Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis, stereocontrol and structural studies of highly luminescent chiral tris-amidepyridyl-triazacyclononane lanthanide complexes †

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1. Experimental

General procedures and instrumentation

Commercially available reagents were used as received from suppliers. Solvents were laboratory grade and dried using an appropriate drying agent when required. Reactions requiring anhydrous conditions were carried out under an atmosphere of dry argon.

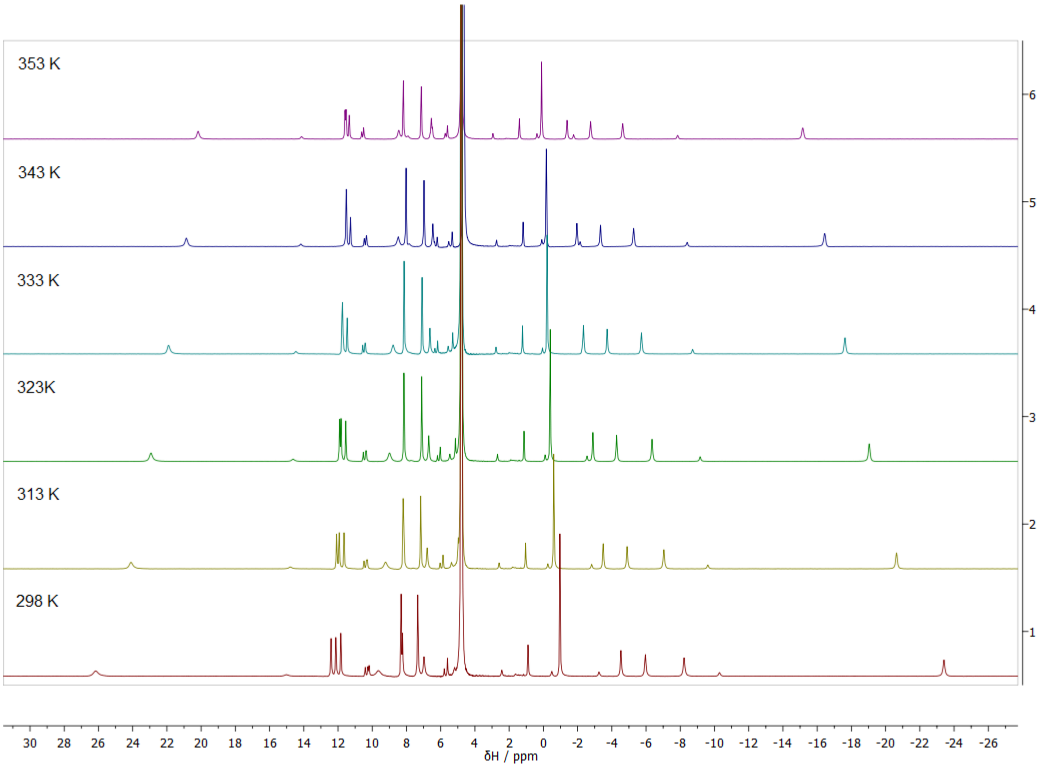
^{1}H and ^{13}C NMR spectra were recorded on spectrometers operating at magnetic inductions corresponding to ^{1}H frequencies at 200, 400, 500, 600 and 700 MHz. Spectra were recorded at 295 K in commercially available deuteriated solvents. ESMS was carried out on a TQD mass spectrometer, and accurate masses were recorded on either a LCT Premier or Thermo Finnigan LTQ-FT.

Reverse phase HPLC purification was performed at 295 K on either a Waters or Perkin Elmer system. The Waters system consisted of a Waters 575 pump, Waters “System Fluidics Organizer”, Waters 2545 “Binary Gradient Module”, Waters 2767 “Sample Manager”, Waters Fraction Collector III, Waters 2998 Photodiode Array Detector and Waters 3100 Mass Detector. The Perkin Elmer system consisted of a Perkin Elmer Series 200 pump, Perkin Elmer Series 200 auto-sampler and Perkin Elmer Series 200 UV/Vis detector. XBridge C18 columns were used with a flow rate of 1 mL/min (analytical) or 4.4 mL/min (semi-prep) or 17 mL/min (prep). Solvent systems of H_2O / CH_3OH with 0.1 % HCOOH (gradient elution) were used. Chiral HPLC was performed on the Perkin Elmer system described above using analytical (4.0 mm × 250 mm) and semi-prep (10 mm × 250 mm) CHIRALPAK-IC or ID columns. An isocratic solvent system of CH_3OH was used in all cases.

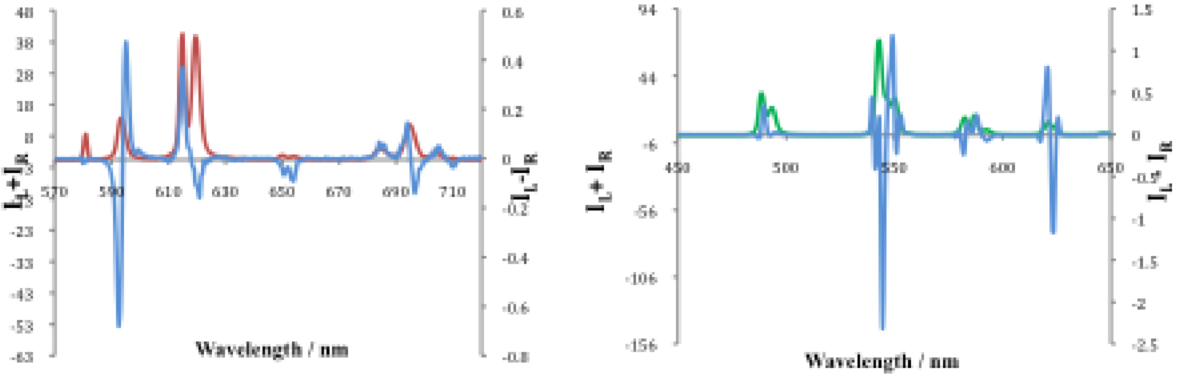
Optical spectroscopy

All samples were contained within quartz cuvettes with a path length of 1 cm and a polished base. Measurements were recorded at 295 K. Absorbance spectra were measured on a Perkin Elmer Lambda 900 UV/Vis/NIR spectrometer using FL Winlab software. Emission spectra were recorded on an ISA Jobin-Yvon Spex-Fluorolog-3 luminescence spectrometer. Lifetime measurements were carried out using a Perkin-Elmer LS55 spectrometer using FL Winlab software. The inner sphere hydration number (q) for europium and terbium complexes was obtained by measuring the excited state lifetime in H_2O and D_2O. The q values were calculated using the equations reported originally by Clarkson.[26]

CPL spectra were recorded on a custom built spectrometer consisting of a laser driven light source (Energetiq EQ-99 LDLS, spectral range 170 to 2100 nm) coupled to an Acton SP2150 monochromator (600 g/nm, 300 nm Blaze) that allows excitation wavelengths to be selected with a 6 nm FWHM band-pass. The collection of the emitted light was facilitated (90 º angle set up, 1 cm path length quartz cuvette) by a Lock-In Amplifier (Hinds Instruments Signaloc 2100) and Photoelastic Modulator (Hinds Instruments PEM-90). The differentiated light was focused onto an Acton SP2150 monochromator (1200 g/nm, 500 nm Blaze) equipped with a high sensitivity cooled Photo Multiplier Tube (Hamamatsu 7155-01 red corrected). Spectra were recorded using a 5 spectral average sequence in the range of 570-720 nm with 0.5 nm spectral intervals and 500 μs integration time. The recorded CPL spectrum underwent a 25% Fourier transformation smoothening protocol using Origin 8.0 Software (Origin Labs) to enhance appearance (all calculations were carried out using raw spectral data).

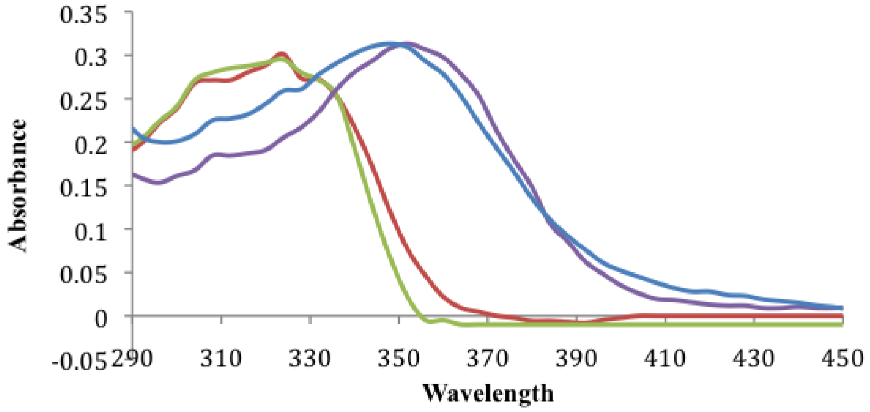


ESI Figure 1 Variable temperature ^{1}H NMR spectra of *S*-[YbL^1]$^{3+}$ (D_2O, 600 MHz).



ESI Figure 2 *Left*: Emission (red) and CPL (blue) spectra of *S*-[EuL^1](OTf)$_3$ (H_2O, pH 5, 295 K, λ_{exc} = 280 nm).

Right: Emission (green) and CPL (blue) spectra of *S*-[TbL^1](OTf)$_3$ (H_2O, pH 5 295 K, λ_{exc} = 280 nm).



ESI Figure 3 UV-absorption spectra of *S*-$[EuL^{2a}]^{3+}$ (red), *S*-$[EuL^{2b}]^{3+}$ (green), *S*-$[EuL^{2c}]^{3+}$ (purple), *S*-$[EuL^{2d}]^{3+}$ (blue), (H_2O, pH 5, 295 K).