

# **C<sub>60</sub>-driven efficient encapsulation of a luminescent Eu(III) complex inside carbon nanotubes**

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## **Supporting Information**

## Instruments and methods

**Nuclear magnetic resonance spectroscopy (NMR).**  $^1\text{H}$  and  $^{13}\text{C}$  spectra were obtained on a 400 MHz Jeol JNM EX-400 NMR. Chemical shifts were reported in ppm according to tetramethylsilane using the solvent residual signal as an internal reference (*d*-chlorophorm:  $\delta_{\text{H}} = 7.26$  ppm,  $\delta_{\text{C}} = 77.16$  ppm). Coupling constants (*J*) were given in Hz. Resonance multiplicity was described as *s* (singlet), *d* (doublet), *t* (triplet), *dd* (doublet of doublets), *dt* (doublet of triplets), *q* (quartet), *m* (multiplet) and *br* (broad signal). Carbon spectra were acquired with a complete decoupling for the proton.

**Thermogravimetric analysis (TGA).** All the TGAs were performed with a *TGA Q500* instrument manufactured by TA instruments (Italy), under  $\text{N}_2/\text{air}$  (80:20) flow of  $55 \text{ ml}\cdot\text{min}^{-1}$  generally employing the following method: equilibration from room temperature to  $50^\circ\text{C}$ , isothermal heating at  $50^\circ\text{C}$  for 20 minutes, then thermal ramp from  $50^\circ\text{C}$  to  $800^\circ\text{C}$  with a heating rate of  $2^\circ\text{C}\cdot\text{min}^{-1}$ . The loss of weight is extracted as a difference by the weight % and evaluated at the plateau of the curve for each derivative.  $\mu\text{mol}/\text{mg}$  are calculated using these two formula:

$$1000 \text{ mg} : x = 100\% : \text{Loss of weight \%} \quad (1)$$

$$\frac{\text{mmol}}{\text{mg}} = \left( \frac{x}{MW} \right) / \text{mg} \quad (2)$$

**X-ray Photoelectron Spectroscopy (XPS).** Studies were performed with a SSX-100 system (Surface Science instrument). The photon source was a mono-chromatized Al  $K\alpha$  line ( $h\nu = 1486.6$  eV) applied with a takeoff angle of  $35^\circ$ . In the spectrum analysis, the background signal was subtracted by Shirley's method. The C 1s core level peak position of carbon atoms was taken as the reference at 284.5 eV. The spectrum analysis was carried out by fitting the peak shape obtained in the same analyzing conditions and other components with mixed (Gaussian + Lorentzian) line shapes. XPS atomic ratios have been estimated from the experimentally determined area ratios of the relevant core lines, corrected for the corresponding theoretical atomic cross-sections and for a square root dependence of the photoelectron kinetics energies. At least three spots of  $800 \mu\text{m}^2$  per sample were characterized and the results are expressed as mean  $\pm$  standard deviation.

## Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR).

Attenuated total reflectance (ATR) investigations in the infrared range ( $400\text{--}4000 \text{ cm}^{-1}$ ) were performed on pristine and functionalized samples. For the measurements a Bruker Tensor 37 spectrometer was used with a Bruker Helios ATR-attachment employing a single-bounce germanium ATR crystal, with spectral resolution  $1 \text{ cm}^{-1}$ . Spectra were taken on the samples as

received, no further sample manipulation was applied. All measured samples were in powder form. All measurements were completed in ambient conditions, each sample studied at 3-4 different spots (spot size  $250\ \mu\text{m}^2$ ).

### **Supercritical CO<sub>2</sub> (scCO<sub>2</sub>) induced peapod synthesis.**

The high-pressure reactor used for the experiments was described in detail elsewhere [György Bánsághi, Edit Székely, David Méndez Sevilano, Zoltán Juvancz, Béla Simándi: Diastereomer salt formation of ibuprofen in supercritical carbon dioxide, *J. of Supercritical Fluids* 69 (2012), 113-116]. Freshly distilled carbon dioxide was carried by a pump through an inlet valve into the 36 ml stainless steel reactor vessel. The reactor is equipped with a pressure transducer, a thermocouple and a rupture disc. Adequate mixing was ensured by a stir bar rotated by a magnetic stirrer. The reactor was maintained at a constant temperature (50 °C) via thermostated water flowing through the reactor's aluminum jacket, circulated by a thermostat. The pressure was kept constant 15 MPa for 96 hours after starting the mixing. When the desired time elapsed, the reactor was cooled to 25 °C (pressure dropped to 6.7 MPa). The reactor was depressurized slowly (approx. 40 min) by taking the gaseous phase of carbon dioxide. Carbon dioxide leaving the reactor passed through a filter and an outlet valve where it expanded to atmospheric pressure and was bubbled through methanol. The dry sample was collected from the reactor after depressurization.

**High Resolution Transmission Electron Microscopy (HRTEM).** Nanotube samples were dispersed in isopropanol and drop cast onto lacey carbon coated copper TEM grids for HRTEM analysis. HRTEM analysis was performed on a JEOL-2100F TEM microscope with a resolution limit of 0.2 nm. The imaging conditions were carefully tuned by lowering the accelerating voltage of the microscope to 100 kV and reducing the beam current density to a minimum in an attempt to minimise the electron beam induced damage of the sample. EDX spectra were recorded for small bundles of nanotubes (3-10 tubes) on a JEOL 2100F TEM equipped with an Oxford Instruments X-rays detector at 100 kV.

**Photoluminescence measurements (PL).** Steady-state emission and excitation spectra were recorded in front face mode on a HORIBA Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W Xenon arc lamp and a TBX-4-X single-photon-counting as excitation source and detector, respectively. Emission spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Photoluminescence decays were measured with a FluoTime 300 "EasyTau" apparatus (PicoQuant) equipped with subnanosecond LDH sources (375, 405, 440, 510 and 640 nm, 50-100 ps pulsewidth)

powered by a PicoQuant PDL 820 variable (0.2-80 MHz) pulsed power supply. A PMA-C and a Hamamatsu H10330 PMT were employed for detection in the UV-visible (200-900 nm) and IR (900-1400 nm) respectively. Measurements were performed using a NanoHarp 250 MCS (Multichannel Scaler Card) histogram accumulating real-time processor. The decays were analyzed by means of PicoQuant FluoFit Global Fluorescence Decay Analysis Software. For solid-state measurements KBr discs were used, characterized by a sample concentration of 1 mg of carbonaceous derivative diluted in 10 mg of KBr. Photoluminescence quantum yields (PLQY) were calculated according to Equation 1, with  $\tau_{obs}$  and  $\tau_{rad}$  representing the measured and radiative lifetimes respectively [D. Parker, J. A. G. Williams, J. Chem. Soc. Dalton Trans. 1996, 3613; J.-C. G. Bünzli, Chem. Rev. 2010, 110, 2729; F. S. Richardson, Chem. Rev. 1982, 82, 541]:

$$F_{Eu} = \frac{t_{obs}}{t_{rad}} \quad (1)$$

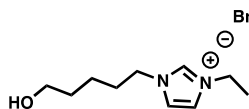
$$\frac{1}{\tau_{rad}} = A_{MD,0} \times n^3 \times \left( \frac{I_{tot}}{I_{MD}} \right) \quad (2)$$

$\tau_{rad}$  can in turn be estimated according to Equation 2 taking in account the amplitude weighted averaged lifetime values for  $\tau_{obs}$ .  $A_{MD,0}$  is the probability of the spontaneous  $^5D_0 \rightarrow ^7F_1$  decay ( $14.65 \text{ s}^{-1}$ ),  $n$  is the refractive index of the medium (air, 1.0008),  $I_{tot}$  is the area of the Eu (III) emission spectrum and  $I_{MD}$  is the area of the  $^5D_0 \rightarrow ^7F_1$  band.

**Materials and reagents.** Chemicals and solvents were purchase from Sigma Aldrich and used without further purification. Deuterated solvents were purchased from Eurisotop. SWCNTs were purchased from Carbon Solutions (P2-SWNT). DWCNTs and MWCNTs were kindly provided by Nanocyl. HeLa cells were obtained from ATCC/LGC Standards GmbH (Wesel, Germany). 4,6-diamidino-2-phenylindole dihydrochloride (DAPI, nuclear stain) was purchased from Polysciences Europe GmbH (Eppelheim, Germany).

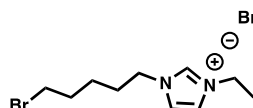
## Synthesis

### 1-(5-Hydroxypentyl)-3-ethylimidazolium bromide (**2**)



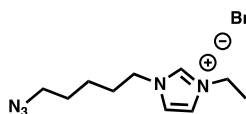
*N*-ethylimidazole (960 mg, 10 mmols) was refluxed with 5-bromopentanol (1.84g, 11 mmols) in 50 ml of toluene for 16 hours. After cooling to r.t., evaporation of the solvent under reduced pressure, afforded the product **2** (95%) as a colorless oil.  $^1\text{H}$ -NMR ( $d_6$ -DMSO):  $\delta$  9.27 (*s*, 1H; -NCHN), 7.83 (*m*, 2H; -NCHCHN), 4.19 (*m*, 4H; the two -NCH<sub>2</sub>), 3.37 (*t*, 2H; -CH<sub>2</sub>OH), 1.80 (*m*, 2H; -(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 1.43 (*m*, 5H; -CH<sub>2</sub>CH<sub>3</sub> and -CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>OH), 1.27 (*m*, 2H; -(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>OH);  $^{13}\text{C}$ -NMR ( $d_6$ -DMSO):  $\delta$  135.65, 122.39, 122.12, 60.25, 48.83, 44.19, 31.64, 29.19, 22.14, 15.03. IR (cm<sup>-1</sup>):  $\nu$  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 183.12 [M]<sup>+</sup>, C<sub>10</sub>H<sub>19</sub>ON<sub>2</sub> requires = 183.14.

### 1-(5-Bromopentyl)-3-ethylimidazolium bromide (**3**)



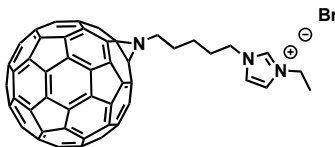
In order to obtain the active complex [Ph<sub>3</sub>P-CBr<sub>3</sub>] $\cdot$ Br, PPh<sub>3</sub> (3.14 g, 12 mmols) is first heated at 60 $^\circ$  C with CBr<sub>4</sub> in CHCl<sub>3</sub> (50 ml) for 1 h. **2** (1.83 g, 10 mmols) was hence added and the reaction kept stirring for 12 hours at the 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 **3** (72%) as a brownish solid. M.p. 100-105  $^\circ$ C;  $^1\text{H}$ -NMR ( $d_6$ -DMSO):  $\delta$  9.40 (*s*, 1H; -NCHN), 7.86 (*m*, 2H; -NCHCHN), 4.19 (*m*, 4H; the two -NCH<sub>2</sub>), 3.30 (*m*, 2H; -(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>Br), 1.84 (*m*, 2H; -(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.42 (*m*, 5H; -CH<sub>2</sub>CH<sub>3</sub> and -(CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>Br), 1.22 (*m*, 2H; -(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Br);  $^{13}\text{C}$ -NMR ( $d_6$ -DMSO):  $\delta$  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<sup>-1</sup>):  $\nu$  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 245.08 [M]<sup>+</sup>, C<sub>10</sub>H<sub>18</sub>BrN<sub>2</sub> requires = 245.06.

### 1-(5-Azidopentyl)-3-ethylimidazolium bromide (**4**)



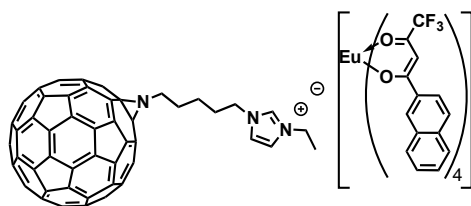
NaN<sub>3</sub> (195 mg, 3 mmols) was added to a solution of **3** (735 mg, 3 mmols) in MeOH (40 ml), and the resulting mixture stirred at reflux temperature for 24 hours. After cooling to r.t., the reaction was filtrated and the solution concentrated under vacuum. The crude was finally purified by hot filtration in CH<sub>2</sub>Cl<sub>2</sub>, affording compound **4** (80%) as a sticky yellow solid. M.p. 62-65 °C; <sup>1</sup>H-NMR (*d*<sub>6</sub>-DMSO): δ 9.36 (*s*, 1H; -NCHN), 7.84 (*m*, 2H; -NCHCHN), 4.20 (*m*, 4H; the two -NCH<sub>2</sub>), 3.32 (*m*, 4H; -CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>), 1.84 (*m*, 2H; -CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>N<sub>3</sub>), 1.56 (*m*, 1H; -(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>N<sub>3</sub> one of the two hydrogens of the group), 1.45 (*t*, 3H; -CH<sub>2</sub>CH<sub>3</sub>), 1.23 (*m*, 1H; -(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>N<sub>3</sub>); <sup>13</sup>C-NMR (*d*<sub>6</sub>-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<sup>-1</sup>): ν 3532.68, 2105.49, 1562.05, 1447.71, 1162.46, 757.46, 636.92. MS (LC-MS, ESI): found 208.10 [M]<sup>+</sup>, C<sub>10</sub>H<sub>18</sub>N<sub>5</sub> requires = 208.15.

### N-5-(3-ethylimidazolium)-pentyl-bromide aza-[60] fullerene (**1·Br**)



To a solution of C<sub>60</sub> (504 mg, 0.7 mmols) in mesitylene/DMSO (1 : 1), a solution of **4** (146 mg, 0.7 mmols) 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 H<sub>2</sub>O. Precipitation upon addition of DMF, to a solution of the precipitate in CS<sub>2</sub> afforded **1·Br** (35%) as a golden solid insoluble in all common organic solvents. M.p. > 150 °C; IR (cm<sup>-1</sup>): ν 3436.1, 2918, 1618, 1429, 1182, 994, 527. MS (LC-MS, APCI): found 900.20 [M]<sup>+</sup>, C<sub>70</sub>H<sub>18</sub>N<sub>3</sub> requires = 900.15.

### N-5-(3-ethylimidazolium)-pentyl-[Eu(III)tetrakis(2-naphthoyltrifluoro-acetonato)] aza-[60] fullerene (**1·[EuL<sub>4</sub>]**)

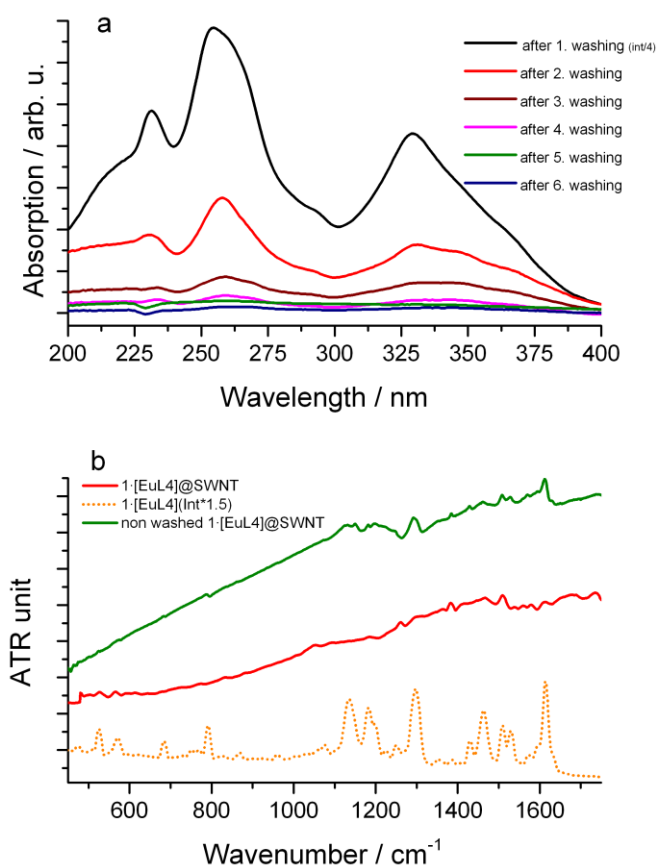


To a dispersion of the C<sub>60</sub>-based carrier (**1-Br**; 10 mg, 0.01 mmols) in toluene an excess of the precursor ionic complex **NEt<sub>4</sub>·[EuL<sub>4</sub>]** (10-fold excess; 100 mg, 0.07 mmols) was added, and the mixture allowed to stir in air atmosphere and at r.t., for 14 hours. Precipitation in CHCl<sub>3</sub>, followed by filtration on a Millipore apparatus and copious rinsing with CHCl<sub>3</sub> afforded the desired supramolecular complex as a brown powder (20 mg, 95 %). M.p. > 150 °C; IR (cm<sup>-1</sup>): ν 3436.1, 2918, 1618, 1500, 1429, 1250, 1182, 1150, 994, 750, 580, 527. MS (MALDI-MS): found 2113.30 [M]<sup>+</sup>, C<sub>134</sub>H<sub>50</sub>N<sub>4</sub>EuF<sub>12</sub>O<sub>8</sub> requires = 2113.15.

### Encapsulation of **1·[EuL<sub>4</sub>]**@CNTs

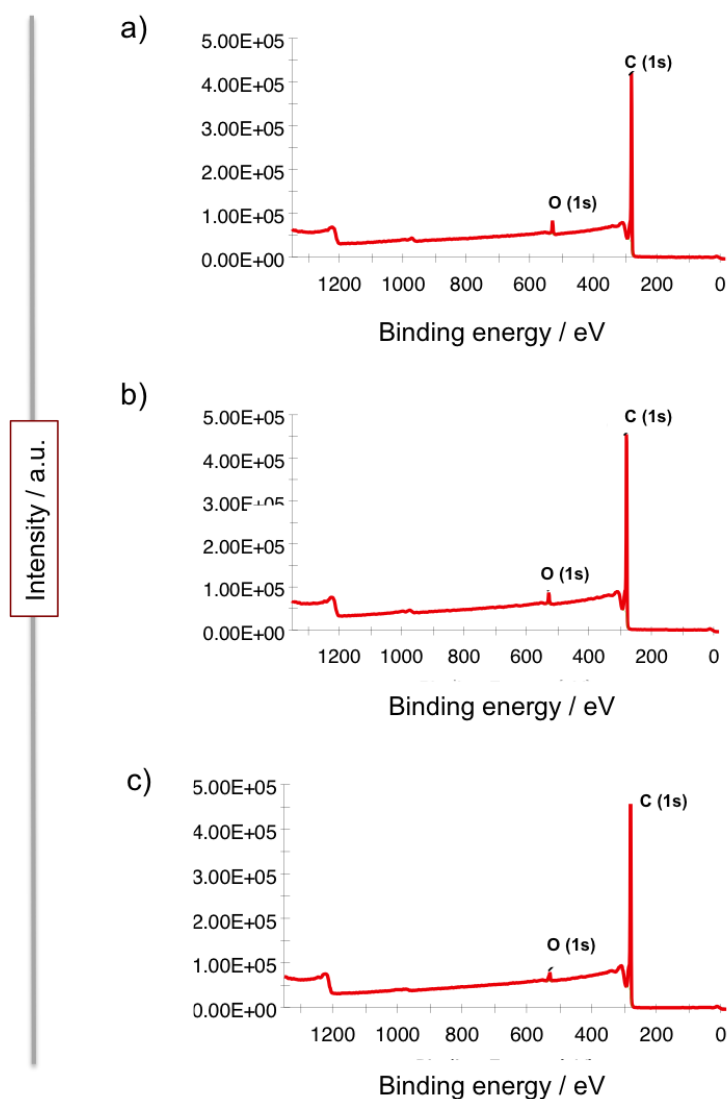
The encapsulation reaction of **1·[EuL<sub>4</sub>]** in SWCNTs, DWCNTs and MWCNTs was performed in a high-pressure closed reactor employing supercritical carbon dioxide (scCO<sub>2</sub>) as solvent. Before starting the reaction, CNTs were oxidized according to the required procedure, and subsequently annealed in air at 570 °C for 20 minutes to remove carboxylic groups at the entrance of the tube which might hamper the efficient encapsulation of the nano-carrier. Approximately 15 mg of **1·[EuL<sub>4</sub>]** was inserted together with the oxidized CNTs (20 mg) in the reactor, which was subsequently sealed and filled with CO<sub>2</sub> at 150 bars (volume of solvent = 30 ml). The reaction was then heated at 50 °C and stirred for 96 hours. At the end of the reaction time the reactor was cooled to 25 °C and the resulting gaseous CO<sub>2</sub> bubbled in 8 ml of methanol until complete depressurization of the reactor. The product, **1·[EuL<sub>4</sub>]**@CNTs, was finally collected and washed with CH<sub>2</sub>Cl<sub>2</sub> to remove **1·[EuL<sub>4</sub>]** adsorbed on the external walls of CNTs. Washings were monitored by UV-Vis absorption and IR-ATR (see Fig. S1).

## Experimental Part

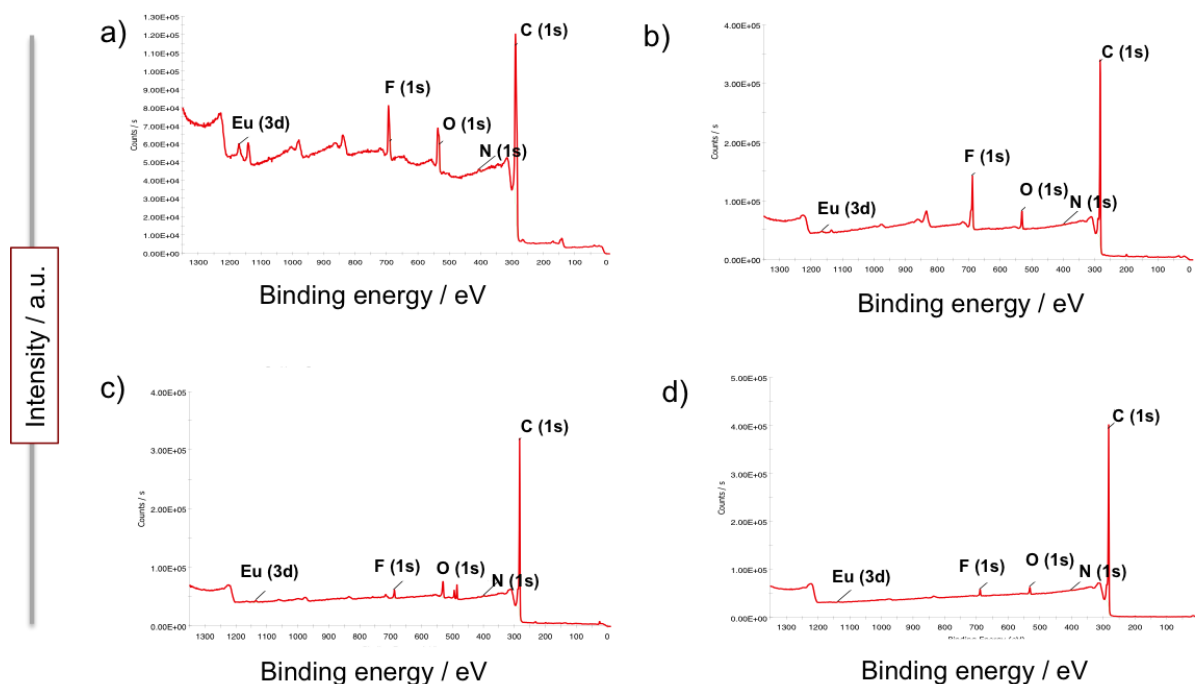


**Figure S1.** a) UV/VIS spectra of the washings performed on **1•[EuL<sub>4</sub>]@SWCNTs**. After the sixth purification treatment, the concentration of **1•[EuL<sub>4</sub>]** decreased below 0.001 mg/ml; b) ATR-IR spectra of **1•[EuL<sub>4</sub>]** and **1•[EuL<sub>4</sub>]@SWCNTs** before washing and after the sixth washing steps. Vibrational features of **1•[EuL<sub>4</sub>]** disappear on washing, indicating that there is no significant amount of adsorbed species on the surface of the nanotubes.

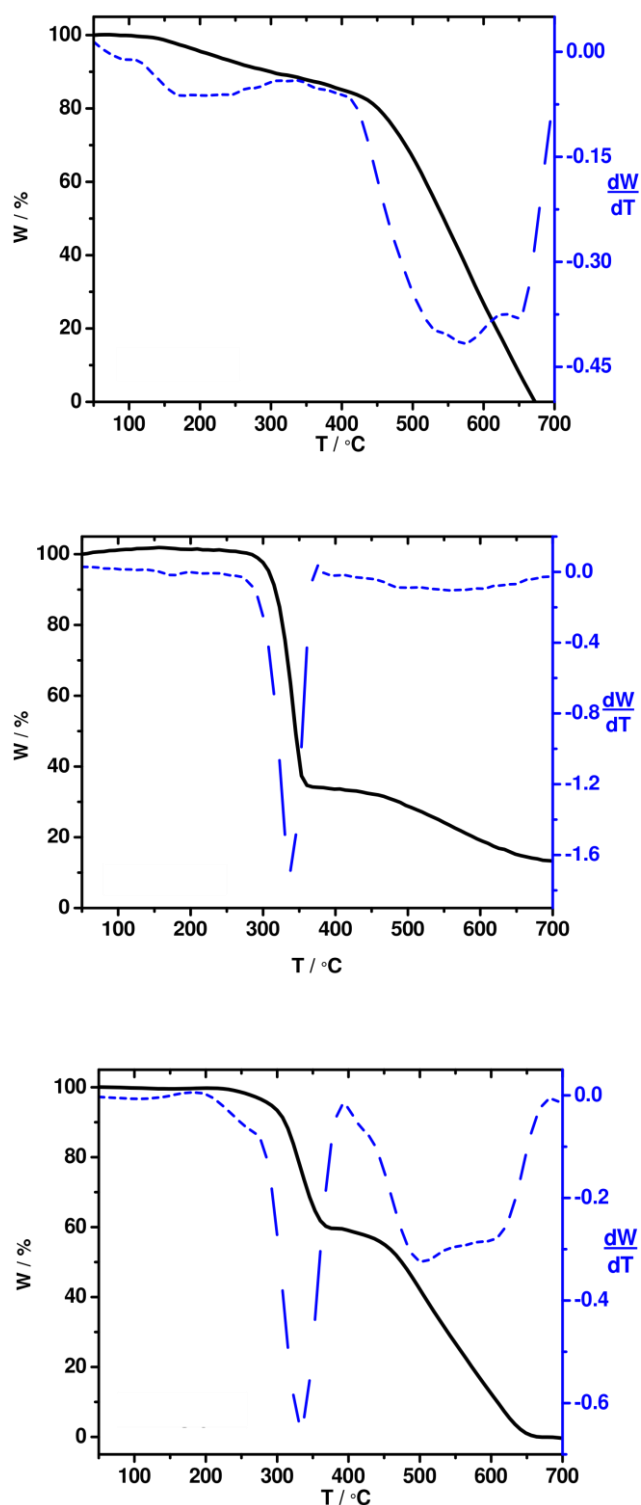




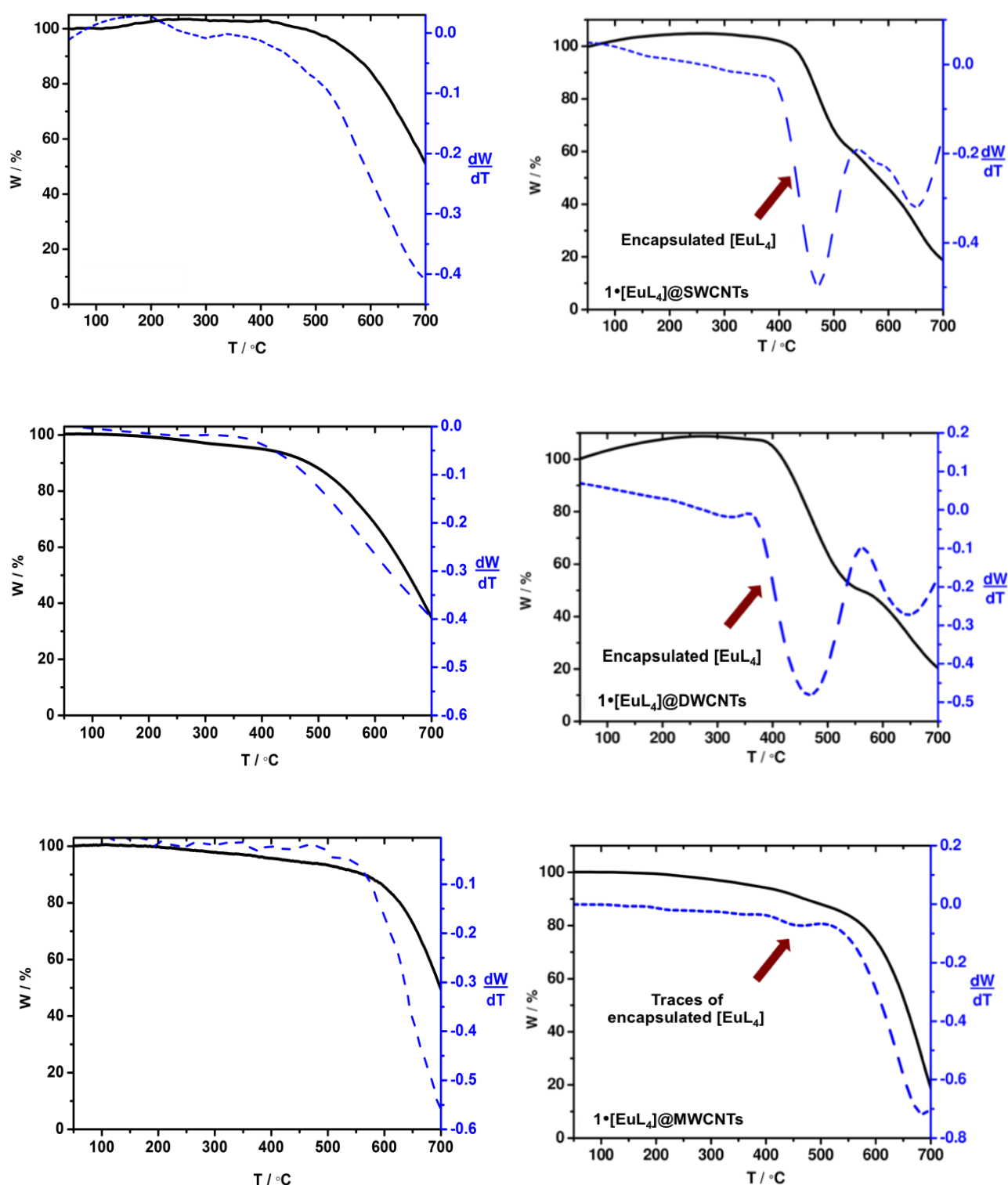
**Figure S2.** XPS survey spectra of: a) **ox-SWCNTs**, b) **ox-DWCNTs**, c) **ox-MWCNTs**. In the X axis the value represents the binding energy, expressed in eV, whilst for the Y axis arbitrary units represent the intensity of the signal.



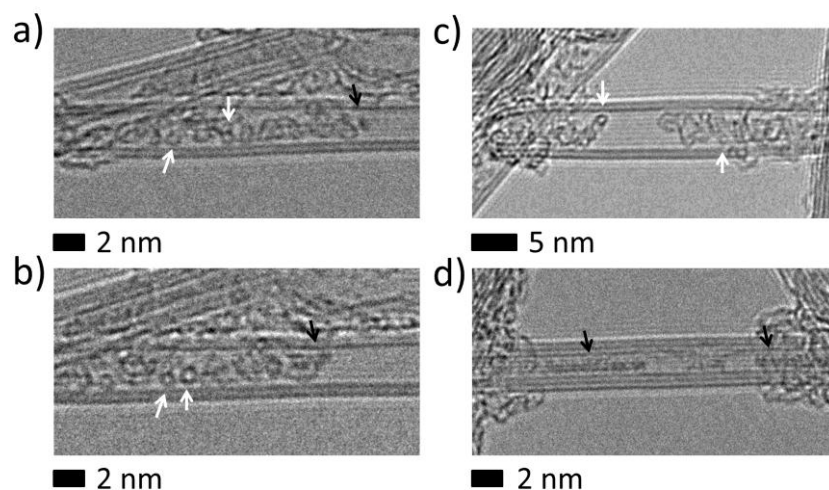
**Figure S3.** XPS survey spectra of: a)  $1\cdot[\text{EuL}_4]$ , b)  $1\cdot[\text{EuL}_4]@\text{SWCNTs}$ , c)  $1\cdot[\text{EuL}_4]@\text{DWCNTs}$ , and d)  $1\cdot[\text{EuL}_4]@\text{MWCNTs}$ . In the X axis the value represents the binding energy, expressed in eV, whilst for the Y axis arbitrary units represent the intensity of the signal.



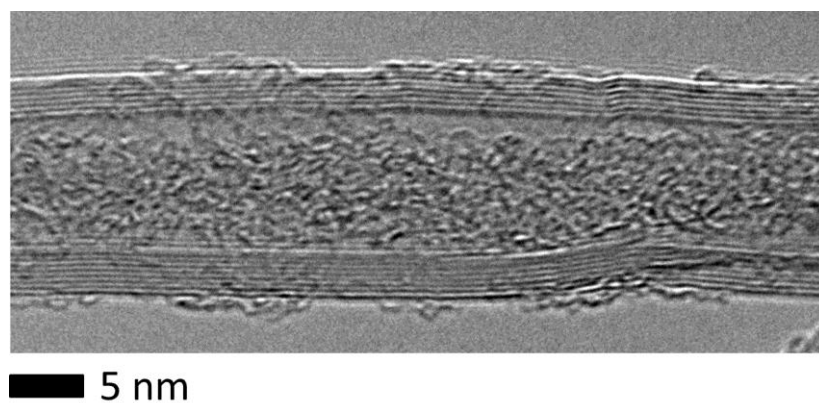
**Figure S4.** Thermogravimetric analysis for (from top to bottom): **4**; **1•Br**; **1•[EuL<sub>4</sub>]**. The traces reported were recorded in N<sub>2</sub>/air (80:20) atmosphere with a heating ramp of 2° C / min.



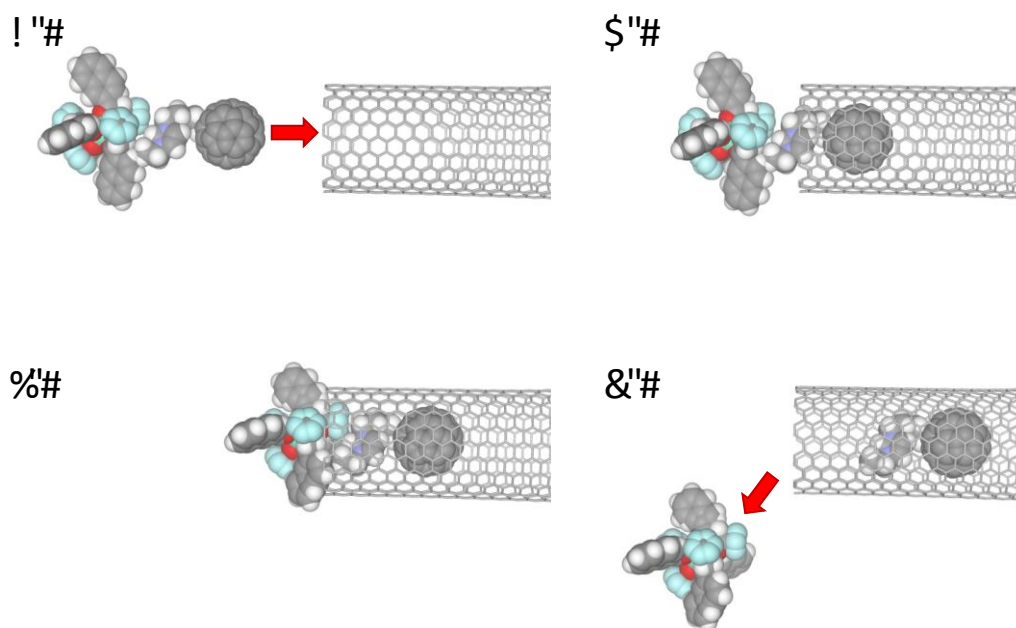
**Figure S5.** Thermogravimetric analysis for (from top to bottom): SW, DW and MWCNTs in their oxidized form (spectrum on the right) and corresponding encapsulation hybrid (spectrum on the left). The traces reported were recorded in  $\text{N}_2/\text{air}$  (80:20) atmosphere with a heating ramp of  $2^\circ \text{C} / \text{min}$ .



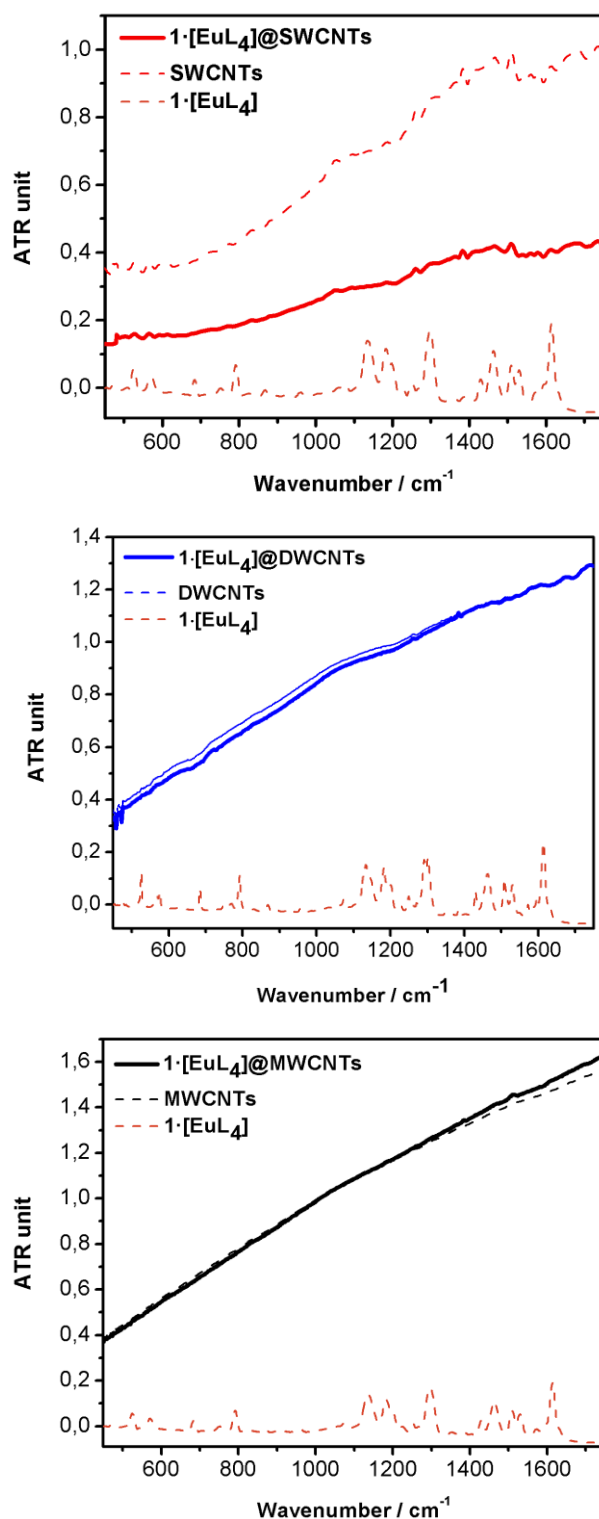
**Figure S6.** HRTEM images taken at 100 kV of a-d) **1•[EuL<sub>4</sub>]@DWCNTs** in which fullerene cages (white arrows) and Eu metal clusters and rods (black arrows) are observed indicating successful introduction of the Eu complex into the internal channel of the DWCNTs.



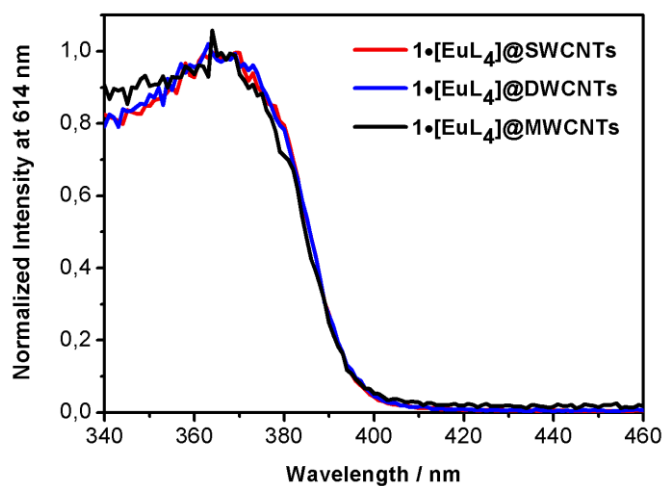
**Figure S7.** HRTEM image taken at 100 kV of **1•[EuL<sub>4</sub>]@MWCNTs** showing significant filling of the internal channel.



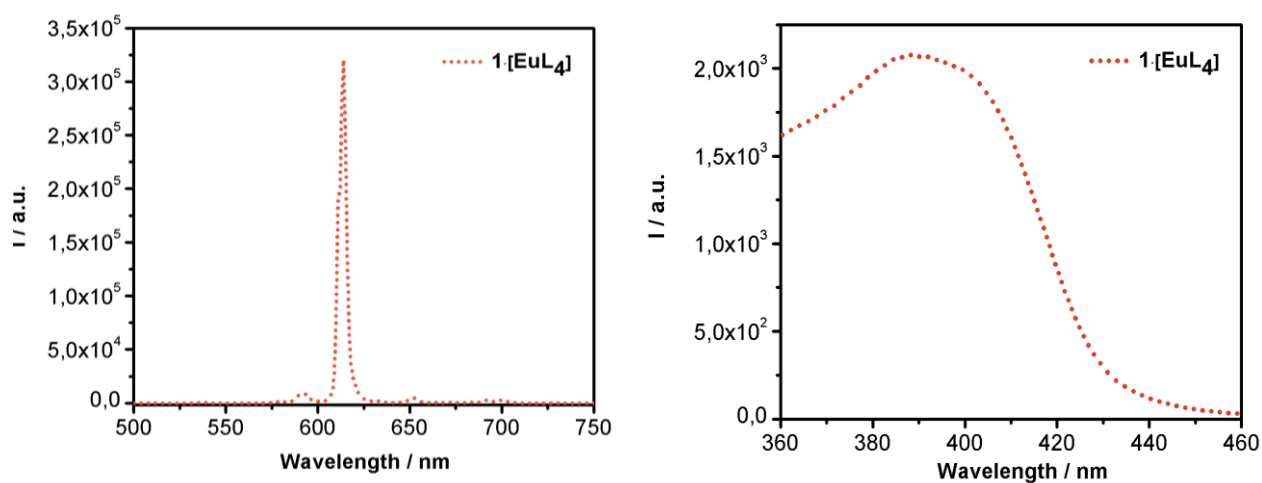
**Figure S8.** Schematic representation of the sequential encapsulation and the subsequent decomposition of  $1\bullet[\text{EuL}_4]$  when entering SWCNTs, showing how the Eu containing complex is forced to dissociate from the fullerene part (d) as the fullerene moves progressively further into the SWCNT during encapsulation ( $d_{\text{NT}} = 1.4\text{--}1.5\text{ nm}$ ).



**Figure S9.** IR-ATR spectra of (from top to bottom):  $1 \cdot [\text{EuL}_4]@\text{SWCNTs}$ ,  $1 \cdot [\text{EuL}_4]@\text{DWCNTs}$ , and  $1 \cdot [\text{EuL}_4]@\text{MWCNTs}$ . The lack of the intense signals of the Eu(III) complex indicates the absence of exohedral  $1 \cdot [\text{EuL}_4]$  confirming the efficiency of the cleaning procedure.



**Figure S10.** Excitation spectra of the Eu(III)-centred emission (recorded at 614 nm) of the three  $1\bullet[\text{EuL}_4]$ @CNTs hybrids.



**Figure S11.** Emission (left,  $\lambda_{\text{exc}} = 475 \text{ nm}$ ) and excitation (right, recorded  $\lambda_{\text{em}} = 614 \text{ nm}$ ) spectra of  $1\bullet[\text{EuL}_4]$ , performed in the solid state.