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Spiral Eu(III) Coordination Polymers with Circular Polarized Luminescence

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Spiral-type chiral Eu(III) coordination polymer showed strong luminescence (emission quantum yield $\Phi_{f\text{-}f}$ = 57%, photosensitized energy transfer efficiency η_{sens} = 53%), effective CD and CPL properties (g_{CPL} = 0.16) compared with mono-nuclear with chiral Eu(III) complex in solid state ($\Phi_{f\text{-}f}$ = 36%, η_{sens} = 14%, g_{CPL} = 0.09).

Luminescent metal complexes with chiral organic ligands have attracted attention due to their unique luminescent properties, such as circularly polarized luminescence (CPL). Enantiopure lanthanide(III) complexes with CPL properties have been explored for their large dissymmetry factor g_{CPL} values, which are several hundred times larger than those of transition metal complexes.[1] Among them, luminescent Eu(III) complex with chiral trifluoroacetylcamphor (+/–tfc) ligands shows g_{CPL} value in solution. Muller and Kaizaki have reported extra-large g_{CPL} value of $Eu(tfc)_4$ with M (tfc: trifluoroacetylcamphor) in solution.[2] We also reported $[Eu(+/–tfc)_3(tppo)_2]$ (tppo: triphenylphosphine oxide) for chiral luminescent material.[3] The emission quantum yield Φ of Eu(III) complexes with chiral camphors, extremely, small. Luminescent Eu(III) complexes with large g_{CPL} and Φ values are expected to be useful in optical application such as a security material with circularly polarized luminescence.[4]

In this study, we report spiral Eu(III) coordination polymers with large g_{CPL} and Φ values. The spiral Eu(III) coordination polymers are composed of chiral $Eu(tfc)_3$ and organic joint dpbp ligand (dpbp: 4,4'-bis(diphenylphosphoryl)biphenyl) units, $[Eu(+/-tfc)_3(dpbp)]_n$ (Figure 1). The tight packing and electronic structures of Eu(III) coordination polymer provides enhanced thermo-stability and characteristic luminescence properties.[5] The characteristic spiral structures of $[Eu(+/-tfc)_3(dpbp)]_n$ are analyzed using X-ray single crystal analysis. Photophysical and chiroptocal properties of mono-nuclear chiral Eu(III) complex $[Eu(+/-tfc)_3(tppo)]$ (tppo: triphenylphosphine oxide) in solid state were also measured as a reference. Here, the characteristic coordination structure and strong luminescent properties of spiral Eu(III) coordination polymer have been performed for novel optical-active materials.

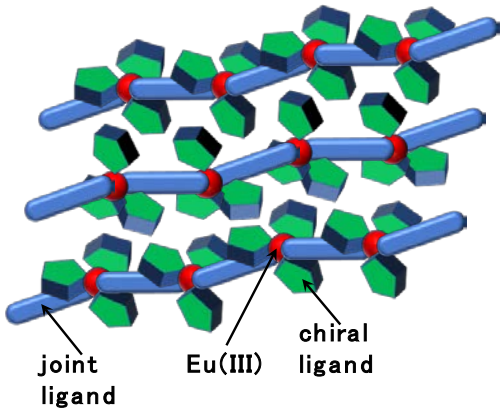

Fig. 1 a) Image and b) chemical structures of poly-nuclear $[Eu(+/-tfc)_3(dpbp)]_n$ and mono-nuclear $[Eu(+/-tfc)_3(tppo)]$.

The spiral Eu(III) coordination polymers $[Eu(+/-tfc)_3(dpbp)]_n$ are prepared by the complexation of chiral $[Eu(tfc)_3(H_2O)_2]$ with dpbp in methanol under reflux. The crystal structure of $[Eu(+/-tfc)_3(dpbp)]_n$ are shown in Figure 2a. Crystal group are categorized to be monoclinic, P_{21} (crystal data: see supporting information Table S1). The Eu(III) ions are coordinated to eight oxygen atoms from three +/-tfc ligands and two bridging dpbp ligands. The geometrical symmetry around Eu(III) ions was

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determined to be an 8-coordinated square-antiprismatic structure (point group=D_{4d}) without an inversion center (see the Supporting Information for details). The coordination chains of[Eu(+tfc)$_3$(tppo)$_2$] and [Eu(+tfc)$_3$(tppo)$_2$] show left- and right-spiral structures (Fig. 2a). Multiple intermolecular CH/F and intramolecular interactions were also observed within the distances of 2.573 Å (Figure 2b). The thermal stability of [Eu(+tfc)$_3$(dpbp)]$_n$ were evaluated using TGA (see supporting information Figure S1 and Table 1).

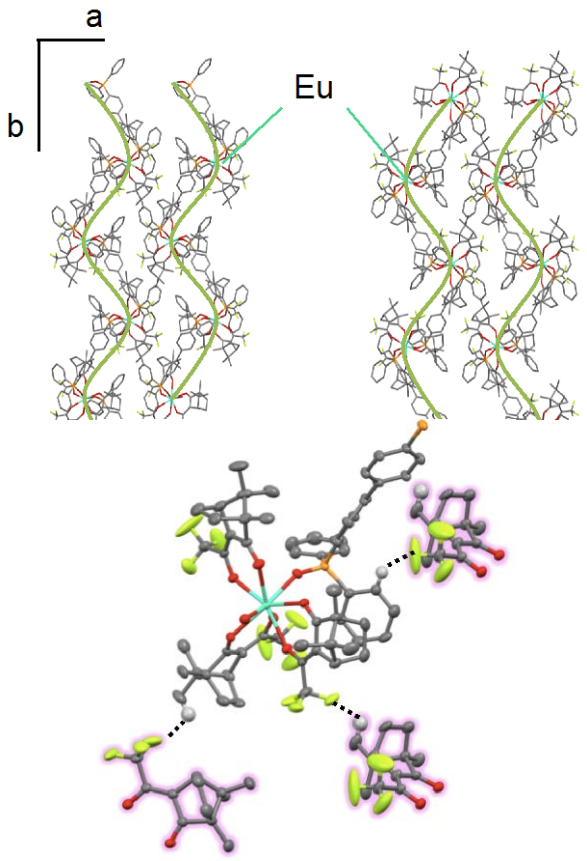

Fig. 2 Ortep views of [Eu(+/-tfc)$_3$(dpbp)]$_n$. Dot lines in ortep view shows CH/F interactions in crystal.

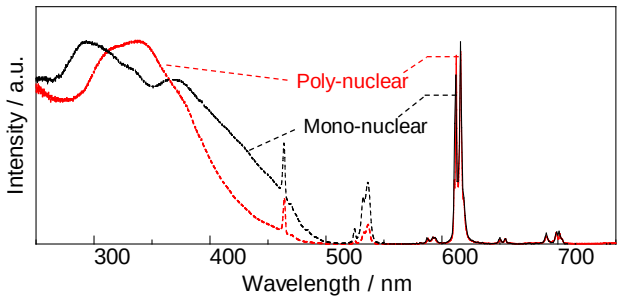

Fig. 3 Emission and excitation spectra of [Eu(+/-tfc)$_3$(dpbp)]$_n$ (poly-nuclear: red line) and [Eu(+/-tfc)$_3$(tppo)] (mono-nuclear: black line) in solid states. Excitation wavelength for emission spectra at 380 nm. Detection wavelength for excitation spectra at 616 nm.

The decomposition temperatures for poly-nuculear [Eu(+tfc)$_3$(dpbp)]$_n$ and mono-nuclear [Eu(+tfc)$_3$(tppo)$_2$] were estimated to be 332 °C and 208 °C, respectively (Table 1). The increase in the decomposition temperatures of [Eu(+tfc)$_3$(dpbp)]$_n$ is caused by tight-packing structures of spiral chain of Eu(III) coordination polymers in solid state.

Steady-state emission spectra of spiral Eu(III) coordination polymers in the solid state are shown in Fig. 3. The spiral Eu(III) coordination polymer exhibit bright red luminescence. Emission bands were observed at around 578, 591, 613, 650, and 698 nm, and are attributed to the f–f transitions of $^5D_0$–^7F_J with J=0, 1, 2, 3, and 4, respectively. The emission band at 613 nm ($^5D_0$–$^7F_2$) is due to electric dipole transitions, which are strongly dependent on the coordination geometry. Spectral shape related to coordination geometry and transition probability of [Eu(+tfc)$_3$(dpbp)]$_n$ at 613 nm is similar to that of [Eu(+tfc)$_3$(tppo)].

Their 4f–4f emission quantum yields ($\Phi_{f\text{-}f}$), radiative and non-radiative rate constants (k_r and k_{nr}) calculated from τ_{obs} and emisiion spectra are also summarized in Table 1. The $\Phi_{f\text{-}f}$ of [Eu(+tfc)$_3$(dpbp)]$_n$ were estimated to be 57%, which is larger than that of [Eu(+tfc)$_3$(tppo)$_2$] ($\Phi_{f\text{-}f}$ = 36%). The larger is $\Phi_{f\text{-}f}$ is caused by small k_{nr} related to tight packing structure of [Eu(+tfc)$_3$(tppo)$_2$] crystal. We estimated the photosensitized energy-transfer efficiency (η_{sens}) using $\Phi_{f\text{-}f}$ and measured values using integrating sphere (excited at 380 nm). The η_{sens} for poly-nuclear [Eu(+tfc)$_3$(dpbp)]$_n$ (53%) is approximately four times larger than that for mono-nuclear [Eu(+tfc)$_3$(tppo)$_2$] (14%). According to the Arrhenius analysis for estimation of relaxation process from emitting level $^5D_0$, we found increase of population factor A and activation energy E_a of poly-nuclear [Eu(+tfc)$_3$(dpbp)]$_n$. The enhanced A may be related to stabilization of excited triplet state of Eu(+tfc)$_3$ unit.[6]

Table 1 Thermal and photophysical properties of [Eu((+)-tfc)$_3$(dpbp)]$_n$ and [Eu((+)-tfc)$_3$(tppo)$_2$] in solid states

	[Eu((+)-tfc)$_3$(dpbp)]$_n$	[Eu((+)-tfc)$_3$(tppo)$_2$]
type	Poly-nuclear	Mono-nuclear
d.p[a] / °C	332	208
$\Phi_{f\text{-}f}$[b] / %	57	36
$\Phi_{380\ nm}$[c] / %	30	5
η_{sens}[d] /%	53	14
τ_{obs}[e] / ms	0.57	0.38
k_r / s^{-1}	1.0×10^3	9.4×10^2
k_{nr} / s^{-1}	7.5×10^2	1.7×10^3
A[f]/ s^{-1}	2.2×10^{10}	1.3×10^9
E_a[g] / cm^{-1}	4.1×10^3	2.9×10^3

a) Decomposition points (see supporting information Fig. S1). b) Emission quantum yields are estimated using emission spectra and lifetimes (see supporting information). c) Total emission quantum yield (excited at 380 nm). d) Photosensitized energy transfer efficiency ($\Phi_{tot} = \Phi_{f\text{-}f} \times \eta_{sens}$). e) Emission lifetime (τ_{obs}) of the Eu(III) complexes were measured by excitation at 355 nm (Nd:YAG 3ω) at room temperature. f) Frequency factor from Arrhenius analysis of the emission lifetime. g) Activation energy form from Arrhenius analysis of the emission lifetime. $\ln(k_{ET}) = \ln(1/\tau - 1/\tau_{100K}) = \ln(A) - (E_a/RT)$

In order to analyze the effective photosensitized energy transfer for [Eu(+tfc)$_3$(dpbp)]$_n$, the energy level calculations

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using Turbomol (B3LYP/def-SV(P) are carried out. The quantum calculation indicates that the absorption energies of ligand moieties in the $[Eu(+tfc)_3(dpbp)]_n$ is higher than those in the $[Eu(+tfc)_3(tppo)_2]$ (see supporting information Figure S4), which is consistent with the blue-shifted excitation spectrum (Fig. 3). The higher energy level of ligand moieties in the $[Eu(+tfc)_3(dpbp)_2]_n$ might promote suppression of back energy transfer from excited Eu(III) to ligands.

The CD and CPL spectra of $[Eu(+/-tfc)_3(dpbp)]_n$ in solid state are shown in Fig. 4b and c, respectively (experimental condition: see supporting information). We observed CD signals of $\pi-\pi*$ transition of the coordinated +/-tfc at around 350 nm. Small CD signals at around 420 and 440 nm are due to 4f-4f transitions of Eu(III) ($^7F_0$-^5L_x). The CPL signals are given by the difference between the left and right circularly polarized emission intensities ($I_{CPL} = I_L - I_R$).

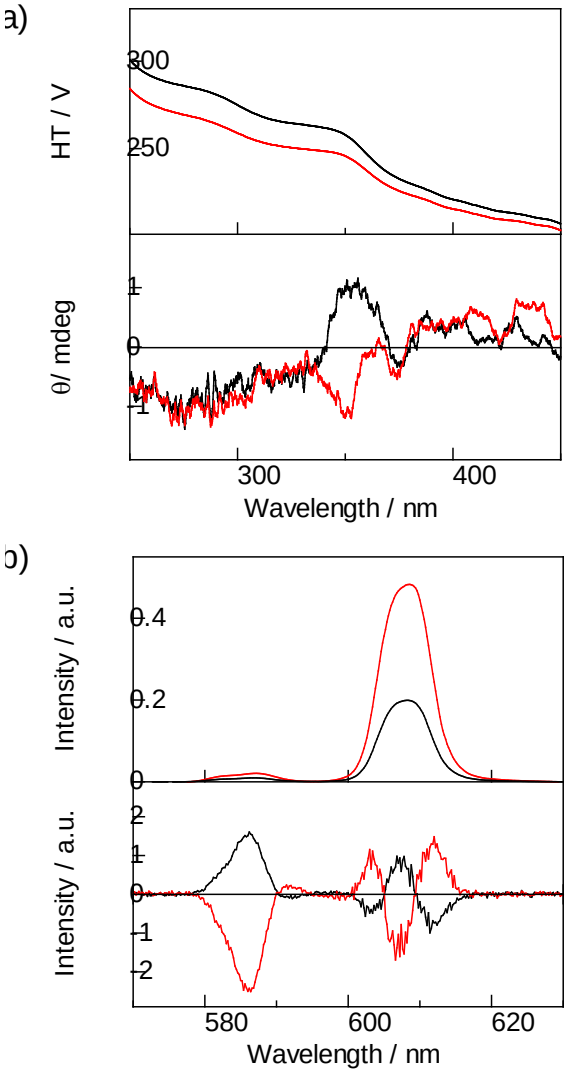

Fig. 4 a) Electronic absorption, CD, b) emission, and CPL spectra of $[Eu(+tfc)_3(dpbp)]_n$ (Back line) and $[Eu(-tfc)_3(dpbp)]_n$ (red line) in solid state.

Effective CPL signals were observed at around 595 and 614 nm, based on $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_2$ transitions, respectively. In general, g_{CPL} values at the magnetic-dipole transition are notably larger than those at the electric-dipole transition in Eu(III) compounds. The g_{CPL} values at the magnetic-dipole and the electric-dipole transitions of $[Eu(+tfc)_3(dpbp)]_n$ were estimated to be 0.17 and – 0.015, respectively. The g_{CPL} value of $[Eu(+tfc)_3(dpbp)]_n$ is two times larger than that of corresponding $[Eu(+tfc)_3(tppo)]_n$ (g_{CPL} at 586 nm = 0.09, see supporting information Figure S5). Recently, Yuasa reported large g_{CPL} value from Aggregation of $Eu(+tfc)_3$.[7] spiral structure of poly-nuclear Eu(III) coordination polymers also promote enhancement of optical activity in solid state.

The spiral Eu(III) coordination polymer $[Eu(+tfc)_3(dpbp)]_n$ successfully provides the large emission quantum yield, thermo-stability and chiroptical optical-activity. We also found the remarkable enhancement of the photosensitized energy transfer efficiency of $[Eu(+tfc)_3(dpbp)]_n$ for luminescent materials. Spiral Eu(III) coordination polymer with CPL are expected to contribute the novel molecular design for optical active molecular materials.

Notes and references

$[Eu(+tfc)_3(dpbp)]_n$: Yield 0.16 g (56%). FT-IR (Kbr) 3060-2870 (m, C-O), 1661 (st, C=O), 1185 (s, P=O) cm^{-1}. FAB-Mass (m/z): $[M - hfa]^+$ calcd for $[C_{60}H_{56}EuF_6O_6P_2]$, 1201.2; found, 1201.2. Anal. Calcd for $[C_{72}H_{70}EuF_9O_8P_2]$: C, 59.71; H, 4.87. Found: C, 59.47; H, 4.86.

$[Eu(-tfc)_3(dpbp)]_n$: Anal. Calcd for $[C_{72}H_{70}EuF_9O_8P_2]$: C, 59.71; H, 4.87. Found: C, **; H, **.

Experimental detail, thermogravimetric analysis, X-ray crystal data, shape measure calculations, temperature dependent emission lifetimes, DFT calculations, chiroptical properties of $[Eu((+)-tfc)_3(tppo)_2]$: see supporting information.

crystallographic data: CCDC-1037529 (for complex 1) and CCDC 1037531 (for complex 2). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.

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