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Electronic Supplementary Information

for

Nitrile *N*-oxides in programmable one-pot functionalization of multi-wall carbon nanotubes *via* 1,3-dipolar cycloaddition

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Materials and methods

Ultrasonication was performed with Bandelin Sonorex Super RK31, 30 W, 35 kHz. Melting points are uncorrected and were determined using Boetius apparatus. ^{1}H NMR spectra and ^{13}C NMR spectra (proton decoupled) were obtained on a Varian Unity INOVA XL-300 (300 MHz / 75 MHz) spectrometer, a Varian Unity INOVA XL-600 (600 MHz /150 MHz) spectrometer. Thermogravimetric data were collected on a Mettler Toledo thermobalance (TGA/DSC 2). SEM microphotographs and EDX spectra were recorded using Phenom PRO microscope (5 kV). Composites microphotographs were taken using Levenhuk D870T optical microscope. Thin layer chromatography (TLC) was conducted on silica pre-coated plates (Merck, silica gel 60 F254 aluminium backed). Spots were visualised with UV light (254 nm), sulphuric acid solution or 2,4-dinitrophenylhydrazine solution. Column chromatography was carried out on a commercial silica gel (Merck, Kieselgel 60, 0.040 - 0.063 mm). PTFE filters used (0.45 μm pore size) were delivered by EMD Milipore.

Synthesis of 1,3-dipole precursors

Propanal oxime

To a vigorously stirred solution of hydroxylamine hydrochloride (13.210 g, 190 mmol) in 80 mL of water, potassium carbonate (27.559 g, 200 mmol) and propanal (11.019 g, 190 mmol) were added. After completion of reaction (TLC), the reaction mixture was extracted three times with 30 mL of diethyl ether. Combined organic phases were dried over magnesium sulphate and evaporated to give crude product. The residue was distilled to give pure propanal oxime as a yellow liquid (bp. 130-132°C) with 74% yield (10.264 g, 140 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.8 (s, 1H, OH) δ 7.01 (t, J = 7.0 Hz) 1H, CHNOH), δ 2.25 (qd, J = 7.4 Hz, J = 7.0 Hz, 2H, -CH2-), δ 1.10 (t, J = 7.4 Hz, 3H, -CH3); 13C NMR ($CDCl_3$, 75 MHz) δ 153.95, δ 23.17, δ 7.97.

2,4,6-trimethoxybenzaldehyde oxime

To a stirred solution of hydroxylamine sulphate (1.642 g, 10 mmol) in water (15 mL) and ethanol (20 mL) potassium hydroxide (1.120 g, 20 mmol) and 2,4,6-trimethoxybenzaldehyde (1.960 g, 10 mmol) was added. The reaction was conducted at room temperature. After 2 h the reaction mixture was concentrated under reduced pressure to approximately 15 mL. Then the residue was extracted with methylene chloride. Combined organic layers were concentrated *in vacuo* and the resulting crude product was purified by column chromatography. Yield: 80% ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.77 (6 H, s), δ 3.80 (3 H, s), δ 6.26 (2 H, s), δ 8.13 (1H, s), 10.8 (1 H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 55.4, δ 55.8, δ 91.0, δ 102.4, δ 142.4, δ 159.2, δ 161.6.

General procedure for synthesis of 4-monosubstitued benzaldoximes

A mixture of aldehyde (50 mmol), hydroxylamine hydrochloride (0.074 mol, 5.13 g), sodium acetate (0.125 mol, 10.26 g), 20 mL ethyl alcohol and 60 mL water was placed in a 250 mL round-bottomed flask equipped with a reflux condenser. Then the mixture was refluxed. The reaction progress was monitored by means of TLC. After the disappearance of starting material, the reaction mixture was poured into a 250 mL beaker. After cooling, the precipitate was filtered, washed with water and dried under vacuum, then recrystallized with ethyl alcohol to obtain a pure solid.

4-bromobenzaldehyde oxime (90%)

^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.09 (s, 1 H), δ 7.70-7.30 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.5, δ 132.1, δ 128.5.

4-hydroxybenzaldehyde oxime (74%)

^{1}H NMR (DMSO-d_6, 600 MHz) δ 6.77 (d, *J* = 10.0 Hz, 2H), δ 7.41 (d, J = 10.0 Hz, 2H), δ 8.00 (s, 1H), δ 9.75 (s, 1H), δ 10.84 (s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ 159.04, δ 149.44, δ 130.00, δ 125.15, δ 117.09.

4-methoxybenzaldehyde oxime (71%)

^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.11 (s, 1 H), δ 7.52 (d, J = 8.7 Hz, 2 H), δ 6.91 (d, J = 8.7 Hz, 2 H), δ 3.84 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.05, δ 129.22, δ 114.11, δ 55.37.

4-trifluoromethylbenzaldehyde oxime (90%)

^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.18 (s, 1 H), δ 8.00 (s, 1 H), δ 7.80-7.50 (m, 4 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 149.2, δ 127.4, δ 125.9, δ 125.9, δ 125.8, δ 125.8.

Isonicotinaldehyde oxime (84%)

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.85 (s, 1H), δ 8.60 (dd, *J* = 4.5 Hz, 1.5 Hz, 2H), δ 8.18 (s, 1H), δ 7.55 (dd, *J* = 4.6 Hz, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.4, δ 145.0, δ 139.6, δ 120.0.

2-(2-(2-methoxyethoxy)ethoxy)acetaldehyde

A dry, two-necked, 250-mL round-bottomed flask equipped a thermometer, and magnetic stirrer was charged with alcohol 2-(2-(2-methoxyethoxy)ethoxy)ethanol (4.105 g, 25 mmol) in dichloromethane (125 mL) under nitrogen atmosphere. The flask was immersed in an ice-water bath. After 15 min dimethyl sulfoxide (4.883 g, 62 mmol) and phosphorus pentoxide (7.097 g, 50 mmol) were added sequentially. The reaction mixture was allowed to stir and warm to room temperature until disappearance of starting material confirmed by TLC (40 min). The flask was immersed again in the ice-water bath; then triethylamine (10.100 g, 100 mmol) was added dropwise over 2 min. Stirring was continued for 1 h. The reaction was quenched with 50 mL of 10% hydrochloric acid and extracted with dichloromethane. The organic layers were washed with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified using column chromatography ($CHCl_3$: MeOH 9:1) to give 3.060 g (76%) of 2-(2-(2-methoxyethoxy)ethoxy)acetaldehyde as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (d, *J* = 0.8 Hz, 1H), δ 4.06 (d, *J* = 0.8 Hz, 2H), δ 3.59-3.67 (m, 4H), δ 3.54 - 3.57 (m, 2H), 3.43 - 3.47 (m, 2H), 3.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, δ 76.7, δ 71.8, δ 70.9, δ 70.7, δ 59.0, δ 40.1.

Hexadecanal

To a cooled and vigorously stirred suspension of PCC (17.000 g, 79 mmol) in 100 mL of dichloromethane, dodecyl alcohol (9.766 12.606 g, 52 mmol) was added in a one lot. Soon after the reaction mixture became dark brown and the ice bath was removed. After 3 hours of stirring at room temperature the reaction was completed. Then the reaction mixture was diluted with 80 mL of anhydrous diethyl ether. The resulting suspension was filtered through silica gel and washed repeatedly with diethyl ether (400 mL). The eluent was dried over magnesium sulphate and subsequently concentrated *in vacuo* to give yellow oil. The crude product was purified with column chromatography (Hexane : Diethyl ether 95:5) to give 8.987 g (38 mmol, 48%) of hexadecanal as a clear liquid. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.76 (t, *J* = 1.8 Hz, 1H), δ 2.43-2.40 (m, 2H,), δ 1.63 (m, 2H,), 1.35-1.23 (m, 16H), 0.89-0.84 (m, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 202.67, δ 43.91, δ 31.92, δ 29.61, δ 29.45, δ 29.38, δ 29.34, δ 29.26, δ 29.19, δ 29.09, δ 22.69, δ 14.10.

Hexadecanal oxime

To a stirred suspension of hexdecanal (3.784 g, 16 mmol) and hydroxylamine hydrochloride (1.668 g, 24 mmol) 1.5 mL (1.470 g, 18 mmol) of pyridine was added. The reaction mixture was stirred at room temperature for 6 hours (progress of the reaction monitored by TLC). Then ethanol was removed under vacuum and the residue was treated with 10 mL of distilled water followed by cooling on an ice bath to 0 °C. When dodecanal oxime crystallised out as a white solid it was filtered off and washed repeatedly with water, then dried in vacuo and recrystallised from ethanol to give pure dodecanal oxime. m.p. 76 - 80 °C (lit. 77°C), ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.04 (s, 1H, OH) δ 7.44 (m, 1H, -CHNOH), δ 1.64-1.59 (m, 2H, -CH_2CHNOH), δ 1.52-1.41 (m, 2H, -CH_2CH_2NOH), 1.41-1.18 (m, 16H, -$(CH_2)_8$-), 0.90-0.86 (m, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.07, δ 32.04, δ 29.73, δ 29.62, δ 29.45, δ 29.26, δ 29.20, δ 26.62, δ 26.14, δ 24.97, δ 22.80, δ 14.20.

Purification of pristine MWCNTs

5.000 g of MWCNTs was added to a round bottom flask containing 250 mL of hydrogen peroxide (30 wt. %). The resulting suspension was sonicated for 24 h at room temperature, filtered off over PTFE filter

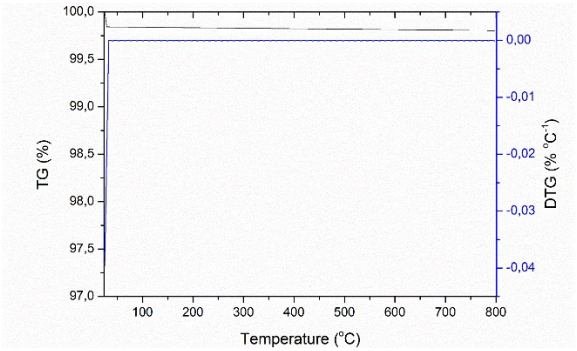
membrane, washed with water and dried in a laboratory oven for 24 h. The solid material was Soxhlet-extracted with methanol and dried to constant weight.

Preparation of Composites

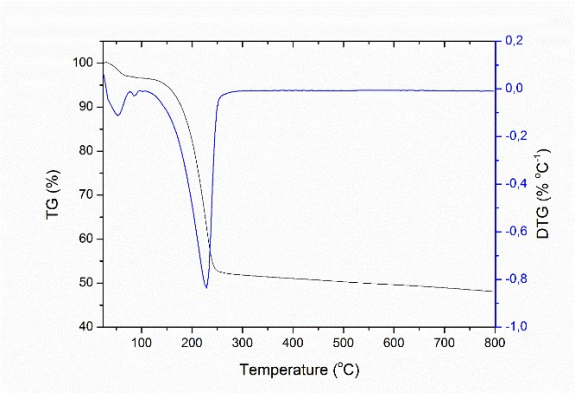
The MWCNTs/PVP composites were obtained by mixing 10 mL of sonicated (2 h) DMF dispersion of pristine/functionalized MWCNTs (0.5 mg/mL) with 7.25 mL of hot DMF solution (60 °C) of polyvinylpyrrolidone) (PVP, Mw ≈ 300 000; 20 mg/mL). After the mixture was stirred for 60 min, the composite film was prepared by casting the solution on a glass Petri dishes (Ø 5 cm) and evaporating to dryness in a fume hood at 40 °C. Samples for microscopic observations were prepared according to the same procedure. However, in order to ensure appropriate conditions for microscopic observations they were diluted 10-times with anhydrous DMF before casting.

Thermogravimetric analysis

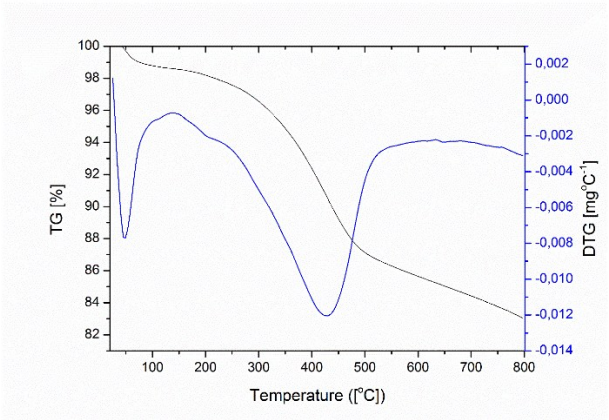
Nanocyl NC 7000™ (functionalizing agents in brackets)



Pristine NC 7000



f-NC 7000 (Propanenitrile oxide)



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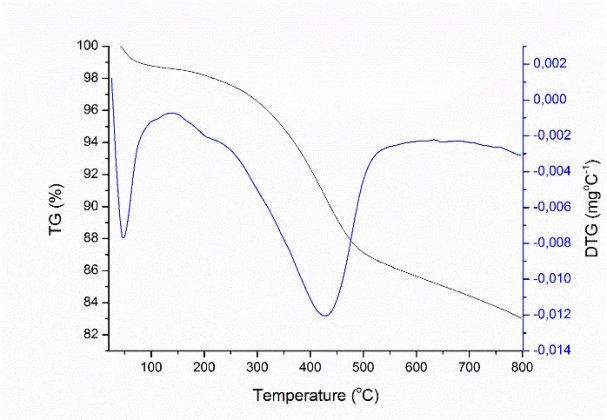
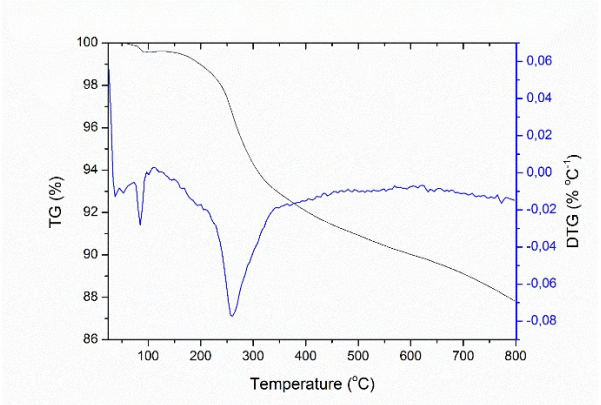
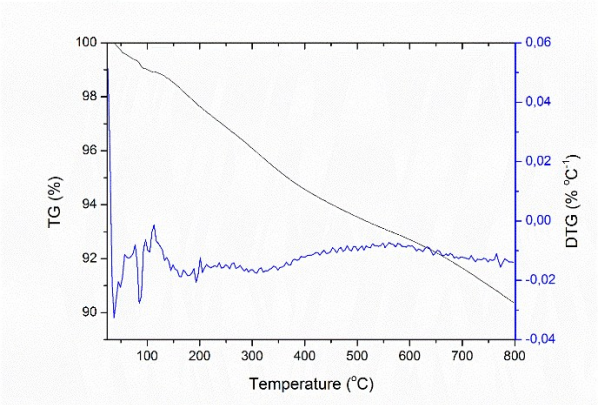


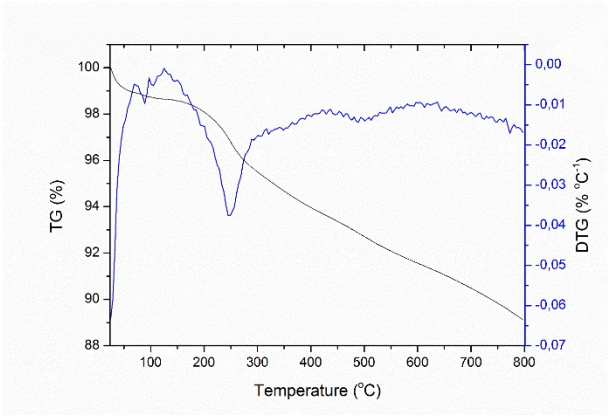
f-NC 7000 Hexadecanitrile oxide



f-NC 7000 (4-trifluoromethylbenzenecarbonitrile oxide)



f-NC 7000 (2-(2-(2-methoxyethoxy)ethoxy)acetonitrile oxide)



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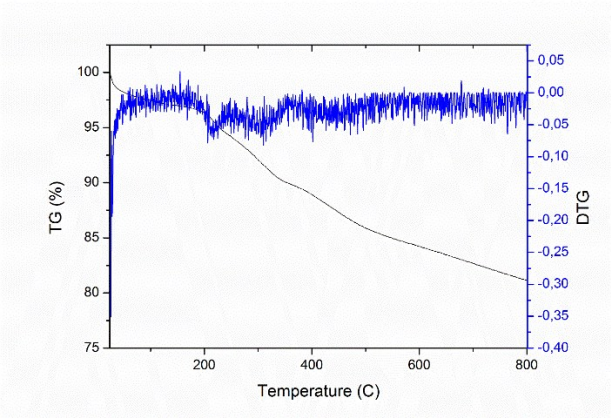
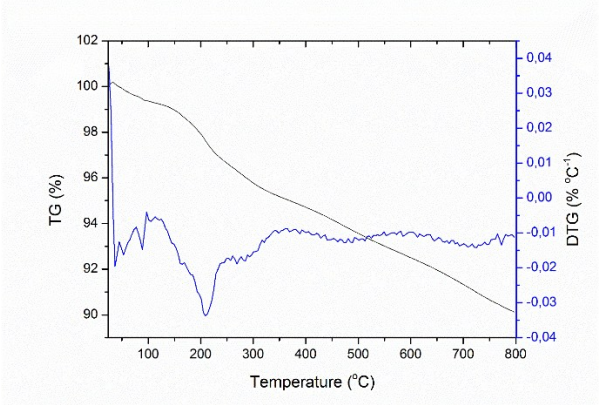
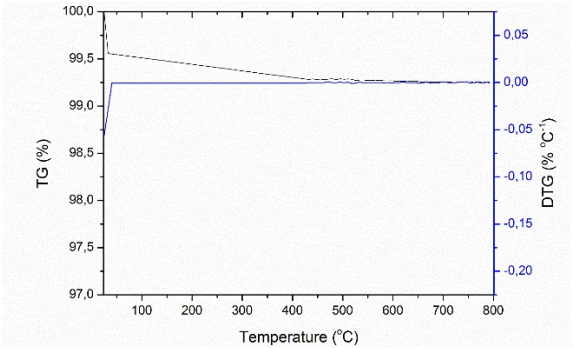


f-NC 7000 (4-hydroxybenzenecarbonitrile oxide)

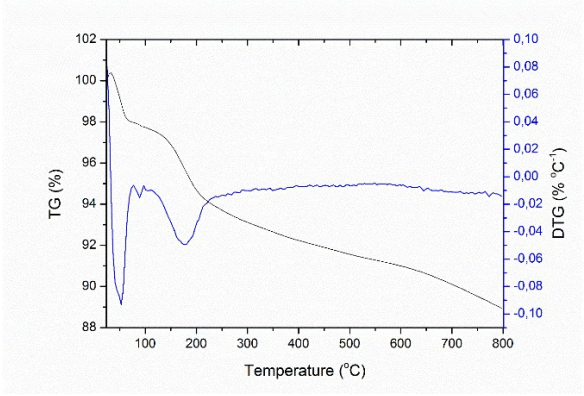


f-NC 7000 (4-methoxybenzenecarbonitrile oxide)

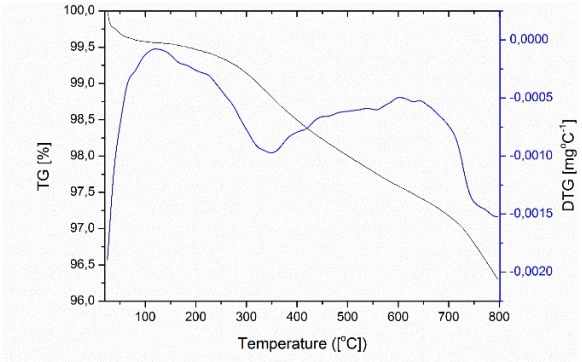
'Our MWCNTs'



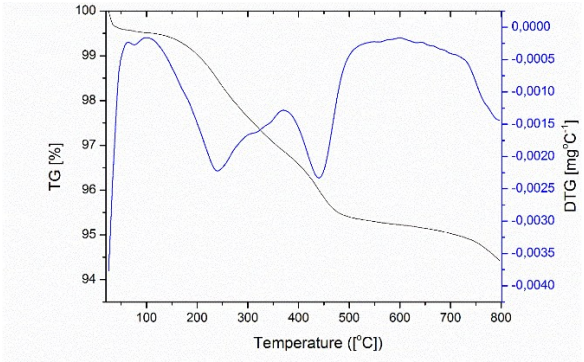
Pristine MWCNTs



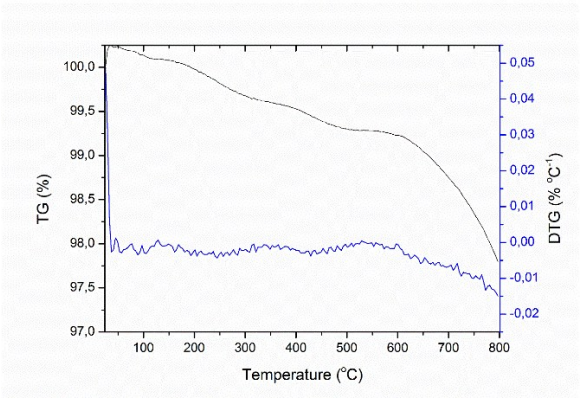
f-NC 7000 (Propanenitrile oxide)



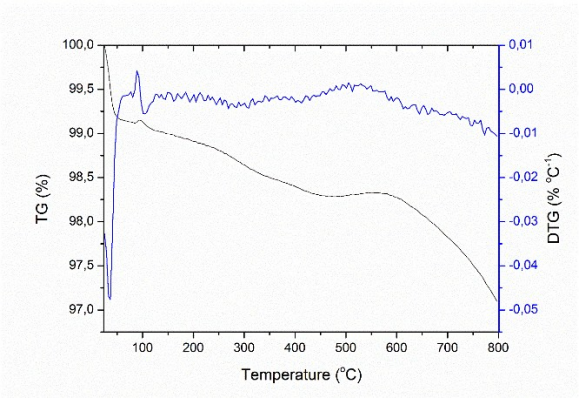
f- MWCNTs (2,4,6-trimethoxybenzonitrile oxide)



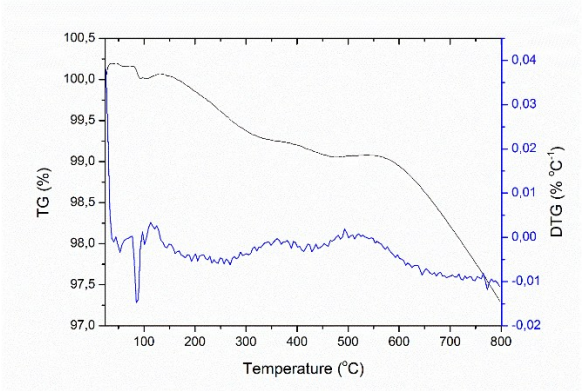
f-MWCNTs (Hexadecanitrile oxide)



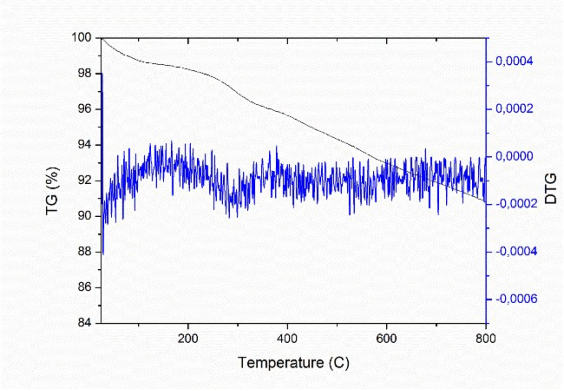
f- MWCNTs (4-trifluoromethylbenzenecarbonitrile oxide)



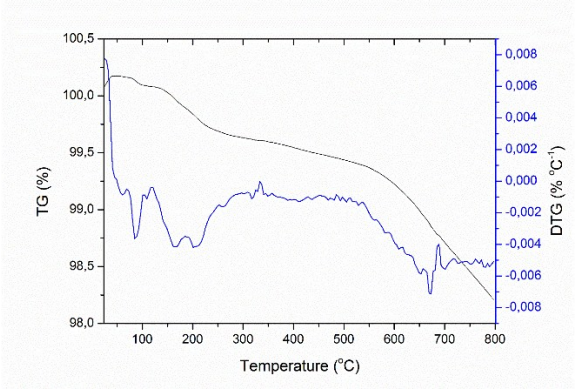
f- MWCNTs (2-(2-(2-methoxyethoxy)ethoxy)acetonitrile oxide)



f- MWCNTs (Pyridine-4-carbonitrile oxide)



f- MWCNTs (4-hydroxybenzenecarbonitrile oxide)

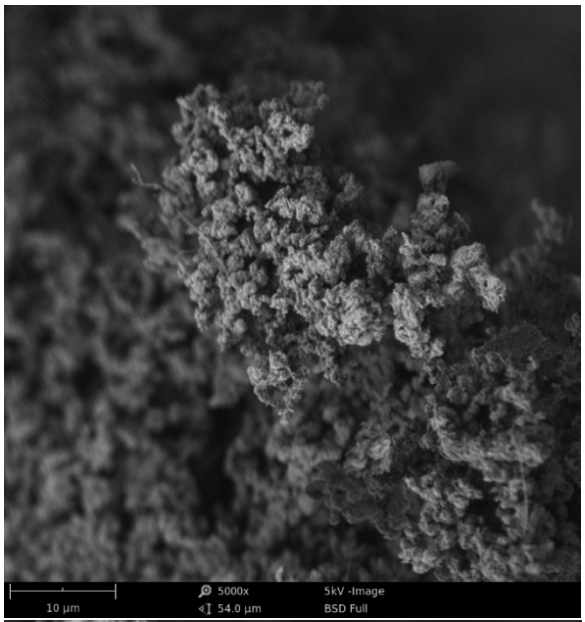


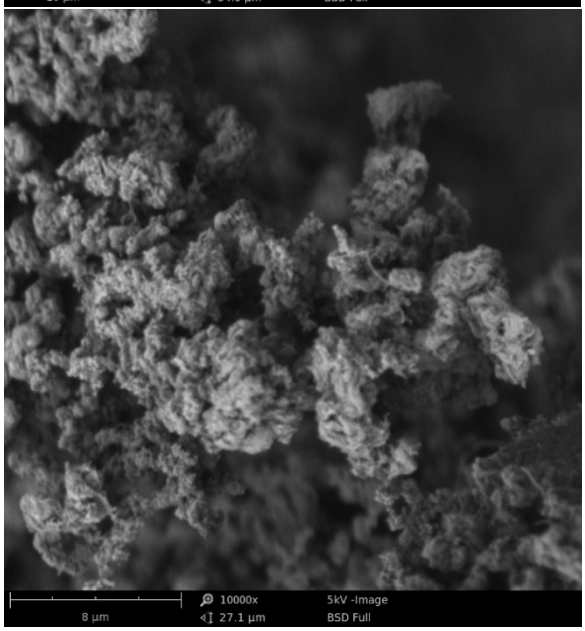
f- MWCNTs (4-methoxybenzenecarbonitrile oxide)

Exemplary SEM images

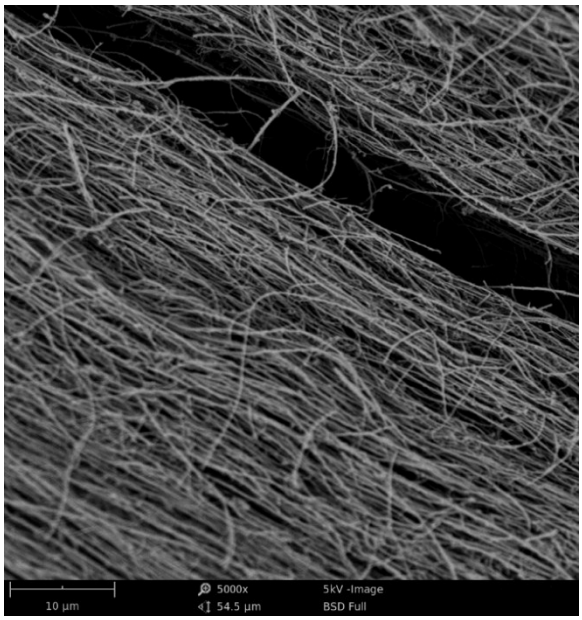
Before functionalization

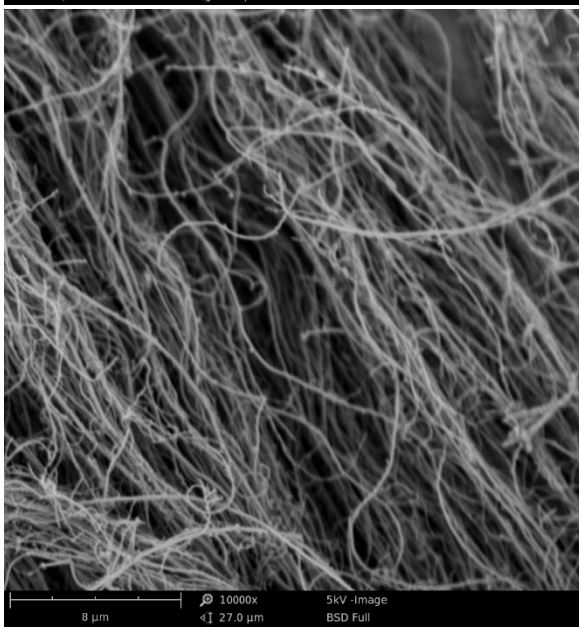
NC7000





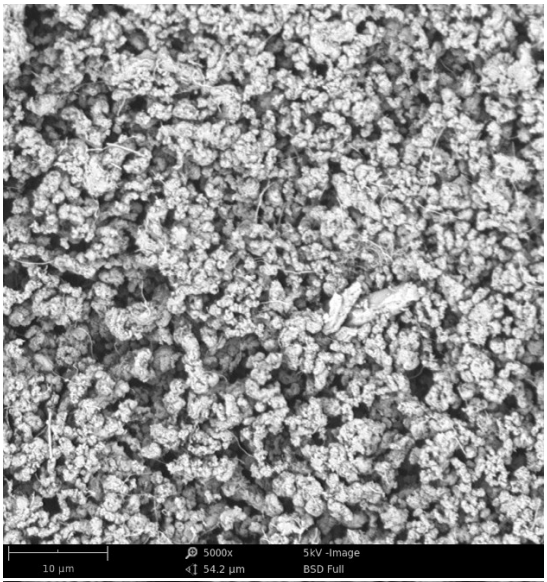
'Our' MWCNTs

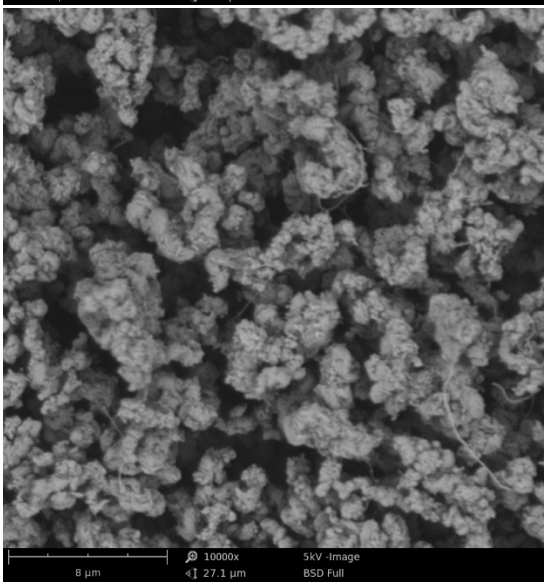




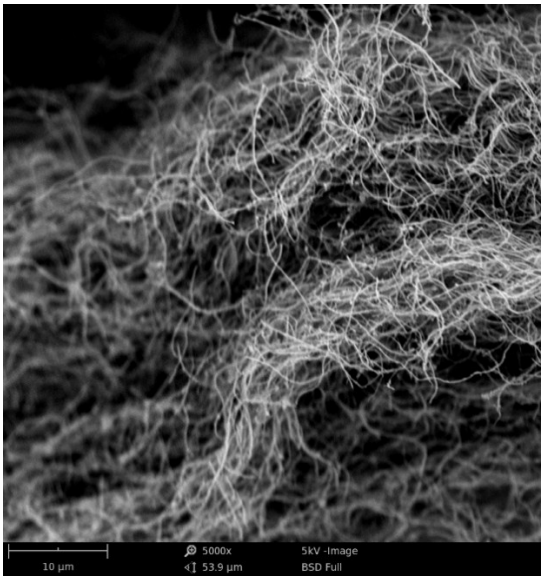
After functionalization (4a and 4b *f*-MWCNTs)

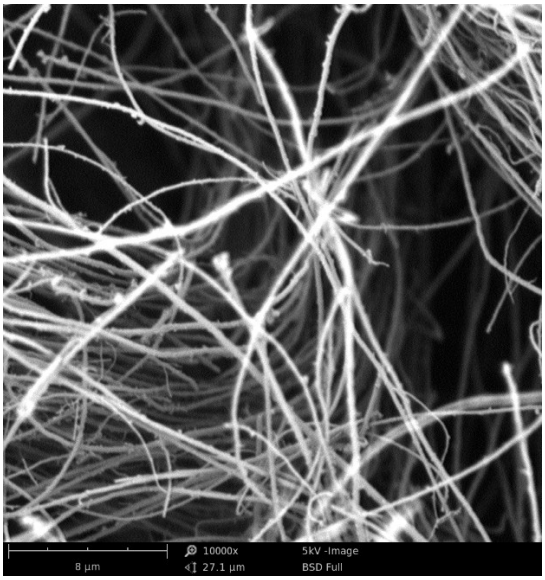
NC 7000



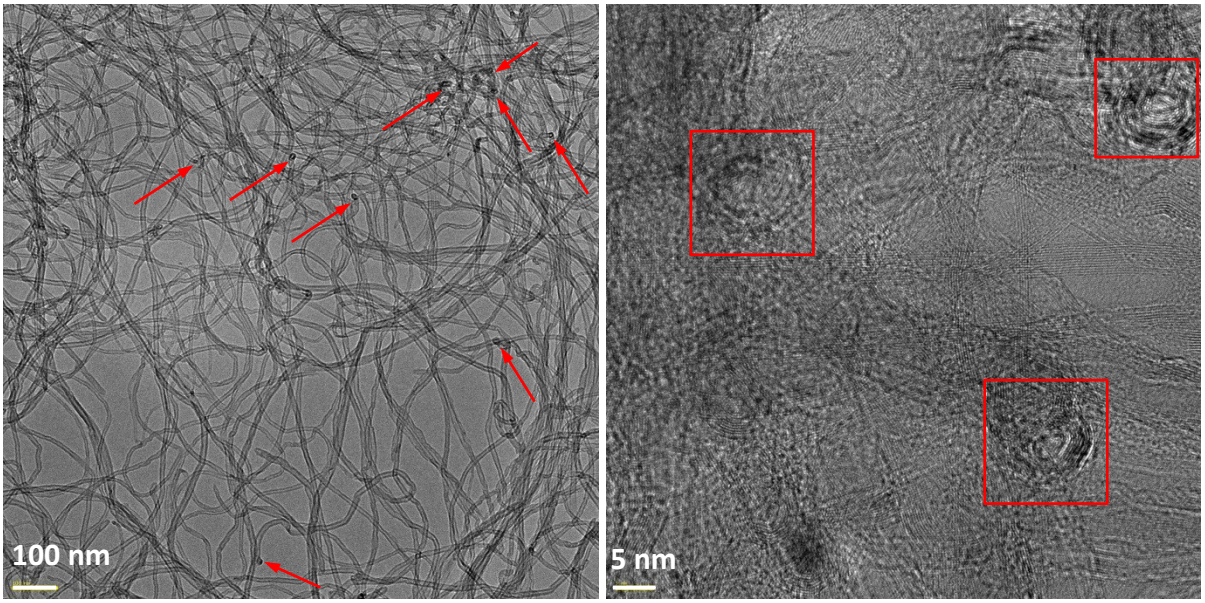


'Our' MWCNTs

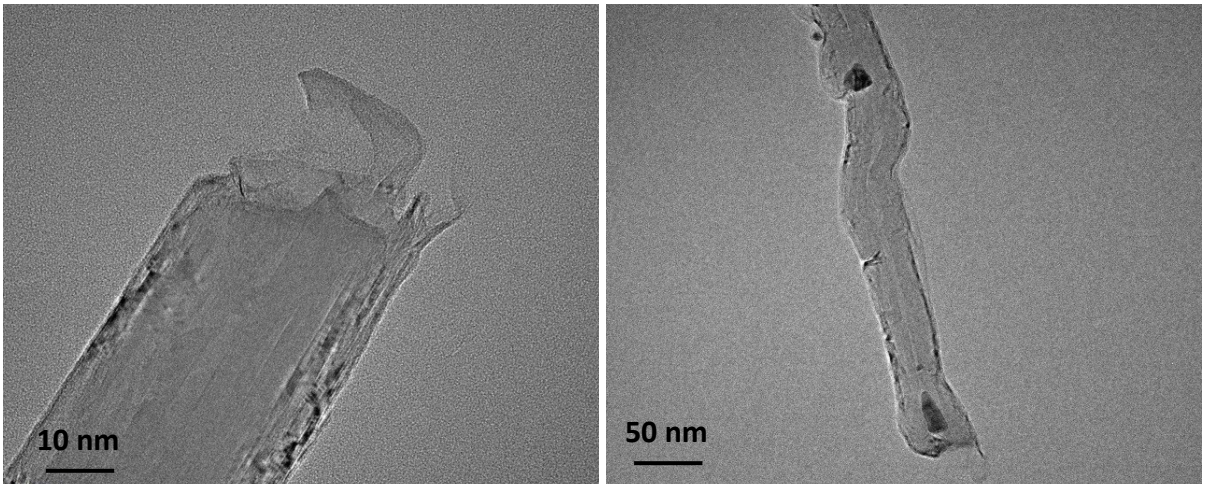




TEM images of open-ended Nanocyl NC7000™



TEM images of open-ended and corked long 'our' MWCNTs



The arrows indicate open-ended nanotube tips, while the squares correspond to the appropriate magnifications thereof