Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information:

Luminescence of a binuclear europium complex bearing a 4-nitrophenolate chromophore: a different way of seeing pH dependence

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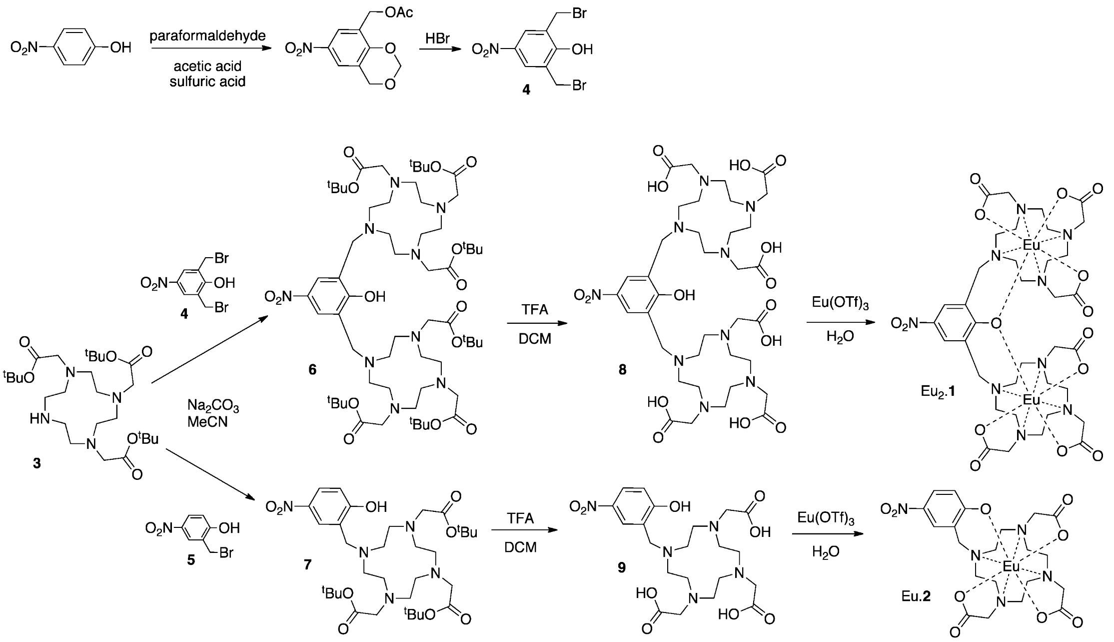
1 Experimental section

1.1 Materials and methods

1,4,7-Tris(tert-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclo-dodecane, hydrobromide salt (**3**),[1] and 2,6-bis(bromomethyl)-4-nitrophenol (**4**)[2] were synthesised by literature procedures. Cyclen was purchased from Chematech, and 2-hydroxy-5-nitrobenzyl bromide (**5**) was purchased from Sigma-Aldrich. Commercially available reagents and solvents were used without further purification. NMR spectra were recorded on a Bruker Avance III HD nanobay 400MHz NMR machine. All coupling constants are quotes in Hz. Mass spectra were obtained using either an Aligent Technology 1260 Infinity or a Waters LCT Premier XS. Absorption spectra were recorded on a T60U spectrometer (PG Instruments Ltd.) using fused silica cells with a path length of 1 cm. Luminescence measurements were obtained using a HORIBA FluoroLog3 fluorimeter except for triplet energy measurements which were conducted on a PerkinElmer LS55 fluorimeter equipped with an Oxford instruments cryostat. A Hanna pH meter was used for pH measurements of solutions of complexes in water and deuterium oxide.



1.2 Synthesis

2,6-Bis(1,4,7-tris(tert-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecane methyl)-4-nitrophenol (6).

4 (0.55 g, 1.7 mmol) dissolved in MeCN (40 mL) was added dropwise to an ice-cooled solution of **3** (2.00 g, 3.4 mmol) and Na_2CO_3 (0.89 g, 8.4 mmol) in MeCN (100 mL). The mixture was stirred at room temperature for 2 d and then heated at reflux for 3 d. A further portion of **4** (0.28 g, 0.85 mmol) was added and the reflux continued for another 12 d. The reaction was cooled to room temperature, the solids filtered off and the filtrate evaporated to dryness. The crude product was purified by column chromatography on alumina eluting with dichloromethane/methanol, the product was eluted at 0.5% methanol (0.69 g, 34%). ES$^+$ MS: *m/z* 1192 $[M + H]^+$, 596 $[M + 2H]^{2+}$. NMR ($CDCl_3$, 400 MHz) δ_H: 1.2 - 1.6 (54 H, *tert*-Bu), 2.1 – 4.4 (48 H, NCH_2), 7.8 – 8.4 (3 H, Ar*H* + O*H*).

2-(1,4,7-Tris(tert-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecane methyl)-4-nitrophenol (7)

5 (0.43 g, 1.7 mmol) dissolved in MeCN (20 mL) was added dropwise to a stirred solution of **3** (1.0 g, 1.7 mmol) and Na_2CO_3 (0.53 g, 5.0 mmol) in MeCN (50 mL).

The mixture was heated at reflux for 13 d. After cooling, the inorganic salt was filtered off and the solvent was removed under reduced pressure. The crude material was purified by silica gel chromatography using DCM/MeOH mixture as eluent (gradient up to 90:10 *v/v*) to obtain the product as a yellow solid (0.60 g, 54 %). ES^+ MS: *m/z* 666 $[M + H]^+$, 688 $[M + Na]^+$. NMR ($CDCl_3$, 400 MHz) δ_H: 1.38 (18H, *tert*-Bu), 1.43 (9H, *tert*-Bu), 2.1 – 4.3 (24 H, NCH_2), 6.7 (1H, *d*, 8 Hz, Ar*H*), 7.9 (2 H, Ar*H* + O*H*), 8.02, (1H, *d*, 8 Hz, Ar*H*).

2,6-Bis(1,4,7-tris(carboxymethyl)-1,4,7,10-tetraazacyclododecane methyl)-4-nitrophenol (8).

6 (0.60 g, 0.50 mmol) was dissolved in dichloromethane (5 mL) and trifluoroacetic acid (5 mL) was added dropwise to this solution. The solution was stirred at room temperature for 2 d. The solvents were removed in vacuo. The residue was dissolved in the minimum amount of methanol and the product precipitated from solution by addition of diethyl ether. The liquid was decanted, the solid was washed several times with diethyl ether and then dried under vacuum to leave a yellow powder (0.40 g, 93%). ES^+ MS: *m/z* 856 $[M + H]^+$, 878 $[M + Na]^+$, 428 $[M + 2H]^{2+}$, 439 $[M + H + Na]^+$. NMR (D_2O, 400 MHz) δ_H: 2.5 – 4.5 (48 H, NCH_2), 8.5 (2 H, Ar*H*).

2-(1,4,7-Tris(carboxymethyl)-1,4,7,10-tetraazacyclododecane methyl)-4-nitrophenol (9)

This compound was prepared in an identical manner to **8** using **7** (60 mg, 0.09 mmol), dichloromethane (5 mL) and trifluoroacetic acid (5 mL) to yield a light yellow powder (28 mg, 51 %). NMR (D_2O, 400 MHz) δ_H: 2.95 – 4.5 (24 H, NCH_2), 7.9 (1 H, Ar*H*), 7.95 (1 H, Ar*H*), 8.2 (1 H, Ar*H*).

Eu_2.1.

8 (0.10 g, 0.12 mmol) was dissolved in water (8 mL) and the pH of the solution was adjusted to 4 by addition of dilute $NaOH_{(aq)}$. Europium trifluoromethanesulfonate (0.14 g, 0.24 mmol) was added to the solution and the reaction heated at 60°C for 4 d. The reaction was cooled and the pH of the solution was raised to 10 by addition of dilute $NaOH_{(aq)}$. The precipitate was removed by centrifugation and filtration, the pH of the solution was adjusted to 7 using dilute $HCl_{(aq)}$, and the solvent was evaporated.

The residue was redissolved in water and purified by dialysis using a 500 Da membrane to give a pale yellow powder (0.15 g, 54%). MALDI$^+$ MS: *m/z* 1154 [M + H]$^+$, 1176 [M + Na]$^+$, 1198 [M − H+ 2Na]$^+$. NMR at neutral pH (D_2O, 400 MHz) δ_H: 44.4, 35.0, 34.6, 32.8, 27.3, 26.5, 23.5, 19.3, 18.3, 15.9, 11.1, 10.2, 8.3, 7.5, 6.7, 5.9, 4.8, 3.9, 2.1, 1.1, 0.1, -0.7, -1.7, -2.3, -3.4, -4.2, -4.7, -6.0, -7.1, -7.9, -8.7, -9.0, -9.7, -10.8, -12.0, -12.5, -13.8, -14.1, -15.1, -15.7, -16.9, -17.2, -19.9, -21.1, -21.7, -22.5.

Gd$_2$.1.

This complex was prepared in an identical manner to Eu$_2$.**1** using **8** (50 mg, 0.058 mmol) and Gd(OTf)$_3$ (71 mg, 0.12 mmol) to give a pale yellow powder (87 mg, 62%). MALDI$^+$ MS: *m/z* 1166 [M + H]$^+$, 1188 [M + Na]$^+$.

Eu.2

This complex was prepared in an identical manner to Eu$_2$.**1** using **9** (28 mg, 0.046 mmol) and Eu(OTf)$_3$ (28 mg, 0.046 mmol). MALDI$^+$ MS: *m/z* 824.1 [M+2CH_3OH+TFA+H$^+$]. NMR at neutral pH (D_2O, 400 MHz) δ_H: 40.1, 36.9, 24.6, 8.3, 8.0, 7.7, 6.8, 5.5, 4.1, 3.7, 1.3, 1.0, -3.7, -4.1, -9.1, -10.3, -11.4, -13.5, -18.3, -22.4.

Gd.2

This complex was prepared in an identical manner to Eu$_2$.**1** using **9** (20 mg, 0.033 mmol) and Gd(OTf)$_3$ (20 mg, 0.033 mmol) to give a yellow powder (12 mg, 56 %). MALDI$^+$ MS: *m/z* 834.3 [M+CH_3OH+TFA+K]$^+$.

2 Photophysics

2.1 Eu_2.**1**

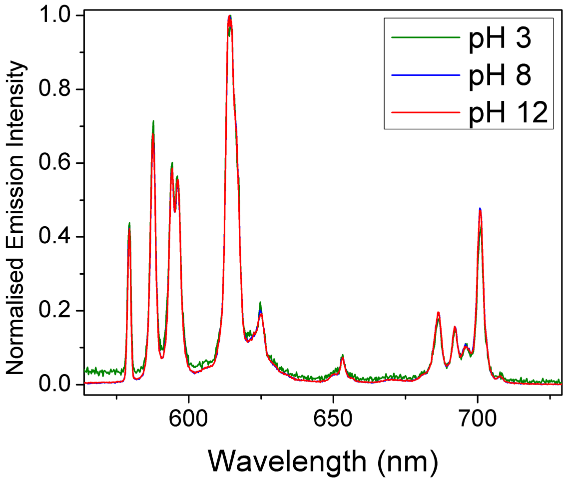


Figure S1. Normalised emission spectra for Eu_2.**1** in H_2O showing a lack of change in structure with change in pH.

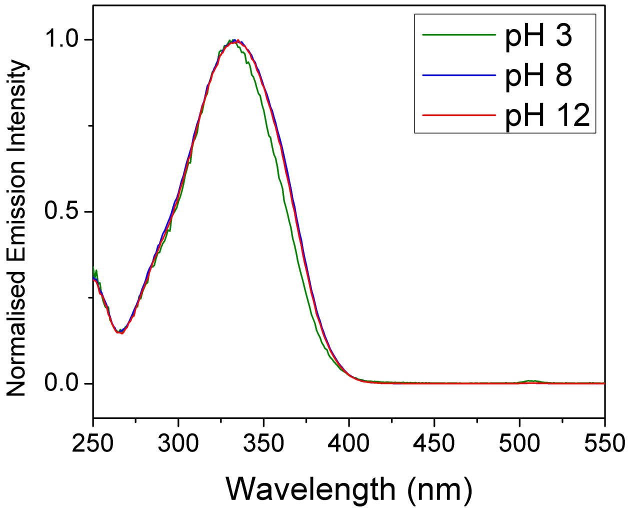


Figure S2. Normalised excitation spectra for Eu_2.**1** in H_2O showing a lack of change in structure with change in pH.

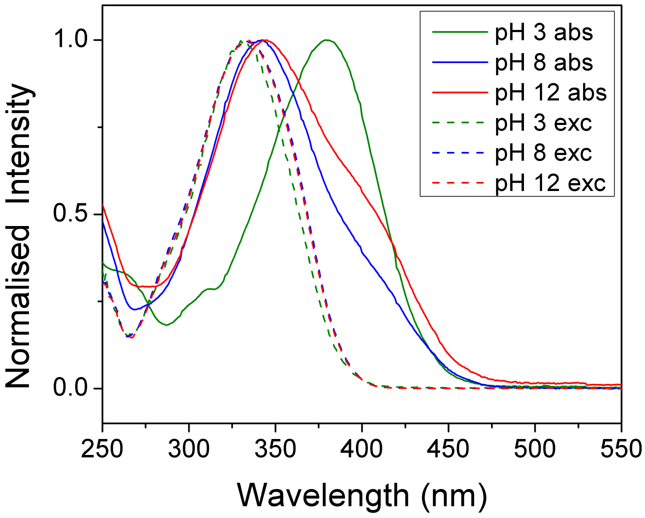


Figure S3. Overlay of normalised absorption and excitation spectra for Eu_2.**1** in H_2O.

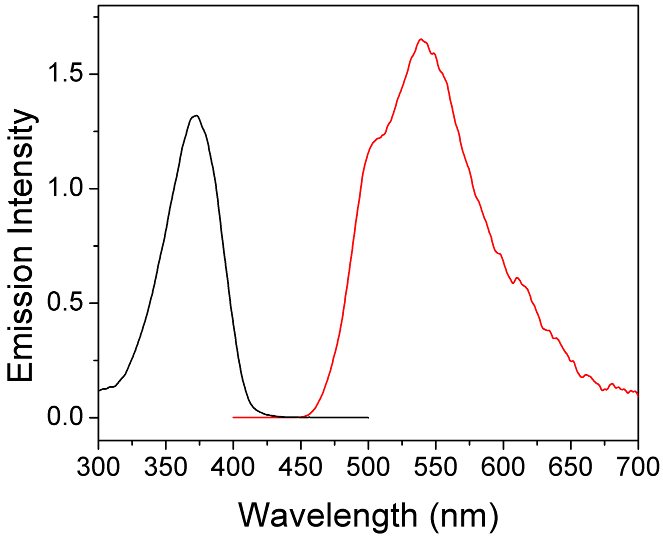


Figure S4. Excitation and emission spectra for Gd_2.**1** at 77 K in an ether-ethanol-isopropyl glass.

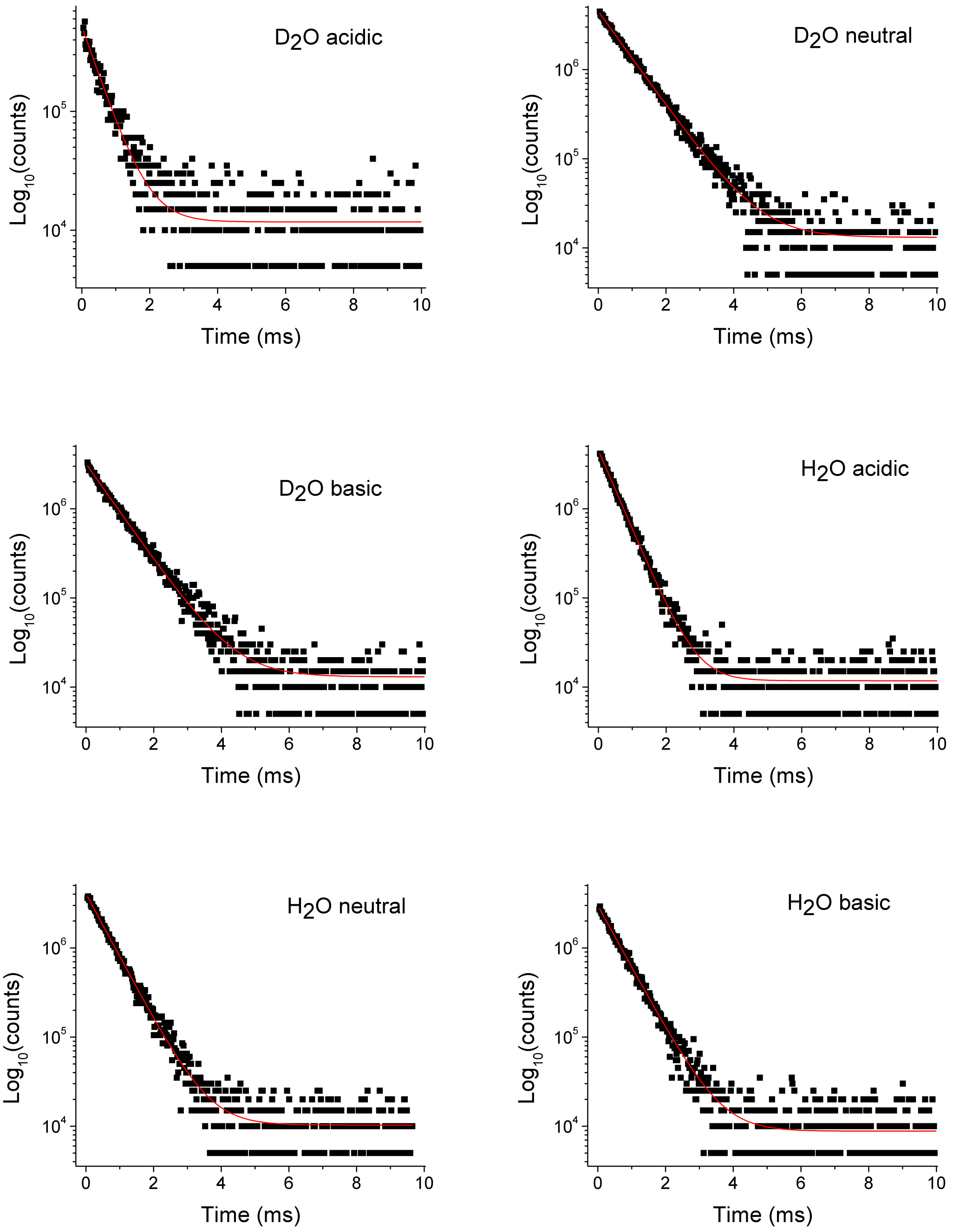


Figure S5. Luminescence decays (black) and fits (red) measured at 616 nm for Eu_2.**1** in D_2O and H_2O at varying pH.

2.2 Eu.2

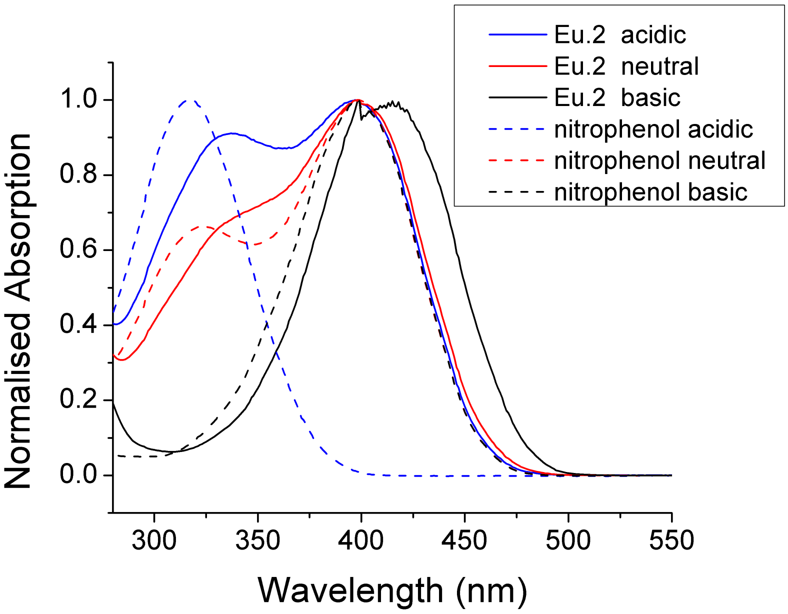


Figure S6. Normalised absorption spectra of Eu.**2** and 4-nitrophenol with varying pH.

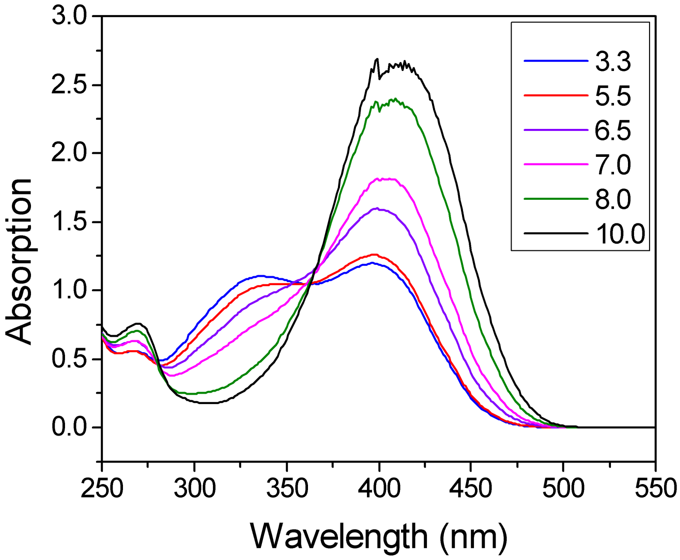


Figure S7. pH dependence of the absorption spectrum of Eu.**2**.

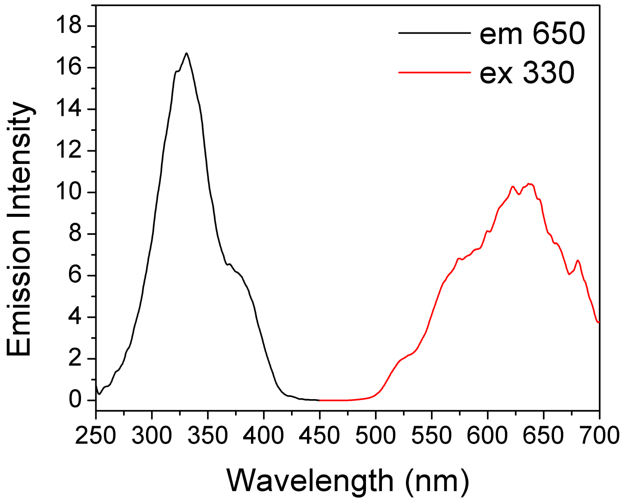


Figure S8. Excitation and emission spectra for Gd.**2** at 77 K in an ether-ethanol-isopropyl glass.

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[1] A. Dadabhoy, S. Faulkner, and P. G. Sammes, *J. Chem. Soc., Perkin Trans. 2*, 2002, 348–357.

[2] J. de Mendoza, P. M. Nieto, P. Prados, and C. Sánchez, *Tetrahedron*, 1990, **46**, 671–682.