

Supplementary Material (ESI) for Chemical Communications  
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## pH driven self-assembly of a ternary lanthanide luminescence complex: The sensing of anions using a $\beta$ -diketonate-Eu(III) displacement assay

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### Electronic Supplementary Information

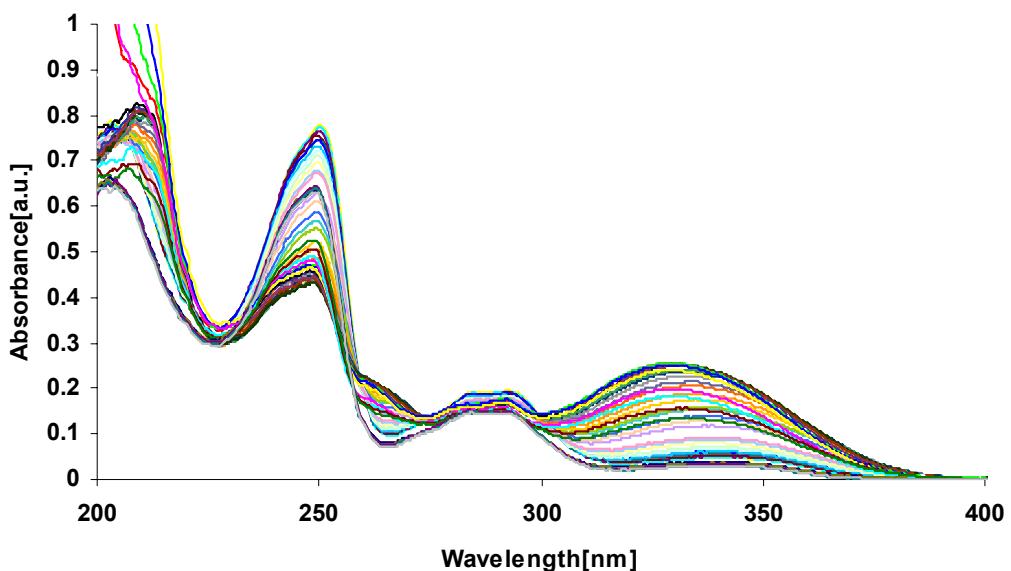
#### 2-(4,10-Bis(dimethylcarbamoylmethyl)-1,4,7,10tetraaza-cyclododec-1-yl)-N,N-dimethyl-acetamide Eu(III) (1.Eu)

Calculated for  $C_{23}H_{41}N_7O_{12}F_9S_3Eu \cdot (H_2O)_2(CHCl_3)_2$ : C, 23.07; H, 3.64; N, 7.53, Found: C, 22.67; H, 3.74; N, 7.55; Calculated for  $C_{21}H_{42}N_7O_6F_3SEu$ : [M+H peak]  $m/z = 730.2082$ , found: 730.2045 ;  $\delta_H$ (CD<sub>3</sub>OCD<sub>3</sub>, 400 MHz) – 13.91, 3.24, 2.60, 2.06, 1.30, 0.89, 0.01, -1.32, -4.95, -8.95, -12.87, -17.65;  $\delta_F$ (CD<sub>3</sub>OCD<sub>3</sub>, 376 MHz) – 78.74; Mass Spec (MeCN, ES+)  $m/z$  Expected :579.56, Found: 878.15 (M[Triflate]<sub>2</sub>+H), 730.20 (M[Triflate]+H); IR  $\nu_{max}(cm^{-1})$  3434, 2982, 2927, 2884, 1625, 1508, 1459, 1438, 1413, 1280, 1258, 1173, 1084, 1031, 960, 824, 762, 641, 573, 518.

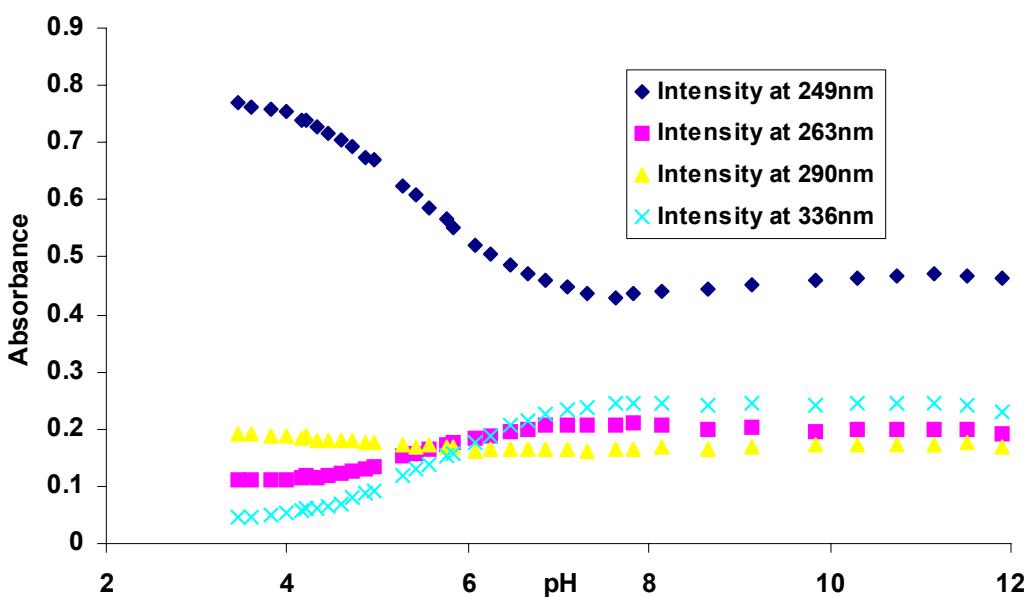
#### X-ray Crystal structure data:

Data were collected on a Bruker SMART APEX diffractometer using the SAINT-NT<sup>13</sup> software with phi/omega scans. A crystal was mounted on to the diffractometer at low temperature *ca.* 123K. The structure was solved using direct methods and refined with the SHELXTL program package<sup>13</sup>. Additional material available from the Cambridge Crystallographic Data Centre comprises relevant tables of atomic coordinates, bond lengths and angles, and thermal parameters (CCDC Number 616591). *Crystal data* for (?), (C<sub>20</sub>H<sub>42</sub>ClN<sub>7</sub>O<sub>3</sub>):-  $M = 464.06$ , monoclinic, space group  $P21/n$ ,  $a = 15.1926$  (14) Å,  $b = 11.0971(10)$  Å,  $c = 15.5763$  (14) Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 111.215$  (2)°,  $U = 2448.09(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu = 0.08$  mm<sup>-1</sup>,  $R_{int} = 0.0256$ , A total of 25078 reflections were measured for the angle range  $2 < 2\theta < 58^\circ$  and 6074 independent reflections were used in the refinement. The final parameters were  $WR2 = 0.1247$  and  $R1 = 0.0477$ , [I > 2σI].

**Figure 1.** a) The changes in the absorption spectra of **4** as a function of pH. b) The changes at various wavelengths.

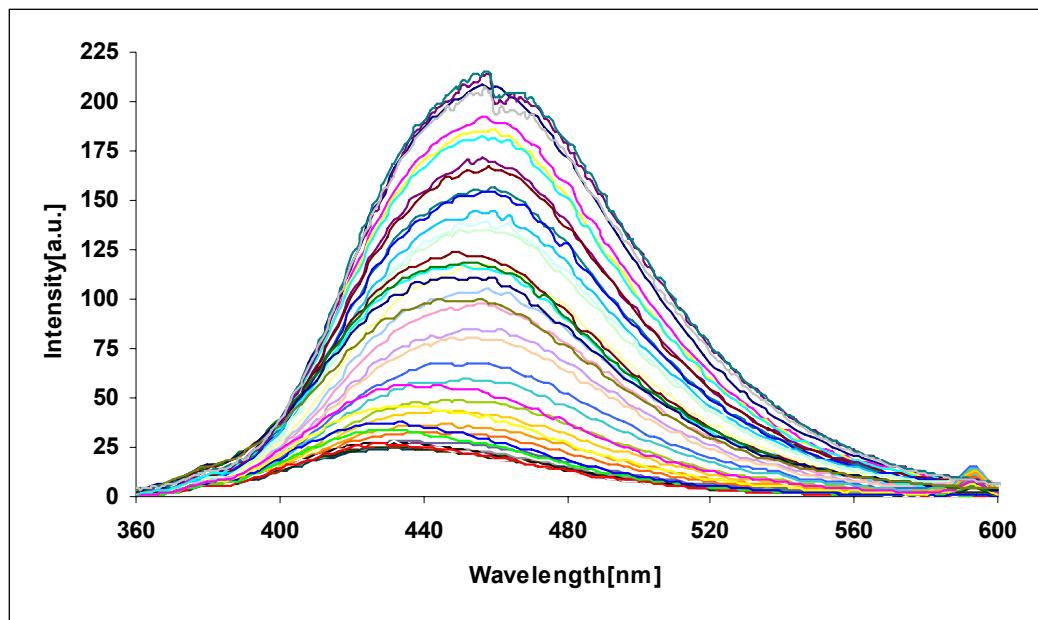


**Figure 1a**

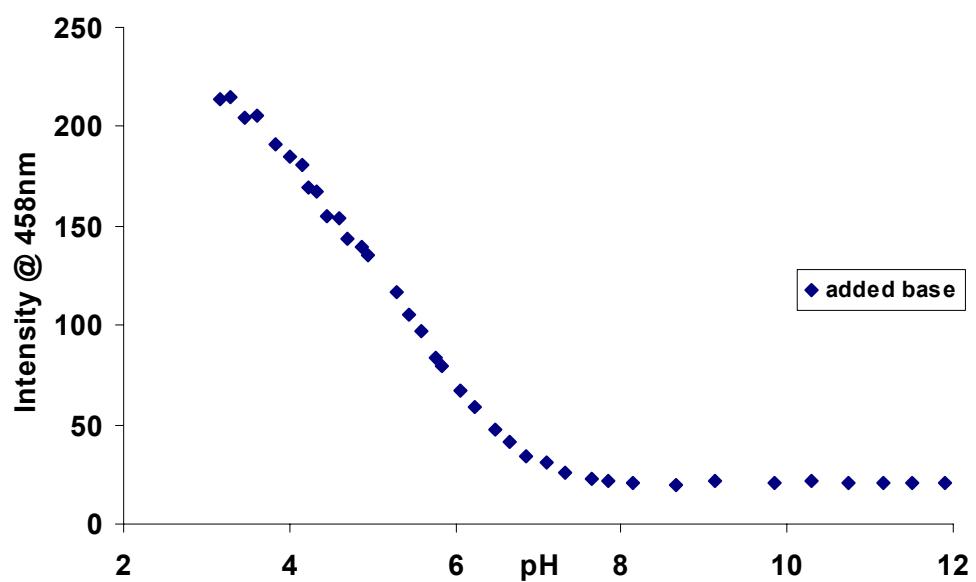


**Figure 1b.**

**Figure 2.** a) The changes in the fluorescence emission spectra of **4** as a function of pH. b) The changes at 485 nm.

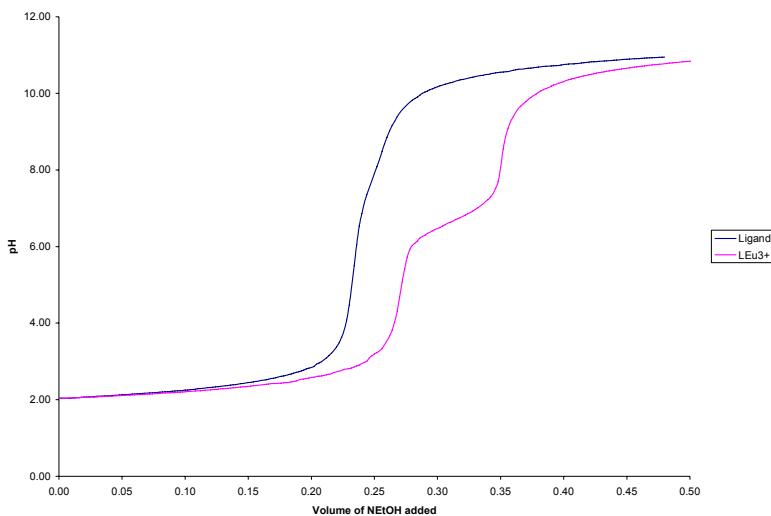


**Figure 2a**

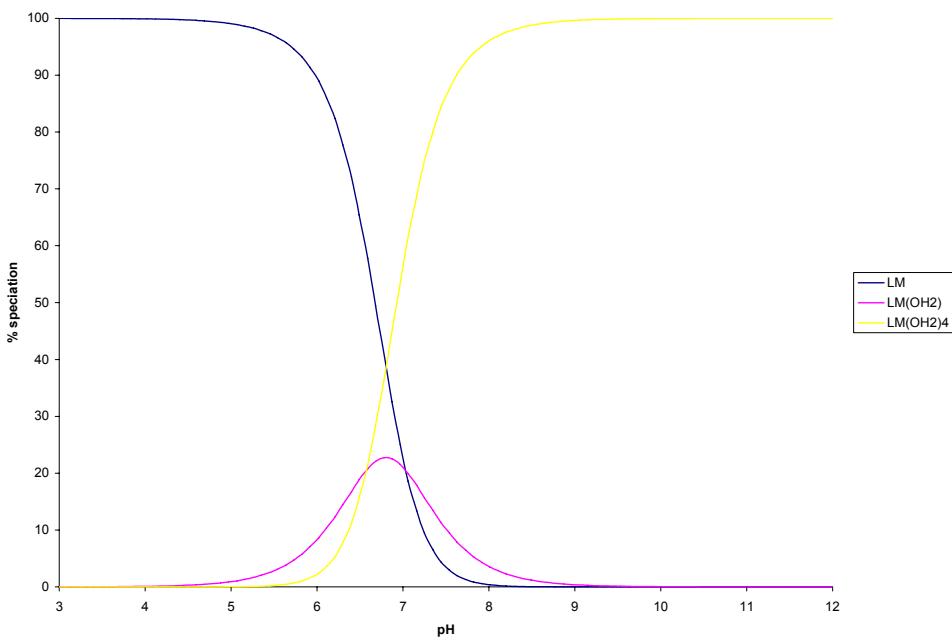


**Figure 2b.**

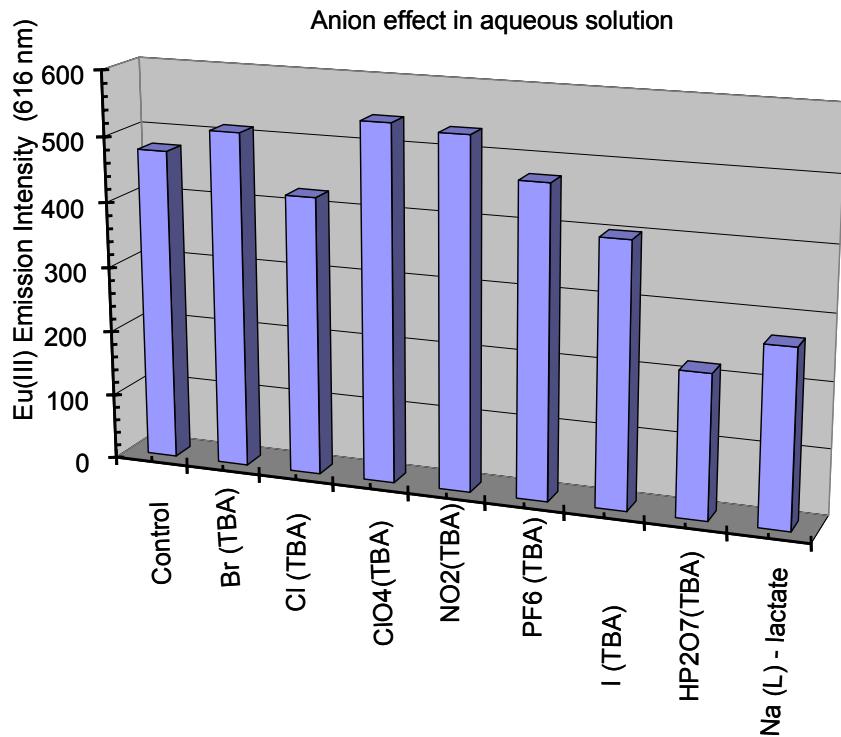
**Figure 3.** The pH titration profile for **1** and **1 + Eu(III)**. Titration curve of the protonated ligand **1** against NEt<sub>4</sub>OH at 25 °C. [1] = 1 x 10<sup>-3</sup> M, [H<sup>+</sup>] = 8.5 x 10<sup>-3</sup> M, [NEt<sub>4</sub>OH] = 0.10 M, I = 0.10 M (NEt<sub>4</sub>ClO<sub>4</sub>), total volume = 3 cm<sup>3</sup>. [Eu(III)]<sub>total</sub> = 1.0 x 10<sup>-3</sup> M, I = 0.10 M (NEt<sub>4</sub>ClO<sub>4</sub>) at 25 °C.



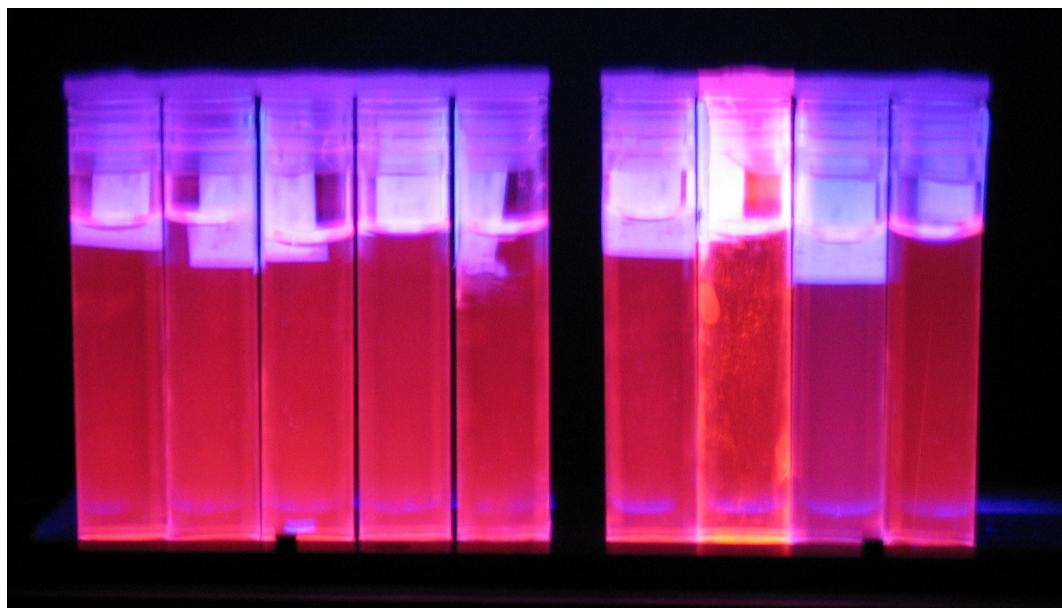
**Figure 4.** Speciation is shown relative to the total concentration of ligand **1**, NEt<sub>4</sub>OH at 25 °C. [1]<sub>total</sub> = 1 x 10<sup>-3</sup> M, [Eu(III)]<sub>total</sub> = 1.0 x 10<sup>-3</sup> M, [H<sup>+</sup>]<sub>total</sub> = 8.5 x 10<sup>-3</sup> M, [NEt<sub>4</sub>OH] = 0.10 M, I = 0.10 M (NEt<sub>4</sub>ClO<sub>4</sub>), total volume = 3 cm<sup>3</sup>.



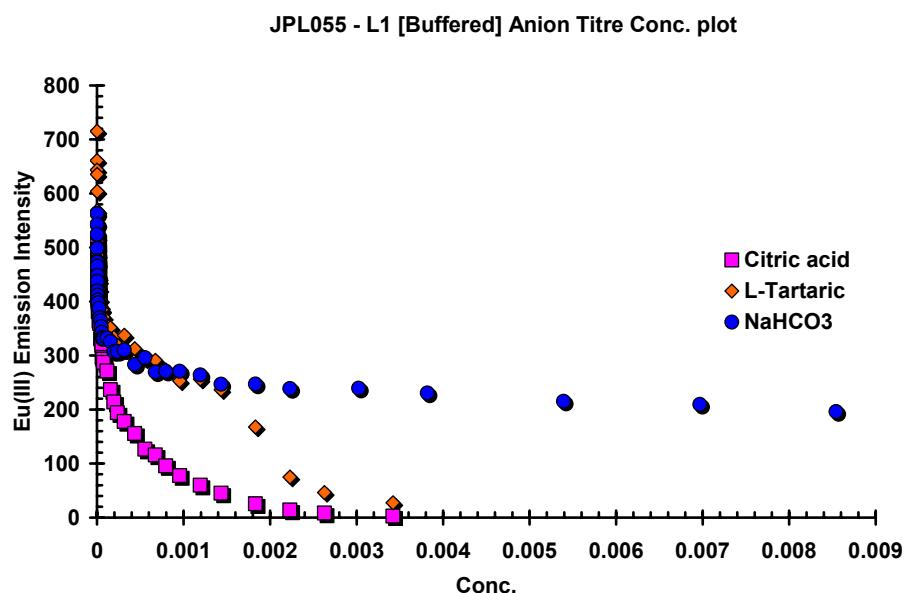
**Figure 5.** The changes in the 616 nm transition with different anions. Moderate changes.



**Figure 6.** Naked-eye detection under a UV-Vis lamp (same order as above for Fig. 5).



**Figure 7.** The pH profile for the titration of the **1.Eu-4** self-assembly with anions.



**Settings for luminescence studies (Varian Carey Eclipse)**

Solutions were made in methanol, water and buffered solutions [0.1M TMACl, 0.1M HEPES, pH 7.5]. Lanthanide concentrations were 10 mM. In all ternary complexes, used in pH studies the lanthanide solutions were 10 mM with 2 equivalents (20 mM) of the ligand. Stock ligand solutions were all made in methanol. Luminescence and lifetimes were measured on a Varian Carey Eclipse Fluorescence spectrophotometer and *Uv-Vis* on a Varian *Uv-Vis* spectrophotometer using with general settings as indicated:

Uv-Vis spectrophotometer settings:

Scan: 200-800 nm, Ex. Slit: 1nm, Em. Slit: 1nm, Scan speed: medium,

Luminescence settings: Lanthanide Luminescence

Mode: Phos, Delay Time: 0.1ms, Gate Time: 10 ms, Cycle: 100, Flash count: 1, Scan: 550-750nm, PMT: 800V, Excitation: 336nm Data Interval: 3 nm, Ex. Slit: 5nm, Em. Slit: 5nm, Average time: 0.10 s, Total decay: 0.02 s

Luminescence settings: Fluorescence

Mode: Fluor, Excitation: 336nm, Scan: 350-[550-750] nm, PMT: 600V, Ex. Slit: 5nm, Em. Slit: 5nm, Scan speed: Fast, Filter: 360-1100 nm

Lanthanide complexes – Life time studies

Lanthanide solutions in H<sub>2</sub>O and D<sub>2</sub>O were all 10 mM. In all ternary complexes, lanthanide solutions were 10 mM with 2 equivalents (20 mM) of the ligand. Lifetimes were measured on a Varian Carey Eclipse Fluorescence spectrophotometer using with general settings as indicated:

Flourimeter settings: Settings for lifetime studies (Varian Carey Eclipse)

Direct excitation: Eu(III) - 395nm, Emission: Eu(III) - 616nm

Mode: Phos, Delay Time: 0.1 ms, Gate Time: 0.1ms, Cycle: 100, Flash count: 1, No. Cycles: 100, Total decay: 3.0 ms, PMT: 800V, Ex. Slit: 5nm, Em. Slit: 5nm