

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/11541953>

# Organic functionalization of carbon nanotubes. J Am Chem Soc 124:760

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · MARCH 2002

Impact Factor: 12.11 · DOI: 10.1021/ja016954m · Source: PubMed

CITATIONS

854

READS

445

6 AUTHORS, INCLUDING:



Vasilios Georgakilas

University of Patras

78 PUBLICATIONS 6,002 CITATIONS

SEE PROFILE



Konstantinos Kordatos

National Technical University of Athens

67 PUBLICATIONS 2,367 CITATIONS

SEE PROFILE



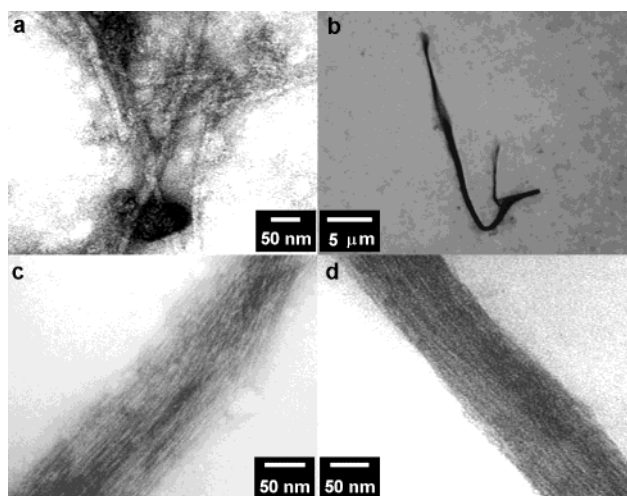
Michael Holzinger

University Joseph Fourier - Grenoble 1

92 PUBLICATIONS 2,895 CITATIONS

SEE PROFILE

Received August 28, 2001



**Figure 1.** TEM image of (a, top left) unreacted SWNTs **1a**, (b, top right) single bundle of product **3**, (c, bottom left) close view of a bundle (b), and (d, bottom right) close view of a bundle of modified SWNTs **6**.

Transmission electron microscopy (TEM) pictures of the product **3** (Figure 1b,c) and of the starting SWNT **1a** (Figure 1a) are compared in Figure 1.

While the original SWNTs aggregate in bundles of the order of 10 nm, the functionalized tubes associate in bundles with typical diameters of 100 nm, and length of several microns. The TEM picture of pyrene-modified tubes **6** (Figure 1d) shows that the bundles are now more compact than tubes **3**, probably as a consequence of a better adhesion between the modified tubes, due to the presence of pyrene.<sup>24</sup> Although it was not possible to judge by TEM if the functional groups were covalently attached to the tubes, the solubility of the material in organic solvents, the NIR data, and the different form of the bundles are decisive arguments in support of the organic functionalization of the tubes.

All reactions were successful with use of either short oxidized or long nonoxidized SWNTs without notable differences in their solubility. The yields of these reactions range between 20 and 80%. This inconsistency, nonspecific of a particular type of tubes, but occurring even inside the same category of tubes, is probably due to the heterogeneous nature of the reaction mixture. Nanotubes will react only when their surface is offered to the reactants, but without sonication, they might remain compact in the form of insoluble bundles. On the other hand, it is known that sonication can affect the length of the SWNTs, such that throughout this work sonication was strictly avoided.

Another piece of evidence for the organic functionalization of NT was obtained by fluorescence experiments. The emission of the pyrene-functionalized SWNT **6** was compared with that of a solution (**3** + pyrene) containing SWNT **3** and unmodified pyrene in approximately the same ratio and the same concentration as in the experiment with **6**. Upon excitation with visible light (350 nm), the emission of SWNT **6** was significantly quenched ( $\Phi = 0.056$ ) relative to the unmodified pyrene ( $\Phi = 0.72$ ). In the (**3** + pyrene) solution, a decrease of the pyrene emission was noted ( $\Phi = 0.46$ ) relative to bare pyrene, which confirms an intermolecular interaction between pyrene and SWNT.<sup>24</sup> However, the 8-fold increase relative to SWNT **6** is the consequence of a less efficient deactivation of the photoexcited chromophore. The fluorescence lifetimes also differ substantially, with values of 8.7 (SWNT **6**) and 124 ns (**3** + pyrene solution). The difference of about 14 substantiates the occurrence of two different quenching mechanisms: intramolecular for **6** and intermolecular for (**3** + pyrene). Importantly, variations of the SWNT **6** concentration did not reveal any significant impact on

the pyrene emission lifetime, whereas in the mixed system, variation of the relative (**3** + pyrene) concentrations led to dramatic changes in the pyrene fluorescence lifetime.

In conclusion, we have described a new, versatile, and powerful methodology for functionalization of different types of carbon nanotubes, using 1,3-dipolar cycloadditions. The modified nanotubes are remarkably soluble in most organic solvents and even in water. Given the better handling of the modified nanotubes, this result opens the way to a high number of opportunities, including the preparation of nanocomposites.<sup>7</sup>

**Acknowledgment.** This work was carried out with partial support from the European Union (HPRNT-CT-1999-00011-FUNCARS) and the Office of Basic Energy Sciences of the U.S. Department of Energy. This is document NDRL-4345 from the Notre Dame Radiation Laboratory. We thank Mr. Claudio Gamboz (CSPA, University of Trieste) for great help with TEM measurements.

**Supporting Information Available:** NIR spectrum of functionalized SWNT **6d** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Traacy, M. M. J.; Ebbesen, T. W.; Gibson, J. M. *Nature* **1996**, *381*, 678.
- (2) Wong, E. W.; Sheehan, P. E.; Lieber, C. M. *Science* **1997**, *277*, 1971–1975.
- (3) Poncharal, P.; Wang, Z. L.; Ugarte, D.; Heer, W. A. d. *Science* **1999**, *283*, 1513.
- (4) Tans, S. J.; Verschuere, A. R. M.; Dekker, C. *Nature* **1998**, *393*, 49–52.
- (5) Dai, H.; Wong, E. W.; Lieber, C. M. *Science* **1996**, *272*, 523.
- (6) Yakobson, B. I.; Smalley, R. E. *Am. Sci.* **1997**, *85*, 324.
- (7) Calvert, P. *Nature* **1999**, *399*, 210.
- (8) Ajayan, P. M. *Chem. Rev.* **1999**, *99*, 1787–1799.
- (9) Bahr, J. L.; Mickelson, I. T.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *Chem. Commun.* **2001**, 193–194.
- (10) Sun, Y.; Wilson, S. R.; Schuster, D. I. *J. Am. Chem. Soc.* **2001**, *123*, 5348–5349.
- (11) Tang, B. Z.; Xu, H. *Macromolecules* **1999**, *32*, 2569–2576.
- (12) 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*, 1721–1725.
- (13) Dalton, A. B.; Stephan, C.; Coleman, J. N.; McCarthy, B.; Ajayan, P. M.; Lefrant, S.; Bernier, P.; Blau, W. J.; Byrne, H. J. *J. Phys. Chem.* **2000**, *104*, 10012–10016.
- (14) Chen, J.; Hannon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Ecklund, P.; Haddon, R. C. *Science* **1998**, *282*, 95–98.
- (15) Riggs, J. E.; Guo, Z.; Carroll, D. L.; Sun, Y. P. *J. Am. Chem. Soc.* **2000**, *122*, 5879–5880.
- (16) Boul, P. J.; Liu, J.; Mickelson, E. T.; 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*, 367–372.
- (17) Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 6536–6542.
- (18) Holzinger, M.; Hirsch, A.; Bernier, P.; Duesberg, G. S.; Burghard, M. *Appl. Phys. A* **2000**, *70*, 599–602.
- (19) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798–9799.
- (20) Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519–526.
- (21) SWNT (**1a**) (6 mg) and paraformaldehyde (20 mg) were suspended in 20 mL of DMF. The heterogeneous mixture was heated at 130 °C while a solution of amino acid **2** in DMF (20 mg in 2 mL of solvent) was added in portions (4 × 0.5 mL every 24 h) and the reaction was continued for 5 days. The reaction was stopped after 5 days and the organic phase was separated from the unreacted material by centrifugation and filtration (filter paper). The solid was washed with DMF and CH<sub>2</sub>Cl<sub>2</sub> leaving 0.5 mg of unreacted material. The combined organics were evaporated and the remaining oily brown residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O. The organic phase was washed five times with water, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to dryness giving, after washing with diethyl ether, 5.2 mg of a brown solid. TEM experiments: One drop of the final solid dissolved in acetone was placed on a TEM grid (copper grid 3.0 mm 200 mesh, coated with Formvar film) together with a drop of uranyl acetate (2% water solution). After air-drying of the grid the sample was investigated by TEM (Philips 208) at an accelerating voltage of 100 kV.
- (22) Haddon, R. C. *Science* **1993**, *261*, 1545–1550.
- (23) Kukovec, A.; Georgakilas, V.; Prato, M.; Kuzmany, H. To be submitted for publication.
- (24) Chen, R. J.; Zhang, Y.; Wang, D.; Dai, H. *J. Am. Chem. Soc.* **2001**, *123*, 3838–3839.

JA016954M