Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Electroactive carbon nanoforms: a comparative study via sequential arylation and click chemistry reactions

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Materials

HiPco SWCNT were purchased from Carbon nanotechnologies (lot: P0261, purity >82 %, <18 % remaining iron particles, length = 100-1000 nm, diameter = 0.8-1.4 nm) and used without any further purification treatment. **MWCNT** were synthesized by CVD using Fe/Al_2O_3 as catalyst at 650 °C.[1] The starting MWCNTs can attain 10 μm in length and most of them exhibit closed ends. The internal diameter varies between 4 and 12 nm, while the external goes from 8 to 21 nm. The **graphite** from TIMCAL (TIMREX SFG15, ρ = 2.26 g/cc, particle size = 8.80 μm, specific surface = 9.50 m^2/g, ashes ≤ 0.100%, interlamelar distance = 3354-3358 nm) was used to obtain graphene. For the exfoliation of **graphene**, graphite flakes (200 mg) were dispersed in NMP (100 mL) and sonicated at a low-power sonication bath for 150 minutes. The dispersion was centrifuged at 500 rpm for 45 minutes, the supernatant was decanted and stored in solution.

Organic solvents and reagents used in this work were purchased from commercial suppliers and used as received, unless stated otherwise. 2-(azidomethyl)-9,10-bis-(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene was synthesized by following the previously reported method.[2]

Instruments

FTIR spectra were carried out using pellets of dispersed samples of the corresponding compounds in dried KBr for solid products. The instrument used was a Bruker TENSOR FTIR. The spectral range was 4000-400 cm^{-1}. **TGA** analyses were carried out under air and nitrogen in a TA-TGA-Q500 apparatus. The sample (~ 0.5 mg) was introduced inside a platinum crucible and equilibrated at 90 ºC followed by a 10 °C min^{-1} ramp between 90 and 1000 °C. **XPS** analyses were carried out using a SPECS GmbH (PHOIBOS 150 9MCD) spectrometer operating in the constant analyzer energy mode. A non monochromatic aluminium X-ray source (1486.61 eV) was used with a power of 200 W and voltage of 12 kV. Pass energies of 75 and 25 eV were used for acquiring both survey and high resolution spectra, respectively. Survey data were acquired from kinetic energies of 1487 - 400 eV with an energy step of 1 eV and 100 ms dwell time per point. The high resolution scans were taken around the emission lines of interest

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[1] M. Corrias, B. Caussat, A. Ayral, J. Durand, Y. Kihn, P. Kalck, P. Serp, *Chem. Eng. Sci.*, 2003, **58**, 4475.

[2] S. González, N. Martín, A. Swartz, D. M. Guldi, *Org. Lett.,* 2003, **5**, 557.

with 0.1 eV steps and 100 ms dwell time per point. SpecsLab Version 2.48 software was used for spectrometer control and data handling. The semi-quantitative analysis were performed from the C 1s (284.3 eV) signal. The samples were introduced as pellets of 8 mm diameter. **Raman** spectra were recorded on Renishaw in Via Microscope at room temperature using two different exciting laser sources (785 and 532 nm). **TEM** micrographs were obtained using a JEOL 2100 microscope operating at 200 kV. The samples were dispersed in organic solvents as DMF or NMP, sonicated for 5 minutes and the resulting suspension dropped onto a holey carbon copper grid (200 mesh), the solvent was allowed to evaporate before analysis. **Cyclic Voltammetry** experiments were carried out on a potentiostat/galvanostat AUTOLAB with PGSTAT30 equipped with a software GPES for windows version 4.8 in a conventional three compartment cell. Measurements were carried out using a GCE (glassy carbon) as working electrode, a $Ag/AgNO_3$ reference electrode, and a Pt wire as counter electrode. $TBAPF_6$ was used as supporting electrolyte and DMF as solvent. **Steady-state absorption** spectra were recorded with a Varian Cary 50 spectrophotometer and a Varian Cary 5000 spectrometer. **Steady-state fluorescence** spectra were taken with a FluoroLog3 spectrometer (Horiba) with an IGA Symphony (5121 1 μm) detector in the NIR detection range. **Transient absorption** measurements based on femtosecond laser photolysis were performed with 387 nm laser pulses (1 kHz, 150 fs pulse width) from an amplified Ti:sapphire laser system (Model CPA-2110 from Clark-MXR Inc.) the laser energy was 200 nJ.

Synthesis

SWCNT-1: 25 mg of pristine SWCNT were reacted in a deoxigenated solution of deionized water (25 mL) with of 4-[(trimethylsilyl)ethynyl]aniline (1 eq., 0.42 mmol) and isoamyl nitrite (2 eq., 0.84 mmol) for 24 hours at 70 °C under argon. The reaction mixture was filtered on a 0.2-μm pore size polycarbonate membrane and washed with deionized water. Afterwards, the solid was washed by filtration over a 0.2-μm poly(tetrafluoroethylene) (PTFE) membrane several times with NMP, CH_2Cl_2, and MeOH (sonicated, centrifuged and filtered) until the filtrated solution remained colorless affording the functionalized **SWCNT-1**. IR (KBr): $\nu = 2900$ (C-H stretching mode), 1599 (C-H in-plane stretching mode) and 2159 (C≡C stretching mode) cm^{-1}; TGA: weight loss and temperature desorption (organic anchoring groups): 26.21 %, 700

°C; Raman: I_D/I_G = 0.283; XPS: % atomic: C (284.6 eV) = 90.89, O (531.6 eV) = 4.91, N (399.6 eV) = 0.64, Si (100.7 eV) = 3.55.

SWCNT-2: The alkyne functionalized **SWCNT-1** (20 mg) was suspended in NMP (20 mL) with 0.08 mL of tetra-*n*-butylammonium fluoride (TBAF) (1M in THF) (0.27 µmol) for two hours to cleavage the TMS protecting groups. Subsequently, 2-(azidomethyl)-9,10-bis-(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (0.05 mmol), copper sulfate (3.1 µm), sodium ascorbate (31.3 µm) and some copper wires were added. After 24 hours at 70 °C, the reaction mixture was filtered and washed over a PTFE membrane several times with NMP, CH_2Cl_2, and MeOH (sonicated, centrifuged and filtered) until the filtrated solution remained colorless to remove the non reacted material. In a second washing step, the solid was washed with water to eliminate the copper catalysts. IR (KBr): ν = 2900 (C-H stretching mode) and 1596 (C-H in-plane stretching mode) cm^{-1}; TGA: weight loss and temperature desorption (organic anchoring groups): 38.33 %, 700 °C; Raman: I_D/I_G = 0.284; XPS: % atomic: C (284.6 eV) = 82.36, O (532.6 eV) = 13.52, N (399.6eV) = 1.03, S (169.6 eV) = 1.04, Si (103.6 eV) = 2.0.

MWCNT-1: To 100 mL of deionizated water were added 100 mg of pristine MWCNT and 4-[(trimethylsilyl)ethynyl]aniline (1 eq., 0.42 mmol). This dispersion was deoxigenated prior to add isoamyl nitrite (2 eq., 0.84 mmol) and left reacting for 24 hours at 70 °C under argon atmosphere. A filtration system provided with a 0.2-µm pore size polycarbonate membrane was used to obtain the **MWCNT-1** cake. Further washing steps with NMP, CH_2Cl_2, and MeOH (sonicated, centrifuged and filtered) over a 0.2-µm poly(tetrafluoroethylene) (PTFE) membrane were needed to purify the **MWCNT-1** conjugate. IR (KBr): ν = 2900 (C-H stretching mode), 1580 (C-H in-plane stretching mode) and 2156 (C≡C stretching mode) cm^{-1}; TGA: weight loss and temperature desorption (organic anchoring groups): 8.07 %, 600 °C; XPS: % atomic: C (284.6 eV) = 91.33, O (532.6 eV) = 4.84, N (399.6 eV) = 0.46, Si (101.6 eV) = 3.36.

MWCNT-2: A NMP (20 mL) solution of **MWCNT-1** (30 mg) containing 0.2 mL of TBAF (1M in THF) (0.27 µmol) was stirred under inert atmosphere for two hours to eliminate the TMS protecting groups. 2-(azidomethyl)-9,10-bis-(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (0.05 mmol), copper sulfate (3.1 µm), sodium ascorbate (31.3 µm) and some copper wires, were added to the previous solution and reacted for 24 hours at 70 °C to obtain the click chemistry resulting product **MWCNT-2**. The reaction mixture was further filtrated and washed over a PTFE membrane subsequently with NMP, CH_2Cl_2, and MeOH (sonicated, centrifuged and filtered) until the filtrated solution remained colorless, to remove the non reacted material. The copper catalyst was removed on a final washing step using water. IR (KBr): ν = 2900 (C-H stretching mode) and 1583 (C-H in-plane stretching mode) cm^{-1}; TGA: weight loss and temperature desorption (organic anchoring groups): 29.59 %, 600 °C; Raman: I_D/I_G = 2.08; XPS: % atomic: C (284.6 eV) = 94.57, O (532.6 eV) = 2.92, N (400.6 eV) = 1.36, S (164.6 eV) = 1.14.

GR-1: Exfoliated graphene suspensions in NMP were utilized as produced for further covalent modification. 50 mL of graphene solution in NMP where reacted with 4-[trimethylsilyl)ethynyl]aniline (1.2 mmol) and isoamyl nitrite (2.5 mmol) under argon atmosphere at 70 °C for 24 hr. The reaction product was washed in a 0.2 μm size PTFE membrane several times with NMP, CH_2Cl_2 and MeOH. The product obtained was redispersed on 50 mL of NMP and submitted to the same reaction conditions to complete a second reaction cycle in order to increase the amount of functional groups presented on the graphene surface, followed by the same filtration step. IR (KBr): ν = 2900 (C-H stretching mode), 1583 (C-H in-plane stretching mode) and 2165 (C≡C stretching mode) cm^{-1}; TGA: weight loss and temperature desorption (organic anchoring groups): 14.42 %, 700 °C**;** Raman: I_D/I_G = 0.18; XPS: % atomic: C (284.6 eV) = 79.26, O (532.6 eV) = 12.53, Si (102.6 eV) = 8.2.

GR-2: To 25 mg of **GR-1** dispersion in 5 mL of NMP was added TBAF (1M in THF) (0.27 μmol) under inert atmosphere. The reaction mixture was stirred for two hours prior to add 2-(azidomethyl)-9,10-bis-(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (0.05 mmol), the copper sulfate (3.1 μm), the sodium ascorbate (31.3 μm) and some copper wires. After 24 hours at 60 °C the solid was separated by filtration onto a PTFE membrane and intensively washed with the organic solvents NMP, CH_2Cl_2, MeOH and finally water. IR (KBr): ν = 2900 (C-H stretching mode) and 1596 (C-H in-plane stretching mode) cm^{-1}; TGA: weight loss and temperature desorption (organic anchoring groups): 21.30 %, 700 °C; Raman: I_D/I_G = 0.18; XPS: % atomic: C (284.6 eV) = 84.32, O (532.6 eV) = 9.02, N (400.6 eV) = 0.95, S (170.5 eV) = 1.4, Si (102.6 eV) = 4.3.

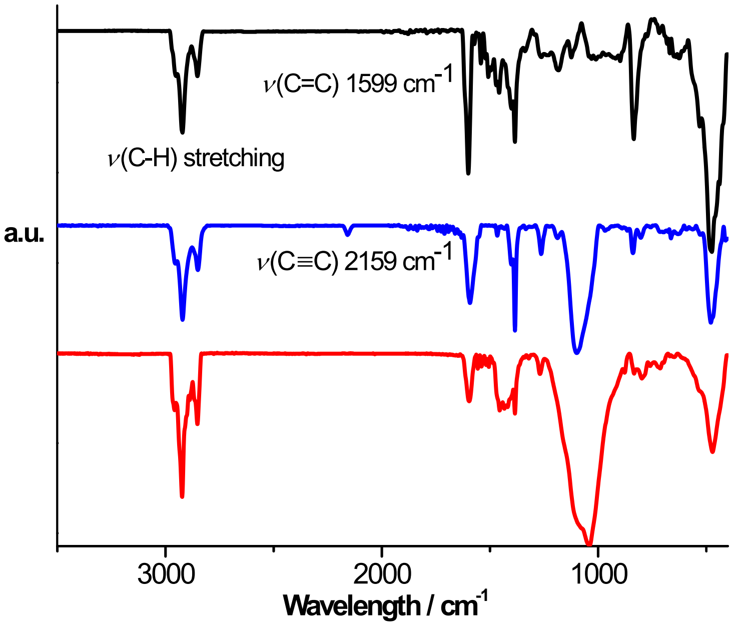


Fig. S1. FTIR spectra of **SWCNT-2** (red) compared to **SWCNT-1** (blue) and pristine MWCNT (black).

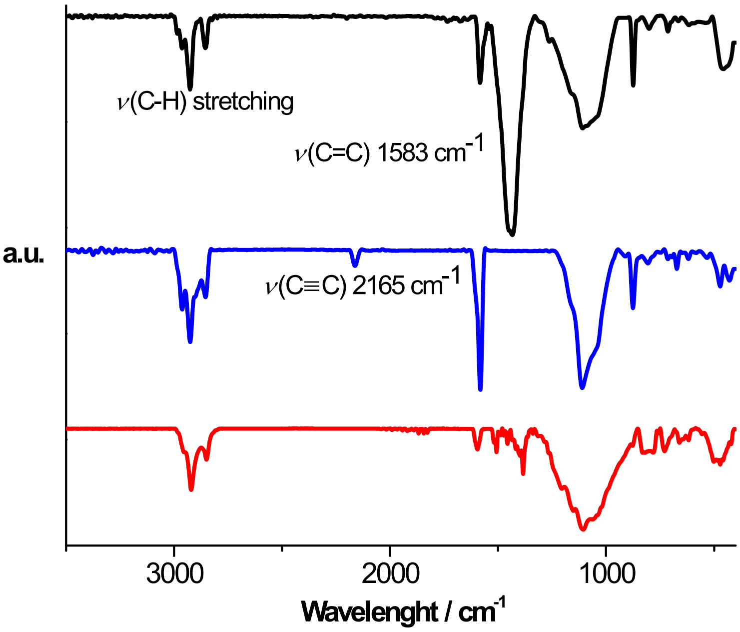
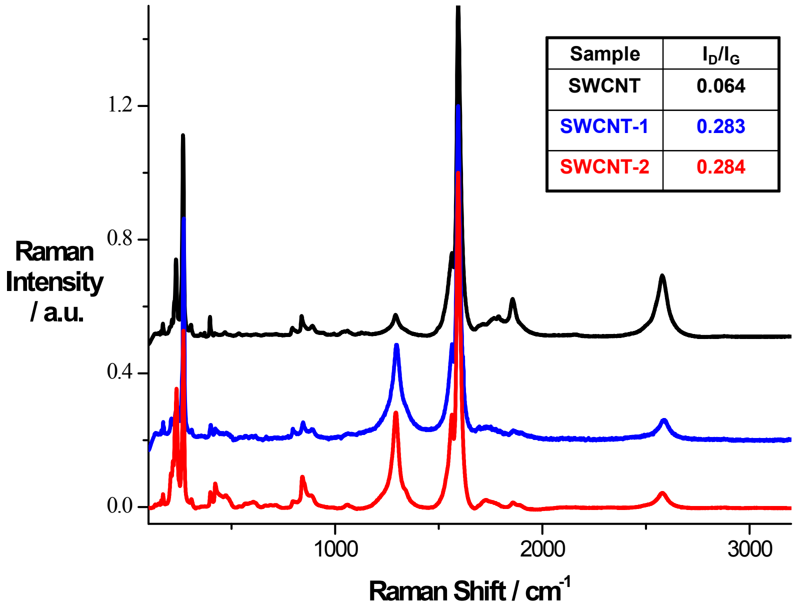


Fig. S2. FTIR spectra of **GR-2** (red) compared to **GR-1** (blue) and pristine graphene (black).



Sample	I_D/I_G
SWCNT	0.064
SWCNT-1	0.283
SWCNT-2	0.284

Fig. S3. Raman spectra of pristine SWCNT (black), **SWCNT-1** (blue) and **SWCNT-2** (red) - 785 nm excitation. Table inserted compares the I_D/I_G ratio between the three samples.

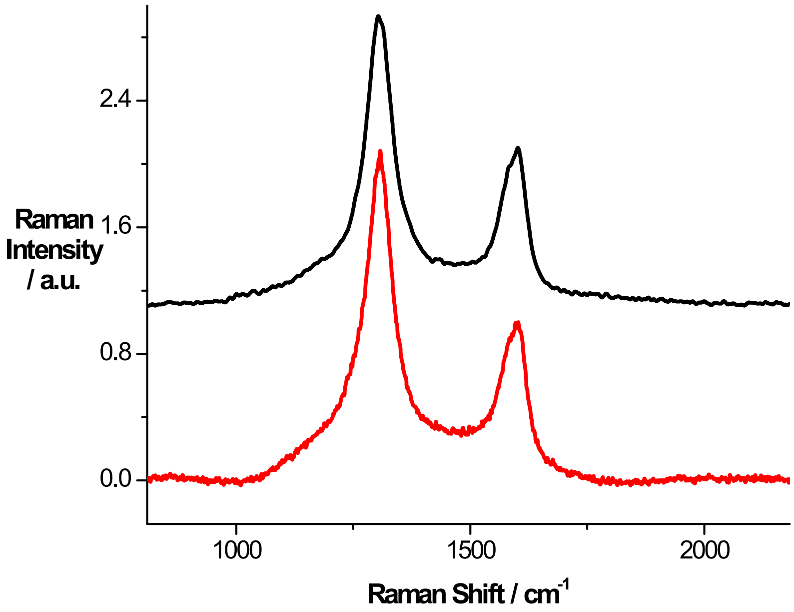


Fig. S4. Raman spectra of pristine MWCNT (black) and **MWCNT-2** (red) - 785 nm excitation.

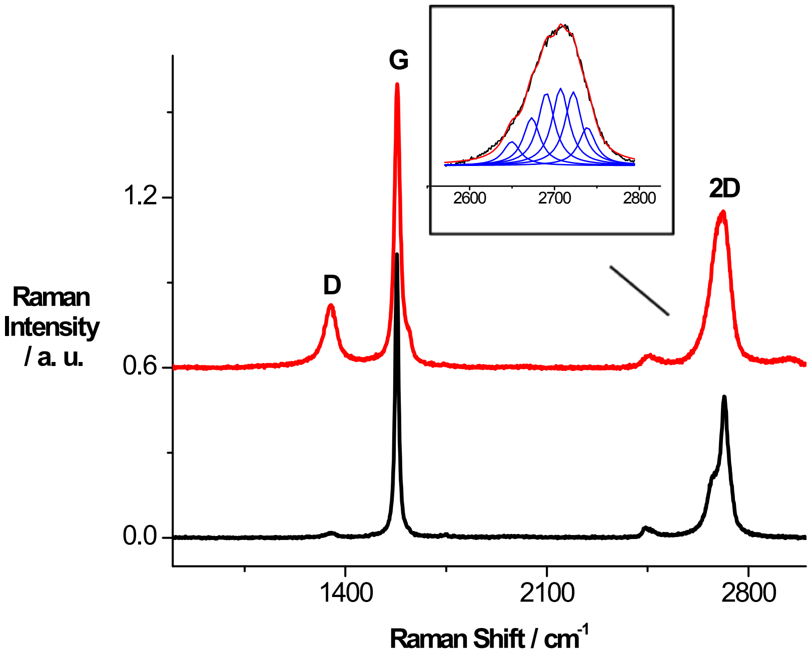
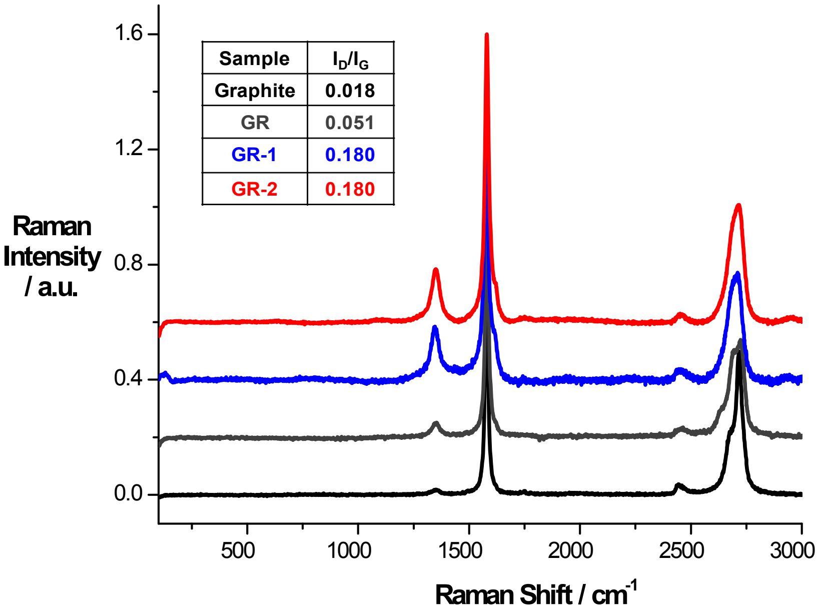


Fig. S5. Raman spectra (λ_{exc} = 532 nm, 100x optical lens) of the exfoliated graphene (red) compared to graphite (black). The inset shows the fit of the 2D band to six Lorentzians of FWHM = 24 cm^{-1}.



Sample	I_D/I_G
Graphite	0.018
GR	0.051
GR-1	0.180
GR-2	0.180

Fig. S6. Raman spectra (λ_{exc} = 532 nm, 100x optical lens) of evaporated suspensions of graphite (black), graphene (dark grey), and both nanoconjugates **GR-1** (blue) and **GR-2** (red) in NMP. Table inserted shows the I_D/I_G ratio.

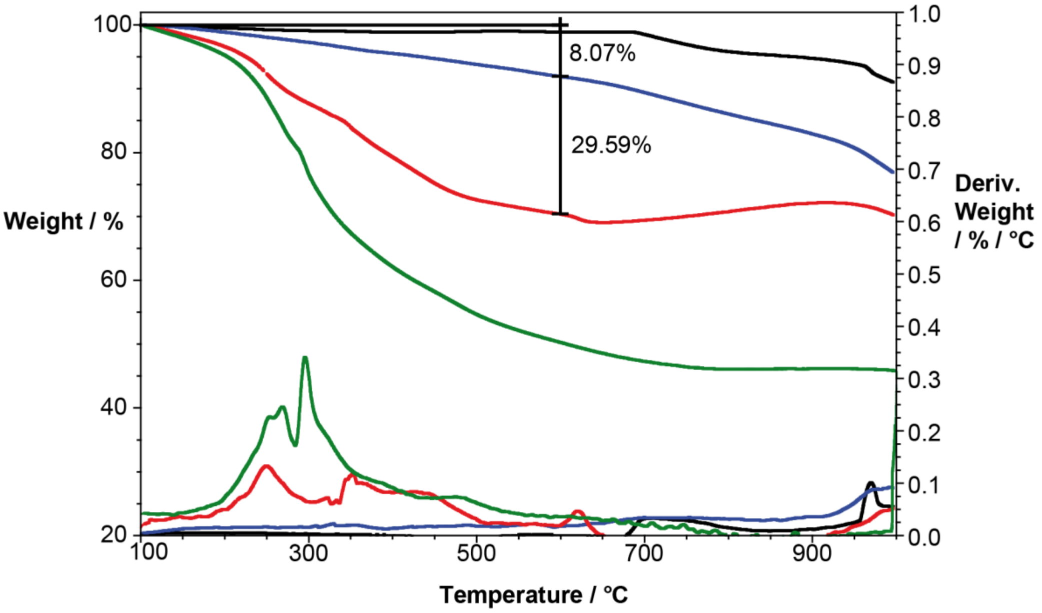


Fig. S7. TGA and first derivative curves under inert conditions of pristine MWCNT (black), the nanoconjugates **MWCNT-1** (blue) and **MWCN-2** (red) and, the thermal decomposition of the exTTF molecule **2** (green).

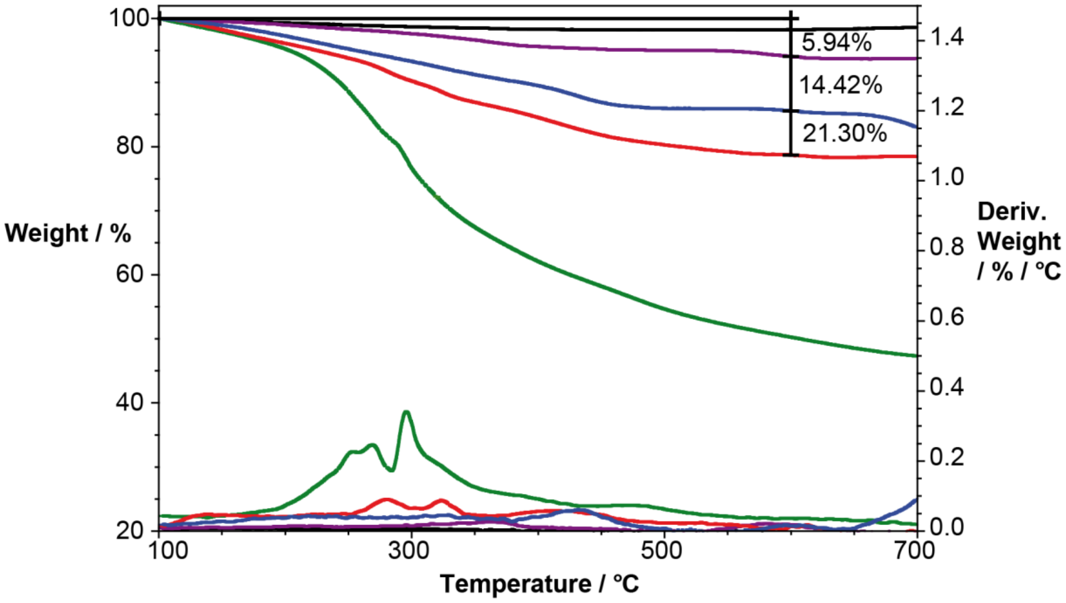


Fig. S8. TGA and first derivative curves under inert conditions of the starting graphite material (black), the exfoliated graphene (purple) and the functionalized **GR-1** (blue) and **GR-2** (red), together with the thermal decomposition of exTTF **2** (green).

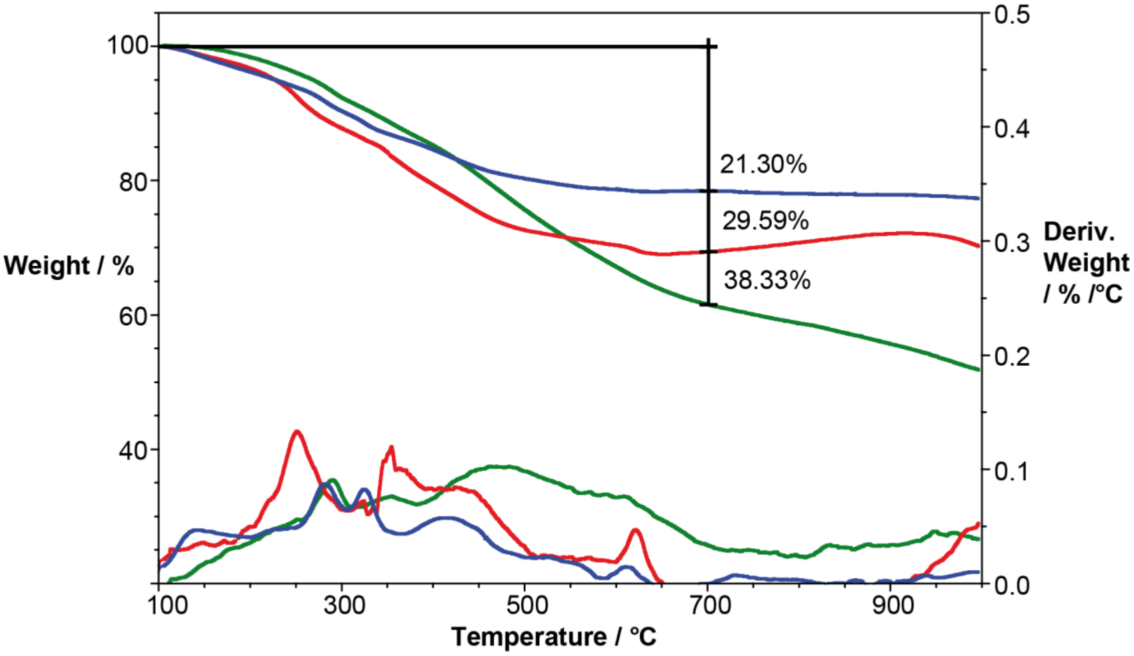


Fig. S9. TGA and first derivative curves under inert conditions of the functionalized carbon nanoforms **SWCNT-2** (green), **MWCNT-2** (red) and **GR-2** (blue).

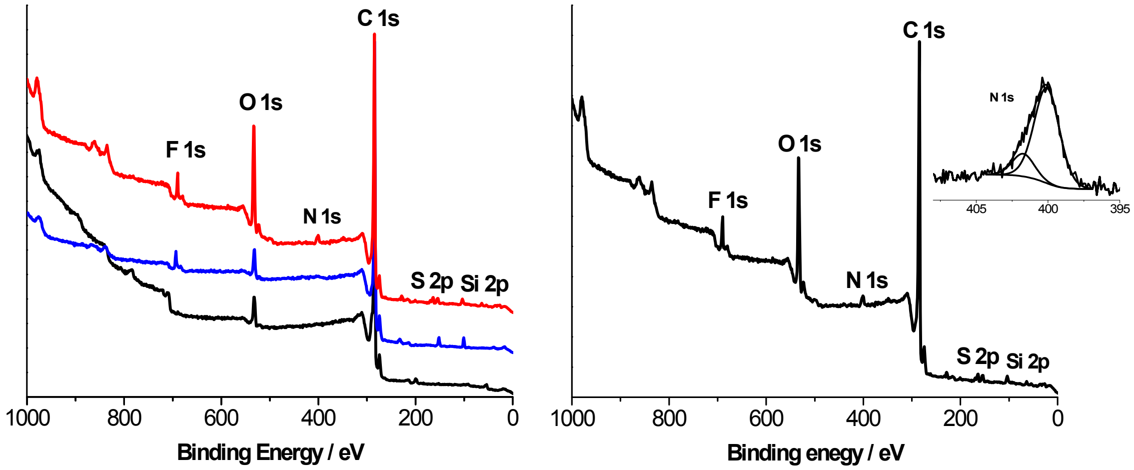


Fig. S10. Left, XPS survey analysis of **SWCNT-2** (red) compared to **SWCNT-1** (blue) and pristine SWCNT (black). Right, XPS analysis of **SWCNT-2**, with N 1s deconvoluted components.

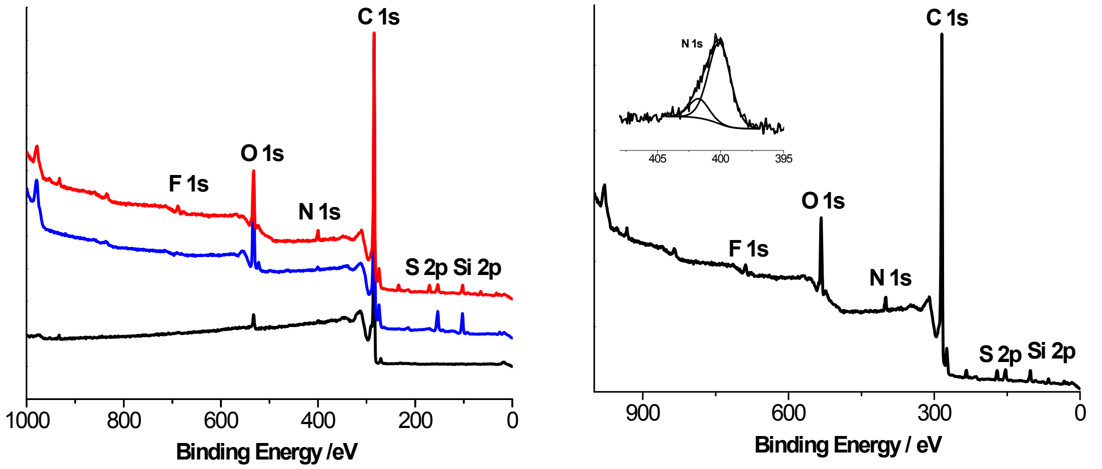


Fig. S11. Left, XPS survey analysis of **GR-2** (red) compared to **GR-1** (blue) and graphene (black). Right, XPS analysis of **GR-2**, with N 1s deconvoluted components.

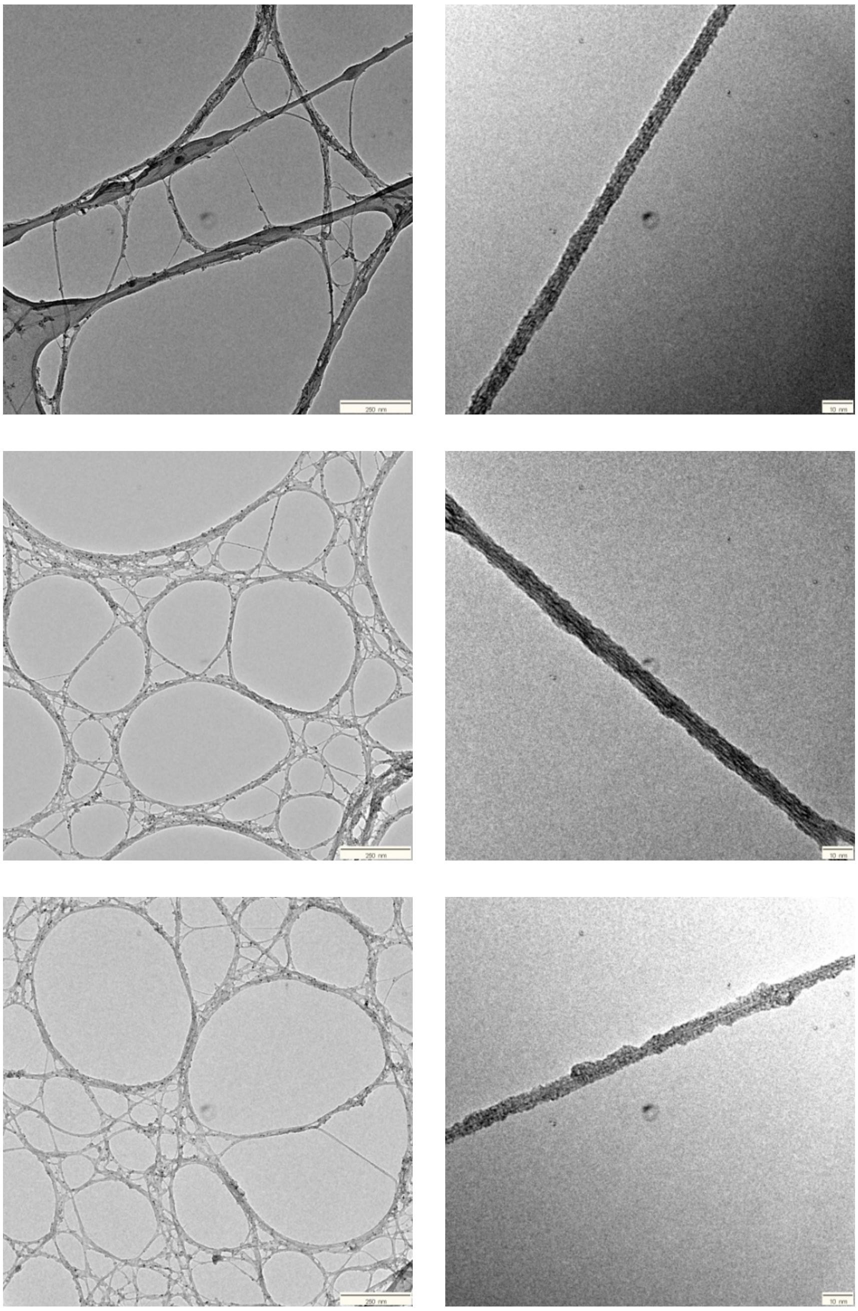


Fig. S12. Representative TEM images on holey carbon grids with scale bars of 250 nm (left) and 10 nm (right) of pristine SWCNT (upper part), **SWCNT-1** (central part) and **SWCNT-2** (lower part).

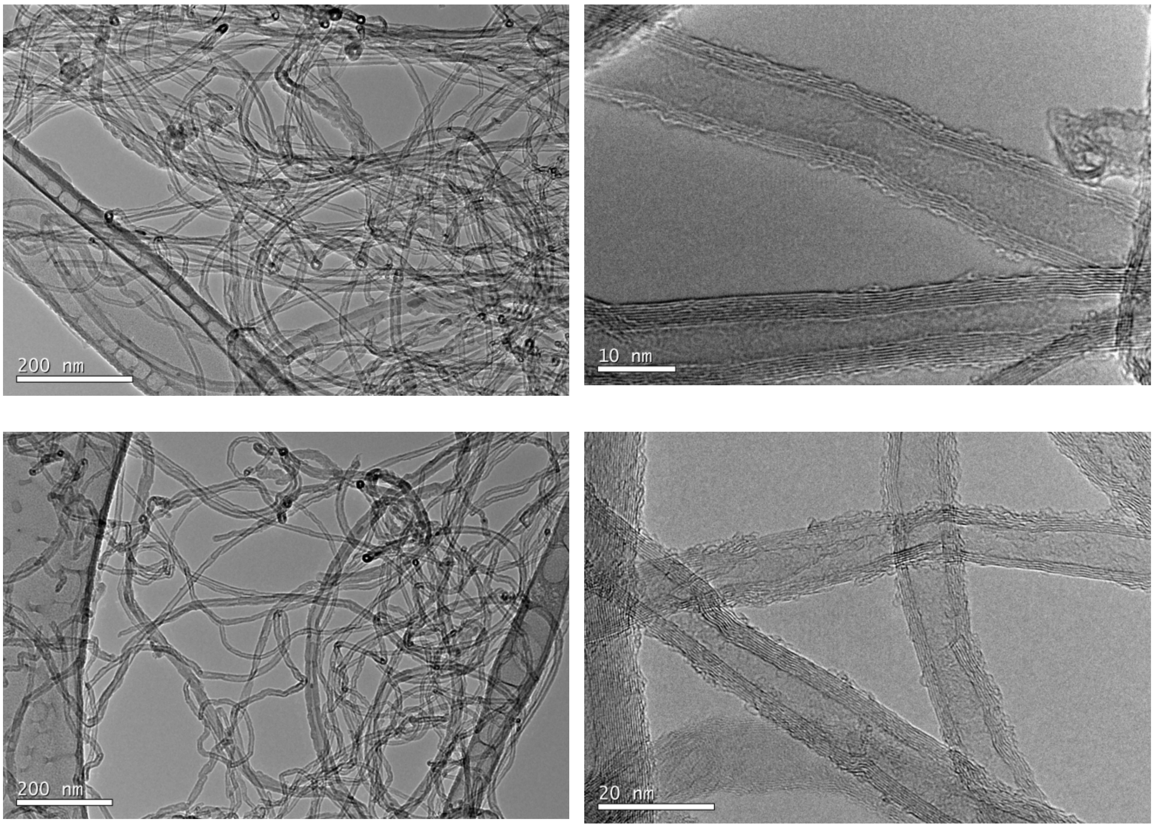


Fig. S13. Representative TEM images on holey carbon copper grids, with scale bars of 200 nm (left) and 10 or 20 nm (right) of pristine MWCNT (upper part) and **MWCNT-2** (lower part).

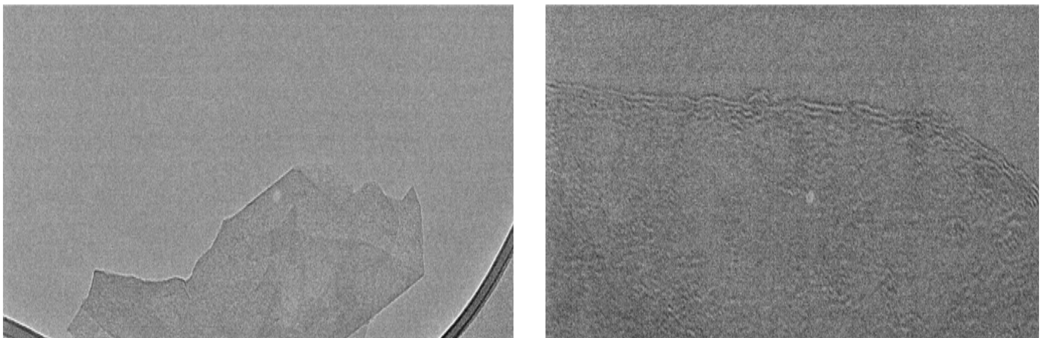


Fig. S14. TEM image of graphene obtained after the exfoliation procedure (left) and magnification of the upper part where can be observed the graphene layers (right).

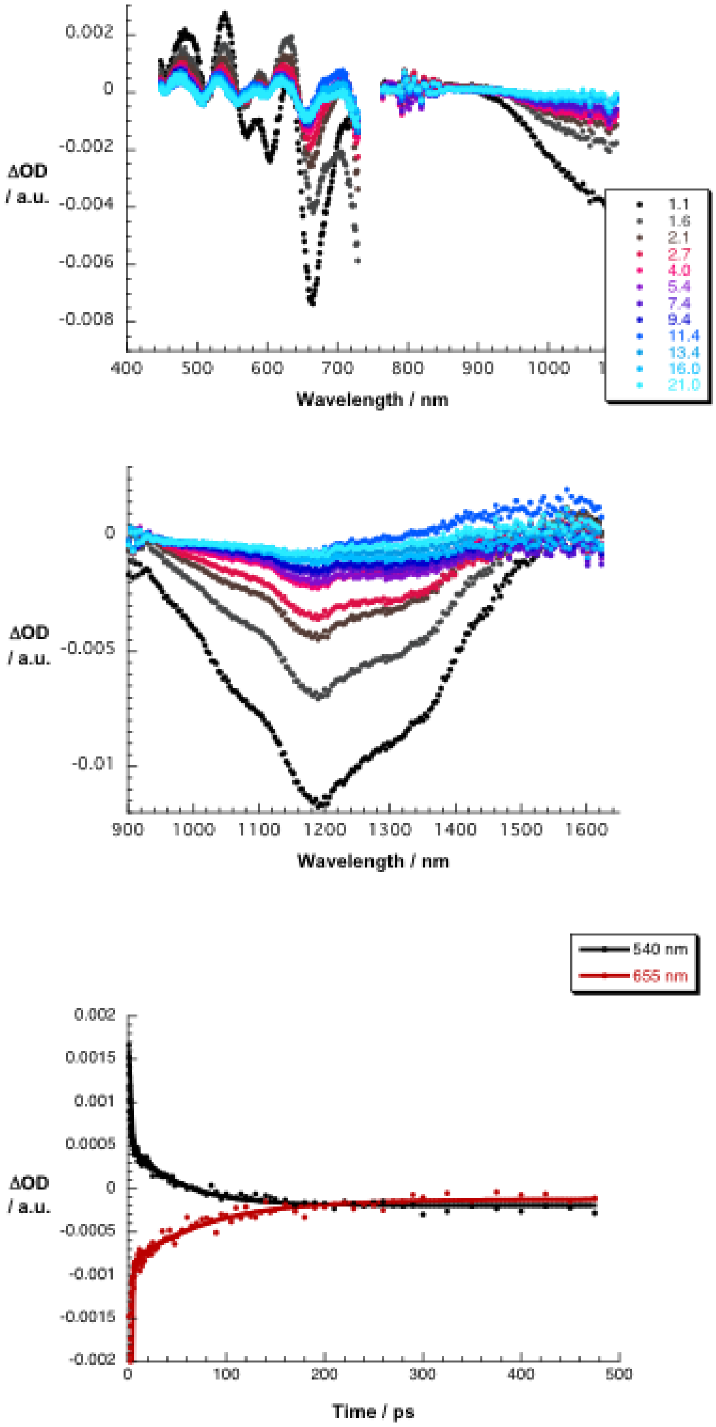


Fig. S15. Upper part – differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (387 nm) of pristine SWCNT with several time delays between 1.1 and 21.0 ps at room temperature. Central part – differential absorption spectra (extended near-infrared) obtained upon femtosecond pump probe experiments (387 nm) of pristine SWCNT with several time delays between 1.1 and 21.0 ps at room temperature. Lower part – time absorption profiles of the spectra shown in the upper part at 540 and 655 nm monitoring the excited state decay.

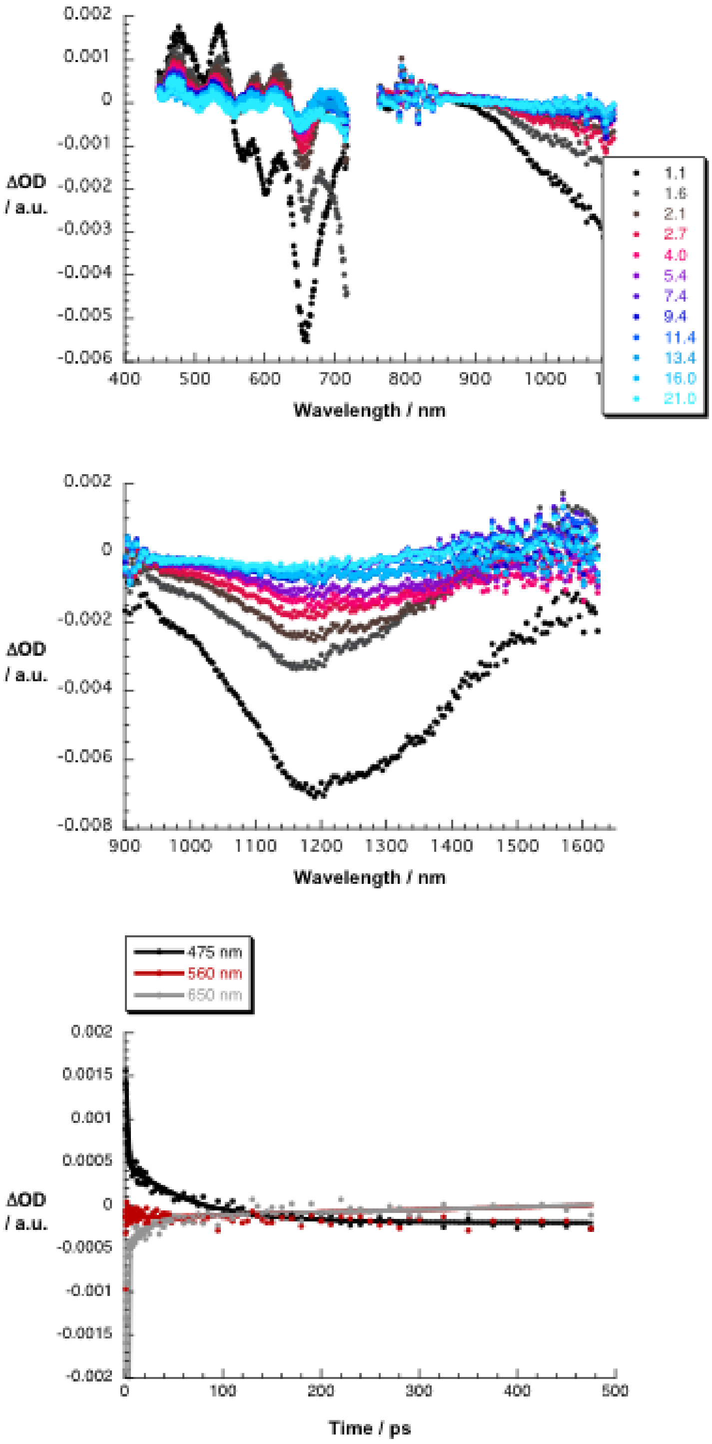
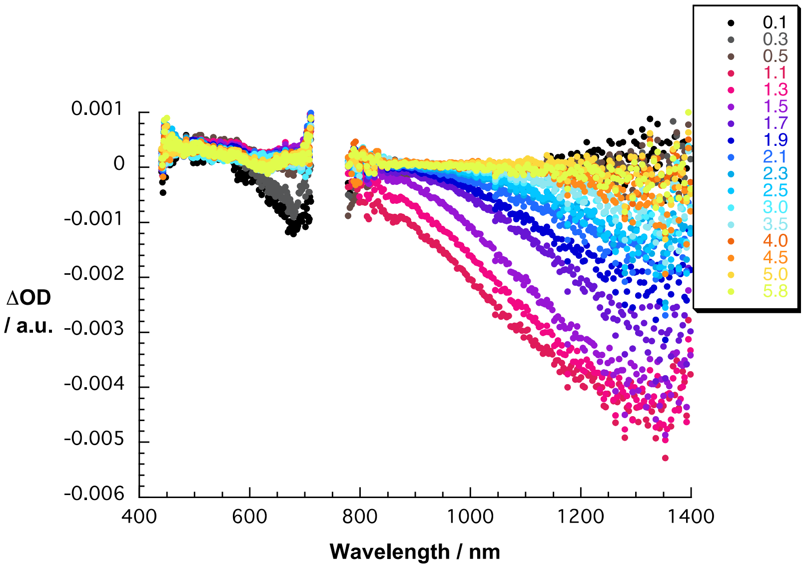


Fig. S16. Upper part – differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (387 nm) of **SWCNT-1** with several time delays between 1.1 and 21.0 ps at room temperature. Central part – differential absorption spectra (extended near-infrared) obtained upon femtosecond pump probe experiments (387 nm) of **SWCNT-1** with several time delays between 1.1 and 21.0 ps at room temperature. Lower part – time absorption profiles of the spectra shown in the upper part at 475, 560, and 650 nm monitoring the excited state decay.



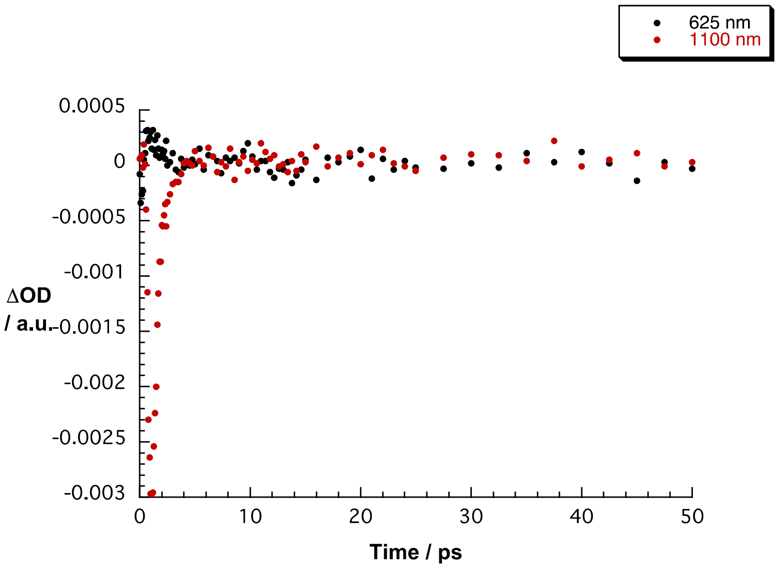


Fig. S17. Upper part – differential absorption spectra (visible) obtained upon pump probe excitation (387 nm, 200 nJ) of **GR-2** in DMF with several time delays between 0.1 and 5.8 ps at room temperature – see legend for details. Lower part – time-absorption profiles of the spectra shown above at 625 and 1100 nm monitoring the excited state decay.