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Electronic supplementary information

Ratiometric luminescence thermometry based on crystal-field alternation at the extremely narrow $^5D_0 \rightarrow {}^7F_2$ transition of europium(III)

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Experimental Section (S1)

Synthesis. Diglycolic acid (ODA) and 6,6'-dimethyl-2,2'-bipyridine were purchased from Tokyo Chemical Industry Co., Lid. Distilled water and D_2O used as solvent were obtained from Wako Pure Chemicals. Europium(III) triflate [$Eu(OTf)_3$; OTf = OSO_2CF_3] was purchased from Aldrich. 2,2'-Bipyridine-6,6'-dicarboxylic acid bis(*N*-hydroxy-succinimide) ester (BP) was synthesized as follows: the dicarboxylic acid (514 mg, 2.10 mmol) was added to 20 mL of $SOCl_2$ and the resulting mixture was refluxed for 21 h. The excess $SOCl_2$ was removed in vacuo and 20 mL of freshly distilled acetonitrile was added. Then 532 mg (2.2 equiv) of N-hydroxysuccinimide was added and after this 700 *m*L (1.9 equiv) of Et_3N via a syringe. The reaction mixture became turbid and after 6 h an off-white precipitate was isolated which was washed with acetonitrile. Recrystallization from acetonitrile gave white crystals of BP. Yield: 506 mg (1.15 mmol, 55%). ^{1}H NMR (300 MHz, DMSO-d_6): d = 2.93 (s, 8H), 8.37 (m, 4H), 8.75 (m, 2H). ESI-MS (positive): m/z calcd. for $C_{20}H_{14}NaN_4O_8$ ($[M+Na]^+$), 461.07; found 461.07.

Preparation of [BP-$(Eu^{III})_2$-$(ODA)_3$]: BP (43.8 mg, 0.10 mmol), ODA (40.2 mg, 0.30 mmol), and $Eu(OTf)_3$ (120 mg, 0.20 mmol) were dissolved in acetonitrile (20 mL) and refluxed under stirring for 6 h. Then, the solution was filtrated and dried to obtain yellow solid. ^{1}H NMR (600 MHz, D_2O, 293 K): d = 1.08 (d, 2H), 2.78 (s, 8H), 3.05–3.45 (br. s, 12H), 4.87 (d, 2H), 5.55 (t, 2H). ESI-MS (positive): m/z calcd. for $C_{32}H_{35}Eu_2N_4O_{27}$ ($[M+4H_2O+H]^+$), 1208.9; found 1208.9. Formation of [BP-$(Eu^{III})_2$-$(ODA)_3$] in acetonitrile was confirmed by UV-vis spectral titration of BP by ODA in the presence of 2 equiv of $Eu(OTf)_3$ in acetonitrile (Fig. S2, ESI†), where one BP ligand reacts with 3 equiv of ODA ligand to provide absorption bands due to [BP-$(Eu^{III})_2$-$(ODA)_3$]. This spectral change has a clear isosbestic point at λ = 296 nm (Fig. S2, ESI†), suggesting perfect conversion of BP to the [BP-$(Eu^{III})_2$-$(ODA)_3$] complex. The isosbestic point (296 nm) indicates conversion of a BP-(Eu^{III}) complex to [BP-$(Eu^{III})_2$-$(ODA)_3$] in acetonitrile.

Measurements. Emission spectra of the Eu^{III} complexes were recorded by a JASCO FP-6500 fluorescence spectrophotometer at various temperatures. Emission quantum yields of the Eu^{III} complexes were measured using a calibrated integrating sphere system in H_2O and D_2O at 293 K. Emission lifetimes of the Eu^{III} complexes (in H_2O and D_2O) were measured with the third harmonics (355 nm) of a Q-swiched 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 to the single-pulse excitation. Monochromator was used to select the desired emission wavelength. In the time-resolved emission spectra of the Eu^{III} complexes (in D_2O), the samples were excited by a N_2 laser (Usho KEC-160; wavelength, 337 nm; pulse width, 600 ps; 10 Hz). The emission profiles were recorded using a streak camera (Hamamatsu, picosecond fluorescence measurement system, C4780).

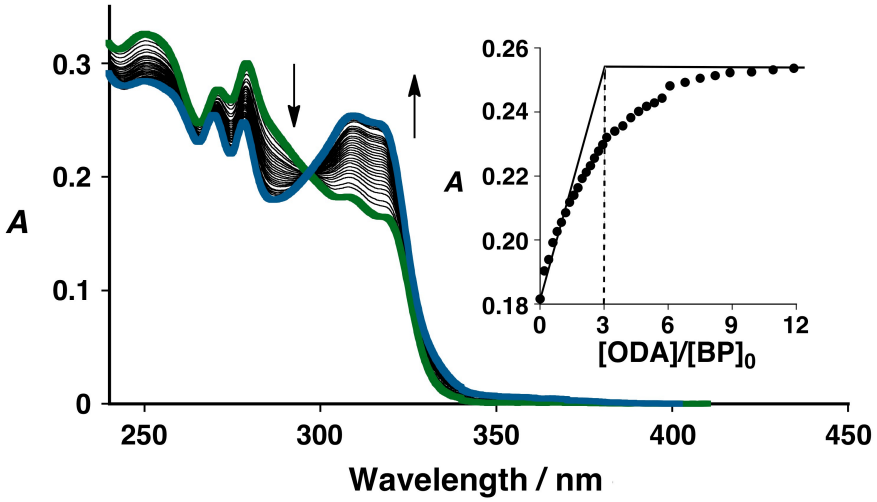

Fig. S2 UV-vis absorption spectra of BP (2.5×10^{-5} M) in the presence of Eu^{3+} (5.0×10^{-5} M) and ODA [0 M (green line) to 3.0×10^{-4} M (blue line)] in MeCN at 298 K. Inset shows plot of absorbance at λ = 309 nm versus $[ODA]/[BP]_0$, where $[BP]_0$ denotes the initial concentration of BP (2.5×10^{-5} M).

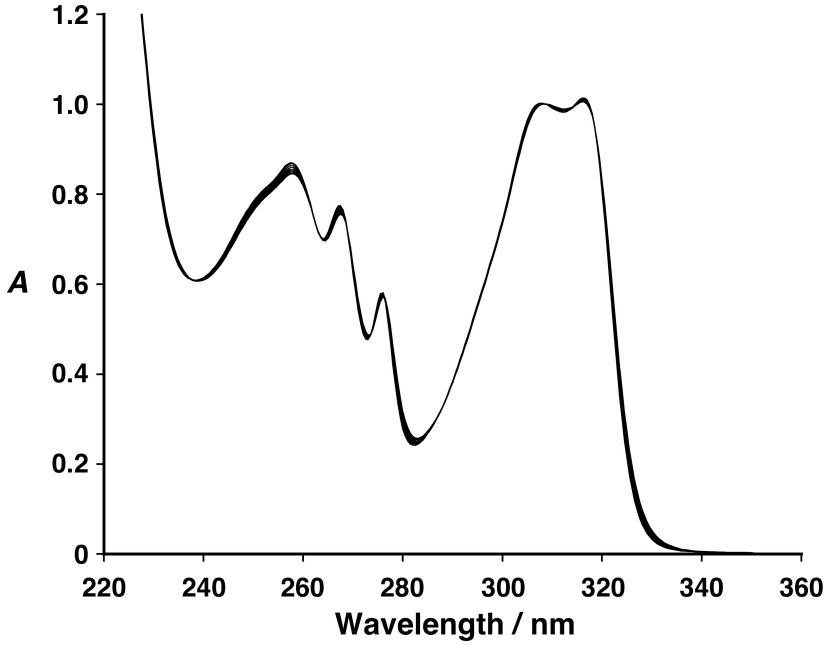

Fig. S3 UV-vis absorption spectra of [BP-$(Eu^{III})_2$-$(ODA)_3$] in H_2O at 298–333 K.

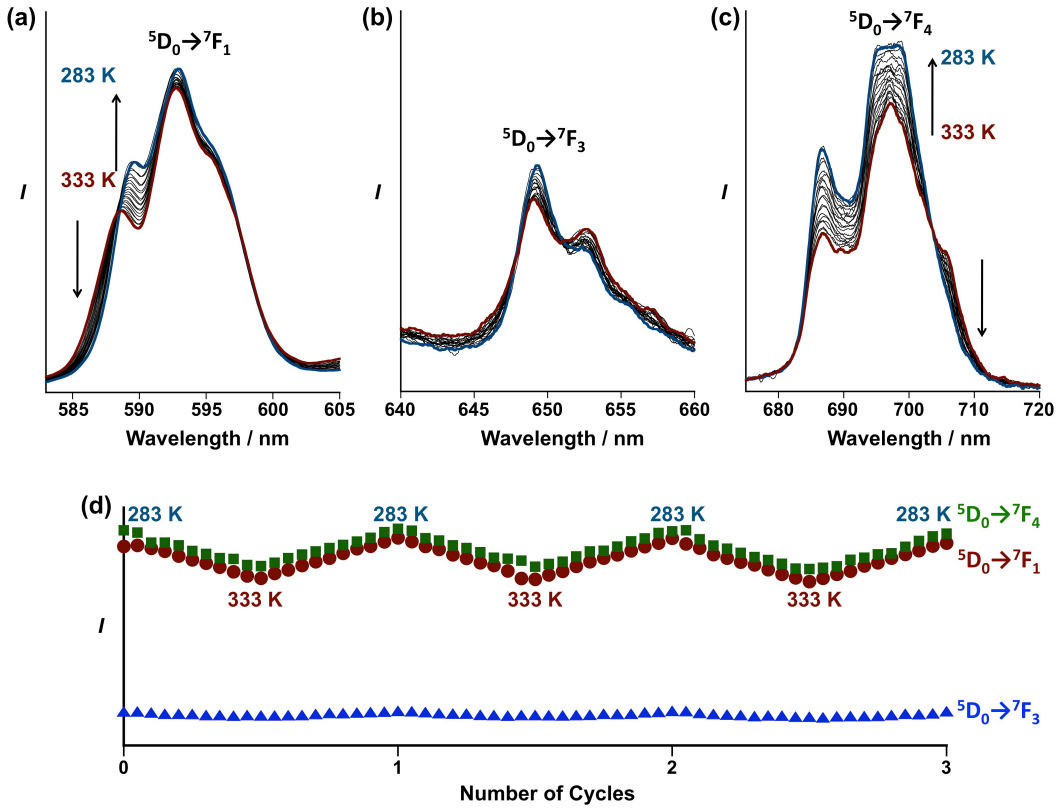

Fig. S4 Emission spectra of [BP-$(Eu^{III})_2$-$(ODA)_3$] (3.9×10^{-5} M) in (a) $^5D_0 \rightarrow {}^7F_1$ (b) $^5D_0 \rightarrow {}^7F_3$ (c) $^5D_0 \rightarrow {}^7F_4$ transition bands in H_2O at 283 K (blue line)–333 K (red line). Excitation wavelength λ = 320 nm. Emission intensity at λ = 589 nm (red circles), 649 nm (blue triangles) and 697 nm (green squares) in H_2O at 283–333 K.

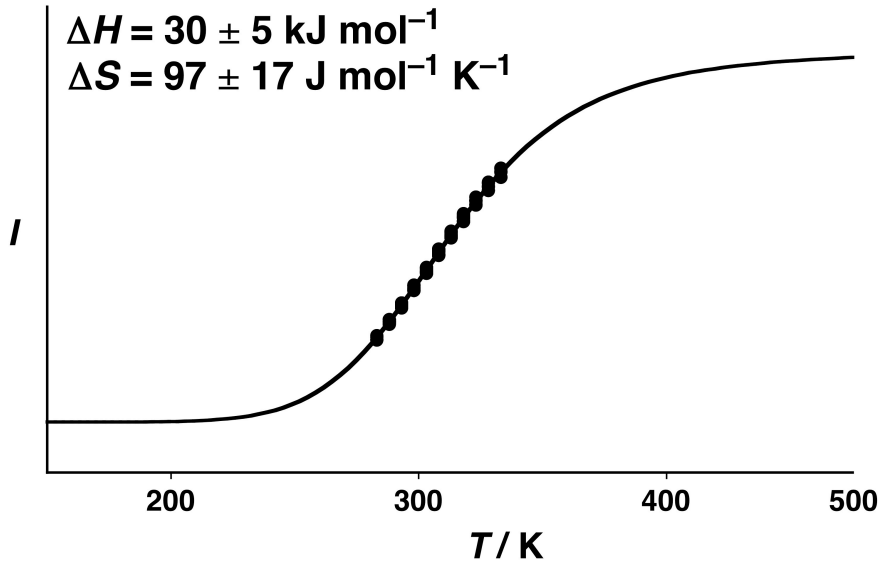

Fig. S5 Temperature dependence of emission intensity (I) of [BP-$(Eu^{III})_2$-$(ODA)_3$] (3.9×10^{-5} M) at 613 nm in H_2O at 283–333 K. Excitation wavelength $\lambda = 320$ nm. The solid line shows a fitting curve using eqn (1).

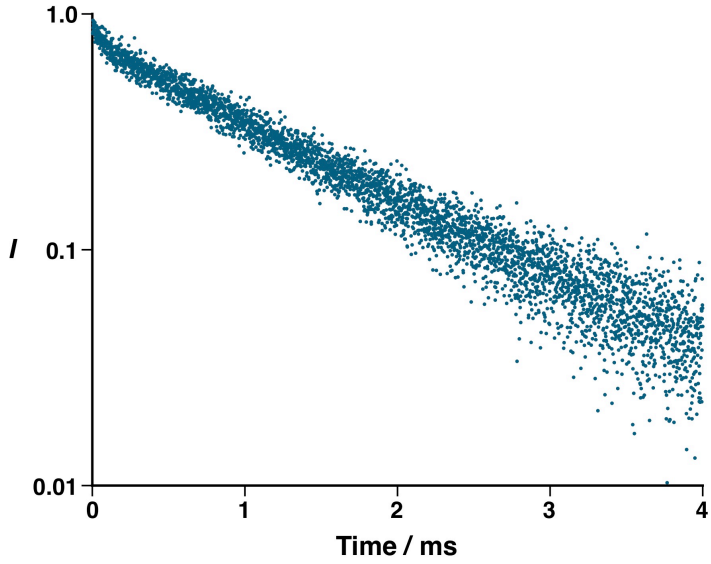

Fig. S6 Emission decay profile at λ = 615 nm of [BP-$(Eu^{III})_2$-$(ODA)_3$] in D_2O at 293 K.

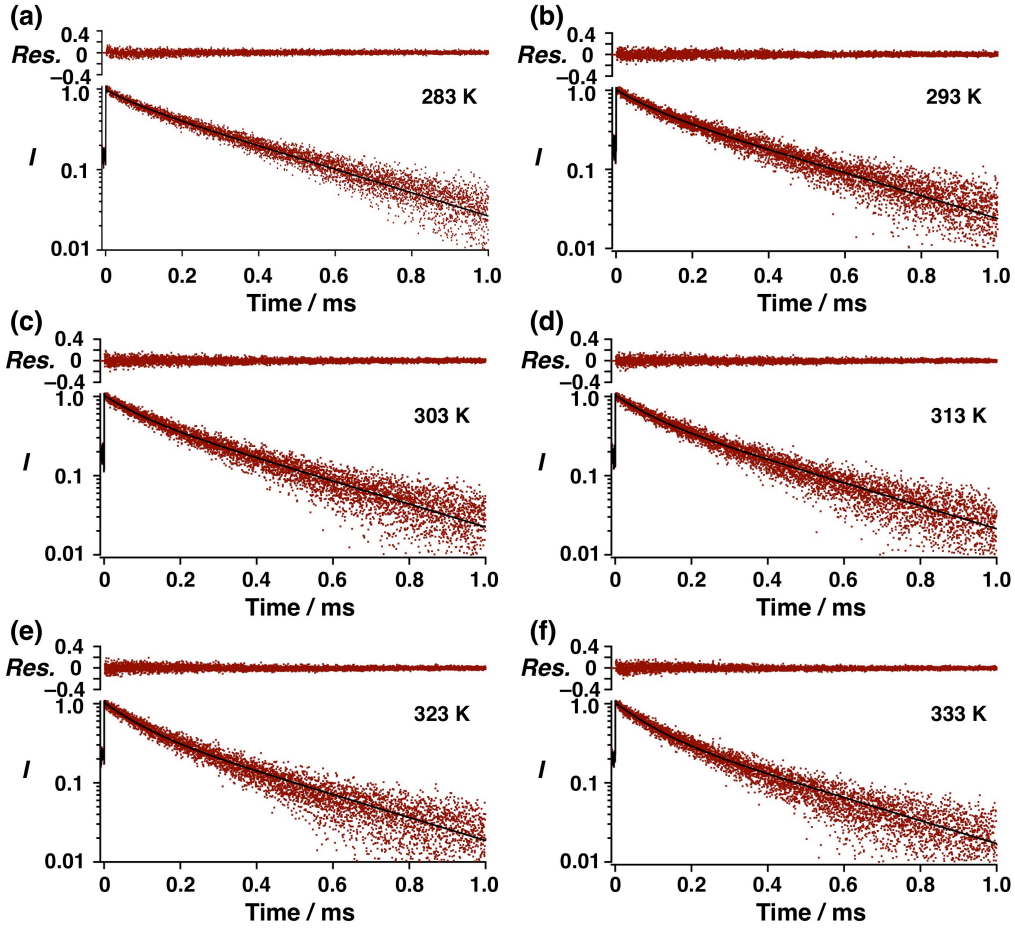

Fig. S7 Emission decay profile at $\lambda = 615$ nm of [BP-$(Eu^{III})_2$-$(ODA)_3$] in H_2O at (a) 283K, (b) 293 K, (c) 303 K, (d) 313 K, (e) 323 K, and (f) 333 K.

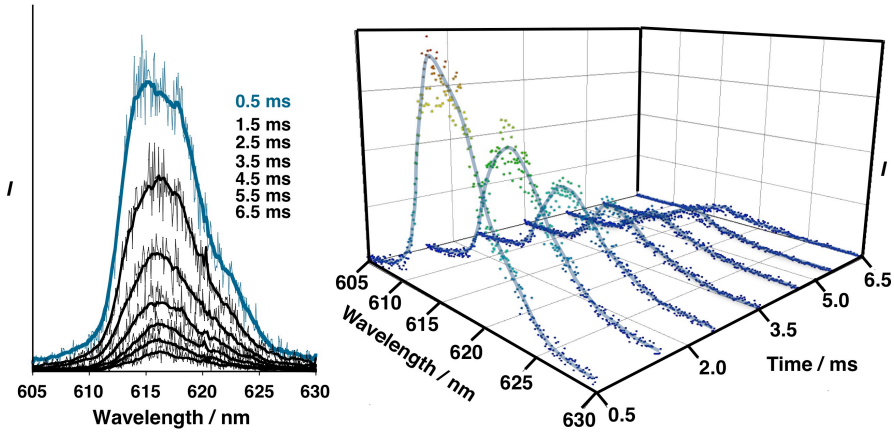

Fig. S8 Time-resolved emission spectra of [BP-$(Eu^{III})_2$-$(ODA)_3$] monitored at 0.5–6.5 ms after laser excitation at λ = 337 nm in D_2O at 293 K.

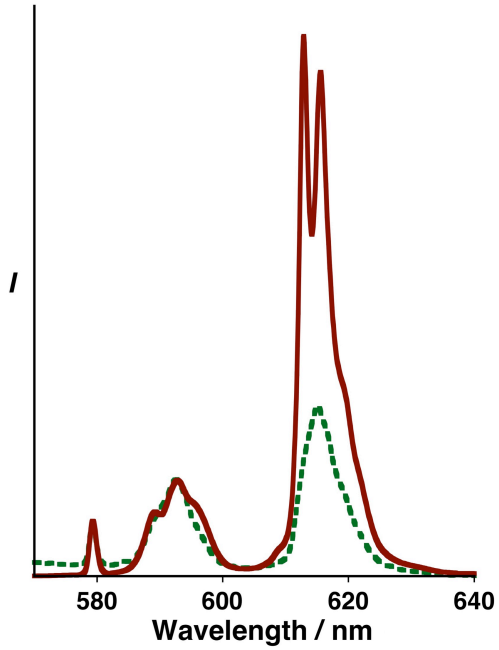

Fig. S9 Emission spectra of [BP-$(Eu^{III})_2$-$(ODA)_3$] in H_2O at 298 K upon excitation at λ = 320 nm (red solid line) and at λ = 395 nm (green dashed line).

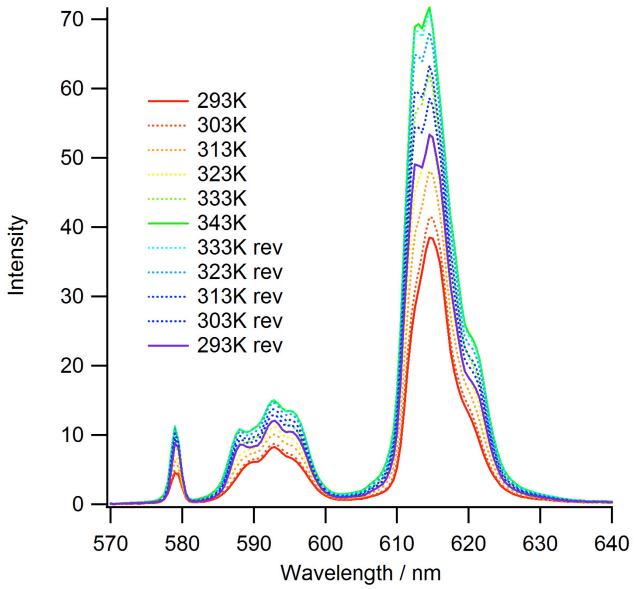

Fig. S10 Emission spectra of [BP-$(Eu^{III})_2$-$(ODA)_3$] in acetonitrile at 293–343 K. Excitation wavelength λ = 329 nm.