J|A|C|S
COMMUNICATIONS

Separation of Semiconducting from Metallic Carbon Nanotubes by Selective Functionalization with Azomethine Ylides

Cécilia Ménard-Moyon,[†] Nicolas Izard,[‡] Eric Doris,*[,†] and Charles Mioskowski*[,†,§]

Service de Marquage Moléculaire et de Chimie Bioorganique, DSV/DBJC, CEA/Saclay, 91191 Gif-sur-Yvette Cedex, France, Laboratoire des Colloïdes, Verres et Nanomatériaux, Université Montpellier II, cc026, Place Eugène Bataillon, 34000 Montpellier, France, and Laboratoire de Synthèse Bioorganique, UMR CNRS 7514, Faculté de Pharmacie, 74 route du Rhin, 67401 Illkirch-Graffenstaden Cedex, France

Received February 2, 2006; E-mail: eric.doris@cea.fr; charles.mioskowski@cea.fr

Since the discovery of carbon nanotubes by Iijima in 1991,[1] intensive studies of their mechanical and electronic properties have been carried out suggesting great potential for applications in nanotechnology.[2] However, covalent functionalization of carbon nanotubes is, in some cases, required to optimize their properties. Few methods have been developed for this purpose and include addition of carbenes, nitrenes, or diazonium salts to the nanotube surface.[3] In addition, Prato et al. reported in 2002 an efficient procedure for the functionalization of single-wall carbon nanotubes (SWNTs).[4] Their approach is based on the 1,3-dipolar cycloaddition of azomethine ylides derived from decarboxylation of iminium salts (Scheme 1, path A). Even though the process developed by Prato is robust, it requires strong thermal activation (130 °C) to induce the formation of the reactive ylide.

In this paper, we report an alternative method for the covalent functionalization of SWNTs by azomethine ylides. Our approach is based on the generation, under mild conditions, of the 1,3-dipole by double deprotonation of the corresponding trialkyl-*N*-oxide[5] (Scheme 1, path B). First experiments were conducted at room temperature. Unfortunately, under these conditions, no covalent functionalization of the nanotubes was detected. Nevertheless, when a solution of lithium diisopropylamide (LDA) was added dropwise to a previously sonicated mixture of SWNTs (HiPco from Carbon Nanotechnologies, Inc.) and trimethylamine-*N*-oxide **1** in refluxing THF (65 °C), we were pleased to observe cycloaddition of the azomethine ylide to the nanotube surface. To enhance the level of functional group coverage, the overall sequence was repeated twice.

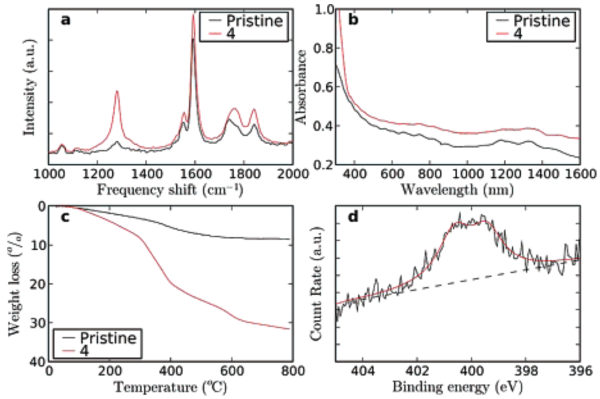
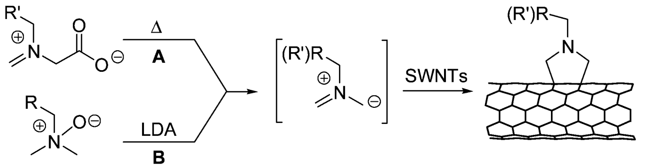


Figure 1. Normalized Raman spectra at 1064 nm (a), UV−vis−NIR in DMF (b), TGA of pristine nanotubes and of functionalized sample **4** (c), and XPS of **4** (d).

Scheme 1



R = H, **1**
R = -(CH$_2$)$_3$-pyrene, **2**
R = -(CH$_2$)$_2$-anthracene, **3**

R = H, **4**
R = -(CH$_2$)$_3$-pyrene, **5**
R = -(CH$_2$)$_2$-anthracene, **6**

Characterization of the functionalized SWNTs has been achieved using different techniques. The Raman spectra of pristine and of functionalized SWNTs **4** are reported in Figure 1a. While the spectrum of the starting material displays a small disorder mode at 1290 cm^{-1}, the functionalized sample shows an increase of the so-called D-band. This rise indicates that a significant amount of the sp^2 carbon atoms have been converted to sp^3 hybridization. This has been further confirmed by UV−vis−NIR absorption spectroscopy. Figure 1b shows the characteristic interband transitions between van Hove singularities of pristine HiPco nanotubes and the loss of these transitions in the functionalized sample **4**. This is also consistent with the covalent grafting of the nanotubes. Thermogravimetric analysis (TGA) of **4** indicates a weight loss of 23% (compared to pristine SWNTs), which was calculated to be ca. 1 functional group in 16 carbon atoms (Figure 1c). The degree of coverage has been confirmed by X-ray Photoelectron Spectroscopy (XPS). Figure 1d shows the N 1s core level spectrum of **4**. The peak at ca. 400 eV is attributed to the nitrogen atom of the pyrrolidine ring which is formed on the nanotube surface during cycloaddition. From the nitrogen-to-carbon ratio (4.6%), we calculated that the level of grafting is ca. 1 functional group in 18 carbon atoms, which correlates rather well with TGA.

Hence, the above mentioned process appears to be highly efficient for the sidewall covalent functionalization of SWNTs. However, our initial objective was to design a method which would operate under mild conditions (i.e., at room temperature). We thus envisioned that if the reactive ylides were generated when in close contact with the nanotube surface, this would facilitate the cycloaddition process. Accordingly, we synthesized two different trialkylamine-*N*-oxides bearing a polycyclic aromatic (PCA) side chain (e.g., pyrene **2** and anthracene **3**). Since aromatic derivatives are capable of π-stacking to the nanotube surface, the side chain could induce adsorption of the *N*-oxide precursors on the nanotube. We found that, upon treatment with LDA of a preorganized mixture of nanotubes and pyrenyl-*N*-oxide **2**, smooth cycloaddition took place at room temperature.

Characterization of the sample unambiguously indicated covalent functionalization of the nanotubes (increase of the Raman D-band and disappearance of the van Hove singularities in the UV−vis−

[†] DSV/DBJC.
[‡] Université Montpellier II.
[§] Laboratoire de Synthèse Bioorganique.

10.1021/ja060802f CCC: $33.50 © 2006 American Chemical Society

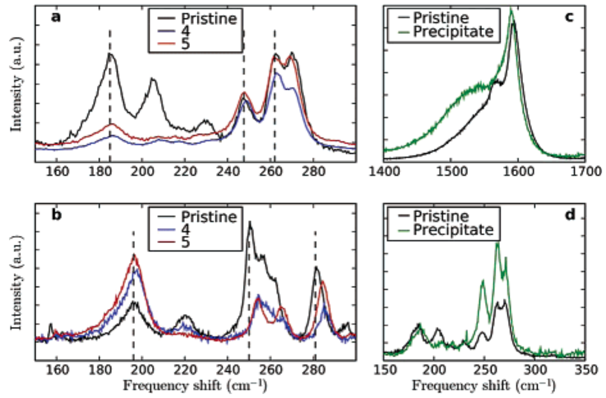


Figure 2. Raman spectra of pristine SWNTs, **4**, and **5** in the RBM at 514.5 (a) and 647.1 nm (b). Raman spectra at 514.5 nm of pristine and of precipitated nanotubes in the TM (c) and RBM (d); intensities were normalized for clarity.

NIR spectrum). TGA of **5** showed a weight loss of 24%, which was calculated to be ca. 1 functional group in 80 carbon atoms. Even though the reaction seems less efficient (to enhance the level of functionalization, the overall sequence was repeated twice) in terms of functional group coverage compared to **4**, preorganization of the substrate permitted the cycloaddition to be effective at room temperature. Furthermore, it has been recently reported that electron-rich compounds, such as porphyrins[6] and alkylamines,[7] are capable of selective interactions with semiconducting nanotubes. With these results in mind, we further analyzed sample **5** by Raman spectroscopy at two specific wavelengths (i.e., 514.5 and 647.1 nm) to determine whether the pyrenyl group permits preferential interaction with one type of nanotubes. As Raman spectroscopy is a resonant process for SWNTs, allowed optical transitions can be reported on a plot as a function of the diameter of the nanotube.[8] Also known as Kataura plot, the latter anticipates that both metallic (met-SWNTs) and semiconducting (sem-SWNTs) HiPco nanotubes are simultaneously probed at 514.5 and 647.1 nm.[9] Figure 2 displays the Raman spectra in the radial breathing mode (RBM) range (ν below 300 cm^{-1}) of pristine and of functionalized samples **4** and **5**. At 514.5 nm, higher frequency RBMs (225−300 cm^{-1}) are attributed to metallic nanotubes and lower frequency RBMs (150−225 cm^{-1}) to semiconducting ones. On the contrary, at 647.1 nm, higher RBMs correspond to sem-SWNTs and lower RBMs to met-SWNTs. Compared to pristine nanotubes, each peak in the radial breathing mode of sample **4** (R = H) exhibits a systematic upshift of a few cm^{-1}. This upshift is associated with an increase of the I_D/I_G ratio (see Figure 1a). This demonstrates successful concomitant functionalization of both met- and sem-SWNTs. The Raman spectrum of the functionalized sample **5** (R = $-(CH_2)_3-$pyrene) displays different features. At 514.5 nm (Figure 2a), no upshift is observed for metallic nanotubes (higher RBMs) while an upshift is observed for semiconducting ones (lower RBMs). On the other hand, at 647.1 nm, lower RBMs are unaffected (met-SWNTs) at the same time as higher RBMs (sem-SWNTs) shift (Figure 2b).

Taken together, these data suggest that selective functionalization of semiconducting nanotubes can be induced when the starting *N*-oxides substrates (ylide precursors) are attached to a polycyclic aromatic substituent (e.g., **2** and **3**). Indeed, the same behavior, albeit less pronounced, was observed with anthracene-linked *N*-oxide **3**. The origin of the selective interaction with sem-SWNTs remains unclear. However, we speculate that PCAs could π-stack preferentially with more aromatic semiconducting nanotubes.[10]

With the mixture of reacted nanotubes **5** in hands, we then set up a process to separate functionalized sem-SWNTs from unreacted met-SWNTs. Our strategy is based on the selective solubilization of the functionalized fraction. This could be achieved by protonation of the pyrrolidine nitrogen atom of the grafted nanotube by lignoceric acid ($C_{23}H_{47}CO_2H$). Since the resulting ammonium carboxylates are bearing long alkyl chains, we assume that sem-SWNTs would become highly soluble in organic solvents while met-SWNTs precipitate. In a typical experiment, a sample of SWNTs that was reacted with ylide **2** (1 mg) is treated with a solution of lignoceric acid in $CHCl_3$ (5 mg/mL, 3 mL). The mixture is sonicated for 3 min and left undisturbed for 48 h. The dark colored chloroform phase is then removed, and the precipitate is analyzed by Raman spectroscopy. The tangential mode ($1400 < \nu_{TM} < 1600$ cm^{-1}) of the precipitate is broader and more asymmetric than that of pristine SWNTs (Breit−Wigner−Fano line shape, Figure 2c). This indicates a substantial enrichment of the precipitate in met-SWNTs[11] which also concurs with a 4 cm^{-1} downshift of the TM. The Raman data in the radial breathing mode region are also consistent with this observation since peaks at ca. 250 cm^{-1} now appear as major components (Figure 2d). These features point out that protonation of functionalized SWNTs (i.e., sem-SWNTs) by lignoceric acid permits the latter to be retained in the chloroform phase, therefore allowing enrichment of the precipitate in unreacted metallic carbon nanotubes.

In summary, we report here a mild and efficient method for the functionalization of SWNTs by cycloaddition of azomethine ylides derived from trialkylamine-*N*-oxides. Selective reaction of semiconducting carbon nanotubes was achieved by preorganizing the starting *N*-oxides on the nanotube surface prior to generating the reactive ylide. Separation of met-SWNTs from functionalized sem-SWNTs was successfully accomplished by inducing solubilization of sem-SWNTs in the presence of lignoceric acid. To the best of our knowledge, this is the first process that permits selective covalent sidewall functionalization of semiconducting SWNTs.[12]

Supporting Information Available: Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Iijima, S. *Nature* **1991**, *354*, 56−58.
(2) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787−792.
(3) Banerjee, S.; Hemraj-Benny, T.; Wong, S. S. *Adv. Mater.* **2005**, *17*, 17−29.
(4) Georgakilas, V.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc.* **2002**, *124*, 760−761.
(5) Beugelmans, R.; Neron, G.; Roussi, G. *J. Chem. Soc., Chem. Commun.* **1983**, *1*, 31−32.
(6) Li, H.; Zhou, B.; Lin, Y.; Gu, L.; Wang, W.; Fernando, K. A. S.; Kumar, S.; Allard, L. F.; Sun, Y.-P. *J. Am. Chem. Soc.* **2004**, *126*, 1014−1015.
(7) Chattopadhyay, D.; Galeska, I.; Papadimitrakopoulos, F. *J. Am. Chem. Soc.* **2003**, *125*, 3370−3375.
(8) Rao, A. M.; Richter, E.; Bandow, S.; Chase, B.; Eklund, P. C.; Williams, K. A.; Fang, S.; Subbaswamy, K. R.; Menon, M.; Thess, A.; Smalley, R. E.; Dresselhaus, G.; Dresselhaus, M. S. *Science* **1997**, *275*, 187−191.
(9) Kataura, H.; Kumazawa, Y.; Maniwa, Y.; Umezu, I.; Suzuki, S.; Ohtsuka, Y.; Achiba, Y. *Synth. Met.* **1999**, *103*, 2555−2558.
(10) Aihara, J.; Yamabe, T.; Hosoya, H. *Synth. Met.* **1994**, *64*, 309−313.
(11) Dresselhaus, M. S.; Dresselhaus, G.; Jorio, A.; Souza Filho, A. G.; Saito, R. *Carbon* **2002**, *40*, 2043−2061.
(12) Methods for covalent functionalization of metallic SWNTs have already been reported. For example, see: Strano, M. S.; Dyke, C. A.; Usrey, M. L.; Barone, P. W.; Allen, M. J.; Shan, H.; Kittrell, C.; Hauge, R. H.; Tour, J. M.; Smalley, R. E. *Science* **2003**, *301*, 1519−1522.

JA060802F