

Supplementary Information

Exploring reversible energy transfer between pyrene complexes and europium ions- potential routes to oxygen sensors

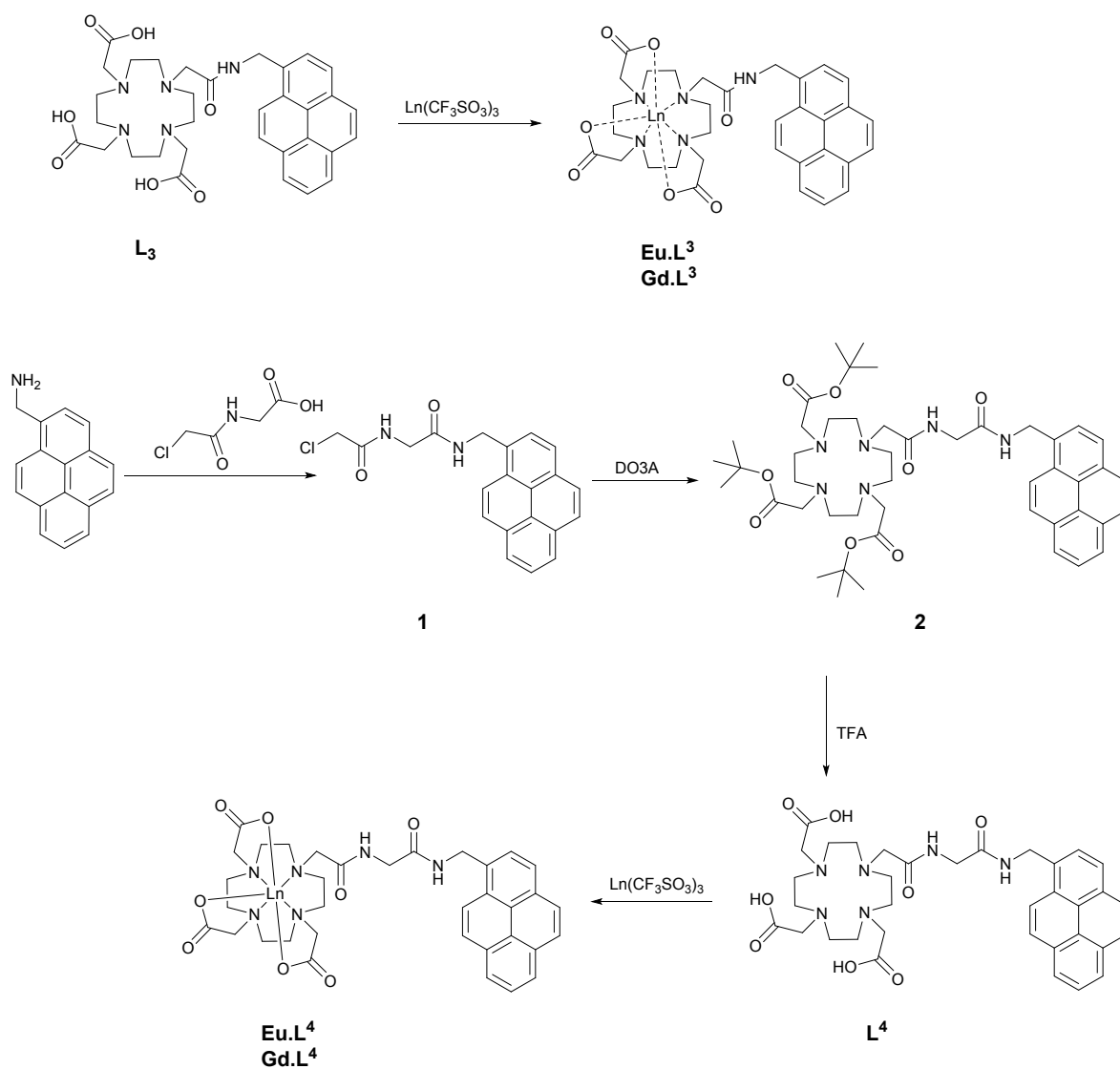
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1. General experimental details

Chemicals were obtained from Acros, Sigma Aldrich, Alfa Aesar, Apollo Scientific or Strem. All solvents used were HPLC grade. TLC, where applicable, was performed on pre-coated aluminium-backed plates (Merck Kieselgel) or and spots were made visible by quenching of UV fluorescence ($\lambda = 254$ nm) and/or by staining with potassium permanganate. Flash Chromatography was performed according to the method by Still, using silica gel (0.040-0.063 mm; Merck) and air pressure. Alumina chromatography was performed on pre-conditioned alumina (EtOAc) under gravity. NMR spectra were recorded on a Varian Mercury VX300 or a Bruker AVANCE AVC500 at frequencies of 300 MHz and 500 MHz for ^1H and 75.5 MHz 126 MHz for ^{13}C respectively, using residual solvent peaks as internal reference. Coupling constants for ^1H spectra have an uncertainty of ± 0.4 Hz. Nominal mass spectra (m/z) were recorded on a Micromass LCT Premier XE spectrometer, under the conditions of positive or negative electrospray ionization (ESI-MS). High resolution mass spectra (HRMS) were recorded under ESI conditions on a BrukerMicroTOF (resolution = 5000 FWHM). Melting points of precursors and ligands were recorded using a Griffin melting point apparatus and are uncorrected. The corresponding Eu- and Gd-analogues were found to undergo thermal decomposition. Luminescence spectra and lifetimes were recorded on a Perkin Elmer LS55 spectrometer: quantum yields were not recorded, as overlap with residual pyrene fluorescence made establishing them impossible with any degree of accuracy.

1,4,7-Tris(tert-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecane (DO3A), *N*-(1-Pyrenylmethyl)-2-chloroacetamide and **L**₃ were prepared as described in the literature.^{1, 2}

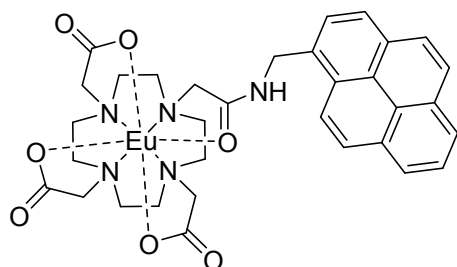
2. Synthetic Strategy



Scheme S1 Synthesis of **L**₃ and **L**₄ ligands and their complexes

3. Synthetic details

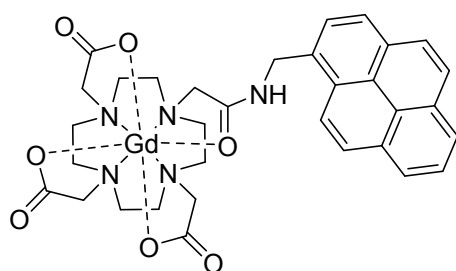
Eu.L³



Eu.L³ 1,4,7,10-Tetraazacyclododecane-10-(N-(1-pyrenyl)acetamide)-1,4,7-triacetic acid (L³) (100 mg, 0.137 mmol) was dissolved in methanol (5 mL). Europium trifluoromethanesulfonate (98 mg, 0.164 mmol) was added, and the solution was heated at 55°C for 48 h.

The hot solution was filtered through cotton wool and the solvent removed *in vacuo*. The residue was re-dissolved in the minimum volume of methanol, and precipitated by addition of diethyl ether. The precipitate was kept and dried *in vacuo*. It was then suspended in the minimum amount of water, sonicated and centrifuged. The supernatant was decanted and the solid was dried *in vacuo* to afford the product as an off-white solid (120 mg, 96 %). ¹H NMR (400 MHz, CD₃OD): δ 26.96, 25.53, 10.23, 9.67, 9.21, 8.27, 8.10, 7.56, 6.78, 6.49, -2.11, -3.11, -3.83, -5.25, -6.18, -6.98, -7.54, -9.32, -10.45, -11.26, -12.64 (only peaks outside the 0 to 5 ppm region were reported). HRMS (ESI⁺): (M+H)⁺ calcd for C₃₃H₃₇¹⁵¹EuN₅O₇⁺ 768.1900; found 768.1900; Elemental Analysis found C, 40.6; H, 4.1; N, 6.6. C₃₃H₃₆EuN₅O₇·3CF₃CO₂H·3H₂O requires C, 40.3; H, 3.9; N, 6.0.

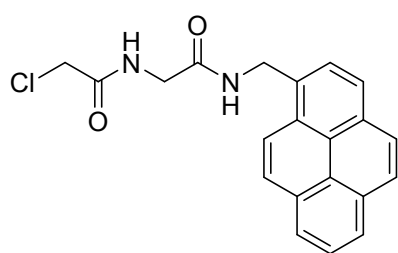
Gd.L³



Gd.L³ was synthesised in an analogous manner to **Eu.L³** using 1,4,7,10-Tetraazacyclododecane-10-(N-(1-pyrenyl)acetamide)-1,4,7-triacetic acid (L³) (50 mg, 0.068 mmol) and gadolinium trifluoromethanesulfonate (42 mg, 0.068 mmol) to afford **Gd.L³** as a light brown solid (38 mg, 72%). HRMS (ESI⁺): (M+H)⁺ calcd for

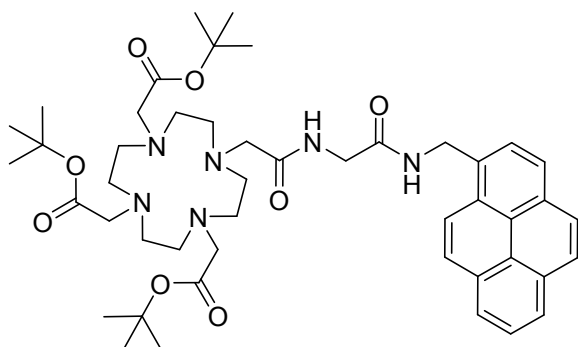
C₃₃H₃₇¹⁵⁸GdN₅O₇⁺ 773.1929; found 773.1934.

2-chloro-N-(2-oxo-2-((pyren-1-ylmethyl)amino)ethyl)acetamide 1



N-(Chloroacetyl)glycine (200 mg, 1.32 mmol), 1-pyrenemethylamine hydrochloride (388 mg, 1.45 mmol) and (Benzotriazol-1-yloxy)tris(dimethylamino)phosphonium hexafluorophosphate (642 mg, 1.42 mmol) were dissolved in the minimum amount of DMF. To this was added diisopropylethylamine (375 mg, 2.9 mmol) and the solution was stirred overnight at ambient temperature. H₂O was then added until formation of a white precipitate. The suspension was sonicated, the precipitate collected by filtration and washed with copious amounts of H₂O, dried, washed with cold Et₂O and dried *in vacuo* to afford the product as an off-white solid (406 mg, 84%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.67 (1H, t, *J* = 5.0 Hz, NHCH₂py), 8.52 (1H, t, *J* = 5.0 Hz, NHCH₂CO), 8.40-8.38 (1H, m, pyH), 8.33-8.24 (4H, m, pyH), 8.19-8.14 (2H, m, pyH), 8.10-8.02 (2H, m, pyH), 5.04 (2H, d, *J* = 5.0 Hz, NHCH₂py), 4.16 (2H, s, CH₂Cl), 3.85 (2H, d, *J* = 5.0 Hz, NHCH₂CO); ¹³C NMR (125.8 MHz, DMSO-*d*₆): δ 168.3, 166.3, 130.8, 130.3, 130.0, 128.0, 127.6, 127.4, 127.0, 126.4, 126.2, 125.2, 125.1, 124.7, 124.0, 123.9, 123.1, 42.6, 42.4, 40.4, 39.5; m.p. 179-182°C; HRMS (ESI⁺): (M+Na)⁺ calcd for C₂₁H₁₇ClN₂NaO₂⁺ 387.0871; found 387.0868.

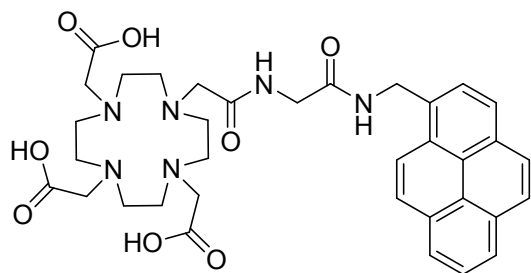
1,4,7-Tris(tert-butyloxycarbonylmethyl)-1,4,7,10-tetraazacyclododecane-10-(N-(2-oxo-2-((pyren-1-ylmethyl)amino)ethyl)acetamide) (2)



DO3A (204 mg, 0.34 mmol), and 2-chloro-N-(2-oxo-2-((pyren-1-ylmethyl)amino)ethyl)acetamide (150 mg, 0.41 mmol) were dissolved in anhydrous CH₃CN (25 mL). K₂CO₃ (95 mg, 0.69 mmol) was added and the solution was heated under reflux for 24 h. The reaction mixture was allowed to cool, filtered to remove the solids and the filtrate was evaporated *in vacuo*. Chromatography on alumina (gradient elution 0% MeOH-10% MeOH in DCM) afforded the product as a light brown solid (220 mg, 76%). ¹H NMR (400 MHz, CDCl₃): δ 9.18 (1H, t, *J* = 6.5 Hz, NHCH₂py), 8.70 (1H, d, *J* = 5.0 Hz, NHCH₂CO), 8.63-8.61 (1H, m, pyH), 8.17-8.06 (5H, m, pyH), 8.00-7.94 (3H, m, pyH), 5.23 (2H, m, NHCH₂py), 5.30-1.46 (28H, m, CH₂) 1.45-1.36 (27H, m, CCH₃); ¹³C NMR (125.8 MHz, CDCl₃): δ 172.10, 172.09, 170.5, 169.9, 133.2, 131.1, 130.9, 130.5,

128.6, 128.0, 127.9, 127.5, 126.8, 125.7, 125.0, 124.9, 124.7, 124.0, 81.8, 55.6, 55.3, 53.4, 43.6, 40.8, 28.1, 27.8; m.p. 141-143°C HRMS (ESI⁺): (M+Na)⁺ calcd for C₄₇H₆₆N₆NaO₈⁺ 865.4834; found 865.4843.

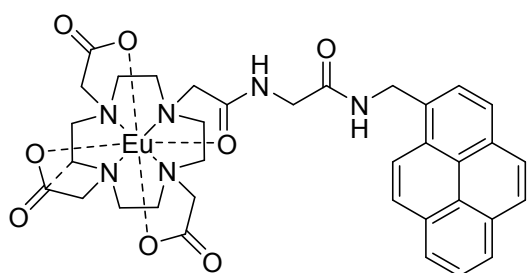
1,4,7,10-Tetraazacyclododecane-10--(N-(2-oxo-2-((pyren-1-ylmethyl)amino)ethyl)acetamide)-1,4,7-triacetic acid **L₄**



2 (250 mg) was dissolved in dichloromethane (5 mL) and trifluoroacetic acid (3 mL) was added dropwise. The solution was stirred at ambient temperature for 24 h. The solvent was removed *in vacuo*, the residue was resuspended in diethyl ether (5 mL) twice followed by removal of the

solvent *in vacuo*. The product was again suspended in diethyl ether, filtered, and dried *in vacuo* to afford **L₄** as a beige solid (190 mg, 95%). ¹H NMR (400 MHz, CD₃OD): δ 8.35-8.32 (1H, m, pyH), 8.22-8.15 (4H, m, pyH), 8.06-8.00 (4H, m, pyH), 4.07-3.03 (28H, m, CH₂); ¹³C NMR (125.8 MHz, CDCl₃): δ 163.5, 163.2, 162.9, 162.7, 133.2, 132.8, 132.3, 129.9, 128.7, 128.4, 127.6, 127.4, 126.5, 126.4, 126.2, 126.1, 126.0, m.p. 192-193°C, HRMS (ESI⁺): (M+Na)⁺ calcd for C₃₅H₄₃N₆O₈⁺ 675.3137; found 675.3122. Elemental Analysis found C, 46.6; H, 4.9; N, 8.1. C₃₅H₄₂N₆O₈·3CF₃CO₂H·3H₂O requires C, 46.8; H, 4.7; N, 8.0.

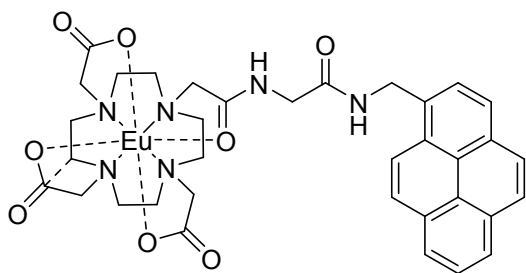
Eu.L₄



Eu.L₄ was synthesised in an analogous manner to **Eu.L₃** using 1,4,7,10-Tetraazacyclododecane-10-(N-(2-oxo-2-((pyren-1-ylmethyl)amino)ethyl)acetamide)-1,4,7-triacetic acid (**L₄**) (100 mg, 0.13 mmol) and europium trifluoromethanesulfonate (76 mg, 0.13 mmol) to afford **Eu.L₄** as an off-

white solid (86 mg, 78%). ¹H NMR (400 MHz, CD₃OD): δ 29.89, 29.45, 28.21, 8.26, 8.08, 7.65, 7.50, 4.04, 3.78, 2.04, 1.59, 1.18, -0.48, -0.98, -2.44, -4.10, 06.70, -7.30, -7.80, -9.09, -10.06, -10.56; HRMS (ESI⁺): (M+Na)⁺ calcd for C₃₅H₃₉¹⁵¹EuN₆NaO₈⁺ 847.1937; found 847.1958.

Gd.L₄



Gd.L₄ was synthesised in an analogous manner to **Eu.L₄** using 1,4,7,10-Tetraazacyclododecane-10-(N-(2-oxo-2-((pyren-1-ylmethyl)amino)ethylacetamide)-1,4,7-triacetic acid (L₄) (40 mg, 0.05 mmol) and gadolinium trifluoromethanesulfonate (31 mg, 0.05 mmol) to afford **Gd.L₄** as a light

brown solid (35 mg, 84%). HRMS (ESI⁺): (M+H)⁺ calcd for C₃₅H₄₀¹⁵⁸GdN₆O₈⁺ 830.2143; found 830.2141.

4. ^1H -NMR spectra of Eu.L₃ and Eu.L₄

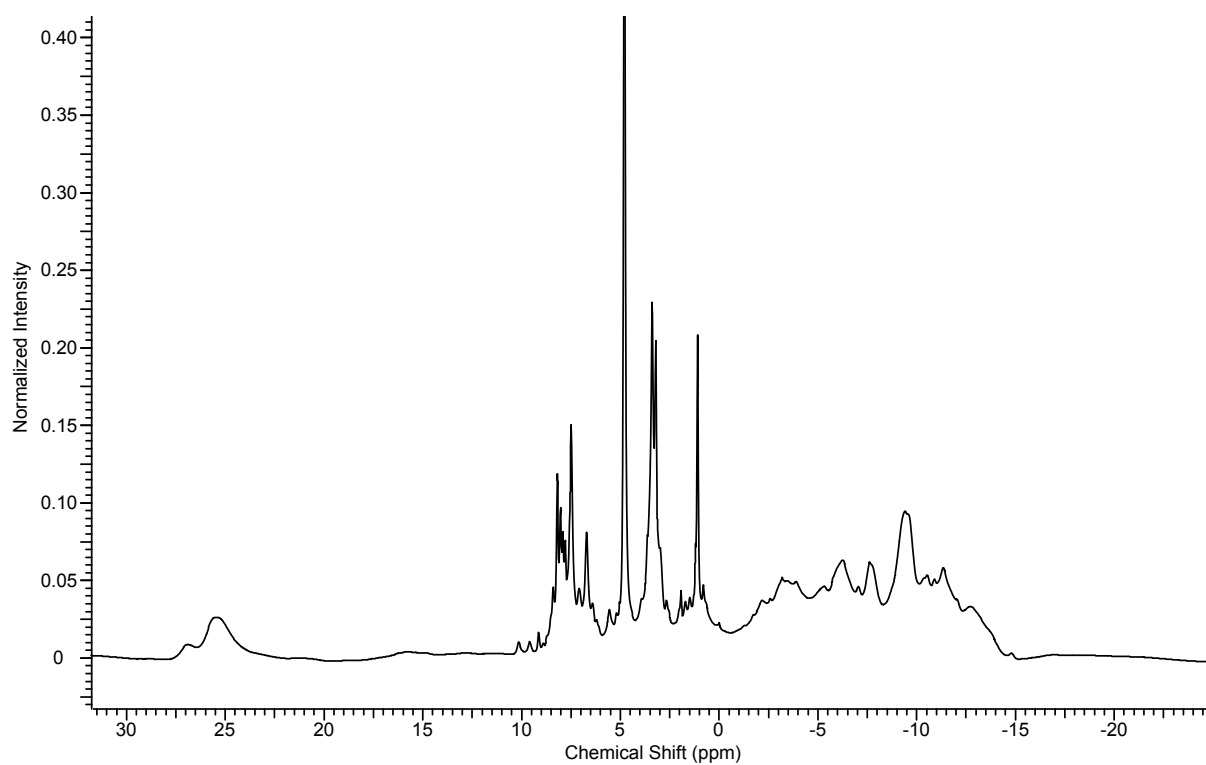


Figure S1 ^1H NMR spectrum of Eu.L₃ in MeOD recorded at 400 MHz

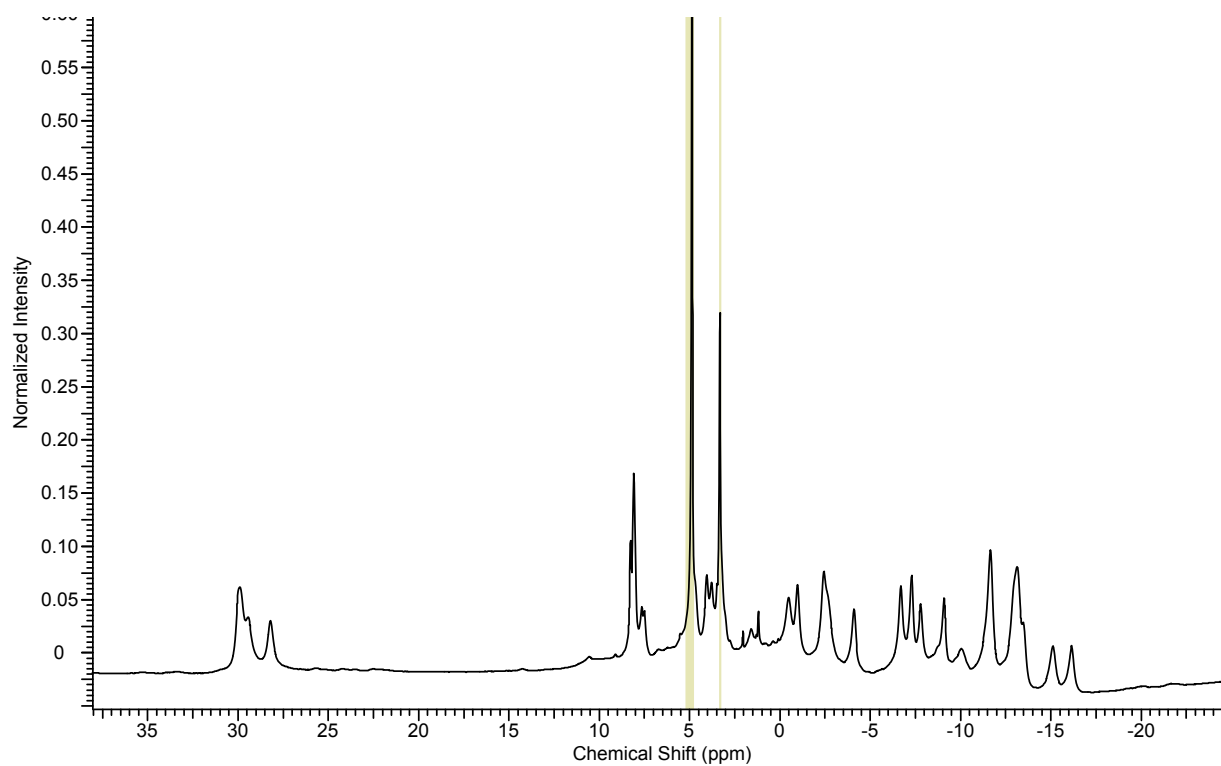


Figure S2 ^1H NMR spectrum of Eu.L₄ in MeOD recorded at 400 MHz

5. Photophysical measurements

UV visible spectroscopy was performed using a PG instruments T60 UV/Vis spectrophotometer.

Steady-state luminescence properties were determined on a Perkin Elmer LS55 fluorimeter operating in phosphorescence mode. For all measurements, both the excitation and emission slit width was 10 nm.

Aerated and degassed luminescence lifetimes of the europium complexes were measured on a Horiba Jobin Yvon FluoroLog-3 (equipped with a Hamamatsu R928 detector and a double-grating emission monochromator) using the 616 nm emission and obtained by tail fitting, using the Fluorescence™ software.

For measurements under anoxic conditions, solutions (2 mL) were degassed (using a degassing cuvette) by five consecutive freeze-pump-thaw cycles and back-filled with N₂ gas.

Lifetimes of the pyrene based fluorescence were determined by time-correlated single-photon counting using an Edinburgh instruments mini- τ EPL 405 diode laser coupled to a Hamamatsu R928 detector and detecting at 450 nm, using tail-fitting on the T900 software.

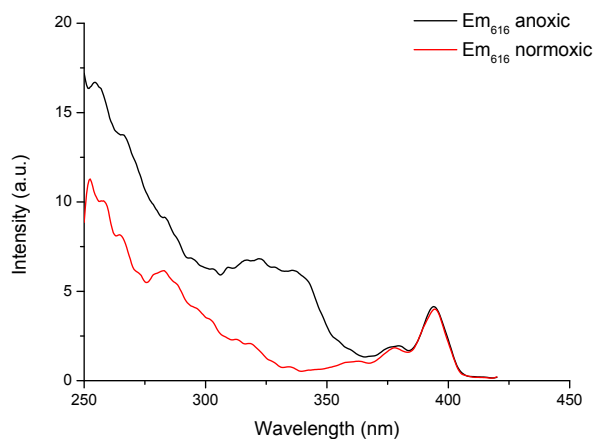


Figure S3 Excitation spectrum of the EuL¹-L² ternary complex

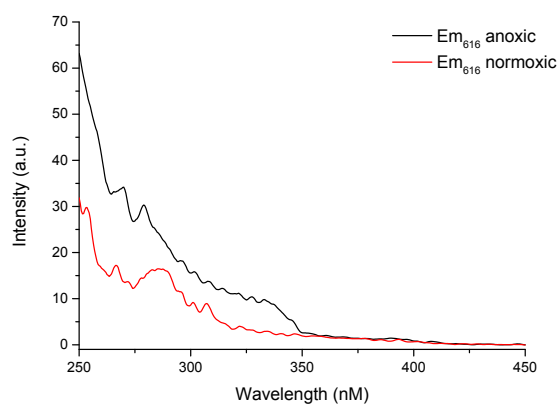


Figure S4 Excitation spectrum of EuL^3

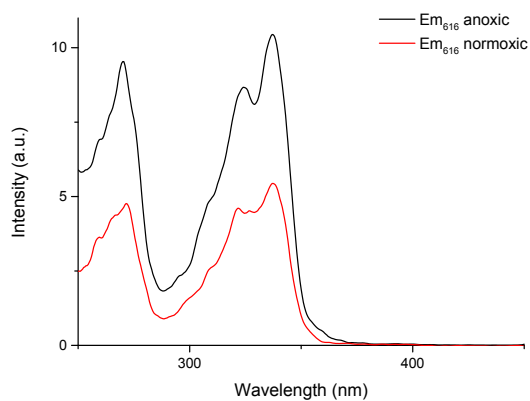


Figure S5 Excitation spectrum of EuL^4

References

1. A. Dadabhoj, S. Faulkner and P. G. Sammes, *Journal of the Chemical Society, Perkin Transactions 2*, 2002, 348-357.
2. S. Faulkner, M.-C. Carrie, S. J. A. Pope, J. Squire, A. Beeby and P. G. Sammes, *Dalton Transactions*, 2004, 1405-1409.