

Supplementary Material (ESI) for Chemical Communications
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SUPPLEMENTARY INFORMATION

FOR

**Rapid and Controllable Covalent Functionalization of Single-
Walled Carbon Nanotubes at Room Temperature**

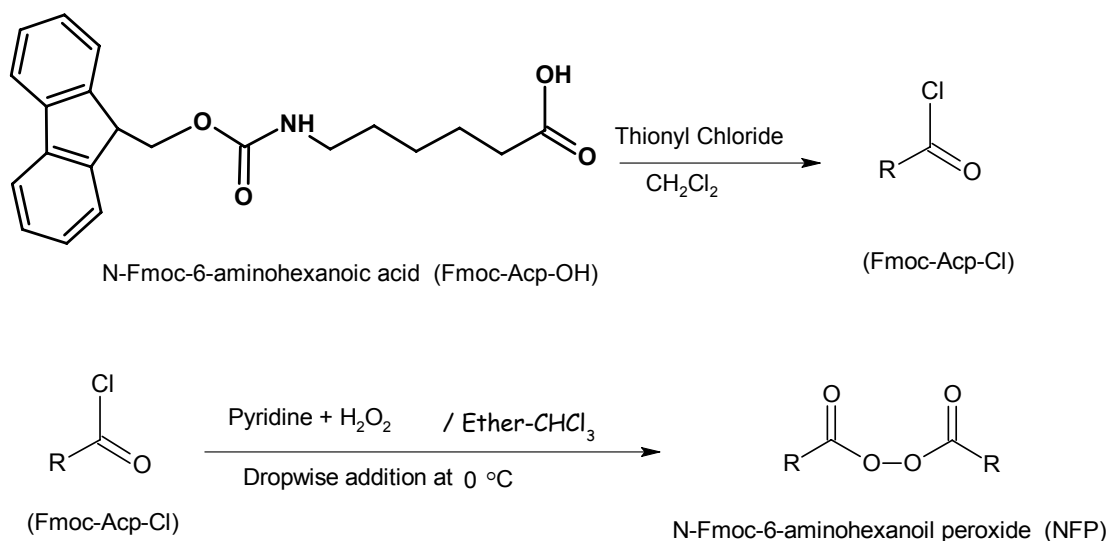
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Dispersion and Functionalization of the SWNT: The dispersion and reduction (charging up negatively) of SWNT was done according to the method described by Penicaud *et al.*⁷ In a typical reaction, 24 mg (2 mmol) of purified SWNT was suspended for about 30 minutes in 20 mL of dry THF, using an ultrasonic probe. Then, 16 mg (0.7 mmol) of sodium and 90 mg (0.7 mmol) of naphthalene were added to the suspension, under nitrogen. A green mixture was formed and the suspension stirred overnight, providing the reduced SWNT (see Scheme 1). About 2 mM of the diacylperoxide was added directly to the reduced SWNT. The reaction was stirred at room temperature for about 30 minutes and then filtered using a 3 μm pore size PTFE membrane (Millipore). The product was washed with toluene, THF, water and methanol. The functionalized SWNTs were repeatedly suspended in THF, methanol and DMF using an ultrasonic bath. The suspensions were centrifuged and finally filtrated to recover the product which was washed with acetone and dried under vacuum at 80 $^{\circ}\text{C}$.

Scheme S1. Synthesis of N-Fmoc-6-aminohexanoyl peroxide (NFP)



Synthesis of N-Fmoc-6-aminohexanoyl acid chloride (Fmoc-Acp-Cl): A solution of 1.76 g (5 mmol) of N-Fmoc-6-aminohexanoic acid (Fmoc-Acp-OH) in 60 mL of CH_2Cl_2 was treated with 3.6 mL (50 mmol) of SOCl_2 and the mixture refluxed for 30 min under

N₂. The solvent and excess SOCl₂, were removed under vacuum and the residue was dissolved in 10 mL of CH₂Cl₂. Addition of 100 mL of hexane precipitated pure Fmoc-Acp-Cl. The product was filtered through a 3 μm PTFE filter, washed with hexane and then dried under vacuum at room temperature for about 24 hours. Approximately 1.7 g of Fmoc-Acp-Cl was obtained (91 % yield). ¹H NMR (400 MHz, CDCl₃, ppm) δ_H 1.39 (q, 2H), 1.54 (q, 2H), 1.74 (q, 2H), 2.91 (t, 2H), 3.2 (c, 2H), 4.22 (t, 2H), 4.43 (d, 2H), 4.77 (s, 1H) 7.33 (t, 2H) 7.41 (t, 2H) 7.60 (d, 2H), 7.78 (d, 2H). ¹³C NMR (400 MHz, CDCl₃, ppm) δ_C 24.88, 25.72, 29.76, 40.85, 47.13, 47.51, 66.71, 120.19, 125.20, 127.24, 127.89, 141.55, 144.17, 156.63, 173.92. The FTIR spectrum shows a new band at 1802 cm⁻¹ that corresponds to the acid chloride ν(C=O) stretching vibrations.

Synthesis of N-Fmoc-6-aminohexanoyl peroxide (NFP): Fmoc-Acp-Cl (5 mmol) was dissolved in 100 mL of a CHCl₃-Ether mixture (1:2) and cooled to 0°C. Hydrogen peroxide (383 μL of 30 % concentration, 3.7 mmol) and pyridine (484 μL, 6mmol) were added dropwise simultaneously. The diacyl peroxide precipitated as it formed. After complete addition of the reagents, the ice bath was removed and the stirring was continued for another 30 min. A homogeneous solution was obtained by addition of more CHCl₃. The solution was transferred to a separatory funnel washed with 4 portions of ice water, dried over anhydrous sodium sulfate and filtered through a plug of glass wool. The organic solution was evaporated down to about 20 mL. Addition of 150 mL of ether and cooling down the solution to -2 °C for 2 hours precipitated pure NFP as a white solid. The product was filtered through a 3 μm PTFE filter, washed with ether, and then dried under vacuum at room temperature for about 24 hours. Approximately 1.25 g of NFP was

obtained (71% yield). Quantofix peroxides test sticks were used for the semi-quantitative determination of the acyl peroxide. ^1H NMR (400 MHz, CDCl_3 , ppm) δ_{H} 1.42 (q, 4H), 1.52 (q, 4H), 1.74 (q, 4H), 2.44 (t, 4H), 3.2 (c, 4H), 4.22 (t, 4H), 4.40 (d, 4H), 4.81 (s, 2H) 7.32 (t, 4H) 7.41 (t, 4H) 7.60 (d, 4H), 7.77 (d, 4H). ^{13}C NMR (400 MHz, CDCl_3 , ppm) δ_{C} 24.80, 26.26, 29.79, 30.28, 41.06, 47.71, 66.91, 120.37, 125.46, 127.44, 128.07, 141.73, 144.41, 156.84, 169.51. The FTIR spectrum shows a pair of bands at 1812 and 1780 cm^{-1} that correspond to the peroxide carbonyls. HRMS calcd for $\text{C}_{42}\text{H}_{44}\text{N}_2\text{O}_8$ (NFP) (M+1): 705.8182, found 705.3179.

Synthesis of succinic acid acyl peroxide (SAP) and glutaric acid acyl peroxide (GAP) according to the literature:⁸ 10 g of succinic anhydride (100 mmol) or 11.4 g of glutaric anhydride (100 mmol) fine powder were added to 20 mL of an ice cold solution of 8 % hydrogen peroxide (52 mmol). The mixture was stirred for about 1 hour at $0\text{ }^\circ\text{C}$. The white gel-like solution was filtered through a $5\text{ }\mu\text{m}$ polycarbonate filter. The resulting acyl peroxide was washed with cold distilled water, and then dried under vacuum at room temperature for about 24 hours. Approximately 6 g of each peroxide was obtained.

Determination of the total percentage of carboxylic acid groups: About 15 mg of purified SWNT, SWNT-SAP and SWNT-GAP were suspended in 40 mL of Na_2CO_3 0.05 mol L^{-1} with the use of a sonication bath for 30 min and stirred under nitrogen for 48 hours. The mixture was filtered through a $3\text{ }\mu\text{m}$ PTFE filter and washed with de-ionized water to remove the excess of Na. Multiple subsamples comprising about 10 mg of the treated SWNT in the form of $\text{SWNT-COO}^-\text{Na}^+$ were weighed and transferred to Teflon bombs by mass difference. Quantitative results were attained by microwave assisted acidic leaching of sample material in 3M HNO_3 and determination of Na by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES).

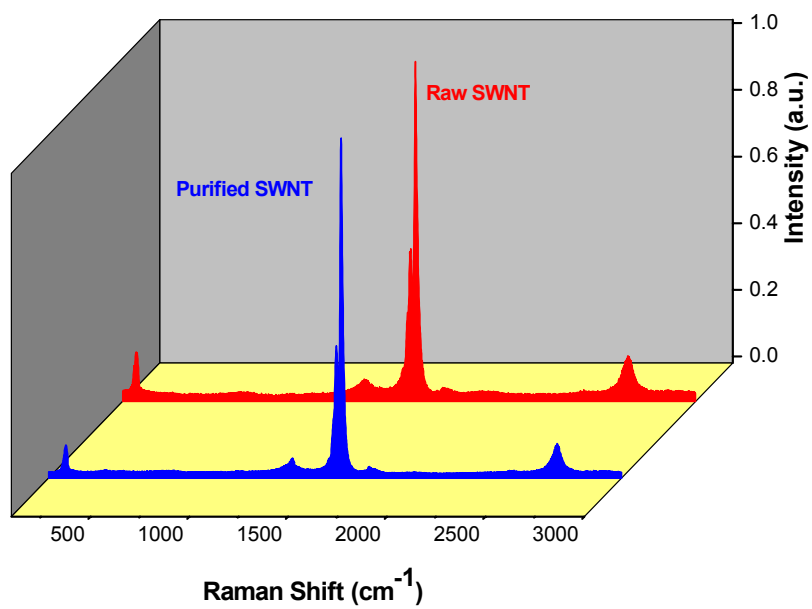


Figure S1: Raman spectra of raw and purified SWNT.

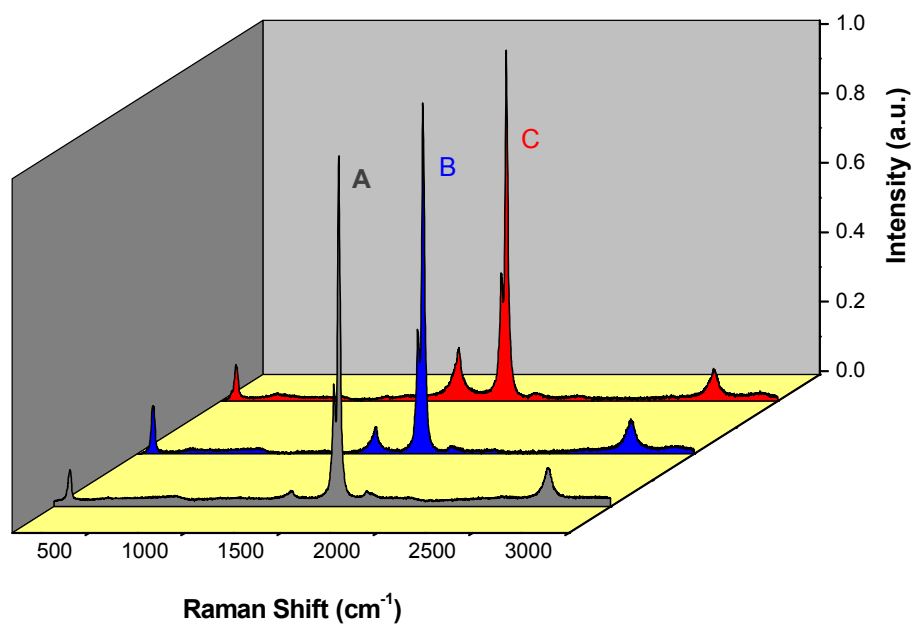


Figure S2. Raman spectra of SWNT resulting from the reaction with NFP A) after refluxing for 2 hours in THF using neutral SWNT. B) Using reduced SWNT according to scheme 1. C) Using reduced SWNT-NFP according to scheme 1

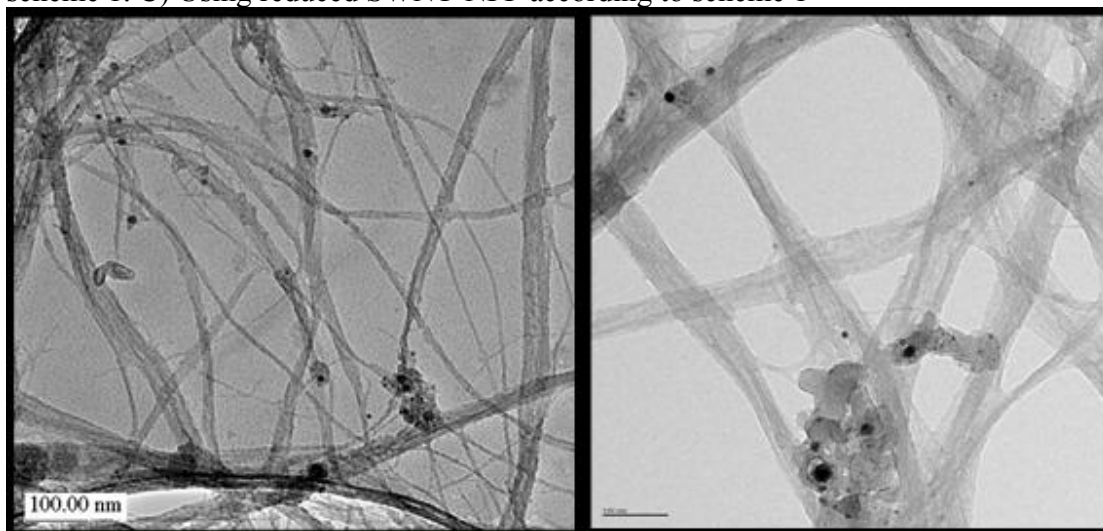


Figure S3. TEM images of SWNT-GAP (left) and Purified SWNT (right) at the same scale.

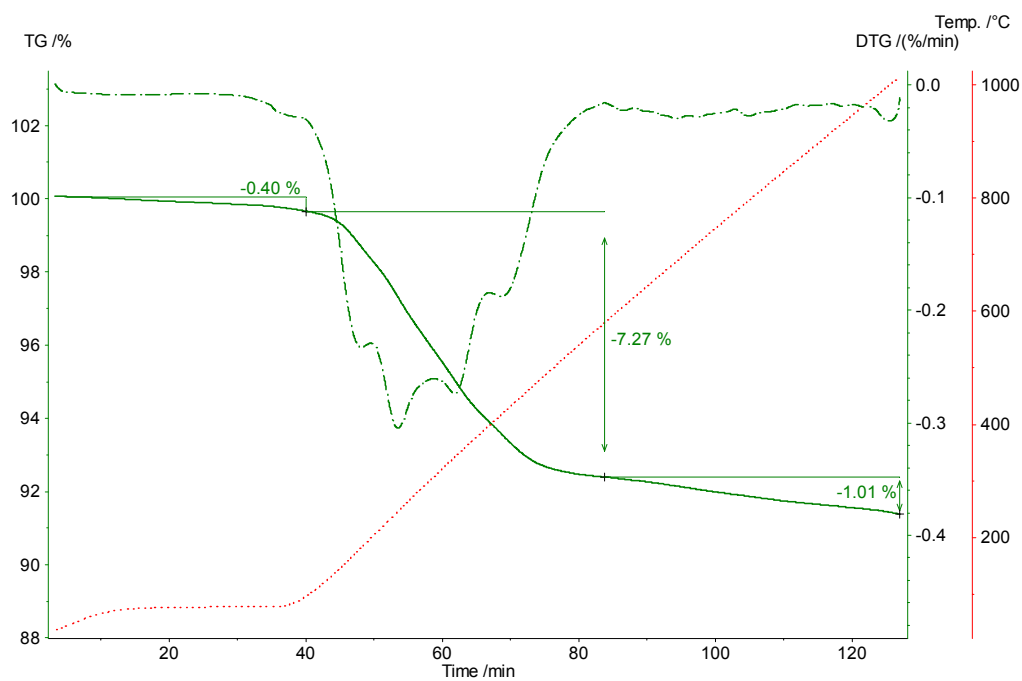


Figure S4. Temperature-dependent mass change (TG) and rate of mass change (DTG) of the sample SWNT-GAP under argon.

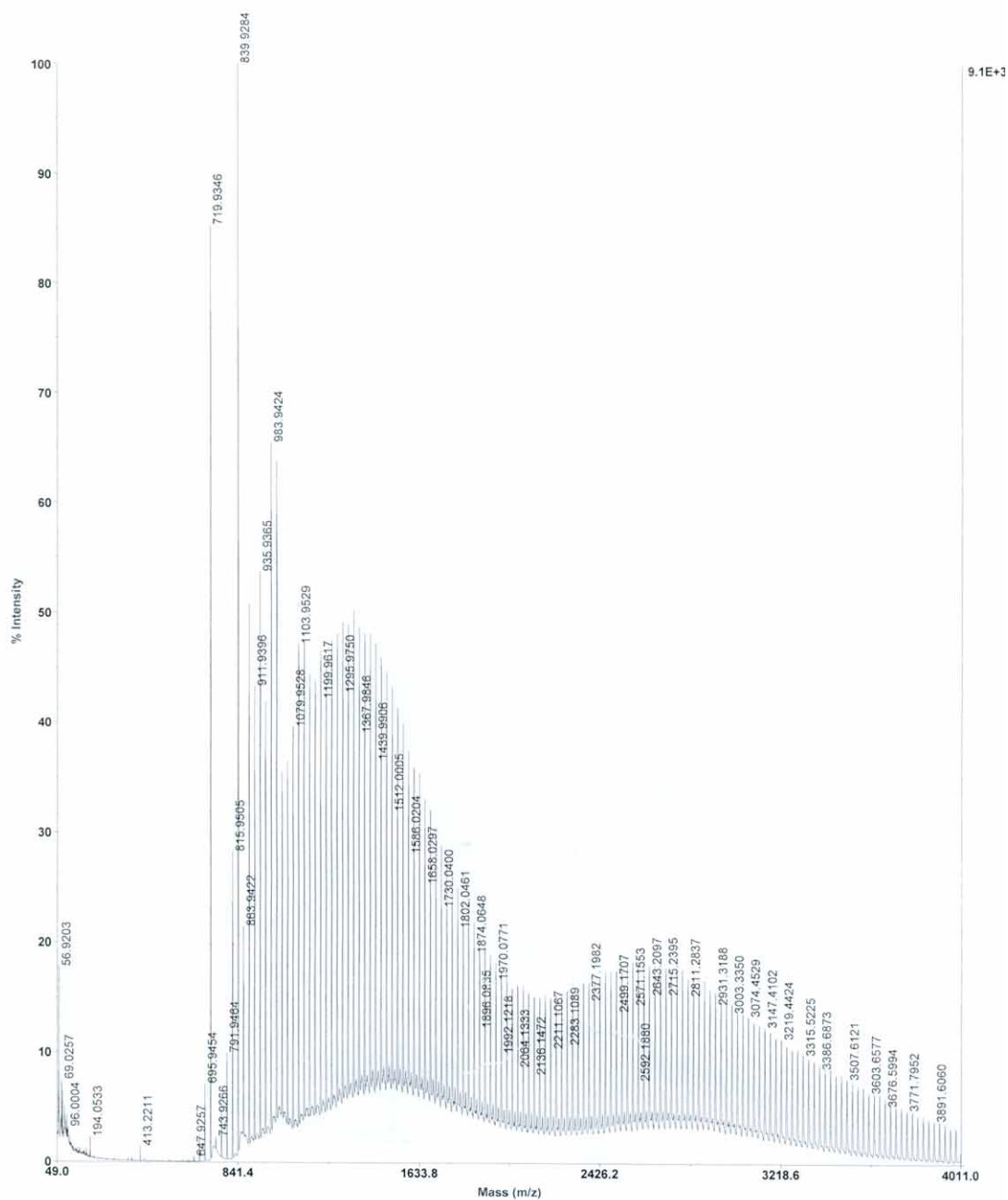


Figure S5. MALDI-TOF-MS Spectrum of purified SWNTs.

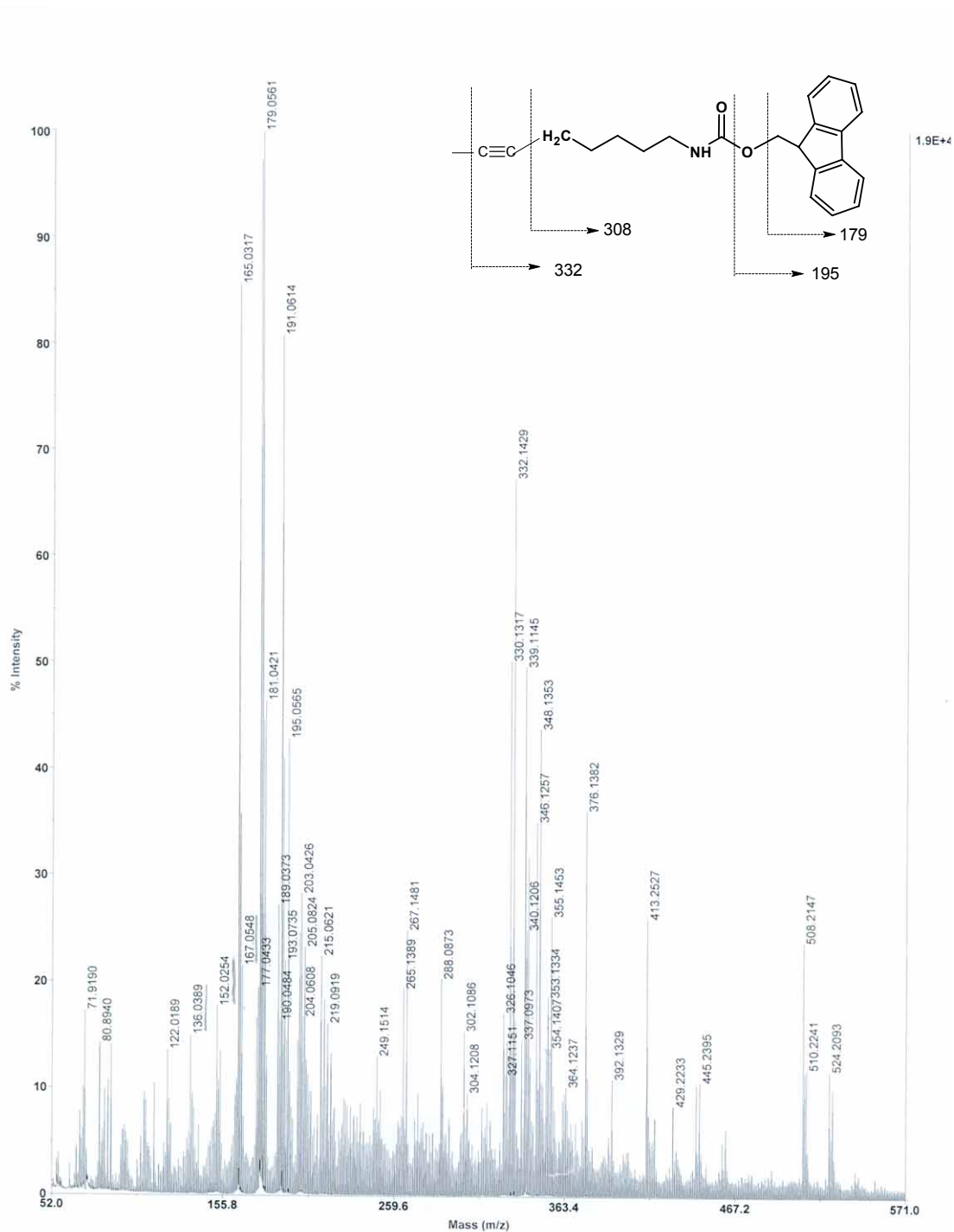


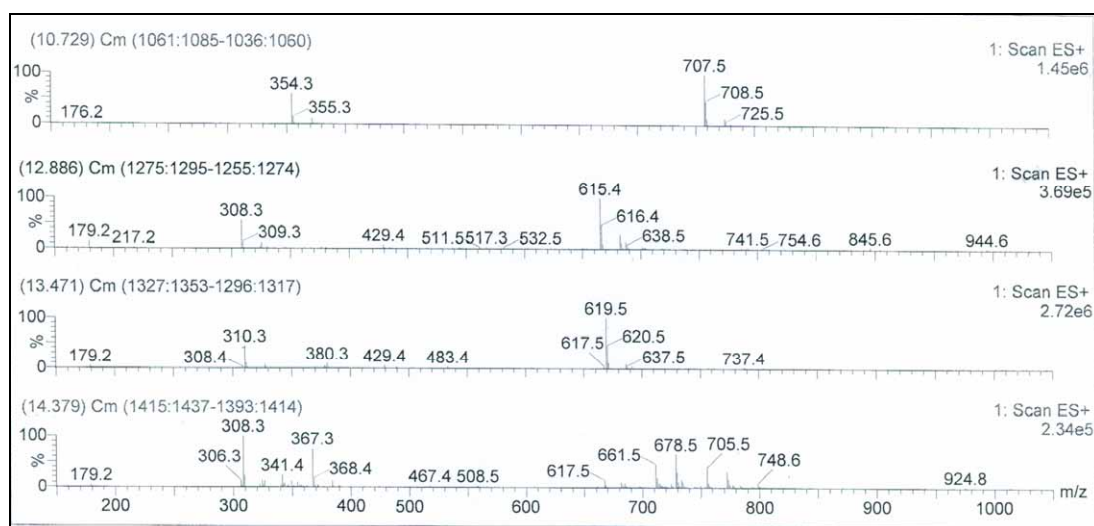
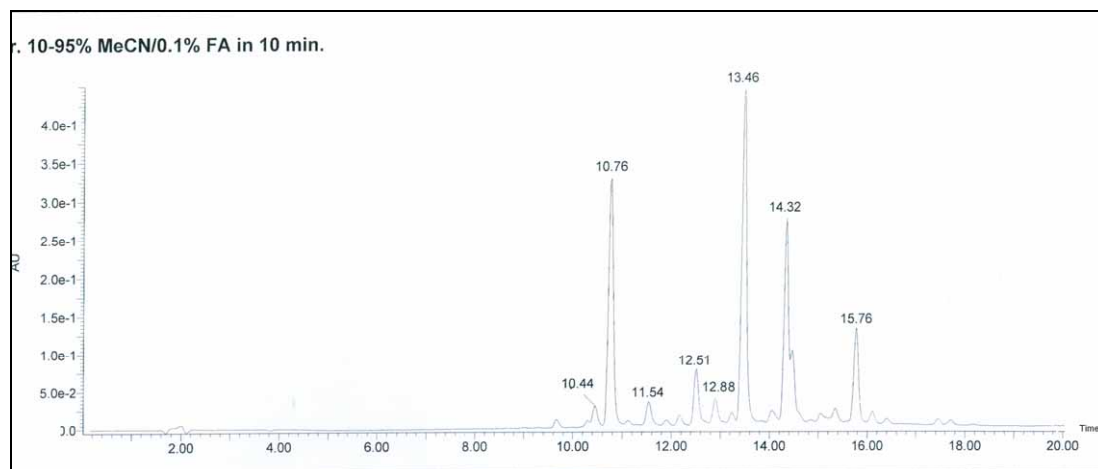
Figure S6. MALDI-TOF-MS Spectrum of SWNT-NFP.

MALDI acquisition was performed on the 4800 TOF-TOF Proteomics Analyzer from Applied Biosystem in the reflector positive mode without matrix. Figure S5 and S6 show MALDI-TOF-MS Spectrum of purified SWNT and SWNT-NFP respectively. Purified SWNT don't show any fragment in the 50-700 mass region. C₆₀ (m/z 719.9) and C₇₀ (m/z 839.9) are observed in the spectrum together with higher molecular weight fragments, each separated by 24 unit of mass (C₂). The same features are observed for that region in the SWNT-NFP spectrum. These results indicate a fragmentation of the SWNT under the experimental conditions of the analysis. On the other hand, in the SWNT-NFP spectrum we can see a fragment with m/z 332 corresponding to the combination of the masses of Fmoc-5-aminopentyl and C₂. C₂ is a stable high temperature leaving group commonly observed in mass spectra of carbonaceous materials. The fragment ions with m/z 179 and 195 are also observed.



Figure S7. Photograph of SWNT-GAP suspended in methanol.

Figure S7 shows a photograph of SWNT-GAP suspended in methanol. To prepare this suspension 40 mg of SWNT-GAP was sonicated for one hour and left to settle for 3 days. The decanted solution (250 mL) was filtered and 15.8 mg of SWNT-GAP was collected after drying the solid in a vacuum oven at 80°C overnight.



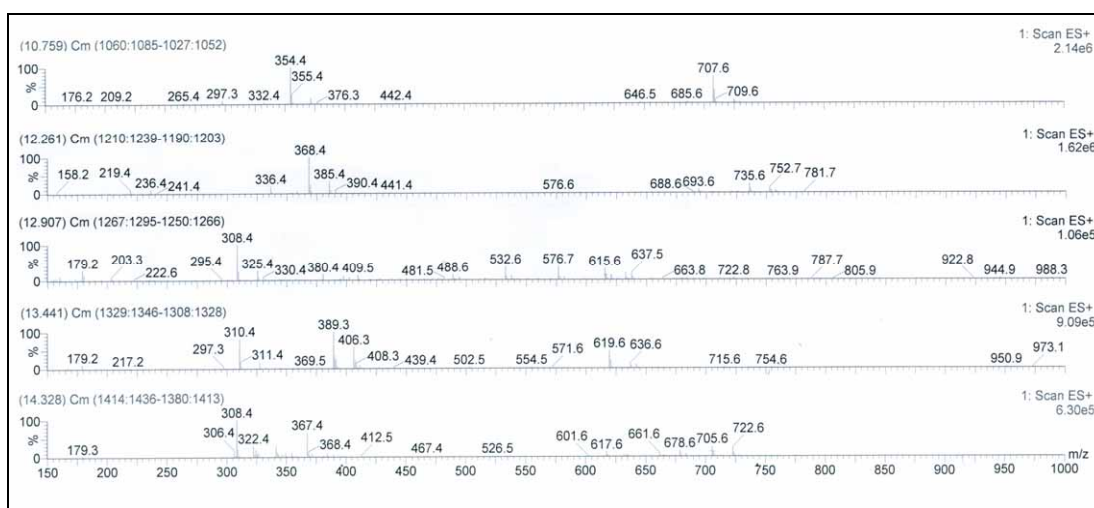
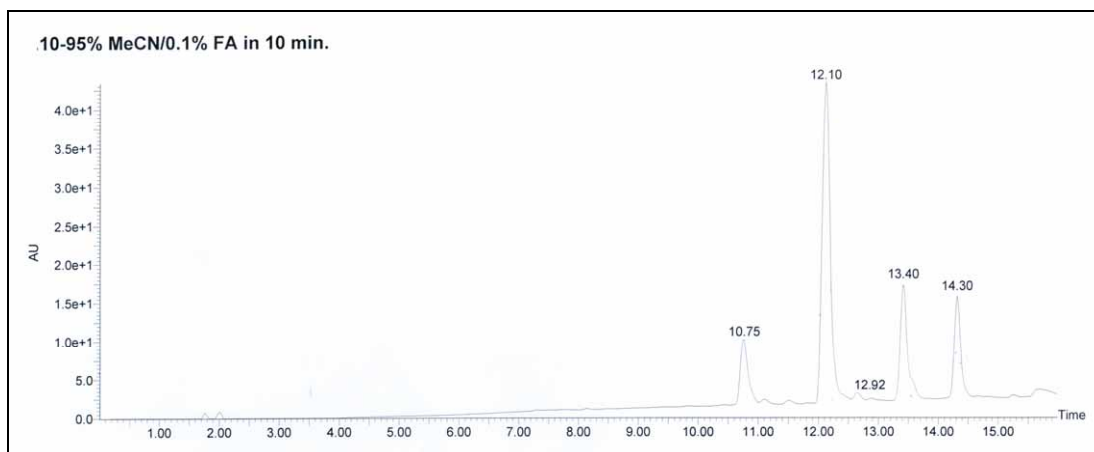
T= 10.76 min: Fmoc-NH-(CH₂)₅-COOH m/z 354.3 ([M+H]⁺) and 707.5 ([2M+H]⁺)

T= 12.88 min: Fmoc-NH-(CH₂)₃-CH=CH₂ ([M+H]⁺ 308.3 and [2M+H]⁺ 615.4)

T= 13.46 min: Fmoc-NH-(CH₂)₃-CH₂-CH₂ ([M+H]⁺ 310.3 and [2M+H]⁺ 619.5)

T= 14.32 min: unreacted NFP ([M+H]⁺ 705.5)

Figure S8. LC-ESI-MS of by-products from the reaction between neutral SWNT and NFP.



T= 10.75 min: Fmoc-NH-(CH₂)₅-COOH ([M+H]⁺ 354.4 and [2M+H]⁺ 707.6)

T= 12.92 min: Fmoc-NH-(CH₂)₃-CH=CH₂ ([M+H]⁺ 308.4 and [2M+H]⁺ 615.6)

T= 13.40 min: Fmoc-NH-(CH₂)₃-CH₂-CH₂ ([M+H]⁺ 310.3 and [2M+H]⁺ 619.6)

T= 14.30 min: unreacted NFP ([M+H]⁺ 705.5)

T= 12.10 min Fmoc-NH-(CH₂)₅-COOCH₃ ([M+H]⁺ 368.4) Probably formed in a competitive reaction.

Figure S9. LC-ESI-MS of by-products from the reaction between reduced SWNT and NFP.

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HPLC/MS analysis was performed with Waters Alliance 2795 liquid chromatograph equipped with Waters 996 PDA diode array detector and connected to a Micromass ZQ2000 mass spectrometer equipped with pneumatically-assisted electrospray ionization source, operating in positive mode. The Waters SunFire C18 (2.1x100mm, 3.5 μ m) column was used. HPLC analysis was performed with gradient (10-95% over 10 min.) elution of acetonitrile/water both with 0.1 % formic acid. Flow rate was 0.2 ml/min and all the eluent was directed first to diode array detector and then to mass spectrometer. The source temperature was set at 80 °C, desolvation gas temperature was set at 200 °C, an electrospray capillary was set at 3.5 kV with a cone voltage set at 10V. Data were collected in centroid scan mode with range 150-2000 amu..

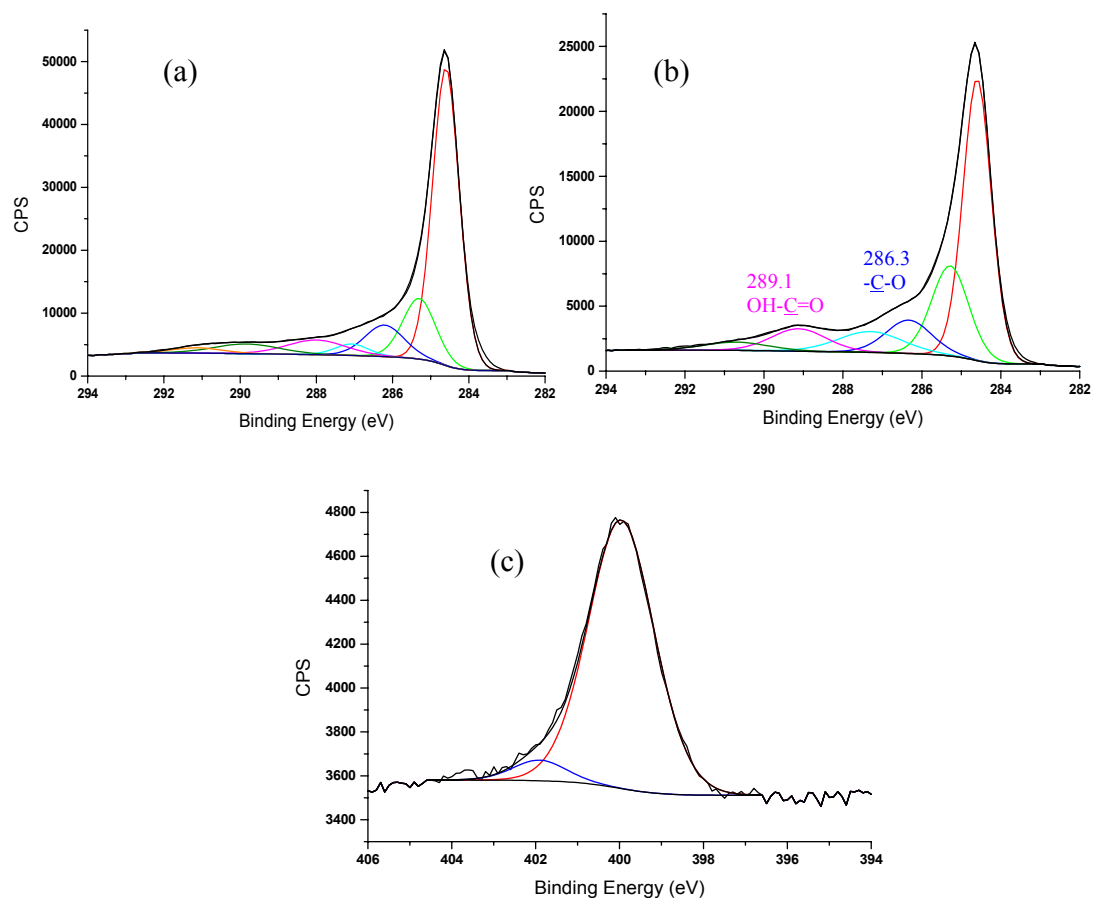


Figure S10. XPS spectra of purified and functionalized SWNTs. (a) C1s spectra of purified SWNTs, (b) C1s spectra of SWNT-GAP, (c) N1s spectra of SWNT-NFP after removing the Fmoc group. Experimental data (black solid line), components attributed at different bonds (colored lines) and fitted results (black solid line).

Table S1. Atomic concentration calculated from XPS Experimental Data

Sample	Concentration of oxygen (atomic %)	Concentration of nitrogen (atomic %)
Purified SWNT	3.86 ± 0.1	0.32 ± 0.01
SWNT-GAP	14.28 ± 0.5	0.23 ± 0.1
SWNT-NFP	8.64 ± 0.03	2.20 ± 0.05

The samples were analyzed, using the Kratos Axis Ultra XPS equipped with a monochromated Al X-ray source. Three analyses were performed on each sample to ensure reproducibility. Analyses were carried out using an accelerating voltage of 14kV, current of 10mA and an X-ray spot size of 400 x 700 μm . Charge build-up was compensated for using the Axis charge balancing system. The pressure in the analysis chamber during analysis was 2.0×10^{-9} torr. High resolution spectra were collected at a pass energy of 40eV and peak fitted using CasaXPS (ver. 2.2.107) data processing software. Shirley background correction procedures were used as provided by CasaXPS. Curve fitting procedures used for the high resolution spectra used a Gaussian-Lorentzian function. The binding energy scale of the spectrometer was externally reference to Ag $3d_{5/2}$ at 368.3 eV. High resolution analyses were calibrated to the adventitious C 1s signal, at 284.6 eV. Quantification was performed using sensitivity factors provided by CasaXPS's Scofield element library.