Electronic Supporting Information

A soluble hybrid material combining carbon nanohorns and C_{60}

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Experimental section

Instrumentation.

Steady-state absorption spectra in the visible and near-IR regions were measured on a Shimatzu UV 3600 spectrometer.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 (^{1}H: 400 MHz; ^{13}C: 100 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = double, t = triplet, m = multiplet, br = broad.

Attenuated-total-reflectance infrared spectra were recorded on an AVATAR 370 Thermo Nicolet spectrometer, equipped with a single reflection diamond ATR accessory. A drop of the solution was placed on the diamond surface, followed by evaporation of the solvent, in stream nitrogen, before recording the spectrum. Typically, 3000 scans were acquired at a 4 cm^{-1} resolution.

Raman spectra were recorded at room temperature using a Renishaw in Via Raman microscope equipped with a CCD camera and a Leica microscope. As an excitation source a Nd:TAG 532 nm and a HPNIR 785 lasers were used. Measurements were taken with 10 seconds of exposure times at varying number of accumulations. The laser spot was focused on the sample surface using a long working distance 50x objective. Raman spectra were collected on numerous spots on the sample and recorded with Peltier cooled CCD camera. All spectra were recorded on solid samples over several regions and were referenced to the silicon line at 520 cm^{-1}. The intensity ratio ID/IG was obtained by taking the peak intensities following any baseline corrections. The data was collected and analysed with Renishaw Wire and Origin software.

X-ray photoelectron spectra (XPS) were obtained with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyser and a MgKα (hν = 1254.6 eV, 1 eV = 1.6302 x 10^{-19} J) X-ray source, powered at 120 W. Survey and high resolution spectra were recorded at pass energy of the analyze of 100 and 20 eV, respectively. Binding energies were calibrated relative to the C 1s peak at 284.8 eV. High resolution spectra envelopes were obtained by curve fitting synthetic peak components using the software "*XPS peak*". Atomic ratios were computed from experimental intensity ratios and normalized by atomic sensitivity factors.

The thermogravimetric analysis was performed using a TGA Q500 instrument by TA in an inert atmosphere of nitrogen, with a rate of 10ºC min^{-1}, and the weight changes were recorded as a function of temperature.

The electrochemical experiments were carried out on an Autolab PGSTAT 30 potentiostat using a BAS MF-2062 Ag/0.01 M $AgNO_3$, 0.1 M $TBAPF_6$ in *o*-dichlorobenzene /acetonitrile reference electrode, an auxiliary electrode consisting of a Pt wire, and a Methrohm 6.1247.000 conventional glassy carbon electrode (3 nm o.d.) as a working electrode, directly immersed in the solution. Before each experiment the cell was purged with high purity argon for 5 min. The working electrode was cleaned before each experiment through polishing using a cloth and 1, 0.3 and 0.05 μm alumina pastes.

Chemicals.

CNHs were produced by CO_2 laser ablation of graphite in the absence of any metal catalyst under an Ar atmosphere (760 Torr) at room temperature; the purity of CNHs was as high as 90% with less amorphous carbons. All other chemicals utilized in the synthesis and spectroscopic measurements were purchased from Aldrich Chemicals (Milwaukee, WI) and were used as received. TLC was performed on Merck silica gel 60 F_{254}, chromatograms were visualized with UV light (254 and 360 nm). Column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh). Compounds **1**[1], **2**[2]and **5**[3] were synthesized according the literature procedure.

Synthesis and characterization of compounds 3, 4, 6, 7 and 8

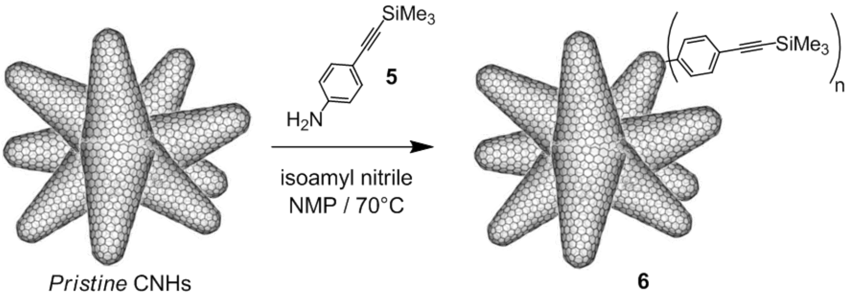
Preparation of compound 3.

DCC (3.02 g, 14.8 mmol) was added to a solution of **1** (7.84 g, 14.8 mmol), **2** (1.00 g, 5.90 mmol), HOBt (160 mg, 1.18 mmol) and DMAP (290 mg, 2.36 mmol) in CH_2Cl_2 (250 mL) at 0ºC. After 1 hour, the mixture was allowed to warm slowly to room temperature and was then stirred for 3 days at this temperature. The resulting mixture was filtered and evaporated. Column chromatography (SiO_2, CH_2Cl_2/cyclohexane 8:2) gave **3** (5.80 g, 81%) as a yellow oil that was used in the next step without further purification. ^{1}H NMR ($CDCl_3$, 300 MHz) δ ppm 7.06 (s, 1H), 6.95 (s, 2H), 6.46 (d, *J* = 2 Hz, 4H), 6.39 (t, *J* = 2 Hz, 2H), 5.14 (s, 4H), 5.09 (s, 4H), 3.91 (t, *J* = 7 Hz, 8H), 3.94 (s, 4H), 1.79-1.71 (m, 8H), 1.45-1.38 (m, 8H) , 1.35-1. 27 (m, 64H), 0.88 (t, *J* = 7 Hz, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ ppm 166.08, 166.06, 160.5, 140.9, 137.7, 137.1, 123.7, 118.3, 106.5, 101.2, 68.1, 67.3, 66.2, 41.4, 31.9, 29.68, 29.65, 29.62, 29.60, 29.42, 29.36, 29.27, 26.1, 22.7, 14.1. IR (neat, cm^{-1}): 2109 (N_3), 1737 (C=O).

Preparation of compound 4.

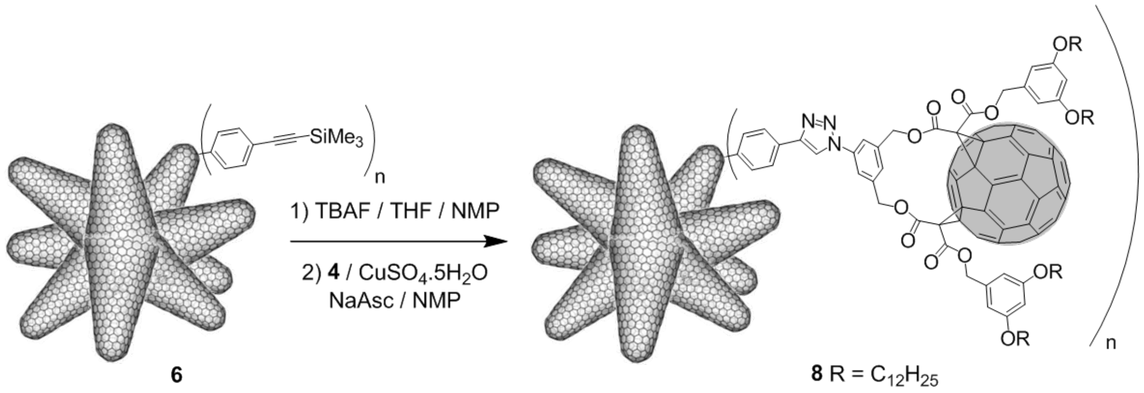
DBU (0.54 mL, 3.62 mmol) was added to a stirred solution of C_{60} (570 mg, 0.79 mmol), I_2 (500 mg, 1.97 mmol) and **3** (1.00 g, 0.79 mmol) in toluene (570 mL) at room temperature. The resulting solution was stirred for 12 hours under Argon, then filtered through a short plug of SiO_2 (CH_2Cl_2) and evaporated. Column chromatography (SiO_2, hexane/ CH_2Cl_2 1:1) gave **4** (652 mg, 42%) as a brown glassy product. UV-Vis (CH_2Cl_2): λ (nm) = 268, 316, 380. ^{1}H NMR ($CDCl_3$, 300 MHz): δ ppm 7.31 (s, 1H), 6.93 (s, 2H), 6.50 (d, J = 2 Hz, 4H), 6.39 (t, J = 2 Hz, 2H), 5.78 (d, J = 13 Hz, 2H), 5.36 (d, J = 12 Hz, 2H), 5.26 (d, J = 12 Hz, 2H), 5.04 (d, J = 13 Hz, 2H), 3.88 (t, J = 7 Hz, 8H), 1.79-1.70 (m, 8H), 1.45-1.38 (t, 8H) , 1.35-1.29 (m, 64H), 0.91 (t, J = 7 Hz, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ ppm 162.6, 162.5, 160.5, 148.6, 147.52, 147.49, 147.37, 146.1, 145.78, 145.76, 145.71, 145.6, 145.4, 145.2, 145.0, 144.9, 144.7, 144.3, 144.2, 144.0, 143.8, 143.6, 143.2, 142.7, 142.3, 141.2, 141.1, 140.6, 140.0, 138.8, 137.9, 136.6, 136.2, 135.9, 134.3, 119.6, 116.9, 107.2, 101.6, 70.6, 68.7, 68.2, 66.9, 66.8, 48.9, 31.9, 29.73, 29.69, 29.67, 29.5, 29.4, 29.3, 26.1, 22.3, 14.2. IR (neat): 2106 (–N3), 1748 (C=O). MALDI-MS: 1984.9 ($[M+H]^+$, calcd for $C_{136}H_{118}N_3O_{12}$: 1984.87). Elemental analysis calcd. for $C_{136}H_{117}N_3O_{12}$: C 82.27, H 5.94, N 2.12; found: C 81.98, H 6.09, N 1.98.

Preparation of modified CNHs 6.



A suspension of CNH (15 mg) in NMP (50 mL) was first sonicated for 10 minutes and then **5**[3] (950 mg, 5 mmol, 4 equiv. C) and isoamyl nitrite (670 µL, 5 mmol, 4eq C) were added. The reaction mixture was stirred at 70°C for 24 hours under Argon. After cooling to room temperature, the suspension was filtered on a PTFE membrane (Millipore, 0.1µm pore) and the black solid was washed several times with DMF and then with CH_2Cl_2 gave **6** (16.5 mg) as a black solid.

Preparation of modified CNHs 8.



To a suspension of **6** (15 mg) in NMP (50 ml) at 0°C was added a solution of tetrabutylammonium fluoride (1 M in THF) (6 mL). The reaction mixture was stirred at room temperature for 2 hours under Argon and then filtered on a PTFE membrane (Millipore, 0.1µm pore). The modified carbon nanohorns (**7**) were washed several times with DMF and then with CH_2Cl_2, suspended in NMP (50 mL) and used directly for the next step.

To a suspension of **7** (15 mg) in NMP (50 ml) were added **4** (15 mg, 9.3 µmol), $CuSO_4 \cdot 5H_2O$ (2.4 mg, 9.3 µmol) and sodium ascorbate (18.6 mg, 93.9 µmol). The reaction mixture was stirred at 70°C for 48 hours under Argon and then filtered on a PTFE membrane (Millipore, 0.1µm pore). In order to remove the catalyst and unreacted **4**, the black solid was sonicated and washed with a DMF/water mixture (v/v:1/4) then a DMF/THF mixture (v/v: 1/4). These operations were repeated two times and the modified carbon nanohorns were finally washed with THF and diethyl ether to afford **8** (20 mg) as a black solid.

Fig. S1. Photograph of a suspension of C_{60}-CNH **8** in dichloromethane.

Fig. S2. Raman spectra of fullerene derivative **4** (magenta), pristine CNHs (black), modified CNHs **6** (red) and **8** (blue) (λ_{exc}: 532 nm).

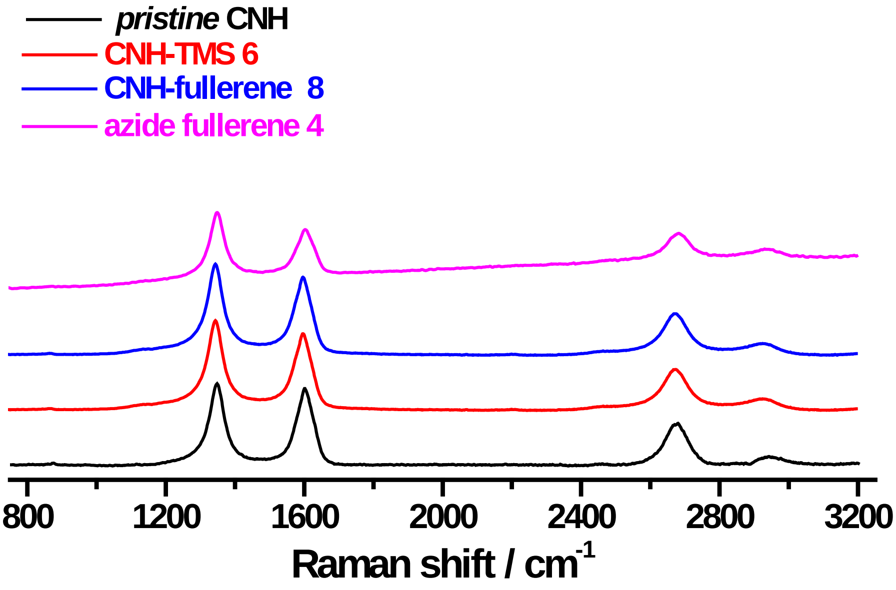


Fig. S3. (a) Survey spectra of CNH-fullerene **8** (blue) and fullerene derivative **4** (magenta) samples; (b) high resolution C1s spectra of **4** and **8**; (c) high resolution N1s spectra of **4** and **8**.

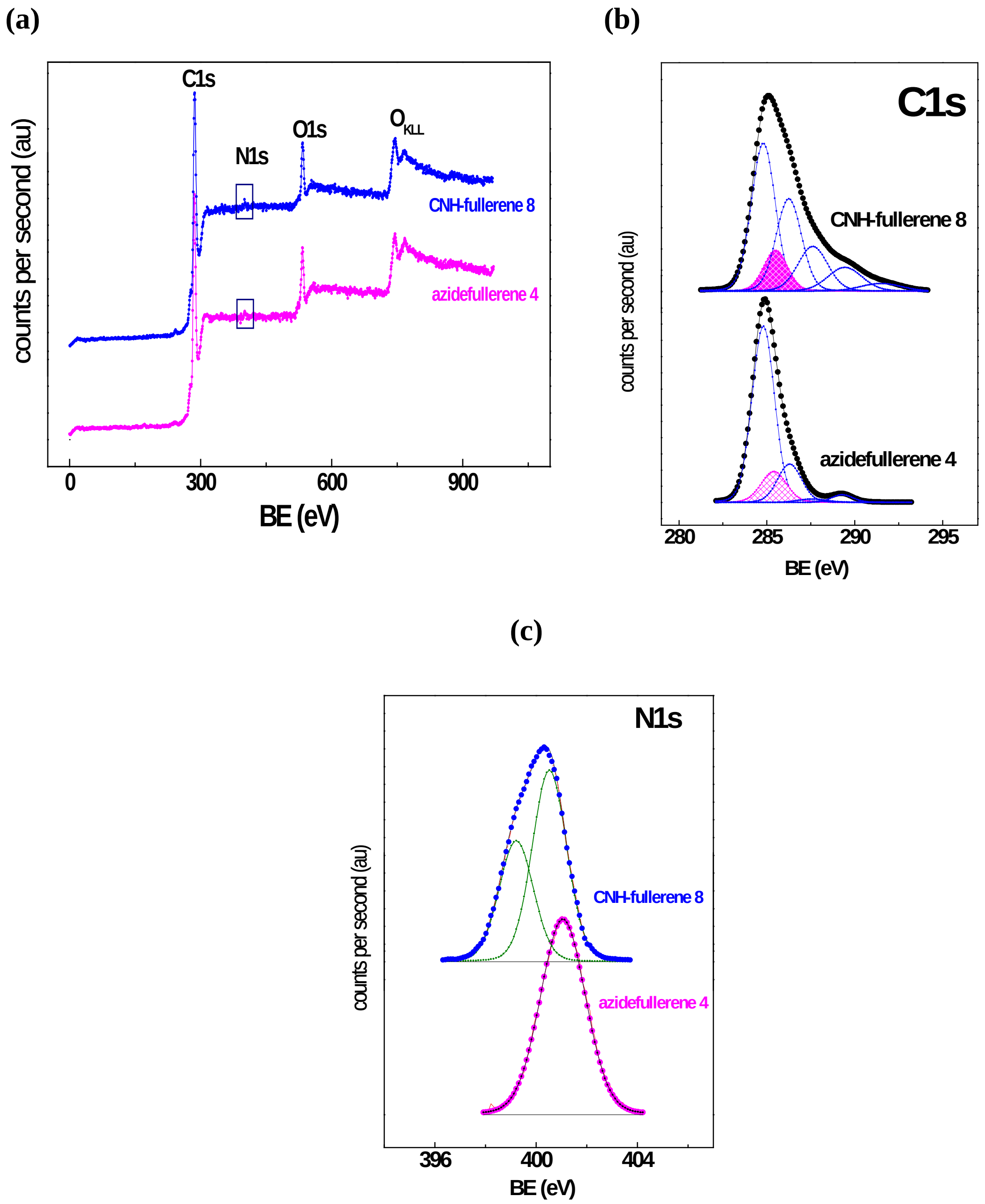


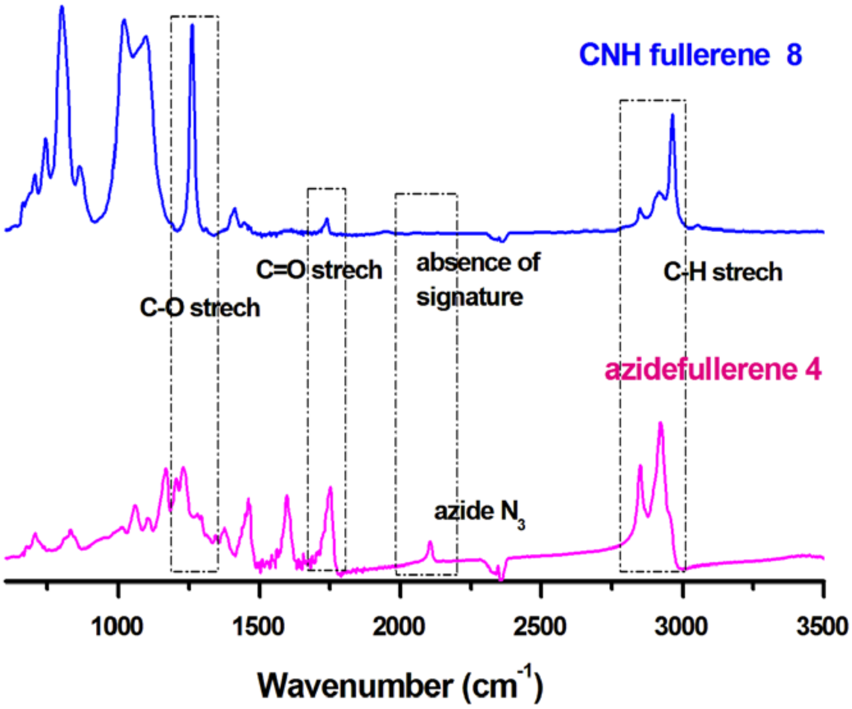
Table S1. Binding energy (eV) of C1s, O1s and N1s core-level spectra of CNH-fullerene **8** and azidefullerene **4**.

Sample	**BE (eV) C1s (%)**							**BE (eV) O1s (%)**		**BE (eV) N1s (%)**	
	sp^2 C	sp^3 C	C-O	C=O	COO	$\pi-\pi*$	C-N*	O-C	O=C	N=N	N-C
CNH-fullerene 8	284.8 (45)	285.4 (13)	286.3 (20)	287.6 (12)	289.2 (8)	291.4 (2)	286.2	533.1 (37)	531.7 (63)	399.2 (31)	400.4 (69)
azidefullerene 4	284.8 (67)	285.4 (14)	286.3 (16)	287.6 (1)	289.3 (2)	-	286.3	533.6 (41)	532.4 (59)	-	401.0 (100)

Table S2. Surface composition (atom percentage) determined by XPS measurements.

Sample	C (%at)	O (%at)	N (%at)
CNH-fullerene 8	86.3	12.5	1.2
azidefullerene 4	86.2	12.8	1.0

Fig. S4 ATR-IR spectrum of fullerene derivative **4** (magenta) and CNH-fullerene **8** (blue). Many of the intense signals which are observed in the case of **4** are also seen for CNH-fullerene **8**: the carbonyl band (C=O) at around 1745 cm^{-1}, and the peaks around 2928 and 2853 cm^{-1} attributed to the stretching of C-H. Importantly, no evidence for azide groups could be observed for CNH-fullerene **8** confirming again the successful functionalization of CNHs *via* click reaction.



Thermogravimetric analysis (TGA). At 600°C, the observed loss of weights are about 1.53% for *pristine* CNHs, 10.75% for modified CNHs **6** and 31.8% for hybrid compound **8** (Fig. S4). The corrected weight losses for **6** and **8** *vs*. pristine CNHs and thus due to the losses of the functional groups on the modified CNHs were estimated to be 9 and 30%, respectively. The number of phenylacetylene functional groups in **6** was thus estimated as 1 *per* 143 carbon atoms. With the same calculation, we estimated the amount of functional groups as 1 *per* 381 carbon atoms for **8**. This number is however not significant because the thermogram of fullerene derivative **4** also reveals a loss of weight (46% at 600ºC, in this case the surprisingly low weight loss can be easily explained by polymerization: the azide units react with the C_{60} under thermal conditions and, as a result, non volatile high molecular weight polymers are obtained). Considering that the difference in weight losses observed for **6** and **8** (*ca*. 21%) corresponds to the clicked fullerene moiety, the amount of fullerene moiety in **8** may correspond to a real ratio of *ca*. 10% (21%*46%). Therefore the number of functional groups can be estimated as *1 fullerene subunit per 191 carbon atoms*. Considering the error range of TGA measurements, we can thus estimate a similar functionalization degree for modified CNHs **6** and **8**. This observation is consistent with a complete functionalization of the alkyne subunits of the modified CNHs with azide **4**. It is however important to stress that retrocycloaddition reactions of the triazole rings may occur upon heating thus liberating azide groups that may further react with C_{60} or the CNH under thermal conditions. In this respect, we believe that analysis of the TGA data is just indicative and the numbers derived should be taken with care.

Fig. S5 Thermograhs of *pristine* CNHs (black), modified CNHs **6** (red) and **8** (blue) and fullerene derivative **4** (magenta). The temperature interval (200-600ºC) represents the steepest weight loss due to organic decompositions.

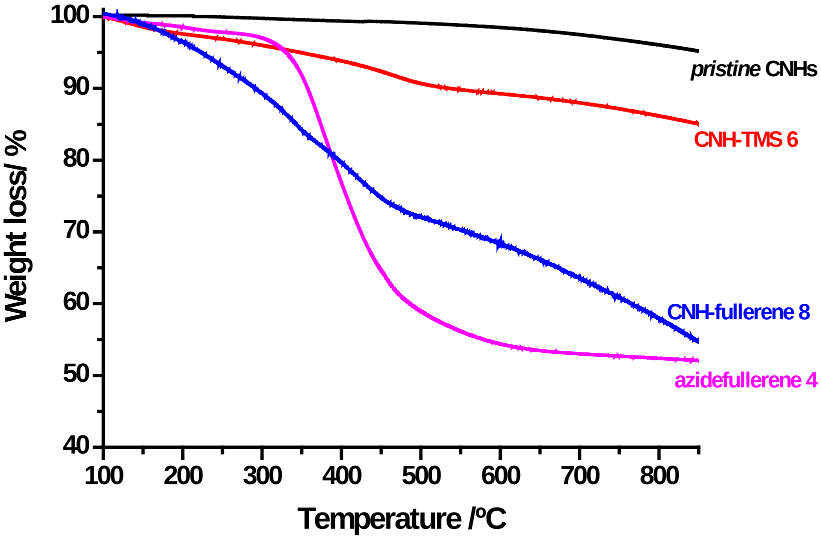
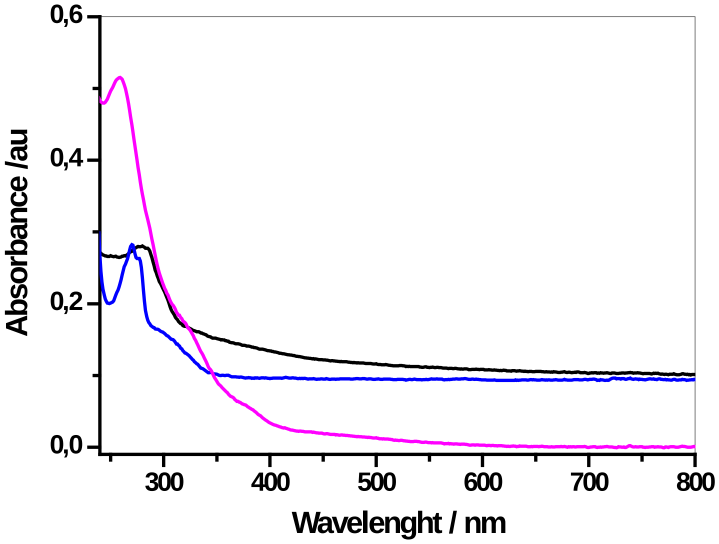


Fig. S6. Absorption spectra of modified CNHs **6** (black) and **8** (blue) and fullerene derivative **4** (magenta)



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