Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Role of Tf_2N^- anions in the ionic liquid–water distribution of europium(III) chelates

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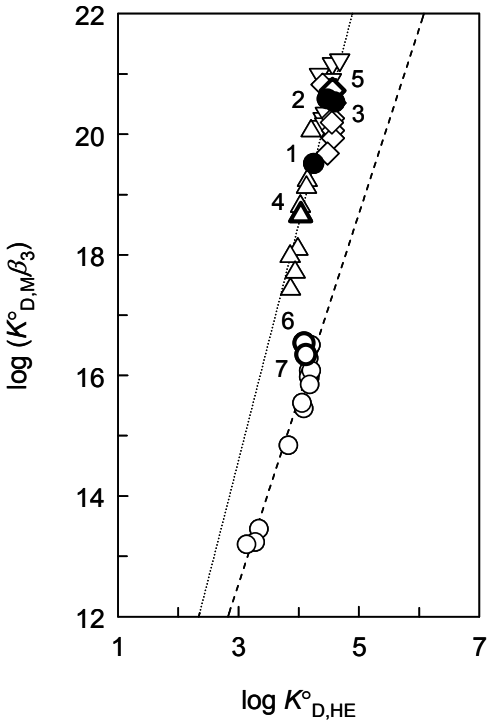

Fig. S1 Relationship between log ($K°_{D,M}\beta_3$) of the neutral $Eu(tta)_3$ chelate and log $K°_{D,HE}$ of the enol form of 2-thenoyltrifluoroacetone (Htta). (●), [$C_n$mim][Tf_2N]; (○), alkanes, aromatic hydrocarbons, and chlorohydrocarbons;[1,2] (◇), ketones;[3,4] (△), ethers;[1] (▽), esters.[3,5] 1, [C_4mim][Tf_2N]; 2, [C_6mim][Tf_2N]; 3, [C_8mim][Tf_2N]; 4, diisopropyl ether (DIPE); 5, isobutyl methyl keton (MIBK); 6, benzene; 7, 1,2-dichloroethane (DCE). The respective straight lines were obtained by a least-squares fitting for the oxygen-containing organic solvents (dotted line) and for alkanes, aromatic hydrocarbons, and chlorohydrocarbons (dashed line).

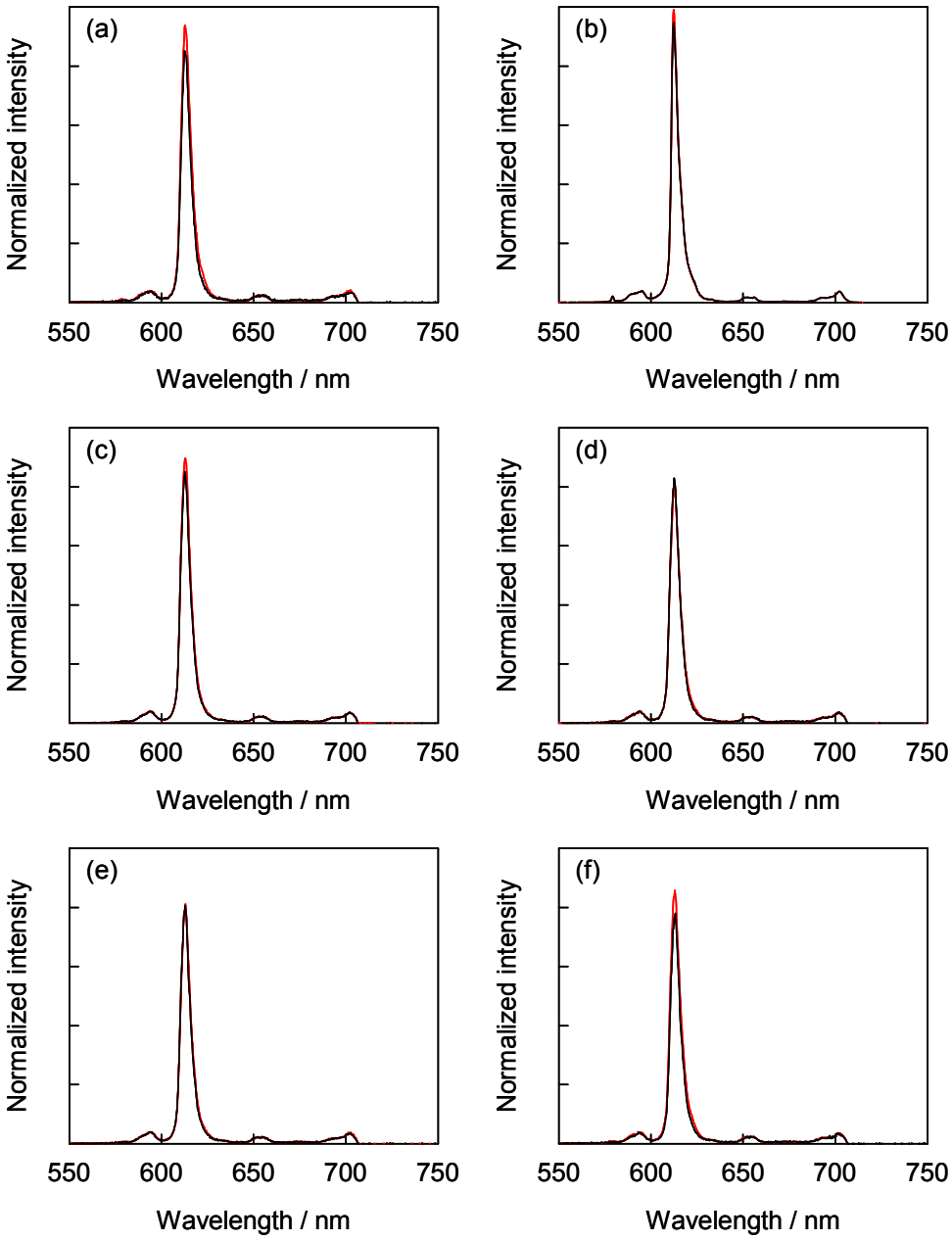

Fig. S2 Fluorescence spectrum of $[Eu(tta)_3(H_2O)_3]$ in $[C_2mim][Tf_2N]$ (a), $[C_4mim][Tf_2N]$ (b), $[C_6mim][Tf_2N]$ (c), $[C_8mim][Tf_2N]$ (d), $[C_{10}mim][Tf_2N]$ (e), and $[C_4dmim][Tf_2N]$ (f) saturated with H_2O (black) and D_2O (red) following pulsed 394 nm excitation. The spectra were normalized by the intensity of the $^5D_0 \rightarrow {}^7F_1$ transition. Concentration of $[Eu(tta)_3(H_2O)_3]$ was 1.0×10^{-4} mol dm^{-3}.

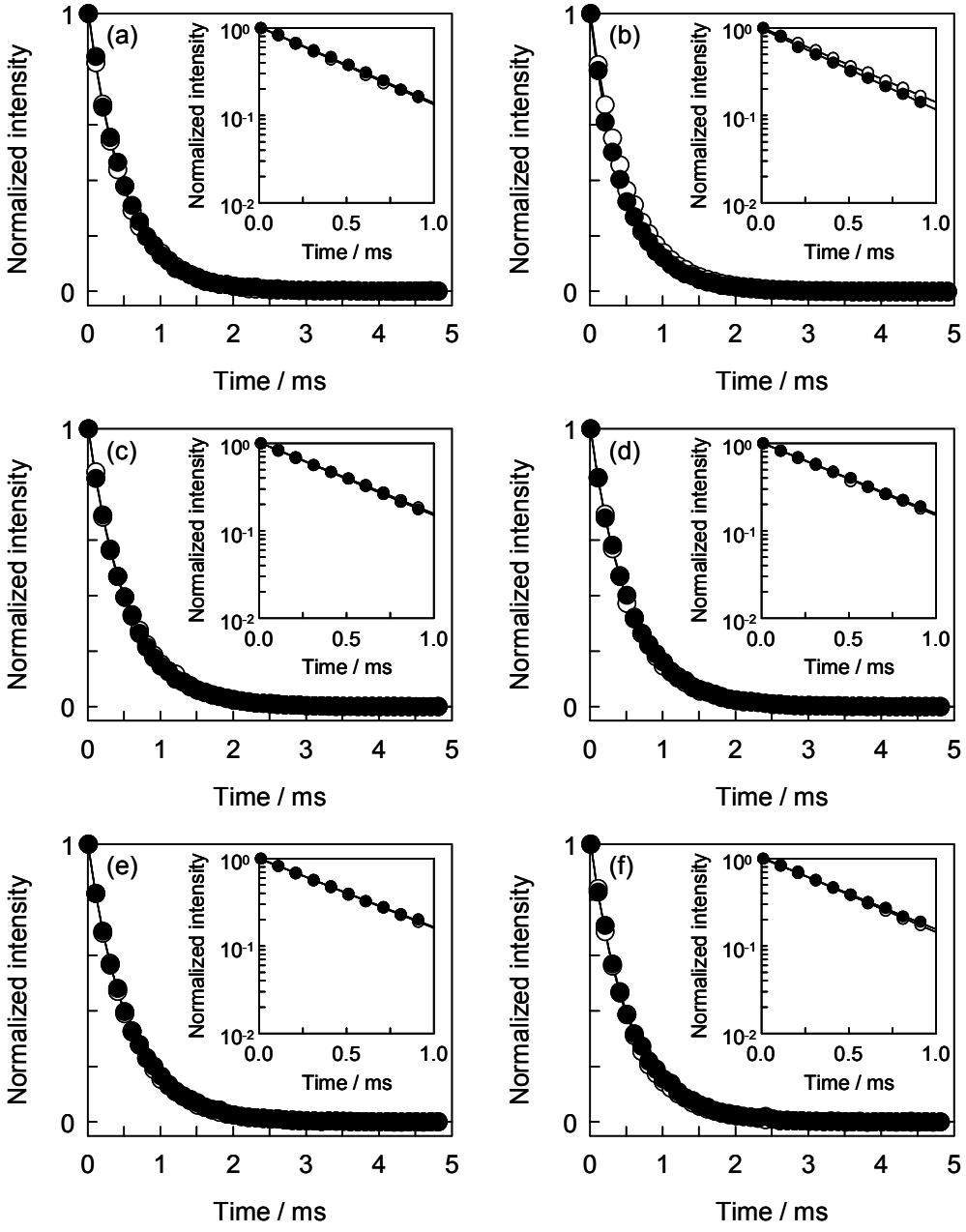

Fig. S3 Fluorescence decay at 613 nm for $[Eu(tta)_3(H_2O)_3]$ in $[C_2mim][Tf_2N]$ (a), $[C_4mim][Tf_2N]$ (b), $[C_6mim][Tf_2N]$ (c), $[C_8mim][Tf_2N]$ (d), $[C_{10}mim][Tf_2N]$ (e), and $[C_4dmim][Tf_2N]$ (f) saturated with H_2O (●) and D_2O (○) following pulsed 394 nm excitation. The decays were normalized at the first data point. The fluorescence decay on a logarithmic scale is presented in the inset graph, and the solid lines were obtained by a least-squares fitting. Concentration of $[Eu(tta)_3(H_2O)_3]$ was 1.0×10^{-4} mol dm^{-3}.

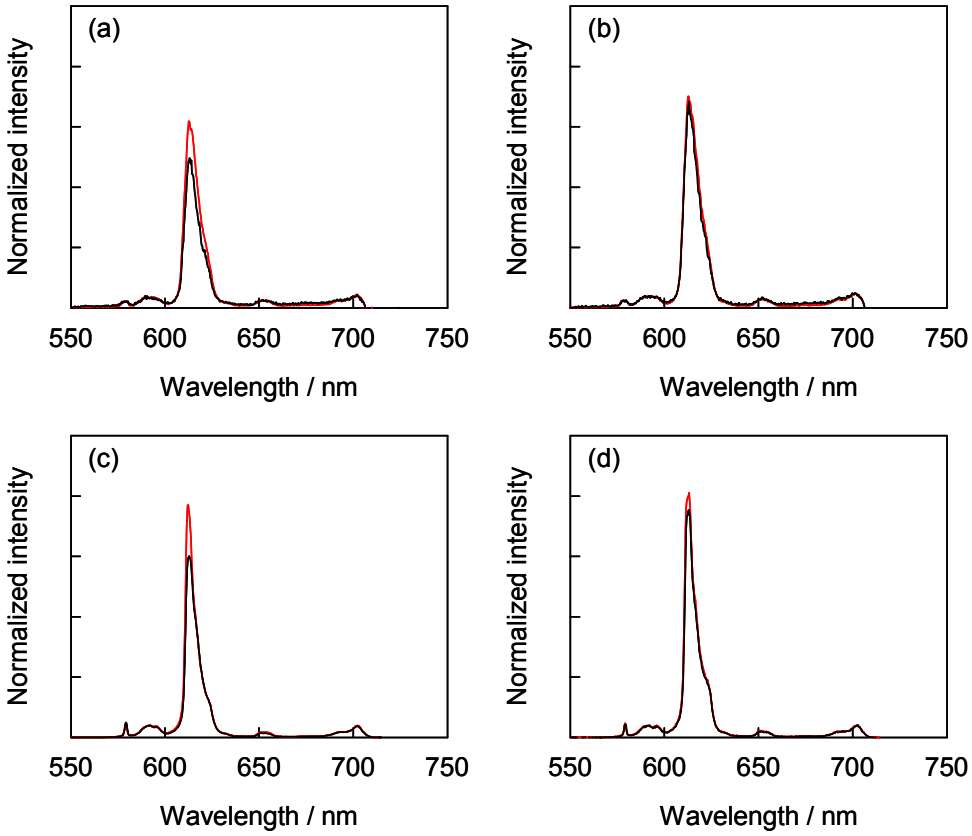

Fig. S4 Fluorescence spectrum of $[Eu(tta)_3(H_2O)_3]$ in DIPE (a), MIBK (b), benzene (c), and DCE (d) saturated with H_2O (black) and D_2O (red) following pulsed 394 nm excitation. The spectra were normalized by the intensity of the $^5D_0 \rightarrow {}^7F_1$ transition. Concentration of $[Eu(tta)_3(H_2O)_3]$ was 1.0×10^{-4} mol dm^{-3}.

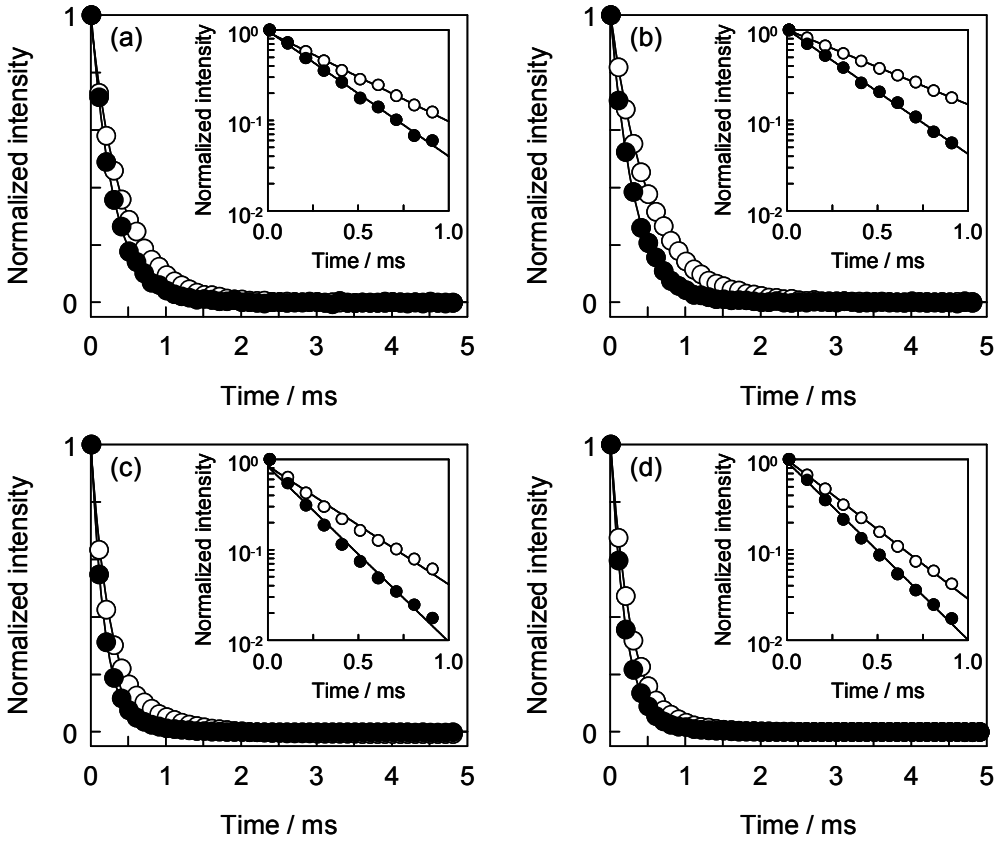

Fig. S5 Fluorescence decay at 613 nm for $[Eu(tta)_3(H_2O)_3]$ in DIPE (a), MIBK (b), benzene (c), and DCE (d) saturated with H_2O (●) and D_2O (○) following pulsed 394 nm excitation. The decays were normalized at the first data point. The fluorescence decay on a logarithmic scale is presented in the inset graph, and the solid lines were obtained by a least-squares fitting. Concentration of $[Eu(tta)_3(H_2O)_3]$ was 1.0×10^{-4} mol dm^{-3}.

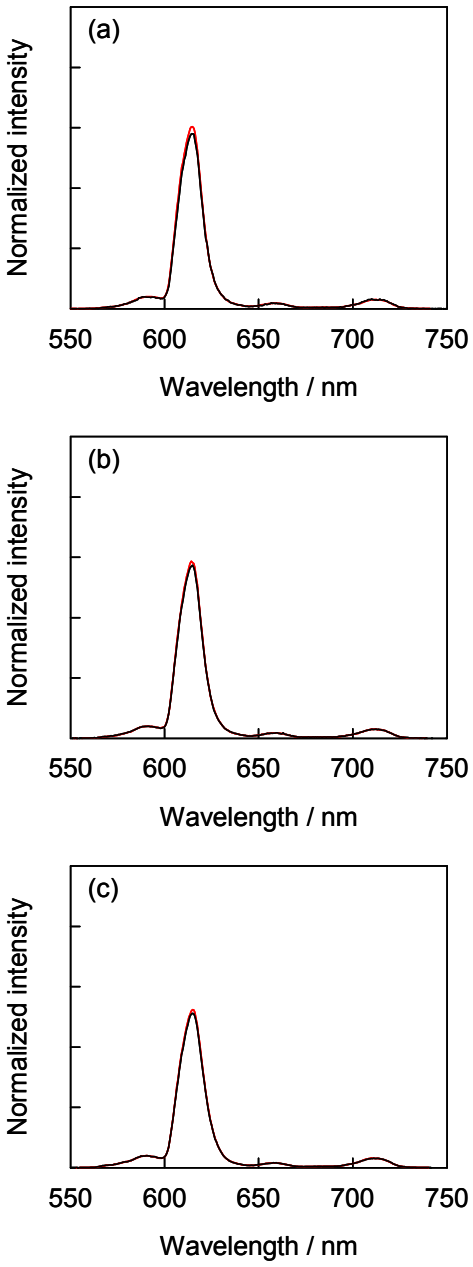

Fig. S6 Fluorescence spectrum of $[Eu(tta)_3(H_2O)_3]$ in $[C_2mim][Tf_2N, ClO_4]$ containing 5.0 mol dm^{-3} H_2O (black) and D_2O (red) (a), $[C_2mim][Tf_2N, ClO_4]$ containing 20 mol dm^{-3} H_2O (black) and D_2O (red) (b), and $[C_2mim][ClO_4]$ containing 20 mol dm^{-3} H_2O (black) and D_2O (red) (c) following pulsed 394 nm excitation. The spectra were normalized by the intensity of the $^5D_0 \rightarrow {}^7F_1$ transition. Concentration of $[Eu(tta)_3(H_2O)_3]$ was 1.0×10^{-4} mol dm^{-3}.

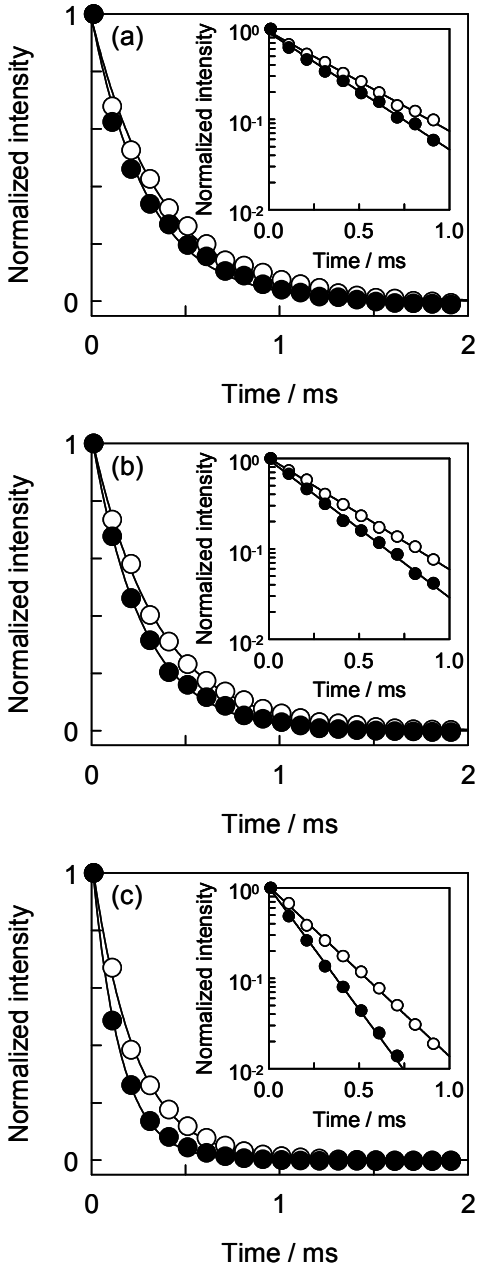

Fig. S7 Fluorescence decay at 613 nm for $[Eu(tta)_3(H_2O)_3]$ in $[C_2mim][Tf_2N, ClO_4]$ containing 5.0 mol dm^{-3} H_2O (●) and D_2O (○) (a), $[C_2mim][Tf_2N, ClO_4]$ containing 20 mol dm^{-3} H_2O (●) and D_2O (○) (b), and $[C_2mim][ClO_4]$ containing 20 mol dm^{-3} H_2O (●) and D_2O (○) (c) following pulsed 394 nm excitation. Tf_2N^- concentration in the $[C_2mim][Tf_2N, ClO_4]$ solution was 0.50 mol dm^{-3}. The decays were normalized at the first data point. The fluorescence decay on a logarithmic scale is presented in the inset graph, and the solid lines were obtained by a least-squares fitting. Concentration of $[Eu(tta)_3(H_2O)_3]$ was 1.0×10^{-4} mol dm^{-3}.

Table S1 Fluorescence decay constants and the number of coordinated water molecules for $[Eu(tta)_3(H_2O)_3]$ dissolved in $[C_2mim][Tf_2N, ClO_4]$ and $[C_2mim][ClO_4]$ containing H_2O or D_2O

Solvent	[water] / mol dm^{-3}	k_{H2O} / ms^{-1}	k_{D2O} / ms^{-1}	n_{H2O}
$[C_2mim][Tf_2N, ClO_4]$	5.0	3.33	2.72	0.6
	20	3.87	3.02	0.9
$[C_2mim][ClO_4]$	20	6.84	4.57	2.4

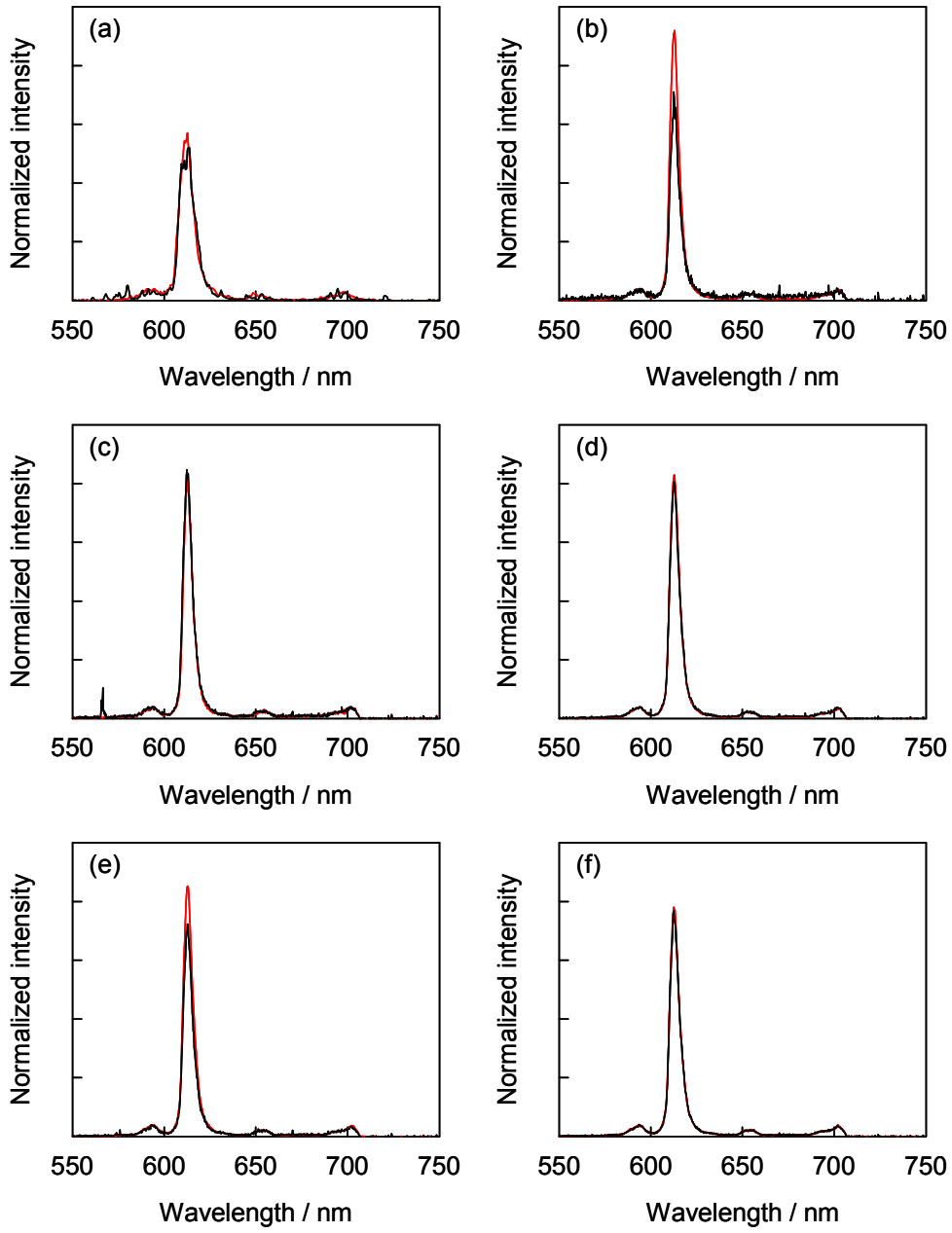

Fig. S8 Fluorescence spectrum of $[Eu(tta)_3(H_2O)_3]$ in DCE containing 0.10 vol% (a), 1.0 vol% (b), 3.0 vol% (c), 15 vol% (d), 30 vol% (e), and 50 vol% (f) $[C_4mim][Tf_2N]$ saturated with H_2O (black) and D_2O (red) following pulsed 394 nm excitation. The spectra were normalized by the intensity of the $^5D_0 \rightarrow {}^7F_1$ transition. Concentration of $[Eu(tta)_3(H_2O)_3]$ was 1.0×10^{-4} mol dm^{-3}.

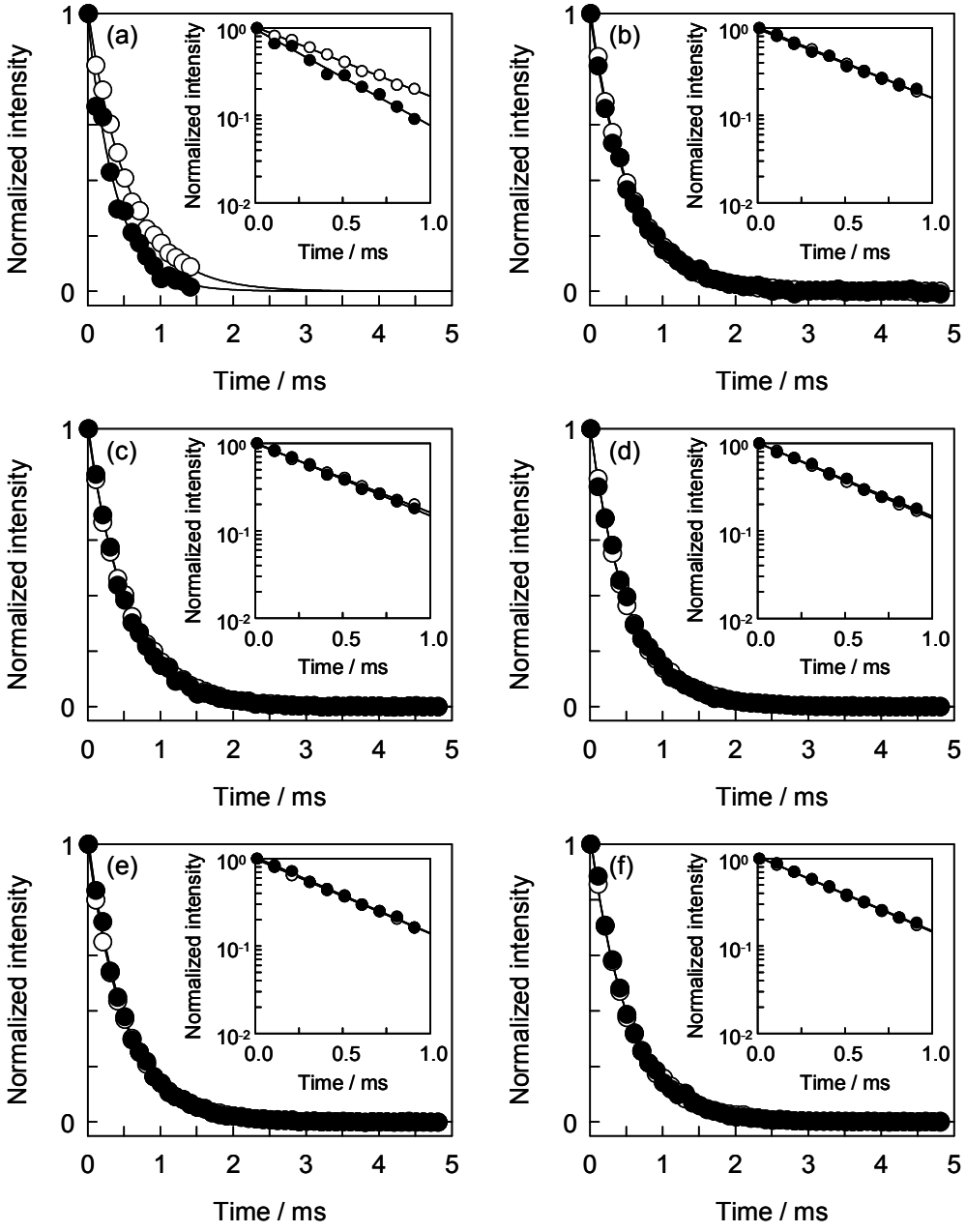

Fig. S9 Fluorescence decay at 613 nm for $[Eu(tta)_3(H_2O)_3]$ in DCE containing 0.10 vol% (a), 1.0 vol% (b), 3.0 vol% (c), 15 vol% (d), 30 vol% (e), and 50 vol% (f) $[C_4mim][Tf_2N]$ saturated with H_2O (●) and D_2O (○) following pulsed 394 nm excitation. The decays were normalized at the first data point. The fluorescence decay on a logarithmic scale is presented in the inset graph, and the solid lines were obtained by a least-squares fitting. Concentration of $[Eu(tta)_3(H_2O)_3]$ was 1.0×10^{-4} mol dm^{-3}.

Table S2 Fluorescence decay constants and the number of coordinated water molecules for $[Eu(tta)_3(H_2O)_3]$ dissolved in $[C_4mim][Tf_2N]$ diluting with DCE, saturated with H_2O or D_2O

Solvent	IL fraction / vol%	$[Tf_2N^-]$ / mol dm^{-3}	k_{H2O} / ms^{-1}	k_{D2O} / ms^{-1}	n_{H2O}
$[C_4mim][Tf_2N]$–DCE	0.10	3.4×10^{-3}	2.85	1.99	0.9
	1.0	3.4×10^{-2}	1.96	1.86	0.1
	3.0	0.10	1.96	1.85	0.1
	15	0.52	1.96	1.95	0
	30	1.0	1.94	1.96	0
	50	1.7	1.96	1.91	0.1

References

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