

Electrostatically-Driven Assembly of MWCNTs with an Europium Complex

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Supplementary Information

Instruments and Materials

NMR spectra were obtained on a JEOL JNM-EX-400 spectrometer (400 MHz ¹H NMR). Chemical shifts (δ) are reported in parts per million using the solvent residual signal as an internal reference (DMSO, $\delta_{\text{H}} = 2.50$ ppm, $\delta_{\text{C}} = 39.52$ ppm). Each resonance multiplicity is described as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet), or *br* (broad signal). IR spectra (KBr) were recorded on a Perkin Elmer 2000 spectrometer. Mass spectrometry *via* electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI), were performed on an Agilent 6210 Time of Flight LC-MS machine. Melting points were measured on a Buchi SMP-20 apparatus.

Thermogravimetric analysis (TGA) data were recorded on 1-3 mg of sample using a Universal V4.5A TA Instrument. Data were recorded in air atmosphere at a ramp rate of $10^{\circ} \text{ C min}^{-1}$ to 800° C after being held at 30° C for 10 min to remove any residual solvent.

XPS studies were performed to investigate the chemical composition of the functionalized MWCNT. For each analysis, 2 mg of material were deposited on a copper thin film, which was then fixed on an XPS sample holder using a double side adhesive conductive carbon tape (SPI supplies). For each compound, the analyses were performed on three different spots using ESCA SPECTROMETER where the photon source was a monochromatised Al K α line ($h\nu = 1486.6$ ev) applied with a takeoff angle of 35° . The survey spectra are the result of the accumulation of 10 scans where the EV/Step is 0.08. The C 1s core level peak was taken as reference at 284.7 eV.

The spectrophotometric titrations were carried out in a Hellma quartz cell ($l = 1$ cm). Absorption spectra were recorded with a Perkin-Elmer Lambda 35 spectrophotometer.

Steady-state photoluminescence spectra were measured in right angle mode with an Edinburgh FLS920 spectrometer (continuous 450 W Xe lamp), equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185–850 nm) or a Hamamatsu R5509-72 supercooled photomultiplier tube (193 K, 800–1700 nm range). Luminescence titrations were carried out (in parallel with the spectrophotometric titrations) at room temperature in dichloromethane (Carlo Erba, spectrofluorimetric grade). For solid state measurements KBr discs were used and the Φ_{em} have been calculated by corrected emission spectra obtained from an apparatus consisting of a barium sulfate coated integrating sphere (6 in.), continuous 450 W Xe lamp as light source and a R928 photomultiplayer tube as signal detector, following the procedure described by De Mello et al. (*Adv. Mater.*, 1997, **9**, 230). Experimental uncertainties are estimated to be $\pm 8\%$ for lifetime determinations, $\pm 20\%$ for emission quantum yields, ± 2 and ± 5 nm for absorption and emission peaks, respectively.

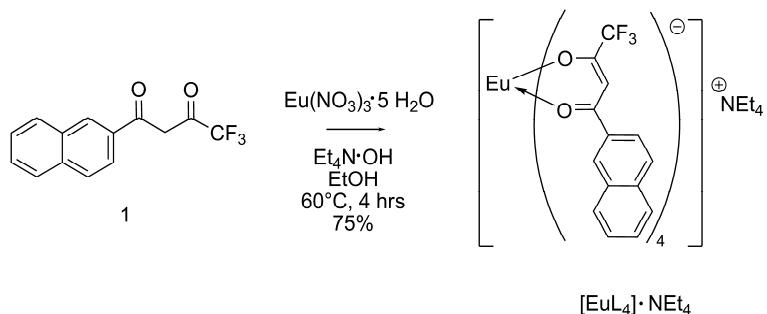
Fluorescence lifetimes were measured with an IBH 5000F time-correlated single-photon counting device, by using pulsed SpectraLED excitation source at 370 nm. Analysis of the luminescence decay profiles against time was accomplished with the Decay Analysis Software DAS6 provided by the manufacturer.

The samples for confocal measurements were prepared dispersing the material in CHCl_3 through mild sonication. $\sim 50 \mu\text{L}$ of this solution was spin coated onto a microscopic glass slide. The images were recorded on a NIKON's A1 confocal laser scanning microscope using 400 nm laser and 60X oil immersion objective lens (N.A. 1.4).

Thin films of PMMA (polymethyl methacrylate) doped with **MWCNT-1-[EuL₄]** were prepared from a 200 g·L⁻¹ PMMA (MW = 35,000) solution in toluene, containing 1% w/w of **MWCNT-1-[EuL₄]**, spin-coated on 2"× 2" borosilicate glass substrates, cut from microscope slides. Spin-coating was then performed by spreading 500 μl of the starting solution onto the spinning substrate (4,000 rpm for 60s).

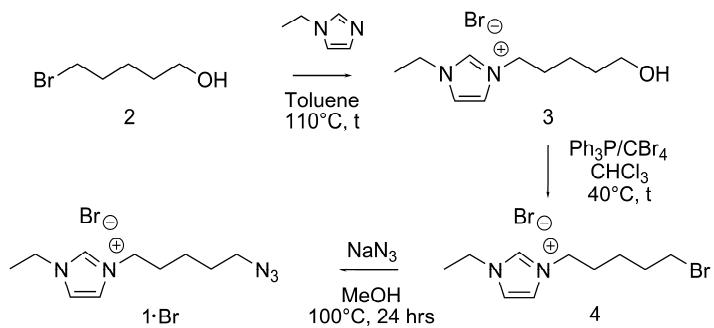
Chemicals were purchased from Aldrich, and used as received. Solvents were purchased from Aldrich and deuterated solvents from Euriso-top. Multi-walled carbon nanotubes (MWCNTs) NC 7000 were kindly provided by Nanocyl.

Synthesis

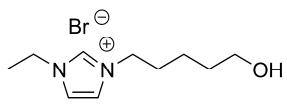


Scheme S1. Synthetic pathway for the preparation of $[\text{EuL}_4]\cdot \text{NEt}_4$

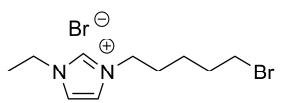
Tetraethylammonium tetrakis[4,4',4''-trifluoro-1-(naphtha-2-yl)-1,3-butandiono]europium(III) ($[\text{EuL}_4]\cdot \text{NEt}_4$): To a solution 4,4',4''-trifluoro-1-(naphtha-2-yl)1,3-butanedione (**1**, 12 mmoles) in EtOH (15 mL), first $\text{NEt}_4\cdot\text{OH}$ 40% (w/w) (12 mmoles), and subsequently $\text{Eu}(\text{NO}_3)_3\cdot 5 \text{ H}_2\text{O}$ (4 mmoles) were added. The solution was then heated at 60° C for 4 hrs, before letting it reach room temperature. The solvent was finally evaporated and water (50 mL) was added to the residual sticky solid under vigorous stirring. The solid was then collected, washed with water and dried. Purification by crystallization from the hot mixture of toluene/acetone (5:1), afforded $[\text{EuL}_4]\cdot \text{NEt}_4$ (75%) as a yellow crystalline solid. M.p. > 150 °C. Elemental Analysis: Calc. for $\text{C}_{64}\text{H}_{52}\text{EuF}_{12}\text{NO}_8$: C, 57.23; H, 3.90; N, 1.04. Found: C, 57.75; H, 4.11; N, 1.02%. IR (KBr, cm^{-1}): ν 3435.05, 1621.44, 1527.42, 1456.49, 1303.91, 1181.13, 1139.79, 957.52, 869.27, 793.40, 682.06, 564.12, 475.87. MS (LC-MS, ESI): found 1211 $[\text{M}]^+$, $\text{C}_{56}\text{H}_{32}\text{EuF}_{12}\text{O}_8$ requires = 1211.11. (See also crystal structure data).



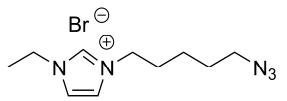
Scheme S2. Synthetic pathway for the preparation of **1-Br**



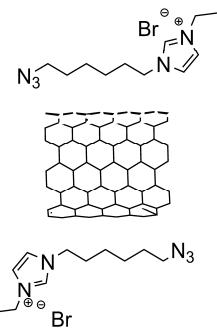
1-(5-Hydroxypentyl)-3-ethylimidazolium bromide (3): N-ethylimidazole (10 mmoles) was refluxed with 5-bromopentanol (11 mmoles) in 50 mL of toluene for 16hrs. After cooling to r.t., evaporation of the solvent under reduced pressure, afforded the product **3** (95%) as a colorless oil. ¹H-NMR (DMSO): δ 9.27 (*s*, 1H; -NCHN), 7.83 (*m*, 2H; -NCHCHN), 4.19 (*m*, 4H; the two -NCH₂), 3.37 (*t*, 2H; -CH₂OH), 1.80 (*m*, 2H; -(CH₂)₃CH₂CH₂OH), 1.43 (*m*, 5H; -CH₂CH₃ and -CH₂CH₂(CH₂)₃OH), 1.27 (*m*, 2H; -(CH₂)₂CH₂(CH₂)₂OH); ¹³C-NMR (DMSO): δ 135.65, 122.39, 122.12, 60.25, 48.83, 44.19, 31.64, 29.19, 22.14, 15.03. IR (cm⁻¹): ν 3374.02, 3136.85, 3078.54, 2934.68, 2865.47, 2069.98, 1567.65, 1452.56, 1164.07, 1048.98, 835.92, 755.05, 633.74. MS (LC-MS, ESI): found 183 [M]⁺, C₁₀H₁₉ON₂ requires = 183.14.



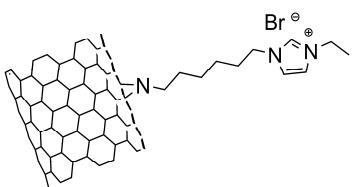
1-(5-Bromopentyl)-3-ethylimidazolium bromide (4): In order to obtain the active complex [Ph₃P-CBr₃]•Br, PPh₃ (12 mmoles) is first heated at 60° C with CBr₄ in CHCl₃ (50 ml) for 1 h. **3** (10 mmoles) was added and the reaction kept stirring for 12 hrs at the reflux temperature. After allowing the reaction to reach r.t., evaporation of the solvent *in vacuo* afforded a residue which was dispersed in a small amount of MeOH (5 mL). Distilled water was then added (50 mL) with vigorous stirring. Filtration and subsequent concentration of the solution under reduced pressure, yielded **4** (72%) as a brownish solid. M.p. 100-105 °C; ¹H-NMR (DMSO): δ 9.40 (*s*, 1H; -NCHN), 7.86 (*m*, 2H; -NCHCHN), 4.19 (*m*, 4H; the two -NCH₂), 3.30 (*m*, 2H; -(CH₂)₄CH₂Br), 1.84 (*m*, 2H; -(CH₂)₃CH₂CH₂Br), 1.42 (*m*, 5H; -CH₂CH₃ and -(CH₂CH₂(CH₂)₃Br), 1.22 (*m*, 2H; -(CH₂)₂CH₂(CH₂)₂Br); ¹³C-NMR (DMSO): δ 135.77, 122.40, 122.12, 48.40, 44.22, 28.58, 22.02, 15.05 (some signals are missing probably due to overlap). IR (cm⁻¹): ν 3416.72, 3087.56, 2059.75, 1631.61, 1563.43, 1454.20, 1166.82, 848.66, 754.82, 644.85. MS (LC-MS, ESI): found 245 [M]⁺, C₁₀H₁₈BrN₂ requires = 245.06.



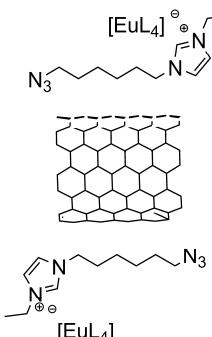
1-(5-Azidopentyl)-3-ethylimidazolium bromide (1-Br): NaN₃ (3 mmoles) was added to a solution of **4** (3 mmoles) in MeOH (40 mL), and the resulting mixture stirred at reflux temperature for 24 hrs. After cooling to r.t., the reaction was filtrated and the solution concentrated under vacuum. The crude was finally purified by hot filtration in CH₂Cl₂, affording compound **1-Br** (80%) as a sticky yellow solid. M.p. 62-65 °C; ¹H-NMR (DMSO): δ 9.36 (*s*, 1H; -NCHN), 7.84 (*m*, 2H; -NCHCHN), 4.20 (*m*, 4H; the two -NCH₂), 3.32 (*m*, 4H; -CH₂CH₂N₃), 1.84 (*m*, 2H; -CH₂CH₂(CH₂)₃N₃), 1.56 (*m*, 1H; -(CH₂)₂CH₂(CH₂)₂N₃ one of the two hydrogens of the group), 1.45 (*t*, 3H; -CH₂CH₃), 1.23 (*m*, 1H; -(CH₂)₂CH₂(CH₂)₂N₃); ¹³C-NMR (DMSO): δ 135.76, 122.40, 122.12, 50.30, 48.39, 44.21, 28.57, 27.4, 22.68, 22.02, 15.05. IR (cm⁻¹): ν 3532.68, 2105.49, 1562.05, 1447.71, 1162.46, 757.46, 636.92. MS (LC-MS, ESI): found 208 [M]⁺, C₁₀H₁₈N₅ requires = 208.15.



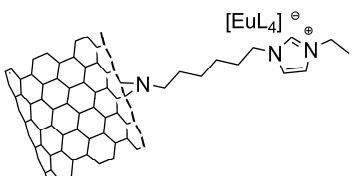
MWCNT-1·Br: MWCNT (50 mg) were first dispersed in mesitylene by ultrasonication for 5 minutes. To the suspension a 20-fold excess of **1·Br** (1.00 g) was added and the mixture refluxed at 170° C under vigorous stirring for 1 h. The reaction was poured onto a Millipore filter, and extensively washed with CH₂Cl₂ (600 mL) to remove the exceeding **1·Br**. The CNTs were then collected as sticky black agglomerate, dried under high vacuum at r.t. and subjected to analytical characterizations (XPS, TGA and photoluminescence studies).



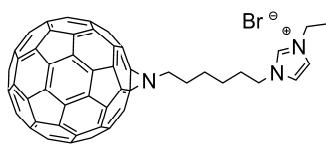
MWCNT-2·Br: MWCNT (50 mg) were first dispersed in mesitylene by ultrasonication for 5 minutes. To the suspension a 20-fold excess of **1·Br** (1.00 g) was added and the mixture refluxed at 170° C under vigorous stirring for 14 hrs. The reaction was then poured onto a Millipore filter, and washed with CH₂Cl₂ (600 mL) to remove the exceeding **1·Br**. The collected CNTs were re-dispersed by sonication in DMF (10 mL) for 10 minutes, the suspension filtered on a Millipore filter, and copiously rinsed with Et₂O (600 mL). The CNTs were collected as a thin black paper, and dried under high vacuum at r.t. and subjected to analytical characterizations (XPS, TGA and photoluminescence studies).



MWCNT-1·[EuL₄]: A suspension of **MWCNT-1·Br** (10 mg) in toluene (25 ml) was sonicated for 5 minutes, before a 10-fold excess of **[EuL₄]·NEt₄** was added to the mixture. Another cycle of sonication (5 minutes) was performed before allowing the suspension to gently stir at r.t. for 14 hrs. Filtration on Millipore filtrating apparatus and copious washings with CH₂Cl₂ (600 ml), allowed the removal of the un-functionalized complex. CNTs were recovered as a colored powder, dried under vacuum at r.t. and subjected to analytical characterizations (XPS, TGA, confocal microscope and photoluminescence studies).



MWCNT-2·[EuL₄]: A suspension of **MWCNT-2·Br** (10 mg) in toluene (25 ml) was sonicated for 5 minutes, before a 10-fold excess of **[EuL₄]·NEt₄** was added to the mixture. Another cycle of sonication (5 minutes) was performed before allowing the suspension to gently stir at r.t. for 14 hrs. Filtration on Millipore filtrating apparatus and copious washings with CH₂Cl₂ (600 ml), allowed the removal of the un-functionalized complex. CNTs were recovered as a black powder, dried under vacuum at r.t. and subjected to analytical characterizations (XPS, TGA and photoluminescence studies).



C₆₀-1·Br: To a solution of C₆₀ (0.7 mmoles) in mesitylene/DMSO (1:1), a solution of **1·Br** (0.7 mmoles) in DMSO (5 mL) was added and the whole stirred at 140 °C for 14 hrs. The precipitate formed during the reaction was filtered off and washed with H₂O. Precipitation upon addition of DMF, to a solution of the precipitate in CS₂ afforded **C₆₀-1·Br** (35%) as a golden solid insoluble in all common organic solvents. M.p. > 150 °C; IR (cm⁻¹): ν 3436.1, 2918, 1618, 1429, 1182, 994, 527. MS (LC-MS, APCI): found 900 [M]⁺, C₇₀H₁₈N₃ requires = 900.15.

Experimental Data

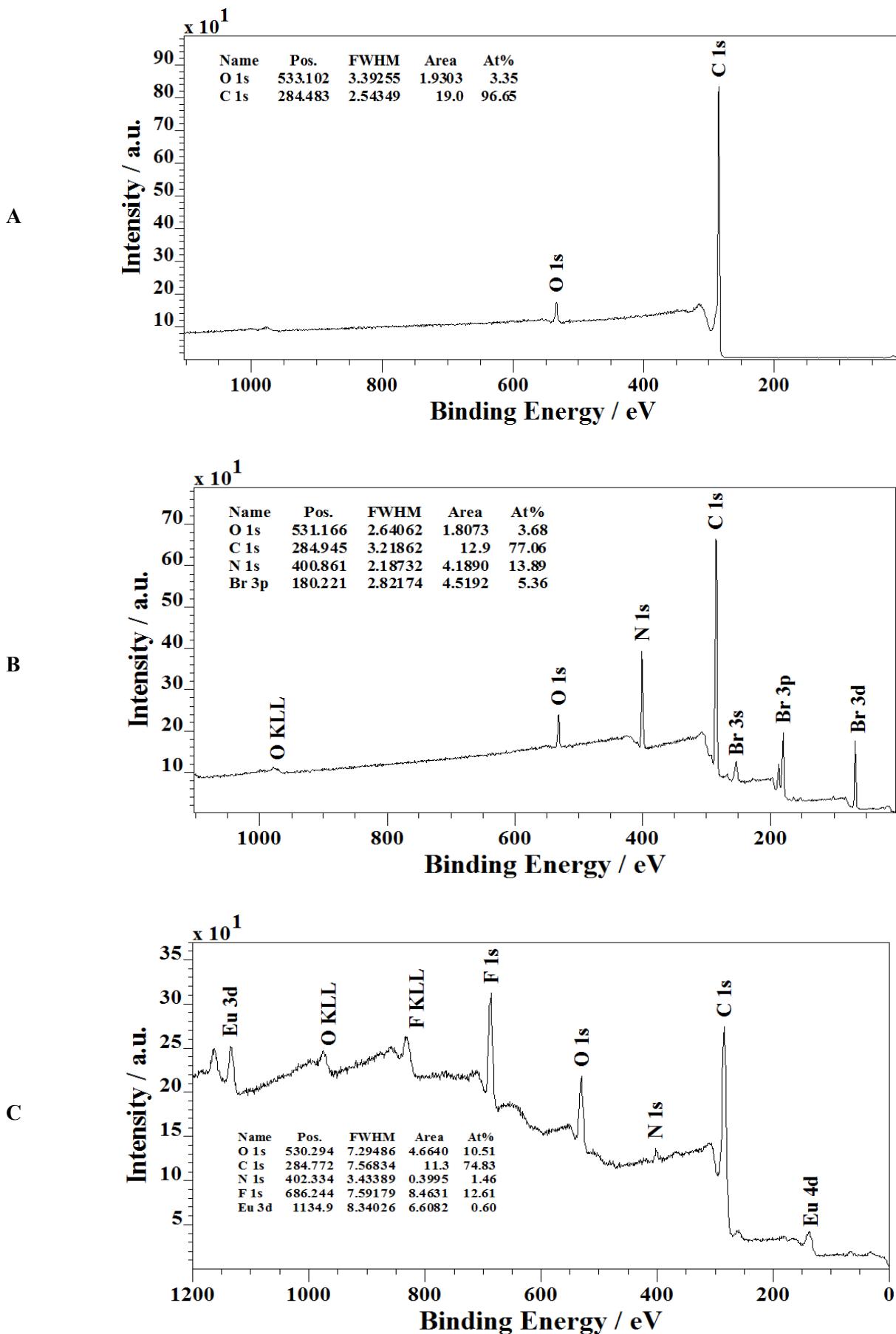
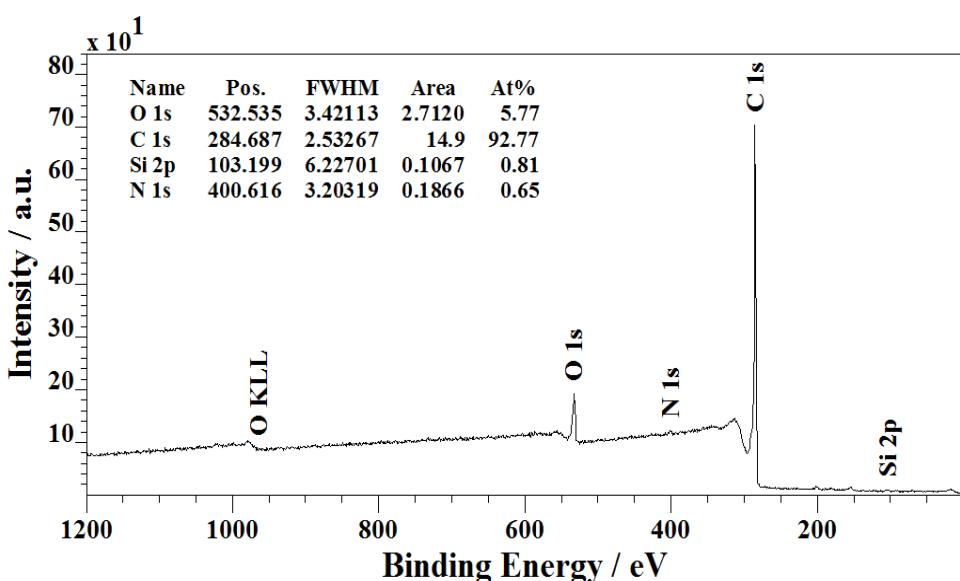
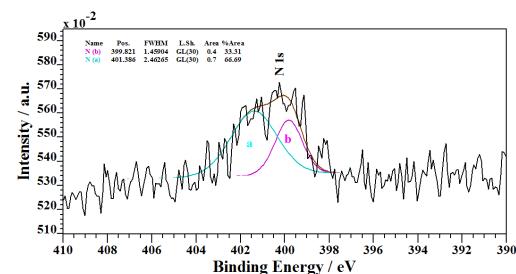


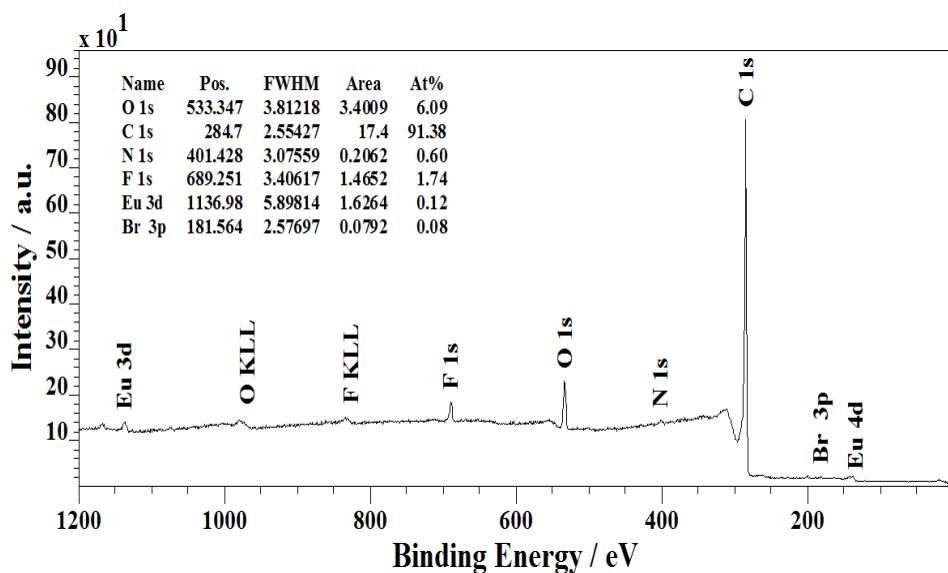
Fig. S1 Examples of XPS survey spectrum of **p**-MWCNT (A), MWCNT-1·Br (B), MWCNT-1·[EuL₄] (C).



A



B



C

Fig. S2 Examples of XPS survey spectra of **MWCNT-2·Br** (A) and **MWCNT-2·[EuL₄]** (C). The N 1s high resolution XPS of **MWCNT-2·Br** (B) shows two contributions at 399.8 eV and 401.4 eV. The peak at lower energy belongs to the aziridyl group, whilst the other can be assigned to the imine group in the form of the imidazolic ring according to the literature (*Langmuir*, 2005, **21**, 4268).

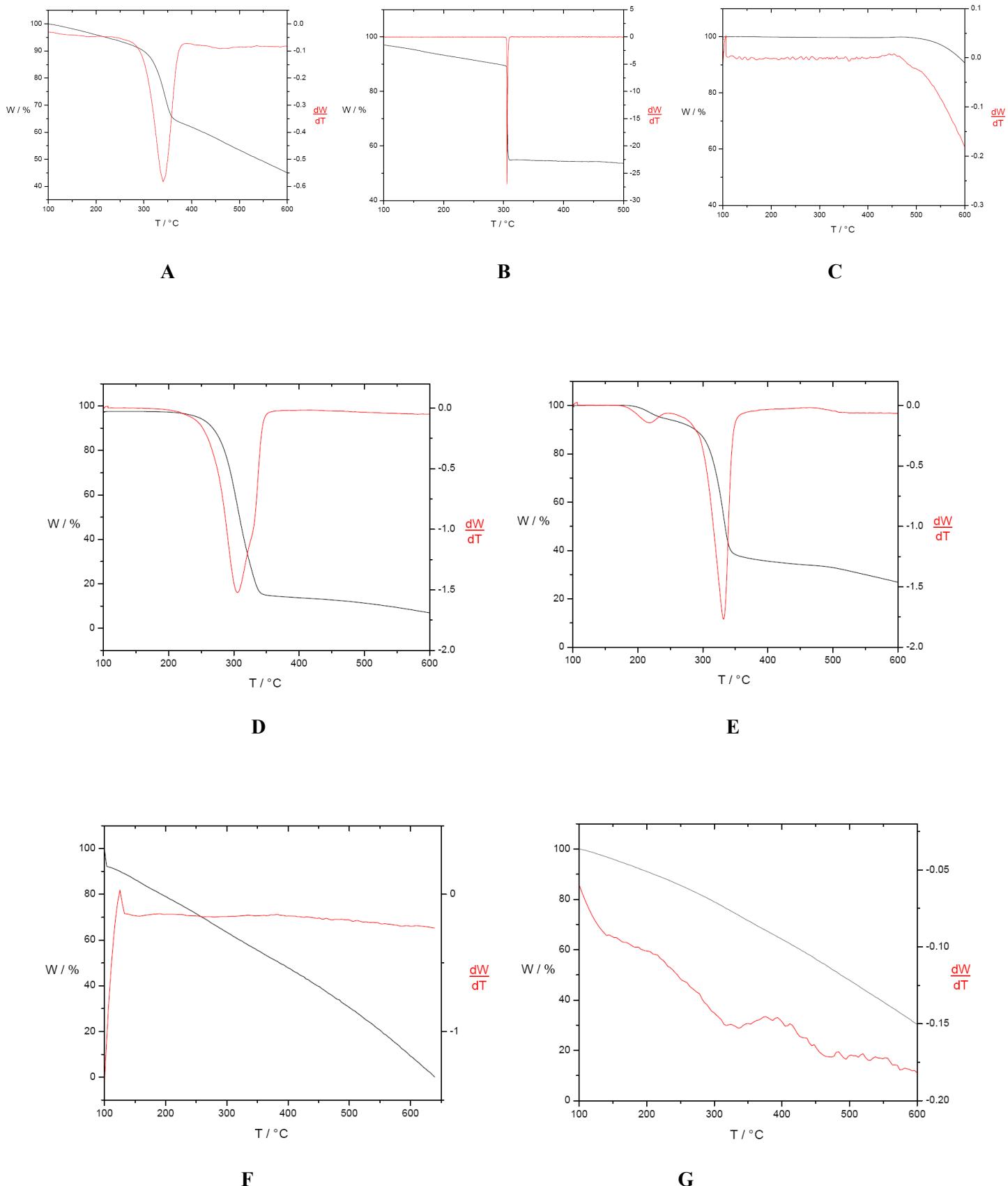


Fig. S3 Thermogravimetric analysis for **[EuL₄]·NEt₄** (A), **1·Br** (B), **p-MWCNTs** (C), **MWCNT-1·Br** (D), **MWCNT-1·[EuL₄]** (E), **MWCNT-2·Br** (F) and **MWCNT-2·[EuL₄]** (G), performed in air atmosphere with a heating ramp of 10° C/min. Before analysis the samples were dried at 0.05 mBar for 14 hrs.

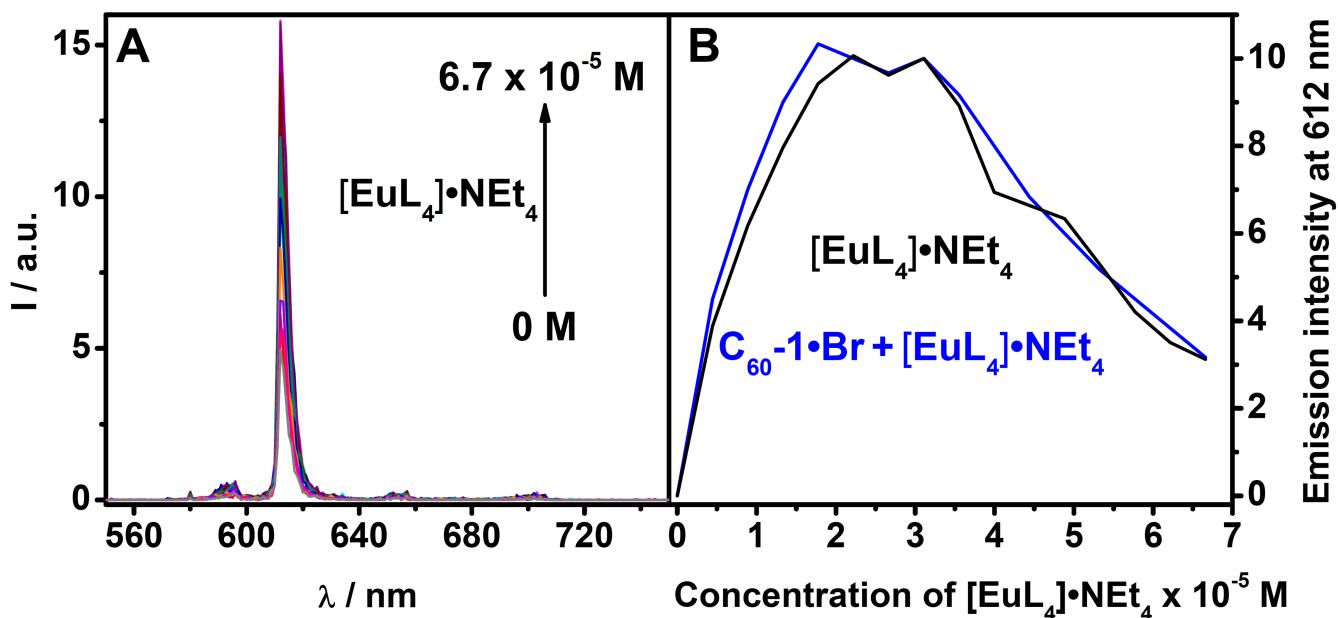


Fig. S4 (A) Emission spectral changes of $[\text{EuL}_4]\cdot\text{NEt}_4$ in CH_2Cl_2 , at various concentrations (blank titration; $C = 0\text{--}6.7 \times 10^{-5} \text{ M}$) and (B) Comparison of changes in the emission intensity of $\text{C}_{60}\text{-1}\cdot\text{Br} : [\text{EuL}_4]\cdot\text{NEt}_4$ and the blank titration at 612 nm as a function of concentration, indicates the similar emission trend in both cases. $\lambda_{\text{ex}} = 370 \text{ nm}$.

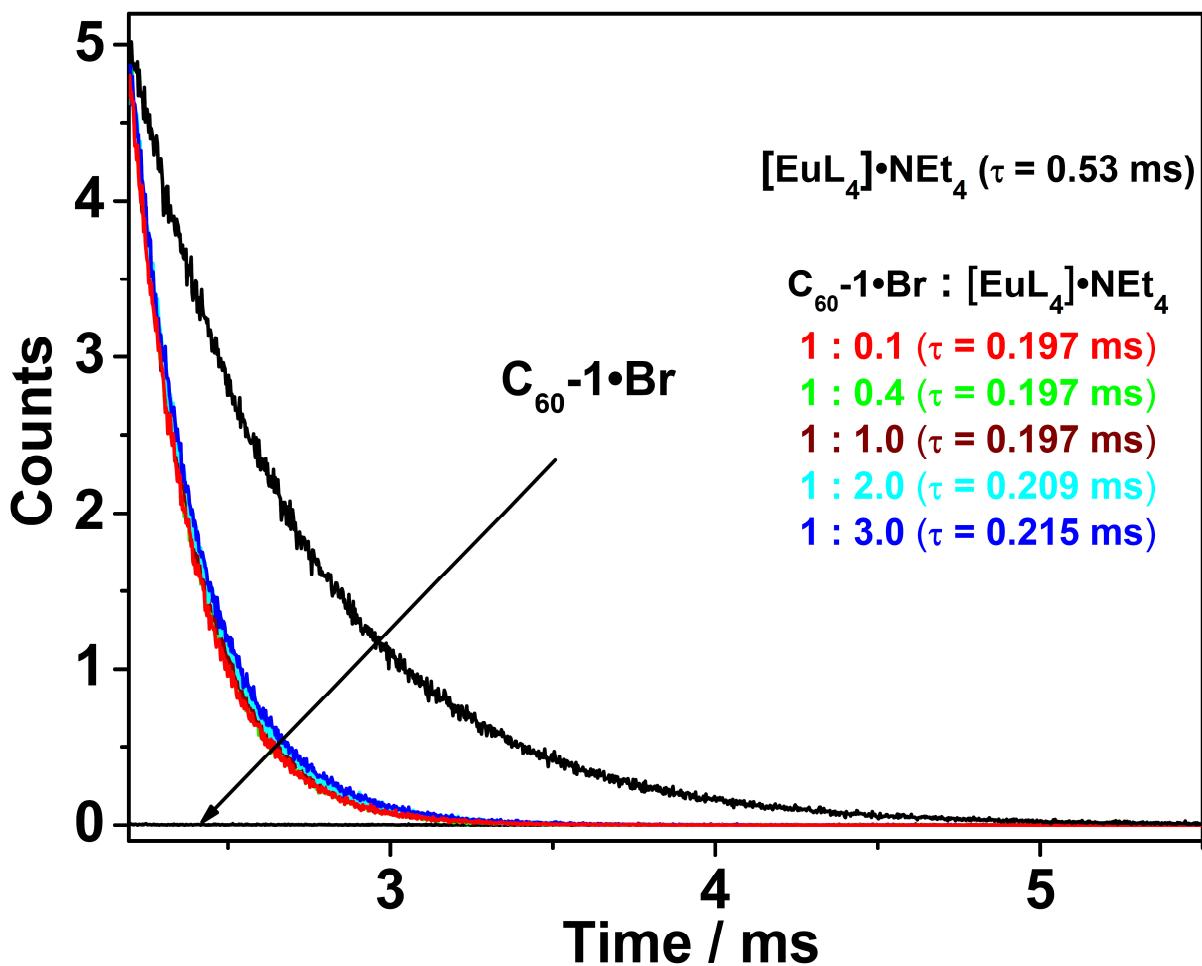


Fig. S5 Luminescence decay profiles of solution containing $\text{C}_{60}\text{-1}\cdot\text{Br} (C = 2.3 \times 10^{-5} \text{ M})$ and various concentrations of $[\text{EuL}_4]\cdot\text{NEt}_4 (C = 0\text{--}6.7 \times 10^{-5} \text{ M})$ in CH_2Cl_2 ; for comparison decay profile of $[\text{EuL}_4]\cdot\text{NEt}_4$ (black curve) is also shown. The decay profiles were collected at 612 nm upon exciting at 370 nm.

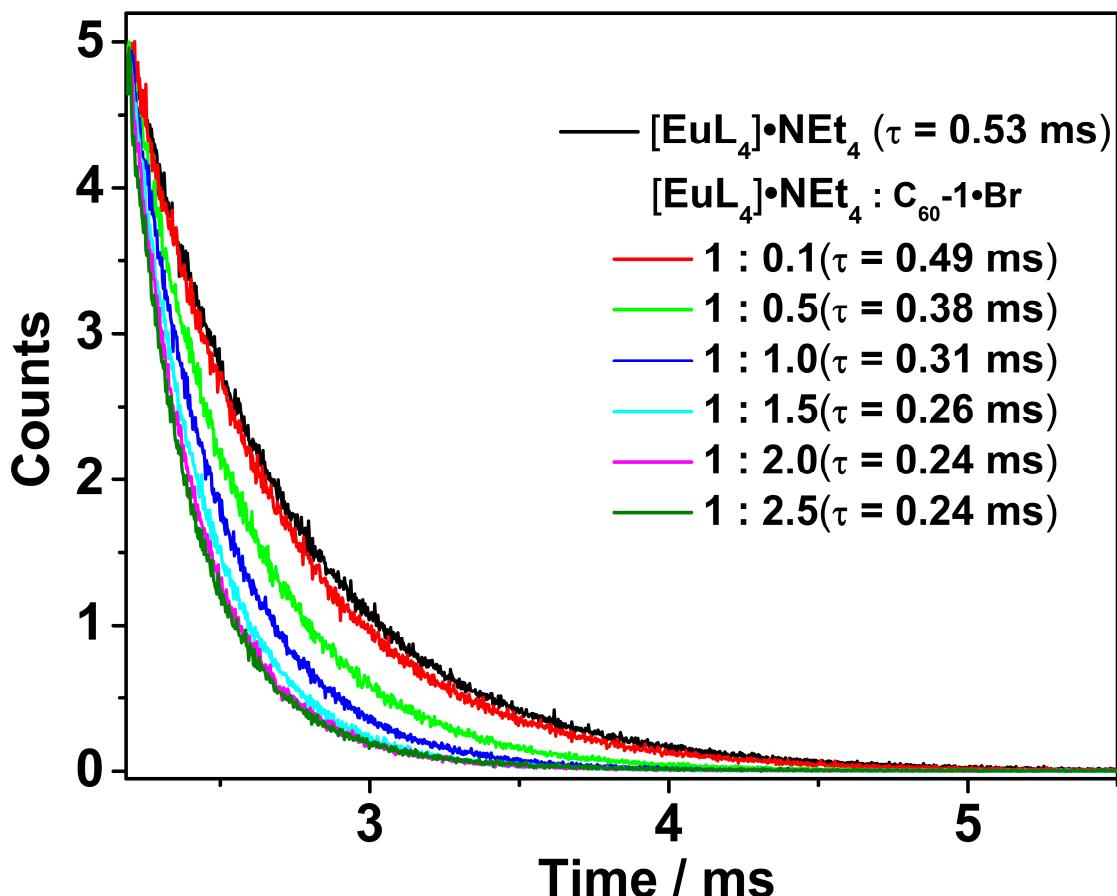


Fig. S6 Luminescence decay profiles in CH_2Cl_2 of $[\text{EuL}_4]\cdot\text{NEt}_4$ ($C = 3.4 \times 10^{-6}$ M) in presence of various concentration of $\text{C}_{60}\text{-}1\cdot\text{Br}$ ($C = 0\text{--}8.5 \times 10^{-6}$ M). The decay profiles were collected at 612 nm upon exciting at 370 nm monitored at 612 nm.

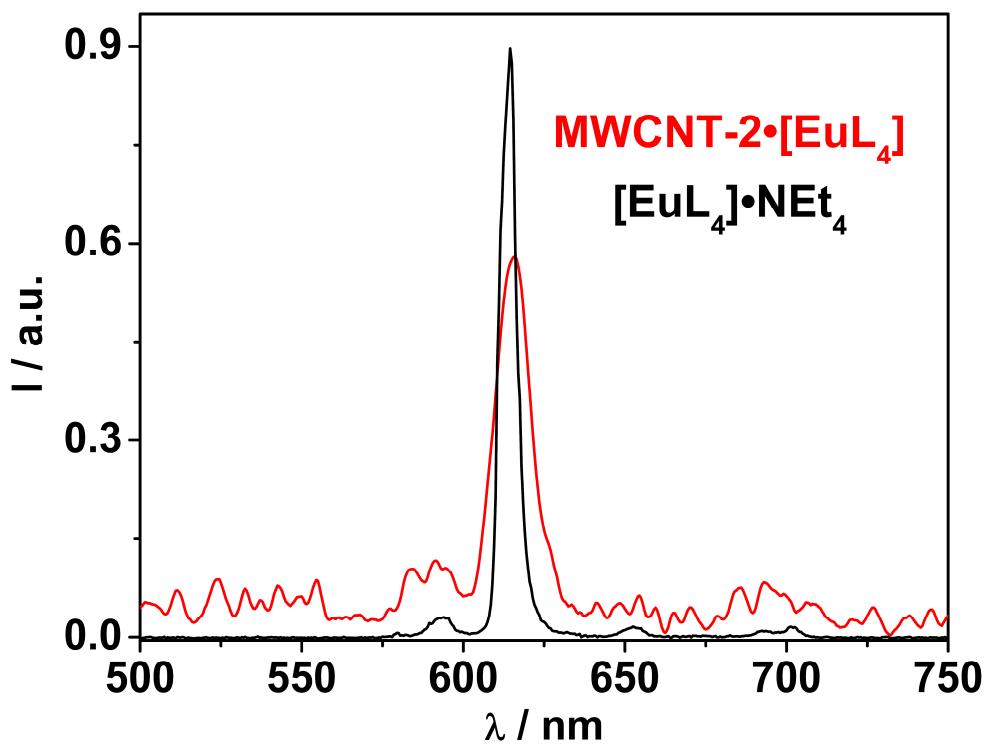


Fig. S7 Luminescence spectra of **MWCNT-2·[EuL₄]** (red) and **[EuL₄]·NEt₄** (black) in the solid state (KBr Disc, Phophorescence mode, $\lambda_{\text{exc}} = 370$ nm).

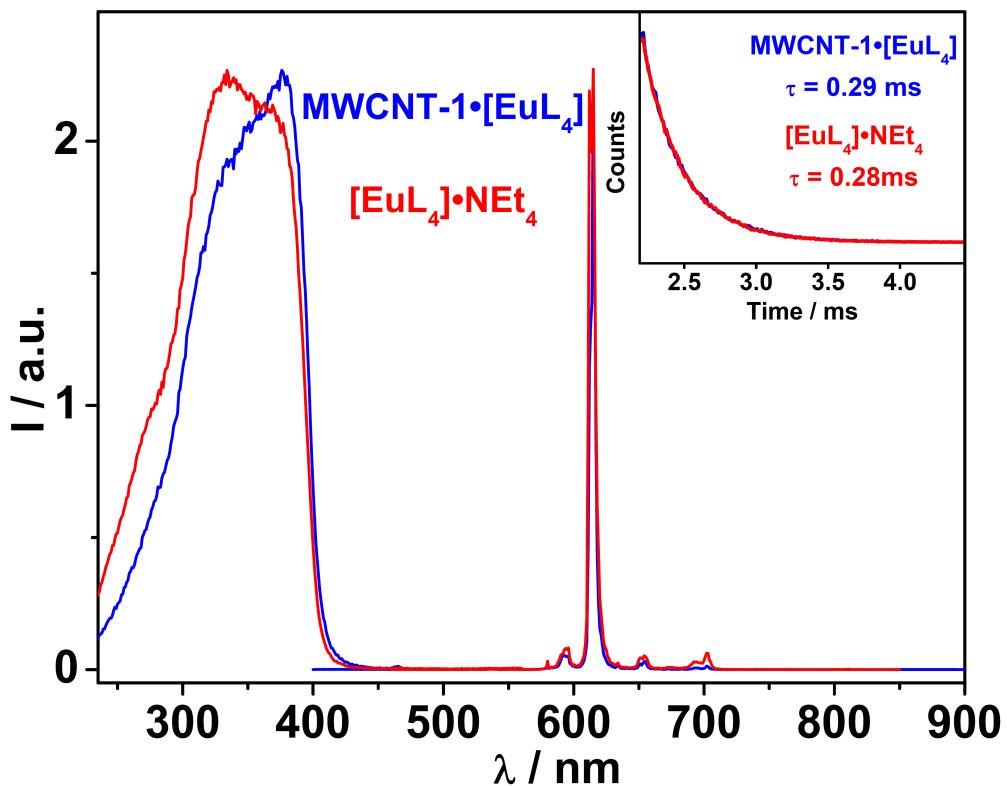
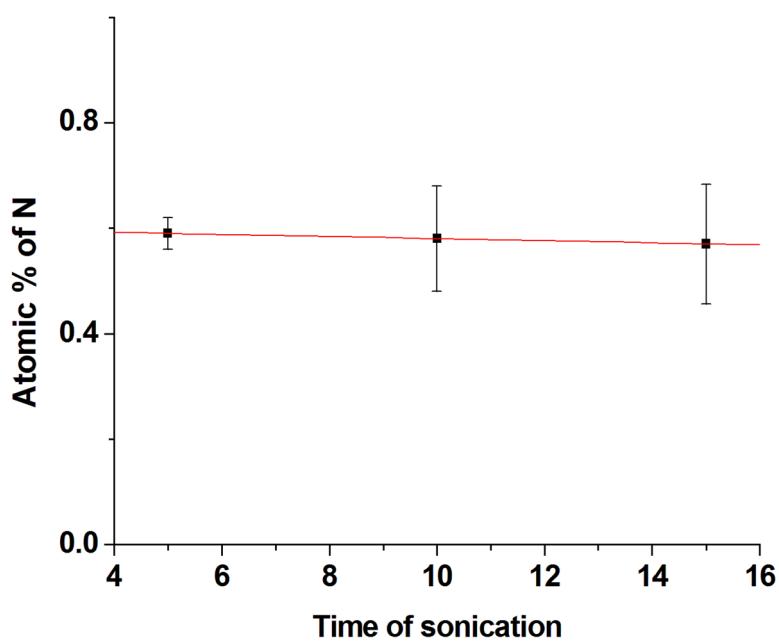
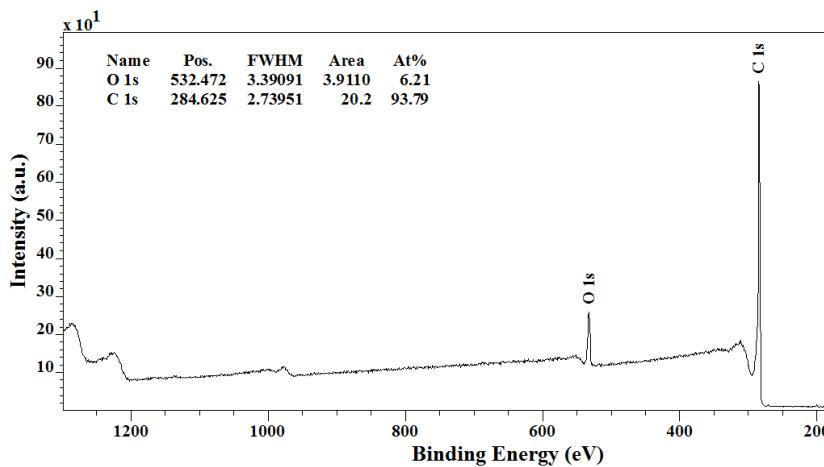


Fig. S8 Excitation (λ_{em} = 612 nm) and emission (λ_{exc} = 370 nm) spectra in the solid state (KBr pellet) of **MWCNT-1-[EuL₄]** (blue) and **[EuL₄]·NEm₄** (red); inset shows the corresponding emission decay profiles.



A



B

Fig. S9 (A) Atomic percentage of nitrogen (obtained by XPS) in **MWCNT-2-[EuL₄]** versus the time of sonication (min). Each value is the average of three analyses. (B) XPS survey spectra of a sample of **MWCNT-1-[EuL₄]** subject to the same sonication treatment in DMF for 15 min.

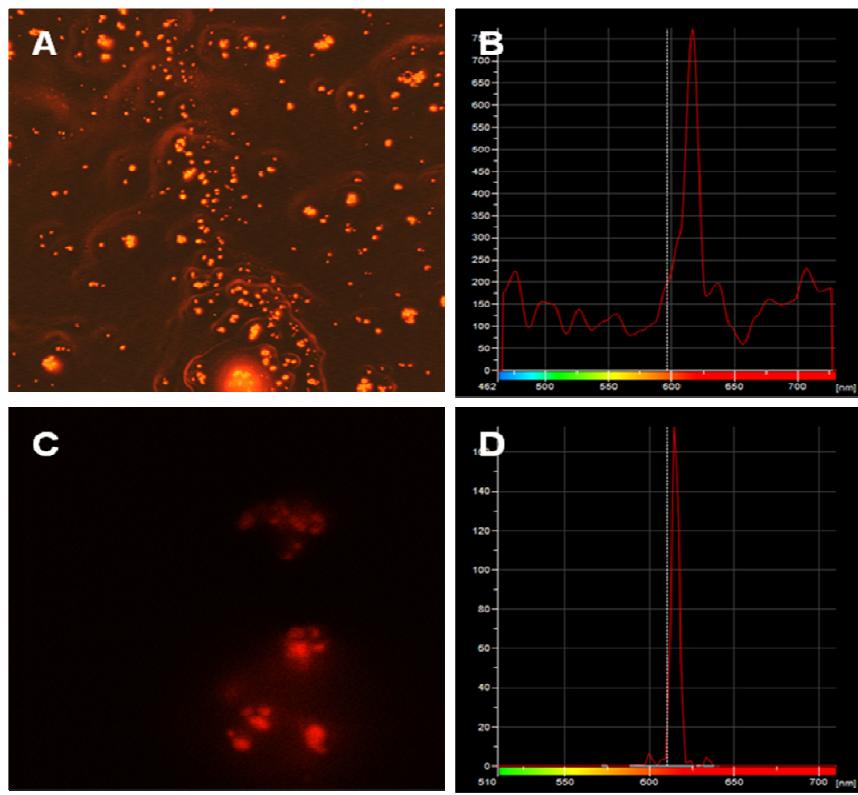


Fig. S10 Confocal images (A,C) recorded from different areas of **MWCNT-1-[EuL₄]** spin-coated onto a glass substrate and representative examples of emission spectra (B,D) recorded on the bright luminescent particles.