# Supporting Information

# Separation of semiconducting from metallic carbon nanotubes by selective functionalization with azomethine ylides

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## **General methods**

Purified SWNTs were purchased from Carbon Nanotechnologies Inc. (Houston, TX) and used without further treatment. Trimethylamine *N*-oxide, 3-chloroperbenzoic acid (*m*-CPBA) and lithium diisopropylamine (LDA) were purchased from Aldrich.

#### Raman Spectroscopy

Raman spectra were measured on a dispersive Jobin-Yvon T64000 spectrometer using 514.5 and 647.1 nm line of an Ar/Kr laser, and on a FT/Bruker RFS 100 using the fundamental laser line of a Nd:YAG laser at 1064 nm. The laser power was maintained below 100 W/cm<sup>2</sup> to prevent the heating of the sample.

#### UV-Vis-nIR

The spectra in the UV-vis-nIR range were obtained using a Perkin-Elmer UV-Vis-nIR Lambda 900 spectrometer.

#### *Thermogravimetric Analysis (TGA)*

Analyses were performed with a TGA 92 apparatus (SETARAM). Experiments were carried out under argon. Samples were heated at 5°C/min from 25°C to 800°C and heated at 800 °C for 30 min.

#### X-Ray Photoelectron Spectroscopy (XPS)

XPS spectra were recorded on a Vacuum Generator ESCALAB 210 spectrometer, using an Al K $\alpha$  source (20 mA, 15 kV) monochromatized at 1486.6 eV and equipped with a hemispherical electron energy analyser. The operating pressure in the analysis chamber was set below 10<sup>-10</sup> mbar (1.33 10<sup>-8</sup> Pa). The instrument calibration was performed by setting Ag 3d<sup>5/2</sup> binding energy at 368.70 eV. The N 1s core level was recorded at fixed pass energy of 20 eV and a take-off angle of 90° with respect to the sample plane. In these conditions the resolution of the spectrometer, referring to the Ag 3d<sup>5/2</sup>, was 0.8 eV.

#### NMR spectroscopy

Spectra were recorded on a BRUKER AC 300 spectrometer. Chemical shifts are given in ppm relative to chloroform (7.25 ppm, <sup>1</sup>H and 77 ppm, <sup>13</sup>C). The resonance multiplicity is indicated as s (singlet), d (doublet), t (triplet), m (multiplet).

#### General procedure for the synthesis of N-oxides (2) and (3)

To a solution of the tertiary amine (1 equiv) in  $CH_2Cl_2$  at 0 °C was added *m*-CPBA (1.1 equiv). The reaction mixture was stirred at 0 °C for 1 h and at room temperature for an additional 1 h. The solution was concentrated under reduced pressure and the residue was purified by chromatography over silica (CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub>: 1/9) to give the desired *N*-oxide.

• *N*,*N*-Dimethyl-4-(pyren-3-yl)butan-1-amine *N*-oxide (**2**): Formula:  $C_{22}H_{23}NO$ . MW: 317. Beige solid. Yield: 86%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  1.88 (m, 2 H), 2.05 (m, 2 H), 3.11 (s, 6 H), 3.23 (m, 2 H), 3.39 (t,  ${}^{3}J = 7.6$  Hz, 2 H), 7.83 (d,  ${}^{3}J = 7.9$  Hz, 1 H), 7.96 (d,  ${}^{3}J = 8.0$  Hz, 1 H), 8.01 (m, 2 H), 8.09 (d,  ${}^{3}J = 7.9$  Hz, 1 H), 8.15 (m, 3 H), 8.21 (d,  ${}^{3}J = 9.8$  Hz, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  23.7, 28.7, 33.1, 58.7, 71.3, 123.0, 124.7, 124.9, 125.0, 125.8, 126.7, 127.2, 127.4, 128.5, 129.9, 130.8, 131.3, 135.6. IR (KBr): v (cm<sup>-1</sup>) = 3222, 3037, 2949, 2864, 1457, 845. MS (ESI / TOF): *m*/*z* = 318 (100, [M + H]<sup>+</sup>), 340 (19, [M + Na]<sup>+</sup>), 635 (39, [2 M + H]<sup>+</sup>). HRMS (ESI / TOF) calcd for  $C_{22}H_{23}NNaO$  340.1677, found 340.1678.

• 3-(Anthracen-10-yl)-*N*,*N*-dimethylpropan-1-amine *N*-oxide (**3**): Formula:  $C_{19}H_{21}NO$ . MW: 279. Yellow solid (m.p.: 151-152 °C). Yield: 91%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  2.46 (m, 2 H), 3.11 (s, 6 H), 3.43 (t, <sup>3</sup>*J* = 8.2 Hz, 2 H), 3.74 (t, <sup>3</sup>*J* = 7.6 Hz, 2 H), 7.50 (m, 4 H), 8.02 (d, <sup>3</sup>*J* = 8.0 Hz, 2 H), 8.24 (d, <sup>3</sup>*J* = 8.8 Hz, 2 H), 8.38 (s, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  24.5, 25.1, 58.7, 71.0, 123.7, 124.8, 125.9, 126.3, 129.2, 129.4, 131.4, 132.4. IR (KBr): v (cm<sup>-1</sup>) = 3386, 3051, 2959, 1664, 1626, 1449, 885, 736. MS (ESI / TOF): *m*/*z* = 280 (100, [M + H]<sup>+</sup>), 302 (40, [M + Na]<sup>+</sup>), 559 (75, [2 M + H]<sup>+</sup>). HRMS (ESI / TOF) calcd for C<sub>19</sub>H<sub>21</sub>NNaO 302.1521, found 302.1546.

## Preparation of functionalized SWNTs 4, 5 and 6

• Preparation of functionalized SWNTs 4

A mixture of SWNTs (20 mg, 1.67 mmol of carbon, 1 equiv) and trimethylamine N-oxide 1 (500 mg, 4 equiv of carbon) in 15 mL of THF was sonicated for 3 min using an ultrasonic probe (Branson Sonifier 450, 60 W, 20 kHz). The flask was air evacuated and backfilled with N2 three times and kept under N2. The heterogeneous mixture was heated at 65 °C and a LDA solution (1.8 M in THF/heptane/ethylbenzene, 7.8 mL, 8.2 equiv) was added dropwise over a period of 1 h. The reaction was heated to 65 °C for 14 h and allowed to cool to 0 °C. Methanol (5 mL) was then added and the reaction mixture was centrifuged at 9000 rpm for 5 min. The supernatant was discarded and the residue was dispersed in THF for 5 min using an ultrasonic bath (Branson 5210, 19 W, 47 kHz). The mixture was centrifuged (9000 rpm, 5 min) and the supernatant was discarded. The same sequence was repeated thrice using DMF. dichloromethane and finally diethyl ether as solvents. Functionalized SWNTs (4) were dried under vacuum overnight. At this stage, Raman spectroscopy indicated an increase in the  $I_D/I_G$ ratio by a factor of 2.4. The overall procedure was repeated twice to enhance the degree of functionalization. Raman spectroscopy after the three sequences of functionalization showed an increase in the  $I_D/I_G$  ratio by a factor 5.1. Control experiments were run without trimethylamine N-oxide, i.e. carbon nanotubes reacted with LDA only. These experiments indicated no reactivity of carbon nanotubes towards LDA.

• Preparation of functionalized SWNTs **5** and **6**: A typical procedure is given for the preparation of **5**.

#### Step 1: pre-organization of the N-oxide on the nanotube surface.

SWNTs (10.2 mg, 0.85 mmol of carbon, 1 equiv) and 1 mg of pyrenyl-*N*-oxide **2** (10% by weight) were suspended for 5 min in 8.5 mL of MeOH using an ultrasonic probe (60 W, 20 kHz). The mixture was further dispersed using an ultrasonic bath (19 W, 47 kHz) for 1 h. The suspension was then vigorously stirred for 14 h. After centrifugation (9000 rpm, 5 min), the

residue was dispersed in methanol (19 W, 47 kHz, 30 min) and centrifuged again at 9000 rpm for 5 min. The same sequence was repeated until no significant amount of pyrenyl-*N*-oxide (2) was detected in the supernatant by UV/Vis spectroscopy. The pre-organized *N*-oxide / SWNTs were dried under vacuum overnight.

#### Step 2: covalent functionalization of the nanotubes.

Under N<sub>2</sub>, pre-organized *N*-oxide / SWNTs were placed in a flame dried flask. LDA (1.8 M in THF/heptane/ethylbenzene; 1.5 mL, 3.2 equiv) was then added slowly at room temperature. The heterogeneous mixture was dispersed in an ultrasonic bath (19 W, 47 kHz) for 1 h and stirred vigorously at rt for 14 h. Methanol (1 mL) was then added and the reaction mixture was centrifuged at 9000 rpm for 5 min. The supernatant was discarded and the residue was dispersed in THF for 5 min using an ultrasonic bath (19 W, 47 kHz). The mixture was centrifuged again (9000 rpm, 5 min) and the supernatant was discarded. The same sequence was repeated four times using DMF, methanol, dichloromethane and diethyl ether as solvents. Functionalized SWNTs **5** were dried under vacuum overnight.

The overall procedure was repeated twice to enhance the degree of functionalization.