Supporting Information

Azobenzene-based Supramolecular Polymer for Processing MWCNTs

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EXPERIMENTAL DETAILS

Photophysical Characterization. Absorption spectra were recorded with a Perkin-Elmer l950 UV/Vis spectrophotometer in Helma 1 cm quartz cuvettes. Irradiation experiments of azobenzene units were carried out using a 100 W mercury lamp, the excitation wavelength was selected by means of Andover Corporation optical bandpass filters (10 ± 2 nm). All measurements were carried out in spectroscopy grade $CHCl_3$, DMSO (Carlo Erba) or tetrahydrofuran used without further purification, and under ambient atmosphere.

X-ray Photoelectron Spectroscopy (XPS). Studies were performed to investigate the chemical composition of the functionalised MWCNTs. For each analysis, 2 mg of material were deposited on a Cu 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 analysis were performed on three different spots using an ESCA SPECTROMETER where the photon source is a monochromatised Al Kα line ($h\nu$ = 1486.6 ev) applied with a take-off 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.

Microscopic Characterisation.

Transmission Electron Microscopy (TEM). All the low resolution TEM images were obtained from the deposition of 40 μL of a dispersions (approximately 1 mg·ml^{-1}) of **1_n⊙MWCNTs** in $CHCl_3$ onto Nickel grids (with carbon layer coating, 200 mesh); these grids were analysed with a *Philips 208* electron microscope at a 100 kV voltage, and the resulting images were collected with an *AMT* high–resolution digital imaging camera.

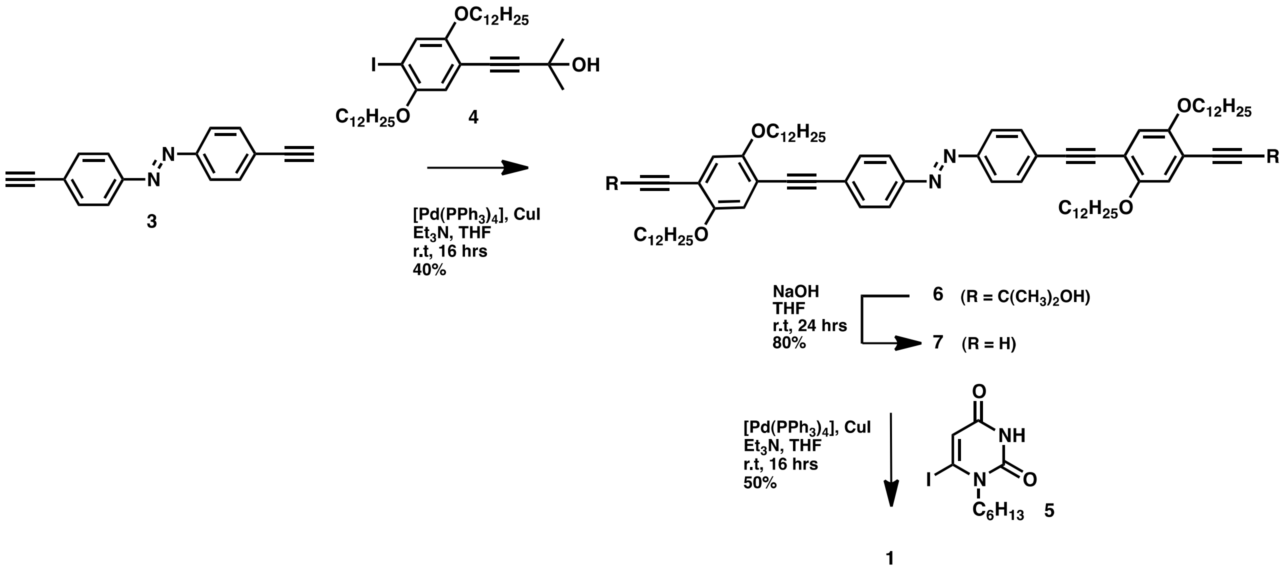
Tapping–mode Atomic Force Microscopy (TM–AFM). TM-AFM of the mica substrates was carried out on air at 298 K using a Nanoscope V (Digital Instruments Metrology Group, model MMAFMLN). The tips used in all measurements were phosphorus-doped silicon cantilevers (T = 20-80 mm, L = 115-135 mm, fo = 200-400 kHz, k = 20-80 N m^{-1}, Veeco) at a resonance frequency of ca. 300 kHz. The collected images were then analyzed with WsXm 4.0 software (Nanotec Electronica S. L.) and with Gwyddion (free and open source software as downloaded from http://gwyddion.net/). For the preparation of the sample twenty microliters of a dispersion (approximately 1 mg·ml^{-1}) of **1_n⊙MWCNTs** in $CHCl_3$ were drop cast onto freshly cleaved mica surfaces and the solvent was removed by environmental evaporation.

Thermogravimetric analysis (TGA). All the TGAs were performed with a *TGA Q500* instrument manufactured by TA instruments (Italy), under a N_2 flow of 60 ml·min^{-1} following this method: equilibration from room temperature to 100 °C in 10 minutes, isothermal heating at 100 °C for 10 minutes to remove eventual residual solvents traces, then thermal ramp from 100 °C to 700 °C in 72 minutes (heating rate of 10 °C·min^{-1}).

SYNTHESIS

Compounds were fully characterised (m.p., IR, ^{1}H and ^{13}C NMR, EI-MS, and ESI–HR-LCMS). NMR spectra were obtained on a Jeol JNM–EX400 (400 MHz ^{1}H–NMR). Chemical shifts are reported in ppm using the solvent residual signal as an internal reference ($CDCl_3$: $^1H = 7.26$ ppm, $^{13}C = 77.16$ ppm). The resonance multiplicity is described as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *dd* (doublet of doublets), *m* (multiplet), *br* (broad signal). IR spectra were recorded on a Perkin Elmer 2000 spectometer. Mass spectrometry measurements were performed on a Time-of-Flight Agilent Name high resolution Liquid Chromatography Mass Analyzer (TOF HR-LCMS), using the Electrospray ionisation mode operating in positive polarity (ESI$^+$). Melting Points (m.p.) were measured on a *Büchi* SMP-20. THF and NEt_3 were distilled from Na/benzophenone and CaH_2 respectively. Molecules **3**, **5** and **8** were synthesized according to previously reported procedures.[1-3]

Synthesis of Molecule 1



Scheme S1. Synthetic procedure to molecule **1**.

4-(2,5-bis(dodecyloxy)-4-iodophenyl)-2-methylbut-3-yn-2-ol (4). To a degassed solution of dry Et_3N (4 mL) and THF (4 mL), 1,4-bis(dodecyloxy)-2,5-diiodidobenzene[1] (0.5 g, 0.7 mmol), $[Pd(PPh_3)_4]$ (32.0 mg, 0.03 mmol), and CuI (11.0 mg, 0.05 mmol) were added and the mixture degassed a second time. 2-methyl-3-butyn-2-ol (0.07 mL, 0.7 mmol) was then added and the reaction mixture degassed one last time, before allowing the whole to stir overnight at r.t. under Ar.

The crude mixture was then filtered over celite, concentrated under vacuum and purified by CC (first cyclohexane, then cyclohexane/CH_2Cl_2 8:2) yielding **4** (260 mg, 57%) as a yellow solid. M.p. 42-46°C. ^{1}H-NMR ($CDCl_3$): δ 7.25 (*s*, 1H; Ar-C*H*); 6.80 (*s*, 1H; Ar-C*H*); 3.92 (*m*, 4H; the two –OCH_2); 1.78 (*m*, 4H; the two -OCH$_2$CH_2); 1.62 (*s*, 6H; the two -C(CH_3)$_2$OH); 1.48 (*m*, 4H; the two -O(CH$_2$)$_2$CH_2); 1.26 (*br*, 32H; the two –O(CH$_2$)$_3$(CH_2)$_8$CH$_3$); 0.88 (*m*, 6H; the two –O(CH$_2$)$_{11}$CH_3). ^{13}C-NMR ($CDCl_3$): δ 154.48, 151.84, 135.02, 123.78, 116.24, 113.06, 87.58, 78.32, 70.21, 69.80, 65.90, 32.06, 31.56, 29.81, 29.60, 26.12, 22.85, 14.28 (peaks in the aliphatic region are missing probably due to overlap). IR (cm^{-1}): ν 3413.9, 2916.5, 2846.4, 2364.2, 1616,9 1465.1, 1380.2, 1218.5, 1068.3, 849.6, 721.1, 519.5. MS (HR-LCMS, ESI$^+$): found 654.3521 [M]$^+$, $C_{35}H_{59}IO_3$ requires = 654.3509.

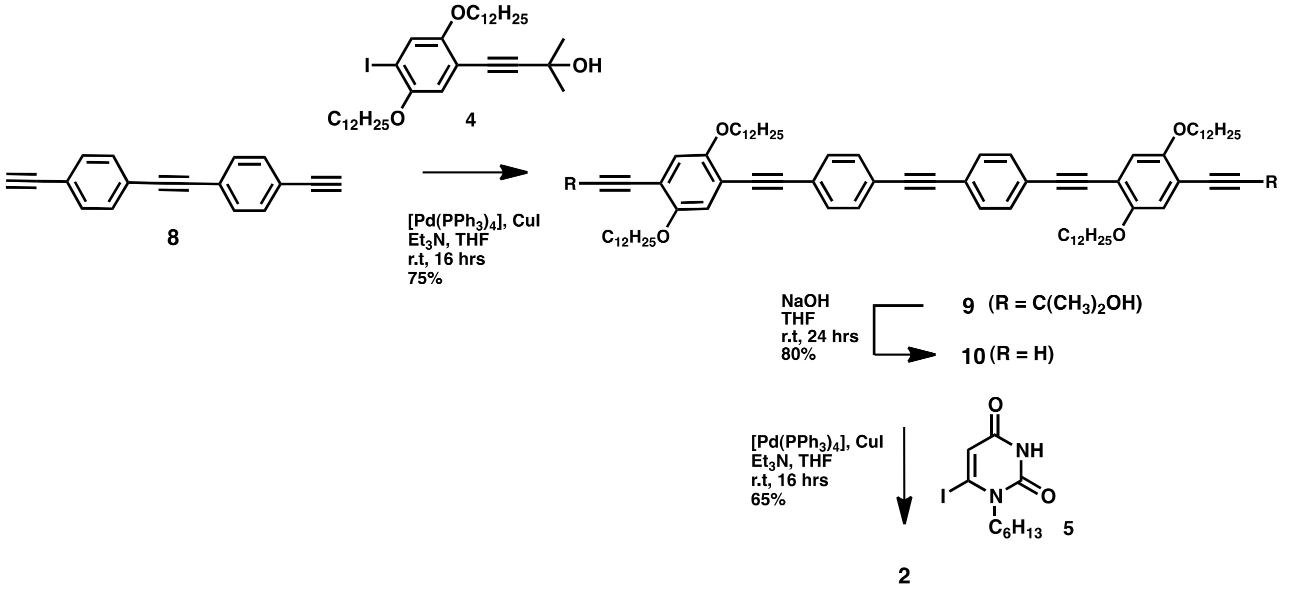
4,4'-(((1,2-diphenyldiazenyl)diethinyl)bis(2,5-bis(dodecyloxy)-4,1-phenylene))bis(2-methylbut-3yn-2-ol) (6). To a degassed solution of dry Et_3N (12 mL) and THF (12 mL), **4** (0.76 g, 1.2 mmol), [Pd(PPh_3)$_4$] (11 mg, 0.01 mmol) and CuI (8 mg, 0.04 mmol) were added before degassing the solution a second time. Finally **3**[2] (92 mg, 0.40 mmol) was added and the solution degassed one last time before allowing it to stir overnight under Ar and at r.t. The reaction was hence filtered over celite and the filtrate concentrated under vacuum. Purification of the crude by CC ($CHCl_3$/EtOAc 3:1) yielded compound **6** (0.2 g, 40%) as a bright red solid. M.p. 95-100°C. ^{1}H-NMR ($CDCl_3$): δ 7.92 (*d*, 4H; Ar-C*H*, *J* = 4 Hz); 7.66 (*d*, 4H; Ar-C*H*, *J* = 4 Hz); 6.99 (*s*, 2H; Ar-C*H*); 6.92 (*s*, 2H; Ar-C*H*); 3.99 (*m*, 8H; -OCH_2); 1.83 (*m*, 8H; -OCH$_2$CH_2); 1.64 (*s*, 12H; -C(CH_3)$_2$OH); 1.53 (*m*, 8H; -O(CH$_2$)$_2$CH_2); 1.26 (*m*, 64H; -O(CH$_2$)$_3$(CH_2)$_8$CH$_3$); 0.85 (*m*, 12H; -O(CH$_2$)$_{11}$CH_3); ^{13}C-NMR could not be performed due to the low solubility of the compound. IR (cm^{-1}): ν 3418.9, 2921.9, 2851.5, 2200.0, 2100.5, 1580.0, 1505.5, 1466.7, 1413.9, 1362.9, 1274.6, 1219.8, 1274.6, 1219.8, 1148.6, 1003.6, 849.4, 774.9, 559.5. MS (HR-LCMS, ESI): found 1282.9624 [M]$^+$, $C_{86}H_{126}N_2O_6$ requires = 1282.9616.

1,2-bis(4-((2,5-bis(dodecyloxy)-4-ethynylphenyl)ethynyl)phenyl)diazene (7). **6** (70 mg, 0.05 mmol) was dissolved in dry toluene (4 mL) under Ar atmosphere. Powdered NaOH (10 mg, 0.2 mmol) was then added to the reaction mixture, which was then heated overnight at 110 °C. After cooling to r.t., the reaction was filtered and the filtrate concentrated under vacuum. Purification of the crude by CC (Cyclohexane/EtOAc 8:2) yielded compound **7** (45 mg, 80%) as a bright red solid. M.p. 185-195 °C. ^{1}H-NMR ($CDCl_3$): δ 7.92 (*d*, 4H; Ar-C*H*, *J* = 4 Hz); 7.68 (*d*, 4H; Ar-C*H*, *J* = 4 Hz); 7.01 (*s*, 2H; Ar-C*H*); 6.99 (*s*, 2H; Ar-C*H*); 4.01 (*m*, 8H; -OCH_2); 3.36 (*s*, 2H; -C*H*); 1.69 (*m*, 8H; -OCH_2); 1.50 (*m*, 8H; -OCH$_2$CH_2); 1.25 (*m*, 64H; -O(CH$_2$)$_3$(CH_2)$_8$CH$_3$); 0.85 (*m*, 12H; -O(CH$_2$)$_{11}$CH_3); ^{13}C-NMR could not be performed due to the low solubility of the compound. IR: ν

= 2922.03, 2852.60, 1734.56, 1465.67, 1377.62, 1211.44, 1033.75, 721.41, 493.53, 487.04, 472.34, 463.49, 451.79. MS (HR-LCMS, ESI$^+$): found 1166.8792 $[M]^+$, $C_{86}H_{126}N_2O_6$ requires = 1166.8779.

4,4'-(((1,2-diphenyldiazenyl)diethinyl)bis(2,5-bis(dodecyloxy)-4,1-phenylene))bisethynyluracyl (1). To a degassed solution of dry Et_3N (2 mL) and THF (2 mL), **5**[1] (16 mg, 0.07 mmol), $[Pd(PPh_3)_4]$ (1 mg, 0.001 mmol) and CuI (0.2 mg, 0.002 mmol) were added before degassing the solution a second time. Finally **7** (30 mg, 0.03 mmol) was added and the solution degassed one last time before allowing it to stir overnight at 85 °C under Ar atmosphere. The reaction was hence filtered over celite and the filtrate concentrated under vacuum. Purification of the crude through several precipitations from $CHCl_3$ with pentane yielded compound **1** (20 mg, 50%) as a bright red solid. M.p. 185-190°C. ^{1}H-NMR ($CDCl_3$): δ 7.94 (*d*, 4H; Ar-C*H*, *J* = 4 Hz); 7.68 (*d*, 4H; Ar-C*H*, *J* = 4 Hz); 6.99 (*s*, 2H; Ar-C*H*); 6.97 (*s*, 2H; Ar-C*H*); 5.98 (*s*, 2H; -C*H*); 4.12 (*m*, 4H; $-NCH_2$); 4.03 (*m*, 8H; $-OCH_2$); 1.82 (*m*, 12H; $-OCH_2CH_2$ and $-NCH_2CH_2$); 1.57 (*m*, 8H; $-O(CH_2)_2CH_2$); 1.26 (*m*, 76H; $-O(CH_2)_3(CH_2)_8CH_3$ and $-N(CH_2)_2(CH_2)_3CH_3$); 0.86 (*m*, 18H; $-O(CH_2)_{11}CH_3$ and $-N(CH_2)_5CH_3$); ^{13}C-NMR could not be performed due to the low solubility of the compound. IR (cm^{-1}): ν = 2921.97, 2852.70, 2209.59, 1669.21, 1588.19, 1504.87, 1464.96, 1415.43, 1260.75, 1217.54,1151.53, 1094.29, 1020.41, 847.21, 800.80, 721.54, 557.62, 502.33, 486.83, 470.51, 458.78. 454.40. MS (HR-LCMS, ESI$^+$): found 1555.0902 $[M]^+$, $C_{100}H_{142}N_6O_8$ requires = 1555.0889.

Synthesis of Molecule 2



Scheme S2. Synthetic procedure to molecule **2**.

4,4'-(((1,2-1,2-diphenylethynel)diethinyl)bis(2,5-bis(dodecyloxy)-4,1-phenylene))bis(2-methylbut-3yn-2-ol) (9). To a degassed solution of dry Et_3N (10 mL) and THF (20 mL), **4** (196 mg, 0.30 mmol), $[Pd(PPh_3)_4]$ (11 mg, 0.01 mmol) and CuI (1 mg, 0.006 mmol) were added before degassing the solution a second time. Finally **8**[3] (30 mg, 0.13 mmol) was added and the solution degassed one last time before allowing it to stir overnight under Ar and at 85 °C. The reaction was hence filtered over celite and the filtrate concentrated under vacuum. Purification of the crude by CC ($CHCl_3$/EtOAc 1:1) yielded compound **9** (125 mg, 75%) as a bright yellow solid. M.p. 200-205°C. ^{1}H-NMR ($CDCl_3$): δ 7.50 (*s*, 8H; Ar-C*H*); 6.96 (*s*, 2H; Ar-C*H*); 6.91 (*s*, 2H; Ar-C*H*); 3.97 (*m*, 8H; $\text{-OC}\mathit{H}_2$); 1.82 (*m*, 8H; $\text{-OCH}_2\text{C}\mathit{H}_2$); 1.64 (*s*, 12H; $\text{-C(C}\mathit{H}_3)_2\text{OH}$); 1.51 (*m*, 8H; $\text{-O(CH}_2)_2\text{C}\mathit{H}_2$); 1.26 (*m*, 64H; $\text{-O(CH}_2)(\text{C}\mathit{H}_2)_8\text{CH}_3$); 0.88 (*m*, 12H; $\text{-O(CH}_2)_{11}\text{C}\mathit{H}_3$). ^{13}C-NMR ($CDCl_3$): δ 153.72, 131.66, 123.60, 122.95, 117.17, 116.82, 113.73, 94.52, 91.18, 88.10, 82.04, 78.64, 69.72, 69.56, 65.95, 60.99, 32.07, 31.58, 29.79, 29.51, 26.23, 22.85, 14.29; (peaks in the aliphatic region missing probably due to overlap). IR (cm^{-1}): ν = 3293.05, 2920.66, 2852.06, 1517.08, 1497.11, 1467.28, 1414.00, 1383.32, 1275.54, 1156.37, 1102.09, 1030.58, 960.04, 908.98, 860.57, 835.79, 721.44, 539.88, 486.91, 479.83, 471.04, 463.22, 454.19. MS (HR-LCMS, ESI$^+$): found 1278.9598 $[M]^+$, $C_{88}H_{126}O_6$ requires = 1278.9554.

1,2-bis(4-((2,5-bis(dodecyloxy)-4-ethynylphenyl)ethynyl)phenyl)-1,2-diphenylethyne (10). 9 (30 mg, 0.02 mmol) was dissolved in dry toluene (10 mL) and kept under Ar atmosphere. Powdered NaOH (6 mg, 0.15 mmol) was ultimately added to the reaction mixture, which was then allowed to stir overnight under Ar and at 110 °C. After cooling to r.t. the reaction was filtered and the recovered solution concentrated under vacuum. Purification of the crude by CC ($CHCl_3$/EtOAc 8:2) yielded compound **10** (19 mg, 80%) as a bright yellow solid. M.p. > 250 °C. ^{1}H-NMR ($CDCl_3$): δ 7.50 (*s*, 8H; Ar-C*H*); 6.99 (*s*, 4H; Ar-C*H*); 5.00 (*m*, 8H; $\text{-OC}\mathit{H}_2$); 3.35 (*s*, 2H; -C*H*); 1.84 (*m*, 8H; $\text{-OCH}_2\text{C}\mathit{H}_2$); 1.49 (*m*, 8H; $\text{-O(CH}_2)_2\text{C}\mathit{H}_2$); 1.26 (*m*, 64H; $\text{O(CH}_2)_3(\text{C}\mathit{H}_2)_8\text{CH}_3$); 0.88 (*m*, 12H; $\text{O(CH}_2)_{11}\text{C}\mathit{H}_3$). ^{13}C-NMR ($CDCl_3$): δ 154.27, 153.63, 132.61, 131.67, 117.84, 116.90, 114.42, 112.94, 94.71, 91.19, 87.94, 82.59, 80.11, 69.74, 32.07, 29.86, 29.74, 29.51, 26.23, 22.85, 14.29. IR: (cm^{-1}): ν = 2921.28, 2852.15, 1707.77, 1516.9, 1496.31, 1467.26, 1410.72, 1385.81, 1274.85, 1218.32, 1017.23, 835.51, 801.92, 539.97, 505.63, 494.15, 480.32, 474.97, 468.22, 458.91; (peaks in the aliphatic region missing probably due to overlap). MS (HR-LCMS, ESI$^+$): found 1162.8726 $[M]^+$, $C_{82}H_{114}O_4$ requires = 1162.8717.

1,4-Bis{[1,4-Bis(dodecyloxy)-2,5-Bis[(2,6-Di(acetylamino)pyridine-4-yl-)ethynyl]benzenyl} 1,2-diphenylethyne (2). To a degassed solution of dry Et_3N (3 mL) and THF (3 mL), **5**[1,3] (18 mg, 0.06 mmol), $[Pd(PPh_3)_4]$ (3 mg, 0.003 mmol) and CuI (2 mg, 0.01 mmol) were added before degassing the solution a second time. Finally **10** (30 mg, 0.03 mmol) was added and the solution degassed one last time before allowing it to stir overnight at 85 °C under Ar atmosphere. The reaction was hence filtered over celite and the filtrate concentrated under vacuum. Purification of the crude through several precipitations from $CHCl_3$ with pentane yielded compound **2** (30 mg, 65%) as a bright yellow solid. M.p. > 250 °C. ^{1}H-NMR ($CDCl_3$): δ 7.52 (*s*, 8H; Ar-C*H*); 7.03 (*s*, 2H; Ar-C*H*); 6.95 (*s*, 2H; Ar-C*H*); 5.97 (*s*, 2H; -C*H*); 4.11 (*m*, 4H; -NCH_2); 4.03 (*m*, 8H; -OCH_2); 1.80 (*m*, 8H; -OCH_2CH_2); 1.68 (*m*, 4H; -NCH_2CH_2); 1.42 (*m*, 8H; -$O(CH_2)_2CH_2$); 1.26 (*m*, 76H; -$O(CH_2)_3(CH_2)_8CH_3$ and -$N(CH_2)_2(CH_2)_3CH_3$); 0.88 (*m*, 18H; -$O(CH_2)_{11}CH_3$ and -$N(CH_2)_5CH_3$). ^{13}C-NMR ($CDCl_3$): δ 167.92, 162.11, 154.70, 153.61, 150.55, 139.13, 131.76, 131.04, 128.94, 123.24, 116.80, 116.28, 110.32, 106.35, 97.86, 96.11, 91.32, 87.69, 85.46, 69.87, 69.43, 68.29, 46.65, 38.76, 32.76, 32.07, 30.49, 29.80, 29.50, 23.14, 22.84, 14.13, 11.10; (peaks in the aliphatic region missing probably due to overlap). IR (cm^{-1}): ν = 2924.38, 2854.26, 1679.30, 1586.63, 1458.97, 1281.01, 1119.97, 722.07, 542.46, 499.39, 486.94, 478.92, 471.54, 463.01, 454.48. MS (HR-LCMS, ESI$^+$): found 1551.0881 $[M]^+$, $C_{102}H_{142}N_4O_8$ requires = 1551.0828.

References

[1] A. Llanes-Pallas, K. Yoosaf, H. Traboulsi, J. Mohanraj, T. Seldrum, J. Dumont, A. Minoia, R. Lazzaroni, N. Armaroli and D. Bonifazi, *J. Am. Chem. Soc.*, 2011, **133**, 15412.

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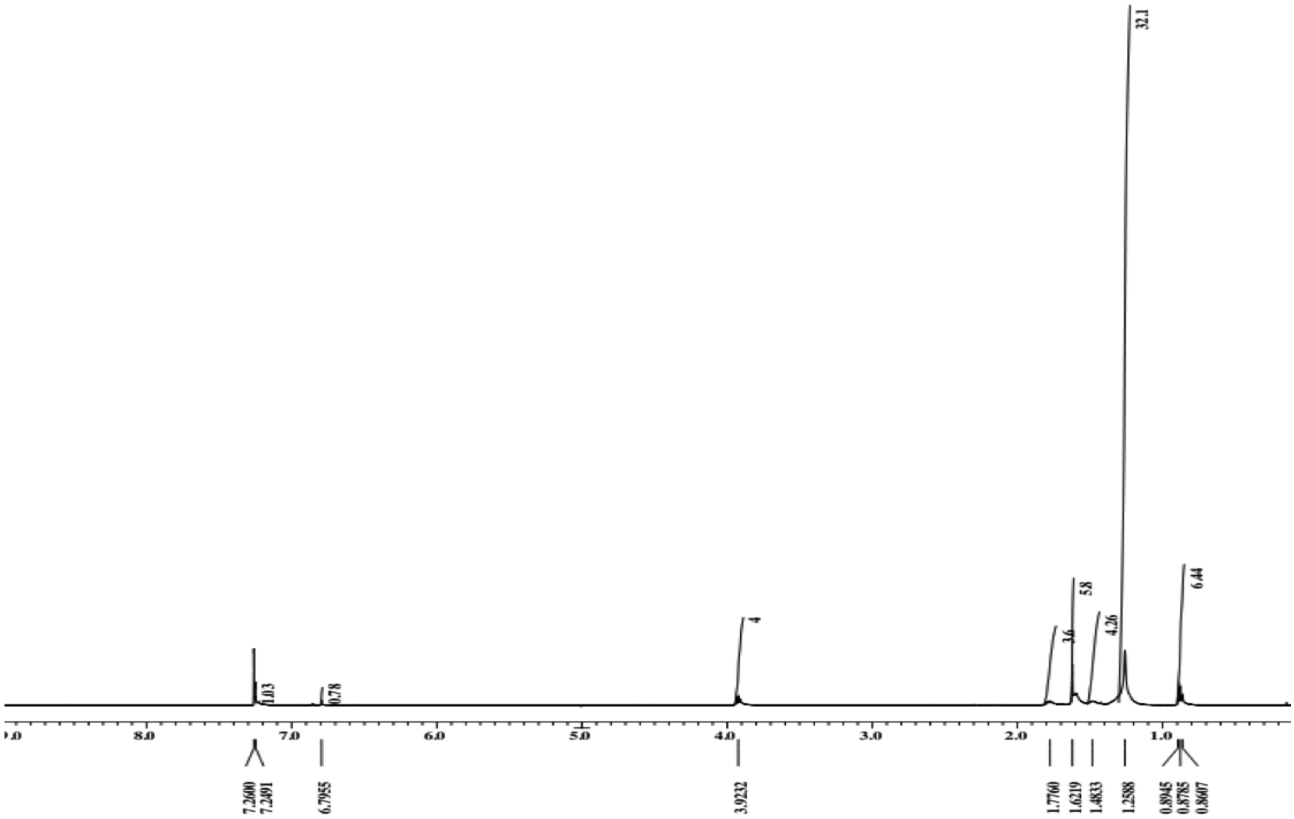
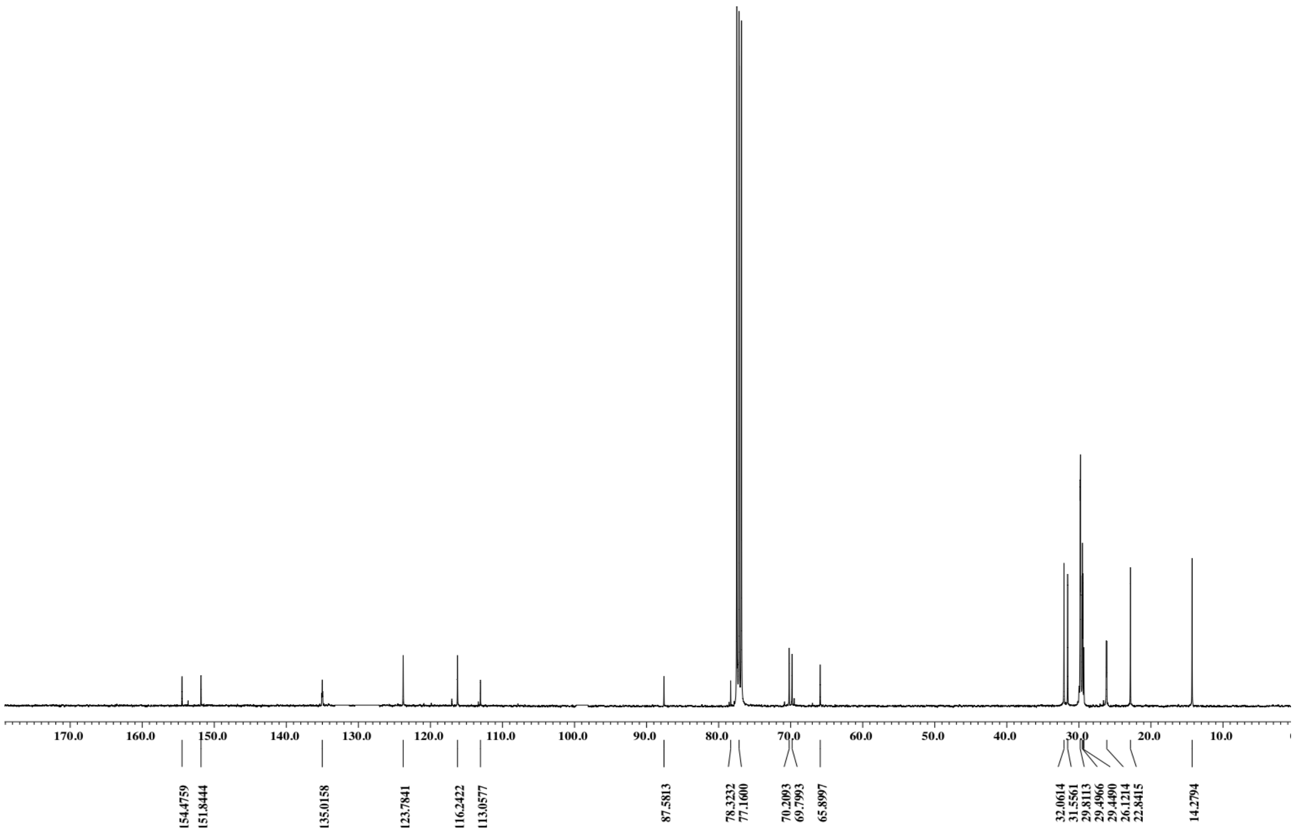
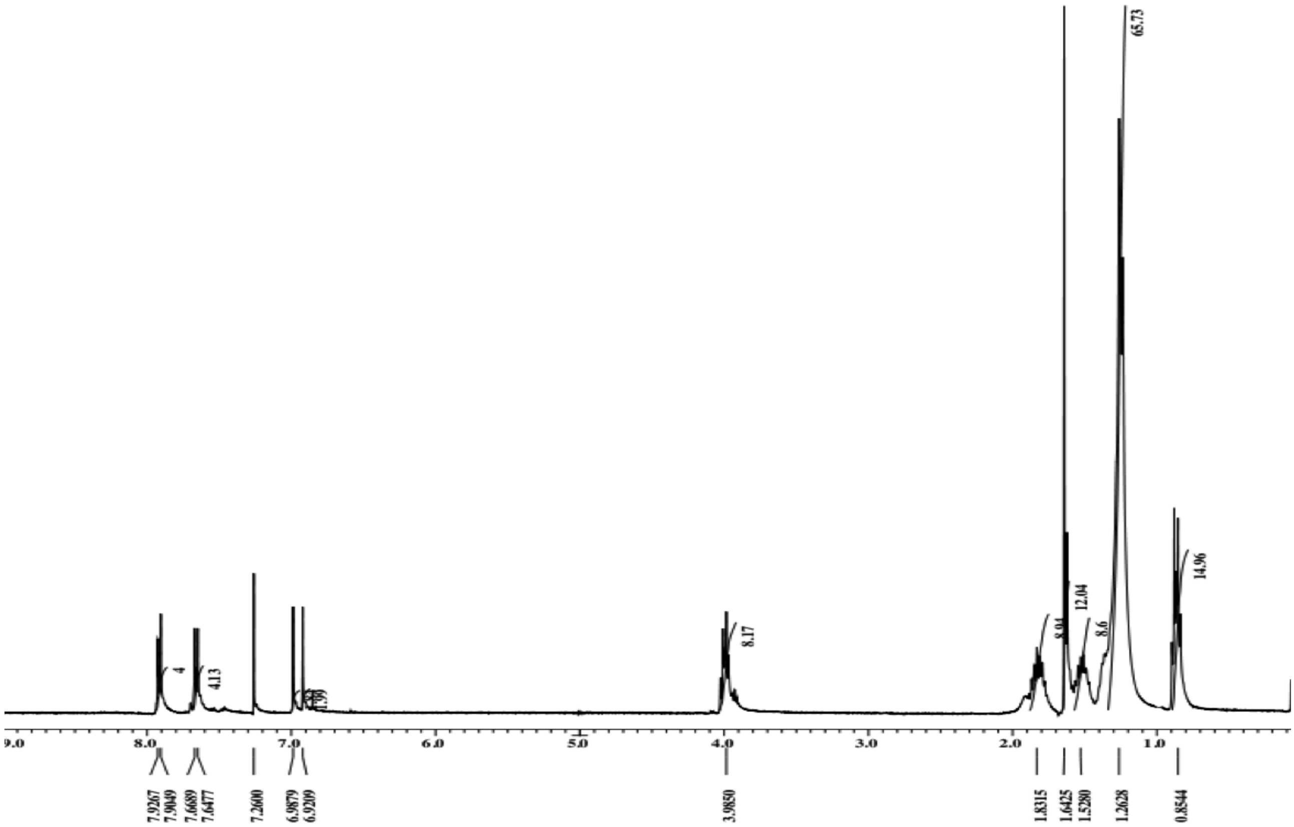
NMR Characterisation

Mol. **4**: ^{1}H-NMR and ^{13}C-NMR





Mol. **6**: ^{1}H-NMR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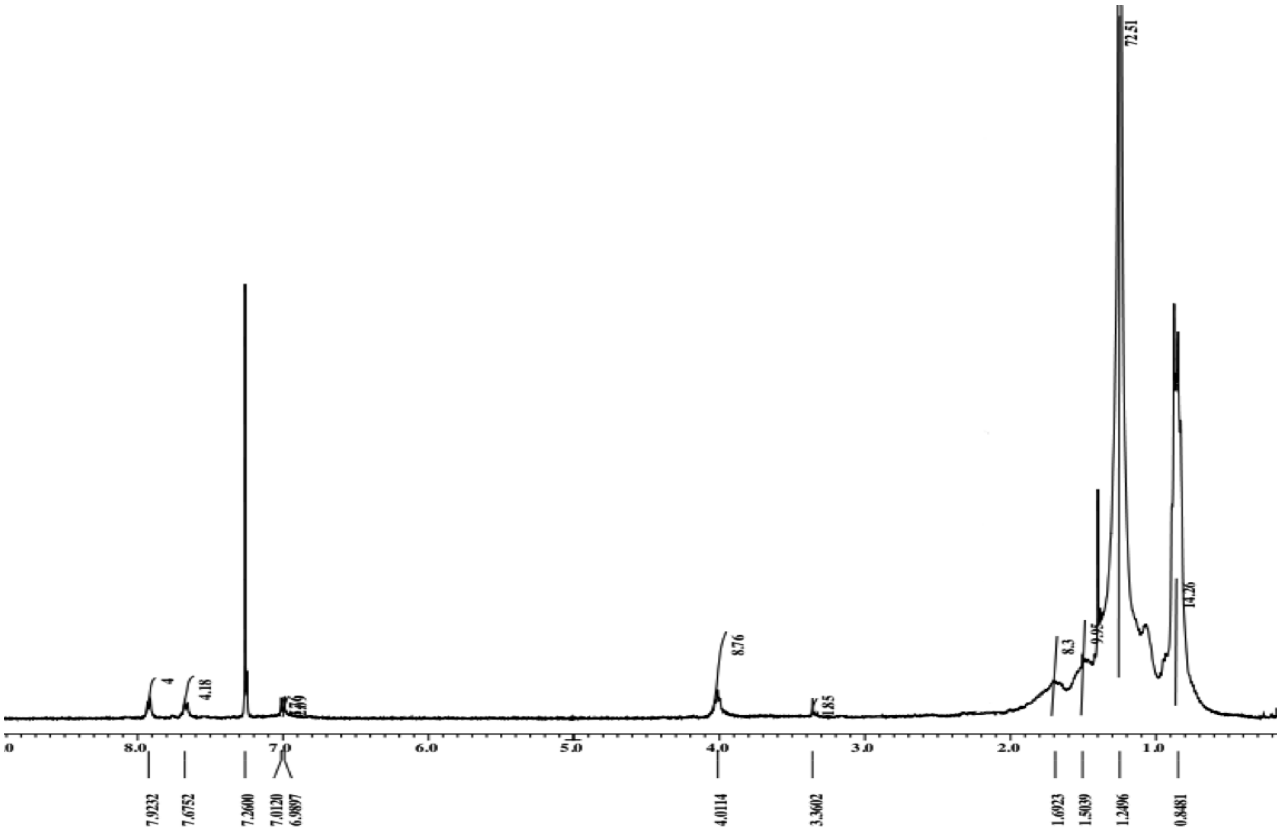
Mol. **7**: ^{1}H-NMR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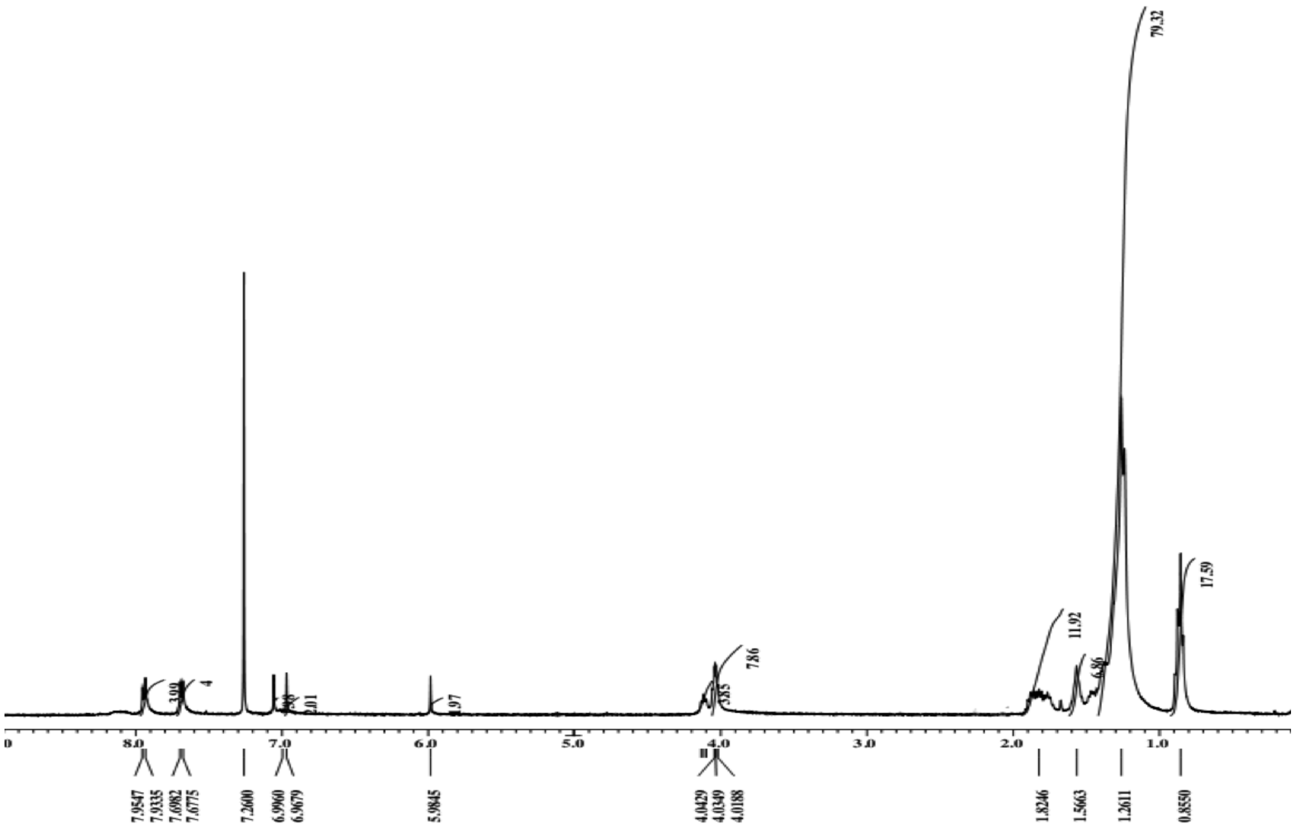
Mol. **1**: ^{1}H-NMR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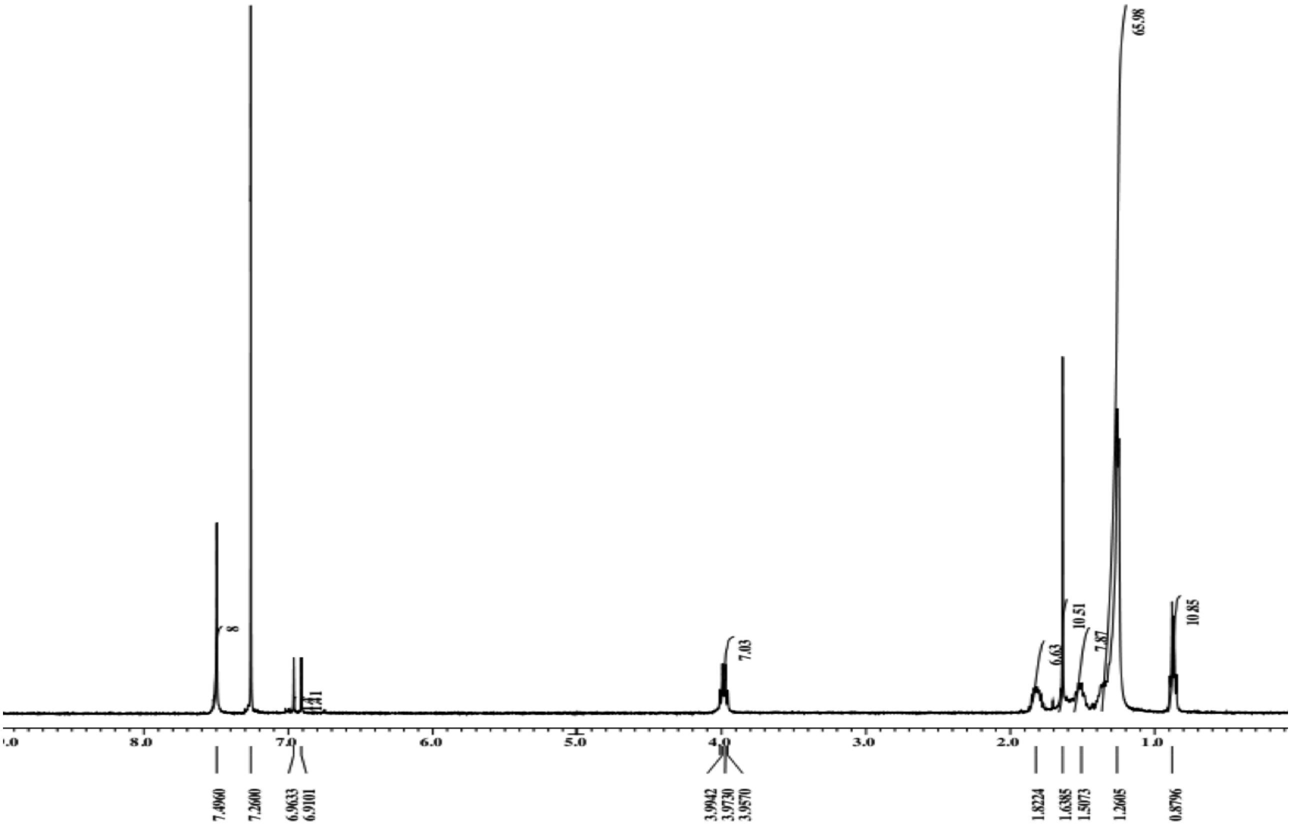
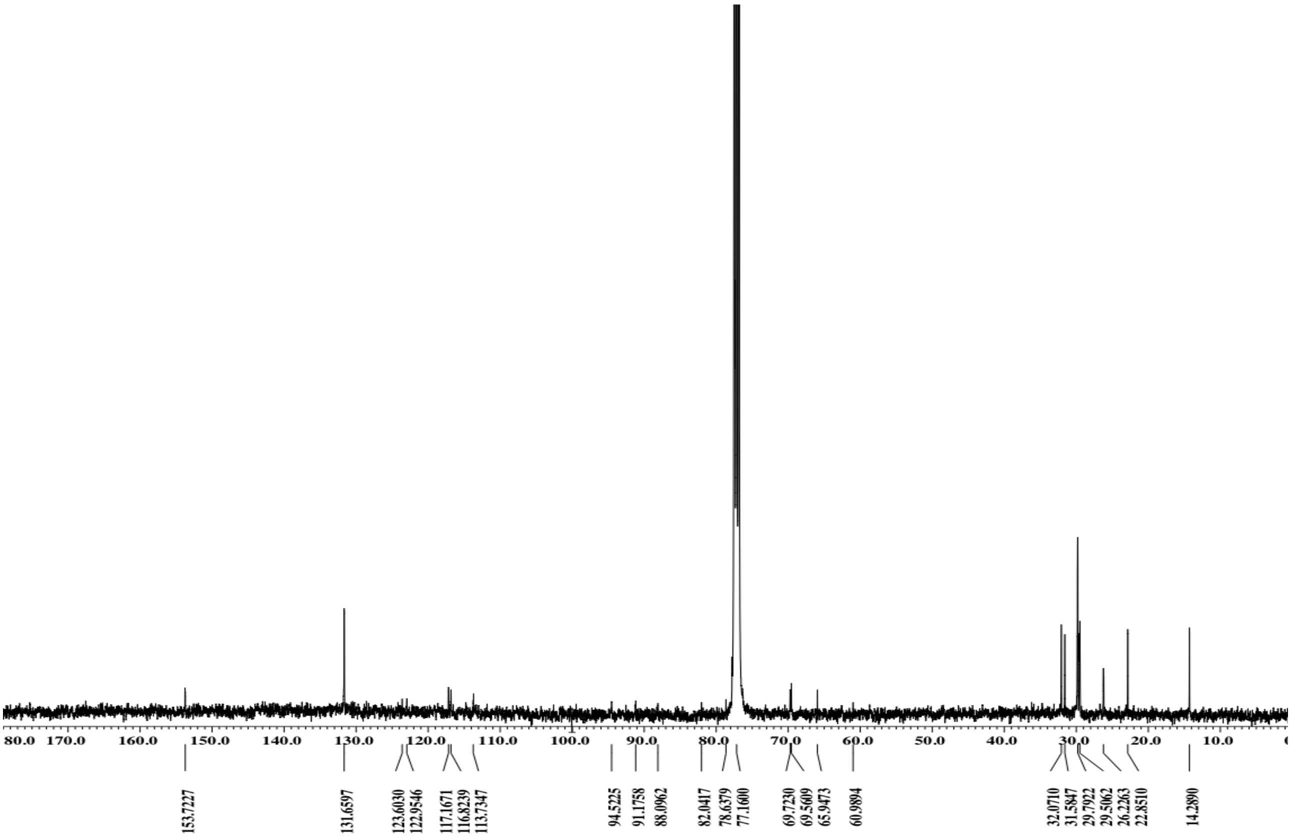
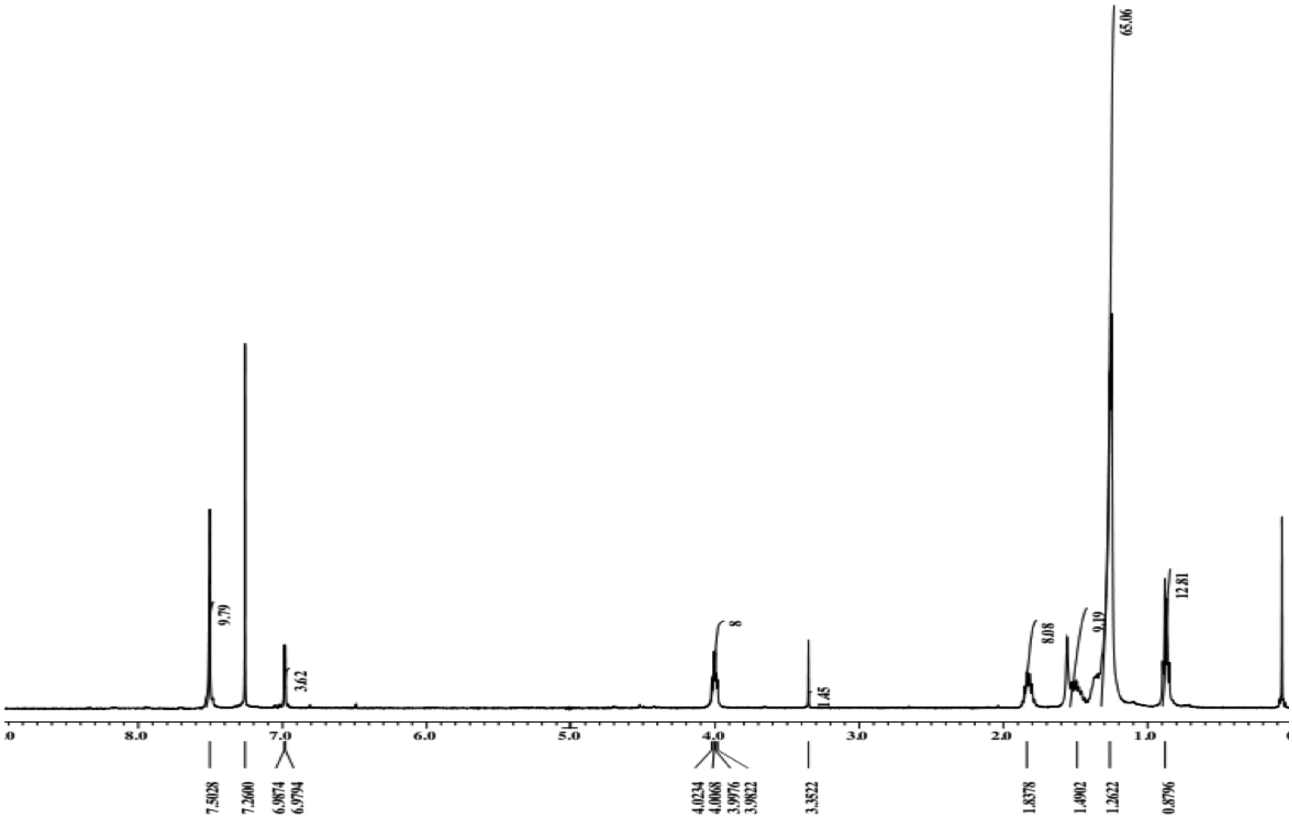
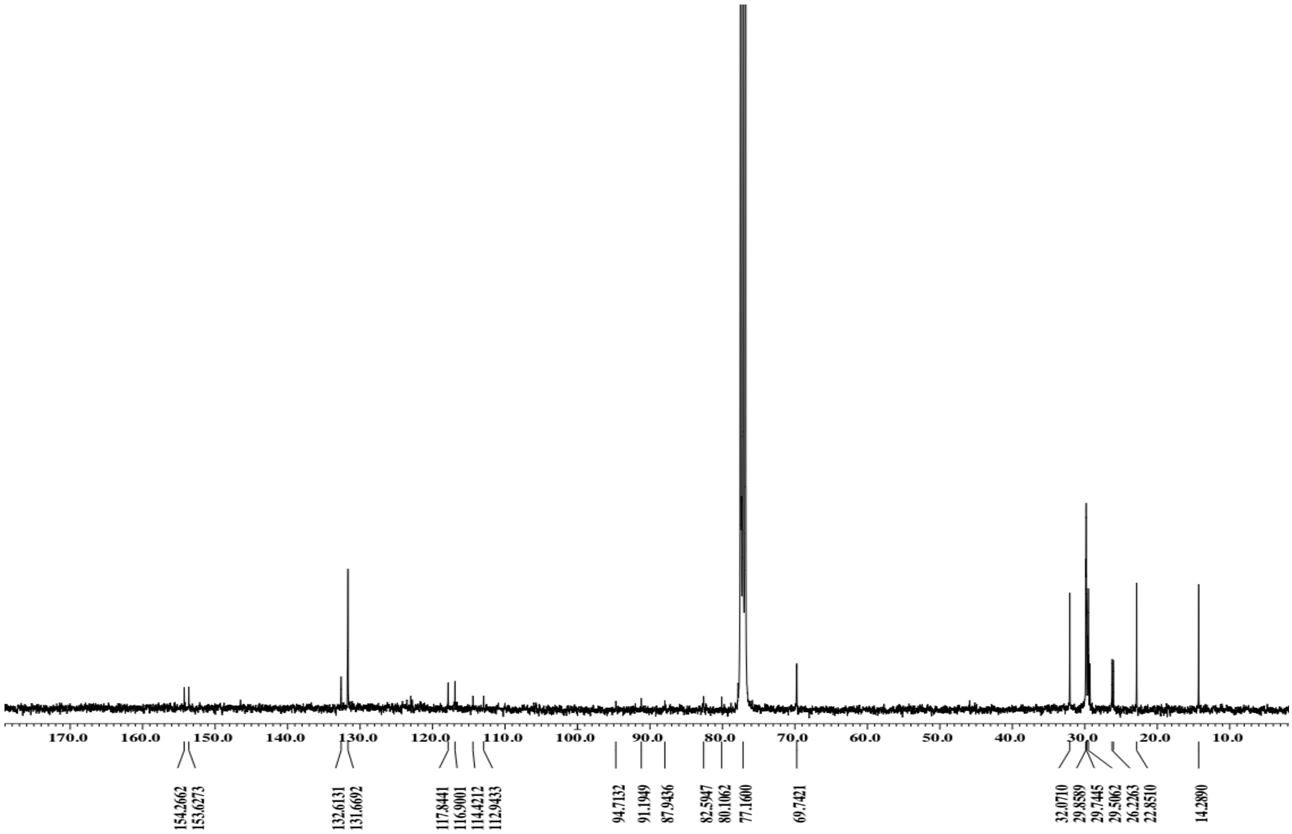
Mol. **9**: ^{1}H-NMR and ^{13}C-NMR



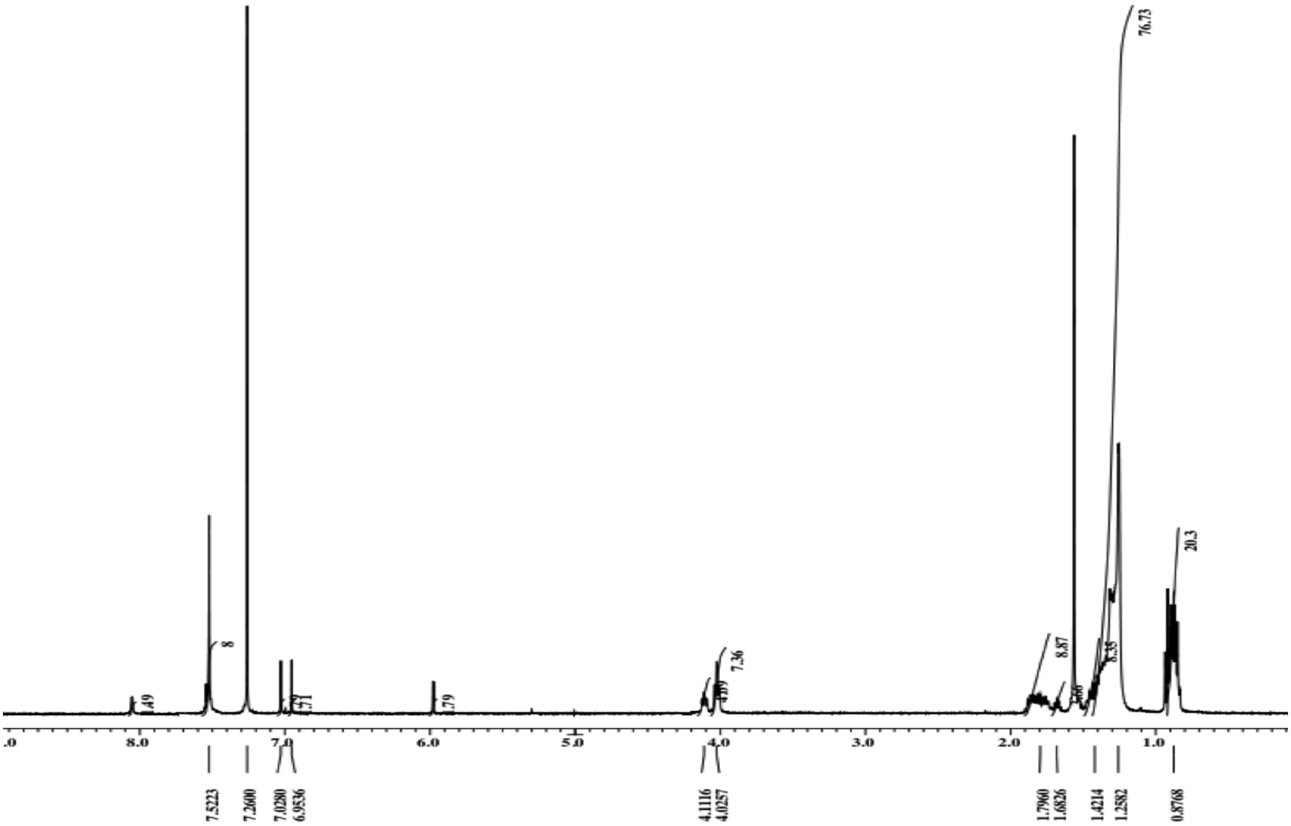


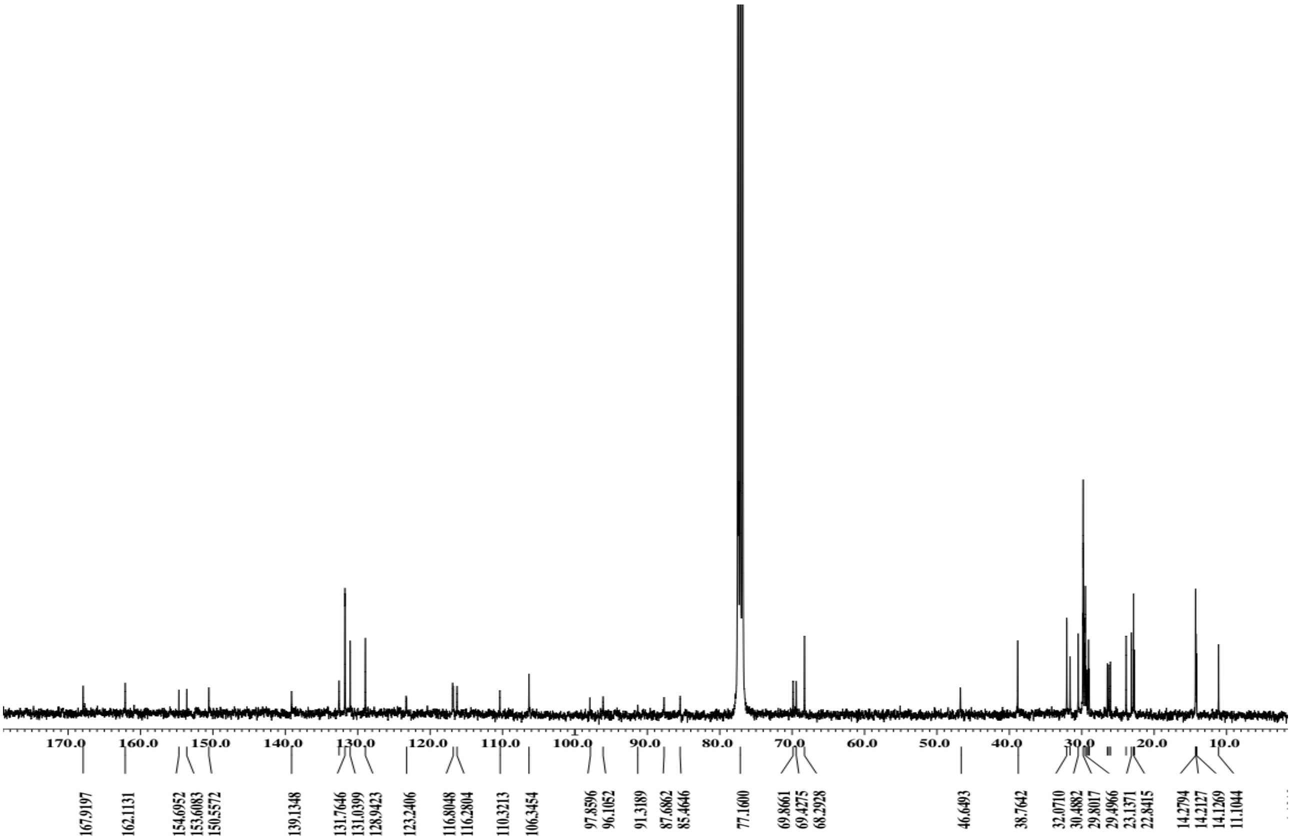
Mol. **10**: ^{1}H-NMR and ^{13}C-NMR





Mol. **2**: ^{1}H-NMR and ^{13}C-NMR





EXPERIMENTAL RESULTS

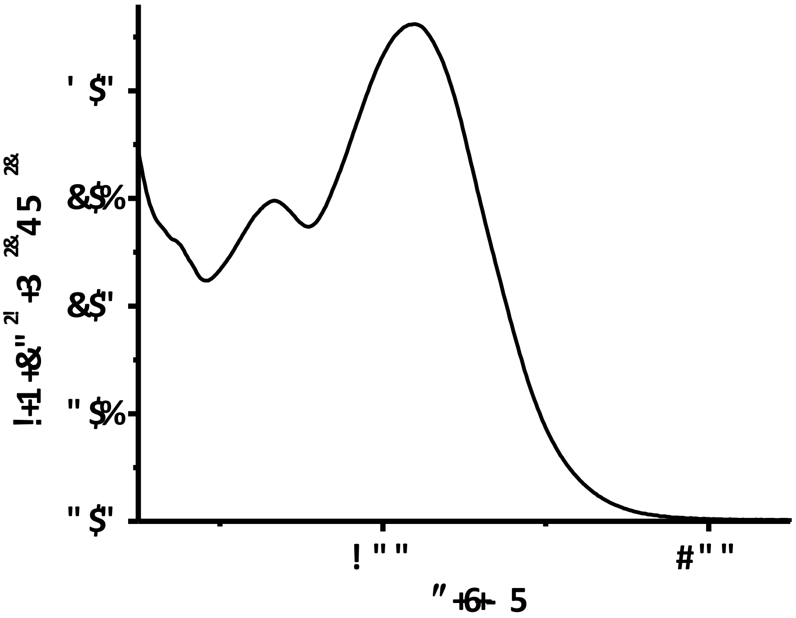


Fig. S1. Absorption spectrum of **1** in tetrahydrofuran.

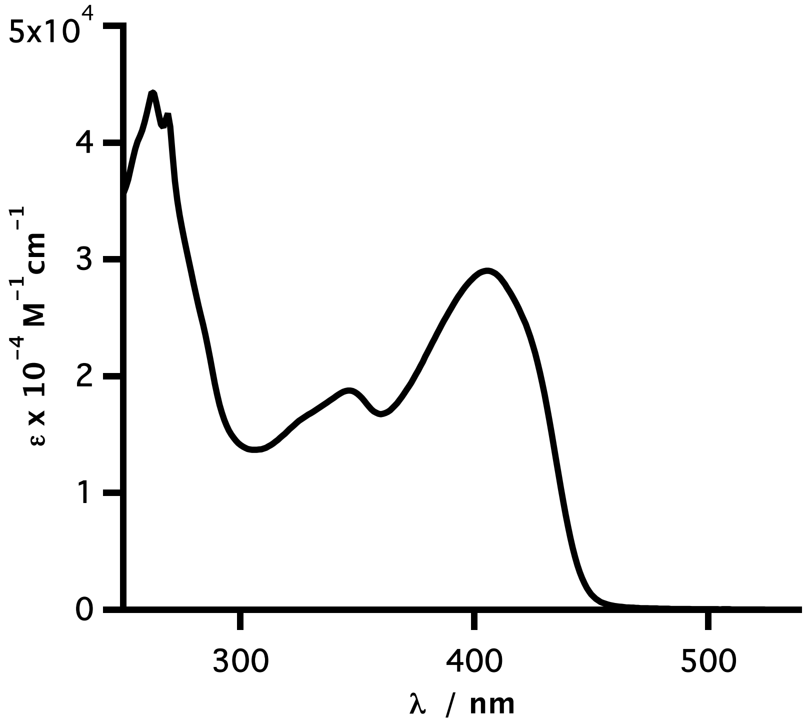


Fig. S2. Absorption spectrum of **2** in chloroform.

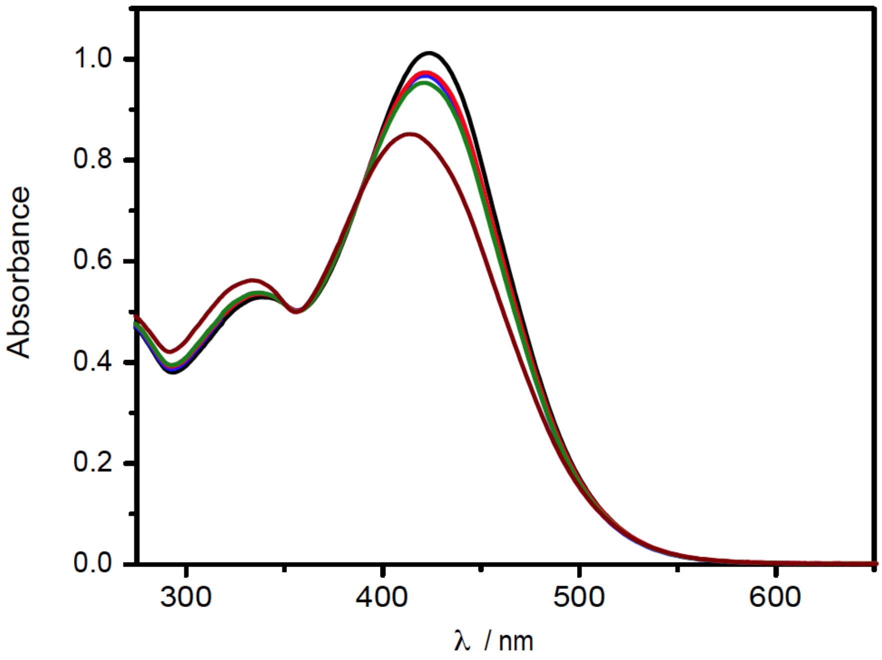


Fig. S3. Absorption spectra of **1** in chloroform (C = 4 x 10^{-4} M) for photostationary states reached after irradiation at 297 nm (blue), 334 nm (red), 365 nm (green) and 436 nm (brown).

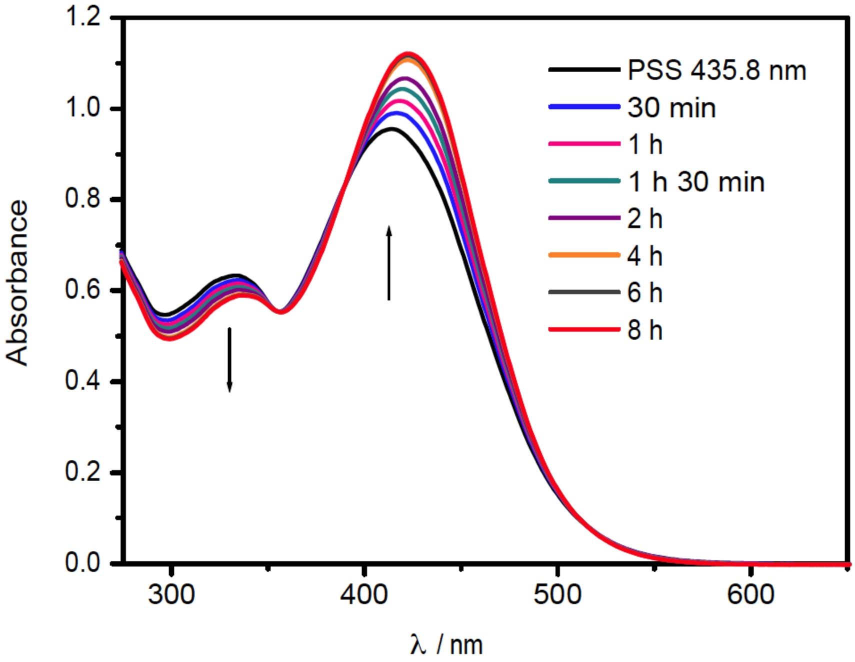


Fig. S4. UV-Vis absorption spectra of **1** in chloroform (C = 4 x 10^{-4} M), showing the thermal *cis* → *trans* thermal process at 20°C of the photostationary mixture obtained after irradiation at 436 nm of the all-*trans* species (black).

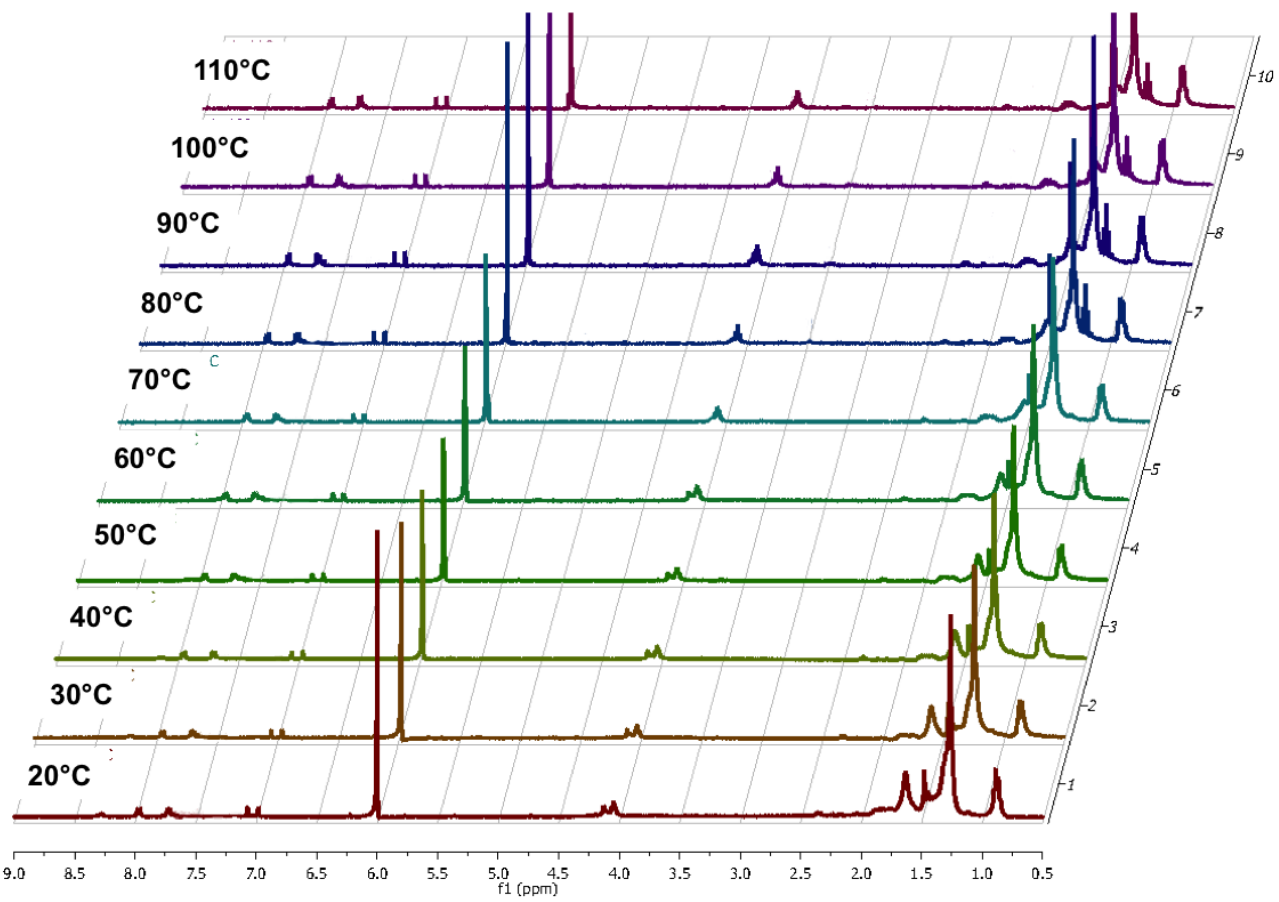


Fig. S5. VT ^{1}H-NMR experiments of a solution of **1** in *d*-tetrachloroethane (C = 10^{-3}). The temperature range spanned from room temperature (20°C, red line) to 110°C (magenta line). The experiments were taken at an interval of 10°C.

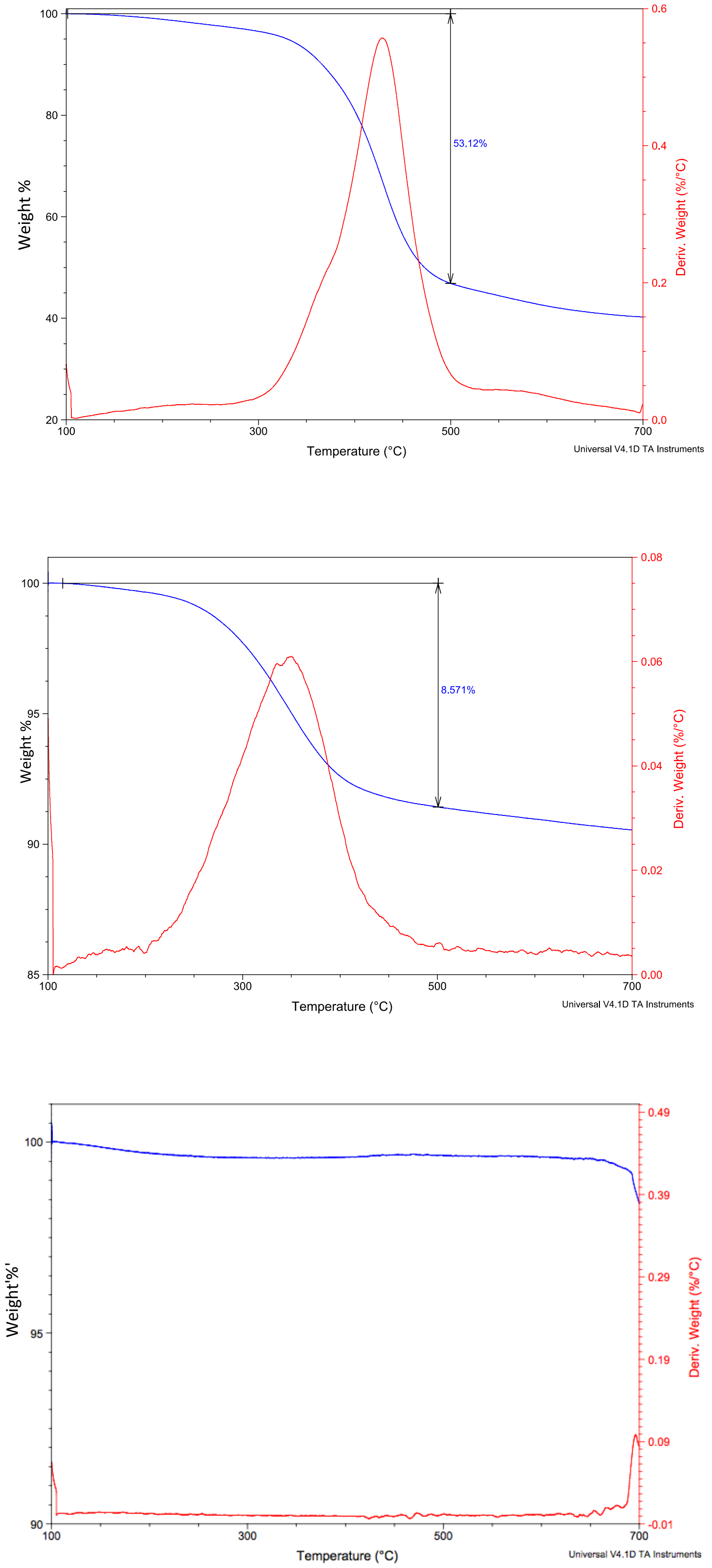
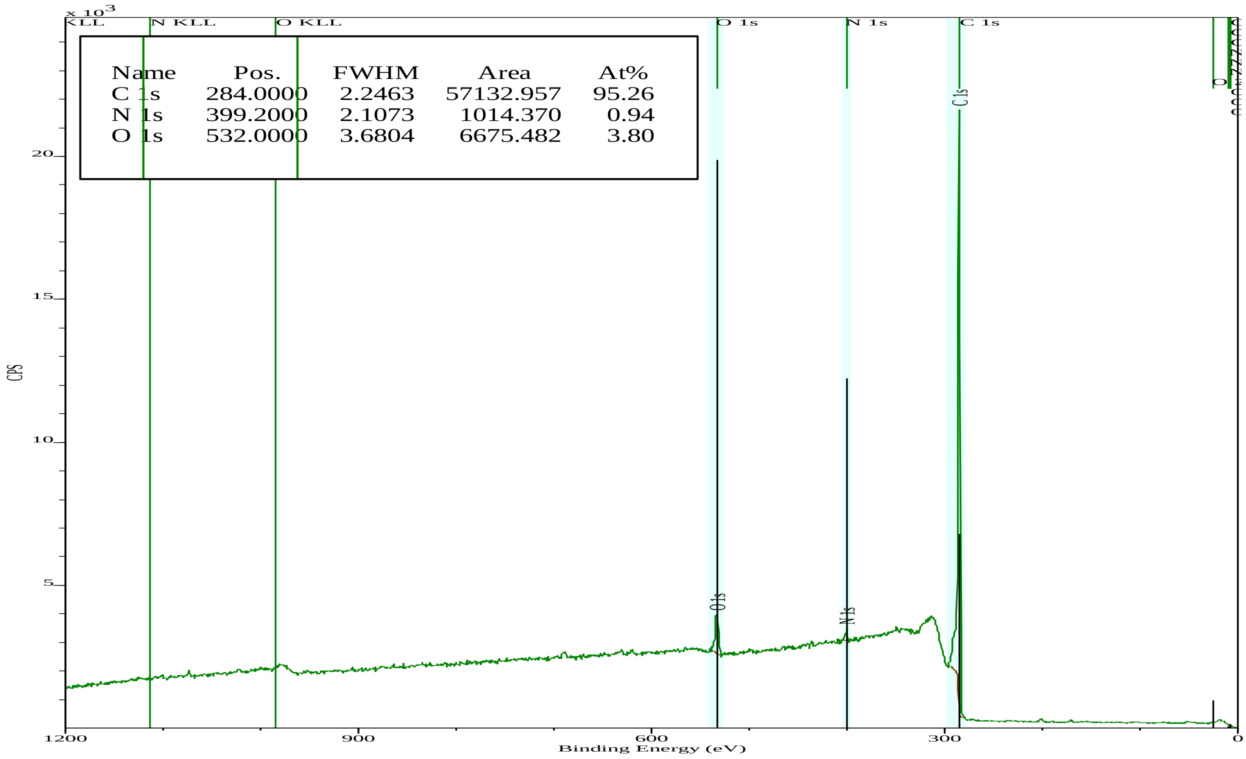


Fig. S6. Original Thermogravimetric profiles (blue lines) and first derivatives (red lines) for (from top to bottom) **1**, **1_n⊙MWCNTs** and the pristine MWCNTs as obtained directly from the TGA measurements.



Name	Pos.	FWHM	Area	At%
C 1s	284.0000	2.2463	57132.957	95.26
N 1s	399.2000	2.1073	1014.370	0.94
O 1s	532.0000	3.6804	6675.482	3.80

Fig. S7. XPS survey spectra of the hybrid $\mathbf{1_n}$⊙**MWCNTs**.

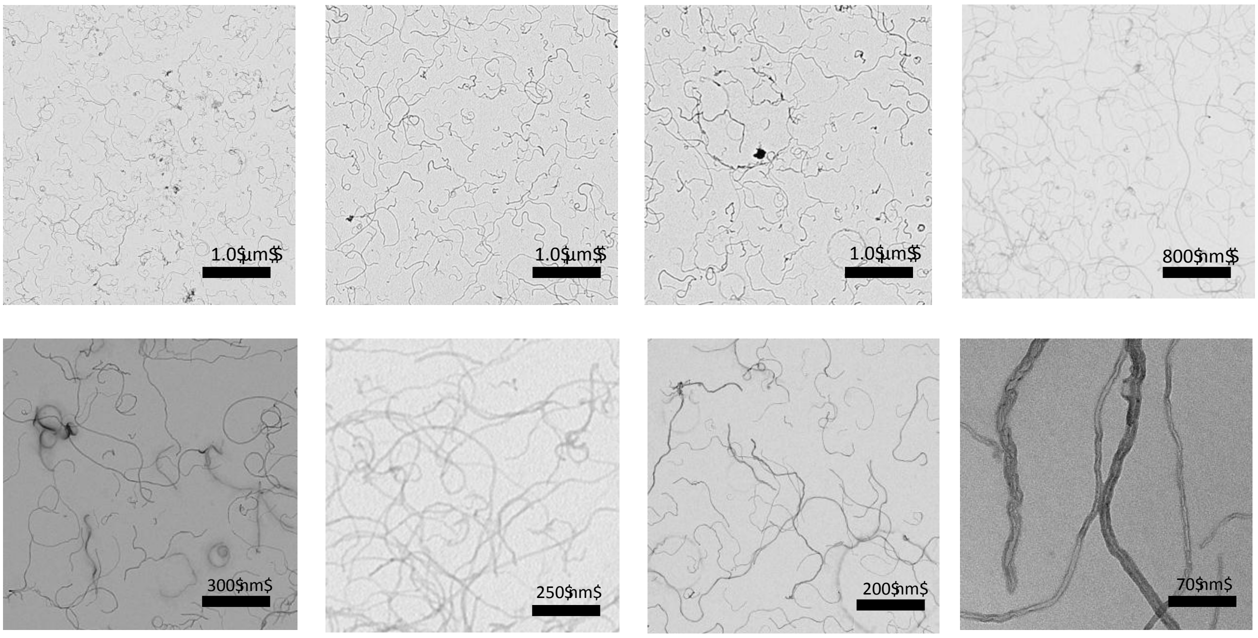


Fig. S8. TEM images at different magnifications of the composite material **1_n⊙MWCNTs** as drop casted onto a Nickel grids from a $CHCl_3$ solution. All the different area examined showed an homogeneus dispersion of the MWCNT structure, with a complete preservation of their sidewall structure.

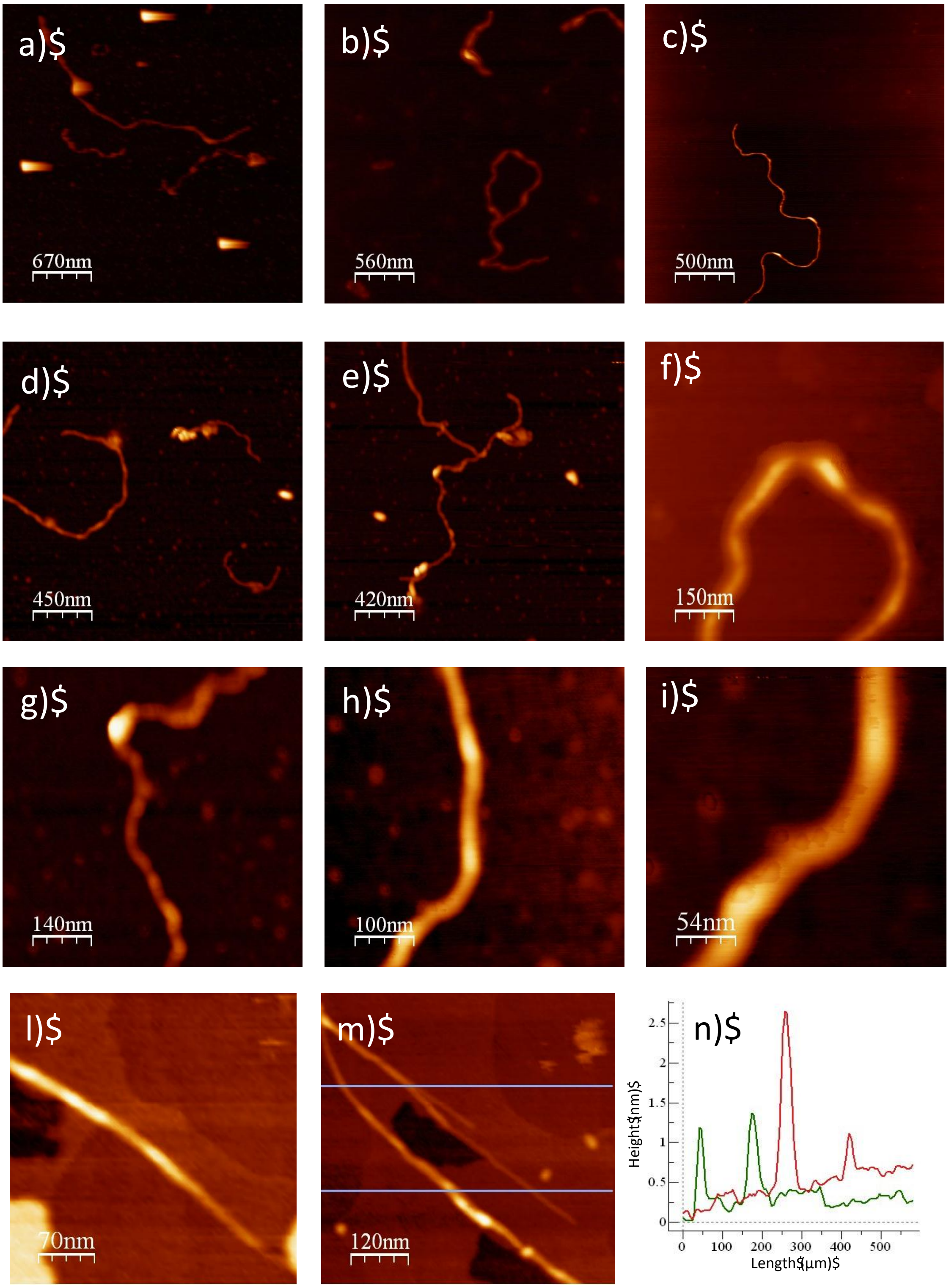


Fig. S9. TM-AFM topographic images of the composite material **1_n⊙MWCNTs** at different magnifications (a-i) and of the nanofibers morphologies (l, m) obtained from the deposition of a CHX solution of molecule **1** on mica surface. Profilometric analysis (n) of the fibers obtained

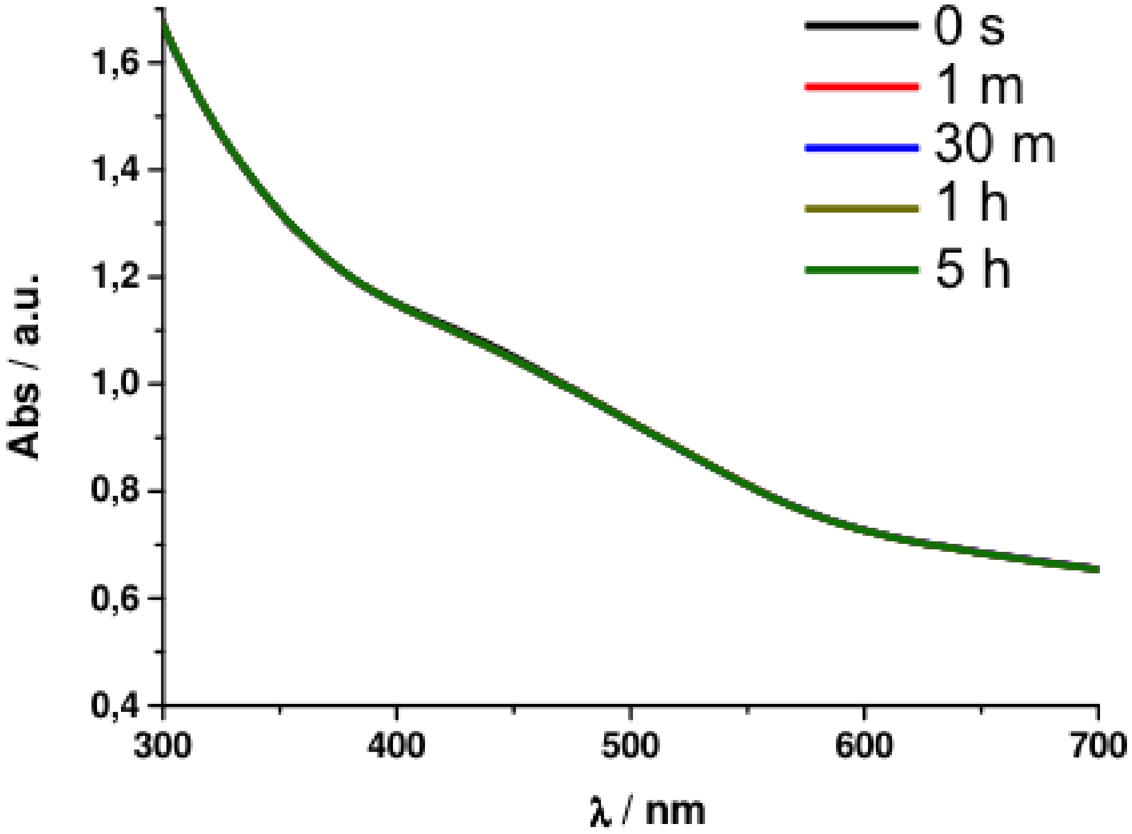


Fig. S10. Irradiation at 436 nm of hybrid **1_n⊙MWCNTs** up to 5 hrs.

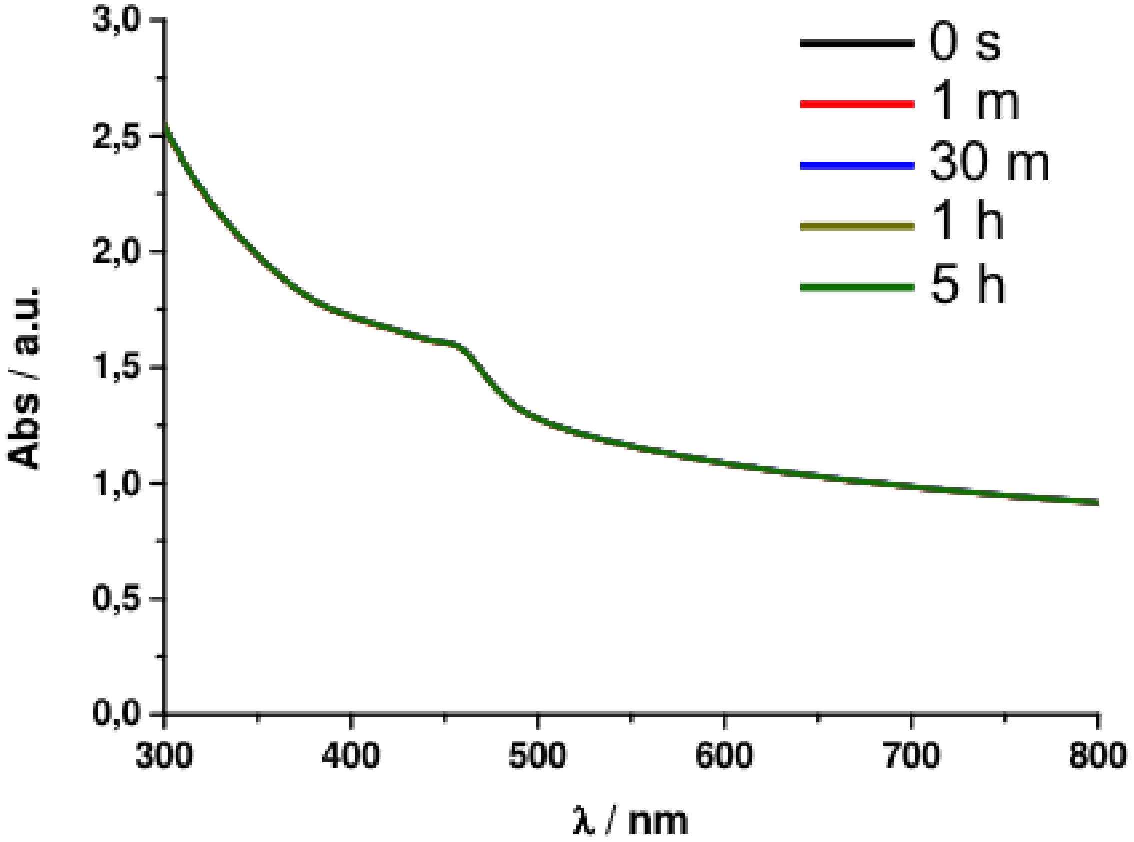


Fig. S11. Irradiation at 436 nm of hybrid **2_n⊙MWCNTs** up to 5 hrs.