

Europium Complexes with High Total Photoluminescence Quantum Yields in Solution and in PMMA

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Supplementary Information

Experimental

Materials: H₂O, Acetone, Ethanol and Hexane (for analysis, Acros) were degassed and used without further purifications. KOtBu, Hexafluoroacetylacetonate (hfac), 1,10-phenanthroline (99%+), EuCl₃·6H₂O, 2,2-Dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (dho) and 1,1,1,2,2,3,3,7,7,8,8,9,9,9-Tetradeca-fluoro-4,6-nonanedione (tfn) are from Aldrich Organics. Ligand bis(2-(diphenylphosphino)phenyl) ether oxide (DPEPO) was synthesized according to a published procedure [i].

General instrumentation and procedures: All reactions were performed in standard glassware under a nitrogen atmosphere. Evaporation and concentration were performed at water aspirator pressure, and drying was *in vacuo* at 10⁻² Torr. Elemental analyses were carried out on a Perkin–Elmer 2400 B analyzer. Mass spectra were obtained using Fast atom bombardment on a Nermag R 10-10H spectrometer. A 9 kV xenon atom beam was used to desorb samples from the 3-nitrobenzyl alcohol matrix. ¹H and ¹³C NMR spectra have been performed at 293 K on a Bruker DPX 360 spectrometer. ¹H and ¹³C NMR spectra are referenced to external tetramethylsilane.

Synthesis of compound 1

In a typical procedure, an aqueous solution (20 mL) of Hexafluoroacetylacetonone (Hhfac) (3 mmol) was added to a KOtBu (3 mmol). The mixture was stirred for 30 min and then $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmol) was added to the resulting clear solution to afford a white precipitate. The mixture was stirred under Nitrogen at 60°C for 1 hour and then at room temperature for 3 hours. The precipitate was filtered off, washed with cold water (100 mL), hexane (5mL) and dried under vacuum for 12h. The product was further purified by recrystallization from Acetone/Hexane and obtained a 71 % yield of white crystals. The precursor diaquo complexes for **4** and **5** were prepared by an analogous method.

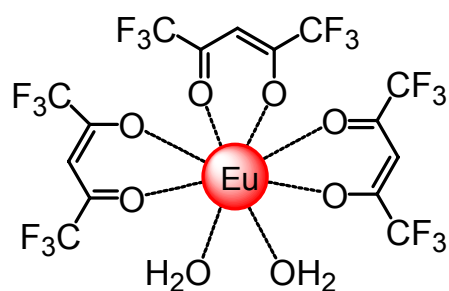


Figure S1: Compound 1

1. Anal. Calc. for **1**, $\text{C}_{15}\text{H}_7\text{EuF}_{18}\text{O}_8$ (809.15): C, 22.27; H, 0.87. Found: C, 22.25; H, 0.77.

Synthesis of compounds 2-3.

Complex **1** (0.175 mmol) and the appropriate ligand, phenanthroline (**2**) or DPEPO (**3**) (0.175 mmol) were mixed in a solution of 1:1 H_2O :Ethanol (30 mL) to form a white precipitate. The mixture was stirred under nitrogen at 60°C for 1 hour and then at room temperature for 3 hours. The white precipitate was filtered off, washed with cold water (100 mL), hexane (5mL) and dried under vacuum for 12h. Compounds **2** and **3** were further purified by recrystallization from Acetone/Hexane, and obtained as white crystals in 65 % and 68 % yield respectively. The compounds were

characterized by ^1H and ^{13}C NMR spectroscopy and their purity was verified by elemental analysis.

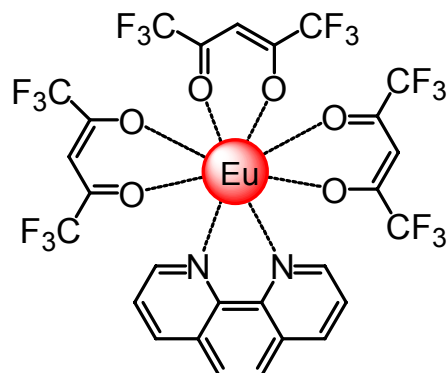


Figure S2: Compound **2**

2. ^1H NMR (300 MHz, $\text{CD}_3\text{CN-d}_3$): δ 3.98 (s, 3 H), 7.57 (s, 2 H), 7.61 (dd, $J = 4$ Hz, $J = 5$ Hz, 2 H), 8.51 (d, $J = 8$ Hz, 2 H), 10.34 (s, 2 H). ^{13}C $\{^1\text{H}\}$ NMR ($\text{CD}_3\text{CN-d}_3$, 75 MHz): δ 59.95, s; 104.09, s; 124.02, s; 146.54, s; 161.23, s. Anal. Calc. for **2**, $\text{C}_{27}\text{H}_{11}\text{EuF}_{18}\text{N}_2\text{O}_6$ (953.32): C, 34.02; H, 1.16; N, 2.94. Found: C, 34.17; H, 1.12; N, 2.89. FAB-MS: 980.2 (100% $[\text{M} + \text{Na}]^+$ calc. for. $\text{C}_{27}\text{H}_{11}\text{EuF}_{18}\text{N}_2\text{O}_6$).

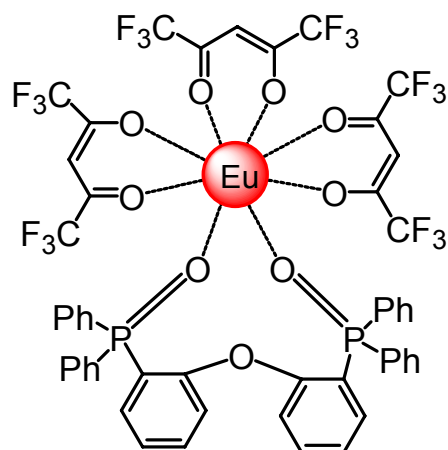


Figure S3: Compound **3**

3. ^1H NMR (300 MHz, CDCl_3): δ 5.61 (s, 3 H), 7.02 (dd, $J = 4.6$ Hz, $J = 4.6$ Hz, 2H), 7.56 (d, $J = 8$ Hz, 2 H), 8.10 (t, $J = 7.5$ Hz, 2 H), 7.21 (m, 4 H), 7.38 (m, 4 H), 7.55 (m, 2 H), 7.87 (m, 4 H), 7.96 (m, 2 H), 8.36 (m, 4 H), 8.97 (m, 4 H). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz): δ 63.55, s; 119.12, s; 123.84, s; 124.05, s; 129.22, m; 133.61, m; 135.04, s; 160.05, s. Anal. Calc. for **3**, for $\text{C}_{51}\text{H}_{31}\text{EuF}_{18}\text{O}_9\text{P}_2$ (1343.67): C, 45.59; H,

2.33. Found: C, 45.50; H, 2.29. FAB-MS: 1344.67 (100% $[M + H]^+$ calc. for. $C_{51}H_{31}EuF_{18}O_9P_2$).

Synthesis of Compounds 4-5

Compounds **4** and **5** were prepared by an analogous route to compound **3**, although purification of **4** was hampered by lower solubility, and were characterized by NMR spectroscopy and elemental analysis.

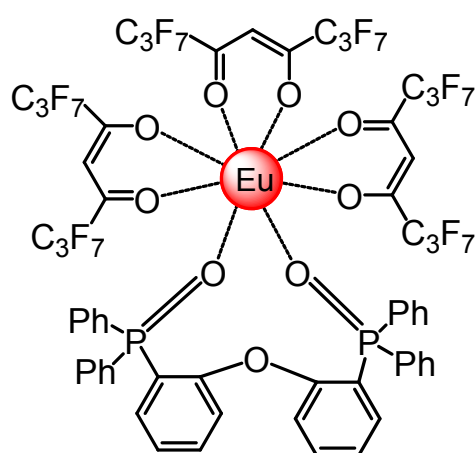


Figure S4: Compound **4**

4. 1H NMR (250 MHz, $(CD_3)_2CO$): δ 6.07 (m, 2 H), 6.13 (m, 2H), 6.34 (s, 3 H), 6.42 (m, 2 H), 6.90 (m, 2 H), 7.17 (m, 2 H), 7.28 (m, 4 H), 7.38 (m, 2 H), 7.66 (m, 2 H), 7.71 (m, 2 H), 7.90 (m, 2 H), 8.47 (m, 2H), 8.62 (m, 2H), 11.56 (m, 2H). Anal. Calc. for **4**, for $C_{63}H_{31}EuF_{42}O_9P_2$ (1943): C, 38.91; H, 1.60. Found: C, 35.07; H, 2.83

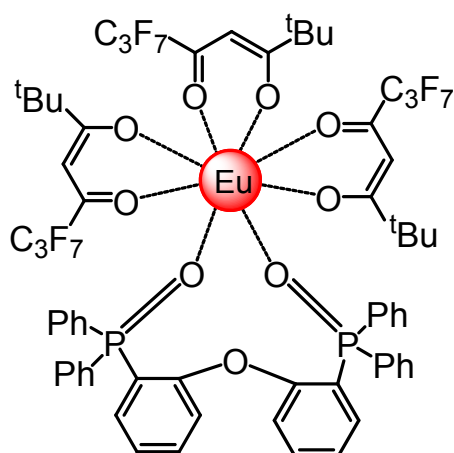


Figure S5: Compound **5**

5. ^1H NMR (250 MHz, CDCl_3): δ 0.82 (s, 27 H), 1.85 (br, 2H), 3.69 (br, 3 H), 5.59 (br, 4 H), 6.25 (br, 6 H), 6.86 (br, 2 H), 7.12 (br, 4 H), 7.69 (br, 2 H), 8.55 (br, 2 H), 9.11 (br, 2 H), 9.67 (br, 4 H). Anal. Calc. for **5**, for $\text{C}_{66}\text{H}_{58}\text{EuF}_{21}\text{O}_9\text{P}_2$ (1607): C, 49.28; H, 3.61. Found: C, 47.91; H, 2.89.

PMMA encapsulation of complexes

The required mass of Eu(III) complex was dissolved in Acros methyl methacrylate monomer (99% stabilised) and combined with Makevale $\text{\textcircled{R}}$ PMMA powder containing 0.3% w/w benzoyl peroxide initiator. After thorough mixing, the resultant mixture was poured into glass moulds and cured at 75°C under 150 psi (10 bar) pressure.

X-ray Crystallographic study:

A partial X-ray structure of $[\text{Eu}(\text{tfn})_3(\text{DPEPO})]$ (**4**) was obtained, however data were too poor to achieve full structure refinement. For information, the general coordination environment and connectivity are shown (Figure S6, S7) and described below. Cell parameters were determined as $a = 14.5690(4)$ $b = 22.7150(6)$ $c = 21.6510(6)$, $\alpha = 90$, $\beta = 90.8370(10)$, $\gamma = 90$. The structure shows two molecules in the asymmetric unit with the expected eight-coordinate environment of the Eu(III) centre, with the exclusion of H_2O or other ligands that might lead to non-radiative decay of the excited state through coupling with high-energy O-H oscillators. The coordinating atoms occupy a square antiprism geometry, with $\text{Eu}\dots\text{O}(\text{DPEPO}) = 2.285 - 2.321$ Å; $\text{Eu}\dots\text{O}(\text{tfn}) = 2.377 - 2.446$ Å. It is notable that the ether oxygen of the DPEPO ligand does not coordinate the Eu and is at distances of 4.360 and 4.282 Å for the two inequivalent molecules. Such an asymmetric geometry is consistent with a short

radiative lifetime of the Eu due to reduction of the parity-forbidden character of the transition, through mixing of the f-orbital states.

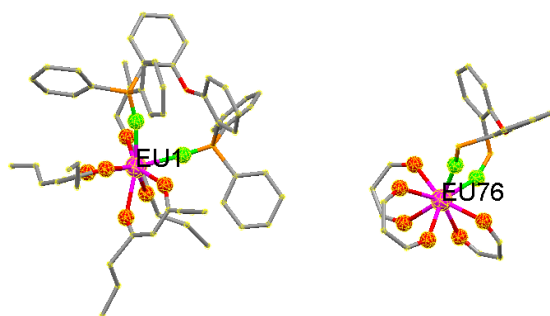


Figure S6: X-ray structure of $[\text{Eu}(\text{tfn})_3(\text{DPEPO})]$ **4** showing the two molecules in the asymmetric unit. For clarity, the complex containing Eu1 has F-atoms removed and the complex containing Eu76 shows only the chelating moieties of the ligands. The latter is viewed down the pseudo-fourfold axis of the square antiprism.

Data were collected at low temperature on an IPDS STOE diffractometer using a graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073\text{\AA}$) and equipped with an Oxford Cryosystem Cryostream Cooler Device. The structure was solved by direct methods using SIR92 [ii], and refined by means of least-squares procedures on F using the programs of the PC version of CRYSTALS [iii]. Atomic scattering factors were taken from the International tables for X-ray Crystallography [iv]. Drawings of molecule are performed with Ortep with 30% probability displacement ellipsoids for non-hydrogen atoms. We thank Anna Collins and Fraser White (University of Edinburgh) for the structure solution and their efforts to achieve a reasonable refinement.

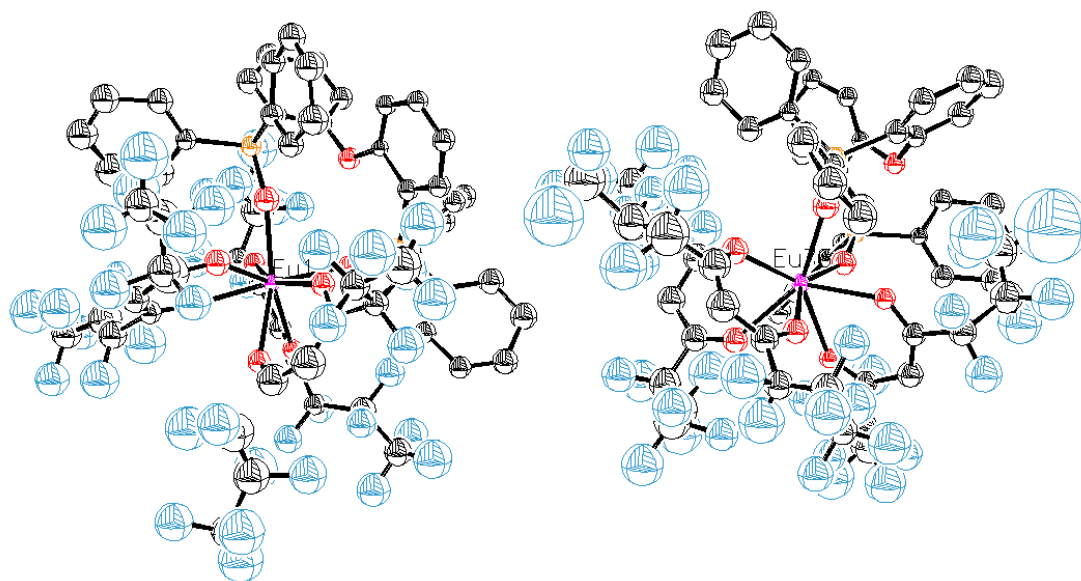


Figure S7: Ortep representation of the structure of **4**, $\text{Eu}(\text{tfn})_3(\text{DPEPO})$. Thermal ellipsoids are drawn at the 30% probability level.

Measurement of fluorescence spectra, lifetimes and total quantum yields

Fluorescence spectra, lifetimes and total quantum yields were measured using a Fluoromax-P spectrofluorimeter (Horiba-Jobin-Yvon). In both DCM and PMMA samples, the concentration of the lanthanide complex was such as to give an absorbance of around 0.1 at the excitation wavelength. Quantum yields were measured at an excitation wavelength of 340 nm, the lower limit of the calibrated range of the integrating sphere.

Excitation and emission spectra and quantum yields were measured using the spectrofluorimeter in photon counting mode, with a continuous xenon lamp excitation source. Spectra were corrected for variations in excitation intensity and the response of the detector. Lifetimes were measured using a pulsed xenon lamp source, with pulse width $< 50 \mu\text{s}$, and time-gated detection. Absolute total quantum yields were measured using an integrating sphere (Horiba-Jobin-Yvon) mounted in the sample

compartment of the spectrofluorimeter, with data processing by software supplied by Horiba-Jobin-Yvon.

Decay data were fitted to exponential functions using an iterative non-linear least squares algorithm in the 'Solver' facility in Microsoft Excel. A typical decay curve, fitted exponential function and residuals are shown in Figure S8.

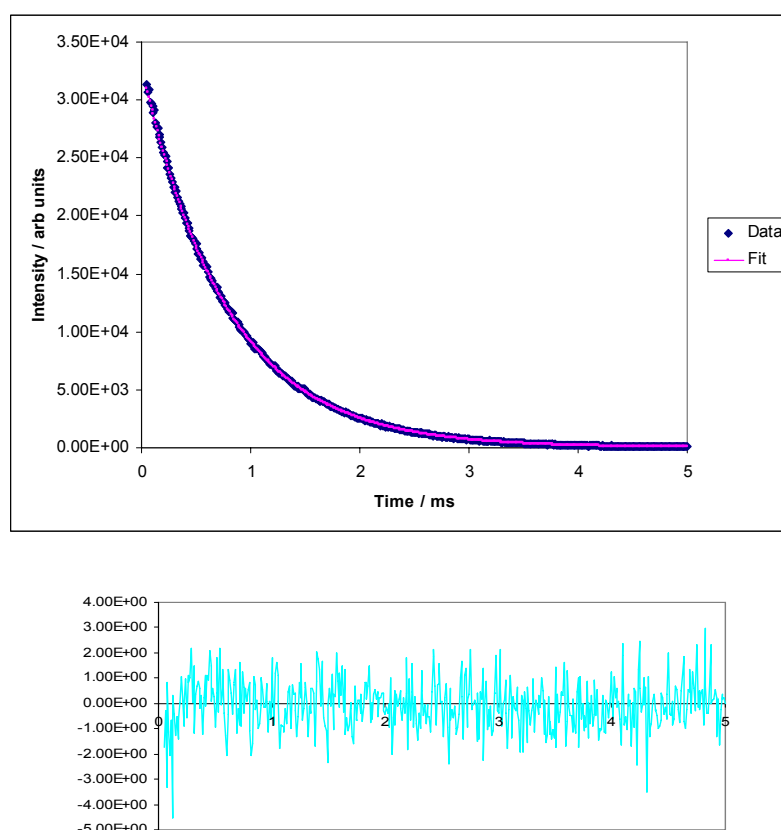


Figure S8 Decay data, fitted single exponential function and weighted residuals for **5** in PMMA.

Electronic Spectra of 3-5

Emission spectra of **3-5**, in DCM and PMMA, together with representative absorption and excitation spectra are shown in Figures S9 to S18

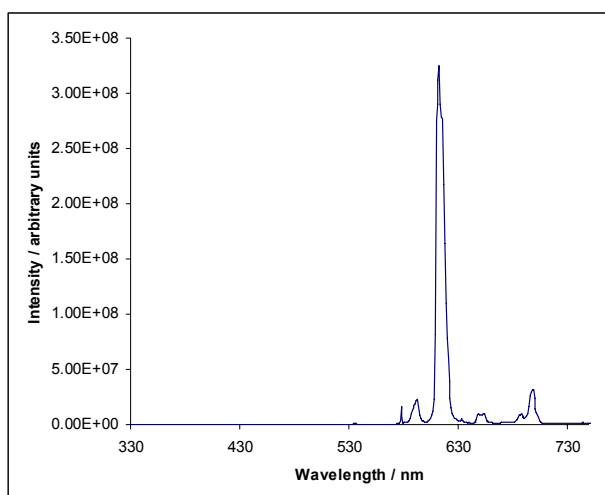


Figure S9: Emission spectrum of **3** in DCM., excited at 320 nm.

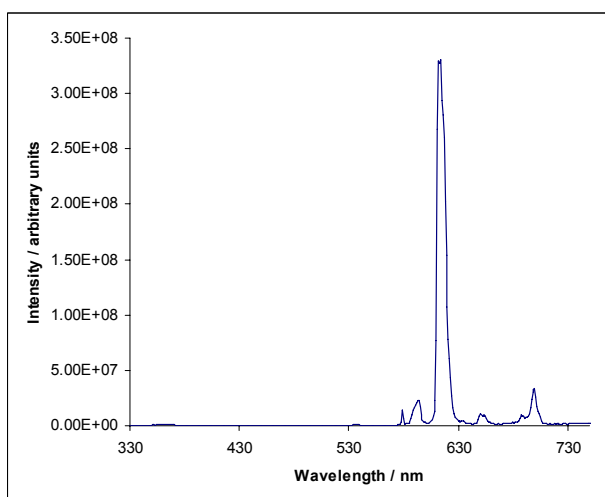


Figure S10: Emission spectrum of **3** in PMMA., excited at 320 nm.

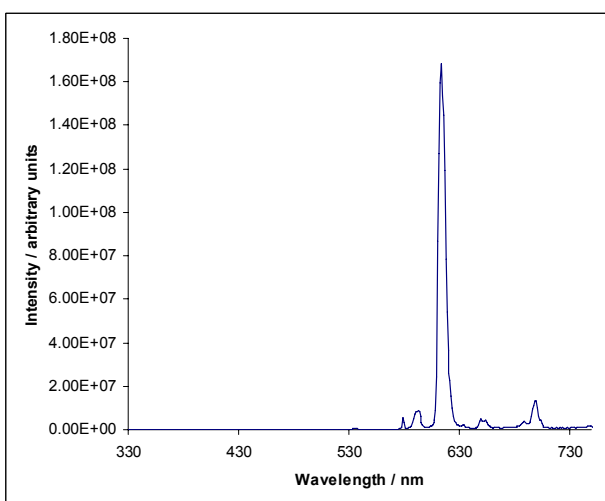


Figure S11: Emission spectrum of **4** in DCM, excited at 320 nm.

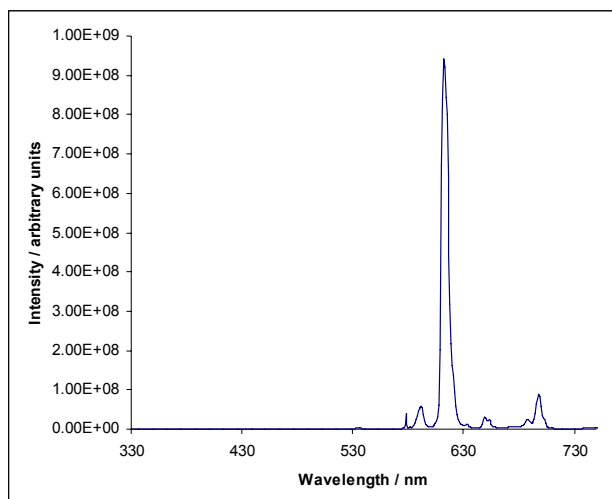


Figure S12: Emission spectrum of **4** in PMMA., excited at 320 nm.

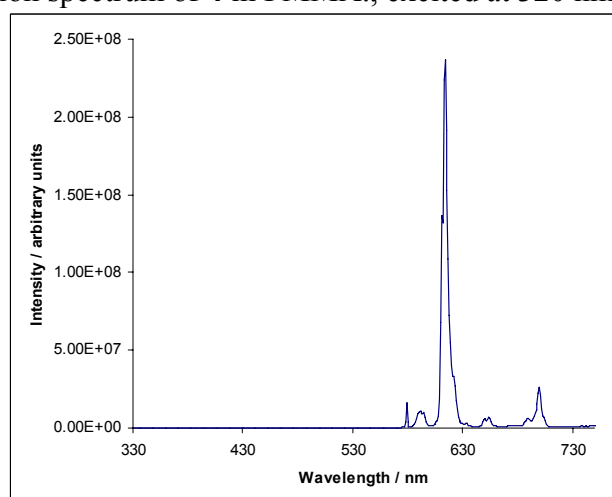


Figure S13: Emission spectrum of **5** in DCM, excited at 320 nm.

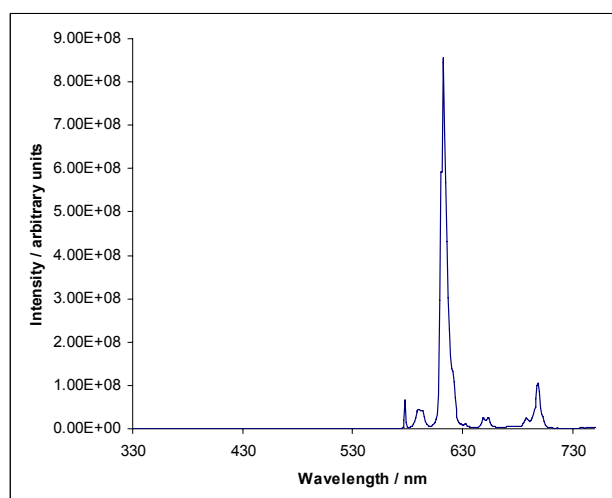


Figure S14: Emission spectrum of **5** in PMMA., excited at 320 nm.

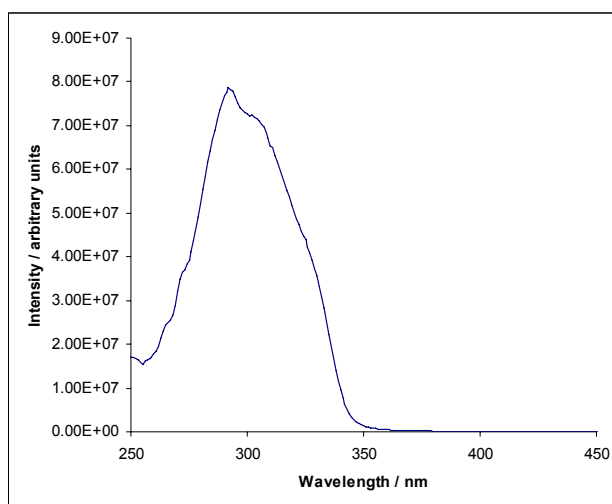


Figure S15: Excitation spectrum of **3** in DCM.

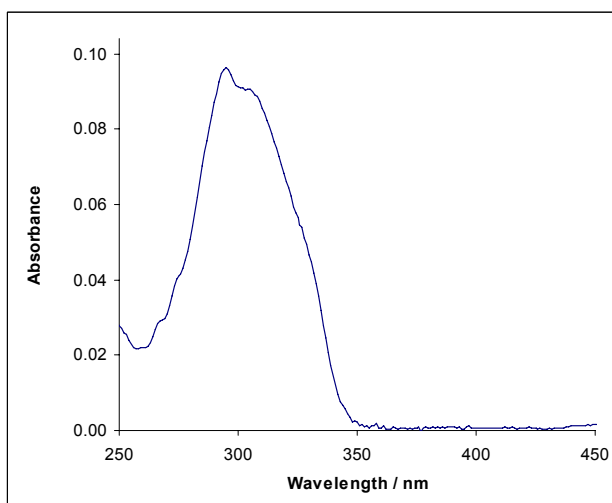


Figure S16: Absorption spectrum of **3** in DCM.

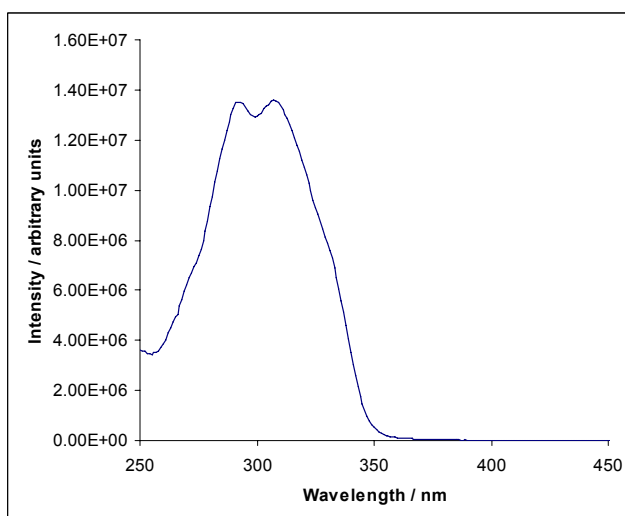


Figure S17: Excitation spectrum of **4** in DCM.

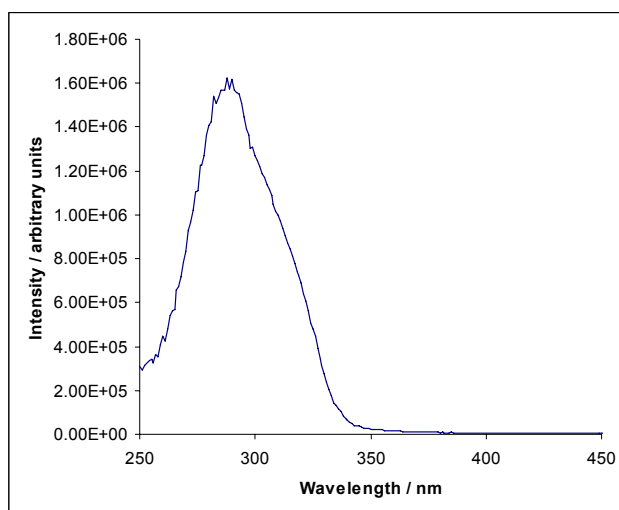


Figure S18: Excitation spectrum of **5** in DCM.

[i] H. Xu, L-H. Wang, X.-H. Zhu, K. Yin, G.-Y., Zhong, X.-Y. Hou, W. Huang, J. Phys. Chem. 110 (2006) 3023-3029

[ii] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 26 (1993) 343-350

[iii] P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout, D.J. Watkin, J. Appl. Crystallogr., 36 (2003) 1487.

[iv] International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, England, 1974, Vol. IV