Supplementary information for:

**Electronic Structure Control of Single Walled Carbon Nanotube Functionalization**

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**4-chlorobenzenediazonium tetrafluoroborate.** To a dry flask was added nitrosonium tetrafluoroborate (3.643 g, 31.19 mmol) in an inert atmosphere. Acetonitrile (20 mL) was added to the flask, and the solution was cooled. To the cold solution (-30°C) was added 4-chloroaniline (3.304 g, 25.90 mmol) dissolved in a minimum of acetonitrile (10 mL) over 0.5 h. After the addition was complete, the reaction mixture was warmed to room temperature. After 1 h, the reaction mixture was diluted with diethyl ether (500 mL). The precipitate was collected, dried to give the diazonium salt as a colorless solid (5.433 g, 93 %): mp 134-135°C; ¹H NMR (400 MHz, CD₃CN) d 8.24 (ABq, J = 9.2 Hz, ? ? = 102.1 Hz, 4 H).

**4-tert-Butylbenzenediazonium tetrafluoroborate.** To a dry flask was added nitrosonium tetrafluoroborate (2.233 g, 19.09 mmol) in an inert atmosphere. Acetonitrile (20 mL) was added to the flask, and the solution was cooled. To the cold solution (-30°C) was added 4-tert-butylaniline (2.5 mL, 15.58 mmol) over 0.5 h. After the addition was complete, the reaction mixture was warmed to room temperature. After 1 h, the reaction mixture was diluted with diethyl ether (500 mL). The precipitate was collected, dried to give the diazonium salt as a colorless solid (3.722 g, 96 %): mp 90-91°C; IR (KBr) 3365, 3107, 2969, 2277, 1579 cm⁻¹; ¹H NMR (400 MHz, CD₃CN) d 8.16 (ABq, J = 9.0 Hz, ? ? = 298.7 Hz, 4 H), 1.30 (s, 9H); ¹³C NMR (100 MHz, CD₃CN) d 168.9, 133.7, 130.4, 111.9, 37.9, 30.8.

**Functionalization of SWNTs.** The sodium dodecylsulfate (SDS)-coated carbon nanotubes (80 mL, 0.16 mmol of carbon) were loaded in a flask. The solid 4-tert-butylbenzenediazonium tetrafluoroborate (0.048 g, 0.32 mmol) was added to the stirred mixture. After 1 h, all of the transitions in the absorption spectra disappeared. The reaction mixture was diluted with acetone (300 mL) and filtered through a PTFE membrane. The collected solid was washed sequentially with water (150 mL) and acetone (150 mL). The functionalized material was resuspended in DMF (40 mL) with sonication (1 min), and filtered through a PTFE membrane. The solid was washed with acetone (250 mL) then diethyl ether (250 mL). The solid was dried in a vacuum oven at 0.5 mm Hg overnight. The dried material (4.5 g) was then characterized by UV/vis, Raman, and TGA. TGA (10°C/min to 750°C in an argon atmosphere) of the material had a weight...
loss of 45% which corresponds to 1 in 13 carbons on the nanotube bearing an aryl substitute. The thermally treated material was then characterized by Raman, which showed restoration of the pristine nanotube structure.

Supporting Figures.

Fig. 1. Raman analysis (633 nm excitation) showing the ability to thermally restore the pristine nanotube structure. The Raman spectra of both the starting nanotubes (black) and thermally regenerated material (blue) are essentially the same compared to highly functionalized material (red). The highly functionalized material has lost its resonance enhancement yet this enhancement returns after thermal treatment.
Fig. 2. Thermal treatment of highly functionalized material in a thermogravimetric analyzer. The functionalized nanotubes were heated to 650°C at 10°C/min in an argon atmosphere. The material treated thermally corresponds to the red trace in Fig. 1 and the material that results from thermal treatment corresponds to the blue trace in Fig. 1. The aryl moieties are lost regenerating the nanotubes electronic properties.
Fig. 3. Absorption spectroscopy also confirms the thermal regeneration of carbon nanotubes. The heavily functionalized carbon nanotubes (black) have lost all van Hove transitions, whereas the electronic properties of the carbon nanotubes has returned upon defunctionalization (red). The defunctionalized trace is characteristic of suspensions of nanotubes generated in organic solvent without centrifugation where the sample is dominated by bundles not individuals. Material suspended in DMF was analyzed.