

Supporting Information

Polymetallic Lanthanide Complexes with PAMAM-Naphthalimide Dendritic Ligands: Luminescent Lanthanide Complexes Formed in Solution

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Experimental Section

The PAMAM generation 3 dendrimer containing 32 end branches terminated by primary amines (PAMAM dendrimer G(3)-NH₂) dissolved in anhydrous methanol (26.03% by weight) and 2,3-naphthalic anhydride were purchased from Dendritech (Michigan) and TCI America (New York), respectively. Anhydrous DMF was purchased from Aldrich (Milwaukee).

¹H-NMR (300 MHz) and ¹³C-NMR (75 MHz) spectra were recorded with a Bruker AC300 spectrometer in deuterated DMSO. FT-IR spectra were obtained from a KBr pellet on a Perkin-Elmer BX spectrometer. Absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer coupled with a personal computer using software supplied by Perkin-Elmer. Metal luminescence emission and excitation spectra were measured using a Jobin Yvon-Horiba Fluorolog-322 spectrofluorimeter equipped for both room temperature and 77K measurements. Luminescence and excitation spectra were corrected for the instrumental function. Metal luminescence quantum yields were measured using quinine sulfate in 0.1N H₂SO₄ ($\Phi = 54.6\%$) as reference.¹

The quantum yields were calculated using the following equation:

$$\Phi_x/\Phi_r = [A_r(\lambda_r)/A_x(\lambda_x)][I(\lambda_r)/I(\lambda_x)][\eta_x^2/\eta_r^2][D_x/D_r]$$

where subscript *r* stands for the reference and *x* for the sample; *A* is the absorbance at the excitation wavelength, *I* is the intensity of the excitation light at the same wavelength, η is the refractive index ($\eta = 1.333$ in 0.1N H₂SO₄, $\eta = 1.479$ in DMSO), and *D* is the measured integrated luminescence intensity.

The Eu³⁺ lifetime measurements were performed by exciting solutions in 1cm quartz cells (NSG Precision Cells, Inc.) using a Nitrogen laser (Oriel model 79110, wavelength 337 nm, pulse width at half-height 15 ns, 5-30 Hz repetition rate). Emission from the solution was collected at a right angle to the excitation beam by a 3" plano-convex lens. The signal was monitored by a photomultiplier (Hamamatsu R 316) coupled to a 500 MHz bandpass digital oscilloscope (Tektronics TDS 754D). Signal (at least 5000 points for each trace) from > 5000 flashes were collected and averaged. Background signals were similarly collected and subtracted from sample signals. Lifetimes are averages of at least three independent determinations.

Synthesis of PAMAM dendrimer G(3)-2,3-Naphthalimide **1**

PAMAM dendrimer G(3)-NH₂ (0.390mg, 0.0561mmol) was treated with a 40 molar excess of 2,3-naphthalic anhydride (445mg, 2.24 mmol) whilst refluxing in DMF (10cm³) for 48 hours under a dinitrogen atmosphere, whilst monitoring for the disappearance of the naphthalic anhydride by thin layer chromatography (silica gel). The functionalized dendrimer was obtained after removal of the solvent and trituration in toluene to yield a pale brown solid. Further purification was achieved by column chromatography (silica gel) using dichloromethane and methanol gradient (from 9:1 to 85:15) to remove any excess 2,3-naphthalic anhydride. The title compound was isolated as a pale brown flocculent solid (716mg, 96%); Found C, 62.16; H, 6.28; N, 12.45, C₆₈₆H₇₃₆N₁₂₂O₁₂₄·32H₂O Requires C, 62.18; H, 6.09; N, 12.9; UV-vis (DMSO) λ_{max} (ε/dm³ mol⁻¹cm⁻¹) 263 nm (202,040), 342 nm (55,320) and 360 nm (74,300); ν_{max} (Nujol/cm⁻¹) 3430 (broad, N-H), 2867, 2733, 1730 (C=O), 1726 (C=O), 1622, 1583, 1370, 1251 and 1148; ¹H-NMR [300MHz; (CD₃)₂SO] 2.09-2.57 (180 H, broad s, N(CH₂)₃), 3.09 (60 H, broad s, NH), 3.31 (120 H, broad s, -CH₂NHCO), 3.54 (120 H, broad s, NCO-CH₂), 3.62 (64H, broad s, N(CO)₂-CH₂) 7.67 (64H, broad s, 1-H and 4-H), 8.09 (64H, broad s, 5-H and 8-H), 8.54 (64H, broad s, 6-H and 7-H), ¹³C-NMR [75MHz; (CD₃)₂SO], 31.28, 32.96, 34.68, 37.64, 38.96, 64.40, 66.29, 68.18, 127.88 (ArC), 128.96 (ArC), 130.02 (ArC), 131.12 (ArC), 134.80 (ArC), 167.40 (NHCO), 171.54 [N(CO)₂].

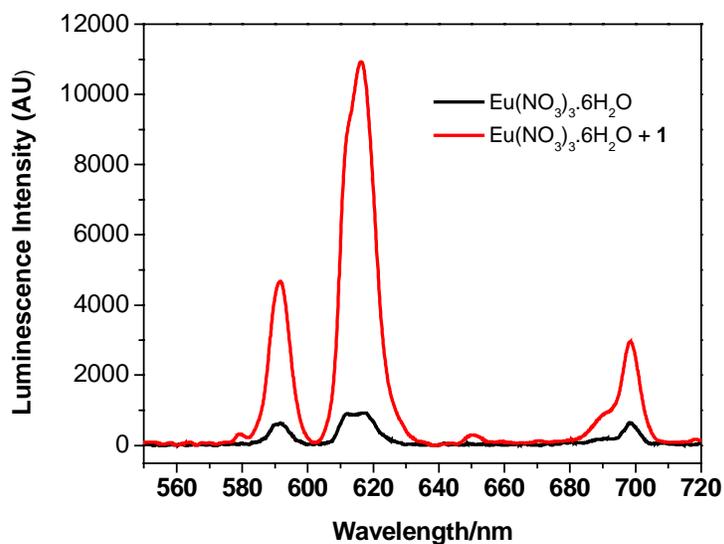


Figure S1. Emission spectra of Eu(NO₃)₃·6H₂O at 8.64x10⁻⁵M in DMSO (black) and **1** at 1.08x10⁻⁵M incubated for one week with 8 equivalents of Eu(NO₃)₃·6H₂O (red, total concentration of Eu³⁺: 8.64x10⁻⁵M in DMSO). λ_{ex} = 360nm, 298K. The integrated emission of **1** + 8Eu³⁺ is 8 times greater than Eu(NO₃)₃·6H₂O.

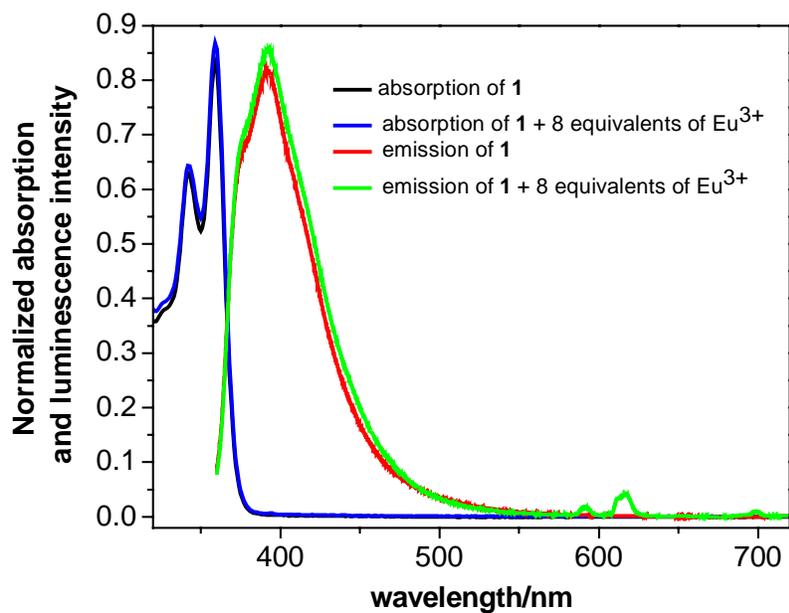


Figure S2. Corrected absorption and emission spectra of **1** with and without 8 equivalents of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in DMSO at $1.08 \times 10^{-5} \text{M}$. $\lambda_{\text{ex}} = 360 \text{nm}$, 298 K.

1. Meech, S. R.; Philips, D. C; *J. Photochem*, **1983**, *65*, 229-235.