# Supporting Information

# Synthesis and characterisation of a trithiocarbonate for the decoration of carbon nanostructures

*Patrizio Salice,*[a] Michele Mauri,[b] Micaela Castellino,[c] Martina De Marco,[a] Alberto Bianchi,[b]*

*Alessandro Virga,[d] Alberto Tagliaferro,[d] Roberto Simonutti,[b] and Enzo Menna[a]*

[a] Università di Padova, Dipartimento di Scienze Chimiche, via Marzolo, 1, 35131, Padova, Italy

[b] Università di Milano-Bicocca, Dipartimento di Scienza dei Materiali, via Cozzi, 53, 20126, Milano, Italy

[c] Center for Space Human Robotics, Istituto Italiano di Tecnologia,, Corso Trento, 21, 10129,Torino, Italy.

[d] Politecnico di Torino, Dipartimento Scienza Applicata e Tecnologia, Corso Duca degli Abruzzi, 24, 10129,Torino, Italy

E-mail: patrizio.salice@unipd.it

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## 1. Instruments, materials and methods

All the reagents and solvents were purchased from Sigma-Aldrich and were used as received if not otherwise specified. Single-walled carbon nanotubes (SWCNTs) and double-walled carbon nanotubes (DWCNTs) were provided by Cheap Tubes Inc and were used as received. Multi-walled carbon nanotubes (MWCNTs) were purchased from Sigma-Aldrich (product # 677248). [60]Fullerene was purchased from Bucky USA and was used as received. Graphite was purchased from Superior Graphite and was used as received.

Dispersions of carbon nanostructures (CNSs) were achieved using the Sonicator 3000 (Misonix) with the following pulse parameters: time on = 3 sec, time off = 3 sec, power level = 2 (4-6 watt). Carbon nanotubes were sonicated for 30 minutes, while graphite for 7 hours. The resulting dispersions were centrifuged with an MR23i Jouan ultracentrifuge equipped with a SWM 180.5 swinging bucket rotor (Thermo electron corporation) at 3000 rpm for 10 minutes. Absorption spectra in air-equilibrated solvents were registered with a Varian Cary 5000 spectrophotometer, at room temperature, between 280 and 1400 nm, data interval = 0.5 nm, scan rate = 300 nm/min, SBW = 2 nm. DLS measurements of CNS samples dispersed in air-equilibrated DMF were performed with a Zetasizer Nano S (Malvern Instruments) at 20 °C setting 20 runs of 10 seconds for each measurement. Raman spectra of CNSs, drop-casted on pre-cleaned glass micro slides (Corning) and annealed at 110°C, were recorded with an Invia Renishaw Raman microspectrometer (50× objective) using the 633 nm line of a He–Ne laser at room temperature with a low laser power. Thermogravimetric analyses (TGA) of CNSs samples, precipitated by adding methanol and dried at 80 °C at 0.2 mbar for 4 h, were carried out with a Q5000IR TGA (TA Instruments) under air by an isotherm at 100 °C for 10 minutes followed by heating at 10 °C/min rate till 1000 °C.

A ZEISS SUPRA 40 Field-Emission Scanning Electron Microscope (FESEM) has been used to analyze the samples surface morphology and degree of dispersion. As the samples were conducting, no special charge suppression was necessary.

A PHI-5000 Versa Probe X-ray Photoelectron Spectroscopy (XPS) device equipped with a monochromatic Al X-ray source (1486.6 eV energy, 15 kV voltage and 25 W), has been used in order to investigate samples surface chemical composition. A spot size of 100 µm has been used. Different Pass Energy (PE) values have been chosen for the various types of spectra acquisition: 187 eV for survey spectra and 23 eV for high resolution peak spectra. XPS analysis have been made with CasaXPS Software (Version 2.3.13).

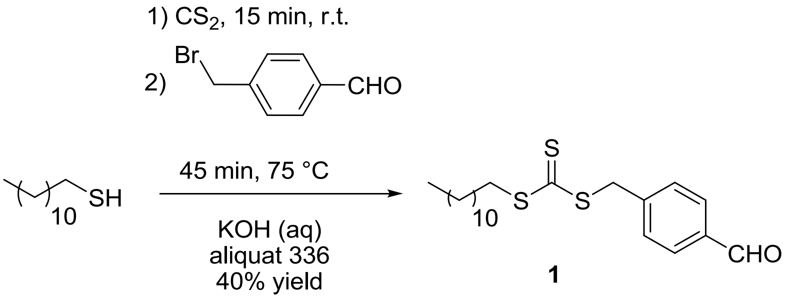
Relative atomic concentration has been evaluated after subtracting the background with a Shirley function. The values measured are reported in the following table.

**Table 1. Properties of the most soluble fractions of functionalized CNSs.**

| | concentration[a] / mg mL$^{-1}$ | aggregate size[b] / nm | *D/G*[c] | *DF*[d] | Relative atomic concentration[e] /% | | |
|---|---|---|---|---|---|---|---|
| | | | | | C | N | S |
| Graphite-TTC | 0.050 | /[f] | 0.48 (0.28) | 1/17 | 77.6 | 0.5 | 1.0 |
| SWCNT-TTC | 0.38 | 60 | 0.13 (0.06) | 1/25 | 89.3 | 0.5 | 2.7 |
| DWCNT-TTC | 0.52 | 30 | 0.14 (0.10) | 1/27 | 91.7 | 1.3 | 3.5 |
| MWCNT-TTC | 1.10 | 60 | 1.68 (1.64) | 1/129 | 93.5 | 0.6 | 1.4 |

[a] Concentration in DMF determined by TGA. Error of ± 5%. [b] Dimension of the aggregates from DLS analysis. Error ± 10%. [c] Ratio between the intensity of the D and the G band of the Raman spectra. The value for the pristine CNSs is reported in brackets. Error ± 5%. [d] Degree of functionalization for the CNSs expressed as the ratio between the moles of functional group and the moles of available reactive sites (C=C) determined by TGA. Error of ± 5%. [e] From XPS measurements. [f] No DLS data due to excessive aggregation.

### 2. Synthesis of dodecyl 4-formylbenzyltrithiocarbonate (1)



The reaction was carried out under nitrogen atmosphere. $CS_2$ (0.30 mL, 5.0 mmol) is added dropwise to a solution of dodecanthiol (1.2 mL, 5.0 mmol) and Aliquat 336 (11 µL, 0.0024 µmol) in aqueous KOH (20% w/w, 1.5 mL). Immediately the solution turned bright yellow. After 15 minutes under magnetic stirring, 4-(bromomethyl)benzaldehyde (1.0 g, 5.0 mmol) was added and the reaction mixture was heated at 75 °C for 45 minutes. The reaction was monitored by TLC on silica gel (eluent: ETP/ $Et_2O$ 9:1, $R_F$(product) = 0.4). The reaction is quenched with deionized water (100 mL) and washed with petroleum ether (4 x 70 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed at reduced pressure obtaining a yellow solid which was purified by column chromatography on silica gel (eluent: ETP/ $Et_2O$ 9:1, $R_F$(product) = 0.4). The desired product was obtained as yellow crystals by recrystallization from methanol. (790 mg, 2.0 mmol). 40% yield.[1]

**$^1$H NMR** (300 MHz, $CDCl_3$, δ): 9.99 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 4.68 (s, 2H), 3.38 (s, 2H), 1.71 (s, 2H -), 1.27 (s, 18H), 0.89 (s, 3H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$, δ): 221, 192.00, 143.05, 136.00, 130.30, 41.21, 41.07, 40.69, 37.71, 32.29, 30.14 , 28.99 , 28.29, 23.08, 14.53.

**mp** 48.3-48-6 °C

**Anal. Calcd** for $C_{21}H_{32}OS_3$: C, 63.59; H, 8.13; O, 4.03; S, 24.25. Found: C, 63.45; H, 8.19; O, 4.14; S, 24.22.

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[1] Formation of byproduct was not observed. Indeed, conversion yield is expected to be higher than the isolated yield. The 40 % yield is obtained after isolating a highly pure portion of the material by column chromatography and crystallization.

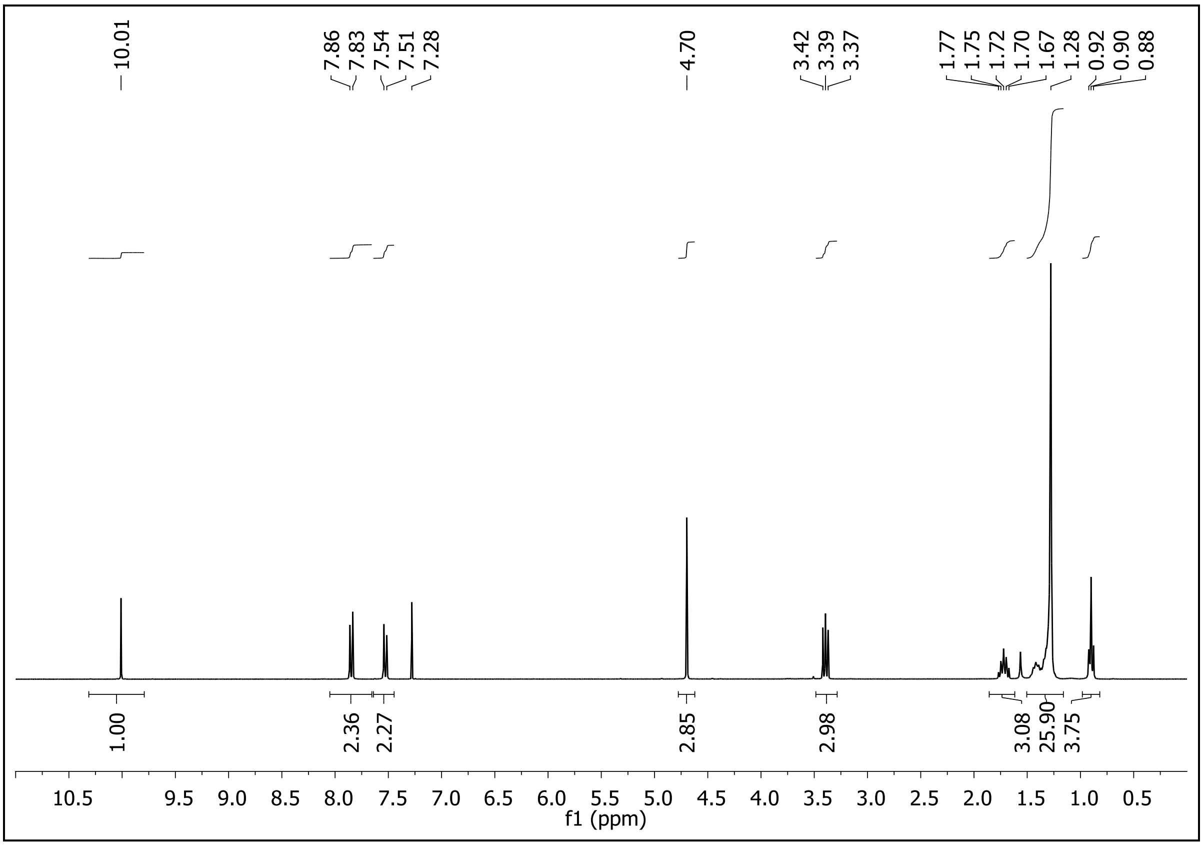


Figure S1: $^1$H-NMR spectrum of **2** (300 MHz, $CDCl_3$).

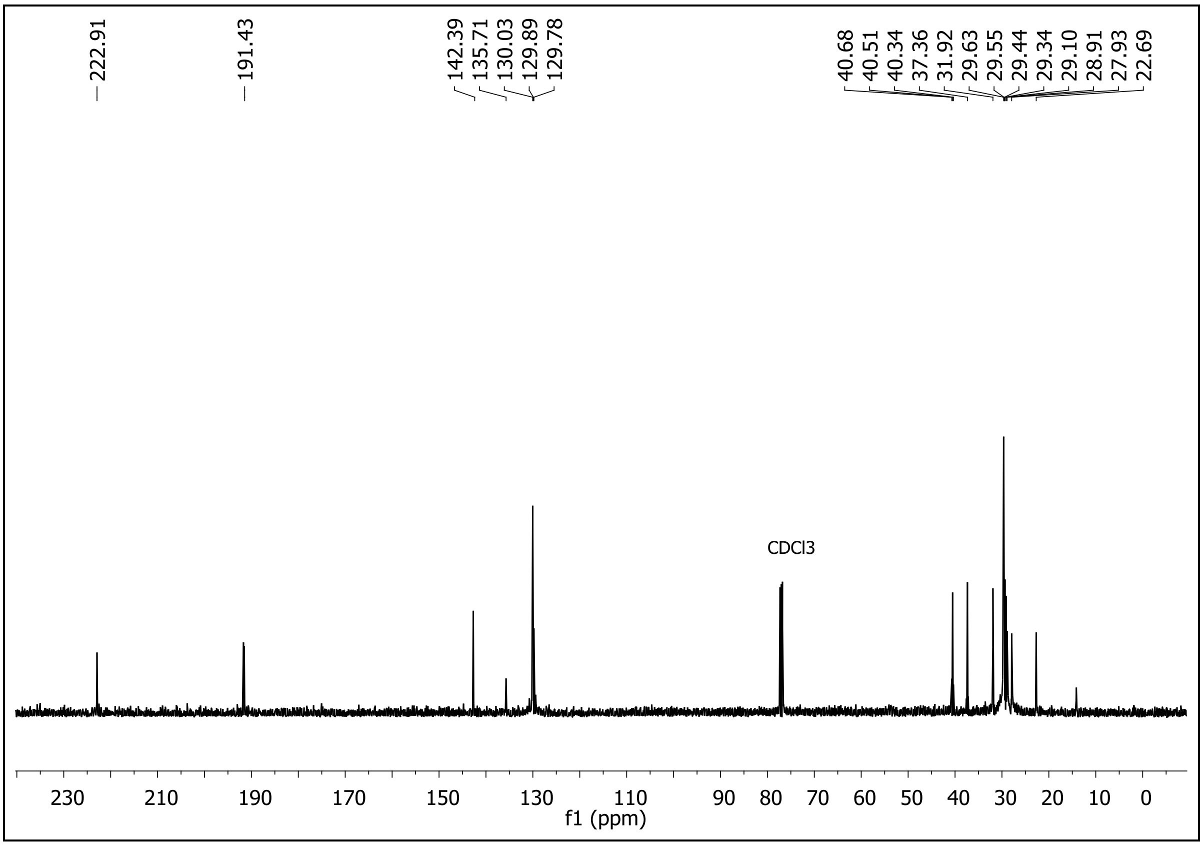


Figure S2: $^{13}$C-NMR spectrum of **1** (125 MHz, $CDCl_3$).

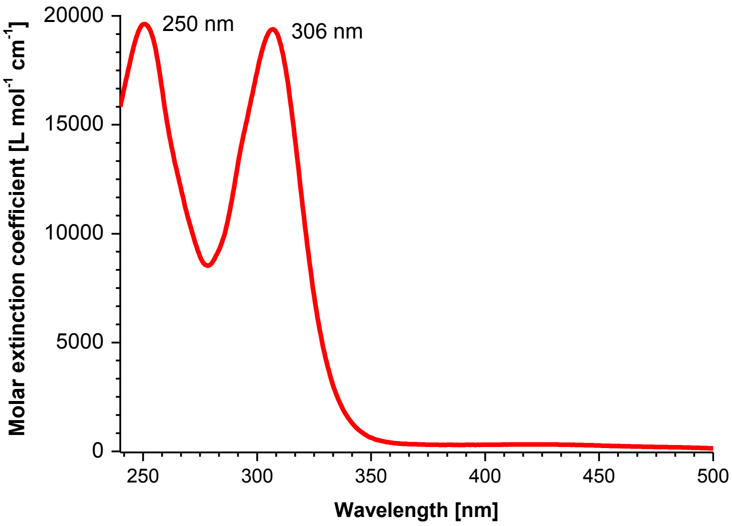


Figure S3: UV-vis absorption spectrum of **1** in air-equilibrated hexane.

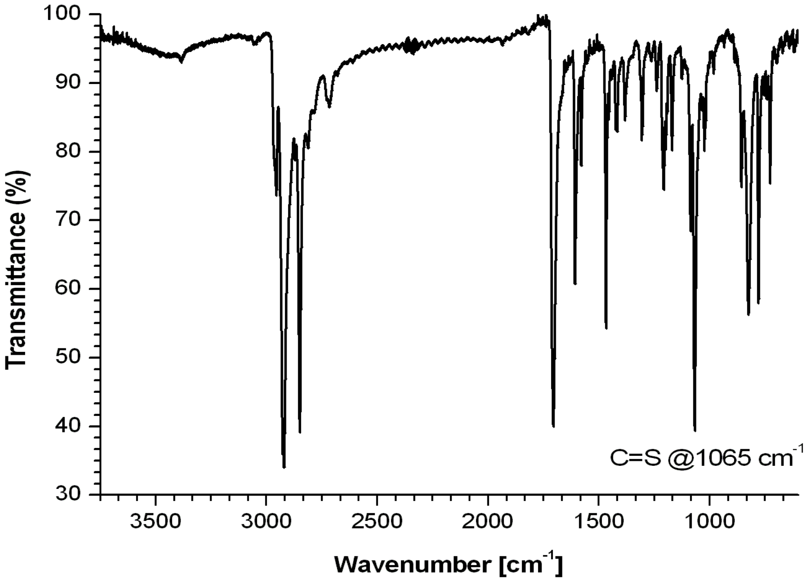


Figure S4: FT-IR absorption spectrum of **1** (KBr pellet).

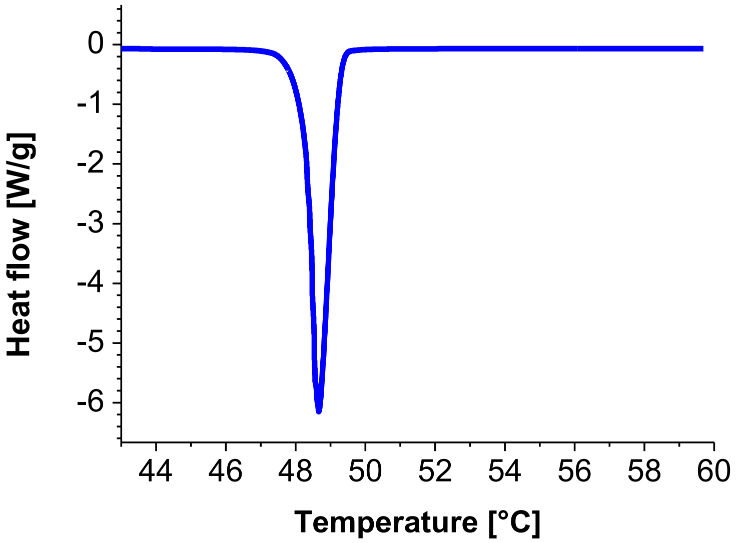


Figure S5: DSC thermogram of **1** (1 °C/min under nitrogen).

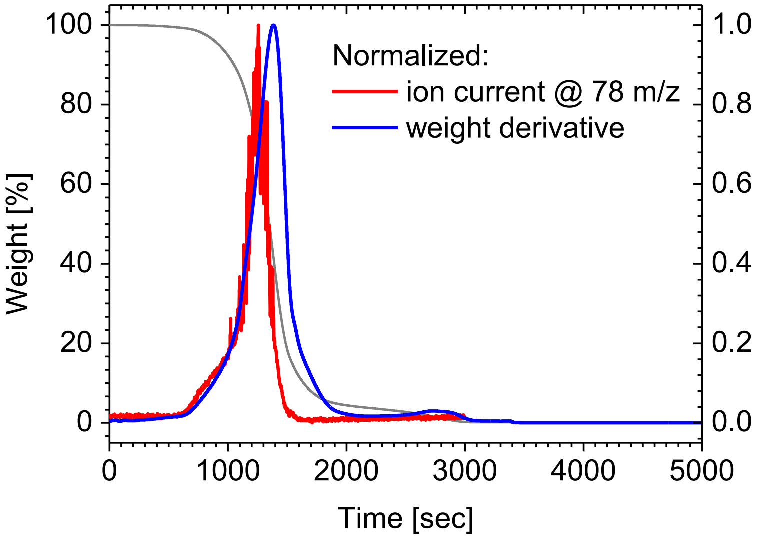
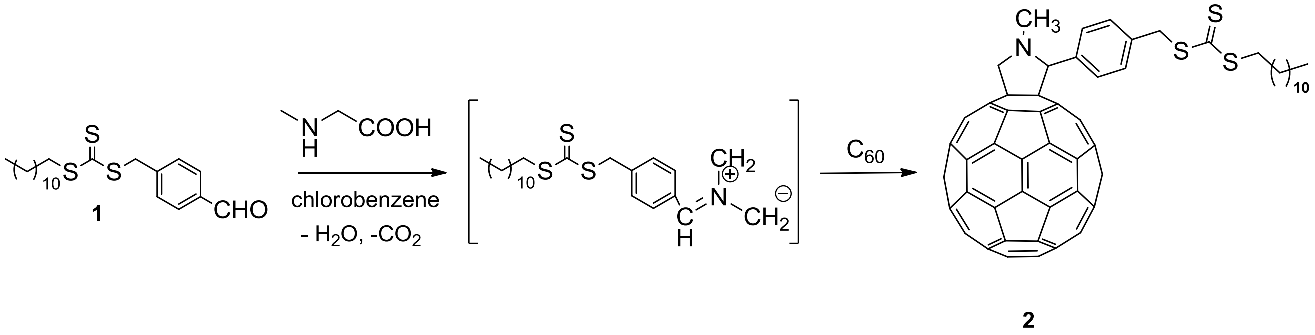


Figure S6: TGA-MS analysis including: (a) weight loss (grey); (b) normalized weight derivative (blue); and (c) normalized ion current at 78 m/z (red) of **1** (10 °C/min under air).

### 3. Synthesis and characterization of the fulleropyrrolidine 2



The reaction was carried out under nitrogen atmosphere. Sarcosine (28 mg, 0.31 mmol) and the aldehyde **1** (84 mg, 0.21 mmo) were added portionwise to a solution of $C_{60}$ (0.10 g, 0.14 mmol) in chlorobenzene (10 mL) heated at 130 °C. The reaction is monitored by TLC (stationary phase: silica gel; eluent: hexane/toluene 2:1; $R_F$(product) = 0.48). After 60 minutes the solvent was removed at reduced pressure obtaining a brown solid which was purified by column chromatography on silica gel (eluent: hexane/toluene 2:1). The desired product was obtained as brown powder (32 mg, 0.028 mmol). 20% yield.

**$^1$H NMR** (300 MHz, $CDCl_3/CS_2$ 1:2) : δ 7.75 (d, *J* = 7.1 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 4.98 (d, *J* = 9.5 Hz, 1H), 4.92 (s, 1H), 4.61 (s, 2H), 4.26 (d, *J* = 9.5 Hz, 1H), 3.35 (t, 2H), 2.80 (s, 3H), 1.68 (m, 2H), 1.26 (s, 18H), 0.88 (s, 3H, $CH_3$).

**$^{13}$C NMR** (126 MHz, $CDCl_3/CS_2$ 1:2) : δ 222.5, 156.04, 153.81, 153.15, 152.98, 147.22, 146.58, 146.34, 146.26, 146.08, 146.00, 145.88, 145.69, 145.49, 145.43, 145.32, 145.20, 145.09, 144.64, 144.56, 144.34, 143.09, 142.96, 142.64, 142.56, 142.51, 142.22, 142.17, 142.11, 141.99, 141.85, 141.79, 141.63, 141.51, 140.17, 140.13, 139.91, 139.50, 136.82, 136.48, 135.82, 135.67, 135.55, 129.76, 129.48, 83.23, 83.11, 70.15, 69.86, 68.89, 41.37, 41.14, 40.92, 40.02, 39.91, 37.57, 37.26, 36.96, 32.17, 29.92, 29.84, 29.75, 29.63, 29.42, 29.22, 28.27, 23.06, 14.45, 14.36.

**APPI-MS** (m/z) $C_{83}H_{37}NS_3$ m/z: 1144 ($M^{+\cdot}$).

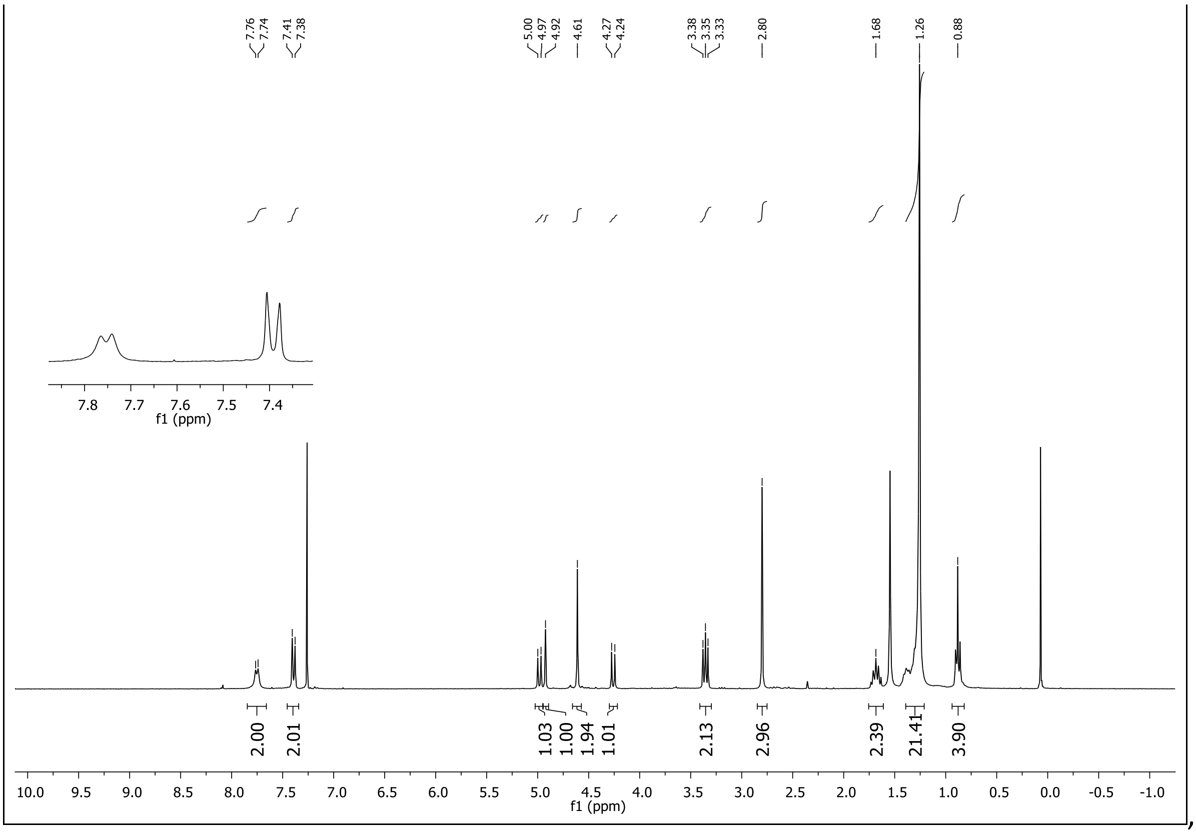


Figure S7. $^{1}$H-NMR spectrum of **2** (300 MHz, $CDCl_3/CS_2$ 4:1).

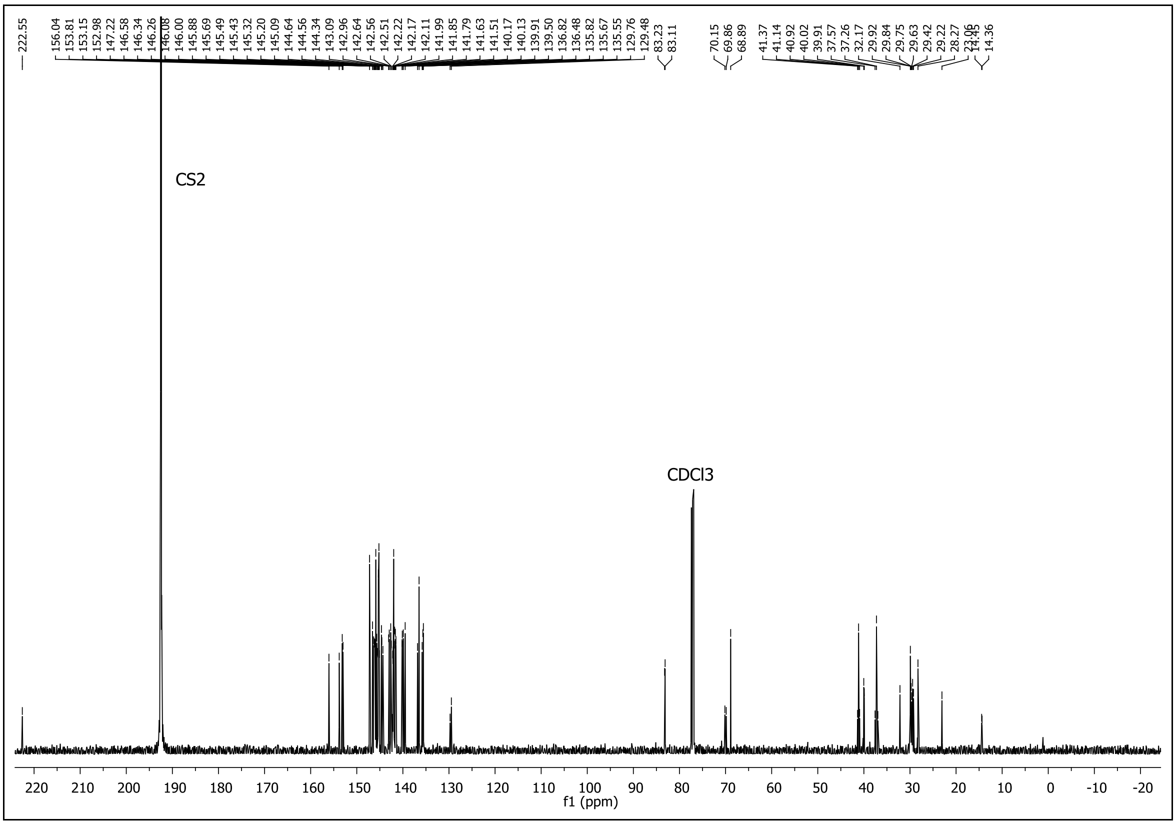


Figure S8. $^{1}$H-NMR spectrum of **2** (300 MHz, $CDCl_3/CS_2$ 4:1).

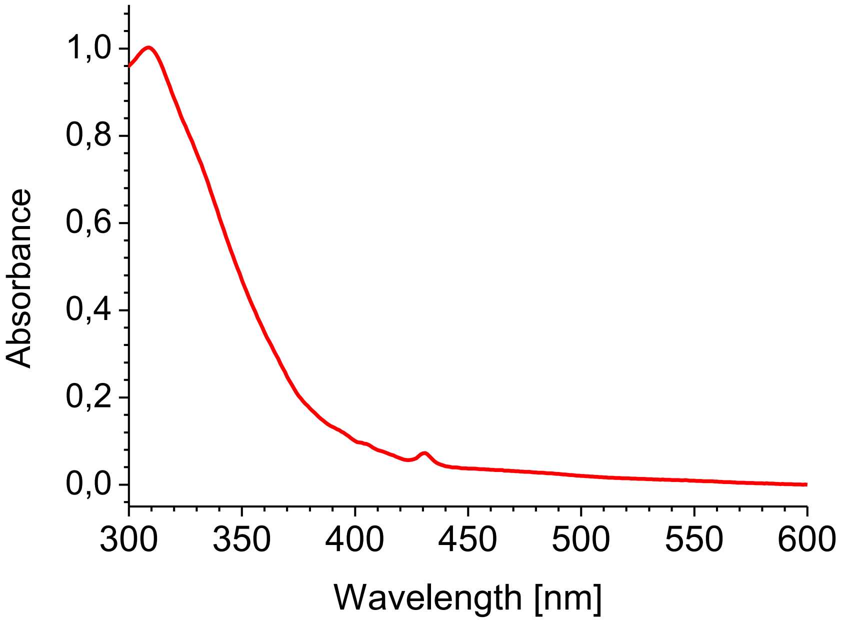


Figure S9. UV-vis absorption spectrum of **2** in air-equilibrated hexane.

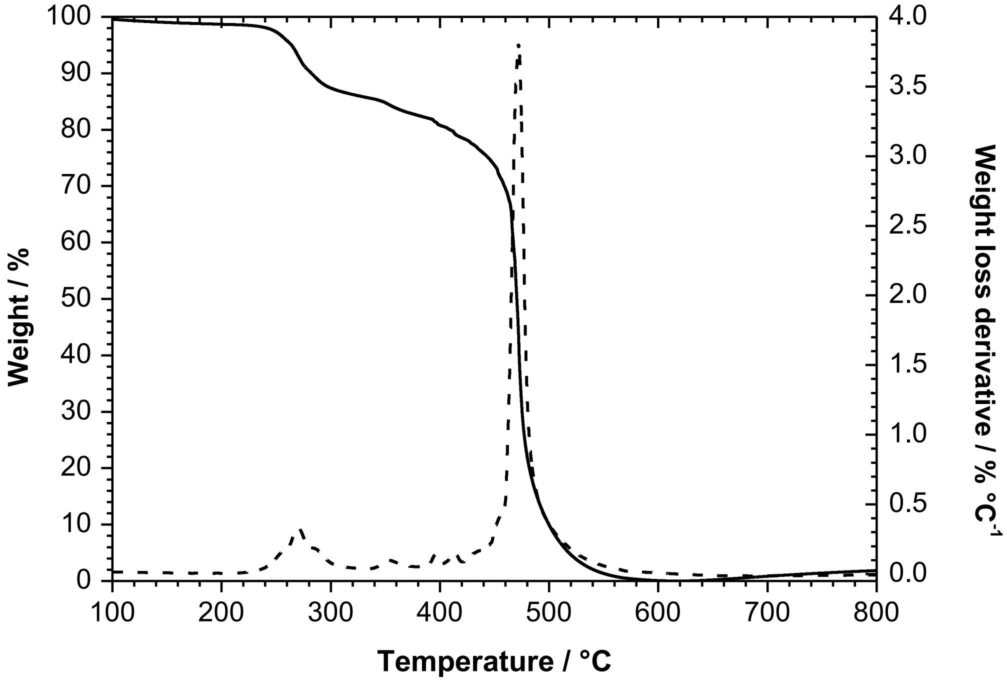


Figure S10. Thermogram of **2** under air with heating rate 10 °C min$^{-1}$. The solid line refers to weight (left axis), the dashed one to weight loss derivative (right axis).

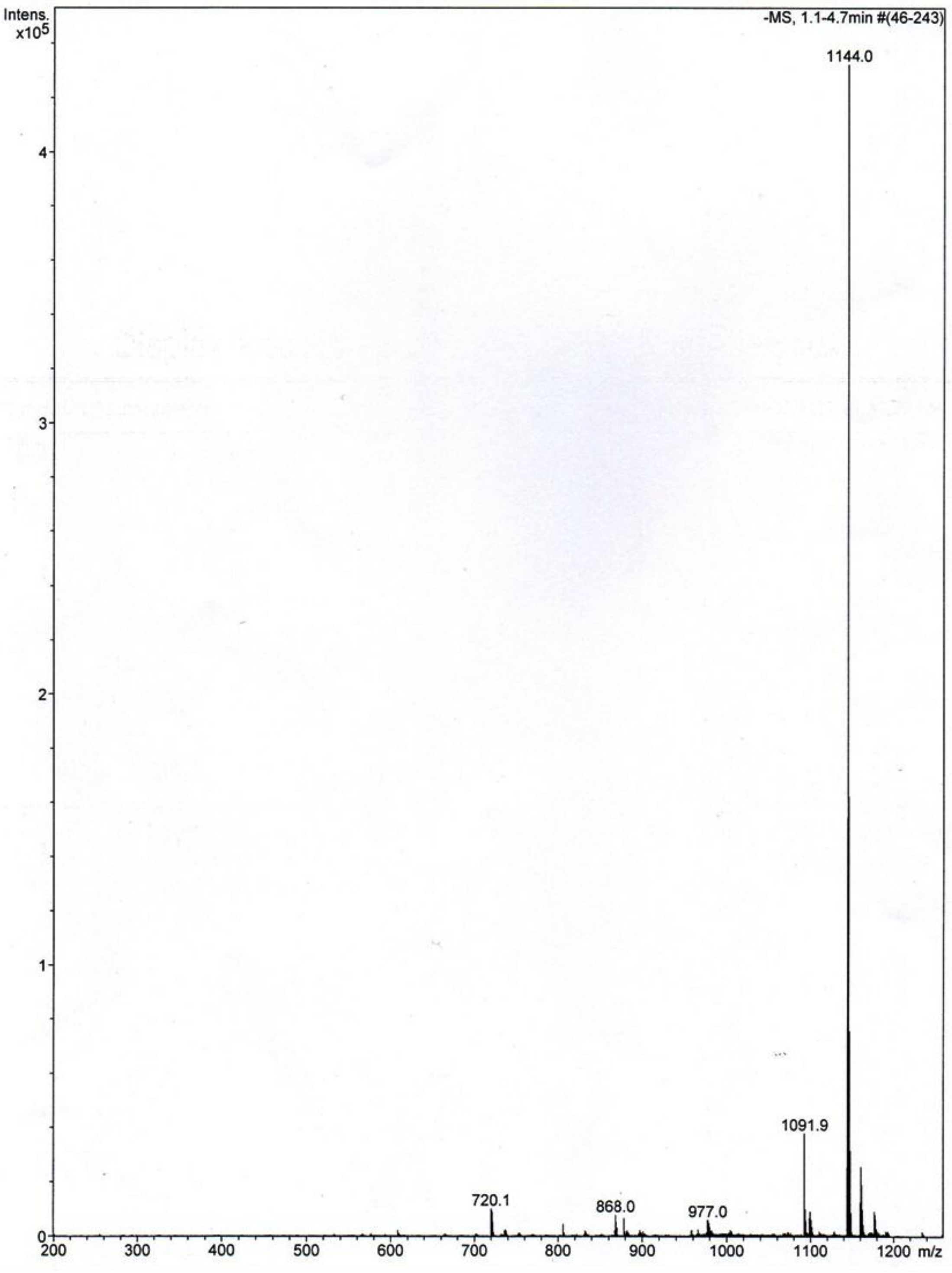
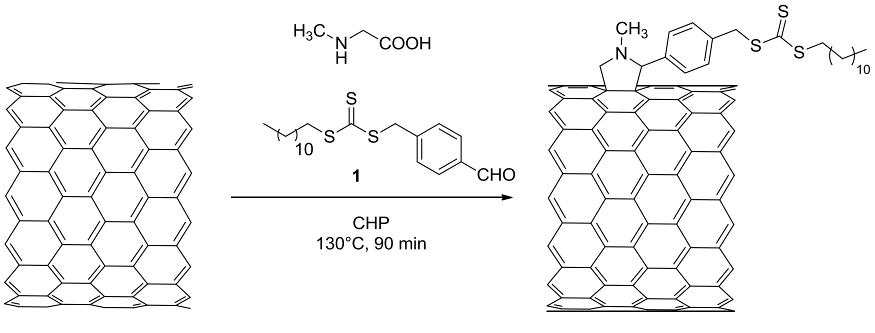


Figure S11. APPI-MS spectrum of **2**; (m/z) $C_{83}H_{37}NS_3$ m/z: 1144 (M+).

## 4. Synthesis and characterization of SWCNT-TTC



SWCNT-TTC

The reaction was carried out under nitrogen. A dispersion of the aldehyde **1** (0.10 g, 0.30 mmol) and sarcosine (30 mg, 0.34 mmol) in 1-cyclohexylpyrrolid-2-one (CHP, 3.0 mL) was added in three portion 30 minutes apart to a dispersion of SWCNT (10 mg, 0.83 mmol of C) in CHP (7.0 mL) pre-sonicated for 30 minutes. After 90 minutes at 130 °C the reaction mixture is diluted with methanol (40 mL) and is centrifuged (10 minutes at 3000 rpm). The precipitate at the bottom of the centrifuge tube is washed with methanol (3 x 5 mL), centrifuged and dried at 80 °C and 0.2 mbar for 30 minutes. Then, the carbonaceous material is extracted with DMF (10 x 5.0 mL) by means of a sonication (power level: 2.0, pulse on: 3 sec, pulse off: 3 sec, time: 1 min) and a centrifugation (5 minutes at 3000 rpm) procedure.

**Solubilities** in DMF for each extract (mg/mL): 0.19 (1), 0.10 (2), 0.09 (3), 0.084 (4), 0.082 (5), 0.063 (6), 0.057 (7), 0.055 (8), 0.032 (9), 0.013 (10).

**Raman** (thin film) /cm$^{-1}$ (relative intensities): 2660 (0.16, 2D), 1920 (0.03, iTOLA) 1586 (1, G), 1332 (0.13, D), 219 (0.16, RBM), 169 (0.04, RBM), 155 (0.06, RBM).

**FD** (weight loss at 350 °C): 1/25 (40.9%).

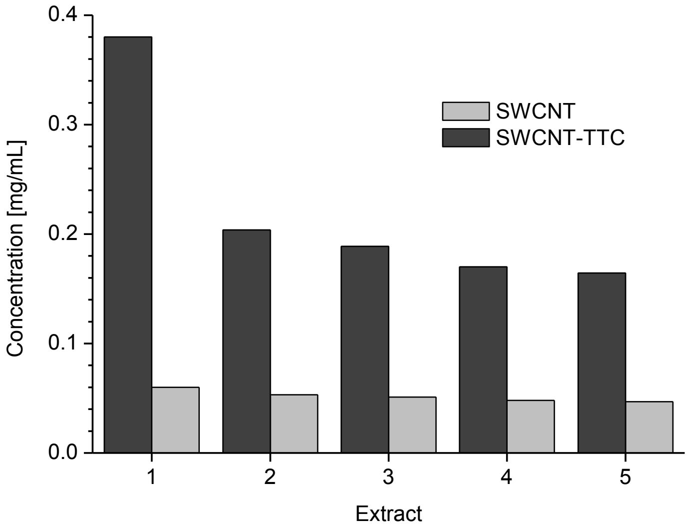


Figure S12. Concentration of pristine SWCNT (light grey) and SWCNT-TTC (dark grey) extracted with DMF (5 fractions, 5 mL each).

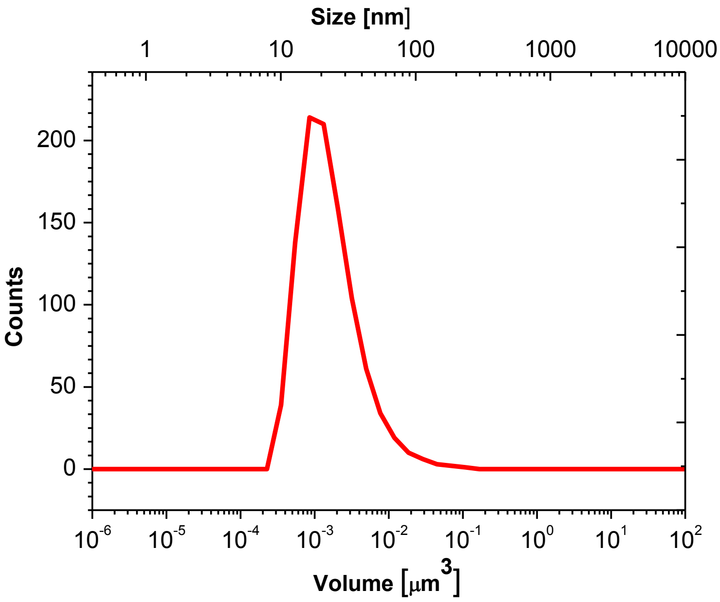


Figure S13. DLS number distributions for SWCNT-TTC present in the first DMF extract.

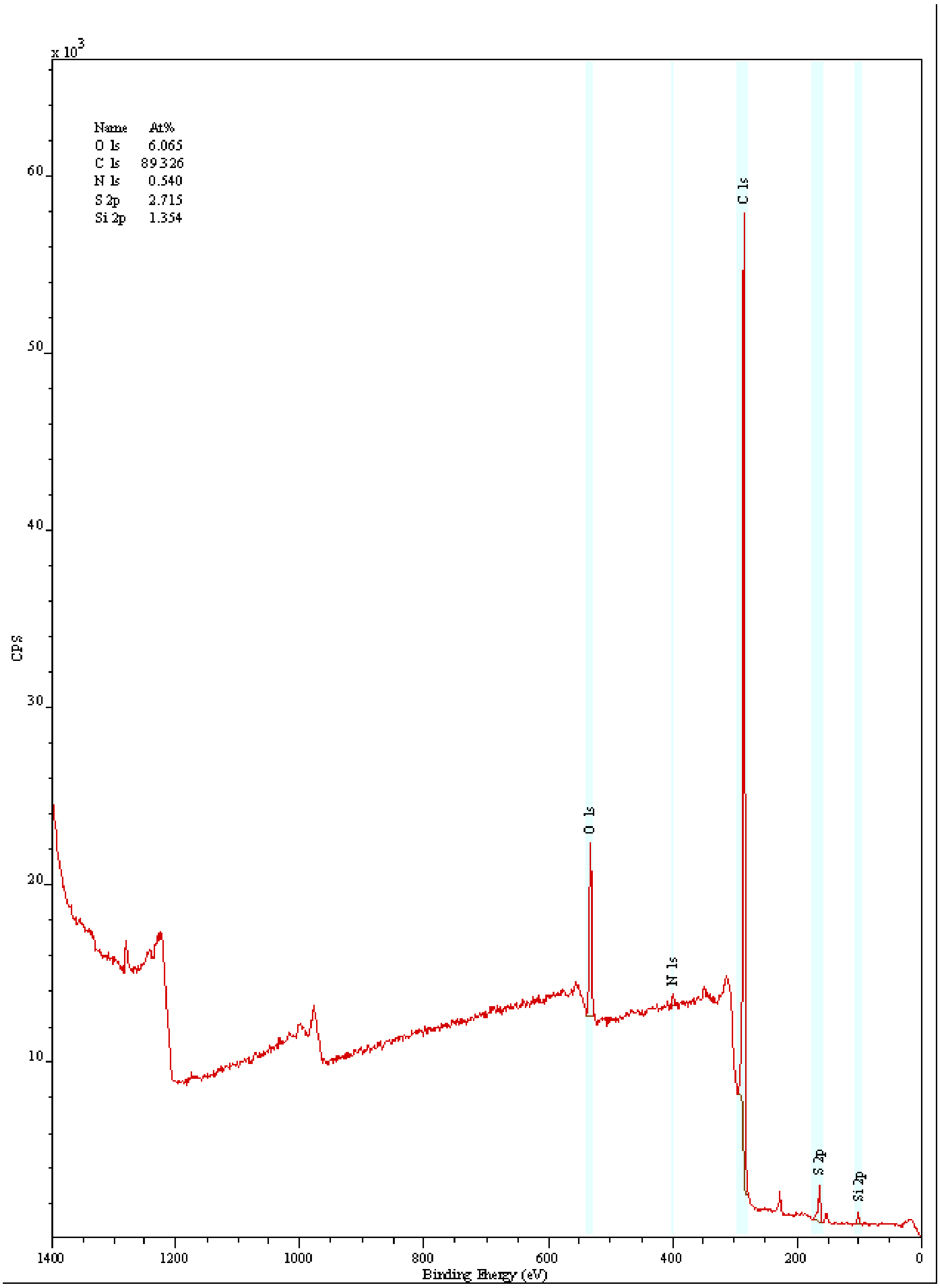


Figure S14. XPS full-scan spectrum of SWCNT-TTC.

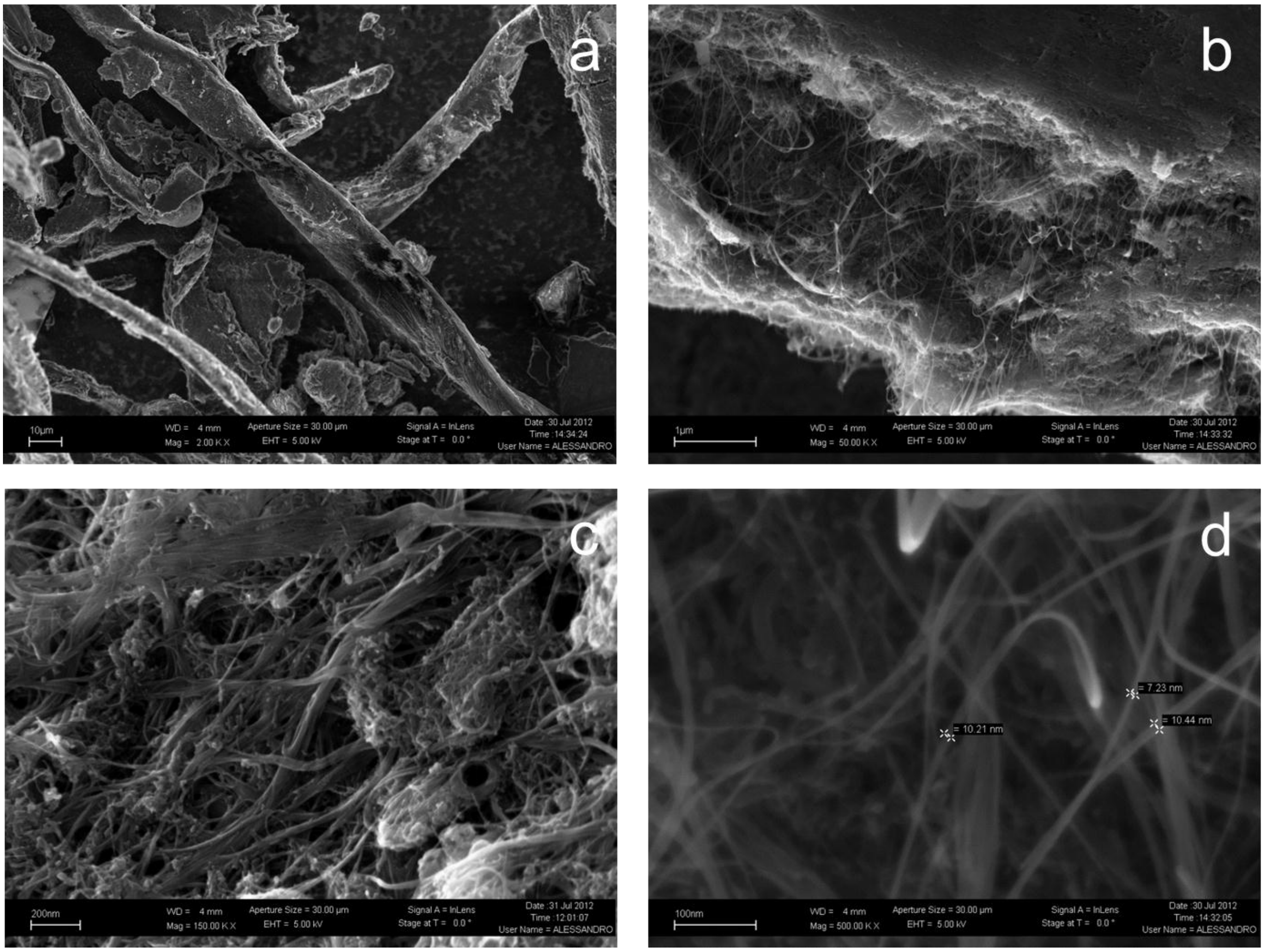


Figure S15. FESEM images of SWCNT-TTC at (a) 2 kX, (b) 50 kX, (c) 150 kX, and (d) 500 kX magnifications.

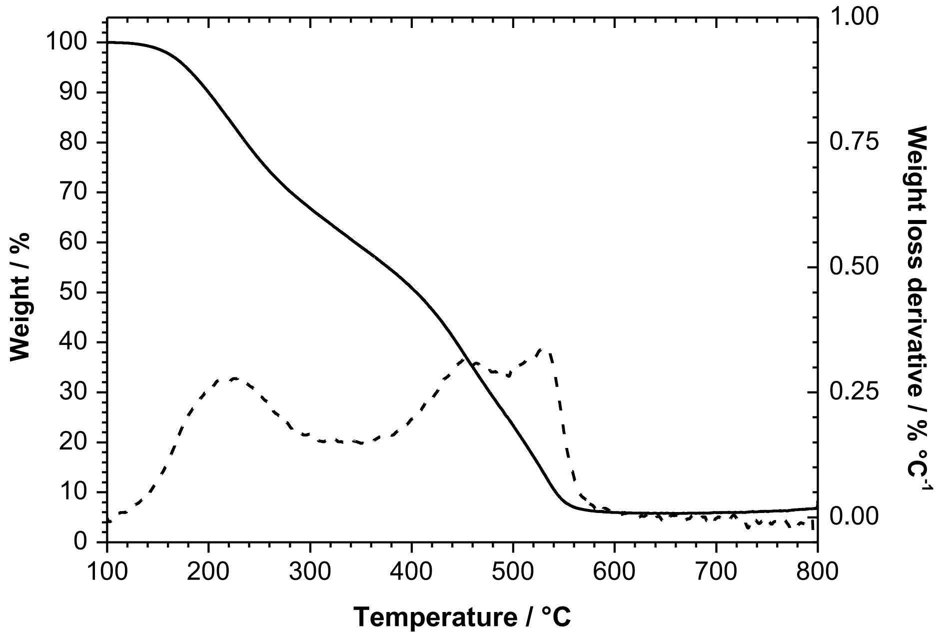


Figure S16. Thermogram of SWCNT-TTC under air with heating rate 10 °C min$^{-1}$. The solid line refers to weight (left axis), the dashed one to weight loss derivative (right axis).

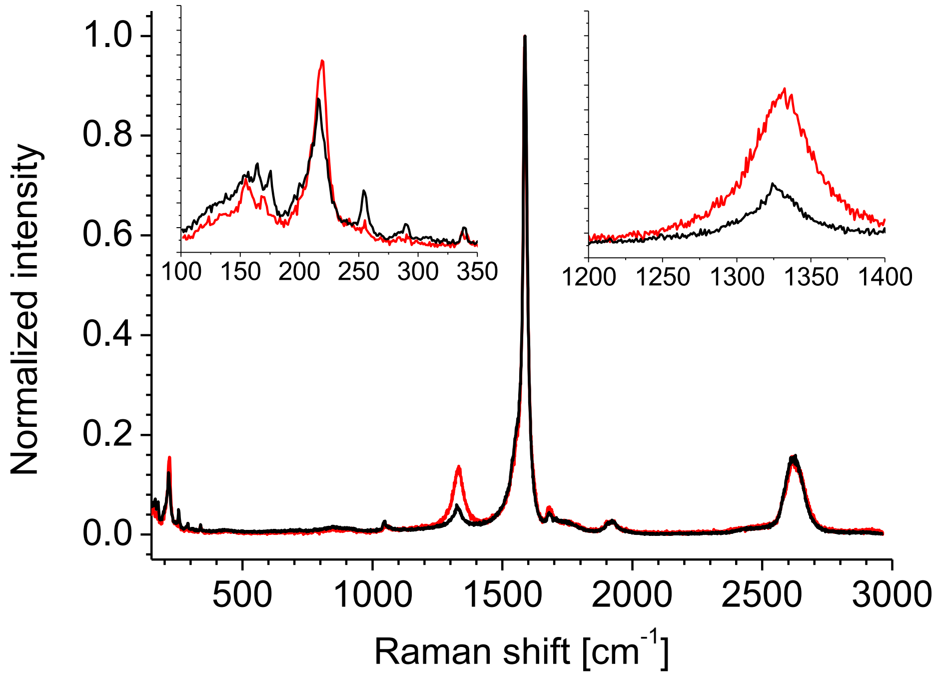
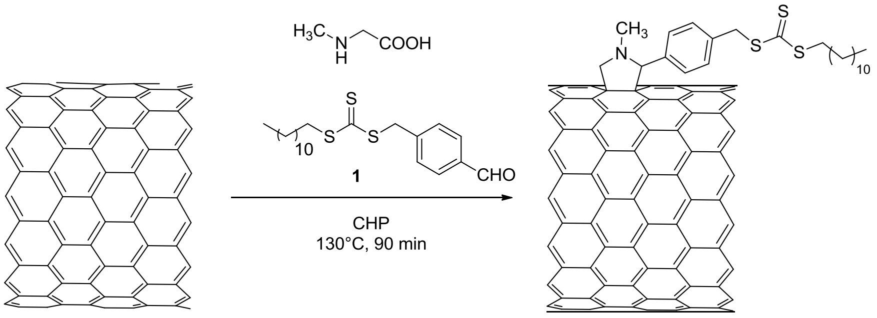


Figure S17. Raman spectra of SWCNT-TTC (red line) and pristine SWCNT (black line). The insets highlight the differences in the RBMs (left) and in the D bands (right) following functionalization.

## 5. Synthesis and characterization of DWCNT-TTC



**DCWNT-TTC**

The reaction was carried out under nitrogen. A dispersion of the aldehyde **1** (0.10 g, 0.30 mmol) and sarcosine (30 mg, 0.34 mmol) in CHP (3.0 mL) was added in three portion 30 minutes apart to a dispersion of DWCNT (10 mg, 0.83 mmol of C) in CHP (7.0 mL) pre-sonicated for 30 minutes. After 90 minutes at 130 °C the reaction mixture is diluted with methanol (40 mL) and is centrifuged (10 minutes at 3000 rpm). The precipitate at the bottom of the centrifuge tube is washed with methanol (3 x 5 mL), centrifuged and dried at 80 °C and 0.2 mbar for 30 minutes. Then, the carbonaceous material is extracted with DMF (10 x 5.0 mL) by means of a sonication (power level: 2.0, pulse on: 3 sec, pulse off: 3 sec, time: 1 min) and a centrifugation (5 minutes at 3000 rpm) procedure.

**Solubilities** in DMF for each extract (mg/mL): 0.26 (1), 0.19 (2), 0.15 (3), 0.13 (4), 0.11 (5), 0.08 (6), 0.069 (7), 0.051 (8), 0.041 (9), 0.037 (10).

**Raman** (thin film) /cm$^{-1}$ (relative intensities): 2627 (0.20, 2D), 1587 (1, G), 1329 (0.13, D), 256 (0.03, RBM), 219 (0.10, RBM), 156 (0.06), 136 (0.04).

**FD** (weight loss at 450 °C): 1/27 (39.2%).

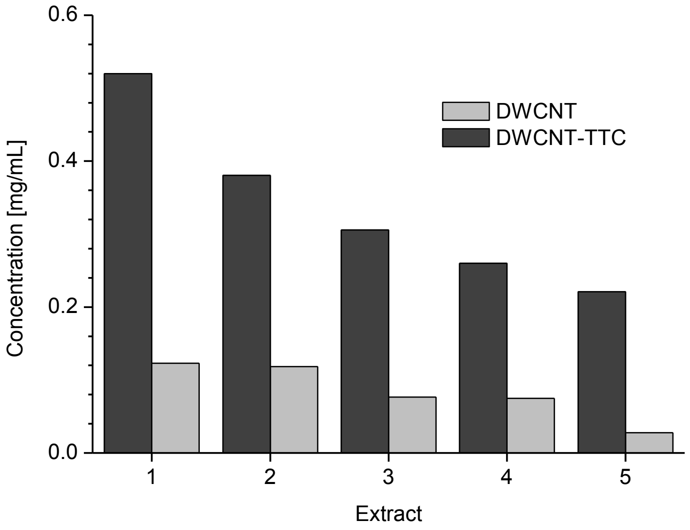


Figure S18. Concentration of pristine DWCNT (light grey) and DWCNT-TTC (dark grey) extracted with DMF (5 fractions, 5 mL each).

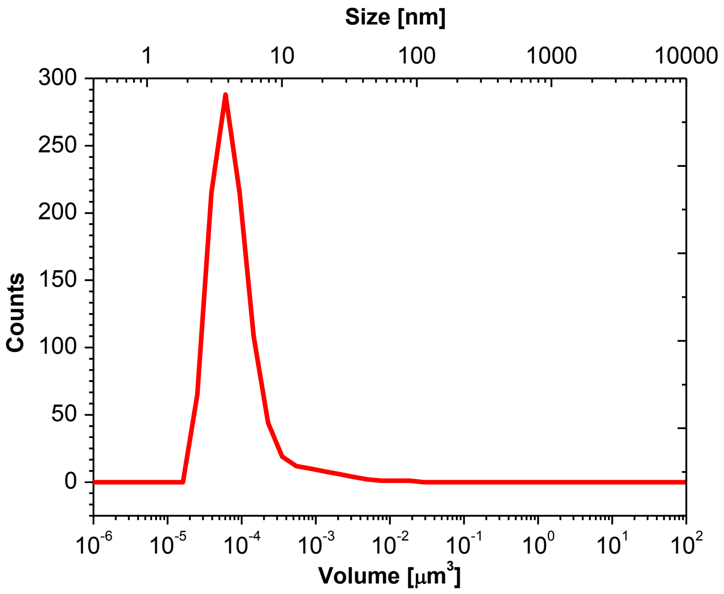


Figure S19. DLS number distributions for DWCNT-TTC present in the first DMF extract.

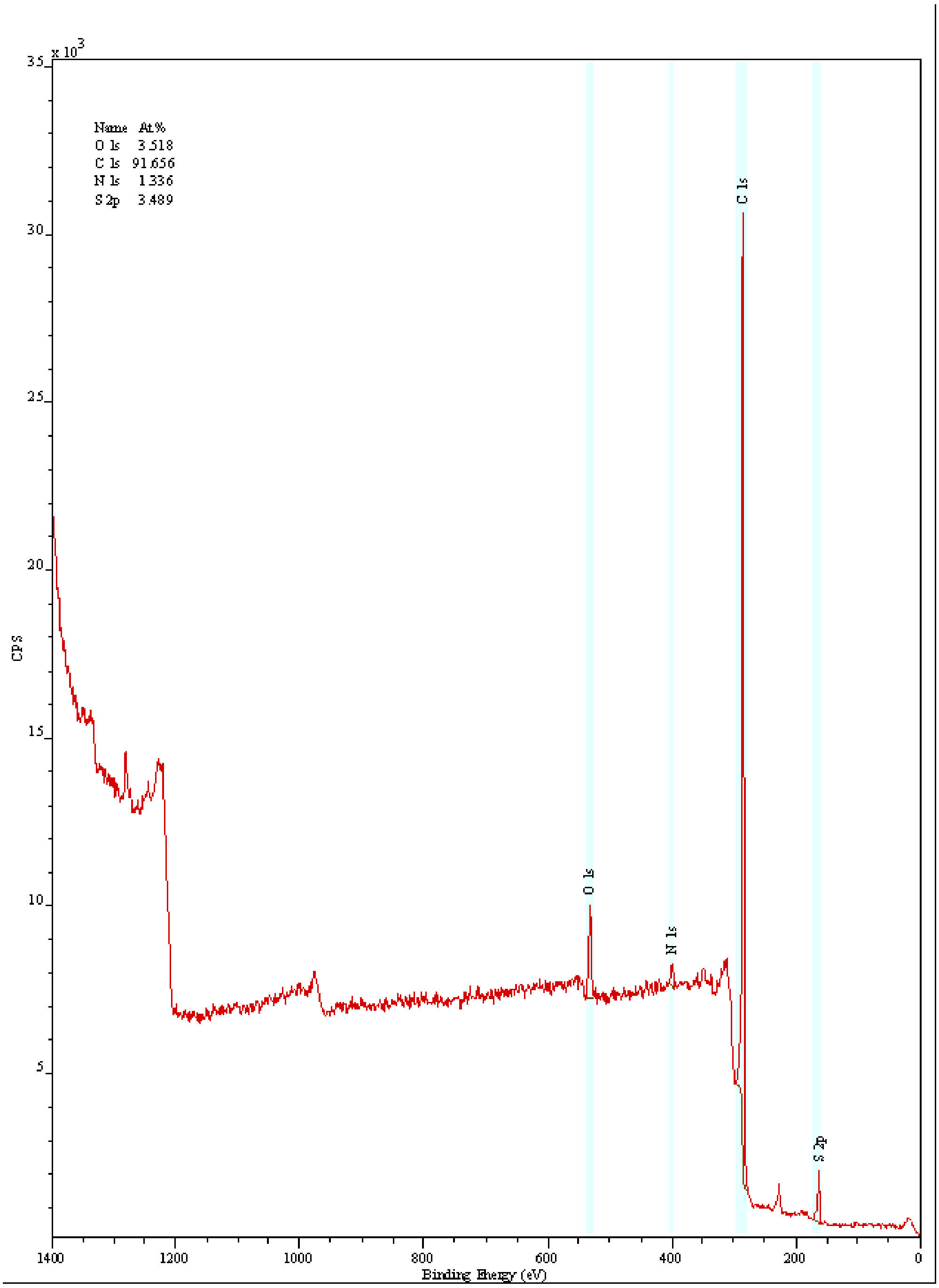


Figure S20. XPS full-scan spectrum of DWCNT-TTC.

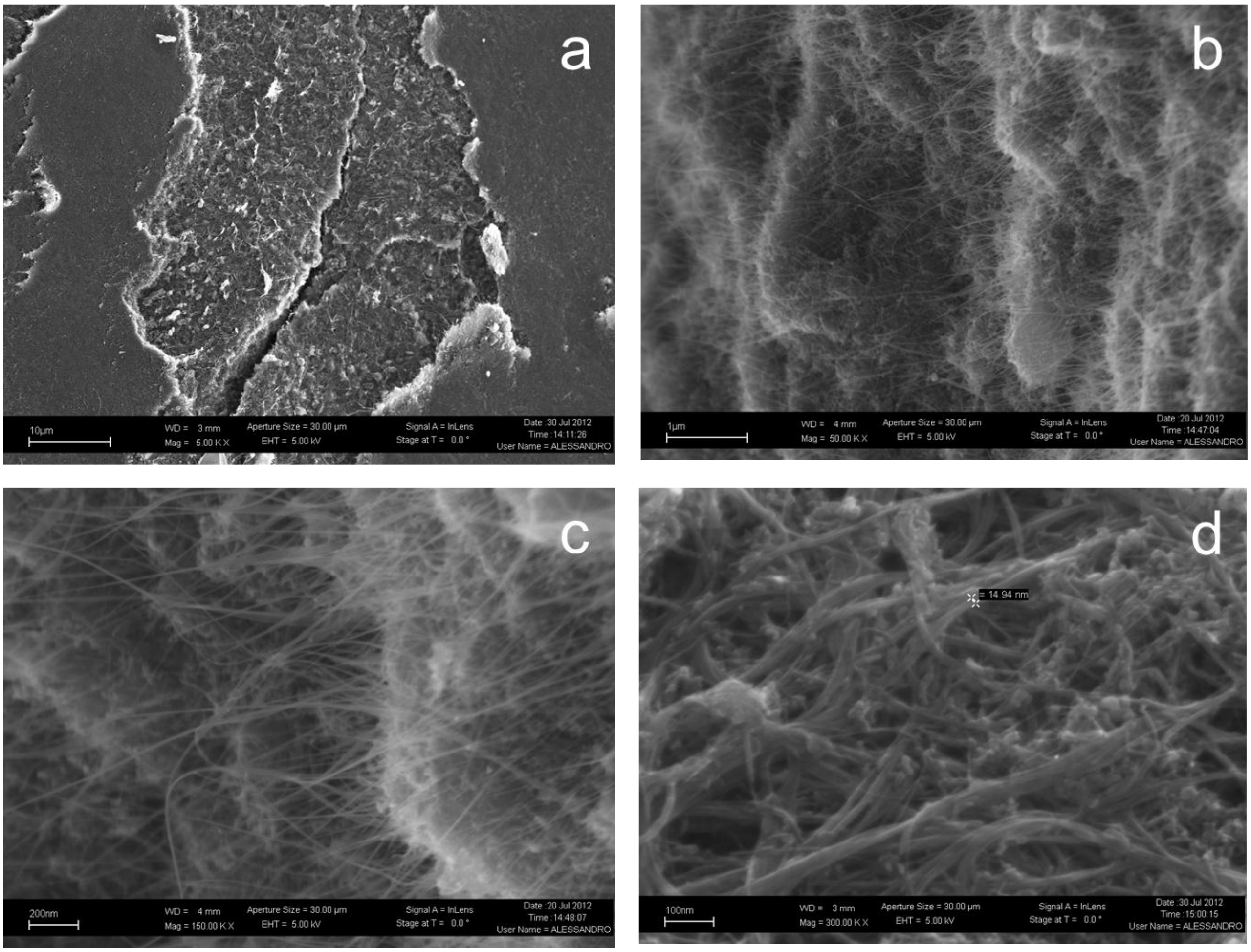


Figure S21. FESEM images of DWCNT-TTC at (a) 5 kX, (b) 50 kX, (c) 150 kX, and (d) 300 kX magnifications.

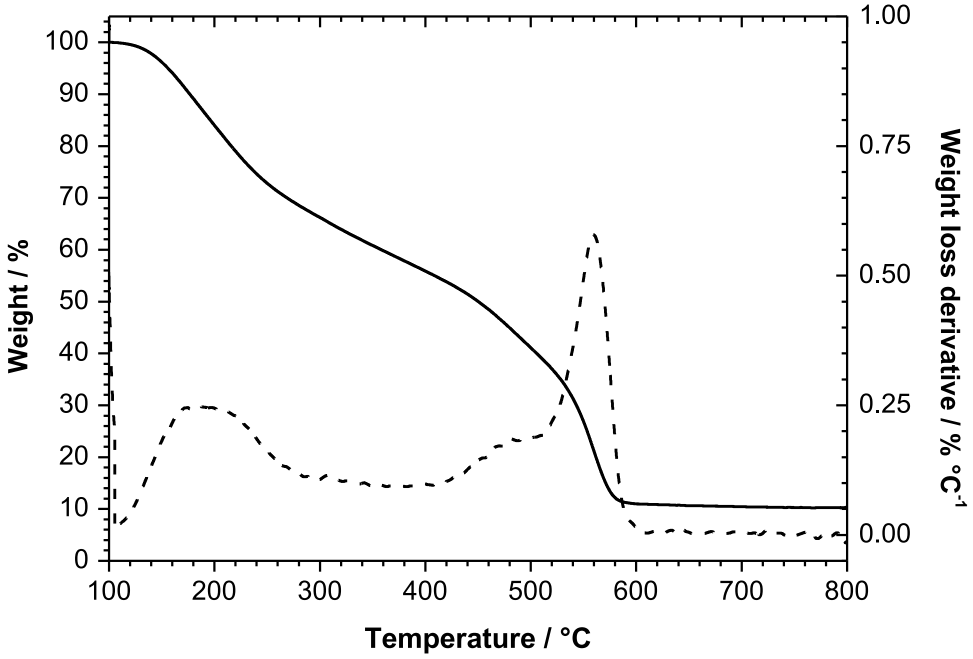


Figure S22. Thermogram of DWCNT-TTC under air with heating rate 10 °C min$^{-1}$. The solid line refers to weight (left axis), the dashed one to weight loss derivative (right axis).

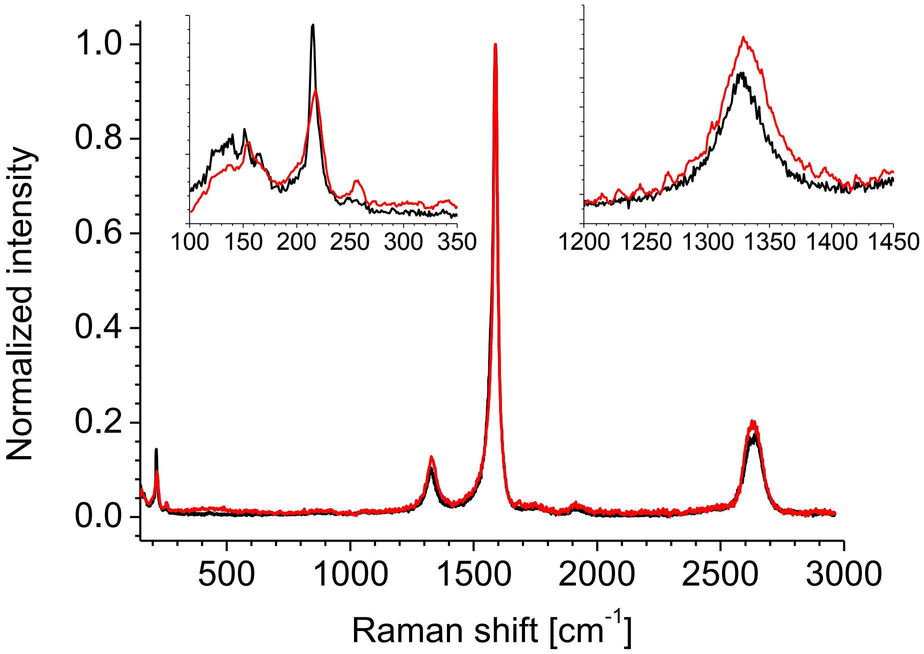
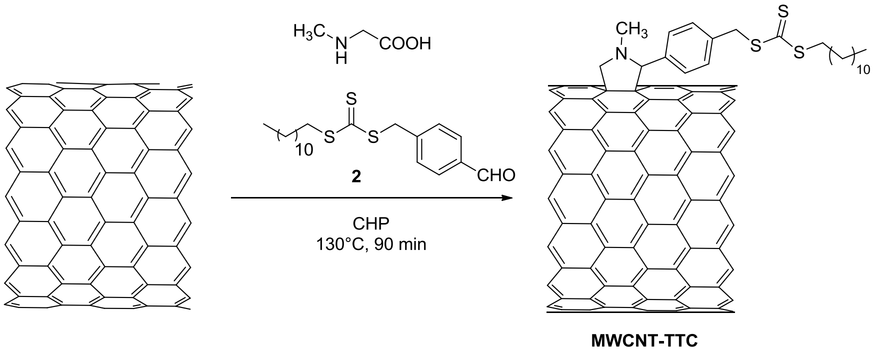


Figure S23. Raman spectra of DWCNT-TTC (red line) and pristine DWCNT (black line). The insets highlight the differences in the RBMs (left) and in the D bands (right) following functionalization.

## 6. Synthesis and characterization of MWCNT-TTC



The reaction was carried out under nitrogen. A dispersion of the aldehyde **1** (0.10 g, 0.30 mmol) and sarcosine (33 mg, 0.28 mmol) in CHP (3.0 mL) was added in three portion 30 minutes apart to a dispersion of MWCNT (10 mg, 0.83 mmol of C) in CHP (7.0 mL) pre-sonicated for 30 minutes. After 90 minutes at 130 °C the reaction mixture is diluted with methanol (40 mL) and is centrifuged (10 minutes at 3000 rpm). The precipitate at the bottom of the centrifuge tube is washed with methanol (3 x 5 mL), centrifuged and dried at 80 °C and 0.2 mbar for 30 minutes. Then, the carbonaceous material is extracted with DMF (10 x 5.0 mL) by means of a sonication (power level: 2.0, pulse on: 3 sec, pulse off: 3 sec, time: 1 min) and a centrifugation (5 minutes at 3000 rpm) procedure.

**Solubilities** in DMF for each extract (mg/mL): 1.10 (1), 0.2 (2), 0.065 (3), 0.019 (4), 0.019 (5), 0.016 (6), 0.013 (7), 0.01 (8), 0.008 (9), 0.008 (10).

**Raman** (thin film) /cm$^{-1}$ (relative intensities): 2660 (0.46, 2D), 1600 (1, G), 1330 (1.59, D).

**FD** (weight loss at 450 °C): 1/129 (16.4%).

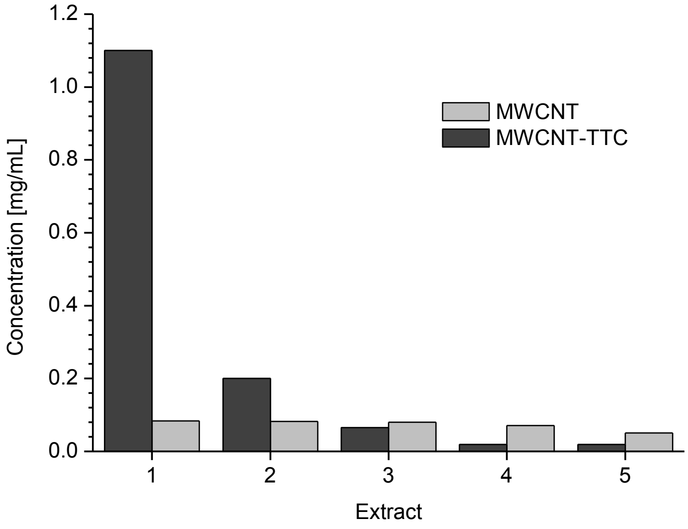


Figure S24. Concentration of pristine MWCNT (light grey) and MWCNT-TTC (dark grey) extracted with DMF (5 fractions, 5 mL each).

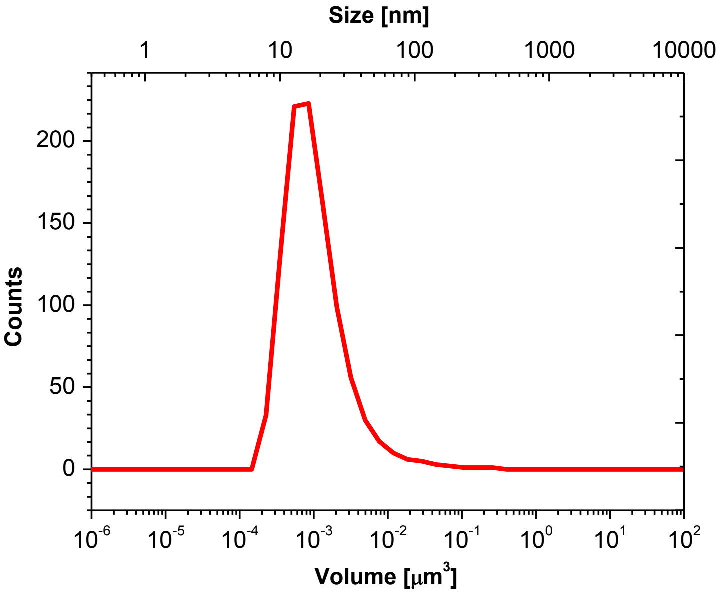
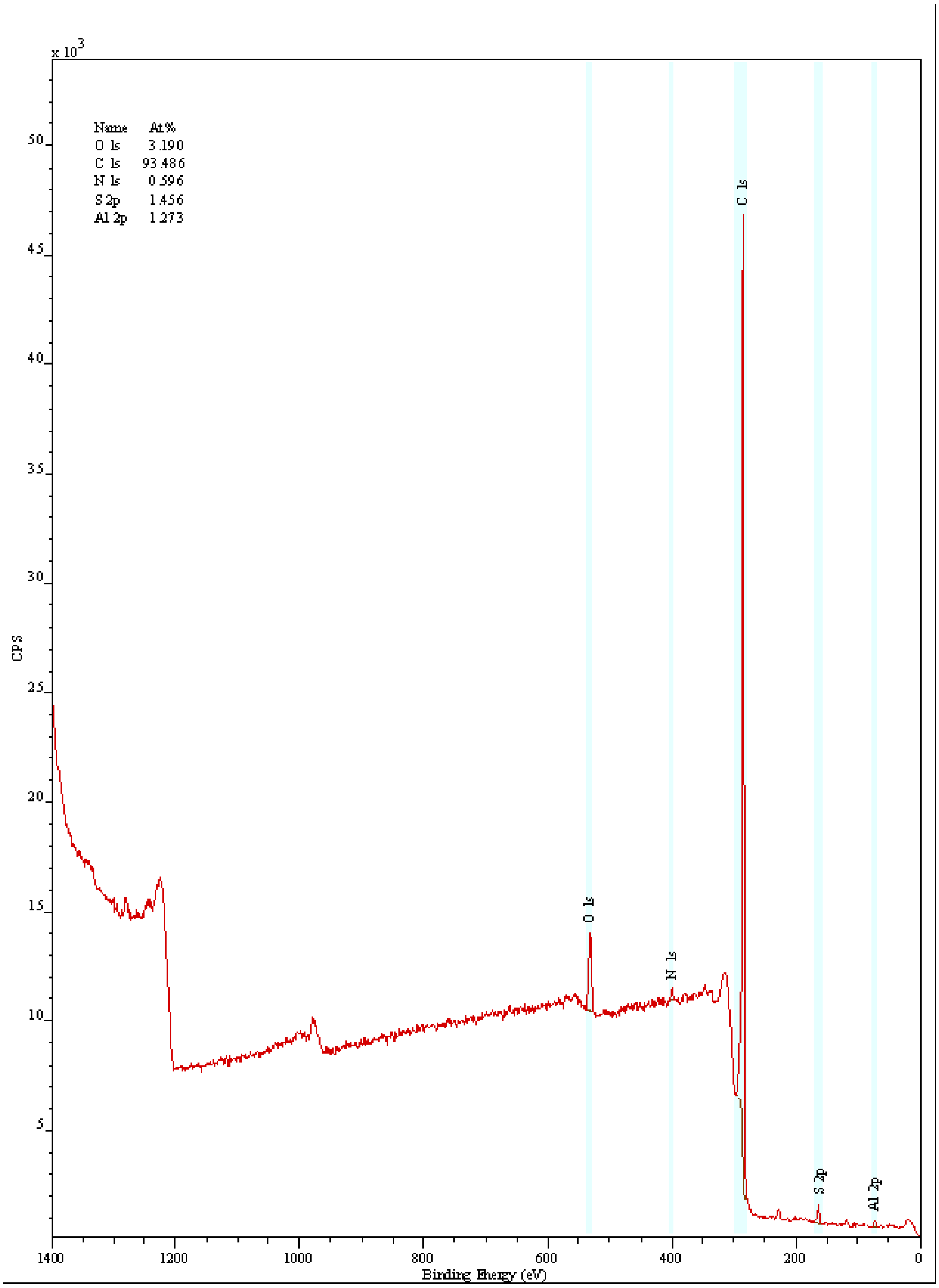


Figure S25. DLS number distributions for MWCNT-TTC present in the first DMF extract.



| Name | At% |
|---|---|
| O 1s | 3.190 |
| C 1s | 93.486 |
| N 1s | 0.596 |
| S 2p | 1.456 |
| Al 2p | 1.273 |

Figure S26. XPS full-scan spectrum of MWCNT-TTC.

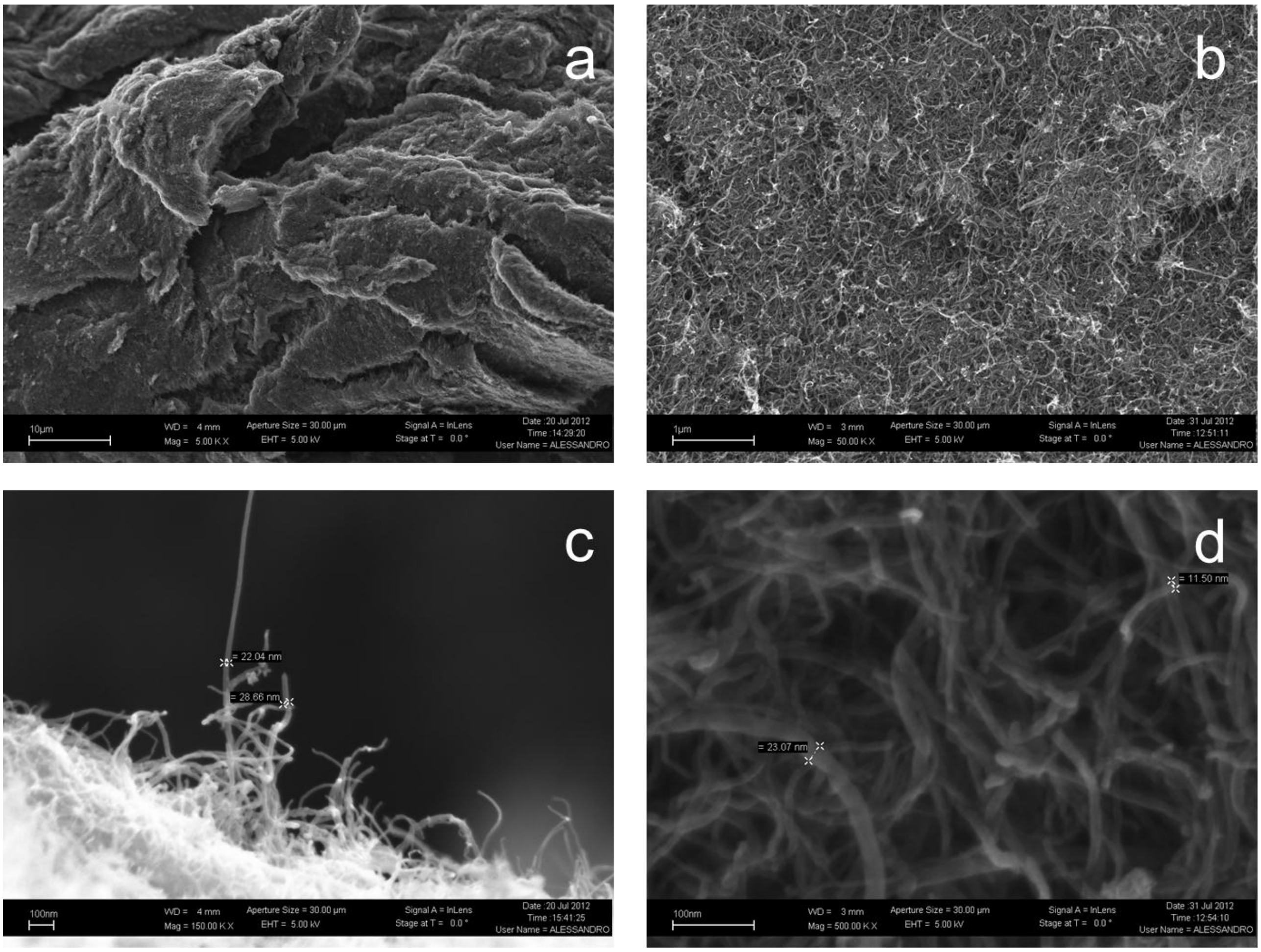


Figure S27. FESEM images of MWCNT-TTC at (a) 5 kX, (b) 50 kX, (c) 150 kX, and (d) 300 kX magnifications.

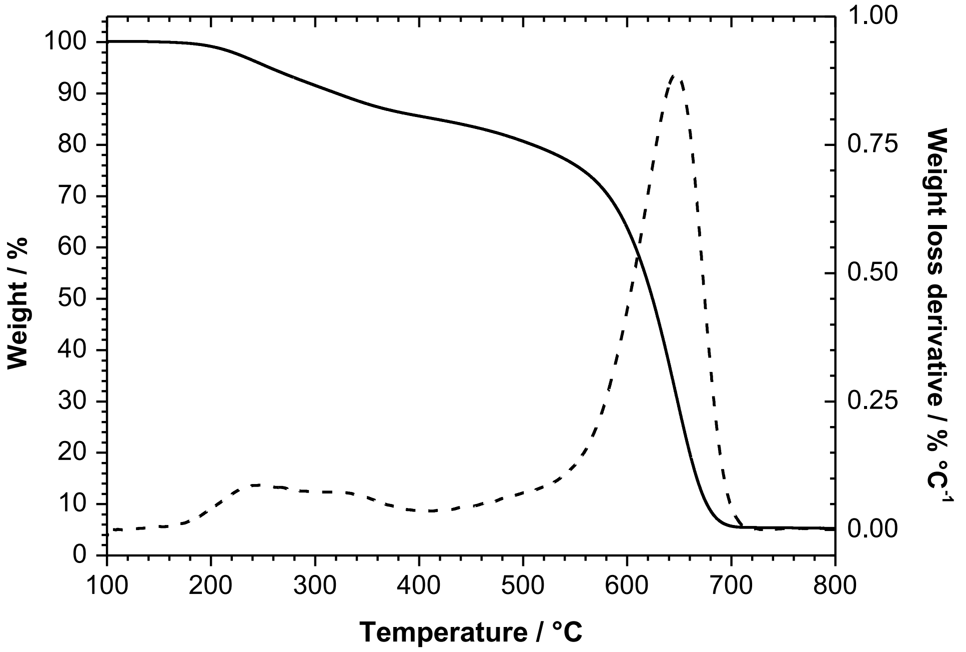


Figure S28. Thermogram of MWCNT-TTC under air with heating rate 10 °C min$^{-1}$. The solid line refers to weight (left axis), the dashed one to weight loss derivative (right axis).

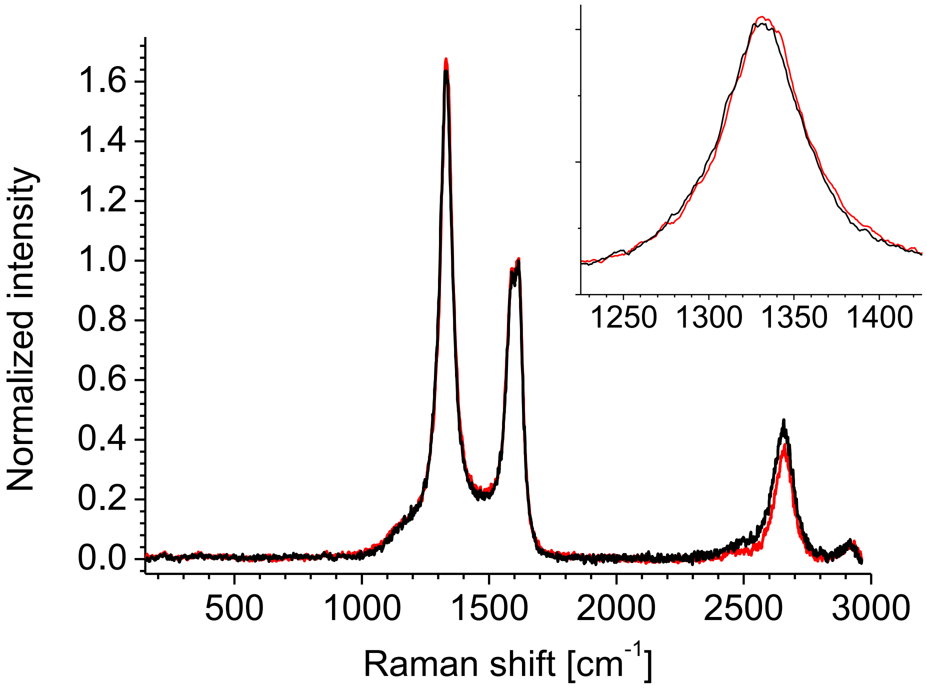
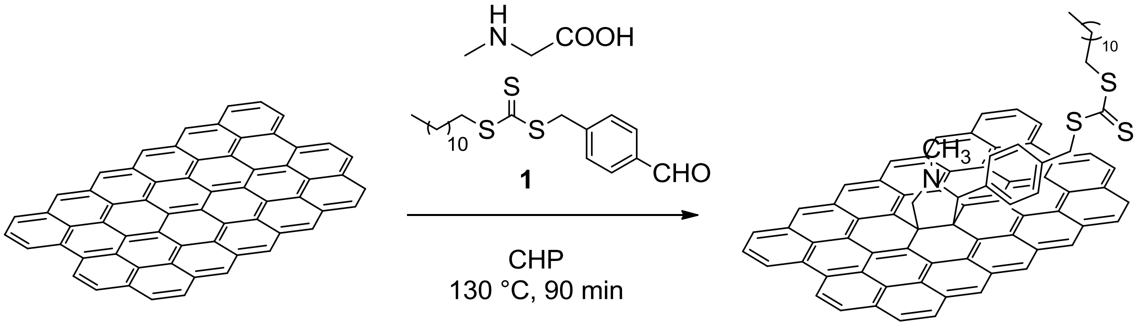


Figure S29. Comparison between the Raman spectra of MWCNT-TTC (red line) and pristine MWCNT (black line). The insets highlight the differences in the D bands (right) following functionalization.

### 7. Synthesis and characterization of graphite-TTC



**Graphite-TTC**

The reaction was carried out under nitrogen. A dispersion of the aldehyde 1 (0.10 g, 0.30 mmol) and sarcosine (40 mg, 0.50 mmol) in CHP (3.0 mL) was added in three portion 30 minutes apart to a dispersion of graphite (10 mg, 0.83 mmol of C) in CHP (7.0 mL) pre-sonicated for 7 hours. After 90 minutes at 130 °C the reaction mixture is diluted with methanol (40 mL) and is centrifuged (10 minutes at 3000 rpm). The precipitate at the bottom of the centrifuge tube is washed with methanol (3 x 5 mL), centrifuged and dried at 80 °C and 0.2 mbar for 30 minutes. Then, the carbonaceous material is extracted with DMF (7 x 5.0 mL) by means of a sonication (power level: 2.0, pulse on: 3 sec, pulse off: 3 sec, time: 1 min) and a centrifugation (5 minutes at 3000 rpm) procedure.

**Solubilities** in DMF for each extract (mg/mL): 0.0509 (1), 0.0299 (2), 0.0210 (3), 0.0183 (4), 0.0153 (5), 0.0143 (6), 0.0137 (7).

**Raman** (thin film) /$cm^{-1}$ (relative intensities): 2676 (0.39, 2D), 1581 (1, G), 1332 (0.0.48, D).

**FD** (weight loss at 450 °C): 1/36 (51 %).

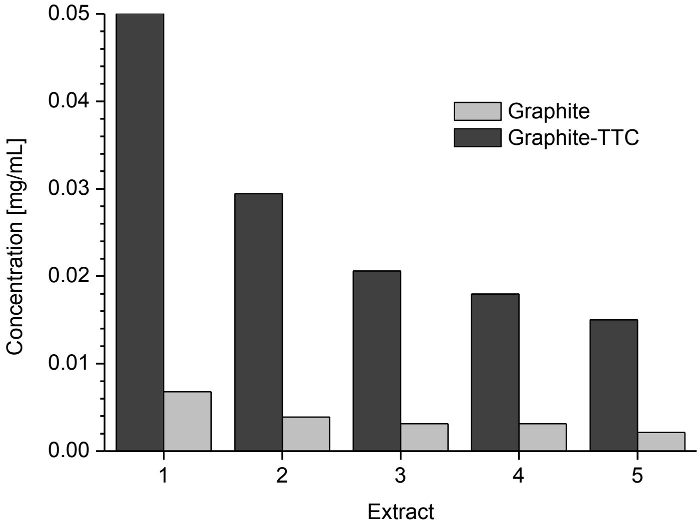


Figure S30. Concentration of pristine graphite (light grey) and graphite-TTC (dark grey) extracted with DMF (5 fractions, 5 mL each).

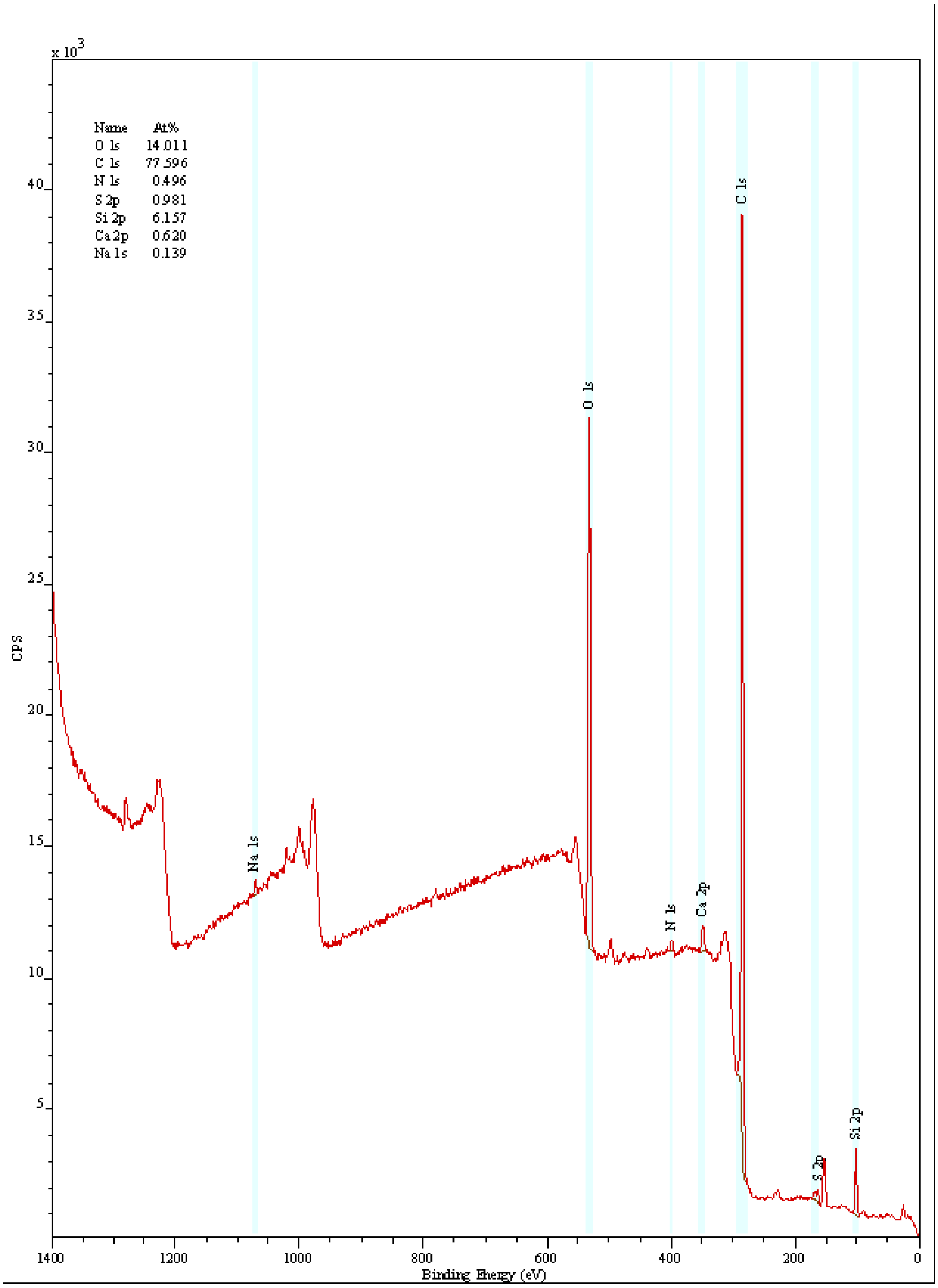


Figure S31. XPS full-scan spectrum of graphite-TTC.

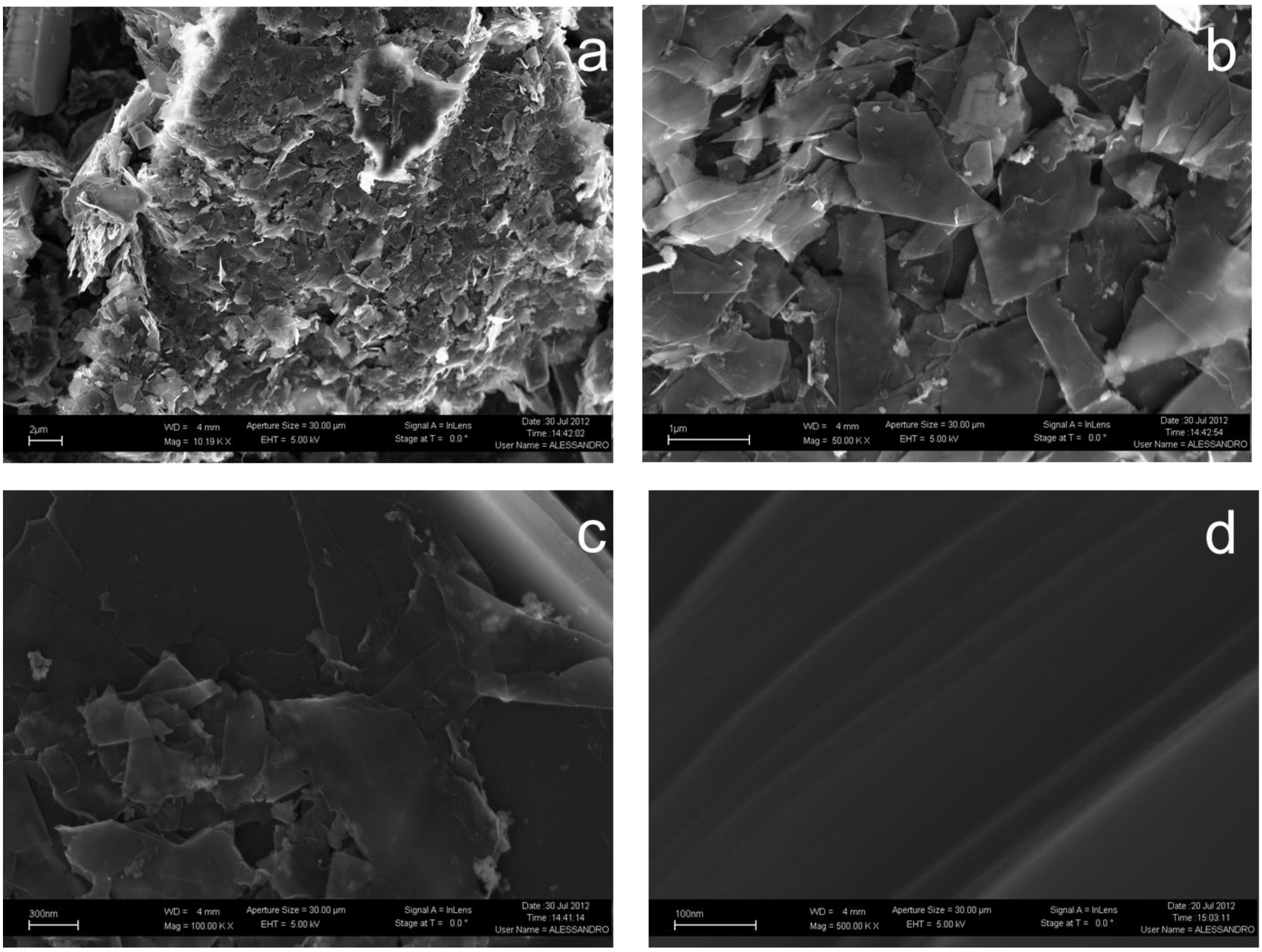


Figure S32. FESEM images of graphite-TTC at (a) 10 kX, (b) 50 kX, (c) 100 kX, and (d) 500 kX magnifications.

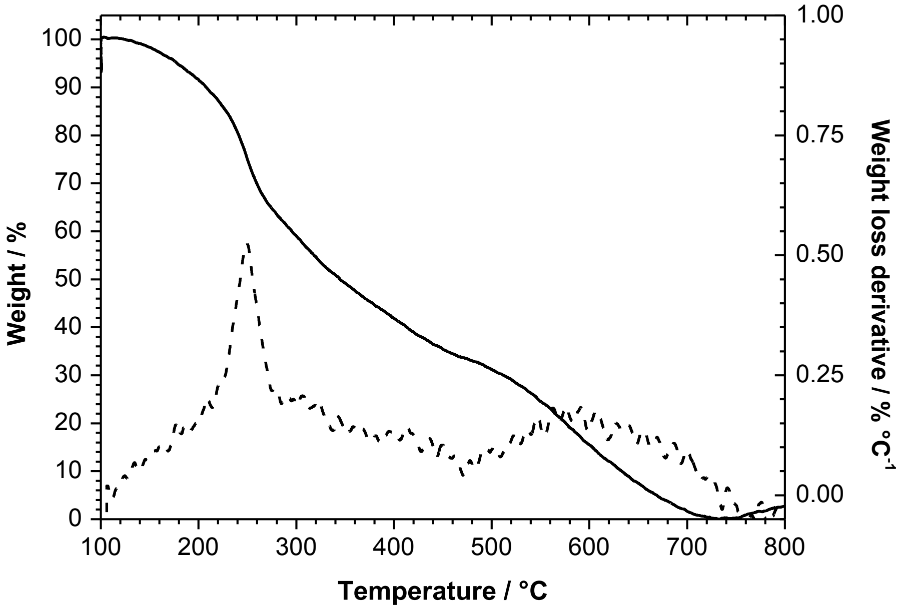


Figure S33. Thermogram of graphite-TTC under air with heating rate 10 °C min$^{-1}$. The solid line refers to weight (left axis), the dashed one to weight loss derivative (right axis).

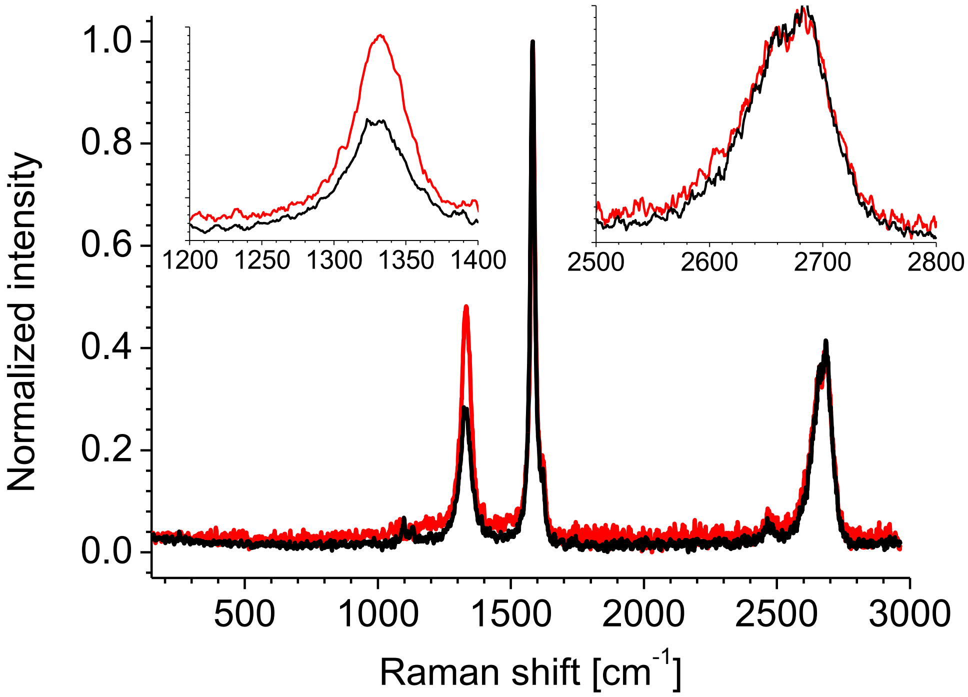
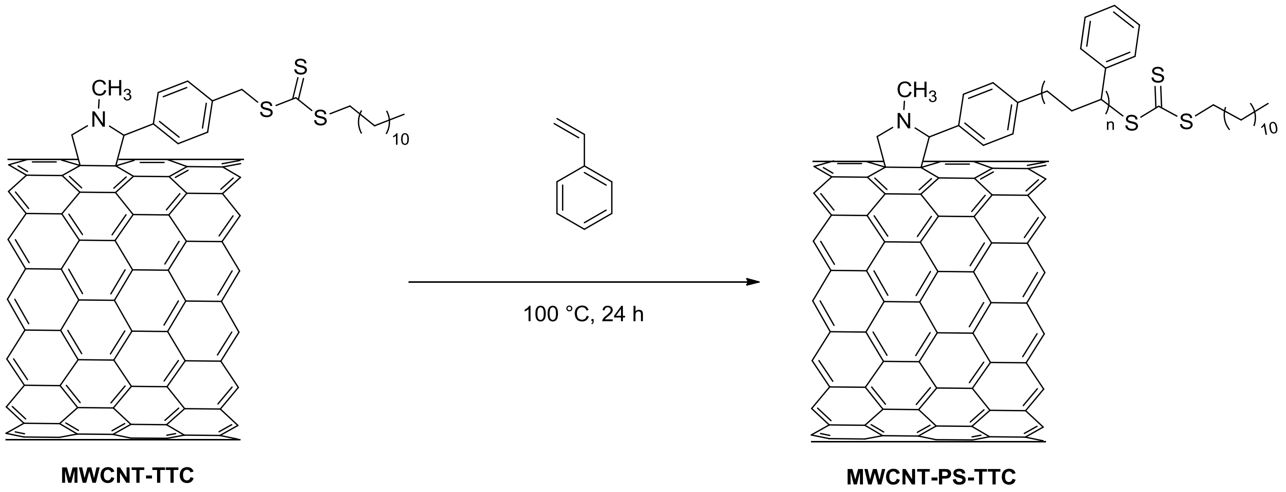


Figure S34. Raman spectra of graphite-TTC (red line) and pristine graphite. The insets highlight the differences in the D band (right) and in the G’ bands (left) following functionalization

## 8. Polymerisation of styrene in the presence of MWCNT-TTC



The reaction was carried out under nitrogen. A dispersion of the MWCNT-TTC (40 mg, 1 eq of RAFT agent) in styrene (1.0 mL, 500 eq) was heated at 100 °C for 24 h. Then the reaction mixture was filtered on a polycarbonate membrane (VCTP 0.1 um, Millipore), washed with 500 mL of toluene and dried under an IR lamp for 2 hours obtaining 51 mg of carbon nanotube derivative. $^1$H-NMR spectroscopy of MWCNT-PS-TTC solubilized in $CDCl_3$ shows four broad peaks centred at 7.08, 6.58, 1.86 and 1.45 consistently with the growth of polystyrene (Figure S35).

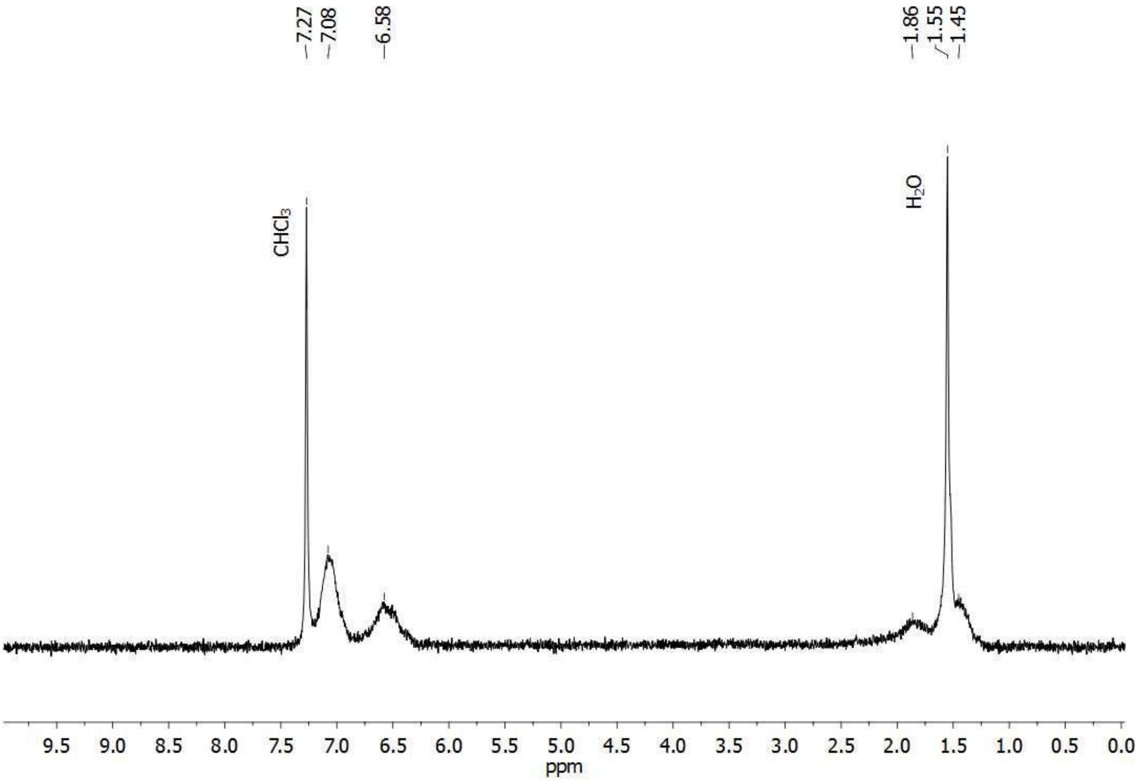


Figure S35. $^1$H-NMR spectrum of MWCNT-PS-TTC in $CDCl_3$.

Uv-vis spectroscopy of the same solution of MWCNT-PS-TTC in $CDCl_3$ shows a peak at 304 nm corresponding to the TTC moiety, a residual absorbance above 400 nm consistent with the plasmonic band of MWCNTs and an intense absorption below 280 nm corresponding to the absorption of polystyrene.

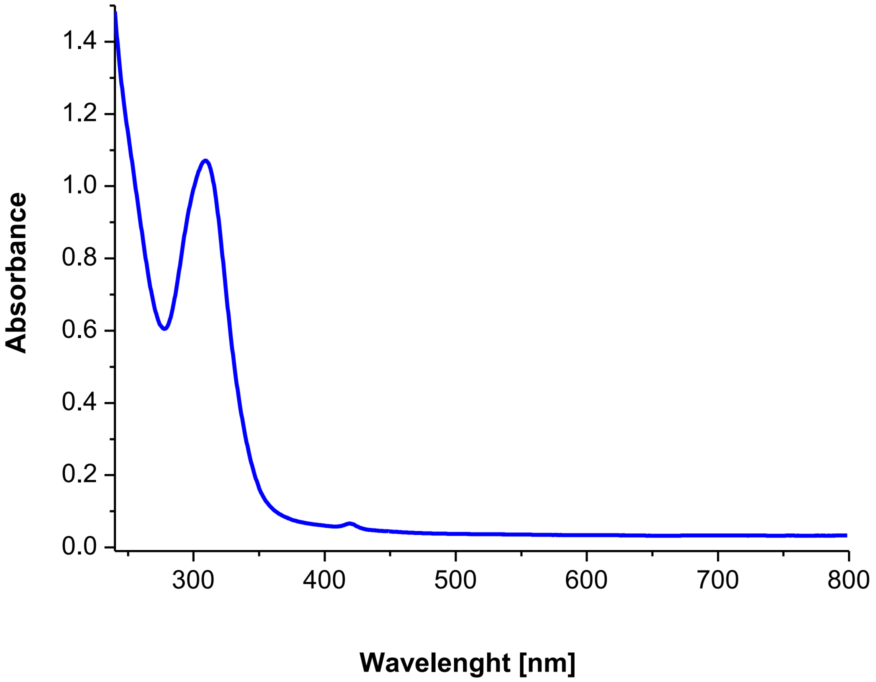


Figure S36. Absorption spectrum of MWCNT-PS-TTC in $CDCl_3$.