Chirogenesis and Pfeiffer Effect in Optically Inactive Eu<sup>III</sup> and Tb<sup>III</sup> Tris(β-diketonate) Upon Intermolecular Chirality Transfer From Poly- and Monosaccharide Alkyl Esters and α-Pinene: Emerging Circularly Polarized Luminescence (CPL) and Circular Dichroism (CD)

Michiya Fujiki<sup>†1</sup>, Laibing Wang<sup>†1</sup>, Nanami Ogata<sup>†1</sup>, Fumio Asanoma<sup>†1</sup>, Asuka Okubo<sup>†1</sup>, Shun Okazaki<sup>†1</sup>, Hiroki Kamite<sup>†1</sup> and Abd Jalil Jalilah<sup>†1,2,3,#</sup>

We report emerging circularly polarized luminescence (CPL) at 4f-4f transitions when lanthanide (Eu<sup>III</sup> and Tb<sup>III</sup>) tris(β-diketonate) embedded to cellulose triacetate (CTA), cellulose acetate butyrate (CABu), D-/L-glucose pentamethyl esters (D-/L-Glu), and D-/L-arabinose tetramethyl esters (D-/L-Ara) are in film states. Herein, 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate (fod) and 2,2,6,6-tetramethyl-3,5-heptanedione (dpm) were chosen as the β-diketonates. The $g_{\text{lum}}$ value of Eu(fod)$_3$ in CABu are +0.0671 at 593 nm ($^5D_0 \rightarrow ^7F_1$) and −0.0059 at 613 nm ($^5D_0 \rightarrow ^7F_2$), respectively, while those in CTA are +0.0463 and −0.0040 at these transitions, respectively. The $g_{\text{lum}}$ value of Tb(fod)$_3$ in CABu are −0.0029 at 490 nm ($^5D_4 \rightarrow ^7F_6$), +0.0078 at 540 nm ($^5D_4 \rightarrow ^7F_5$), and −0.0018 at 552 nm ($^5D_4 \rightarrow ^7F_5$), respectively, while those in CTA are −0.0053, +0.0037, and −0.0059 at these transitions, respectively. $D-/L$-Glu and $D-/L$-Ara induced weaker $g_{\text{lum}}$ values at 4f-4f transitions of Eu(fod)$_3$, Tb(fod)$_3$, and Tb(dpm)$_3$. For comparison, Tb(dpm)$_3$ in α-pinene showed clear CPL characteristics, though Eu(dpm)$_3$ did not. A surplus charge neutralization hypothesis was applied to the origin of attractive intermolecular interactions between the ligands and saccharides. This idea was supported from the concomitant opposite tendency in upfield $^{19}$F-NMR and downfield $^1$H-NMR chemical shifts of Eu(fod)$_3$ and the opposite Mulliken charges between F-C bonds (fod) and H-C bonds (CTA and $D-/L$-Glu). An analysis of CPL excitation (CPLE) and CPL spectra suggests that (+)- and (−)-sign CPL signals of Eu<sup>III</sup> and Tb<sup>III</sup> at different 4f-4f transitions in the visible region are the same with the (+)- and (−)-sign exhibited by CPLE bands at high energy levels of Eu<sup>III</sup> and Tb<sup>III</sup> in the near-UV region.

**Keywords:** non-covalent interaction, circularly polarized luminescence, circular dichroism, europium, terbium, cellulose, saccharide, terpene
INTRODUCTION

In recent years, controlled chirogenesis led by several scenarios of intermolecular chirality transfer endowed with natural and human-made resources has become the most popular phenomenon allowing for an efficient generation of the desired optically active substances in the realms of organic chemistry (Bosnich, 1967; Hayward and Totty, 1969; Noack, 1969; Soai et al., 1999), supramolecular chemistry (Kobayashi et al., 1993; Huang et al., 1998; Prince et al., 2000; Borovkov et al., 2004; Hembury et al., 2008; Aida et al., 2012; Borovkov, 2014; Liu et al., 2015; Goto et al., 2017), polymer chemistry (Green et al., 1993; Yashima et al., 1995; Nakashima et al., 2001; Kawagoe et al., 2010; Numata and Shinkai, 2011; Lee et al., 2012; Duan et al., 2014; Fujiki, 2014; Wang et al., 2014; Akagi, 2019), and molecular aggregation/colloidal/gel chemistry (Palmons and Meijer, 2007; Isare et al., 2010; George et al., 2011; Mei et al., 2015; Roose et al., 2016; Sang et al., 2019). Particularly, chirogenesis in metal coordination chemistry by the chirality transfer has long been one of the central subjects in inorganic chemistry (Mason and Norman, 1965; Kirschner and Ahmad, 1968; Kirschner and Bakkar, 1982; Mason, 1982; Brittain, 1983, 1989; Riehl and Richardson, 1986; Tsukube and Shinoda, 2002; Di Bari and Salvadori, 2005; Muller, 2009, 2014; Bünzli, 2010; Carr et al., 2016). In the early 1930s, Pfeiffer and Quehl were hypothesizing the Pfeiffer effect (formula = \( M^+ \text{[Eu(dpdm)]}^{3-} \) (M\(^7^+\); counter cationic species and dpa; dipicolinate) at the photoexcited state (ES) in achiral solvents are in the range of 12 and 17 kcal mol\(^{-1}\); higher viscosity cosolvents of water-ethylene glycol corresponded to higher barrier heights (Glover-Fischer et al., 1998).

Historically, in 1898, Kipping and Pope investigated the first chirogenesis of \( L \)-NaClO\( _3 \) crystals (P\( _2 \)I\( 3 \) space group) in an enantiomer excess (ee) of several % that were preferentially grown in a water solution of \( D \)-glucose and \( D \)-mannitol (Kipping and Pope, 1898). In 1919, Perucca found the first chirogenesis of triarylmethane textile dye by observing an anomalous optical rotational dispersion (ORD) in visible region when he dispersed an ORD-silent triarylmethane textile dye in polycrystalline \( L \)-NaClO\( _3 \) (Perucca, 1919; Kahr and Gurney, 2001; Jacoby, 2008; Bing et al., 2010). In the early 1930s, Pfeiffer and Quehl were aware that optical rotation of amino acids increased and/or decreased in the presence of racemic labile metal (Zn\(^{2+}\), Cd\(^{2+}\), and Ni\(^{2+}\)) complexes (Pfeiffer and Quehl, 1931, 1932). This anomaly is called as the Pfeiffer effect (Mayer and Brasted, 1973; Mason, 1982; Brittain, 1983, 1989; Lunkley et al., 2018).

In 1965, Mason and Norman reported the first circular dichroism (CD) signals at 3d-3d transitions of Eu\(^{3+}\)(NH\( _3 \))\( _6 \)(ClO\( _4 \))\( _3 \) in the presence of (+)-diethyl tartrate (Mason and Norman, 1965). In 1977, the first circularly polarized luminescence (CPL) spectra from optically inactive Eu\(^{3+}\)(dpm)\( _3 \), Eu\(^{3+}\)(dpdm)\( _3 \), and other two Eu\(^{3+}\) complexes dissolved in (R)-(S)-\( \alpha \)-phenylethylamine are reported by hypothesizing the Pfeiffer effect (fod = 6,6,7,7,8,8,8-heptafluorooctyl-2,2-dimethyl-3,5-octanediode, dpm: dipivaloylmethane or 2,2,6,6-tetramethyl-3,5-heptanedione) (British and Richardson, 1977a, 1980). These pioneering CPL studies further stimulated many researchers to investigate CPL and CD spectroscopic characteristics of optically inactive lanthanide complexes in the presence of amino acids, monosaccharides, malic acid ascorbic acid, cyclic glycols, DNA, and other chiral chemical influences (Luk and Richardson, 1974; Brittain and Richardson, 1977b, 1981a; Madaras and Brittain, 1981, 1984; Richardson, 1982; Van et al., 1982; Huskowska and Riehl, 1995; Muller and Riehl, 2005; Muller, 2009; Iwamura et al., 2012, 2016; Miyake et al., 2014; Wu et al., 2016, 2019; Jalilah et al., 2018; Lunkley et al., 2018; Wu and Bouf, 2018; Taniguchi et al., 2019). An outer-sphere intermolecular interaction between the \( \Delta-\Lambda \) mixture lanthanide\(^{III}\)(\( Ln^{III} \)) complex and the chiral additives is responsible for the equilibrium shift, as detectable by emerging CPL spectra. Richardson et al. evaluated that the barrier heights in \( \Delta-\Lambda \) stereoremutation between charged \( M^+\text{[Eu(dpdm)]}^{3-} \) (M\(^4^+\); counter cationic species and dpa; dipicolinate) at the photoexcited state (ES) in chiral solvents are in the range of 12 and 17 kcal mol\(^{-1}\); higher viscosity cosolvents of water-ethylene glycol corresponded to higher barrier heights (Glover-Fischer et al., 1998).

New knowledge and understanding of several weak inter- and intramolecular interactions known as C-H/\( \pi \), C-H/O-C, C-H/F-C, C-F/H/\( \alpha \)-C, C-F/Si, and \( \pi-\pi \) (Nishio et al., 1998; Desiraju and Steiner, 1999; Matsuura et al., 2003; Mele et al., 2003; Tsuzuki et al., 2003; Kim et al., 2004; Mahadevi and Sastry, 2016; Pitts et al., 2017) lead us to hypothesize that multiple point chirality and/or main chain helicity of non-charged bioresources impose the capability of non-symmetrical force transfer to non-charged achiral or optically inactive chromophores and luminophores. Non-charged terpene hydrocarbons, e.g., (S)-(R)-(L)-limonene, (1S)-(1R)-(1)-\( \alpha \)-pinene, and (1S)-(1R)-(1)-\( \beta \)-pinene, can efficiently work as chiral liquified scaffolds in the ground state (GS) and the ES of several colloidal \( \pi-\pi \)-conjugated polymers (Kawagoe et al., 2010; Nakano et al., 2010, 2012; Lee et al., 2012; Fujiki, 2014; Wang et al., 2014), colloidal vinyl polymers bearing azobenzene (Jiang et al., 2015), and non-charged Eu(fod)\( _3 \) (Figure 1; Jalilah et al., 2018). However, to realize practical photonic applications, solution-processable and/or thermoplastic solid materials are inevitably needed because terpenes are volatile, flammable liquids.

Among solidified chiral bioresources, poly- and monosaccharides are incredible biomaterials that are abundant on earth and have a wide variety of functions (Klemm et al., 2005), e.g., allowing growth and maintenance of homochiral life resulting chiral foods (Coultaite, 2016), recognition and sorting of enantiomers (Ikai and Okamoto, 2009), service as a building block of optically active supramolecular complexes (Numata and Shinkai, 2011), and fabrication of liquid crystals, solid films, fibers, sheets, and nano-composites for industrial purposes (Dubois et al., 1998; Henriksson et al., 2007; Wang et al., 2007; Iwatake et al., 2008). More recently, poly- and monosaccharides are excellent chiroptical platforms to generate and boost CD/CPL/circularly polarized reflection bands because of their helicoidal and cholesteric higher-order structures (Wilton et al., 2017; De La Cruz et al., 2018; Yu et al., 2018, 2019; Zheng et al., 2018). We have proved that three cellulose derivatives (cellulose triacetate (CTA), cellulose acetate butyrate (CABu), and cellulose tri(phenyl carbamate) (CTPC) in Figure 1 possess...
FIGURE 1 | The chemical structures of cellulose alkyl esters (CABu and CTA), cellulose tris(phenoxy carbamate) (CTPC), D-(+)- and L-(−)-glucose pentamethylester (D-Glu/L-Glu), D-(−)- and L-(+)−arabinose tetramethylester (D-Ara/L-Ara), (1S)-(−)/(1R)+(+)−α-pine, and four optically inactive EuIII and TbIII complexes coordinated with achiral tris(β-diketonate) [Eu(fod)3, Tb(fod)3, Eu(dpm)3, and Tb(dpm)3].

an efficient ambidextrous scaffolding capability toward CD-inactive oligo- and polyfluorenes, leading to the corresponding (+)- or (−)-sign CPL-active/CD-active species as the solid film states (Guo et al., 2017, 2018).

These results encourage us to propose that CTA, CABu, D-/L-glucose permethyl esters (D-Glu/L-Glu), and D-/L-arabinose permethyl esters (D-Ara/L-Ara) should work as chirality transferring solid platforms, enabling several optically inactive and/or racemic EuIII and TbIII complexes to the corresponding CPL-active/CD-active, non-racemic species (Figure 1). For comparison, we tested the chirality transfer capability of (1S)-(−)/(1R)+(+)−α-pine as chiral liquid molecules to Eu(dpm)3 and Tb(dpm)3.

Herein, we showcase that Eu(fod)3, Tb(fod)3, and Tb(dpm)3, except Eu(dpm)3 commonly exhibited CPL signals at 4f−4f transitions and CD bands due to n-π*/π−π* transitions of the ligands when CABu, CTA, D-Glu/L-Glu, and D-Ara/L-Ara were employed as embedding films. In α-pine, although Tb(dpm)3 showed clear CPL characteristics, Eu(dpm)3 did not. Unresolved inherent nature between EuIII and TbIII causes considerable differences of CPL characteristics as well as emission wavelengths at 4f−4f transitions. Although the current $\xi_{\text{Lum}}$ values of our CPL-active lanthanide complex in the films are not very outstanding, the hypothesis of these non-covalent weak chiral intermolecular interactions in the ES and GS led us to freely design solution processible CPL- and/or CD-functioned composite films made of several optically inactive lanthanide complexes coordinated with achiral organic ligands upon chirality/helicity transfer of inexpensive soluble polysaccharide, oligosaccharide, and monosaccharide derivatives as the solidified chiral bioresources, in addition to a conventional multi-step synthesis of optically active lanthanide complexes coordinated with chiral ligands designed strategically.

EXPERIMENTAL

Materials

CTA and CABu

CTA (Wako Pure Chemicals, Osaka, Japan) and CABu (Sigma-Aldrich Japan, Tokyo, Japan) were used without further purification (Figures S1, S2, SM). Chloroform, tetrahydrofuran (THF), methanol (MeOH), and other solvents (Dojindo, Kumamoto, Japan) were used as received. CDCl3 and hexafluorobenzene (C6F6) were purchased from Stable Isotope
Lab (SIL) (Japanese vendor, Wako Pure Chemicals) and Wako Pure Chemicals, respectively. (1S)- and (1R)-α-Pinene (Tokyo Chemical Industry (TCI), Tokyo, Japan) were purified by distillation in a reduced pressure.

Monosaccharide Permethylesters

**L-(-)-Glu.** To a mixture of L-(-)-glucose (0.5 g) and stoichiometric acetic anhydride (4 mL), freshly dried Cu(OTf)$_2$ (0.03 mol % of L-(-)-glucose) at 0°C was added under nitrogen [Scheme S1 in Supplementary Materials (SM)]. The mixture was stirred for 1 h in an ice bath and then stirred at room temperature for 12 h. Methanol (5 mL) was slowly added to quench the acylation reaction, and the mixture was stirred for another 0.5 h, followed by evaporation under reduced pressure. Chloroform (25 mL) was added to dissolve the residue, and the mixture was consecutively washed twice with saturated NaHCO$_3$ brine and water, respectively. The organic layer was dried over anhydrous Na$_2$SO$_4$, and the mixture was filtered. The filtrate was concentrated in a vacuum and purified by silica gel column chromatography, and eluted with petroleum ether/ethyl acetate (v/v, 50/1) to yield a white powder (yield: 0.42 g, 70%; Analysis: Calcd (%) for C$_{16}$H$_{22}$O$_{11}$: C, 49.23; H, 5.68; Found (%): C, 49.53; H, 5.43. $^1$H-NMR (in CDCl$_3$), FT-IR (onto CaF$_2$) and ESI (positive mode)-MS spectra of L-Glu and D-Glu are shown in Figure S3, SM and Figure S4, SM, respectively. Elemental analysis of L-Glu and D-Glu are given in Figure S5, SM.

**D-(-)-Glu.** Donated from Prof. Wei Zhang (Soochow University, China) prepared by a similar method. $^1$H-NMR, FT-IR, and ESI (positive mode) MS spectra are displayed in Figure S4, SM. Solid-state $^{13}$C-NMR and $^1$H-NMR in CDCl$_3$ solution are shown in Figures 5, SM, respectively. Analysis: Calcd (%) for C$_{16}$H$_{22}$O$_{11}$: C, 49.23; H, 5.68; Found (%): C, 49.51; H, 5.40.

**D-Ara and L-Ara.** D(-)-Arabinose tetramethyl ester and L-(-)-arabinose tetramethyl ester were synthesized utilizing the same procedure as described for the synthesis of L-Glu. A viscous liquid was obtained as D-Ara. Yield: 2.4 g, 32%. Analysis for D-Ara: Calcd (%) for C$_{15}$H$_{20}$O$_{6}$: C, 49.06; H, 5.70; Found (%): C, 48.97; H, 5.56. **L-Ara.** Yield (2.4 g, 32%). Analysis: Calcd (%) for C$_{15}$H$_{20}$O$_{6}$: C, 49.06; H, 5.70, Found (%): C, 49.01; H, 5.60. $^1$H-NMR, FT-IR, and ESI-MS (positive mode) spectra of D-Ara and L-Ara are shown in Figures S6, S7, SM, respectively. The results of the elemental analysis of L-Ara and D-Ara are shown in Figure S8, SM.

**Tb(fod)$_3$**

The starting material, 0.19 g (0.74 mmol) of TbCl$_3$ (99% purity, Sigma-Aldrich, now Merck) was dissolved in the minimum amount of methanol (3.0 mL), and 1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanediene (Hfod, 0.636 g (2.15 mmol, 0.5 mL), TCI) was adjusted to pH 5–6 by adding the required amount of aqueous NaOH solution. The above two solutions were mixed by vigorous stirring with a magnetic stir bar for 10 min, followed by addition of 200 mL distilled water dropwise into the solution. A pale-yellow Tb(fod)$_3$ was precipitated under vigorous stirring with a magnetic bar for 12 h. The crude product adhered to the bottom of the reaction vessel was purified by a short-column silica gel chromatography (Wakogel C-200, Chart S1 in SI) as shown below, with chloroform as an eluent to yield a pale yellow oil, followed by drying in a vacuum oven 90°C to obtain a white solid. Yield, 200 mg (40%). The purification of Tb(fod)$_3$ using a 5 mL pipette tip made of polypropylene, as a short-column apparatus, is illustrated below. Analysis: Calcd (%) for C$_{30}$H$_{35}$O$_{11}$Tb: C, 34.50; H, 2.90. Found (%): C, 34.58; H, 2.80. The elemental analysis suggested that Tb(fod)$_3$ has no water adducts.

Before we utilized the purification method (see Chart S1, SM) for Tb(fod)$_3$, we were aware of some impurity peaks approximately 450 nm in the PL spectrum of Tb(fod)$_3$. After the purification by silica gel column chromatography and elution with chloroform, we obtained a pure Tb(fod)$_3$ (based on the expected fluorescent emission spectrum). $^1$H-NMR (CDCl$_3$), $^{19}$F-NMR (CDCl$_3$), FT-IR (CaF$_2$), and ESI-MS (positive mode) spectra and elemental analysis of Tb(fod)$_3$ are shown in Figure S9, SM.

Other Lanthanide Complexes

Eu(fod)$_3$, Eu(dpm)$_3$, and Tb(dpm)$_3$ were purchased from Sigma-Aldrich-Merck, TCI, and Sigma-Aldrich-Merck, respectively, and were used as received. $^1$H-NMR (CDCl$_3$) and FT-IR spectra of Eu(fod)$_3$ are shown in Figure S10, SM. $^1$H-NMR and FT-IR spectra of Eu(dpm)$_3$ are shown in Figure S11, SM. $^1$H- and $^{19}$F-NMR (CDCl$_3$) and FT-IR (CaF$_2$) spectra of Tb(dpm)$_3$ are shown in Figure S12, SM.

**Instrumentation**

The UV-vis and CD spectra of the solutions were measured with a JASCO J-820 spectropolarimeter (Hachioji-Tokyo, Japan) equipped with Peltier-controlled housing units. Synthetic quartz (SQ) cuvette with a 10-mm path length (scanning rate: 100 nm min$^{-1}$; bandwidth: 1.0 nm; response time: 1.0 s; 0.5-nm interval sampling; single accumulation) at 25°C were used. To avoid second- and third-order stray light due to diffraction grating, CPL and PL spectra were recorded on a JASCO CPL-200, that was designed as a prism-based spectrfluoropolarimeter with a forward scattering of 0° angle equipped with focusing and collecting lenses, and a manually movable film holder onto an optical rail enables to adjust the best focal point to maximize CPL/PL signal amplitudes. Measurement conditions were bandwidths of 10 nm for excitation and emission, a scanning rate of 100 nm min$^{-1}$, and a data sampling of 0.5 nm interval. IR spectra were measured on CaF$_2$ plate using a Horiba FT-730 Fourier-transform (FT) infrared (IR) spectrometer (Horiba, Kyoto, Japan) over a wavenumber range between 800 and 4,000 cm$^{-1}$ with a resolution of 2 cm$^{-1}$ and a scanning speed of 5 mm s$^{-1}$ for 128 scans and a Perkin-Elmer Spectrum One/100 FT-IR spectrometer (Winter Street Waltham, MA 02451, USA) over a wavenumber range between 900 and 4,000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ for 64 scans. Electrospray ionization mass spectrometry (ESI-MS) was conducted with a JEOL (Akishima, Tokyo, Japan) AccuTOF JMS-T100 LC mass spectrometer (accelerating voltage,
10 kV). Electron ionization mass spectrometry with high-resolution (HR-ESI-MS) mode was recorded with a JEOl JMS-700 double-focusing mass spectrometer (accelerating voltage, 10 kV). The ionic species were often attached with Na⁺ ion. The hybridized polymers were characterized by a JEOl JNM-ECX400 cross-polarization (CP) magic-angle-spinning (MAS) solid-state (ss)-13C{H}-FT-NMR spectrometer (resonance frequency 100.5 MHz, contact time 2.0 ms, 550 scans, relaxation delay 5.0 s, spinning 8.0 kHz, repetition time 5.05 s). Elemental analysis was performed on a Perkin-Elmer 2400II CHNS/O. The solution \(^1\)H- and \(^{19}\)F-FT-NMR spectra were recorded on the JEOl ECP-400 spectrometer. The resonance frequencies of \(^{19}\)F- and \(^1\)H-NMR are 376 MHz and 400 MHz, respectively. Representative measurement conditions for \(^{19}\)F-NMR spectra had an acquisition time of 0.432 sec, 64 acquisitions, a relaxation delay of 4.0 sec, at a temperature of \(~20^\circ\)C, a pulse angle of 45° and a pulse width of 7.0 sec were used. Raw NMR data were processed and analyzed by JEOl Delta (Ver. 5) software. Hexafluorobenzene (HFB, -163.0 ppm) and tetramethylsilane (Me$_4$Si, 0.0 ppm) were used as internal standards for the \(^{19}\)F- and \(^1\)H-NMR measurements, respectively. Photodynamic decay of six solid films (Eu(fod)$_3$) with CTA and CABu (detected at 610–620 nm), Eu(dpm)$_3$ with CTA and CABu (detected at 610–620 nm), and Tb(dpm)$_3$ with CTA and CABu (detected at 542–551 nm) excited by an N$_2$ laser (Usho KEC-160; wavelength 337.1 nm; pulse width 600 ps; 10 Hz) were measured with the help of streak camera (Hamamatsu, picosecond fluorescence measurement system C4780 with Grating 150 lines per mm and slit width 100 μm). The 337.1 nm of N$_2$ laser source was used to excite shoulder UV/CD signals of the lanthanide complexes. Photodynamic measurements of other Eu$^{III}$ and Tb$^{III}$ complexes in the solid films were not obtained due to lack of an integrating sphere. The all processed data saved as raw text data were re-organized by KaleidaGraph ver. 4.53 (Synergy software, Reading, PA 19606, USA).

**Preparation of the Hybridized Films**

In fabricating the hybridized film, 10 mg of lanthanide complexes and 20 mg of saccharide derivatives (Glu and Ara) or cellulose derivatives (CABu and CTA) were completely dissolved in 1.0 mL of the desired solvent (chloroform or tetrahydrofuran (THF)) at ambient temperature. The hybridized film was deposited onto a polished circular quartz plate or borosilicate glass (Tempax Float®, Schott AG, Germany) (25 mm in diameter and 1 mm in thickness) by spin coating using a spin coater (MIKASA, MS-B100, Tokyo, Japan), then, 800 μL of the solution was placed onto the center of the plate and spun at 1,500 rpm for 60 s. The films on the glass were attached on both sides (front and back surfaces) to ensure an **optically symmetrical geometry** with air-sample-(quartz or borosilicate substrate)-sample-air contact by spin coating chloroform or THF solutions that consist of saccharides (chiral host) and lanthanide complex (achiral guest) (Guo et al., 2017, 2018; Yamada et al., 2018). Although the film thicknesses of both sides were not determined, we assumed to be on the order of several μm for each. The hybridized double-side coating films were scattering-free and transparent by the naked eye. To measure CPL/PL/CPLE/PLE/CD/UV-visible spectra, the optical density of the double-side coating specimen was controlled to 0.3–1.0 in the range of 280 and 330 nm. CD, CPL, and CPLE spectra of the hybridized films were measured at ambient temperature (24–26°C). The double-sided coating in the symmetrical optical geometry avoids chiroptical inversion artifacts that could be originated from linear dichroism induced by mechanical stress on anisotropic specimens due to spin coating. Based on our experience, single-side coating in the dissymmetrical optical geometry can often cause artifact inversion in signs of CPL and CD signals. In the case of single-side coating, the probability of the chiroptical sign inversion was approximately 2–3 out of 10, while double-side coating prevented the artifact origin sign inversion.

**RESULTS AND DISCUSSION**

The chirogenesis characteristics of oligo-/polyfluorenes originate from rotatable C–C bonds between fluorene rings and from C–O/C–C bonds of the cellulose derivatives (Figure 1) (Guo et al., 2017, 2018; Yamada et al., 2018) in the GS and ES because rotational barrier heights of the single bonds are as small as 1.5–2.5 kcal mol$^{-1}$. Eu$^{III}$ and Tb$^{III}$ complexes with three fod ligands should coexist as racemic mixtures of D- and L-species of C$_3$-symmetrical facial (fac)- and C$_1$-meridional (mer) motifs (Brittain and Richardson, 1977a; Jalilah et al., 2018), while even Eu$^{III}$ and Tb$^{III}$ with three dpm should coexist as a racemic mixture of D- and L-species of D$_3$-geometry. Although barrier heights of D-L stereomutation and/or fac-mer isomerism are considerably high on the order of 10–20 kcal mol$^{-1}$ (Glover-Fischer et al., 1998; Carr et al., 2012; Miyake, 2014), multiple intermolecular C-H/O-C, C-H/π, and C-H/F-C interactions (Murray-Rust et al., 1983; Nishio et al., 1998; Desiraju and Steiner, 1999; Tsuzuki et al., 2003; Yuasa et al., 2011; Koiso et al., 2017; Jalilah et al., 2018) should overcome the barriers when solidified matrices are employed. Note that solidified matrices are regarded as solid-like solvents with a very high viscosity. In this work, we applied a double-side, spin-coating technique (Guo et al., 2017, 2018) to fabricate CPL/CD-functioned films deposited onto fused quartz and/or borosilicate glass to obtain artifact-free CPL/photoluminescence (PL), CPLE/PL excitation (PLE), and CD/UV-visible spectra. CPL and CPLE spectral characterizations of Eu$^{III}$ and Tb$^{III}$ at 4f-4f transitions were assigned based on the literature (Fulgêncio et al., 2012; Tanner, 2013; Binnemans, 2015; de Queiroz et al., 2015; Xue et al., 2015; Yang et al., 2017). Dimensionless Kuhn’s anisotropic ratios in the ES and GS, being popularly known as $g_{\text{abs}}$ and $g_{\text{lam}}$ were manually evaluated at a specific extreme wavelength ($\lambda_{\text{ext}}$) of the corresponding CPL and CD spectral profiles in line with the literature (Elie and Wilen, 1994). All CPL characteristics ($g_{\text{lam}}$ value at $\lambda_{\text{ext}}$) of Eu$^{III}$ and Tb$^{III}$ complexes are summarized in Table 1.
These alkyl esters of \( \text{CABu} \) differ in the solidified films only as external chirality. For comparison, the original raw CD and UV-visible spectra of Eu(fod)\(_3\) and (–)-sign CD bands at 205 and 215 nm in the solid film are shown in Figure 2C,D, respectively. Obviously, while those in CTA film are \(-1.6 \times 10^{-4} \) at 290 nm and \(+1.1 \times 10^{-4} \) at 300 nm, respectively. Note that the \( \lambda_{\text{max}} \) values at non-polarized UV-visible spectra of Eu(fod)\(_3\) in CTA films are approximately \( \sim 291 \) nm. Although these CD bands at \( \sim 290 \) nm and \( \sim 310 \) nm are ascribed to \( n-\pi^* \)/\( \pi-\pi^* \) bands of the three fod ligands, their signs appear to be determined solely by preferential helix sense and/or local chirality of multiple alkyl esters of \( \text{CABu} \) and CTA. Contrarily, the normalized bisignate-like CPL spectral profiles between Eu(fod)\(_3\) in CABA and CTA films are apparently the same, as shown in Figures 2C,D, respectively. Obviously, bisignate CPL band profiles at \( \sim 593 \) nm and \( \sim 613 \) nm in CABA and CTA are definitively similar. The \( g_{\text{abs}} \) values of Eu(fod)\(_3\) in CABA film are \(-6.71 \times 10^{-4} \) at 290 and \( \sim 3.5 \times 10^{-4} \) at 310 nm, respectively, while those in CTA film are \(-3.5 \times 10^{-4} \) at 290 nm and \( +3.5 \times 10^{-4} \) at 310 nm, respectively. Note that the \( \lambda_{\text{max}} \) values at non-polarized UV-visible spectra of Eu(fod)\(_3\) in CABA and CTA films are \( \sim 291 \) nm. Although these CD bands at \( \sim 290 \) nm and \( \sim 310 \) nm are ascribed to \( n-\pi^* / \pi-\pi^* \) bands of the three fod ligands, their signs appear to be determined solely by preferential helix sense and/or local chirality of multiple alkyl esters of \( \text{CABu} \) and CTA.

TABLE 1 | CPL characteristics (dissymmetry ratio, \( g_{\text{abs}} \) in \( 10^{-2} \)) at specific wavelength of Eu\(^{III}\) and Tb\(^{III}\) coordinated with three \( \beta\)-diketonates as achiral ligands embedded in two polysaccharide alkyl esters (\( \text{CABu} \) and CTA), \( \text{D-/L-glucose} \) pentamethyl esters (\( \text{D-/L-Glu} \)), and \( \text{D-/L-Arabino} \) tetraceta methyl esters (\( \text{D-/L-Ara} \)).

| Ln\(^{III}\) | polysaccharide alkyl esters | CTA | Glu | Ara | \( \alpha\)-pinene |
|----------|--------------------------|-----|-----|-----|--------------------|
| \( n\text{tris}(\beta\text{-diketonates}) \) | \( g_{\text{abs}} \) in \( 10^{-2} \) (nm) | \( g_{\text{abs}} \) in \( 10^{-2} \) (nm) | \( g_{\text{abs}} \) in \( 10^{-2} \) (nm) | \( g_{\text{abs}} \) in \( 10^{-2} \) (nm) | \( g_{\text{abs}} \) in \( 10^{-2} \) (nm) |
| Eu(fod)\(_3\) | +0.61 (593) | −0.59 (613) | +0.15 (594) | −0.19 (612) | −0.02 (607) |
| Eu(dpm)\(_3\) | n.d. | n.d. | n.d. | n.d. | n.d. |
| Tbx(fod)\(_3\) | −0.29 (490) | −0.10 (490) | +0.35 (542) | −0.07 (553) | n.d. |
| Tbx(dpm)\(_3\) | −0.53 (491) | −0.44 (489) | − | n.d. | n.d. |

All numerical values in bracket mean wavelength extremum for CPL signals. \( a \) Eu\(^{III}\) \( \rightarrow \) \( D_0 \) \( \rightarrow \) \( F_1 \) (593 nm), \( b \) Eu\(^{III}\) \( \rightarrow \) \( D_0 \) \( \rightarrow \) \( F_2 \) (613 nm), \( c \) Tb\(^{III}\) \( \rightarrow \) \( D_0 \) \( \rightarrow \) \( F_2 \) (490 nm), \( d \) Tb\(^{III}\) \( \rightarrow \) \( D_0 \) \( \rightarrow \) \( F_1 \) (540 nm), \( e \) Tb\(^{III}\) \( \rightarrow \) \( D_0 \) \( \rightarrow \) \( F_2 \) (552 nm). \( f \) Not characterized or no data.

Chirality Transfer Capability From Cellulose Alkyl Esters to Eu(fod)\(_3\)

The normalized CD and UV-visible spectra of Eu(fod)\(_3\) in \( \text{CABu} \) and CTA films are shown in Figures 2A,B, respectively. For comparison, the original raw CD and UV-visible spectra of the Eu(fod)\(_3\)-hybridized films were given in Figure S1A, SM. Bisignate profile at Cotton CD bands at 290 and 310 nm between \( \text{CABu} \) and CTA films are obviously opposite. These Cotton CD bands at 290 and 310 nm, however, do not originate from \( \text{CABu} \) and CTA. Broad monosignate CD bands due to \( n-\pi^* \) transition from alkyl esters of \( \text{CABu} \) and CTA thin films appeared at \( \sim 215 \) nm with (+)-sign and \( \sim 205 \) nm with (−)-sign, respectively (Guo et al., 2018). These (+)- and (−)-sign CD bands at 205 and 215 nm in the solid film reflect from left-handed helicity of \( \text{CABu} \) and right-handed helicity of CTA in solutions, respectively (Dubois et al., 1998; Onofrei et al., 2015), though \( \text{CABu} \) and CTA are \( \beta\)-l(1–4) linked polymers made of \( D\)-glucose framework as a common repeating unit.

Although the alkyl ester itself does not have a stereogenic center, the ester can adopt particular chiral conformational geometry by the direct connection of the \( D\)-glucose ring. Two lone pairs at ethereal “O–” and two C–H groups at “–CH\(_2\)–” are no longer to be equal because of C–O=C single bonds in R-C(=O)-O–CH\(_2\)- side group act as pseudochiral stereogenic bonds, similar to gauche n-butane. The unequal lone pairs at ethereal oxygen and unequal CH\(_2\) groups may be responsible for the induction of chiral intermolecular C–O/H–C and C–H/F–C interactions between the alkyl ester moieties and lanthanide ligands. However, any CD/CPL signals of Eu(fod)\(_3\) in the presence of \( \text{CABu} \) and CTA in dilute chloroform solutions (\( \sim 10^{-3} \) M) were not able to detect because the postulated chiral intermolecular C–O/H–C and C–H/F–C interactions are inherently weak in the fluid solution. The postulated chiral alkyl esters of \( \text{CABu} \) and CTA can thus act efficiently and differently in the solidified films only as external chirality inducible scaffoldings toward optically inactive Eu(fod)\(_3\) and several lanthanide complexes, as discussed in later sections.

The \( g_{\text{abs}} \) values at \( \lambda_{\text{max}} \) of Eu(fod)\(_3\) at 290 and 310 nm in \( \text{CABu} \) film are \(-3.5 \times 10^{-4} \) at 280 nm and \(-3.5 \times 10^{-4} \) at 310 nm, respectively, while those in CTA film are \(-1.6 \times 10^{-4} \) at 290 nm and \(-1.1 \times 10^{-4} \) at 300 nm, respectively. Note that the \( \lambda_{\text{max}} \) values at non-polarized UV-visible spectra of Eu(fod)\(_3\) in CABA and CTA films are \( \sim 291 \) nm. Although these CD bands at \( \sim 290 \) nm and \( \sim 310 \) nm are ascribed to \( n-\pi^* / \pi-\pi^* \) bands of the three fod ligands, their signs appear to be determined solely by preferential helix sense and/or local chirality of multiple alkyl esters of \( \text{CABu} \) and CTA.
to efficiently induce and magnify $|\delta_{\text{L}}|$ values to optically inactive Eu(fod)$_3$ as a potent CPL emitter regardless of achiral ligands.

To confirm the apparent inconsistency between the retention in CPL bands at 4f-4f transitions in CABu and CTA films and between the inversion in CD bands at n-$\pi^1$/1-$\pi^3$ transitions in CABu and CTA films, we applied CPLE and PLE spectroscopy (Duong and Fujiki, 2017) by monitoring at $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions in CABu and CTA films, as shown in Figures 2E,F, respectively. Disregard of CABu and CTA, it is obvious that the CPLE band at 310 nm is commonly (+)-sign monitored at $^5D_0 \rightarrow ^7F_1$ transition and that the CPLE band at 310 nm is commonly (–)-sign monitored at $^5D_0 \rightarrow ^7F_2$ transition. The magnitudes of the CPLE bands in CABu film are $+4.86 \times 10^{-2}$ monitored at 589 nm and $-0.30 \times 10^{-2}$ monitored at 615 nm, respectively. Similarly, the magnitude of the CPLE bands in CTA film somewhat weaken, and $+2.96 \times 10^{-2}$ monitored at 590 nm and $-0.33 x 10^{-2}$ monitored at 615 nm, respectively.

The origin of the inconsistency between the sign at the first Cotton CD band (310 nm) and the opposite CPL sign at this wavelength that depends on the wavelengths monitored at $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions is an unresolved question and obscure. However, the n-$\pi^1$/1-$\pi^3$ bands at $\sim$310 nm with the opposite sign originates from the three fod ligands, is obviously degenerative, and is responsible for LMCT (from the
ligands to high energy levels of Eu\textsuperscript{III}, for example, $^5\Delta_2$ state, leading to $^5\Delta_0 \rightarrow ^7\Gamma_1$ and $^5\Delta_0 \rightarrow ^7\Gamma_2$ transitions with the opposite CPL sign. The broader ~310 nm transition is likely to be a convolution of two nearly degenerate transitions with an opposite chirality; one (+)-sign band at ~310 nm is responsible for $^5\Delta_0 \rightarrow ^7\Gamma_1$ and another (–)-sign band at ~310 nm for $^5\Delta_0 \rightarrow ^7\Gamma_2$ bands. The $^5\Delta_2$ state of Eu\textsuperscript{III} is close to the lowest photoexcited $^3\Pi$ states of the ligands. When one excite simultaneously at couplet-like $^1\pi-\pi^*$ transitions (~310 nm) of CD-active Eu(fod)\textsubscript{3} using monochromated non-polarized light, the photoexcited Eu(fod)\textsubscript{3} decays into the $^7\Gamma_1$ and $^7\Gamma_2$ states with two different pathways because $^5\Delta_0 \rightarrow ^7\Gamma_1$ and $^5\Delta_0 \rightarrow ^7\Gamma_2$ states are magnetic dipole (MD) allowed transition with an electric dipole (ED) forbidden transition and MD forbidden transition with a forced induced ED transition, so-called, hypersensitive transition, respectively (Tanner, 2013; Binnemans, 2015).

**Chirality Transfer Capability From Cellulose Alkyl Esters to Tb(fod)\textsubscript{3}**

The normalized CD and UV-visible spectra of Tb(fod)\textsubscript{3} in CTA and CABu films are compared in Figure 3A. For comparison, the original CD and UV-visible spectra of the films were given in Figure S13B, SM. Unlike the case of Eu(fod)\textsubscript{3}, trisignate profile at CD bands appeared at (–)-sign at 315 nm, (+)-sign at 292 nm and (–)-sign at 273 nm in CABu while (+)-sign at 322 nm, (–)-sign at 300 nm and (–)-sign at 275 nm in CTA. The apparent $g_{\text{abs}}$ values at the first Cotton band of Tb(fod)\textsubscript{3} in CABu and CTA films are $-3.5 \times 10^{-4}$ at 315 nm and $+2.0 \times 10^{-4}$ at 324 nm, respectively. CABu efficiently induced the Cotton CD band of Tb(fod)\textsubscript{3} rather than CTA, similar to the case of Eu(fod)\textsubscript{3}.

The different CD inducibility of Tb(fod)\textsubscript{3} between CABu and CTA reflects the corresponding CPL spectra at $4f-4f$ transitions of Tb(fod)\textsubscript{3}. Figure 3B shows the normalized CPL and PL spectra excited at 310 nm of Tb(fod)\textsubscript{3} in CTA and CABu films. Obviously, three CPL bands are ascribed to $^5\Sigma_4 \rightarrow ^5\Pi_6$ transition (490 nm) and $^5\Delta_4 \rightarrow ^7\Gamma_3$ transitions (540 and 552 nm), respectively (Table 1). On the other hand, we did not detect any CPL bands at $^5\Sigma_4 \rightarrow ^5\Pi_4$ transition (585 nm) and $^5\Delta_4 \rightarrow ^7\Gamma_3$ transition (622 nm) clearly though the corresponding PL band was obvious. The $g_{\text{ lum}}$ values of Tb(fod)\textsubscript{3} in CABu are $-2.91 \times 10^{-3}$ at $^5\Delta_4 \rightarrow ^5\Pi_6$ transition (490 nm), $+7.82 \times 10^{-3}$ at $^5\Delta_4 \rightarrow ^7\Gamma_3$ transition (540 nm) and $-1.75 \times 10^{-3}$ at $^5\Delta_4 \rightarrow ^7\Gamma_3$ transition (552 nm), respectively (Table 1). Those values in CTA weaken with $-1.01 \times 10^{-3}$ at $^5\Delta_4 \rightarrow ^7\Gamma_3$ transition (490 nm), $+3.53 \times 10^{-3}$ at $^5\Delta_4 \rightarrow ^7\Gamma_3$ transition (542 nm) and $-0.68 \times 10^{-3}$ at $^5\Delta_4 \rightarrow ^7\Gamma_3$ transition (553 nm), respectively (Table 1).
The first Cotton CD bands and $g_{\text{lum}}$ values of CPL bands at 4$f$-4$f$ transitions between Eu(fod)$_3$ and Tb(fod)$_3$ remain, CABu and CTA commonly induced clear CD and CPL bands.

Although the $[g_{\text{lum}}]$ values ($0.35–0.78 \times 10^{-2}$ at 540 nm, Table 1) at $^5D_4 \rightarrow ^7F_5$ transition of Tb(fod)$_3$ in CABu and CTA films are comparable to those ($0.83 \times 10^{-2}$ at 542 nm) of Tb$^{III}$(hfa)$_3$ (hfa: hexafluoroacetonate) with chiral 4,12-bis(diphenylphosphino)-[2.2]-paracyclophane (Taniguchi et al., 2019) and weaken by one order of magnitude compared to those ($4–8 \times 10^{-2}$ at $\sim$540 nm) of Tb$^{III}$ complexes coordinated with chiral bis(oxazolinyl)pyridine (Yuasa et al., 2011). The well-designed chiral ligands induce CPL-functionality to Tb$^{III}$ complexes in solution more efficiently than solidified polysaccharide alkyl esters.

**Chirality Transfer Capability From Cellulose Alkyl Esters to Eu(dpm)$_3$ and Tb(dpm)$_3$**

The dpm ligand is a symmetrical $\beta$-diketonate, in which two methyl groups of acetylacetonate are replaced by two electron-donating (ED) tert-butyl groups. Therefore, Tb(dpm)$_3$ and
Eu(dpm)$_3$ can adopt a single $D_3$-symmetrical configuration (Brittain and Richardson, 1977a; Brittain, 1980). In a recent paper (Jalilah et al., 2018) and the present work, we confirmed that Eu(fod)$_3$ in $\alpha$-pinene has shown clear CPL signals due to the presence of electron-withdrawing (EW) fluoroalkyl groups. Eu(dpm)$_3$ in $\alpha$-pinene shows no detectable CPL signals due to the lack of EW fluoroalkyl groups (Figure S14B, SM).

Tb(dpm)$_3$ in CABu and CTA films shows clear CD and UV-visible spectra in the range of 200 nm and 340 nm, as shown in Figure 4A. For comparison, the original CD and UV-visible spectra of the films are given in Figure S13C, SM. Tb(dpm)$_3$ in CABu and CTA films, however, showed detectable but weak CPL spectra at 4f-4f' transitions, as shown in Figure 4B. The $g_{\text{ lum}}$ values in CABu film are $-0.53 \times 10^{-3}$ at $^5D_4 \rightarrow ^7F_6$ (491 nm), +0.37 $\times 10^{-3}$ at $^5D_4 \rightarrow ^7F_5$ (537 nm), $-0.59 \times 10^{-3}$ at $^5D_4 \rightarrow ^7F_5$ (547 nm), while the $g_{\text{ lum}}$ values in CTA are $-0.44 \times 10^{-3}$ at $^5D_4 \rightarrow ^7F_6$ (489 nm) and $-0.80 \times 10^{-3}$ at $^5D_4 \rightarrow ^7F_5$ (547 nm) (Table 1). The absolute magnitudes of $g_{\text{ lum}}$ values with fod ligands greatly diminished compared to Tb$^{3+}$ complexes with fod ligands. Tb(dpm)$_3$ and Eu(dpm)$_3$ showed different behaviors toward external chiral chemical perturbations regardless of the same fod and dpm as the ligands. Eu(dpm)$_3$ in CABu and CTA did not demonstrate obvious CPL spectra although the corresponding PL spectra are evident (Figures S14A,B, SM).

We ascertained many times that there were no detectable CPL signals of Eu(dpm)$_3$ in CABu films. This could be because Eu(dpm)$_3$ is lack of EW-fluoroalkyl groups that can cause efficient chiral C-F/H-C interactions. Chiral C-O/H-C interactions seem not efficient to induce the chiral perturbation.

**Chirality Transfer Capability From Monosaccharide Permethyl Esters to Eu(fod)$_3$ and Tb(fod)$_3$**

Kipping and Pope found that preferential crystallization of $L$-NaClO$_3$ in the presence of naturally occurring $D$-glucose and $D$-mannitol (Kipping and Pope, 1898). Currently, non-naturally occurring $L$-glucose is available commercially, although it is costly. $L$-$\alpha$- and $D$-$\alpha$-arabinose are also available, but the $L$-form is more abundant in nature than the $D$-form due to unknown reasons. To verify whether chirogenesis of Eu(fod)$_3$ is solely determined by point chirality of monosaccharides, we measured CD and CPL spectra of Eu(fod)$_3$ embedded in $D$-$/L$-Glu and $D$-$/L$-Ara films, as displayed in Figures 5A–D.

Firstly, CD and UV-visible spectra between Eu(fod)$_3$ in $D$- and $L$-Glu films are compared in Figure 5A. The original CD and UV-visible spectra of the films are given in Figure S13D, SM. Eu(fod)$_3$ showed nearly mirror-image bisignate CD bands, though the value of $\lambda_{\text{ext}}$ at the first and second Cotton bands are considerably different from each other. The $g_{\text{ abs}}$ values of Eu(fod)$_3$ in $D$-Glu film are $+0.89 \times 10^{-4}$ at 321 nm and $-0.42 \times 10^{-4}$ at 284 nm, while in $L$-Glu film, these values are $-0.80 \times 10^{-4}$ at 321 nm and $+0.44 \times 10^{-4}$ at 282 nm (Table 1).

CD and UV-visible spectra between Eu(fod)$_3$ in $D$- and $L$-Ara films are compared in Figure 5B. The original CD and UV-visible spectra of the films are given in Figure S13E, SM. Similarly, Eu(fod)$_3$ shows nearly mirror-image bisignate CD bands, though the value of $\lambda_{\text{ext}}$ at the first and second Cotton bands are subtly different. The $g_{\text{ abs}}$ values of Eu(fod)$_3$ in $D$-$\text{Ara}$ are $-0.96 \times 10^{-4}$ at 321 nm and $+0.55 \times 10^{-4}$ at 281 nm, respectively, while in $L$-$\text{Ara}$ film, these values are $+1.08 \times 10^{-4}$ at 316 nm and $-0.39 \times 10^{-4}$ at 275 nm, respectively (Table 1).

Next, we compared CPL and PL spectra excited at 315 nm of Eu(fod)$_3$ in $D$- and $L$-Glu films, shown in Figure 5C. Eu(fod)$_3$ displays nearly mirror-image trisignate CPL bands at 4f-4f' transitions associated with emission wavelengths, though the absolute $g_{\text{ lum}}$ values at these transitions are somewhat different. The $g_{\text{ lum}}$ values in $D$-Glu are $+1.05 \times 10^{-2}$ at $^5D_0 \rightarrow ^7F_1$ (594 nm), $-0.19 \times 10^{-2}$ at $^5D_0 \rightarrow ^7F_2$ (612 nm) and $+0.19 \times 10^{-2}$ at $^5D_0 \rightarrow ^7F_2$ (626 nm), while in $L$-Glu, these values are $-0.81 \times 10^{-2}$ at $^5D_0 \rightarrow ^7F_1$ (596 nm), $+0.08 \times 10^{-2}$ at $^5D_0 \rightarrow ^7F_2$ (613 nm), and $-0.04 \times 10^{-2}$ at $^5D_0 \rightarrow ^7F_2$ (627 nm) (Table 1).

For comparison, CPL and PL spectra of Eu(fod)$_3$ in $D$- and $L$-Ara films were excited at 315 nm, and the results are presented in Figure 5D. Eu(fod)$_3$ exhibits no longer mirror-image trisignate CPL bands at 4f-4f' transitions, though the absolute $g_{\text{ lum}}$ values at these transitions weaken several times. The $g_{\text{ lum}}$ values in $D$-Ara are $+0.19 \times 10^{-2}$ at $^5D_0 \rightarrow ^7F_1$ (593 nm), $-0.02 \times 10^{-2}$ at $^5D_0 \rightarrow ^7F_2$ (607 nm), and $+0.42 \times 10^{-2}$ at $^5D_0 \rightarrow ^7F_2$ (630 nm), while in $L$-Ara, these values are $-0.30 \times 10^{-2}$ at $^5D_0 \rightarrow ^7F_1$ (591 nm), $+0.06 \times 10^{-2}$ at $^5D_0 \rightarrow ^7F_2$ (611 nm), and $-0.72 \times 10^{-2}$ at $^5D_0 \rightarrow ^7F_2$ (622 nm) (Table 1).

CPL and PL spectra of Tb(fod)$_3$ excited at 315 nm in $D$-$/L$-Glu and $D$-$/L$-Ara films are given in Figures 5E,F, respectively. Regardless of Glu and Ara, although Tb(fod)$_3$ shows very weak CPL bands at 4f-4f' transitions, CPL signs are likely to depend on the chirality of Glu and Ara. Because the absolute $g_{\text{ lum}}$ values at these 4f-4f' transitions considerably weaken, the $g_{\text{ lum}}$ values cannot be precisely evaluated.

Although $L$-cellulose is not available on earth, we can conclude that $D$-chirality of CTA, CABu, Glu, and Ara determines the (+)- and (-)-sign CPL characteristics of Eu(fod)$_3$ at $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions. Conversely, (-)- and (+)-signs at these transitions are from the $L$-chirality of Glu and Ara, although the inversion in the bisignate CD bands of Eu(fod)$_3$ at 280–290 nm and 300–310 nm are considerably dependent on the nature of the alkyl groups of CTA and CABu. Similarly, $D$-chirality of CTA, CABu, Glu, and Ara determines the (+)- and (-)-sign CPL characteristics of Tb(fod)$_3$ at two $^5D_4 \rightarrow ^7F_3$ transitions. Conversely, $L$-chirality of Glu and Ara determines the (-)- and (+)-signs at the transitions.

**Chirality Transfer Capability From $\alpha$-Pinene to Eu(fod)$_3$, Tb(fod)$_3$, Eu(dpm)$_3$, and Tb(dpm)$_3$**

Bicyclic terpenes, (1S)/(1R)-$\alpha$-pinene and (1S)/(1R)-$\beta$-pinene, are chiral rigid hydrocarbons and are transparent in the near-UV and visible region. This feature is beneficial to gain an insight into higher energy states responsible for CPL transitions by measuring CPLE spectra monitoring at a specific CPL wavelength. Actually, the chirality of $\alpha$-/$\beta$-pinenes is transferred to achiral or racemic Eu(fod)$_3$ with considerably large $g_{\text{ lum}}$ values at 4f-4f' transitions,
that were verified by CPLE spectra (Jalilah et al., 2018). This result prompted us to test whether Tb(fod)$_3$ in α-pinene reveals CPL signals, although Tb(fod)$_3$ did not show clear CPL signals because of an unknown reason.

On the other hand, Tb(dpm)$_3$ dissolved in α-pinene shows clear CPL signals, in which signs are determined solely by the chirality of the α-pinene (Figure 4C). The $g_{\text{Lum}}$ values in (1S)-α-pinene are $+4.35 \times 10^{-3}$ at $^5\text{D}_4 \rightarrow 7\text{F}_5$ (537 nm) and $-1.28 \times 10^{-3}$ at $^5\text{D}_4 \rightarrow 7\text{F}_3$ (547 nm), while in (1R)-α-pinene are $-4.94 \times 10^{-3}$ at $^5\text{D}_4 \rightarrow 7\text{F}_3$ (537 nm) and $+3.44 \times 10^{-3}$ at $^5\text{D}_4 \rightarrow 7\text{F}_5$ (548 nm), though the CPL bands at $^5\text{D}_4 \rightarrow 7\text{F}_6$ (490 nm) are not obvious (Table 1). Evidently, (+)- and (−)-sign CPL characteristics of Eu(fod)$_3$ at $^5\text{D}_0 \rightarrow 7\text{F}_1/7\text{F}_2$ transitions and Tb(dpm)$_3$ at two $^5\text{D}_4 \rightarrow 7\text{F}_2$ transitions are determined by S- and R-chirality of α-pinene, respectively. In comparison to Tb(dpm)$_3$, Eu(dpm)$_3$ in α-pinene has shown no detectable CPL signals (Figure S14C, SM). From PL spectrum of Tb(dpm)$_3$ in (R)-α-pinene excited at 320 nm associated with the corresponding CPL signals ranging of 500 and 800 nm (Figure 4F), seven characteristic $4f-4f$ transitions were assigned
to $^5D_4 \rightarrow {^7F}_6$ (490.0 nm, 20408 cm$^{-1}$), $^5D_4 \rightarrow {^7F}_5$ (545.5 nm, 18330 cm$^{-1}$), $^3D_4 \rightarrow {^7F}_4$ (584.5 nm, 17,109 cm$^{-1}$), $^5D_4 \rightarrow {^7F}_3$ (620.0 nm, 16129 cm$^{-1}$), $^5D_4 \rightarrow {^7F}_2$ (652.5 nm, 15,326 cm$^{-1}$), $^5D_4 \rightarrow {^7F}_1$ (682.0 nm, 14,663 cm$^{-1}$), and $^5D_4 \rightarrow {^7F}_3$ (702.5 nm, 14,235 cm$^{-1}$) (Fulgêncio et al., 2012; de Queiroz et al., 2015; Xue et al., 2015; Yang et al., 2017).

We further verified these CPL signals of Tb(dpm)$_3$ by the broad CPLE spectra centered at $\sim 300$ nm associated with the corresponding PLE spectra with several shoulders, as marked by blue, pink, and green bars in Figures 4D,E. The signs of the CPLE spectra depend on the signs at monitor wavelengths (535 and 548 nm) and $\alpha$-pinine chirality; (+)-sign in CPLE spectrum is identical to (+)-sign CPL signal at 546 nm in (R)-pinene, while (+)-sign in CPLE spectrum is the same of (+)-sign CPL signal at 535 nm in (S)-pinene. The broad CPLE/PLE spectra may arise from at least three different origins of $n$-$\pi^*$/$\pi$-$\pi^*$ transitions of three dpm ligands associated with high energy levels (e.g., $^3D_1$ and $^5D_2$) of Tb$^{III}$ (Fulgêncio et al., 2012; de Queiroz et al., 2015; Xue et al., 2015). A similar tendency can be seen in the broad CPLE/PLE spectra of Tb(fod)$_3$ in CABu, as marked in blue, pink, and green bars in Figures 3C,D.

Unresolved factors between Tb$^{III}$ and Eu$^{III}$ associated with ligands (fod and dpm) and chiral matrices ($\alpha$-pinine and monosaccharide alkyl esters) are other critical parameters to generate CPL signals and boost $g_{\text{lum}}$ characteristics. Although the inherent nature of the differences between Tb$^{III}$ and Eu$^{III}$ is unresolved, we assume that the interactions of C($\delta$--)-$H$($\delta$+) bonds of dpm of Tb(dpm)$_3$ and C($\delta$+)-C($\delta$--) double bond of $\alpha$-pinine are more crucial while the C-$F$/H-C interactions between C($\delta$+)-F($\delta$--) bonds of fod ligands and H($\delta$+)-C($\delta$--) bonds of $\alpha$-pinine are crucial (Jalilah et al., 2018).

### Intermolecular Interactions Between Eu(fod)$_3$ and CTA/Glu by Solid-State $^{13}$C($^1$H)-NMR and Solution $^1$H/$^{19}$F-NMR Spectra

We do not yet know what kinds of intermolecular noncovalent interactions exist between the lanthanide tris($\beta$-diketonate) and the poly-$\alpha$-monosaccharide alkyl esters. Among lanthanide tris($\beta$-diketonate)$_3$, we chose Eu(fod)$_3$ for simplicity and excellent solubility in CDCl$_3$. The three fod ligands have $^1$H, $^{19}$F, and $^{13}$C-NMR active elements to discuss the possible interactions. Additionally, we chose CTA and D-/L-Glu for simplicity in these solid-state ($ss$-$^{13}$C-NMR and solution $^1$H/$^{19}$F-NMR spectra. According to the hard-soft-acid-base theory proposed by Pearson (Pearson, 1963), the lone pairs of the hard base O atom(s) of ester groups can coordinate with the hard acid Eu$^{III}$ of Eu(fod)$_3$. A marked chemical shift in $^{13}$C-NMR spectra of ester (C=O and O) and ethereal C--O--C atoms was expected.

The $ss$-$^{13}$C($^1$H)-NMR spectra of Eu(fod)$_3$, CTA, and a mixture of Eu(fod)$_3$ and CTA in 1/1 (w/w) are compared in Figures 6A,B. The $ss$-$^{13}$C-NMR spectra of the Eu(fod)$_3$-CTA mixture are merely a convolution of those of CTA and Eu(fod)$_3$. Any noticeable chemical shift in the $^{13}$C-NMR spectra was not seen. $^{13}$C-NMR chemical shift at $\sim 170$ ppm due to O=C=O of CTA was unchanged after mixing with Eu(fod)$_3$.

The $ss$-$^{13}$C($^1$H)-NMR spectra of Eu(fod)$_3$, D-Glu, and a mixture of Eu(fod)$_3$ and D-Glu in 1/1 (w/w) are compared in Figures 6C-G. Similarly, the $ss$-$^{13}$C-NMR spectra of the Eu(fod)$_3$-D-Glu mixture are merely a convolution of those of D-Glu and Eu(fod)$_3$. Any remarkable chemical shift in the $^{13}$C-NMR spectra was not seen. Even five well-resolved O=C=O peaks of D-Glu pentamethyl ester ranging of $\sim 169$ ppm and $\sim 173$ ppm showed no detectable chemical shifts (Figure 6D). Similarly, no noticeable chemical shifts of three well-resolved methyl groups ranging from $\sim 19$ ppm to $\sim 22$ ppm were observed (Figure 6E). Among five well-resolved $^{13}$C peaks assignable to O=C=O of five esters, C--O=C--pyranose ring ranging from $\sim 64$ to $\sim 72$ ppm and at $\sim 83$ ppm does not show remarkable chemical shifts of D-glucose ring. These $ss$-$^{13}$C($^1$H)-NMR data led us to the conclusion that any O atom(s) of glucose ring and ester moieties do not coordinate directly to Eu$^{III}$ ions.

On the other hand, alterations in the chemical shifts of the solution $^{19}$F-NMR spectra of Eu(fod)$_3$ in the absence and presence of CTA, D-Glu, and L-Glu in CDCl$_3$ are apparent, as shown in Figures 7A–C. The outer CF$_3$ signal of Eu(fod)$_3$ in CDCl$_3$ resonates at $\sim 81.73$ ppm as a single peak, indicating C$_3$-symmetrical geometry (Figure 7B). The single peak resonates at $\sim 82.21$ ppm and $\sim 82.26$ ppm in the absence and presence of L-Glu and D-Glu, respectively, and shifts upfield by 0.48 ppm and 0.53 ppm, respectively (Figure 7B). In the presence of CTA, the CF$_3$ signal resonates at $\sim 82.31$ ppm and shifts upfield by 0.58 ppm (Figure 7B). Although the middle CF$_2$ signal of fod ligand resonates broadly at $\sim 126$ ppm, in the presence of L-Glu and D-Glu, this signal resonates at $\sim 127.4$ ppm and $\sim 127.5$ ppm, that is shifted upfield by 1.4 ppm and 1.5 ppm, respectively (Figure 7C). Similarly, the middle CF$_2$ peak at $\sim 127.5$ ppm shifts upfield by 1.5 ppm in the presence of CTA (Figure 7C). The inner CF$_2$ of fod shows a broad resonance at $\sim 129.2$ ppm, but this signal appears at $\sim 130.1$ ppm in the presence of L- and D-Glu and shifts upfield by 0.9 ppm (Figure 7C). Similarly, the signal appears at $\sim 130.3$ ppm in the presence of CTA and shifts upfield by 1.1 ppm. These upfield shifts in the $^{19}$F-NMR spectra indicate intermolecular interactions between the F atoms and CTA, L-Glu, and D-Glu, possibly, C-F($\delta$+)-(of the three fod ligands)/H($\delta$+)-C (of CTA and Glu) interactions. It is thus evident that there were no marked alterations in ss-$^{13}$C-NMR spectra between CPL-inactive and CPL-active Eu(fod)$_3$ in CTA, L-Glu, and D-Glu, while the remarkable upfield chemical shifts in $^{19}$F-NMR of fod ligands in dilute CDCl$_3$ solution was distinct. These characteristics should arise from outer or second-sphere effects perturbed by chiral chemicals that are non-coordinating to Eu$^{III}$, the so-called ‘Pfeiffer effect’. The multiple H($\delta$+)-C($\delta$--) bonds of chiral chemical species (CTA, D-/L-Glu, possibly, D-/L-Ara and CABu) interact with multiple F($\delta$+)-C($\delta$--) bonds of the three fod ligands but do not directly coordinate with Eu$^{III}$.

The noticeable downfield chemical shifts in $^1$H-NMR spectra of D-Glu and CTA support the postulated C($\delta$+)-F($\delta$--) (of fod) and H($\delta$+)-C($\delta$--) (of CTA and D-/L-Glu) interaction. Figure 8A displays the changes in $^1$H-NMR spectra of D-Glu in the absence and presence of Eu(fod)$_3$. All protons are assigned in the inset of the Figure. The degree of the downfield shifts is summarized...
FIGURE 6 | (A) Solid-state (ss)-CP/MAS-\(^{13}\)C\{\(^{1}\)H\}-NMR spectra of Eu(fod)\(_3\), CTA, and a mixture of Eu(fod)\(_3\) and CTA in 1/1 (w/w). (B) Its magnified spectrum in the range of 150–200 ppm. (C) ss-\(^{13}\)C\{\(^{1}\)H\}-NMR spectra of Eu(fod)\(_3\), D-Glu, and a mixture of Eu(fod)\(_3\) and D-Glu in 1/1 (w/w) (D,E). Their magnified spectra of methyl groups in D-Glu in the range of 150–200 ppm and 16–24 ppm (F,G). (D,E). Their magnified spectra of D-glucose ring in the range of 62–90 ppm. A broad \(^{13}\)C-NMR signal at 130 ppm (Figures 5A,C) was attributable to \(\beta\)-diketonate.
in Table 2. Notably, protons H1, H3, H5, H6 shift downfield significantly and protons H2, H4, H6 (one of two), H7 also considerably shift downfield. We noticed that H1, H3, H5 are the glucose ring protons and H6 is the CH$_2$ attached to C5 carbon. Possibly, Eu(fod)$_3$ molecule is placed on top of the D-glucose ring. All H1–H7 protons are close to Eu(fod)$_3$ molecule with the help of multiple C($\delta$+)/F($\delta$–)/H($\delta$+)/C($\delta$–) and C($\delta$–)/H($\delta$+)/O($\delta$–)/C($\delta$+) interactions.

Figure 8B exhibits similar changes in $^1$H-NMR spectra of CTA in the absence and presence of Eu(fod)$_3$. Protons are assigned in the insets of the figure. The degree of downfield shifts is summarized in Table 2. Notably, protons H1, H3, H5, H6 shift downfield significantly and protons H2, H4, H6 (one of two), H7 also considerably shift downfield. We noticed that H1, H3, H5 are the glucose ring protons and H6 is the CH$_2$ attached to C5 carbon. Possibly, Eu(fod)$_3$ molecule is placed on top of the D-glucose ring. All H1–H7 protons are close to Eu(fod)$_3$ molecule with the help of multiple C($\delta$+)/F($\delta$–)/H($\delta$+)/C($\delta$–) and C($\delta$–)/H($\delta$+)/O($\delta$–)/C($\delta$+) interactions.

For comparison, FT-IR spectra between Eu(fod)$_3$, D-Glu, and Eu(fod)$_3$ mixed with D-Glu in the ranges of 2,700 and 3,700 cm$^{-1}$, 2,800 and 3,100 cm$^{-1}$, and 1,000 and 2,000 cm$^{-1}$ are shown in Figures S15A–C, SM. We observed no noticeable frequency shifts in $\nu$(C-H) at 2,850–3,000 cm$^{-1}$ and $\nu$(C-F) at 1,250–1,050 cm$^{-1}$. Since the postulated C-F/H-C and C-H/O-C interactions are very weak, the resulting frequency shifts might be minimal, possibly, within 10 cm$^{-1}$. One $\nu$(C-H) at 2973 cm$^{-1}$ and $\nu$(C-H) at 2873 cm$^{-1}$ due to methyl groups of fod in the absence of D-Glu shift to lower frequencies at 2967 cm$^{-1}$ by 7 cm$^{-1}$ and 2871 by 2 cm$^{-1}$, respectively (Figure S15B, SM). These small shifts may be the consequence of the C-H/O-C interactions. On the other hand, $\nu$(C=O) at $\sim$1,750 cm$^{-1}$ characteristic of five ester group of D-Glu does not coordinate to Eu$_{III}$ directly because there are no noticeable frequency shifts (Figure S15C,
Comparison of $^1$H-NMR spectra in CDCl$_3$ at room temperature between (A) $D$-Glu (blue) and Eu(fod)$_3$ with $D$-Glu (red) and between (B) CTA (blue) and Eu(fod)$_3$ with CTA (red). Sharper and broader $^1$H-NMR peaks at $\sim$1.5 ppm are assumed to be free water in CDCl$_3$ and bounded waters at Eu(fod)$_3$, respectively. Although 20 mg of $D$-Glu and 10 mg of Eu(fod)$_3$ were able to co-dissolve in 0.6 mL of CDCl$_3$, 10 mg of CTA and 10 mg of Eu(fod)$_3$ were co-dissolved in 0.6 mL of CDCl$_3$ because of the limited solubility of 20 mg CTA in 0.6 mL of CDCl$_3$. 

**FIGURE 8** | Comparison of $^1$H-NMR spectra in CDCl$_3$ at room temperature between (A) $D$-Glu (blue) and Eu(fod)$_3$ with $D$-Glu (red) and between (B) CTA (blue) and Eu(fod)$_3$ with CTA (red). Sharper and broader $^1$H-NMR peaks at $\sim$1.5 ppm are assumed to be free water in CDCl$_3$ and bounded waters at Eu(fod)$_3$, respectively. Although 20 mg of $D$-Glu and 10 mg of Eu(fod)$_3$ were able to co-dissolve in 0.6 mL of CDCl$_3$, 10 mg of CTA and 10 mg of Eu(fod)$_3$ were co-dissolved in 0.6 mL of CDCl$_3$ because of the limited solubility of 20 mg CTA in 0.6 mL of CDCl$_3$. 

*Frontiers in Chemistry* | *www.frontiersin.org*  
*August 2020 | Volume 8 | Article 685*
SM). Although, in the absence of D-Glu, Eu(fod)$_3$ has one broad and one shoulder $\nu$(C=O) band at 1621 cm$^{-1}$ and 1594 cm$^{-1}$ due to the $\beta$-diketonate, in the presence of D-Glu, the shoulder $\nu$(C=O) may disappear and merge to 1621 cm$^{-1}$ or shift to 1642 cm$^{-1}$ due to specific alteration of $\beta$-diketonates. Other frequency shifts such as $\nu$(C-O-C) at $\sim$1200 cm$^{-1}$ and 1150 cm$^{-1}$ of the ester groups and glucose rings of D-Glu are not apparent because of significant overlapping with other intense $\nu$(C-F) bands. The C-F/H-C interactions are not obvious due to the significant overlapping.

**Table 2** Comparison of chemical shifts in the $^1$H-NMR spectra in CDCl$_3$ at room temperature between (a) D-Glu without and with Eu(fod)$_3$ and between (b) CTA without and with Eu(fod)$_3$, whereas (+)-sign stands for the downfield shift.

|            | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   |
|------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| D-Glu      | 6.31| 5.45| 5.14| 5.09| 4.26| 4.09| 2.17| 2.08| 2.01|
| Eu(fod)$_3$ in D-Glu | 7.55| 6.53| 6.53| 6.17| 5.93| 5.61| 4.99| 3.16| 2.58|
| Relative shifts of $^1$H-NMR | +1.24| +1.08| +1.39| +1.08| +1.67| +1.52| +0.90| +0.99| +0.50| +0.41| +0.43|
| CTA        | 5.05| 4.78| 4.37| 4.04| 3.70| 3.52| 2.10| 1.99| 1.92|
| Eu(fod)$_3$ in CTA | 6.38| 6.31| 5.12| 5.05| 4.67| 4.49| 4.13| 2.40| 2.31|
| Relative shifts of $^1$H-NMR | +1.33| +1.53| +0.75| +1.01| +0.93| +0.79| +0.61| +0.30| +0.32| +0.11|

**Table 3** Lifetimes of photoexcited Eu(fod)$_3$, Eu(dpm)$_3$, and Tb(dpm)$_3$ embedded to CTA and CABu films$^a$.

| Lanthanide complexes | Eu(dpm)$_3$ | Eu(dpm)$_3$ | Eu(fod)$_3$ | Eu(fod)$_3$ | Tb(dpm)$_3$ | Tb(dpm)$_3$ |
|----------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Poly(D-saccharides)  |             |             |             |             |             |             |
| CABu                 | 0.22$^a$    |             |             |             |             |             |
| CTA                  |             | 0.29$^b$    |             |             |             |             |
| CABu                 |             | 0.44$^a$    |             |             |             |             |
| CTA                  |             | 0.50$^b$    |             |             |             |             |
| CABu                 |             | 0.59$^a$    |             |             |             |             |
| CABu                 |             | 0.92$^b$    |             |             |             |             |

$^a$Pulsed Nd laser, 337.1 nm, 10 Hz repetition, Grating 150 lines per mm, slit width 100 μm.

$^b$At room temperature, detected at 615 nm (collected from 610 to 620 nm), $^c$detected at 546 nm (collected from 542 to 551 nm).

Photodynamics of Eu(fod)$_3$, Eu(dpm)$_3$, and Tb(dpm)$_3$ in CTA and CABu Films

Lifetimes of Eu(fod)$_3$, Eu(dpm)$_3$, and Tb(dpm)$_3$ species embedded to CTA and CABu films excited at an N$_2$ pulsed laser 337.1 nm are summarized in Table 3 based on decay curves (semilog and linear plots) of these emitters (Figures S17A–K, SM). The decay times ($\tau$) of these emitters in CABu are somewhat long by the magnitude of 15–56 % compared to those in CTA. Possibly, these emitters have differently interacted with CTA and CABu, that depends on the nature of alkyl esters. Alternatively, regardless of CTA and CABu, the values of $\tau$ belong to the order of Eu(fod)$_3$, Eu(dpm)$_3$, and Tb(dpm)$_3$, depending on the nature of lanthanides and ligands.

**Mulliken Charges of Sc$^{III}$ Tris($\beta$-diketonate) as Models of Eu$^{III}$/Tb$^{III}$ Tris($\beta$-diketonate), D-Glu and D-Glu Dimer as a Model of CTA Obtained With MP2 (6-311G) Calculation**

To theoretically discuss possible intermolecular interactions, we calculated Mulliken charges (Mulliken, 1955) by the Møller–Plesset second-order perturbation theory (MP2) (Møller and Plesset, 1934; Head-Gordon et al., 1988) (6-311G basis set) method of the model compounds optimized by MM (UFF force filed), followed by DFT [6-31G(d)] methods (Frisch et al., 2013). Time-consuming MP2 calculation allows for reliable Mulliken charges compared to DFT calculation. Figure 9 and Figure S18, SM display the numbering for all the atoms in the D-Glu and D-Glu dimer as a model of CTA. All the peripheral hydrogen atoms of D-Glu and D-Glu dimer show positive Mulliken charges ranging from +0.215 to +0.261. The O=C atoms of methyl esters have substantial negative Mulliken charges of −0.464. We observed that the O=C atoms of methyl esters and the C–O=C atom in pyranose rings and C–O=C linkage between two pyranose rings show more substantial negative Mulliken charges ranging from −0.652 to −0.690, respectively. When $\delta$(−)$-H(\delta+)$ bond of the ligands (fod and dpm) feels the force
of oxygen atoms, the $\text{C(δ+)−O(δ−)−C(δ+)−O(δ−)−}$ bond of esters, leading to (ligand, C−H)/O (D-Glu, possibly, CTA, CABu, Glu, and Ara) interactions.

In the previous paper (Jalilah et al., 2018), we proposed that the surplus charge neutralization obtained with Mulliken charges is a driving force of attractive forces between several ligands in the lanthanide complexes and CPL-inducible chiral substances. The fluorine atoms of Sc(fod)$_3$ have negative Mulliken charges ranging from $-0.341$ to $-0.373$; conversely, the hydrogen atoms of Sc(fod)$_3$ and Sc(dpm)$_3$ have positive Mulliken charges ranging from $+0.153$ to $+0.193$.

The Mulliken charge neutralization between multiple (δ−) fluorines of fod and multiple (δ+) hydrogens of D-Glu and the saccharides is possible. Total surplus charge between C(δ+)-F(δ−) (fod) and H(δ+)−C(δ−) (saccharides, in this work) is that $3 \times (-0.35) \times (4\sim5) \times (+0.20 \sim +0.24) \times (\alpha$-pinene) is $-0.05 \sim -0.09$. Additionally, the Mulliken charge neutralization between multiple (δ+) hydrogens of the ligands (fod and dpm) and multiple (δ−) oxygen atoms of the saccharides are possible. Total surplus charge between (fod or dpm) C(δ−)-H(δ+) and O(δ−)-C(δ+) (saccharides) is that $(4) \times (+0.17) \times (−0.62 \sim −0.69) \times (O-C or O-C=O) = +0.06 \sim −0.01$. Moreover, total surplus charge between (dpm and fod) C(δ−)-H(δ+) and O(δ−)-C(δ+) (α-pinene) is that $(1) \times (+0.17) \times (H-C) + (1) \times (C-C) = −0.01$; Tb(dpm)$_3$ is a dominant factor, while Eu(dpm)$_3$ is unimportant. However, it is reasonably assumed that the same Mulliken charges between multiple (δ+) hydrogen atoms of ligands (fod and dpm) and multiple (δ+) hydrogen atoms of the saccharides should cause repulsive interactions.

**The Degree of Chirogenesis and the Pfeiffer Effects**

Since the serendipitous finding by an anomaly in an optical rotation of chiral substances in the presence of optically inactive labile metal ions in aqueous solutions (Pfeiffer and Quehl, 1931, 1932), the chirogenesis in the GS and ES from
optically inactive labile metal complexes induced by chiral additives has been often observed in the titles of several papers in the past and currently: e.g., Pfeiffer effect (Kirschner and Ahmad, 1968; Mayer and Brasted, 1973; Schipper, 1978; Brittain, 1982, 1984; Kirschner and Bakkar, 1982; Lunkley et al., 2018); outer-sphere coordination and complexation (Mason and Norman, 1965; Madaras and Brittain, 1980; Kirschner and Bakkar, 1982); second-phase coordination (Colquhoun et al., 1986). Pfeiffer effect and/or outer-sphere/second-phase coordination are mainly investigated in their solution states of the metal complexes.

An equilibrium shift from dynamic racemic mixtures (Δ : A = 50/50) of labile metal complexes is responsible for the Pfeiffer effect and chirogenesis by outer-sphere/second-sphere coordination. A barrier height of racemization should be rather small to permit dynamic racemization at ambient temperatures. In 1975, Schipper theoretically discussed chemical discrimination between racemic substances (A’ and A") and chiral substance B surrounded by achiral solvent (discrimination between racemic substances (A’ and A") and chiral substance B). Collectively, we thus conclude that the Pfeiffer effect and chirogenesis by outer-sphere/second-sphere coordination is responsible for multiple pseudo chiral O/H–C interactions in dynamic association system is devoted to overcome thermal fluctuation k_BT.

To quantitatively discuss the degree of chirogenesis in six-coordinate labile lanthanide tris(β-diketone) led by chiral additives in solution, we compare four solution PL spectra of Eu(fod)₃ itself (10 mg, 0.8 × 10⁻² M, red line) and in the presence of D-Glu (20 mg, 4 × 10⁻² M, blue line), L-Glu (20 mg, 4 × 10⁻² M, green line), and CTA (10 mg, 3 × 10⁻² M, black line) in 1.2 mL of CDCl₃ (Figure S19, SM). These CDCl₃ solutions were used prior to measurements of ¹⁹F- and ¹H-NMR spectra (Figure 7). Among ⁵D₀-⁵F₁ (J = 0,1,2,3,4) transitions, ⁵D₀-⁵F₁ transition at 594 nm is known to be susceptible to alterations in molecular symmetry and geometry coordinated with external ligands. Our previous investigation suggests that Eu(fod)₃ is likely to adopt a facial C₃-symmetrical structure and exists as a mixture of labile Δ - and Δ-isomers in solutions (Jalilah et al., 2018). Similar Pfeiffer effect was reported for D₃-symmetrical labile TbIII(dpa)₃ in the absence and presence of L-histidine, revealing no significant alteration in PL and CPL spectral profiles at 7F5-5D4 transition (Wu et al., 1989).

From Figure S19A in SM, we can see minimal alterations in magnitudes, wavelengths, and profiles in PL bands of Eu(fod)₃ (non-chiral additive (red line), D-Glu (blue line), L-Glu (green line), and CTA (black line)) at the five ⁵D₀-⁵F₁ (J = 0,1,2,3,4) transitions. Any apparent change in PL wavelength (593.0 nm) of Eu(fod)₃ (non-chiral additive, D-Glu, L-Glu) is not detectable, while subtle changes in wavelength and magnitude in PL spectra of Eu(fod)₃ (non-chiral additive, D-Glu) is discernable. Clearly, PL intensity at ⁵D₀-⁵F₁ transition (580 nm) of non-chiral additive Eu(fod)₃ increases in the presence of chiral additive in the order of L-Glu < D-Glu < CTA. Similar alterations in subtle increases and subtle spectral shifts at ⁵D₀-⁵F₁ (J = 2,3,4) transitions between Eu(fod)₃ (non-chiral additive, D-Glu, L-Glu, and CTA) is observable (Figures S19C–E, SM). We thus conclude that C₃-symmetrical Eu(fod)₃ in CDCl₃ (0.8 x10⁻² M) maintains in the presence of L-Glu, D-Glu, CTA (3–4 × 10⁻² M, 4–5-folds excess relative to Eu(fod)₃).

To confirm the dynamic equilibrium shift of the Δ-Δ isomers, we compare CPL and PL spectra of (a) Eu(fod)₃ (0.8 × 10⁻² M, 10 mg) and CTA (3 × 10⁻² M, 20 mg) in 1.2 mL of CDCl₃ (red line) and (b) thin solid films of Eu(fod)₃ (10 mg, ~5 × 10⁻¹ M) in CTA (20 mg) annealed at 100 °C in a vacuum overnight (blue line).

Previously, a simple thermodynamic analysis confirmed that the binding constant K_B using g_lum value at ⁵D₀-⁵F₁ transition between Eu(fod)₃ and rigid chiral hydrocarbon, α-pinene, was on the order of 10⁻³ M⁻¹; 0.7 × 10⁻³ M⁻¹ for (1S)-α-pinene and 1.0 × 10⁻³ M⁻¹ for (1R)-α-pinene (Jalilah et al., 2018). When a solvent quantity of α-pinene was used, even minimal K_B value was characterized as g_lum by CPL spectroscopy.

When a similar analysis was applied to Eu(fod)₃ and non-rigid chiral CTA, we obtained K_B = 0.09 M⁻¹ (Figures S21A,B, SM). This K_B value is more significant than that of α-pinene by two orders of magnitude and it is reasonable because a chiral repeating unit in CTA (though non-rigid and floppy) contains five oxygen atoms with the substantial (−)-Mulliken charges responsible for multiple pseudo chiral O/H–C interactions with achiral ligands (Figure 9 and Figure S18, SM). When solidified film and high concentrations of CTA were employed as chirality inducible scaffolds and platforms, the degree of chirogenesis was characterizable as g_lum values from CPL spectral characteristics. This idea can be extended to CABu and other four monosaccharide alkyl esters (Table 1).

CONCLUSION

Two polysaccharide alkyl esters (CTA and CABu) as the films, two enantiopairs of monosaccharide permethyl esters (D-L/Glu and D/L-Ara) as the films, and (1S)/(1R)-α-pinene in solution were capable of transferring their chirality to several optically inactive EuIII and TbIII tris(β-diketone) (= fod and dpm), which impart the shining CPL characteristics at 4f-4f transitions. The greatest g_lum values at ⁵D₀ → ⁷F₁ transitions (λ_ex = 315 nm) of Eu(fod)₃ in CABu and CTA films are +0.067 and +0.046, respectively. Tb(fod)₃ in CABu and CTA exhibited moderately large g_lum values of +0.008 and +0.004 at ⁵D₄ → ⁷F₅ transitions (λ_ex = 315 nm), respectively. Meanwhile, D-L/Glu and D-L-Ara films induced weaker g_lum values for Eu(fod)₃, Tb(fod)₃, and Tb(dpm)₃. CTA and CABu induced CPL signals more efficiently for Eu(fod)₃ than D-L/Glu and D-L-Ara. Noticeably, the chirality of α-pinene enabled Tb(dpm)₃ to shine similar CPL characteristics of Tb(fod)₃ in CABu. However, Eu(dpm)₃ in CABu films and α-pinene did not reveal CPL. From the analyses of solution ¹H-/¹⁹F-NMR, solid-state ¹³C-NMR with the help of MP2 (6–311G basis set) calculation, we propose that the surplus charge neutralization evaluated by the opposite Mulliken charges between H(δ+)–C(δ−) bonds of the poly- and monosaccharides and F(δ−)–C(δ+) bonds of the fluorinated ligands are the attractive driving forces to induce the CPL characteristics of Tb(fod)₃ and Eu(fod)₃. The present knowledge should enable the
fabrication of films, sheets, fibers, and nanocomposites that emit Eu\textsuperscript{III}-origin red-color and Tb\textsuperscript{III}-origin green-color CPL spectra with narrow spectral bandwidths. As demonstrated, Eu\textsuperscript{III}(fod)\textsubscript{3} and Tb\textsuperscript{III}(dpm)\textsubscript{3} containing transparent CTA films deposited on the Tempax substrate displayed clear Eu\textsuperscript{III}-origin red-color and Tb\textsuperscript{III}-origin green-color emissions upon 365-nm excitation (see, photographs in Figure S22, SM). These materials were obtainable by a chiral ligand-free process at room temperature by co-mixing soluble poly saccharide derivatives (and bacterial cellulose) and several optically inactive Eu\textsuperscript{III}/Tb\textsuperscript{III} complexes. The challenging issue remains to boost the rather small \(g_{\text{lu}}\) values [Eu(fod)]\textsubscript{3}: 6 \(\times\) 10\textsuperscript{-2} at 593 nm and Tb(fod)\textsubscript{3}: 0.8 \(\times\) 10\textsuperscript{-2} at 540 nm toward an ultimate \(g_{\text{lu}} = \pm 2.0\), i.e., obtaining purely left- or right-CPL forms (Elie and Wilen, 1994). Symmetry-oriented designing of emitters should be considered by precisely controlling the topology shape associated with an efficient lens and an optofluidic effect (Wang et al., 2007; Di Pietro and Di Bari, 2012; Kruk et al., 2014; Khorasaninejad et al., 2016; Yeung et al., 2017; Tanaka et al., 2018; Zhou et al., 2019). A deeper understanding of the Pfeiffer effect in the GS and ES, magnetic dipole transitions of Eu\textsuperscript{III} and Tb\textsuperscript{III} complexes, colloidal aggregations, hybridization by other chromophores/luminophores, chain-like polymers, supramolecular motifs and polymers, and nature of oligo- and polysaccharides with conformational freedom are the next challenges (Wormald et al., 2002; Zou et al., 2019) in addition to several approaches to elaborate CPL and CD functions as polymeric colloids, revealing moderately high \(|g_{\text{lu}}|\) and \(|K_{\text{an}}|\) values (\(>10\textsuperscript{-2}-10\textsuperscript{-1}\)) in the range of 300 and 800 nm (Nakano and Fujiki, 2011; Duong and Fujiki, 2017; Fujiki and Yoshi moto, 2017; Wang et al., 2017).

However, our approaches of chirogenesis from optically inactive labile Ln\textsuperscript{III} tris(\(\beta\)-diketonate) (Ln: lanthanide) induced by soluble chiral biomaterials is very limited to common organic solvents of Ln\textsuperscript{III} complexes and biomaterials. If watersoluble optically inactive labile Ln\textsuperscript{III} complexes are designed in the future, our approaches are applicable as a thin film state to sense and detect various water-soluble chiral substances including biomaterials, drug, medicine, pesticide, and virus consisting of illness-causing single-strand (ss)/double-strand (ds) RNA.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation. Requests for the original CPL/CPL/CD/UV-visible/NMR/IR spectral and photodynamic data sets, followed by the processed data (#.qpc with #.qda and #.txt) using KaleidaGraph (mac, ver 4.53), and the calculation results (#.com, #.log, and #.chk up to 20 GB) of Gaussian09 (mac) to support the conclusion of this article should be sent to MF (fujikim@ms.naist.jp).

AUTHOR CONTRIBUTIONS

All the authors co-designed this work. MF, LW, and AJ co-wrote the paper. LW, NO, AJ, and MF co-measured and co-analyzed the CPL, CPLE, CD, UV-visible, PL, and PLE spectra of Tb(fod)\textsubscript{3}, Eu(fod)\textsubscript{3}, Tb(dpm)\textsubscript{3}, and Eu(dpm)\textsubscript{3} and other several lanthanide complexes in the presence of chiral additives and chiral solvents. LW and FA co-acquired and co-analyzed ss-\(^{13}\)C[\(1\)H]-FT-NMR and solution \(^1\)H-NMR/\(^{19}\)F-NMR spectra. FA conducted the elemental analysis of the products. MF performed MP2 and DFT calculations. LW, NO, AJ, AO, SO, HK, and MF contributed to a joint project of emerging CPL spectra from achiral organic, polymeric, and lanthanide luminophores endowed with chiral polymers and chiral solvents. All authors discussed the data and commented on the manuscript. All authors have given approval to the final version of the manuscript. These authors contributed equally. The manuscript was written through contributions of all authors.

FUNDING

MF thanks for the funding for Japan Society for the Promotion of Science (KAKENHI, 16H04155). AJ would like to acknowledge the support from the Fundamental Research Grant Scheme (FRGS) under a grant number RACER/1/2019/TK05/UNIMAP//1 from the Ministry of Higher Education Malaysia.

ACKNOWLEDGMENTS

MF and AJ owe a debt of gratitude to Prof. Victor Borovcov (South-Central University for Nationalities, Wuhan, China) for giving us the opportunity to contribute to this special issue. LW and MF acknowledge Prof. Wei Zhang (Soolochow University, China) for providing D-Glu. We thank Dr. Sibo Guo for assisting the chiroptical measurements. We thank Yoshiko Nishikawa for measuring and analyzing mass spectral data sets of D-/L-Glu, D-/L-Ara, Tb(fod)\textsubscript{3}, Eu(fod)\textsubscript{3}, Tb(dpm)\textsubscript{3}, and Eu(dpm)\textsubscript{3}, Yasuo Okajima for measuring photodynamics of Eu(fod)\textsubscript{3}, Eu(dpm)\textsubscript{3}, and Tb(dpm)\textsubscript{3} embedded to CTA and CABu specimens, and Prof. Tsuyoshi Ando for the permission to use Perkin Elmer FT-IR spectrometer.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2020.00685/full#supplementary-material Characterization (\(^1\)H-/\(^{19}\)F-NMR, CP-MAS-\(^{13}\)C-FT-NMR, FT-IR, HR-ESI-MS spectra) of CTA, CABu, D-/L-Glu, D-/L-Ara, Eu(fod)\textsubscript{3}, Tb(dpm)\textsubscript{3}, and Eu(dpm)\textsubscript{3}. Detailed measurement and analytical conditions of all instruments (solution \(^1\)H-/\(^{19}\)F-FT-NMR, solid-state CP-MAS-\(^{13}\)C-FT-NMR). CPL/PL spectra of Eu(dpm)\textsubscript{3} in CABu and Eu(dpm)\textsubscript{3} in (S)-/(R)-\(\alpha\)-pinene. Mulliken charges of D-Glu dimer obtained with MP2 (6-311G basis set) calculation. Photodynamic decay curves of Eu(dpm)\textsubscript{3} in CTA, Eu(dpm)\textsubscript{3} in CABu, Eu(fod)\textsubscript{3} in CTA, Eu(fod)\textsubscript{3} in CABu, Tb(dpm)\textsubscript{3} in CTA, and Tb(dpm)\textsubscript{3} in CABu, raw CD and UV-visible spectra of Eu(fod)\textsubscript{3}, Tb(fod)\textsubscript{3}, and Tb(fod)\textsubscript{3} in CTA and CABu films and Eu(fod)\textsubscript{3} in D-/L-Glu and D-/L-Glu films.
compounds. Anal. Chem. 88, 8878–8885. doi: 10.1021/acs.analchem.6b02505

Xue, X., Cheng, T., Suzuki, T., and Ohishi, Y. (2015). Upconversion emissions from high energy levels of Tb³⁺ under near-infrared laser excitation at 976 nm. Opt. Mater. Exp. 5, 2768–2776. doi: 10.1364/OME.5.002768

Yamada, T., Nomura, K., and Fujiki, M. (2018). Noticeable chiral center dependence of signs and magnitudes in circular dichroism (CD) and circularly polarized luminescence (CPL) spectra of all-trans poly(9,9-dialkylfluorene-2,7-vinylene) bearing chiral alkyl side chains in solution, aggregates, and in thin films. Macromolecules 51, 2377–2387. doi: 10.1021/acs.macromol.8b00241

Yan, F., Copeland, R. A., and Brittain, H. G. (1982). Optical activity induced in the terbium(III) and europium(III) tris complexes of pyridine-2,6-dicarboxylate through association with monoamino- and diamino-carboxylic acids. Inorg. Chem. 21, 1180–1185. doi: 10.1021/ic00133a059

Yang, X., Lin, X., Zhao, Y., Zhao, Y. S., and Yan, D. (2017). Lanthanide metal–organic framework microrods: colored optical waveguides and chiral polarized emission. Angew. Chem. Int. Ed. 56, 7853–7857. doi: 10.1002/anie.201703917

Yashima, E., Matsushima, T., and Okamoto, Y. (1995). Poly((4-carboxyphenyl)acetylene) as a probe for chirality assignment of amines by circular dichroism. J. Am. Chem. Soc. 117, 11596–11597. doi: 10.1021/ja00151a032

Yeung, C.-T., Yim, K.-H., Wong, H.-Y., Pal, R., Lo, W.-S., Yan, S.-C., et al. (2017). Chiral transcription in self-assembled tetrahedral Eu₄L₆ chiral cages displaying sizable circularly polarized luminescence. Nat. Commun. 8:1128. doi: 10.1038/s41467-017-01025-1

Yu, H., Pan, K., and Deng, J. (2018). Cellulose concurrently induces predominantly one-handed helicity in helical polymers and controls the shape of optically active particles thereof. Macromolecules 51, 5656–5664. doi: 10.1021/acs.macromol.8b01282

Yu, Y., Gim, S., Kim, D., Arnon, Z. A., Gazit, E., Seeberger, P. H., et al. (2019). Oligosaccharides self-assemble and show intrinsic optical properties. J. Am. Chem. Soc. 141, 4833–4838. doi: 10.1021/jacs.8b11882

Yuasa, J., Ohno, T., Miyata, K., Tsunatori, H., Hasegawa, Y., and Kawai, T. (2011). Noncovalent ligand-to-ligand interactions alter sense of optical chirality in luminescent Tris(β-diketone) Lanthanide(III) complexes containing a chiral bis(oxazolinyl) pyridine ligand. J. Am. Chem. Soc. 133, 9892–9902. doi: 10.1021/ja201984u

Zheng, H., Li, W., Li, W., Wang, X., Tang, Z., Zhang, S. X.-A., et al. (2018). Uncovering the circular polarization potential of chiral photonic cellulose films for photonic applications. Adv. Mater. 30:1705948. doi: 10.1002/adma.201705948

Zhou, Y., Li, H., Zhu, T., Gao, T., and Yan, P. A. (2019). Highly luminescent chiral tetrahedral Eu₄L₆(UC)₄ cage: chirality induction, chirality memory, and circularly polarized luminescence. J. Am. Chem. Soc. 141, 19634–19643. doi: 10.1021/jacs.9b07178

Zinna, F., and Di Bari, L. (2015). Lanthanide circularly polarized luminescence: bases and applications. Chirality 27, 1–13. doi: 10.1002/chir.22382

Zou, C., Qu, D., Jiang, H., Lu, D., Ma, X., Zhao, Z., et al. (2019). Bacterial cellulose: a versatile chiral host for circularly polarized luminescence. Molecules 24:1008. doi: 10.3390/molecules24061008

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Copyright © 2020 Fujiki, Wang, Ogata, Asanoma, Okubo, Okazaki, Kamite and Jalilah. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.