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Organic Functionalization of Carbon Nanotubes

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Received August 28, 2001

Carbon nanotubes (NTs) exhibit extraordinary mechanical[1-3] and electronic[4,5] properties.[6-8] However, manipulation and processing of NTs has been limited by their insolubility in most common solvents, although some dissolution has recently been obtained.[9,10] Wrapping with polymers has also provided a supramolecular approach to solubilization of NTs.[11-13] Considerable effort has therefore been devoted to the chemical modification of NTs, which might pave the way to many useful applications, including composite preparations.[7] Attachment of long alkyl chains[14] and polymers,[15] fluorination,[16] and radical reactions[17] have provided access to tip and sidewall functionalization, eventually leading to relatively soluble materials.

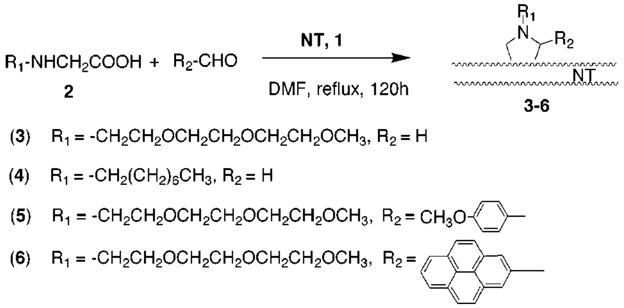
In this paper, we report our approach to the organic functionalization of NTs, which has led to a high level of solubility of the resulting products. Besides being very powerful, this approach proved consistent for all types of NTs tested, including single-wall (SWNTs) and multiwall (MWNTs) carbon nanotubes.

The NTs used in this work were obtained from Bucky USA (long purified SWNT (**1a**), short oxidized SWNT (**1b**), and purified MWNTs (**1c**)) or Carbon Nanotechnologies, Inc. (HiPCO SWNTs, **1d**) or were prepared and purified according to a reported procedure (short oxidized SWNT, **1e**).[18] For the sake of clarity, the data reported herein refer to a single type of nanotubes, specifically SWNT **1a**, although very similar results were obtained with all the other samples.

The functionalization methodology is based on the 1,3-dipolar cycloaddition of azomethine ylides, generated by condensation of an α-amino acid and an aldehyde, a reaction that we have widely applied to the organic modification of fullerene C_{60} (Scheme 1).[19,20]

The SWNTs were suspended in DMF, together with excess aldehyde and modified glycine **2**. The heterogeneous reaction mixture was heated at 130 °C for 5 days, although after only a few hours the color changed to dark brown, giving a hint for the occurrence of the reaction. After workup,[21] a brown solid was obtained, which was very soluble in $CHCl_3$, CH_2Cl_2, acetone, methanol, ethanol, and also water, less soluble in toluene and THF, and practically insoluble in less polar solvents, including diethyl ether and hexane. The solubility was similar for all the functionalized nanotubes. As an example, the solubility of SWNT **3** in $CHCl_3$ was close to 50 mg/mL—*without sonication!* The functionalized NTs remained in solution indefinitely long, and no precipitation was observed after two weeks.

Scheme 1



The ^1H NMR spectrum of **3**, **4**, and **6** in $CDCl_3$ shows the presence of the triethylene glycol monomethyl ether chain consisting of two broad peaks at 3.4 and 3.6 ppm. When an aromatic aldehyde was used instead of formaldehyde (4-methoxybenzaldehyde), the corresponding aromatic resonances were observed in product **5** at 6.8 ppm, together with those of the methoxy group (at 3.3 ppm). The presence of the pyrrolidine protons, which would corroborate the occurrence of the 1,3-dipolar cycloaddition, was difficult to confirm. However, it is expected that these signals would be very broad, therefore ranging over a wide chemical shift interval, depending on the different magnetic environment. In the ^1H NMR spectrum of the *n*-heptyl derivative (**4**), the peaks belonging to the aliphatic protons were clearly visible at 0.84 and 1.23 ppm, uncovering a broad peak between 2 and 4 ppm. These signals are tentatively assigned to the pyrrolidine protons. The chemical shift of these protons is at higher fields relative to the fullerene analogue (~ 4.5 ppm[19]), which may be justified by the absence of paramagnetic five-membered rings in SWNT.[22]

In general, the UV−vis absorption spectrum in CH_2Cl_2 showed a broad band around 250 nm, which monotonically decreased in intensity, reaching the near-infrared region. The NIR spectrum (Figure S1, see Supporting Information) shows that some of the electronic properties of the SWNT are lost during the functionalization process. This is expected on the basis of previous work.[17] However, Raman spectroscopy indicates that the SWNT structure is still present in the functionalized tubes, with the characteristic tangential mode at around 1600 cm^{-1}. A full report of the Raman characteristics will be reported shortly.[23] When an aromatic aldehyde was used, the corresponding UV−vis bands were observed in the products. For example, the UV−vis absorption spectrum of product **6** in CH_2Cl_2 contained the characteristic absorption bands of the pyrene group (at 346, 331, 316, 278, 267, 243, and 235 nm) shifted by 5−10 nm to higher wavelengths with respect to pyrene itself. It should be noted that these transitions are completely different from the absorption bands of the starting pyrene aldehyde (at 396, 374, 363, 289, 278, 244, and 234 nm), which confirms the successful chemical transformation. A calibration curve was used to measure the concentration of the pyrene group in the sample, which indicated that one pyrene and therefore one pyrrolidine ring correspond to about 95 carbon atoms of the SWNT.

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10.1021/ja016954m CCC: $22.00

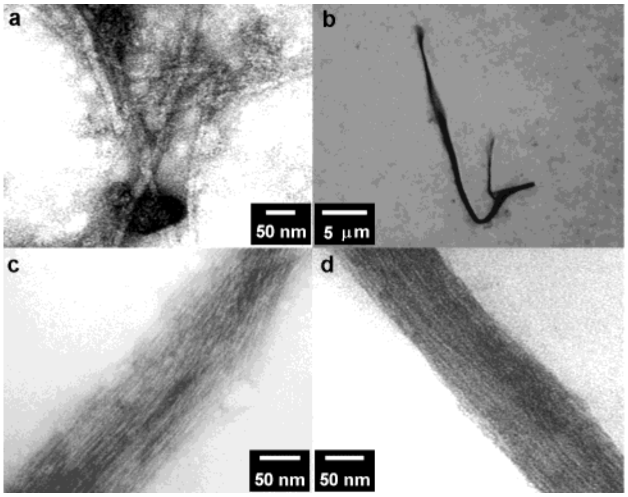

Figure 1. TEM image of (a, top left) unreacted SWNTs **1a**, (b, top right) single bundle of product **3**, (c, bottom left) close view of a bundle (b), and (d, bottom right) close view of a bundle of modified SWNTs **6**.

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.[24] 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.[24] 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.[7]

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.

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(21) SWNT (**1a**) (6 mg) and paraformaldeyde (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_2Cl_2 leaving 0.5 mg of unreacted material. The combined organics were evaporated and the remaining oily brown residue was extracted with CH_2Cl_2/H_2O. The organic phase was washed five times with water, dried over Na_2SO_4, 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.
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JA016954M