Steric and Electronic Control of Chiral Eu(III) Complexes for Effective Circularly Polarized Luminescence

Yuichi Kitagawa,* Makoto Tsurui, and Yasuchika Hasegawa*

ABSTRACT: Circularly polarized luminescence (CPL) is characterized by the differential emission of right and left circularly polarized light by a chiral molecule. This mini-review describes the recent developments in chiral trivalent europium (Eu(III)) complexes with effective CPL. CPL has many potential applications in security tags, lasers, and three-dimensional organic electroluminescence devices, which is one of the most intensely investigated topics in molecular luminophores. Eu(III) complexes have attracted considerable attention as effective CPL luminophores for the above-mentioned applications. In this review, recent studies on the Eu(III) CPL, including the steric (dimer, tetramer, aggregates, and coordination polymers) and electronic control (mononuclear) of Eu(III) complexes for the construction of a luminophore with effective CPL, are discussed. The characteristic CPL applications employing the chiral mononuclear Eu(III) complexes are also described. Chiral Eu(III) complexes with well-designed organic ligands can result in the establishment of new research areas in the fields of photochemistry and materials science.

1. INTRODUCTION

Chiral molecules exhibit circularly polarized luminescence (CPL), which is characterized by the differential emission of right- and left-handed circularly polarized light.1−2 CPL has attracted considerable attention owing to its applications in security tags, lasers, and organic electroluminescent (EL) devices for 3D displays.3 Many studies on various chiral luminophores such as organic dyes, transition-metal complexes, and lanthanide metal complexes have been reported. Among these chiral luminophores, enantiopure lanthanide complexes exhibit the most effective CPL as chiral luminophores.4−7

Lanthanoids include La and 14 other elements (lanthanides: Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) (Figure 1a), which form stable trivalent ions. Chiral lanthanide(III) complexes are composed of lanthanide(III) ions (i.e., a luminescent center) and organic ligands (i.e., chiral indicators) as shown in Figure 1b. The trivalent lanthanide ions are characterized by an incompletely filled 4f shell (with the exception of La(III) and Lu(III)). The 4f orbital is shielded from the surroundings by the filled 5s and 5p orbitals. On the basis of the electronic characteristics, 4f−4f transitions produce sharp emission lines (full width at half-maximum, fwhm <10 nm), which is considerably different from the emission properties of the organic dyes and transition-metal complexes.7−10

Chiral ligands induce a high CPL activity for the 4f−4f transition.

Figure 1. (a) Lanthanoids in the periodic table and (b) image of the chiral lanthanide luminophore ([Eu((+)-hfbc)_4]^-) with high CPL activity.

Herein, we introduce the history of the studies on CPL using the lanthanide complex. In 1975, Richardson et al. discovered CPL in Eu(III) and Tb(III) complexes with chiral carboxylic acid for the first time.11 Following this discovery, they also observed high CPL activity in a Eu(III) complex with chiral 3-
trifluoroacetylcamphorate ligands,\(^\text{12}\) and there are several reports on CPL.\(^\text{13,14}\) During that time, the reports on the CPL were limited because of the weak effect and the lack of conventional measurement systems. In the 21st century, the CPL measurement systems became widespread, resulting in a gradual increase in the number of CPL reports. In 2011, Kaizaki and Muller reported the chiroptical properties of Cs[Eu((+)-hfbc)]\(_4\) (hfbc: 3-heptfluoro butyryl camphorate).\(^\text{15}\) The emission intensity (in the \(5D_0 \rightarrow 7F_1\) transition) of the left-handed light is approximately 5 times greater than that of the right-handed light. This finding further accelerated the CPL research on lanthanide(III) complexes. Various studies on lanthanide CPLs are summarized in several reviews by Muller,\(^\text{1}\) Parker,\(^\text{5}\) and Di Bari.\(^\text{6}\) The focus of this review is on the recent progress in the lanthanide CPL from Eu(III) complexes. Various mononuclear Eu(III) complexes are also described.

2. GENERAL THEORY

CPL spectroscopy measures the difference between the intensities (\(\Delta I\)) of the left (\(I_L\)) and right (\(I_R\)) circularly polarized emissions from the chiral luminescence, which is defined by following equation.\(^\text{1,2}\)

\[
\Delta I(\lambda) = I_L(\lambda) - I_R(\lambda) \tag{1}
\]

The degree of dissymmetry of CPL is quantified by the difference in the relative intensities of the left and right circularly polarized emissions and is known as the luminescence dissymmetry factor (\(g_{\text{CPL}}\)).

\[
g_{\text{CPL}} = 2 \frac{\Delta I(\lambda)}{I_L(\lambda) + I_R(\lambda)} \tag{2}
\]

By definition, the \(g_{\text{CPL}}\) values should be in the range of \(-2\) to \(+2\). \(g_{\text{CPL}}\) is also expressed in terms of the transition electric dipole moment \(\mu\) and transition magnetic dipole moment \(\mu_m\) as shown below.

\[
g_{\text{CPL}} = \frac{4|\mu||\mu_m|\cos \theta}{|\mu|^2 + |\mu_m|^2} \tag{3}
\]

where \(\theta\) is the angle between \(\mu\) and \(\mu_m\). When \(\mu = \mu_m\) (\(\theta = 0\), eq 3 affords the highest \(g_{\text{CPL}}\) value (= 2) mathematically. The equation indicates that the lanthanide(III) complexes are plausible candidates for CPL with high \(g_{\text{CPL}}\) values because the magnitude of the electric dipole moment (\(|\mu|\)) is similar to that of the magnetic dipole moment (\(|\mu_m|\)). Among lanthanide(III) emissions, the \(5D_0 \rightarrow 7F_1\) transition of Eu(III) complexes shows an enormous \(g_{\text{CPL}}\) based on the allowed magnetic dipole nature.

3. STERIC STRUCTURAL CONTROL BY MOLECULAR INTEGRATION

In contrast to many reports for the lanthanide CPL based on mononuclear complexes,\(^\text{1–6}\) few reports exist on the polynuclear lanthanide CPL. Polynuclear complexes show interior intramolecular interaction by integration. Herein, recent progress in the lanthanide CPL from Eu(III) tetratertartrate,\(^\text{10}\) dimers,\(^\text{17}\) aggregates,\(^\text{18}\) and coordination polymers\(^\text{19,20}\) is reviewed.

3.1. Highly Active CPL for the Eu(III) Tetramer and Dimer. Morphology control on the molecular scale can produce effective CPL properties. Teat demonstrated that the point chirality of a ligand decisively influenced its supramolecular assembly behavior.\(^\text{16}\) They produced a Eu(III) tetrahedral cage using 2,6-diaminothraquinone-based chiral ligands with different point chirality (Figure 2). Ligand 1 shows an enormous CPL.\(^\text{16}\) The Eu(III) complexes were arranged closely in a chiral orientation by the unit. This structural modulation also induces emission intensity change based on the back-energy transfer from the Eu(III) ion to the photochromic unit. The chiral arrangement of the complex units was switched by a photoinduced structural change in the system, resulting in on–off switching.

Figure 2. Tetranuclear chiral Eu(III) complexes.

(Figure 2) allowed the formation of highly diastereoselective Eu tetrahedral cages, although ligands 2 and 3 (Figure 2) led to the generation of a mixture of isomers. The homochiral cages exhibit excellent CPL (\(g_{\text{CPL}}\) up to 0.16), but other cages show relatively low \(g_{\text{CPL}}\) values. All cages show the same long emission lifetimes (1.6 ms). From these results, we consider that the cages do not exhibit the quenching states around the emitting level of the Eu(III) ion. The cage framework also shows effective energy transfer and a high emission quantum yield (\(\Phi_{\text{tot}} = 16–18\%\)). These results (different CPLs and similar \(\Phi_{\text{tot}}\)'s) indicate that the precise steric control of the Eu(III) cage system provides the effective chiroptical change in the solution.

A characteristic CPL luminescence was also reported for the dynamic CPL control using a photochemical reaction. The combination of Eu(III) complexes and photochromic chiral molecule induces unique chiroptical phenomena. Nakashima and Kawai reported the photoswitching of the CPL property in the Eu(III) dimer system (Figure 3).\(^\text{17}\) The Eu(III) complex shows nine coordination structures composed of \(\beta\)-diketonate and terpyridine derivative with a chiral photochromic unit. The Eu(III) complexes were arranged closely in a chiral orientation by the unit. This structural modulation also induces the emission intensity change based on the back-energy transfer from the Eu(III) ion to the photochromic unit. The chiral arrangement of the complex units was switched by a photoinduced structural change in the system, resulting in on–off switching.

Figure 3. Photoresponsive chiral Eu(III) dimer. Adapted from ref 17.
of the CPL with high contrast ($g_{\text{CPL}}$ values of 0.1 and <0.01). Nanoscale studies on the chiroptical properties of a chiral Eu(III) complex have been recently explored, although numerous studies have been historically carried out on chiral dye oligomers based on the coupled exciton theory.

3.2. Enhanced CPL for Eu(III) Aggregation and Coordination Polymers. Polynuclear Eu(III) complexes show highly active circular polarized emission as described in the last chapter. Recently, enhanced $g_{\text{CPL}}$ through the aggregation of chiral units was also reported for the chiral Eu(III) complex with 3-heptafluorobutyl camphorate (hfbc) and the Cs(I) ion (Figure 4a).\textsuperscript{18} The helical 1D aggregation of

\[ \text{Cs}[\text{Eu}(+\text{hfbc})_4] \]

resulted in the highest $g_{\text{CPL}}$ value (1.45: $^5D_0 \rightarrow ^7F_1$ transition), although $g_{\text{CD}}$ ($\pi-\pi^*$ transition) of Cs[Eu(+–hfbc)$_4$] was the same as the aggregates. The emission intensity of the left-handed light is approximately 6 times larger than that of the right-handed light, which allowed the visualization of CPL with the naked eye using circularly polarized filters.

Compared to the large $g_{\text{CPL}}$ of the Eu(III) complexes with chiral $\beta$-diketonate ligands that contain a camphorate framework, the emission quantum yields are extremely low because of the existence of an energy quenching state for the emissive Eu(III) ion (1D aggregation of Cs[Eu(+–hfbc)$_4$]); emission quantum yield, $\Phi_{\text{tot}} = 1\%$.\textsuperscript{18} Our research group determined that the spiral polymerization of the Eu(III) complex with 3-trifluoroacetyl camphorate significantly increased the emission quantum yield.\textsuperscript{19} Herein, the Eu(III) coordination polymers were composed of chiral Eu(tfc)$_3$(dpbp)\textsubscript{4} complexes (Figure 5a, Eu(tfc)$_3$+tppo and Eu(tfc)$_3$+ac) provides a dramatic change in the CPL property (Figure 5b). In this paper, large negative CPL signal of Eu(tfc)$_3$+ac at 594 nm was observed, although a small positive signal for Eu(tfc)$_3$+tppo was observed. The electronic

4. ELECTRONIC STRUCTURE CONTROL FOR HIGH CPL ACTIVITY

In section 3, the recent research which describes the achievement of high CPL activity by steric control through molecular integration is discussed. The CPL magnitude and sign can also be affected by the chiral electronic structure of the Eu(III) ion surrounded by external ligands in addition to the chiral steric structure. The electronic structural modulation of chiral Eu(+tfc)$_3$ complexes (Figure 5a, Eu(tfc)$_3$+tppo and Eu(tfc)$_3$+ac) provides a dramatic change in the CPL property (Figure 5b). In this paper, large negative CPL signal of Eu(tfc)$_3$+ac at 594 nm was observed, although a small positive signal for Eu(tfc)$_3$+tppo was observed. The electronic
transitions at 583 nm of Eu(tfc)$_3$+tppo and Eu(tfc)$_3$+ac show the same CPL sign and similar magnitudes.

The characteristic photophysical phenomena was analyzed using the eq 3 for $g_{\text{CPL}}$. The equation can be modified as follows

$$g_{\text{CPL}} = 4 \frac{\mu_1 |\mu| \cos \theta}{|\mu_1|^2 + |\mu|^2} = 4 \left( \frac{|\mu_1|}{|\mu|} \right) \cos \theta + 1$$

(4)

where $\theta$ is the angle between $\vec{\mu}$ and $\vec{m}$. In the region $|\mu_1|/|\mu| < 1$, the Eu(III) complex with a large $|\mu_1|$ provides a high $g_{\text{CPL}}$ value (Figure 5c). In general, the $|\mu_1|$ value in the $^5D_0 \rightarrow ^5F_1$ transition is greater than the $|\mu_1|$ value ($|\mu_1|/|\mu| < 1$).

Therefore, an enhanced $|\mu_1|$ is important for the construction of the Eu(III) complex with large $g_{\text{CPL}}$. The intensity of $|\mu_1|$ in the $^5D_0 \rightarrow ^5F_1$ transition depends on the crystal field around the Eu(III) ion. The $^5F_1$ energy level of the Eu(III) ion in a typical eight-coordinate structure ($C_{4v}$ or $D_{4d}$) splits into two Stark sublevels (Figure 5d). The two bands at 583 and 594 nm in the CPL spectra are assigned to the $A_2 \rightarrow A_1$ and $A_1 \rightarrow E$ transitions, respectively, in Figure 5d.e. The observed CPL signals for the $A_1 \rightarrow E$ transition are reversed for Eu(tfc)$_3$+tppo with tppo compared to Eu(tfc)$_3$+ac with acetone, whereas those for the $A_1 \rightarrow A_2$ transition show the same minus sign for Eu(tfc)$_3$+tppo with tppo and acetone.

In $C_{4v}$ or $D_{4d}$ symmetry, the direct product $A_2 (= A_1 \times A_2)$ is expressed in terms of the ED-forbidden (ED: electric dipole) and MD-allowed (MD: magnetic dipole) transitions on the character table in group theory (Figure 5e). Alternately, the direct product $E (= A_1 \times E)$ produces ED- and MD-allowed transitions (Figure 5e). The CPL signal at 583 nm (for the ED-forbidden $A_1 \rightarrow A_2$ transition) reflects the intrinsic $\Lambda$- or $\Delta$-type structure because of the insensitive electronic state mixing. Considering the same CPL signal at 583 nm for Eu(tfc)$_3$+tppo with acetone, the structure type ($\Lambda$ or $\Delta$) with tppo is the same as that with acetone in the experiments. In contrast, the CPL sign in the ED- and MD-allowed $A_1 \rightarrow E$ transition is sensitive to the electronic state mixing even for the same chiral structure type ($\Lambda$ or $\Delta$).

The drastic change in the intensity of the CPL signal in the $A_1 \rightarrow E$ transition is also considered to be caused by the change in $\vec{\mu}$ based on electronic state mixing. In the $^5D_0 \rightarrow ^5F_1$ transition, $\vec{\mu}$ is mainly altered by the $J$ mixing of $^5F_2$ or $^5F_3$ sublevels into $^5F_1$. In the photoluminescence spectra, the Stark splitting energy of Eu(tfc)$_3$+tppo with acetone is greater than that of Eu(tfc)$_3$+ac. The large Stark splitting energy suggests a large amount of $J$ mixing in the $A_1 \rightarrow E$ transition of the Eu(III) complex with acetone. The $J$ mixing increases the $|\mu_1|$ values of the ED-forbidden $A_1 \rightarrow E$ transition relative to that of the ED-forbidden $A_1 \rightarrow A_2$ transition. An increase in $|\mu_1|$ results in a high $g_{\text{CPL}}$ value in eq 4. In the case of the previously reported mononuclear Eu(III) complexes with chiral steric structures, a strong $A_1 \rightarrow E$ transition is also related to a large $g_{\text{CPL}}$. The angle ($\theta$) between $\vec{\mu}$ and $\vec{m}$ for the Eu(tfc)$_3$ complex with acetone is greater than 90°, whereas for the Eu(tfc)$_3$ complex with tppo is less than 90°, suggesting that the angle is established by the change in the $\vec{\mu}$ vector due to $J$ mixing. The significant enhancement of $g_{\text{CPL}}$ from +0.013 to −1.0 also indicates that $J$ mixing promotes the antiparallel direction of $\vec{\mu}$ and $\vec{m}$, leading to a large $g_{\text{CPL}}$. This paper demonstrates that the CPL sign and intensity are strongly influenced by the chiral electronic structure depending on $\vec{\mu}$ under $J$ mixing in the same chiral structure type. This CPL study provides a novel aspect for the molecular design of chiral Eu(III) complexes by maximizing the $g_{\text{CPL}}$ value and altering its sign. In the future, a detailed description of the electronic structure based on calculation science may accelerate research on electronic structure control.

5. RECENT CPL APPLICATIONS

5.1. Recent CPL-Based Devices. Circularly polarized (CP) electroluminescence (CP-OLEDs) is rapidly attracting considerable interest owing to its possible applications in 3D displays. The development of more efficient CP-OLEDs is required for such applications. Di Bari and co-workers found that the chiroptical properties strongly depend on the thickness of Al as a cathode layer. The authors also demonstrated that the chiral Eu complex-based CP-OLEDs (Al thickness: 6 nm) show a remarkable CPL with a large dissymmetry factor ($g_{\text{CPL}} = -1.0$). Furthermore, the chiral Eu(III) complexes can be applied not only to the electrical devices but also to the optical devices. Parker demonstrated a chiral image contrast using Eu(III) complexes with efficient light-absorption ability and a high emission quantum yield for CPL microscopy.

Nakamura and Kobayashi described the DNA-based functional materials, which are of significant interest for applications in electrical and optical devices. They prepared novel DNA-based photofunctional materials fabricated by the association of a DNA–cetyltrimethylammonium chloride (CTMA) complex with a luminescent Eu(III) complex. The emission intensity, quantum yield, and thermal stability of the Eu(III) complex hosted by the DNA–CTMA matrix were superior to those of the complex in a conventional poly(methyl methacrylate) matrix. Furthermore, the Eu(III) complex in the DNA–CTMA film also exhibited high CPL activity through the excitation of the ligand moiety. The CPL originated from the chiral environment produced by the DNA matrix. The composite films of DNA–CTMA and luminescent lanthanide(III) complexes provide new insights for the construction of materials with high CPL activity for future applications.

5.2. CPL-Based Monitoring Methods around the Lanthanide Ion. The effective Eu(III) CPL provides information about the chiral environment around the Eu(III) ion. Researchers have developed CPL-based probes for various organic compounds. Neil and co-workers successfully demonstrated that CPL probes are useful for investigating the reversible binding of anionic chiral species such as phosphorylated amino acids and peptides. CPL probes are also useful for the determination of the reversible binding and competitive binding of different proteins. Recently, methods for monitoring the ADP/ATP ratio or sialic acid via the induced CPL of Eu(III) complexes have been demonstrated. These results illustrate the utility of thoughtfully designed Eu(III) probes to signal changes in the local chiral environment.

6. CONCLUSION

In this mini-review, the recent developments in lanthanide CPL that evaluate the steric and electronic structures to construct a luminophore with high CPL activity are described. The tetramer, dimer, aggregates, and coordination polymertype Eu(III) complexes show high CPL activity with a large $g_{\text{CPL}}$ and emission quantum yields. The CPL applications based on the Eu(III) complexes are also described from the
viewpoint of their practical use in devices. Further studies on the luminescent Eu(III) complexes with high CPL activity can open frontier areas in the fields of photochemistry and materials science.

■ AUTHOR INFORMATION

Corresponding Authors
Yuichi Kitagawa — Faculty of Engineering and Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo, Hokkaido 060-8628, Japan; orcid.org/0000-0003-1487-2531; Email: y-kitagawa@eng.hokudai.ac.jp
Yasuchika Hasegawa — Faculty of Engineering and Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo, Hokkaido 060-8628, Japan; orcid.org/0000-0002-6622-8011; Email: hasegaway@eng.hokudai.ac.jp

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b03613

Notes
The authors declare no competing financial interest.

Biographies
Yuichi Kitagawa obtained his Ph.D. (2012) from the School of Engineering, University of Tokyo. He was a research fellow of the Japan Society for the Promotion of Science (JSPS) (2013) at Ritsumeikan University. He was an assistant professor (2014–2018) at Hokkaido University. Since 2019, he has been a lecturer at Hokkaido University. His interests are molecular photophysics and photochemistry. He is now studying the luminescence, chiroptical, and magneto-optical properties of lanthanide (III) complexes.

Makoto Tsurui is a first-year master course student at Hokkaido University under the supervision of Prof. Yasuchika Hasegawa. He completed his undergraduate degree from Hokkaido University. He is now studying the luminescence and chiroptical properties of lanthanide (III) complexes.

Yasuchika Hasegawa obtained his Ph.D. (1997) at the Graduate School of Engineering, Osaka University and was a researcher (1994–1999) at New Japan Chemical Co. Ltd. He was an assistant professor (1999–2005) at Osaka University and an associate professor (2005–2010) at Nara Institute of Science and Technology. Since 2010, he has been a professor at Hokkaido University. He received the JPA Award (2013) and the CSJ (The Chemical Society of Japan) Award for Creative Work (2014) and an Award of the MEXT (Minister of Education, Culture, Sports, Science and Technology, Japan). His focus is the study of lanthanide photochemistry.

■ ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Grant numbers 17K14467, 19H04556, 18H04497, and 18H02041. This work was also supported by the Institute for Chemical Reaction Design and Discovery (ICReDD), established by the World Premier International Research Initiative (WPI) of MEXT, Japan. This study was supported in part by Grants-in-Aid for the regional R&D proposal-based program from the Northern Advancement Center for Science & Technology of Hokkaido, Japan.

■ REFERENCES

(1) Mason, S. F. Molecular Optical Activity and the Chiral Discriminations; Cambridge University Press, 1982.
(2) Riehl, J. P.; Richardson, F. S. Circularly polarized luminescence spectroscopy. Chem. Rev. 1986, 86, 1–16.
(3) Sang, Y. T.; Han, J. L.; Zhao, T. H.; Duan, P. F.; Liu, M. H. Circularly Polarized Luminescence in Nanoassemblies: Generation, Amplification, and Application. Adv. Mater. 2019, 1900110, DOI: 10.1002/adma.201900110.
(4) Muller, G. Luminescent Chiral Lanthanide(iii) Complexes as Potential Molecular Probes. Dalton Trans. 2009, 9692–9707.
(5) Carr, R.; Evans, N. H.; Parker, D. Lanthanide Complexes as Chiral Probes Exploiting Circularly Polarized Luminescence. Chem. Soc. Rev. 2012, 41, 7673–7686.
(6) Zinna, F.; Di Bari, L. Lanthanide Circularly Polarized Luminescence: Bases and Applications. Chirality 2015, 27, 1–13.
(7) Circularly Polarised Luminescence. In Luminescence of Lanthanide Ions in Coordination Compounds and Nanomaterials; de

Figure 6. (a) CP-OLED architecture (adapted from ref 27) and (b) a chiral Eu(III) complex with high CPL activity, CPL microscopy images, and CPL spectra. (The reproduction of material is from ref 28.) (c) DNA-based chiral Eu(III) complex. Redrawn from ref 29. Copyright (2018) The Royal Society of Chemistry.
Bettencourt-Dias, A., Ed.; John Wiley & Sons: Chichester, U.K., 2014; pp 77–124.

(8) Bünzli, J.-C. G. On the Design of Highly Luminescent Lanthanide Complexes. Coord. Chem. Rev. 2015, 293–294, 19–47.

(9) Binnemans, K. Interpretation of Europium(III) Spectra. Coord. Chem. Rev. 2015, 295, 1–45.

(10) Hasegawa, Y.; Kitagawa, Y.; Nakashima, T. Efective Photo-sensitized, Electrosensitized, and Mechanosensitized Luminescence of Lanthanide Complexes. NPG Asia Mater. 2018, 10, 52–70.

(11) Luk, C. K.; Richardson, F. S. Circularly polarized luminescence and energy transfer studies on carboxylic acid complexes of europium(III) and terbium(III) in solution. J. Am. Chem. Soc. 1975, 97, 6666–6675.

(12) Brittain, H. G.; Richardson, F. S. Circularly Polarized Emission Studies on the Chiral Nuclear Magnetic Resonance Lanthanide Shift Reagent Tris(3-trifluoroacetyl-d-camphorato)europium(III). J. Am. Chem. Soc. 1976, 98, 5858–5863.

(13) Brittain, H. G.; Richardson, F. S.; Martin, R. B. Terbium(III) Emission as a Probe of Calcium(II) Binding Sites in Proteins. J. Am. Chem. Soc. 1976, 98, 8255–8260.

(14) Spaulding, L.; Brittain, H. G. Complexation of Amino Acids by Terbium(III) Ethylenediaminetetraacetate. Inorg. Chem. 1985, 24, 3692–3698.

(15) Lunkley, J. L.; Shirotani, D.; Yamanari, K.; Kaizaki, S.; Muller, G. Chiroptical Spectra of a Series of Tetraakis(+-3-heptfluoroacetyl-butyrylcamphorato)lanthanide(III) with an Encapsulated Alkali Metal Ion: Circularly Polarized Luminescence and Absolute Chiral Structures for the Eu(III) and Sm(III) Complexes. Inorg. Chem. 2011, 50 (12), 12724–12732.

(16) Yeung, C.-T.; Yim, K.-H.; Wong, H.-Y.; Pal, R.; Lo, W.-S.; Yan, S.-C.; Yee-Man Wong, M.; Yim, D.; Smiles, D. E.; McCormick, L. J.; Teat, S. J.; Shah, D. K.; Wong, W.-T.; Law, G.-L. Chiral Transcription in Self-Assembled Tetrahedral Eu4L6 Chiral Cages Displaying Sizable Circularly Polarized Luminescence. Nat. Commun. 2017, 8, 1128.

(17) Hashimoto, Y.; Nakashima, T.; Yamada, M.; Yuasa, J.; Rapenne, G.; Kawai, T. Hierarchical Emergence and Dynamic Control of Chirality in a Photosensitive Dinuclear Complex. J. Phys. Chem. Lett. 2018, 9, 2151–2157.

(18) Kumar, J.; Marydasan, B.; Nakashima, T.; Kawai, T.; Yuasa, J. Chiral Supramolecular Polymerization Leading to Eye Differentiable Circular Polarization in Luminescence. Chem. Commun. 2016, 52, 9885–9888.

(19) Hasegawa, Y.; Miura, Y.; Kitagawa, Y.; Wada, S.; Nakashima, T.; Fushimi, K.; Seki, T.; Ito, H.; Iwasa, T.; Taketsuga, T.; Goi, M.; Tanaka, K.; Chujo, Y.; Hattori, S.; Karasewa, M.; Ishii, K. Spiral Eu(III) Coordination Polymers with Circularly Polarized Luminescence. Chem. Commun. 2018, 54, 10695–10697.

(20) Koiso, N.; Kitagawa, Y.; Takayuki, N.; Koji, F.; Yasuchika, H. Eu(III) Chiral Coordination Polymer with a Structural Transformation System. Inorg. Chem. 2017, 56, 5741–5747.

(21) Wada, S.; Kitagawa, Y.; Nakashima, T.; Goi, M.; Tanaka, K.; Fushimi, K.; Chujo, Y.; Hasegawa, Y. Electronic Chirality Inversion of Lanthanide Complex Induced by Acharal Molecules. Sci. Rep. 2018, 8, 16395.

(22) Richardson, F. S.; Berry, M. T.; Reid, M. F. Ligand Polarization Contributions to Lanthanide 4f → 4f Magnetic Dipole Transition Moments and Rotatory Strengths. Mol. Phys. 1986, 58, 929–945.

(23) Forsberg, J. H. Complexes of Lanthanide (III) Ions with Nitrogen Donor Ligands. Coord. Chem. Rev. 1973, 10, 195–226.

(24) Ma, C. G.; Brik, M. G.; Kisk, V.; Kangur, T.; Sidlos, I. Spectroscopic and Crystal-field Analysis of Energy Levels of Eu3+ in SnO2 in Comparison with ZrO2 and TiO2. J. Alloys Compd. 2011, 509, 3441–3451.

(25) Gendron, F.; Moore, B.; Cador, O.; Pointillart, F.; Autschbach, J.; Le Guennic, B. Ab Initio Study of Circular Dichroism and Circularly Polarized Luminescence of Spin-Allowed and Spin-Forbidden Transitions: From Organic Ketones to Lanthanide Complexes. J. Chem. Theory Comput. 2019, 15, 4140–4155.