J|A|C|S
COMMUNICATIONS

Functionalization of Single-Wall Carbon Nanotubes by Tandem High-Pressure/$Cr(CO)_6$ Activation of Diels−Alder Cycloaddition

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

Service de Marquage Moléculaire et de Chimie Bioorganique, DSV/DBJC, CEA/Saclay, 91191 Gif-sur-Yvette Cedex, France, BioCIS, UMR 8076, Centre d'Etude Pharmaceutique, Université Paris-Sud, 5 rue J-B. Clément, 92296 Châtenay-Malabry, France, Laboratoire de Synthèse Bioorganique, UMR CNRS 7514, Faculté de Pharmacie, 74 route du Rhin, 67401 Illkirch-Graffenstaden Cedex, France

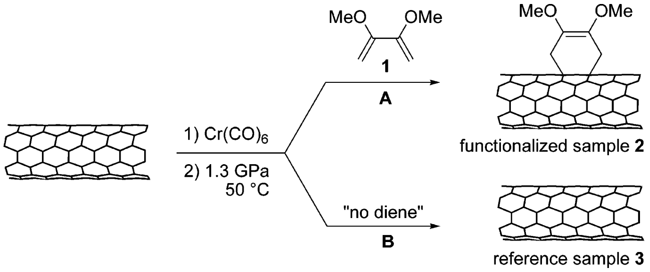
Received August 7, 2006; E-mail: eric.doris@cea.fr; charles.mioskowski@cea.fr

Since their discovery by Iijima in 1991,[1] carbon nanotubes have attracted considerable interest due to their unique mechanical,[2] electronic,[3] and optical[4] properties. Their potential in nanotechnology has however been hampered by difficulties associated with processing and manipulation. Considerable efforts have thus been devoted to nanotube functionalization to improve solubility and to enhance compatibility in composite materials.[5] A few methods have been developed for this purpose, which include oxidation at defects sites,[6] addition of azomethine ylides,[7] diazonium salts,[8] carbenes,[9] nitrenes,[10] and radicals[11] to single-wall carbon nanotubes (SWNTs). In addition to these known processes, the Diels−Alder reaction has also been theoretically predicted to be favored.[12] Nevertheless, it is only recently that experimental validation was reported, i.e., the reaction under microwave irradiation of *o*-quinodimethane with soluble SWNTs,[13] and the cycloaddition of dienes with fluorinated SWNTs.[14] Diels−Alder reaction on SWNTs thus appears viable, starting from previously derivatized carbon nanotubes.

In the present paper we report an alternative method which avoids prior covalent modification of SWNTs. Our approach is based on the simultaneous activation of the Diels−Alder cycloaddition using a transition metal together with pressure. Indeed, cycloaddition reactions are known to be accelerated under high pressure.[15] Also, the electrophilic character of aromatic compounds has been reported to be enhanced upon complexation with $Cr(CO)_6$.[16] We therefore investigated the combined effect of pressure and chromium hexacarbonyl on the Diels−Alder reaction of various dienes with carbon nanotubes.

In a typical experiment, 3 mg of SWNTs (HiPCO from Carbon Nanotechnologies, Inc.) were first reacted with $Cr(CO)_6$ in 1,4-dioxane (see Supporting Information for details). The resulting chromium−SWNTs complex was added to a solution of 2,3-dimethoxy-1,3-butadiene **1** in THF, and the suspension was sonicated for 5 min. The mixture was then heated at 50 °C and 1.3 GPa (Scheme 1, path A). After 60 h, pressure was released and the suspension was irradiated with visible light to induce decomplexation of chromium.[17] The nanotubes were collected by centrifugation and washed several times with organic solvents. Control experiments were also run in parallel to ensure that the experimental conditions were innocuous toward the nanotube structure. Accordingly, a sample of SWNTs was treated as above but without diene **1** (Scheme 1, path B). Sample **3** was analyzed by Raman spectroscopy which indicated that pressure combined with chromium had little effect on the nanotube since we only observed a minute increase of the relative intensity of the D-band at ca. 1280 cm^{-1} (Figure 1a). This band is related to defects in the nanotube lattice. Sample **3** will be used as a reference to allow comparison with the functionalized carbon nanotubes **2**.

Scheme 1



The functionalized sample **2** was characterized using two spectroscopic techniques along with thermogravimetric analysis (Figure 1). Direct evidence for covalent sidewall functionalization of nanotubes was provided by Raman spectroscopy (Figure 1a).

Indeed, the relative intensity of the D-band is increased in the functionalized SWNTs **2** compared to reference sample **3**. This indicates a significant conversion of sp^2- to sp^3-hybridized carbon atoms.[18] Functionalization has been further confirmed by UV−vis−NIR absorption spectroscopy. Figure 1b exhibits the characteristic interband transitions between van Hove singularities of reference SWNTs **3**, and the loss of these absorptions in the functionalized sample **2**. This is also indicative of a disruption of the extended π-network due to a significant number of sp^2 carbon atoms which have been converted to sp^3 hybridization. Thermogravimetric analysis (TGA) of **2** (under Ar, 10 °C/min to 800 °C) shows a weight loss of 22% (compared to pristine SWNTs), which was calculated to be ca. 1 functional group in 33 carbon atoms[19] (Figure 1c). Taken together, these data suggest that the Diels−Alder cycloaddition did occur on the nanotube surface.

The synergistic effect of pressure and chromium has been highlighted by supplementary experiments which indicated that neither the reaction of diene **1** with pristine SWNTs at 50 °C and 1.3 GPa nor the reaction of **1** with the chromium−SWNTs complex at 50 °C at atmospheric pressure led to covalent modification of the nanotube. Therefore, the combined effect of high pressure and $Cr(CO)_6$ is crucial to activate the nanotube toward Diels−Alder cycloadditions.

To determine the scope and limitation of this process, the Diels−Alder reaction was attempted using other dienes. The first, experiments were conducted with 1,3-cyclohexadiene, **4**, 2,3-dimethylbutadiene, **5**, and 9,10-dimethylanthracene, **6**. Results are summarized in Table 1.

To detect and quantify covalent functionalization of the nanotube surface, the intensity of the D-band relative to that of the G-band (I_D/I_G) in the Raman spectra was used as a probe. As an example,

---

[†] Service de Marquage Moléculaire et de Chimie Bioorganique.
[‡] BioCIS.
[§] Laboratoire de Synthèse Bioorganique.

10.1021/ja065698g CCC: $33.50 © 2006 American Chemical Society

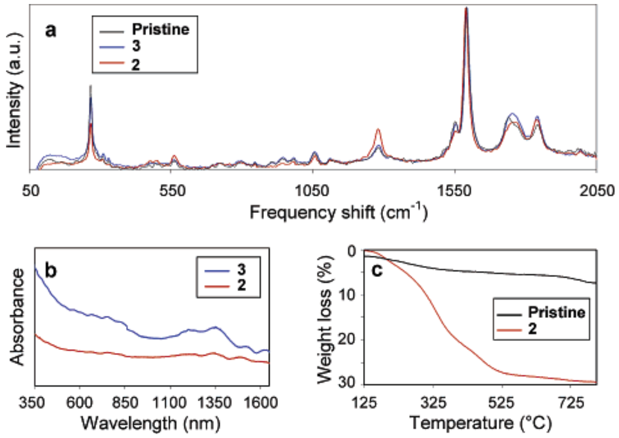
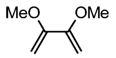
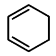
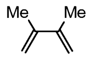
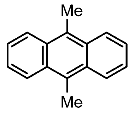
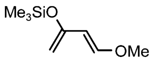


Figure 1. (a) Normalized Raman spectra at 1064 nm of pristine carbon nanotubes, reference sample **3**, and functionalized SWNTs **2**, (b) UV−vis−NIR in DMF of **3** and **2**, (c) TGA of pristine SWNTs and of functionalized nanotubes **2**.

Table 1. Increase of the I_D/I_G Ratio for Various Dienes

Entry	Diene		Increase of the I_D/I_G ratio
1		**1**	2.3
2		**4**	1
3		**5**	1
4		**6**	1.1
5		**7**	2.6

functionalized sample **2** shows an amplification of the I_D/I_G ratio by a factor of 2.3 (entry 1) compared to reference sample **3**. Unfortunately, no covalent functionalization of the nanotube was detected using the abovementioned dienes (entries 2−4), although a small increase was measured for **6**. We were pleased, however, to observe that Diels−Alder cycloaddition took place with the electron-rich Danishefsky's diene[20] **7** (entry 5). Indeed, the Raman spectrum of SWNTs that were reacted with **7** showed an increase of the I_D/I_G ratio by a factor of 2.6 in comparison with that of sample **3**. This enhancement of the relative intensity of the D-band is in the same range as that of SWNTs **2**. Functionalization was further confirmed by UV−vis−NIR spectroscopy with the disappearance of the van Hove singularities. The Diels−Alder process is therefore operative with dienes bearing strong electron-donating groups (e.g., **1** and **7**). The preferential reactivity of electron-rich dienes with chromium−SWNTs can be rationalized using frontier molecular orbital (FMO) theory which anticipates that the lower the energy gap between the HOMO (diene) and the LUMO (dienophile), the more efficient the Diels−Alder reaction will be. In our case, the process is concomitantly favored by the electron-donating ability of the diene and by the enhanced electrophilicity of the carbon nanotube due to its complexation to chromium. We speculate that the transition metal induces the formation of nanotube-based species analogous to arene chromium tricarbonyl complexes.[21]

In summary, we report here an efficient method to induce Diels−Alder reactions on SWNTs. The synergistic effect of pressure and complexation of chromium hexacarbonyl is an original method to transiently boost the reactivity of the nanotube toward the cycloaddition of electron-rich dienes.

Acknowledgment. E. Anglaret, N. Izard, N. Mackiewicz, and M. Paternostre are gratefully acknowledged for helpful discussions. C.M.M. thanks the "Délégation Générale pour l'Armement" for financial support.

Supporting Information Available: Experimental procedures, Raman and UV−vis−NIR spectra of SWNTs functionalized with **7**. 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) Falvo, M. R.; Clary, G. J.; Taylor, R. M.; Chi, V.; Brooks, F. P.; Washburn, S.; Superfine, R. *Nature* **1997**, *389*, 582−584.
(3) Ouyang, M.; Huang, J.-L.; Lieber, C. M. *Acc. Chem. Res.* **2002**, *35*, 1018−1025.
(4) Izard, N.; Ménard, C.; Riehl, D.; Doris, E.; Mioskowski, C.; Anglaret, E. *Chem. Phys. Lett.* **2004**, *391*, 124−128.
(5) Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. *Chem. Rev.* **2006**, *106*, 1105−1136.
(6) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95−98.
(7) (a) Georgakilas, V.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc.* **2002**, *124*, 760−761. (b) Ménard-Moyon, C.; Izard, N.; Doris, E.; Mioskowski, C. *J. Am. Chem. Soc.* **2006**, *128*, 6552−6553.
(8) 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.
(9) (a) Holzinger, M.; Vostrowsky, O.; Hirsch, A.; Hennrich, F.; Kappes, M.; Weiss, R.; Jellen, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 4002−4005. (b) Hu, H.; Zhao, B.; Hamon, M. A.; Kamaras, K.; Itkis, M. E.; Haddon, R. C. *J. Am. Chem. Soc.* **2003**, *125*, 14893−14900.
(10) Holzinger, M.; Abraham, J.; Whelan, P.; Graupner, R.; Ley, L.; Hennrich, F.; Kappes, M.; Hirsch, A. *J. Am. Chem. Soc.* **2003**, *125*, 8566−8580.
(11) (a) Ying, Y.; Saini, R. K.; Liang, F.; Sadana, A. K.; Billups, W. E. *Org. Lett.* **2003**, *5*, 1471−1473. (b) Peng, H.; Alemany, L. B.; Margrave, J. M.; Khabashesku, V. N. *J. Am. Chem. Soc.* **2003**, *125*, 15174−15182.
(12) Lu, X.; Tian, F.; Wang, N.; Zhang, Q. *Org. Lett.* **2002**, *4*, 4313−4315.
(13) Delgado, J. L.; de la Cruz, P.; Langa, F.; Urbina, A.; Casado, J.; López Navarrete, J. T. *Chem. Commun.* **2004**, *15*, 1734−1735.
(14) Zhang, L.; Yang, J.; Edwards, C. L.; Alemany, L. B.; Khabashesku, V. N.; Barron, A. R. *Chem. Commun.* **2005**, *26*, 3265−3267.
(15) Matsumoto, K.; Hamana, H.; Iida, H. *Helv. Chim. Acta* **2005**, *88*, 2033−2234.
(16) Semmeihack, M. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier Science: Oxford, 1995; Vol. 12, pp 979−1038.
(17) Pape, A. R.; Kaliappan, K. P.; Kündig, P. E. *Chem. Rev.* **2000**, *100*, 2917−2940.
(18) Dresselhaus, M. S.; Dresselhaus, G.; Jorio, A.; Souza Filho, A. G.; Saito, R. *Carbon* **2002**, *40*, 2043−2061.
(19) For comparison of the level of grafting with other known methods, see: Dyke, C. A.; Tour, J. M. *J. Phys. Chem. A* **2004**, *108*, 11151−11159.
(20) Danishefsky, S. *Acc. Chem. Res.* **1981**, *14*, 400−406.
(21) Nunzi, F.; Mercuri, F.; Sgamellotti, A.; Re, N. *J. Phys. Chem. B* **2002**, *106*, 10622−10633.

JA065698G