DOI: 10.1002/ejoc.200600196

A Co-Functionalization Approach to Soluble and Functional Single-Walled Carbon Nanotubes

Matteo D'Este,[a] Marco De Nardi,[a] and Enzo Menna*[a]

Keywords: Nanotubes / Synthetic methods / Amides / Fluorescence spectroscopy

A new class of single-walled carbon nanotube (SWNT) derivatives have been synthesized by means of an oxidation route that leads to shortened nanotubes bearing carboxylic acid end groups. The simultaneous attachment of poly(ethylene glycol)amine (PEG–NH_2) and amine derivatives of aromatic fluorophores was achieved through the formation of amide bonds. Different soluble products have been obtained from 2-aminofluorene, 2-aminoanthracene and 1-aminomethylnaphthalene. Basic spectroscopic characterization revealed peculiar features, such as quenching of the fluorescence, that suggest intramolecular interactions between the tubes and the attached aromatic moieties. The proposed co-functionalization procedure could be easily extended to obtain a wide range of soluble organic derivatives of SWNTs.

Introduction

Since their first observation in 1991[1] carbon nanotubes (NTs), and especially single-walled carbon nanotubes (SWNTs)[2,3] have attracted great attention because of their unique properties.[4–7] After the earlier example of chemically functionalized NTs, that was reported at the end of the 1990s,[8] a great deal of functionalized NTs appeared in the literature.[9–14] In fact, the route toward application of SWNTs in biology and material science passes through the chemical modification of NTs, that allows the preparation of soluble compounds and the derivatization with functional molecular moieties. Sidewall functionalizations[15–18] with different methods[19–27] have been reported, while a different approach is based on the end functionalization through oxidation routes[8,13,28–30] that lead to shortened nanotubes bearing carboxylic acid end groups.[11,31–35]

Recently, covalent and noncovalent functionalization strategies have been employed for the preparation of several derivatives of SWNTs bearing dye units.[36–41] Despite the interesting properties shown by such compounds, their solubility, when reported, is found to be of the order of 10^{-1} mg/mL or less. Besides, the nature of the molecular moiety grafted to the NT rules the method of preparation and the solubility of the product.

We now report an application of the end-functionalization route to soluble derivatives of SWNTs bearing polycyclic aromatics with fluorescence properties. Poly(ethylene glycol) (PEG) was selected as solubilizing moiety because it is widely used for such purpose,[42] especially in medicinal chemistry, and also in the field of NTs it has been already experimented.[31,43–45] We ourselves reported a procedure for the microwave-assisted synthesis of an SWNT-PEG derivative.[46]

Results and Discussion

Co-functionalization of SWNTs with PEG and polycyclic aromatics with fluorescence properties was obtained by an amidation reaction, on the basis of established literature procedures (Scheme 1).

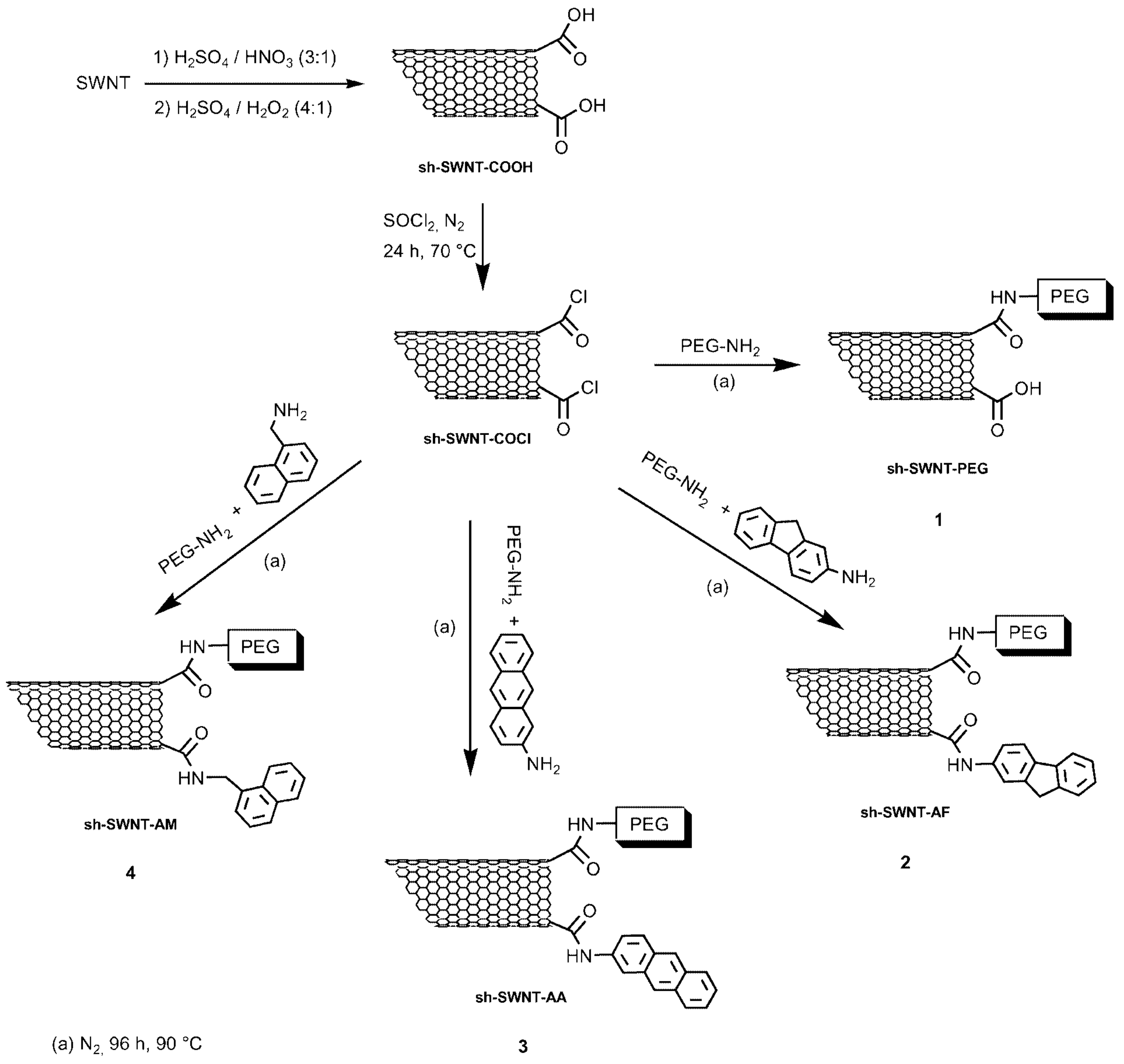
Commercial HiPco SWNTs were cut and etched according to a reported procedure,[28] to give shortened SWNTs bearing carboxylic groups at their ends and also as defect sites on the sidewalls (sh-SWNT-COOH). Sonication during the cutting protocol was reduced to 35 min. In a previously reported study on HiPco SWNTs, we found that this treatment time leads to a good degree of functionalization while avoiding excessive degradation of SWNTs.[47] According to the original work by Haddon and coworkers,[8] carboxylic groups were activated through $SOCl_2$ treatment to obtain the corresponding acyl chlorides (sh-SWNT-COCl), that were then allowed to react with excess of poly(ethylene glycol)monoamine (PEG–NH_2, molecular weight 5000) together with an amine derivative (25% by weight) of three different polycyclic aromatics: 2-aminofluorene, 2-aminoanthracene and 1-aminomethylnaphthalene. According to Scheme 1, the resulting co-functionalized products have been named sh-SWNT-AF (**2**), sh-SWNT-AA (**3**), sh-SWNT-AM (**4**), while the reaction of sh-SWNT-COCl with neat PEG–NH_2 afforded sh-SWNT-PEG (**1**).

All amidation reactions were carried out under the same conditions, without solvent, under inert gas at 90 °C for

---

[a] Dipartimento di Scienze Chimiche, Università di Padova,
Via Marzolo 1, 35131 Padova, Italy
Fax: +39-049-827-5239
E-mail: enzo.menna@unipd.it

Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.



Scheme 1.

96 h. At such temperature PEG–NH_2 (m.p. ca. 70 °C) forms a viscous fluid that can be stirred and homogeneously mixed with the other reactants. The reaction mixture was diluted with warm water, then filtered through a 0.1-µm membrane and washed successively with water, ethanol and methanol. From the black solid a soluble fraction was extracted by means of sonication/centrifugation cycles with different portions of CH_2Cl_2 (DCM). From the combined colored DCM supernatants, functionalized SWNTs were precipitated with cyclohexane. The product was repeatedly washed with cyclohexane and the washings checked by UV/Vis spectroscopy to assess the absence of any residual fluorophore. Then the samples were dried in vacuo at 70 °C overnight.

The SWNT derivatives **1**–**4** were found to exhibit good solubility (up to 5 mg/mL) in chloroform, tetrahydrofuran, dichloromethane, and slightly lower (about 1 mg/mL) in water.

In order to confirm the amide nature of the bond between the SWNTs and the functionalizing moieties, a test was done by applying the same procedure, but omitting the $SOCl_2$ activation. No soluble SWNT derivatives were obtained under these conditions, thus excluding any hypothesis of non-covalent linkages, such as polymer wrapping or salt formation. Moreover, the absence of unreacted fluorophores in the final material has been confirmed by GC-MS, that showed the release of the polycyclic moieties only for the mixtures of SWNTs and fluorophores and not for the derivatives **2**–**4**.

Soluble products were characterized by thermogravimetric analysis (TGA), Raman, NMR, IR, UV/Vis and fluorescence spectroscopy.

The Raman spectra of the derivatives **1**–**4** show all the features of original HiPco NTs, confirming that the basic structure of the NTs is substantially unperturbed upon the chemical processing.

The loading of PEG in functionalized SWNTs can be determined from TGA.[31] Figure 1 shows the TGA graph for sh-SWNT-PEG (**1**), where two distinct decompositions are visible. The first one (below 450 °C) is assigned to the PEG chain, by comparing with the thermogram for PEG–NH_2 (dotted line), while the second one (above 450 °C) is related to the depletion of SWNTs with diverse diameters (continuous line). The amount of PEG loading estimated from the graph is about 45% by weight. The fraction of carbon atoms that are functionalized with PEG (molecular weight 5000) can then be calculated with the following equation: $(0.45/5000)/(0.55/12) = 0.2\%$.

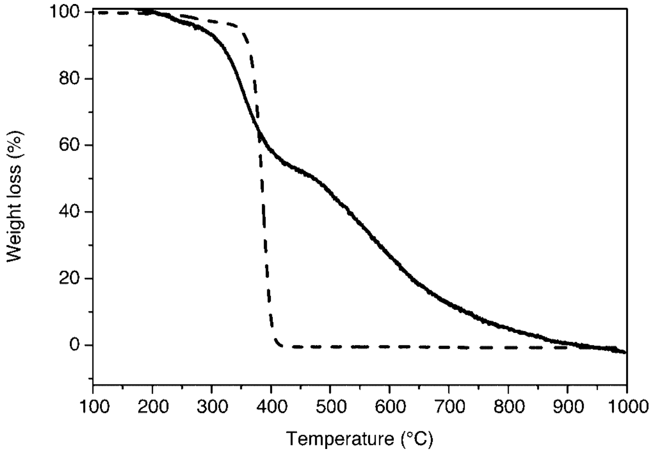


Figure 1. TGA graph for sh-SWNT-PEG **1** (continuous) and PEG–NH_2 (dashed).

Unfortunately, TGA measurements on co-functionalized derivatives (**2**–**4**) do not allow to distinguish between the decomposition of the two functional moieties.

^1H NMR (250 MHz, $CDCl_3$) spectra of the derivatives **1**–**4** show a resonance centered at $\delta = 3.64$ ppm due to the methylene groups of PEG chains and, for co-functionalized derivatives **2**–**4**, also some signals of aromatic protons on the fluorophore units can be recognized. Compared with the amine precursors,[48–50] such resonances are strongly broadened, in agreement with previous functionalization studies reporting the widening and weakening of signals for protons in proximity to SWNTs.[8,25,29,51,52] Such effect can be ascribed to the slow tumbling of SWNT derivatives in solution and to the presence of strong ring currents in the tube walls.[8,25,29] It is worthy of note that the band broadening is especially pronounced for the protons closer to the amide group and thus to the NT wall. Such protons are in fact subjected to a wide range of chemical environments depending on their position along the tube. For sh-SWNT-AA (**3**) these weak signals are at $\delta = 6.98$ and 7.08 ppm (Figure 2).

IR spectra of the products show some characteristic features of carboxylic derivatives of SWNTs.[8,29,35] The spectrum of derivative **2**, for example, is shown in Figure 3, where the band at 1647 cm^{-1} can be assigned to the C=O stretching of the amide carbonyl vibration, while the band at 1731 cm^{-1} can be assigned to the C=O stretching of the residual carboxylic acid groups on functionalized SWNTs. Similar bands in the same spectral regions are found also for the products **3** and **4**.

Compound **1** shows non-vanishing absorption in the UV/Vis range, with characteristic van Hove singularities in the Vis/NIR region of the spectrum. Superimposed to those features, the derivatives **2**–**4** show also the characteristic absorption bands of each fluorophore (Figure 4).

These bands appear substantially unchanged except for a broadening and a shift of the maximum (up to 5 nm for compound **3**).[53] Such variations are symptomatic of electronic communication between the π-structures of the fluorophore moiety and the nanotube.[40]

UV/Vis spectroscopy can also be used to obtain a rough estimate of fluorophore loading. By subtracting the absorp-

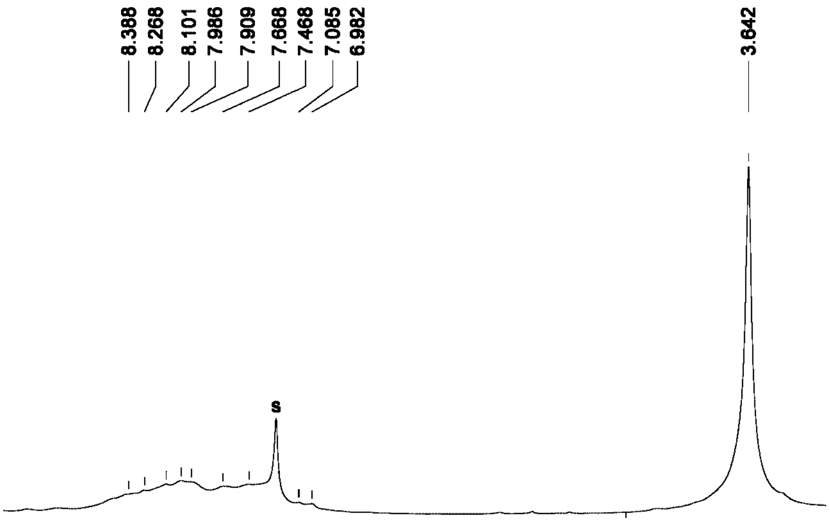


Figure 2. ^1H NMR spectrum of sh-SWNT-AA (**3**).

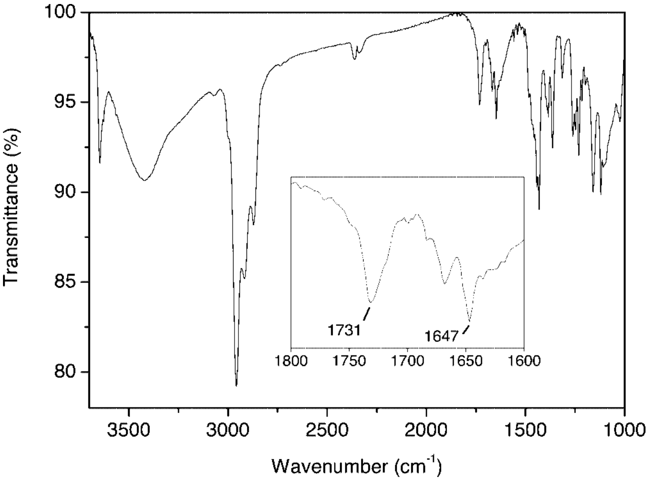


Figure 3. IR spectrum (KBr pellet) of sh-SWNT-AF (**2**). Inset: enlargement of the C=O stretching region.

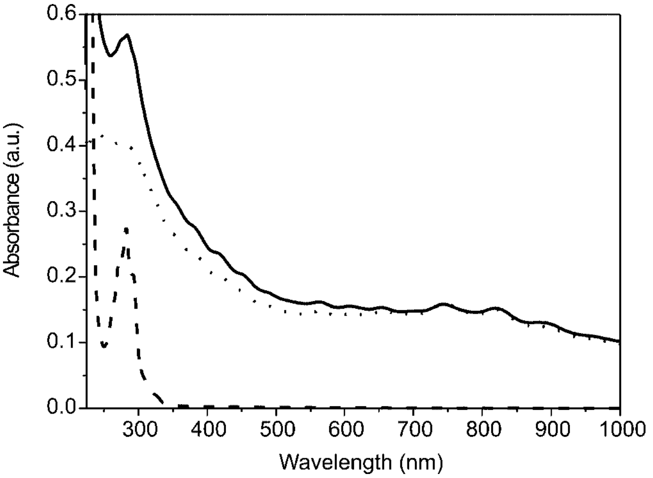


Figure 4. UV/Vis spectra of derivatives **1** (dotted), **4** (continuous), and 1-(aminomethyl)naphthalene (dashed).

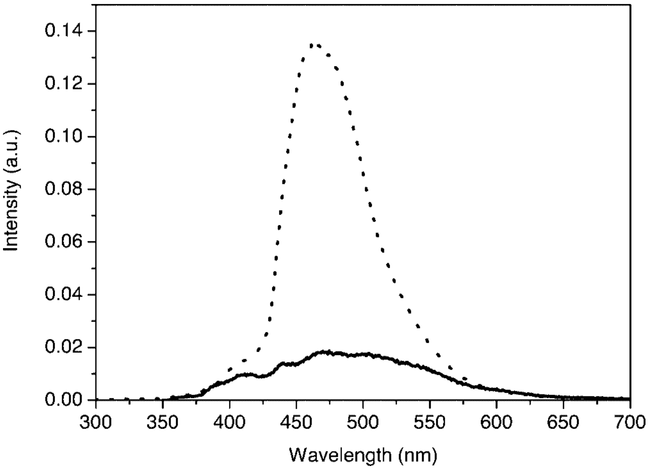


Figure 5. Emission spectra (in CH_2Cl_2) of 2-aminoanthracene ($3.80 \cdot 10^{-6}$ M) (dotted) and derivative **3** with equivalent absorbance at 261 nm (continuous) in CH_2Cl_2.

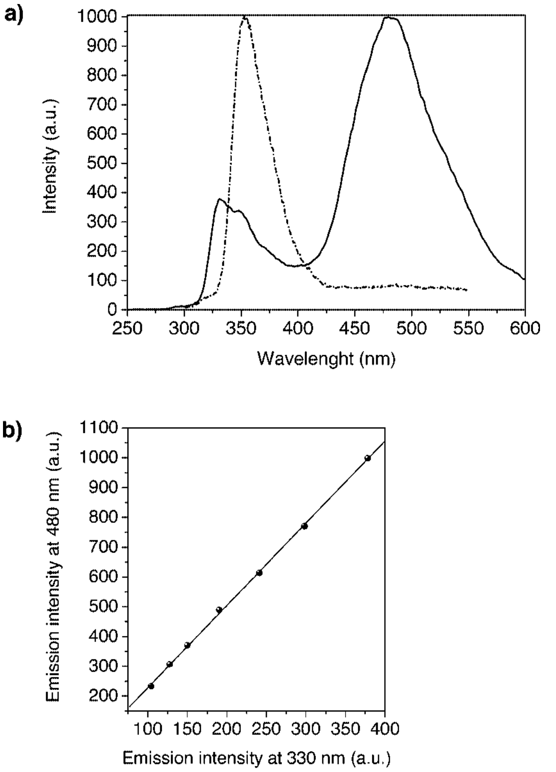


Figure 6. a) Emission spectra of derivative **2** (continuous) and 2-aminofluorene (dashed) in CH_2Cl_2. b) Plot of emission intensity of **2** at 480 nm vs. emission intensity at 330 nm at different concentrations.

tion spectrum of soluble SWNTs (without fluorophores) from those of the adducts **2**–**4**, we calculated the fluorophore amount as weight fraction: 4% for derivative **2**, 6% for derivative **3**, and 2% for derivative **4**.

The emission spectrum of each co-functionalized derivative has been compared with that of the corresponding aminofluorophore, considering pairs of solutions with matching absorption. All the species show substantial quenching of fluorescence, again suggesting an energy exchange between the excited fluorophore and the NT.[40,41] Figure 5 shows the fluorescence spectra of compound **3** and 2-aminoanthracene for solutions of matching absorption.

The quenching factor is 6.4, while for compound **4** it is quantitative. For derivative **2** (Figure 6), fluorescence quenching is accompanied by the growth of a second broader emission band at longer wavelengths (480 nm), that can be ascribed to the formation of a complex at the excited state.

In order to confirm that the observed spectroscopic features are originated by a covalently bound SWNT–fluorophore system, simple solution mixtures of derivative **1** and 2-aminofluorene have been examined, while varying the concentration ratio in a wide range. No one of such mixtures showed the band at 480 nm observed for material **2**. Moreover, the intensity ratio between the emission at 480 nm to that at 330 nm is independent of the solution concentration (see Figure 6). This behavior is consistent with the formation of a complex of intramolecular nature (i.e. a covalent link between the NT and the fluorophore).

Conclusions

In summary, we propose here a strategy to obtain soluble SWNT derivatives bearing a functional moiety that, in principle, can be extended to a wide range of functional addends. Good solubility, independent from the functional moiety, is provided by PEG chains, that usually do not influence physico-chemical properties such as photophysical and electrochemical behaviors, and that is also compatible with biological environments. In particular we have tested our co-functionalization method with three functional units belonging to the family of polycyclic aromatic fluorophores. The resulting SWNT derivatives show interesting spectroscopic properties that are worthy of deeper investigations. Thanks also to their solubility properties, the reported products could be useful models for a further development of SWNT-based advanced materials.

Experimental Section

General: For all sonications a 150-W ultrasonic cleaning bath, operating at 45 kHz, was used. NMR spectra were recorded with a Bruker AC 250 spectrometer (5.9 T, 250.1 MHz for ^{1}H). UV/Vis spectra were recorded with a Perkin–Elmer Lambda 45 spectrometer, fluorescence spectra were recorded with a Perkin–Elmer LS 55 spectrometer with excitation wavelength at the absorption maximum, Raman spectra were registered with a Renishaw InVia microraman spectrometer, IR spectra were recorded with a Nicolet 5700 FT-IR spectrometer. GC-MS was performed with a Agilent 6850 series GC system.

Starting Materials: Purified HiPco SWNTs were purchased from Carbon Nanotechnologies Inc., Houston, TX. Poly(ethylene glycol)monoamine (PEG–NH$_2$, molecular weight 5000) was purchased from Nektar Therapeutics, Huntsville, AL. All remaining reagents and solvents were purchased from Sigma–Aldrich.

Cutting and Activation of SWNTs: Shortened SWNTs bearing carboxylic groups (sh-SWNT-COOH) at their open ends were prepared from HiPco SWNTs according to ref.[28] with a cutting time reduced to 35 min.[47] Carboxylic groups were activated by SOCl$_2$ according to ref.[8] to obtain the corresponding acyl chlorides (sh-SWNT-COCl).

sh-SWNT-PEG (1): PEG–NH$_2$ (300 mg) and sh-SWNT-COCl (13 mg) were stirred at 90 °C under dry nitrogen for 96 h. The black solid obtained after cooling the viscous reaction mixture was diluted with warm water, then filtered through a polycarbonate membrane (Millipore VCTP, 0.1 μm pore size) and washed with water (8 × 30 mL), ethanol (15 mL) and methanol (15 mL). The solid material was dispersed in CH$_2$Cl$_2$ (DCM, 10 mL), sonicated for 15 min and centrifuged. The solid residue was separated from the supernatant and further washed with DCM (5 × 10 mL). The combined DCM washings were concentrated at reduced pressure, and the solid product was precipitated upon addition of cyclohexane (5 mL) and centrifuged. The product was then washed with cyclohexane (6 × 5 mL), and dried in vacuo to afford 7.5 mg of a black solid material.

SWNTs Derivatives 2–4: The fluorophore-grafted derivatives **2**–**4** were obtained according to the same procedure as for **1**, by replacing neat PEG–NH$_2$ with a mixture of PEG–NH$_2$ and the proper aminofluorophore (25% by weight): 2-aminofluorene for sh-SWNT-AF (**2**), 2-aminoanthracene for sh-SWNT-AA (**3**) and 1-(aminomethyl)naphthalene for sh-SWNT-AM (**4**).

Supporting Information (see footnote on the first page of this article): Raman spectrum for compound **2**; NMR spectra for **2** and **4**. IR spectra for **3** and **4**. UV/Vis spectra for **2** and **3**; emission spectra for **3** and **4**.

Acknowledgments

Thanks are due to M. Meneghetti and G. Marcolongo for Raman spectra and to M. Maggini for helpful discussions. Funding from MIUR (GR/No. 2004035502, RBAU017S8R, RBNE01P4JF) and from ITM-CNR is gratefully acknowledged.

[1] S. Iijima, *Nature* **1991**, *354*, 56–58.
[2] D. S. Bethune, C. H. Kiang, M. S. Devries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, *Nature* **1993**, *363*, 605–607.
[3] S. Iijima, T. Ichihashi, *Nature* **1993**, *363*, 603–605.
[4] M. S. Dresselhaus, G. Dresselhaus, P. Avouris, *Carbon Nanotubes: Synthesis Structure, Properties, and Applications*, Springer, Heidelberg, **2001**, p. 447.
[5] R. Saito, G. Dresselhaus, M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, London, **1998**, p. 258.
[6] T. W. Ebbesen, *Carbon Nanotubes: Preparation and Properties*, CRC Press, Boca Raton, FL, **1996**, p. 304.
[7] M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, New York, **1996**, p.
[8] J. Chen, M. A. Hamon, H. Hu, Y. S. Chen, A. M. Rao, P. C. Eklund, R. C. Haddon, *Science* **1998**, *282*, 95–98.
[9] A. Hirsch, *Angew. Chem. Int. Ed.* **2002**, *41*, 1853–1859.
[10] S. Banerjee, T. Hemraj-Benny, S. S. Wong, *Adv. Mater.* **2005**, *17*, 17–29.
[11] Y. P. Sun, K. F. Fu, Y. Lin, W. J. Huang, *Acc. Chem. Res.* **2002**, *35*, 1096–1104.
[12] A. Hirsch and O. Vostrowsky, in: *Functionalization of carbon nanotubes*, Springer-Verlag Berlin, Berlin, **2005**, vol. 245, pp. 193–237.
[13] S. Niyogi, M. A. Hamon, H. Hu, B. Zhao, P. Bhowmik, R. Sen, M. E. Itkis, R. C. Haddon, *Acc. Chem. Res.* **2002**, *35*, 1105–1113.
[14] Y. Lin, S. Taylor, H. P. Li, K. A. S. Fernando, L. W. Qu, W. Wang, L. R. Gu, B. Zhou, Y. P. Sun, *J. Mater. Chem.* **2004**, *14*, 527–541.
[15] C. A. Dyke, J. M. Tour, *J. Phys. Chem. A* **2004**, *108*, 11151–11159.
[16] J. E. Riggs, Z. X. Guo, D. L. Carroll, Y. P. Sun, *J. Am. Chem. Soc.* **2000**, *122*, 5879–5880.
[17] D. B. Mawhinney, V. Naumenko, A. Kuznetsova, J. T. Yates, J. Liu, R. E. Smalley, *J. Am. Chem. Soc.* **2000**, *122*, 2383–2384.
[18] E. Dujardin, T. W. Ebbesen, A. Krishnan, M. M. J. Treacy, *Adv. Mater.* **1998**, *10*, 1472–1475.
[19] H. Hu, B. Zhao, M. A. Hamon, K. Kamaras, M. E. Itkis, R. C. Haddon, *J. Am. Chem. Soc.* **2003**, *125*, 14893–14900.
[20] Y. Chen, R. C. Haddon, S. Fang, A. M. Rao, W. H. Lee, E. C. Dickey, E. A. Grulke, J. C. Pendergrass, A. Chavan, B. E. Haley, R. E. Smalley, *J. Mater. Res.* **1998**, *13*, 2423–2431.
[21] M. Holzinger, J. Abraha, P. Whelan, R. Graupner, L. Ley, F. Hennrich, M. Kappes, A. Hirsch, *J. Am. Chem. Soc.* **2003**, *125*, 8566–8580.
[22] M. Holzinger, O. Vostrowsky, A. Hirsch, F. Hennrich, M. Kappes, R. Weiss, F. Jellen, *Angew. Chem. Int. Ed.* **2001**, *40*, 4002–4005.
[23] V. Georgakilas, D. M. Guldi, R. Signorini, R. Bozio, M. Prato, *J. Am. Chem. Soc.* **2003**, *125*, 14268–14269.
[24] V. Georgakilas, N. Tagmatarchis, D. Pantarotto, A. Bianco, J. P. Briand, M. Prato, *Chem. Commun.* **2002**, 3050–3051.

[25] V. Georgakilas, K. Kordatos, M. Prato, D. M. Guldi, M. Holzinger, A. Hirsch, *J. Am. Chem. Soc.* **2002**, *124*, 760–761.
[26] J. L. Bahr, J. P. Yang, D. V. Kosynkin, M. J. Bronikowski, R. E. Smalley, J. M. Tour, *J. Am. Chem. Soc.* **2001**, *123*, 6536–6542.
[27] E. T. Mickelson, C. B. Huffman, A. G. Rinzler, R. E. Smalley, R. H. Hauge, J. L. Margrave, *Chem. Phys. Lett.* **1998**, *296*, 188–194.
[28] J. Liu, A. G. Rinzler, H. J. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, S. Young-Seok, T. R. Lee, D. T. Colbert, R. E. Smalley, *Science* **1998**, *280*, 1253–1256.
[29] M. A. Hamon, J. Chen, H. Hu, Y. S. Chen, M. E. Itkis, A. M. Rao, P. C. Eklund, R. C. Haddon, *Adv. Mater.* **1999**, *11*, 834–840.
[30] S. Banerjee, S. S. Wong, *Nano Lett.* **2002**, *2*, 49–53.
[31] B. Zhao, H. Hu, A. P. Yu, D. Perea, R. C. Haddon, *J. Am. Chem. Soc.* **2005**, *127*, 8197–8203.
[32] Y. C. Ni, H. Hu, E. B. Malarkey, B. Zhao, V. Montana, R. C. Haddon, V. Parpura, *J. Nanosci. Nanotechnol.* **2005**, *5*, 1707–1712.
[33] N. W. S. Kam, H. J. Dai, *J. Am. Chem. Soc.* **2005**, *127*, 6021–6026.
[34] A. Kitaygorodskiy, W. Wang, S. Y. Xie, Y. Lin, K. A. S. Fernando, X. Wang, L. W. Qu, B. Chen, Y. P. Sun, *J. Am. Chem. Soc.* **2005**, *127*, 7517–7520.
[35] H. Hu, Y. C. Ni, S. K. Mandal, V. Montana, N. Zhao, R. C. Haddon, V. Parpura, *J. Phys. Chem. B* **2005**, *109*, 4285–4289.
[36] D. M. Guldi, G. M. A. Rahman, F. Zerbetto, M. Prato, *Acc. Chem. Res.* **2005**, *38*, 871–878.
[37] G. M. A. Rahman, D. M. Guldi, R. Cagnoli, A. Mucci, L. Schenetti, L. Vaccari, M. Prato, *J. Am. Chem. Soc.* **2005**, *127*, 10051–10057.
[38] N. Nakashima, Y. Tomonari, H. Murakami, *Chem. Lett.* **2002**, 638–639.
[39] D. M. Guldi, G. M. A. Rahman, N. Jux, N. Tagmatarchis, M. Prato, *Angew. Chem. Int. Ed.* **2004**, *43*, 5526–5530.
[40] D. M. Guldi, G. M. A. Rahman, N. Jux, D. Balbinot, N. Tagmatarchis, M. Prato, *Chem. Commun.* **2005**, 2038–2040.
[41] D. Baskaran, J. W. Mays, X. P. Zhang, M. S. Bratcher, *J. Am. Chem. Soc.* **2005**, *127*, 6916–6917.
[42] J. M. Harris, S. Zalipsky, *Chemistry and Biological Applications of Polyethylene Glycol*, ACS Books, Washington, DC, **1997**, p.
[43] M. Sano, A. Kamino, J. Okamura, S. Shinkai, *Langmuir* **2001**, *17*, 5125–5128.
[44] M. Shim, N. W. S. Kam, R. J. Chen, Y. M. Li, H. J. Dai, *Nano Lett.* **2002**, *2*, 285–288.
[45] W. J. Huang, S. Fernando, L. F. Allard, Y. P. Sun, *Nano Lett.* **2003**, *3*, 565–568.
[46] F. Della Negra, M. Meneghetti, E. Menna, *Fullerenes, Nanotubes, Carbon Nanostruct.* **2003**, *11*, 25–34.
[47] E. Menna, F. Della Negra, M. Dalla Fontana, M. Meneghetti, *Phys. Rev. B* **2003**, *68*, 193412.
[48] M. E. Jason, P. R. Kurzweil, *J. Org. Chem.* **1991**, *56*, 3664–3669.
[49] S. Berger, B. W. K. Diehl, *Magn. Reson. Chem.* **1989**, *27*, 201–203.
[50] E. M. Hampe, D. M. Rudkevich, *Tetrahedron* **2003**, *59*, 9619–9625.
[51] M. G. C. Kahn, S. Banerjee, S. S. Wong, *Nano Lett.* **2002**, *2*, 1215–1218.
[52] M. J. O'Connell, P. Boul, L. M. Ericson, C. Huffman, Y. Wang, E. Haroz, C. Kuper, J. Tour, K. D. Ausman, R. E. Smalley, *Chem. Phys. Lett.* **2001**, *342*, 265–271.

[53] We cannot exclude the presence of unreacted fluorophores in our samples. However, we have verified that by mixing sh-SWNT-PEG (**1**) with 2-aminoanthracene, followed by washing with cyclohexane, the residual fluorophore, if any, does not affect the UV/Vis spectrum which is identical to that of the starting sh-SWNT-PEG (**1**) sample.

Received: March 6, 2006