Supplementary Information

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

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S1. Synthesis of 4,4-bis(diphenylphosphoryl)biphenyl (dpbp): The dpbp was synthesized according to the previously reported procedure.[S1]

S2. Synthesis of Tris(3-trifluoroacetyl-(+)-camphorato)Ln(III) ($Ln(+tfc)_3(H_2O)_n$, Ln = Eu, Gd, and Sm): The $Ln(+tfc)_3(H_2O)_n$ were synthesized according to the previously reported procedure.[S1]

S3. $[Eu(+tfc)_3(dpbp)]_n$: The $[Eu(+tfc)_3(dpbp)]_n$ was synthesized according to the previously reported procedure.[S1] Methanol (8 mL) containing $Eu(+tfc)_3(H_2O)_2$ (190 mg, 0.20 mmol) and dpbp (112 mg, 0.20 mmol) was refluxed at 65 ^{o}C under stirring for 14 h. The reaction mixture was filtrated to afford the white powder (Yield: 51%, 150 mg).

FTIR = 1659 (st, C=O), 1181 (st, P=O) cm^{-1}. Elemental analysis calcd. (%) of $C_{144}H_{140}Eu_2F_{18}O_{16}P_4$, C 59.71, H 4.87; found C 59.07, H 4.73. Under the same experimental procedure of $[Eu (+tfc)_3(dpbp)]_n$, all other mixed lanthanide polymers were synthesized.

S4. $[Gd_{0.5}Eu_{0.5}(+tfc)_3(dpbp)]_n$: White powder, yield: 43%. To determine the Eu/Gd ratios of $[Gd_{0.5}Eu_{0.5}(+tfc)_3(dpbp)]_n$, ICP-AES analysis was conducted (AMETEK Materials Analysis Division, SPECTRO ARCOS). Concentrations were calculated from the emission intensities of Eu and Gd (λ = 393.048 and 342.247 nm, respectively) for each sample using the appropriate calibration curves. The analysis results revealed that the Eu/Gd ratio was 0.485 : 0.515 (calcd, 1 : 1).

FTIR = 1661 (st, C=O), 1183 (st, P=O) cm^{-1}. Elemental analysis calcd. (%) of $C_{144}H_{140}GdEuF_{18}O_{16}P_4$, C 59.60, H 4.86; found C 59.07, H 4.73.

S5. [Sm$_{0.5}$Eu$_{0.5}$ (+tfc)$_3$(dpbp)]$_n$: White powder, yield: 33 %. To determine the Eu/Gd ratios of [Sm$_{0.5}$Eu$_{0.5}$(+tfc)$_3$(dpbp)]$_n$, ICP-AES analysis was conducted (AMETEK Materials Analysis Division, SPECTRO ARCOS). Concentrations were calculated from the emission intensities of Eu and Sm (λ = 393.048 and 442.434 nm, respectively) for each sample using the appropriate calibration curves. The analysis results revealed that the Eu/Sm ratio was 0.499 : 0.501 (calcd, 1 : 1). FTIR = 1658 (st, C=O), 1182 (st, P=O) cm^{-1}. Elemental analysis calcd. (%) of $C_{144}H_{140}SmEuF_{18}O_{16}P_4$, C 59.75, H 4.87; found C 59.09, H 4.78.

S6. Instruments

Electrospray ionization mass spectrometry (ESI-MS) was performed using JEOL JMS-T100 LP. Elemental analyses were performed using a J-SCIENCE MICRO CORDER JM10 system. IR analyses were performed by JASCO FTIR-4600 spectrometer. XRD data were recorded at on a Rigaku SmartLab diffractometer with Cu-K$_\alpha$ radiation and D/teX Ultra detector. Emission spectra were measured at room temperature using a Horiba/Jobin-Yvon FluoroLog-3 spectrofluorometer. Excitation light source was 450 W Xe arc lamp. The emission quantum yield (Φ_{tot}) was determined using an FP-6300 spectrofluorometer attached with an integrating sphere (ILF-533). Emission lifetimes were measured using the third harmonics (355 nm) of a Q- switched Nd: YAG laser (Spectra Physics, INDI-50, fwhm = 5 ns, λ = 1064 nm) and a photomultiplier (Hamamatsu Photonics, R5108, response time ≤ 1.1 ns). The Nd:YAG laser response was monitored with a digital oscilloscope (Sony Tektronix, TDS3052, 500 MHz) synchronized the Nd: YAG laser. The temperature-dependent emission lifetime measurements were performed using Nd: YAG laser with a cryostat (Thermal Block Company, SASB245T) and a temperature controller (Oxford, Instruments, ITC502S). Diffuse reflection spectra were obtained using a JASCO V-670 spectrophotometer with an ISN-723 integrating sphere unit. CPL spectra were measured using a JASCO CPL-300 spectrofluoropolarimeter for pure Eu(III) and Eu(III)-Ln(III) coordination polymers (0.5 mg) mixed with KBr (150 mg). Tablets (diameter: 10 mm, Eu(III) complexes/KBr) were prepared using a tablet forming machine (48.2 kN, press time: 3min).

S7. ESI-MS spectra

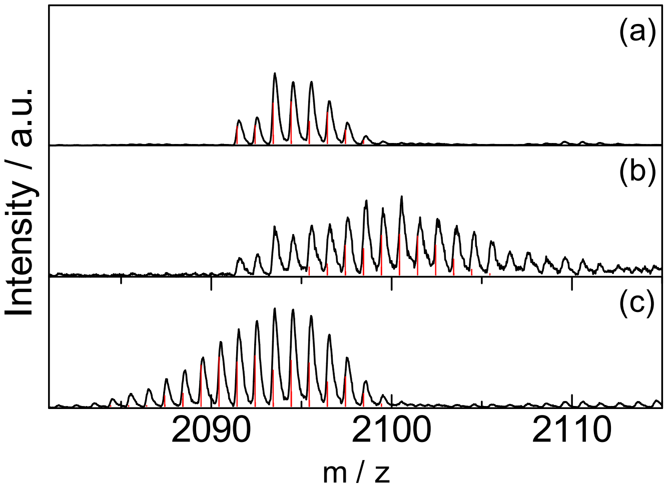

Fig. S1. ESI-MS spectra of (a)[Eu(+tfc)$_3$(dpbp)]$_n$, (b)[Eu$_{0.5}$Gd$_{0.5}$(+tfc)$_3$(dpbp)]$_n$, and (c) [Eu$_{0.5}$Sm$_{0.5}$(+tfc)$_3$(dpbp)]$_n$. Red bar: Calculation MS spectra of (a) [Eu$_2$(+tfc)$_5$(dpbp)]$^+$, (b) [EuGd(+tfc)$_5$(dpbp)]$^+$, and (c) [EuSm(+tfc)$_5$(dpbp)]$^+$. The ESI-MS results indicate the existence of the [EuLn(+tfc)$_5$dpbp]$^+$ (Ln = Gd and Sm) frameworks in Eu(III)-Ln(III) (Ln = Gd and Sm) coordination polymers.

S8. XRD spectra

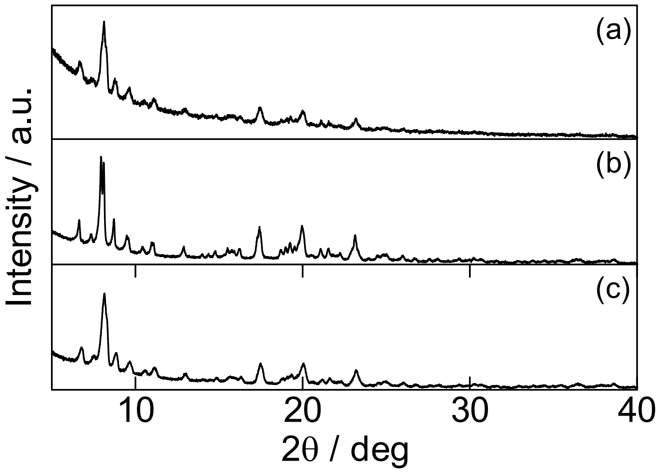

Fig. S2. XRD patterns of (a)[Eu(+tfc)$_3$(dpbp)]$_n$, (b)[Eu$_{0.5}$Gd$_{0.5}$(+tfc)$_3$(dpbp)]$_n$, and (c) [Eu$_{0.5}$Sm$_{0.5}$(+tfc)$_3$(dpbp)]$_n$.

S9. Calculation of photophysical parameter[S1]

The intrinsic emission quantum yields (Φ_{ff}), the radiative (k_r), and the nonradiative (k_{nr}) rate constants were estimated using equations as follows.

$$\tau_{rad} = \frac{1}{k_r} \qquad \text{(S1)}$$

$$\tau_{obs} = \frac{1}{k_r + k_{nr}} \qquad \text{(S2)}$$

$$k_r = A_{MD,0} n^3 \times \left(\frac{I_{tot}}{I_{MD}}\right) \qquad \text{(S3)}$$

$$\Phi_{ff} = \frac{k_r}{k_r + k_{nr}} = \frac{\tau_{obs}}{\tau_{rad}} \qquad \text{(S4)}$$

$$k_{nr} = \frac{1}{\tau_{obs}} - \frac{1}{\tau_{rad}} \qquad \text{(S5)}$$

$$\eta_{sens} = \frac{\Phi_{tot}}{\Phi_{ff}} \times 100 \qquad \text{(S6)}$$

where $A_{MD,0}$ is the spontaneous luminescence probability for the $^5D_0 \rightarrow {}^7F_1$ transition in vacuo (14.65 s^{-1}), n is the refractive index of the medium (1.5), and (I_{tot}/I_{MD}) is the ratio of the total area of the Eu(III) luminescence spectrum to the area of the $^5D_0 \rightarrow {}^7F_1$ transition band. τ_{obs} and τ_{rad} are emission lifetime and the inverse of the rate of radiative decay, respectively.

S10. Calculation of Activation Energy (ΔE_a) and Frequency factor (A) of back energy transfer, based on the temperature dependent PL-LT[2].

Adopting an established method, we calculate activation energy (ΔE_a) and frequency factor (A). To estimate the effect of BEnT, the temperature-dependent emission lifetimes in the solid state were measured in the range 100–400 K (Fig. S3). To analyze the energy transfer mechanism, we estimated the back-energy transfer rate constants (k_{BEnT}). The temperature dependence of k_{BEnT} was expected to follow an Arrhenius-type equation with an activation energy ΔE_a,[S2] which is defined by the given equation:

$$ln\left(\frac{1}{\tau_{obs}} - \frac{1}{\tau_{100K}}\right) = lnk_{BEnT} = ln\,A - \frac{\Delta E_a}{R}.\frac{1}{T} \qquad \text{(S7)}$$

in which τ_{obs}, τ_{100K}, A, ΔE_a, R and T are the observed emission lifetime, emission lifetime at 100 K, frequency factor, activation energy, gas constant, and temperature, respectively. From these calculations, the E_a and A values are given in Table S1.

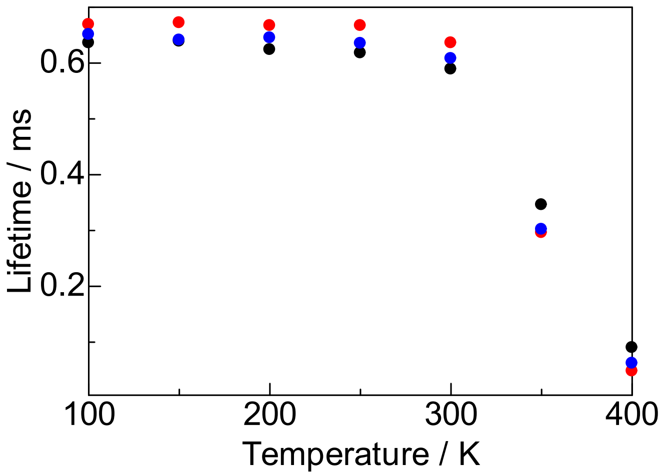

Fig. S3. Temperature dependent emission lifetimes of $[\mathrm{Eu}(+\mathrm{tfc})_3(\mathrm{dpbp})]_n$ (black dot), $[\mathrm{Eu}_{0.5}\mathrm{Gd}_{0.5}(+\mathrm{tfc})_3(\mathrm{dpbp})]_n$ (red dot), and $[\mathrm{Eu}_{0.5}\mathrm{Sm}_{0.5}(+\mathrm{tfc})_3(\mathrm{dpbp})]_n$ (blue dot).

Table S1. ΔE_a and A of $[\mathrm{Eu}(+\mathrm{tfc})_3(\mathrm{dpbp})]_n$, $[\mathrm{Eu}_{0.5}\mathrm{Gd}_{0.5}(+\mathrm{tfc})_3(\mathrm{dpbp})]_n$, and $[\mathrm{Eu}_{0.5}\mathrm{Sm}_{0.5}(+\mathrm{tfc})_3(\mathrm{dpbp})]_n$.

	ΔE_a / cm^{-1}	A / s^{-1}
$[\mathrm{Eu}(+\mathrm{tfc})_3\mathrm{dpbp}]_n$	3600	3.0×10^9
$[\mathrm{Eu}_{0.5}\mathrm{Gd}_{0.5}(+\mathrm{tfc})_3\mathrm{dpbp}]_n$	4610	2.0×10^{11}
$[\mathrm{Eu}_{0.5}\mathrm{Sm}_{0.5}(+\mathrm{tfc})_3\mathrm{dpbp}]_n$	4090	2.6×10^{10}

References

S1. Y. Hasegawa, Y. Miura, Y. Kitagawa, S. Wada, T. Nakanishi, K. Fushimi, T. Seki, H. Ito, T. Iwasa, T. Taketsugu, M. Gon, K. Tanaka, Y. Chujo, S. Hattori, M. Karasawa and K. Ishii, *Chem. Commun.*, 2018, **54**, 10695–10697.

S2. M. Yamamoto, Y. Kitagawa T. Nakanishi, K. Fushimi, Y. Hasegawa, *Chem.–Eur. J.* 2018, **24**, 17719–17726.