A_y} = \cos(kz - \omega t + \phi) \quad (1.13)$$

$$= \cos(kz - \omega t)\cos\phi - \sin(kz - \omega t)\sin\phi$$

Substituting equation (1.12) into equation (1.13), equation (1.14) and (1.15) are obtained.

$$\frac{E_y}{A_y} = \frac{E_x}{A_x} \cos \phi - \sqrt{1 - \cos^2(kz - \omega t)} \sin \phi \quad (1.14)$$

$$\left(\frac{E_y}{A_y}\right)^2 + \left(\frac{E_x}{A_x}\right)^2 - 2\frac{E_x E_y}{A_y A_x} \cos \phi = \sin^2 \phi \quad (1.15)$$

Since equation (1.15) is an elliptic equation, the electric field vector draws an ellipse when the phase difference between the x and y components is other than 0, $\pm\pi/2$, and $\pm\pi$, and light at that time is called elliptically polarized light.

1.2.3 Circularly polarized luminescence

Circularly polarized luminescence (CPL) is a specific photophysical phenomenon in which chiral compounds emit light with different intensities of left and right circularly polarized light.^[15,16] It has a wide range of applications, including asymmetric light reactions,^[17] plant growth,^[18] three-dimensional displays^[19], security inks,^[20] etc. The intensity of CPL is described using the dissymmetry factor g_{CPL} , which is defined using the intensity of left circularly polarized light I_L and right circularly polarized light I_R as in Equation (1.16)^[15,21]

$$g_{\text{CPL}} = \frac{2(I_L - I_R)}{I_L + I_R} \quad (1.16)$$

From equation (1.16), g_{CPL} takes values from -2 to 2 . $g_{\text{CPL}} = -2$ and 2 mean that only right and left circularly polarized light are observed, respectively, while $g_{\text{CPL}} = 0$ means that there is no intensity difference between left and right circularly polarized light. The ratio of I_R to I_L according to g_{CPL} is summarized as **Table 1.2**.

Table 1.2 The relationship between g_{CPL} and the intensity of left- and right-handed circularly polarized light.

g_{CPL}	$I_L / \%$	$I_R / \%$
0	50	50
0.0001	50.0025	49.9975
0.001	50.025	49.975
0.01	50.25	49.75
0.1	52.5	47.5
1	75	25
2	100	0

The g_{CPL} can also be written in terms of electric and magnetic dipole moments by the following equation. ^[15,21]

$$g_{\text{CPL}} = 4 \frac{|\vec{\mu}| |\vec{m}| \cos \theta_{\mu,m}}{|\vec{\mu}|^2 + |\vec{m}|^2} \quad (1.17)$$

From the equation, when $\vec{\mu}$ and $\vec{m}$ are equal in magnitude and the angle between the vectors is 0° , the g_{CPL} takes a maximum value of 2. It is important to approach this condition in order to create an ideal circularly polarized luminescent material. In general, the magnitude of the electric dipole moment is much larger than that of the magnetic dipole moment in the electronic transitions of organic compounds and transition metal complexes. Therefore, in order to create an ideal circularly polarized luminescent material, it is necessary to reduce the magnitude of the electric dipole moment and increase the magnitude of the magnetic dipole moment.

1.2.4 Chiral lanthanide complexes

Lanthanide complexes with chiral organic ligands exhibit CPL. In 1975, Richardson reported the observation of CPL from Tb(III) and Eu(III) complexes with chiral ligands containing carboxy groups such as L-malic acid and L-aspartic acid.^[22] Brittain synthesized Eu(III) complexes with chiral β -diketonate (camphorate derivatives) ligands.^[23] Since these reports, the Eu(III) complexes with various types of chiral ligands have been reported. Typical chiral ligands have the chiral moieties such as BINAP (2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl),^[24] Pybox (bis(oxazolonyl)pyridine),^[25] DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid),^[26] 1,4,7-

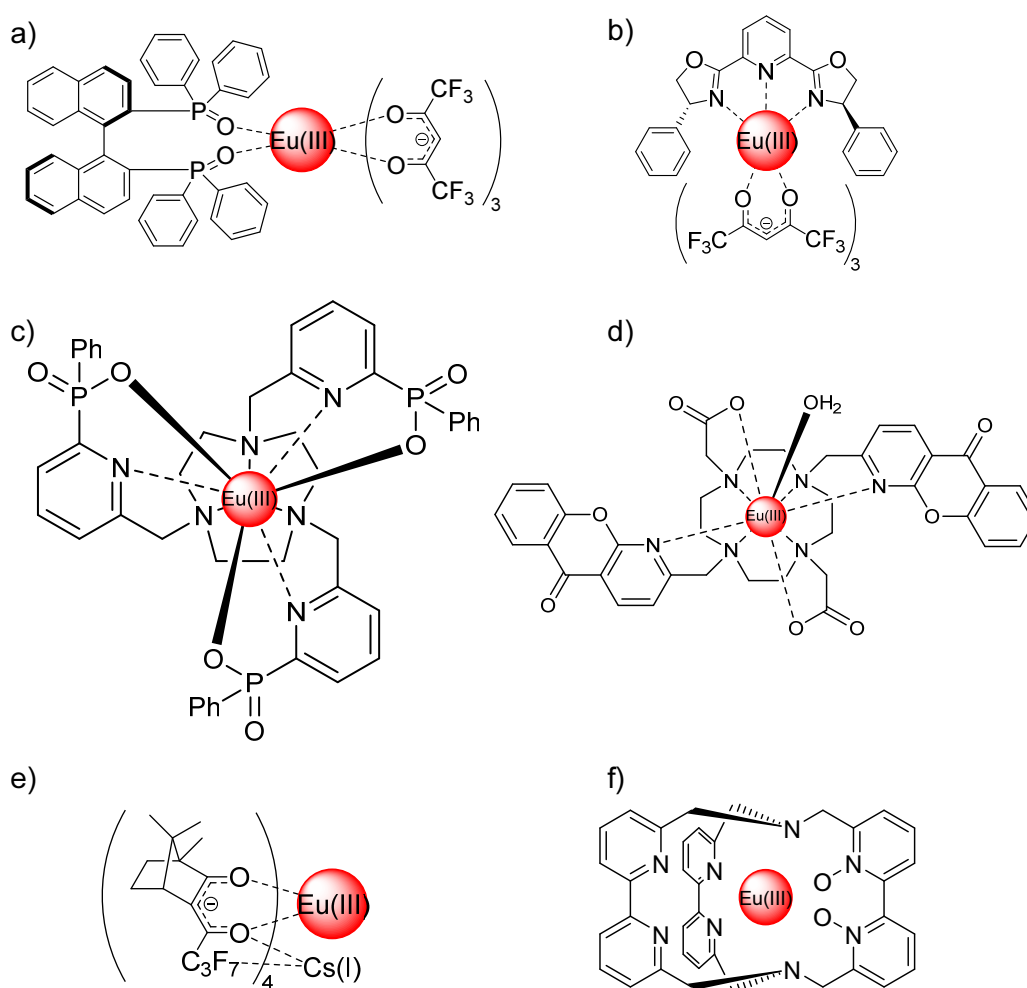


Figure 1.10 The molecular structure of various types of chiral Eu(III) complexes.

triazacyclononane,^[27] cryptate,^[28] and camphor.^[29] The CPL properties in these chiral lanthanide complexes are greatly affected not only by the structure of chiral ligands but also by the surrounding environment and other additive molecules. Kumar achieved enhancement of g_{CPL} by helical aggregation of chiral Eu(III) complexes with camphor ligands.^[30] Minami reported strong luminescence intensity and CPL by interaction of chiral Eu(III) complexes with DNA.^[31]

Considering the application of these chiral lanthanide complexes as luminescent materials such as security inks, it is crucial that they exhibit large g_{CPL} ($g_{\text{CPL}} > 1.5$, $I_{\text{L}}/I_{\text{R}} > 7$). Recently, Kitagawa reported chiral Eu(III) complexes with large g_{CPL} ($g_{\text{CPL}} = 1.2$) in amorphous state and applications to the security ink. Generally, chiral Eu(III) complexes exhibit a relatively large g_{CPL} compared to the organic molecules and transition metal complexes. As shown in equation (1.17), the balance between $\vec{\mu}$ and $\vec{m}$ is important to achieve a large g_{CPL} . In the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition of Eu(III) is electric dipole forbidden and magnetic dipole allowed ($|\vec{\mu}| < |\vec{m}|$). This characteristic transition leads to a large g_{CPL} . Furthermore, Wada reported that mixing of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition with an electric dipole-allowed transition (J-mixing) enhances $\vec{\mu}$ and increases g_{CPL} .^[32] There are several reports of large g_{CPL} in other lanthanides. Cotter reported a large g_{CPL} of 0.272 in the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ transition of a Sm(III) complex with a binaphthyl frameworks.^[33] Relatively large g_{CPL} values have also been reported for Tb(III), Dy(III),^[34] Yb(III),^[35] Tm(III), and Er(III)^[36,37] complexes, but in comparison to the Eu(III) complexes, the number of reported instances remains scarce.

1.3 Objective and outline

Lanthanide complexes with chiral organic ligands exhibit strong CPL. CPL luminophores are expected to be applied to next-generation optical materials. As mentioned above, the CPL properties of chiral lanthanide complexes are strongly affected by the steric and electronic structure, and construction of molecular design for large g_{CPL} ($g_{\text{CPL}} \sim 2$) is required.

From this viewpoint, the objective of this study is elucidation of the mechanism for enhancement of g_{CPL} and providing the guideline for effective CPL properties of chiral Eu(III) complexes. The CPL properties of the chiral Eu(III) complexes strongly affected by the coordination geometry and electronic structure. The author focused on control of electronic structure of the complexes with same coordination geometry to evaluate the effect of electronic structure on the CPL properties precisely.

This thesis consists of six chapters.

In **Chapter 1**, the theoretical background and current research topics of lanthanide chemistry and circularly polarized luminescence focused on the chiral Eu(III) complexes are overviewed, and the objective of this study is described.

In **Chapter 2**, highly luminescent chiral Eu(III) complexes are provided. The characteristic chiral phosphine ligands lead to the creation of Eu(III) complexes with high emission quantum yields. Additionally, it is suggested that their CPL properties are related to the ligand-to-metal charge transfer (LMCT) transition.

In **Chapter 3**, introducing bulky substituents in the chiral ligands of Eu(III) coordination polymer is demonstrated for controlling their LMCT properties. The combination of rigid linker ligand and bulky chiral ligands provided the crystal packing without crystal field change. According to the molecular design, elucidation of the effect of ligand strain on the LMCT characteristics and the CPL properties can be achieved.

In **Chapter 4**, phase-transformable chiral Eu(III) coordination polymers are proposed. The bended-type linker ligands with ethynyl groups provided characteristic crystal-to-crystal phase transition behavior upon heat treatment, which significantly changes the CPL properties. Quantum chemical calculations also suggest that the molecular orientation affects the LMCT and CPL properties.

In **Chapter 5**, the CPL properties of chiral Eu(III) complexes with ammonium cations were systematically evaluated depending on the cation species. The counterions affect the coordination structure and photophysical properties of the complexes. The precise tuning of the structure and LMCT characteristics provide the strong CPL properties. The molecular design guideline for effective CPL are also provided.

In **Chapter 6**, summary and outlook of the research are described.

1.4 References

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Chapter 2

***CIRCULARLY POLARIZED LUMINESCENCE OF
Eu(III) COMPLEXES WITH POINT CHIRAL
PHOSPHINE OXIDE LIGANDS***

2.1 Introduction

Lanthanide complexes with chiral organic ligands provide effective CPL properties. Various types of bidentate, tridentate, and tetradentate chiral ligands, such as camphorate, DOTA, Pybox, and other derivatives were reported.^[1–4] The kind of chiral ligand closely related to the CPL properties of the chiral lanthanide complexes. Recently, Wada reported that the CPL properties are related to the chiral electronic structure of $[\text{Eu}(\text{tfc})_3(\text{tppo})_2]$ (tfc: 3-trifluoroacetylcamphorate, tppo: triphenylphosphine oxide) in liquid media.^[5] The g_{CPL} value of a spiral-shaped Eu(III) coordination polymer can also be enhanced by the characteristic ligand environment in the solid state.^[6] Their chiral electronic and geometrical structures are dominated by the conformation of the Eu(III) coordination sphere. Controlling the conformation is linked to the development of chiral Eu(III) complexes with large g_{CPL} values.

In this chapter, the author selected bidentate chiral phosphine oxide ligands to control the chiral geometrical conformation of the luminescent Eu(III) complex. Previously, strong luminescence and CPL properties of $\text{Eu}(\text{hfa})_3$ complexes (hfa : hexafluoroacetylacetonato) including axis-chiral bidentate phosphine oxide ligands with binaphthyl frameworks, 2,2'-bis(diphenylphosphoryl)-1,1'-binaphthyl and 1,1'-binaphthyl-2,2'-bis(diphenylphosphine oxide) were reported.^[7,8] Combination of low-vibrational frequency hfa and phosphine oxide ligands in the Eu(III) complex leads to decrease in non-radiative relaxation, resulting in high emission quantum yields.^[9] Based on these strong luminescent designs, $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ (B2QPO: 2,3-bis(*tert*-butylmethylphosphineoxide)quinoxaline) and $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$ (B3QPO: 2-*tert*-butylmethylphosphineoxide-3-(di-*tert*-butylphosphineoxide)quinoxaline) were synthesized (**Figure 2.1**). The B3QPO and B2QPO ligands contain two and one phosphorus stereocenters, respectively. The coordination structures were characterized using single crystal X-ray structural analysis. The photophysical properties of

[Eu(hfa)₃((R)-B3QPO)] and [Eu(hfa)₃((R,R)-B2QPO)] were estimated using emission spectra, emission quantum yields, and emission lifetime measurements. [Eu(hfa)₃((R,R)-B2QPO)] exhibits a relatively high emission quantum yield (Φ_{f-f} in CH₂Cl₂ = 55%, Φ_{f-f} in solid = 63%) and a large g_{CPL} value (g_{CPL} = 0.08) when compared with previously reported Eu(III) complexes with chiral phosphine oxide ligands ([Eu(hfa)₃((R)-BINAPO)]; g_{CPL} = 0.014).^[10] To analyze the driving force for the large g_{CPL} value, the electronic configurations of the Eu(III) complexes were also estimated using the differential circular dichroism (CD) spectra recorded for their corresponding chiral Eu(III) and Gd(III) complexes. From these chiroptical and structural measurements, we found that the ligand-to-metal charge transfer (LMCT) transition from the hfa ligands to the Eu(III) center is key to the enhancing the g_{CPL} value of the Eu(III) complexes. The presence of LMCT is triggered by chiral coordination strain. The electronic strain effect in chiral Eu(III) complexes opens up a novel research area in the fields of future optical materials, coordination chemistry, and applied photochemical science.

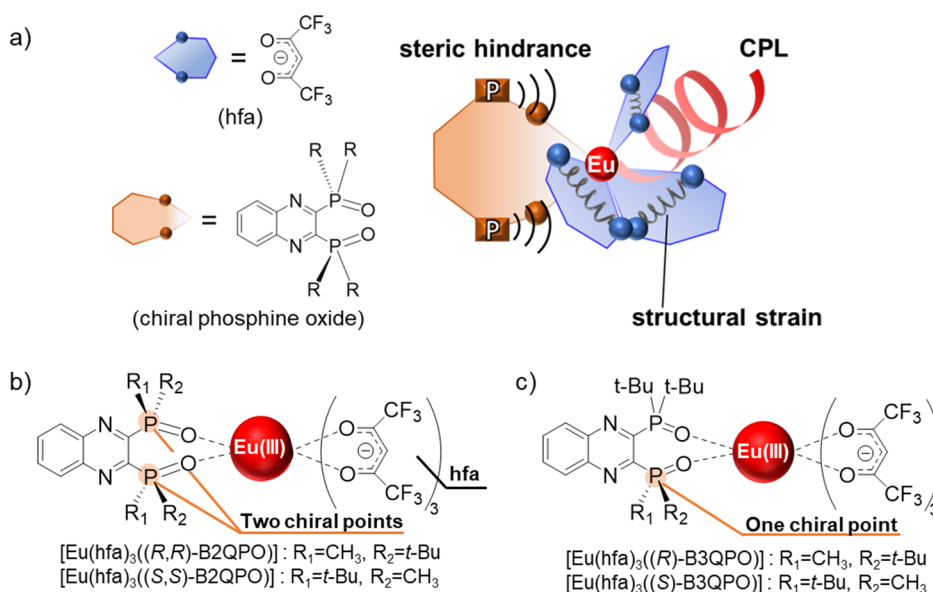


Figure 2.1 (a) Conceptual molecular design. (b), (c) Chemical structures of [Eu(hfa)₃((R,R)-B2QPO)], [Eu(hfa)₃((S,S)-B2QPO)], [Eu(hfa)₃((R)-B3QPO)], and [Eu(hfa)₃((S)-B3QPO)].

2.2 Methods

2.2.1 Materials and apparatus

B2QP and B3QP were obtained from Nippon Chemical Industrial Co., Ltd. The other chemicals were of reagent grade and used without further purification. Infrared spectra were recorded on a JASCO FT/IR-4600 spectrometer. ESI-MS spectra were measured using a JEOL JMS-T100LP. APCI-MS spectra were measured using an Advion CMS-L01. Elemental analyses were performed using an Exeter Analytical CE440. ^1H NMR (400 MHz), ^{19}F NMR (176 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). ^{19}F chemical shifts were determined with fluorobenzene as an external standard ($\delta = -116.3$ ppm). ^{31}P chemical shifts were determined with 85% H_3PO_4 as an external standard ($\delta = 0$ ppm).

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, $\lambda = 1064$ nm) and a photomultiplier (Hamamatsu Photonics, R5108, response time ≤ 1.1 ns). The Nd:YAG laser response was monitored with a digital oscilloscope (Sony Tektronix, TDS3052, 500 MHz) synchronized to the single-pulse excitation. The emission lifetimes were determined from the slope of logarithmic plots of the decay profiles. The emission quantum yields excited at 380 nm (Φ_{tot}) were estimated using a JASCO FP-6300 spectrometer attached with a JASCO ILF-533 integrating sphere unit ($\varphi = 100$ mm). The wavelength dependence of the detector response and the beam intensity of the Xe light source for each spectrum were calibrated using a standard light source. UV-vis absorption and CD spectra were recorded on a JASCO J-1500 spectro-polarimeter. The CPL spectra

were recorded on a JASCO CPL-200 spectro-fluoropolarimeter calibrated with d-10-camphorsulfonic acid ammonium salt as a standard reference.

2.2.2 Crystallography

Single crystal X-ray structural analyses were carried out using a Rigaku XtaLAB Synergy diffractometer with graphite monochromatic Mo-K α radiation. The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically using the SHELX system.^[11] Hydrogen atoms were refined using the riding model. All calculations were performed using the crystal structure crystallographic and Olex 2 software package.^[12] The CIF data were confirmed by the checkCIF/PLATON service.

CCDC 1979796 (for [Eu(hfa)₃((R,R)-B2QPO)]), 1980042 (for [Eu(hfa)₃((S,S)-B2QPO)]), 1980043 (for [Eu(hfa)₃((R)-B3QPO)]), 1980045 (for [Eu(hfa)₃((S)-B3QPO)]), 1980048 (for [Gd(hfa)₃((R,R)-B2QPO)]) and 1980319 (for [Gd(hfa)₃((R)-B3QPO)]) contain the supplementary crystallographic data for this chapter.

2.2.3 Computational details

The energy calculations from the structures obtained from crystallography were carried out using the Gaussian 09 program package^[13] at the B3LYP level with the basis set 6-31G(d). For simplification of the calculations, Al(III) ions were used instead of Eu(III) ions.

2.2.4 Syntheses

Preparation of (*R,R*)-2,3-bis(*tert*-butylmethylphosphineoxide)quinoxaline ((*R,R*)-B2QPO)

(*R,R*)-B2QPO was synthesized by the oxidation of ((*R,R*)-2,3-Bis(*tert*-butylmethylphosphino)quinoxaline) ((*R,R*)-B2QP). (*R,R*)-B2QP (98 mg, 0.29 mmol) was dissolved in dichloromethane (2 mL). The solution was cooled to 0 °C, and then a 30% hydrogen peroxide solution (2 mL) was added dropwise to the above solution. The solution was stirred for 4 h. The product was extracted by dichloromethane. Magnesium sulfate dehydrate was added to the organic phases for dehydration. After filtration, the organic phase was evaporated using a rotary evaporator, which gave a light yellow powder. Yield: 67 mg (63%). ¹H NMR (400 MHz, CDCl₃/TMS, 25 °C): δ = 8.14 (dd, *J* = 6.4, 3.7 Hz, 2H), 7.92 (dd, *J* = 6.4, 3.7 Hz, 2H), 2.11 (d, *J* = 12.8 Hz, 6H), 1.43 (d, *J* = 14.6 Hz, 18H) ppm. ³¹P NMR (162 MHz, CDCl₃, 25 °C): δ = 51.0 ppm. IR (ATR): ν = 2820–2992 (m, C–H), 1152 (s, P=O) cm^{–1}. APCI-MS (*m/z*): calcd for C₁₈H₂₉N₂O₂P₂ [*m* + H]⁺: 367.2, found 367.2.

Preparation of ((*R*)-2-*tert*-butylmethylphosphineoxide-3-(di-*tert*-butylphosphineoxide)quinoxaline) ((*R*)-B3QPO)

(*R*)-B3QPO was synthesized by the oxidation of ((*R*)-2-*tert*-butylmethylphosphino-3-(di-*tert*-butylphosphino)quinoxaline) ((*R*)-B3QP). (*R*)-B3QP (203 mg, 0.54 mmol) was dissolved in dichloromethane (4 mL). The solution was cooled to 0 °C, and then a 30% hydrogen peroxide solution (4 mL) was added dropwise to the above solution. The solution was stirred for 2 h. The product was extracted by dichloromethane. Magnesium sulfate dehydrate was added to the organic phases for dehydration. After filtration, the organic phase was evaporated using a rotary evaporator, which gave a light yellow powder. Yield: 178 mg (81%). ¹H NMR (400 MHz, CDCl₃/TMS, 25 °C): δ = 8.23–8.05

(m, 2H), 8.01–7.79 (m, 2H), 2.21 (d, $J = 12.8$ Hz, 3H), 1.54–1.22 (m, 27H) ppm. ^{31}P NMR (162 MHz, CDCl_3 , 25 °C): $\delta = 52.3$ (s), 49.0 (s) ppm. IR (ATR): $\nu = 2861$ – 2967 (m, C–H), 1161 (s, P=O) cm^{-1} . APCI-MS (m/z): calcd for $\text{C}_{21}\text{H}_{35}\text{N}_2\text{O}_2\text{P}_2$ [$m + \text{H}$] $^+$: 409.2, found 409.2.

Preparation of $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$

(R,R)-B2QPO (67 mg, 0.18 mmol) and $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$ (160 mg, 0.20 mmol) were dissolved in dichloromethane (5 mL). The solution was stirred for 2 h. The solution was filtered, and then concentrated by an evaporator to afford a white powder. The powder was recrystallized from methanol to give colourless dendritic crystals. Yield 82 mg (40%). ^{19}F NMR (376 MHz, CDCl_3 , 25 °C): $\delta = -78.9$ ppm. ^{31}P NMR (162 MHz, CDCl_3 , 25 °C): $\delta = -3.6$ ppm. ESI-Mass (m/z): $[\text{M} - \text{hfa}]^+$ calcd for $\text{C}_{28}\text{H}_{30}\text{EuF}_{12}\text{N}_2\text{O}_6\text{P}_2$, 933.06; found, 933.09. Elemental analysis: calcd for $\text{C}_{33}\text{H}_{31}\text{EuF}_{18}\text{N}_2\text{O}_8\text{P}_2$, C 34.78, H 2.74, N 2.46; found, C 34.50, H 2.50, N 2.33%. FT-IR (ATR): 1653 (st, C=O), 1252 (st, C–F), 1139 (st, P=O) cm^{-1} .

Preparation of $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$

(R)-B3QPO (74 mg, 0.18 mmol) and $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$ (195 mg, 0.24 mmol) were dissolved in dichloromethane (5 mL). The solution was stirred for 2 h. The solution was filtered, and then concentrated by an evaporator to afford a white powder. The powder was recrystallized from methanol to give colourless block crystals. Yield 92 mg (43%). ^{19}F NMR (376 MHz, CDCl_3 , 25 °C): $\delta = -78.4$ ppm. ^{31}P NMR (162 MHz, CDCl_3 , 25 °C): $\delta = -57.2$ (s), -70.2 (s) ppm. ESI-Mass (m/z): $[\text{M} - \text{hfa}]^+$ calcd for $\text{C}_{31}\text{H}_{36}\text{EuF}_{12}\text{N}_2\text{O}_6\text{P}_2$, 975.11; found, 975.13. Elemental analysis: calcd for $\text{C}_{36}\text{H}_{37}\text{EuF}_{18}\text{N}_2\text{O}_8\text{P}_2$, C 36.59, H 3.16, N 2.37; found, C 36.53, H 2.97, N 2.30%.

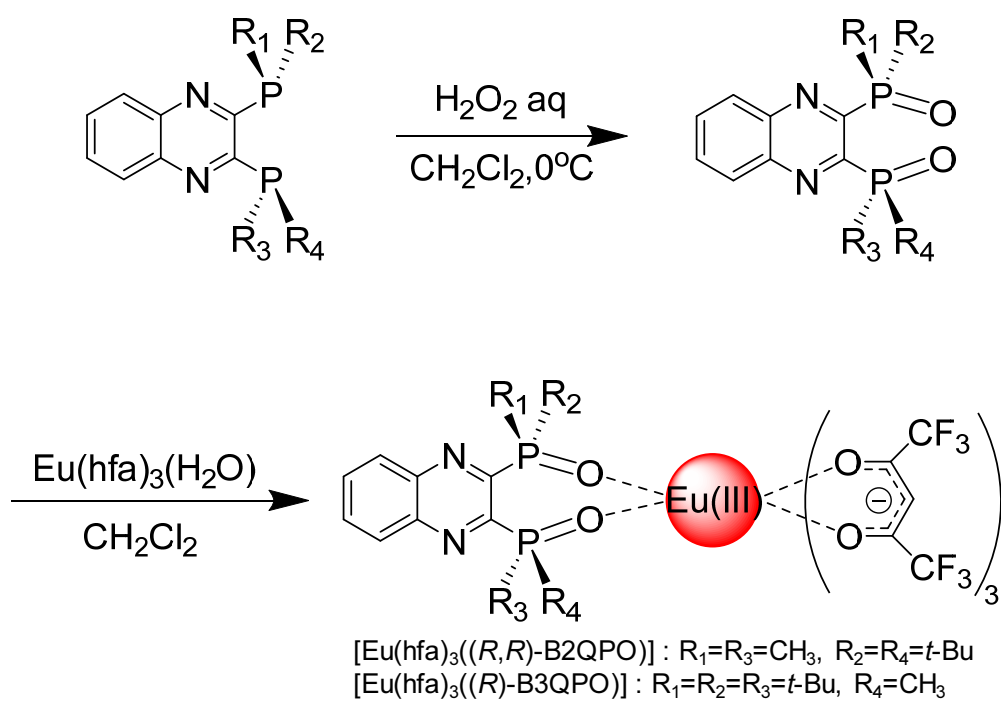


Figure 2.2 Synthetic schemes of Eu(III) complexes.

2.3 Results and discussion

2.3.1 Chiral coordination structures

Four chiral Eu(III) complexes, $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$, $[\text{Eu}(\text{hfa})_3((S,S)\text{-B2QPO})]$, $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$, and $[\text{Eu}(\text{hfa})_3((S)\text{-B3QPO})]$, were synthesized by the complexation of a chiral phosphine oxide ligand ((*R,R*)-B2QPO, (*S,S*)-B2QPO, (*R*)-B3QPO, and (*S*)-B3QPO) with a precursor complex, $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$, in dichloromethane at room temperature. Single crystals of these chiral Eu(III) complexes were obtained via recrystallization from methanol. The crystal structures of these complexes were determined using single-crystal X-ray structural analyses and their crystallographic data are summarized in **Figure 2.3** and the parameters are listed in **Table 2.1**.

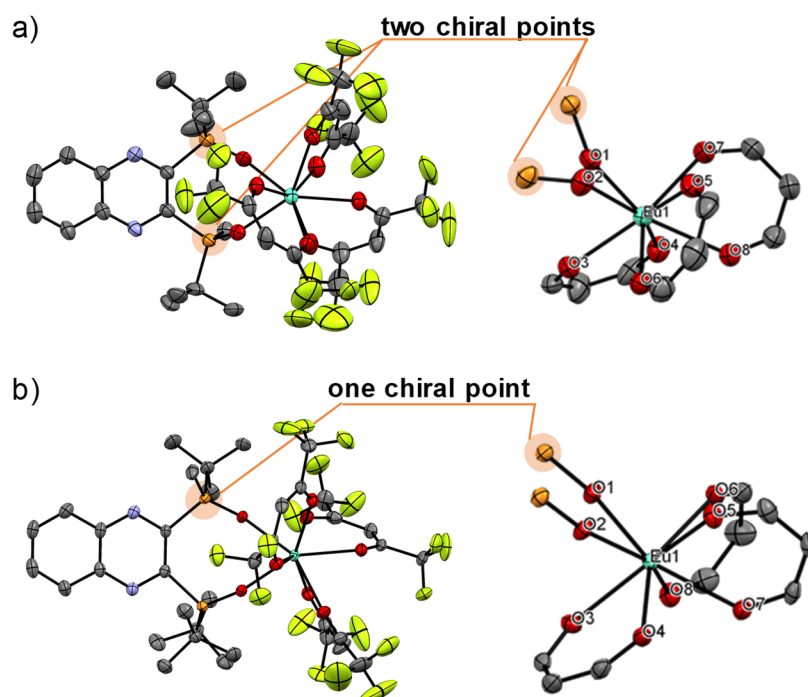


Figure 2.3 ORTEP drawings (left) and coordination geometries around Eu(III) (right) of (a) $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$, (b) $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$.

Table 2.1 X-ray crystal data of Eu(III) complexes.

	[Eu(hfa) ₃ ((R,R)-B2QPO)]	[Eu(hfa) ₃ ((R)-B3QPO)]
Chemical formula	C ₃₃ H ₃₁ EuF ₁₈ N ₂ O ₈ P ₂	C ₃₆ H ₃₇ EuF ₁₈ N ₂ O ₈ P ₂
Formula weight	1139.50	1181.57
Crystal system	monoclinic	monoclinic
Space group	P2 ₁	P2 ₁
<i>a</i> / Å	11.6631(2)	11.19040(10)
<i>b</i> / Å	19.2898(2)	20.5895(2)
<i>c</i> / Å	20.1981(2)	20.3663(2)
α / deg.	90	90
β / deg.	93.5450(10)	99.7900(10)
γ / deg.	90	90
Volume / Å ³	4535.45(10)	4624.16(8)
<i>Z</i>	4	4
Temperature / K	123.15	123.15
<i>d</i> _{calc} / g cm ⁻³	1.669	1.697
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
Reflections collected	85714	137245
Goodness-of-fit on F ²	1.053	1.031
<i>R</i> ₁	0.0439	0.0240
<i>WR</i> ₂	0.1177	0.0572
Flack parameter	0.000(4)	-0.012(3)

The space groups of these complexes were categorized as $P2_1$, which is the chiral space group with helices along the b -axis. The ORTEP views of these Eu(III) complexes exhibit eight-coordinate structures comprised of one Eu(III), one bidentate phosphine oxide and three hfa ligands. Based on their crystal data, continuous shape measures (CShM) calculations using SHAPE^[14–16] were performed to determine the geometrical structures around the Eu(III) ions in the first coordination sphere. The CShM factor (S_{CShM}) expresses the degree of deviation from the ideal coordination structure. The S_{CShM} value is given by,

$$S_{\text{CShM}} = \min \frac{\sum_k^N |Q_k - P_k|^2}{\sum_k^N |Q_k - Q_0|^2} \times 100 \quad (2.1)$$

where N , Q_k , Q_0 , and P_k are the number of vertices, vertices of an actual structure, position vectors of the geometrical center, and vertices of the ideal structure, respectively. The S_{CShM} values obtained for these complexes for 8-SAP and 8-TDH (SAP: square antiprism, TDH: triangular dodecahedron) are summarized in **Table 2.2**. The S_{CShM} values in the 8-SAP structures are smaller than those of 8-TDH in [Eu(hfa)₃((*R,R*)-B2QPO)] and [Eu(hfa)₃((*R*)-B3QPO)]. Thus, the coordination geometry of [Eu(hfa)₃((*R,R*)-B2QPO)] and [Eu(hfa)₃((*R*)-B3QPO)] were categorized to be 8-SAP.

Table 2.2 S_{CShM} value of Eu(III) complexes.

Compounds	S_{CShM} (8-SAP)	S_{CShM} (8-TDH)
[Eu(hfa) ₃ ((<i>R,R</i>)-B2QPO)]	0.289	2.142
[Eu(hfa) ₃ ((<i>R</i>)-B3QPO)]	0.695	1.872

In order to estimate the structural strain in the hfa ligands (**Figure 2.4**), the O...O distances in the hfa ligands and the L...Eu...L dihedral angles in the coordination sphere obtained from the X-ray single crystal data were summarized in **Table 2.3**.

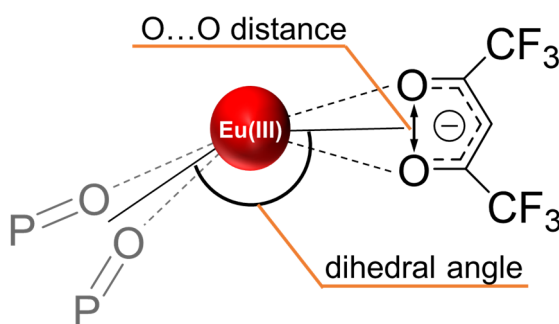


Figure 2.4 O...O distance and dihedral angle of Eu(III) complex.

Table 2.3 O...O distance and dihedral angle between phosphine oxide and hfa ligands.

Compounds	O...O distance / Å			
	hfa1	hfa2	hfa3	avg.
[Eu(hfa) ₃ ((R,R)-B2QPO)]	2.808	2.846	2.870	2.841
[Eu(hfa) ₃ ((R)-B3QPO)]	2.803	2.806	2.829	2.813
Compounds	Dihedral angle between phosphine oxide and hfa ligands / deg.			
	hfa1	hfa2	hfa3	avg.
[Eu(hfa) ₃ ((R,R)-B2QPO)]	97.32	130.49	107.61	111.81
[Eu(hfa) ₃ ((R)-B3QPO)]	129.86	112.46	94.79	112.37

The longer O...O distance observed in $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ was attributed to the increase in strain between the photosensitized hfa and chiral phosphine oxide ligands. The average dihedral angle between the phosphine oxide and hfa ligands in $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ is smaller than that observed in $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$, which indicates that the hfa ligands are close to the chiral phosphine oxide ligands in $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$. The postulated structures of $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ and $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$ are shown in **Figure 2.5**. The author propose that the electronic structure of $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ is affected by structural strain due to the longer O...O distance and smaller dihedral angle.

Their coordination structures in liquid media were estimated using ^{19}F and ^{31}P NMR spectra (**Figure 2.6**). The ^{19}F chemical shifts of $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ and $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$ were located at around -80 ppm, which were similar to that of $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$ (-80.54 ppm).^[10] In contrast, drastic ^{31}P chemical shift in the low-magnetic field of $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ (-3.6 ppm), compared with those of $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$ (-57.2 , -70.2 ppm) was found. The characteristic chemical shift of $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ might be due to formation of specific electronic structure.

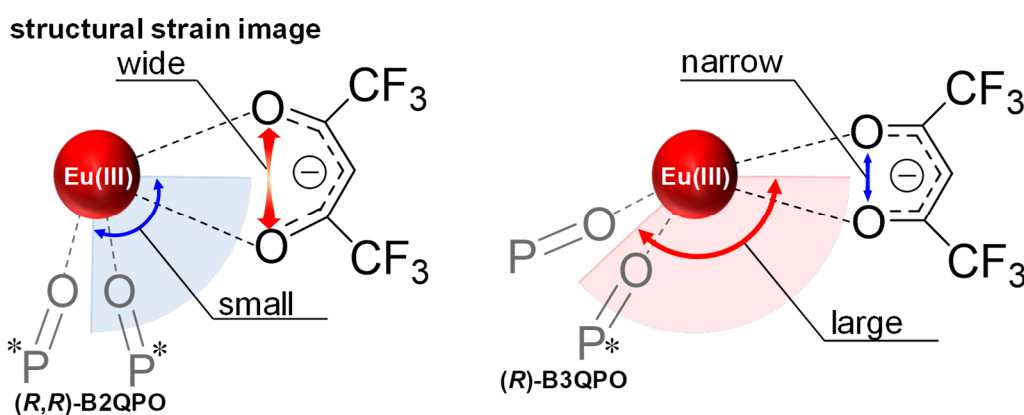


Figure 2.5 Postulated images of $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ and $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$.

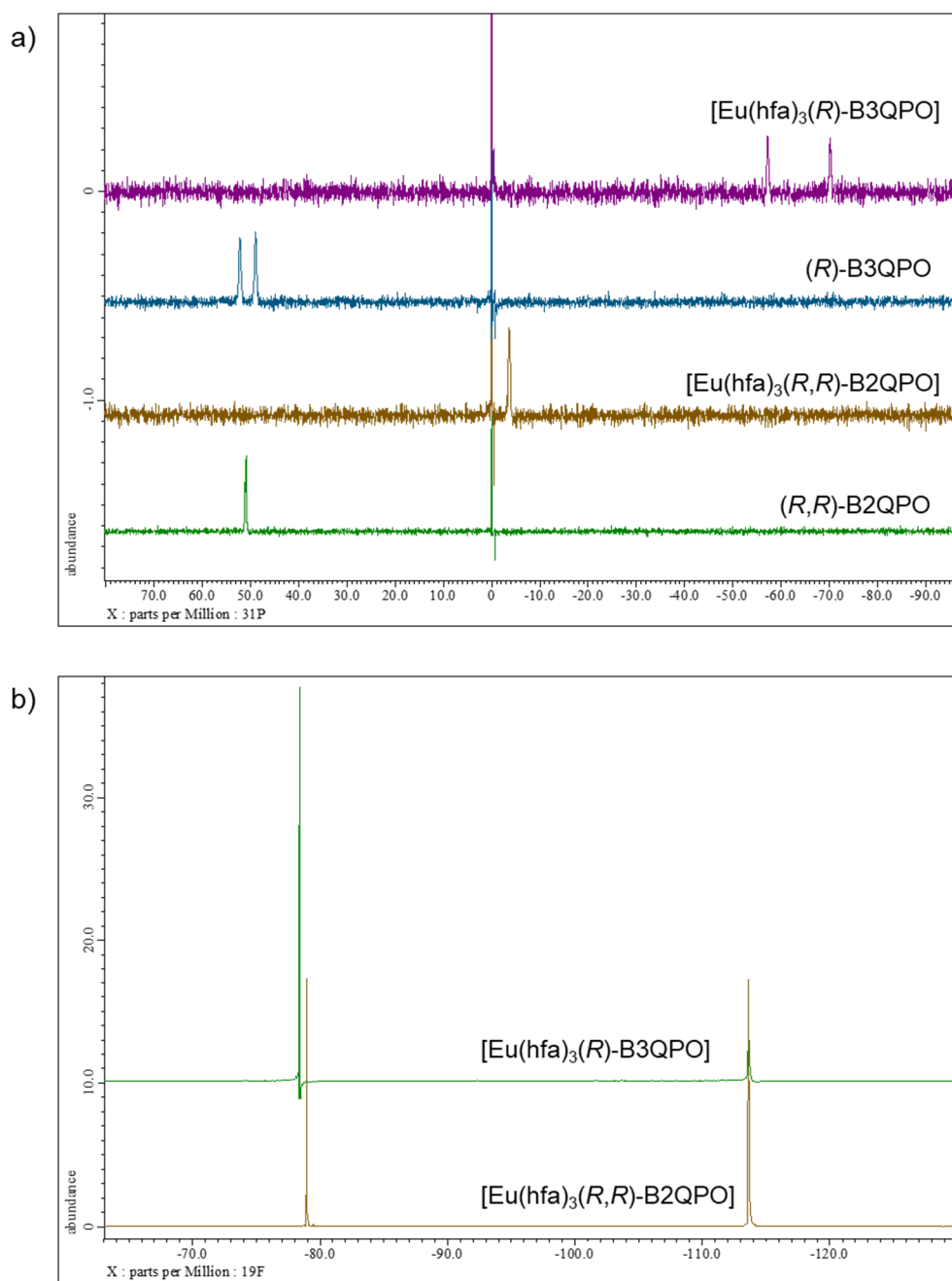


Figure 2.6. (a) ^{31}P (162 MHz) and (b) ^{19}F NMR (376 MHz) spectra of ligands ((*R,R*)-B2QPO, (*R*)-B3QPO) and complexes ([Eu(hfa)₃((*R,R*)-B2QPO)], [Eu(hfa)₃((*R*)-B3QPO)]).

2.3.2 Photophysical properties

The excitation and emission spectra of $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ and $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$ in dichloromethane (1.0×10^{-4} M) are shown in **Figure 2.7**. The excitation bands observed in the UV region (250–350 nm) are attributed to the $\pi\text{-}\pi^*$ transitions in the organic ligands. The characteristic bands of $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ and $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$ at around 380 nm were assigned to the $\pi\text{-}\pi^*$ transitions in the quinoxaline units.

The emission bands at 578, 590, 610, 652, and 700 nm are attributed to the 4f-4f transitions of Eu(III) ($^5\text{D}_0 \rightarrow ^7\text{F}_J$: $J = 0, 1, 2, 3$, and 4, respectively).^[3] The emission spectra were normalized with the area of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition band, which is known to be insensitive to the surrounding environment of the Eu(III) ion.^[17] The spectral shape and stark splitting of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition in $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$, which is directly related to the geometrical symmetry, are much similar to those observed for $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$ (**Figure 2.7**, inset).^[18] In order to estimate the relative transition probability of the electric-dipole transition, the relative integrated intensity (A_{rel}) of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ band with respect to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ were evaluated ($A_{\text{rel}} = A_{\text{ED}}/A_{\text{MD}}$, A_{ED} : integrated intensity at the electric-dipole transition, A_{MD} : integrated intensity at the magnetic-dipole transition, **Table 2.4**). The A_{rel} value of $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ is the same as $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$, which indicates that the transition probability of $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ was also much similar to $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$.

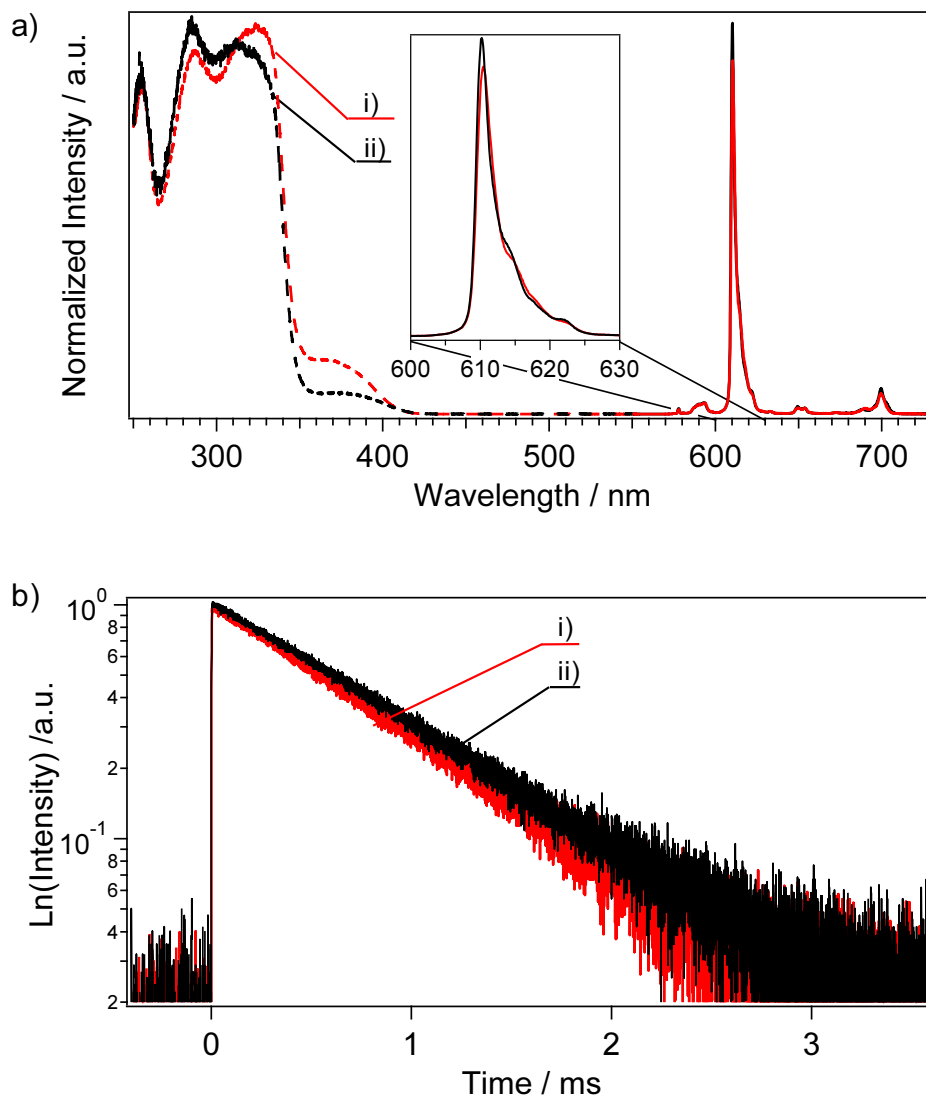


Figure 2.7 (a) Normalized emission (solid line, $\lambda_{\text{ex}} = 350$ nm) and excitation (dashed line, $\lambda_{\text{em}} = 611$ nm) spectra. (b) Emission decay profiles of i) $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ (red line), ii) $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$ (black line) in dichloromethane (1.0×10^{-4} M) at room temperature.

Table 2.4 Photophysical properties of Eu(III) complexes.

Compounds	media	A_{rel}	k_r / s^{-1}	$k_{\text{nr}} / \text{s}^{-1}$	
[Eu(hfa) ₃ ((R,R)-B2QPO)]	sol. ^[a]	16.2	7.8×10^2	6.3×10^2	
	solid ^[b]	15.0	9.3×10^2	5.4×10^2	
[Eu(hfa) ₃ ((R)-B3QPO)]	sol. ^[a]	16.5	8.0×10^2	4.5×10^2	
	solid ^[b]	15.4	9.7×10^2	4.2×10^2	
Compounds	media	$\tau_{\text{obs}} / \text{ms}$	$\Phi_{\text{f-f}} / \%$	$\Phi_{\text{tot}} / \%$	$\eta_{\text{sens}} / \%$
[Eu(hfa) ₃ ((R,R)-B2QPO)]	sol. ^[a]	0.71	55	31	56
	solid ^[b]	0.68	63	60	95
[Eu(hfa) ₃ ((R)-B3QPO)]	sol. ^[a]	0.80	64	32	50
	solid ^[b]	0.72	70	64	91

[a] in dichloromethane solution (1.0×10^{-4} M), [b] in powder

The time-resolved emission decay profiles obtained for [Eu(hfa)₃((R,R)-B2QPO)] and [Eu(hfa)₃((R)-B3QPO)] in dichloromethane (1.0×10^{-4} M) at room temperature are shown in **Figure 2.7**. Single-exponential decays with sub-milli-second scale lifetimes were observed. The emission lifetimes (τ_{obs}) were determined from the slope of the logarithmic decay profiles. The τ_{obs} values for [Eu(hfa)₃((R,R)-B2QPO)] and [Eu(hfa)₃((R)-B3QPO)] were determined to be 0.71 and 0.80 ms, respectively. Based on the emission lifetime, the 4f-4f emission quantum yield ($\Phi_{\text{f-f}}$), radiative rate constant (k_r), the non-radiative rate constant (k_{nr}), and energy transfer efficiency (η_{sens}) were estimated using the equations (1.1)-(1.4). These photophysical parameters of two Eu(III) complexes are also summarized in **Table 2.4**. The k_r value of [Eu(hfa)₃((R,R)-B2QPO)] is the same as that of [Eu(hfa)₃((R)-B3QPO)]. On the other hand, the k_{nr} value obtained for [Eu(hfa)₃((R,R)-B2QPO)] is larger than that of [Eu(hfa)₃((R)-B3QPO)], which suggests that a quenching state, such as an LMCT band, exists in [Eu(hfa)₃((R,R)-B2QPO)]. The $\Phi_{\text{f-f}}$ values of [Eu(hfa)₃((R,R)-B2QPO)] (55%) and [Eu(hfa)₃((R)-B3QPO)] (64%) are much larger than those of chiral Eu(III) complexes prepared from camphor derivatives ($\Phi_{\text{f-f}} < 5\%$).^[10] The photosensitized energy transfer efficiency η_{sens} of [Eu(hfa)₃((R,R)-B2QPO)] and [Eu(hfa)₃((R)-B3QPO)] in the solution and solid are greater than 50 and 90%, respectively.

Their Φ_{f-f} and η_{sens} values are comparable to those previously reported for bright luminescent Eu(III) complexes.^[19,20] Generally, Eu(III) complexes prepared using camphor derivatives have an energy quenching state around the emitting energy level of Eu(III) ($^5D_0 \rightarrow ^7F_J$; $J = 0-4$), resulting in a decrease in the emission quantum yield.^[10,21] The energy levels of the LMCT bands in [Eu(hfa)₃((*R,R*)-B2QPO)] and [Eu(hfa)₃((*R*)-B3QPO)] are much higher than those of Eu(III) complexes prepared from camphor derivatives. A higher LMCT band may promote a higher emission quantum yield in chiral Eu(III) complexes.

2.3.3 Chiroptical properties

The CD spectra of chiral phosphine oxide ligands and chiral Eu(III) complexes in dichloromethane (1.0×10^{-4} M) are shown in **Figure 2.8**, respectively. The CD signals observed for (*R,R*)-B2QPO are in agreement with those obtained for (*R*)-B3QPO in the UV and visible light regions shown in **Figure 2.8**. In contrast, [Eu(hfa)₃((*R,R*)-B2QPO)] shows a large positive CD signal at around 320 nm (π - π^* transition of the hfa ligand), although [Eu(hfa)₃((*R*)-B3QPO)] exhibits a negative and weak CD signal in the same region. This effective difference is caused by the exciton coupling depending on the coordination geometry. The opposite CD signs at around 320 nm are based on the orientation difference between [Eu(hfa)₃((*R,R*)-B2QPO)] and [Eu(hfa)₃((*R*)-B3QPO)].

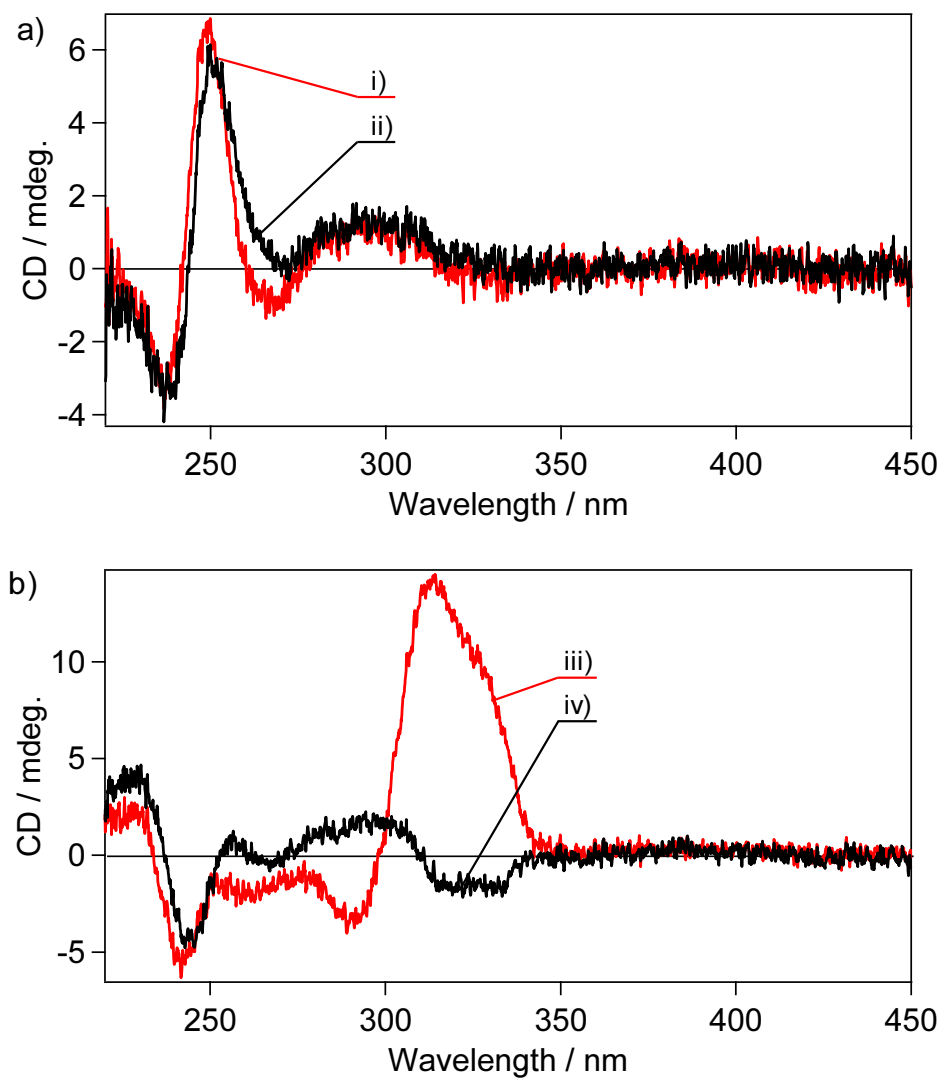


Figure 2.8 The CD spectra of (a) (*R,R*)-B2QPO ((i), red line) and (*R*)-B3QPO ((ii), black line), (b) [Eu(hfa)₃](*R,R*)-B2QPO] ((iii), red line) and [Eu(hfa)₃](*R*)-B3QPO] ((iv), black line) in dichloromethane (1.0×10^{-4} M) at room temperature.

Consequently, the electronic state of the hfa ligand using $[\text{Gd}(\text{hfa})_3((R,R)\text{-B2QPO})]$ and $[\text{Gd}(\text{hfa})_3((R)\text{-B3QPO})]$ were estimated. The energy level of the LMCT state in the Gd(III) complexes was much higher than that of the Eu(III) complexes.^[22] The g_{CD} spectra of the chiral Eu(III) and Gd(III) complexes are shown in **Figure 2.9**. A significant difference was observed in the spectra recorded for $[\text{Gd}(\text{hfa})_3((R,R)\text{-B2QPO})]$ and $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ at around 320 nm, while the CD signal of $[\text{Gd}(\text{hfa})_3((R)\text{-B3QPO})]$ was the same as that observed for $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$. Their molecular orbitals and calculated energy levels are estimated using DFT calculations (B3LYP, 6-31G(d)) with Al(III) ion (**Figure 2.10** and **Table 2.5**). The quantum calculations provide localized electronic structure and higher HOMO energy levels of hfa ligands in $[\text{Al}(\text{hfa})_3((R,R)\text{-B2QPO})]$. From these photophysical findings, the significant difference observed in the spectra recorded for $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ and $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$ may be affected by the LMCT transition from hfa to the Eu(III) ion.

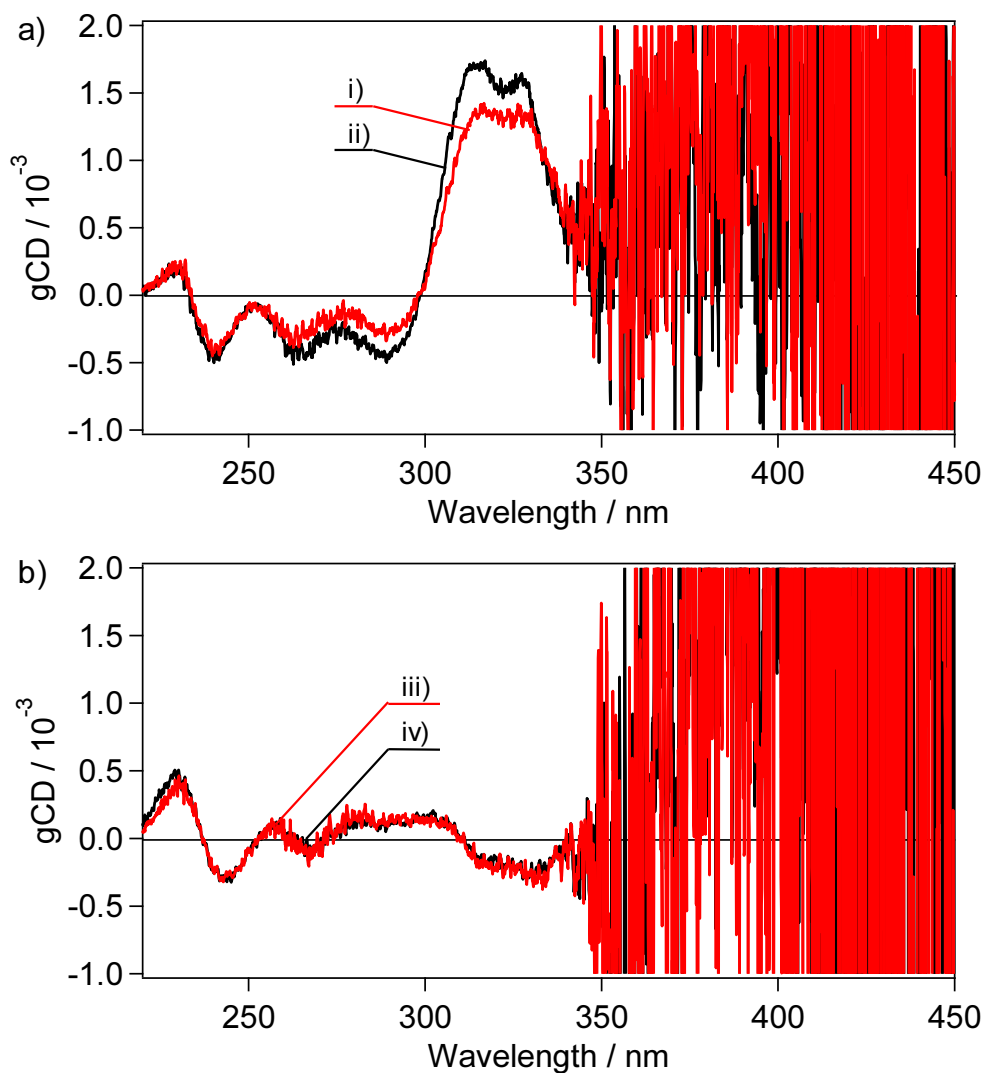
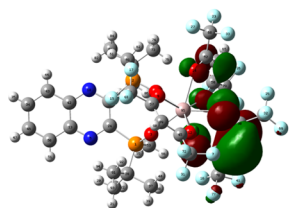
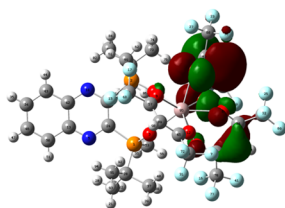


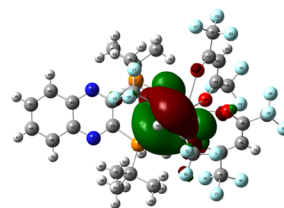
Figure 2.9 The g_{CD} spectra of (a) $[Eu(hfa)_3((R,R)\text{-B2QPO})]$ ((i), red line) and $[Gd(hfa)_3((R,R)\text{-B2QPO})]$ ((ii), black line), (b) $[Eu(hfa)_3((R)\text{-B3QPO})]$ ((iii), red line) and $[Gd(hfa)_3((R)\text{-B3QPO})]$ ((iv), black line) in dichloromethane (1.0×10^{-4} M) at room temperature.

[Al(hfa)₃(*R,R*)-B2QPO]

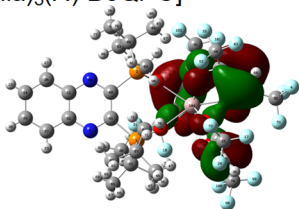
HOMO



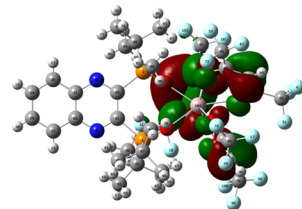
HOMO-1



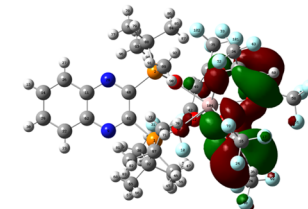
HOMO-2

[Al(hfa)₃(*R*)-B3QPO]

HOMO



HOMO-1



HOMO-2

Figure 2.10 Molecular orbitals of [Al(hfa)₃((*R,R*)-B2QPO)] and [Al(hfa)₃((*R*)-B3QPO)]**Table 2.5** Calculated HOMO, HOMO-1, and HOMO-2 energy levels of [Al(hfa)₃((*R,R*)-B2QPO)] and [Al(hfa)₃((*R*)-B3QPO)] obtained by DFT calculations.

Complex	Energy level / eV		
	HOMO	HOMO-1	HOMO-2
[Al(hfa) ₃ ((<i>R,R</i>)-B2QPO)]	-6.050	-6.173	-6.437
[Al(hfa) ₃ ((<i>R</i>)-B3QPO)]	-6.216	-6.259	-6.302

The CPL spectra of chiral Eu(III) complexes in dichloromethane (1.0×10^{-4} M) are shown in **Figure 2.11**. The CPL signals are given by the difference between the left- and right-handed circularly polarized light. The characteristic CPL signals were observed around 590 ($^5D_0 \rightarrow ^7F_1$) and 610 ($^5D_0 \rightarrow ^7F_2$) nm. In the region corresponding to the $^5D_0 \rightarrow ^7F_1$ transition, a large negative CPL signal in [Eu(hfa)₃((R,R)-B2QPO)] (**Figure 2.11** (i)) compared with small positive CPL signal in [Eu(hfa)₃((R)-B3QPO)] (**Figure 2.11** (ii)) was observed. The maximum g_{CPL} value of [Eu(hfa)₃((R,R)-B2QPO)] ($g_{\text{CPL}} = -0.083$ for $^5D_0 \rightarrow ^7F_1$ and 0.011 for $^5D_0 \rightarrow ^7F_2$ transition) was also larger than [Eu(hfa)₃((R)-B3QPO)] ($g_{\text{CPL}} = 0.012$ for $^5D_0 \rightarrow ^7F_1$ and -0.0023 for $^5D_0 \rightarrow ^7F_2$ transition). This CPL signal behavior should be related to the CD signals of the hfa ligands observed at 320 nm.

The electronic perturbation of the LMCT state in the Eu(III) complex affects the oscillator strength of the 4f-4f transition.^[23] In this study, structural strain in the chiral coordination structure promotes the formation an LMCT state, resulting in the enhanced CPL signals observed for chiral Eu(III) complexes.

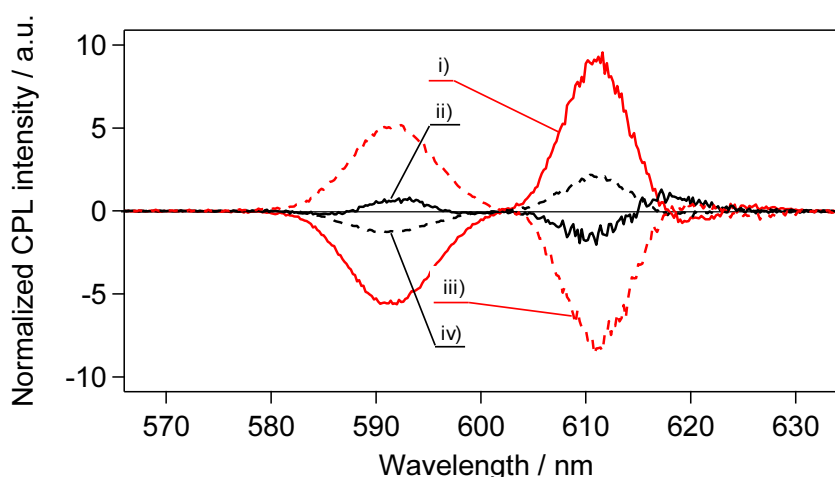


Figure 2.11 CPL spectra of [Eu(hfa)₃((R,R)-B2QPO)] ((i), red solid line), [Eu(hfa)₃((R)-B3QPO)] ((ii), black solid line), [Eu(hfa)₃((S,S)-B2QPO)] ((iii), red dashed line) and [Eu(hfa)₃((S)-B3QPO)] ((iv), black dashed line) in dichloromethane (1.0×10^{-4} M) at room temperature excited at 350 nm.

2.4 Conclusion

Four novel Eu(III) complexes containing point-chiral phosphine oxide ligands, [Eu(hfa)₃((*R,R*)-B2QPO)], [Eu(hfa)₃((*R*)-B3QPO)], [Eu(hfa)₃((*S,S*)-B2QPO)], and [Eu(hfa)₃((*S*)-B3QPO)], have been synthesized. [Eu(hfa)₃((*R,R*)-B2QPO)] exhibits both high emission quantum yields ($\Phi_{\text{f-f in CH}_2\text{Cl}_2} = 55\%$, $\Phi_{\text{f-f in solid}} = 63\%$) and relatively large g_{CPL} value ($g_{\text{CPL}} = 0.08$). The development of highly luminescent Eu(III) complexes with large g_{CPL} values is expected to be useful in chiroptical applications, such as three-dimensional displays, advanced chiral security tags, and bio-imaging luminophores.^[24] The increased structural strain observed in [Eu(hfa)₃((*R,R*)-B2QPO)] promotes an extra LMCT band in the CD signals, which is related to the magnitude of the g_{CPL} value. The photophysical relationship between the structural and electronic strains in chiral Eu(III) complexes opens up a novel area of research in the field of future optical materials, coordination chemistry, and applied photochemical science.

2.5 Appendix

Preparation of (*S,S*)-2,3-Bis(*tert*-butylmethylphosphineoxide)quinoxaline ((*S,S*)-B2QPO)

(*S,S*)-B2QPO was synthesized by the same procedure as described for the (*R,R*)-B2QPO. Yield: 61%. ¹H NMR (400 MHz, CDCl₃/TMS, 25°C): δ = 8.14 (dd, *J* = 6.4, 3.7 Hz, 2H), 7.92 (dd, *J* = 6.4, 3.7 Hz, 2H), 2.11 (d, *J* = 12.3 Hz, 6H), 1.43 (d, *J* = 14.6 Hz, 18H) ppm. IR (ATR): ν = 2822-2999 (m, C-H), 1151 (s, P=O) cm⁻¹. APCI-MS (*m/z*): calcd for C₁₈H₂₉N₂O₂P₂ [*m* + H]⁺: 367.2, found 367.2.

Preparation of (*S*)-2-*tert*-butylmethylphosphineoxide-3-(di-*tert*-butylphosphineoxide)quinoxaline ((*S*)-B3QPO)

(*S*)-B3QPO was synthesized by the same procedure as described for the (*R*)-B3QPO. Yield: 82%. ¹H NMR (400 MHz, CDCl₃/TMS, 25°C): δ = 8.23-8.09 (m, 2H), 7.98-7.85 (m, 2H), 2.24 (d, *J* = 12.8 Hz, 3H), 1.55-1.25 (m, 27H) ppm. IR (ATR): ν = 2861-2967 (m, C-H), 1161 (s, P=O) cm⁻¹. APCI-MS (*m/z*): calcd for C₂₁H₃₅N₂O₂P₂ [*m* + H]⁺: 409.2, found 409.2.

Preparation of [Eu(hfa)₃(H₂O)₂] (hfa: hexafluoroacetylacetonato)

[Eu(hfa)₃(H₂O)₂] was prepared with the procedure described in previous report^[25].

Preparation of [Eu(hfa)₃((*S,S*)-B2QPO)]

[Eu(hfa)₃((*S,S*)-B2QPO)] was synthesized by the same procedure as described for the [Eu(hfa)₃((*R,R*)-B2QPO)]. Yield: 45%. ESI-Mass (*m/z*): [M-hfa]⁺ calcd. for C₂₈H₃₀EuF₁₂N₂O₆P₂, 933.06; found, 933.10. Elemental analysis: calcd. for C₃₃H₃₁EuF₁₈N₂O₈P₂, C 34.78, H 2.74, N 2.46; found, C 34.36, H 2.53, N 2.29%. FT-IR (ATR): 1652 (st, C=O), 1252 (st, C-F), 1141 (st, P=O) cm⁻¹.

Preparation of [Eu(hfa)₃((S)-B3QPO)]

[Eu(hfa)₃((S)-B3QPO)] was synthesized by the same procedure as described for the [Eu(hfa)₃((R)-B3QPO)]. Yield: 42%. ESI-Mass (m/z): [M-hfa]⁺ calcd. for C₃₁H₃₆EuF₁₂N₂O₆P₂, 975.11; found, 975.11. Elemental analysis: calcd. for C₃₆H₃₇EuF₁₈N₂O₈P₂, C 36.59, H 3.16, N 2.37; found, C 36.55, H 2.99, N 2.28%. FT-IR (ATR): 1650 (st, C=O), 1251 (st, C-F), 1140 (st, P=O) cm⁻¹.

Preparation of [Gd(hfa)₃(H₂O)₂]

[Gd(hfa)₃(H₂O)₂] was synthesized by the same procedure as described for the [Eu(hfa)₃(H₂O)₂].

Preparation of [Gd(hfa)₃((R,R)-B2QPO)]

[Gd(hfa)₃((R,R)-B2QPO)] was synthesized by the same procedure as described for the [Eu(hfa)₃((R,R)-B2QPO)]. Yield 45%. ESI-Mass (m/z): [M-hfa]⁺ calcd. for C₂₈H₃₀GdF₁₂N₂O₆P₂, 938.06; found, 938.06. Elemental analysis: calcd. for C₃₃H₃₁GdF₁₈N₂O₈P₂, C 34.62, H 2.73, N 2.45; found, C 34.34, H 2.56, N 2.34%. FT-IR (ATR): 1653 (st, C=O), 1253 (st, C-F), 1139 (st, P=O) cm⁻¹.

Preparation of [Gd(hfa)₃((R)-B3QPO)]

[Gd(hfa)₃((R)-B3QPO)] was synthesized by the same procedure as described for the [Eu(hfa)₃((R)-B3QPO)]. Yield 43%. ESI-Mass (m/z): [M-hfa]⁺ calcd. for C₃₁H₃₆GdF₁₂N₂O₆P₂, 980.11; found, 980.11. Elemental analysis: calcd. for C₃₆H₃₇GdF₁₈N₂O₈P₂, C 36.43, H 3.14, N 2.36; found, C 36.34, H 3.00, N 2.29%. FT-IR (ATR): 1650 (st, C=O), 1250 (st, C-F), 1137 (st, P=O) cm⁻¹.

Table 2.6 X-ray crystal data of Gd(III) complexes

	[Gd(hfa) ₃ ((<i>R,R</i>)-B2QPO)]	[Gd(hfa) ₃ ((<i>R</i>)-B3QPO)]
Chemical formula	C ₃₃ H ₃₁ F ₁₈ GdN ₂ O ₈ P ₂	C ₃₆ H ₃₇ F ₁₈ GdN ₂ O ₈ P ₂
Formula weight	1144.79	1186.86
Crystal system	monoclinic	monoclinic
Space group	P2 ₁	P2 ₁
<i>a</i> / Å	11.6565(2)	11.16540(10)
<i>b</i> / Å	19.2883(3)	20.5710(2)
<i>c</i> / Å	20.1991(3)	20.3672(2)
α / deg.	90	90
β / deg.	93.4630(10)	99.6950(10)
γ / deg.	90	90
Volume / Å ³	4533.15(12)	4611.20(8)
<i>Z</i>	4	4
Temperature / K	123.15	123.15
<i>d</i> _{calc} / g cm ⁻³	1.677	1.710
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
Reflections collected	127032	119067
Goodness-of-fit on F ²	1.031	1.026
<i>R</i> ₁	0.0395	0.0212
<i>WR</i> ₂	0.1070	0.0512
Flack parameter	-0.006(3)	-0.007(2)

The absorption spectra of chiral phosphine oxide ligands, precursor complex ($[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$), and chiral Eu(III) complexes are shown in **Figure 2.12**. The absorption bands at 300–350 nm are attributed to π - π^* transitions of hfa and phosphine oxide ligands. The bands at around 250 nm are attributed to the existing of phosphine oxide ligands.

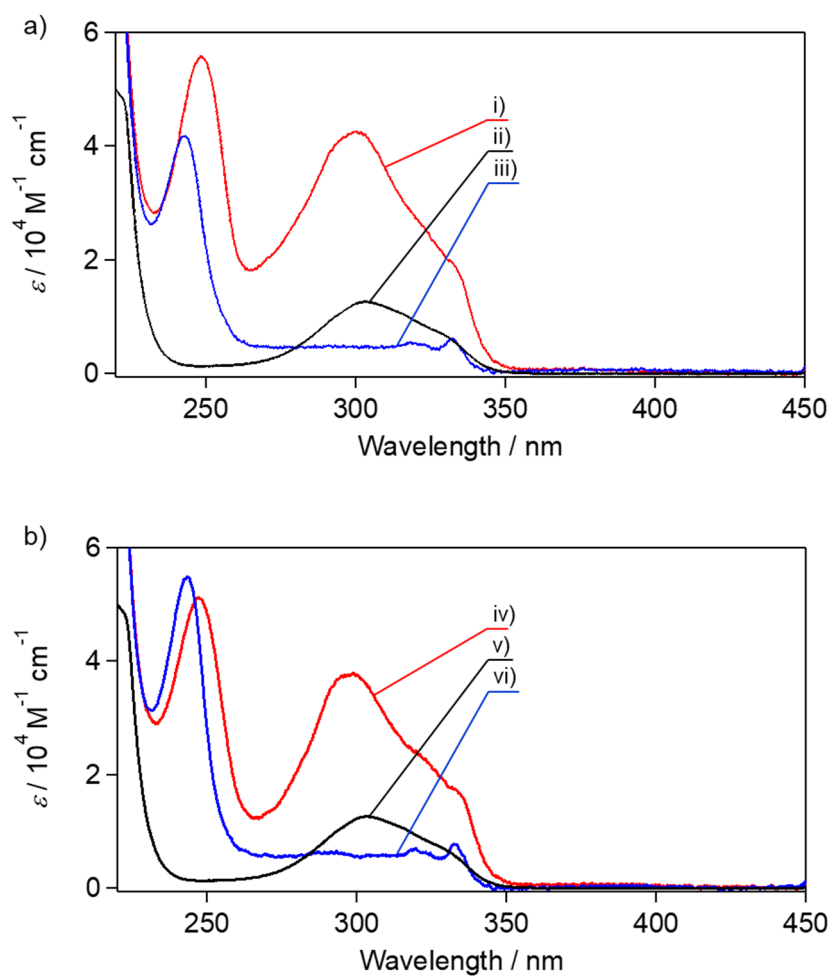


Figure 2.12 UV-vis absorption spectra of (a) $[\text{Eu}(\text{hfa})_3((R,R)\text{-B2QPO})]$ ((i), red line), $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$ ((ii), black line) and $(R,R)\text{-B2QPO}$ ((iii), blue line), (b) $[\text{Eu}(\text{hfa})_3((R)\text{-B3QPO})]$ ((iv), red line), $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$ ((v), black line) and $(R)\text{-B3QPO}$ ((vi), blue line) in dichloromethane ($1.0 \times 10^{-4} \text{ M}$) at room temperature.

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Chapter 3

***ENHANCEMENT OF CIRCULARLY POLARIZED
LUMINESCENCE WITH CONTROLLING
STRUCTURAL STRAIN IN CHIRAL Eu(III)
COORDINATION POLYMERS***

3.1 Introduction

In **Chapter 2**, the author provided the highly luminescent chiral Eu(III) complexes with point chiral phosphine oxide ligands. The characteristic chiral ligands provided the LMCT states which is potentially related to the CPL properties of chiral Eu(III) complexes. Generally, the LMCT states of Eu(III) complexes are produced by the electronic transition from the HOMO level of the ligand to the LUMO level of the Eu(III) ion.^[1,2] The steric strain of the ligand may affect the energy level and direction of the transition dipole moment of the LMCT states in Eu(III) complexes (**Figure 3.1a** and **b**).

In this chapter, the author focused on the electronic structure of the ligands based on the LMCT characteristics for evaluating the CPL properties of chiral Eu(III) compounds. From this concept, chiral Eu(III) coordination polymers with rigid and long linker ligands were selected. The linker ligands provide wide space for packing the bulky chiral ligands without crystal field change (**Figure 3.1c**). This molecular design allows to understand the direct effect of ligand strain on the LMCT characteristics and the CPL properties. The chiral Eu(III) coordination polymers are composed of chiral luminescent Eu(III) units and rigid linker parts. Three chiral ligands with perfluoroalkyl groups of different length, (+)-3-(trifluoroacetyl)camphorate (+tfc), (+)-3-(pentafluoropropionyl)camphorate (+pfc), and (+)-3-(heptafluorobutyryl)camphorate (+hfc), were selected to systematically control the strain factor in the Eu(III) coordination polymer (**Figure 3.1d**). The ethynyl-linked phosphine oxide, 1,4-bis(diphenylphosphorylethynyl)benzene (*p*-dpeb), was synthesized as a linear rigid linker to create a wide space to hold the large camphorate ligands without crystal field change (**Figure 3.1c**).^[3,4] Three chiral Eu(III) coordination polymers, [Eu(+tfc)₃(*p*-dpeb)]_n, [Eu(+pfc)₃(*p*-dpeb)]_n, and [Eu(+hfc)₃(*p*-dpeb)]_n (**Figure 3.1d**) were synthesized using these ligands to tune the steric hindrance of the chiral ligands in the Eu(III) coordination polymers.

The coordination structures of the chiral Eu(III) coordination polymers were characterized by single-crystal X-ray structural analyses. The strain factors in the camphorate ligands were estimated from their crystallographic data. The photophysical properties of the Eu(III) coordination polymers were evaluated using the emission spectra, lifetimes, and CPL measurements. Time-dependent density-functional theory (TD-DFT) calculations were then carried out for estimation of the LMCT states. The large steric hindrance of the camphorate ligands provides characteristic interaction between LMCT states and 4f-4f excited states in Eu(III), resulting in effective CPL properties.

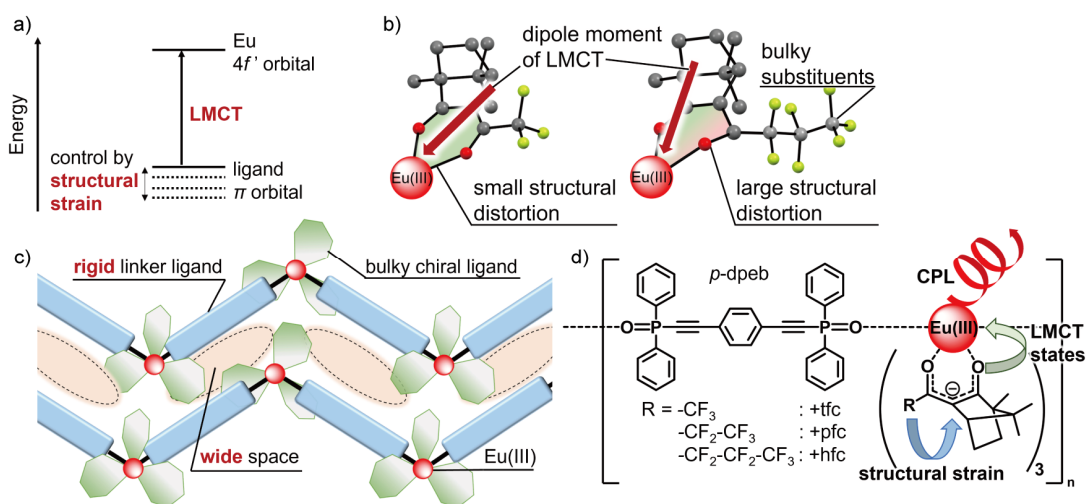


Figure 3.1 Illustrations of (a) controlling the LMCT energy level, (b) the direction of the dipole moments due to structural strain, and (c) the conceptual design of a chiral Eu(III) coordination polymer. (d) Chemical structures of the chiral Eu(III) coordination polymers.

3.2 Methods

3.2.1 Materials and apparatus

(+)-3-(Trifluoroacetyl)camphor (98%) and (+)-3-(heptafluorobutyryl)camphor (96%) were purchased from Sigma-Aldrich Co. LLC. (+)-Camphor (>98.0%) was purchased from Tokyo Chemical Industry Co., Ltd. Europium(III) acetate *n*-hydrate (99.9%) was purchased from FUJIFILM Wako Pure Chemical Corporation. All other reagents were of reagent grade and used without further purification.

Fourier transform infrared spectra were recorded on a JASCO FT/IR-4600 spectrometer. ESI-MS spectra were recorded using a JEOL JMS-T100LP and Thermo Scientific Exactive. Elemental analyses were performed on an Exeter Analytical CE440. ^1H NMR (400 MHz), ^{19}F NMR (376 MHz), and ^{31}P NMR (162 MHz) spectra were recorded on a JEOL ECS400, JEOL ECZ400S, and JEOL ECX400 at 298 K, respectively. Tetramethylsilane ($\delta_{\text{H}} = 0.00$ ppm), hexafluorobenzene ($\delta_{\text{F}} = -164.9$ ppm), and phosphoric acid ($\delta_{\text{P}} = 0.00$ ppm) were used as references for ^1H , ^{19}F , and ^{31}P NMR, respectively. A triple resonance ^{13}C $\{^1\text{H}, ^{19}\text{F}\}$ NMR (151 MHz) spectrum was recorded on a JEOL JNM-ECZR equipped with a ROYAL-HFX probe. Powder X-ray diffraction was performed on a Rigaku SmartLab using Cu-K α radiation ($\lambda = 1.5418$ Å).

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, $\lambda = 1064$ nm) and a photomultiplier (Hamamatsu Photonics, R5108, response time ≤ 1.1 ns). The Nd:YAG laser response was monitored with a digital oscilloscope (Sony Tektronix, TDS3052, 500 MHz) synchronized to the single-pulse excitation. The emission lifetimes were determined from the slope of logarithmic plots of the decay profiles. Emission lifetimes in the range of

150–370 K were measured using a cryostat (Thermal Block Company, SA-SB245T) and a temperature controller (Oxford Instruments, ITC 502S). Diffuse reflection spectra were measured using a JASCO V-770 spectrophotometer with an ISN-923 integrating sphere unit. CPL spectra were recorded on a JASCO CPL-300 spectro-fluoropolarimeter for Eu(III) coordination polymers (0.5 mg) mixed with KBr (150 mg). KBr tablets (diameter: 10 mm, Eu(III) coordination polymers/KBr) were prepared using a PT-10 tablet forming machine (48.2 kN, press time: 3 min).

3.2.2 Crystallography

Single crystals of $[\text{Eu}(\text{+pfc})_3(\text{p-dpeb})]_n$ and $[\text{Eu}(\text{+hfc})_3(\text{p-dpeb})]_n$ were obtained by recrystallization from ethanol solution. 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, $\lambda = 0.71073 \text{ \AA}$). The structure was resolved using direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically using the SHELX system.^[5] 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.^[6] The CIF data were confirmed by the checkCIF/PLATON service. CCDC 2213525 (for $[\text{Eu}(\text{+pfc})_3(\text{p-dpeb})]_n$) and 2213526 (for $[\text{Eu}(\text{+hfc})_3(\text{p-dpeb})]_n$) contain the supplementary crystallographic data for this chapter.

3.2.3 Computational details

All quantum chemical calculations were performed using the density functional theory (DFT) using the Gaussian 16 package.^[7] Structural optimization was carried out using DFT with the B3LYP-D3 functional^[8–10] (basis set: Stuttgart RSC 1997 (ECP28MWB)^[11,12] for the Eu atoms and 6-31G(d) for other elements). The excited

states were investigated using time-dependent (TD)-DFT with the long-range corrected LC-BLYP functional.^[13] Spin-unrestricted self-consistent field calculations were performed. The Stuttgart RSC 1997 (ECP28MWB) basis set was adopted for the Eu atoms, while the cc-pVDZ basis set^[14] was used for the other atoms.

3.2.4 Syntheses

Preparation of 1,4-bis(diphenylphosphorylethynyl)benzene (*p*-dpeb)

p-dpeb was prepared with the procedure described in a previous report.^[3] 1,4-diethynylbenzene (0.63 g, 6.6 mmol) was dissolved in dry diethyl ether (50 mL), and the mixture was degassed by Ar bubbling. A solution of *n*-BuLi (ca. 1.6 mol L⁻¹, 7.5 mL, 12 mmol) was added dropwise to the solution at -80 °C. The mixture was stirred for 3.5 h at -10 °C, after which chlorodiphenylphosphine (2.2 mL, 12 mmol) was added dropwise at -80 °C. The mixture was gradually brought to room temperature and stirred for 21 h. The reaction mixture was poured into distilled water and extracted with dichloromethane. The extracts were washed with brine three times and dried over anhydrous MgSO₄. The solvent was evaporated, and the obtained yellow oil was placed with dichloromethane (10 mL) in a flask. The solution was cooled to 0 °C, and then an aqueous 30% hydrogen peroxide solution (10 mL) was added dropwise to the above solution. The solution was stirred for 16 h. After the separation of the aqueous hydrogen peroxide solution, the solution was washed with distilled water. Anhydrous MgSO₄ was added to the organic phases for dehydration. After filtration, the organic phase was evaporated to give a white powder. The powder was recrystallized from methanol and dichloromethane solution to give prism crystals. Yield: 1.97 g (3.7 mmol, 75%). ¹H NMR (CDCl₃): δ = 7.85–7.92 (m, 8H), 7.60 (s, 4H), 7.55–7.59 (m, 4H), 7.48–7.54 ppm (m, 8H). ³¹P NMR (CDCl₃): δ = 8.37 ppm. IR (ATR): ν = 3030–3076 (st, ArC-H), 2180 (st, C≡C), 1196 cm⁻¹ (st, P=O).

ESI-MS (m/z): $[M + H]^+$ calcd for $C_{34}H_{25}O_2P_2$, 527.13; found, 527.13. Elemental analysis: calcd for $C_{34}H_{24}O_2P_2$, C 77.56, H 4.59; found, C 77.44, H 4.49%.

Preparation of (+)-3-(pentafluoropropionyl)camphor

(+)-Camphor (3.0 g, 20 mmol) and sodium hydride (60% dispersion in paraffin liquid, 2.1 g) were dissolved in tetrahydrofuran (super dehydrated, 30 mL) under an argon atmosphere. The mixture was stirred for 30 min at room temperature, after which ethylpentafluoropropionate (3.3 mL) was added dropwise to the solution at 0 °C. The mixture was stirred for 10 min and refluxed for 20 h. The dark brown reaction solution was cooled to room temperature and methanol was added to consume the excess sodium hydride. Hydrochloric acid (1 mol L⁻¹, 60 mL) was added to the mixture. The product was extracted with ethyl acetate and washed with brine. The extracts were dried over anhydrous Na₂SO₄ and evaporated to give a deep red oil. The crude material was purified by silica gel (Silica gel 60N, spherical, neutral, particle size 100–210 µm, Kanto Chemical Co., Inc.) column chromatography (ethyl acetate : *n*-hexane = 1 : 5) to afford a light red liquid. The liquid was further purified by distillation which gave a colourless liquid.

Yield: 2.1 g (7.1 mmol, 36%). ¹H NMR (CDCl₃): δ = 11.73 (br, 1H), 2.81–2.95 (m, 1H), 2.02–2.15 (m, 1H), 1.69–1.86 (m, 1H), 1.37–1.55 (m, 2H), 1.02 (s, 3H), 0.97 (s, 3H), 0.83 ppm (s, 3H). ¹³C NMR (CDCl₃): δ = 214.0, 148.3, 120.2, 118.4, 109.3, 58.0, 49.0, 47.3, 30.0, 26.6, 20.3, 18.2, 8.5 ppm. ¹⁹F NMR (CDCl₃): δ = –86.9, –124.4 ppm. ESI-MS (m/z): $[M - H]^-$ calcd for $C_{13}H_{15}F_5O_2$, 297.09; found, 297.09.

Preparation of [Eu(+tfc)₃(*p*-dpeb)]_n

Europium(III) acetate *n*-hydrate (0.36 g) was dissolved in distilled water (150 mL). (+)-3-Trifluoroacetylcamphor (0.50 g, 2.0 mmol) in methanol (15 mL) was added to the solution, and the mixture was stirred for 4 h at room temperature. The obtained powder

was washed with distilled water, and the powder was dried *in vacuo* ($[\text{Eu}(+\text{tfc})_3(\text{H}_2\text{O})_2]$, 0.41 g). $[\text{Eu}(+\text{tfc})_3(\text{H}_2\text{O})_2]$ (0.37 g, 0.40 mmol) and *p*-dpeb (0.18 g, 0.33 mmol) were dissolved in methanol (10 mL) and refluxed for 5 h. The reaction mixture was cooled to room temperature and evaporated to give a light yellow powder. The obtained powder was washed with diethyl ether and recrystallized from ethanol to give a light yellow powder.

Yield: 35% for monomer. IR (ATR): 2865–2990 (st, ArC–H), 2183 (st, C≡C), 1660 (st, C=O), 1120 cm^{-1} (st, P=O). ESI-MS (m/z): $[\text{M} - \text{tfc}]^+$ calcd for $\text{C}_{58}\text{H}_{52}\text{EuF}_6\text{O}_6\text{P}_2$, 1173.24; found, 1173.25. Elemental analysis: calcd for $\text{C}_{70}\text{H}_{66}\text{EuF}_9\text{O}_8\text{P}_2$, C 59.20, H 4.68; found, C 58.87, H 4.57%.

Preparation of $[\text{Eu}(+\text{pfc})_3(\text{p}\text{-dpeb})]_n$

Europium(III) acetate *n*-hydrate (0.42 g) was dissolved in distilled water (150 mL). (+)-3-(Pentafluoropropionyl)camphor (0.71 g, 2.4 mmol) in methanol (20 mL) was added to the solution, and the mixture was stirred for 18 h at room temperature. The obtained powder was washed with distilled water, and the powder was dried *in vacuo* ($[\text{Eu}(+\text{pfc})_3(\text{H}_2\text{O})_n]$, 0.56 g). $[\text{Eu}(+\text{pfc})_3(\text{H}_2\text{O})_n]$ (0.11 g) and *p*-dpeb (62 mg, 0.12 mmol) were dissolved in methanol (10 mL) and refluxed for 20 h. The reaction mixture was cooled to room temperature and evaporated to give a light yellow powder. The obtained powder was recrystallized from ethanol to give a light yellow crystal.

Yield: 53 mg (0.034 mmol, 28%; for monomer). IR (ATR): 2868–2995 (st, ArC–H), 2183 (st, C≡C), 1654 (st, C=O), 1126 cm^{-1} (st, P=O). ESI-MS (m/z): $[\text{M} - \text{pfc}]^+$ calcd for $\text{C}_{60}\text{H}_{52}\text{EuF}_{10}\text{O}_6\text{P}_2$, 1273.23; found, 1273.22. Elemental analysis: calcd for $\text{C}_{73}\text{H}_{66}\text{EuF}_{15}\text{O}_8\text{P}_2$, C 55.84, H 4.24; found, C 55.63, H 4.11%.

Preparation of $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$

Europium(III) acetate *n*-hydrate (0.38 g) was dissolved in distilled water (200 mL), and a few drops of 28% ammonia solution were added (pH = 8). (+)-3-(Heptafluorobutyryl)camphor (1.1 g, 3.2 mmol) in methanol (40 mL) was added to the solution, and the mixture was stirred for 22 h at room temperature. The obtained powder was washed with distilled water, and the powder was dried *in vacuo* ($[\text{Eu}(+\text{hfc})_3(\text{H}_2\text{O})_n$, 0.94 g). $[\text{Eu}(+\text{hfc})_3(\text{H}_2\text{O})_n]$ (78 mg) and *p*-dpeb (40 mg, 0.08 mmol) were dissolved in methanol (10 mL) and refluxed for 5 h. The reaction solution was cooled to room temperature and evaporated to give a light yellow powder. The obtained powder was recrystallized from ethanol to give a light yellow crystal.

Yield: 37 mg (0.022 mmol, 27%; for monomer). IR (ATR): 2870–2999 (st, ArC–H), 2183 (st, C≡C), 1652 (st, C=O), 1187 cm^{-1} (st, P=O). ESI-MS (*m/z*): $[\text{M} - \text{hfc}]^+$ calcd for $\text{C}_{62}\text{H}_{52}\text{EuF}_{14}\text{O}_6\text{P}_2$, 1373.22; found, 1373.22. Elemental analysis: calcd for $\text{C}_{76}\text{H}_{66}\text{EuF}_{21}\text{O}_8\text{P}_2$, C 53.06, H 3.87; found, C 52.85, H 3.75%.

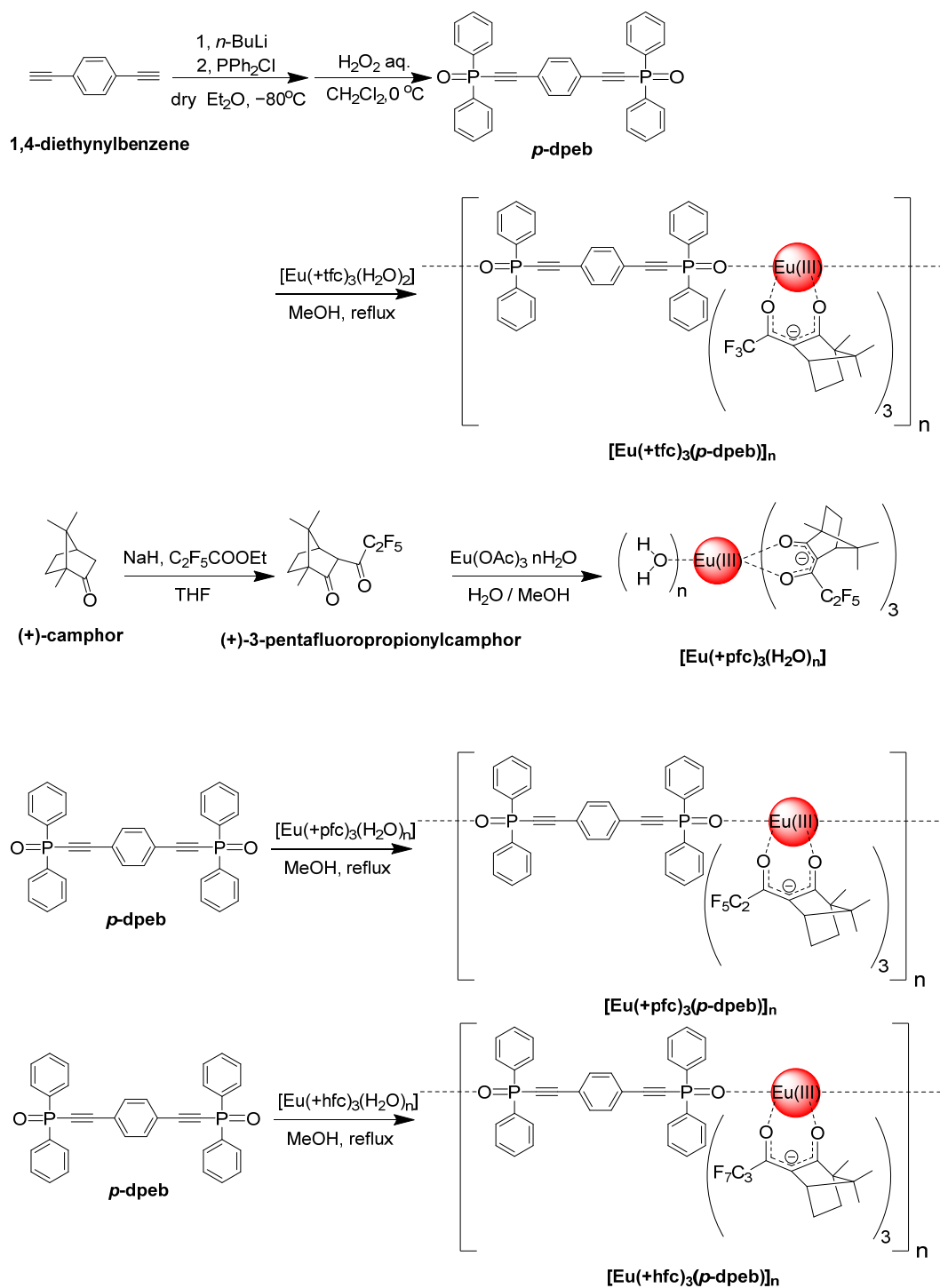


Figure 3.2 Synthetic scheme of chiral Eu(III) coordination polymers.

3.3 Results and discussion

3.3.1 Structural characterizations

Chiral Eu(III) luminescent centers were obtained by the reaction of Eu(III) acetate and chiral camphorate ligands (+tfc, +pfc, and +hfc) in methanol and water.^[15] The chiral Eu(III) coordination polymers with diethynylbenzene linkers, $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$, $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$, and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$, were synthesized by complexation of *p*-dpeb with precursor chiral Eu(III) units in methanol and purified by recrystallization from ethanol solution. The ESI-MS spectra and simulated mass patterns of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ are shown in **Figure 3.3**. The observed signals with mass numbers (*m/z*) of 1173.25, 2593.63, 4013.94, and 5434.32 were assigned to the $[\text{Eu}(+\text{tfc})_2(p\text{-dpeb})]^+$, $[\text{Eu}_2(+\text{tfc})_5(p\text{-dpeb})_2]^+$, $[\text{Eu}_3(+\text{tfc})_8(p\text{-dpeb})_3]^+$, and $[\text{Eu}_4(+\text{tfc})_{11}(p\text{-dpeb})_4]^+$ fragments, respectively. Assignments were made by comparing the observed isotope distribution of $[\text{Eu}_n(+\text{tfc})_{3n-1}(p\text{-dpeb})_n]^+$ (*m/z* at approximately 1173.2, 2593.7, 4013.9, and 5434.2) with the calculated data. The observed ESI-MS signals of $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ were also assigned to the $[\text{Eu}_n(+\text{pfc})_{3n-1}(p\text{-dpeb})_n]^+$ and $[\text{Eu}_n(+\text{hfc})_{3n-1}(p\text{-dpeb})_n]^+$ fragments, respectively (**Figure 3.14** and **Figure 3.15**).

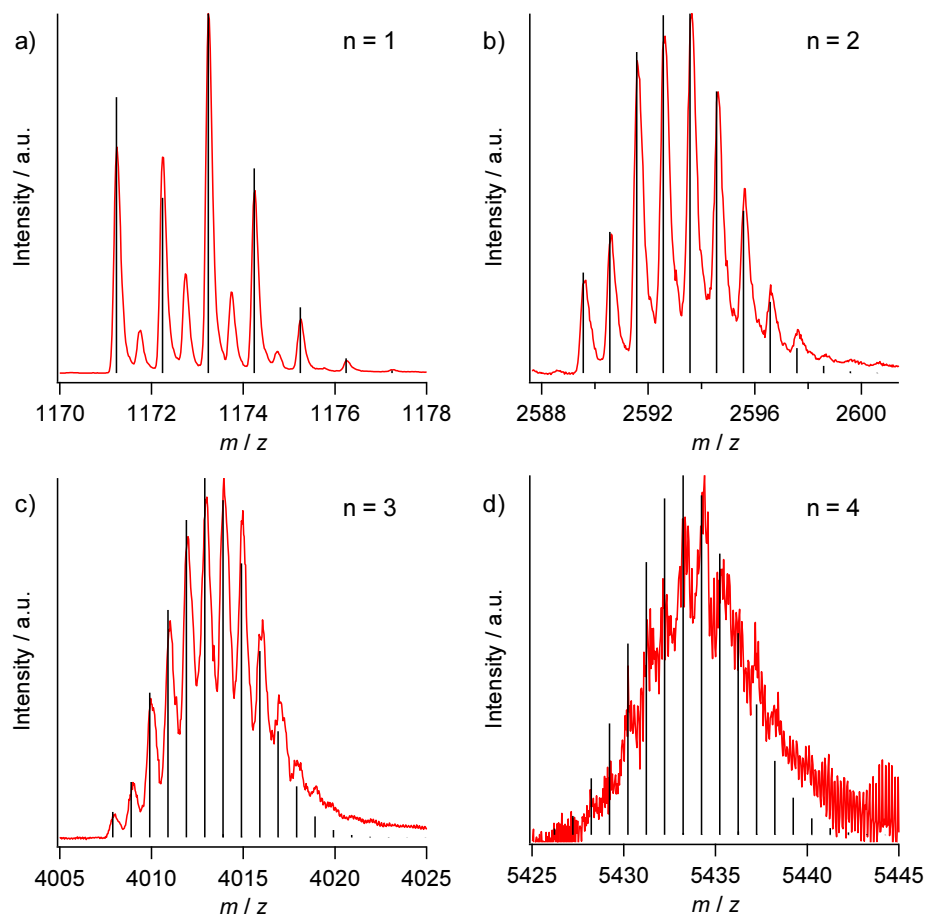


Figure 3.3 ESI-MS spectra (red) and simulated mass pattern (black) of $[\text{Eu}_n(+\text{tfc})_{3n-1}(\text{p-dpeb})_n]^+$ (a) $n = 1$, b) $n = 2$, c) $n = 3$, d) $n = 4$.

The powder X-ray diffraction (PXRD) patterns of the chiral Eu(III) coordination polymers are shown in **Figure 3.4**. Characteristic sharp diffraction maxima were observed for each coordination polymer because of its high crystallinity. The single crystals of $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ were successfully obtained by recrystallization from ethanol solution and their structures were determined by single-crystal X-ray structural analyses. The crystallographic data are summarized in **Figure 3.5** and **Table 3.1**. The space groups of these Eu(III) coordination polymers were categorized as $P2_12_12_1$, which is a chiral space group. The ORTEP views of these chiral Eu(III) coordination polymers exhibited eight-coordinated structures in which three chiral camphorate ligands and two phosphine oxide groups were coordinated to one Eu(III) ion. Two phosphine oxide groups in the *p*-dpeb ligand were attached with different Eu(III) ions to form the coordination polymer structure.

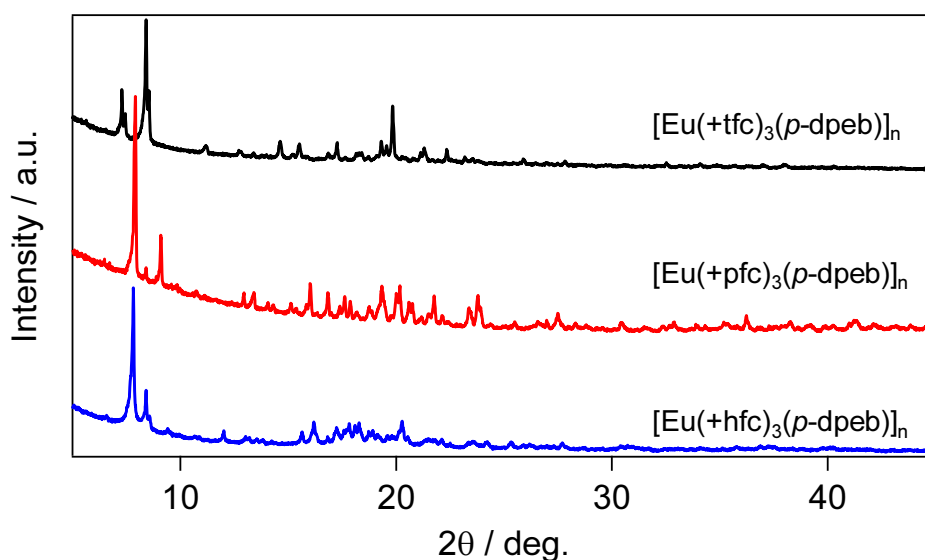
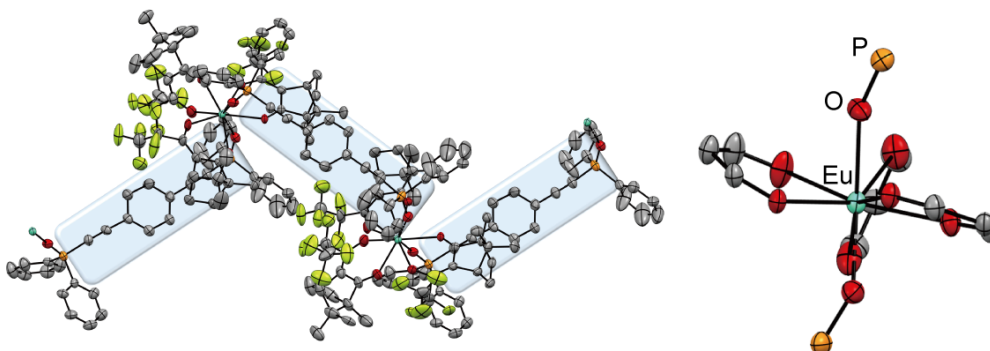
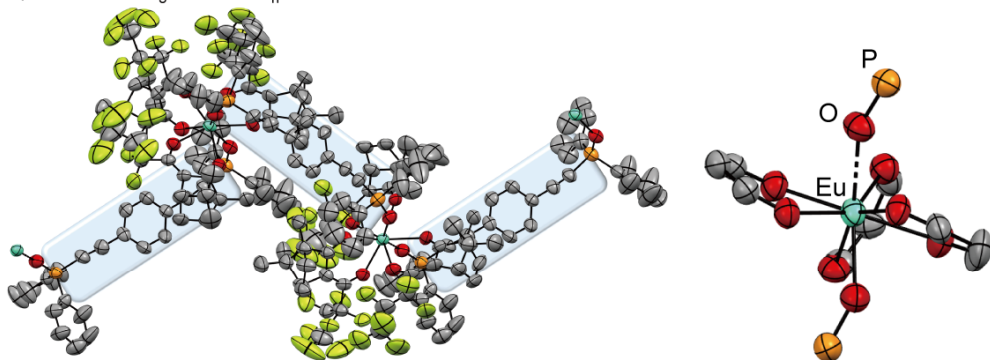


Figure 3.4 PXRD patterns of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ (black), $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ (red), and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ (blue).

a) $[\text{Eu}(\text{+pfc})_3(\text{p-dpeb})]_n$



b) $[\text{Eu}(\text{+hfc})_3(\text{p-dpeb})]_n$



c)

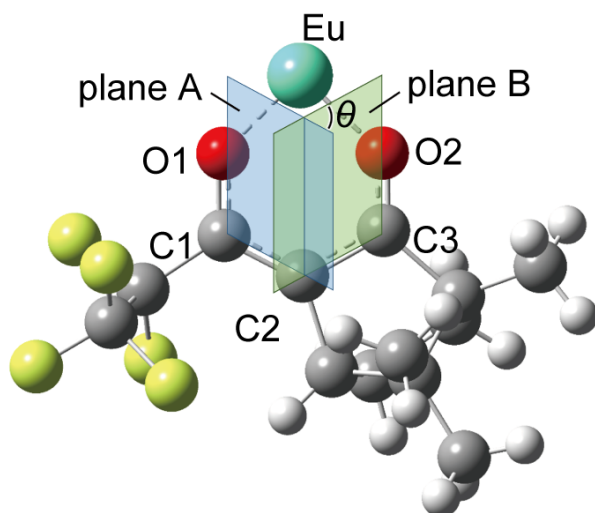


Figure 3.5 ORTEP drawings (ellipsoids set at 50 % probability, hydrogen atoms were omitted for clarity) of a) $[\text{Eu}(\text{+pfc})_3(\text{p-dpeb})]_n$ and b) $[\text{Eu}(\text{+hfc})_3(\text{p-dpeb})]_n$. c) Illustration of dihedral angle θ in camphorate ligand.

Table 3.1 Crystallographic data of chiral Eu(III) coordination polymers.

Compounds	[Eu(+pfc) ₃ (<i>p</i> -dpeb)] _n	[Eu(+hfc) ₃ (<i>p</i> -dpeb)] _n
Chemical formula	C ₇₃ H ₆₆ EuF ₁₅ O ₈ P ₂	C ₇₆ H ₆₆ EuF ₂₁ O ₈ P ₂
Crystal system	orthorhombic	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
<i>a</i> / Å	17.7325(3)	17.6036(3)
<i>b</i> / Å	19.2862(3)	20.5986(5)
<i>c</i> / Å	21.0290(3)	20.7174(5)
β / deg.	90	90
Volume / Å ³	7191.76(19)	7512.3(3)
<i>Z</i>	4	4
ρ _{calc} / g cm ⁻³	1.450	1.521
Temperature / K	123	123
μ (Mo Kα) / mm ⁻¹	1.009	0.984
max 2θ / deg.	62.164	61.978
No. of reflns collected	67773	57738
No. of independent reflns	17870	19014
R ₁	0.0576	0.0648
wR ₂	0.1546	0.1828
Flack parameter	−0.004(7)	0.000(6)

Based on their crystal data, continuous shape measure (CShM) calculations were performed using SHAPE^[16–18] to determine the geometrical structures around the Eu(III) ions in the first coordination sphere (equation (2.1)). The CShM factor (S_{CShM}) values obtained for these complexes for 8-SAP and 8-TDH (SAP: square antiprism, TDH: triangular dodecahedron) are summarized in **Table 3.2**. The S_{CShM} values in the 8-SAP structures are smaller than those of 8-TDH in the synthesized chiral Eu(III) coordination polymers. Thus, the coordination geometries of $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ were categorized as 8-SAP.

To estimate the strain magnitude of the chiral Eu(III) coordination polymers, the author focused on the orientation and planarity of the coordinated β -diketonate ligands. The orientation of the chiral ligands in $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ were classified as Λ form (**Figure 3.5**). The dihedral angles θ of planes A (O1, C1, and C2 atoms in **Figure 3.5**) and B (O2, C2, and C3 atoms in **Figure 3.5**) are listed in **Table 3.3**. The dihedral angles θ in $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ (β -diketonate 4, 5, 6) were larger than those in $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ (β -diketonate 1, 2, 3). These large dihedral angles of $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ indicate large β -diketonate plane distortion.

Table 3.3 Dihedral angles of the camphorate ligands.

Compounds	Ligands	Dihedral angles θ / deg.
[Eu(+pfc) ₃ (<i>p</i> -dpeb)] _n	β -diketonate 1	2.92
	β -diketonate 2	2.35
	β -diketonate 3	5.10
	average	3.46
[Eu(+hfc) ₃ (<i>p</i> -dpeb)] _n	β -diketonate 4	11.68
	β -diketonate 5	6.67
	β -diketonate 6	5.39
	average	6.91

Table 3.2 S_{CSHM} values of the chiral Eu(III) coordination polymers.

Compounds	S_{CSHM} (8-SAP)	S_{CSHM} (8-TDH)
[Eu(+pfc) ₃ (<i>p</i> -dpeb)] _n	0.704	1.422
[Eu(+hfc) ₃ (<i>p</i> -dpeb)] _n	0.526	1.433

3.3.2 Luminescence properties

The emission spectra of the chiral Eu(III) coordination polymers in the solid state are shown in **Figure 3.6**. The emission spectra were normalized with the area of the $^5D_0 \rightarrow ^7F_1$ transition band, which is known to be insensitive to the surrounding environment of the Eu(III) ion.^[19] The emission bands at approximately 580, 590, 615, 650, and 700 nm were assigned to the 4f-4f transitions of Eu(III) ($^5D_0 \rightarrow ^7F_J$: $J = 0, 1, 2, 3$, and 4).^[20] The emission band of $^5D_0 \rightarrow ^7F_2$ transition, which is directly related to the coordination geometrical symmetry, are also shown in **Figure 3.7**.^[21] The Stark splitting of the $^5D_0 \rightarrow ^7F_2$ transition in $[Eu(+pfc)_3(p-dpeb)]_n$ is the same as that in $[Eu(+hfc)_3(p-dpeb)]_n$. The coordination geometry of $[Eu(+pfc)_3(p-dpeb)]_n$ is identical to that of $[Eu(+hfc)_3(p-dpeb)]_n$. On the other hand, the Stark splitting of $[Eu(+tfc)_3(p-dpeb)]_n$ is different from those in $[Eu(+pfc)_3(p-dpeb)]_n$ and $[Eu(+hfc)_3(p-dpeb)]_n$.

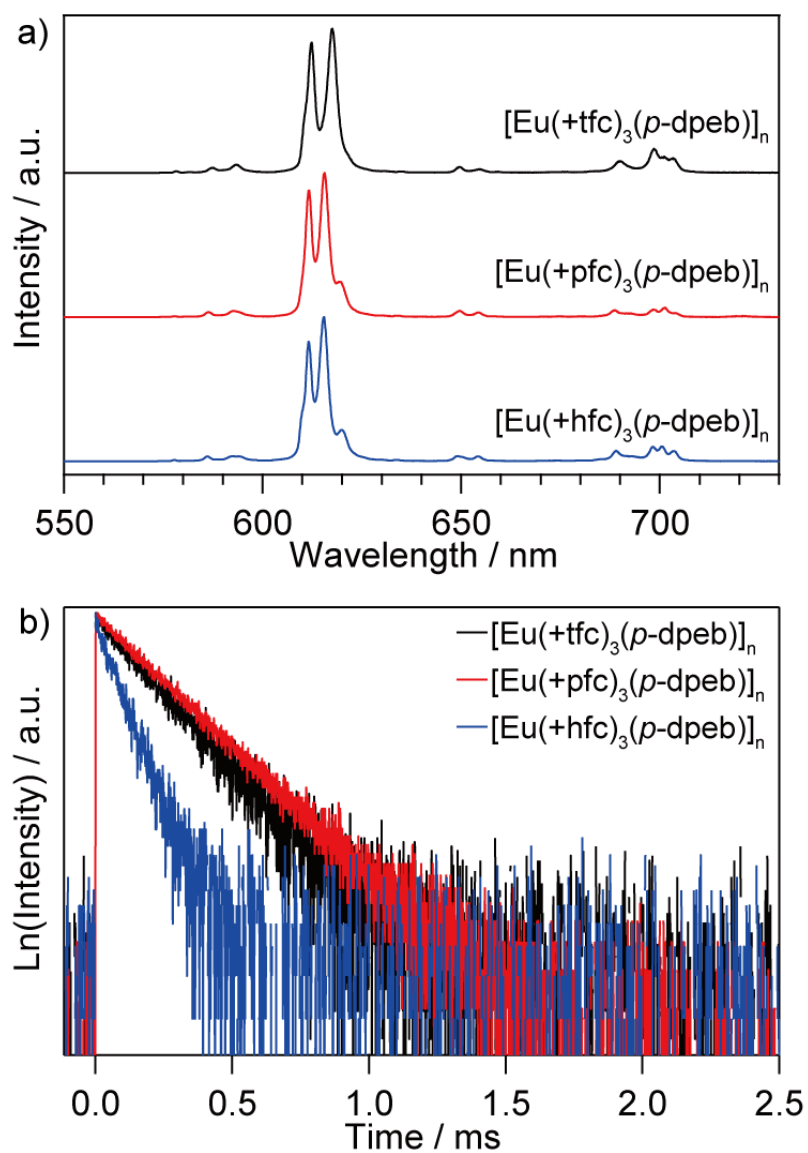


Figure 3.6 a) Emission spectra ($\lambda_{\text{ex}} = 360$ nm) and b) time-resolved emission decay profiles ($\lambda_{\text{ex}} = 355$ nm) of $[\text{Eu}(\text{+tfc})_3(\text{p-dpeb})]_n$ (black), $[\text{Eu}(\text{+pfc})_3(\text{p-dpeb})]_n$ (red), and $[\text{Eu}(\text{+hfc})_3(\text{p-dpeb})]_n$ (blue) in the solid state measured at room temperature.

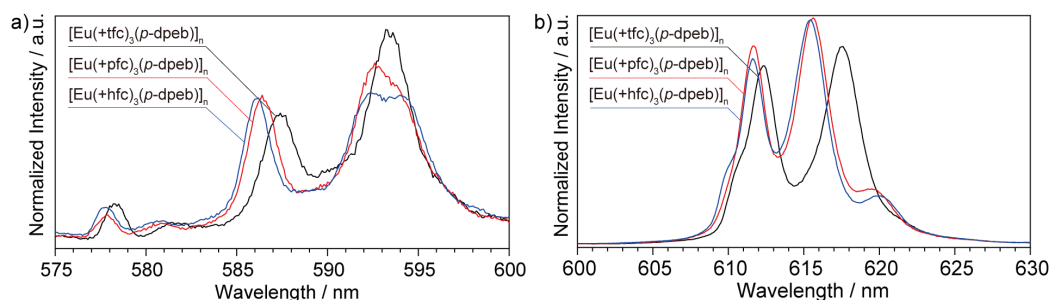


Figure 3.7 Emission spectra ($\lambda_{\text{ex}} = 360$ nm) of $[\text{Eu}(+\text{tfc})_3(\text{p-dpeb})]_n$ (black), $[\text{Eu}(+\text{pfc})_3(\text{p-dpeb})]_n$ (red), and $[\text{Eu}(+\text{hfc})_3(\text{p-dpeb})]_n$ (blue) expanded in the region of a) $^5\text{D}_0 \rightarrow ^7\text{F}_{0,1}$ and b) $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions.

The emission decay profiles of the chiral Eu(III) coordination polymers in the solid state measured at room temperature are shown in **Figure 3.6b**. Single-exponential decays with sub-milli second scale lifetimes were observed. The emission lifetimes were estimated using an exponential function and are summarized in **Table 3.4**. Based on the emission lifetimes and spectra, the 4f-4f emission quantum yield ($\Phi_{\text{f-f}}$), radiative rate constant (k_{r}), and non-radiative rate constant (k_{nr}) were estimated using the equations (1.1)-(1.4).

Table 3.4 Photophysical parameters of chiral Eu(III) coordination polymers.

Compounds	$k_{\text{r}} / \text{s}^{-1}$	$k_{\text{nr}} / \text{s}^{-1}$	$\tau_{\text{obs}}^{[\text{a}]} / \text{ms}$	$\Phi_{\text{f-f}} / \%$
$[\text{Eu}(+\text{tfc})_3(\text{p-dpeb})]_n$	1.2×10^3	2.0×10^3	0.31	37
$[\text{Eu}(+\text{pfc})_3(\text{p-dpeb})]_n$	1.2×10^3	1.5×10^3	0.37	43
$[\text{Eu}(+\text{hfc})_3(\text{p-dpeb})]_n$	1.2×10^3	7.1×10^3	0.12	15

The k_r value of the chiral Eu(III) coordination polymer with large structural strain, $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$, is the same as those of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ and $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$. The magnitude of the k_r enhancement by the LMCT perturbation in $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ is similar to those in $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ and $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$. On the other hand, the k_{nr} values of the chiral Eu(III) coordination polymers (1.5×10^3 – $7.1 \times 10^3 \text{ s}^{-1}$) were strongly dependent on the substituents of the chiral camphorate ligands (+tfc, +pfc, and +hfc). The drastic changes in the k_{nr} values were derived from the LMCT quenching process. This LMCT quenching leads to decreases in both the emission lifetimes and Φ_{f-f} values.

The temperature-dependent emission lifetimes in the solid state measured in the range of 150–350 K are shown in **Figure 3.8a**. The energy transfer rate constants (k_{EnT}) between Eu(III) and LMCT states were estimated using kinetic Arrhenius analysis (**Figure 3.8b**). The k_{EnT} was defined by the following equation: ^[22–24]

$$\ln\left(\frac{1}{\tau_{\text{obs}}} - \frac{1}{\tau_{150\text{K}}}\right) = \ln k_{\text{EnT}} = \ln A - \frac{\Delta E_a}{RT} \quad (3.1)$$

where τ_{obs} , $\tau_{150\text{K}}$, A , ΔE_a , R , and T are the observed emission lifetime, standard emission lifetime at 150 K, frequency factor, activation energy, gas constant, and temperature, respectively. The calculated ΔE_a and A values are summarized in **Table 3.5**. The Arrhenius plots were well fitted to the equation (3.1) with high coefficient of determination ($R^2 = 0.996$ ($[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$), and 0.999 ($[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$)), indicating the single temperature-dependent quenching state.

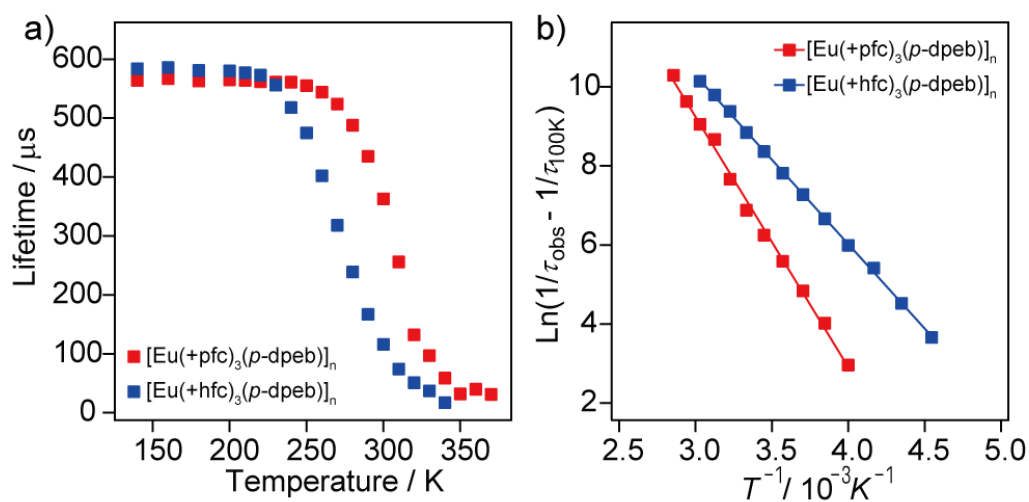


Figure 3.8 a) Temperature-dependent emission lifetimes and b) Arrhenius plots of $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ (red) and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ (blue) ($\lambda_{\text{ex}} = 355\text{ nm}$, $\lambda_{\text{em}} = 610\text{ nm}$).

Table 3.5 Arrhenius parameters of chiral Eu(III) coordination polymers.

Compounds	$\Delta E_a / \text{cm}^{-1}$	A / s^{-1}
$[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$	4.4×10^3	4.0×10^{11}
$[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$	3.0×10^3	1.1×10^{10}

3.3.3 Theoretical calculations

TD-DFT calculations were performed to estimate the LMCT characteristics in $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$. These calculations were based on the structural parameters obtained by single-crystal X-ray structural analyses. The selected molecular orbitals of $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ are shown in **Figure 3.9**.

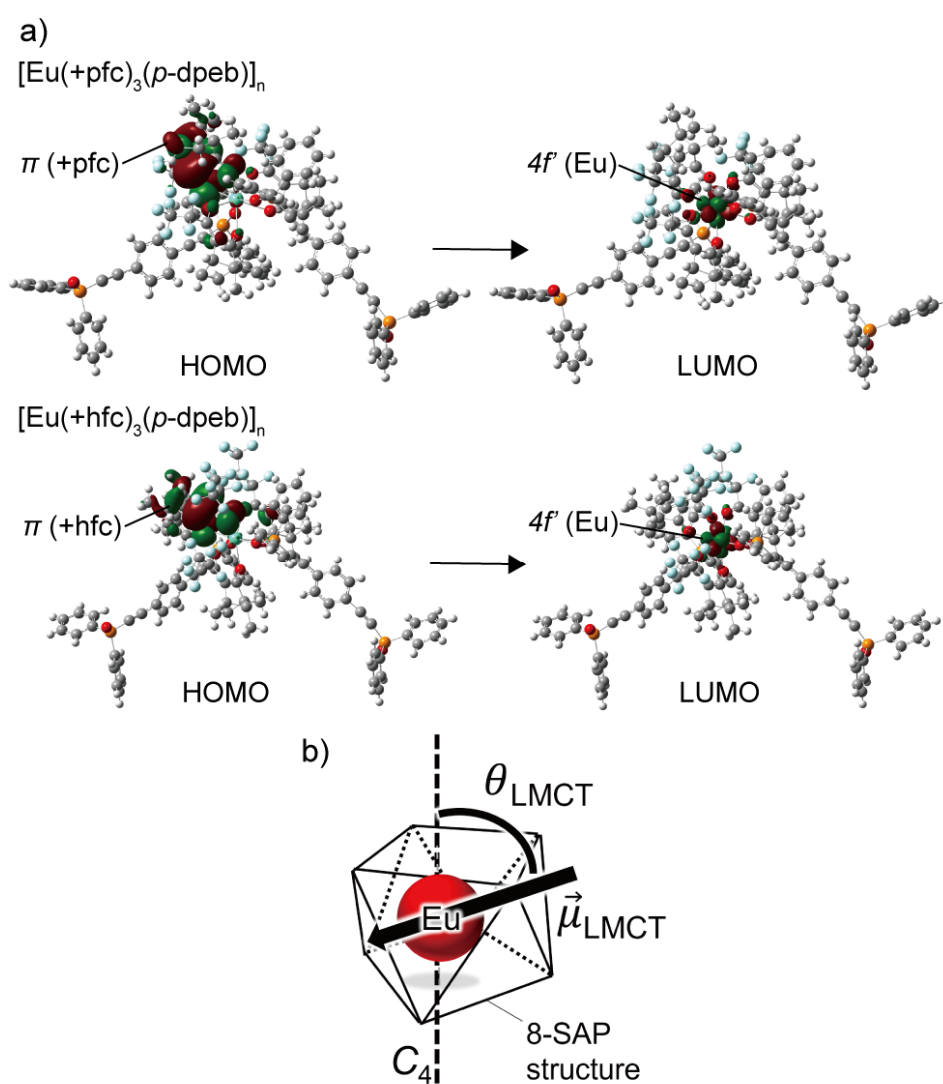


Figure 3.9 a) Selected α -spin molecular orbitals of $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$.
b) Illustration of θ_{LMCT} .

The calculated HOMO and LUMO are located in the camphorate ligands and Eu(III), respectively. The excitation energies and oscillator strengths of the lowest LMCT transition (π (camphorate ligand) $\rightarrow 4f^0$ (Eu)) are summarized in **Table 3.6**. The LMCT excitation energy of $[\text{Eu}(\text{+hfc})_3(\text{p-dpeb})]_n$ ($20,810 \text{ cm}^{-1}$) is lower than that of $[\text{Eu}(\text{+pfc})_3(\text{p-dpeb})]_n$ ($22,530 \text{ cm}^{-1}$). The calculated energy levels of $[\text{Eu}(\text{+hfc})_3(\text{p-dpeb})]_n$ and $[\text{Eu}(\text{+pfc})_3(\text{p-dpeb})]_n$ are qualitatively consistent with the results of diffuse reflection measurements (**Figure 3.10**). The absorption edge of $[\text{Eu}(\text{+hfc})_3(\text{p-dpeb})]_n$ (c.a. 400 nm) is longer than that of $[\text{Eu}(\text{+tfc})_3(\text{p-dpeb})]_n$ and $[\text{Eu}(\text{+pfc})_3(\text{p-dpeb})]_n$ (c.a. 380 nm). These lower LMCT excited states lead to energy transfer between Eu(III) and the LMCT state, resulting in a decrease of the emission quantum yield ($\Phi_{\text{f-f}}$). The moment angles between the transition electric dipole moments of the LMCT ($\vec{\mu}_{\text{LMCT}}$) and C_4 axis in the 8-SAP structure (θ_{LMCT} , **Figure 3.9** and **Table 3.6**) were also calculated. The results revealed that the θ_{LMCT} of $[\text{Eu}(\text{+hfc})_3(\text{p-dpeb})]_n$ (79.3°) is smaller than that of $[\text{Eu}(\text{+pfc})_3(\text{p-dpeb})]_n$ (82.5°), indicating that the bulky substituents in $[\text{Eu}(\text{+hfc})_3(\text{p-dpeb})]_n$ affected the direction of the transition electric dipole moments.

Table 3.6 Characteristics of the LMCT states and the energy of T1 states obtained by TD-DFT calculations.

Compounds	Excitation energies of the lowest LMCT states / cm^{-1}	Oscillator strengths	θ_{LMCT} / deg.	Energy levels of T ₁ states / cm^{-1}
$[\text{Eu}(\text{+tfc})_3(\text{p-dpeb})]_n$ ^[a]	22,310	0.0046	84.0	20,400
$[\text{Eu}(\text{+pfc})_3(\text{p-dpeb})]_n$ ^[b]	22,530	0.0043	82.5	20,300
$[\text{Eu}(\text{+hfc})_3(\text{p-dpeb})]_n$ ^[b]	20,810	0.0050	79.3	20,110

[a] Based on the structure obtained by structural optimization of $[\text{Eu}(\text{+tfc})_3(\text{p-dpeb})_2]$. [b] Based on the structure obtained by single-crystal X-ray structural analyses.

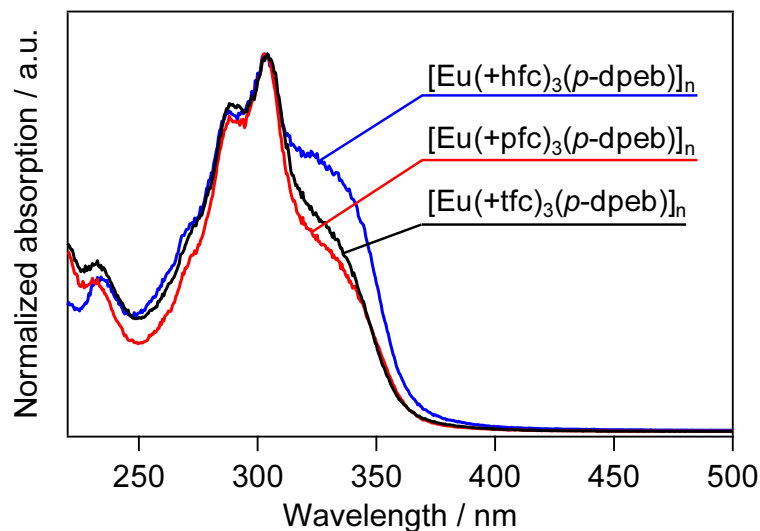


Figure 3.10 Diffuse reflection spectra of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ (black), $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ (red), and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ (blue).

Additionally, structural optimization of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})_2]$ unit by DFT calculations to estimate the structure of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ was performed. The optimized structure and the cartesian coordinates of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})_2]$ are shown in **Figure 3.11** and **Table 3.8**, respectively. The LMCT characteristics of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ were also evaluated using TD-DFT calculations based on the optimized structure. The characteristics of the LMCT states were summarized in **Table 3.6**. The LMCT excitation energy of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ ($22,310\text{ cm}^{-1}$) is similar to that of $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ ($22,530\text{ cm}^{-1}$). The θ_{LMCT} of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ (84.0°) is larger than that of $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$. The structural strain of the camphorate ligands was closely related to the characteristics of the LMCT excited states in the chiral Eu(III) coordination polymers.

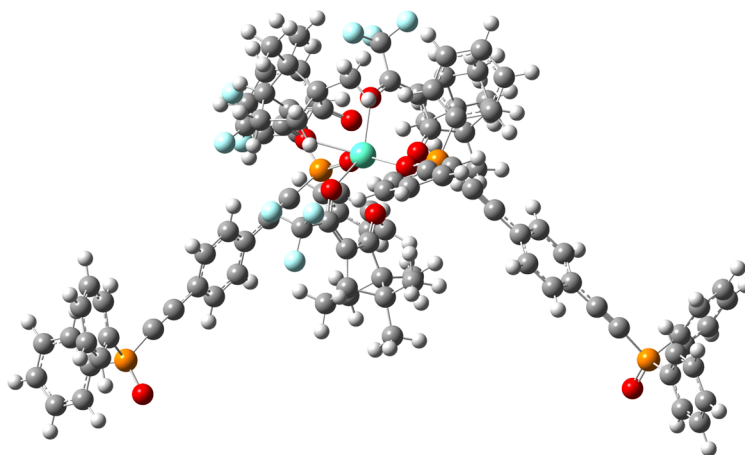


Figure 3.11 Optimized structure of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})_2]$ obtained by DFT calculations.

The energy level of T_1 states, which are strongly related to the energy transfer process of Eu(III) complexes,^[25] are also estimated (**Table 3.6**). The T_1 energy level of $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ ($20,110\text{ cm}^{-1}$) is similar to those of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ ($20,400\text{ cm}^{-1}$) and $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ ($20,300\text{ cm}^{-1}$). From these results, the drastically change of $\Phi_{\text{f-f}}$ is mainly caused by the LMCT excited states.

3.3.4 CPL properties

The CPL spectra of the chiral Eu(III) coordination polymers in the solid state (in KBr pellets) are shown in **Figure 3.12**. Characteristic CPL signals were observed at approximately 590 ($^5D_0 \rightarrow ^7F_1$) and 615 nm ($^5D_0 \rightarrow ^7F_2$). The g_{CPL} values of each transition band are summarized in **Table 3.7**.

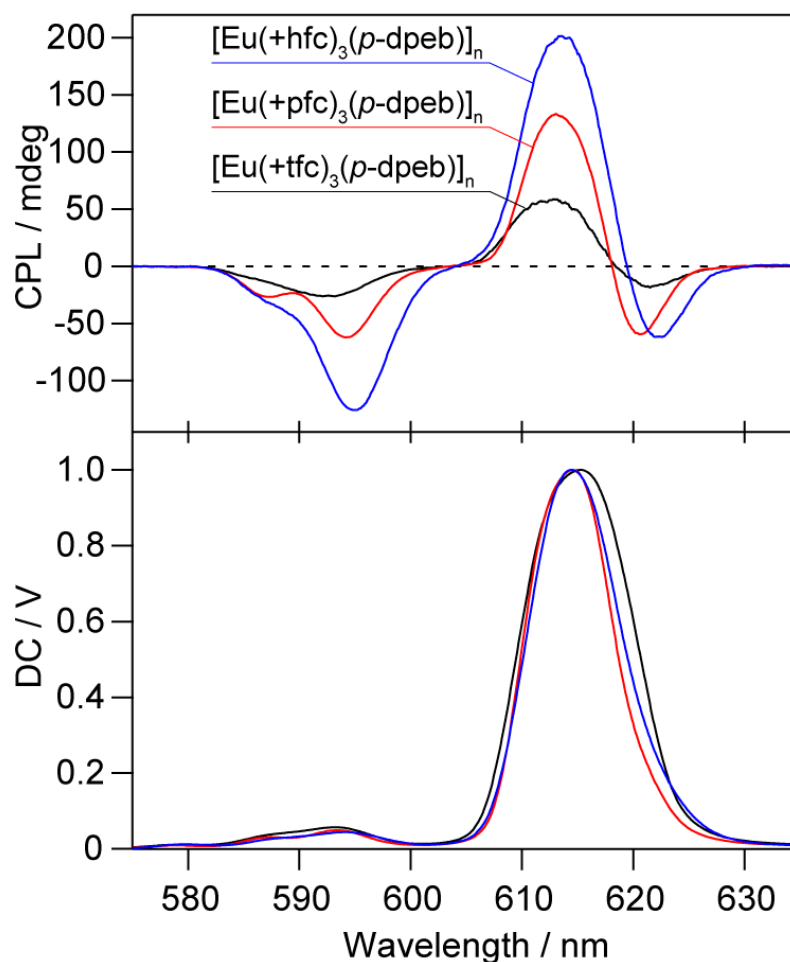


Figure 3.12 CPL (upper) and emission (lower) spectra ($\lambda_{\text{ex}} = 350$ nm) of $[\text{Eu}(+\text{tfc})_3(\text{p-dpeb})]_n$ (black), $[\text{Eu}(+\text{pfc})_3(\text{p-dpeb})]_n$ (red) and $[\text{Eu}(+\text{hfc})_3(\text{p-dpeb})]_n$ (blue) in KBr pellet.

Table 3.7 The g_{CPL} values of the chiral Eu(III) coordination polymers in their $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions.

Compounds	$g_{\text{CPL}}(^5\text{D}_0 \rightarrow ^7\text{F}_1)$	$g_{\text{CPL}}(^5\text{D}_0 \rightarrow ^7\text{F}_2)$
$[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$	-0.05	+0.005
$[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$	-0.10	+0.010
$[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$	-0.22	+0.017

The CPL signal intensities of $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ ($g_{\text{CPL}} = -0.10$) and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ ($g_{\text{CPL}} = -0.22$) were larger than that of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ ($g_{\text{CPL}} = -0.05$). Three types of enantiomeric coordination polymers, $[\text{Eu}(-\text{tfc})_3(p\text{-dpeb})]_n$, $[\text{Eu}(-\text{pfc})_3(p\text{-dpeb})]_n$, and $[\text{Eu}(-\text{hfc})_3(p\text{-dpeb})]_n$ showed mirror images in the CPL spectra (**Figure 3.13**). The enhancement of the $|g_{\text{CPL}}|$ values in both $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions can be explained by the J -mixing between $^7\text{F}_1$ and $^7\text{F}_2$ sublevels.^[26] The J -mixing is estimated by the Stark splitting energy of magnetic dipole transition band ($^5\text{D}_0 \rightarrow ^7\text{F}_1$).^[27,28] In the emission band of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, the Stark splitting energies of $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ were larger than that of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ (**Figure 3.7**). The large $|g_{\text{CPL}}|$ of $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ are caused by large J -mixing effect. Indeed, the $|g_{\text{CPL}}|$ value of $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ was twice that of $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$ in both the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions. The Stark splitting energy and k_r value of $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ are the same as those of $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$, resulting in constant $|\vec{\mu}_{f-f}|^2 + |\vec{m}_{f-f}|^2$ and $|\vec{\mu}_{f-f} / \vec{m}_{f-f}|$ units in equation (1.17). From these results, the enhanced $|g_{\text{CPL}}|$ value of $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ is caused by the change in $\cos \theta_{\mu,m}$. The moment angle of $\vec{\mu}_{f-f}$ is affected by $\vec{\mu}_{\text{LMCT}}$ through LMCT perturbation, which is related to the change in $\theta_{\mu,m}$. Thus, the steric hindrance control in camphorate

ligands of chiral Eu(III) coordination polymers is one of the important factors for enhancing their CPL properties.

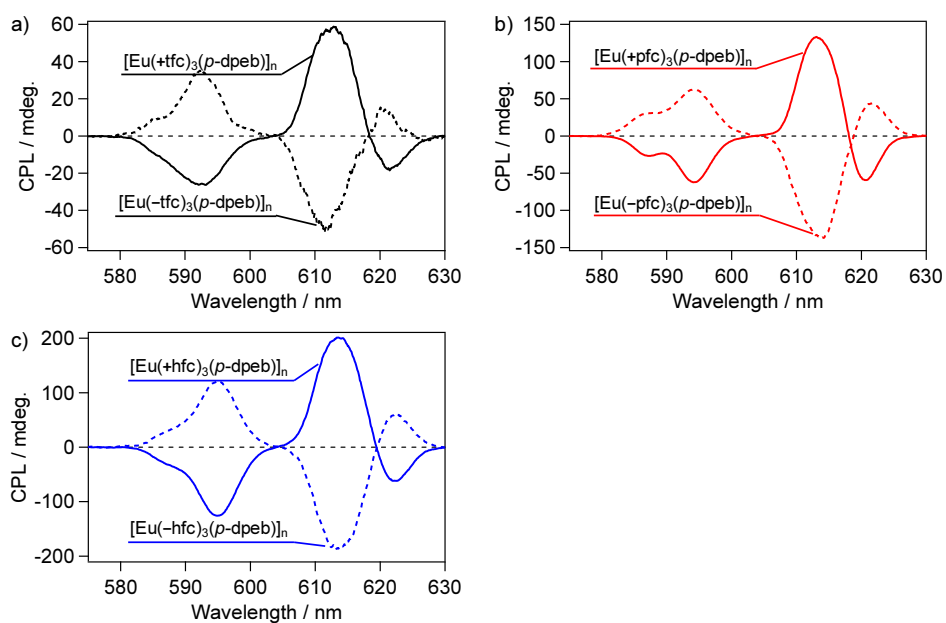


Figure 3.13 CPL spectra of a) $[\text{Eu}(+\text{tfc})_3(\text{p-dpeb})]_n$ (solid) and $[\text{Eu}(-\text{tfc})_3(\text{p-dpeb})]_n$ (dotted), b) $[\text{Eu}(+\text{pfc})_3(\text{p-dpeb})]_n$ (solid) and $[\text{Eu}(-\text{pfc})_3(\text{p-dpeb})]_n$ (dotted), and c) $[\text{Eu}(+\text{hfc})_3(\text{p-dpeb})]_n$ (solid) and $[\text{Eu}(-\text{hfc})_3(\text{p-dpeb})]_n$ (dotted).

3.4 Conclusion

Three types of chiral Eu(III) coordination polymers, $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$, $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$, and $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ were synthesized. The structural distortion of $[\text{Eu}(+\text{hfc})_3(p\text{-dpeb})]_n$ was larger than that of $[\text{Eu}(+\text{pfc})_3(p\text{-dpeb})]_n$. The large structural strain affects the direction of the transition dipole moments and leads to a large $|g_{\text{CPL}}|$ value. In this study, the electronic structure of the ligands in a chiral Eu(III) coordination polymer is directly linked to the characteristics of the LMCT excited states and $|g_{\text{CPL}}|$ value. The precise tuning of the structural distortion of the chiral ligands can enhance the $|g_{\text{CPL}}|$ value for optical applications. The relationship between the CPL properties and LMCT excited states in chiral Eu(III) compounds provides novel insights in the fields of lanthanide chemistry, coordination chemistry, and photophysical science.

3.5 Appendix

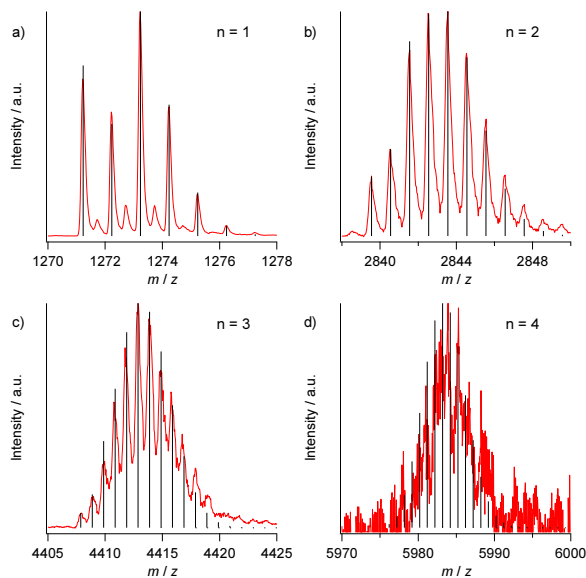


Figure 3.14 ESI-MS spectra (red) and simulated mass pattern (black) of $[\text{Eu}_n(+\text{pfc})_{3n-1}(\text{p-dpeb})_n]^+$ (a) $n = 1$, b) $n = 2$, c) $n = 3$, d) $n = 4$.

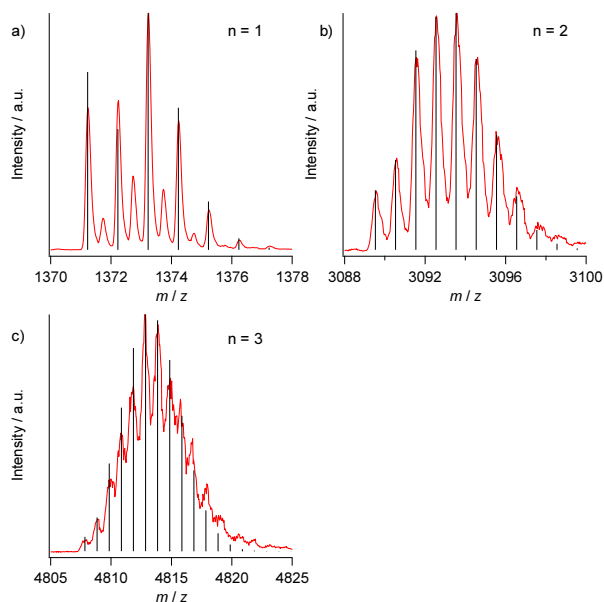


Figure 3.15 ESI-MS spectra (red) and simulated mass pattern (black) of $[\text{Eu}_n(+\text{hfc})_{3n-1}(\text{p-dpeb})_n]^+$ (a) $n = 1$, b) $n = 2$, c) $n = 3$.

Table 3.8 Cartesian coordinates (in Å) of [Eu(+tfc)₃(*p*-dpeb)₂] for optimized structure obtained by DFT calculations.

Atom	X	Y	Z	Atom	X	Y	Z
P	-9.19144	6.46651	0.060322	H	4.269938	-1.41087	1.588213
P	-1.73203	-1.82383	3.306254	H	5.213164	-2.16582	2.895127
O	-8.49847	7.781126	-0.14049	C	5.709428	0.957488	-1.48149
C	-11.5897	7.929844	3.017292	C	3.99269	-5.69766	1.15331
H	-11.7295	8.893318	3.500071	H	4.751975	-6.39063	1.532707
C	-4.63744	1.27532	2.179704	H	3.64865	-6.08255	0.190533
C	-10.0071	5.846056	-1.44979	C	0.594008	-5.06216	0.763562
C	-10.4522	6.551627	1.381444	C	-1.71186	0.858623	-1.36092
C	-10.2946	4.49232	-1.67385	C	2.804381	-5.54233	2.147546
H	-9.98789	3.742445	-0.94974	H	2.44606	-6.48076	2.576663
C	-8.14622	5.125639	0.560394	C	-2.55008	-3.80656	-3.96462
C	-3.71372	0.274856	2.597052	C	9.813183	4.12604	0.221181
C	-5.38555	1.097582	0.997373	C	12.27974	4.065834	1.612245
H	-5.26891	0.190066	0.417034	C	0.68665	3.509383	-0.33214
C	-7.35857	4.265651	0.913279	C	2.329699	-4.05394	4.225561
C	-12.3592	6.832652	3.4075	H	2.740093	-3.26454	4.866716
H	-13.1007	6.94063	4.194766	H	2.061448	-4.89546	4.876707
C	-4.80466	2.454309	2.934729	H	1.409981	-3.67147	3.776299
H	-4.22672	2.591698	3.84301	C	2.212574	-0.39366	-6.68836
C	-6.272	2.081628	0.581453	H	2.872556	-0.41024	-7.55135
H	-6.838	1.948315	-0.33455	C	1.889228	2.349745	1.748417
C	-10.6369	7.792045	2.005681	H	1.687275	1.681995	2.592606
H	-10.0277	8.634013	1.691208	H	2.277292	3.293773	2.148884
C	-6.44362	3.259229	1.336767	H	2.674219	1.880598	1.145628
C	-2.92964	-0.59434	2.932619	C	6.497938	0.572889	-0.37791
C	-0.87057	-1.19095	4.781109	H	6.278413	-0.35839	0.134045
C	-10.9497	4.099939	-2.84151	C	-4.50594	-3.79038	-2.79576
H	-11.1658	3.048873	-3.013	H	-5.43002	-4.16658	-2.35313
C	-5.69822	3.431956	2.521124	C	-2.80091	1.288586	-2.3539
H	-5.8269	4.338765	3.102921	C	0.159907	-6.53858	0.779095
C	-11.2269	5.45159	1.776667	C	4.539625	-4.2404	1.058317
H	-11.0897	4.484369	1.300721	H	4.47224	-3.82789	0.046435
C	-2.64857	-3.32031	3.759744	H	5.591569	-4.17849	1.360059
C	0.348583	-0.52544	4.580312	C	4.261542	-3.52152	-3.20369
H	0.745927	-0.4349	3.573448	H	4.979328	-2.71311	-3.31087
C	-12.1772	5.593106	2.786775	C	-1.53324	3.748579	0.632793
H	-12.7753	4.738194	3.090611	H	-1.63541	4.838256	0.675965
C	1.037235	0.002352	5.673468	H	-2.5378	3.324671	0.708903
H	1.981041	0.517817	5.517567	C	11.80664	5.965342	-0.59804
C	-11.021	6.403584	-3.57925	C	-0.56896	3.216539	1.736649
H	-11.2942	7.145966	-4.32422	H	-1.03857	2.475733	2.392434
C	-2.67334	-5.73834	3.88334	H	-0.19738	4.022102	2.379705
H	-2.18744	-6.68889	3.686065	C	12.56986	4.230279	2.972913
C	-11.3164	5.055376	-3.79261	H	12.06178	5.013088	3.527827
H	-11.8235	4.747319	-4.70309	C	4.681828	-4.84535	-3.33543
C	-2.02049	-4.55482	3.54042	H	5.722258	-5.06135	-3.5622
H	-1.03651	-4.59039	3.086345	C	-3.26726	-6.07467	-2.89135
C	-3.9473	-5.69342	4.453749	H	-2.63968	-6.71617	-3.52265
H	-4.45682	-6.61635	4.717512	H	-4.14148	-6.66787	-2.5948
C	-10.3667	6.800139	-2.41237	H	-2.70331	-5.84132	-1.98434
H	-10.1139	7.842937	-2.24552	C	13.49964	3.393974	3.594357
C	-3.93367	-3.278	4.318053	H	13.72208	3.523868	4.650011
H	-4.43985	-2.32618	4.451017	C	0.078014	0.167605	-5.68997

C	-4.57611	-4.46493	4.671383	H	-0.91834	0.592353	-5.76466
H	-5.57436	-4.43087	5.098862	C	12.95272	7.886589	-1.53011
C	-1.38792	-1.33079	6.076128	H	13.35743	8.88796	-1.41158
H	-2.32165	-1.86173	6.238749	C	0.928803	0.151159	-6.79605
C	0.517503	-0.1336	6.962998	H	0.593891	0.561226	-7.74515
H	1.05771	0.276138	7.812355	C	-3.54469	-2.93494	-0.49303
C	-0.69314	-0.80122	7.163922	C	12.33488	7.255879	-0.44966
H	-1.09338	-0.91538	8.167594	H	12.24095	7.761053	0.506971
Eu	-0.39327	-1.98933	-0.11325	C	13.04359	7.23553	-2.76239
P	2.307823	-1.53709	-2.73721	H	13.52323	7.728765	-3.60363
P	11.0548	5.208037	0.881819	C	1.645149	3.009961	-1.4281
O	0.246398	0.155438	0.715752	H	2.6874	3.07914	-1.09315
F	1.122215	-7.34245	0.259232	H	1.547916	3.633409	-2.32601
O	10.55702	6.214951	1.874901	H	1.454722	1.974226	-1.72074
O	1.184283	-1.3942	-1.73797	C	-3.34055	-2.57517	-4.54142
O	-0.17708	-4.28037	0.12209	H	-3.4762	-2.69862	-5.62196
F	-5.7889	-2.11244	-0.56651	H	-2.78922	-1.64282	-4.38958
F	-0.96249	-6.75102	0.083921	C	-3.71532	-4.82293	-3.66785
O	1.791263	-2.35834	0.836142	C	-3.43267	-3.35374	-1.80604
F	-3.02525	2.617448	-2.40544	C	-2.20614	-3.35546	-2.53808
F	-4.94921	-2.48537	1.400508	C	4.613129	-4.97704	3.940677
O	-1.64629	-0.40923	-1.25824	H	5.438108	-5.28763	3.295278
O	-1.05555	-3.01443	-2.16895	H	4.357507	-5.83002	4.582036
O	-2.61019	-2.54057	0.274011	H	4.9884	-4.18102	4.595258
C	0.006772	1.320197	0.320347	C	0.50521	-0.35965	-4.46921
F	-2.47555	0.891653	-3.61356	H	-0.15389	-0.36296	-3.60847
C	2.434852	-5.60968	-2.8566	C	-4.95179	-2.92952	0.133997
H	1.729711	-6.42036	-2.69693	C	11.88842	5.320747	-1.84044
C	7.822436	2.595653	-0.60285	H	11.44997	4.335356	-1.97341
C	1.794239	-0.8984	-4.35935	C	1.056267	4.972818	-0.03325
C	1.755171	-4.70825	1.425341	H	0.476324	5.422361	0.775911
C	2.919202	-3.23935	-2.90763	H	0.903	5.587672	-0.92915
C	3.36413	-4.50181	3.178322	H	2.115838	5.053307	0.237976
C	2.647982	-0.91697	-5.47229	C	-1.37146	-4.25761	-4.8094
H	3.646624	-1.33908	-5.39382	H	-1.6976	-4.53891	-5.81776
C	3.728571	-0.58501	-2.30524	H	-0.86144	-5.11968	-4.36462
C	0.626329	2.580932	0.937277	H	-0.63441	-3.45336	-4.9063
C	8.892045	3.423997	-0.15682	C	12.50816	5.954562	-2.91802
C	7.030738	2.981351	-1.70377	H	12.56591	5.452732	-3.88018
H	7.24173	3.919075	-2.20735	C	-4.69679	-2.59446	-3.77455
C	-0.90851	1.765186	-0.69194	H	-4.87753	-1.66624	-3.22731
C	-0.82611	3.287965	-0.67545	H	-5.54428	-2.75249	-4.45114
H	-1.17256	3.791274	-1.5781	C	-4.47435	-5.30325	-4.91695
C	4.638599	0.128941	-1.9232	H	-4.80513	-4.49505	-5.57342
C	3.769684	-5.88894	-3.15906	H	-5.36473	-5.87072	-4.6176
H	4.101641	-6.91969	-3.25026	H	-3.84695	-5.9768	-5.51353
C	2.279538	-3.37791	1.373024	C	12.9275	3.061601	0.878477
C	7.539887	1.380917	0.054686	H	12.71263	2.928363	-0.1784
H	8.143854	1.085169	0.90623	C	14.14128	2.394503	2.861133
C	5.988894	2.173615	-2.13766	H	14.86538	1.744596	3.345338
H	5.379015	2.474033	-2.9834	C	13.85515	2.228806	1.502597
C	2.001151	-4.28812	-2.73684	H	14.35593	1.452148	0.930852
H	0.962604	-4.07215	-2.50346	O	-0.7114	-2.06543	2.210701
C	3.650719	-3.42396	2.064421	F	-3.97831	0.7001	-2.04976
C	4.210037	-2.06933	2.462166	F	-5.51755	-4.15789	0.136967
H	3.567286	-1.56882	3.194749	F	-0.06153	-6.97015	2.052854

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Chapter 4

***CIRCULARLY POLARIZED LUMINESCENCE OF
PHASE TRANSFORMABLE CHIRAL Eu(III)
COORDINATION POLYMERS***

4.1 Introduction

In **Chapter 2** and **3**, the author discovered the LMCT characteristics of chiral Eu(III) complexes affected to their CPL properties. Generally, the CPL properties are also affected to the steric or electronic structure of the organic ligands. The evaluation of the CPL properties using same organic ligands were required for the precisely elucidation of the relationship between LMCT characteristics and CPL properties. Herein, chiral Eu(III) coordination polymers with phase-transition behaviors are proposed for the evaluation of molecular orientations in crystalline solids. Through the phase-transition, the packing structure of the chiral Eu(III) coordination polymers can be changed with same ligands. In molecular designs for the thermal phase-transition, a flexible transformation ability and a thermostable rigid structure of Eu(III) coordination compounds are required. Eu(III) coordination polymers exhibit tight stacking structures of one-dimensional polymer chains in the crystal, resulting in the formation of thermostable properties (decomposition temperature > 300 °C).^[1–3] Hirai reported that the ethynyl groups of the linker ligands in Eu(III) coordination polymers exhibit phase-transition behavior in the solid state.^[4,5]

In this chapter, chiral Eu(III) coordination polymers with ethynyl groups in the linker ligands, $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ and $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$, were prepared by the reaction of $[\text{Eu}(+\text{tfc})_3(\text{H}_2\text{O})_2]$ with *m*- or *p*-dpeb (**Figure 4.1a**, +tfc: (+)-3-trifluoroacetylcamphorato, *m*-dpeb: 1,3-bis(diphenylphosphorylethynyl)benzene, *p*-dpeb: 1,4-bis(diphenylphosphorylethynyl)benzene). The coordination polymers are composed of Eu(III) ions, chiral camphorate ligands (+tfc), and *m*- or *p*-linked phosphine oxide ligands, including ethynyl groups (*m*-dpeb or *p*-dpeb). The *o*-linked ethynyl ligand (*o*-dpeb: 1,2-bis(diphenylphosphorylethynyl)benzene) provides a mononuclear Eu(III) complex $[\text{Eu}(+\text{tfc})_3(o\text{-dpeb})]$. The phase-transition behavior of Eu(III) coordination polymers was characterized using thermogravimetry (TG), differential scanning calorimetry (DSC), and powder X-ray diffraction (PXRD). The chiral Eu(III) coordination polymer,

$[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$, exhibit phase-transition behavior without changes in the coordination geometry (see **Figure 4.1b** for images of Type-A and Type-B), although $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ has no phase-transition temperature. The phase-transition of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ leads to a considerable change in the CPL signal intensity without a spectral shape change in the emission. Transformable chiral Eu(III) coordination polymer has been demonstrated for understanding the orientation effect on CPL properties in solid systems.

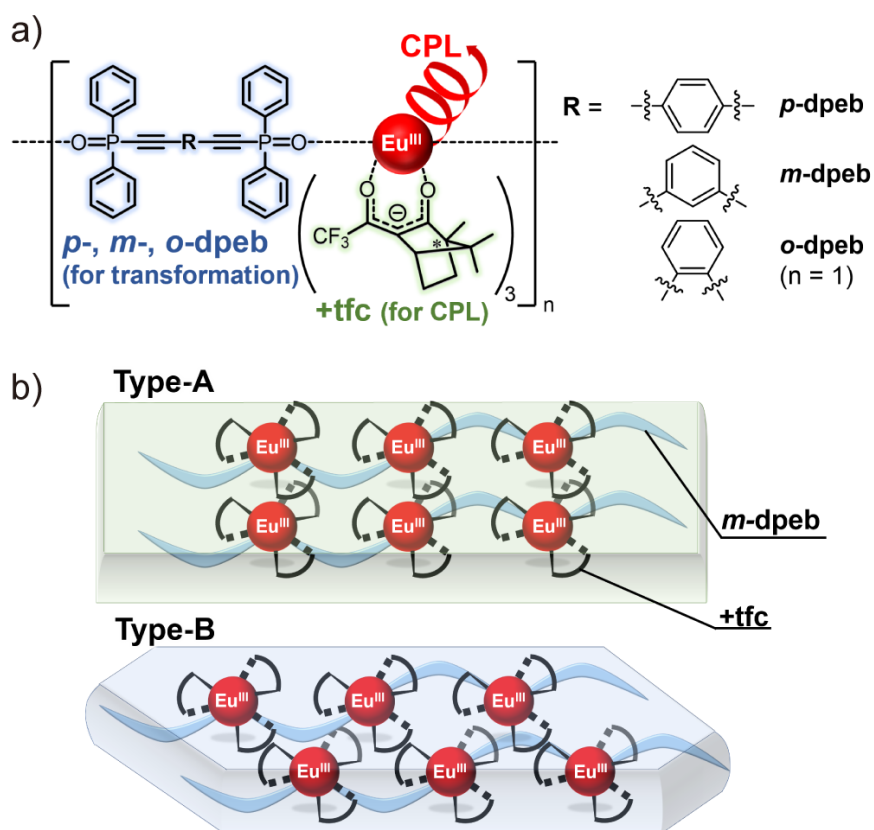


Figure 4.1. (a) Chemical structures of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$, $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$, and $[\text{Eu}(+\text{tfc})_3(o\text{-dpeb})]$.
(b) Schematic image of phase transition in $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$.

4.2 Methods

4.2.1 Materials and apparatus

All chemicals were of reagent grade and used without further purification. Fourier transform infrared (FT-IR) spectra were recorded on a JASCO FT/IR-4600 spectrometer. ESI-MS spectra were measured using a JEOL JMS-T100LP. Elemental analyses were performed on an Exeter Analytical CE440. ^1H NMR (400 MHz) and ^{31}P NMR (162 MHz) spectra were recorded on a JEOL ECS400 at 298 K. Tetramethylsilane ($\delta_{\text{H}} = 0.00$ ppm) and phosphoric acid ($\delta_{\text{P}} = 0.00$ ppm) were used as internal references for ^1H and ^{31}P NMR, respectively. DSC was performed on a Hitachi High-Tech DSC 7020 under a nitrogen atmosphere at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$. TG analysis was performed on a Hitachi High-Tech TG/DTA6300 analyzer under a nitrogen atmosphere at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$. Synchrotron X-ray powder diffraction data were acquired using a large Debye–Scherrer camera installed at the SPring-8 BL02B2 beamline, employing an autosampler with a multiple MYTHEN detector.^[6] The wavelength of the incident X-ray was $0.800168\text{ }\text{\AA}$, which was calibrated using a cerium oxide standard powder sample by the National Institute of Standards and Technology. Temperature-dependent X-ray diffractometry was performed on a Rigaku SmartLab using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418\text{ }\text{\AA}$).

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. Emission lifetimes in the range of 100–

350 K were measured using a cryostat (Thermal Block Company, SA-SB245T) and a temperature controller (Oxford, Instruments, ITC 502S). CPL spectra were recorded on a JASCO CPL-300 for Eu(III) complexes (0.5 mg) mixed with KBr (150 mg). Tablets (diameter: 10 mm, Eu(III) complexes/KBr) were prepared using a PT-10 tablet forming machine (48.2 kN, press time: 3 min).

4.2.2 Computational details

All quantum chemical calculations were performed by the density functional theory (DFT) with the long-range and dispersion-corrected ω B97X-D functional^[7] using the Gaussian 16 package.^[8] The spin-unrestricted self-consistent field calculations were performed. Excited states were investigated using time-dependent (TD)-DFT. The Stuttgart RSC 1997 (ECP28MWB)^[9,10] basis set was adopted for Eu atoms, while the cc-pVDZ basis set^[11] was used for the other atoms.

4.2.3 Syntheses

Preparation of 1,3-Bis(diphenylphosphorylethynyl)benzene (*m*-dpeb)

m-dpeb was prepared with the procedure described in a previous report.^[4] 1,3-Diethynylbenzene (1.0 g, 7.9 mmol) was dissolved in dry diethyl ether (50 mL), and the mixture was degassed by Ar bubbling. A solution of *n*-BuLi (ca. 1.6 mol L⁻¹, 12 mL, 19 mmol) was added dropwise to the solution at -80 °C. The mixture was stirred for 3.5 h at -10 °C, after which chlorodiphenylphosphine (3.5 mL, 19 mmol) was added dropwise at -80 °C. The mixture was gradually brought to room temperature and stirred for 19 h. The reaction mixture was poured into distilled water and extracted with dichloromethane. The extracts were washed with brine three times and dried over anhydrous MgSO₄. The solvent was evaporated, and the obtained yellow oil was placed with dichloromethane (10 mL) in a flask. The solution was cooled to 0 °C, and then an aqueous 30% hydrogen

peroxide solution (10 mL) was added dropwise to the above solution. The solution was stirred for 3 h. After the separation of the aqueous hydrogen peroxide solution, the solution was washed with distilled water. Anhydrous MgSO_4 was added to the organic phases for dehydration. After filtration, the organic phase was evaporated to give a white powder. The powder was recrystallized from methanol solution to give prism crystals. Yield: 3.48 g (6.6 mmol, 84%). ^1H NMR (CDCl_3): δ = 7.92–7.86 (m, 8H), 7.83 (s, 1H), 7.68 (d, J = 1.8 Hz, 1H), 7.66 (d, J = 1.3 Hz, 1H), 7.61–7.49 (m, 12H), 7.42 ppm (t, J = 7.9 Hz, 1H). ^{31}P NMR (162 MHz, CDCl_3 , 25 °C): δ = 8.26 ppm. IR (ATR): ν = 3020–3050 (st, ArC-H), 2168 (st, $\text{C}\equiv\text{C}$), 1205 cm^{-1} (st, $\text{P}=\text{O}$). ESI-MS (m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{34}\text{H}_{25}\text{O}_2\text{P}_2$, 527.13; found, 527.13. Elemental analysis: calcd for $\text{C}_{34}\text{H}_{24}\text{O}_2\text{P}_2$, C 77.56, H 4.59; found, C 77.41, H 4.49%.

Preparation of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ (+tfc: (+)-3-Trifluoroacetylcamphorato)

Europium(III) acetate n -hydrate (0.36 g) was dissolved in distilled water (150 mL), and a few drops of 28% ammonia solution were added. (+)-3-Trifluoroacetylcamphor (0.50 g, 2.0 mmol) in methanol (15 mL) was added to the solution, and the mixture was stirred for 4 h at room temperature. The reaction mixture was evaporated. The obtained powder was washed with distilled water, and the powder was dried in vacuo ($[\text{Eu}(+\text{tfc})_3(\text{H}_2\text{O})_2]$, 0.41 g). $[\text{Eu}(+\text{tfc})_3(\text{H}_2\text{O})_2]$ (0.37 g, 0.40 mmol) and m -dpeb (0.19 g, 0.36 mmol) were dissolved in methanol (10 mL) and refluxed for 5 h. The reaction solution was cooled to room temperature and evaporated to give a light yellow powder. The obtained powder was washed with diethyl ether and hexane. The powder was dried in vacuo and heated at 140 °C for 30 min to crystallize. Yield: 0.09 g (0.06 mmol, 18% for monomer). IR (ATR): ν = 2870–2990 (st, ArC-H), 2172 (st, $\text{C}\equiv\text{C}$), 1654 (st, $\text{C}=\text{O}$), 1197 cm^{-1} (st, $\text{P}=\text{O}$). ESI-MS (m/z): $[\text{M} - \text{tfc}]^+$ calcd for $\text{C}_{58}\text{H}_{52}\text{EuF}_6\text{O}_6\text{P}_2$, 1173.24; found, 1173.24. Elemental analysis: calcd for $\text{C}_{70}\text{H}_{66}\text{EuF}_9\text{O}_8\text{P}_2$, C 59.20, H 4.68; found, C 58.61, H 4.66%.

Preparation of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$

$[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ was synthesized by the same procedure to that described in Chapter 3.

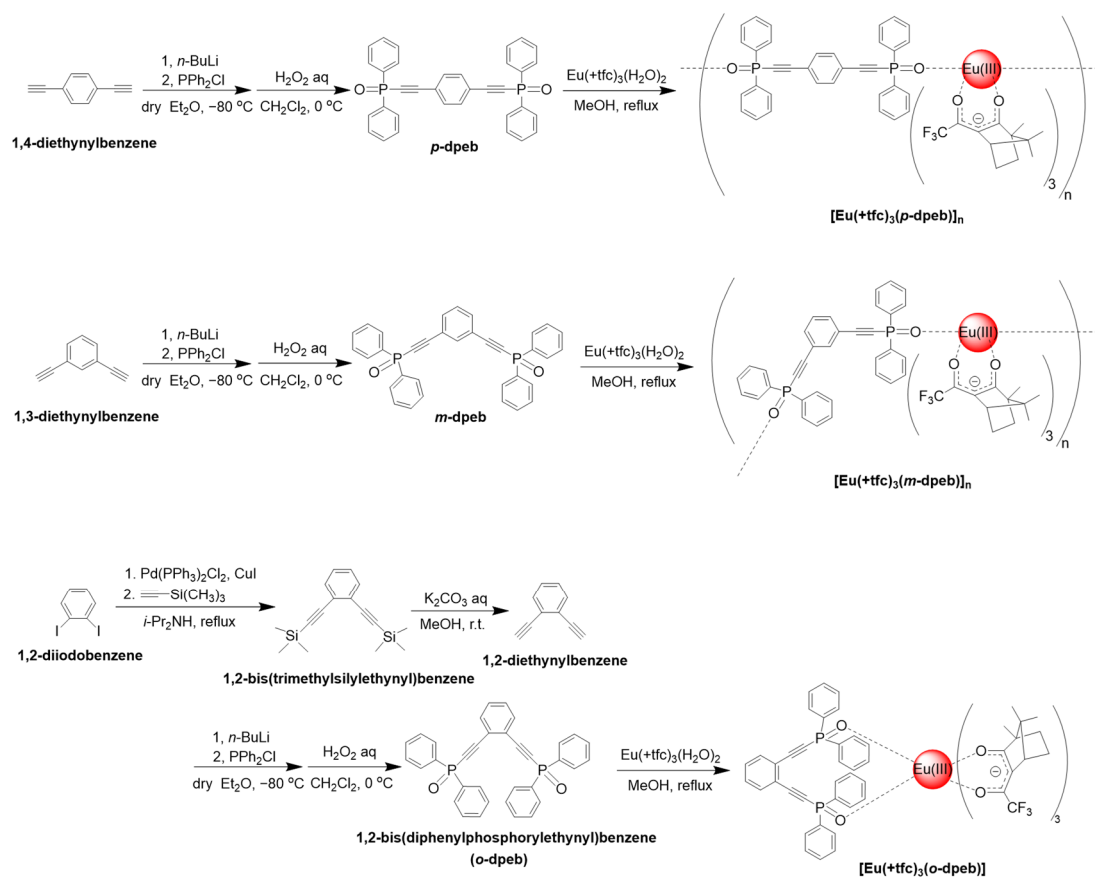


Figure 4.2. Synthetic scheme of Eu(III) coordination polymers and complex.

4.3 Results and discussion

4.3.1 Structural characterizations

Chiral Eu(III) coordination polymers with ethynyl linkers, $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ and $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$, were synthesized by complexation of *m*-dpeb and *p*-dpeb with $[\text{Eu}(+\text{tfc})_3(\text{H}_2\text{O})_2]$ in a methanol solution, respectively. The formation of the coordination polymers was characterized using FT-IR and ESI-MS spectroscopy. The FT-IR spectra of *m*-dpeb, $[\text{Eu}(+\text{tfc})_3(\text{H}_2\text{O})_2]$, and $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ are shown in **Figure 4.3**. The precursor $[\text{Eu}(+\text{tfc})_3(\text{H}_2\text{O})_2]$ shows significant O-H stretching vibrational signals for coordinated water at approximately $3,400\text{ cm}^{-1}$. The disappearance of O-H stretching vibrational signals was observed in the IR spectrum of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$. The disappearance of coordinated water in *p*-linked $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ was also confirmed (**Figure 4.3**).

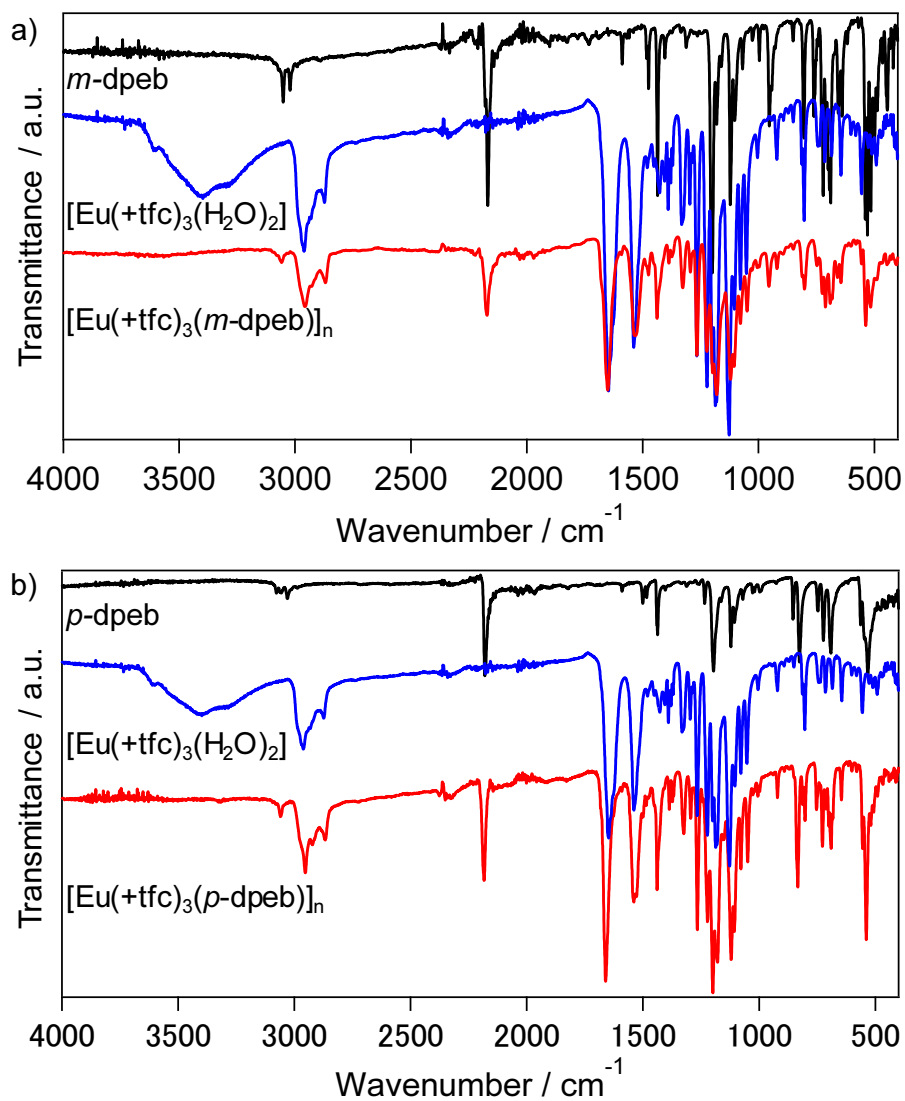


Figure 4.3. FT-IR spectra of a) *m*-dpeb (black line), $[\text{Eu}(+\text{tfc})_3(\text{H}_2\text{O})_2]$ (blue line), and $[\text{Eu}(+\text{tfc})_3(\textit{m}\text{-dpeb})]_n$ (red line) and b) *p*-dpeb (black line), $[\text{Eu}(+\text{tfc})_3(\text{H}_2\text{O})_2]$ (blue line), and $[\text{Eu}(+\text{tfc})_3(\textit{p}\text{-dpeb})]_n$ (red line).

The ESI-MS spectra and simulated mass patterns of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ are shown in **Figure 4.4**. The observed signals with mass numbers (m/z) of 1173.2, 2592.5, 4013.8, and 5434.1 were assigned to the fragments of $[\text{Eu}(+\text{tfc})_2(m\text{-dpeb})]^+$, $[\text{Eu}_2(+\text{tfc})_5(m\text{-dpeb})_2]^+$, $[\text{Eu}_3(+\text{tfc})_8(m\text{-dpeb})_3]^+$, and $[\text{Eu}_4(+\text{tfc})_{11}(m\text{-dpeb})_4]^+$, respectively. Assignments were made by comparing the observed isotope distribution of $[\text{Eu}_n(+\text{tfc})_{3n-1}(m\text{-dpeb})_n]^+$ (m/z at approximately 1173.2, 2592.5, 4013.8, and 5434.1) with the calculated data. The observed ESI-MS signals of p -linked $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ were also assigned to fragments of $[\text{Eu}_n(+\text{tfc})_{3n-1}(p\text{-dpeb})_n]^+$ (**Figure 4.18**).

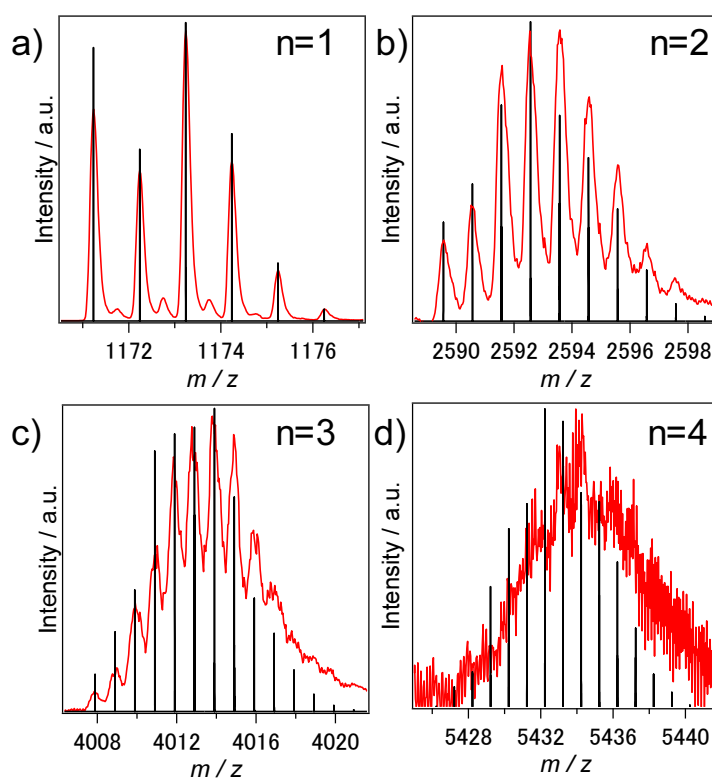


Figure 4.4. ESI-MS spectra (red) and simulated mass pattern (black) of $[\text{Eu}_n(+\text{tfc})_{3n-1}(m\text{-dpeb})_n]^+$: (a) $n = 1$, b) $n = 2$, c) $n = 3$, and d) $n = 4$).

TG measurements were conducted in a nitrogen atmosphere to evaluate the thermophysical properties of $[\text{Eu}(\text{+tfc})_3(m\text{-dpeb})]_n$, $[\text{Eu}(\text{+tfc})_3(p\text{-dpeb})]_n$, and the precursor $[\text{Eu}(\text{+tfc})_3(\text{H}_2\text{O})_2]$. Although the elimination of coordinated water in the precursor $[\text{Eu}(\text{+tfc})_3(\text{H}_2\text{O})_2]$ was observed at approximately 90 °C, the decomposition temperatures (T_d) of $[\text{Eu}(\text{+tfc})_3(m\text{-dpeb})]_n$ and $[\text{Eu}(\text{+tfc})_3(p\text{-dpeb})]_n$ were 306 and 298 °C, respectively (**Figure 4.5**). The high decomposition temperatures of $[\text{Eu}(\text{+tfc})_3(m\text{-dpeb})]_n$ and $[\text{Eu}(\text{+tfc})_3(p\text{-dpeb})]_n$ are similar to those of previously reported chiral lanthanide coordination polymers ($T_d > 300$ °C).^[12,13]

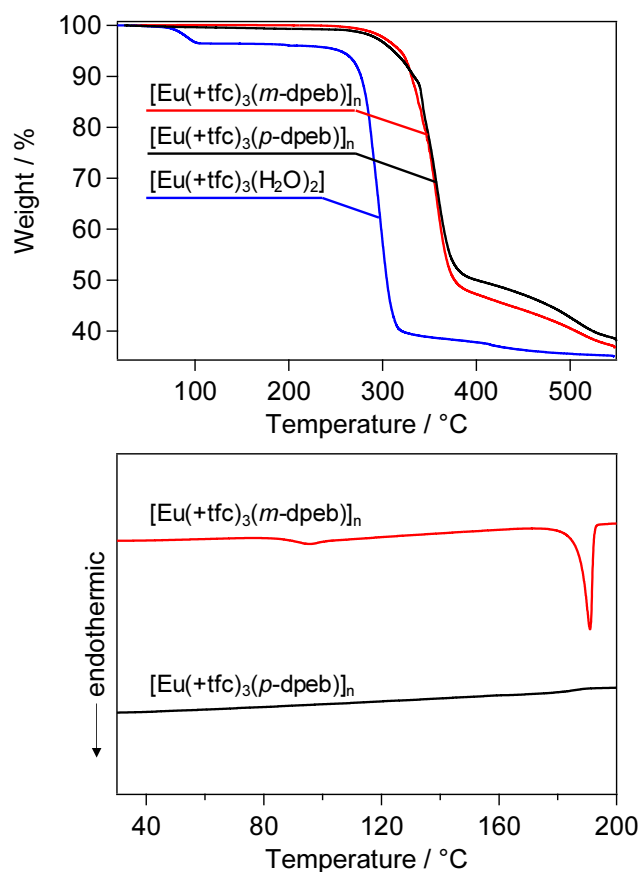


Figure 4.5. a) TG and b) DSC thermograms of $[\text{Eu}(\text{+tfc})_3(m\text{-dpeb})]_n$ (red line), $[\text{Eu}(\text{+tfc})_3(p\text{-dpeb})]_n$ (black line), and $[\text{Eu}(\text{+tfc})_3(\text{H}_2\text{O})_2]$ (blue line) in a nitrogen atmosphere at a heating and cooling rate of 5 °C min⁻¹.

PXRD patterns of $[\text{Eu}(\text{+tfc})_3(\text{m-dpeb})]_n$ at various temperatures are shown in **Figure 4.6**. The characteristic peaks at $2\theta = 7.5^\circ, 8.0^\circ, 8.4^\circ, 11.0^\circ, 12.9^\circ, 14.3^\circ, 15.0^\circ, 15.3^\circ, 19.3^\circ, 20.2^\circ$, and 20.8° were observed under 160°C (Type-A). The drastic changes in the PXRD patterns of $[\text{Eu}(\text{+tfc})_3(\text{m-dpeb})]_n$ at $2\theta = 7.9^\circ, 9.1^\circ, 15.1^\circ, 19.9^\circ$, and 20.4° at 180°C were observed, which were related to the phase-transition behavior. The peaks disappeared due to the melting of the Eu(III) coordination polymer at 200°C .

Based on the DSC measurements, characteristic endothermic peaks corresponding to the phase-transition and melting phenomena of $[\text{Eu}(\text{+tfc})_3(\text{m-dpeb})]_n$ were observed at 192°C (**Figure 4.5**). Since the endothermic value during the heating process is 10.0 J g^{-1} while the exothermic value during the cooling process is 8.76 J g^{-1} , the phase transition from Type-A to Type-B is irreversible (**Figure 4.19**). A significant endothermic peak of $[\text{Eu}(\text{+tfc})_3(\text{p-dpeb})]_n$ was not visible. These results indicate that $[\text{Eu}(\text{+tfc})_3(\text{m-dpeb})]_n$ exhibits three stable structures (Type-A, Type-B, and melting states) depending on the temperature.

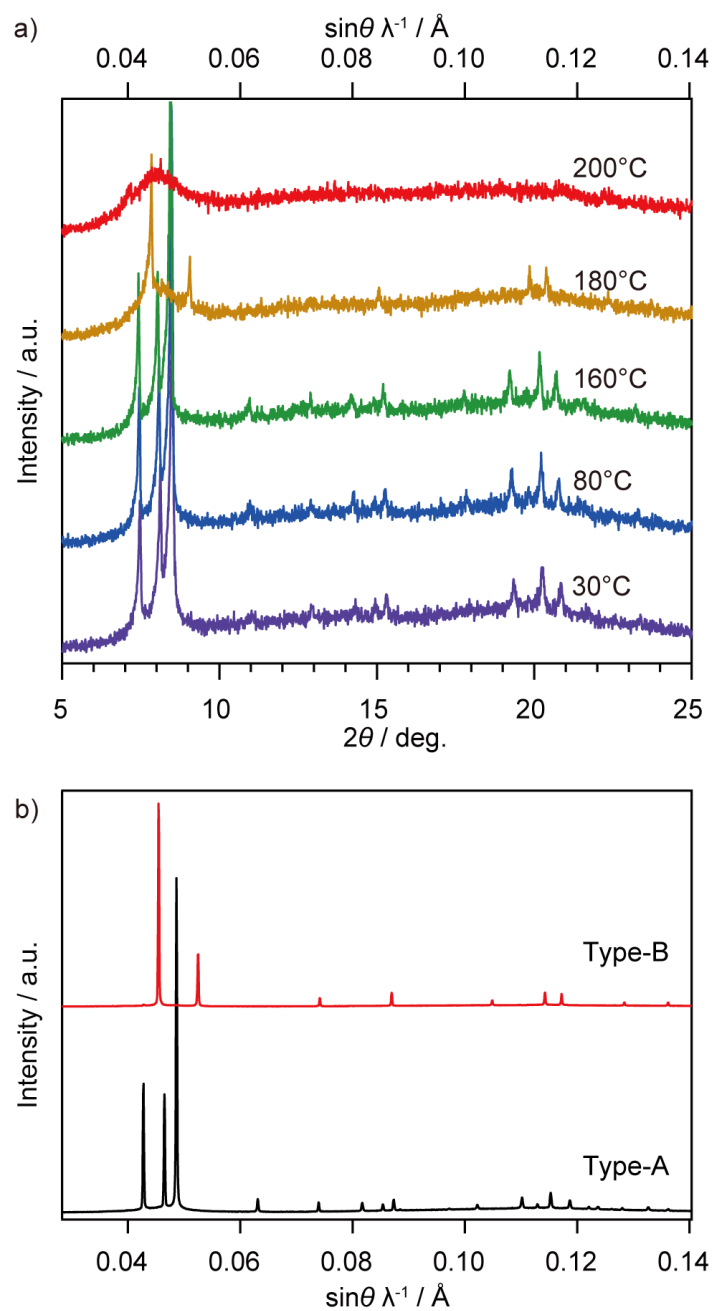


Figure 4.6. a) PXRD patterns of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ in the temperature range of 30–200 °C. b) Synchrotron PXRD patterns of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ measured at 23 °C after the heat-treatment (black line: Type-A; red line: Type-B).

To confirm the stable structure of the coordination polymer at room temperature, synchrotron PXRD measurements of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ were performed after heat-treatment (**Figure 4.6**). The PXRD patterns of phase-transformed $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ after heat-treatment at 180 °C for 30 min and rapid cooling (Type-B) agreed with those obtained under heating (**Figure 4.6**; at 180 °C). The Type-B structure of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ was maintained in air at room temperature. The additional PXRD measurements were conducted to check the stable structure of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ after heating at 200 °C (melting state) and cooling. The PXRD patterns of the coordination polymer after heat-treatment at 200 °C and rapid (c.a. 100 °C min⁻¹, Type-C) or slow (c.a. 1 °C min⁻¹, Type-D) cooling are shown in **Figure 4.7**. The PXRD patterns of Type-C (rapid cooling from 200 °C) agreed with those of Type-B (rapid cooling from 180 °C). On the other hands, the PXRD patterns of Type-D (slow cooling from 200 °C) showed presence of phase A and B. This result indicates that the structural phase of Type-B was metastable and partially transformed back into phase A.

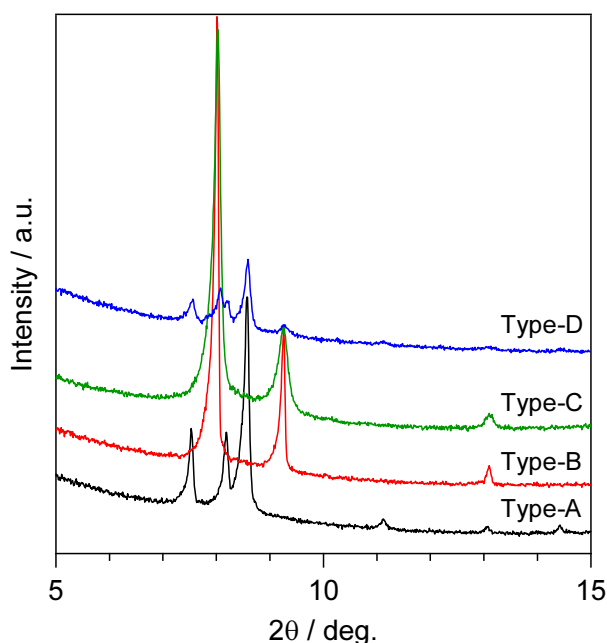


Figure 4.7. PXRD patterns of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ measured at room temperature after heating treatment (black line: Type-A, red line: Type-B, green line: Type-C, blue line: Type-D).

The PXRD patterns of *p*-linked $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ were not transformed in the heat-treatment below the decomposition temperature (**Figure 4.8**). The orientation-change Type-A and Type-B samples of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ based on the phase-transition were successfully prepared.

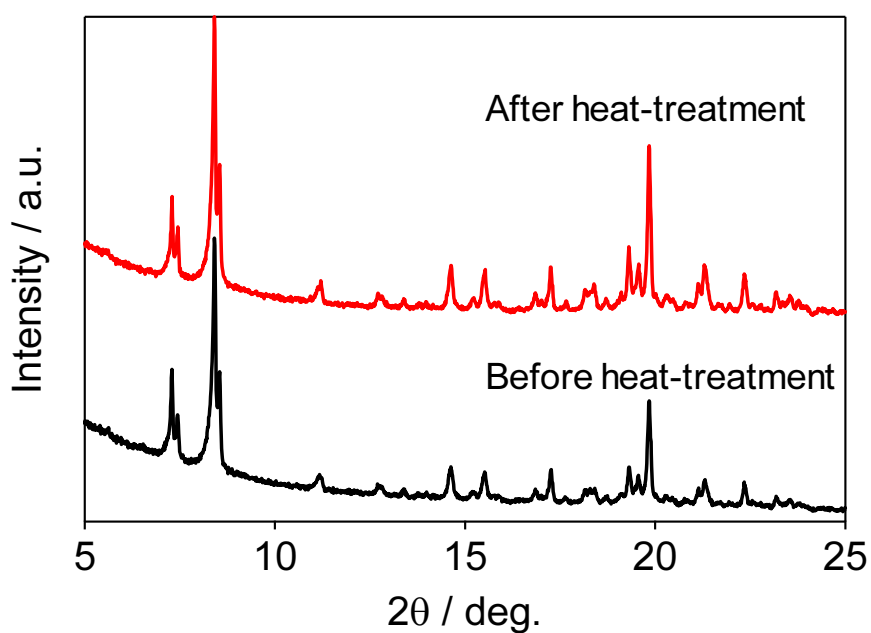


Figure 4.8. PXRD patterns of $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ measured at room temperature before and after heating treatment (black line: without heating, red line: after heating treatment at 200 °C for 30 min and rapid cooling).

4.3.2 Photophysical properties

The excitation and emission spectra of Type-A at room temperature are shown in **Figure 4.9**. The sharp excitation bands at 464, 525, and 534 nm are attributed to the 4f-4f transitions of Eu(III) ($^5D_2 \leftarrow ^7F_0$, $^5D_1 \leftarrow ^7F_0$, and $^5D_1 \leftarrow ^7F_1$).^[14] The broad excitation bands are attributed to the π - π^* transitions in the organic ligands. The emission bands at 578, 590, 612, 652, and 700 nm are attributed to the 4f-4f transitions of Eu(III) ($^5D_0 \rightarrow ^7F_J$: $J = 0, 1, 2, 3$, and 4).^[14] The emission spectra of Type-A and Type-B expanded in the region of $^5D_0 \rightarrow ^7F_{0,1}$ and $^5D_0 \rightarrow ^7F_2$ transitions are shown in **Figure 4.9**, respectively. The spectral shape with Stark splitting at the magnetic dipole transition ($^5D_0 \rightarrow ^7F_1$) and electric dipole transition ($^5D_0 \rightarrow ^7F_2$) of Type-A agreed with that of Type-B. The agreement between the transition bands reveals that the geometrical structure around the Eu(III) center in Type-A is the same as that in Type-B.

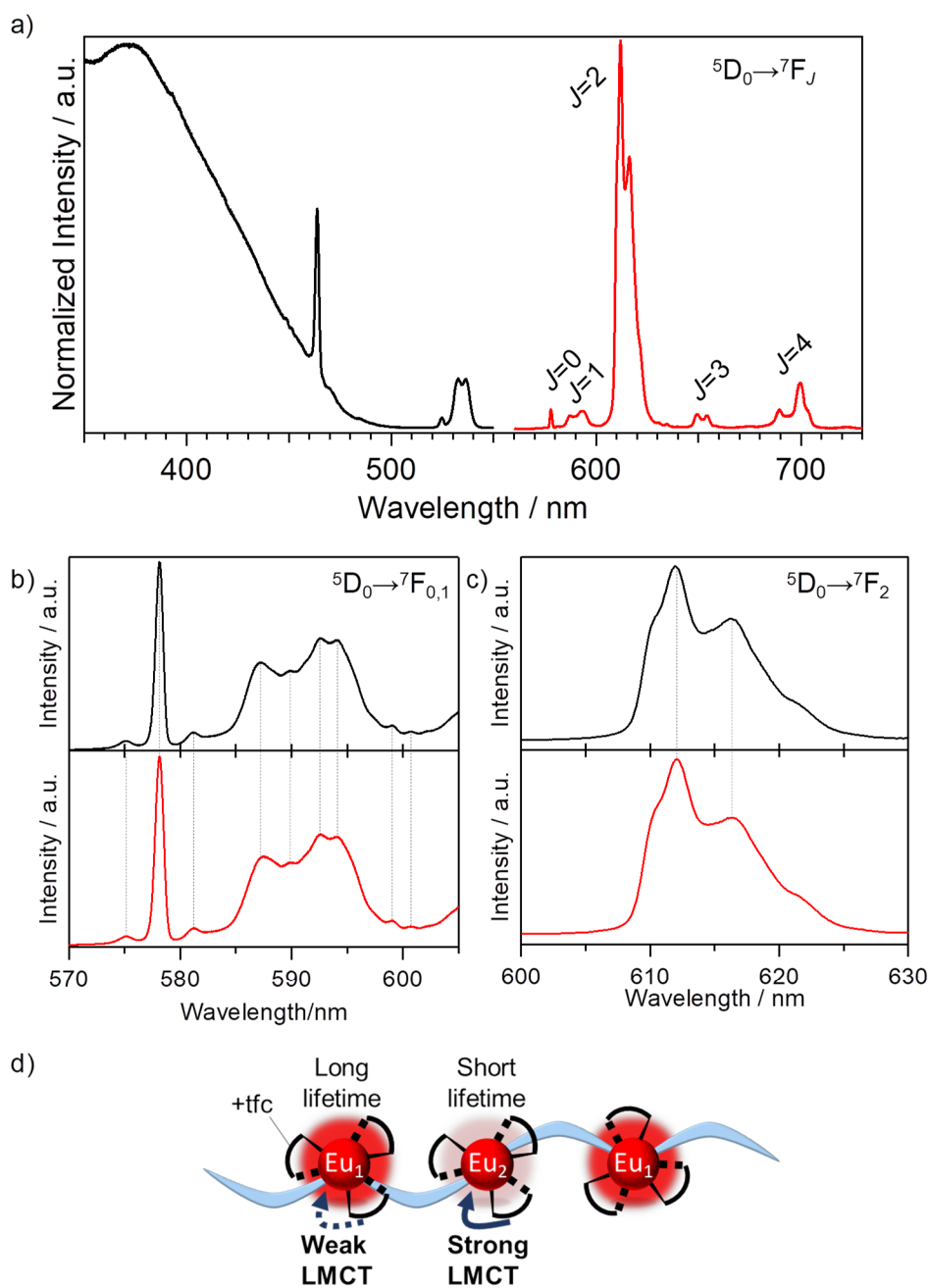


Figure 4.9. a) Excitation ($\lambda_{em} = 612$ nm) and emission spectra ($\lambda_{ex} = 360$ nm) of Type-A measured at room temperature; b), c) Emission spectra ($\lambda_{em} = 612$ nm) of Type-A (black) and Type-B (red) expanded the region of $^5D_0 \rightarrow ^7F_{0,1}$ and $^5D_0 \rightarrow ^7F_2$ transitions, respectively. d) Schematic image of two emission sites of Eu(III) coordination polymer.

The time-resolved emission decay profiles obtained for Type-A and -B at room temperature are shown in **Figure 4.10**. Double-exponential decays with sub-millisecond scale lifetimes were observed. The multi-exponential decay might arise from the two emission sites of the Eu(III) ion (**Figure 4.9d**), which is a common behavior in inorganic phosphors including lanthanide ions.^[15] The emission lifetimes and their ratios were estimated using an exponential function (**Table 4.1**). The shorter lifetime (τ_2) may be due to non-radiative relaxation via the LMCT quenching process. That LMCT quenching process often occurs in chiral Eu(III) complexes with camphor ligands.^[16,17] The average emission lifetime (τ_{avg}) of Type-B (270 μs) was slightly longer than that of Type-A (253 μs).

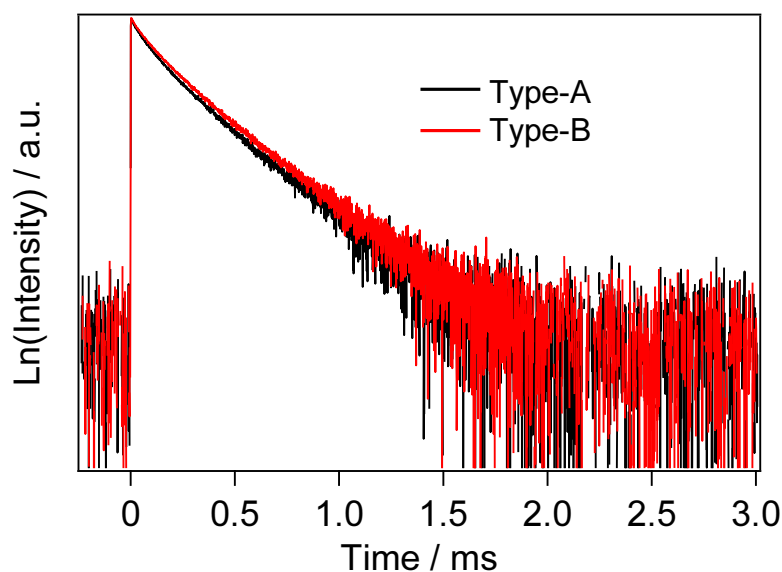


Figure 4.10. Emission decay profiles ($\lambda_{\text{ex}} = 355 \text{ nm}$) of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ measured at room temperature after heating treatment (in powder, red line: Type-A, blue line : Type-B).

Based on the emission lifetime and emission spectra, the 4f-4f emission quantum yield (Φ_{f-f}), radiative rate constant (k_r), and non-radiative rate constant (k_{nr}) were estimated using the equations (1.1)-(1.3). These photophysical parameters of Type-A and Type-B are summarized in **Table 4.1**. The k_r value of Type-A ($1.07 \times 10^3 \text{ s}^{-1}$) was almost the same as that of Type-B ($1.06 \times 10^3 \text{ s}^{-1}$). On the other hand, the k_{nr} value of Type-A ($2.88 \times 10^3 \text{ s}^{-1}$) was slightly larger than that of Type-B ($2.64 \times 10^3 \text{ s}^{-1}$).

To estimate the effect of energy transfer from Eu(III) to the LMCT states in Type-A and Type-B, the temperature-dependent emission lifetimes in the solid state were measured in the range of 100–350 K (**Figure 4.11**). The emission decay profiles measured at 100–250 K displayed a single exponential decay, whereas double exponential decays were observed in the higher temperature range. The double exponential decay might arise from the two emission sites of the Eu(III) ion. Each emission sites exhibit different emission lifetime in the higher temperature range because of the difference in LMCT contribution.

Table 4.1 Photophysical properties of $[\text{Eu}(\text{+tfc})_3(\text{m-dpeb})]_n$.

	$\tau_1 / \mu\text{s}$	$\tau_2 / \mu\text{s}$	$\tau_{\text{avg}} / \mu\text{s}$	k_r / s^{-1}	k_{nr} / s^{-1}	$\Phi_{f-f} / \%$	g_{CPL} (594 nm)	g_{CPL} (613 nm)
Type-A	322 (69%)	98 (31%)	253	1.07×10^3	2.88×10^3	27	−0.092	+0.008
Type-B	340 (70%)	109 (30%)	270	1.06×10^3	2.64×10^3	29	−0.030	+0.002

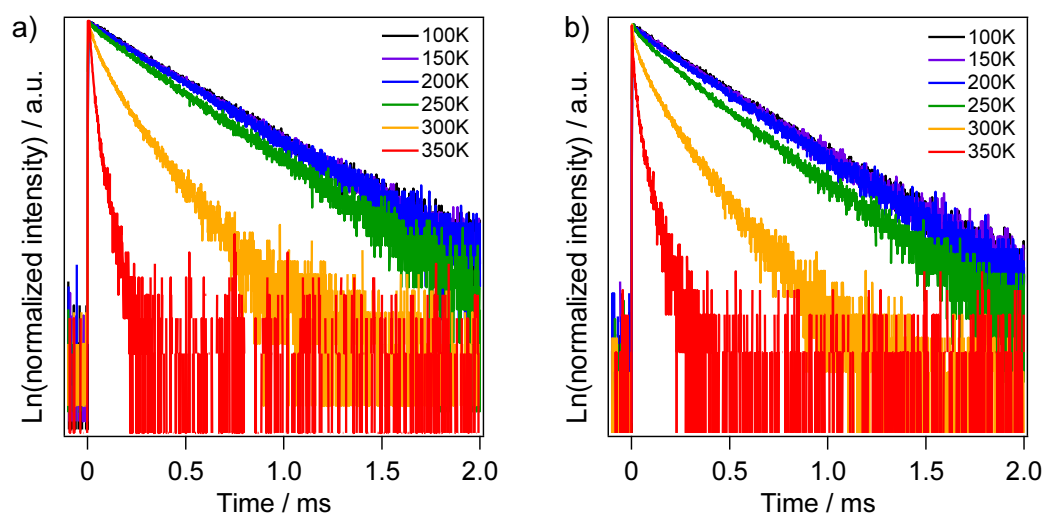


Figure 4.11. Temperature-dependent emission decay profiles of a) Type-A and b) Type-B ($\lambda_{\text{ex}} = 355$ nm, $\lambda_{\text{em}} = 612$ nm).

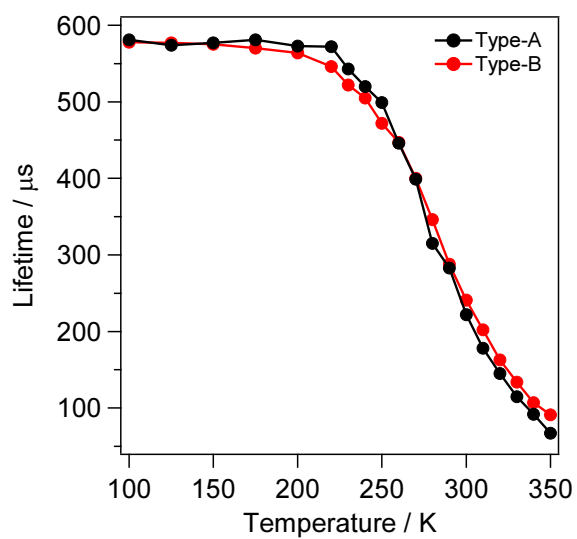


Figure 4.12. Temperature-dependent emission lifetime of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ (black line: Type-A, red line: Type-B, $\lambda_{\text{ex}} = 355$ nm, $\lambda_{\text{em}} = 612$ nm).

The relationship between the average emission lifetime and temperature is shown in **Figure 4.12**. Based on the temperature-dependent emission lifetimes, the back energy transfer rate constants (k_{BET}) were estimated using kinetic analysis (equation (3.1)). In the 4f-4f transitions in Eu(III) compounds, the vibrational deactivation of 4f-4f transition is usually insensitive to the temperature because of the large energy gap between excited and ground states.^[18] From the Arrhenius analysis, the non-radiative rate factor in k_{BET} is only depended on the back energy transfer process from Eu(III) to the LMCT states. Arrhenius plots of Type-A and Type-B are shown in **Figure 4.13**, and the calculated ΔE_a and A values are summarized in **Table 4.2**. The Arrhenius plots were well fitted to the equation (3.1) with high coefficient of determination ($R^2 = 0.995$ (Type-A), and 0.998 (Type-B)), suggesting the single temperature-dependent quenching state. The calculated activation energy (ΔE_a) value of Type-A ($2,200 \text{ cm}^{-1}$) was larger than that of Type-B ($1,880 \text{ cm}^{-1}$). The calculated frequency factor (A) value of Type-A ($1.1 \times 10^8 \text{ s}^{-1}$) was almost five times larger than that of Type-B ($2.0 \times 10^7 \text{ s}^{-1}$). The large difference in the ΔE_a

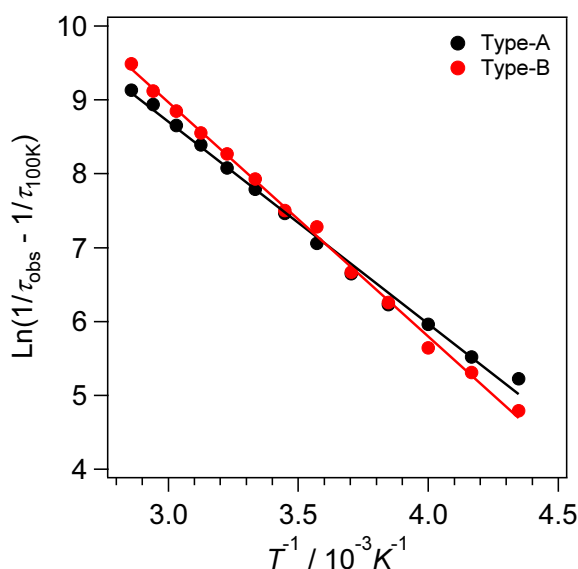


Figure 4.13. Arrhenius plots of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ (black: Type-A, red: Type-B).

and A values between Type-A and Type-B indicates that the LMCT characteristics can be affected by the molecular orientation change based on the phase-transition.

Table 4.2 Arrhenius parameters of $[\text{Eu}(\text{+tfc})_3(\text{m-dpeb})]_n$.

	$\Delta E_a / \text{cm}^{-1}$	A / s^{-1}
Type-A	2,200	1.1×10^8
Type-B	1,880	2.0×10^7

The CPL spectra of the two types of $[\text{Eu}(\text{+tfc})_3(\text{m-dpeb})]_n$ (Type-A and Type-B) in the solid state (in KBr pellets) are shown in **Figure 4.14**. Characteristic CPL signals were observed at approximately 580–600 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) and 610–620 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$). In the magnetic dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), two significant peaks were observed at 586 and 594 nm for each coordination polymer. The intensity of the negative CPL signal in Type-A was larger than that in Type-B in this region. The maximum $|g_{\text{CPL}}|$ value for Type-A ($g_{\text{CPL}} = -0.092$) was three times larger than that for Type-B ($g_{\text{CPL}} = -0.030$). In the electric dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), the $|g_{\text{CPL}}|$ value of Type-A was also larger than that of Type-B. The significantly large difference in the $|g_{\text{CPL}}|$ values between Type-A and Type-B might be affected by the molecular orientation of the polymer chains.

To confirm the effect of molecular orientation on the CPL properties in Eu(III) coordination polymer, amorphization via an additive phosphine oxide ligand was demonstrated (**Figure 4.20**, **Figure 4.21**). After amorphization, amorphized Type-A exhibited a decreasing $|g_{\text{CPL}}|$ value ($g_{\text{CPL}} = -0.076$), which agrees with that for amorphized Type-B ($g_{\text{CPL}} = -0.077$). These additional experiments indicated that the g_{CPL} value depends on the orientation of the polymer chains in the solid state.

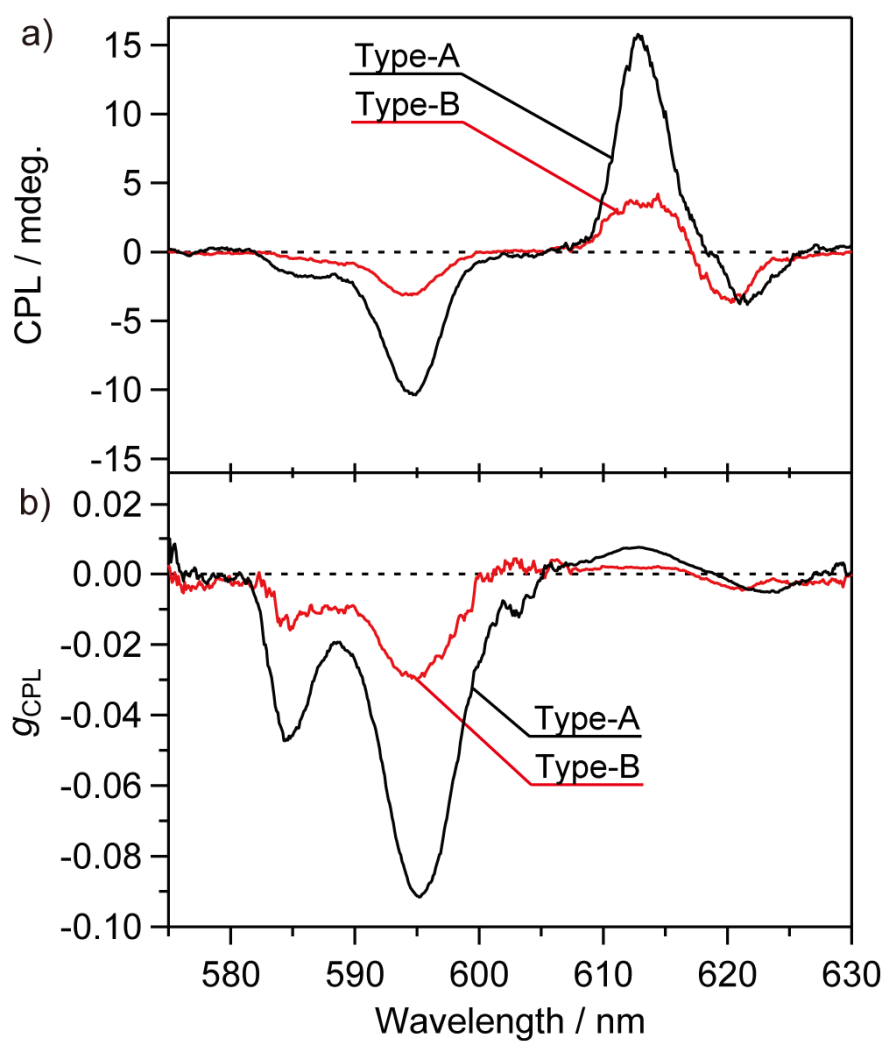


Figure 4.14. CPL spectra ($\lambda_{\text{ex}} = 350$ nm) of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ measured at room temperature after heating treatment (in solid state (in KBr pellet), red line: Type-A, blue line : Type-B).

4.3.3 DFT calculations

Recently, the photophysical and theoretical analyses of the LMCT excited states, which affect the 4f-4f transition probability in Eu(III) complexes, have been focused.^[19–21] The chiroptical properties of chiral Eu(III) compounds are also affected by the LMCT transition. Thus, the transition electric dipole moments of the LMCT states were estimated by TD-DFT calculations to understand the mechanism of the g_{CPL} change under structural transformation. The TD-DFT calculations in vacuum condition were performed using a mononuclear chiral Eu(III) complex with camphor ligands, $[\text{Eu}(+\text{tfc})_3(\text{tppo})_2]$ (tppo: triphenylphosphine oxide), as a one-unit model.^[22] A dimer model (Eu-Eu distance: $d_{\text{Eu-Eu}} = 12.79 \text{ \AA}$) was constructed from the X-ray crystallographic data. The modified structures elongating the Eu-Eu distance of the original dimer model to $d_{\text{Eu-Eu}} = 13, 14, \text{ and } 15 \text{ \AA}$ (**Figure 4.15**) were also examined by the TD-DFT calculations.

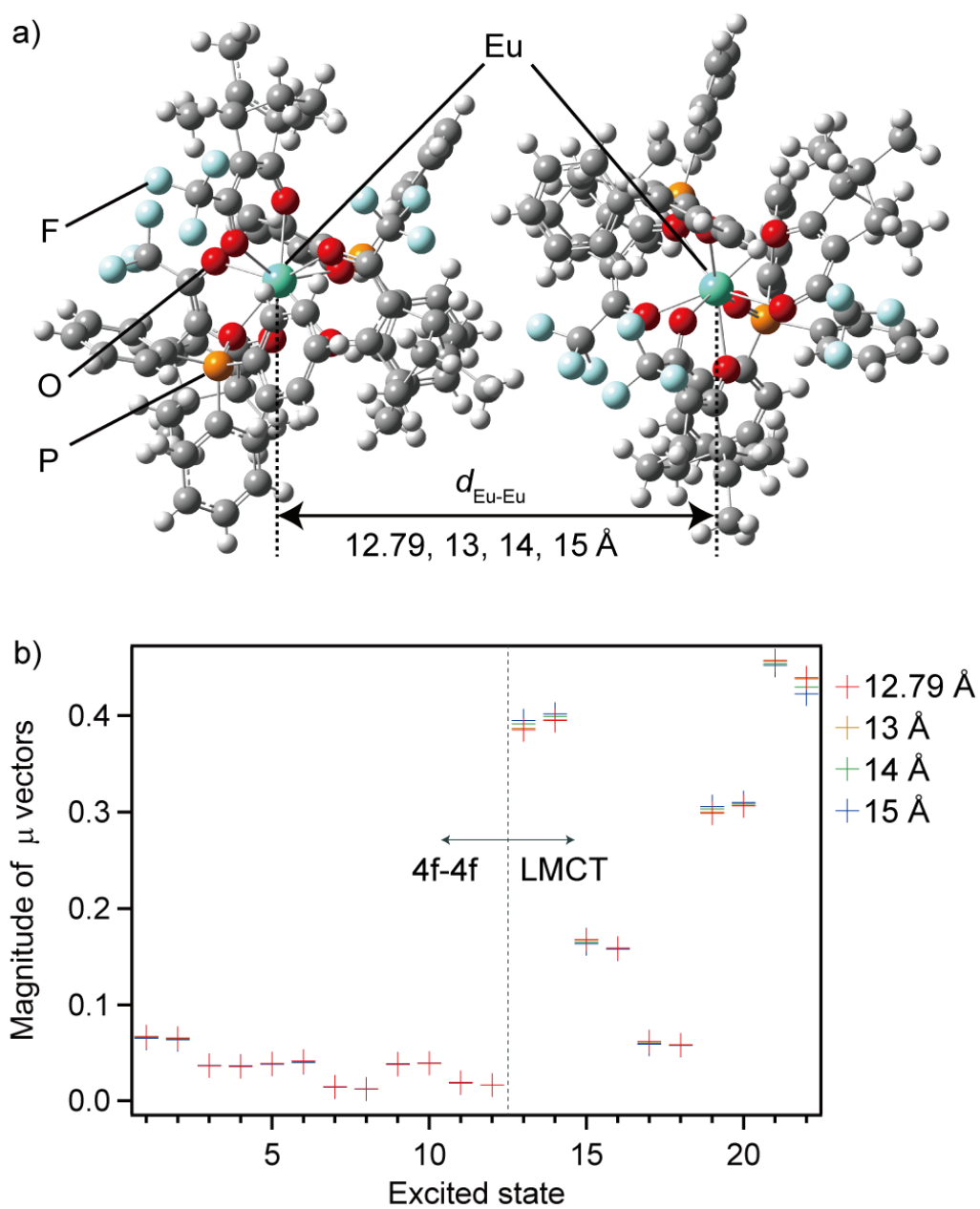


Figure 4.15. a) Molecular structure of $\text{Eu}(+\text{tfc})_3(\text{tppo})_2$ dimer model. b) Magnitude of transition electric dipole moment vectors ($|\vec{\mu}|$) in 4f-4f or LMCT excited states.

The calculated excitation energies and transition assignments are summarized in **Table 4.3**, **Table 4.4**, **Table 4.5**, **Table 4.6**, and **Figure 4.22**. The 4f-4f transition character was observed for the excited states 1 through 12 in **Table 4.3**. LMCT nature was observed for the excited states 13 to 22. Based on the calculation data, the magnitudes of the transition electric dipole moments ($|\vec{\mu}|$) in the excited states 1–22 are shown in **Figure 4.15b**. The $|\vec{\mu}|$ in the LMCT transitions was slightly dependent on the Eu-Eu distance, although the $|\vec{\mu}|$ in the region of 4f-4f transitions was almost unchanged. Furthermore, the $|\vec{\mu}|$ in the LMCT transitions was also dependent on the direction between the units (**Figure 4.16**).

Table 4.3 Excitation energies of $\text{Eu}(+\text{tfc})_3(\text{tppo})_2$ dimer model ($d_{\text{Eu-Eu}} = 12.79 \text{ \AA}$) obtained by TD-DFT calculation.

excited state	excitation energy / cm^{-1}	oscillator strength	largest configuration	character	splitting energy gap (ΔE_{split}) / cm^{-1}
1	1,047	0.0000	HOMO-128 $\rightarrow$ LUMO+1 (α)	4f-4f	7
2	1,054	0.0000	HOMO-132 $\rightarrow$ LUMO (α)	4f-4f	
3	1,776	0.0000	HOMO-148 $\rightarrow$ LUMO+1 (α)	4f-4f	2
4	1,778	0.0000	HOMO-157 $\rightarrow$ LUMO (α)	4f-4f	
5	1,972	0.0000	HOMO-148 $\rightarrow$ LUMO+1 (α)	4f-4f	4
6	1,976	0.0000	HOMO-149 $\rightarrow$ LUMO (α)	4f-4f	
7	2,429	0.0000	HOMO-114 $\rightarrow$ LUMO+1 (α)	4f-4f	7
8	2,436	0.0000	HOMO-120 $\rightarrow$ LUMO (α)	4f-4f	
9	3,431	0.0000	HOMO-100 $\rightarrow$ LUMO (α)	4f-4f	6
10	3,437	0.0000	HOMO-95 $\rightarrow$ LUMO+1 (α)	4f-4f	
11	3,671	0.0000	HOMO-117 $\rightarrow$ LUMO (α)	4f-4f	2
12	3,673	0.0000	HOMO-110 $\rightarrow$ LUMO+1 (α)	4f-4f	
13	12,110	0.0055	HOMO-1 $\rightarrow$ LUMO (α)	LMCT	203
14	12,313	0.0058	HOMO $\rightarrow$ LUMO+1 (α)	LMCT	
15	15,675	0.0013	HOMO-3 $\rightarrow$ LUMO (α)	LMCT	198
16	15,873	0.0012	HOMO-2 $\rightarrow$ LUMO+1 (α)	LMCT	
17	16,393	0.0002	HOMO-4 $\rightarrow$ LUMO+1 (α)	LMCT	577
18	16,970	0.0002	HOMO-5 $\rightarrow$ LUMO (α)	LMCT	
19	20,169	0.0055	HOMO-8 $\rightarrow$ LUMO (α)	LMCT	191
20	20,360	0.0058	HOMO-7 $\rightarrow$ LUMO+1 (α)	LMCT	
21	20,584	0.0131	HOMO-6 $\rightarrow$ LUMO+1 (α)	LMCT	101
22	20,685	0.0121	HOMO-9 $\rightarrow$ LUMO (α)	LMCT	

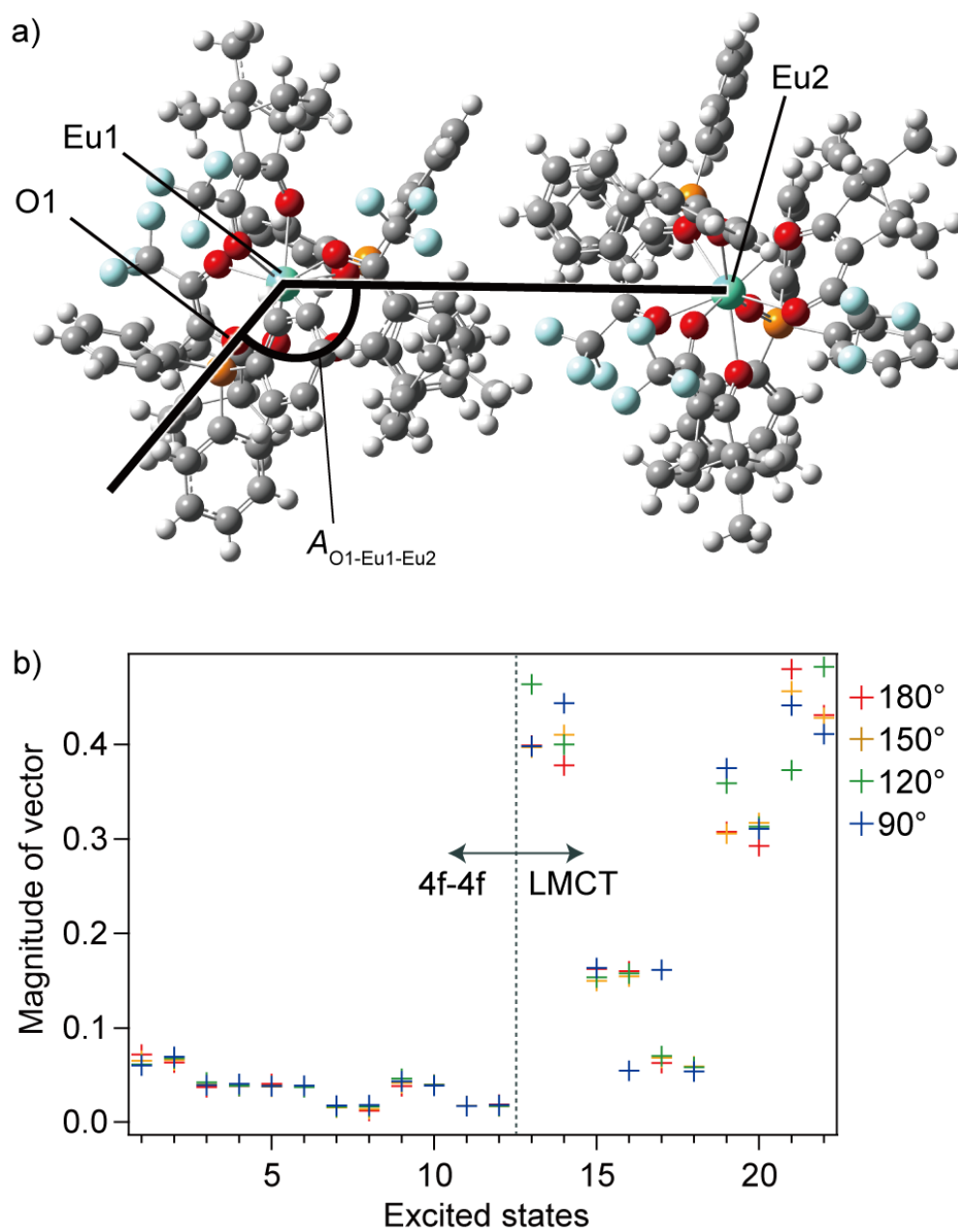


Figure 4.16. a) Molecular structure of $\text{Eu}(+\text{tfc})_3(\text{tppo})_2$ dimer model. b) Magnitude of transition electric dipole moment vectors ($|\vec{\mu}|$) in 4f-4f or LMCT excited states.

Theoretically, the energy levels of the LMCT transition in the dimer model are split into LMCT states 1 and 2 because of the interactions between the two Eu(III) units (**Figure 4.17**). To estimate the quantum mixing between the LMCT and 4f-4f states, the contribution of the splitting energy gap (ΔE_{split}) was calculated. The relationship between ΔE_{split} and $d_{\text{Eu-Eu}}$ is shown in **Figure 4.17b**. The large ΔE_{split} in short $d_{\text{Eu-Eu}}$ leads to a small energy gap between the LMCT and 4f-4f states ($\Delta E_{\text{LMCT-4f}}$ in **Figure 4.17a**), resulting in a large quantum mixing of the LMCT and 4f-4f states. The images of the molecular orbitals with the largest ΔE_{split} (excited states 17 and 18) are shown in **Figure 4.17c**, where the characteristic LMCT transitions ($\pi (+\text{tfc}) \rightarrow 4f (\text{Eu})$) were observed. These results suggest that the molecular orientation of chiral Eu(III) compounds affects the splitting energy of LMCT states (ΔE_{split}) and their quantum mixing ($\Delta E_{\text{LMCT-4f}}$), resulting in a change in g_{CPL} because of structural transformation.

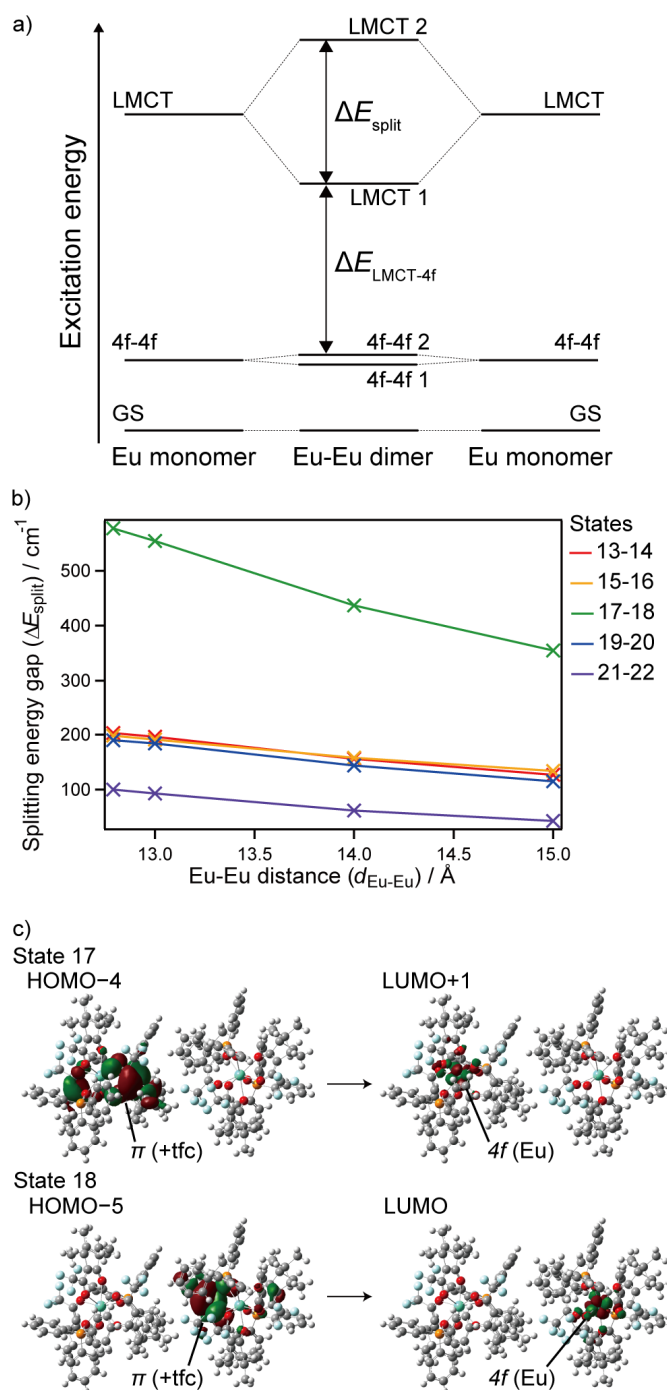


Figure 4.17. a) Energy diagrams of correlations between 4f-4f and LMCT states for monomer and dimer model. b) Relationship between splitting energy gap (ΔE_{split}) and Eu-Eu distance ($d_{\text{Eu-Eu}}$). c) Selected α -spin molecular orbitals of $\text{Eu}(\text{+tfc})_3(\text{tppo})_2$ dimer model ($d_{\text{Eu-Eu}} = 12.79 \text{ \AA}$).

4.4 Conclusion

Novel chiral Eu(III) coordination polymers, $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ and $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$, were synthesized. $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ showed phase-transition behavior at 180 °C, whereas $[\text{Eu}(+\text{tfc})_3(p\text{-dpeb})]_n$ showed no phase-transition behavior. The phase-transition behavior of Eu(III) coordination polymers was depended on the position of the ethynyl groups in the phosphine oxide ligands. The emission spectra (coordination geometrical analyses) and CPL measurements (chiroptical properties) showed that the dissymmetry factor (g_{CPL}) is related to the orientation of the polymer chains in the crystalline solid. The photophysical findings were confirmed by performing quantum chemical calculations.

Further control of the orientation of the polymer chains in chiral Eu(III) coordination polymers can improve the $|g_{\text{CPL}}|$ value for optical applications such as security tags and three-dimensional displays. The relationship between the molecular orientation and the CPL properties of chiral Eu(III) compounds opens up a frontier fields of coordination chemistry, material science, and solid-state photophysical chemistry.

4.5 Appendix

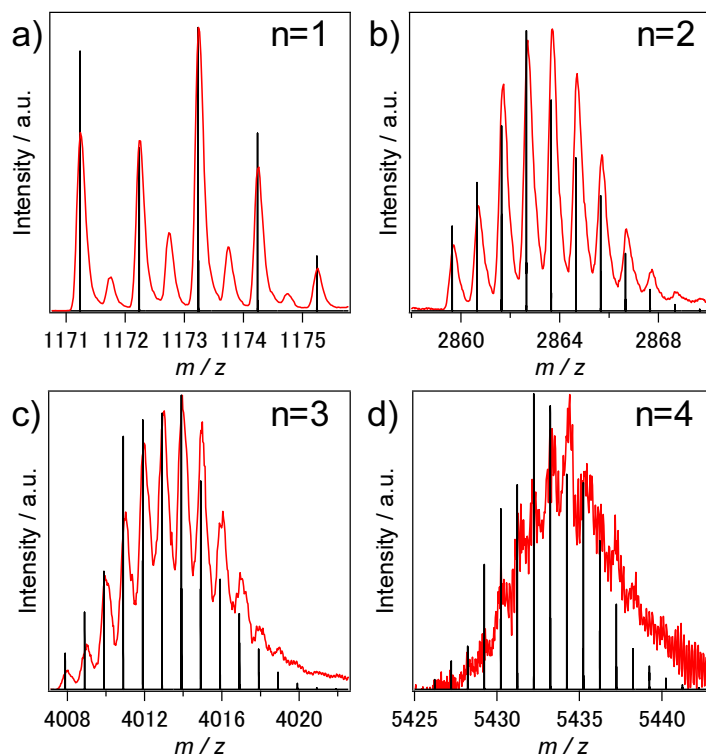


Figure 4.18. ESI-MS spectra (red) and simulated mass pattern (black) of $[\text{Eu}_n(+\text{tfc})_{3n-1}(\text{p-dpeb})_n]^+$ (a) $n = 1$, b) $n = 2$, c) $n = 3$, d) $n = 4$).

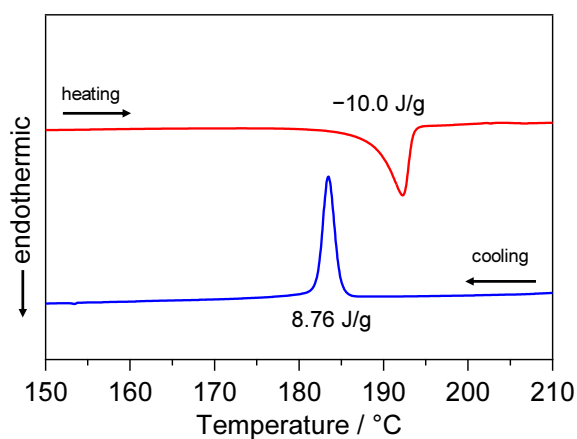


Figure 4.19. DSC thermograms of $[\text{Eu}(+\text{tfc})_3(\text{m-dpeb})]_n$ in a nitrogen atmosphere at a heating (red) and cooling (blue) rate of $5\text{ }^\circ\text{C min}^{-1}$.

Amorphization by additive phosphine oxide ligand to Eu(III) coordination polymers

Monodentate phosphine oxide tppo (tppo: triphenylphosphine oxide) was used for amorphization of the coordination polymer. The tppo molecules were added to the Eu(III) coordination polymers using the following procedure.

The Eu(III) coordination polymer (1 eq.) and tppo molecules (2 eq.) were ground using an agate mortar for 5 min. For comparison, pure Type-A and Type-B were also ground before PXRD measurements. The PXRD patterns before and after adding the tppo ligand to the Type-A and -B coordination polymers are shown in **Figure 4.20**. The mixture of Type-A and tppo (Type-A+tppo) shows broad signals at approximately $2\theta = 8^\circ$, although tppo and pure Type-A show characteristically sharp peaks. The mixture of Type-B and tppo (Type-B+tppo) exhibits a decrease in crystallinity. The typical molecular orientation of chiral Eu(III) coordination polymers disappeared with the addition of TPPO molecules.

The emission and CPL spectra of the chiral Eu(III) coordination polymers before and after adding the tppo molecule are shown in **Figure 4.21**. The emission spectral shape with Stark splitting remains unchanged by the addition of tppo. The coordination geometries around Eu(III) ions are unaffected by the addition of tppo molecules. On the other hand, the CPL intensities of these coordination polymers change substantially. After the addition of TPPO molecules, the g_{CPL} value of Type-A+tppo (-0.076) was similar to that of Type-B+tppo (-0.077), although the g_{CPL} value of pure Type-A was three times larger than that of pure Type-B. These phenomena might occur owing to a breakage in the molecular orientation, which affects the CPL properties of Eu(III) coordination polymers. These results indicate that the characteristic macroscopic structures of Type-A and Type-B effectively affected the CPL properties of chiral Eu(III) coordination polymers in a solid system.

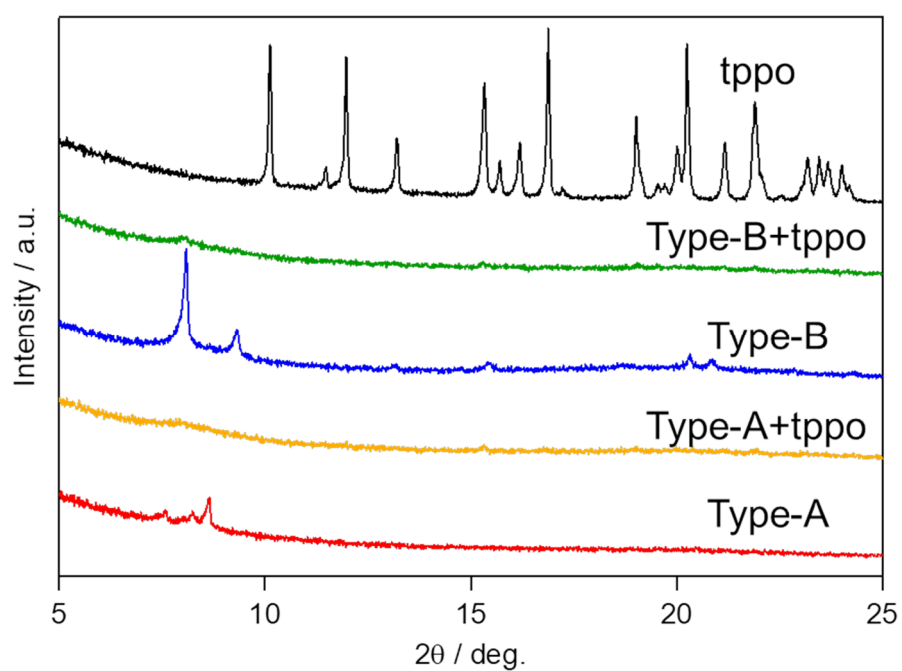


Figure 4.20. PXRD patterns of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ measured at room temperature after adding tppo molecule (black line: tppo, red line: Type-A, yellow line: Type-A+tppo, blue line: Type-B, green line: Type-B+tppo).

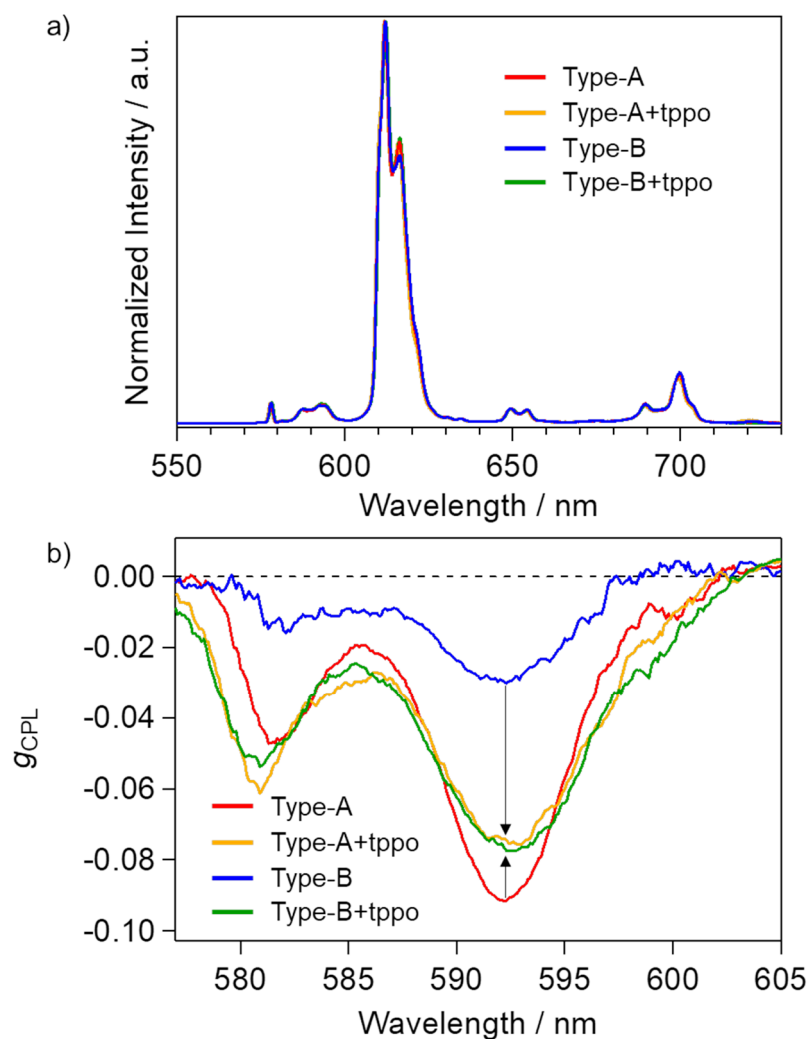


Figure 4.21. (a) Emission and (b) g_{CPL} spectra of $[\text{Eu}(+\text{tfc})_3(m\text{-dpeb})]_n$ measured at room temperature after adding tpo molecule ($\lambda_{\text{ex}} = 360$ nm, black line: tpo, red line: Type-A, yellow line: Type-A+tpo, blue line: Type-B, green line: TypeB+tpo).

Table 4.4 The excitation energies of $\text{Eu}(\text{+tfc})_3(\text{tppo})_2$ dimer model ($d_{\text{Eu-Eu}} = 13 \text{ \AA}$) obtained by TD-DFT calculation.

excited state	excitation energy / cm^{-1}	oscillator strength	largest configuration	character	splitting energy gap (ΔE_{split}) / cm^{-1}
1	1047	0.0000	HOMO-128 $\rightarrow$ LUMO+1 (α)	4f-4f	7
2	1054	0.0000	HOMO-132 $\rightarrow$ LUMO (α)	4f-4f	
3	1776	0.0000	HOMO-148 $\rightarrow$ LUMO+1 (α)	4f-4f	
4	1778	0.0000	HOMO-157 $\rightarrow$ LUMO (α)	4f-4f	2
5	1972	0.0000	HOMO-148 $\rightarrow$ LUMO+1 (α)	4f-4f	
6	1977	0.0000	HOMO-149 $\rightarrow$ LUMO (α)	4f-4f	4
7	2429	0.0000	HOMO-114 $\rightarrow$ LUMO+1 (α)	4f-4f	
8	2436	0.0000	HOMO-120 $\rightarrow$ LUMO (α)	4f-4f	7
9	3432	0.0000	HOMO-100 $\rightarrow$ LUMO (α)	4f-4f	
10	3437	0.0000	HOMO-98 $\rightarrow$ LUMO+1 (α)	4f-4f	5
11	3671	0.0000	HOMO-117 $\rightarrow$ LUMO (α)	4f-4f	
12	3674	0.0000	HOMO-110 $\rightarrow$ LUMO+1 (α)	4f-4f	2
13	12100	0.0055	HOMO-1 $\rightarrow$ LUMO (α)	LMCT	
14	12297	0.0059	HOMO $\rightarrow$ LUMO+1 (α)	LMCT	196
15	15682	0.0013	HOMO-3 $\rightarrow$ LUMO (α)	LMCT	
16	15873	0.0012	HOMO-2 $\rightarrow$ LUMO+1 (α)	LMCT	191
17	16409	0.0002	HOMO-4 $\rightarrow$ LUMO+1 (α)	LMCT	
18	16963	0.0002	HOMO-5 $\rightarrow$ LUMO (α)	LMCT	554
19	20161	0.0055	HOMO-8 $\rightarrow$ LUMO (α)	LMCT	
20	20345	0.0058	HOMO-7 $\rightarrow$ LUMO+1 (α)	LMCT	184
21	20592	0.0130	HOMO-6 $\rightarrow$ LUMO+1 (α)	LMCT	
22	20685	0.0120	HOMO-9 $\rightarrow$ LUMO (α)	LMCT	93

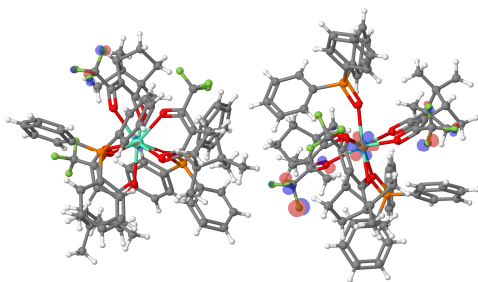
Table 4.5 The excitation energies of $\text{Eu}(\text{+tfc})_3(\text{tppo})_2$ dimer model ($d_{\text{Eu-Eu}} = 14 \text{ \AA}$) obtained by TD-DFT calculation.

excited state	excitation energy / cm^{-1}	oscillator strength	largest configuration	character	splitting energy gap (ΔE_{split}) / cm^{-1}
1	1048	0.0000	HOMO-128 $\rightarrow$ LUMO+1 (α)	4f-4f	8
2	1056	0.0000	HOMO-134 $\rightarrow$ LUMO (α)	4f-4f	
3	1777	0.0000	HOMO-148 $\rightarrow$ LUMO+1 (α)	4f-4f	2
4	1779	0.0000	HOMO-156 $\rightarrow$ LUMO (α)	4f-4f	
5	1974	0.0000	HOMO-144 $\rightarrow$ LUMO+1 (α)	4f-4f	4
6	1978	0.0000	HOMO-149 $\rightarrow$ LUMO (α)	4f-4f	
7	2428	0.0000	HOMO-114 $\rightarrow$ LUMO+1 (α)	4f-4f	6
8	2434	0.0000	HOMO-127 $\rightarrow$ LUMO (α)	4f-4f	
9	3435	0.0000	HOMO-100 $\rightarrow$ LUMO (α)	4f-4f	4
10	3438	0.0000	HOMO-98 $\rightarrow$ LUMO+1 (α)	4f-4f	
11	3673	0.0000	HOMO-116 $\rightarrow$ LUMO (α)	4f-4f	2
12	3674	0.0000	HOMO-110 $\rightarrow$ LUMO+1 (α)	4f-4f	
13	12075	0.0056	HOMO-1 $\rightarrow$ LUMO (α)	LMCT	156
14	12232	0.0059	HOMO $\rightarrow$ LUMO+1 (α)	LMCT	
15	15707	0.0013	HOMO-3 $\rightarrow$ LUMO (α)	LMCT	158
16	15865	0.0012	HOMO-2 $\rightarrow$ LUMO+1 (α)	LMCT	
17	16486	0.0002	HOMO-4 $\rightarrow$ LUMO+1 (α)	LMCT	437
18	16923	0.0002	HOMO-5 $\rightarrow$ LUMO (α)	LMCT	
19	20143	0.0056	HOMO-8 $\rightarrow$ LUMO (α)	LMCT	144
20	20288	0.0059	HOMO-7 $\rightarrow$ LUMO+1 (α)	LMCT	
21	20620	0.0129	HOMO-6 $\rightarrow$ LUMO+1 (α)	LMCT	62
22	20683	0.0116	HOMO-9 $\rightarrow$ LUMO (α)	LMCT	

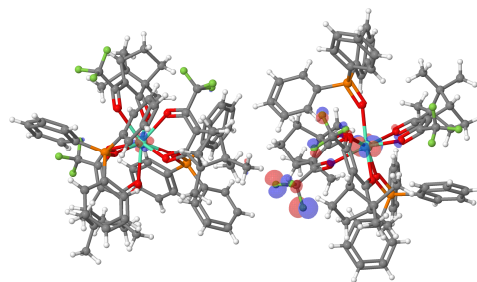
Table 4.6 The excitation energies of $\text{Eu}(\text{+tfc})_3(\text{tppo})_2$ dimer model ($d_{\text{Eu-Eu}} = 15 \text{ \AA}$) obtained by TD-DFT calculation.

excited state	excitation energy / cm^{-1}	oscillator strength	largest configuration	character	splitting energy gap (ΔE_{split}) / cm^{-1}
1	1049	0.0000	HOMO-129 $\rightarrow$ LUMO+1 (α)	4f-4f	8
2	1056	0.0000	HOMO-133 $\rightarrow$ LUMO (α)	4f-4f	
3	1778	0.0000	HOMO-148 $\rightarrow$ LUMO+1 (α)	4f-4f	2
4	1780	0.0000	HOMO-155 $\rightarrow$ LUMO (α)	4f-4f	
5	1975	0.0000	HOMO-145 $\rightarrow$ LUMO+1 (α)	4f-4f	4
6	1979	0.0000	HOMO-149 $\rightarrow$ LUMO (α)	4f-4f	
7	2428	0.0000	HOMO-117 $\rightarrow$ LUMO+1 (α)	4f-4f	5
8	2433	0.0000	HOMO-123 $\rightarrow$ LUMO (α)	4f-4f	
9	3436	0.0000	HOMO-103 $\rightarrow$ LUMO (α)	4f-4f	2
10	3439	0.0000	HOMO-98 $\rightarrow$ LUMO+1 (α)	4f-4f	
11	3673	0.0000	HOMO-116 $\rightarrow$ LUMO (α)	4f-4f	1
12	3674	0.0000	HOMO-110 $\rightarrow$ LUMO+1 (α)	4f-4f	
13	12062	0.0057	HOMO-1 $\rightarrow$ LUMO (α)	LMCT	127
14	12189	0.0060	HOMO $\rightarrow$ LUMO+1 (α)	LMCT	
15	15721	0.0013	HOMO-3 $\rightarrow$ LUMO (α)	LMCT	134
16	15855	0.0012	HOMO-2 $\rightarrow$ LUMO+1 (α)	LMCT	
17	16544	0.0002	HOMO-4 $\rightarrow$ LUMO+1 (α)	LMCT	355
18	16899	0.0002	HOMO-5 $\rightarrow$ LUMO (α)	LMCT	
19	20135	0.0057	HOMO-8 $\rightarrow$ LUMO (α)	LMCT	115
20	20249	0.0059	HOMO-7 $\rightarrow$ LUMO+1 (α)	LMCT	
21	20638	0.0128	HOMO-6 $\rightarrow$ LUMO+1 (α)	LMCT	43
22	20681	0.0112	HOMO-9 $\rightarrow$ LUMO (α)	LMCT	

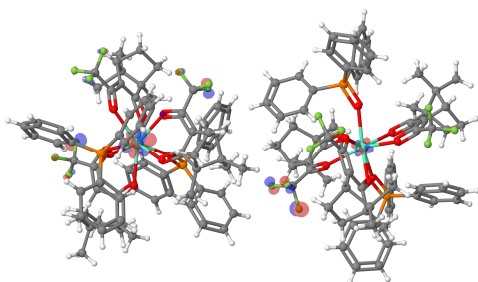
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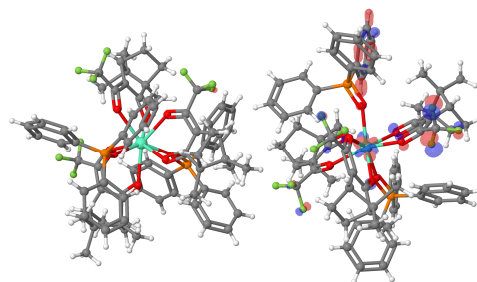
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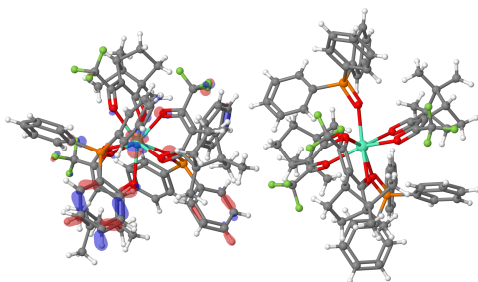
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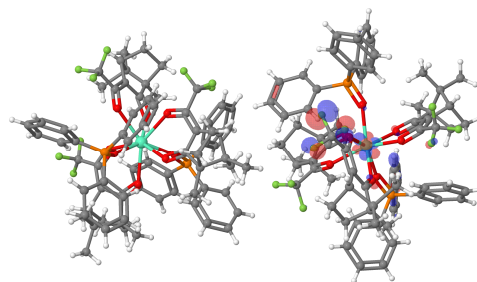
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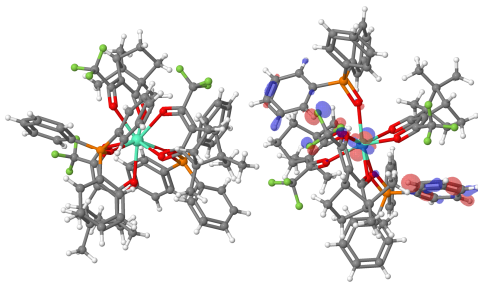
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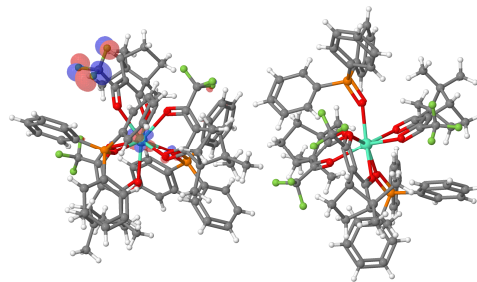
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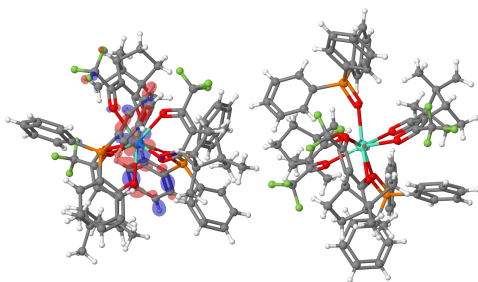
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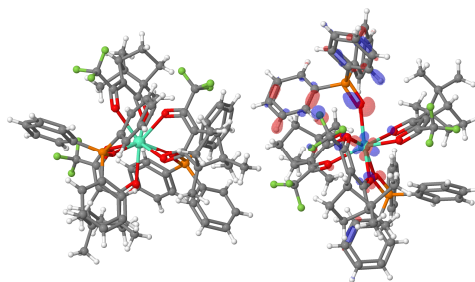
h) HOMO-114



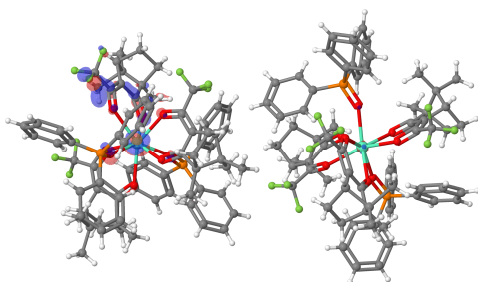
i) HOMO-110



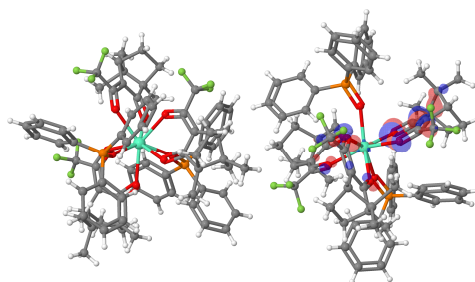
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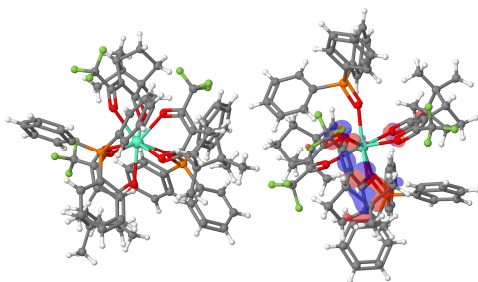
k) HOMO-95



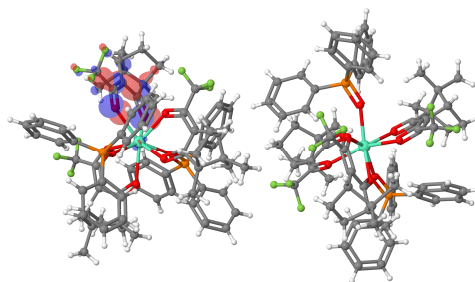
l) HOMO-9



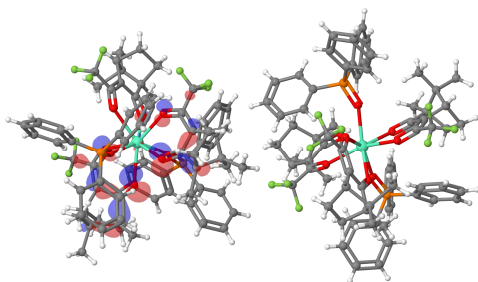
m) HOMO-8



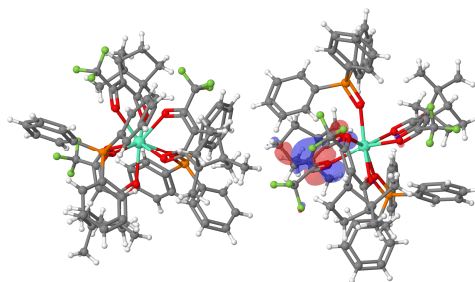
n) HOMO-7



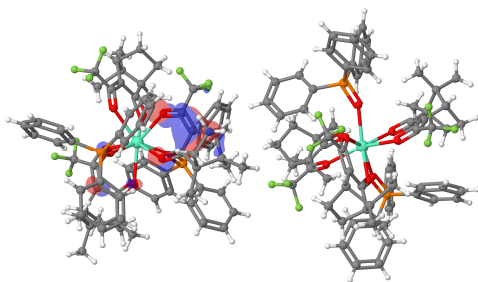
o) HOMO-6



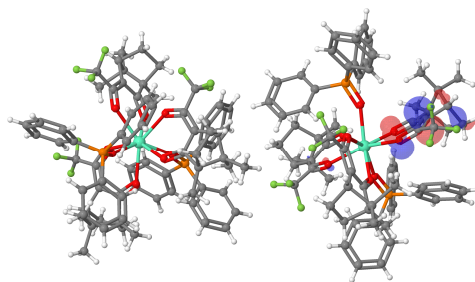
p) HOMO-5



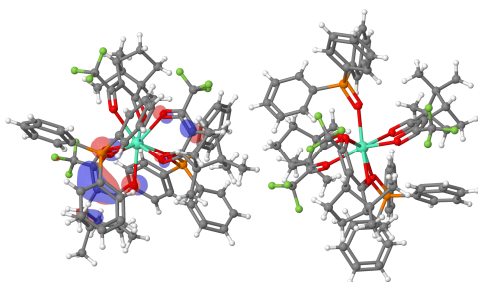
q) HOMO-4



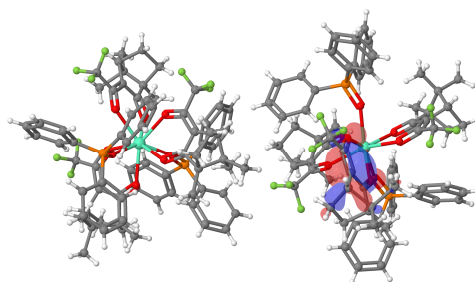
r) HOMO-3



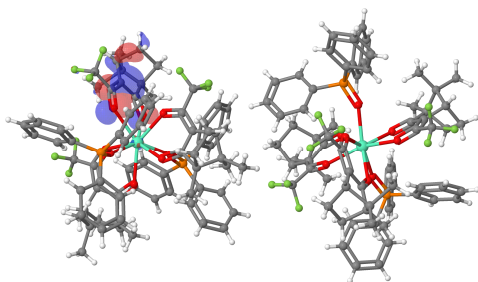
s) HOMO-2



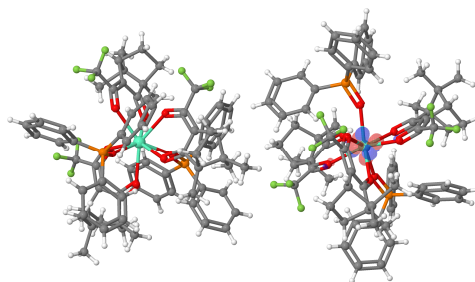
t) HOMO-1



u) HOMO



v) LUMO



w) LUMO+1

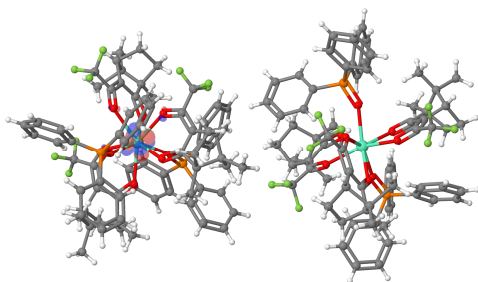


Figure 4.22 Selected α -spin molecular orbitals of $\text{Eu}(+\text{tfc})_3(\text{tppo})_2$ dimer model ($d_{\text{Eu-Eu}} = 12.79 \text{ \AA}$).

4.6 References

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Chapter 5

***SYSTEMATICALLY CONTROL OF STERIC AND
ELECTRONIC STRUCTURE IN CHIRAL Eu(III)
COMPLEXES***

5.1 Introduction

In **Chapter 4**, the author demonstrated the CPL properties change thorough the phase-transition behavior of chiral Eu(III) coordinaiton polymers. The molecular orientation of the chiral Eu(III) coordination polymerrrs affects the CPL and LMCT properties. However, since the single crystal before and after phase transition was not obtained, further investigation such as quantum chemical calculations based on the crystal structure could not be performed.

Here, the author focused on the tetrakis(β -diketonate) Eu(III) complexes in which four camphorate ligands were coordinated to one Eu(III) ion for evaluating the relationship between the CPL and LMCT characteristics. The tetrakis(β -diketonate) Eu(III) complexes with alkali metal ion (Na^+ , K^+ , Rb^+ , Cs^+) as a counterion showed efficient CD and CPL properties.^[1-3] Di Bari concluded that the large g_{CPL} value in the $\text{Cs}^+[\text{Eu}(\text{hfc})_4]^-$ is related to the combination of D_{4d} symmetric structure and the dynamic coupling involving the diketonate π - π^* transition.^[4] The aggregation structure of the tetrakis(β -diketonate) Eu(III) complexes also affects the CPL properties of them.^[5,6] Here, the author considered the introduction of organic cations instead of metal ions into the tetrakis(β -diketonate) Eu(III) complexes. Since the organic cations can easily control of their structure, the CPL properties of the complexes can be precised tuning. Regarding the introduction of organic cations into the Eu(III) complexes, Nakamura and Kobayashi reported that the effect of ammonium salts with different counter anions on the photophysical properties of tris(β -diketonate) Eu(III) complexes.^[7,8]

In this chapter, twelve types of chiral tetrakis(β -diketonate) Eu(III) complexes with combination of three different chiral ligands and four different ammonium cations were synthesized (**Figure 5.1**). Their structures were estimated by single crystal X-ray analysis, and the photophysical properties were evaluated emission spectra and CPL measurements.

The quantum chemical calculations were performed for evaluating the polarizability and LMCT characteristics of the complexes.

Tetrakis(camphorate)Eu(III) Ammonium cation

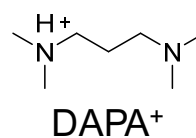
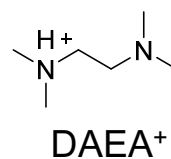
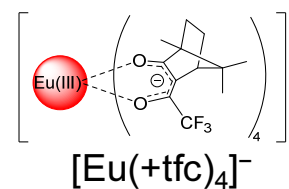
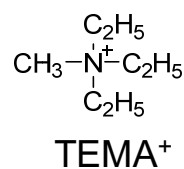
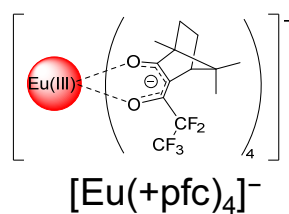
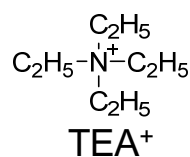
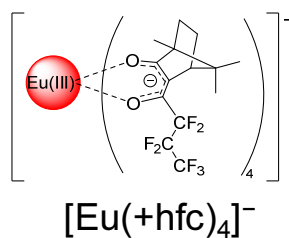


Figure 5.1 Molecular structures of three types of chiral tetrakis(camphorate)Eu(III) complexes and four types of ammonium cations.

5.2 Methods

5.2.1 Materials and apparatus

(+)-3-(Trifluoroacetyl)camphor (98%) and (+)-3-(heptafluorobutyryl)camphor (96%) were purchased from Sigma-Aldrich Co. LLC. (+)-Camphor (>98.0%) was purchased from Tokyo Chemical Industry Co., Ltd. Europium(III) chloride hexahydrate (99.9%) was purchased from FUJIFILM Wako Pure Chemical Corporation. All other reagents were of reagent grade and used without further purification.

ESI-MS spectra were measured using a JEOL JMS-T100LP. Elemental analyses were performed on an Exeter Analytical CE440. Emission 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, $\lambda = 1064$ nm) and a photomultiplier (Hamamatsu Photonics, R5108, response time ≤ 1.1 ns). The Nd:YAG laser response was monitored with a digital oscilloscope (Sony Tektronix, TDS3052, 500 MHz) synchronized to the single-pulse excitation. Emission lifetimes were determined from the slope of logarithmic plots of the decay profiles. CPL spectra were recorded on a JASCO CPL-300 circularly polarized luminescence spectrometer. For evaluating the CPL properties in the solid state, the KBr pellets (Eu(III) complexes (0.5 mg) and KBr (150 mg)) were prepared using PT-10 tablet forming machine (48.2 kN, press time: 3 min).

5.2.2 Crystallography

Single crystals of chiral Eu(III) complexes were obtained by recrystallization from acetonitrile or ethanol solution. 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.^[9] 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.^[10] The CIF data were confirmed by the checkCIF/PLATON service. 2329097 (for $\text{TEA}^+[\text{Eu}(+\text{tfc})_4]^-$), 2329098 (for $\text{TEA}^+[\text{Eu}(+\text{hfc})_4]^-$), 2329099 (for $\text{TEMA}^+[\text{Eu}(+\text{hfc})_4]^-$), 2329100 (for $\text{DAEA}^+[\text{Eu}(+\text{pfc})_4]^-$), 2329101 (for $\text{DAEA}^+[\text{Eu}(+\text{hfc})_4]^-$), 2329102 (for $\text{DAPA}^+[\text{Eu}(+\text{tfc})_4]^-$), 2329103 (for $\text{DAPA}^+[\text{Eu}(+\text{pfc})_4]^-$), and 2329104 (for $\text{DAPA}^+[\text{Eu}(+\text{hfc})_4]^-$) contain the supplementary crystallographic data for this chapter.

5.2.3 Computational details

All quantum chemical calculations were performed by the density functional theory (DFT) with the long-range corrected LC-BLYP functional using the Gaussian 16 package.^[11] Solvent effects of the structure were estimated using self-consistent reaction field (SCRF), solvation model density (SMD) and solvent-accessible surface (SAS) options. For the evaluating of the LMCT characteristics, the spin-unrestricted self-consistent field time-dependent (TD)-DFT calculations were performed. The Stuttgart RSC 1997 (ECP28MWB) basis set^[12,13] was adopted for Eu atoms, while the cc-pVDZ^[14] basis set was used for the other atoms.

5.2.4 Syntheses

Preparation of (+)-3-(pentafluoropropionyl)camphor (+pfc)

(+)-3-(pentafluoropropionyl)camphor was prepared using the same procedure described in Chapter 3.

Preparation of $\text{TEA}^+[\text{Eu}(+\text{hfc})_4]^-$ (TEA^+ : tetraethylammonium)

(+)-3-(heptafluorobutyryl)camphor (225 μL , 0.53 mmol) was dissolved in ethanol (3 mL). Ethanol solutions (3 mL) of Tetraethylammonium chloride (62.3 mg, 0.37 mmol) and Europium (III) Chloride Hexahydrate (68.1 mg, 0.19 mmol) were dropwised to the solution. The saturated ethanol solution of sodium hydroxide was slowly dropwised to the mixture until the pH increased to 7. After stirring 1 h, white precipitate was removed from the reaction mixture. The reaction solution was evaporated to give a light yellow powder. The obtained powder was recrystallized from acetonitrile to give a light yellow crystal.

Yield: 106.8 mg, 34%. ESI-MS (m/z): $[\text{Eu}(+\text{hfc})_4]^-$ calcd. for $\text{C}_{56}\text{H}_{56}\text{EuF}_{28}\text{O}_8$, 1541.28; found, 1541.24. Elemental analysis: calcd. for $\text{C}_{64}\text{H}_{76}\text{EuF}_{28}\text{NO}_8$, C 46.00, H 4.58, N 0.84; found, C 45.74, H 4.46, N 0.79 %.

Preparation of Eu(III) complexes with TEA^+ / TEMA^+ (TEMA^+ : triethylmethylammonium)

The complexes were synthesized using similar procedure to the $\text{TEA}^+[\text{Eu}(+\text{hfc})_4]^-$, with (+)-3-(heptafluorobutyryl)camphor, (+)-3-(pentafluoropropionyl)camphor, or (+)-3-(Trifluoroacetyl)camphor was used for β -diketonate and tetraethylammonium chloride or Triethylmethylammonium was used for ammonium salt.

$\text{TEMA}^+[\text{Eu}(+\text{hfc})_4]^-$: Yield: 23%. ESI-MS (m/z): $[\text{Eu}(+\text{hfc})_4]^-$ calcd. for $\text{C}_{56}\text{H}_{56}\text{EuF}_{28}\text{O}_8$, 1541.28; found, 1541.28. Elemental analysis: calcd. for $\text{C}_{63}\text{H}_{74}\text{EuF}_{28}\text{NO}_8$, C 45.66, H 4.50, N 0.85; found, C 45.16, H 4.38, N 0.81 %.

$\text{TEA}^+[\text{Eu}(+\text{pfc})_4]^-$: Yield: 16%. ESI-MS (m/z): $[\text{Eu}(+\text{pfc})_4]^-$ calcd. for $\text{C}_{52}\text{H}_{56}\text{EuF}_{20}\text{O}_8$, 1341.29; found, 1341.30. Elemental analysis: calcd. for $\text{C}_{60}\text{H}_{76}\text{EuF}_{20}\text{NO}_8$, C 48.98, H 5.21, N 0.95; found, C 48.92, H 5.16, N 0.91 %.

TEMA⁺[Eu(+pfc)₄]⁻: Yield: 8%. ESI-MS (*m/z*): [Eu(+pfc)₄]⁻ calcd. for C₅₂H₅₆EuF₂₀O₈, 1341.29; found, 1341.27. Elemental analysis: calcd. for C₅₉H₇₄EuF₂₀NO₈, C 48.63, H 5.12, N 0.96; found, C 48.47, H 5.06, N 0.88 %.

TEA⁺[Eu(+tfc)₄]⁻: Yield: 5%. ESI-MS (*m/z*): [Eu(+tfc)₄]⁻ calcd., 1141.30; found, 1141.28. Elemental analysis: calcd. for C₅₆H₇₆EuF₁₂NO₈, C 52.91, H 6.03, N 1.10; found, C 52.49, H 5.94, N 1.07 %.

TEMA⁺[Eu(+tfc)₄]⁻: 47%. ESI-MS (*m/z*): [Eu(+tfc)₄]⁻ calcd., 1141.30; found, 1141.29. Elemental analysis: calcd. for C₅₅H₇₄EuF₁₂NO₈, C 52.55, H 5.93, N 1.11; found, C 52.52, H 5.92, N 1.08 %.

Preparation of DAEA⁺[Eu(+hfc)₄]⁻ (DAEA⁺: 2-(dimethylamino)-*N,N,N*-trimethylethan-1-aminium)

(+)-3-(heptafluorobutyryl)camphor (170 μ L, 0.40 mmol) was dissolved in ethanol (2 mL). Ethanol solutions (3 mL) of europium (III) Chloride Hexahydrate (55 mg, 0.15 mmol) was dropwised to the solution. The *N,N,N',N'*-Tetramethyl-ethylenediamine (100 μ L) was slowly dropwised to the mixture and refluxed 4 h. After the reaction, the reaction was cooled to room temperature and slowly evaporated to give a light yellow crystal.

Yield 195 mg (78 %). ESI-MS (*m/z*): [Eu(+hfc)₄]⁻ calcd. for C₅₆H₅₆EuF₂₈O₈, 1541.28; found, 1541.27. Elemental analysis: calcd. for C₆₂H₇₃EuF₂₈N₂O₈, C 44.91, H 4.44, N 1.69; found, C 44.81, H 4.43, N 1.59 %.

Preparation of Eu(III) complexes with DAEA⁺ / DAPA⁺ (DAPA⁺: 3-(dimethylamino)-*N,N,N*-trimethylpropan-1-aminium)

The complexes were synthesized using similar procedure to the DAEA⁺[Eu(+hfc)₄]⁻, with (+)-3-(heptafluorobutyryl)camphor, (+)-3-(pentafluoropropionyl)camphor, or (+)-3-(Trifluoroacetyl)camphor was used for β -diketonate and *N,N,N',N'*-Tetramethyl-ethylenediamine or *N,N,N',N'*-Tetramethyl-1,3-diaminopropane was used for amine.

DAPA⁺[Eu(+hfc)₄]⁻: Yield 87 %. ESI-MS (*m/z*): [Eu(+hfc)₄]⁻ calcd. for C₅₆H₅₆EuF₂₈O₈, 1541.28; found, 1541.27. Elemental analysis: calcd. for C₆₃H₇₅EuF₂₈N₂O₈, C 45.25, H 4.52, N 1.68; found, C 45.46, H 4.47, N 1.67 %.

DAEA⁺[Eu(+pfc)₄]⁻: Yield 36 %. ESI-MS (*m/z*): [Eu(+pfc)₄]⁻ calcd. for C₅₂H₅₆EuF₂₀O₈, 1341.29; found, 1341.28. Elemental analysis: calcd. for C₅₈H₇₃EuF₂₀N₂O₈, C 47.78, H 5.05, N 1.92; found, C 47.63, H 4.99, N 1.88 %.

DAPA⁺[Eu(+pfc)₄]⁻: Yield 64 %. ESI-MS (*m/z*): [Eu(+pfc)₄]⁻ calcd. for C₅₂H₅₆EuF₂₀O₈, 1341.29; found, 1341.28. Elemental analysis: calcd. for C₅₉H₇₅EuF₂₀N₂O₈, C 48.14, H 5.14, N 1.90; found, C 48.03, H 5.10, N 1.85 %.

DAEA⁺[Eu(+tfc)₄]⁻: Yield 41 %. ESI-MS (*m/z*): [Eu(+tfc)₄]⁻ calcd., 1141.30; found, 1141.29. Elemental analysis: calcd. for C₅₄H₇₃EuF₁₂N₂O₈, C 51.55, H 5.85, N 2.23; found, C 51.45, H 5.84, N 2.19 %.

DAPA⁺[Eu(+tfc)₄]⁻: Yield 66 %. ESI-MS (*m/z*): [Eu(+tfc)₄]⁻ calcd., 1141.30; found, 1141.28. Elemental analysis: calcd. for C₅₅H₇₅EuF₁₂N₂O₈, C 51.93, H 5.94, N 2.20; found, C 51.87, H 5.94, N 2.14 %.

5.3 Results and discussion

5.3.1 Structural characterizations

Twelve types of chiral Eu(III) complexes with ammonium cations were obtained by complexation of chiral camphorate ligands and europium chloride hexahydrate with ammonium chloride or amine. The complexes were purified by recrystallization of acetonitrile or ethanol solution. Among them, the single crystals of $\text{TEA}^+[\text{Eu}(+\text{hfc})_4]^-$, $\text{TEMA}^+[\text{Eu}(+\text{hfc})_4]^-$, $\text{DAEA}^+[\text{Eu}(+\text{hfc})_4]^-$, $\text{DAPA}^+[\text{Eu}(+\text{hfc})_4]^-$, $\text{DAEA}^+[\text{Eu}(+\text{pfc})_4]^-$, $\text{DAPA}^+[\text{Eu}(+\text{pfc})_4]^-$, $\text{TEA}^+[\text{Eu}(+\text{tfc})_4]^-$, and $\text{DAPA}^+[\text{Eu}(+\text{tfc})_4]^-$ were successfully obtained and single-crystal X-ray analyses were performed to determine their structures. These crystallographic data were summarized in **Figure 5.2** and **Table 5.1**. All of these chiral Eu(III) complexes were eight-coordinated structures in which four chiral camphorate ligands were coordinated to one Eu(III) ion. One ammonium cation is existed per tetrakis(β -diketonate)europium(III) unit as a counterion. Although DAEA and DAPA could potentially be dications, their presence in a one-to-one ratio with the Eu(III) ion indicates that they are monovalent cations. The Eu(III) complexes with +hfc or +pfc ligands showed almost the same structure, which four fluoroalkyl chains of the camphorate ligands were oriented toward the ammonium cation. Several CH-F interactions were observed between the ammonium cations and fluorine atoms in fluoroalkyl chains. The configurations of the chiral β -diketonate ligands were classified as Δ form. In contrast to the $[\text{Eu}(+\text{hfc})_4]^-$ and $[\text{Eu}(+\text{pfc})_4]^-$ complexes, two fluoroalkyl chains of $[\text{Eu}(+\text{tfc})_4]^-$ complexes were faced to the upper side, and the others were faced to the downside. The configurations of the ligands were categorized as Λ form.

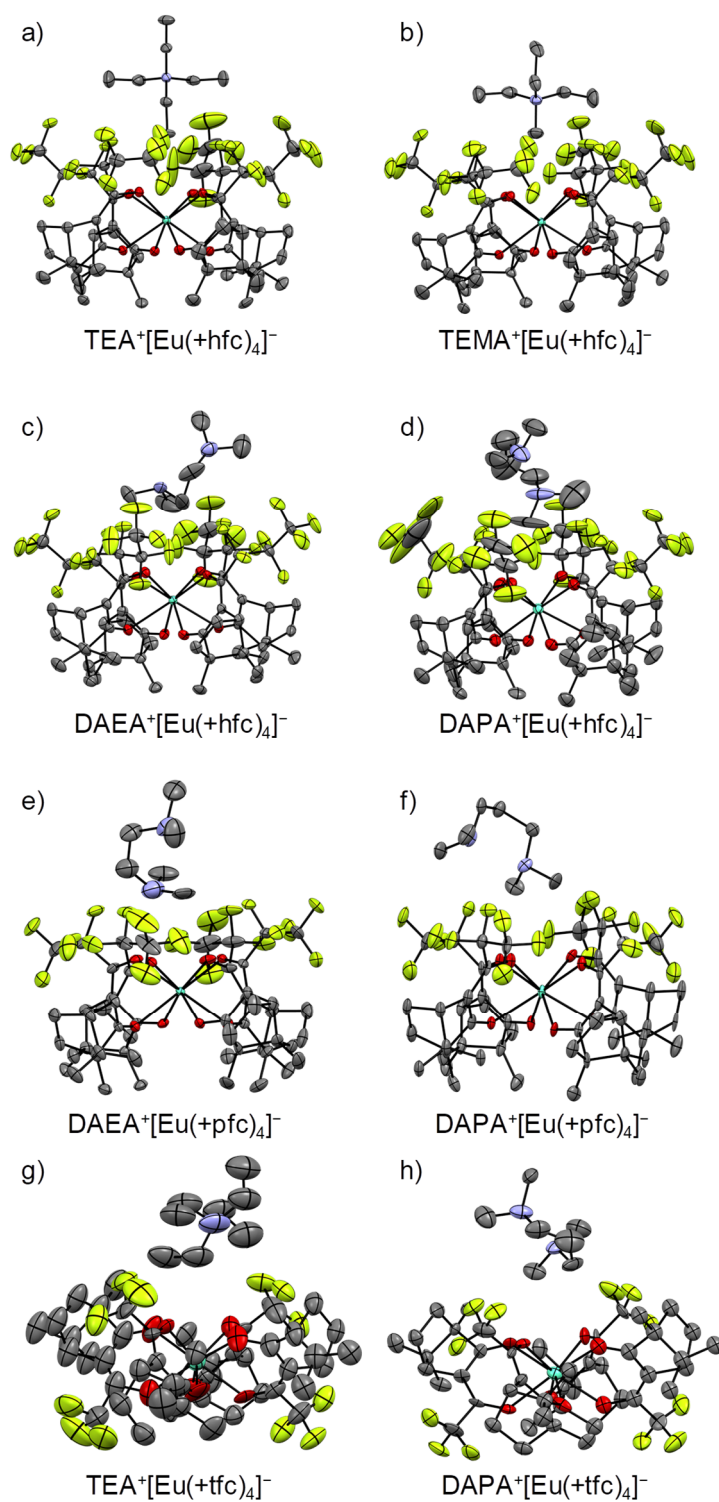


Figure 5.2 ORTEP drawings (ellipsoids set at 50 % probability, hydrogen atoms were omitted for clarity) of a) $\text{TEA}^+[\text{Eu}(\text{+hfc})_4]^-$, b) $\text{TEMA}^+[\text{Eu}(\text{+hfc})_4]^-$, c) $\text{DAEA}^+[\text{Eu}(\text{+hfc})_4]^-$, d) $\text{DAPA}^+[\text{Eu}(\text{+hfc})_4]^-$, e) $\text{DAEA}^+[\text{Eu}(\text{+pfc})_4]^-$, f) $\text{DAPA}^+[\text{Eu}(\text{+pfc})_4]^-$, g) $\text{TEA}^+[\text{Eu}(\text{+tfc})_4]^-$, and h) $\text{DAPA}^+[\text{Eu}(\text{+tfc})_4]^-$.

Table 5.1 Crystallographic data of chiral Eu(III) complexes.

Compounds	TEA ⁺ [Eu(+hfc) ₄] [−]	TEMA ⁺ [Eu(+hfc) ₄] [−]	DAEA ⁺ [Eu(+hfc) ₄] [−]	DAPA ⁺ [Eu(+hfc) ₄] [−]
Chemical formula	C ₆₈ H ₈₂ EuF ₂₈ N ₃ O ₈	C ₆₉ H ₈₃ EuF ₂₈ N ₄ O ₈	C ₆₂ H ₇₃ EuF ₂₈ N ₂ O ₈	C ₆₃ H ₇₇ EuF ₂₈ N ₂ O ₉
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	P2 ₁	P2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
a / Å	14.3413(2)	14.0766(3)	13.9299(2)	13.9014(2)
b / Å	17.0866(2)	17.0228(3)	22.2178(4)	22.1826(4)
c / Å	16.3500(2)	16.3800(3)	24.0965(4)	23.9333(3)
β / deg.	91.9770(10)	93.628(2)	90	90
Volume / Å ³	4004.09(9)	3917.16(13)	7457.7(2)	7380.29(19)
R ₁	0.0334	0.0323	0.0342	0.0423
wR ₂	0.0877	0.0858	0.0852	0.1140
Flack parameter	−0.019(2)	−0.021(2)	−0.012(4)	−0.015(4)
Compounds	DAEA ⁺ [Eu(+pfc) ₄] [−]	DAPA ⁺ [Eu(+pfc) ₄] [−]	TEA ⁺ [Eu(+tfc) ₄] [−]	DAPA ⁺ [Eu(+tfc) ₄] [−]
Chemical formula	C ₅₈ H ₇₃ EuF ₂₀ N ₂ O ₈	C ₅₉ H ₇₅ EuF ₂₀ N ₂ O ₈	C ₅₆ H ₇₆ EuF ₁₂ NO ₈	C ₅₅ H ₇₃ EuF ₁₂ N ₂ O ₈
Crystal system	orthorhombic	monoclinic	tetragonal	tetragonal
Space group	C222 ₁	P2 ₁	P4 ₃	P4 ₃
a / Å	18.7730(3)	13.2845(3)	16.8183(2)	16.3835(5)
b / Å	18.5793(3)	38.9837(7)	16.8183(2)	16.3835(5)
c / Å	37.3769(5)	13.3168(3)	20.5009(4)	21.4906(6)
β / deg.	90	106.542(2)	90	90
Volume / Å ³	13036.7(3)	6611.1(3)	5798.79(18)	5768.5(4)
R ₁	0.0484	0.0708	0.0712	0.0887
wR ₂	0.1180	0.1828	0.1952	0.2303
Flack parameter	0.001(3)	−0.015(8)	0.003(10)	−0.038(8)

Based on their crystal data, continuous shape measure (CShM) calculations using SHAPE^[15–17] were performed to determine the geometrical structures around the Eu(III) ions. The CShM factor (S_{CShM}) values obtained for these eight complexes for 8-SAP and 8-TDH (SAP: square antiprism, TDH: triangular dodecahedron) are summarized in **Table 5.2**. The S values for 8-SAP of all chiral Eu(III) complexes were smaller than that for 8-TDH, indicating that the coordination geometries of all chiral Eu(III) complexes were classified as 8-SAP. However, the ratio of S_{SAP} and S_{TDH} were slightly different that means the coordination geometry around Eu(III) ion differ depending on the kinds of counter ions.

Table 5.2 S_{CShM} values of the chiral Eu(III) complexes.

Compounds	S_{CShM} (8-SAP)	S_{CShM} (8-TDH)	S_{CShM} (8-SAP)/ S_{CShM} (8-TDH)
TEA ⁺ [Eu(+hfc) ₄] [−]	0.400	2.069	0.19
TEMA ⁺ [Eu(+hfc) ₄] [−]	0.459	1.943	0.24
DAEA ⁺ [Eu(+hfc) ₄]	0.837	0.877	0.95
DAPA ⁺ [Eu(+hfc) ₄] [−]	0.843	0.893	0.94
DAEA ⁺ [Eu(+pfc) ₄] [−]	0.619	1.059	0.58
DAPA ⁺ [Eu(+pfc) ₄] [−]	0.561	0.619	0.91
TEA ⁺ [Eu(+tfc) ₄] [−]	0.831	1.506	0.55
DAPA ⁺ [Eu(+tfc) ₄] [−]	0.567	1.617	0.35

5.3.2 Photophysical properties

The emission spectra of the chiral Eu(III) complexes are shown in **Figure 5.3**. The emission spectra were normalized with the area of the $^5D_0 \rightarrow ^7F_1$ transition band, which is known to be insensitive to the surrounding environment of the Eu(III) ion.^[18] The emission bands at approximately 575, 590, 610, 650, and 700 nm were assigned to the 4f-4f transitions of Eu(III) ($^5D_0 \rightarrow ^7F_J : J = 0, 1, 2, 3, \text{ and } 4$).^[19] The weak $^5D_0 \rightarrow ^7F_0$ band and strong $^5D_0 \rightarrow ^7F_4$ band suggest that the higher symmetry around the Eu(III) coordination sphere. The intensity and spectral shape of $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_4$ transition were depends on the kind of ammonium cations, which represented the oscillator strength and Judd-Ofelt parameters of the complexes were slightly changed.

The emission lifetimes of the chiral Eu(III) complexes are shown in **Table 5.3**. Based on the emission lifetimes and spectra, the 4f-4f emission quantum yield (Φ_{f-f}), radiative rate constant (k_r), and non-radiative rate constant (k_{nr}) were estimated using the equations (1.1)-(1.3), and the parameters are also summarized in **Table 5.3**.

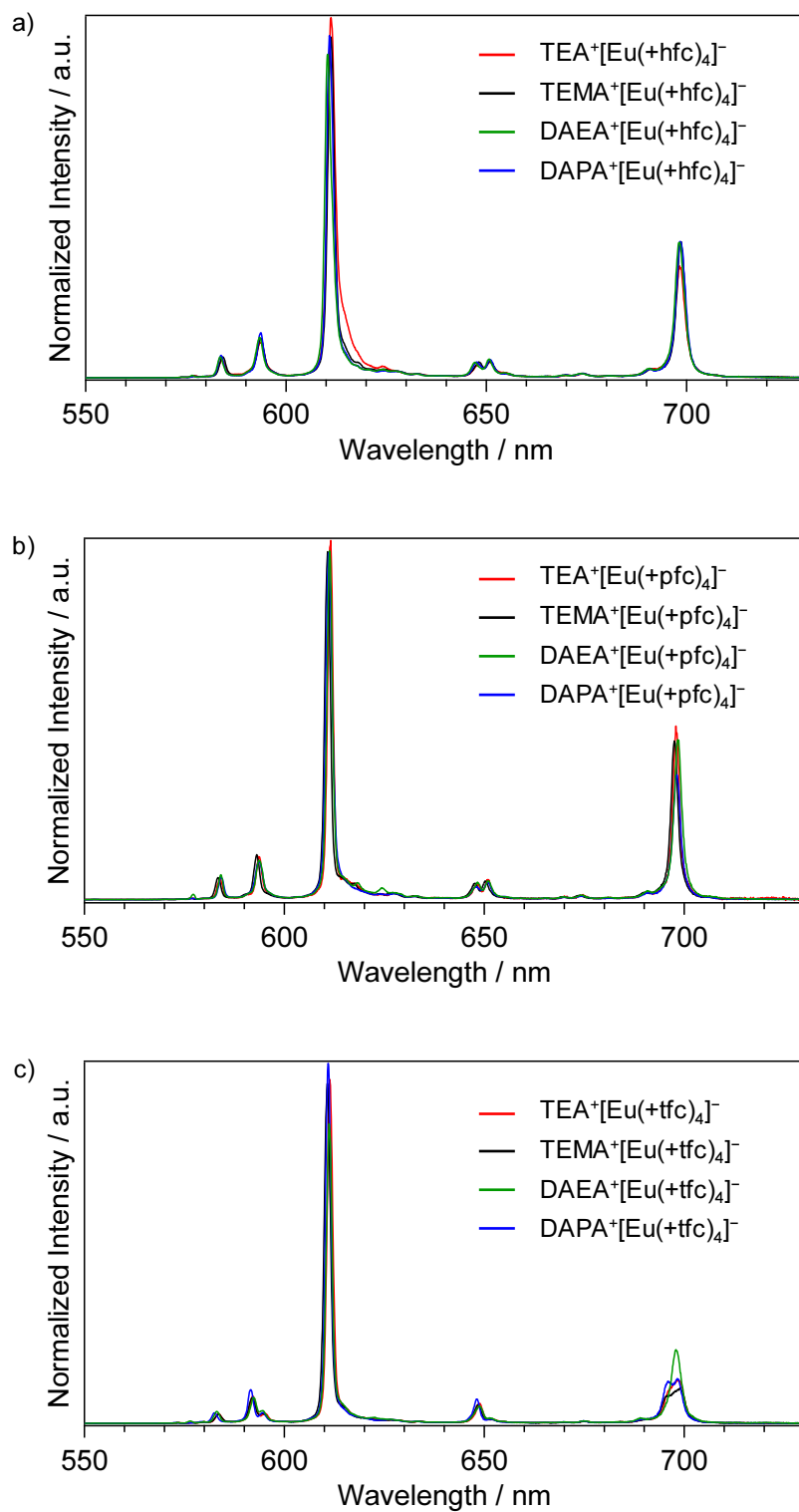


Figure 5.3 Emission spectra ($\lambda_{\text{ex}} = 360$ nm) of a) [Eu(+hfc)₄]⁻, b) [Eu(+pfc)₄]⁻, and c) [Eu(+tfc)₄]⁻ complexes.

Table 5.3 Photophysical parameters of the chiral Eu(III) complexes.

Compounds	k_r / s^{-1}	k_{nr} / s^{-1}	τ_{obs} / ms	$\Phi_{f-f} / \%$	I_{tot}/I_{MD}	g_{CPL}
TEA ⁺ [Eu(+hfc) ₄] [−]	5.9×10^2	2.0×10^3	0.385	23	11.91	+0.70
TEMA ⁺ [Eu(+hfc) ₄] [−]	5.0×10^2	2.1×10^3	0.389	19	10.04	+1.03
DAEA ⁺ [Eu(+hfc) ₄]	5.3×10^2	3.6×10^3	0.240	13	10.66	+0.76
DAPA ⁺ [Eu(+hfc) ₄] [−]	5.2×10^2	1.2×10^3	0.587	31	10.58	+0.80
TEA ⁺ [Eu(+pfc) ₄] [−]	5.1×10^2	5.2×10^2	0.979	49	10.20	+0.97
TEMA ⁺ [Eu(+pfc) ₄] [−]	5.0×10^2	5.9×10^2	0.922	46	10.07	+1.08
DAEA ⁺ [Eu(+pfc) ₄]	5.4×10^2	3.5×10^3	0.246	13	10.87	+0.72
DAPA ⁺ [Eu(+pfc) ₄] [−]	5.1×10^2	5.9×10^2	0.912	47	10.33	+0.93
TEA ⁺ [Eu(+tfc) ₄] [−]	5.2×10^2	2.6×10^3	0.322	17	10.51	−1.11
TEMA ⁺ [Eu(+tfc) ₄] [−]	5.3×10^2	2.6×10^3	0.323	17	10.63	−1.10
DAEA ⁺ [Eu(+tfc) ₄]	5.3×10^2	6.2×10^3	0.148	8	10.66	−1.02
DAPA ⁺ [Eu(+tfc) ₄] [−]	5.4×10^2	2.1×10^3	0.378	21	10.98	−0.87

The CPL spectra of the chiral Eu(III) complexes in the solid state (in KBr pellets) are shown in **Figure 5.4**. Characteristic CPL signals were observed at approximately 590 ($^5D_0 \rightarrow ^7F_1$) and 615 nm ($^5D_0 \rightarrow ^7F_2$). In [Eu(+hfc)₄][−] and [Eu(+pfc)₄][−] complexes, the positive and negative CPL signals were observed in their $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions, respectively. On the other hand, the CPL signs of [Eu(+tfc)₄][−] complexes were inverted, which is related to the Δ or Λ configuration in the Eu(III) coordination sphere. The g_{CPL} values of $^5D_0 \rightarrow ^7F_1$ transition are summarized in **Table 5.3**.

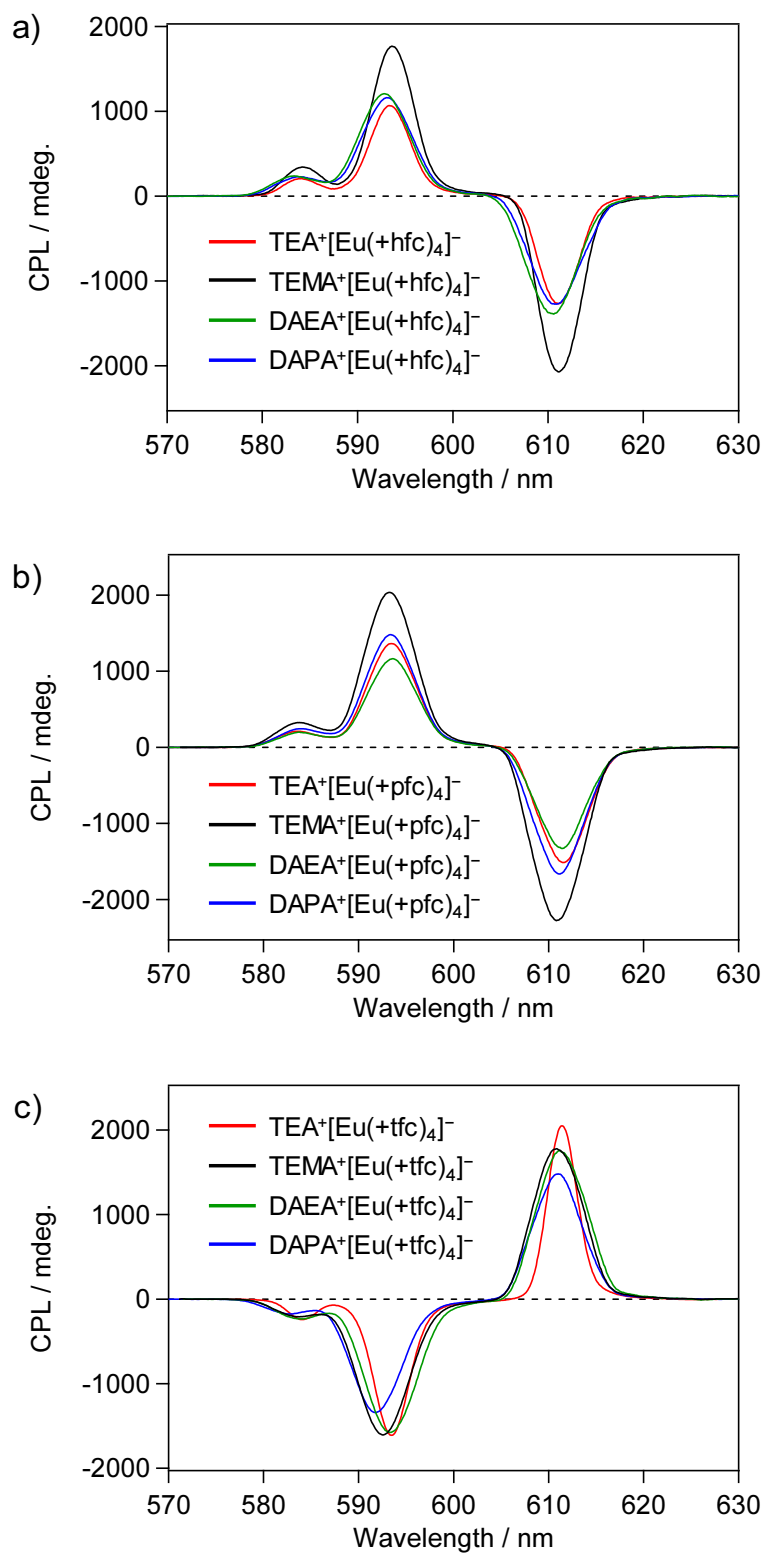


Figure 5.4 CPL spectra ($\lambda_{\text{ex}} = 360$ nm) of a) $[\text{Eu}(\text{+hfc})_4]^-$, b) $[\text{Eu}(\text{+pfc})_4]^-$, and c) $[\text{Eu}(\text{+tfc})_4]^-$ complexes.

Here, the author focused on the relationship between the g_{CPL} and emission spectral intensity in chiral Eu(III) complexes. The plots of g_{CPL} and $I_{\text{tot}}/I_{\text{MD}}$ are shown in **Figure 5.5a**. In both solid and solution state, there are clearly trends that the small $I_{\text{tot}}/I_{\text{MD}}$ value with large absolute g_{CPL} ($|g_{\text{CPL}}|$) values. Theoretically, the $I_{\text{tot}}/I_{\text{MD}}$ is corresponding to the oscillator strength of f-f transition. Hatanaka reported that the enhancement of 4f-4f transition probability is related to the coordination geometrical structure, polarizability of the ligand, and mixing of charge transfer state.^[20,21] In the case of coordination geometrical effect, the plots of g_{CPL} and $S_{\text{SAP}}/S_{\text{TDH}}$ is shown in **Figure 5.5b**. Compared to $\text{TEA}^+[\text{Eu}(+\text{hfc})_4]^-$ and $\text{TEMA}^+[\text{Eu}(+\text{hfc})_4]^-$, their S_{SAP} values are almost identical but the g_{CPL} values are quite different. The $I_{\text{tot}}/I_{\text{MD}}$ value is depended not only geometrical parameters but also the electronic structure of the complexes.

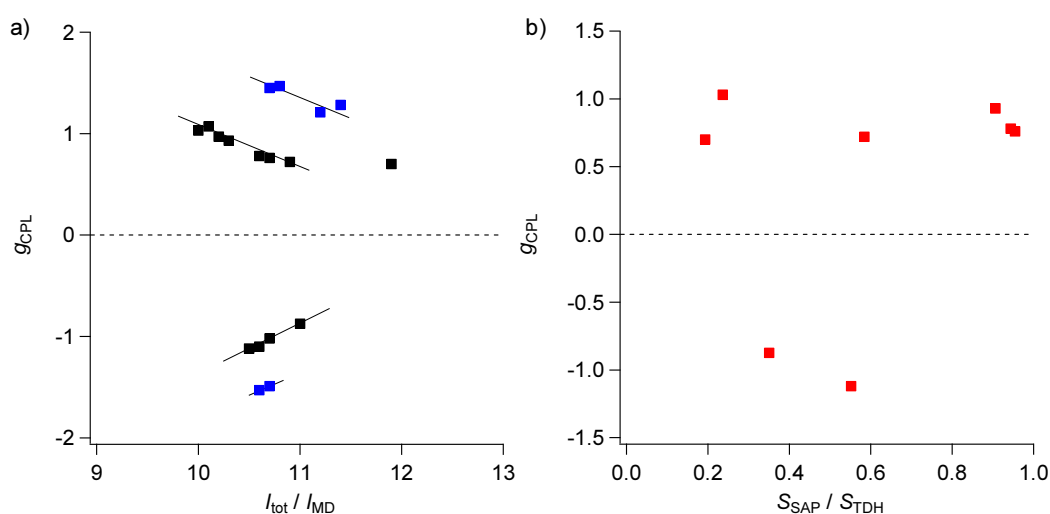


Figure 5.5 The relationship between a) $I_{\text{tot}}/I_{\text{MD}}$ and g_{CPL} (black: solid, blue: solution (2 mM in CHCl_3)) and b) $S_{\text{SAP}}/S_{\text{TDH}}$ and g_{CPL} .

5.3.3 DFT calculations

To evaluate the polarizability and the LMCT characteristics of the chiral Eu(III) complexes, quantum chemical calculations were conducted. From dynamic coupling models, the Ω_2 parameter is proportional to the square of the polarizability (α) and minus eight power of the distance between metal ion and ligands (R) ($\Sigma\alpha^2R^{-8}$: **Table 5.4**).^[22] The magnitude of the polarizability and $\Sigma\alpha^2R^{-8}$ values are strongly affected by the kind of camphorate ligands and weakly depended on the kind of ammonium cations. From these results, the polarizability is expected to have negligible effect on the emission spectral shape ($I_{\text{tot}}/I_{\text{MD}}$) and CPL properties dependent on the counter-cationic species.

Table 5.4 Calculated polarizability and LMCT characteristics of the chiral Eu(III) complexes.

Compounds	$\alpha(\text{average}) / \text{Bohr}^3$	$\Sigma\alpha^2R^{-8} / \text{\AA}^{-2}$	$\Sigma\alpha^2R^{-8}$	$E_{\text{CT}}^{-3}P_{\text{CT}} / 10^{-16} \text{ cm}^3$	$\theta_{\text{LMCT}} / \text{deg.}$
TEA ⁺ [Eu(+hfc) ₄] [−]	142.61	0.412	18.76	6.97	70.5
TEMA ⁺ [Eu(+hfc) ₄] [−]	139.62	0.398	18.13	5.60	57.7
DAEA ⁺ [Eu(+hfc) ₄] [−]	141.41	0.403	18.36	5.60	72.5
DAPA ⁺ [Eu(+hfc) ₄] [−]	141.80	0.413	18.79	5.62	73.9
DAEA ⁺ [Eu(+pfc) ₄] [−]	130.95	0.340	15.49	7.30	76.6
DAPA ⁺ [Eu(+pfc) ₄] [−]	129.53	0.344	15.66	5.61	67.3
TEA ⁺ [Eu(+tfc) ₄] [−]	122.83	0.316	14.41	5.45	76.0
DAPA ⁺ [Eu(+tfc) ₄] [−]	119.76	0.282	12.83	7.86	80.9

From the TD-DFT calculations based on the structure obtained by single crystal X-ray analysis, the LMCT characteristics were evaluated. The strength of LMCT perturbation in 4f-4f transition is proportional to the oscillator strength and minus three power to the excitation energy ($E_{CT}^{-3}P_{CT}$).^[23] From the lower excitation energy, each complex has four LMCT excited states near the emitting level of Eu(III) ion. The summation of $E_{CT}^{-3}P_{CT}$ values of these transitions and average angle of the electric dipole moments of LMCT transition (θ_{LMCT} , Chapter 3) were summarized in **Table 5.4**. From the comparison of $TEA^+[Eu(+hfc)_4]^-$ (with small g_{CPL} value (+0.70)) and $TEMA^+[Eu(+hfc)_4]^-$ (with large g_{CPL} value (+1.03)), the $E_{CT}^{-3}P_{CT}$ value of $TEA^+[Eu(+hfc)_4]^-$ (6.97×10^{-16}) is larger than that of $TEMA^+[Eu(+hfc)_4]^-$ (5.60×10^{-16}), which suggests that the large LMCT perturbation influences the decreasing of the $|g_{CPL}|$ values. On the other hands, the $E_{CT}^{-3}P_{CT}$ values of $TEMA^+[Eu(+hfc)_4]^-$ (5.60×10^{-16}), $DAPA^+[Eu(+hfc)_4]^-$ (5.62×10^{-16}), $DAEA^+[Eu(+hfc)_4]^-$ (5.60×10^{-16}), and $DAPA^+[Eu(+pfc)_4]^-$ (5.61×10^{-16}), whose g_{CPL} values are almost identical, are nearly the same. When the $E_{CT}^{-3}P_{CT}$ are same level, $TEMA^+[Eu(+hfc)_4]^-$ with the smallest θ_{LMCT} and nearly to the ideal SAP structure (the lowest S_{SAP} value) shows the largest g_{CPL} values in these complexes. Assuming that the $\vec{\mu}_{f-f}$ and $\vec{m}_{f-f}$ are parallel to each other and orthogonal to the C_4 axis of the coordination sphere (**Figure 5.6** left), the small θ_{LMCT} have little effect on the $\vec{\mu}_{f-f}$, resulting in large g_{CPL} values (**Figure 5.6** middle). As θ_{LMCT} increases, the mixing of $\vec{\mu}_{LMCT}$ and $\vec{\mu}_{f-f}$ becomes stronger. The increasing of $\theta_{\mu,m}$ related to the LMCT mixing leads to the decreasing of g_{CPL} values of the tetrakis(camphorate)Eu(III) complexes (**Figure 5.6** right). Therefore, it is clear that a structure close to the SAP structure and weak perturbation of LMCT transition are required to achieve strong CPL characteristics. Even

focusing on complexes with +tfc ligands, the complexes with weak LMCT perturbations show larger $|g_{\text{CPL}}|$ values than that with strong LMCT perturbations.

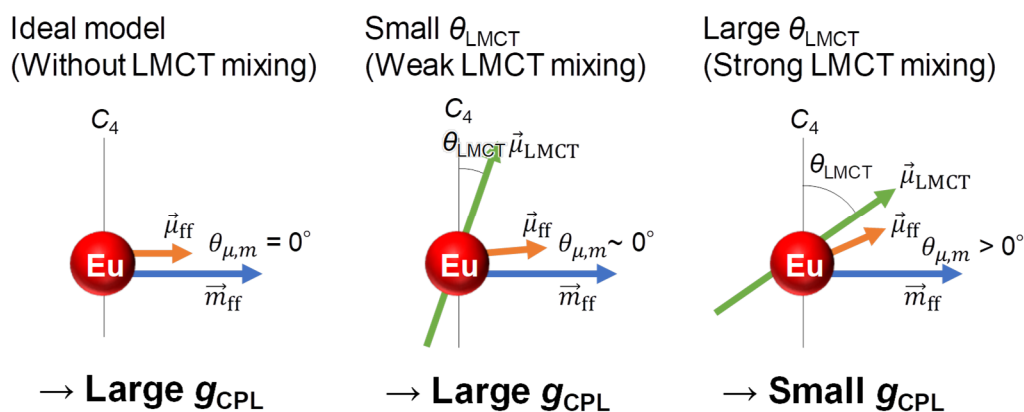


Figure 5.6 The illustration of dipole moments of f-f transition and LMCT transition in tetrakis(camphorate)Eu(III) complexes.

5.3.4 CPL properties in solution state

As shown in **Figure 5.5**, the chiral Eu(III) complexes exhibited stronger g_{CPL} values in solution state (CHCl_3) than in KBr pellet even the $I_{\text{tot}}/I_{\text{MD}}$ values are similar. The emission spectra, CPL spectra, and photophysical parameters of them are shown in **Figure 5.7**, **Figure 5.8**, and **Table 5.5**, respectively.

The photophysical parameters of chiral Eu(III) complexes in chloroform solution are depended on the kinds of camphorate ligand, and the kinds of counterion are not strongly affected their photophysical properties. The interaction between fluoroalkyl chain and ammonium cation, which was observed by single crystal X-ray crystal analysis, became weak in the solution.

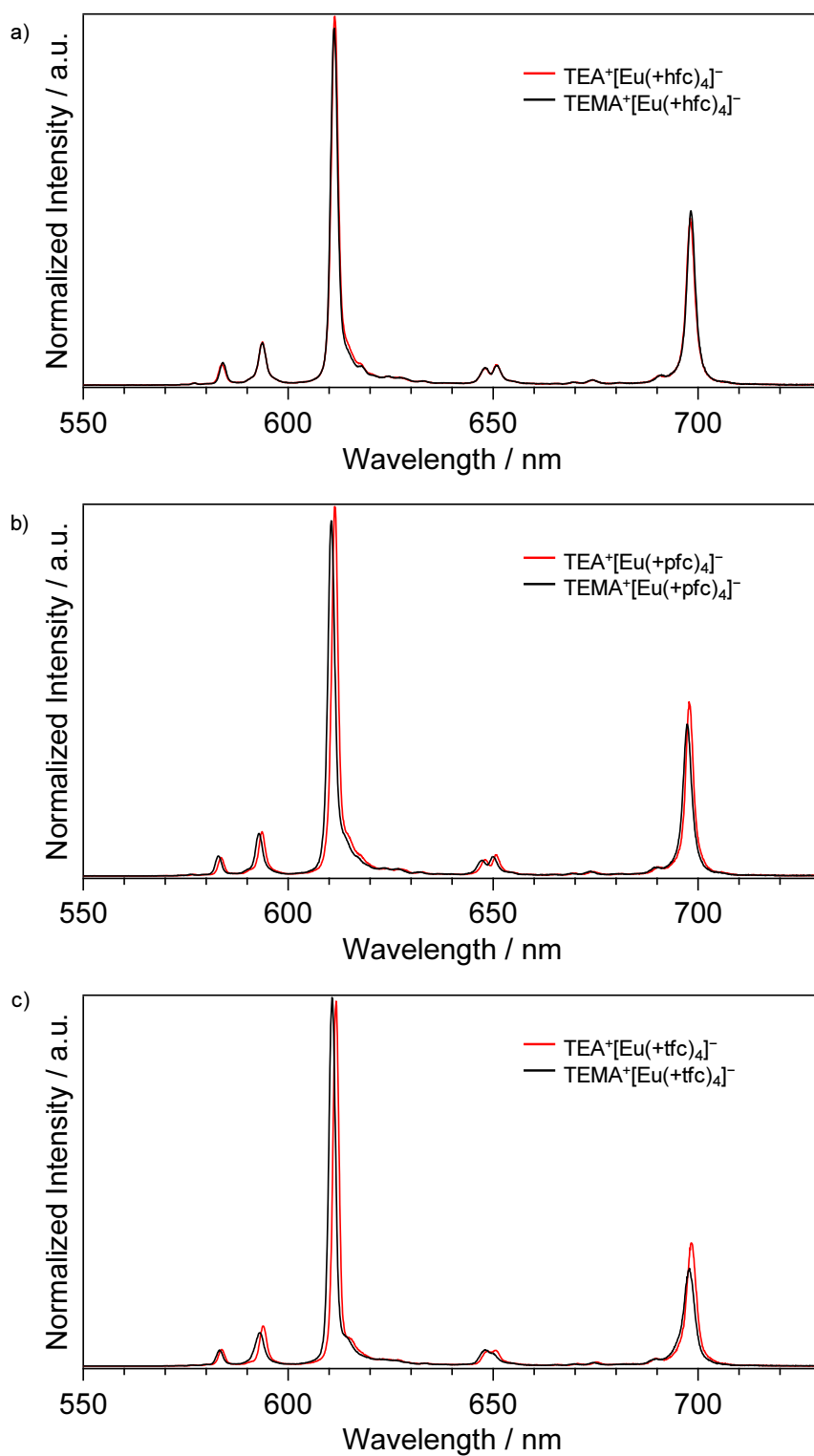


Figure 5.7 Emission spectra ($\lambda_{\text{ex}} = 360$ nm, in 2 mM CHCl_3) of a) $[\text{Eu}(+\text{hfc})_4]^-$, b) $[\text{Eu}(+\text{pfc})_4]^-$, and c) $[\text{Eu}(+\text{tfc})_4]^-$ complexes.

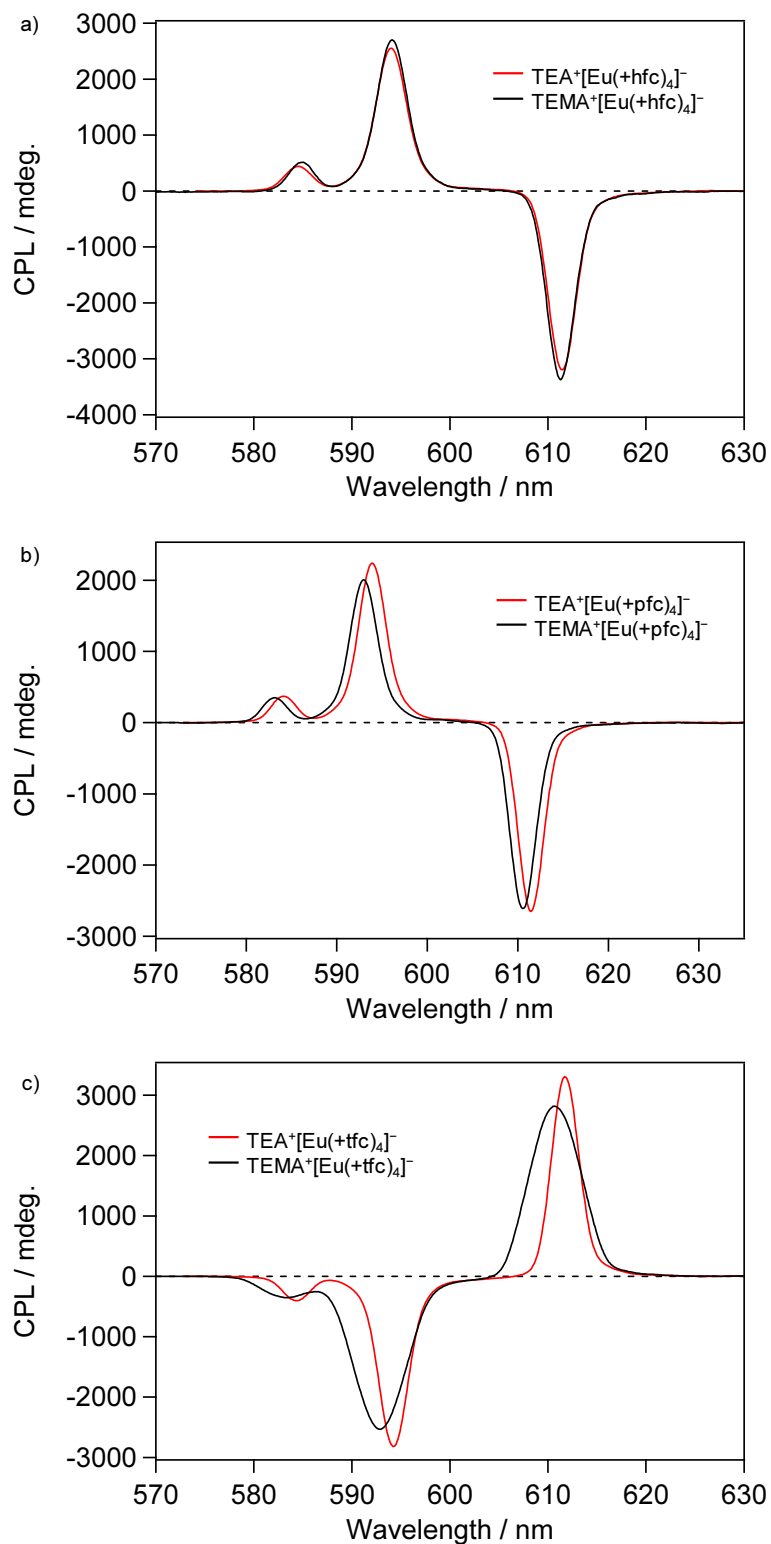


Figure 5.8 CPL spectra ($\lambda_{\text{ex}} = 360$ nm, in 2 mM CHCl_3) of a) $[\text{Eu}(+\text{hfc})_4]^-$, b) $[\text{Eu}(+\text{pfc})_4]^-$, and c) $[\text{Eu}(+\text{tfc})_4]^-$ complexes.

Table 5.5 Photophysical parameters of the chiral Eu(III) complexes (in 2 mM CHCl₃).

Compounds	k_r / s^{-1}	k_{nr} / s^{-1}	τ_{obs} / ms	$\Phi_{f-f} / \%$	I_{tot}/I_{MD}	g_{CPL}
TEA ⁺ [Eu(+hfc) ₄] [−]	4.8×10^2	3.3×10^3	0.263	13	10.85	+1.45
TEMA ⁺ [Eu(+hfc) ₄] [−]	4.7×10^2	2.5×10^3	0.332	16	10.66	+1.46
TEA ⁺ [Eu(+pfc) ₄] [−]	5.0×10^2	2.7×10^3	0.317	16	11.41	+1.28
TEMA ⁺ [Eu(+pfc) ₄] [−]	5.0×10^2	2.4×10^3	0.345	17	11.24	+1.21
TEA ⁺ [Eu(+tfc) ₄] [−]	4.7×10^2	2.2×10^3	0.371	17	10.56	−1.54
TEMA ⁺ [Eu(+tfc) ₄] [−]	4.7×10^2	2.3×10^3	0.367	17	10.66	−1.49

Since the structural and electronic structure of the complexes in solution could be different from those in crystal, the structural optimization of the chiral Eu(III) complexes in chloroform solution were demonstrated (**Figure 5.9**). The Cartesian coordinates of the optimized chiral Eu(III) complexes are shown in **Table 5.7** to **Table 5.12**. For estimating the LMCT characteristics, TD-DFT calculations were also conducted using optimized structure (**Table 5.6**). Similar to the solid state, TEA⁺[Eu(+tfc)₄][−] with the smallest θ_{LMCT} showed the largest $|g_{CPL}|$ values ($g_{CPL} = -1.54$). The structural relaxation in the solution state leads to the weakness of the LMCT mixing, resulting in the large $|g_{CPL}|$ value compared to the solid state.

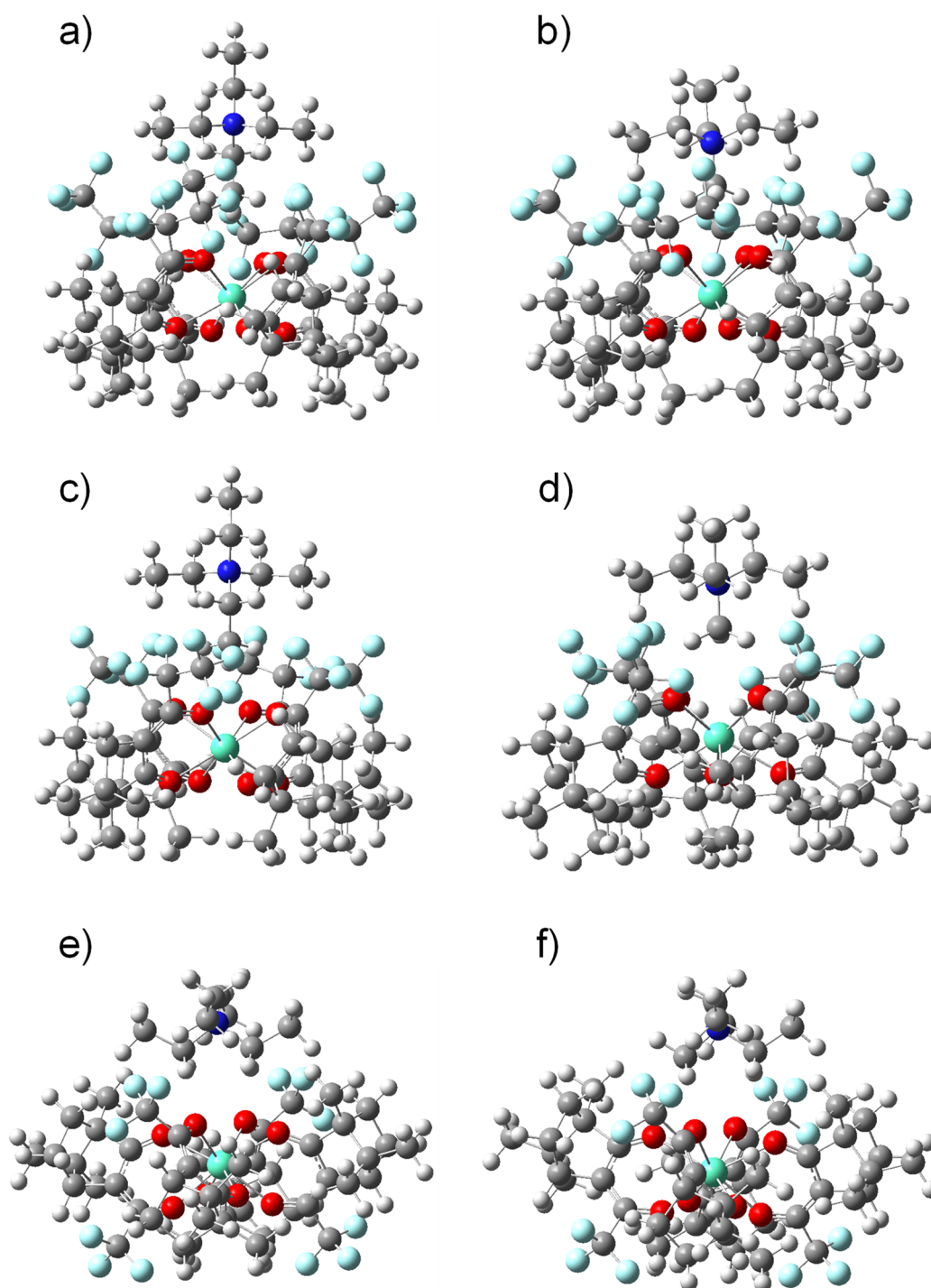


Figure 5.9 Optimized structure of a) TEA⁺[Eu(+hfc)₄]⁻, b) TEMA⁺[Eu(+hfc)₄]⁻, c) TEA⁺[Eu(+pfc)₄]⁻, d) TEMA⁺[Eu(+pfc)₄]⁻, e) TEA⁺[Eu(+tfc)₄]⁻, and f) TEMA⁺[Eu(+tfc)₄]⁻ in chloroform solution.

Table 5.6 Calculated the LMCT characteristics of the chiral Eu(III) complexes based on the optimized structure in chloroform solution.

Compounds	$E_{CT}^{-3}P_{CT} / 10^{-16} \text{ cm}^3$	$\theta_{LMCT} / \text{deg.}$
TEA ⁺ [Eu(+hfc) ₄] ⁻	5.08	67.2
TEMA ⁺ [Eu(+hfc) ₄] ⁻	5.52	67.3
TEA ⁺ [Eu(+pfc) ₄] ⁻	8.00	80.2
TEMA ⁺ [Eu(+pfc) ₄] ⁻	5.74	75.0
TEA ⁺ [Eu(+tfc) ₄] ⁻	5.48	52.1
TEMA ⁺ [Eu(+tfc) ₄] ⁻	5.88	68.5

5.4 Conclusion

Tetrakis(camphorate)Eu(III) complexes with ammonium cations were synthesized. The Δ and Λ configuration of the complexes were dependent on the length of the fluoroalkyl chains in the camphorate ligand. The CPL intensity of the complexes were related to the area of emission spectra of them. The narrow emission bands standard as magnetic dipole transition of the Eu(III) offered to the large g_{CPL} values. From the result of quantum chemical calculations and single crystal X-ray analyses, the weak LMCT perturbation and SAP structures leads to the enhancement of CPL intensity in the tetrakis(camphorate)Eu(III) complexes. The control of the LMCT transition is important for the formation of chiral Eu(III) complexes with large $|g_{\text{CPL}}|$, and can be extended to the Eu(III) complexes with other substituents of the camphorate ligands. In the future, these results provide a basis for the prediction of the CPL properties by the quantum chemical calculations.

5.5 Appendix

Table 5.7 Cartesian coordinates (in Å) of TEA⁺[Eu(+hfc)₄]⁻ for optimized structure obtained by DFT calculations.

Atom	X	Y	Z	Atom	X	Y	Z
Eu	0.036906	0.429711	-1.185441	H	2.556334	6.182989	-1.189288
F	3.688485	0.133618	1.753486	C	-4.496395	0.287266	1.370363
F	4.819406	-0.120599	-0.096938	C	-4.901803	-3.481931	-4.434367
F	2.826045	-2.276405	1.744639	H	-5.868254	-3.109788	-4.076108
F	4.388051	-2.981655	0.420828	H	-4.918395	-4.579097	-4.349805
F	1.900767	1.866126	2.908230	H	-4.834366	-3.241309	-5.505302
F	-2.722428	1.007602	2.684400	C	1.988885	2.471154	0.631266
F	3.512232	3.191977	2.323500	C	-3.363662	5.101026	0.037501
O	0.905148	-1.096344	-2.828313	H	-4.113307	5.894407	0.159287
O	-1.709988	0.850117	0.301236	H	-2.862929	4.973578	1.004756
O	-0.999969	2.504094	-1.862802	C	-4.604528	2.785836	-2.719500
O	1.831417	1.669802	-2.192196	H	-3.956031	1.914297	-2.566987
F	6.194665	0.064265	2.289839	H	-4.645399	2.989323	-3.799792
F	-2.729747	-4.440978	0.153738	H	-5.620784	2.507061	-2.402234
C	-1.706108	-2.412107	-0.651039	C	5.032052	2.457602	-2.033460
F	5.351044	-1.827887	2.877471	H	5.859196	2.714933	-2.709407
O	-0.743306	-1.637884	-0.399517	H	4.928874	1.364157	-2.056666
F	-5.184723	0.591625	0.256854	F	-4.191793	2.484595	2.072612
F	1.584092	4.291512	3.813428	C	-2.378849	5.419170	-1.104422
F	-4.915528	-0.207079	3.631084	H	-2.583744	6.395231	-1.565301
O	0.939008	1.785796	0.497450	H	-1.333436	5.436887	-0.771297
C	2.652516	2.461004	-1.712361	C	-2.076944	4.573110	-3.519331
C	2.631625	-1.623557	-0.511945	H	-0.987437	4.711107	-3.480971
F	1.859263	5.168463	1.838694	H	-2.522807	5.480017	-3.952360
C	3.554702	-1.948655	0.649596	H	-2.267082	3.731524	-4.199955
C	5.661244	-1.058841	1.835181	C	1.403452	4.093737	2.500682
C	4.407534	-0.729465	1.025277	F	0.628383	-5.925558	1.769115
C	-3.730603	-1.378558	-3.526581	C	-5.031998	5.175352	-2.336588
F	-6.236094	-1.042869	2.152201	H	-6.067637	4.961569	-2.031714
C	2.825592	2.890082	-0.360394	H	-5.039757	5.322161	-3.426475
F	-2.167149	-2.917192	1.587217	H	-4.745498	6.129262	-1.879786
C	-2.037483	3.063424	-1.489060	C	-0.586856	-5.497570	1.462902
C	4.359081	-3.967469	-4.654719	C	-5.019203	-2.424938	-1.735723
H	5.406222	-4.112036	-4.348328	H	-5.002609	-2.187151	-0.665157
H	4.372324	-3.625530	-5.699779	H	-5.922371	-3.019976	-1.926834
H	3.872705	-4.949370	-4.638972	C	-3.667375	-0.516276	-4.754507
F	-3.834015	-0.859214	1.172573	H	-3.659909	0.546846	-4.480211
C	-3.746340	-3.172055	-2.160387	H	-4.532021	-0.693526	-5.410190
H	-3.711551	-4.225041	-1.868329	H	-2.750352	-0.704488	-5.330151
C	-2.574322	-1.189507	-2.568531	F	-1.241739	-5.260360	2.600128
F	-0.690233	5.028421	2.887869	C	3.732715	3.149512	-2.515896
O	1.849547	-0.684532	-0.198601	C	4.946519	5.396870	-2.205675
F	-1.212817	-6.447759	0.797955	H	5.052783	6.245223	-1.512717
C	2.746912	-4.614345	-2.338494	H	4.753198	5.816518	-3.203653
H	3.338813	-5.491247	-2.633220	H	5.913800	4.883608	-2.249061
H	2.290798	-4.834805	-1.366958	C	-2.631541	1.697281	0.433684
C	-3.497613	1.409376	1.651611	C	3.691130	-2.934640	-3.763864
C	1.702904	-4.245964	-3.410338	C	-1.809189	-3.493138	0.410685
H	0.682094	-4.202994	-3.005647	C	4.389187	-1.602779	-3.987792
H	1.687422	-4.965562	-4.240521	H	5.449312	-1.672587	-3.700796
C	-3.708068	-2.918108	-3.683915	H	3.943044	-0.782669	-3.410329
C	-0.105406	4.019286	2.252211	H	4.357996	-1.319333	-5.050007
C	2.227231	2.880664	2.074350	C	-0.473039	-4.208141	0.647368
F	-6.340226	1.052679	2.617273	C	3.504571	3.132156	-3.999781
C	-2.904693	2.743564	-0.398536	H	3.442134	2.098254	-4.366447
C	-2.580721	-2.325966	-1.696437	H	4.320790	3.637278	-4.535883
O	-1.844958	-0.191509	-2.564317	H	2.557467	3.621860	-4.266033
F	6.559696	-1.683914	1.097679	C	-4.968700	-1.165522	-2.622116

C	1.812881	-1.933110	-2.784207	H	-4.878164	-0.242390	-2.035372
C	5.254662	2.998828	-0.608021	H	-5.867452	-1.060180	-3.245423
H	5.333971	2.203971	0.141451	N	0.072358	-1.486593	4.764107
H	6.167721	3.605703	-0.543487	C	-0.105073	-0.225442	3.963365
C	-5.522530	0.026205	2.470963	H	-1.085414	0.178562	4.240001
F	-0.370532	4.141195	0.962446	H	0.651534	0.478737	4.325973
F	0.376756	-3.417558	1.320186	C	-0.956902	-2.504375	4.372633
C	3.795912	4.506947	-1.769399	H	-0.715501	-2.795743	3.348655
C	-4.128894	4.013977	-1.960470	H	-0.781669	-3.380751	5.007566
C	3.607303	-3.345286	-2.276071	C	-0.000615	-0.415258	2.484166
H	4.572511	-3.467216	-1.776931	H	-0.787030	-1.053633	2.072248
C	3.996822	3.845655	-0.386375	H	0.976138	-0.786893	2.157167
H	4.046953	4.541661	0.456589	H	-0.122529	0.565488	2.020932
C	2.717740	-2.253835	-1.720280	C	0.098257	-2.212821	7.208846
C	1.576062	-2.445654	-5.253318	H	-0.022584	-1.776607	8.209565
H	1.862948	-3.147190	-6.049830	H	1.089030	-2.684478	7.184478
H	1.908919	-1.438335	-5.539615	H	-0.667025	-2.992904	7.106628
H	0.478918	-2.416647	-5.203679	C	-0.051874	-1.102521	6.200724
C	2.153376	-2.859101	-3.930245	H	0.699285	-0.323199	6.372321
F	0.069663	-4.529585	-0.534481	H	-1.031542	-0.621621	6.301318
C	-2.446004	-3.436201	-4.354802	C	1.405141	-2.108656	4.469898
H	-2.434696	-3.171530	-5.422341	H	1.471321	-3.002563	5.101223
H	-2.400089	-4.533998	-4.291703	H	1.357457	-2.448622	3.431224
H	-1.528848	-3.039335	-3.900977	C	-2.392159	-2.052285	4.444582
F	-0.627956	2.889091	2.709219	H	-2.710417	-1.760832	5.455181
C	-3.997677	3.785459	-0.436795	H	-3.016598	-2.902311	4.139124
H	-4.926136	3.507754	0.072559	H	-2.612558	-1.235268	3.748070
C	-2.616265	4.300059	-2.144909	C	2.602273	-1.214931	4.664046
C	2.513792	5.318841	-1.869277	H	2.722978	-0.871874	5.700996
H	1.617184	4.740941	-1.610157	H	2.593527	-0.345956	3.994108
H	2.377643	5.711120	-2.887848	H	3.495870	-1.797019	4.406108

Table 5.8 Cartesian coordinates (in Å) of TEMA⁺[Eu(+hfc)₄]⁻ for optimized structure obtained by DFT calculations.

Atom	X	Y	Z	Atom	X	Y	Z
Eu	0.045988	-0.043088	-0.926426	C	-3.360861	-3.993668	-2.814884
O	-1.717725	-0.971867	-2.258190	C	4.215081	-3.237478	-1.271100
F	-4.549839	2.575821	1.269992	H	5.165285	-3.025503	-0.771665
F	-3.081762	1.471038	2.423181	C	2.494244	2.865786	-0.844392
F	3.963211	0.759402	1.246693	F	4.533768	-2.677141	1.459066
F	-1.882956	-2.711474	2.532824	F	5.117274	-0.056941	3.569506
O	0.822048	1.758440	0.384553	C	-3.437544	-2.471852	-3.097133
F	1.180319	5.834093	1.991483	C	-1.957094	2.409608	-2.023686
C	-2.434298	-1.966241	-2.084843	C	5.721527	-0.199431	2.395690
O	1.043707	-1.875273	-2.127829	C	-3.214682	-1.973051	-4.495988
F	-6.706442	1.156277	1.834908	H	-3.964198	-2.382826	-5.188126
O	-1.784087	0.731910	0.306041	H	-2.215555	-2.244674	-4.864367
F	-1.373207	-5.537890	0.585419	H	-3.282408	-0.877388	-4.531712
O	-0.873141	1.824107	-2.141953	C	-1.810416	-2.617778	0.183965
O	1.895065	0.907011	-2.121124	C	2.730428	-3.416486	-2.960601
F	0.771491	-3.318825	2.201261	C	4.900568	2.221162	-2.137690
C	-4.634612	0.252606	1.190490	H	4.952105	1.186012	-1.774050
C	0.705826	4.758816	1.352722	H	5.751859	2.362739	-2.817720
F	-6.385957	-0.946213	2.142476	C	3.577421	2.481884	-2.898908
C	2.137190	-2.431979	-1.976448	C	-2.448705	3.480594	-2.971966
F	-5.388950	0.485454	3.403445	F	-1.258678	-5.223157	2.738631
O	-0.870974	-1.793392	0.350021	C	-2.550310	-2.817944	-0.943865
C	-4.952312	-3.064887	-1.273728	C	3.696760	-4.673499	-1.103587
H	-5.089320	-2.546681	-0.316964	H	4.497701	-5.413817	-1.232022
H	-5.808855	-3.738962	-1.408182	H	3.267757	-4.825144	-0.105632
C	1.746070	3.626915	1.416621	C	3.768534	-1.572857	1.384541
C	-2.957090	2.284518	-1.010276	C	2.783753	-1.603790	0.225179

C	5.168896	-4.028964	-3.521448	C	-2.041097	-3.469993	1.420165
H	5.102386	-3.894184	-4.610805	C	-0.651505	4.444460	1.987754
H	4.971948	-5.085888	-3.309549	C	3.524691	3.923486	-1.167759
H	6.210957	-3.823555	-3.233485	H	3.407357	4.876928	-0.643372
F	-0.539786	4.356537	3.309486	C	2.099819	-3.379988	-4.322933
F	0.494327	5.093491	0.069300	H	2.577724	-4.099223	-5.003362
F	1.524592	2.943823	2.567503	H	2.167414	-2.378522	-4.770142
C	-1.736859	3.519426	-4.293543	H	1.031574	-3.629878	-4.258573
H	-2.158674	4.294773	-4.949103	C	-3.511278	4.653576	-1.107907
H	-1.800721	2.552618	-4.811943	H	-3.172274	4.737355	-0.068731
H	-0.669906	3.738096	-4.153093	H	-4.274950	5.426921	-1.265846
F	6.442877	0.886078	2.163265	C	-4.817229	4.217567	-3.656959
C	3.387157	4.006622	-2.701740	H	-4.579618	5.251534	-3.382144
F	0.716180	-4.034299	0.159620	H	-5.882438	4.052748	-3.434750
C	-3.619262	-3.824259	-1.301438	H	-4.697559	4.132448	-4.746688
H	-3.599489	-4.752195	-0.721893	C	-2.002173	-4.599542	-3.132254
F	-5.146748	0.140881	-0.044945	H	-1.167290	-4.026322	-2.708107
F	1.114159	-5.395348	1.767891	H	-1.848265	-4.662288	-4.219594
C	3.066983	-2.328837	-0.894700	H	-1.937434	-5.623289	-2.733791
F	5.383457	-0.456738	0.124072	C	3.497992	1.917345	-4.288219
C	-4.052651	3.248821	-1.403276	H	2.518073	2.115749	-4.744457
H	-5.040173	3.032881	-0.982950	H	3.631160	0.828222	-4.275229
F	-3.897462	-0.838195	1.451580	H	4.275858	2.347184	-4.935557
F	-1.164507	3.314243	1.533501	O	1.774139	-0.874239	0.431241
C	-1.076380	-4.647016	1.542597	C	-4.320773	1.813087	-3.508639
C	4.451638	4.855818	-3.373126	H	-4.192673	1.799102	-4.601072
H	4.326201	4.842495	-4.465526	H	-5.374690	1.572778	-3.301840
H	5.477305	4.535532	-3.157337	H	-3.705439	1.007034	-3.088884
H	4.357961	5.903592	-3.049840	F	3.102151	-1.474212	2.557501
C	2.529291	1.956811	-1.942411	C	1.679607	2.667571	0.233700
C	4.233852	-3.069882	-2.806409	C	-4.418977	-4.810935	-3.534227
F	6.529452	-1.243059	2.456349	H	-4.417307	-5.845166	-3.158206
F	-1.491213	5.430939	1.706287	H	-4.205819	-4.858397	-4.612002
C	4.697698	-0.363288	1.274962	H	-5.436479	-4.420639	-3.418544
C	-2.750423	1.511257	0.094809	N	-0.076256	0.030467	4.266015
C	2.643424	-4.773823	-2.224207	C	0.909926	1.026194	4.793067
H	1.630792	-4.954625	-1.841590	H	0.553617	2.002042	4.441492
H	2.867527	-5.585686	-2.929499	H	0.818197	1.011091	5.886051
C	-2.359224	4.774837	-2.125202	C	-0.143155	0.133885	2.785781
H	-2.472869	5.651711	-2.777341	H	-0.373471	1.162425	2.501529
H	-1.376968	4.864593	-1.640575	H	-0.913226	-0.540185	2.406094
C	0.413795	-4.324755	1.413005	H	0.815188	-0.166147	2.351654
F	-3.279763	-3.988126	1.480868	C	2.339907	0.811290	4.374387
C	4.894045	3.251595	-0.990943	H	2.767967	-0.118121	4.769143
H	5.718076	3.971212	-1.087213	H	2.932695	1.642881	4.778644
H	4.977121	2.784438	-0.002070	H	2.465572	0.825082	3.288025
C	4.575319	-1.658626	-3.254781	C	0.450249	-1.667011	6.066823
H	3.900979	-0.903325	-2.832168	H	0.704020	-2.729458	6.181032
H	4.526966	-1.578252	-4.350846	H	-0.479812	-1.497135	6.625943
H	5.601732	-1.398671	-2.954813	H	1.255274	-1.092172	6.543659
C	-3.968443	3.180121	-2.943827	C	-1.406855	0.407643	4.842590
C	2.025879	4.508676	-3.156639	H	-1.641875	1.385152	4.402835
H	1.867885	5.544838	-2.821200	H	-1.256182	0.552215	5.919609
H	1.197471	3.903735	-2.766235	C	0.312958	-1.373024	4.596137
H	1.957422	4.507608	-4.254515	H	1.250390	-1.560720	4.060599
F	2.952279	4.202159	1.538147	H	-0.437410	-2.015684	4.124515
C	-4.798454	-2.095446	-2.461771	C	-2.534240	-0.558295	4.589846
H	-4.812293	-1.042440	-2.151548	H	-2.395891	-1.516850	5.106716
H	-5.597818	-2.220187	-3.205155	H	-2.697916	-0.750594	3.526142
C	-5.809847	0.245230	2.165920	H	-3.454676	-0.103379	4.978804
C	-3.745063	1.496175	1.245368				

Table 5.9 Cartesian coordinates (in Å) of TEA⁺[Eu(+pfc)₄]⁻ for optimized structure obtained by DFT calculations.

Atom	X	Y	Z	Atom	X	Y	Z
Eu	-0.014928	0.097982	-1.014678	C	-3.004495	4.985727	-0.314938
F	3.663479	0.546971	1.959966	H	-3.627512	5.887858	-0.248738
F	5.209366	-0.221311	0.666337	H	-2.509956	4.853117	0.654012
F	2.727338	-1.927403	2.396371	C	-4.637814	2.703748	-2.887714
F	4.379986	-2.787429	1.290997	H	-4.148340	1.749458	-2.653560
F	1.820448	2.326759	2.792216	H	-4.642136	2.818861	-3.981550
F	-2.743748	1.398719	2.676188	H	-5.686787	2.625455	-2.564372
F	2.629752	4.181200	2.010223	C	4.927657	2.106660	-1.694593
O	1.071853	-1.546079	-2.370287	H	5.848216	2.211906	-2.285164
O	-1.912478	0.603875	0.257120	H	4.805626	1.035142	-1.485588
O	-1.074304	1.974345	-2.071794	F	-4.354078	2.552018	1.792901
O	1.787398	1.265484	-2.104683	C	-2.000702	5.069752	-1.480831
F	-2.505901	-4.677967	0.982607	H	-2.044181	6.038251	-1.997893
C	-1.629232	-2.693650	-0.060741	H	-0.962168	4.929613	-1.150555
O	-0.673583	-1.874977	0.060318	C	-1.898154	4.050477	-3.846867
F	-5.190185	0.175148	0.533054	H	-0.799652	4.027166	-3.838075
F	0.530250	4.771868	3.289224	H	-2.217712	4.986476	-4.327066
O	0.598943	1.872123	0.381176	H	-2.228799	3.208501	-4.470879
C	2.533128	2.168923	-1.714983	C	0.334469	4.008389	2.219309
C	2.716706	-1.554031	0.074690	C	-4.697226	5.149520	-2.661444
F	-0.058494	4.790638	1.218976	H	-5.736321	5.129680	-2.299286
C	3.548828	-1.732235	1.333913	H	-4.738217	5.208554	-3.758830
C	4.401833	-0.516872	1.679127	H	-4.240798	6.078451	-2.301336
C	-3.693404	-2.133859	-3.043312	C	-4.960602	-2.818426	-1.073632
C	2.520750	2.907411	-0.485178	H	-4.910413	-2.394129	-0.064253
F	-2.130072	-2.937607	2.220910	H	-5.880116	-3.415847	-1.136798
C	-2.019180	2.685896	-1.718323	C	-3.639165	-1.492854	-4.400015
C	4.859302	-4.312224	-3.603628	H	-3.595680	-0.399015	-4.305528
H	5.902527	-4.298279	-3.253258	H	-4.524182	-1.750464	-4.999334
H	4.881056	-4.150147	-4.691106	H	-2.741588	-1.799944	-4.954712
H	4.467680	-5.321252	-3.431812	C	3.728278	2.661985	-2.500080
F	-3.756072	-0.866734	1.763652	C	4.955879	4.922433	-2.545639
C	-3.712653	-3.658570	-1.382605	H	4.983578	5.912309	-2.065476
H	-3.693219	-4.643580	-0.909626	H	4.925037	5.090781	-3.631971
C	-2.515165	-1.805988	-2.153920	H	5.903478	4.420599	-2.319674
O	1.843631	-0.654042	0.220070	C	-2.726545	1.566460	0.329021
C	3.211221	-4.723781	-1.255340	C	4.061676	-3.217549	-2.917077
H	3.888953	-5.579431	-1.377318	C	-1.685996	-3.626409	1.133779
H	2.732990	-4.817000	-0.273502	C	4.643191	-1.877895	-3.339842
C	-3.560151	1.485870	1.595921	H	5.691130	-1.794473	-3.014301
C	2.187185	-4.638586	-2.403518	H	4.097128	-1.023758	-2.918980
H	1.149913	-4.628099	-2.040644	H	4.633426	-1.775433	-4.434939
H	2.273853	-5.482694	-3.101475	C	-0.311787	-4.187988	1.513706
C	-3.703562	-3.677089	-2.927863	C	3.705389	2.295966	-3.956247
C	1.636355	3.291677	1.853182	H	3.674692	1.204451	-4.078056
C	-2.891294	2.566009	-0.586511	H	4.597692	2.672979	-4.476353
C	-2.524336	-2.767075	-1.089320	H	2.814262	2.697841	-4.458240
O	-1.758154	-0.852103	-2.354686	C	-4.906779	-1.736781	-2.169259
C	2.061199	-2.256260	-2.169442	H	-4.787038	-0.725695	-1.757076
C	4.958416	2.960061	-0.412201	H	-5.816589	-1.723928	-2.785118
H	4.896278	2.353387	0.498087	N	-0.061826	-0.713942	5.138292
H	5.874784	3.561921	-0.346619	C	-0.229597	0.375691	4.115290
F	0.440482	-3.286227	2.136293	H	-1.197514	0.845108	4.320356
C	3.727771	4.154279	-2.089360	H	0.543131	1.121252	4.328667
C	-3.965650	3.893476	-2.221568	C	-1.088917	-1.785667	4.928793
C	3.951479	-3.385925	-1.384945	H	-0.853270	-2.243667	3.964566
H	4.902145	-3.329355	-0.847550	H	-0.907946	-2.541358	5.702356
C	3.710593	3.838330	-0.576348	C	-0.148842	-0.093876	2.697550
H	3.674152	4.713802	0.077419	H	-0.958325	-0.775098	2.417811
C	2.942509	-2.310500	-1.041048	H	0.812958	-0.549294	2.440633
C	1.973253	-3.184444	-4.522180	H	-0.250638	0.787438	2.060610

H	2.339441	-3.985182	-5.180585	C	-0.066317	-0.973595	7.674777
H	2.237792	-2.216607	-4.970348	H	-0.201347	-0.360373	8.575905
H	0.875848	-3.234399	-4.499204	H	0.924211	-1.439928	7.752320
C	2.533260	-3.319025	-3.135614	H	-0.830748	-1.760648	7.707273
F	0.337827	-4.619334	0.440707	C	-0.201448	-0.069244	6.476738
C	-2.468494	-4.334939	-3.521182	H	0.549813	0.728138	6.508744
H	-2.470177	-4.251752	-4.617890	H	-1.180737	0.422691	6.474881
H	-2.450314	-5.407651	-3.276370	C	1.273906	-1.378092	4.980364
H	-1.532063	-3.895816	-3.153272	H	1.335259	-2.134425	5.771611
C	-3.830838	3.748009	-0.688789	H	1.235048	-1.910215	4.025839
H	-4.777278	3.644801	-0.150842	C	-2.524748	-1.328737	4.938109
C	-2.435526	3.942747	-2.449030	H	-2.845594	-0.921950	5.907084
C	2.499622	4.911879	-2.567332	H	-3.149659	-2.207377	4.729798
H	1.558704	4.407893	-2.310810	H	-2.740311	-0.597751	4.149715
H	2.522480	5.043809	-3.659013	C	2.469334	-0.460826	5.010119
H	2.470044	5.916340	-2.118829	H	2.585364	0.069128	5.965737
C	-4.457500	0.251615	1.639202	H	2.462942	0.268936	4.190947
C	-4.924769	-4.336195	-3.544822	H	3.365640	-1.078585	4.867877
H	-5.875342	-3.883921	-3.240325	F	-0.466263	-5.214272	2.345154
H	-4.961577	-5.400555	-3.267394	F	5.151183	-0.784677	2.746801
H	-4.876260	-4.289584	-4.642519	F	-0.644485	3.160514	2.505083
C	1.590826	2.650814	0.479661	F	-5.280669	0.329631	2.680640

Table 5.10 Cartesian coordinates (in Å) of TEMA⁺[Eu(+pfc)₄]⁻ for optimized structure obtained by DFT calculations.

Atom	X	Y	Z	Atom	X	Y	Z
Eu	-0.005910	-0.022620	-0.604040	C	0.446864	-3.199785	-1.535037
O	2.035664	-0.208682	-1.846470	C	3.939991	-0.373568	-3.982447
F	2.380607	-4.551761	1.935955	H	4.826032	-0.451310	-4.628731
F	1.876226	-2.692803	2.933639	H	3.197172	0.260992	-4.485511
F	-4.048530	1.532241	1.326366	H	3.497887	-1.374511	-3.891565
F	2.764563	2.159637	2.698557	C	2.787362	1.533352	0.423183
O	-1.550761	-1.176702	0.723189	C	-0.339569	4.242301	-2.698294
F	-3.373082	-4.371100	0.434931	C	-5.370616	0.382981	-1.773415
C	3.131916	0.341593	-1.688262	H	-4.923498	1.318153	-1.409597
O	0.125756	2.009123	-1.866665	H	-6.189116	0.665542	-2.449714
O	1.190687	-1.539635	0.721217	C	-4.335326	-0.471151	-2.543857
F	3.510275	4.305162	0.061590	C	0.343847	-4.407806	-2.439469
O	-0.137721	-2.129745	-1.746086	F	3.410332	4.712167	2.174500
O	-2.082074	0.059234	-1.803988	C	3.577892	1.205742	-0.639718
C	3.821486	-2.764868	1.684402	C	-0.470258	5.823383	-0.842107
C	-2.828470	-3.886132	1.548799	H	-0.695365	6.889191	-0.981658
C	-0.448548	3.094718	-1.719825	H	-0.069169	5.698388	0.170574
O	1.588651	1.194535	0.623901	C	-2.504851	3.290138	1.513849
C	5.827753	0.286099	-0.728258	C	-1.582014	2.766395	0.424750
H	5.653976	-0.083389	0.289419	C	3.315705	2.467373	1.499687
H	6.905644	0.465775	-0.837677	C	-4.968434	-1.773358	-0.815552
C	-3.219704	-2.425667	1.731384	H	-5.312473	-2.669992	-0.291456
C	1.288786	-3.582615	-0.444874	C	0.193851	3.859322	-4.048778
C	-1.968920	6.139413	-3.310827	H	0.216928	4.725095	-4.726044
H	-1.964713	5.990751	-4.400363	H	-0.415356	3.070794	-4.511919
H	-1.203383	6.888805	-3.079560	H	1.216552	3.467342	-3.965669
H	-2.945586	6.572791	-3.047389	C	0.448856	-5.870277	-0.485699
F	-1.510496	-4.009224	1.458315	H	0.041157	-5.684620	0.514535
F	-2.650211	-2.014134	2.888927	H	0.671596	-6.943092	-0.560366
C	-0.173571	-4.111701	-3.817788	C	1.967164	-6.349077	-2.912191
H	-0.198938	-5.020792	-4.435658	H	1.191350	-7.076132	-2.646603
H	0.447811	-3.361988	-4.327081	H	2.935723	-6.773027	-2.606738
H	-1.192738	-3.705349	-3.770936	H	1.980775	-6.269322	-4.008859
C	-4.894079	-1.904408	-2.352030	C	4.022859	2.685311	-3.069584
C	5.005627	1.554659	-0.994918	H	3.001507	2.625558	-2.671780
H	5.396523	2.466284	-0.534094	H	3.959853	2.639691	-4.166853

F	4.368774	-3.244946	0.571305	H	4.424606	3.675155	-2.805812
C	-1.301468	3.542055	-0.662642	C	-4.004042	0.005381	-3.928862
F	-4.381530	3.283035	0.110229	H	-3.227286	-0.618303	-4.392711
C	1.694147	-5.009751	-0.737513	H	-3.617514	1.033231	-3.903519
H	2.604080	-5.350988	-0.234753	H	-4.892941	-0.006622	-4.575805
F	3.911748	-1.439123	1.657010	O	-1.206323	1.581320	0.639112
C	2.960449	3.920632	1.211247	C	2.857954	-4.058965	-2.810861
C	-6.237807	-2.140242	-3.018172	H	2.843337	-4.034306	-3.910534
H	-6.126542	-2.182426	-4.111377	H	3.852256	-4.419107	-2.506129
H	-6.986044	-1.371339	-2.794536	H	2.752877	-3.027694	-2.450340
H	-6.652719	-3.107874	-2.697821	F	-2.141418	2.792162	2.721379
C	-3.154102	-0.525540	-1.600720	C	-2.740732	-1.563338	0.574797
C	-1.774552	4.817808	-2.589486	C	6.278078	1.713675	-3.219350
C	-3.948607	2.856504	1.293859	H	6.741216	2.678704	-2.963830
C	1.540835	-2.745099	0.603239	H	6.162672	1.689964	-4.312675
C	0.489758	5.296162	-1.926257	H	6.989451	0.925335	-2.947921
H	1.403450	4.854337	-1.505321	N	-0.004482	0.195425	4.480855
H	0.809868	6.088557	-2.616695	C	-1.283371	-0.279088	5.096239
C	-0.499316	-5.405216	-1.608324	H	-1.369435	-1.333368	4.806141
H	-0.821410	-6.237241	-2.249546	H	-1.148679	-0.238742	6.184348
H	-1.412328	-4.930413	-1.223134	C	-0.058152	-0.047102	3.019730
F	4.649342	2.404049	1.656595	H	-0.203734	-1.112247	2.829069
C	-5.851665	-0.532100	-0.630394	H	0.870188	0.297054	2.558053
H	-6.919304	-0.772054	-0.723676	H	-0.877907	0.528044	2.584363
H	-5.696355	-0.087387	0.359433	C	-2.525658	0.466475	4.680309
C	-2.848324	3.854482	-3.071148	H	-2.528829	1.513484	5.008948
H	-2.740559	2.847841	-2.646705	H	-3.381966	-0.030354	5.156180
H	-2.823900	3.761348	-4.166974	H	-2.694760	0.436842	3.598514
H	-3.847242	4.226018	-2.797206	C	0.292282	2.100488	6.122146
C	1.773734	-4.982776	-2.278964	H	0.445507	3.187918	6.136699
C	-3.938721	-2.991538	-2.818972	H	1.136733	1.651314	6.662005
H	-4.290545	-3.979752	-2.486394	H	-0.629992	1.899762	6.683925
H	-2.918827	-2.855953	-2.436560	C	1.097647	-0.625799	5.072450
H	-3.885452	-3.016595	-3.917475	H	0.860772	-1.663056	4.806721
F	-4.551997	-2.384447	1.909843	H	1.016546	-0.530759	6.162433
C	5.297491	-0.678689	-1.807315	C	0.212595	1.659123	4.684315
H	4.806304	-1.563961	-1.379794	H	-0.602667	2.162065	4.154436
H	6.098014	-1.046605	-2.463734	H	1.127291	1.908745	4.136855
C	2.369595	-3.215893	1.786161	C	2.487851	-0.283312	4.601874
C	4.928617	1.586770	-2.535589	H	2.812576	0.717868	4.912180
C	-1.710976	4.944559	-1.052342	H	2.596200	-0.370270	3.515840
H	-2.626757	5.315486	-0.582912	H	3.177929	-1.009608	5.052639
C	-3.557027	-1.336883	-0.495694	F	4.520665	-3.205866	2.721111
F	-2.497920	4.629214	1.623499	F	1.646323	4.075107	1.118573
C	4.301683	0.172962	-2.631376	F	-4.736429	3.358903	2.233077

Table 5.11 Cartesian coordinates (in Å) of TEA⁺[Eu(+tfc)₄]⁻ for optimized structure obtained by DFT calculations.

Atom	X	Y	Z	Atom	X	Y	Z
Eu	-0.001450	0.000970	-0.303166	H	0.898951	4.867933	0.335577
F	4.919249	-0.061006	-2.637864	H	0.758040	6.320930	-0.675810
O	1.810226	-0.118327	-1.745025	F	-4.018661	1.694816	-3.682186
F	3.543730	1.021913	2.542106	C	-5.441979	2.002425	0.213207
F	3.192683	0.283390	-3.874208	H	-5.593208	0.929925	0.039701
O	-1.543441	1.578278	0.767152	H	-6.431891	2.477514	0.230553
F	4.001760	-1.693085	-3.699573	C	-2.946547	4.607596	-0.999891
F	4.686136	2.101313	1.078414	H	-3.382926	4.994001	-1.933195
F	3.484199	3.168087	2.510413	H	-2.104207	3.959670	-1.273938
O	1.542884	-1.577928	0.760163	H	-2.547642	5.470726	-0.446258
O	-1.818176	0.120780	-1.738688	C	4.651272	-2.290763	1.481094
O	-1.405904	-1.222565	1.129011	H	4.344234	-1.363438	1.983736
O	0.275915	2.183642	-1.350463	H	5.236302	-2.874463	2.205384

O	-0.283555	-2.181179	-1.352469	C	-2.371399	-4.996867	-1.286054
F	-4.681402	-2.097117	1.100065	C	-1.474903	-5.613706	-0.225076
F	-3.208469	-0.280632	-3.862927	H	-0.761919	-6.318443	-0.677494
O	1.410620	1.222638	1.125818	H	-2.075236	-6.179999	0.502794
C	3.277589	-1.758708	-0.907705	H	-0.898703	-4.865973	0.335230
C	4.524695	-2.611058	-0.889138	C	-3.512062	-2.084755	1.737548
H	4.999254	-2.768245	-1.862829	C	-1.631228	-4.011108	-2.223265
C	2.333598	2.865064	-0.293424	C	-2.325052	-2.036491	0.788933
C	3.996698	-3.886309	-0.200630	C	-2.336454	-2.863292	-0.286570
F	-3.527557	-1.025384	2.560644	C	-4.648989	2.289666	1.503623
C	-4.535030	2.605731	-0.868043	H	-4.339615	1.363441	2.006896
H	-5.015100	2.760741	-1.839372	H	-5.231050	2.874525	2.229331
F	-4.931501	0.060045	-2.620615	C	2.932816	-4.611187	-1.008951
C	3.737831	-0.571683	-3.021422	H	2.534250	-5.471486	-0.450666
C	3.320807	3.913595	-0.746252	H	3.364010	-5.001724	-1.942945
H	4.026040	4.256752	0.019078	H	2.090900	-3.961965	-1.281226
C	2.852115	-0.825207	-1.808919	C	-2.862306	0.824806	-1.796842
F	-3.473218	-3.171530	2.521066	C	-3.423141	3.107538	1.025149
C	1.265543	2.911509	-1.253752	C	-3.075838	-6.127399	-2.015210
C	2.364225	4.999067	-1.292427	H	-3.718800	-6.685974	-1.318316
C	3.520639	2.084248	1.722771	H	-2.343418	-6.839842	-2.422129
C	2.585037	-2.063254	0.298915	H	-3.704940	-5.793473	-2.847833
C	1.619527	4.013843	-2.226427	C	-3.751720	0.572383	-3.006868
C	2.696123	-3.886762	2.070563	C	-0.488937	-4.499986	-3.065878
H	3.365976	-4.601804	2.569267	H	0.284824	-4.989496	-2.458047
H	1.852102	-4.446804	1.644229	H	-0.010797	-3.655138	-3.580534
H	2.282761	-3.221017	2.838143	H	-0.832080	-5.216477	-3.825694
C	5.076794	-4.888945	0.165630	C	-5.084351	4.884722	0.185906
H	4.642366	-5.756359	0.683714	H	-5.867073	4.476505	0.835602
H	5.862647	-4.480964	0.811699	H	-5.575237	5.262859	-0.723358
H	5.563426	-5.267972	-0.745544	H	-4.648310	5.752746	0.701611
C	-2.588502	2.062032	0.310735	C	-2.691818	3.889783	2.078810
C	-3.325632	-3.911734	-0.735051	H	-1.854826	4.454379	1.644690
H	-4.027152	-4.255095	0.033623	H	-2.267514	3.226648	2.842584
C	3.966337	3.366344	-2.026888	H	-3.360931	4.601393	2.583384
H	4.377097	2.361835	-1.868318	N	0.018745	-0.001400	4.627972
H	4.790534	4.005843	-2.370050	C	-1.062582	0.519271	3.725299
C	2.786362	3.375352	-3.018018	H	-0.614413	1.314572	3.119926
H	2.520721	2.370903	-3.367245	H	-1.298138	-0.279697	3.013315
H	2.998379	3.983071	-3.908285	C	-1.186054	-2.229055	4.814692
C	3.422291	-3.108342	1.010644	H	-1.472836	-2.968007	5.575198
C	2.327909	2.036819	0.781133	H	-0.532101	-2.739327	4.096487
C	0.473262	4.503187	-3.063362	H	-2.099248	-1.926616	4.290754
H	0.812747	5.220488	-3.824060	C	1.103506	-0.524297	3.730819
H	-0.297836	4.991903	-2.451510	H	0.657821	-1.321109	3.125581
H	-0.007003	3.658713	-3.576650	H	1.340268	0.272856	3.017370
C	-3.286710	1.755339	-0.892066	C	-0.503444	-1.083042	5.517568
C	-1.272796	-2.909050	-1.251815	H	0.352252	-1.439728	6.101825
C	-4.005068	3.882729	-0.184509	H	-1.190039	-0.600982	6.223414
C	5.438260	-2.007220	0.186262	C	2.344332	-0.995191	4.442819
H	6.427455	-2.483937	0.199516	H	2.846672	-0.198524	5.006355
H	5.590382	-0.935341	0.009794	H	3.053805	-1.324704	3.676000
C	-3.977250	-3.364166	-2.012445	H	2.174493	-1.850032	5.111897
H	-4.803005	-4.003616	-2.351937	C	-2.306494	0.992222	4.430248
H	-4.387367	-2.359750	-1.851634	H	-3.007491	1.325378	3.657397
C	3.065546	6.129682	-2.024455	H	-2.139375	1.845474	5.101995
H	3.712175	6.687641	-1.330468	H	-2.815755	0.195751	4.987759
H	2.331439	6.842636	-2.427412	C	1.225264	2.225523	4.812880
H	3.690378	5.795903	-2.860350	H	1.506696	2.968151	5.571845
C	-2.801978	-3.372761	-3.009150	H	0.576969	2.732432	4.087237
H	-3.018113	-3.980524	-3.898395	H	2.142219	1.920199	4.297331
H	-2.538221	-2.368278	-3.359652	C	0.537089	1.083230	5.516340
C	1.472844	5.615718	-0.227030	H	1.218762	0.603408	6.228436
H	2.076724	6.181461	0.498331	H	-0.321718	1.443228	6.093887

Table 5.12 Cartesian coordinates (in Å) of TEMA⁺[Eu(+tfc)₄]⁻ for optimized structure obtained by DFT calculations.

Atom	X	Y	Z	Atom	X	Y	Z
Eu	-0.030495	0.036364	-0.311120	C	-1.918475	-5.430407	-0.123797
F	-5.091863	0.379766	-2.281943	H	-2.531159	-5.946502	0.630587
O	-1.891950	0.329783	-1.669962	H	-1.279236	-4.712833	0.406826
F	-3.553796	-0.750546	2.709656	H	-1.265751	-6.185684	-0.585591
F	-3.486613	-0.019528	-3.657557	F	3.835171	-2.072414	-3.627604
O	1.326112	-1.678911	0.788862	C	5.185566	-2.415253	0.316503
F	-4.188630	1.988579	-3.388791	H	5.416145	-1.358327	0.133909
F	-4.850831	-1.504100	1.169012	H	6.138121	-2.960207	0.357373
F	-3.838064	-2.867102	2.490538	C	2.513362	-4.836418	-0.908931
O	-1.345388	1.775167	0.797011	H	2.933358	-5.270529	-1.828623
O	1.761837	-0.289344	-1.744284	H	1.729573	-4.128514	-1.207514
O	1.556902	1.108757	1.078418	H	2.037734	-5.656367	-0.350290
O	-0.539386	-2.104772	-1.340580	C	-4.342183	2.518238	1.885470
O	0.440427	2.153688	-1.391310	H	-3.981675	1.606602	2.380936
F	4.896642	1.590735	0.841873	H	-4.839542	3.127775	2.652717
F	3.235607	-0.024338	-3.831855	C	2.779568	4.764818	-1.402144
O	-1.550282	-1.010372	1.144726	C	1.985315	5.462522	-0.310090
C	-3.263250	1.952728	-0.651668	H	1.336069	6.240869	-0.736922
C	-4.496400	2.808850	-0.489485	H	2.663239	5.957867	0.401224
H	-5.086495	2.960053	-1.399078	H	1.350726	4.774943	0.264196
C	-2.602018	-2.631340	-0.208158	C	3.781013	1.741287	1.554582
C	-3.885564	4.088687	0.119916	C	1.914467	3.854247	-2.307775
F	3.723146	0.707508	2.408438	C	2.537319	1.820633	0.682126
C	4.254910	-2.964102	-0.774329	C	2.580767	2.644543	-0.394810
H	4.739681	-3.171446	-1.733625	C	4.351524	-2.627467	1.595487
F	4.896465	-0.532026	-2.563272	H	4.109044	-1.677076	2.089268
C	-3.922499	0.843583	-2.751849	H	4.872976	-3.254201	2.332439
C	-3.670834	-3.619407	-0.607772	C	-2.923210	4.806772	-0.812895
H	-4.367557	-3.902766	0.189458	H	-2.467499	5.673736	-0.311723
C	-2.930060	1.041396	-1.613832	H	-3.458872	5.186213	-1.695830
F	3.932752	2.843017	2.303046	H	-2.113473	4.159083	-1.173368
C	-1.573318	-2.761600	-1.200345	C	2.747218	-1.075135	-1.766060
C	-2.805978	-4.772857	-1.167827	C	3.072428	-3.347678	1.103158
C	-3.698354	-1.728046	1.803016	C	3.559809	5.824405	-2.160033
C	-2.435579	2.260187	0.462920	H	4.276993	6.320413	-1.488705
C	-2.032695	-3.850693	-2.143318	H	2.883159	6.602275	-2.542907
C	-2.322716	4.089587	2.227304	H	4.124330	5.432815	-3.013539
H	-2.912894	4.853102	2.753951	C	3.675607	-0.923171	-2.963672
H	-1.488057	4.590290	1.716858	C	0.785950	4.446186	-3.101459
H	-1.884973	3.424731	2.983597	H	0.069848	4.975085	-2.456147
C	-4.913804	5.097458	0.600795	H	0.229760	3.651348	-3.617097
H	-4.422245	5.961989	1.070508	H	1.155949	5.153765	-3.857001
H	-5.629498	4.692470	1.325290	C	4.601538	-5.264034	0.318939
H	-5.491959	5.480492	-0.253416	H	5.408519	-4.907556	0.969355
C	2.337651	-2.249618	0.358349	H	5.069245	-5.699257	-0.576875
C	3.647726	3.593477	-0.885718	H	4.090835	-6.083095	0.846166
H	4.407503	3.868452	-0.145319	C	2.261097	-4.046413	2.156704
C	-4.325475	-3.051738	-1.874391	H	1.382394	-4.541897	1.720681
H	-4.668134	-2.022263	-1.716362	H	1.887183	-3.334316	2.903419
H	-5.199009	-3.643779	-2.178568	H	2.858055	-4.805177	2.682631
C	-3.183688	-3.149140	-2.904704	N	0.156012	0.255981	4.549858
H	-2.867614	-2.167873	-3.277859	C	1.175516	-0.543509	3.795590
H	-3.464589	-3.753158	-3.778284	H	0.622537	-1.299414	3.226430
C	-3.174000	3.316991	1.260841	H	1.596756	0.125743	3.037305
C	-2.518050	-1.780166	0.845346	C	1.737457	2.245915	4.529597
C	-0.949821	-4.424743	-3.010344	H	2.019407	3.097633	5.163195
H	-1.359503	-5.133900	-3.743621	H	1.292866	2.651904	3.612833
H	-0.187455	-4.948038	-2.416193	H	2.657821	1.718797	4.258034
H	-0.438344	-3.620811	-3.557411	C	-0.788101	0.815535	3.553164
C	3.079137	-2.017935	-0.835343	H	-0.249794	1.479433	2.872441
C	1.492656	2.790163	-1.321550	H	-1.222377	0.014102	2.945976

C	3.611950	-4.185133	-0.084244	C	0.783313	1.381131	5.312610
C	-5.271872	2.211308	0.694650	H	-0.055348	1.974980	5.699295
H	-6.257971	2.678813	0.818252	H	1.291013	0.936615	6.177158
H	-5.430945	1.135248	0.552024	C	2.245504	-1.157550	4.658674
C	4.194907	2.988561	-2.185833	H	2.965894	-1.656067	3.999025
H	5.063633	3.547844	-2.557980	H	1.862954	-1.919529	5.352157
H	4.515369	1.950487	-2.036393	H	2.811655	-0.412848	5.234034
C	-3.602846	-5.866378	-1.857143	C	-1.292341	-1.787157	4.977823
H	-4.260067	-6.370945	-1.132896	H	-1.808703	-2.289722	5.806953
H	-2.930053	-6.631215	-2.271833	H	-0.598864	-2.515584	4.538883
H	-4.232916	-5.505359	-2.677652	H	-2.050439	-1.527251	4.231112
C	2.988466	3.109189	-3.137139	C	-0.587624	-0.580043	5.540482
H	3.226426	3.694001	-4.036189	H	-1.307450	0.096767	6.020065
H	2.618636	2.133185	-3.472853	H	0.137942	-0.877653	6.306975

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Chapter 6

SUMMARY

6.1 Summary and outlook

The CPL properties of chiral Eu(III) complexes are affected by the steric and electronic structure. The purpose of this study is to elucidate of the mechanism for enhancement of the CPL and to provide molecular design for effective CPL luminophore.

In **Chapter 1**, overviews of the lanthanide chemistry, circularly polarized luminescence are provided. In particular, the author focused on the current research topics of chiral Eu(III) complexes.

In **Chapter 2**, the author described the synthesis of Eu(III) complexes with chiral phosphine oxide ligands possessing point chirality. The combination of low-vibrational β -diketonate and phosphine oxide ligands provides high emission quantum yield ($\Phi_{\text{ir}} = 63\%$) and energy transfer efficiency ($\eta_{\text{sens}} > 90\%$). The crystal field strain caused by the steric hindrance of phosphine oxide ligands affected to the CPL and LMCT properties of the Eu(III) complexes.

In **Chapter 3**, the chiral Eu(III) coordination polymers with bulky substituents in the chiral β -diketonate ligands were investigated. The synthesis of a novel chiral ligand has enabled a systematic evaluation of the effect of steric hindrance on the distortion of β -diketonate plane. The characteristic structural strain affected to the LMCT characteristics. The angle of electric dipole moments of the LMCT transition were changed without crystal field change. The control of ligand field change without crystal field change provides the new concept for evaluating the CPL properties in chiral Eu(III) complexes.

In **Chapter 4**, phase-transformable chiral Eu(III) coordination polymers were demonstrated. The control of molecular packings with the same ligands were successfully achieved. The CPL properties were affected by not only the kinds of ligands, but also molecular packings in the crystals. As a result of quantum chemical calculations, while f-f transitions were not affected by the molecular packings, the dipole moment of LMCT transitions were strongly affected by them. These photophysical findings provide the

novel insight that the CPL properties of chiral Eu(III) complexes were changeable by the LMCT characteristics.

In **Chapter 5**, chiral tetrakis(camphorate)Eu(III) complexes with ammonium cations were synthesized. The structure and photophysical properties of the complexes were successfully controlled by the structural change of the counter cation species. From systematic evaluation of the structure, CPL, and LMCT characteristics of the complexes, the weak LMCT perturbation to the f-f transition and SAP structure leads to the enhancement of the $|g_{\text{CPL}}|$ values in tetrakis(camphorate)Eu(III) complexes. These molecular design can be applied to the effective CPL luminophores.

Circularly polarized luminescence has potential of application as a next-generation optical material. Because of their characteristic luminescence properties, lanthanide complexes are candidates for applying the effective CPL materials that cannot be achieved with organic molecules and transition metal complexes. However, the expectation of lanthanide complexes with effective CPL properties were still difficult due to its difficulty of quantum chemical calculation. Previously, the magnitude of the electric and magnetic dipole moments was considered to be important for achieving the large $|g_{\text{CPL}}|$ value. In addition to the previous theory, the author focused on the angles between these dipole moments. In this study, the LMCT transition of chiral Eu(III) complexes was shown to affect the angles between electric and magnetic dipole moments of f-f transition and change the CPL properties. These results would open up the new concept for the design of chiral Eu(III) complexes that exhibit strong CPL. The author hopes that this work will contribute to the development of chiral lanthanide chemistry and evolution of next-generation optical materials.

6.2 Abbreviations

ISC: intersystem crossing

SAP: square anti prism

TDH: trigonal dodecahedron

CPL: circularly polarized
luminescence

g_{CPL} : dissymmetry factor of CPL

LMCT: ligand-to-metal charge transfer

BEnT: back energy transfer

k_r : radiative rate constant

k_{nr} : non-radiative rate constant

ISC: intersystem crossing

BEnT: back energy transfer

HOMO: highest occupied molecular
orbitals

LUMO: lowest unoccupied molecular
orbitals

6.3 List of Publications

For thesis

- [1] **Makoto Tsurui**, Yuichi Kitagawa, Koji Fushimi, Masayuki Gon, Kazuo Tanaka, and Yasuchika Hasegawa “**Electronic strain effect on Eu(III) complexes for enhanced circularly polarized luminescence**”, *Dalton Transactions*, **2020**, 49, 5352-5361. (Chapter 2)
- [2] **Makoto Tsurui**, Yuichi Kitagawa, Sunao Shoji, Hitomi Ohmagari, Miki Hasegawa, Masayuki Gon, Kazuo Tanaka, Masato Kobayashi, Tetsuya Taketsugu, Koji Fushimi, and Yasuchika Hasegawa “**Asymmetric Lumino-Transformer: Circularly Polarized Luminescence of Chiral Eu(III) Coordination Polymer with Phase-Transition Behavior**”, *The Journal of Physical Chemistry B*, **2022**, 126, 3799-3807. (Chapter 4)
- [3] **Makoto Tsurui**, Yuichi Kitagawa, Sunao Shoji, Koji Fushimi, and Yasuchika Hasegawa “**Enhanced circularly polarized luminescence of chiral Eu(III) coordination polymers with structural strain**”, *Dalton Transactions*, **2023**, 52, 796-805. (Chapter 3)

Other Publications

- [1] Tomoki Yoneda, Chika Kasai, Yumehiro Manabe, **Makoto Tsurui**, Yuichi Kitagawa, Yasuchika Hasegawa, Parantap Sarkar, and Yasuhide Inokuma “**Luminescent Coordination Polymers Constructed from a Flexible, Tetradentate Diisopyrazole Ligand and Copper(I) Halides**”, *Chemistry – An Asian Journal*, **2020**, 15, 601-605.
- [2] Yuichi Kitagawa, **Makoto Tsurui**, and Yasuchika Hasegawa “**Steric and Electronic Control of Chiral Eu(III) Complexes for Effective Circularly Polarized Luminescence**”, *ACS Omega*, **2020**, 5, 3786-3791.
- [3] Yasuchika Hasegawa, Katsumasa Koide, **Makoto Tsurui**, Yuichi Kitagawa, Takayuki Nakanishi, Yoshihiro Doi, Yukio Hinatsu, and Koji Fushimi “**Circularly Polarized Absorption and Luminescence of Semiconductor Eu-OCN Nanocrystals in the Blue Region of the Electromagnetic Spectrum**”, *ChemPhysChem*, **2020**, 21, 2019-2024.

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6.4 List of Presentations

- [1] ◦**Makoto Tsurui**, Yuichi Kitagawa, Koji Fushimi, Tomohiro Seki, Hajime Ito, Masayuki Gon, Kazuo Tanaka, and Yasuchika Hasegawa, “**Synthesis and photophysical properties of chiral Eu(III) coordination polymers with phase transition abilities**”, 日本化学会第 99 春季年会, 2C2-42, 甲南大学, 2019.3.17 (Oral Presentation).
- [2] ◦**鶴井真**, 北川裕一, 伏見公志, 長谷川靖哉, 「**カンファー骨格を導入した Eu(III)配位高分子の相転移挙動とキラル光学特性**」, 第 40 回 光化学若手の会, P7, 大学セミナーハウス (東京都八王子市), 2019.6.15 (Poster Presentation).
- [3] ◦**鶴井真**, 北川裕一, 伏見公志, 関朋宏, 伊藤肇, 権正行, 田中一生, 長谷川靖哉, 「**キラル分子を導入した Eu(III)配位高分子の相転移挙動と光物性**」, 日本化学会北海道支部 2019 年夏季研究発表会, A08, 苫小牧工業高等専門学校, 2019.7.20 (Oral Presentation).
- [4] ◦**鶴井真**, 北川裕一, 伏見公志, 長谷川靖哉, 「**エチニル基含有リンカー配位子を用いたキラル型 Eu(III)配位高分子の光物性評価**」, 第 15 回 錯体化学若手の会 夏の学校, P1-24, 天童温泉 栄屋ホテル (山形県天童市), 2019.7.31 (Poster Presentation).
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- [7] ◦**鶴井真**, 北川裕一, 伏見公志, 関朋宏, 伊藤肇, 権正行, 田中一生, 長谷川靖哉, 「**カンファー誘導体を有するキラル型 Eu(III)配位高分子の構造と発光特性**」, 第 68 回 高分子討論会, 3Pa079, 福井大学, 2019.9.27 (Poster Presentation).

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- [20] ○Makoto Tsurui, Yuichi Kitagawa, Sunao Shoji, Koji Fushimi, Yasuchika Hasegawa, “**Circularly polarized luminescence of Eu(III) coordination polymers with distorted chiral moieties**”, 第 72 回 錯体化学討論会, 2Fb-09, 九州大学, 2022.9.27 (Oral Presentation).
- [21] ○Makoto Tsurui, Yuichi Kitagawa, Mengfei Wang, Sunao Shoji, Koji Fushimi, Yasuchika Hasegawa, “**Circularly polarized luminescence of chiral Eu(III) coordination polymers with ligand field strain**”, The 31st International Conference on Photochemistry, P25-136, 札幌パークホテル, 2023.7.25 (Poster Presentation).
- [22] ○Makoto Tsurui, Yuichi Kitagawa, Mengfei Wang, Sunao Shoji, Koji Fushimi, Yasuchika Hasegawa, “**Circularly polarized luminescence and charge transfer characteristics of chiral Eu(III) coordination polymers**”, The 11th International Conference on f Elements, University of Strasbourg, France, 2023.8.22 (Poster Presentation).

6.5 Awards

- [1] 「優秀ポスター賞」 第9回 CSJ 化学フェスタ 2019.
- [2] 「優秀ポスター賞」 錯体化学若手の会北海道地区 第8回勉強会.
- [3] 「優秀発表賞」 第8回元素ブロック研究体合同修論発表会.
- [4] 「学生講演賞」 第38回希土類討論会.
- [5] 「優秀ポスター賞」 第71回 高分子討論会.

6.6 Patent

- [1] 長谷川靖哉, 北川裕一, 鶴井真, 田村健, 佐野夏博, 「ビスホスフィンオキシド希土類錯体及び光学機能性材料」 (特開 2021-017403)

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