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Carbon Nanotube Salts. Arylation of Single-Wall Carbon Nanotubes

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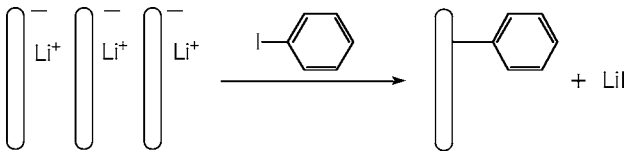
ABSTRACT



Carbon nanotube salts prepared by treating single-wall carbon nanotubes (SWNTs) with lithium in liquid ammonia react readily with aryl iodides to give SWNTs functionalized by aryl groups.

Carbon nanotubes have attracted considerable interest since their discovery by Iijima in 1991.[1] Despite extraordinary promise, realistic applications of these materials have been slow to emerge and still face challenges due to poor solubility and reactivity that is comparable with the basal plane of graphite.[2] Chemical functionalization enhances solubility[3] and leads to materials that are more amenable for some of the anticipated applications. Sidewall functionalizations[4] using fluorine,[5] aryl diazonium salts[6] (Tour reaction), azomethine ylides,[7] nitrenes,[8] carbenes,[9] Bingel reaction,[10] and organic radicals[9,11,12] have been reported previously. The fluorinated nanotubes[5,13] reported by Margrave and co-workers in 1998 can be reacted with alkyllithium[14,15] and Grignard reagents[16] to give SWNTs functionalized by alkyl groups. End functionalization has been explored through oxidation routes[17−21] that lead to shortened nanotubes bearing carboxylic acid end groups.[22]

Nevertheless, a more accommodating and direct approach to functionalized nanotubes is desirable. A cheap, scalable,

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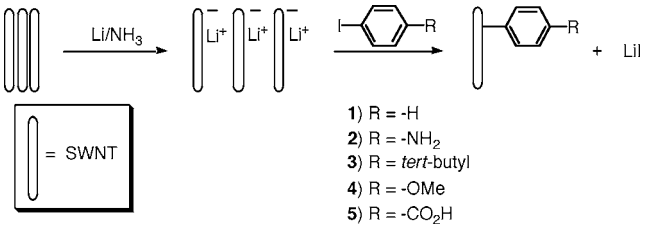
Scheme 1

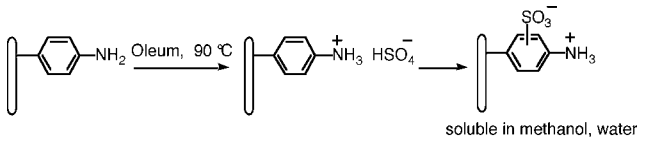


and efficient way to functionalize SWNTs that exhibit greater solubility in common organic solvents has been reported recently.[23,24] We now report an application of this route to arylated SWNTs as illustrated in Scheme 1.

The arylation reactions were carried out by adding the SWNTs (20 mg) under an atmosphere of argon to a dry 100 mL, three-neck, round-bottomed flask fitted with a dry ice condenser. Ammonia (60 mL) was then condensed into the flask followed by the addition of lithium metal (0.12 g). The aryl iodide (6.4 mol, 4 equiv) was then added and the mixture stirred at −33 °C for 12 h with the slow evaporation of ammonia. The reaction mixture was quenched by slow addition of ethanol followed by water. The mixture was acidified (10% HCl), filtered through a 0.2 μm PTFE membrane, and washed successively with water and ethanol. The functionalized SWNTs were dried overnight in vacuo at 80 °C.

The zwitterion obtained by sulfonation of **2** (Scheme 2) was found to exhibit moderate solubility (ca. 50 mg/L) in methanol.

Scheme 2



Functionalized SWNTs were characterized by Raman spectroscopy, infrared spectroscopy (FTIR-ATR), and thermogravimetric analysis (TGA). Direct covalent sidewall attachment of aryl groups can be determined by Raman spectra. As shown in Figure 1(A), pristine SWNTs exhibit a tangential mode at 1590 cm^{-1} and a radial breathing mode around 230 cm^{-1}, indicating different diameter distribution of HiPco SWNTs. After functionalization (B and C), the relative intensity of the disorder mode (D band) at 1290 cm^{-1} is enhanced due to chemically induced disruption of sp^2-hybridized carbons in the hexagonal framework of the nanotube walls.

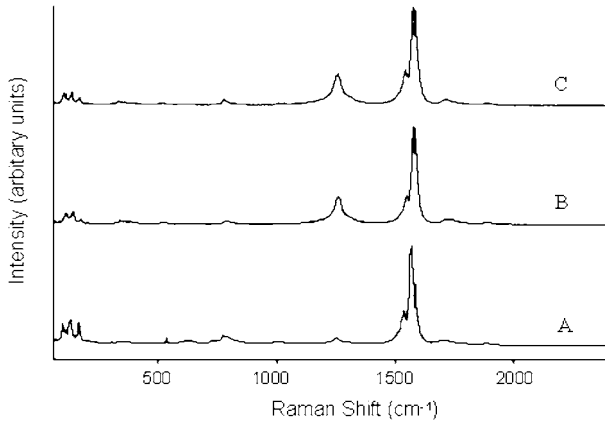


Figure 1. Raman spectra (780 nm excitation) of (A) purified SWNTs, (B) phenyl SWNTs **1**, and (C) aniline SWNTs **2**.

Although the infrared spectra of the pristine materials are featureless, FTIR spectroscopy using an ATR accessory was used to record the infrared spectrum of **1**. This material exhibits a peak at 3100 cm^{-1} that is characteristic of sp^2-hybridized C−H stretching. Similar results were obtained for other aryl-functionalized SWNTs. An absorption at 2980 cm^{-1} is indicative of sp^3-hybridized C−H stretching, suggesting that some hydrogen may have been added to the SWNTs.

Thermogravimetric analysis (TGA) of degassed (800 °C) functionalized SWNTs was used to evaluate the extent of functionalization. The carbon/aryl ratios could be determined (Table 1) on the basis of weight loss between 200 and 500 °C. A higher degree of functionalization was observed, as expected, when the aryl group was functionalized by electron-donating substituents.

Table 1. Weight Loss of Different Compounds from TGA Analysis at 800 °C in Argon

compd	weight loss (%) obsd	carbon/aryl ratio
phenyl	22	21:1
aniline	28	16:1
tert-butylphenyl	38	15:1
methoxyphenol	21	32:1
benzoic acid	14	54:1

Additional evidence for the covalent attachment of aryl groups was provided by thermal degradation (TGA) of **1** in the 50−800 °C range coupled with on-line monitoring of

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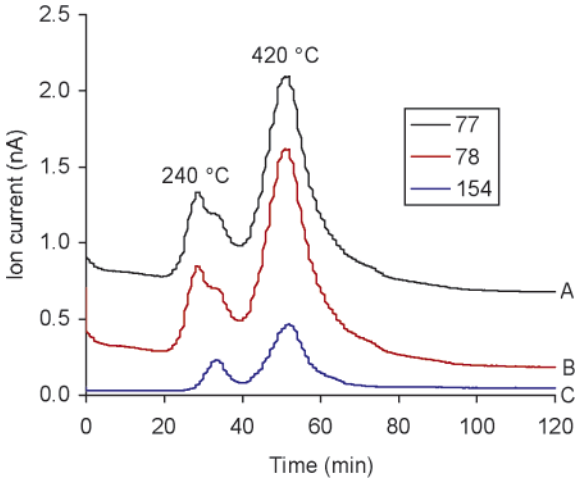

Figure 2. TGA-MS of the products evolved from phenylated SWNTs **1**. Ion current vs time plots for ions corresponding to (A) *m*/*z* 77 $\{C_6H_5^+\}$, (B) *m*/*z* 78 $\{C_6H_6^+\}$, and (C) *m*/*z* 154 $\{C_{12}H_{10}^+\}$.

the volatile products by a mass spectrometer. Evolution curves (Figure 2) were obtained for ions *m*/*z* 77 $\{C_6H_5^+\}$, *m*/*z* 78 $\{C_6H_6^+\}$, and *m*/*z* 154 $\{C_{12}H_{10}^+\}$. Since each curve was observed at the same time (evolution temperature), the ions observed at *m*/*z* 78 and 154 must arise by subsequent reactions of phenyl radicals. Similarly, a high-temperature mass spectrum (HT-MS) of compound **3** exhibited masses corresponding to 4,4′-di-*tert*-butylbiphenyl and *tert*-butylbenzene, products derived from the *tert*-butylphenyl radical.

X-ray photoelectron spectroscopy (XPS) also provides a measure of the degree of functionalization. XPS analysis of compound **2** shows 3.3% atomic nitrogen, which compares favorably with the TGA analysis.

The aniline-derivatized zwitterion is soluble in methanol. An atomic force microscopy (AFM) image recorded in methanol is shown in Figure 3. The average diameter of this zwitterionic complex is 2−3 nm as determined by height, demonstrating that extensive debundling has occurred.

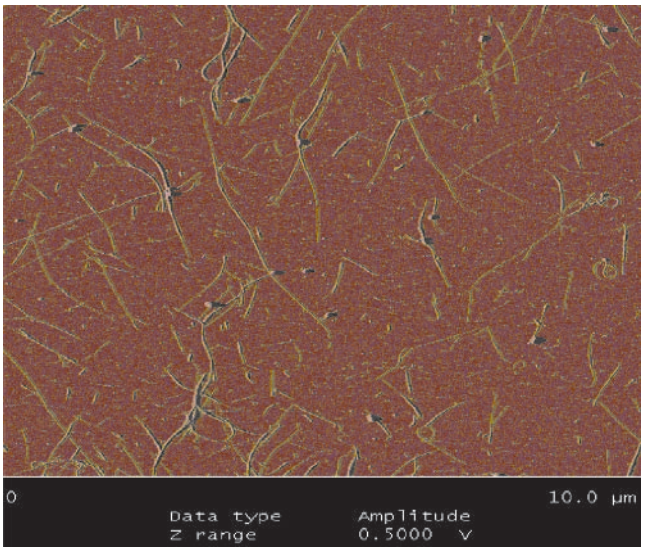

Figure 3. Tapping-mode AFM image of the zwitterion formed by sulfonation of the aniline derivative **2** spin-coated onto mica from methanol.

Further evidence for extensive debundling is provided by inspection of the high-resolution transmission electron microscopy (HRTEM) image (Supporting Information) of the zwitterion illustrated in Figure 1. The functionalized SWNTs were observed to exhibit characteristic irregular sidewall morphology.

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Supporting Information Available: HR-TEM image. This material is available free of charge via the Internet at http://pubs.acs.org.

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