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Citation	Dalton transactions, 50(16), 5433-5436 https://doi.org/10.1039/d1dt00519g
Issue Date	2021-04-28
Doc URL	http://hdl.handle.net/2115/85181
Type	article (author version)
File Information	Dalton-rev2.pdf



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COMMUNICATION

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

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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

Advanced optical systems based on circularly polarized luminescence (CPL) allow the construction of future three-dimensional displays¹⁻³ and biosensing applications⁴⁻⁵. The CPL is composed of electric ($\vec{\mu}$) and magnetic (\vec{m}) dipole transitions⁶ and evaluated using dissymmetry factor which is defined by the following equation:

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

where θ is the angle between $\vec{\mu}$ and \vec{m} . The CPL of typical chiral organic compounds are based on π - π^* electronic transitions ($\vec{\mu} \gg \vec{m}$), resulting in small g_{CPL} (< 0.01).^{7,8} 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} .⁶ Among them, Eu(III) complexes with chiral 3-(trifluoroacetyl)camphor (tfc) ligands have been reported to have extra-large g_{CPL} values ($g_{\text{CPL}} > 0.10$).^{6,9-13} Chiral Eu(III) coordination compounds with tfc ligands exhibit a characteristic ligand-to-metal charge transfer (LMCT) band at around 400 nm¹⁴ (Fig. 1), resulting in an effective decrease in emission quantum yield (Φ_{tot}). The problem of the trade-off relationship between large g_{CPL} and small Φ_{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.¹⁵ 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 Φ_{tot} values.

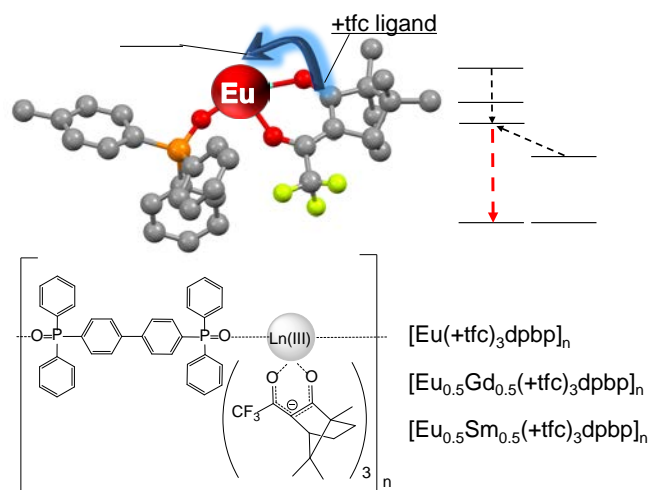


Fig. 1. Schematic of LMCT in Eu(+tfc)₃ derivative and chemical structures of coordination polymer.

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

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

oxide)biphenyl (dppb). The Eu(III)-Ln(III) coordination polymers were identified and characterized by elemental analysis, IR spectroscopy, ESI-MS, and XRD analysis. The ESI-MS results indicate the existence of the $[\text{EuLn}(\text{+tfc})_3\text{dppb}]^+$ frameworks in 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 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 $\sigma\text{-}\pi^*$ and $\pi\text{-}\pi^*$ 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 $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$, and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions, respectively, 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 $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ 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.

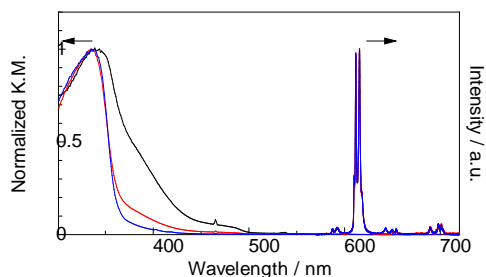


Fig. 2. Diffuse reflectance and emission spectra ($\lambda_{\text{ex}} = 350$ nm) of pure Eu(III) and mixed Eu(III)-Ln(III) coordination polymers (black line: $[\text{Eu}(\text{+tfc})_3\text{dppb}]_n$, red line: $[\text{Eu}_{0.5}\text{Gd}_{0.5}(\text{+tfc})_3\text{dppb}]_n$, blue line: $[\text{Eu}_{0.5}\text{Sm}_{0.5}(\text{+tfc})_3\text{dppb}]_n$).

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 ($\tau \approx 0.6$ ms, $k_r = 1.0 \times 10^3$ s⁻¹). The large k_r and small k_{nr} ($\approx 6.0 \times 10^2$ s⁻¹) of each coordination polymer leads to highly internal emission quantum yields ($\Phi_{\text{ff}} \geq 60\%$). In contrast, the ligand-excited emission quantum yield

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 band¹⁵. The LMCT bands are classified into ⁷LMCT and ⁹LMCT bands.^{15,18} The delocalized ⁹LMCT states are formed in the pure Eu(III) coordination polymer owing to ligand(tfc)-ligand(dppb) interactions (Fig. 3a). The characteristic localized ⁹LMCT 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 (ΔE_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 ΔE_a values of the Eu(III)-Ln(III) coordination polymers are larger than that of pure the Eu(III) coordination polymer.

The Φ_{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 T₁ 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

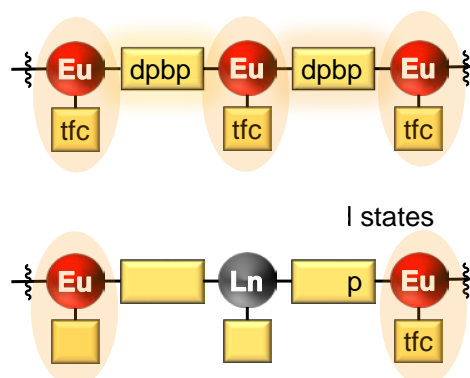


Fig. 3. Schematic of (a) delocalized LMCT excited states and (b) localized LMCT excited states.

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

	^a τ / ms	^b Φ_{tot} / %	Φ_{ff} / %	^c n_{sens} / %	^c k_r / s ⁻¹	^c k_{nr} / s ⁻¹	ΔE_a / cm ⁻¹
$[\text{Eu}(\text{+tfc})_3\text{dppb}]_n$	0.61	36	61	59	1.0×10^3	6.4×10^2	^e 3600
$[\text{Eu}_{0.5}\text{Gd}_{0.5}(\text{+tfc})_3\text{dppb}]_n$	0.63	34	63	54	1.0×10^3	5.9×10^2	4600
$[\text{Eu}_{0.5}\text{Sm}_{0.5}(\text{+tfc})_3\text{dppb}]_n$	0.60	52 ^d (54) ^f	60	87	^d 1.0×10^3	^d 6.6×10^2	4090

[a] $\lambda_{\text{ex}} = 355$ nm under Ar. [b] $\lambda_{\text{ex}} = 380$ nm under Ar. [c] η_{sens} : Photosensitized energy transfer efficiency, k_r : Radiative rate constant, k_{nr} : Non-radiative rate constant. [d] Calculations were performed by omitting Sm(III) emission contribution. [e] The previously reported value is 4,100 cm⁻¹. Previously reported data show a large error bar for temperature-dependent emission lifetime [Fig S2, in Ref14]. We re-measured the temperature dependent emission lifetime (Fig S3 and Table S1). [f] The value in a parenthesis is emission quantum yield containing Sm(III) emission.

The g_{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 g_{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.

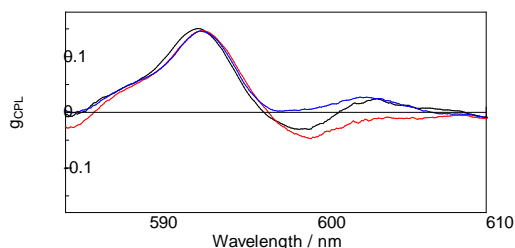


Fig. 4. g_{CPL} spectra of pure Eu(III) and mixed Eu(III)-Ln(III) coordination polymers (black line: $[\text{Eu}(\text{+tfc})_3\text{dppb}]_n$, red line: $[\text{Eu}_{0.5}\text{Gd}_{0.5}(\text{+tfc})_3\text{dppb}]_n$, blue line: $[\text{Eu}_{0.5}\text{Sm}_{0.5}(\text{+tfc})_3\text{dppb}]_n$)

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 ($g_{\text{CPL}} = 0.15$). The obtained emission quantum yield of the Eu-Sm mixed coordination polymer (52%) was highest in the reported Eu(III) complexes with *tfc*-type ligands.^{9-12,14,22-24} We consider that the key factors for the enhancement of the emission quantum yields of the $\text{Eu}(\text{+tfc})_3$ polymer are control of the LMCT energy by lanthanide doping and the paramagnetic effect of the doping lanthanide ions. Control of the 4f electronic structure in lanthanide coordination polymers offers new avenues in photochemistry and materials chemistry.

This work was supported by grant-in-aid for grant numbers 20H02748, 19H04556, 18H04497, 18H02041, 20H04653, and 20H05197. This work was also supported by the Institute for Chemical Reaction Design and Discovery (ICReDD), established by the World Premier International Research Initiative (WPI) of MEXT, Japan. We are particularly grateful for experimental assistance by Professor H. Ito, Associate Professor K. Fushimi, and Mr. A. Fujimura of Hokkaido University.

Conflicts of interest

There are no conflicts to declare.

Notes and references

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

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