Supplementary Information

Lanthanide tweezer complexes for luminescence detection of aromatic pollutants in water

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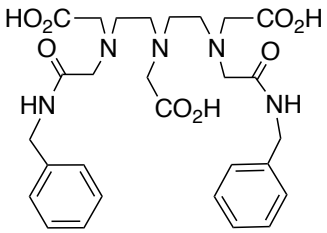
Synthesis

Materials Starting materials were of reagent grade, obtained from Aldrich, Acros or Avocado, and used without further purification unless otherwise stated. Tetrabutylammonium hydroxide (TBAOH) (40% wt H_2O) was purchased from Aldrich or Fluka. The Ln(III)Cl_3•$6H_2O$ salts were of >99.9% purity, stored in a dry atmosphere (desiccator) and used as received from Acros or Aldrich. Deuterated solvents were obtained from Goss Scientific and used as received. Deionised water was used from an Elga "Option 3" water purifier.

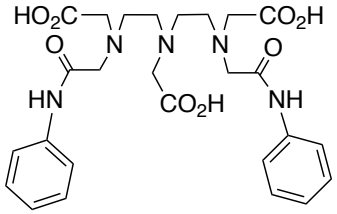
N,N''-bis(benzylcarbamoylmethyl)diethylenetriamineN,N'N''-triacetic acid (H_3L^1).



ca.DTPA (5 g, 14 mmol) was slowly added to benzylamine (10 cm^3, 78 mmol) whilst stirring at 0°C. After 30 minutes the solution was allowed to warm to room temperature and water (15 cm^3) added to the solution. The reaction was then stirred for 24 h. The resulting yellow solution was reduced in volume to an oil, then diluted with water (10 cm^3). The pH of the solution was lowered to pH 3 by dropwise addition of conc. HCl. The flask was then stoppered and stored in a fridge for 2 days. The white crystals that formed were collected by filtration, washed with water (2 x 25 cm^3), ethanol (2 x 25 cm^3) and diethyl ether (2 x 25 cm^3), then dried on a vacuum line. (Yield 5.80 g, 68 %).

^{1}H NMR (300 MHz, $(CD_3)_2SO$), δ_H: 8.52 (2H, t, -CONH-, $^3J_{HH}$ 6 Hz), 7.21 (10H, m, Ar H), 4.28 (4H, d, -CH_2Ph, $^3J_{HH}$ 6 Hz), 3.37 (4H, s, terminal -NCH_2COO), 3.34 (2H, s, central NCH_2COO), 3.29 (4H, s, -NCH_2CO-), 2.86 (4H, m, -NCH_2CH_2N-), 2.80 (4H, m, -NCH_2CH_2N-).^{1}H NMR (300 MHz, (D_2O/NaOD), δ_H: 7.40-7.10 (10H, m, ArH), 4.36 (4H, s, CH_2Ph), 3.19/3.11 (8H, 2 x s, terminal -CH_2COO, -NCH_2CO-), 2.94 (2H, central –CH_2COO), 2.51 (8H, m, -NCH_2CH_2N-). $^{13}C\{^1H\}$ NMR (75.5 MHz, $(CD_3)_2SO$), δ_C: 172.6 (2C, –CH_2CONH-), 170.4 (2 x –COOH), 169.5 (2C, cent. –COOH), 139.4 (2C, ArC), 128.2 (4C ArCH), 127.1 (4C, ArCH), 126.7 (2C ArCH), 57.3 (2x –NCH_2CONH-), 55.2 (2C, -CH_2COOH), 55.0 (1C, cent -CH_2COOH), 52.0 and 50.7 (4C -NCH_2CH_2N-), 41.9 (2C, -CH_2Ph). MS (ES+) *m/z* 572 $[M+H]^+$, 594 $[M+Na]^+$.

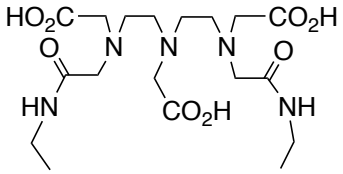
N,N''-bis(phenylcarbamoylmethyl)diethylenetriamineN,N'N''-triacetic acid (H_3L^2).



ca.DTPA (5 g, 14 mmol) was added slowly to aniline (7.4 cm^3, 78 mmol) whilst stirring at 0 ^oC for 30 minutes. The pH of the resulting suspension was raised to pH 7 by dropwise addition of conc. ammonium hydroxide, giving a clear light yellow solution. The reaction was then stirred for 24 h at room temperature. The yellow solution was reduced in volume to a thick oil, then diluted with water (10 cm^3). The pH of the solution was lowered to pH3 by dropwise addition of conc. HCl resulting in two layers in the flask, a top water layer and a thick product layer at the bottom. The top layer was decanted, and the bottom layer washed with water (3 x 20 cm^3), then diethyl ether (40 cm^3) suspended on top of the resulting sticky solid for 2 days. A white solid was collected by filtration, crushed brought to reflux in ethanol (50 cm^3) for 2 hours. The white powder from this was collected by filtration and dried under vacuum. (Yield 2.96 g, 38%).

^{1}H NMR (300 MHz, $(CD_3)_2SO$), δ_H: 10.03 (2H, s, -CONH-), 7.64 (4H, d, *o*-ArCH, $^3J_{HH}$ = 7.5 Hz), 7.27 (4H, dd, *m*-ArCH, $^3J_{HH}$ = 7.5 Hz), 7.03 (2H, dd, *p*-ArCH, $^3J_{HH}$ = 7.5 Hz), 3.48 (2H, s, central -NCH_2COOH), 3.45 (4H, s, terminal -NCH_2COOH), 3.43 (4H, s, -NCH_2CO-), 2.97 (4H, m, -NCH_2CH_2N-), 2.91 (4H, m, -NCH_2CH_2N-). ^{1}H NMR (300 MHz, d_7-DMF), δ_H: 10.2 (2H, s, -CONH-), 7.80 (4H, d, *o*-ArCH), 7.33 (4H, t, *m*-Ar CH), 7.07 (2H, t, *p*-Ar CH), 3.71 (2H, s, central -NCH_2COOH), 3.63 (4H, s, terminal -NCH_2COOH), 3.57 (4H, s, -NCH_2CO-), 3.19 (4H, m, -NCH_2CH_2N-), 3.10 (4H, m, -NCH_2CH_2N-). $^{13}C\{^1H\}$ NMR (75.5 MHz, $(CD_3)_2SO$), δ_C: 172.9 (2 x –CH_2CONH-), 169.3 (2 x –COOH), 138.6 (2 x Ar C), 128.5 (4 x Ar CH), 123.2 (2 x Ar CH), 119.2 (4 x Ar CH), 57.3 (2x –NCH_2CONH-), 55.2 (2 x -CH_2COOH), 52.2 and 51.1(4 x -NCH_2CH_2N-). MS (ES+) *m/z* 544 ($M+H^+$), 566 ($M+Na^+$). Calculated for $C_{26}H_{33}N_5O_8.H_2O$: C 55.6 % H 6.3 % N 12.5 % Found: C 55.8 %, H 6.3 % N 12.6 %.

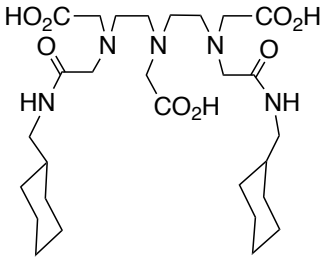
1, 11-(bis(ethylamino)-1, 11-dioxo-3,6,9-triaza-3,6,9-triscarboxymethyl)undecane: H_3L^3



DTPA-dianhydride (15.0 g, 0.042 mol) was added slowly over 30 minutes to a stirring, ice cold solution of ethylamine (30 cm^3, 0.37 mol, 70% w/w H_2O). The mixture was then diluted with 30 cm^3 H_2O, allowed to warm to ambient temperature and stirring continued overnight. The yellow solution was filtered and the volume reduced to an oil by rotary evaporation. The oil was then diluted with 10 cm^3 H_2O and acidified to around pH 2 with conc. HCl. The colourless crystals that formed were collected by filtration, washed with water (100 cm^3), ethanol (50 cm^3) and diethyl ether (50 cm^3) then dried under vacuum. The solid was recrystallised from H_2O to yield the title compound, H_3**L^3** $2H_2O$ (4.46 g, 22 %). ^{1}H NMR (400 MHz, D_2O) δ 3.89 (s, 4H, NCH_2CO_2H, terminal), 3.77 (s, 4H, NCH_2CONH), 3.71 (s, 2H, NCH_2CO_2H, central), 3.41 (t, *J* = 6.3 Hz, 4H, NCH_2CH_2N), 3.31 (t, *J* = 6.23 Hz, 4H, NCH_2CH_2N), 3.27 (q, *J* = 7.3 Hz, 4H, NCH_2CH_3),

1.14 (t, *J* = 7.3 Hz, 6H, $NCH_2C\underline{H}_3$). ^{13}C NMR (62.9 MHz): δ_C 172.7 ($\underline{C}O_2H$); 172.4 ($\underline{C}O_2H$); 168.2 ($\underline{C}ONH$); 57.3, 57.1, 55.0 ($N\underline{C}H_2CO$); 52.2, 51.5 ($N\underline{C}H_2\underline{C}H_2N$), 35.0 ($N\underline{C}H_2CH_3$); 13.9 ($\underline{C}H_3$); MS $[M+1]^+$ 448 ; CHN: Calculated for $C_{18}H_{37}N_5O_{10}$: 44.70% C; 7.73% H; 14.49% N. Found: 44.60% C; 7.77% H; 14.49% N.

1,11-(bis(methylenecyclohexylamino)-1,11-dioxo-3,6,9-triaza-3,6,9-triscarboxymethyl) undecane ($H_3\mathbf{L^4}$)



DTPA-dianhydride (12.85 g, 0.036 mol) was added in small portions over 30 minutes to neat ice cold, stirring cyclohexanemethylamine (23 cm^3, 0.18 mol). The viscous suspension was then diluted with water (20 cm^3), and allowed to warm to room temperature, at which temperature stirring was continued for 24 hours. The volume of the yellow solution was reduced by rotary evaporation and the oil diluted with 50 cm^3 H_2O before acidification to pH~2 with conc. HCl. The colourless solid which quickly formed was collected by filtration, washed with water (500 ml), EtOH (500 cm^3) and diethyl ether then dried under vacuum to yield the title compound, DTPA-mcyHA (12.9 g, 62 %). MS: $[M+1]^+$ 584. ^1H NMR (400 MHz MeOD) δ_H (ppm): 3.83 (2H, s, $NC\underline{H}_2CO_2$ central); 3.51 (4H, s, $NC\underline{H}_2CO_2$ terminal); 3.47 (4H, s, $NC\underline{H}_2CONH$); 3.41 (t, 4H, ^3J = 5.9 Hz, $NCH_2C\underline{H}_2N$); 3.16 (t, 4H, ^3J = 5.9 Hz, $NC\underline{H}_2CH_2N$) 3.09 (4H, d, $CONHCH_2C\underline{H}C_5H_{10}$, ^3J = 6.9 Hz); 1.78-1.75 (10H, m, cyhex); 1.52 (2H, m, cyhex); 1.35-1.15 (6H, m, cyhex); 1.0-0.9 (4H, m, cyhex). CHN: Calculated for $C_{28}H_{49}N_5O_8$: 57.60% C; 8.64% H; 12.00% N. Found: 57.40% C; 8.64% H; 11.30% N.

Eu$\mathbf{L^1}$ To a solution of $EuCl_3.6H_2O$ (0.823 mmol) in H_2O (3 cm^3) was added H_3L^1 (0.500 g, 0.823 mmol). The solution was diluted with water (25 cm^3) then sonicated and gently heated until all the ligand had dissolved. The pH of the resulting colourless solution was raised from pH 3 to pH 5 by dropwise addition of tetrabutylammonium hydroxide (40 % wt in water). The volume of the solution was reduced to ~1 cm^3 and then acetonitrile (20 cm^3) added, resulting in a cloudy white suspension. The solid product was collected by filtration then washed with acetonitrile and diethyl ether. The resulting powder was dried in *vacuo* (yield 93 %). MS (ES^+) *m/z* 722 $[M+H]^+$, 744 $[M+Na]^+$. UV/Vis (H_2O) λ nm (ε mol^{-1} dm^3 cm^{-1}): 247 (sh), 252 (560), 257 (580), 262 (sh), 267 (sh). Calculated for $C_{28}H_{34}N_5O_8Tb.3.5H_2O$: C 42.5 % H 5.2 % N 8.9 % Found: C 42.6 %, H 5.0 % N 8.7 %.

Ln$\mathbf{L^1}$ Same procedure as for Eu$\mathbf{L^1}$ was followed for other Ln:

Tb$\mathbf{L^1}$: (Yield 97 %) MS (ES^+) *m/z* 728 $[M+H]^+$, 750 $[M+Na]^+$. UV/Vis (H_2O) λ nm (ε mol^{-1} dm^3 cm^{-1}): 247 (sh), 252 (344), 257 (410), 262 (sh), 267 (sh). Calculated for $C_{28}H_{34}N_5O_8Tb.4.5H_2O$: C 42.0 % H 5.4 % N 8.7 % Found: C 42.0 %, H 5.4 % N 8.4 %.

LaL^1: (yield 98 %) MS (ES$^+$) *m/z* 708 [M+H]$^+$. ^{1}H NMR (300 MHz, D_2O): δ_H 7.6-7.1 (10H, m, ArH), 4.6-4.1 (4H, m, CH_2-Ph), 3.8-2.0 (18H, br, aliphatic CH_2).

YL^1: (yield 81 %) ^{1}H NMR (300 MHz, *d_4*-methanol): δ_H 7.6-7.2, (10H, m, ArH), 4.7-4.3 (4H, m, CH_2-Ph), 3.8-2.2 (18H, br, aliphatic CH_2).MS (ES+) *m/z* 680 [M+Na]$^+$ Accurate ESI-MS: m/z: calc. 680.1364 [M+Na]$^+$, found. 680.1359.

EuL^2 To a solution of $EuCl_3.6H_2O$ (0.890 mmol) dissolved in H_2O (3 cm^3) was added H_3**L^2** (0.500 g, 0.890 mmol). The solution was diluted with water (25 cm^3) then sonicated and gently heated until all the ligand had dissolved. The resulting colourless solution was raised from pH 3 to pH 5 by dropwise addition of tetrabutylammonium hydroxide (40% wt in water). The volume of the solvent was reduced to ~1 cm^3 resulting in a light yellow oil and then acetonitrile (20 cm^3) added giving a cloudy white suspension. The product was filtered off then washed with acetonitrile (20 cm^3) and diethyl ether (20 cm^3), then dried *in vacuo* (Yield 96 %). MS (ES$^-$) *m/z*: 617 [M-Bz-H]$^+$, 692 [M-H]$^+$. Calculated for $C_{26}H_{30}N_5O_8Eu.4H_2O$ $0.25(C_{16}H_{36}NCl)$: C 43.2 % H 5.7 % N 8.8 % Found: C 43.3 %, H 5.5 % N 8.8 %. UV**/**Vis (H_2O) λ nm (ε mol^{-1} dm^3 cm^{-1}): 239.4 (17900).

TbL^2: Same procedure as **EuL^2** (Yield 91 %) MS (ES$^-$) *m/z*: 698 [M-H]$^+$. Calculated for $C_{26}H_{30}N_5O_8Tb.4H_2O$ $0.3(C_{16}H_{36}NCl)$: C 43.6 % H 5.8 % N 8.6 % Found: C 43.7 %, H 5.8 % N 8.7 %.

EuL^3 The ligand, H_3**L^3**, (0.242 g, 0.500 mmol) was combined with 2 ml aqueous $EuCl_3{\cdot}6H_2O$ (0.179 g, 0.489 mmol), the mixture diluted to 20 cm^3 with water before sonicating and heating gently until all of the powder had dissolved (pH ~1). The colourless solution was raised to pH 5 by dropwise addition of TBAOH (40 % w/w H_2O) then the volume reduced to ~0.5 ml by rotary evaporation. Addition of CH_3CN to the concentrated solution instantly afforded a colourless solid which was collected by filtration, washed with CH_3CN (50 cm^3) and Et_2O (50 cm^3) then dried under vacuum to yield the title complex, [EuBEA.H_2O] (0.288 g, 96%). ES-MS (+): [M+1]$^+$ 596/598 D, [TBA]$^+$ 242 D. The solid was dissolved in methanol (5 ml), the volume reduced and the complex re-precipitated with acetonitrile to remove the excess TBACl. CHN: Calculated for $[EuC_{18}H_{34}N_5O_{10}]$: 34.17% C; 5.43% H; 11.07% N. Found: 34.44% C; 5.26% H; 10.92% N

EuL^4 H_3**L^4** (0.326 g, 0.558 mmol) was added to an aqueous solution (2 cm^3) of $EuCl_3{\bullet}6H_2O$ (0.203 g, 0.554 mmol). The mixture was diluted to 20 cm^3 with water then heated and sonificated until all the ligand had dissolved (pH~1). TBAOH (40% w/w H_2O) was added dropwise raising the colourless solution to pH 5 before reducing the volume by rotary evaporation. Addition of CH_3CN (20 cm^3) instantly afforded a colourless precipitate. This was collected by filtration, washed with CH_3CN (50 cm^3) and Et_2O (50 cm^3) then dried under vacuum to yield the title compound, $[EumcyHA{\bullet}H_2O]2H_2O$ (0.339 g, 82 %). LC-MS (ES+): [M$^+$] 731/733 D (2.57 mins).

Methods for guest binding experiments. The guest binding experiments were carried out using for a Ln-complex concentration of 4 x 10^{-5} mol dm^3 in water. Toluene and benzene were either added neat or as a solution dissolved in methanol such that the final volume was 1.5 % methanol in water. In samples where the guest was added neat to the host, the solution was mixed thoroughly to saturate the host solution with the guest molecule. ^{19}F guest binding

studies were carried out on a Bruker AVI 400 NMR spectrometer using CF_3COOH as an external reference for 0 ppm.

Determination of the number of bound water molecules (q) for EuL^1 and EuL^2. Based on the below equation by Parker *et al.*[1]

$$q^{Eu} = 1.2[\left(\frac{1}{\tau_{H2O}} - \frac{1}{\tau_{D2O}}\right) - (0.25 + 0.075n)]$$

where n = the number of -NH amide groups which are bound to Eu via oxygen; for both complexes, n = 2.

Table 1. Emission Lifetimes and *q* values for Eu**L**^{1} and Eu**L**^{2}

	τ_{H_2O} / ms	τ_{D_2O} / ms	$1/\tau_{H_2O}$ / ms^{-1}	$1/\tau_{D_2O}$ / ms^{-1}	*q*
Eu**L**^{1}	0.55	2.5	1.82	0.40	1.2
Eu**L**^{2}	0.51	2.2	1.96	0.45	1.3

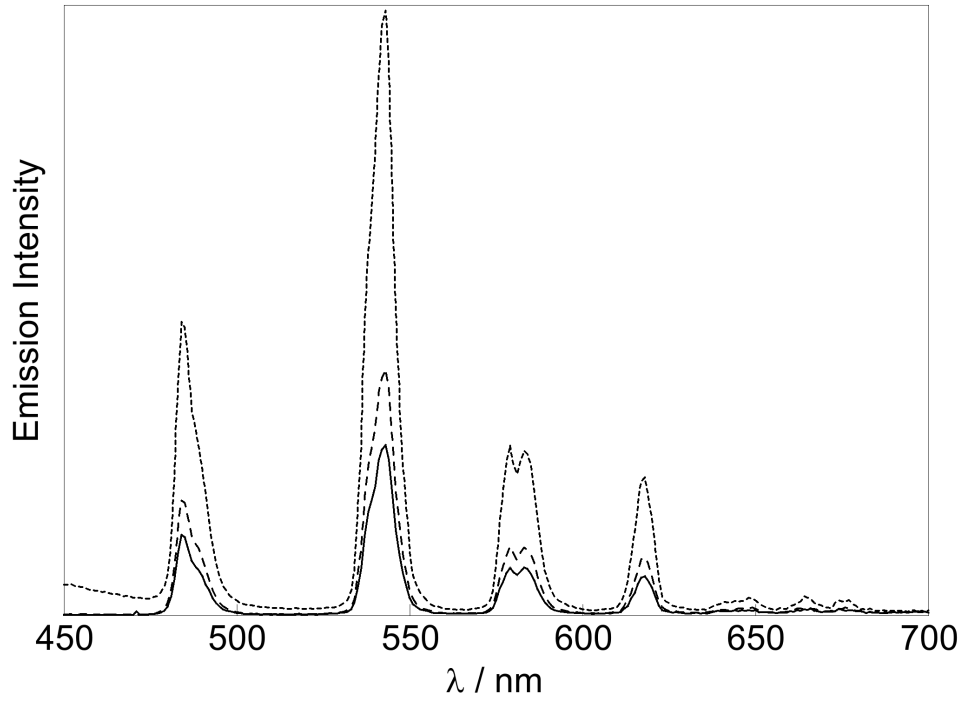


Figure S1. Emission spectra of [TbL^1] (4 x 10^{-5} mol dm^{-3}) in water alone (solid line), with excess toluene (dashed), and with 10 equivalents of phenol (dotted) (λ_{exc} = 270 nm).

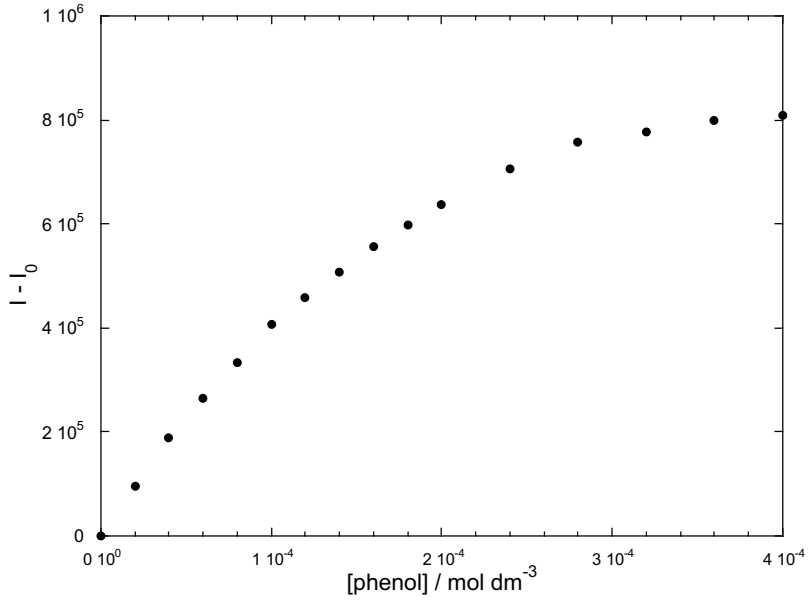


Figure S2. Emission intensities (λ_{exc} = 270 nm) of [Tb**L**^{1}] (4 x 10^{-5} mol dm^{-3}) in water upon addition of 1 – 10 equivalents of phenol.

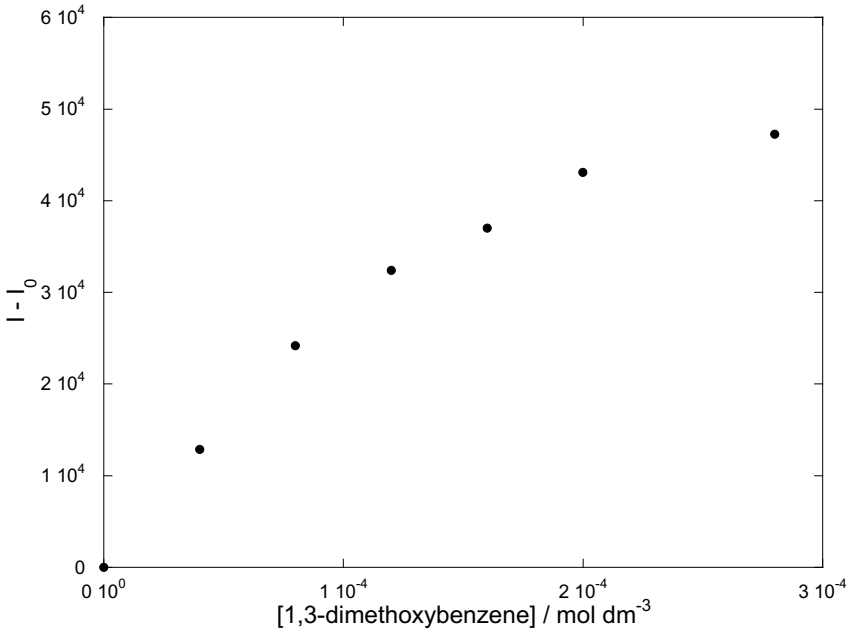


Figure S3. Emission intensities (λ_{exc} = 270 nm) of [Eu**L**^{1}] (4 x 10^{-5} mol dm^{-3}) in water upon titration of 1-10 equivalents of dimethoxybenzene.

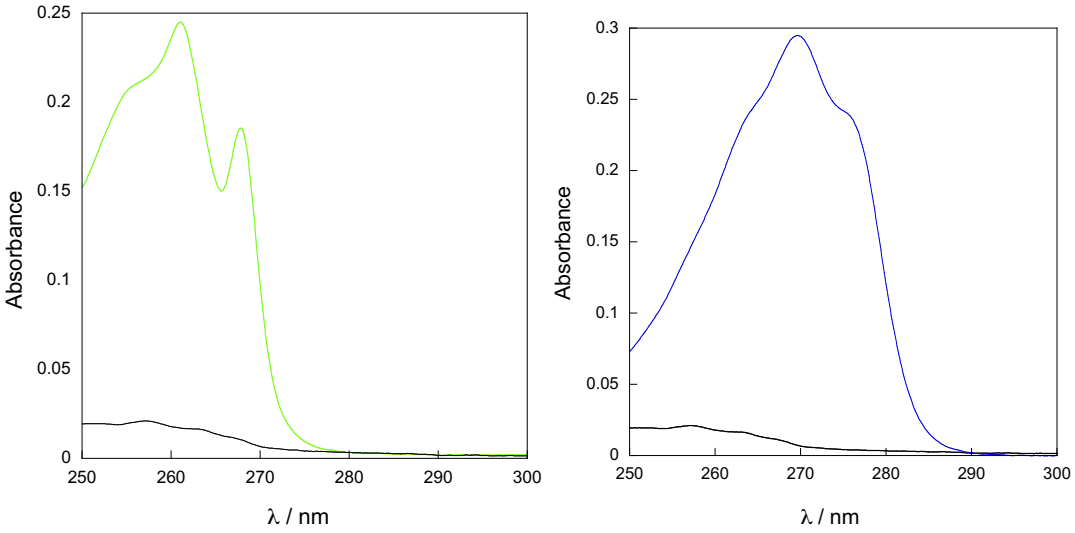


Figure S4. Absorption spectra of Eu**L**^{1} (black) upon addition of (a) toluene (green) and (b) phenol (blue).

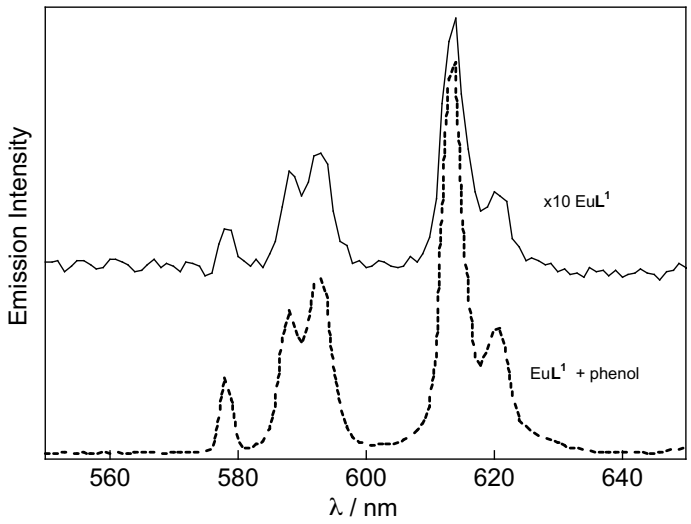


Figure S5. Expanded emission spectra showing the hypersensitive band for Eu**L**^{1} (4 x 10^{-5} mol dm^{-3}) in water upon addition of phenol (λ_{exc} = 270 nm).

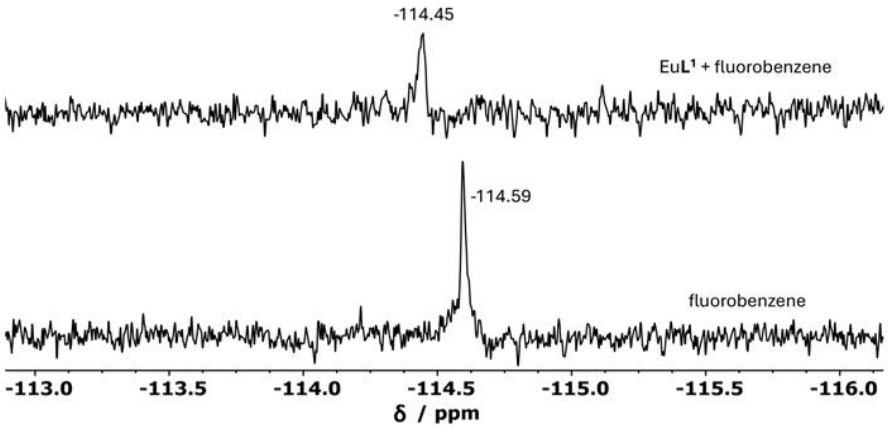


Figure S6. ^{19}F-NMR (D_2O) of Eu**L^1** with excess fluorobenzene (top) and fluorobenzene alone (bottom); external reference CF_3COOH.

Binding studies

For a 1:1 binding event, A + B $\rightleftharpoons$ AB the equation of the inclusion complexation is rearranged to:

$$K[A]_0[B]_0 - (K[A]_0[AB] - [K[B]_0[AB]\text{-}[AB]) + K[AB]^2 = 0$$

Considering $I_{obs} = I_A \frac{[A]_0 - [AB]}{[A]_0} + I_{AB} \frac{[AB]}{[A]_0}$

$$I_{obs} - I_A = \frac{\Delta I_{max}[AB]}{[A]_0}$$

Data are fitted to:

$$I_{obs} - I_A = \frac{\Delta I_{max}}{[A]_0}\left(\frac{1}{2}\left([A]_0 + [B]_0 + \frac{1}{k}\right) \pm \frac{1}{2}\sqrt{\left([A]_0 + [B]_0 + \frac{1}{k}\right)^2 - 4[A]_0[B]_0}\right)$$

Crystal structure determination

For the determination of X-ray crystal structures, intensity data were collected on a Nonius Kappa CCD diffractometer using Mo radiation. SHELXS was used for structure solution and SHELXL for refinement. Non-hydrogen atoms were refined anisotropically using the Rydberg model for hydrogen atoms. The structures have been deposited in the CSD with reference numbers Deposition Number 1031054-1031055.

Table 1. Crystal and structure refinement data.

Empirical formula	$C_{28}H_{40}EuN_5O_{11}$	$C_{58}H_{94}Eu_2N_{10}O_{31}$
Formula weight	774.61	1731.35
Temperature / K	296(2)	296(2)
Wavelength / Å	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic
Space group	P_2_1/a	C 2/c
a / Å	11.1136(11)	49.451(4)
b / Å	29.324(2)	13.7239(7)
c / Å	10.9950(10)	23.828(2)
a / °	90°.	90
b / °	117.575(3)	99.982(2)
g / °	90°.	90
Volume / $Å^3$	3176.2(5)	15926(2)
Z	4	8
Density (calculated) / Mg m^{-3}	1.620	1.444
Absorption coefficient/ mm^{-1}	2.041	1.644
F(000)	1576	7088
Crystal size / mm^3	0.220 x 0.201 x 0.200	0.500 x 0.200 x 0.200
Theta range for data collection / °	1.389 to 25.256	1.542 to 25.378
Reflections collected	19947	37050
Independent reflections	5735	14369
R(int)	0.0760	0.1120

Goodness-of-fit on F^2	1.054	1.066
R1 [I>2sigma(I)]	0.0449	0.0547
wR2 [I>2sigma(I)]	0.1084	0.1490
Largest diff. peak and hole / e.$Å^{-3}$	1.031 and -1.911	1.035 and -1.329

References

1. A. Beeby, I. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. de Sousa, J. A. Gareth Williams and M. Woods, *Journal of the Chemical Society, Perkin Transactions 2*, 1999, DOI: 10.1039/A808692C, 493-504.