

Deuterium Attachment to Carbon Nanotubes in Solution

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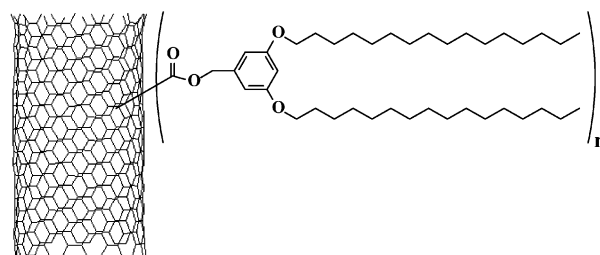
ABSTRACT

Strong attachment of deuterium to carbon nanotubes was observed in solution under mild experimental conditions when deuterated ethanol was used as a co-reactant in nanotube functionalization reactions. The solubility of samples in common organic solvents has allowed unambiguous ^2H NMR characterization. The broad ^2H NMR signal at ~ 6.5 ppm is assigned to carbon-nanotube-bound deuterium species. The assignment is supported by the results from FT-IR measurements. The results from the use of selectively deuterated ethanols suggest that the labile deuterium is responsible for the attachment to carbon nanotubes.

Chemical modification and functionalization of carbon nanotubes have received much recent attention.^{1–11} The functionalization reactions reported in the literature can be divided roughly into two categories, corresponding to two somewhat different approaches. One is to use the carboxylic acid moieties in both shortened and as-prepared single-walled (SWNT) and multiple-walled (MWNT) carbon nanotubes to attach oligomeric or polymeric functional groups.^{1–8} The other is functionalization via direct addition to or interaction with the graphitic surface of carbon nanotubes.^{9–11} Examples for the additions include the fluorination of SWNTs and the derivatization of nanotubes in the decomposition of diazonium salts.^{9,10} However, of particular interest and importance is the hydrogenation of carbon nanotubes because it not only represents the most basic addition to the nanotube graphitic surface but also has potential implications in hydrogen storage.¹² For example, Birch reduction has been applied to the hydrogenation of carbon nanotubes, with an estimated coverage of hydrogen atoms on the nanotube surface of $\sim 9\%$.¹¹

In this letter we report that deuterium can be attached to carbon nanotubes in the functionalization reactions in the presence of labile deuterium species. The solution-phase ^2H NMR spectra of the soluble samples exhibit a characteristic broad signal in the aromatic region. The NMR results may be explained in terms of unusually strong interactions of deuterons with the carbon nanotube surface. The explanation is supported by the results from FT-IR measurements.

Purified SWNTs and MWNTs^{13–15} were functionalized with 3,5-dihexadecyloxybenzyl alcohol (**I**) in esterification reactions, as already reported in the literature (see also Supporting Information).^{4,5} For ^2H NMR characterization, ethanol- d_6 was used as a co-reactant in the functionalization reactions. In a typical experiment, a purified SWNT sample (20 mg) was refluxed in thionyl chloride for 24 h to convert the nanotube-bound carboxylic acids into acyl chlorides. After thorough evaporation of the residual thionyl chloride, the nanotubes were mixed with **I** (200 mg) and ethanol- d_6 (200 mg). The mixture (pH ~ 7) was stirred at 70 °C for 48 h, and then cooled to ambient for repeated extractions with chloroform. Upon simple filtration, the chloroform solution was vigorously centrifuged at a high speed (7800 rpm) to remove residual insoluble nanotubes. The solution was evaporated in a gentle nitrogen flow to yield the functionalized SWNT sample (**I**–SWNT–ethanol- d_6) as black solids. The same procedure was used in the functionalization of MWNTs with **I** and ethanol- d_6 , yielding the functionalized MWNT sample (**I**–MWNT–ethanol- d_6) also as black solids.



I–SWNT

The functionalized carbon nanotube samples (**I**–SWNT–ethanol- d_6 and **I**–MWNT–ethanol- d_6) are soluble in com-

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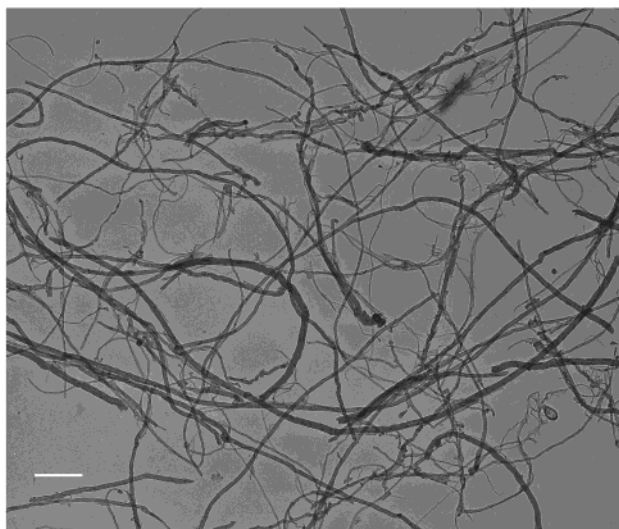


Figure 1. TEM image of the **I-MWNT-ethanol- d_6** sample deposited on a carbon-coated copper grid (scale bar = 500 nm).

mon organic solvents such as chloroform to form a homogeneous solution. The properties of the samples obtained with ethanol- d_6 as a co-reactant are generally similar to those without ethanol- d_6 . For example, the absorption spectra of **I-SWNT-ethanol- d_6** and **I-MWNT-ethanol- d_6** in room-temperature chloroform are similarly featureless curves.^{4,10} The TEM results provide more direct evidence for the presence of carbon nanotubes in the samples. Shown in Figure 1 is a typical TEM image of the MWNTs functionalized with **I** and ethanol- d_6 as a co-reactant. The soluble samples obviously contain nanotubes of different lengths and diameters.

The ^1H and ^{13}C NMR results of the functionalized nanotube samples obtained with ethanol- d_6 as a co-reactant are essentially the same as those of the samples without ethanol- d_6 .^{4,5} However, the samples with ethanol- d_6 have allowed a new dimension of characterization using ^2H NMR. Shown in Figure 2 is a ^2H NMR spectrum of **I-SWNT-ethanol- d_6** in chloroform. Surprisingly, in addition to the expected CD_2CD_3 signals, there is a broad peak centered at ~ 6.5 ppm (Figure 2). The ^2H NMR results were found to be easily reproducible among different sets and batches of solubilized nanotubes with ethanol- d_6 as a co-reactant.

The deuterium signal centered at ~ 6.5 ppm in all these samples is considerably broader than those of free ethanol- d_6 and CD_2CD_3 side chains from the esterification of nanotube-bound carboxylic acids by ethanol- d_6 (Figure 2). According to the quadrupolar mechanism for deuterium relaxation, there should be a strong dependence of the relaxation times and line-width on correlation times of molecular motions. Thus, the broadness of the 6.5 ppm signal may be explained by extremely long correlation time of molecular motion for deuterium atoms attached to the carbon skeleton in such a large species (nanotube). For nuclei of the side chains the correlation times are considerably shorter because they are controlled by internal segmental motions rather than the whole molecular motion. At room temperature the line width of the 6.5 ppm signal is almost 0.8 ppm,

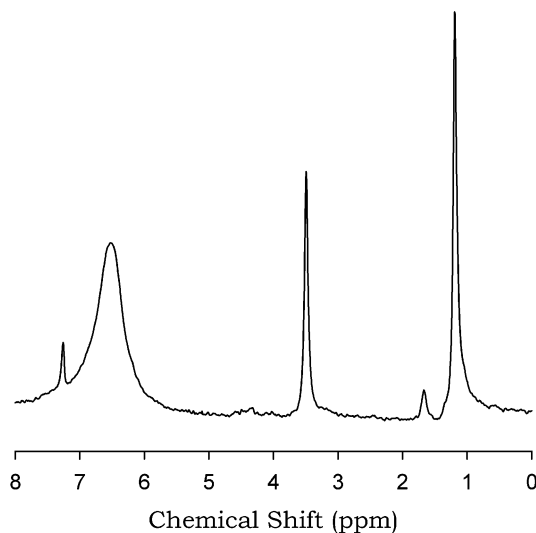


Figure 2. The ^2H NMR spectrum of **I-SWNT-ethanol- d_6** in room-temperature chloroform solution.

corresponding to 60 Hz. The signal also has a symmetric shape with no indication for a distribution of contributions from sharp deuterium signals of slightly different chemical shifts.

The deuterium source responsible for the broad ^2H NMR signal was identified by use of selectively deuterated ethanols, including ethanol- d_1 ($\text{CH}_3\text{CH}_2\text{OD}$) and ethanol- d_2 ($\text{CH}_3\text{CD}_2\text{OH}$). When ethanol- d_1 instead of ethanol- d_6 was used as a co-reactant in the functionalization reaction of MWNTs with **I** under the same experimental conditions, the same results as those with the use of ethanol- d_6 were obtained. The ^2H NMR spectrum shows a similarly broad signal centered at ~ 6.5 ppm, but no meaningful CD_2 and CD_3 signals as expected (Figure 3). However, when ethanol- d_2 was used as a co-reactant, no deuterium attachment to carbon nanotubes was observed. The ^2H NMR spectrum of the **I-MWNT-ethanol- d_2** sample in room-temperature chloroform shows no 6.5 ppm signal (Figure 3). These results suggest that the ^2H NMR signal is not due to reductive deuterium addition to carbon nanotubes, despite the fact that ethanol is capable of serving as a reductant, and is also inconsistent with any deuterium abstraction by free radicals. Instead, the results point to a scenario in which the labile deuterium ($-\text{O}-\text{D}$) is responsible for the broad ^2H NMR signal in the spectra of the functionalized nanotube samples, namely a deuterium transfer mechanism. In a separate note, the fact that the reaction with ethanol- d_2 yields no deuterium addition eliminates completely the remote possibility for the broad ^2H NMR signal at ~ 6.5 ppm being associated with any deuterated ethanol molecules physically encapsulated inside the nanotubes.

The ^2H NMR results may be explained in terms of unusually strong interactions of the graphitic surface of solubilized carbon nanotubes with deuterons in homogeneous solution.¹⁶ The deuterium species responsible for the characteristic NMR signal cannot be displaced by protons under usual exchange conditions. For example, after a solution of the **I-SWNT-ethanol- d_6** sample in ethanol was stirred for

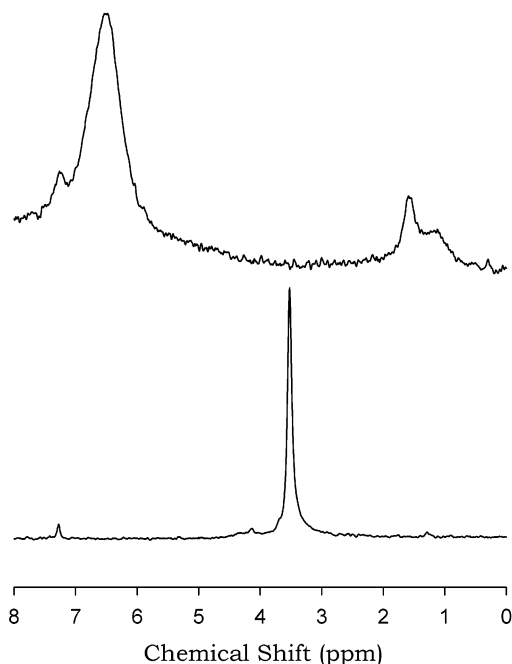


Figure 3. ^2H NMR spectra of **I**-MWNT-ethanol- d_1 (top) and **I**-MWNT-ethanol- d_2 (bottom) in room-temperature chloroform.

24 h at room temperature or refluxed for 48 h, the same ^2H NMR spectrum was obtained. Here the relationship between the nanotube carbon and deuterium probably resembles that in a C–D bond. This is supported by the results from FT-IR measurements. The C–D stretching mode is typically in the $1800\text{--}2500\text{ cm}^{-1}$ region, where there are hardly any contributions from the vibrational modes associated C–H and C–O bonds. Thus, even weak signals from the C–D (or C–D-like) vibrations may be detected. In the FT-IR spectrum of the **I**-MWNT-ethanol- d_6 sample in room-temperature carbon tetrachloride solution, there are indeed several weak absorption peaks in the $1900\text{--}2500\text{ cm}^{-1}$ region. Especially pronounced is the peak at 2030 cm^{-1} , whose intensity exhibits a clear dependence on the solution concentration (Figure 4). Also illustrated in Figure 4 is the fact that the concentration dependence follows the Lambert–Beer’s law.

The strong attachment of deuterium to carbon nanotubes is a rather unusual phenomenon. For fullerenes as a related class of nanoscale carbon materials, the addition of hydrogen and deuterium to form hydrides and deuterides has been studied extensively.^{17–21} The NMR signals for the C–H and C–D bonds on the fullerene molecular surface are rather diverse, showing up in a broad region downfield from ~ 3 ppm, depending on the addition pattern. The carbon–deuterium relationship in the functionalized carbon nanotube samples is likely different from those in the fullerene hydrides and deuterides. For hydrogenated fullerenes prepared in Birch reduction, as an example, the reaction with an oxidant such as DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) results in a quick loss of hydrogens and the recovery of pristine fullerenes.¹⁷ However, the same treatment by refluxing the **I**-SWNT-ethanol- d_6 sample with an excessive amount of DDQ in toluene for several hours caused little change in the

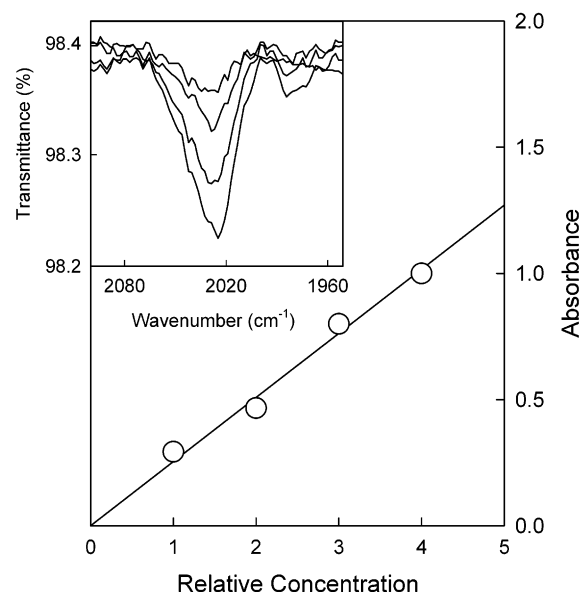


Figure 4. The dependence of the absorbance at 2030 cm^{-1} on the **I**-MWNT-ethanol- d_6 solution concentration follows Lambert–Beer’s law. Shown in the inset are the FT-IR spectra from which the absorbance data are obtained.

^2H NMR results. The exact nature of the apparently strong attachment of deuterium to carbon nanotubes remains to be determined in further investigations.

The deuterium contents in the deuterium-attached soluble carbon nanotube samples were determined by using quantitative NMR signal integration with multiple internal standards (chloroform, ethanol- d_2 , and DMSO- d_6). The deuterium contents in the SWNT samples are generally higher than those in the MWNT samples. For example, the **I**-SWNT-ethanol- d_6 sample contains 0.15% (wt/wt) deuterium. Since the nanotube contents in the **I**-functionalized SWNT samples are typically 5–15% (wt/wt),^{4,5} the deuterium to the nanotube-carbon ratio is 0.01–0.03 (wt/wt) or 0.06–0.18 (mol/mol). Obviously, an accurate estimate of the deuterium coverage on carbon nanotubes depends on the development of more precise methods for determining the nanotube contents in the solubilized samples. The latter is still a challenge.

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Supporting Information Available: Experimental data for studied compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, 282, 95.
- (2) (a) Chen Y.; Haddon, R. C.; Fang, S.; Rao, A. M.; Lee, W. H.; Dickey, E. C.; Grulke, E. A.; Pendergrass, J. C.; Chavan, A.; Haley, B. E.; Smalley, R. E. *J. Mater. Res.* **1998**, 13, 2423. (b) 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. (c) Niyogi, S.; Hu, H.; Hamon, M. A.; Bhowmik, P.; Zhao, B.; Rozenzhak, S. M.; Chen, J.; Itkis, M. E.; Meier, M. S.; Haddon, R. C. *J. Am. Chem. Soc.* **2001**, 123, 733.
- (3) Riggs, J. E.; Guo, Z.; Carroll, D. L.; Sun, Y.-P. *J. Am. Chem. Soc.* **2000**, 122, 5879.
- (4) Sun, Y.-P.; Huang, W.; Lin, Y.; Fu, K.; Kitaygorodskiy, A.; Riddle, L. A.; Yu, Y. J.; Carroll, D. L. *Chem. Mater.* **2001**, 13, 2864.
- (5) Fu, K.; Huang, W.; Lin, Y.; Riddle, L. A.; Carroll, D. L.; Sun, Y.-P. *Nano Lett.* **2001**, 1, 439.
- (6) (a) Riggs, J. E.; Walker, D. B.; Carroll, D. L.; Sun, Y.-P. *J. Phys. Chem. B* **2000**, 104, 7071. (b) Czerw, R.; Guo, Z.; Ajayan, P. M.; Sun, Y.-P.; Carroll, D. L. *Nano Lett.* **2001**, 1, 423. (c) Lin, Y.; Rao, A. M.; Sadanadan, B.; Kenik, E.; Sun, Y.-P. *J. Phys. Chem. B* **2002**, 106, 1294.
- (7) Chen, J.; Rao, A. M.; Lyuksyutov, S.; Itkis, M. E.; Hamon, M. A.; Hu, H.; Cohn, R. W.; Eklund, P. C.; Colbert, D. T.; Smalley, R. E.; Haddon, R. C. *J. Phys. Chem. B* **2001**, 105, 2525.
- (8) Jin, Z.; Sun, X.; Xu, G.; Goh, S. H.; Ji, W. *Chem. Phys. Lett.* **2000**, 318, 505.
- (9) (a) Mickelson, E. T.; Chiang, I. W.; Zimmerman, J. L.; Boul, P. J.; Lozano, J.; Liu, J.; Smalley, R. E.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem. B* **1999**, 103, 4318. (b) Boul, P. J.; Liu, J.; Mickelson, E. T.; Huffman, C. B.; Ericson, L. M.; Chiang, I. W.; Smith, K. A.; Colbert, D. T.; Hauge, R. H.; Margrave, J. L.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, 310, 367.
- (10) (a) Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J. Am. Chem. Soc.* **2001**, 123, 6536. (b) Bahr, J. L.; Tour, J. M. *Chem. Mater.* **2001**, 13, 3823.
- (11) Pekker, S.; Salvétat, J.-P.; Jakab, E.; Bonard J.-M.; Forró, L. *J. Phys. Chem. B* **2001**, 105, 7938.
- (12) (a) Ajayan, P. M. *Chem. Rev.* **1999**, 99, 1787. (b) Khare, B. N.; Meyyappan, M.; Cassell, A. M.; Nguyen, C. V.; Han, J. *Nano Lett.* **2002**, 2, 73. (c) Rao, C. N. R.; Satishkumar, B. C.; Govindaraj, A.; Nath, M. *ChemPhysChem* **2001**, 2, 78. (d) Ajayan, P. M.; Zhou, O. Z. *Top. Appl. Phys.* **2001**, 80, 391. (e) Cheng, H. M.; Yang, Q. H.; Liu, C. *Carbon* **2001**, 39, 1447. (f) Wang, Q. Y.; Johnson, J. K. *J. Phys. Chem. B* **1999**, 103, 4809. (g) Lee, S. M.; Lee, Y. H. *Appl. Phys. Lett.* **2000**, 76, 2877.
- (13) (a) Tsang, S. C.; Chen, Y. K.; Harris, P. J. F.; Green, M. L. H. *Nature* **1994**, 372, 159. (b) Hiura, H.; Ebbesen, T. W.; Tanigaki, K. *Adv. Mater.* **1995**, 7, 275. (c) Rinzler, A. G.; Liu, J.; Dai, H.; Nikolaev, P.; Huffman, C. B.; Rodríguez-Macías, F. J.; Boul, P. J.; Lu, A. H.; Heymann, D.; Colbert, D. T.; Lee, R. S.; Fischer, J. E.; Rao, A. M.; Eklund, P. C.; Smalley, R. E. *Appl. Phys. A* **1998**, 67, 29.
- (14) Liu, J.; Rinzler, A. G.; Dai, H.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodríguez-Macías, F.; Shon, Y.-S.; Lee, T. R.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, 280, 1253.
- (15) Rao, A. M.; Jacques, D.; Haddon, R. C.; Zhu, W.; Bower, C.; Jin, S. *Appl. Phys. Lett.* **2000**, 76, 3813.
- (16) The alkoxy-derivatized phenyl moieties in the side chains in I-functionalized carbon nanotubes play no role in the deuterium attachment. When I was replaced by H₂NCH₂CH₂(OCH₂CH₂)_nNH₂ (average molecular weight ~1500) in the functionalization reactions, similar ²H NMR results were obtained.
- (17) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, 94, 8634.
- (18) Banks, M. R.; Dale, M. J.; Gosney, I.; Hodgson, P. K. G.; Jennings, R. C. K.; Jones, A. C.; Lecoultre, J.; Langridge-Smith, P. R. R.; Maier, J. P.; Scrivens, J. H.; Smith, M. J. C.; Smyth, C. J.; Taylor, A. T.; Thorburn, P.; Webster, A. S. *J. Chem. Soc., Chem. Commun.* **1993**, 1149.
- (19) Rüchardt, C.; Gerst, M.; Ebenhoch, J.; Beckhaus, H.-D.; Campbell, E. E. B.; Tellgmann, R.; Schwarz, H.; Weiske, T.; Pitter, S. *Angew Chem., Int. Ed. Engl.* **1993**, 32, 584.
- (20) Hirsch, A. *Synthesis* **1995**, 895.
- (21) (a) Darwish, A. D.; Abdul-Sada, A. K.; Langley, G. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Synth. Met.* **1996**, 77, 303. (b) Darwish, A. D.; Abdul-Sada, A. K.; Langley, G. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2359.

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