Supplementary information

10-(4-aminobenzyl)-1,4,7,10-tetrazacyclododecane-1,4,7-triacetic acid 5: To a solution of tris tert butyl 1,4,7,10- tetrazacyclododecane-1,4,7-triacetate (1.5 g, 2.9×10^{-3} mol) in acetonitrile (30 cm³) under dinitrogen, was added an excess of NaHCO₃ (1.0g, 1.19×10^{-2} mol). 4-nitrobenzene bromide (0.626 g, 2.9×10^{-3} mol) was added to the mixture and the reaction heated to reflux for 24 h. The mixture was then cooled to room temperature, filtered and the solvent removed *in vacuo* yielding triester, 2, as a light yellow solid. The residue was purified using Al₂O₃ column chromatography eluting with dichloromethane/methanol (95:5) [ES⁺ MS: m/z 672 {M + Na}⁺, 649 {M}⁺; ¹H NMR: 1.3-1.5 (27H, m, tert-Bu), 2.1-2.9 (24H, m, NCH₂), 7.6 (2H, d, ArH, 9 Hz), 8.1 (2H, d, ArH, 9 Hz)]. Treatment of the purified nitrobenzyl ester (1.0 g, 1.54×10^{-3} mol) with H₂ (delivered via a balloon) in the presence of Pd/C for 24 h. in methanol (15 cm³) giving the corresponding aminobenzyl derivative as a yellow, oily solid. Finally, hydrolysis of the ester was achieved with trifluroacetic acid (10 cm³ in 10 cm³ CH₂Cl₂) for 24 h. The solvents were removed in situ leaving a residue which was subjected to repeated washings and evaporation of methanol $(3 \times 20 \text{ cm}^3)$ and dichloromethane $(3 \times 20 \text{ cm}^3)$. Dissolution of the residue with the minimum volume of methanol, followed by addition of diethyl ether, precipitated the hydrolysed ligand as a yellow solid which was washed with diethyl ether and dichloromethane (0.515 g, 74%). IR (solid) v_{max} 3344 (br), 3221, 3086, 2966, 2850, 1683, 1629, 1611, 1521, 1457, 1395, 1351, 1314, 1285, 1184, 1124, 1087, 1022 cm⁻¹. UV-vis (H₂O) λ_{max} = 285 sh (900), 243 (4200), 198 sh (21200) nm. AP⁺ CI MS (MeCN/MeOH): m/z 452 {M + H}⁺, 347 {M - CH₂(C₆H₄)NH₂}⁺; AP⁻ CI MS (MeCN/MeOH): m/z 450 {M - H}⁻, 345 {M - CH₂(C₆H₄)NH₂}⁻. ¹H NMR (400 MHz, D_2O , 300K) δ_H 2.8-3.4 (24H, m, NCH₂), 3.7 (2H, NH₂), 7.3 (2H, d, ArH, 9 Hz), 7.6 (2H, d, ArH, 8 Hz). ¹³C{¹H} NMR (400 MHz, D₂O, 300K) δ_{c} 42.7, 47.9, 48.3, 48.5, 49.2, 49.4, 50.7, 51.4, 51.9, 54.1, 56.1, 56.5, 56.8, (NCH₂), 116.7 (q, CF₃CO₂H), 123.5, 132.1, (Ar), 163.2 (q, CF₃CO₂H), 170.1 (br), 175.4 (CO). Found C, 42.78; H, 5.91; N, 11.05; calc. for C₂₁H₃₃N₅O₆.2.25 CF₃CO₂H: C, 43.25; H, 4.98; N, 9.89%.

Terbium complex of 10-(4-aminobenzyl)-1,4,7,10-tetrazacyclododecane-1,4,7triacetic acid, 6: The triacid 5 (0.1 g, 2.22×10^{-4} mol) and Tb(OTf)₃ (0.135 g, 2.22×10^{-4} mol) were dissolved in methanol (5 cm³). The reaction mixture was heated to 60°C and allowed to stir for 24 h. The solvent was then removed *in vacuo* and the residue redissolved with a minimum volume of methanol and a yellow solid precipitated with the addition of diethyl ether. Further reprecipitation was achieved from acetonitrile again using diethyl ether. The hygroscopic product was filtered, washed (diethyl ether) and isolated as a light beige powder (0.103 g, 76 %). IR (solid) v_{max} 2974, 2863, 1576 (br), 1443, 1396, 1302, 1209, 1156, 1085, 1031, 1004 cm⁻¹. UV-vis (H₂O) λ_{max} = 292 sh (530), 241 sh (1400), 199 (11000) nm. ES⁻ MS (MeCN): *m/z* 609{M}⁻¹. ¹H NMR (500 MHz, D₂O, 300K) δ_{H} -435, -412, -320, -280, -260, -210, -120, -110, -100, -95, -90, -75, -60, -20, 10, 25, 80, 125, 180, 215, 260, 310 (all br). Found H, 4.88; N, 12.16; calc. for C₂₁H₃₀N₅O₆Tb: H, 4.94; N, 11.53% [NOTE: carbon and metal analyses low indicative of incomplete combustion and metal carbide formation] **[Tb₂(L)], 7**: To a solution of **6** (0.05 g, 8.24×10^{-5} mol) in dimethylformamide (10 cm³) was added 0.5 equivalents of diethylenetriamine pentaacetic acid anhydride (0.015 g, 4.12×10^{-5} mol) and triethylamine (0.033 g, 3.3×10^{-4} mol). The reaction mixture was then heated to 60 °C for 24 h. The solution was cooled and filtered. The solvents were removed *in vacuo*, the residue redissolved in methanol (1 cm³) and then precipitated with diethyl ether. The light brown solid was filtered and washed with diethyl ether. The desired complex was isolated as a hygroscopic solid (0.068 g, 53 %). IR (solid) v_{max} 3381 (br), 2982, 2872, 1579 (br), 1441, 1389, 1319, 1248, 1223, 1085, 1029, 1003 cm⁻¹. UV-vis (H₂O) $\lambda_{max} = 332$ sh (1200), 285 sh (1300), 239 (4300), 196 (24400) nm. ES⁺ MS (MeCN/H₂O): m/z 1607 {M + 2H₂O}⁺. Found H, 5.62; N, 11.51; calc. for C₅₆H₈₁N₁₃O₂₀Tb₂: H, 5.16; N, 11.58%. [NOTE: see above]

[**Tb**₂(**L**)**Yb**], 1: The diterbium complex 7 (0.02 g, 1.27×10^{-5} mol) was dissolved in methanol (5 cm³) and one equivalent of Yb(OTf)₃ (0.008 g, 1.27×10^{-5} mol) added. The mixture was stirred and gently heated to 50°C for 24 h. Concentration of the reaction mixture to *ca*. 2 cm³ followed by addition of diethyl ether precipitated the desired complex as a light brown solid (0.018 g, 81%). IR (solid) v_{max} 2975, 2873, 1574 (br), 1449, 1411, 1320, 1254, 1230, 1085, 1026 cm⁻¹. UV-vis (H₂O) λ_{max} = 968 (90), 330 (900), 290 sh (1000), 238 sh (3400), 197 sh (18600) nm. MALDI TOF⁺ (dithranol): shows large fragments incorporating dtpa.

Luminescence measurements

Luminescence properties of the terbium complexes were determined using a PerkinElmer LS55 fluorimeter.

In the case of the ytterbium complex, the sample was excited using a pulsed nitrogen laser (PTI-3301, 337 nm) or a nitrogen pumped dye laser (PTI-330, 520 nm), operating at 10Hz. Light emitted at right angles to the excitation beam was focused onto the slits of a monochromator (PTI120), which was used to select the appropriate wavelength. The growth and decay of the luminescence at selected wavelengths was detected using a germanium photodiode (Edinburgh Instruments, EI-P) and recorded using a digital oscilloscope (Tektronix TDS220) before being transferred to a PC for analysis. Time resolved emission(TRES) spectra were obtained by measuring the growth and decay of the luminescence at each of a series of wavelengths. Luminescence lifetimes were obtained by iterative reconvolution of the detector response (obtained by using a scatterer) with exponential components for growth and decay of the metal centred luminescence, using a spreadsheet running in Microsoft Excel. The details of this approach have been discussed elsewhere (A. Beeby, A; Faulkner, S *Chem. Phys. Lett.* **1997**, *266*, 116). Fitting to a double exponential decay yielded no improvement in fit as judged by minimisation of residual squared and reduced chi squared.

Energy level diagram for Terbium and Ytterbium

Tb states above 5D4 are omitted for clarity and emissive states are shown in italic typeface

