Supporting Information

Functionalization of Single-Wall Carbon Nanotubes by Tandem High Pressure/$Cr(CO)_6$ Activation of Diels-Alder Cycloaddition

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General methods

Purified SWNTs were purchased from Carbon Nanotechnologies Inc. (Houston, TX) and used without further treatment. 2,3-dimethoxy-1,3-butadiene **1**, 1,3-cyclohexadiene **4**, 2,3-dimethylbutadiene **5**, 9,10-dimethylanthracene **6**, *trans*-1-methoxy-3-trimethylsiloxy-1,3-butadiene **7** (Danishefsky's diene), chromium hexacarbonyl, and anhydrous 1,4-dioxane were purchased from Aldrich. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under an atmosphere of N_2.

Raman Spectroscopy
Raman spectra were measured 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^2 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 SETARAM SETSYS 16/18 apparatus. Experiments were carried out under argon. Samples were heated at 10 °C/min from 25 °C to 800 °C and heated at 800 °C for 30 min.

Preparation of chromium-SWNTs complex

Chromium hexacarbonyl (55 mg, 0.25 mmol, 1 equiv.) was added to a suspension of SWNTs (3 mg, 1 equiv.) in 6 mL of anhydrous 1,4-dioxane. The mixture was sonicated for 5 min using an ultrasonic probe (Branson Sonifier 450, 60 W, 20 kHz) and then freeze-thawed three times (purged with N_2). The mixture was heated to 100 °C for 96 h in the dark, after which it was cooled to room temperature. The suspension was filtered through a 5 μm PTFE membrane and the solid was washed with anhydrous 1,4-dioxane. The resulting chromium-SWNTs complex was dried under vacuum in the dark.

Functionalization of SWNTs with 2,3-dimethoxy-1,3-butadiene **1** and Danishefsky's diene **7**

A typical procedure is given for the preparation of sample **2**.

To a suspension of the chromium-SWNTs complex in freshly distilled THF (0.8 mL) was added 2,3-dimethoxy-1,3-butadiene **1** (76 μL, 2.5 equiv.). The mixture was sonicated for 5 min using an ultrasonic probe (Branson Sonifier 450, 60 W, 20 kHz). The resulting suspension was introduced, by means of a syringe, into the capillary inlet of a 1 mL pyrex glass cell. The cell was immersed into hexane, used as piezotransmitter liquid which was contained in the high pressure apparatus,

closed on the bottom side with a steel stopper. The mobile piston was then inserted and the whole assembly was placed between the pistons of a hydraulic press. The reaction was run at 1.3 GPa and 50 °C for 60 h. After decompression, the mixture was exposed to visible light for 30 min to induce decomplexation of chromium. The reaction mixture was centrifuged at 9000 rpm for 5 min. The supernatant was discarded and the precipitate 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 five times using dichloromethane, DMF, methanol, acetone, and diethyl ether as solvents. Functionalized SWNTs **2** were finally dried under vacuum overnight.

Figure S1. Normalized Raman spectra at 1064 nm of reference sample **3** and of SWNTs functionalized with Danishefsky's diene **7**

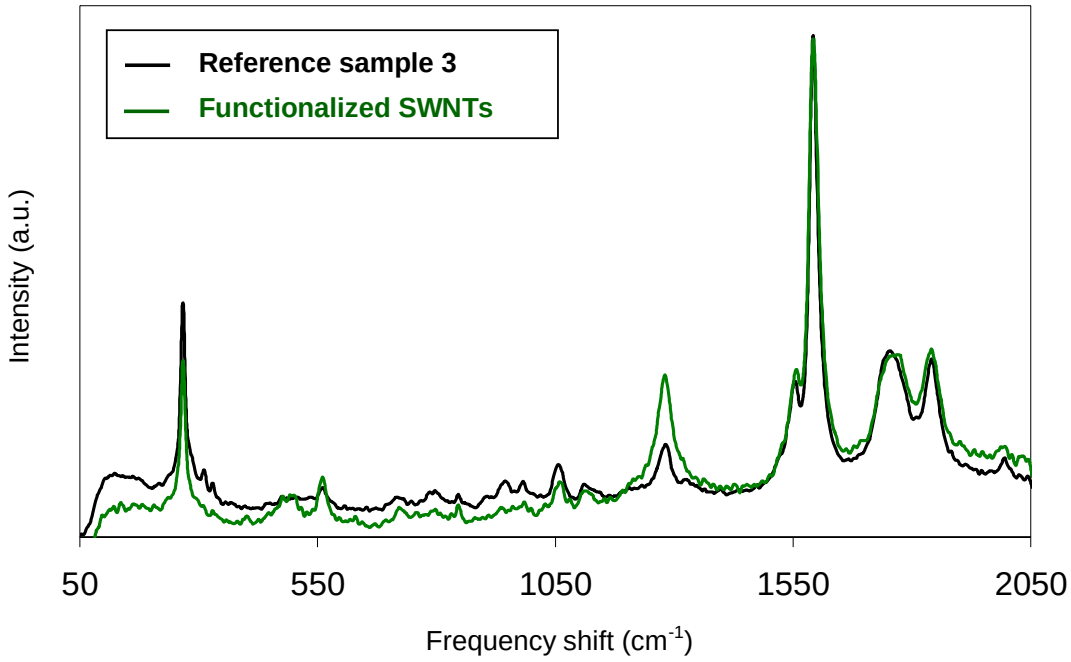

Figure S2. UV-vis-NIR in DMF of reference sample **3** and of SWNTs functionalized with Danishefsky's diene **7**