

## Solution studies of tri-metallic lanthanide luminescent anion sensors: Towards ratiometric sensing using an internal reference channel

Sally E. Plush and Thorfinnur Gunnlaugsson\*

### Electronic Supplementary Information

#### Synthesis

##### Compound 2

1-Amino naphthalene (1 g, 6.9 mmol) was dissolved in a solution of DCM (40 cm<sup>3</sup>) and triethylamine (1.78 cm<sup>3</sup>, 13 mmol), the mixture was cooled to 0 °C. A solution of Chloroacetyl chloride (0.828 cm<sup>3</sup>, 10.4 mmol) in DCM (30 cm<sup>3</sup>) was then added dropwise to the reaction mixture at 0 °C. The reaction was left to warm to room temperature overnight. The reaction was quenched with a dropwise addition of water (15 cm<sup>3</sup>). The organic layer was then washed with 0.1 mol dm<sup>-3</sup> hydrochloric acid and a saturated solution of sodium hydrogen carbonate. The organic layer was then dried and the solvent removed under reduced pressure to give a brown solid. Purification by means of a silica squat column [100% DCM, R<sub>f</sub> 0.8] yielded an off white solid (1.11 g, 74 %),  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 4.38 (2H, s, CH<sub>2</sub>Cl), 7.51 – 7.60 (3H, m, Ar-H), 7.77 (1H, d, Ar-H), 7.91 (2H, t, Ar-H), 8.00 (1H, d, Ar-H);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 42.9 (CH<sub>2</sub>Cl), 119.7, 120.1, 125.5, 125.8, 126.0, 126.2, 126.4, 128.4, 130.6, 133.6 (Ar-H), 163.9 (C=O); *m/z* (ESMS) 242 (M-Na<sup>+</sup>); HRMS: *m/z* (ESMS) Found: 242.0341. C<sub>12</sub>H<sub>10</sub>NONaCl requires 242.0349

##### Compound 3

1-Aza-18-crown-6 (100 mg, 0.38 mmol) was dissolved in a solution of DCM (5 cm<sup>3</sup>) and triethylamine (0.158 cm<sup>3</sup>, 1.14 mmol), the mixture was cooled to 0 °C. A solution of Chloroacetyl chloride (0.03 cm<sup>3</sup>, 0.38 mmol) in DCM (10 cm<sup>3</sup>) was then added dropwise to the reaction mixture at 0 °C. The reaction was left to warm to room temperature overnight. The reaction was quenched with a dropwise addition of water (15 cm<sup>3</sup>). The organic layer was then washed with 0.1 mol dm<sup>-3</sup> hydrochloric acid and a saturated solution of sodium hydrogen carbonate. The organic layer was then dried and the solvent removed under reduced pressure to give a yellow oil (7.05 g, 79 %),  $\delta_{\text{H}}$  (400 MHz;

CDCl<sub>3</sub>) 3.63 – 37.1 (24H, m, CH<sub>2</sub>), 4.26 (2H, s, CH<sub>2</sub>Cl); δ<sub>C</sub> (100 MHz; CDCl<sub>3</sub>) 21.1 (CH<sub>2</sub>Cl) 48.7 (CH<sub>2</sub>), 49.7 (CH<sub>2</sub>) 143.1 (C=O); *m/z* (ESMS) 378 (M-K<sup>+</sup>) 362 (M-Na<sup>+</sup>); HRMS: *m/z* (ESMS) Found: 362.1338. C<sub>14</sub>H<sub>26</sub>NO<sub>6</sub>NaCl requires 362.1346.

**Compound 4:** Compound **2** (51.9 mg, 0.147 mmol), compound **3** (50 mg, 0.220 mmol), CsCO<sub>3</sub> (31 mg, 0.16 mmol) and a catalytic amount of KI were dissolved in DMF and the solution was heated at 80 °C for 3 days. The reaction was then filtered through celite and the solvent removed under reduced pressure. The residue was then redissolved in DCM and the product extracted into water to yield the desired product as a white solid (1.35 g, 65 %) δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>) 2.75 – 2.97 (16H, m cyclen CH) 3.49 – 3.66 (28H, m, CH<sub>2</sub>O and CH<sub>2</sub>Cl), 7.51 (3H, m, Ar-H), 7.75 (1H, d, Ar-H), 7.86 (1H, d, Ar-H), 8.05 (1H, d, Ar-H), 8.19 (1H, d, Ar-H); δ<sub>C</sub> (100 MHz; CDCl<sub>3</sub>) 47.6, 47.7 (broad, cyclen CH), 52.3, 52.4 (CH<sub>2</sub>N), 54.3 (CH<sub>2</sub>Cl), 116.0, 116.4 (CH=CH<sub>2</sub>), 132.1, 132.6 (CH=CH<sub>2</sub>), 170 (C=O); *m/z* (ESMS) 659 721(M<sup>+</sup>)

**Ligand 1:** Compounds **4** (20 mg, 0.015 mmol) and *N,N*-dimethyl- $\alpha$ -chloroamide (7.2 mg, 0.03 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub>(5 cm<sup>3</sup>) and to this solution was added diisopropylethylamine (0.036 cm<sup>3</sup>, 0.1 mmol). The resulting solution was left to stir overnight at room temperature, after which the solvent was removed under reduced pressure to yield **1** as a yellow oil (10 mg, 80 %). δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>) 2.41 – 3.21 (22H, m, CH<sub>3</sub> and cyclen CH<sub>2</sub>), 3.50 – 3.74 (54H, m, CH<sub>2</sub>O and CH<sub>2</sub>Cl), 4.11, (2H, m, CH<sub>2</sub>Cl) 7.51 (3H, m, Ar-H), 7.83 (4H, m, Ar-H); δ<sub>C</sub> (100 MHz; CDCl<sub>3</sub>) 14.4 (CH<sub>3</sub>), 29.7 (cyclen CH<sub>2</sub>), 65.1 (CH<sub>2</sub>C=O), 70.0 (aza-crown CH<sub>2</sub>), 87.7 (aza-crown CH<sub>2</sub>), 123.0, 123.1, 125.5, 126.0, 126.1, 128.1, 133.9 (ArH), 170.4, 171.2 (C=O); *m/z* (ESMS) 1047.6 (M<sup>+</sup>); HRMS: *m/z* (ESMS) Found: 1047.6298. C<sub>52</sub>H<sub>87</sub>N<sub>8</sub>O<sub>14</sub> requires 1047.6342.

#### **Eu(III) and Tb(III) Complexes of 1:**

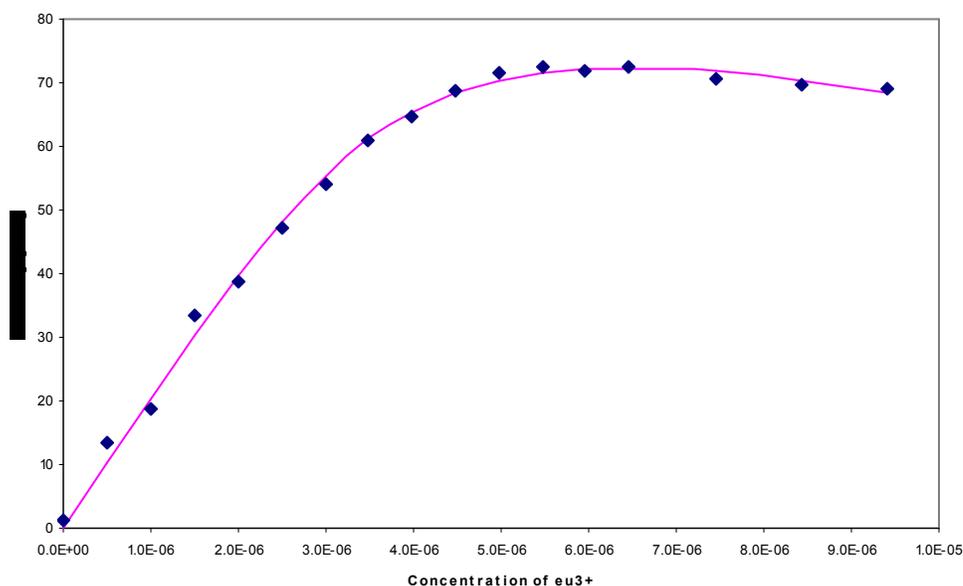
**Eu(III) complex of 1:** Eu(ClO<sub>4</sub>)<sub>3</sub> (19 mg, 0.043 mmol) was added to a stirred solution of ligand **1** (15 mg, 0.015 mmol) in MeOH (2 cm<sup>3</sup>) a precipitate formed, which was redissolved in CH<sub>3</sub>CN (2 cm<sup>3</sup>). The solvent was then left to evaporate and the resultant solid dried under reduced pressure to yield a yellow solid in 60% yield. The <sup>1</sup>H NMR was

broad due to the presence of three Eu(III) ions. Hence, we could not assign it accurately, Elemental analysis found: C 21.28, H 3.62, N 3.69; Expected for:  $C_{52}H_{86}N_8O_{14} \cdot (Eu^{3+})_3 \cdot (ClO_4^-)_{15} \cdot (CH_3OH)_3$ : C 21.37, H 3.20, N 3.63

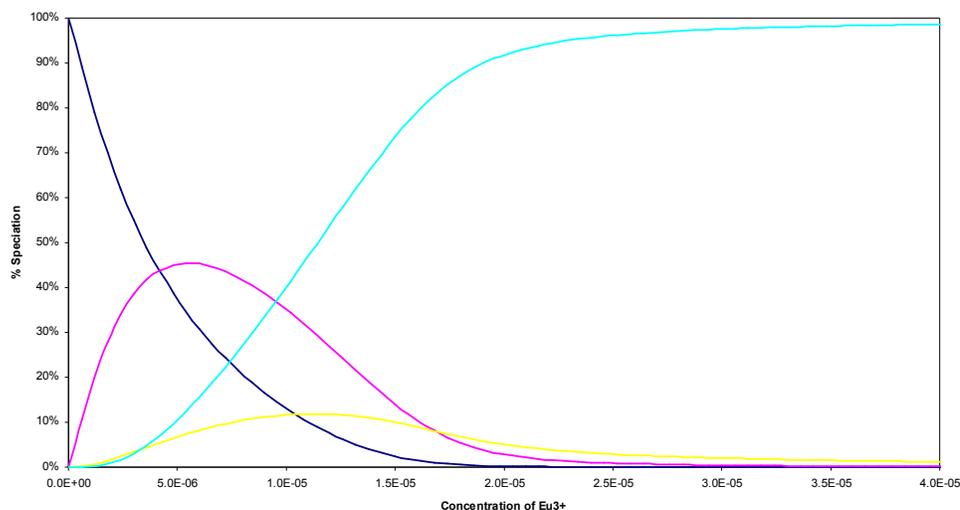
**Tb(III) complex of 1:** Same procedure was used as above, using  $Tb(ClO_4)_3$  (50 mg, 0.045 mmol), **1** (16 mg, 0.015 mmol). Elemental analysis: found: C 41.74, H 5.17, N 7.64. Expected for : C 41.36, H 5.87, N 7.89.  $C_{52}H_{86}N_8O_{14} \cdot Tb^{3+} \cdot 3 \cdot CH_3OH \cdot CH_3CN$ .

### Solution studies of the formation of the trimetallic complexes of 1:

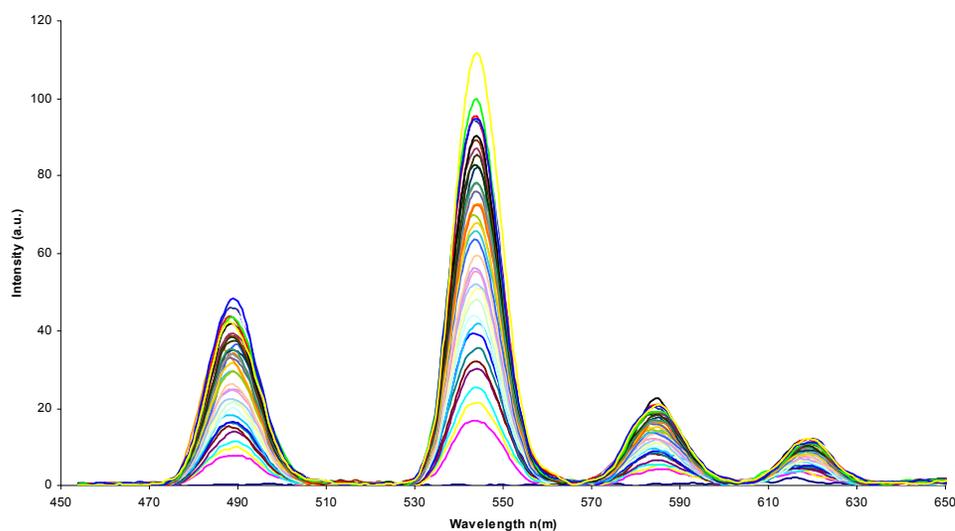
**Figure S1.** Fit obtained from Specfit for the changes in  $Eu^{3+}$  emission intensity upon titration of **1** ( $5 \times 10^{-6} \text{ mol dm}^{-3}$ ) with  $Eu^{3+}$  ( $0 - 5 \times 10^{-5} \text{ mol dm}^{-3}$ ), pH 6.5 (MES),  $I = 0.10 \text{ mol dm}^{-3}$  ( $NEt_4ClO_4$ ) in 50/50 MeOH/ $H_2O$  (v/v).



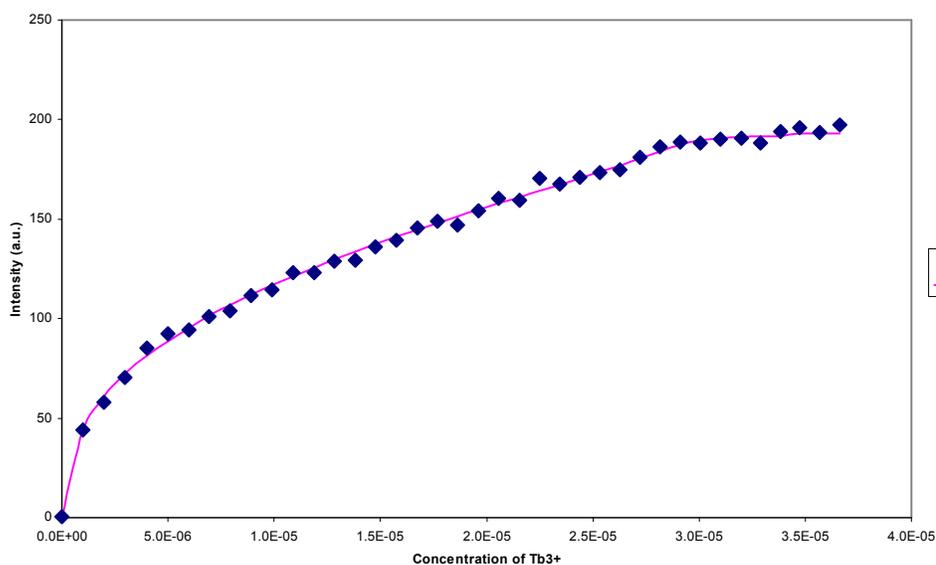
**Figure S2.** Speciation diagram for the changes in  $\text{Eu}^{3+}$  emission intensity upon titration of **1** ( $5 \times 10^{-6} \text{ mol dm}^{-3}$ ) with  $\text{Eu}^{3+}$  ( $0 - 3.5 \times 10^{-5} \text{ mol dm}^{-3}$ ), pH 6.5 (MES),  $I = 0.10 \text{ mol dm}^{-3}$  ( $\text{NEt}_4\text{ClO}_4$ ) in 50/50 MeOH/ $\text{H}_2\text{O}$  (v/v).



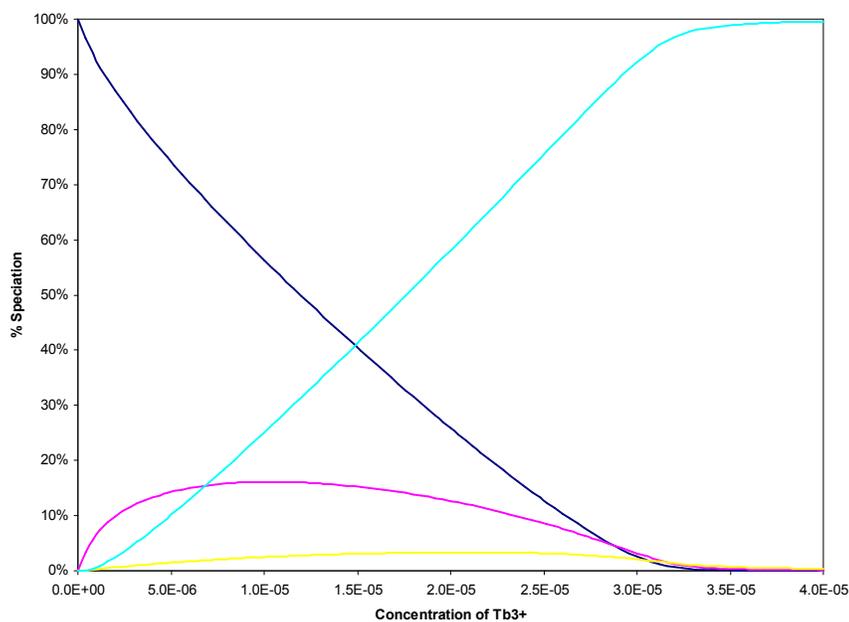
**Figure S3:** Changes in the  $\text{Tb}^{3+}$  emission upon titrations of complex **1** ( $1 \times 10^{-5} \text{ mol dm}^{-3}$ ) with  $\text{Tb}(\text{ClO}_4)_3$  ( $0 - 5 \times 10^{-5} \text{ mol dm}^{-3}$ ), pH 6.5 (MES),  $I = 0.10 \text{ mol dm}^{-3}$  ( $\text{NEt}_4\text{ClO}_4$ ) in 50/50 MeOH/ $\text{H}_2\text{O}$  (v/v); Inset: Changes in  $\text{Tb}^{3+}$  emission at 616 nm.



**Figure S4.** Fit obtained from Specfit for the changes in  $\text{Tb}^{3+}$  emission intensity upon titration of **1** ( $5 \times 10^{-6} \text{ mol dm}^{-3}$ ) with  $\text{Tb}^{3+}$  ( $0 - 5 \times 10^{-5} \text{ mol dm}^{-3}$ ), pH 6.5 (MES),  $I = 0.10 \text{ mol dm}^{-3}$  ( $\text{NEt}_4\text{ClO}_4$ ) in 50/50 MeOH/ $\text{H}_2\text{O}$  (v/v).

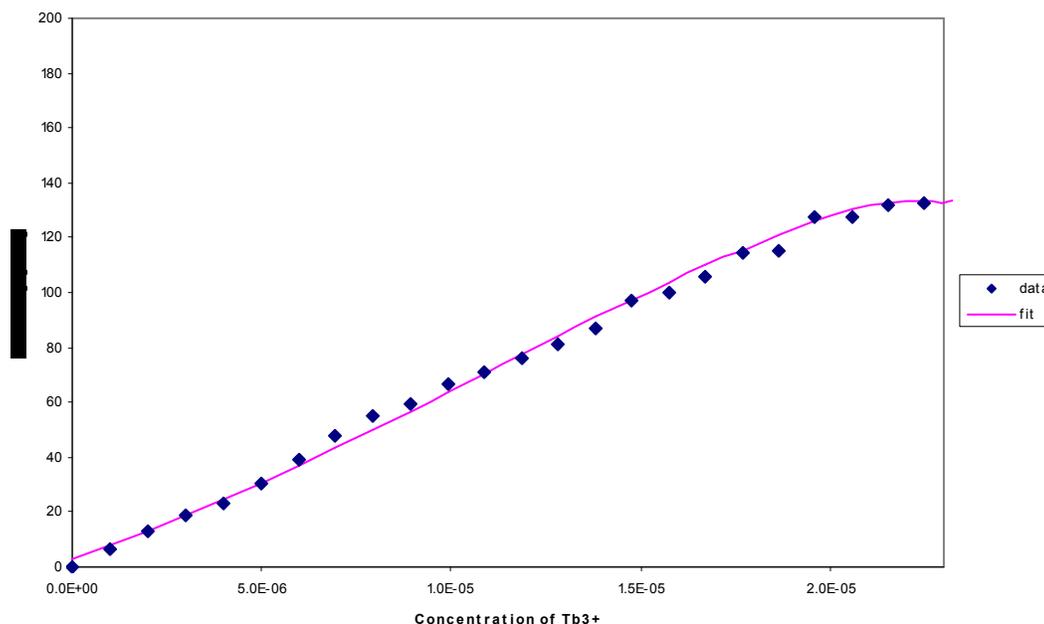


**Figure S5.** Speciation diagram for the changes in  $\text{Tb}^{3+}$  emission intensity upon titration of **1** ( $1 \times 10^{-5} \text{ mol dm}^{-3}$ ) with  $\text{Tb}^{3+}$  ( $0 - 4 \times 10^{-5} \text{ mol dm}^{-3}$ ), pH 6.5 (MES),  $I = 0.10 \text{ mol dm}^{-3}$  ( $\text{NEt}_4\text{ClO}_4$ ) in 50/50 MeOH/ $\text{H}_2\text{O}$  (v/v).

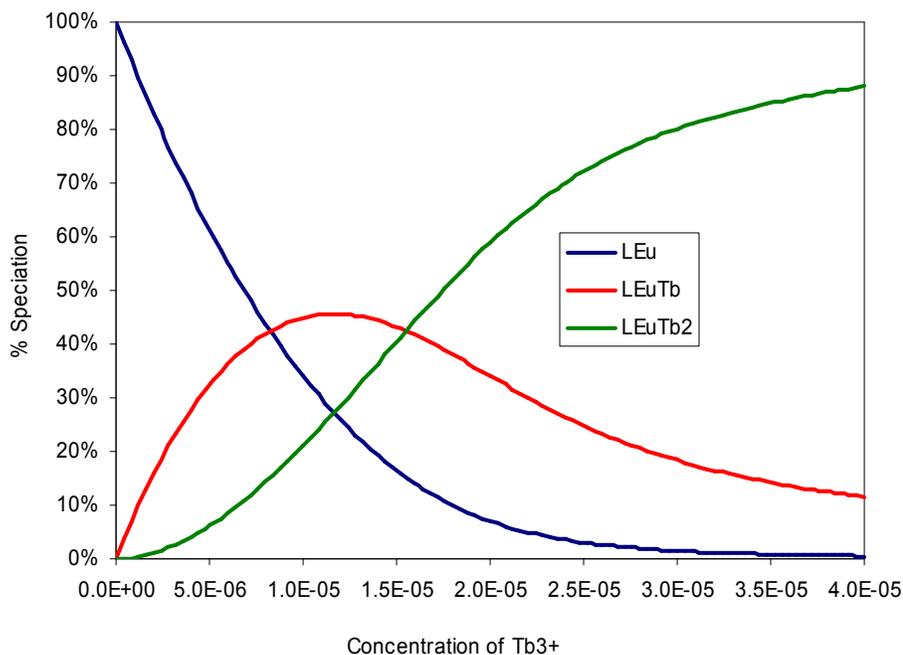


### Formation of the mixed lanthanide ion complex

**Figure S6.** Fit obtained from Specfit for the changes in  $\text{Eu}^{3+}$  emission intensity upon titration of **1** ( $5 \times 10^{-6} \text{ mol dm}^{-3}$ ) with  $\text{Tb}^{3+}$  ( $0 - 5 \times 10^{-5} \text{ mol dm}^{-3}$ ), pH 6.5 (MES),  $I = 0.10 \text{ mol dm}^{-3}$  ( $\text{NEt}_4\text{ClO}_4$ ) in 50/50 MeOH/ $\text{H}_2\text{O}$  (v/v).

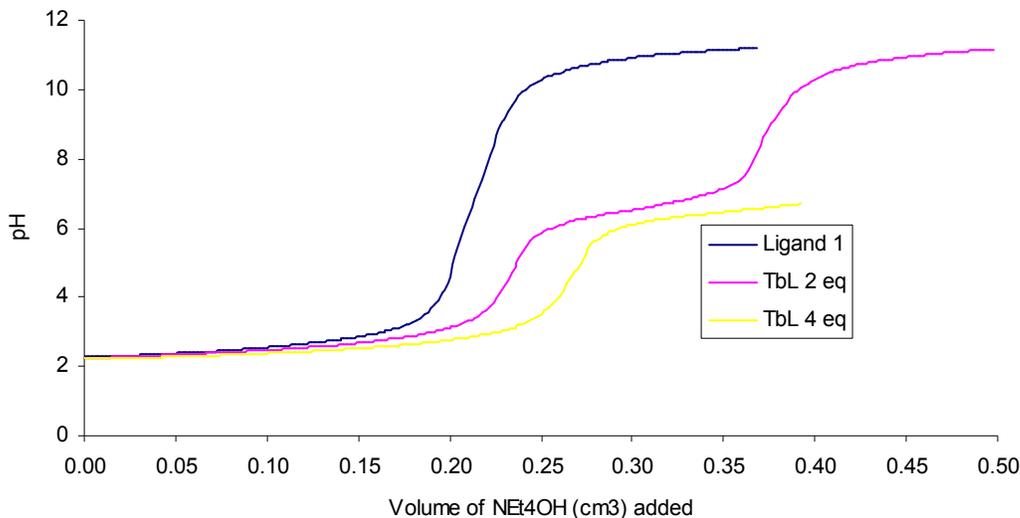


**Figure S7.** Speciation diagram for the changes in  $\text{Tb}^{3+}$  emission intensity upon titration of **1** ( $1 \times 10^{-5} \text{ mol dm}^{-3}$ ) with  $\text{Tb}^{3+}$  ( $0 - 4 \times 10^{-5} \text{ mol dm}^{-3}$ ), pH 6.5 (MES),  $I = 0.10 \text{ mol dm}^{-3}$  ( $\text{NEt}_4\text{ClO}_4$ ) in 50/50 MeOH/ $\text{H}_2\text{O}$  (v/v).

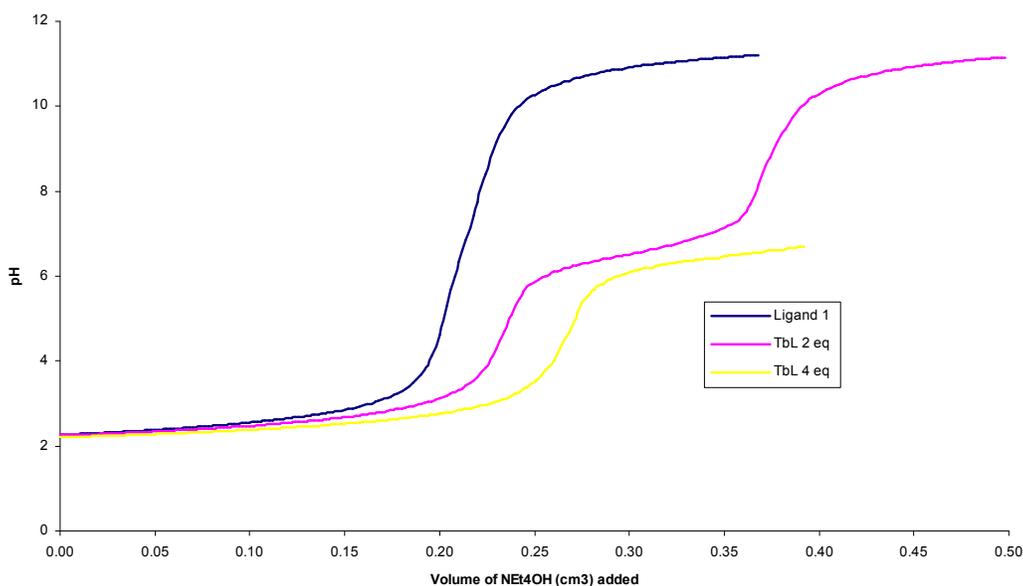


### Potentiometric titration of **1** and resulting Eu(III) and Tb(III) complexes

**Figure S8.** Typical titration curve of the protonated ligand **1** in the absence and presence of  $\text{Eu}(\text{ClO}_4)_3$  against  $\text{NEt}_4\text{OH}$  at 25 °C in a methanol/water solution 50/50(v/v).  $[\text{L56}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 7.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{Eu(III)}] = 1 \times 10^{-3} - 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{NEt}_4\text{OH}] = 0.093 \text{ mol dm}^{-3}$ ,  $I(\text{NEt}_4\text{ClO}_4) = 0.1 \text{ mol dm}^{-3}$ .

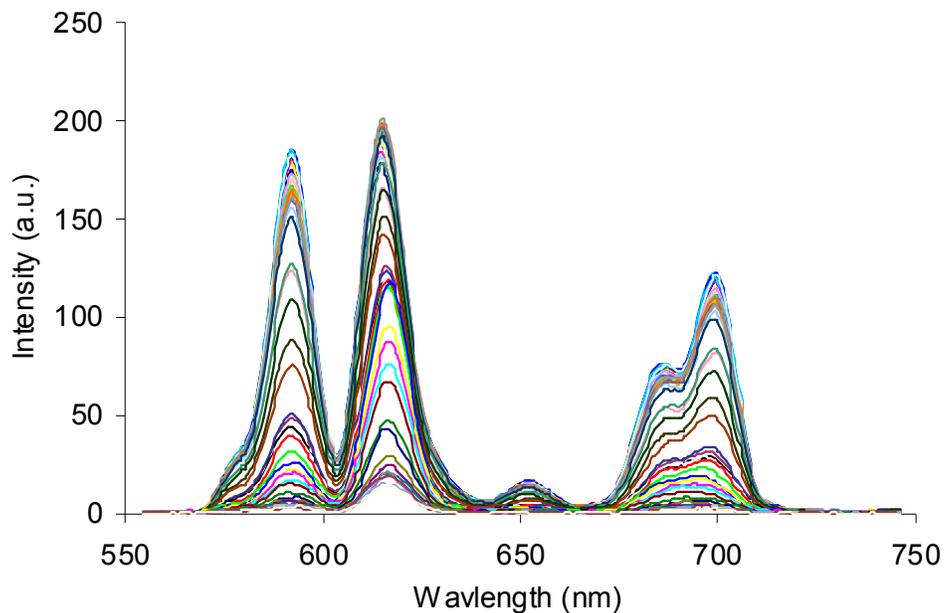


**Figure S9.** Typical titration curve of the protonated ligand **1** in the absence and presence of  $\text{Tb}(\text{ClO}_4)_3$  against  $\text{NEt}_4\text{OH}$  at 25 °C in a methanol/water solution 50/50(v/v).  $[\text{L56}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 7.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{Tb(III)}] = 1 \times 10^{-3} - 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{NEt}_4\text{OH}] = 0.093 \text{ mol dm}^{-3}$ ,  $I(\text{NEt}_4\text{ClO}_4) = 0.1 \text{ mol dm}^{-3}$ .

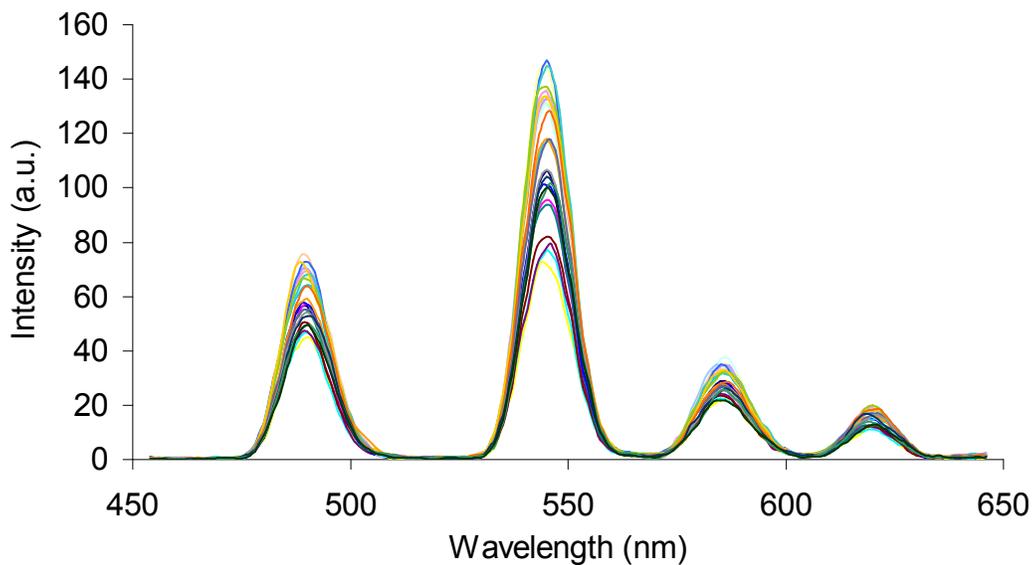


### Luminescent pH dyes of **1.Eu<sub>3</sub>** and **1.Tb<sub>3</sub>**

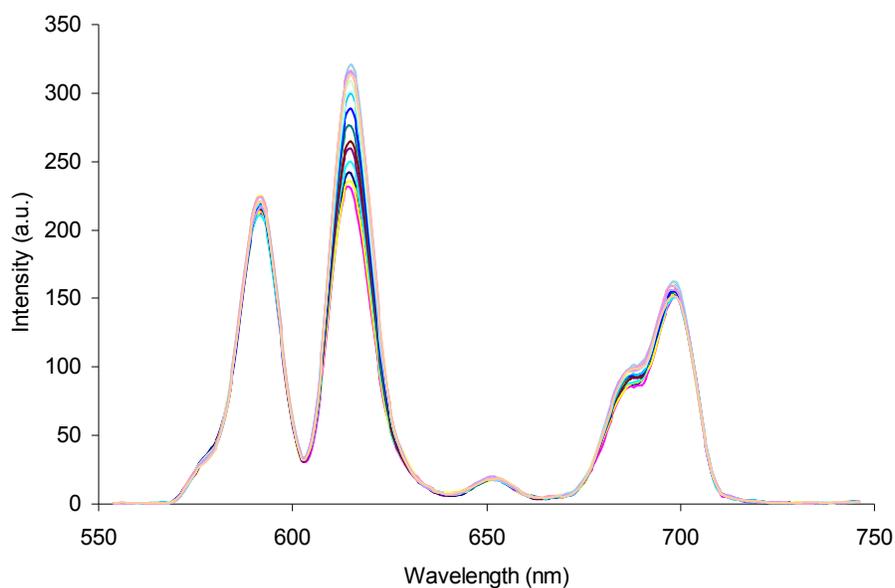
**Figure S10.** The pH titration profile of the acidified complex, **1.Eu<sub>3</sub>** ( $5 \times 10^{-6}$  mol dm<sup>-3</sup>) on titration with NEt<sub>4</sub>OH at 298.2 ( $\pm$  0.2) K,  $I=0.01$  M (NEt<sub>4</sub>ClO<sub>4</sub>) in 100% H<sub>2</sub>O



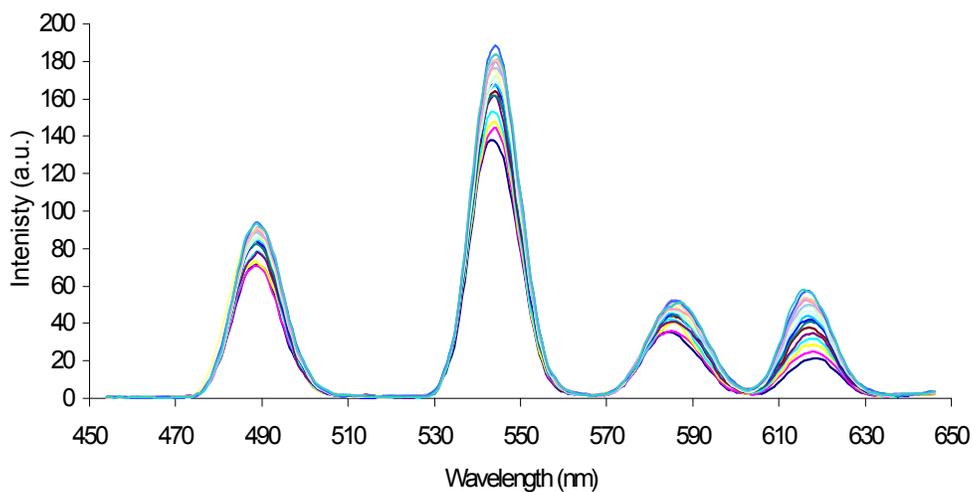
**Figure S11.** The pH titration profile of the acidified complex, **1.Tb<sub>3</sub>** ( $5 \times 10^{-6}$  mol dm<sup>-3</sup>) on titration with NEt<sub>4</sub>OH at 298.2 ( $\pm$  0.2) K,  $I=0.01$  M (NEt<sub>4</sub>ClO<sub>4</sub>) in 100% H<sub>2</sub>O;



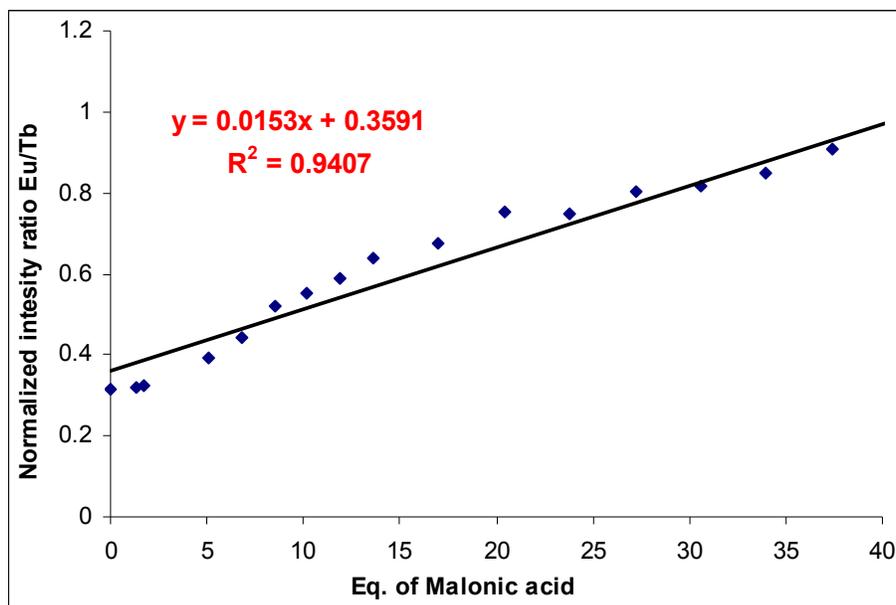
**Figure S12.** Changes in  $\text{Eu}^{3+}$  emission upon titrations of  $\mathbf{1.Eu}_3$  ( $5 \times 10^{-6} \text{ mol dm}^{-3}$ ) with Oxalic acid ( $0 - 3.5 \times 10^{-5} \text{ mol dm}^{-3}$ ), pH 6.5 (MES),  $I = 0.10 \text{ mol dm}^{-3}$  ( $\text{NEt}_4\text{ClO}_4$ ) in 100 %  $\text{H}_2\text{O}$ .



**Figure S13.** Changes in  $\text{Tb}^{3+}$  emission upon titrations of  $\mathbf{1.Tb}_3$  ( $5 \times 10^{-6} \text{ mol dm}^{-3}$ ) with oxalic acid ( $0 - 5 \times 10^{-5} \text{ mol dm}^{-3}$ ), pH 6.5 (MES),  $I = 0.10 \text{ mol dm}^{-3}$  ( $\text{NEt}_4\text{ClO}_4$ ) in 100%  $\text{H}_2\text{O}$ .



**Figure S14.** The ratiometric changes observed by comparing the changes in the Eu(III) emission with that of the Tb(III), demonstrating the liner relationship observed when titrated for malonic acid.



**Tables S1-4**

**Table S1:** The  $pK_a$  values of the protonated ligand **1** obtained at 25 °C with  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{NEt}_4\text{ClO}_4$ ) in a methanol/water solution 60/40(v/v).

	$pK_a$
$pK_{a1}$	$8.30 \pm 0.06$
$pK_{a2}$	$5.94 \pm 0.03$
$pK_{a3}$	$2.36 \pm 0.01$

**Table S2:** The stability constants expressed as  $\log K$  values for the metal complex ion of Eu(III) or Tb(III) perchlorate with **1**, at 25 °C with  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{NEt}_4\text{ClO}_4$ ) in a methanol/water solution 60/40(v/v).

	1.5 eq of $\text{Eu}^{3+}$	1.5 eq of $\text{Tb}^{3+}$
ML	$27.58 \pm 0.04$	$23.00 \pm 0.05$
$\text{M}_2\text{L}$	$4.41 \pm 0.04$	$8.99 \pm 0.05$

Complex	$\log K$	$\log K$
	1.5 eq of $\text{Eu}^{3+}$	1.5 eq of $\text{Tb}^{3+}$
$\text{MLH}_1$	$5.01 \pm 0.05$	$5.36 \pm 0.03$
$\text{MLH}_2$	$5.39 \pm 0.04$	$5.87 \pm 0.04$
$\text{MLH}_3$	$6.83 \pm 0.06$	$5.19 \pm 0.05$
$\text{MLH}_4$	-	$6.97 \pm 0.02$
$\text{MLH}_5$	-	$10.02 \pm 0.04$

**Table S3.** The  $pK_a$  values of the metal complex ion of Eu(III) or Tb(III) perchlorate with **1** at 25 °C with  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{NEt}_4\text{ClO}_4$ ) in a methanol/water solution 60/40(v/v).

Complex	$pK_a$	$pK_a$
	1.5 eq of $\text{Eu}^{3+}$	1.5 eq of $\text{Tb}^{3+}$
MLH <sub>1</sub>	$6.17 \pm 0.05$	$5.96 \pm 0.03$
MLH <sub>2</sub>	$6.52 \pm 0.06$	$6.35 \pm 0.03$
MLH <sub>3</sub>	$8.39 \pm 0.06$	$6.78 \pm 0.04$
MLH <sub>4</sub>	-	$7.57 \pm 0.03$
MLH <sub>5</sub>	-	$10.10 \pm 0.11$

**Table S4.** Lifetimes measurements for **1.Eu<sub>3</sub>** and **1.Tb<sub>3</sub>**

Excitation of antenna at 283 nm	$\tau_1$	$\tau_2$	$\tau_1$	$\tau_2$	$q_1$	$q_2$
	H <sub>2</sub> O		D <sub>2</sub> O			
<b>1.Eu<sub>3</sub></b>	0.313	0.695	0.568	3.04	1.33	<b>0.94</b>

Excitation of antenna at 283 nm	$\tau_1$	$\tau_2$	$\tau_1$	$\tau_2$	$q_1$	$q_2$
	H <sub>2</sub> O		D <sub>2</sub> O			
<b>1.Tb<sub>3</sub></b>	0.229	1.29	0.216	1.77	1.67	<b>1.05</b>