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Strong circularly polarized luminescence of mixed lanthanide coordination polymers with control of 4f electronic structure

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This paper reports chiral mixed Eu(III)-Ln(III) coordination polymers (Ln = Gd and Sm) with a large dissymmetry factor of circularly polarized luminescence ($g_{CPL} = 0.15$) for the enhancement of the emission quantum yield ($\Phi_{tot} \geq 50\%$), achieved via the control of 4f electronic structures.

Advanced optical systems based on circularly polarized luminescence (CPL) allow the construction of future three-dimensional displays and biosensing applications. The CPL is composed of electric ($\vec{\mu}$) and magnetic ($\vec{m}$) dipole transitions and evaluated using dissymmetry factor which is defined by the following equation:

$$g_{CPL} = 4 \cdot \frac{||\vec{\mu}||^2 + ||\vec{m}||^2}{||\vec{\mu}||^2} \cdot \frac{\cos \theta}{1 + \frac{||\vec{\mu}||^2}{||\vec{m}||^2}}$$

where $\theta$ is the angle between $\vec{\mu}$ and $\vec{m}$. The CPL of typical chiral organic compounds are based on $\pi$-$\pi$ electronic transitions ($\vec{\mu} \gg \vec{m}$), resulting in small $g_{CPL} (< 0.01)$. On the other hand, the CPL in trivalent lanthanide (Ln(III)) complexes have almost equal contributions from electric and magnetic dipole transitions ($\vec{\mu} \approx \vec{m}$), resulting in large $g_{CPL}$. Among them, Eu(III) complexes with chiral 3-(trifluoroacetyl)camphor (tfc) ligands have been reported to have extra-large $g_{CPL}$ values. Chiral Eu(III) coordination compounds with tfc ligands exhibit a characteristic ligand-to-metal charge transfer (LMCT) band at around 400 nm, resulting in an effective decrease in emission quantum yield ($\Phi_{tot}$). The problem of the trade-off relationship between large $g_{CPL}$ and small $\Phi_{tot}$ of the Eu-tfc complex can be solved by controlling the electronic structure in LMCT band. Formation of a chiral Eu(III) coordination polymer with control of 4f electronic structure leads to an increase in the LMCT level for suppression of Eu(III) emission quenching.

Recently, our group has reported the increase of LMCT energy level upon mixing Gd(III) in Eu(III) coordination polymer. Their characteristic spin configurations should reduce the LMCT delocalization, leading to enhanced emission quantum yield. Based on this concept, chiral mixed-lanthanide coordination polymers are introduced for obtaining large $g_{CPL}$ with high emission quantum yield. Here, we selected Gd(III) and Sm(III) for preparing mixed Eu(III)-Ln(III) coordination polymers (Fig. 1), because they show extra small 4f-4f and LMCT absorption bands in the visible region. Herein we report on the novel molecular design and photophysical analysis of chiral Eu(III) coordination compounds with large $g_{CPL}$ and $\Phi_{tot}$ values.

Fig. 1. Schematic of LMCT in Eu(+tfc)3 derivative and chemical structures of coordination polymer.

The Eu(III)-Ln(III) (Ln = Gd and Sm) coordination polymers were obtained by the reaction of Eu(+tfc)3(H2O)n and Ln(+tfc)3(H2O)n (Ln = Gd and Sm) with 4,4’-Bis(diphenylphosphine...
Eu(III)-Ln(III) coordination polymers (Fig. S1). The XRD patterns of these coordination polymers are similar to that of the pure Eu(III) coordination polymer (Fig. S2). The XRD patterns of these coordination polymers are shown in Fig. 2. The strong absorption bands at around 350 nm are originated from the \( \sigma-\pi^* \) and \( \pi-\pi^* \) transitions. The LMCT bands of the pure Eu(III) coordination polymer are observed at around 400 nm, while no significant LMCT bands were observed for Eu-Gd and Eu-Sm coordination polymers. The emission spectra of pure Eu(III) and mixed Eu(III)-Ln(III) coordination polymers are also shown in Fig. 2. These spectra were normalized by intensity maxima. For each coordination polymer, the sharp emission bands at around 590, 610, 650, and 700 nm are assigned to the \( \lambda_{\text{max}} \) of the Eu(III) ion.16 The Eu(III)-Sm(III) polymer also showed an additional band at around 640 nm, which is assigned to the \( \Delta G_{5f/2} \) transition of the Sm(III) ion.17 The Eu(III) emission spectral shapes of the Eu(III)-Ln(III) coordination polymers agree well with that of the pure Eu(III) coordination polymer, which is directly linked to the Eu(III) coordination geometry.

The diffuse reflectance spectra of pure Eu(III) and mixed Eu(III)-Ln(III) coordination polymers are shown in Fig. 2. The strong absorption bands at around 350 nm are originated from the \( \sigma-\pi^* \) and \( \pi-\pi^* \) transitions. The LMCT bands of the pure Eu(III) coordination polymer are observed at around 400 nm, while no significant LMCT bands were observed for Eu-Gd and Eu-Sm coordination polymers. The emission spectra of pure Eu(III) and mixed Eu(III)-Ln(III) coordination polymers are also shown in Fig. 2. These spectra were normalized by intensity maxima. For each coordination polymer, the sharp emission bands at around 590, 610, 650, and 700 nm are assigned to the \( \lambda_{\text{max}} \) of the Eu(III) ion.16 The Eu(III)-Sm(III) polymer also showed an additional band at around 640 nm, which is assigned to the \( \Delta G_{5f/2} \) transition of the Sm(III) ion.17 The Eu(III) emission spectral shapes of the Eu(III)-Ln(III) coordination polymers agree well with that of the pure Eu(III) coordination polymer, which is directly linked to the Eu(III) coordination geometry.

The photophysical properties are summarized in Table 1. The emission lifetimes and radiative rate constants of the Eu(III)-Ln(III) coordination polymers are similar to those of the pure Eu(III) coordination polymer, which is directly linked to the Eu(III) coordination geometry. The photophysical properties are summarized in Table 1. The emission lifetimes and radiative rate constants of the Eu(III)-Ln(III) coordination polymers are similar to those of the pure Eu(III) coordination polymer, which is directly linked to the Eu(III) coordination geometry.

Table 1: Photophysical properties of pure Eu(III) and mixed Eu(III)-Ln(III) coordination polymers.

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<tr>
<th></th>
<th>( \tau/\text{ms} )</th>
<th>( \Phi_{\text{tot}}/% )</th>
<th>( \Phi_{\text{ff}}/% )</th>
<th>( \eta_{\text{abs}}/% )</th>
<th>( k_r/\text{s}^{-1} )</th>
<th>( k_{\text{nr}}/\text{s}^{-1} )</th>
<th>( \Delta E_a/\text{cm}^{-1} )</th>
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<tbody>
<tr>
<td>[Eu(tfc)3dpbp]n</td>
<td>0.61</td>
<td>36</td>
<td>61</td>
<td>59</td>
<td>1.0 \times 10^3</td>
<td>6.4 \times 10^2</td>
<td>( *3600 )</td>
</tr>
<tr>
<td>[Eu0.5Gd0.5(tfc)3dpbp]n</td>
<td>0.63</td>
<td>34</td>
<td>63</td>
<td>54</td>
<td>1.0 \times 10^3</td>
<td>5.9 \times 10^2</td>
<td>4600</td>
</tr>
<tr>
<td>[Eu0.5Sm0.5(tfc)3dpbp]n</td>
<td>0.60</td>
<td>52 (54) (^{1})</td>
<td>60</td>
<td>87</td>
<td>1.0 \times 10^3</td>
<td>6.6 \times 10^2</td>
<td>4090</td>
</tr>
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\(^{1}\) \( \lambda_{\text{max}} = 355 \) nm under Ar. \(^{2}\) \( \lambda_{\text{max}} = 380 \) nm under Ar. \(^{\#}\) \( \eta_{\text{phot}} \): Photosensitized energy transfer efficiency. \( k_r \): Radiative rate constant, \( k_{\text{nr}} \): Non-radiative rate constant. \(^{\dagger}\) Calculations were performed by omitting Sm (III) emission contribution. \(^{\ddagger}\) The previously reported value is 4.100 cm\(^{-1}\). Previously reported data show a large error bar for temperature-dependent emission lifetime (Fig S3 and Table S1). \(^{\circ}\) The value in a parenthesis is emission quantum yield containing Sm(III) emission.

Fig. 2. Diffuse reflectance and emission spectra (\( \lambda_{\text{ex}} = 350 \) nm) of pure Eu(III) and mixed Eu(III)-Ln(III) coordination polymers (black line: [Eu(tfc)3dpbp]n, red line: [Eu0.5Gd0.5(tfc)3dpbp]n, blue line: [Eu0.5Sm0.5(tfc)3dpbp]n).

Fig. 3. Schematic of (a) delocalized LMCT excited states and (b) localized LMCT excited states.

Strongly depends on Ln(III) doping (pure Eu(III): 36\%, Eu-Gd(III): 34\%, and Eu-Sm(III): 54\%). These results indicated that the photosensitized energy transfer efficiency of the Eu(III)-Ln(III) coordination polymer are strongly affected by the incorporated Ln(III) ion. The significant enhancement of the energy transfer efficiency in the Eu(III)-Sm(III) coordination polymer should be related to the energy modulation of the LMCT band.15 The LMCT bands are classified into \( ^{6}\)LMCT and \( ^{9}\)LMCT bands.15,18 The delocalized \( ^{6}\)LMCT states are formed in the pure Eu(III) coordination polymer owing to ligand(tfc)-ligand(dpbb) interactions (Fig. 3a). The characteristic localized \( ^{9}\)LMCT states (Fig. 3b) are also formed in the mixed Eu(III)-Ln(III) coordination polymers induced by Ln(III) doping (Ln = Gd, Sm). The energy modulation is consistent with the activation energies (\( \Delta E_a \)) from the Eu(III) ion to the LMCT quenching states in each coordination polymer, as estimated by Arrhenius analysis (Table 1, See ESI). The \( \Delta E_a \) values of the Eu(III)-Ln(III) coordination polymers are larger than that of pure the Eu(III) coordination polymer.

The \( \phi_{\text{tot}} \) of the Eu(III)-Gd(III) coordination polymer was similar to that of the pure Eu(III) coordination polymer, probably due to the fast deactivation of ligand \( T_1 \) states, which was induced by the paramagnetic effect of the Gd(III) ion on the +tfc ligands.19,20 We consider that the control of the 4f electronic structure in the mixed lanthanide coordination polymers allows the manipulation of excited-state dynamics.21

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The $\epsilon_{\text{CPL}}$ spectra of pure Eu(III) and mixed Eu(III)-Ln(III) coordination polymers are shown in Fig. 4. The CPL intensity and spectral shape are almost same for all the coordination polymers. The maximum $\epsilon_{\text{CPL}}$ was 0.15 for both Eu(III)-Gd(III) and Eu(III)-Sm(III) coordination polymers, same as that of the pure Eu(III) coordination polymer.

In summary, we demonstrated the significant enhancement in the emission quantum yield by Ln(III) doping in Eu(III) coordination polymers with large chiroptical property ($\epsilon_{\text{CPL}} = 0.15$). The obtained emission quantum yield of the Eu-Sm mixed coordination polymer (52%) was highest in the reported Eu(III) polymers. The maximum spectral shape are almost same for all the coordination polymers. The maximum spectral shape are almost same for all the coordination polymers.

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**Conflicts of interest**

There are no conflicts to declare.

**Notes and references**

Experimental detail, Mass spectra, XRD spectra: see Supplementary Information.