Electronic supplementary information

Ratiometric luminescence thermometry based on crystal-field alternation at the extremely narrow $^5\text{D}_0 \rightarrow ^7\text{F}_2$ 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., Ltd. Distilled water and D$_2$O used as solvent were obtained from Wako Pure Chemicals. Europium(III) triflate [Eu(OTf)$_3$; OTf = OSO$_2$CF$_3$] 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-hydroxy succinimide was added and after this 700 mL (1.9 equiv) of Et$_3$N 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$_{30}$H$_{14}$NaN$_4$O$_8$ ([M+Na$^+$]), 461.07; found 461.07.

Preparation of [BP(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$_2$O, 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$_{16}$Eu$_2$N$_4$O$_{27}$ ([M+4H$_2$O+H$^+$]), 1208.9; found 1208.9. Formation of [BP(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(III)$_2$-(ODA)$_3$]. This spectral change has a clear isosbestic point at $\lambda = 296$ nm (Fig. S2, ESI†), suggesting perfect conversion of BP to the [BP(III)$_2$-(ODA)$_3$] complex. The isosbestic point (296 nm) indicates conversion of a BP(III) complex to [BP(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$_2$O and D$_2$O at 293 K. Emission lifetimes of the Eu$^{III}$ complexes (in H$_2$O and D$_2$O) were measured with the third harmonics (355 nm) of a Q-switched Nd:YAG laser (Spectra Physics, INDI-50, fwhm = 5 ns, $\lambda = 1064$ nm) and a photomultiplier (Hamamatsu photonics, R5108, response time $\leq 1.1$ 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$_2$O), 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 $\times$ 10$^{-5}$ M) in (a) $^5$D$_0$ $\rightarrow$ $^7$F$_4$ (b) $^5$D$_0$ $\rightarrow$ $^7$F$_3$ (c) $^5$D$_0$ $\rightarrow$ $^7$F$_4$ transition bands in H$_2$O at 283 K (blue line)–333 K (red line). Excitation wavelength $\lambda$ = 320 nm. Emission intensity at $\lambda$ = 589 nm (red circles), 649 nm (blue triangles) and 697 nm (green squares) in H$_2$O at 283–333 K.
Fig. S5 Temperature dependence of emission intensity ($I$) of [BP-(Eu$^{III}$)$_2$-(ODA)$_3$] (3.9 $\times$ 10$^{-5}$ M) at 613 nm in H$_2$O 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 $\lambda = 615$ nm of [BP-(Eu$^{III}$)$_2$-(ODA)$_3$] in D$_2$O at 293 K.
Fig. S7 Emission decay profile at $\lambda = 615$ nm of [BP-(Eu$^{III}$)$_2$(ODA)$_3$] in H$_2$O at (a) 283 K, (b) 293 K, (c) 303 K, (d) 313 K, (e) 323 K, and (f) 333 K.
**Fig. S8** Time-resolved emission spectra of [BP-(EuIII)$_2$-(ODA)$_3$] monitored at 0.5–6.5 ms after laser excitation at $\lambda = 337$ nm in D$_2$O at 293 K.
**Fig. S9** Emission spectra of [BP-(Eu$^{III}$)$_2$-(ODA)$_3$] in H$_2$O at 298 K upon excitation at $\lambda = 320$ nm (red solid line) and at $\lambda = 395$ nm (green dashed line).
Fig. S10  Emission spectra of [BP-(Eu(III))$_2$(ODA)$_3$] in acetonitrile at 293–343 K. Excitation wavelength $\lambda = 329$ nm.