Supplementary Information:

Substituent Effects on Fluoride Binding by Lanthanide Complexes of DOTA-tetraamides

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1 Materials and Methods

1.1 Synthesis of Compounds

Scheme S1. Synthesis of benzyl-substituted ligands and complexes.

Commercially available reagents and solvents were used without further purification. Compounds 9, 10, 11, 12, 4, L1, 5, L2, 6, L3, 7, L4, 8, L6 were synthesised by literature procedures. All complexes were isolated as their trifluoromethanesulfonate salts.
NMR spectra were recorded on a Bruker Avance III HD nanobay 400MHz NMR with EXSY spectra and VT on a Bruker Avance III 500MHz NMR at 298 K unless expressed otherwise. All coupling constants are quoted in Hz. Abbreviations when quoting NMR data are as follows: singlet (s), doublet (d), triplet (t), multiplet (m), doublet of doublet of doublets (ddd), broad (br).

Mass spectra were obtained using either an Agilent Technology 1260 Infinity or a Waters LCT Premier XS. Luminescence measurements were obtained using a HORIBA FluoroLog3 fluorimeter. All data fitting was done in Dynafit.

2,2',2'',2''''-(1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetrayl)tetrakis(N-(4-methoxybenzyl)acetamide) (L₅) Cyclen (0.12 g, 0.70 mmol), 10 (0.60 g, 2.81 mmol) and triethylamine (0.49 mL, 3.51 mmol) were dissolved in dry tetrahydrofuran (50 mL). The mixture was heated at 70°C for 48 h. The resultant solid was filtered off, washed with water and ethanol, and recrystallized from acetonitrile and chloroform (1:1, v/v) to give a white solid (0.15 g, 24%). m/z (ES+): 452 [M+Na+H]²⁺, 441 [M+2H]²⁺. NMR (400 MHz, CDCl₃) δH (ppm) 2.44 (s, 16H, ring CH₂), 2.89 (s, 8H, CH₂CO), 3.76 (s, 12H, OC₆H₃), 4.25 (s, 8H, CH₂NH), 6.84 (d, J = 8.7, 8H, Ar), 7.06 (t, 4H, NH), 7.11 (d, J = 8.6, 8H Ar). Anal. Calcd (%) for C₄₈H₆₄N₈O₈: C, 65.43; H, 7.32; N, 12.72. Found: C, 65.37; H, 7.36; N, 12.53.

2,2',2'',2''''-(1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetrayl)tetrakis(N-(4-fluorobenzyl)acetamide) (L₇) Cyclen (0.20 g, 1.18 mmol), 12 (1.00 g, 4.97 mmol) and triethylamine (1.4 mL, 10.0 mmol) in DMF (50 mL) were heated overnight at 85 °C. Water (170 mL) was added and the solution was heated at 100 °C for 30 min. After cooling, the beige precipitate was filtered, washed with H₂O (30 mL) and dried. The solid was suspended in DMF (12 mL) and water (8 mL) and the mixture heated at 100 °C for 30 min. After cooling, the solid was filtered and dried to give a beige solid (0.26 g, 27 %). m/z (ES+): 833.4 [M + H]⁺. HR-ESMS found m/z 833.41235, calculated m/z 833.41204 for [C₄₄H₅₃O₄N₈F₄]⁺. NMR (400 MHz, DMSO-d₆) δH (ppm) 8.46 (t, J = 6.1, 4H, NH), 7.25 - 7.22 (m, 8H, Ar), 7.11 - 7.07 (m, 8H, Ar), 4.22 (d, J = 5.9, 8H, NCH₂CO), 2.97 (s, 8H, NCH₂Ar), 2.52 (s, 16H, NCH₂). NMR (376 MHz, DMSO-d₆) δF (¹H) (ppm) 116.7. δC 170.3, 161.1 (d, ¹JCF = 242.2 Hz, C), 135.7 (d, ¹JCF = 3.2 Hz, C), 129.1 (d, ³JCF = 8.1 Hz, CH), 114.9 (d, ²JCF = 21.1 Hz, CH), 57.8,
53.6, 41.1 ppm. Found: C, 63.34; H, 6.27; N, 13.34. Calc. for \( \text{C}_{44}\text{H}_{52}\text{F}_{4}\text{N}_{8}\text{O}_{4} \): C, 63.45; H, 6.29; N, 13.45 %.

**Ytterbium (III)** \( 2,2',2'',2'''\)-(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayl)tetrakis(N-benzylacetamide) (YbL\(^4\)) \( \text{L}^4 \) (0.10 g, 0.13 mmol) and Yb(OTf)\(_3\) (0.10 g, 0.13 mmol) were dissolved in acetonitrile (10 mL). The mixture was heated to 60°C for 2 d. Any unreacted ligand was filtered off and the remaining solution was concentrated in vacuo. Dichloromethane was added until a precipitate formed and the mixture was cooled to 5°C for 18 h. The precipitate was filtered off, yielding a white solid (0.047 g, 40%). \( m/z \) (ES+): 311 \([\text{M}–3\text{OTf}]^{3+}\). NMR (400 MHz, D\(_2\)O) \( \delta_{\text{H}} \) (ppm) 98.95, 18.25, 15.22, 4.55, 3.60, 3.06, 2.40, 0.02, -4.48, -26.79, -32.49, -62.13. Anal. Calcd (%) for \( \text{C}_{47}\text{H}_{56}\text{F}_{9}\text{N}_{8}\text{O}_{13}\text{S}_{3}\text{Yb} \): C, 40.87; H, 4.09; N, 8.11. Found: C, 40.54; H, 3.91; N, 8.02.

**Europium (III)** \( 2,2',2'',2'''\)-(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayl)tetrakis(N-benzylacetamide) (EuL\(^4\)) This compound was prepared in a manner identical to YbL\(^4\) using \( \text{L}^4 \) (0.08 g, 0.011 mmol) and Eu(OTf)\(_3\) (0.06 g, 0.011 mmol) in acetonitrile (10 mL) to yield a white solid (0.08 g, 79%). \( m/z \) (ES+): 1211 \([\text{M}–\text{OTf}]^{+}\), 531 \([\text{M}–2\text{OTf}]^{2+}\). NMR (400 MHz, D\(_2\)O) \( \delta_{\text{H}} \) (ppm) 26.73, 6.31, 6.11, 3.02, 2.35, -2.53, -6.39, -7.95, -13.40, -13.93. Anal. Calcd (%) for \( \text{C}_{47}\text{H}_{56}\text{F}_{9}\text{N}_{8}\text{O}_{13}\text{S}_{3}\text{Eu} \): C, 41.50; H, 4.15; N, 8.24. Found: C, 41.56; H, 4.07; N, 8.19.

**Yttrium (III)** \( 2,2',2'',2'''\)-(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayl)tetrakis(N-benzylacetamide) (YL\(^4\)) This compound was made in a manner identical to YbL\(^4\) with \( \text{L}^4 \) (0.08 g, 0.011 mmol), Y(OTf)\(_3\) (0.06 g, 0.011 mmol) in acetonitrile (10 mL) to give a white solid (0.06 g, 68%). \( m/z \) (ES+): 498 \([\text{M}–2\text{OTf}]^{2+}\). NMR (400 MHz, D\(_2\)O) \( \delta_{\text{H}} \) (ppm) 1.96-2.44 (16H, m, ring NCH\(_2\)), 2.85-3.14 (8H, m, CH\(_2\)CO), 4.40 (8H, t, CH\(_2\)NH), 7.34 (20H, s, Ar). Anal. Calcd (%) for \( \text{C}_{47}\text{H}_{56}\text{F}_{9}\text{N}_{8}\text{O}_{13}\text{S}_{3}\text{Y} \): C, 43.52; H, 4.35; N, 8.64. Found: C, 43.23; H, 4.76; N, 8.57.

**Lutetium (III)** \( 2,2',2'',2'''\)-(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayl)tetrakis(N-benzylacetamide) (LuL\(^4\)) This compound was made in a manner identical to YbL\(^4\) with L\(^4\) (0.10 g, 0.13 mmol), Lu(OTf)\(_3\) (0.081 g, 0.13 mmol) in acetonitrile (10 mL) to give a white solid (0.097 g 53%). \( m/z \): 1233 \([\text{M}–\text{OTf}]^{+}\), 542
M–OTf\(^{2+}\), NMR (400MHz, D\(_2\)O) \(\delta\) (ppm) 1.86-2.56 (16H, m, ring NCH\(_2\)), 2.85-3.20 (8H, m, CH\(_2\)CO), 4.41 (8H, s, CH\(_2\)NH), 7.35 (20H, m, Ar).

**Ytterbium (III) 2,2',2'',2''''-(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayl)tetrakis(N-(4-methoxybenzyl)acetamide) (YbL\(^5\))** The compound was prepared in a manner identical to YbL\(^4\) using L\(^5\) (0.05 g, 0.056 mmol) and Yb(OTf)\(_3\) (0.04 g, 0.056 mmol) dissolved in acetonitrile (10 mL). This yielded a white solid (0.06 g, 65%). \(m/z\): 458 [M–2OTf+Na]\(^{3+}\). NMR (400 MHz, D\(_2\)O) \(\delta\) (ppm) 97.82, 18.32, 15.60, 5.83, 4.70, 3.48, 2.05, 1.10, -1.07, -4.46, -26.09, -31.64, -60.58. Anal. Calcd (%) for C\(_{51}\)H\(_{64}\)F\(_9\)N\(_8\)O\(_{17}\)S\(_3\)Y: C, 40.80; H, 4.30; N, 7.46. Found: C, 39.72; H, 4.04; N, 7.72.

**Europium (III) 2,2',2'',2''''-(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayl)tetrakis(N-(4-methoxybenzyl)acetamide) (EuL\(^5\))** The compound was prepared in a manner identical to YbL\(^4\) using L\(^4\) (0.05 g, 0.06 mmol) and Eu(OTf)\(_3\) (0.03 g, 0.06 mmol) dissolved in acetonitrile (10 mL) to yield a white solid (0.02 g, 34%). \(m/z\): 591 [M–2OTf]\(^{2+}\). NMR (400 MHz, D\(_2\)O) \(\delta\) (ppm) 26.29, 6.61, 6.10, 3.48, 3.21, 2.75, 2.24, 1.10, 0.33, -2.61, -6.10, -7.88, -12.79, -13.62. Anal. Calcd for C\(_{51}\)H\(_{64}\)F\(_9\)N\(_8\)O\(_{17}\)S\(_3\)Eu: C, 41.38; H, 4.36; N, 7.57. Found: C, 41.38; H, 4.13; N, 7.97.

**Yttrium (III) 2,2',2'',2''''-(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayl)tetrakis(N-(4-methoxybenzyl)acetamide) (YL\(^5\))** The compound was prepared in a manner identical to YbL\(^4\) using L\(^5\) (0.05 g, 0.06 mmol) and Y(OTf)\(_3\) (0.03 g, 0.06 mmol) in acetonitrile (10 mL) to yield a white solid (0.07 g, 85%). NMR (400 MHz, D\(_2\)O) \(\delta\) (ppm) 2.07-2.52 (m, ring, 16H, NC\(_2\)H\(_2\)), 3.01-3.22 (8H, CH\(_2\)CO), 4.32 (t, 8H, CH\(_2\)NH), 6.86 (d, \(J = 1.2\), 8H, Ar), 7.30 (d, \(J = 1.2\), 8H, Ar). Anal. Calcd (%) for C\(_{51}\)H\(_{64}\)F\(_9\)N\(_8\)O\(_{17}\)S\(_3\)Y: C, 43.22; H, 4.55; N, 7.61. Found: C, 44.47; H, 3.97; N, 8.15.

**Ytterbium (III) 2,2',2'',2''''-(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayl)tetrakis(N-(4-nitrobenzyl)acetamide) (YbL\(^6\))** The compound was prepared in a manner identical to YbL\(^4\) using L\(^6\) (0.051 g, 0.061 mmol) and Yb(OTf)\(_3\) (0.038 g, 0.061 mmol) dissolved in acetonitrile (5 mL) to yield a yellow solid (0.054 g, 61%). \(m/z\) (ES+): 1412 [M–OTf]\(^+\), 631 [M–2OTf]\(^{2+}\). NMR (400 MHz, D\(_2\)O) \(\delta\) (ppm) 88.45, 16.59, 13.81 (7.01, .031, -3.28), -23.21, -28.37, -52.72. Anal. Calcd (%) for
C_{47}H_{52}F_{9}N_{12}O_{21}S_{3}Yb: C, 36.25; H, 3.11; N, 10.98. Found: C, 36.18; H, 3.16; N, 10.66.

**Europium (III)** $2,2',2'',2'''$-(1,4,7,10-tetraazacyclododecane-$1,4,7,10$-tetracyl)tetrakis(N-(4-nitrobenzyl)acetamide) ($\text{EuL}^6$) This compound was prepared in a manner identical to YbL$_4$ using L$^6$ (0.051 g, 0.061 mmol) and Eu(OTf)$_3$ (0.036 g, 0.061 mmol) in acetonitrile (5 mL) to yield a white solid (0.051 g, 59%). $m/z$ (ES+): 1391 [M–OTf]$^+$, 621 [M–2OTf]$^{2+}$. NMR (400 MHz, D$_2$O) $\delta_H$ (ppm) 23.95, 7.79, 3.40, 2.86, -3.00, -5.23, -8.43, -10.68, -12.78. Anal. Calcd (%) for C$_{47}$H$_{52}$F$_9$N$_{12}$O$_{21}$S$_3$Eu: C, 36.75; H, 3.15; N, 10.94. Found: C, 36.88; H, 3.26; N, 10.84.

**Yttrium (III)** $2,2',2'',2'''$-(1,4,7,10-tetraazacyclododecane-$1,4,7,10$-tetracyl)tetrakis(N-(4-nitrobenzyl)acetamide) ($\text{YL}^6$) This compound was prepared in a manner identical to YbL$_4$ using L$^6$ (0.045 g, 0.053 mmol) and Y(OTf)$_3$ (0.029 g, 0.053 mmol) dissolved in acetonitrile (5 mL) to yield a white solid (0.048 g, 65%). $m/z$ (ES+): 589 [M–2OTf]$^{2+}$. NMR (400 MHz, D$_2$O) $\delta_H$ (ppm) 2.09–2.65 (16H, m, ring NCH$_2$), 3.18–3.32 (8H, m, CH$_2$CO), 4.47–4.60 (8H, t, CH$_2$NH), 7.53 (8H, d, $J$ = 8.6, Ar), 8.14 (8H, d, $J$ = 8.7, Ar) Anal. Calcd (%) for C$_{47}$H$_{52}$F$_9$N$_{12}$O$_{21}$S$_3$: C, 38.22; H, 3.55; N, 11.36 Found: C, 38.06; H, 3.79; N, 11.28.

**Ytterbium** $2,2',2'',2'''$-(1,4,7,10-tetraazacyclododecane-$1,4,7,10$-tetracyl)tetrakis(N-(4-fluorobenzyl)acetamide) ($\text{YbL}^7$) This compound was prepared in a manner identical to YbL$_4$ using L$^7$ (0.051 g, 0.061 mmol) and Yb(OTf)$_3$ (0.038 g, 0.061 mmol) dissolved in acetonitrile (5 mL) to yield a white solid (0.054 g, 61%). NMR (400 MHz, D$_2$O) $\delta_H$ (ppm) 95.0, 17.6, 14.7, 4.6, 3.7, -0.2, -4.2, -25.5, -31.0, -59.1. NMR (376 MHz, DMSO-$d_6$) $\delta_F$ {$_1$H} (ppm) -118.6. $m/z$ (ES+): 577.7 [M–2OTf]$^{2+}$. HR-ESMS found $m/z$ 1302.24866, calculated $m/z$ 1302.24464 for [C$_{46}$H$_{52}$O$_{10}$N$_8$F$_{10}$S$_2$Yb]$^+$. Anal. Calcd (%) for C$_{47}$H$_{52}$F$_9$N$_{12}$O$_{21}$S$_3$: C, 38.85; H, 3.61; N, 7.71. Found: C, 38.66; H, 3.52; N, 7.62.

**Europium (III)** $2,2',2'',2'''$-(1,4,7,10-tetraazacyclododecane-$1,4,7,10$-tetracyl)tetrakis(N-(4-fluorobenzyl)acetamide) ($\text{EuL}^7$) This compound was prepared in a manner identical to YbL$_4$ using L$^7$ (0.051 g, 0.061 mmol) and Eu(OTf)$_3$ (0.036 g, 0.061 mmol) dissolved in acetonitrile (5 mL) to yield a white solid (0.051 g, 59%).
NMR (400 MHz, D2O) δH (ppm) 25.9, 6.7, 6.3, 3.7, 3.1, 2.5, -2.6, -6.0, -8.0, -12.5, -13.4. NMR (376 MHz, DMSO-d6) δF {1H} (ppm) -115.9. m/z (ES+): 567.3 for [M–2OTf]2+. HR-ESMS found m/z 328.44150, calculated m/z 328.44145 for [C44H52O4N8EuF4]3+. Anal. Calcd (%) for C47H52EuF13N8O13S3: C, 39.42; H, 3.66; N, 7.82. Found: C, 39.54; H, 3.54; N, 7.75.

Yttrium (III) 2,2’,2”’,2”’’-(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayl)tetrakis(N-(4-fluorobenzyl)acetamide) (YL7) This compound was prepared in a manner identical to YbL4 using L7 (0.045 g, 0.053 mmol) and Y(OTf)3 (0.029 g, 0.053 mmol) dissolved in acetonitrile (5 mL) to yield a white solid (0.048 g, 65%).

1H NMR (400 MHz, D2O) δH 7.40 - 7.37 (m, 8H, Ar), 7.10 (t, J = 8.7, 8H, Ar), 4.48 - 4.39 (m, 8H, ArCH2), 3.25 (t, J = 14.3, 4H, ring NCH2), 3.08 (d, J = 16.5, 4H, NCH2CO), 2.57 (d, J = 14.3, 4H, ring NCH2), 2.33 - 2.23 (m, 8H, ring NCH2 and NCH2CO), 2.03 (t, J = 14.3, 4H, ring NCH2) NMR (376 MHz, DMSO-d6) δF {1H} (ppm) -114.9. m/z (ES+): 535.1 [M–2OTf]2+. HR-ESMS found m/z 307.10287, calculated m/z 307.10299 for [C44H52O4N8F4Y]3+. Anal. Calcd (%) for C47H52YF13N8O13S3: C, 41.23; H, 3.83; N, 8.18. Found: C, 41.06; H, 3.71; N, 8.66.
NMR Studies

Figure S1. Bleaney plots and associated gradients for YbL<sup>1-7</sup>-OH<sub>2</sub> (black) and YbL<sup>1-7</sup>-F (red) in D<sub>2</sub>O using crystal structures from references 6 (YbL<sup>1-3</sup>) and 10 (YbL<sup>4-7</sup>).
Table S1. Values of $\chi_\parallel$ and $\chi_\perp$ calculated from the slopes of the Bleaney plots in Figure S1,\textsuperscript{11} using an estimate of $\chi_{av} T$ as 2.50 cm$^3$mol$^{-1}$K to determine $\chi_{av}$.

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Figure S2. $^1$H EXSY spectra (500 MHz, D$_2$O, 298 K) of complexes YbL$^{1-7}$ with added fluoride showing the exchange between hydrated and fluoride-bound species.
Figure S3. $^1$H NMR spectra (D$_2$O, 298 K) of complexes EuL$^{1-7}$ in the absence (black) and presence (red) of an excess of sodium fluoride.
3 Titration data

3.1 Luminescence titrations

Figure S5. Left: Changes to the EuL₁ emission spectrum on addition of sodium fluoride start of titration (black), end of titration (red), intermediate concentrations (grey). Right: Binding isotherms and fits using the intensity ratios ΔJ = 2/ΔJ = 0, ΔJ = 2/ΔJ = 1, ΔJ = 2/ΔJ = 3 and ΔJ = 2/ΔJ = 4.
Figure S6. Left: Changes to the EuL³ emission spectrum on addition of sodium fluoride start of titration (black), end of titration (red), intermediate concentrations (grey). Right: Binding isotherms and fits using the intensity ratios.

Figure S7. Left: Changes to the EuL⁴ emission spectrum on addition of sodium fluoride start of titration (black), end of titration (red), intermediate concentrations (grey). Right: Binding isotherms and fits using Binding isotherms and fits using the intensity ratios.

Figure S8. Left: Changes to the EuL⁵ emission spectrum on addition of sodium fluoride start of titration (black), end of titration (red), intermediate concentrations
(grey). Right: Binding isotherms and fits using Binding isotherms and fits using the intensity ratios.

Figure S9. Left: Changes to the EuL\textsuperscript{6} emission spectrum on addition of sodium fluoride start of titration (black), end of titration (red), intermediate concentrations (grey). Right: Binding isotherms and fits using Binding isotherms and fits using the intensity ratios.

Figure S10. Left: Changes to the EuL\textsuperscript{7} emission spectrum on addition of sodium fluoride start of titration (black), end of titration (red), intermediate concentrations (grey). Right: Binding isotherms and fits using the Binding isotherms and fits using the intensity ratios.
3.2 NMR titrations

Figure S11. Binding isotherms and fits for titration of EuL\textsuperscript{1} with NaF monitoring \textsuperscript{1}H NMR integrals relative to DSS at 298 K.

Figure S12. Binding isotherms and fits for titration of EuL\textsuperscript{3} with NaF monitoring \textsuperscript{1}H NMR integrals relative to DMF and \textsuperscript{19}F NMR integrals relative to OTf\textsuperscript{-} at 278 K.
Figure S13. Binding isotherms and fits for titration of EuL$^4$ with NaF monitoring $^1$H NMR integrals relative to DSS at 298 K.

Figure S14. Binding isotherms and fits for titration of EuL$^5$ with NaF monitoring $^1$H NMR integrals relative to DSS at 298 K.
Figure S15. Binding isotherms and fits for titration of EuL\textsuperscript{6} with NaF monitoring \textsuperscript{1}H NMR integrals relative to DSS at 298 K.

Figure S16. Binding isotherms and fits for titration of EuL\textsuperscript{7} with NaF monitoring \textsuperscript{19}F NMR integrals of the ligand fluorines relative to OTf\textsuperscript{-} at 298 K.
4 lnK vs. D₁

Figure S17. Correlation between lnK (measured by luminescence) of the Eu complexes of L₁⁻⁷ and D₁ values for the Yb complexes from ¹H Bleaney plots.

5 Rates of Exchange

5.1 LuL₁ ¹H NMR spectra

Figure S18. ¹H NMR spectra (D₂O, 298 K) of LuL₁ upon addition of increasing amounts of sodium fluoride.
Figure S19. $^1$H NMR spectra ($\text{D}_2\text{O}, 298 \text{ K}$) of LuL$_3$ upon addition of increasing amounts of sodium fluoride.

Figure S20. $^1$H NMR spectra ($\text{D}_2\text{O}, 298 \text{ K}$) of LuL$_4$ upon addition of increasing amounts of sodium fluoride.

Figure S21. $^1$H NMR spectra ($\text{D}_2\text{O}, 298 \text{ K}$) of LuL$_4$ (bottom) with added sodium fluoride at 298 K (red) and 323 K (black).
5.2 $^1$H/$^19$F Inversion recovery data

Figure S22. $^1$H intensities of the methyl groups of YbL$_2$-OH$_2$ and YbL$_2$-F following selective inversion (top) and non-selective inversion (bottom) at 278 K, fits are shown in red.

Figure S23. $^1$H intensities of the methyl groups of YbL$_2$-OH$_2$ and YbL$_2$-F following selective inversion (top) and non-selective inversion (bottom) at 283 K, fits are shown in red.
Figure S24. $^1H$ intensities of the methyl groups of Yb$^2$-OH$_2$ and Yb$^2$-F following selective inversion (top) and non-selective inversion (bottom) at 288 K, fits are shown in red.

Figure S25. $^1H$ intensities of the methyl groups of Yb$^2$-OH$_2$ and Yb$^2$-F following selective inversion (top) and non-selective inversion (bottom) at 293 K, fits are shown in red.
Figure S26. $^1H$ intensities of the methyl groups of YbL$_2$-OH$_2$ and YbL$_2$-F following selective inversion (top) and non-selective inversion (bottom) at 298 K, fits are shown in red.

Figure S27. $^1H$ intensities of the methyl groups of YbL$_2$-OH$_2$ and YbL$_2$-F following selective inversion (top) and non-selective inversion (bottom) at 303 K, fits are shown in red.
Figure S28. $^{19}$F intensities of the ligand benzyl substituent of YbL$_7$-OH$_2$ and YbL$_7$-F following selective inversion (top) and non-selective inversion (bottom) at 278 K, fits are shown in red.

Figure S29. $^{19}$F intensities of the ligand benzyl substituent of YbL$_7$-OH$_2$ and YbL$_7$-F following selective inversion (top) and non-selective inversion (bottom) at 283 K, fits are shown in red.
Figure S30. $^{19}$F intensities of the ligand benzyl substituent of Yb$^7$-OH$_2$ and Yb$^7$-F following selective inversion (top) and non-selective inversion (bottom) at 288 K, fits are shown in red.

Figure S31. $^{19}$F intensities of the ligand benzyl substituent of Yb$^7$-OH$_2$ and Yb$^7$-F following selective inversion (top) and non-selective inversion (bottom) at 293 K, fits are shown in red.
Figure S32. $^{19}$F intensities of the ligand benzyl substituent of $\text{YbL}^7$-$\text{OH}_2$ and $\text{YbL}^7$-$\text{F}^-$ following selective inversion (top) and non-selective inversion (bottom) at 298 K, fits are shown in red.

Figure S33. $^{19}$F intensities of the ligand benzyl substituent of $\text{YbL}^7$-$\text{OH}_2$ and $\text{YbL}^7$-$\text{F}^-$ following selective inversion (top) and non-selective inversion (bottom) at 303 K, fits are shown in red.
Table S2. Rates of exchange at multiple temperatures measured using selective inversion and fit using CIFIT\textsuperscript{12} for YbL\textsuperscript{2} and YbL\textsuperscript{7} with fluoride in D\textsubscript{2}O at 500 MHz.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>YbL\textsuperscript{2} k (s\textsuperscript{-1})</th>
<th>Temperature (K)</th>
<th>YbL\textsuperscript{7} k (s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>278</td>
<td>50.0 ± 1.0</td>
<td>278</td>
<td>14.8 ± 0.3</td>
</tr>
<tr>
<td>283</td>
<td>71.0 ± 1.1</td>
<td>283</td>
<td>22.7 ± 1.0</td>
</tr>
<tr>
<td>288</td>
<td>108.3 ± 1.6</td>
<td>288</td>
<td>31.5 ± 1.0</td>
</tr>
<tr>
<td>293</td>
<td>160.7 ± 4.0</td>
<td>293</td>
<td>42.8 ± 2.0</td>
</tr>
<tr>
<td>298</td>
<td>215.7 ± 3.0</td>
<td>298</td>
<td>61.2 ± 3.6</td>
</tr>
<tr>
<td>303</td>
<td>283.1 ± 6.0</td>
<td>303</td>
<td>84.2 ± 7.8</td>
</tr>
</tbody>
</table>


\textsuperscript{11} From equations 2 and 3 in the main paper, it should be clear that

\[ \delta_{PC} = D_1 \frac{(3\cos^2\theta - 1)}{r^3} = \frac{1}{2N_A} \left[ \frac{(3\cos^2\theta - 1)}{r^3} (\chi_\parallel - \chi_{av}) \right] \]

so,

\[ D_1 = \frac{1}{2N_A} [(\chi_\parallel - \chi_{av})] \]