Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Quantitative Determination of Fluoride in Pure Water using Luminescent Europium Complexes

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Contents

1. Experimental Section

1.1 General Procedures

NMR Spectroscopy and Mass Spectrometry

^{1}H, ^{13}C, ^{19}F and NMR spectra were recorded in commercially-available deuteriated solvents on a Varian Mercury-200 (^{1}H at 199.975 MHz, ^{13}C at 50.289 MHz, ^{19}F at 188.090 MHz), Varian Mercury-400 or Bruker Avance-400 (^{1}H at 399.960 MHz, ^{13}C at 100.572 MHz), Varian Inova-500 (^{1}H at 499.772 MHz, ^{13}C at 125.671 MHz) or Varian VNMRS-700 (^{1}H at 699.731 MHz, ^{13}C at 176.939 MHz) spectrometer. All chemical shifts are given in ppm and coupling constants are in Hz. Electrospray mass spectra were recorded on a Waters Micromass LCT or Thermo-Finnigan LTQ FT instrument operating in positive or negative ion mode as stated, with methanol as the carrier solvent. Accurate mass spectra were recorded using the Thermo-Finnigan LTQ FT mass spectrometer.

Chromatography

Flash column chromatography was performed using flash silica gel 60 (230 - 400 mesh) from Merck. Thin layer chromatography (TLC) was performed on aluminum sheet silica gel plates with 0.2 mm thick silica gel 60 F_{254} (E. Merck) using different mobile phase. The compounds were visualized by UV irradiation (254 nm).

Reverse phase HPLC traces were recorded at 298 K using a Perkin Elmer system equipped with a Perkin Elmer Series 200 Pump, a Perkin Elmer Series 200 Autosampler and a Perkin Elmer Series 200 Diode array detector (operated at 254 nm). Separation was achieved using a semi-preparative Waters XBridge RP-C_{18} column (5 µm, 10 × 100 mm) at a flow rate maintained at 4.4 mL/min. For the purification of ligand $\mathbf{L^1}$ a solvent system composed of water (0.1% formic acid) / methanol was used over the stated linear gradient. Analytical RP-HPLC was performed using a Waters XBridge RP-C_{18} column (3.5 µm, 4.6 × 100 mm) at a flow rate maintained at 1.0 mL/ min over the stated linear gradient.

pH and ISE Measurements

Measurements of pH were carried out using a Jenway 3510 pH/mV meter with a Jenway combination electrode or a Jenway 3020 pH meter with an Aldrich glass combination pH electrode, both calibrated using buffer solutions of pH 4.00 ± 0.01, 7.00 ± 0.01 and 10.00 ± 0.01. ISE measurements were performed using a Jenway 3510 pH/mV meter, equipped with a Mettler Toledo DX219 fluoride selective electrode and a Ag/AgCl reference electrode (Mettler Toledo). Calibration was achieved by a standard addition method.

Optical Spectroscopy

Unless otherwise specified, quartz cuvettes with a pathlength of 1 cm or disposable UV-grade methacrylate cuvettes were used to contain all samples. UV/Vis absorbance spectra were measured on an ATI Unicam UV/Vis spectrometer (Model UV2) using Vision version 3.33 software. Molar extinction coefficients were determined by first dissolving a known amount of complex in a known amount of solvent to give a bulk solution. Four solutions of known concentration, with absorbances ranging between 0.1 and 1.0, were made up by dilution of the bulk solution. Molar extinction coefficients, ε, were calculated in accordance with the Beer-Lambert law, by plotting absorbance, A, against complex concentration, c.

Emission spectra were recorded on an ISA Joblin-Yvon Spex Fluorolog-3 luminescence spectrometer using DataMax version 2.2.10 software. An integration time of 0.5 seconds, increment of 0.5 nm and excitation and emission slits of 2.5 and 1.5 nm respectively were used.

Lifetime measurements were measured using a Perkin Elmer LS55 luminescence spectrometer with FL Winlab Molecular Spectroscopy version 4.00.02 software. Lifetime measurements were typically obtained by indirect excitation of the lanthanide (III) ion *via* the chromophore using a short pulse of light (at λ_{max}) followed by monitoring the integrated intensity of the light emitted at 615 nm during a fixed gate time, t_g, after a delay time, t_d. Measurements were made for a minimum of 20 delay times, covering 3 or more lifetimes. A gate time of 0.1 ms was used, and the excitation and emission slits were set to 10 and 5 nm respectively. The obtained decay curves were plotted in Microsoft Excel and fitted to the equation:

$$I = A_0 + A_1 e^{-kt}$$

I: intensity at time t following excitation; A_0: intensity when decay has ceased

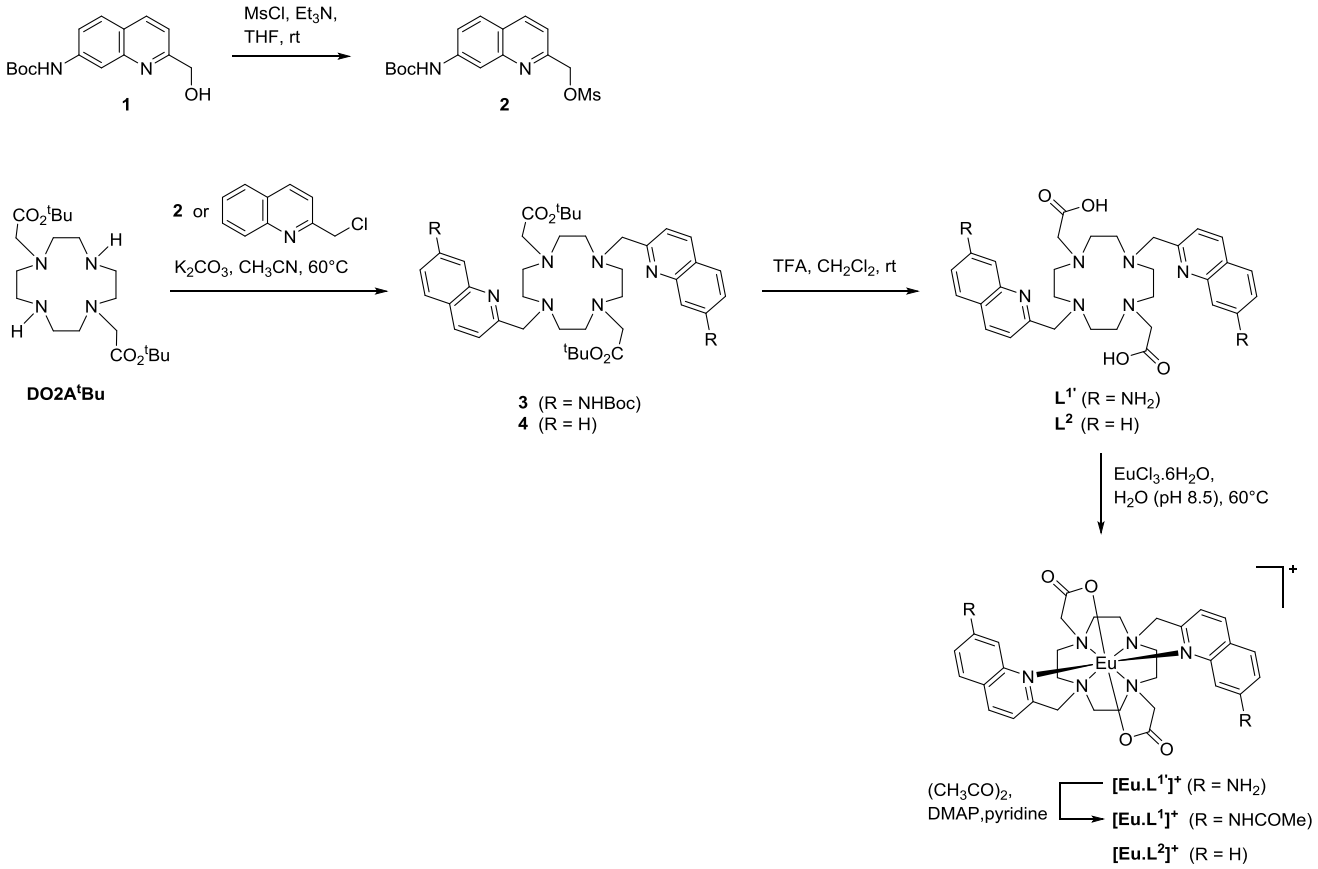
A_1: pre-exponential factor; k: rate constant for the depopulation of the excited state

General procedure for titrating $[Eu.L^{1\text{-}2}]^+$ with anions

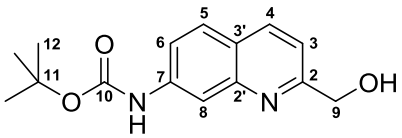
A stock solution of $[\mathbf{Eu.L^{1\text{-}2}}]^+$ (2 mM) was prepared in the stated aqueous buffer solution. Stock solutions of the anion (sodium salt, 0.025 M and 0.1 M) were also prepared. To a 1 cm quartz glass cuvette was added a solution of the probe (20 μM, 1.0 mL) and the luminescence emission spectrum was recorded (λ_{exc} = 332 nm for $[\mathbf{Eu.L^1}]^+$; 318 nm for $[\mathbf{Eu.L^2}]^+$). Aliquots of the anion solution were then added, ensuring that the total added volume did not exceed 50 uL. After each addition, the solution was mixed with a pipette and the emission spectrum was recorded. Typically, 1000 equivalents of the anion were added to the solution. Each titration was repeated at least twice.

To determine association constants (reported as log K_a values) for the bound anions, two wavelength bands were selected and the emission intensity ratio was plotted as a function of anion concentration. The titration data was analysed using a nonlinear least-squares curve fitting procedure, based on a 1:1 binding model.

1.2 Compound Synthesis and Characterisation



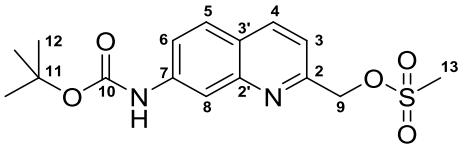
Scheme S1. Synthesis of complexes **[Eu.L$^{1\text{-}2}$]$^{+}$**.



7-(*t*-Butoxycarbonylamino)-2-quinolinylmethanol (1)

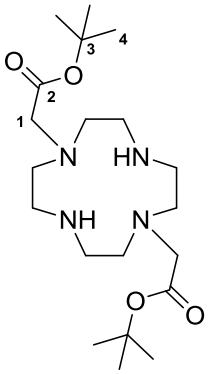
The experimental procedure for the synthesis of alcohol **1** has been reported previously.[1]

m.p. 71–73 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.05 (1H, d, $^{3}J_{H\text{-}H}$ 8.3 Hz, H^{4}), 8.02 (1H, d, $^{4}J_{H\text{-}H}$ 1.8 Hz, H^{8}), 7.74 (1H, d, $^{3}J_{H\text{-}H}$ 8.8 Hz, H^{5}), 7.67 (1H, d, $^{3}J_{H\text{-}H}$ 8.8 Hz, $^{4}J_{H\text{-}H}$ 1.8 Hz, H^{6}), 7.16 (1H, d, $^{3}J_{H\text{-}H}$ 8.3 Hz, H^{3}), 6.81 (1H, br s, CONH), 4.89 (2H, s, H^{9}), 1.57 (9H, s, H^{12}), O-H signal not observed; ^{13}C NMR (176 MHz, $CDCl_3$) δ 159.5 (C^{2}), 152.6 (C^{10}), 147.7 (C$^{2'}$), 140.1 (C^{7}), 136.7 (C^{4}), 128.6 (C^{5}), 124.0 (C$^{3'}$), 119.4 (C^{6}), 117.0 (C^{3}), 114.9 (C^{8}), 81.3 (C^{11}), 64.1 (C^{9}), 28.5 (C^{12}); ESI-LRMS (+) *m*/*z* 275 [M + H]$^{+}$; ESI-HRMS (+) *m*/*z* 275.1386 [M + H]$^{+}$ ($C_{15}H_{19}N_2O_3$ requires 275.1396); R_f = 0.55 (silica gel; hexane/EtOAc 1:1 v/v).



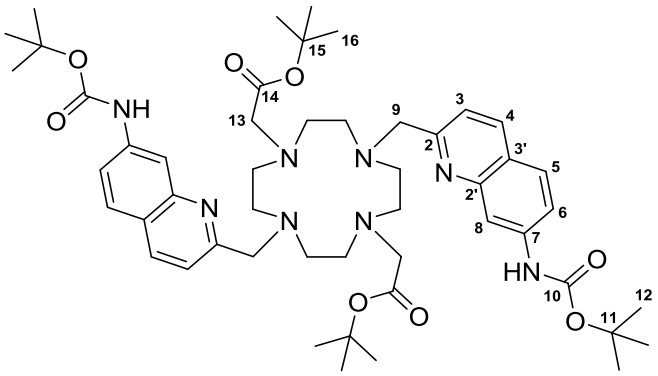
7-(*t*-Butoxycarbonylamino)-2-((methylsulfonyloxy)methyl)quinoline (2)

Alcohol **1** (0.500 g, 1.82 mmol) was dissolved in anhydrous THF (15 mL) and cooled to 5 °C. Triethylamine (0.51 mL, 3.65 mmol) and methanesulfonyl chloride (0.22 mL, 2.74 mmol) were added and the mixture was stirred under argon for 30 min. The progress of the reaction was monitored by TLC [silica gel; hexane/EtOAc 1:1 v/v, R_f(product) = 0.83, R_f(reactant) = 0.55]. The solvent was removed under reduced pressure and the residue was partitioned between CH_2Cl_2 (30 mL) and sat. aq. brine solution (30 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give 7-(*t*-butoxycarbonylamino)-2-((methylsulfonyloxy)methyl)quinloline **2** as a yellow oil (0.642 g, quant.), which was used immediately in the next step; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.16 (1H, d, $^3J_{H\text{-}H}$ 8.3 Hz, H^4), 7.97 (1H, d, $^4J_{H\text{-}H}$ 1.8 Hz, H^8), 7.78 (2H, m, H^5 and H^3), 7.47 (1H, d, $^3J_{H\text{-}H}$ 8.6 Hz, H^6), 6.95 (1H, br s, CONH), 5.48 (2H, s, H^9), 3.16 (3H, s, H^{13}), 1.55 (9H, s, H^{12}); ESI-LRMS (+) *m*/*z* 353 $[M + H]^+$; R_f = 0.85 (silica gel; hexane/EtOAc 1:1 v/v).



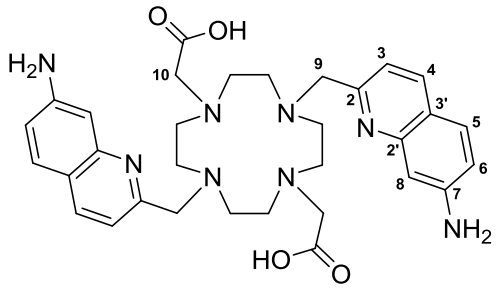
(7-*tert*-Butoxycarbonylmethyl-1,4,7,10-tetraazacyclododec-1-yl)-acetic acid *tert*-butyl ester (DO2A^{t}Bu)

The procedure for the preparation of the macrocyclic diester, DO2A^{t}Bu, was followed according to that reported previously.[2] The bis-amine was isolated as a brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.31 (4H, s, H^1), 2.82 (8H, br m, ring CH_2), 2.71 (8H, br m, ring CH_2), 1.45 (18H, s, H^4); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9 (C^2), 82.7 (C^3), 60.1 (C^1), 53.4 (ring CH_2), 51.8 (ring CH_2), 27.3 (C^4); the spectral data were consistent with those previously reported for DO2A^{t}Bu.[2] ESI-LRMS (+) *m*/*z* 401.6 $[M + H]^+$; ESI-HRMS (+) *m*/*z* 401.3121 $[M + H]^+$ ($C_{20}H_{41}N_4O_4$ requires 401.3128).



Compound (3)

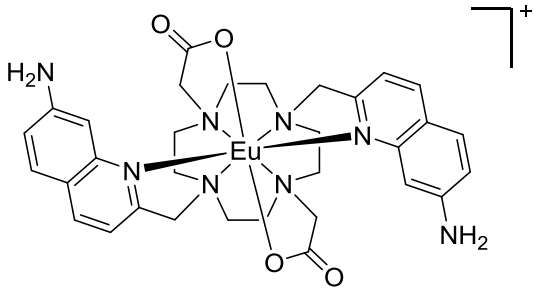
To a solution of 7-(*t*-butoxycarbonylamino)-2-((methylsulfonyloxy)methyl)quinoline **2** (142 mg, 0.402 mmol) and the macrocyclic diester, DO2A^{t}Bu (73 mg, 0.183 mmol), in anhydrous CH_3CN (15 mL) was added K_2CO_3 (56 mg, 0.402 mmol) and the mixture was stirred under argon at 60 °C. The progress of the reaction was monitored by LC-MS analysis at regular intervals, which revealed complete consumption of starting material after 24 h. The reaction mixture was cooled to room temperature and the solution decanted from excess potassium salts. The solvent was removed under reduced pressure and the crude material was purified by column chromatography (silica, CH_2Cl_2/2–10% CH_3OH in 1% increments) to give compound **3** as a yellow oil; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.16 (2H, d, $^3J_{H\text{-}H}$ 8.3 Hz, H^4), 7.91 (2H, d, $^4J_{H\text{-}H}$ 1.8 Hz, H^8), 7.76 (2H, d, $^3J_{H\text{-}H}$ 8.7 Hz, $^4J_{H\text{-}H}$ 1.8 Hz, H^6), 7.69 (2H, d, $^3J_{H\text{-}H}$ 8.7 Hz, H^5), 7.32 (2H, d, $^3J_{H\text{-}H}$ 8.3 Hz, H^3), 6.77 (2H, br s, CONH), 4.02–3.70 (8H, br m, ring CH_2), 3.09 (4H, s, H^{13}), 2.86 (4H, s, H^9), 2.73–2.38 (8H, br m, ring CH_2), 1.43 (18H, s, H^{12}), 1.17 (18H, s, H^{16}); ^{13}C NMR (176 MHz, $CDCl_3$) δ 171.8 (C^{14}), 159.4 (C^2), 152.6 (C^{10}), 148.6 (C$^{2'}$), 140.2 (C^7), 137.0 (C^4), 128.2 (C^5), 123.6 (C$^{3'}$), 120.2 (C^6), 120.0 (C^3), 115.8 (C^8), 82.4 (C^{15}), 80.6 (C^{11}), 60.5 (C^9), 57.4 (C^{13}), 51.3–49.8 (ring CH_2), 28.3 (C^{16}), 28.0 (C^{12}); ESI-LRMS (+) *m*/*z* 914 $[M + H]^+$; ESI-HRMS (+) *m*/*z* 913.5549 $[M + H]^+$ ($C_{50}H_{73}N_8O_8$ requires 913.5551); R_f = 0.33 (silica gel; CH_2Cl_2/CH_3OH 9:1 v/v).



Ligand 1' (L$^{1'}$)

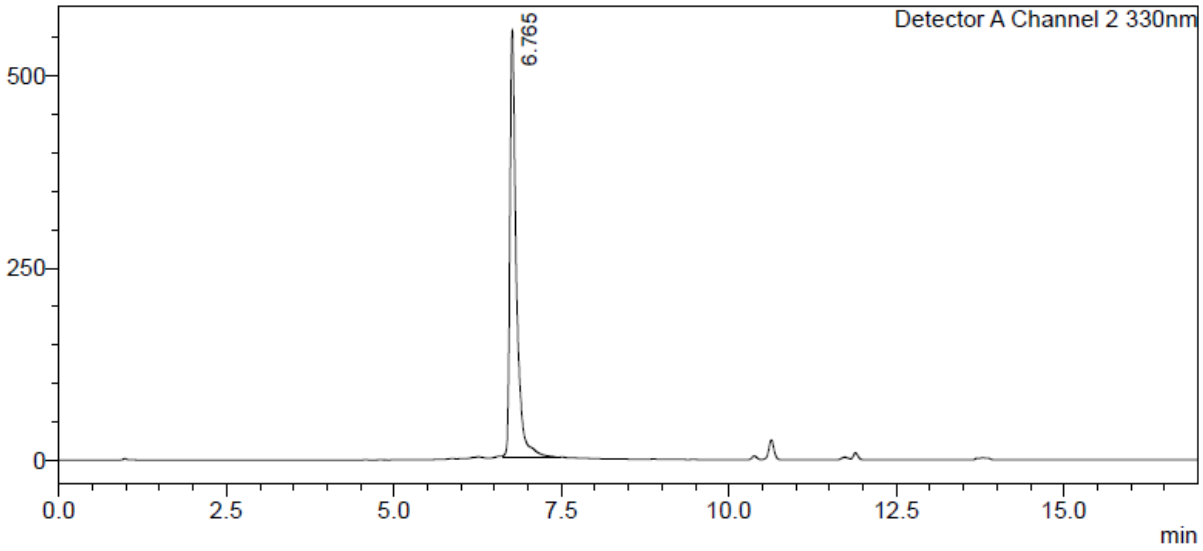
Compound **3** (45 mg, 0.049 mmol) was dissolved in CH_2Cl_2 (1 mL) and TFA (1 mL) added slowly to give a dark brown solution. The reaction mixture was stirred at rt for 6 h, and the solvent was removed under reduced pressure to afford ligand **L$^{1'}$** as the tetra(trifluoroacetate) salt (52 mg,

quant.). The crude ligand **L$^{1'}$** was used directly in the following complexation step. ^{1}H NMR (400 MHz, D_2O) δ 8.60 (2H, d, $^{3}J_{H\text{-}H}$ 7.6 Hz, H^{4}), 7.88 (2H, d, $^{3}J_{H\text{-}H}$ 8.3 Hz, H^{5}), 7.64 (2H, d, $^{3}J_{H\text{-}H}$ 7.6 Hz, H^{3}), 7.24 (2H, d, $^{3}J_{H\text{-}H}$ 8.3 Hz, H^{6}), 7.01 (2H, s, H^{8}), 4.10 (4H, s, H^{9}), 3.64 (4H, s, H^{10}), 3.58 (8H, m, ring CH_2), 3.18 (4H, m, ring CH_2), 3.03 (4H, m, ring CH_2), N-H signals not observed; ESI-LRMS (+) *m/z* 601 $[M + H]^+$; ESI-HRMS (+) *m/z* 601.3244 $[M + H]^+$ ($C_{32}H_{40}N_8O_4$ requires 601.3251).

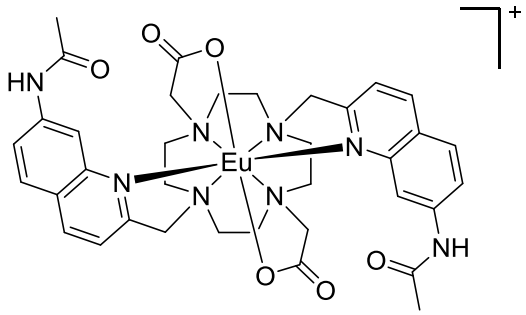


[**Eu.L$^{1'}$**]$^+$

Ligand **L$^{1'}$** (52 mg, 0.049 mmol) was dissolved in a mixture of methanol/water (4 mL, 1:1 v/v) and the pH of the solution was raised to 9 by the addition of KOH (1 M). $EuCl_3.6H_2O$ (19.7 mg, 0.054 mmol) was added and the solution was stirred at 60 °C under argon for 24 h. The mixture was cooled to room temperature and the crude material was purified by preparative RP-HPLC [gradient: 2 − 100% acetonitrile in 25 mM NH_4CO_3 over 15 min; t_R = 6.77 min], to give [**Eu.L$^{1'}$**]$^+$ as a colourless solid (20 mg, 54%); ESI-LRMS (+) *m/z* 749 [M(^{151}Eu)]$^+$; ESI-HRMS (+) *m/z* 749.2209 [M(^{151}Eu)]$^+$ ($C_{32}H_{38}N_8O_4{}^{151}$Eu requires 749.2215).

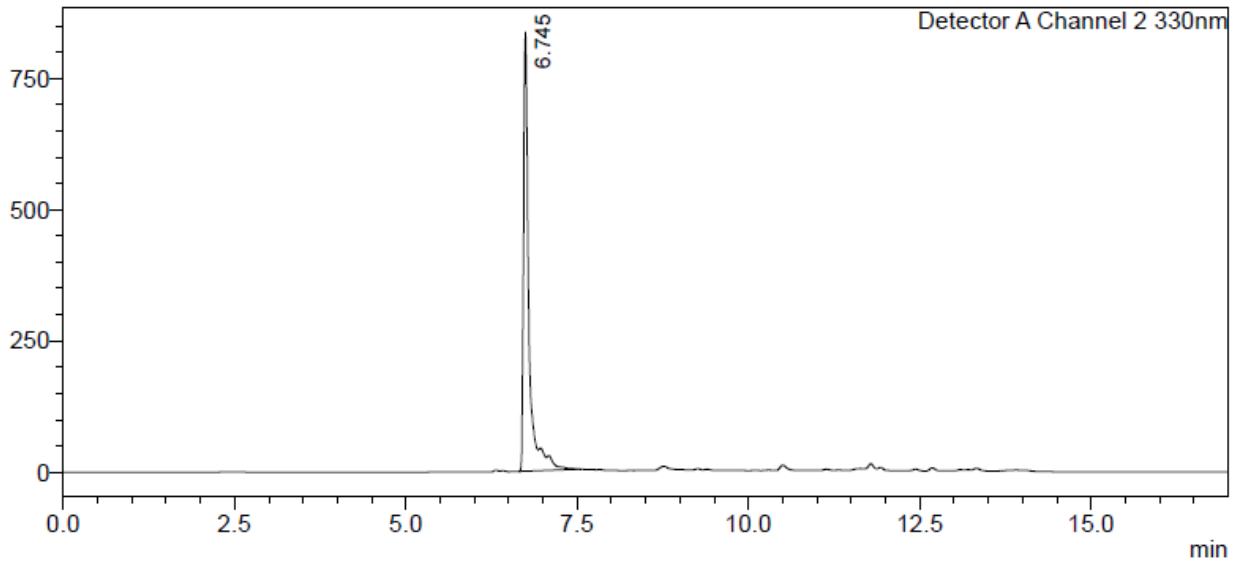


Analytical RP-HPLC trace of **[Eu.L$^{1'}$]$^+$**; t_R = 6.77 min [gradient: 2 − 100% acetonitrile in 25 mM NH_4CO_3 over 15 min]



[**Eu.L^{1}**]$^{+}$

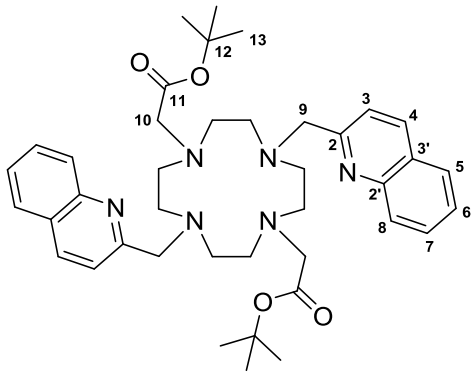
To a solution of the bis-amine [**Eu.L$^{1'}$**]$^{+}$ (10 mg, 0.013 mmol) in anhydrous pyridine (1 mL) was added DMAP (0.5 mg, 0.004 mmol) and acetic anhydride (12 µL, 0.13 mmol) and the solution was stirred at 30 °C under argon for 24 h. The mixture was cooled to room temperature and the crude material was purified by preparative RP-HPLC [gradient: 2 − 100% acetonitrile in 25 mM NH_4CO_3 over 15 min; t_R = 6.75 min], to give [**Eu.L^{1}**]$^{+}$ as a colourless solid (7 mg, 65%); ^{1}H NMR (400 MHz, D_2O) spectral range of 77 ppm (+47.2 to -30.0 ppm), 47.3, 29.6, 17.8, 16.4, 16.0, 15.2, 14.7, 13.1, 11.8, 11.0, 9.4, 9.1, 7.0, 6.0, 4.0, 3.4, 2.8, 2.4, 1.9, 1.7, -0.5, -2.1, -2.2, -5.6, -6.5, -7.3, -12.0, -12.4, -14.0, -17.4, -18.7, -27.8, -28.1, -30.0, two signals obscured or overlapping, N-H signals not observed; ESI-LRMS (+) *m/z* 833[M(^{151}Eu)]$^{+}$; ESI-HRMS (+) *m/z* 833.2444 [M(^{151}Eu)]$^{+}$ ($C_{36}H_{42}N_8O_6{}^{151}$Eu requires 833.2426); τ_{H2O} = 0.45 ms; τ_{D2O} = 1.54 ms; Φ^{em}_{H2O} = 5% (± 15%); ε_{H2O} (332 nm) = 12,500 M^{-1} cm^{-1}.



Analytical RP-HPLC trace of **[Eu.L^{1}]$^{+}$**; t_R = 6.75 min [gradient: 2 − 100% acetonitrile in 25 mM NH_4CO_3 over 15 min]

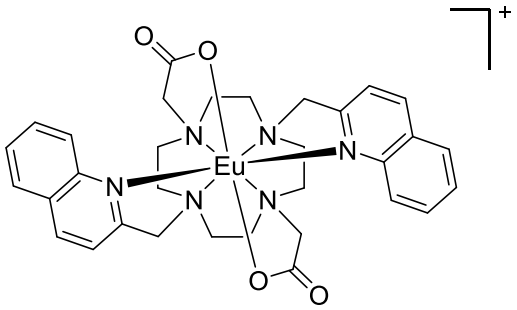
Stability of Complexes $[Eu.L^{1\text{-}2}]^+$

Complexes **$[Eu.L^{1\text{-}2}]^+$** were found to be kinetically stable in aqueous solution over extended time periods, as determined by mass spectrometric data and by comparing the emission spectral form, intensity and lifetime at various stages over a six month time period. Furthermore, the fluoride and bicarbonate adducts of **$[Eu.L^{1\text{-}2}]^+$** are kinetically inert in aqueous solutions containing a range of other anions (e.g. Cl^-, Br^-, I^-, HSO_4^-, HPO_4^{2-}, NO_3^-). For examples of analogous stable europium complexes, bearing trans-related azaxanthone units, see reference 3.



Compound (4)

To a solution of 2-(chloromethyl)quinoline hydrochloride (94 mg, 0.440 mmol) and the macrocyclic diester, DO2A^{t}Bu (80 mg, 0.200 mmol) in anhydrous CH_3CN (15 mL) was added K_2CO_3 (121 mg, 0.880 mmol) and the mixture was stirred under argon at 60 °C. The progress of the reaction was monitored by LC-MS analysis at regular intervals, which revealed complete consumption of starting material after 24 h. The reaction mixture was cooled to room temperature and the solution decanted from excess potassium salts. The solvent was removed under reduced pressure and the crude material was purified by column chromatography (silica, CH_2Cl_2/2–10% CH_3OH in 1% increments) to give compound **4** as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (2H, d, $^3J_{H\text{-}H}$ 8.5 Hz, H^4), 7.92 (2H, d, $^3J_{H\text{-}H}$ 7.6 Hz, $^4J_{H\text{-}H}$ 1.5 Hz, H^5), 7.82 (2H, dd, $^3J_{H\text{-}H}$ 7.6 Hz, $^4J_{H\text{-}H}$ 1.5 Hz, H^8), 7.44 (2H, td, $^3J_{H\text{-}H}$ 7.6, $^4J_{H\text{-}H}$ 1.5 Hz, H^7), 7.37 (2H, d, $^3J_{H\text{-}H}$ 8.5 Hz, H^3), 7.26 (2H, td, $^3J_{H\text{-}H}$ 7.6 Hz, $^4J_{H\text{-}H}$ 1.5 Hz, H^6), 3.95 (6H, br m, ring CH_2), 3.29 –2.30 (14H, br m, ring CH_2 and H^9), 2.89 (4H, s, H^{10}), 1.14 (18H, s, H^{13}); ^{13}C NMR (176 MHz, $CDCl_3$) δ 171.9 (C^{11}), 159.2 (C^2), 147.9($C^{2'}$), 137.4 (C^4), 129.7 (C^7), 129.6 (C^8), 127.8 (C^5), 127.5 ($C^{3'}$), 126.4 (C^6), 121.7 (C^3), 82.4 (C^{12}), 60.3 (C^9), 57.9 (C^{10}), 51.3–50.5 (ring CH_2), 28.1 (C^{13}); ESI-LRMS (+) *m*/*z* 683 $[M + H]^+$; ESI-HRMS (+) *m*/*z* 683.4296 $[M + H]^+$ ($C_{40}H_{55}N_6O_4$ requires 683.4285); R_f = 0.38 (silica gel; CH_2Cl_2/CH_3OH 9:1 v/v).

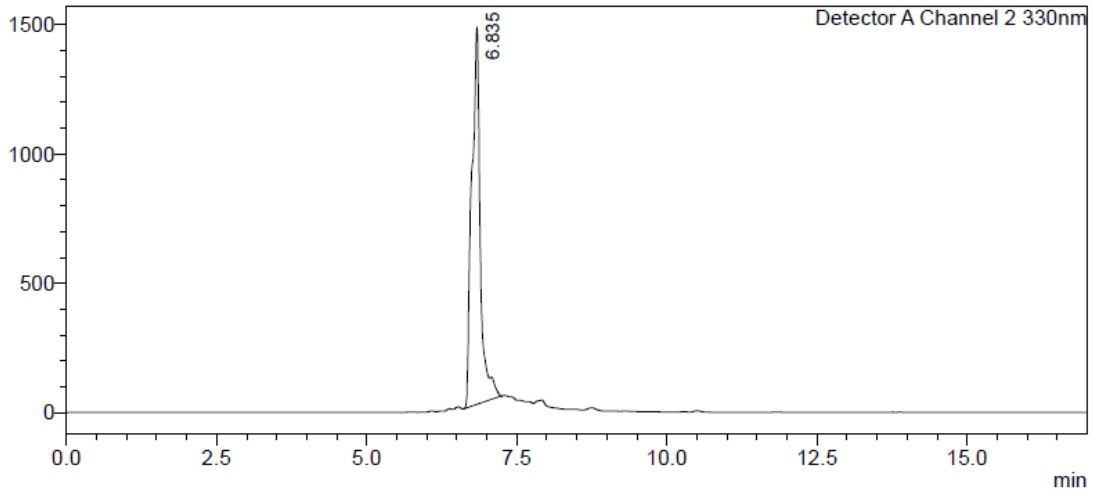


[Eu.L^1]$^+$

[Eu.L^2]$^+$

Step 1. Compound **4** (20 mg, 0.029 mmol) was dissolved in CH_2Cl_2 (1 mL) and TFA (1 mL) added slowly. The reaction mixture was stirred at rt for 4 h, and the solvent was removed under reduced pressure, to afford ligand **L^2** as the bis(trifluoroacetate) salt (21 mg, quant.); ESI-LRMS (+) *m/z* 571 $[M + H]^+$; ESI-HRMS (+) *m/z* 571.3046 $[M + H]^+$ ($C_{32}H_{39}N_6O_4$ requires 571.3033). The crude ligand **L^2** was used directly in the following complexation step.

Step 2. The crude ligand **L^2** (21 mg, 0.029 mmol) was dissolved in a mixture of methanol/water (2 mL, 1:1 v/v) and the pH of the solution was raised to 8.5 by the addition of KOH (1 M). $EuCl_3.6H_2O$ (11.6 mg, 0.032 mmol) was added and the solution was stirred at 60 °C under argon for 24 h. The mixture was cooled to room temperature and the crude material was purified by preparative RP-HPLC [gradient: 2 − 100% acetonitrile in 25 mM NH_4CO_3 over 10 min; t_R = 6.84 min], to give **[Eu.L^2]$^+$** as a colourless solid (10 mg, 48%); ^{1}H NMR (400 MHz, D_2O) spectral range of 76 ppm (47.0 to -29.2 ppm), 46.9, 29.4, 17.8, 16.5, 15.1, 14.7, 12.8, 11.2, 11.0, 9.4, 9.1, 7.0, 6.0, 3.9, 3.6, 3.2, 3.0, 2.7, 2.2, 2.1, 0.2, -1.9, -2.5, -5.9, -6.2, -7.4, -11.9, -12.5, -13.5, -17.2, -18.6, -27.3, -27.4, -27.9, -29.2; ESI-HRMS (+) *m/z* 719.2000 $[M(^{151}Eu)]^+$ ($C_{32}H_{36}N_6O_4{}^{151}Eu$ requires 719.1997); τ_{H2O} = 0.51 ms; τ_{D2O} = 1.37 ms; Φ^{em}_{H2O} = 23% (± 15%); ε_{H2O} (318 nm) = 11,800 M^{-1} cm^{-1}.



Analytical RP-HPLC trace of **[Eu.L^2]$^+$**; t_R = 6.84 min [gradient: 2 − 100% acetonitrile in 25 mM NH_4CO_3 over 15 min]

2. Spectroscopic studies conducted in aqueous solution.

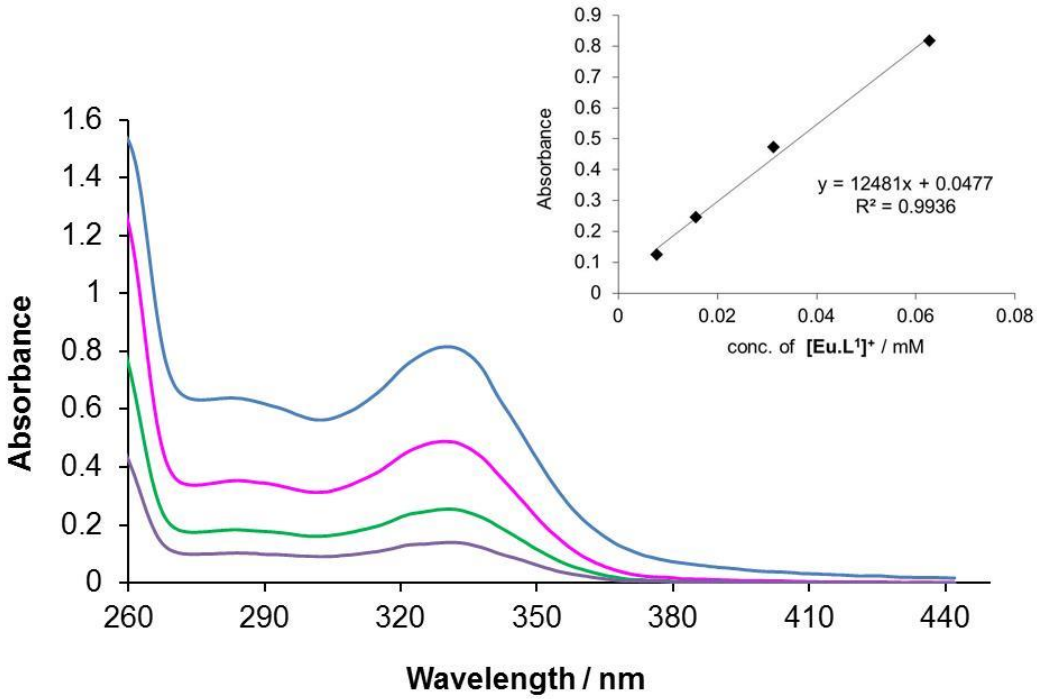


Figure S1. Change in absorption spectra of $[\mathbf{Eu.L^1}]^+$ in water as a function of concentration. Inset shows the fit to the experimental data, with a molar extinction coefficient, ε = 12,500 M^{-1} cm^{-1}.

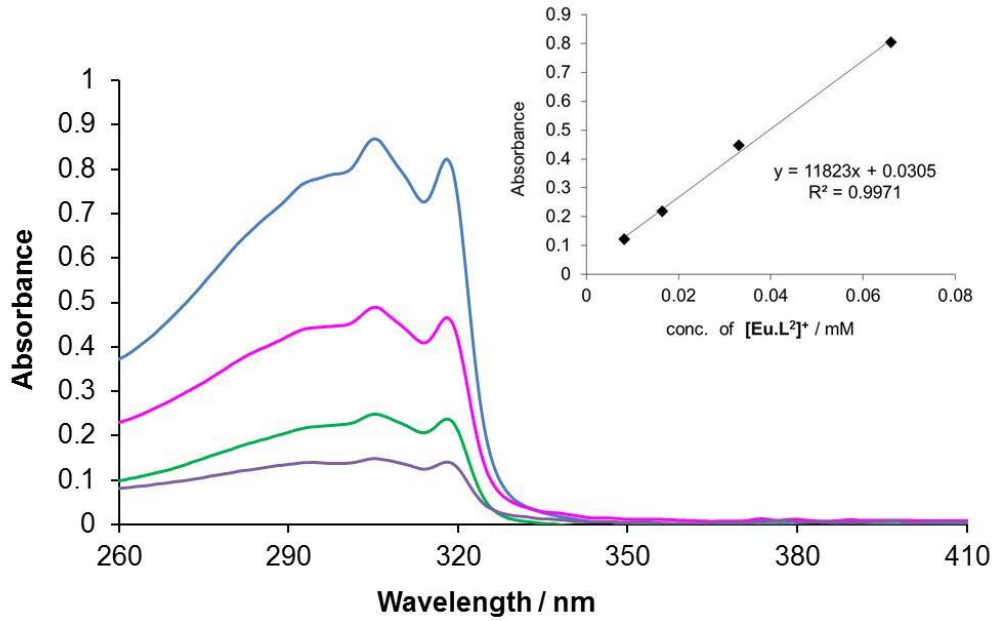


Figure S2. Change in absorption spectra of $[\mathbf{Eu.L^2}]^+$ in water as a function of concentration. Inset shows the fit to the experimental data, with a molar extinction coefficient, ε = 11,800 M^{-1} cm^{-1}.

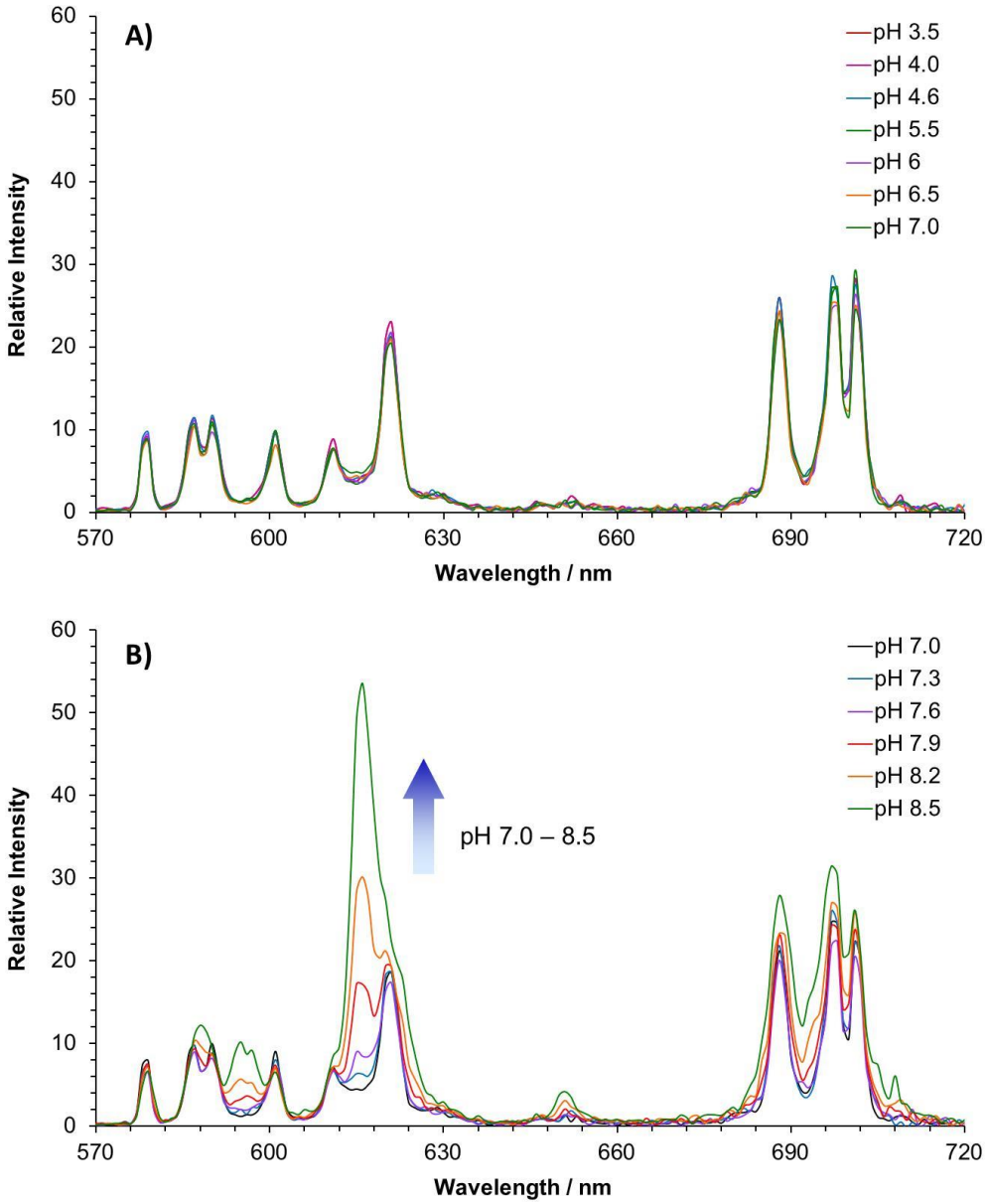


Figure S3. Change in emission spectra of $[\mathbf{Eu.L^1}]^+$ (20 μM) as a function of pH: A) negligible spectral change over the pH range 3.5–7.0; B) increase in emission intensity over the pH range 7.0–8.5. Conditions: deionized water, λ_{exc} 332 nm, 25 °C.

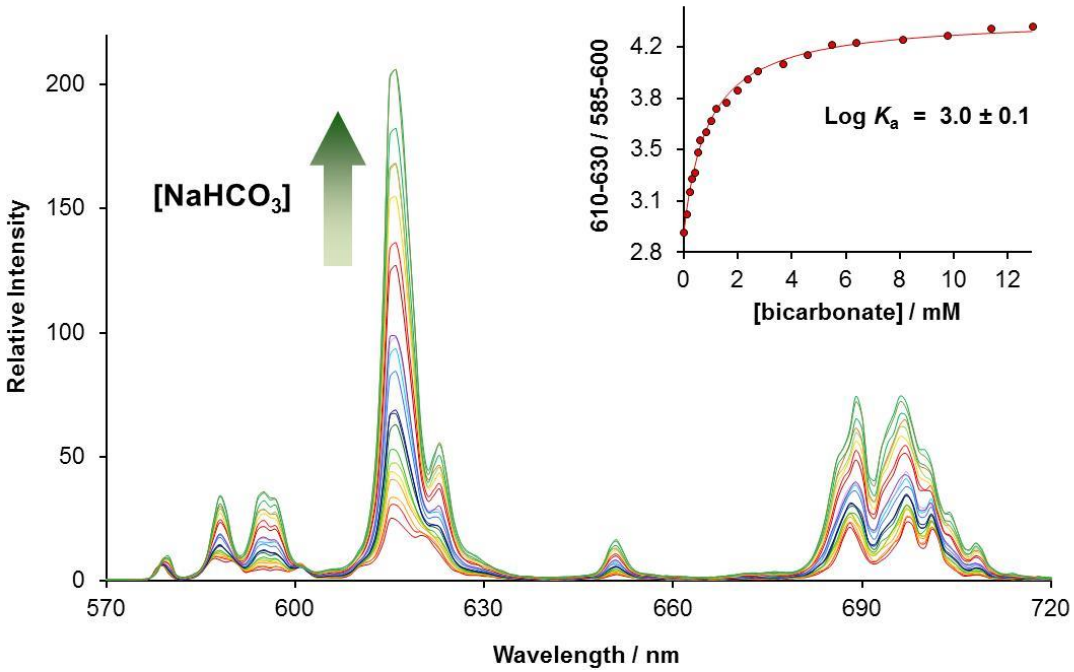


Figure S4. Change in emission spectra of $[\mathbf{Eu.L^1}]^+$ (20 μM) as a function of added $NaHCO_3$ in water at pH 7.4. The inset shows the fit to the experimental data, for log K_a = 3.0 (± 0.1). Conditions: HEPES buffer (25 mM, pH 7.4), λ_{exc} 332 nm, 25 °C.

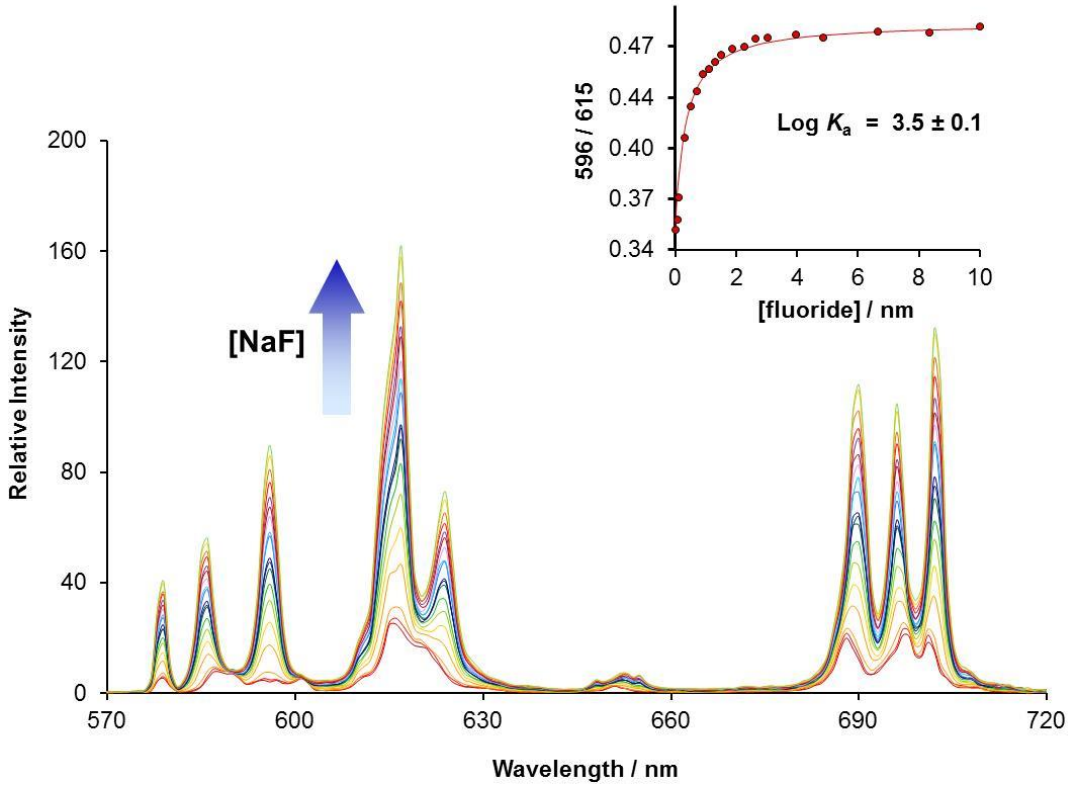


Figure S5. Change in emission spectra of $[\mathbf{Eu.L^1}]^+$ (20 μM) as a function of added NaF in water at pH 7.4. The inset shows the fit to the experimental data, for log K_a = 3.5 (± 0.1). Conditions: HEPES buffer (25 mM, pH 7.4), λ_{exc} 332 nm, 25 °C.

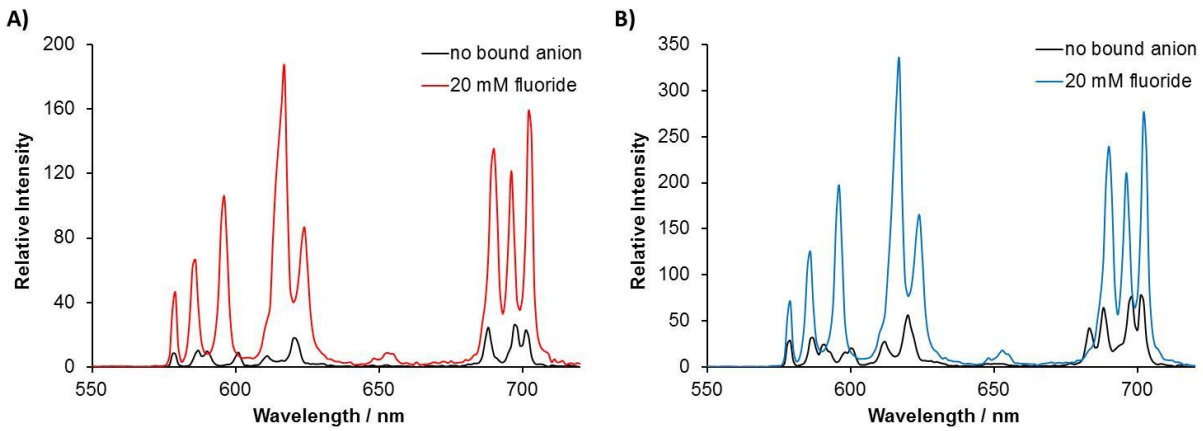


Figure S6. Comparison of the emission spectra of: A) **[Eu.L^{1}]$^{+}$** in the absence of a coordinating anion (*black line*) and after the addition of excess NaF (*red line*), resulting in a 9-fold overall emission enhancement; B) **[Eu.L^{2}]$^{+}$** in the absence of a coordinating anion (*black line*) and in the presence of excess NaF (*blue line)*, resulting in 3.5-fold overall emission enhancement. Conditions: H_2O (25 mM MES, pH 6), λ_{exc} = 332 nm and 318 nm for **[Eu.L$^{1\text{-}2}$]$^{+}$** respectively, 298 K.

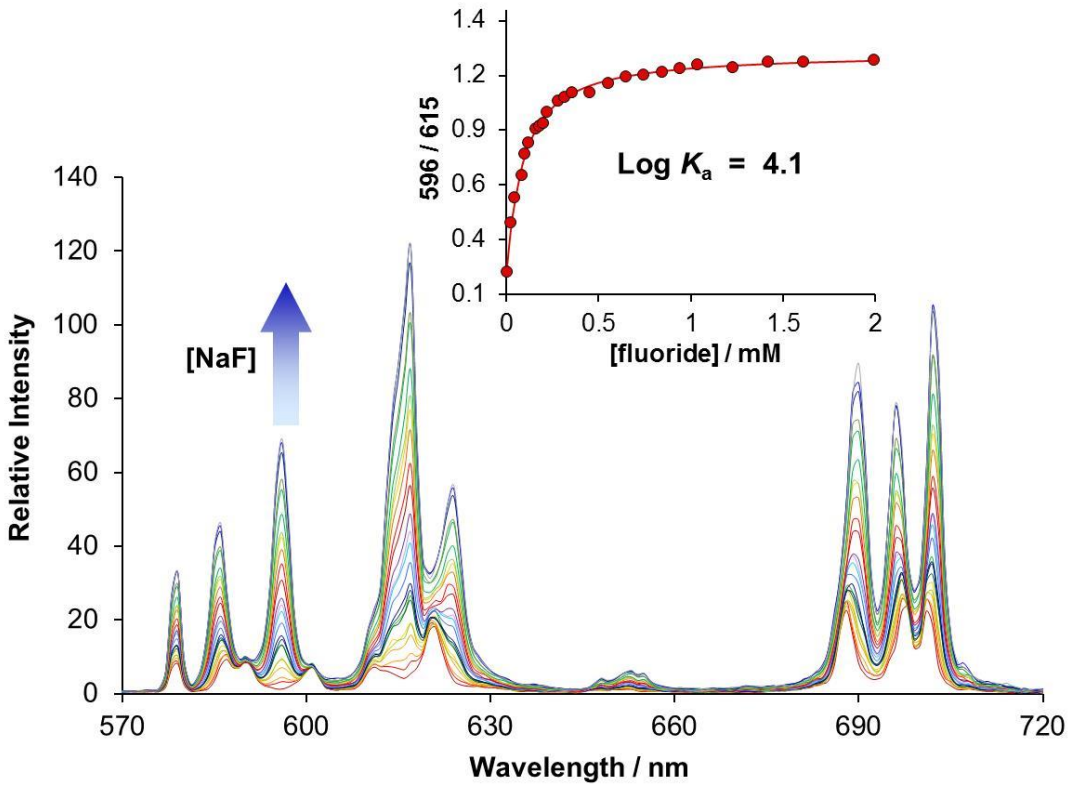


Figure S7. Change in emission spectra of [**Eu.L^{1}**]$^{+}$ (20 μM) as a function of added NaF in water pH 6.0. The inset shows the fit to the experimental data, for log K_a = 4.1 (± 0.1). Conditions: MES buffer (25 mM), λ_{exc} 332 nm, 25 °C.

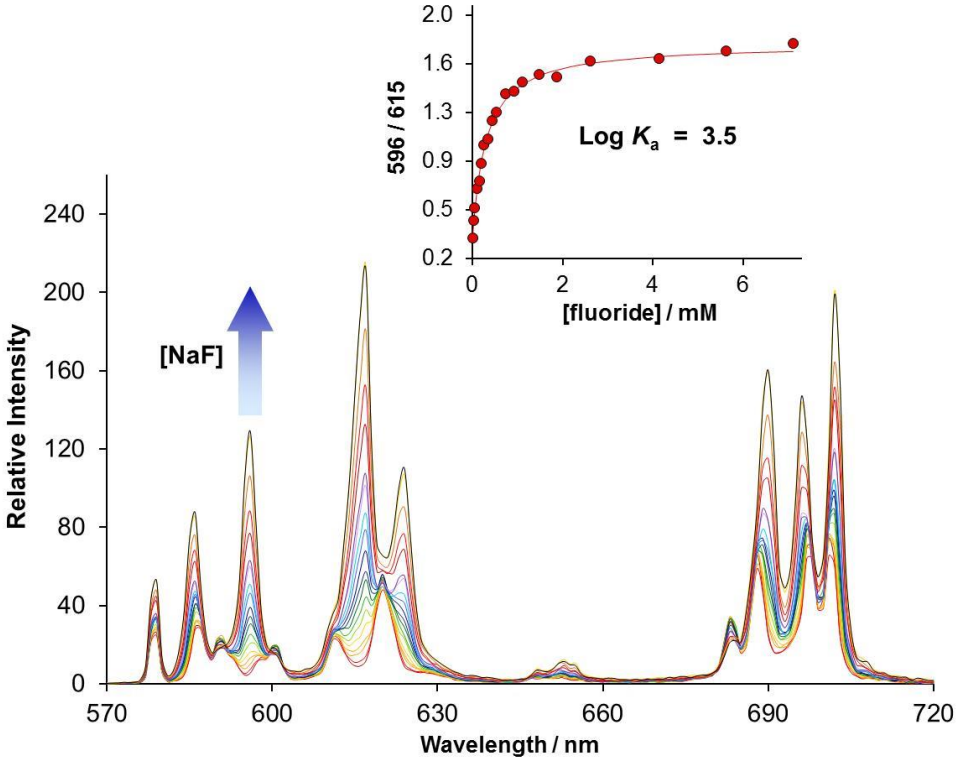


Figure S8. Change in emission spectra of $[\mathbf{Eu.L^2}]^+$ (20 μM) as a function of added NaF in water pH 6.0. The inset shows the fit to the experimental data, for log K_a = 3.5 (± 0.1). Conditions: MES buffer (25 mM), λ_{exc} 318 nm, 25 °C.

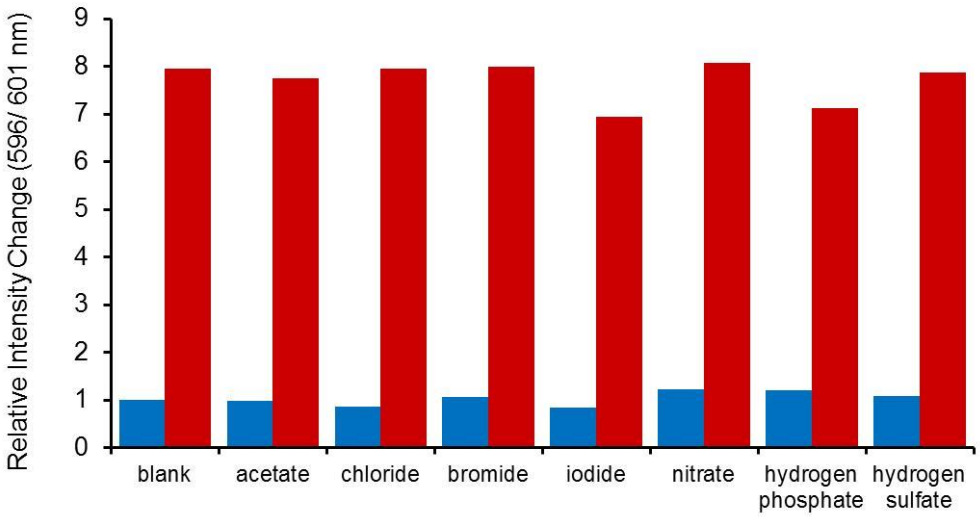


Figure S9. Competition experiments showing the relative change in emission intensity ratio, 596/601 nm, of $[\mathbf{Eu.L^1}]^+$ (20 μM) in the presence of different anions (5 mM sodium salts, *blue*), followed by addition of NaF (0.5 mM, *red*). Conditions: H_2O (25 mM MES buffer, pH 6.0), λ_{exc} = 332 nm.

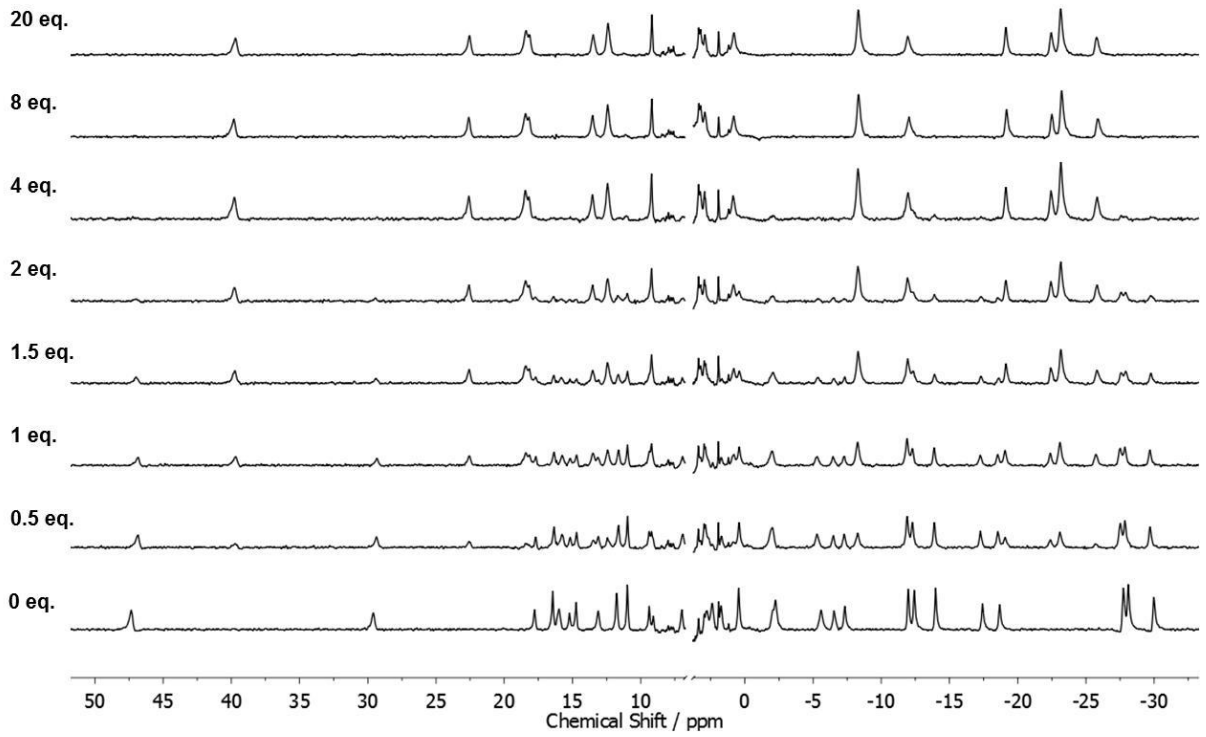


Figure S10. Change in the ^{1}H NMR spectra of [**Eu.L^{1}**]$^{+}$ (1.2 mM) as a function of added NaF (0–20 eq.). Measured in D_2O (pD 6.4, 25 °C). Addition of NaF resulted in the appearance of a new set of resonances corresponding to the fluoride-bound species, whereas the original signals for the mono-hydrated complex disappeared.

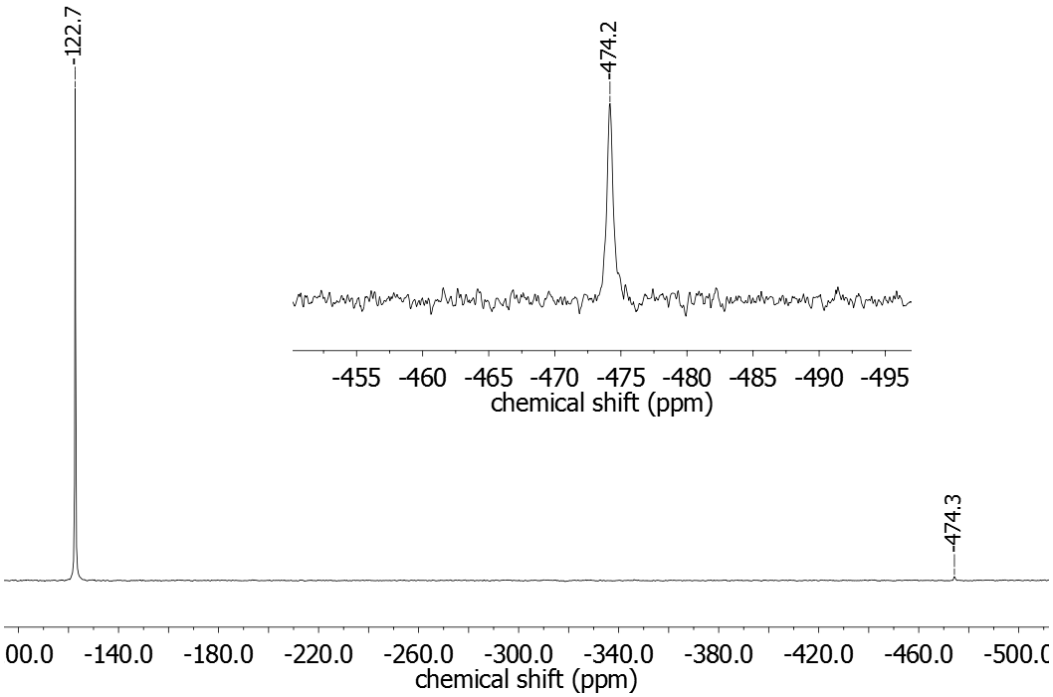


Figure S11. ^{19}F NMR spectrum of [**Eu.L^{1}**]$^{+}$ (1.2 mM) in the presence of 1 eq. NaF. Measured in D_2O (pD 6.4, 25 °C).

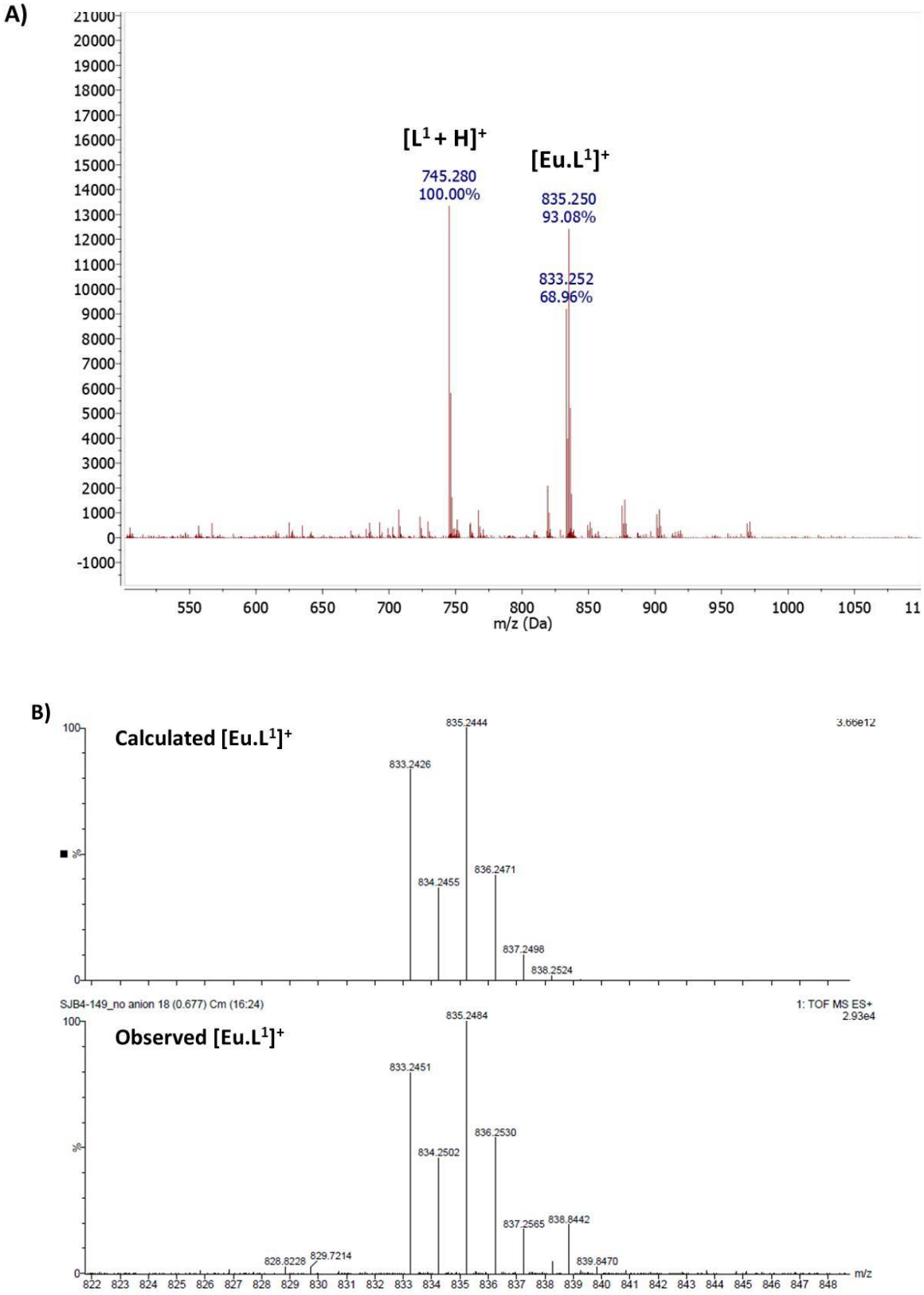


Figure S12. A) ESI high resolution mass spectrum (HRMS^{+}) of [**Eu.L^{1}**]$^{+}$; B) observed and calculated isotopic distribution of **[Eu.L^{1}]$^{+}$** ($EuC_{36}H_{42}N_8O_6$).

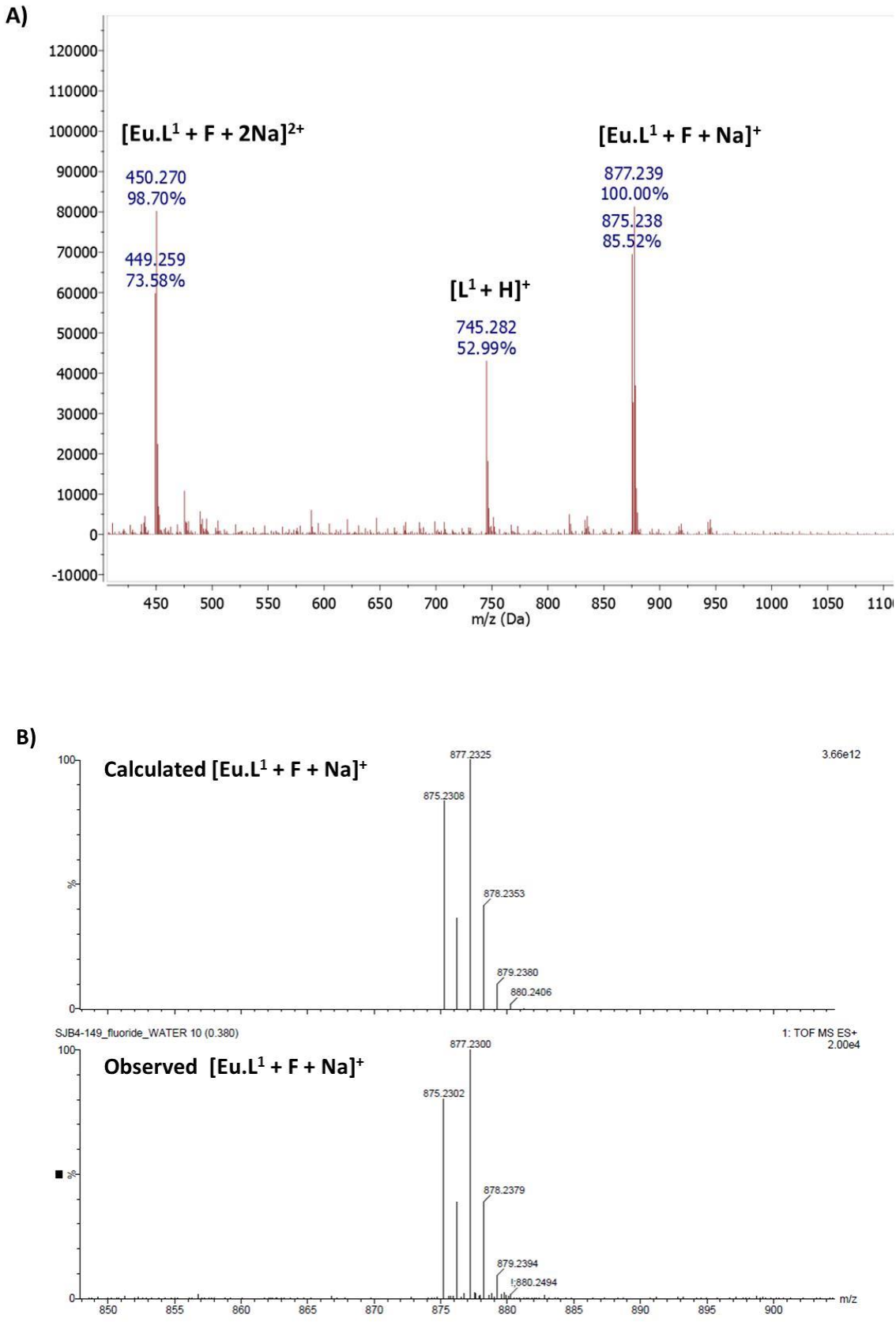


Figure S13. A) ESI high resolution mass spectrum ($HRMS^+$) of the fluoride adduct of $[\mathbf{Eu.L^1}]^+$; B) observed and calculated isotopic distribution of $\mathbf{[Eu.L^1+F+Na]^+}$ ($EuC_{36}H_{42}N_8O_6FNa$).

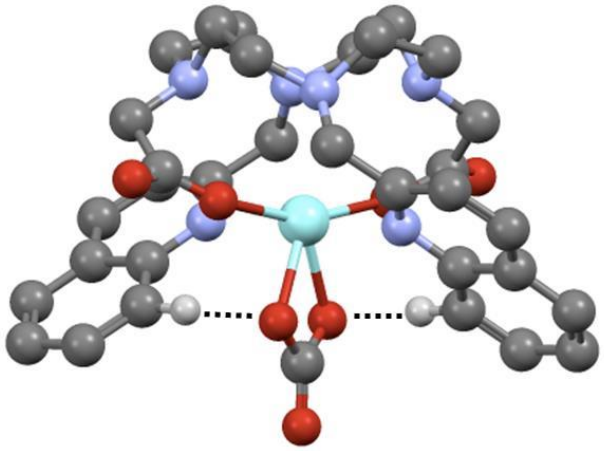


Figure S14. An optimised structure of [**Eu.L^2**]$^+$ with a coordinated carbonate ion. The tendency of carbonate to chelate Ln ions has previously been shown by X-ray crystallography and relaxometric studies.[4-5] The Eu-bound carbonate ion is stabilised by two C-H···O$^-$ contacts (avg. C-H···O$^-$ distance is 2.99 Å, avg. C-H···O$^-$ angle is 161°). The model geometry was optimised at B3LYP/3-21G* (Gaussian 09 package) using the polarised continuum solvent model, using water as solvent.

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