Enhanced photolabelling of luminescent Eu^{III} centres with a chelating antenna in micellar media

Martine Cantuel,[a] Christophe Lincheneau,[b] Thierry Buffeteau,[a] Laura Jonusauskaite,[a] Thorfinnur Gunnlaugsson,[b] Gediminas Jonusauskas,[c] and Nathan D. McClenaghan*[a]

[a] Groupe Nanostructures Organiques, Institut des Sciences Moléculaires, University of Bordeaux/CNRS, UMR 5255, 33405 Talence cedex, France. Fax: +33 540 00 33 21; Tel:= +33 540 00 61 58; E-mail: n.mc-clenaghan@ism.u-bordeaux1.fr.
[b] School of Chemistry, Centre for Synthesis and Chemical Biology, Trinity College Dublin, Dublin 2, Ireland
[c] Centre de Physique Moléculaire Optique et Hertzienne, University of Bordeaux/CNRS, UMR 5798, 33405 Talence cedex, France.

Supporting Information

1- Materials and methods

The syntheses of [Eu·**1**]$(CF_3SO_3)_3 \cdot 2H_2O$[1] and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS)[2] have been reported previously. Naphthylacetic acid was used as its sodium salt **3**·Na^+, obtained by mixing 1 equivalent of NaOH with **3**·H^+ in water. Dichloromethane was distilled over calcium hydride before use.

^1H and ^{13}C-NMR experiments were performed at 295 K on a Brüker Avance DPX 300 or a Brüker AC-D50 spectrometer. Chemical shifts are reported in ppm (d) and are referenced to the NMR solvent residual peaks. Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. ESI Mass spectra were recorded on a LCQ (positive mode) on methanolic solutions containing 0.05% v/v of trifluoroacetic acid..

Electronic absorption spectra were measured on a Varian Cary 5000 UV-vis-NIR spectrometer. Steady-state emission and excitation spectra were measured with optically dilute samples in 1 cm-quartz cells or films deposited onto quartz slides, with either right angle or front-face detection, on a Fluorolog 212 (SPEX) fluorimeter equipped with a Hamamatsu R928 photomultiplier.

$^5D_0$(Eu) lifetimes were measured on a Varian Carey Eclipse Fluorimeter. The inner sphere hydration number q was calculated according to equation:

$$q = 1.2[(\tau_{H2O}^{-1} - \tau_{D2O}^{-1}) - 0.25]$$

where the constant 1.2 represents the sensitivity of Eu^{III} to quenching by coordinated H_2O molecules, and -0.25 is a correction term taking into account the quenching by second-sphere H_2O molecules.[3] No satisfactory correction term for deexcitation due to the contribution of amine NH groups is available, which may lead to slightly overestimated values.

Photochemical irradiation experiments were carried out by using a high pressure Hg/Xe lamp equipped with a monochromator set at 296 nm. The light intensity at 296 nm, measured by ferrioxalate actinometry, was $2.2 \cdot 10^{-8}$ Einstein.min^{-1} on a 3 ml volume.[4]

Infrared spectra were recorded with a ThermoNicolet Nexus 670 FTIR spectrometer at a resolution of 4 cm^{-1}, by coadding 50 scans. Experiments were performed in D_2O and CD_3OD at a concentration of 10 mM. D_2O and CD_3OD solutions were held in a CaF_2 cell with fixed path lengths of 45 mm (BioCell™, BioTools) and 100 mm (Omni-Cell™, Eurolabo), respectively. All infrared spectra were shown with solvent absorption subtracted out.

The LETAGROP-SPEFO method[5] was used to determine the stoichiometry and association constants at room temperature. The LETAGROP-SPEFO program calculates the global binding constants K_{ass} for a chemical scheme by iterative comparison of calculated data with experimental data, searching for the global minimum of the error function. Equations that do not fit the data are rejected.

1 T. Gunnlaugsson, A. J. Harte, J. P. Leonard and M. Nieuwenhuyzen, *Supramol. Chem.*, 2003, **15**, 505.
2 J. S. Moore and S. I. Stupp, *Macromolecules*, 1990, **23**, 65.
3 A. Beeby, I. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. De Sousa, J. A. G. Williams and M. Woods, *J. Chem. Soc., Perkin Trans. 2*, 1999, 493.
4 M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, *Handbook of Photochemistry - Third Edition*, Taylor and Francis group LLC ed., CRC press, 2006.
5 (a) L. G. Sillen, B. Warnqvist, *Ark. Kemi* 1968, **31**, 315; (b) L. G. Sillen, B. Warnqvist, *Ark. Kemi* 1968, **31**, 377; (c) J. Havel, Haltafal-Spefo program; Mazaryle University: Brno, Moravia, Czech Republic; (d) K. A. Connors, *Binding Constants: The Measurement of Molecular Complex Stability*, Wiley-interscience, 1987..

2- Synthesis of 2-nitrobenzyl 2-(naphthalen-1-yl)acetate (2)

A mixture of 1-naphthyl acetic acid (2.46 g, 13.2 mmol), 2-nitrobenzyl alcohol (2.02 g, 13.2 mmol) and DPTS (7.8 g, 26.4 mmol) in 100 ml of dry dichloromethane is stirred under nitrogen. Diisopropylcarbodiimide (3.3 g, 26.4 mmol) is added and the stirring is pursued for 24 hours. The mixture is filtered over celite and the solvent is evaporated. The solid obtained is washed with methanol, and finally recrystallized in diethylether to yield 2.32 g (7.2 mmol, 54 %) of pale yelow crystals.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 8.08-7.99 (m, 2H), 7.91-7.81 (m, 2H), 7.55-7.37 (m, 6H), 7.17 (m, 1H), 5.53 (s, 2H), 4.19 (s, 2H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 170.9, 147.4, 134.0, 133.7, 132.2, 132.1, 130.2, 128.9, 128.7, 128.7, 128.4, 128.3, 126.6, 126.0, 125.7, 125.1, 123.8, 63.4, 39.3. ESI-MS *m/z* =344.09 (MNa$^+$).

3- Figures

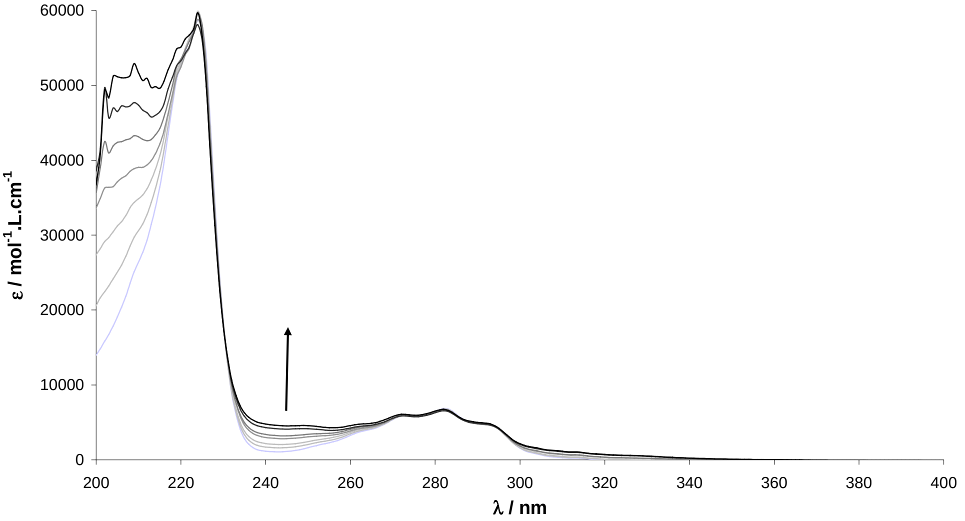


Figure S1: Electronic absorption spectra of **3** (concn = 6.10^{-5}M) in MeOH, in the presence of increasing amounts (0-1.5eq) of [Eu·**1**]$^{3+}$.

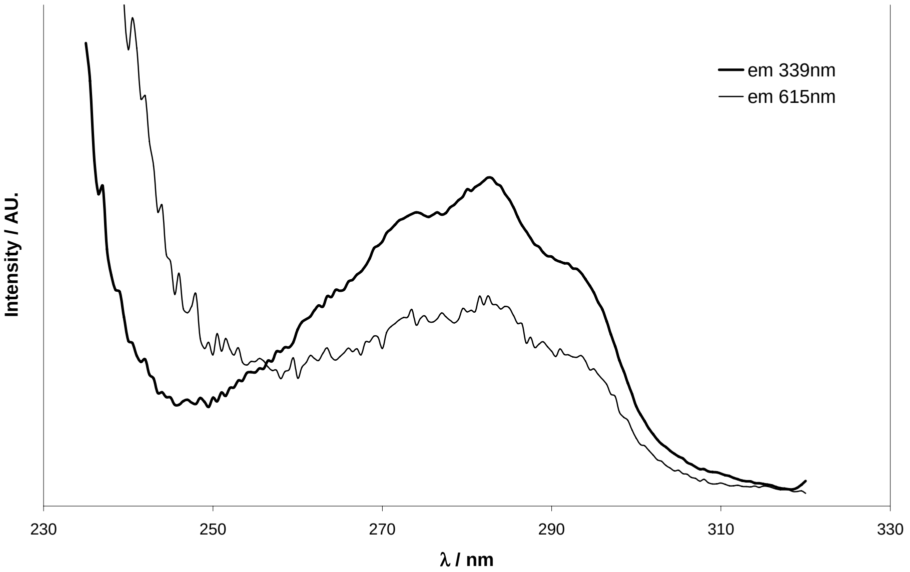
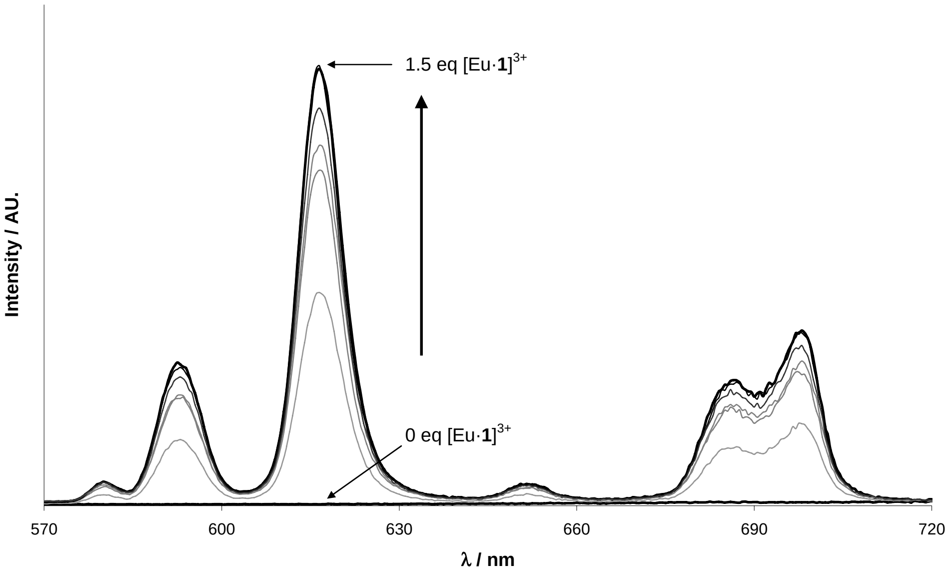


Figure S2: Fluorescence excitation spectra of a MeOH solution containing [Eu·**1**]$^{3+}$ (concn = 2 x 10^{-5} M) and **3** in a 1:2 ratio, upon monitoring the emission in the naphthalene region (339 nm) or in the europium region (615 nm).

a)



b)

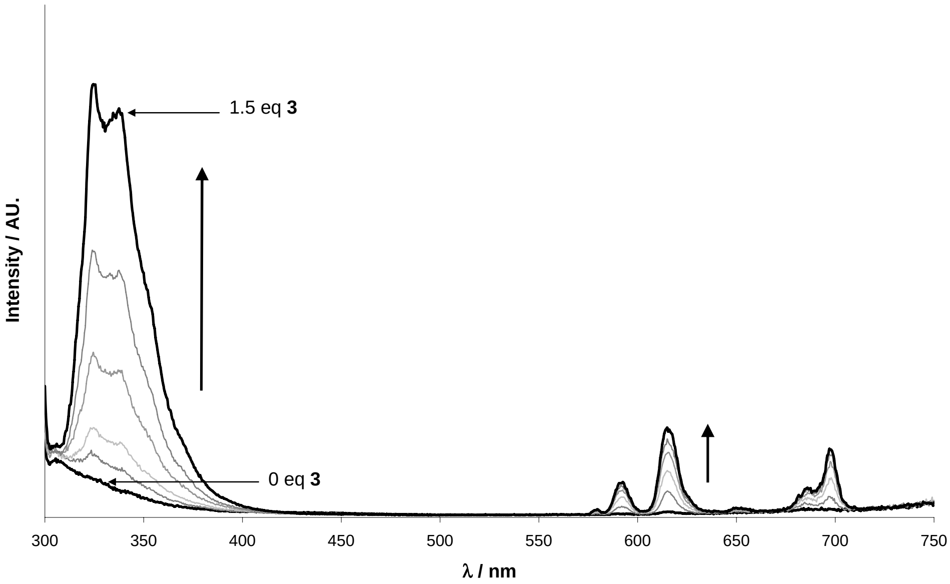


Figure S3: a) Emission spectra of **3** (concn = 6·10^{-5}M) in MeOH in the presence of increasings amounts (0-1.5 eq) of [Eu·**1**]$^{3+}$ (Zoom on the Eu emission region). b) Emission spectra of [Eu·**1**]$^{3+}$ (concn = 2·10^{-5}M) in MeOH in the presence of increasings amounts (0-1.5 eq) of **3**.

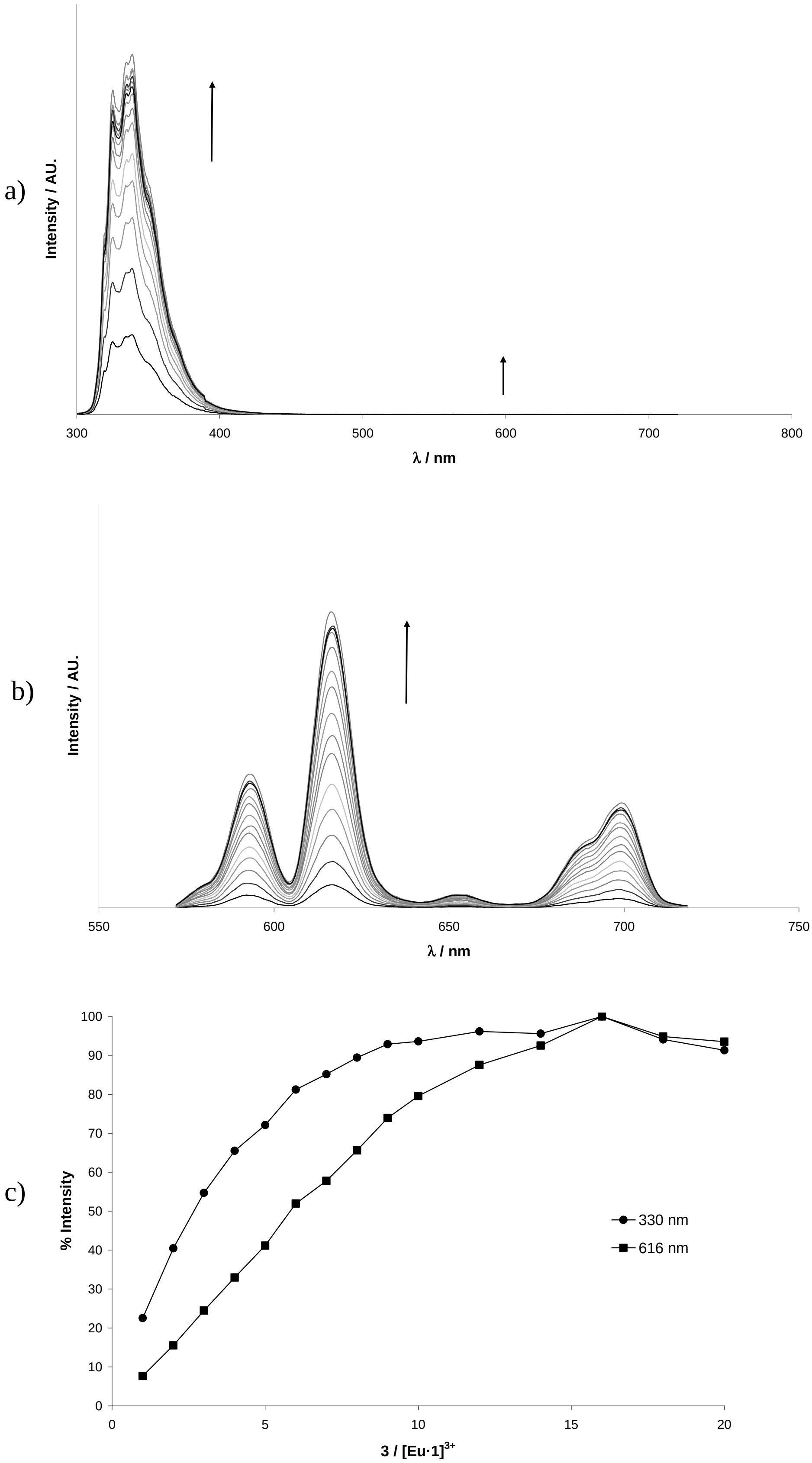


Figure S4: a), b) Emission spectra of $[Eu{\cdot}\mathbf{1}]^{3+}$ (concn = 2.10^{-5}M) in H_2O, in the presence of increasing amounts (0-20eq) of **3**, and c) percentage variation of the intensity of emission at 330 and 615 nm. λ_{exc} = 282 nm.

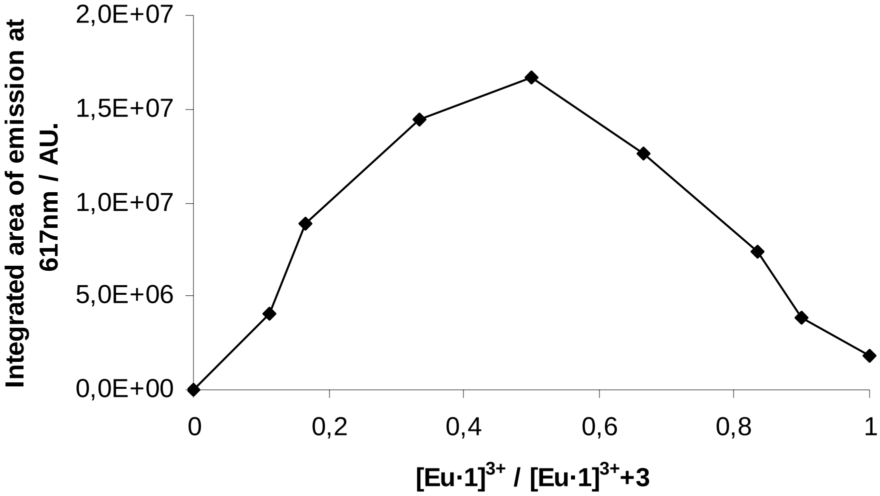


Figure S5: Job plot of mixture of [Eu·**1**]$^{3+}$ and **3** in MeOH. Total concn = 2 x 10^{-5}M. λ_{exc} = 282 nm.

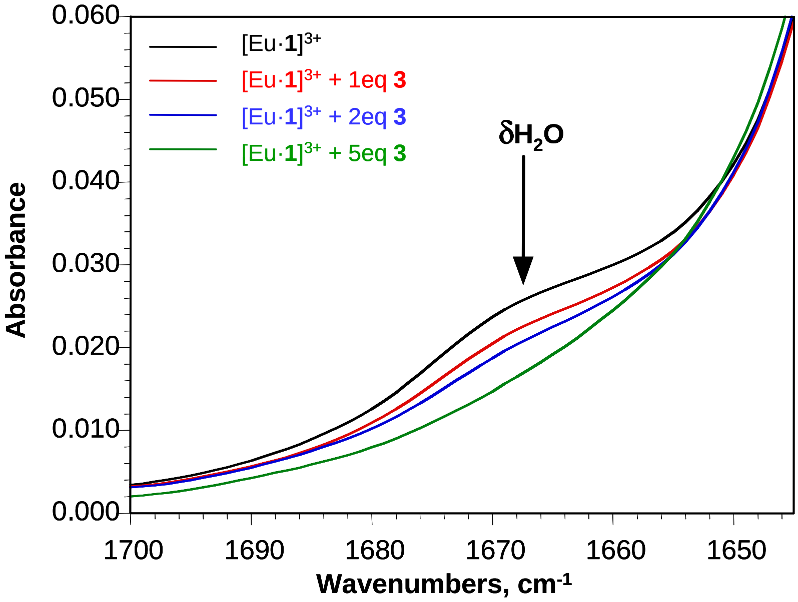


Figure S6: Infrared spectra of **3**, [Eu·**1**]$^{3+}$ and various [Eu·**1**]$^{3+}$:**3** ratios in CD_3OD in the region of the lanthanide-bound water bending vibrations. Concn = 10 mM.

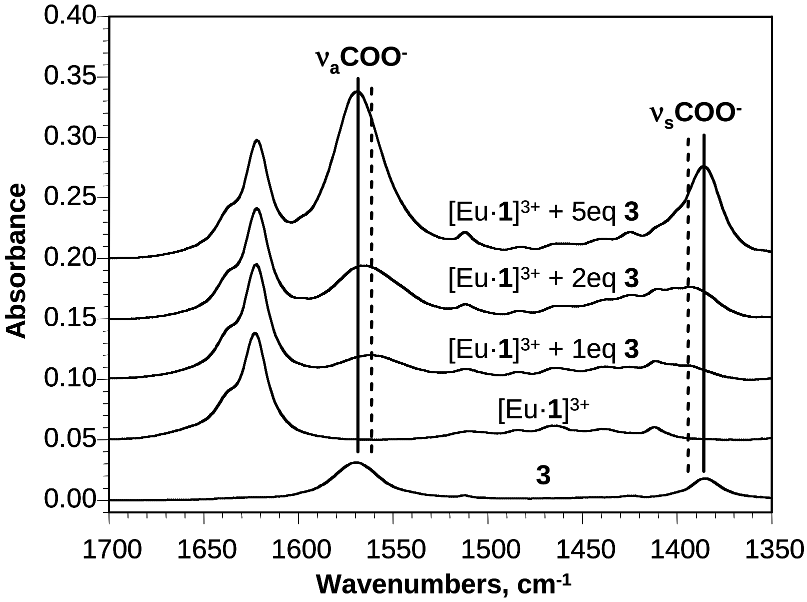


Figure S7: Infrared spectra of **3**, [Eu.**1**]$^{3+}$ and various [Eu.**1**]$^{3+}$:**3** ratios in D_2O in the region of the carboxylate stretching vibrations. Concn = 10 mM.

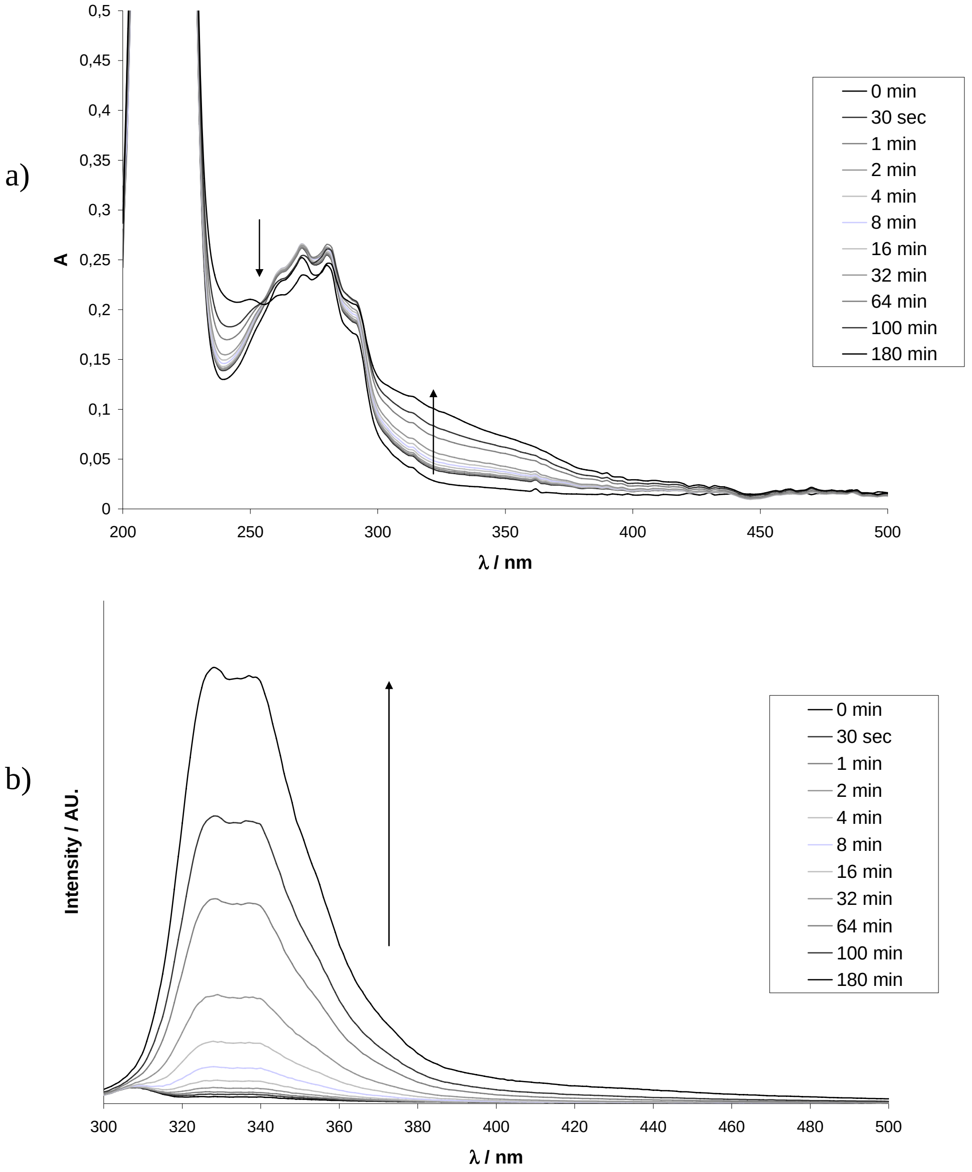


Figure S8: Variation of a) absorption and b) emission spectra (λ_{exc} = 282 nm), of **2** in MeOH, after increasing irradiation times. Concn = 2 x 10^{-5} M.

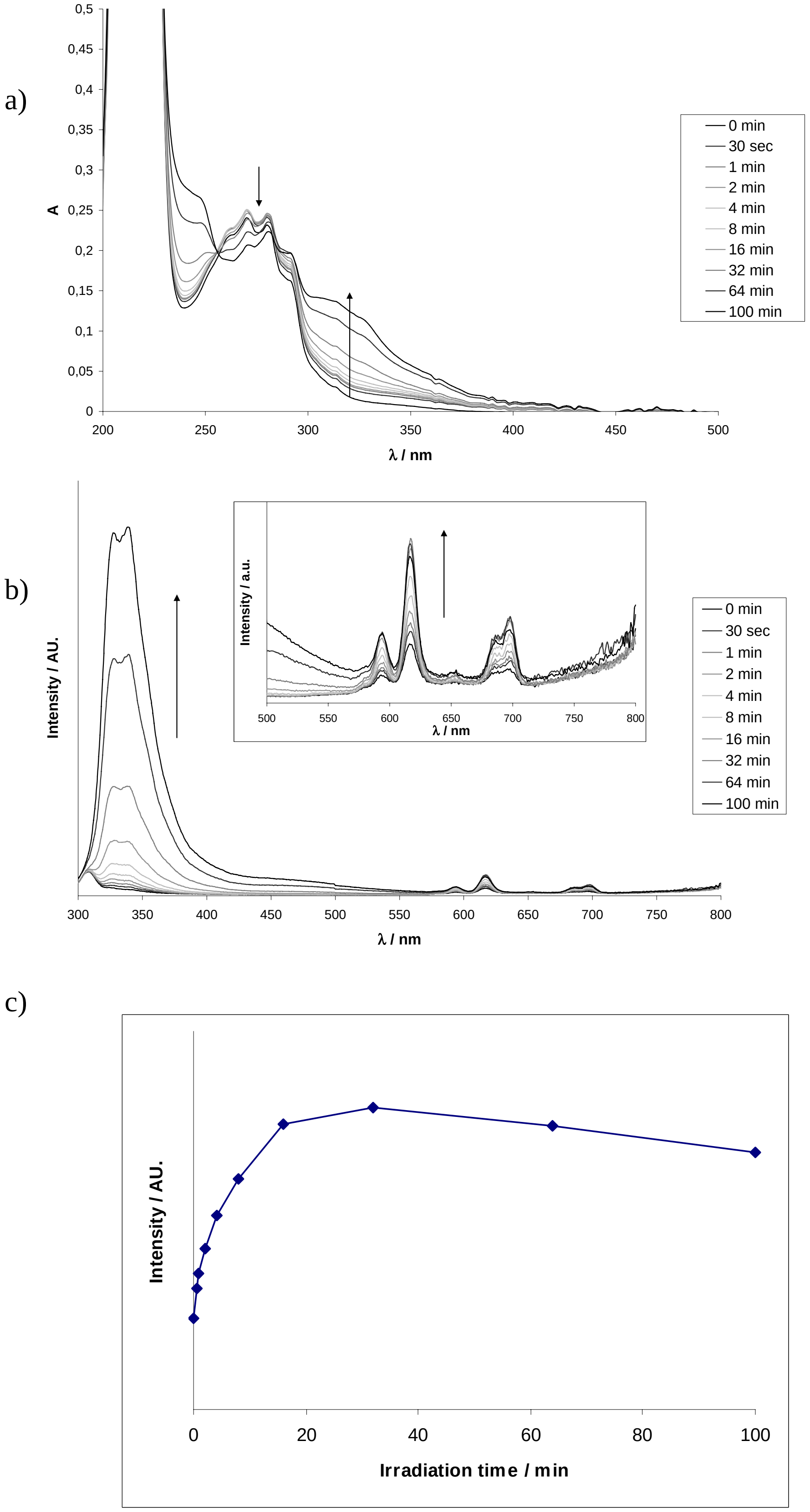


Figure S9: Variation of a) absorption and b) emission spectra (λ_{exc} = 282 nm) of a 1:1 mixture of $[\mathrm{Eu}\cdot\mathbf{1}]^{3+}$ and **2** in MeOH, upon various irradiation times. Concn ($[\mathrm{Eu}\cdot\mathbf{1}]^{3+}$) = 1×10^{-5} M. c) Increasing europium luminescence (at 615nm) as a function of irradiation time, concentration and irradiation time as Figure S9b.

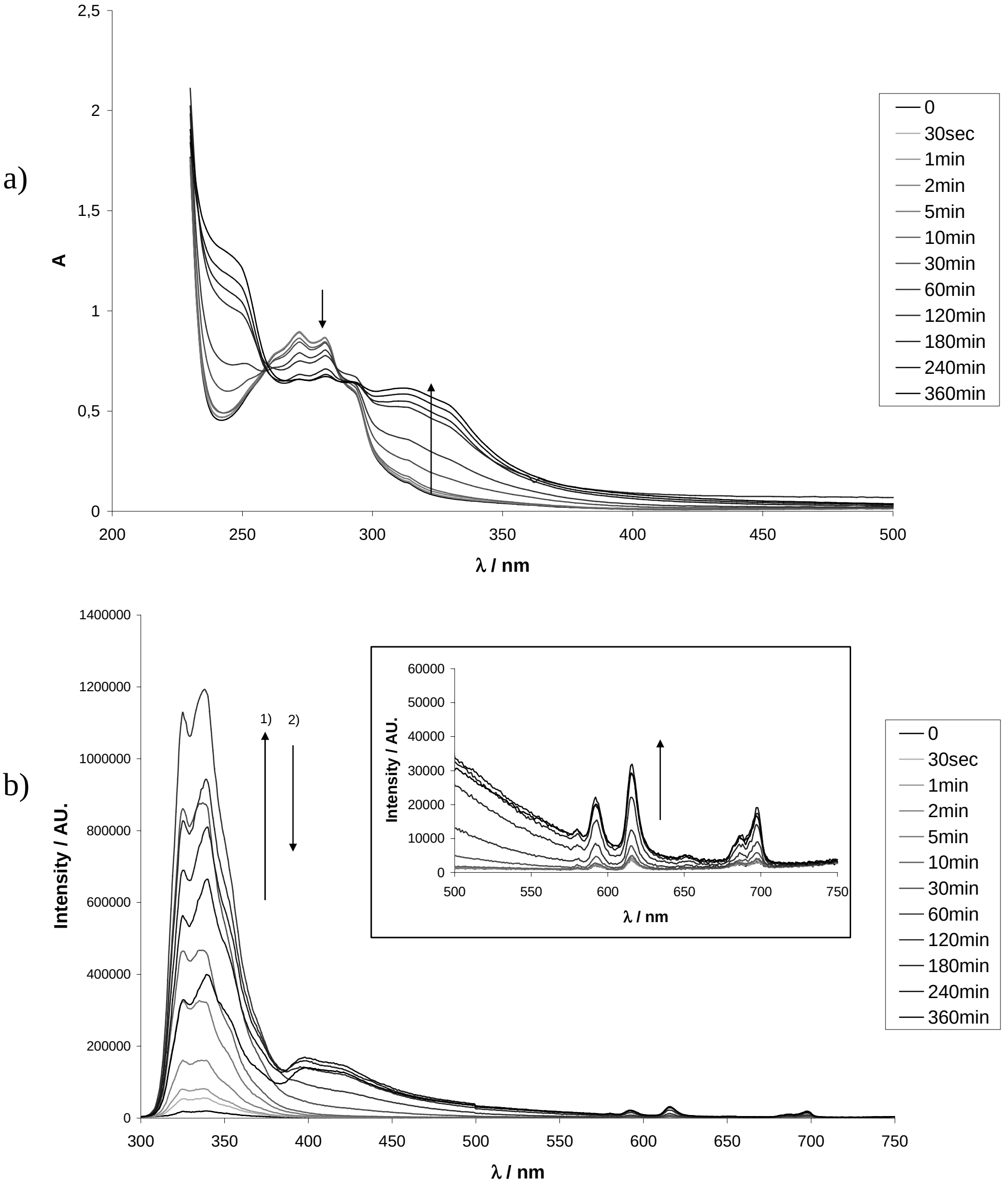


Figure S10: Variation of a) absorption and b) emission spectra (λ_{exc} = 282 nm), of a 1:1 mixture of [Eu·**1**]$^{3+}$ (concn = 2 x 10^{-4}M) and 2 in TMADS (20 mM) in H_2O, upon various irradiation times.

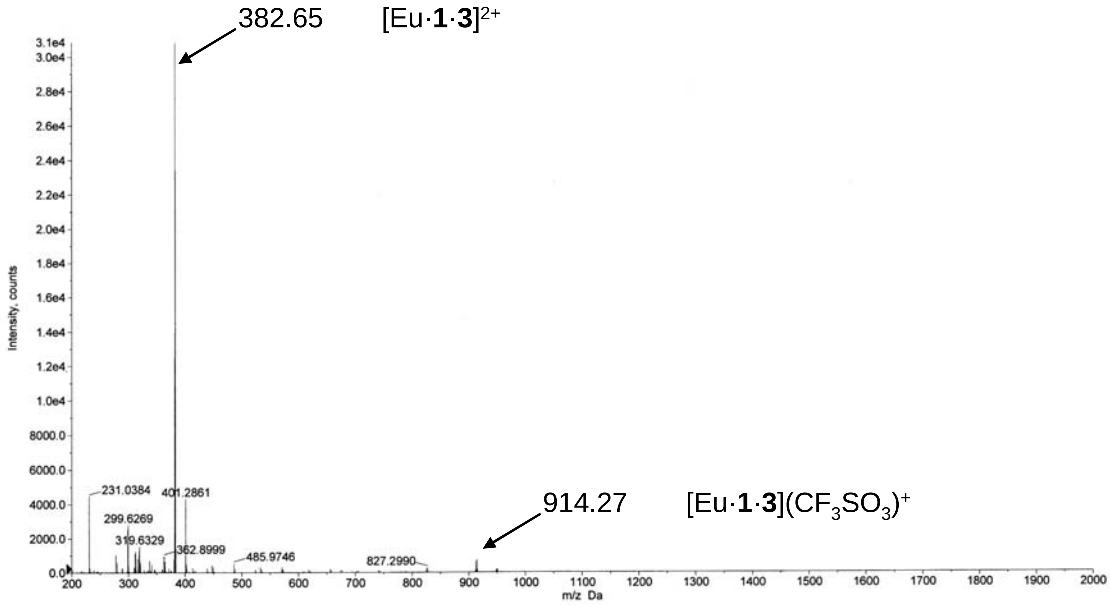


Figure S11: ESI-MS spectrum (positive mode) of [Eu.**1.3**]$(CF_3SO_3)_2$.

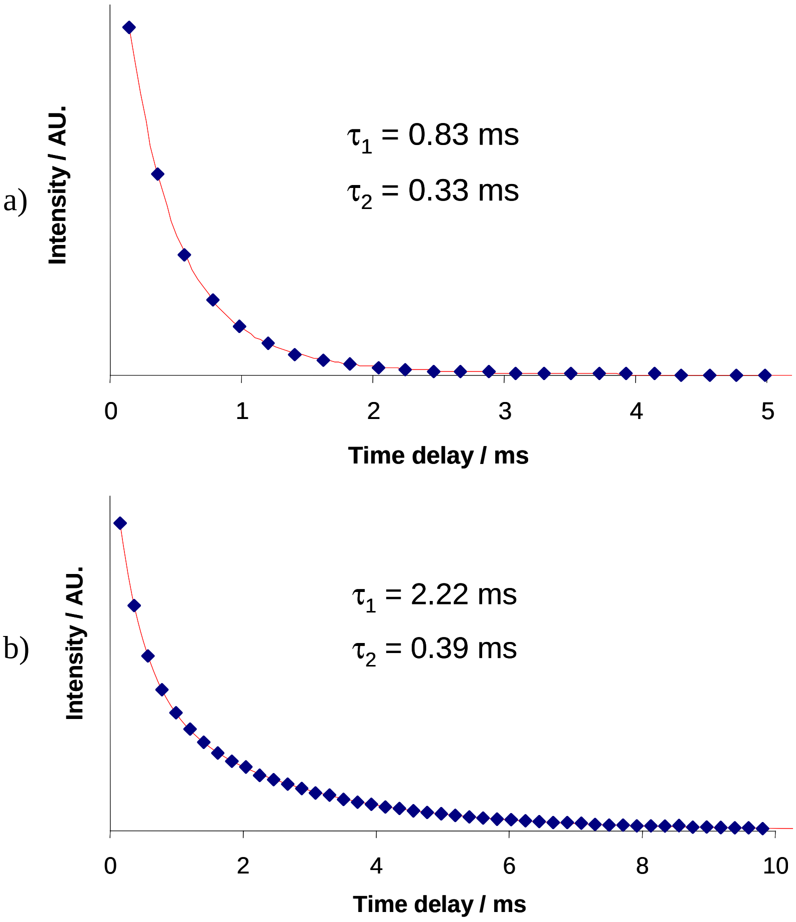


Figure S12: Emission decays (diamonds) and associated biexponential fittings (lines) of [Eu.**1**]$^{3+}$ in the presence of 2 eq. of **3** in H_2O (a) and in D_2O (b). λ_{exc}=282nm, λ_{em}=615nm. Concn = 10^{-4} M.