Supplementary Information

Controllable three-component luminescence from a 1,8-naphthalimide / Eu(III) complex: white light emission from a single molecule

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Part 1: Experimental Details

Part 2: Additional figures

Fig. S1. UV/Vis absorption spectra of H3L (blue), GdL (black) and EuL (red) in MeCN.

Fig. S2. ^{1}H NMR spectra of H_3L in D_2O (red) and MeCN (black) illustrating the broadening due to aggregation in the latter case.

Fig. S3. UV/Vis Transient absorption spectrum of EuL in MeCN.

Fig. S4. Time-resolved emission of Eu(III) at 615 nm in EuL (in degassed MeCN) following excitation of the naphthalimide unit.

Fig. S5. Normalised emission spectra (taken from Fig. 4 in main text) of thin films of H_3L (black) and GdL (blue) showing the relatively reduced red component in the emission of solid GdL.

Part 1: Experimental Details

Instrumentation

UV/Vis absorption spectra were measured on a Varian Cary 50 Bio spectrophotometer; luminescence spectra were measured on a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer. CIE coordinates were calculated using the CIE (1964) 10-degree color matching functions[1] generously provided by Prof. J. Gareth Williams of the University of Durham. NMR spectra were measured on a Bruker Avance I or a Bruker Avance III 400 MHz spectrometer. Mass spectra and elemental analysis samples were analyzed by the Department of Chemistry's Centre for Chemical Instrumentation and Analytical Services.

Time-resolved measurements

Flash photolysis experiments were performed on a home-built setup. The samples were excited at 355 nm with the third harmonic (355 nm) of a Q-switched Nd:YAG laser LS-2137U (LOTIS TII). The energy of excitation pulses delivered to the sample were between 2.0 – 2.5 mJ at a 10 Hz repetition rate and a 7 ns pulse width. The probe light source was a 150 W Xe arc lamp (Hamamatsu). The probe light was detected through a SPEX MiniMate monochromator by a custom-built detector unit based on a FEU-118 PMT. Detector current output was coupled into a Tektronix TDS 3032B digital oscilloscope and subsequently transferred to a computer.

Time-resolved emission measurements were completed on either the flash photolysis setup (with the only difference being that the probe lamp was blocked), or an Edinburgh Instruments mini-Tau fitted with a 272.4 nm pulsed LED picosecond laser as excitation source and a Hamamatsu H5773-03 PMT detector, utilizing the time correlated single photon counting (TCSPC) technique.

Flash photolysis and time-resolved emission experiments denoted as 'degassed' were deoxygenated by by the freeze-pump-thaw technique and the saturated with argon. Flash photolysis experiments noted as 'bubble degassed' utilized a flow system that was continuously bubbled with nitrogen starting a minimum of 20 minutes before the start of the experiment. All samples were measured in a quartz cell with a path length of 10 mm.

The analysis of data from the home-built setup was performed using Igor Pro software (WaveMetrics, Inc.). The decay kinetics were fitted to the exponential decay law using least-squares algorithm built-in into Igor Pro. Global fitting was applied to analyze simultaneously decay kinetics obtained for numerous spectral points for the transient absorbance spectra which enabled us to reconstruct the shape of transient spectra and considerably increased reliability of the lifetime values. TCSPC data on the mini-Tau was analyzed with the provided T900 software to extract luminescenve decay lifetimes.

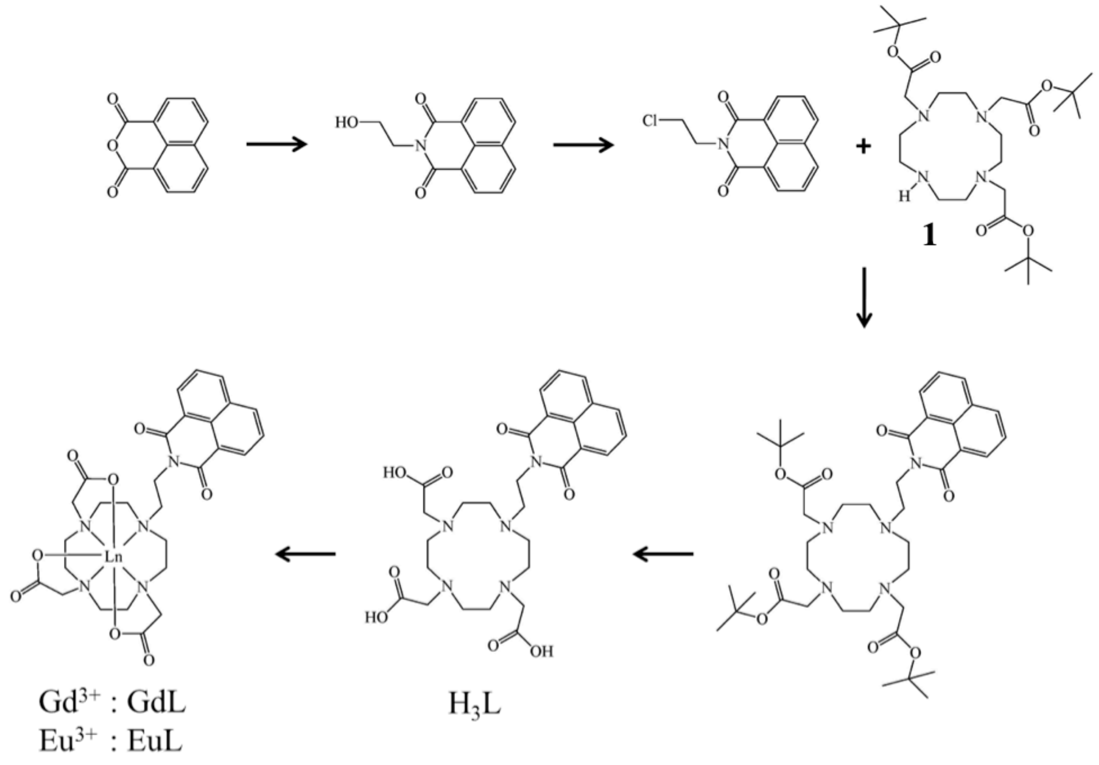
Materials

Commercially available compounds were obtained from either Sigma Aldrich, Fisher Scientific or VWR with the exception of 1,4,7,10-tetraazacyclododecane which was purchased from Strem Chemicals, Inc. Solvents denoted as 'dry' were obtained from a Grubbs solvent purification system.

1,4,7-Tris(*tert*-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecane (**1**, as its hydrobromide salt) was synthesized according to the method of Sammes and coworkers.[2]

Syntheses

The synthesis is summarized in the Scheme below.



N-(2-ethoxy)-1,8-naphthalimide

Ethanolamine (4.6 cm^3, 76.2 mmol) was added to a suspension of 1,8-naphthalic anhydride (5.0 g, 25.2 mmol) in *i*-propanol (300 cm^3). The suspension was refluxed for 5.5 hrs, cooled to 0 ^{o}C overnight and filtered to yield a light brown solid. The filter cake was washed with *i*-propanol (3 x 50 cm^3) and subsequently dried. Yield: 91 %. ^{1}H NMR ($CDCl_3$) in ppm: δ 3.49 (s, 1H), 4.00 (t, 2H), 4.48 (t, 2H), 7.78 (dd, 2H), 8.25 (dd, 2H), 8.63 (dd, 2H). ESI-MS: 242.08 (M + H)$^+$.

N-(2-chloroethyl)-1,8-naphthalimide

N-(2-ethoxy)-1,8-naphthalimide (1 g, 4.14 mmol) and thionyl chloride (0.33 cm^3, 4.55 mmol) were combined in chloroform (20 cm^3). The mixture was refluxed for 2.5 hrs, cooled, and purified by column chromatography on silica with CH_2Cl_2 as the eluent to afford the product as a white solid (83 %). ^{1}H NMR ($CDCl_3$) in ppm: 3.85 (t, 2H), 4.58 (t, 2H), 7.78 (t, 2H), 8.24 (d, 2H), 8.63 (d, 2H). ESI-MS:

260.0487 (*M* + H)$^+$. Elemental analysis: calc'd for $C_{14}H_{10}NO_2Cl$•0.1$CHCl_3$: C, 62.7; H, 3.5; N, 5.2%. Found: C, 62.4; H, 3.7; N, 5.2.

(N-{2-[4,7,10-Tris(carboxymethyl)-1,4,7,10-tetraazacyclododecan-1-yl]ethyl}-1,8-naphthalimide) (H_3L)

A mixture of 4,7,10-tris(^{t}Bu-carboxymethyl)-1,4,7,10-tetraazacyclododecane (compound **1** in the scheme; 1.505 g, 2.9 mmol) and cesium carbonate (1.890 g, 5.8 mmol) in acetonitrile (75 cm^3) was stirred under N_2 at 50°C for 30 minutes. Subsequently, *N*-(2-chloroethyl)-1,8-naphthalimide (0.939 g, 3.6 mmol) was added and the reaction was refluxed overnight under N_2. The reaction mixture was cooled, filtered and then evaporated to dryness. The resulting residue was dissolved in CH_2Cl_2 (20 cm^3) to which trifluoroacetic acid (20 cm^3) was added; the mixture was stirred for 48 hours. The solution was evaporated under reduced pressure and the residue was washed with CH_2Cl_2 and methanol. The residue was then purified by preparative HPLC on a reverse-phase C_8-silica column by isocratic elution with 35 % MeCN/H_2O for 3 minutes (the product eluted between 1.58 and 2.18 minutes). The product was precipitated from MeCN solution by addition of ether to yield the product as a white solid in 10% yield. ^{1}H NMR (MeCN-d_3 + 2 drops D_2O) in ppm: δ 2.99 – 3.73 (m, 24 H), 4.37 (t, 2H), 7.81 (t, 2H), 8.35 (d, 2H), 8.54 (d, 2H). ESI-MS: 570 (*M* + H)$^+$. Elemental analysis: calc'd for $C_{28}H_{35}N_5O_8$•1.5CF_3CO_2H• 0.5H_2O: C, 49.3; H, 5.4; N, 9.8%. Found: C, 49.7; H, 5.0; N, 9.3%.

EuL and GdL

A mixture of H_3L (0.1 g, 0.15 mmol) and europium(III) triflate (0.1 g, 0.17 mmol) in methanol was heated at 50 °C for 48 hrs. The solvent was then removed under reduced pressure and the residue purified by size-exclusion chromatography on Sephadex LH20 with methanol as the eluent. A white solid was obtained by precipitation with ether (60 %). ESI-MS: 720.1607 (*M* + H)$^+$. Elemental analysis: calc'd for $C_{28}H_{35}N_5O_8Eu$•1.25CF_3CO_2H•2.75H_2O: C, 40.1; H, 4.3; N, 8.0%. Found: C, 40.2; H, 4.3; N, 7.7.

GdL was synthesized and purified in exactly the same way from H_3L (0.1 g, 0.15 mmol) and gadolinium(III) triflate (0.1 g, 0.17 mmol). ESI-MS: 725.2 (*M* + H)$^+$. Elemental analysis: calc'd for $C_{28}H_{35}N_5O_8Gd$•2CF_3CO_2H•5.5H_2O: C, 36.3; H, 4.1; N, 7.1%. Found: C, 36.6; H, 4.3; N, 6.7%.

References

1. CIE Proceedings (1964) Vienna Session, **1963**, Vol. B, pp. 209-220 (Committee Report E-1.4.1), Bureau Central de la CIE, Paris

2. A. Dadabhoy, S. Faulkner and P. G. Sammes, *J. Chem. Soc., Perkin Trans. 2*, 2002, 348.

3. M. Placidi, A. J. L. Villaraza, L. S. Natrajan, D. Sykes, A. M. Kenwright and S. Faulkner, *J. Am. Chem. Soc.*, 2009, **131**, 9916.

Part 2: Additional figures

Fig. S1. UV/Vis absorption spectra of H3L (blue), GdL (black) and EuL (red) in water.

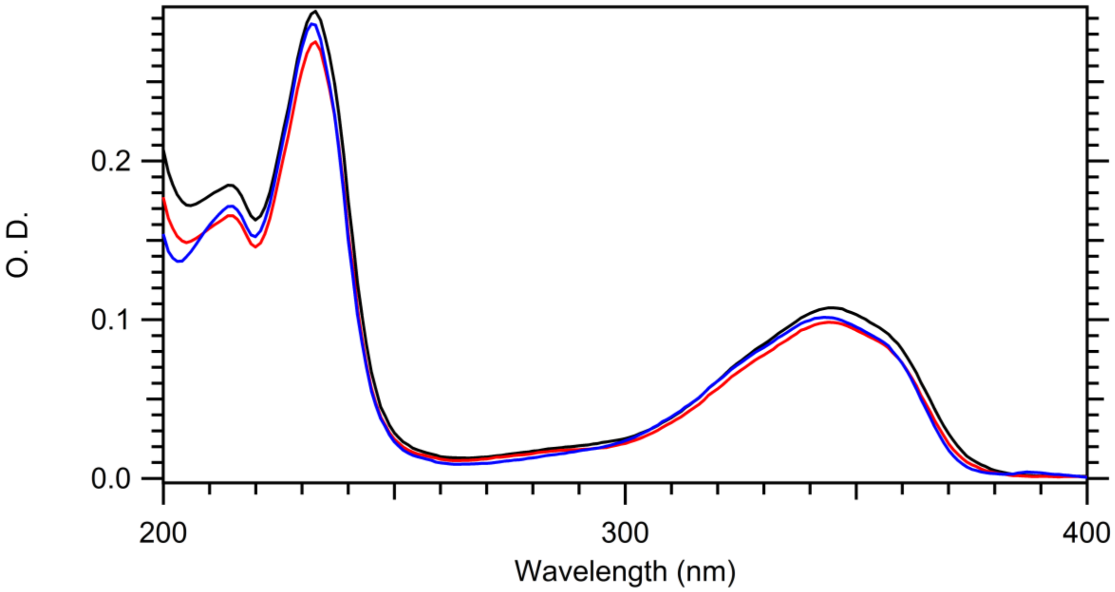


Fig. S2. ^{1}H NMR spectra of H_3L in D_2O (red) and MeCN (black) illustrating the broadening due to aggregation in the latter case.

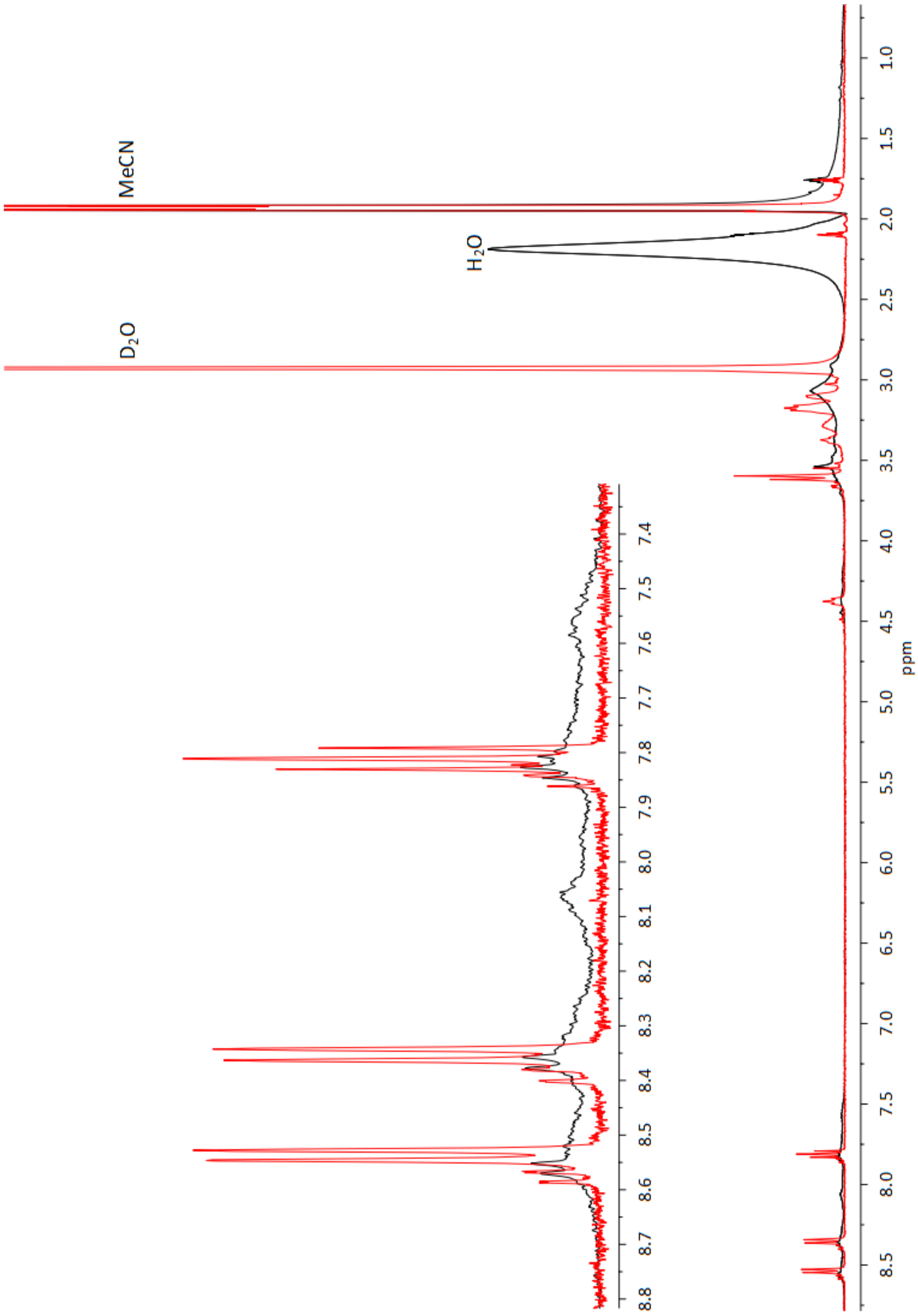


Fig. S3. UV/Vis Transient absorption spectrum of EuL in MeCN. The transient absorption spectrum was calculated using global fitting of multiple wavelength decays.

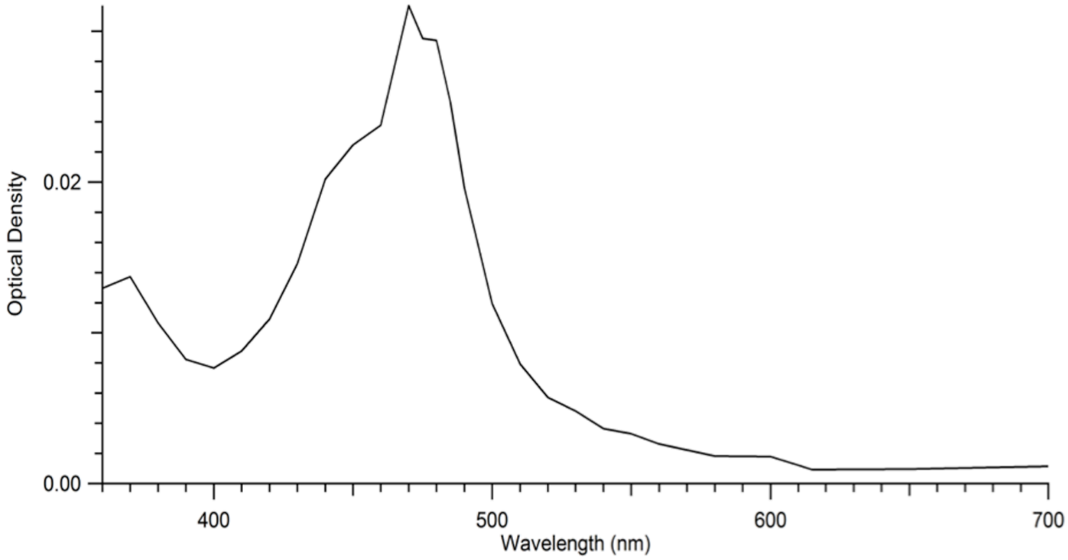


Fig. S4. Time-resolved emission of Eu(III) at 615 nm in EuL (in degassed MeCN) following excitation of the naphthalimide unit at 355 nm. Note the grow-in at early times (τ = 14 µs) arising from naphthalimide→Eu(III) energy-transfer. The red line shows the best fit of the observed data to two lifetime components (grow-in of 14 µs and decay of 1.1 ms; see main text); the bottom panel shows the residuals arising from this fit.

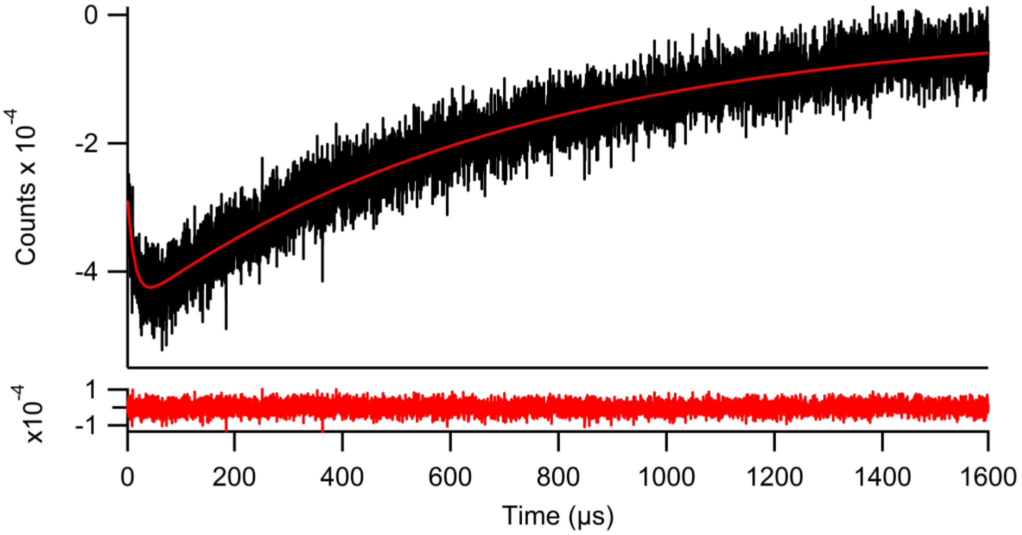


Fig. S5. Normalised emission spectra (taken from Fig. 4 in main text) of thin films of H_3L (black) and GdL (blue) showing the relatively reduced red component in the emission of solid GdL.