Highly Functionalized and Soluble Multiwalled Carbon Nanotubes by Reductive Alkylation and Arylation: The Billups Reaction

Jason J. Stephenson, Anil K. Sadana, Amanda L. Higginbotham, and James M. Tour*

Departments of Chemistry and Mechanical Engineering and Materials Science, The Smalley Institute for Nanoscale Science and Technology, Rice University, MS 222, 6100 Main Street, Houston, Texas 77005

Single-walled carbon nanotubes (SWNTs) have been directly sidewall functionalized with a variety of organic addends, which renders them organic soluble or water soluble, depending on the precise functionalities used. However, multiwalled carbon nanotubes (MWNTs) are generally less reactive toward organic group functionalizations. Here, we demonstrate the formation of heavily functionalized MWNTs using the Billups reaction, which is a method of reductive alkylation or arylation (using lithium or sodium) of nanotubes in liquid ammonia. The resulting functionalized MWNTs can be soluble in either water or organic solvents. Raman spectroscopy and high-resolution transmission electron microscopy verify the high degrees of sidewall addends on the MWNTs. Making MWNTs soluble can be critical for efficient composite applications.

Introduction

Carbon nanotubes (CNTs) are considered as broad-based nanotechnological materials due to their structural, mechanical, and electronic properties.[1] The mechanical properties and very high aspect ratios of CNTs suggest that they may be used as reinforcing fillers in nanocomposites where stiffness, strength, and light weight are important considerations.[2] For applications such as polymer nanocomposites, the CNTs must be available in large volumes at low cost, they must be dispersible in the bulk material matrix, and there needs to be robust interactions between the CNTs and their surrounding host. Unfortunately, the limited availability and high cost of single-walled carbon nanotubes (SWNTs) have slowed their use in nanocomposites for large-scale consumer applications.[3] Although multiwalled carbon nanotubes (MWNTs) do not mirror the properties of SWNTs, they still provide a unique combination of mechanical, electrical, and thermal properties to materials.[4] MWNTs are more economical[5] and offer an inexpensive route to exploiting the physical properties of CNTs until the price of SWNTs can be substantially lessened. However, rendering MWNTs soluble and dispersible in host matrices will be essential for their wide-scale usage in composites. Major routes developed for dispersing SWNTs in liquids are sidewall functionalization,[6] including oxidative treatment[7] and polymer wrapping.[8]

Likewise, because of the smooth surface of MWNTs,[9] there is little interfacial interaction with the polymer matrix. Furthermore, the sidewall functionalization of CNTs is strongly dependent on their diameter, and the smaller the diameter, the more reactive their sidewalls. But MWNTs possess a much larger diameter than do SWNTs and thus are more difficult to sidewall functionalize and disperse in common solvents. Other than harsh acid-based etching, many of the organic appendage methods reported for dispersing MWNTs deal with endwall or defect site modifications.[10] In this study we have successfully applied the Billups reaction protocol (reductive alkylation or arylation using

(6) (a) Dujardin, E.; Ebbesen, T. W.; Krishnan, A.; Treacy, M. M. *Adv. Mater.* **1998,** *10,* 1472. (b) Mawhinney, D. B.; Naumenko, V.; Kuznetsova, A.; Yates, J. T., Jr.; Liu, J.; Smalley, R. E. *J. Am. Chem. Soc.* **2000,** *122,* 238. (c) Riggs, J. E.; Guo, Z.; Carroll, D. L.; Sun, Y. P. *J. Am. Chem. Soc.* **2000,** *122,* 5879. Jaffe, R. L. *Proc. Electrochem. Soc.* **1999,** *99,* 153. (d) Mickelson, E. T.; Huffman, C. B.; Rinzler, A. G.; Smalley, R. E.; Hauge, R. H.; Margrave, J. L. *Chem. Phys. Lett.* **1998,** *296,* 188. (e) Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J. Am. Chem. Soc.* **2001,** *123,* 6536. (f) Georgakilas, V.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc.* **2002,** *124,* 760. (g) Georgakilas, V.; Tagmatarchis, N.; Pantarotto, D.; Bianco, A.; Briand, J. P.; Prato, M. *Chem. Commun.* **2002,** 3050. (h) Pantarotto, D.; Partidos, C. D.; Graff, R.; Hoebeke, J.; Briand, J. P.; Prato, M.; Bianco, A. *J. Am. Chem. Soc.* **2003,** *125,* 6160.

(7) (a) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P.; Haddon, R. C. *Science* **1998,** *282,* 95. (b) Hamon, M. A.; Hu, H.; Bhowmik, P.; Niyogi, S.; Zhao, B.; Itkis, M. E.; Haddon, R. C. *Chem. Phys. Lett.* **2001,** *347,* 8. (c) Hamon, M. A.; Hui, H.; Bhowmik, P.; Itkis, M. E.; Haddon, R. C. *Appl. Phys. A* **2002,** *74,* 333. (d) Sun, Y. P.; Fu, K.; Lin, Y.; Huang, W. *Acc. Chem. Res.* **2002,** *35,* 1096. (e) Niyogi, S.; Hamon, M. A.; Hu, H.; Zhao, B.; Bhowmik, P.; Sen, R.; Itkis, M. E.; Haddon, R. C. *Acc. Chem. Res.* **2002,** *35,* 1105. (f) Banerjee, S.; Wong, S. S. *Nano Lett.* **2002,** *2,* 49. (g) Hamon, M. A.; Chen, J.; Hu, H.; Chen, Y.; Itkis, M. E.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Adv. Mater.* **1999,** *11,* 834.

(8) Star, A.; Stoddart, J. F.; Steuerman, D.; Diehl, M.; Boukai, A.; Wong, E. W.; Yang, X.; Chung, S. W.; Choi, H.; Heath, J. R. *Angew. Chem., Int. Ed.* **2001,** *40,* 1721.

(9) Takahashi, H.; Numao, S.; Bandow, S.; Iijima, S. *Chem. Phys. Lett.* **2006,** *418,* 535.

(10) Lin, Y.; Rao, A. M.; Sadanadan, B.; Kenik, E. A.; Sun, Y. P. *J. Phys. Chem. B.* **2002,** *106,* 1294.

* To whom correspondence should be addressed. E-mail: tour@rice.edu.

(1) *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications;* Dresselhaus, M. S., Dresselhaus, G., Avouris, P., Eds.; Springer-Verlag: Berlin, Germany, 2001.

(2) (a) Vaia, R. A.; Wagner, H. D. *Mater. Today* **2004,** *7,* 32. (b) Dyke, C. A.; Tour, J. M. *J. Phys. Chem. A* **2004,** *51,* 11151. (c) Breuer, O.; Sunderaraj, U. *Polym. Compos.* **2004,** *25,* 630. (d) Pulickel, M. A.; Linda, S. S.; Paul, V. B. *Nanocomposites Science and Technology;* Wiley-VCH: Weinheim, 2003. (e) Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. *Chem. Rev.* **2006,** *106,* 1105.

(3) http://www.cnanotech.com (accessed Apr 2006).

(4) http://www.xnri.com/English/index.html (accessed Apr 2006).

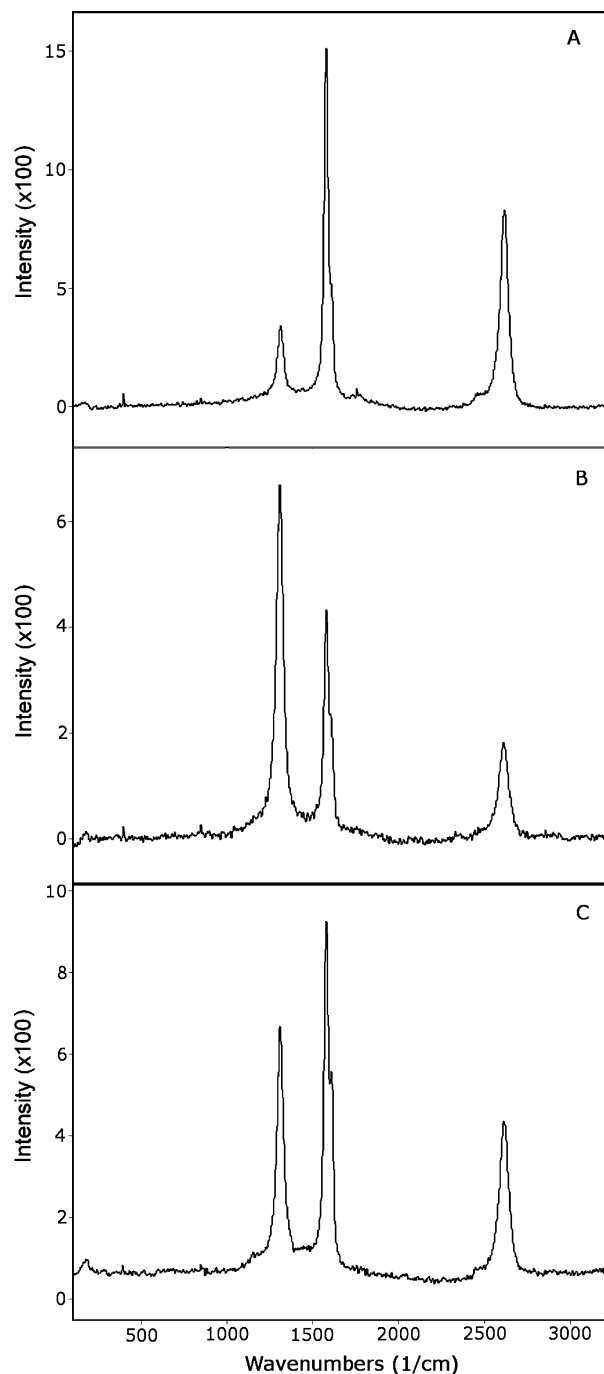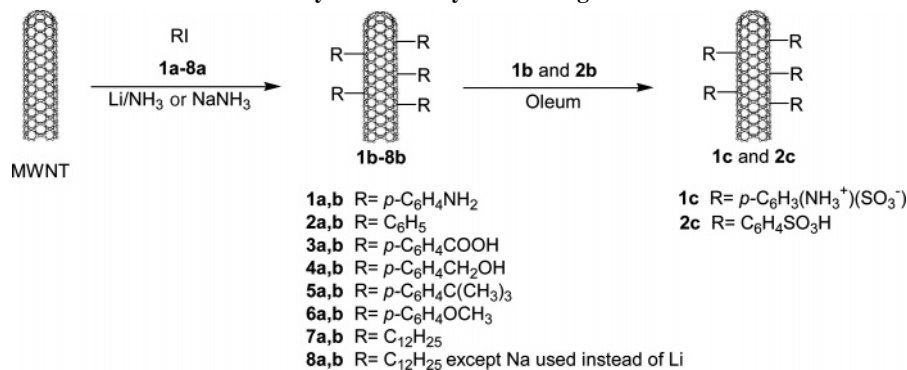(5) http://www.helixmaterial.com (accessed Apr 2006).

Figure 1. Raman spectra (780 nm excitation) of (A) pristine MWNTs, (B) functionalized MWNTs **5b** and (C) **5b** after 850 °C TGA treatment in argon.

Table 1. Raman *D/G* Ratio, TGA-Determined Weight Loss, and Solubilities

compound	Raman *D/G* [a]	% TGA wt loss [b]	solubility [c] (H$_2$O, CHCl$_3$)
1b	1.5	10	<2 mg/L (H$_2$O)
			<2 mg/L (CHCl$_3$)
1c	1.5	11	30 mg/L (H$_2$O)
2b	1.4	5	<2 mg/L (H$_2$O)
			<2 mg/L (CHCl$_3$)
2c	1.4	4	15 mg/L (H$_2$O)
3b	1.7	12	<2 mg/L (H$_2$O)
			<2 mg/L (CHCl$_3$)
4b	1.9	7	<2 mg/L (H$_2$O)
			<2 mg/L (CHCl$_3$)
5b	1.5	4	60 mg/L (CHCl$_3$)
6b	1.6	8	<2 mg/L (CHCl$_3$)
7b	1.7	18	100 mg/L (CHCl$_3$)
8b	1.9	17	120 mg/L (CHCl$_3$)

[a] Representative Raman (780 nm excitation) *D/G* values averaged over five scans per sample. [b]TGA weight loss was obtained by ramping at 10 °C/min to 850 °C in argon. [c]Solubility determined by filtering sonicated solution through the glass wool plug to remove any particulate and measuring the weight of nanotubes in known volumes of solvent.[2b]

Table 2. Sheet Resistivity of MWNT Bucky Papers

entry	sample	resistivity (Ω/square) [a]
1	unfunctionalized MWNTs	213−235
2	**1b**	9−38
3	**1c**	39−906
4	**2b**	170−175
5	**2c**	19−30
6	**3b**	41−89
7	**4b**	52−177
8	**5b**	110−115
9	**7b**	1120−1476

[a] The resistivities were recorded by the four-point probe method using five to six measurements per sample over a period of 2−3 days per sample. Some water adsorption might account for the large deviation in measurements for **1c**.

lithium or sodium in liquid ammonia), initially developed for the debundling, alkylation, and arylation of SWNTs,[11] to the sidewall functionalization of MWNTs.

Results

Scheme 1 shows the reaction procedure where MWNTs are functionalized after an electron transfer from the lithium to the sidewall of the nanotube. This lithiation of MWNTs causes them to disperse in ammonia, leading to high degrees of coverage of functional groups through radical addition.
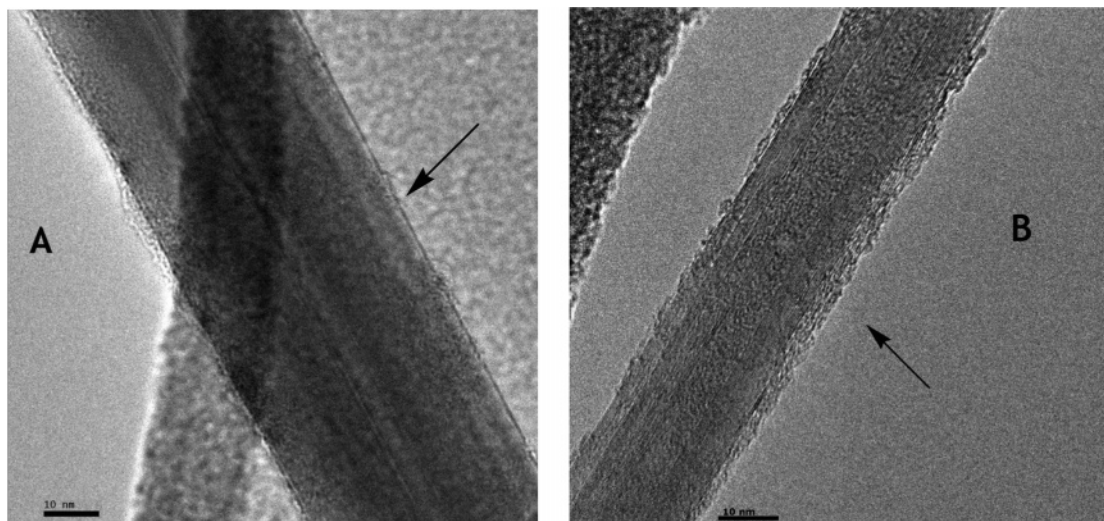
Scheme 1. Functionalization of MWNTs to Produce 1b−8b through Dispersions in Alkali Metal/Ammonia Followed by Reductive Alkylation or Arylation Using Iodides 1a−8a [a]

1a,b R= *p*-C$_6$H$_4$NH$_2$
2a,b R= C$_6$H$_5$
3a,b R= *p*-C$_6$H$_4$COOH
4a,b R= *p*-C$_6$H$_4$CH$_2$OH
5a,b R= *p*-C$_6$H$_4$C(CH$_3$)$_3$
6a,b R= *p*-C$_6$H$_4$OCH$_3$
7a,b R= C$_{12}$H$_{25}$
8a,b R= C$_{12}$H$_{25}$ except Na used instead of Li

1c R= *p*-C$_6$H$_3$(NH$_3$$^+$)(SO$_3$$^-$)
2c R= C$_6$H$_4$SO$_3$H

[a] Sulfonation of **1b** and **2b** by oleum produced arylsulfonated products **1c** and **2c** that exhibited significant solubility in protic solvents.

Figure 2. (A) HRTEM of purified MWNTs showing predominantly smooth sidewall edges with some levels of moderate sidewall roughening coverage on the other side of the same MWNT. (B) HRTEM of **7b** showing heavy functional group attachment on the sidewalls of MWNTs displayed as thick roughening throughout their length. These images are characteristic of the entire sample areas observed. Scale bars are 10 nm. Samples were imaged using 300 mesh lacey carbon grids.

Aryl iodides as well as alkyl iodides work well in this procedure. The MWNTs functionalized in this method of reductive arylation and alkylation show very high disorder bands in Raman spectra compared to the original unfunctionalized material, as well as significant solubilities in aqueous and organic solvents, depending on the addends. For water solubility, MWNTs **1b** and **2b** were treated with oleum to sulfonate the pendent aryl rings.[11c] The water solubility of MWNT **1c** was 30 mg/L, and that of MWNT **2c** was 15 mg/L. Organic solubility can be achieved by appending long alkyl chains or *tert*-butyl arenes onto the MWNTs. Remarkably, solubilities in $CHCl_3$ up to 120 mg/L were conferred to these MWNT materials. Solubility was determined by first sonicating MWNTs in the respective solvents followed by filtering through a tightly wadded glass wool plug to remove any insoluble particulate.[2b] The solutions had no visible particulate and were stable for over 1 month. Metallic sodium also can be used in the place of lithium as in the reduction process to **8b**, carried out on a gram scale of MWNTs. Sodium salts are less expensive and less hazardous for disposal than are lithium salts, producing a process that may be easier to scale.

Characterization

Raman spectroscopy (shown in Figure 1 for **5b**) is an indication of the degree of functionalization. From the pristine MWNTs in Figure 1A to the functionalized MWNTs in Figure 1B, an increase in the ratio of the disorder band (1320 cm^{-1}) to the graphite band (1594 cm^{-1}) for MWNT **5b** indicates a substantial increase in functionalization. Unlike SWNTs, however, thermogravimetric analysis (TGA) weight loss is less informative with MWNTs. Because MWNTs are comprised of concentric tubes, there are several layers of

carbon that are not available for functionalization, making the TGA unreliable for determining the coverage of functional groups per nanotube carbon. Nevertheless, the TGA data is recorded in Table 1 along with Raman D/G values and sample solubilities, where available. Furthermore, Figure 1C demonstrates the ability to effect partial defunctionalization via addend cleavage by thermolysis.

The functional group attachment to MWNTs was confirmed through the use of high-resolution transmission electron microscopy (HRTEM). Figure 2 shows an image of MWNT **7b** as well as the starting unfunctionalized MWNTs, confirming the significant buildup of sidewall addends on the treated material.

When a standard retractable four-point probe technique was used on thin sheets of the bucky paper prepared from filtration, sheet resistivity measurements were made on the starting unfunctionalized MWNTs as well as on several of the products. This was done to determine if functionalizing the outer sidewalls affected the overall resistivity of the materials. The sheet resistivities are shown in Table 2. The general observed trend is that functionalization of the outer sidewalls slightly lowers the sheet resistivities except in the case of the long-chain alkylated product **7b**. These resistive properties of the functionalized MWNTs are likely dominated by the inner, non-functionalized tubes, and the reaction conditions probably serve to remove the small amount of impurities such as amorphous carbon, which could raise the resistivity of the untreated material.

Conclusion

The Billups reaction protocol involving dissolving metal reduction of MWNTs and their subsequent alkylation or arylation has been shown to produce functionalized MWNTs that are soluble in either organic or aqueous solvents. This method allows for the attachment of alkyl or aryl pendent groups, using either lithium or sodium, and has been used to produce gram quantities of alkylated MWNTs. Raman spectral analysis, TGA, HRTEM imaging, and solubility

(11) (a) Liang, F.; Sadana, A. K.; Peera, A.; Chattopadhyay, J.; Gu, Z.; Hauge, R. H.; Billups, W. E. *Nano Lett.* **2004**, *4*, 1257. (b) Chattopadhyay, J.; Sadana, A. K.; Liang, F.; Beach, J. M.; Xiao, Y.; Hauge, R. H.; Billups, W. E. *Org. Lett.* **2005**, *7*, 4067. (c) Liang, F.; Beach, J. M.; Rai, P. K.; Guo, W.; Hauge, R. H.; Pasquali, M.; Smalley, R. E.; Billups, W. E. *Chem. Mater.* **2006**, *18*, 1520.

studies confirmed the high degree of MWNT functionalization. In addition, the conductive properties of the MWNTs are generally retained even after functionalization of the outer walls, as observed by four point probe analysis. With a MWNT sidewall functionalization protocol established, composite formulation can now be explored.

Experimental Section

All reagents except the MWNTs were used as received from Sigma-Aldrich. MWNTs (99.79% carbon purity) were received from Bussan Nanotech Research Institute, Inc., a subsidiary of Mitsui & Co., Ltd., and used as received. These MWNTs were found to contain only small amounts of amorphous carbon.

General Procedure for Functionalization of MWNTs. MWNTs (50 mg, 4.1 mequiv C) were added to a flame-dried 100 mL three-necked flask fitted with a cold finger condenser and homogenizer. NH_3 (65 mL) was condensed into the flask using a dry ice and acetone bath. Once the NH_3 was collected, the solution was homogenized using an adjustable speed Dremel tool (model 400xpr) equipped with a standard-capacity rotor-stator generator (Cole-Parmer no. A-36904-52) at the lowest setting. During homogenization, lithium metal (40 mg, 5.7 mequiv Li) was added to the ammonia solution, which remained a dark blue color indicating an excess of lithium had been added and all possible sites on the MWNT had been lithiated. After the solution homogenized for 10 min, an aryl or alkyl iodide (16.4 mmol, 4 equiv) was added, and homogenization continued for 1 h at −78 °C. After 1 h, the homogenization was stopped, and the solution was removed from the dry ice acetone bath and allowed to warm to room temperature while the NH_3 was distilled into a scrubber system. Reaction workup included the successive additions of methanol (30 mL) and water (30 mL). This mixture was then filtered using a 1 μm polycarbonate filter. The bucky paper filter cake was dispersed via sonication (Cole-Parmer 12 W, 55 kHz) and successively washed and filtered with acetone, dimethylformamide, acetone, water, and acetone. Each filtration was over a 0.2-μm poly(tetrafluoroethylene) filter. Finally the MWNTs were dried as a bucky paper.

4-Aminophenyl MWNTs (1b and 1c). The general reaction procedure was followed. 4-Iodoaniline (3.59 g, 16.4 mmol) was used as the electrophile. The product **1b** was isolated as a bucky paper (50 mg). **1c** was formed by treating **1b** (20 mg) with 50 mL of oleum (20% excess SO_3) for 2 h at room temperature. The solution was then diluted over ice and filtered over a 0.2-μm polycarbonate filter. The MWNTs were then dispersed and washed according to the general procedure and were isolated as a bucky paper (20 mg).

Phenyl MWNTs (2b, 2c). The general reaction procedure was followed. Iodobenzene (3.34 g, 16.4 mmol) was used as the electrophile. The product **2b** was isolated as a bucky paper (50 mg). **2c** was formed by treating **2b** (20 mg) with 50 mL of oleum (20% excess SO_3) for 2 h at room temperature. The solution was then diluted over ice and filtered with 0.2-μm polycarbonate filter. The MWNTs were then dispersed and washed according to the general procedure and were isolated as a bucky paper (20 mg).

4-Benzoic Acid MWNTs (3b). The general reaction procedure was followed. 4-Iodobenzoic acid (4.06 g, 16.4 mmol) was used as the electrophile. The product **3b** was isolated as a bucky paper (50 mg).

4-Benzyl Alcohol MWNTs (4b). The general reaction procedure was followed. 4-Iodobenzyl alcohol (3.83 g, 16.4 mmol) was used as the electrophile. The product **4b** was isolated as a bucky paper (52 mg).

4-*tert*-Butylphenyl MWNT (5b). The general reaction procedure was followed. 4-Iodo-*tert*-butylbenzene (4.26 g, 16.4 mmol) was used as the electrophile. The product **5b** was isolated as a bucky paper (50 mg).

4-Methoxy Benzene MWNTs (6b). The general reaction procedure was followed. 4-Iodoanisole (3.83 g, 16.4 mmol) was used as the electrophile. The product **6b** was isolated as a bucky paper (51 mg).

Dodecyl MWNT (7b, 8b). The general reaction procedure was followed for **7b.** The product **7b** was isolated as a bucky paper (56 mg). For **8b** (sodium used instead of lithium), MWNTs (1.19 g, 0.099 equiv C), sodium (9.10 g, 0.40 mol), and 1-iodododecane (58.6 g, 0.197 mol) were used.