

Supporting Information

Suzuki Coupling Reactions for the Surface Functionalization of Single-Walled Carbon Nanotubes

Fuyong Cheng and Alex Adronov*

*Department of Chemistry and the Brockhouse Institute for Materials Research, McMaster University,
Hamilton, Ontario L8S 4M1, Canada*

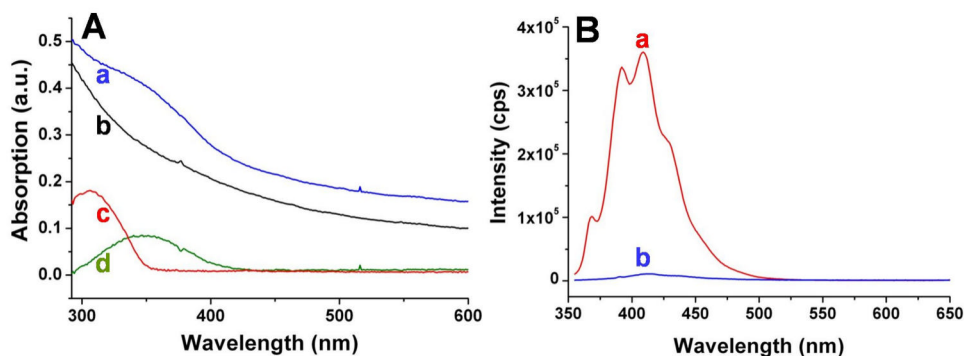


Figure S1. (A) Absorption spectra for compound **3b** (a), compound **1** (b), model compound **5** (c), and nanotube-bound fluorene with nanotube absorption subtracted (d). (B) Normalized emission spectra of **5** (a) and **3b** (b).

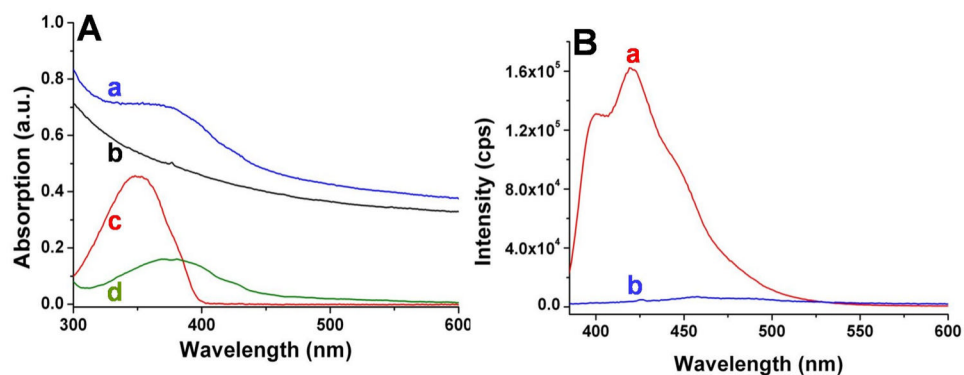


Figure S2. (A) Absorption spectra for compound **3c** (a), compound **1** (b), model compound **6** (c), and nanotube-bound fluorene with nanotube absorption subtracted (d). (B) Normalized emission spectra of **6** (a) and **3c** (b).

Experimental Section

General

Single-walled carbon nanotubes (SWNTs), prepared by the HiPco process, were purchased from Carbon Nanotechnologies, Inc. (Houston, TX) and used without further purification. The porphyrin borate **2a**, 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(4-cyanophenyl)-20-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)porphyrinato(2-)- $\kappa N^{21}, \kappa N^{22}, \kappa N^{23}, \kappa N^{24}$]zinc(II), was prepared as described elsewhere.¹ 9,9-Didodecylfluorene-2,7-bis(trimethyleneborate) (**2b**) and 5-hexyl-5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophene (**2c**) were purchased from Aldrich and used as received. All other reagents and solvents were purchased from commercial suppliers and used as received. Laser Raman spectroscopy was performed on a Bruker RFS 100 instrument equipped with a YAG laser and a Ge high-sensitivity detector. FTIR was performed on a Bio-Rad FTS-40 instrument. All samples were prepared as pellets using spectroscopic grade KBr in a Carver press at 15 000 psi. Atomic force microscopy was done using a Digital Instruments NanoScope IIIa Multimode AFM, with samples prepared by spin-coating (4000 rpm) sample solutions onto freshly cleaved mica substrates. The images were recorded with standard tips in tapping mode at a scan rate of 1.0 Hz. TEM analysis was performed using a Philips CM12 operating at 120 keV. NMR was performed on a Bruker 200 MHz instrument in CDCl₃. The chemical shifts (δ) are given in ppm with respect to the residual non-deuterated solvent. Coupling constants (J) are given in Hz. All ¹³C NMR were proton wide-band decoupled. High resolution EI-MS was run on the Micromass GCT (time-of-flight). Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 409 PC instrument under Argon with a temperature range from 20 to 800°C and a temperature gradient of 5 deg/min.

Ultrasonication was done in a Banson Ultrasonics B1510 bath sonicator. Filtration was done through a 200 nm-pore Teflon membrane (Millipore). UV/vis absorption spectra measured using a Cary 50 UV-visible spectrophotometer. Fluorescence spectra were measured using a Jobin-Yvon SPEX Fluorolog 3.22 equipped with a 450 W Xe lamp, double-excitation and double-emission monochromators, and a digital photon-counting photomultiplier. Slit widths were set to 2 nm band-pass on both excitation and emission. Correction for variations in lamp intensity over time and λ was achieved using a reference silicon photodiode.

Preparation of *p*-iodophenyl functionalized SWNTs (1)

In a typical experiment, SWNTs (250 mg, 20.83 mmol of carbon) and 4-iodoaniline (15.0 g, 64 mmol) were added to a flask equipped with a reflux condenser and a magnetic stir bar. The flask was degassed and backfilled with nitrogen. The mixture was stirred and heated to 65 °C to allow 4-iodoaniline completely melt and mix well with the carbon nanatubes. Subsequently, isoamyl nitrite (20 mL, 149 mmol) was added slowly via syringe. The mixture was then stirred vigorously at 60 °C for 3 h. The resulting paste was diluted with DMF and filtered through a PTFE (450 nm pore diameter) membrane. The collected solid was then taken up in DMF (100 mL) and sonicated (20 min), followed by filtration and washing with DMF (100 mL). This process was repeated 6 times until the filtrate was colorless. The solid was finally washed with diethyl ether (100 mL), and was dried in a vacuum oven (55 °C) overnight.

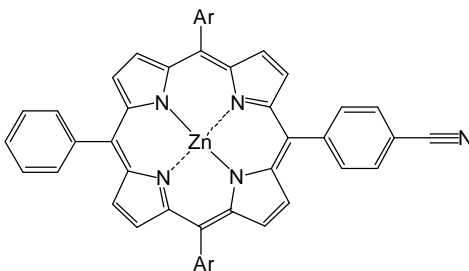
Suzuki cross-coupling on the SWNT surface

A 50 mL flask was charged with *p*-iodophenyl functionalized SWNTs **1** (20 mg) and DMF

(20 mL). After sonicating for 10 min at room temperature a black suspension was formed. Cs_2CO_3 (0.8 g, 2.5 mmol) and a 0.5 M solution of 9,9-didodecylfluorene-2,7-bis(trimethyleneborate) (**2b**) in toluene (0.5 mL, 0.25 mmol) were added to the reaction mixture. This mixture was then degassed via three freeze-pump-thaw cycles and refilled with Ar. $\text{Pd}(\text{PPh}_3)_4$ (10 mg) was added and the reaction mixture was stirred at 100 °C under argon for 24 h. After cooling to room temperature, the mixture was diluted with 200 mL of THF, bath sonicated for 5 min, and filtered through a 200 nm PTFE membrane. The product was washed thoroughly with THF, methanol, water, methanol, and THF (100 mL of each) and then dried under vacuum overnight to yield compound **3b**.

This procedure for Suzuki coupling was identically applied to porphyrin borate **2a** and 5-hexyl-5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophene **2c**.

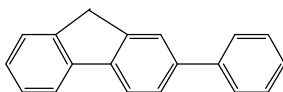
5-Phenyl-15-(4-cyanophenyl)-10,20-Bis(3,5-di-*tert*-butylphenyl)porphyrinato- $N^{21},N^{22},N^{23},N^{24}$ zinc(II) (4**)**



To a 100 mL round-bottomed flask charged with [5,15-Bis(3,5-di-*tert*-butylphenyl)-10-bromo-20-(4-cyanophenyl)porphyrinato(2-)- $\kappa N^{21},\kappa N^{22},\kappa N^{23},\kappa N^{24}$]-zinc(II)¹ (150 mg, 0.16 mmol) in toluene (60 mL) was added 2-phenyl-1,3,2-dioxaborinane (0.16 mL, 0.96 mmol), $\text{Pd}(\text{PPh}_3)_4$ (23 mg, 0.02 mmol), and

Cs₂CO₃ (0.52 g, 1.6 mmol). The reaction mixture was degassed using three freeze-pump-thaw cycles and refluxed under Ar for 18 h. The mixture was filtered through a pad of celite and the solvent was evaporated *in vacuo*. Flash chromatography (SiO₂, hexane/CH₂Cl₂, 1:1) afforded the title compound as a red solid (138 mg, 93%). UV-Vis (THF): 425 nm. ¹H-NMR (CDCl₃, 200 MHz): δ 1.54 (*s*, 36 H), 7.79-7.53(*m*, 3 H), 7.82 (*t*, *J* = 1.4, 2 H), 8.06 (*d*, *J* = 8.0, 2 H), 8.10 (*d*, *J* = 1.4, 4 H), 8.26-8.21 (*m*, 2 H), 8.37 (*d*, *J* = 8.0, 2 H), 8.84 (*d*, *J* = 4.7, 2 H), 9.06-8.97 (*m*, 6 H). ¹³C NMR (CDCl₃, 50 MHz): δ 31.77, 35.07, 111.42, 118.00, 119.18, 120.95, 121.67, 122.98, 126.57, 127.57, 129.84, 130.34, 130.98, 132.22, 132.53, 132.89, 134.33, 134.85, 141.56, 142.75, 148.17, 148.68, 149.13, 150.30, 150.49, 150.79. HR-MS (ESI): 925.3988 (*M*⁺, C₆₁H₅₉N₅Zn, calc. 925.4062).

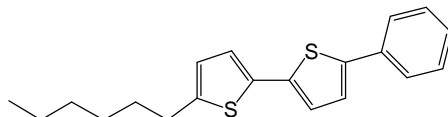
2-Phenyl-9H-fluorene (5)



To a 50 mL flask charged 2-bromofluorene (98 mg, 0.4 mmol) in toluene (20 mL) was added 2-phenyl-1,3,2-dioxaborinane (0.20 mL, 1.2 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and Cs₂CO₃ (1.3 g, 4.0 mmol). The reaction mixture was degassed using three freeze-pump-thaw cycles and refluxed under Ar for 18 h. The mixture was filtered through a pad of celite, and the solvent was concentrated *in vacuo*. The product was precipitated by adding MeOH to the resulting solution, affording the product as a white solid (85 mg, 88%). UV-Vis (THF): 306 nm. ¹H-NMR (CDCl₃, 200 MHz): δ 3.96 (*s*, 2 H), 7.35 (*m*, 3 H), 7.47 (*m*, 2 H), 7.56 (*m*, 1 H), 7.66 (*m*, 3 H), 7.81 (*m*, 3 H). ¹³C NMR

(CDCl₃, 50 MHz): δ 37.02, 101.97, 119.92, 120.11, 123.84, 125.06, 126.03, 126.71, 126.85, 127.11, 127.24, 128.83, 139.92, 140.95, 141.51, 143.52, 143.94. HRMS (EI): 242.1107 (M^+ , C₁₉H₁₄, calc. 242.1096).

5-Hexyl-5'-phenyl-2,2'-bithiophene (6)



To a 100 mL flask charged with bithiophene borate **2c** (378 mg, 1.0 mmol) in toluene (60 mL) was added iodobenzene (0.34 mL, 3.0 mmol), Pd(PPh₃)₄ (12 mg, 0.01 mmol), and Cs₂CO₃ (3.25 g, 10.0 mmol). The reaction mixture was degassed and refluxed under Ar for 18 h. The mixture was filtered through a pad of celite and the solvent was evaporated *in vacuo*. Flash chromatography (SiO₂, hexane) afforded the product as a yellow solid (293 mg, 90%). UV-Vis (THF): 378 nm. ¹H-NMR (CDCl₃, 300 MHz): δ 0.89 (*t*, *J* = 7.4, 3 H), 1.32-1.68 (*m*, 8 H), 2.79 (*t*, *J* = 7.3, 2 H), 6.68-7.61 (broad *m*, 9 H). ¹³C NMR (CDCl₃, 75 MHz): δ 14.09, 22.57, 28.75, 30.18, 31.56, 123.26, 123.62, 123.78, 124.77, 125.50, 127.39, 128.88. HR-MS (EI): 326.1169 (M^+ , C₂₀H₂₂S₂, calc. 326.1163).

Measurement of solubility

A vial charged with a functionalized SWNT sample (10 mg) and spectrophotometric grade THF (10 mL) was sonicated for 5 min. Then the vial was centrifuged at 5000 rpm for 20 min and subsequently allowed to stand undisturbed overnight. The supernatant was carefully separated and diluted with THF to appropriate concentrations for UV/vis absorption measurement. The specific extinction coefficient for shortened SWNTs (0.0103

L mg⁻¹ cm⁻¹) was used to calculate the solubility of the functionalized full-length SWNTs.

References

- (1) Cheng, F.; Zhang, S.; Adronov, A.; Echehoyen, L.; Diederich, F. *Chem. Eur. J.* **2006**, *12*, 6062-6070.