

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

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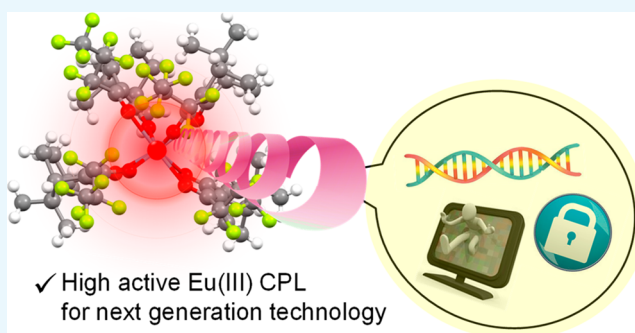
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ABSTRACT: Circularly polarized luminescence (CPL) is characterized by the differential emission of right and left circularly polarized light by a chiral molecule. This mini-review describes the recent developments in chiral trivalent europium (Eu(III)) 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.

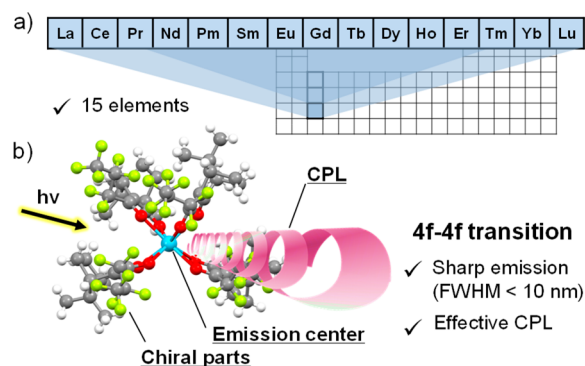


Figure 1. (a) Lanthanoids in the periodic table and (b) image of the chiral lanthanide luminophore ($[\text{Eu}((+)\text{-hfbc})_4]^-$) with high CPL activity.

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-

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trifluoroacetylcamphorate ligands,¹² and there are several reports on CPL.^{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-heptafluoro butyryl camphorate).¹⁵ The emission intensity (in the ⁵D₀ → ⁷F₁ 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,⁴ Parker,⁵ and Di Bari.⁶ The focus of this review is on the latest progress in polynuclear Eu(III) CPL and the electronic control of chiral mononuclear Eu(III) complexes to realize effective CPL. The CPL applications using the chiral mononuclear Eu(III) complexes are also described.

2. GENERAL THEORY

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

$$\Delta I(\lambda) = I_L(\lambda) - I_R(\lambda) \quad (1)$$

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_{CPL}).

$$g_{\text{CPL}} = 2 \frac{\Delta I(\lambda)}{I_L(\lambda) + I_R(\lambda)} \quad (2)$$

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

$$g_{\text{CPL}} = 4 \frac{|\vec{\mu}||\vec{m}|\cos\theta}{|\vec{\mu}|^2 + |\vec{m}|^2} \quad (3)$$

where θ is the angle between $\vec{\mu}$ and \vec{m} . When $\vec{\mu} = \vec{m}$ ($\theta = 0$, eq 3 affords the highest g_{CPL} value ($= 2$) mathematically. The equation indicates that the lanthanide(III) complexes are plausible candidates for CPL with high g_{CPL} values because the magnitude of the electric dipole moment ($|\vec{\mu}|$) is similar to that of the magnetic dipole moment ($|\vec{m}|$). Among lanthanide(III) emissions, the ⁵D₀ → ⁷F₁ transition of Eu(III) complexes shows an enormous g_{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,^{4–6} 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) tetramers,¹⁶ dimers,¹⁷ aggregates,¹⁸ and coordination polymers^{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.¹⁶ They produced a Eu(III) tetrahedral cage using 2,6-diaminoanthraquinone-based chiral ligands with different point chirality (Figure 2). Ligand 1

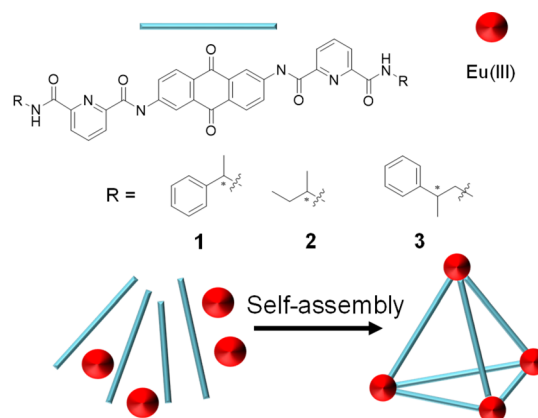


Figure 2. Tetranuclear chiral Eu(III) complexes.

(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_{CPL} : up to 0.16), but other cages show relatively low g_{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 ($\Phi_{\text{tot}} = 16\text{--}18\%$). These results (different CPLs and similar Φ_{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 luminophore 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).¹⁷ The Eu(III) complex

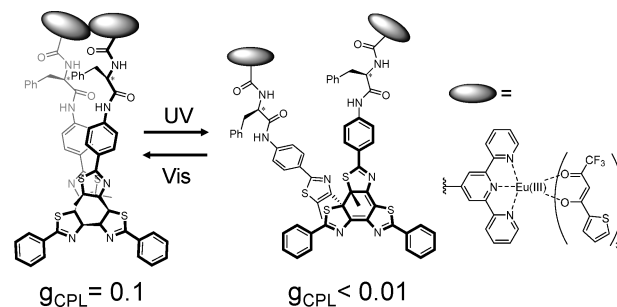


Figure 3. Photoresponsive chiral Eu(III) dimer. Adapted from ref 17.

shows nine coordination structures composed of β -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 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

of the CPL with high contrast (g_{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

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_{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).¹⁸ The helical 1D aggregation of

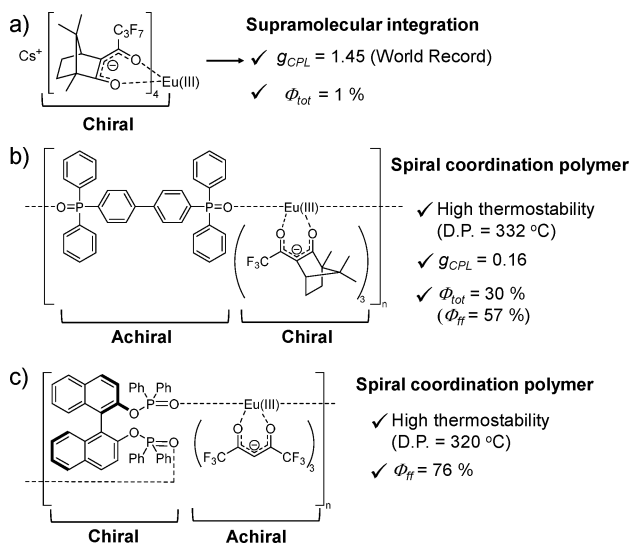


Figure 4. (a) Supramolecular and (b, c) coordination-polymer-type chiral Eu(III) complexes.^{18–20}

$\text{Cs}[\text{Eu}((+)\text{-hfbc})_4]$ resulted in the highest g_{CPL} value (1.45: $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition), although g_{CD} ($\pi\text{-}\pi^*$ transition) of $\text{Cs}[\text{Eu}((+)\text{-hfbc})_4]$ 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_{CPL} of the Eu(III) complexes with chiral β -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 $\text{Cs}[\text{Eu}((+)\text{-hfbc})_4]$; emission quantum yield, $\Phi_{\text{tot}} = 1\%$).¹⁸ Our research group determined that the spiral polymerization of the Eu(III) complex with 3-trifluoroacetyl camphorate significantly increased the emission quantum yield.¹⁹ Herein, the Eu(III) coordination polymers were composed of chiral $\text{Eu}(\text{tfc})_3$ [$\text{tfc} = 3\text{-trifluoroacetylcamphorate}$] and dpbp joint ligand, $[\text{Eu}(\pm\text{tfc})_3(\text{dpbp})_n]$ ($\text{dpbp} = 4,4'\text{-bis(diphenylphosphoryl)biphenyl}$, Figure 4b). The tight packing of the Eu(III) coordination polymer afforded enhanced thermostability (332 °C). The rigid spiral-type chiral Eu(III) coordination polymer exhibited strong luminescence ($\Phi_{\text{tot}} = 30\%$) and high CPL activity ($g_{\text{CPL}} = 0.16$) in comparison to those of the mononuclear chiral Eu(III) complex $[\text{Eu}(\text{tfc})_3(\text{tppo})_2]$, $\text{tppo} = \text{triphenylphosphine oxide}$] in the solid state. The high Φ_{tot} is due to an effective photosensitized efficiency ($\eta_{\text{sens}} = 53\%$) and internal emission quantum yield obtained by excitation of the lanthanide ion (Φ_{ff}

$= 57\%$). The modulation of the ligand electronic structure through molecular integration is also presumed to suppress the energy quenching from the emissive Eu(III) ion, which results in a high emission quantum yield. The spiral coordinated Eu(III) polymer with the chiral phosphine oxide ligands and achiral β -diketonate ligands was also successfully synthesized by Hasegawa and co-workers (Figure 4c).²⁰ The Eu(III) coordination polymer had a helical polymer structure with the characteristic hydrogen–fluorine/ π interactions in the crystal. This polymer also exhibited high thermostability (320 °C) and an extremely high emission quantum yield obtained by the excitation of the lanthanide ion ($\Phi_{\text{ff}} = 76\%$) in the solid state. The Eu(III) polymer shows an effective transformation from a polymer to a monomer structure in solution. This paper shows the g_{CPL} ($= 0.013$) of the mononuclear structure in solution.

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 $\text{Eu}(\text{tfc})_3$ complexes (Figure 5a, $\text{Eu}(\text{tfc})_3 + \text{tppo}$ and $\text{Eu}(\text{tfc})_3 + \text{ac}$) provides a dramatic change in the CPL property (Figure 5b). In this paper, large negative CPL signal of $\text{Eu}(\text{tfc})_3 + \text{ac}$ at 594 nm was observed, although a small positive signal for $\text{Eu}(\text{tfc})_3 + \text{tppo}$ was observed. The electronic

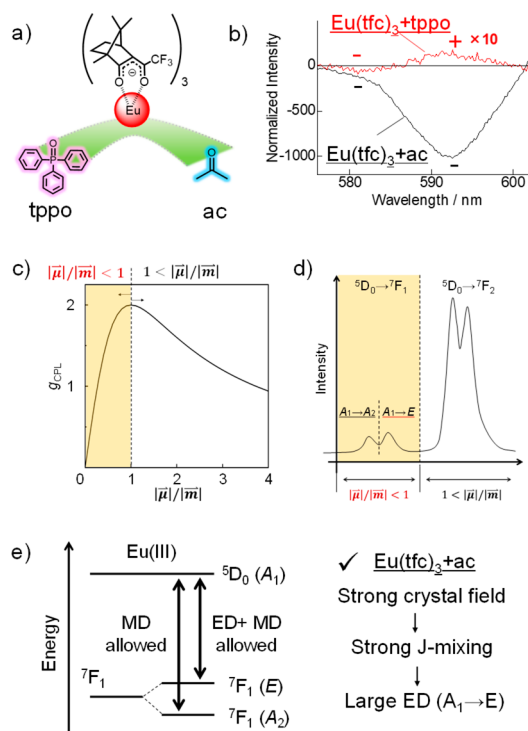


Figure 5. (a) Chiral Eu(III) complexes with achiral ligands. (b) Circularly polarized luminescence spectra and (c) a simulated g_{CPL} curve as a function of the $|\bar{m}_l|/|\bar{m}|$ ratio in eq 4 with $\theta = 0^\circ$. (d) Photoluminescence spectrum and (e) energy diagram of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition of the Eu(III) complex (C_{4v} or D_{2d}) based on the electronic structure and group theory. Redrawn from ref 21.

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_{CPL} . The equation can be modified as follows

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

where θ is the angle between $\vec{\mu}$ and \vec{m} . In the region $|\vec{\mu}|/|\vec{m}| < 1$, the Eu(III) complex with a large $|\vec{\mu}|$ provides a high g_{CPL} value (Figure 5c). In general, the $|\vec{m}|$ value in the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition is greater than the $|\vec{\mu}|$ value ($|\vec{\mu}|/|\vec{m}| < 1$).²² Therefore, an enhanced $|\vec{\mu}|$ is important for the construction of the Eu(III) complex with large g_{CPL} . The intensity of $|\vec{\mu}|$ in the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition depends on the crystal field around the Eu(III) ion.^{23,24} The ${}^7\text{F}_1$ energy level of the Eu(III) ion in a typical eight-coordinate structure (C_{4v} or D_{2d}) splits into two Stark sublevels (Figure 5d).⁹ The two bands at 583 and 594 nm in the CPL spectra are assigned to the $A_1 \rightarrow A_2$ 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 with tppo compared to Eu(+tfc)₃ with acetone, whereas those for the $A_1 \rightarrow A_2$ transition show the same minus sign for Eu(+tfc)₃ with tppo and acetone.

In C_{4v} or D_{2d} 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 sign at 583 nm (for the ED-forbidden $A_1 \rightarrow A_2$ transition) reflects the intrinsic Λ - or Δ -type structure because of the insensitive electronic state mixing. Considering the same CPL sign at 583 nm for Eu(+tfc)₃ with tppo and acetone, the structure type (Λ or Δ) 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 (Λ or Δ).

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 ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition, $\vec{\mu}$ is mainly altered by the J mixing of ${}^7\text{F}_2$ or ${}^7\text{F}_3$ sublevels into ${}^7\text{F}_1$. In the photoluminescence spectra, the Stark splitting energy of Eu(+tfc)₃ with acetone is greater than that of Eu(+tfc)₃ with tppo. 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 $|\vec{\mu}|$ value of the ED-allowed $A_1 \rightarrow E$ transition relative to that of the ED-forbidden $A_1 \rightarrow A_2$ transition. An increase in $|\vec{\mu}|$ results in a high g_{CPL} value in eq 4. In the case of the previously reported mononuclear Eu(III) complexes with chiral structures,¹⁵ a strong $A_1 \rightarrow E$ transition is also related to a large g_{CPL} . The angle (θ) between $\vec{\mu}$ and \vec{m} for the Eu(tfc)₃ complex with acetone is greater than 90° , whereas that 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_{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_{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_{CPL} value and altering its sign. In the future, a detailed description of the electronic structure based on calculation science^{25,26} 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 ($g_{\text{CPL}} = -1.0$).²⁷ 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 (Figure 6b).²⁸

Nakamura and Kobayashi described the DNA-based functional materials, which are of significant interest for applications in electrical and optical devices.²⁹ 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.³⁰ CPL probes are also useful for the determination of the reversible binding and competitive binding of different proteins.³¹⁻³³ Recently, methods for monitoring the ADP/ATP ratio or sialic acid via the induced CPL of Eu(III) complexes have been demonstrated.^{34,35} 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 polymer-type Eu(III) complexes show high CPL activity with a large g_{CPL} and emission quantum yields. The CPL applications based on the Eu(III) complexes are also described from the

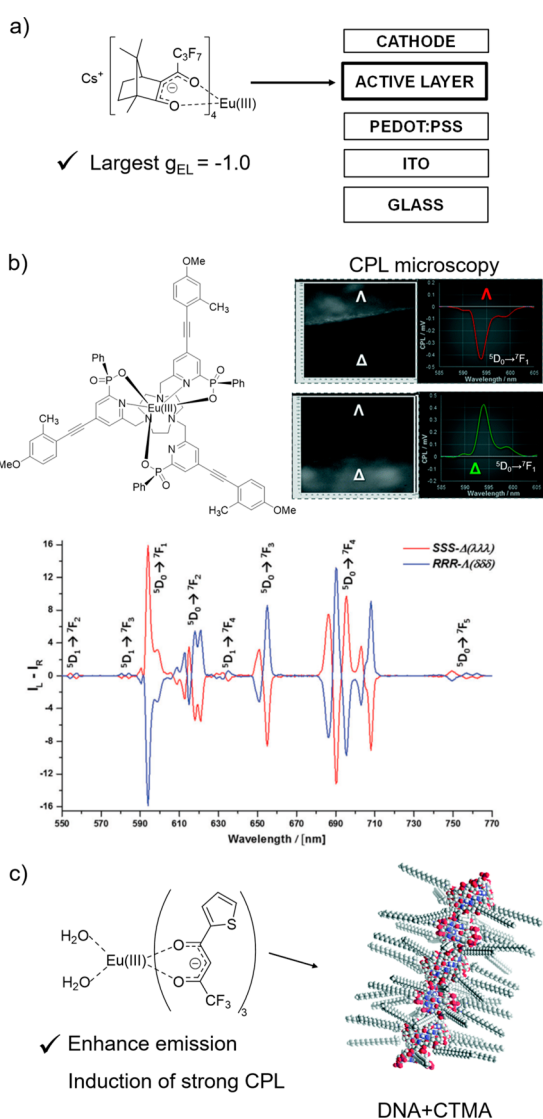


Figure 6. (a) CP-OLED architecture (adapted from ref 27) and (b) a chiral Eu(III) complex with high CPL activity, CPL microscopy images, and CPL spectra. (The reproduction of material is from ref 28.) (c) DNA-based chiral Eu(III) complex. Redrawn from ref 29. Copyright (2018) The Royal Society of Chemistry.

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.

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Notes

The authors declare no competing financial interest.

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