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Microwave-Induced Multiple Functionalization of Carbon Nanotubes

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Abstract: We describe a new synthetic strategy to produce multifunctionalized carbon nanotubes using a combination of two different addition reactions, the 1,3-dipolar cycloaddition of azomethine ylides and the addition of diazonium salts, both via a simple and fast microwave-induced method. The presence of multifunctionality on the SWNTs has been confirmed using the most useful techniques for the characterization of carbon nanotubes. The doubly functionalized SWNTs can be considered potentially useful for many interesting applications.

Introduction

Carbon nanotubes (CNTs) are considered most promising materials for applications in many fields.¹ Although much work has been devoted to facilitate their manipulation and to enhance their solubility, we are still far from considering CNTs as entities easy to integrate into organic, inorganic, or biological systems. One of the most powerful approaches to improve CNT handling is the covalent functionalization of their side walls and tips.² A wide variety of reactions have been described, most of them employing conventional chemical techniques, such as refluxing and/or sonication in organic solvents or mineral acids, often making use of high temperatures and/or pressures,³ long reaction times,⁴ or highly reactive species.⁵ While all this work has demonstrated that under harsh conditions nanotubes can be

chemically modified, only a few examples are known where carbon nanotubes have been functionalized with more than one functional group.⁶ This type of multifunctional CNTs would be very attractive for drug delivery applications,⁷ sensors,⁸ or in the preparation of composites.⁹ However, taking into account practical applications, where usually large amounts of materials are required, the reaction conditions are most often too lengthy and impractical. Therefore, alternative functionalization approaches are still highly desirable to enable new protocols, simple to execute and easy to scale up. Up to now, only the reaction of diazonium salts, explored at Rice University in J. Tour's group, has been scaled up to a reasonable extent.¹⁰

With the aim of optimizing a multiple functionalization approach, we developed a new synthetic strategy to produce multifunctional CNTs avoiding the use of long reaction times, toxic solvents, and extreme conditions. In 2002, our group described that 1,3-dipolar cycloaddition of azomethine ylides can readily occur on CNTs.¹¹ However, a severe limitation to this process is the great amount of DMF needed to disperse CNTs and the long reaction times necessary to make the reaction efficient (five days). It is known in organic chemistry that certain reactions can be microwave-assisted to improve selectivity and reduce reaction times.¹² Recent work has explored the use of this radiation to assist CNT functionalization in the presence

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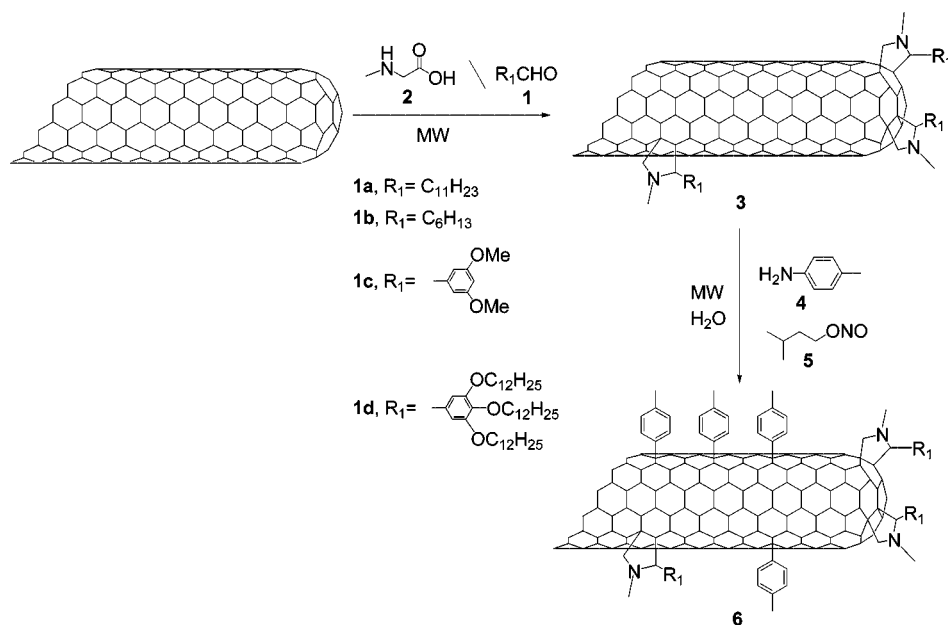
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Scheme 1



of strong oxidants,¹³ to synthesize a soluble derivative of short oxidized single-walled carbon nanotubes (SWNTs),¹⁴ to enable cycloadditions to prefunctionalized CNTs,¹⁵ and to perform radical¹⁶ or electrophilic¹⁷ additions. Recently, our group has also shown that a solvent-free technique combined with microwave irradiation produces functionalized nanotubes in just 1 h of reaction, paving the way to large-scale functionalization.¹⁸ This procedure provides a fundamentally different approach when considering the chemistry of CNTs, because under microwave irradiation and in the absence of solvents, pristine nanotubes behave in a way completely different from regular organic compounds.¹⁹

Diazonium salt chemistry is also a well-known method to functionalize carbon nanotubes in a very efficient manner.²⁰ Formation of diazonium salts in situ from aniline precursors is one method developed to avoid the direct use and long-term storage of diazonium compounds, thereby avoiding their potential laboratory hazard. Recently, Price and Tour described a synthetic route to obtain purified SWNTs “on water” in the presence of a substituted aniline and an oxidizing agent, which represents a “green” or environmentally friendly process.²¹

In the present work, we explore a new strategy for the double functionalization of as-produced, non-oxidized SWNTs with a

1,3-dipolar cycloaddition in solvent-free conditions and an arene radical addition in water; both reactions were performed via a microwave-induced method. The short reaction times, the absence of harsh conditions, and the wide range of products that can be obtained open the way to a green chemical protocol. By using this procedure, it is possible to obtain multifunctional SWNTs with a variety of groups that could be customized to fit a desired application. The multifunctional SWNTs have been characterized using several techniques, such as Raman and UV–vis–NIR spectroscopies, thermogravimetric analysis (TGA), and transmission electron microscopy (TEM), which not only have confirmed the double functionalization but also have allowed a better study of the efficiencies of both types of reactions.

Results and Discussion

In a first approach, pristine HiPco SWNTs were functionalized by 1,3-dipolar cycloaddition using different aldehydes (**1a–d**) and sarcosine (**2**) in solvent-free conditions under microwave irradiation (Scheme 1). The reactions were carried out in a CEM focused microwave reactor, model Discover, in a closed quartz tube with control of pressure. Different powers and ramp times were used to control the temperature (for details, see the Experimental Section), because in the absence of solvents the nanotubes display an extremely high microwave absorption. After 1 h of reaction, the crude was suspended in dichloromethane (DCM). The functionalized SWNTs (f-SWNTs) (**3**) were separated by filtration over a Millipore membrane (Fluoropore, 0.2 μm), washed with DCM and methanol, and dried. Characterization of the reaction products was performed using different spectroscopic, analytical, and microscopic techniques.

The Raman spectrum of the pristine SWNTs starting material shows a disorder-induced mode (D-band) with a very low intensity at 1314 cm^{-1} . Spectra of the functionalized material exhibit an increased intensity of the D band, indicating functionalization of the SWNTs since functional groups introduce sp^3 defects on the sp^2 network of the nanotube^{22,23} (Figure 1, exciting line = 632.8 nm).

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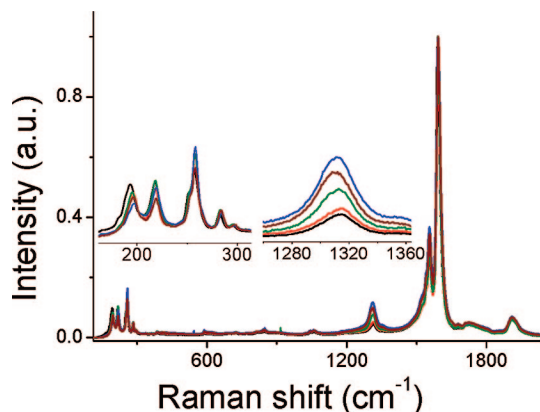


Figure 1. Raman spectra (633 nm) of pristine SWNTs (black line), f-SWNTs **3a** (green line), f-SWNTs **3b** (brown line), f-SWNTs **3c** (blue line), and f-SWNTs **3d** (red line).

Table 1. Comparative Study of the Functionalization of Compounds **3a–d**

| product | TGA wt loss (%) ^a | functional group coverage ^b | Raman D/G ratio ^c |
|-----------|------------------------------|--|------------------------------|
| 3a | 13 | 118 | 0.08 |
| 3b | 11 | 96 | 0.10 |
| 3c | 16 | 87 | 0.12 |
| 3d | 21 | 216 | 0.05 |

^a TGA-determined weight loss. ^b See ref 24. ^c Calculated D/G ratios from Raman spectra.

The ratios of the Raman D- to G-band intensities are reported in Table 1, together with the functionalization group coverage (number of SWNT carbon atoms per functional group) based on TGA weight loss.²⁴ These results suggest different degrees of functionalization and, accordingly, reactivity among the aldehydes reported in Scheme 1. Although no quantitative relationship between the D- over G-band ratio and the degree of functionalization calculated from TGA data have been found thus far, we clearly observe a qualitative and consistent trend (Table 1).

The Raman spectra also show that the microwave-assisted functionalization does not determine a preferential reactivity of metallic or semiconducting nanotubes. In fact, the radial breathing mode (RBM) spectral region below 400 cm⁻¹ (see inset to Figure 1) shows that the spectra of the pristine SWNTs and those of **3a–d** have the same bands for both semiconducting nanotubes, above 230 cm⁻¹, and metallic nanotubes, below this frequency.²⁵ One can only observe some intensity variation for metallic nanotubes, which are probably more easily functionalized, than semiconducting nanotubes.²⁶ However, the different intensity variation is not due to a selection of nanotubes operated by the reaction, but can be related to a variation of the resonance condition that can be particularly important for metallic nanotubes. This can be traced back to many effects such as debundling of nanotubes, which can also account for shifts of the van Hove singularities in the density of states of the order

of 0.1 eV.²⁷ Nevertheless, we cannot discard a doping effect introduced by the functional groups since it is known that doping suppresses the RBM intensities and in particular those of metallic nanotubes.²⁸ It is also worth noting that the bands at higher frequency, which are related to semiconducting nanotubes with small diameters, are preserved by the reaction, contrary to what happens when strong oxidation is used since in this latter case small diameter nanotubes, which are more reactive because of their increased curvature, are destroyed.²⁹

UV–vis–NIR spectra were recorded as DMF solution. The absorption spectrum of pristine SWNTs shows the characteristic van Hove singularities,²⁵ while the spectra of the functionalized material indicate a partial loss of these transitions as often observed upon functionalization, as a consequence of the change in hybridization of a high number of carbon atoms in the extended π -system³⁰ (Figure 2a; for clarity, only the spectrum of compound **3a** is reported). A very recent analysis of the variation of the electronic spectra of SWNT as a function of the number of functionalizing groups³¹ shows that only when the functional groups are of the order of 1 per 30–20 carbon atoms can one observe significant differences of the electronic spectra. Therefore, the ratios reported in Table 1 agree with the small variations of the intensity of the absorptions related to the van Hove singularities. All products **3a–d** exhibit similar spectral features (Supporting Information).

TEM indicates that f-SWNTs **3a–d** are present in small bundles. Figure 2b shows a representative image of **3a**.

Finally, the experimental data seem to show that the number of functionalized groups attached to the nanotubes does not depend on the aromatic or aliphatic nature of the aldehyde. There is some indication, though, that the steric hindrance of the aldehyde could influence the reaction course. When the experiments focused on the optimization of the reaction time, we observed that shorter times of irradiation lead to a smaller degree of functionalization (Table 2).

The novel f-SWNTs were subjected to diazonium salt reaction to introduce other functional groups on the same SWNTs. Therefore, f-SWNTs (**3a–d**) were dispersed in water with *p*-toluidine (**4**) in a microwave glass vessel. After being sonicated for a few minutes, isoamyl nitrite (**5**) was added and a condenser was connected to the flask. The mixture was irradiated for 90 min at 80 °C in the microwave reactor (Scheme 1). When heating was interrupted, the doubly functionalized SWNTs (ff-SWNTs) (**6a–d**) were separated from the solution by filtration over a Millipore membrane (Fluoropore, 0.2 μ m) and washed with methanol, acetone, and DCM.

Figure 3 reports representative Raman spectra showing an increase in the D-band of **6c** relative to that of **3c** and that of pristine nanotubes, which supports further functionalization after the arene radical addition. Table 3 gives the functional group coverage, obtained by TGA, along with the D/G ratio.

These values reveal that this second reaction introduces a higher number of functionalities relative to 1,3-dipolar cycloadd-

- (24) Total mass loss was attributed to functional groups covalently attached to the side walls. The number of functional groups was calculated considering the mass loss and the molecular weight of the molecular fragment. The residual mass was attributed to pristine SWNT, which was used to determine the mequiv of SWNT carbons present.
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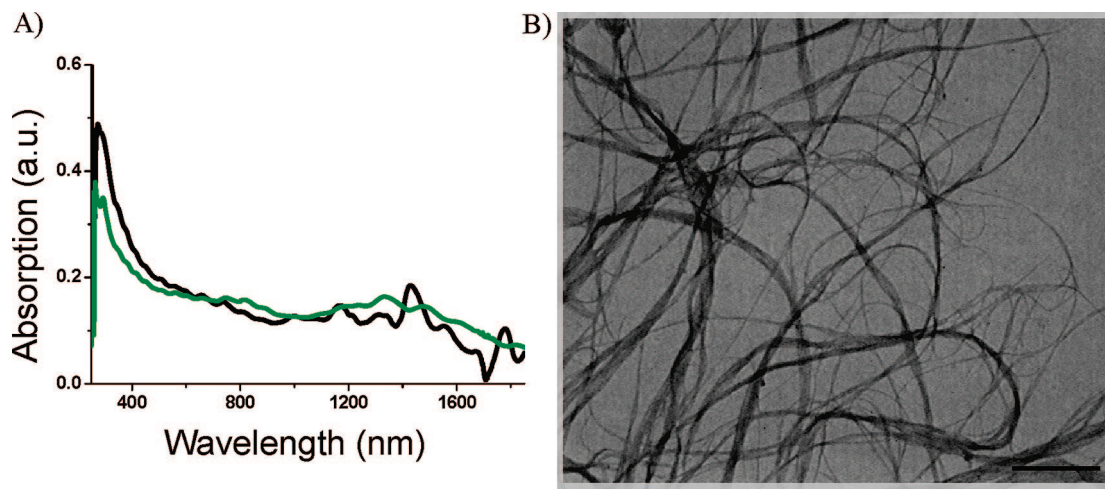


Figure 2. (A) UV-vis-NIR absorption spectrum in DMF of pristine SWNTs (black line) and f-SWNTs **3a** (green line). (B) TEM image of the f-SWNTs **3a** (scale bar is 500 nm).

Table 2. Comparative Study of the Functionalization of **3c** at Different Reaction Times

| reaction time (min) | TGA wt loss (%) ^a | functional group coverage ^b | Raman D/G ratio ^c |
|---------------------|------------------------------|--|------------------------------|
| 60 | 16 | 87 | 0.12 |
| 40 | 8 | 187 | 0.08 |
| 10 | 6 | 252 | 0.06 |

^a TGA-determined weight loss. ^b The functional group coverage was calculated following ref.²⁴ ^c Calculated D/G ratios from Raman spectra.

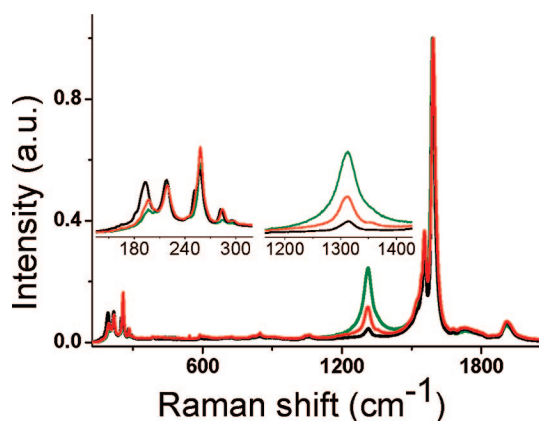


Figure 3. Raman spectra (633 nm) of pristine SWNTs (black line), f-SWNTs **3c** (red line), and ff'-SWNTs **6c** (green line).

Table 3. Comparative Study of the Functionalization of Compounds **6a–d**

| product | TGA wt loss (%) ^a | functional group coverage (1,3-dipolar cycloaddition) ^b | functional group coverage (arene radical addition) ^c | Raman D/G ratio ^d |
|-----------|------------------------------|--|---|------------------------------|
| 6a | 21 | 118 | 89 | 0.30 |
| 6b | 23 | 96 | 57 | 0.24 |
| 6c | 36 | 87 | 31 | 0.24 |
| 6d | 25 | 216 | 192 | 0.18 |

^a TGA results show total weight loss. ^b Coverage of the 1,3-dipolar cycloaddition is taken from Table 1. ^c The difference between the total weight loss and the weight loss after the first reaction (Table 1) gives the functional group coverage of the arene radical addition. ^d The Raman D/G ratios are considered after the two reactions.

dition. Nevertheless, it seems that, with the same number of groups added, the functionalization by 1,3-dipolar cycloaddition produces a smaller increase in the D-band than the radical addition (Tables 1–3). In principle, this might mean that

cycloadditions occur at close sites, leaving large parts of the π -system untouched, whereas the arene radical addition is more spread out. These results also confirm the fact that all the parameters that govern the D/G intensity band ratio are not completely understood, especially when comparing different functionalities.³²

Analysis of the RBM spectral region shows that all the bands observed for the pristine SWNT are always present, although one can note that not only the bands of the metallic nanotubes have intensity variations but also those related to semiconducting nanotubes (above 230 cm^{-1}) show some decrease in intensity. This probably derives from the fact that the larger functionalization obtained after the second reaction increases the number of “defects” to the level where all the nanotubes show some electronic perturbation of the van Hove singularities and therefore of the resonance condition of the Raman spectrum.

Table 3 also reveals that even though we have used pristine tubes and different reaction conditions from the classical conditions described by Price and Tour,²¹ the degrees of functionalization are comparable.

UV-vis-NIR spectrophotometry confirms an increase of the functionalization degree. Figure 4b shows a dramatic decrease in the van Hove singularities for ff'-SWNTs **6c** compared to that of f-SWNTs **3c**. This loss of features is particularly indicative of a heavy side wall functionalization, which has a large effect on the perturbation of the electronic structure of nanotubes. The different UV-vis-NIR spectra and the different Raman spectra seem to suggest differences in the functionalization, but in this case we increase, after the second reaction, the overall functionalization. Thus, in agreement with previous results, we confirm that the arene radical addition introduces “defects” that perturb the intrinsic periodicity of the conjugated nanotube π -system.³³

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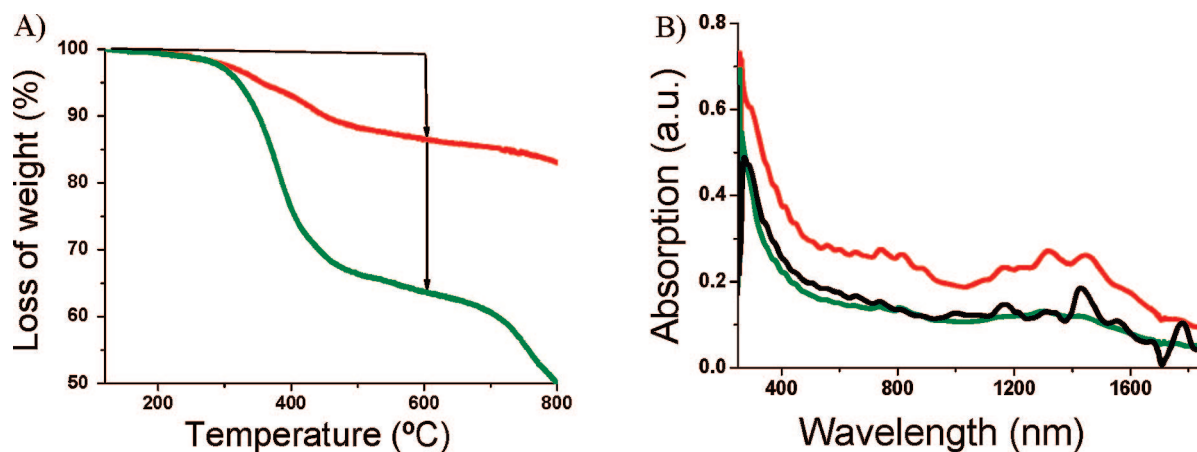


Figure 4. (A) TGA analysis of the f-SWNTs **3c** (red line) and ff'-SWNTs **6c** (green line). (B) UV-vis-NIR absorption spectra in DMF of pristine SWNTs (black line), f-SWNTs **3c** (red line), and ff'-SWNTs **6c** (green line).

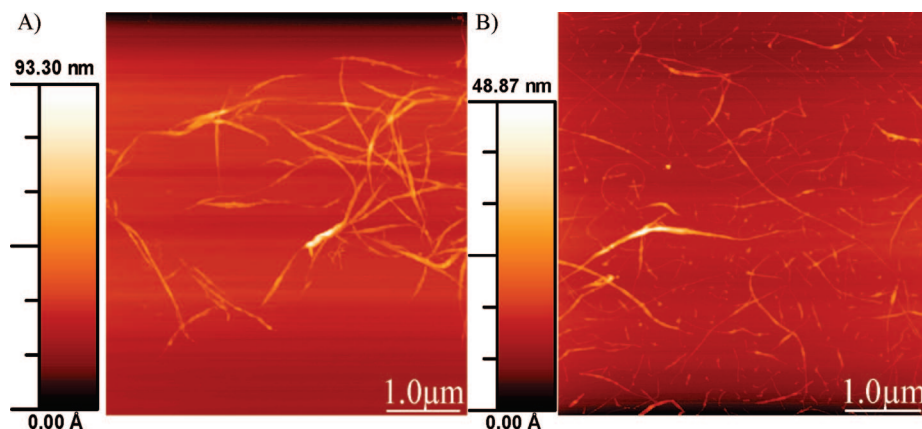


Figure 5. AFM images prepared by spin-coating on silicon wafer from DMF solution. Two representative images of (A) f-SWNTs **3c** and (B) ff'-SWNTs **6c**. TEM images agree with the AFM observations. Compound **3c** shows small bundles of functionalized SWNTs, whereas ff'-SWNT **6c** presents as individuals and well-dispersed thin bundles (Figure 6).

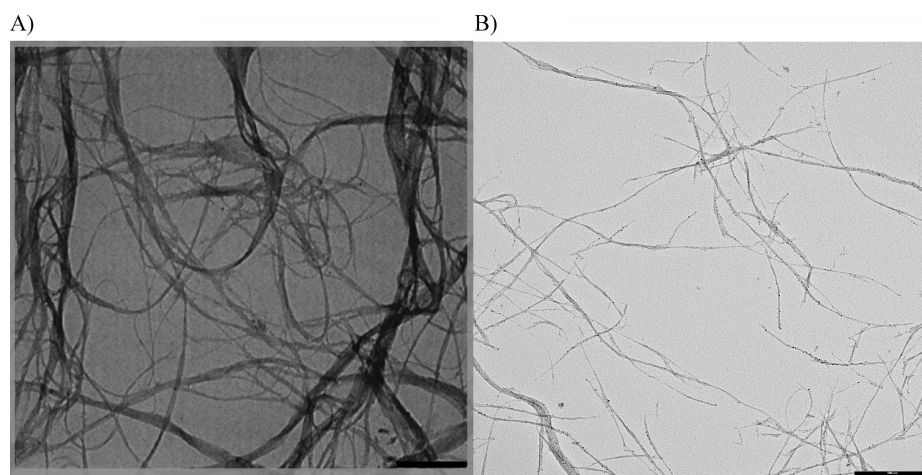


Figure 6. TEM images of (A) f-SWNTs **3c** (scale bar of 500 nm) and (B) ff'-SWNTs **6c** (scale bar of 500 nm).

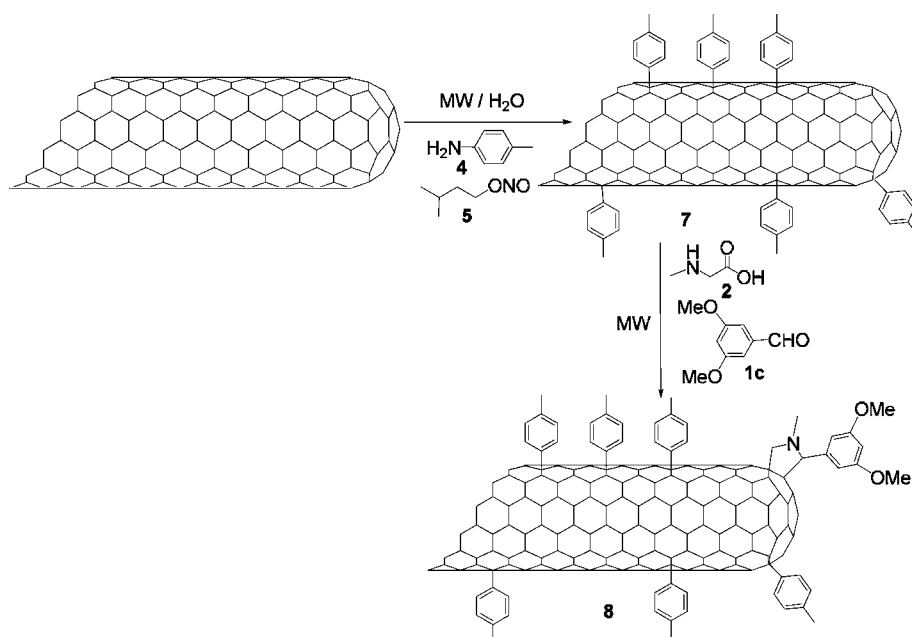
The same compounds have also been investigated by atomic force microscopy (AFM). The samples were prepared by spin-coating on a silicon wafer from a DMF solution. Two representative images of f-SWNTs **3c** and ff'-SWNTs **6c** are shown in Figure 5. The mean length of both types of functionalized nanotubes is typically on the order of several micrometers, while their diameters are quite different. f-SWNTs **3c** show heights between 3 and 18 nm, diameters that are consistent with small aggregates, whereas

ff'-SWNTs **6c** present diameters between 1 and 3 nm, which corresponds to individual SWNTs and thin bundles.

In view of these results and to better study the double functionalization, we changed the order of reactions and performed first the arene radical addition and then the 1,3-dipolar cycloaddition. (Scheme 2).

In this case, the Raman spectrum shows an increase of the D-band (D/G ratio) when the arene radical addition is performed,

Scheme 2



compared to that of the pristine nanotubes, while the same band does not increase after the second reaction (Figure 7).

The RBM modes show little activity also after the first reaction, and only for the metallic tubes is it possible to observe some variation, as before. However, TGA and UV–vis–NIR spectra show some evident changes after the second reaction (cycloaddition). On the basis of the TGA weight loss, we calculate that we have introduced one functional group every 56 SWNT carbons in the arene radical addition and only one functional group every 216 carbons in the 1,3-dipolar cycloaddition (Figure 8). This reaction using the same aldehyde and the same amino acid but carried out with pristine nanotubes introduced one functional group for 87 SWNT carbons (c.f. Table 1). This indicates that, once performed the radical addition, the 1,3-dipolar cycloaddition proceeds to a much lesser extent, probably because most of the reactive sites are saturated by arene groups. The UV–vis–NIR spectrum shows a more evident loss of the van Hove singularities. Thus, taken together, all these results suggest that the 1,3-dipolar cycloaddition shows a certain reactivity only for the more reactive positions, while the arene radical addition seems to be less selective and could also take

place on the less reactive points of the nanotubes. More experiments are needed to corroborate this hypothesis.

Conclusions

We have performed a comprehensive study of the microwave-induced reactivity of SWNT using two different well-established addition reactions. The 1,3-dipolar cycloaddition of azomethine ylides can be achieved in only 1 h using MW instead of 5 days, necessary for the conventional thermal conditions. The addition of diazonium salts can also be performed using microwaves with results very similar to the classical conditions reported by Price and Tour.²¹ The two reactions can be performed in series. The results show that the radical arene addition saturates more reactive sites than the cycloaddition. Therefore, to attach two different functional groups to SWNTs, the order of reaction should be first the cycloaddition and then the arene addition. This gives rise to comparable functionalization degrees for the two additions. If only a few functional groups are required along with an excess of other organic/inorganic groups, then the functionalization order can be reversed. This latter could be the case of some biomedical applications, where, for example, much more drug molecules are needed with respect to a contrast agent. Work along these lines is currently under development in our laboratories.

Experimental Section

Techniques. Microwave irradiations were carried out in a CEM Discover reactor, with infrared pyrometer, pressure control system, stirring, and air-cooling option. UV–vis–NIR spectra were recorded in 1-cm quartz cuvettes on a Varian Cary 5000 spectrophotometer. The thermogravimetric analyses were performed with a TGA Q500 (TA Instruments) at 10 °C/min under N₂. Raman spectra were recorded with an InVia Renishaw microspectrometer equipped with a He–Ne laser. For the TEM analyses, a small amount of the functionalized SWNTs was suspended in DMF and a drop of the suspension was placed on a copper grid (3.00 mm, 200 mesh, coated with carbon film). After being air-dried, the sample was investigated by TEM Philips EM 208, accelerating voltage of 100 kV. For the AFM analyses, the samples were prepared by spin-coating on silicon wafers from a solution of

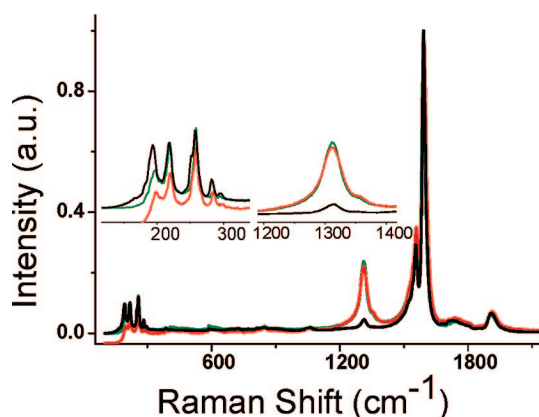


Figure 7. Raman spectra (633 nm) of pristine SWNTs (black line), f-SWNTs 7 (green line), and ff-SWNTs 8 (red line).

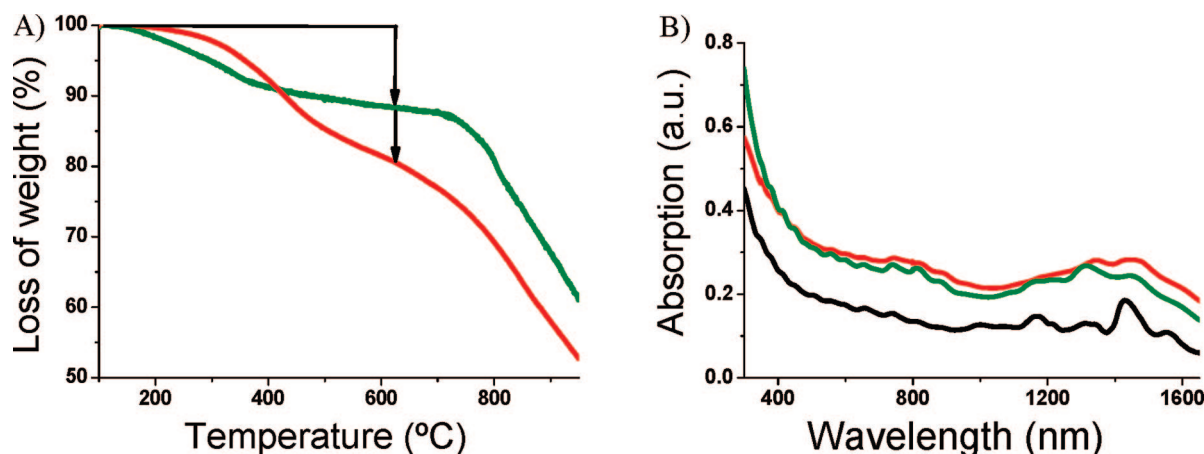


Figure 8. (A) TGA analysis of the f-SWNTs **7** (green line) and ff'-SWNTs **8** (red line). (B) UV-vis-NIR absorption spectra in DMF of the pristine SWNTs (black line), f-SWNTs **7** (green line), and ff'-SWNTs **8** (red line).

SWNTs in CH_2Cl_2 or DMF and then investigated with a Veeco multimode scanning probe microscope equipped with a Nanoscope IIIa controller.

Materials. Solvents were purchased from SDS and Fluka. All dry solvents were freshly distilled under argon over an appropriate drying agent before use. Chemicals were purchased from Sigma-Aldrich or Across Organics and used as received without further purification. Aldehyde **1d** was synthesized following the literature procedure.^{33b} HiPCO SWNTs were purchased from Carbon Nanotechnologies, Inc., lot # R0496 (<http://www.cnanotech.com>) and used without purification.

Synthesis. SWNTs 3a–c. In a typical experiment, 25 mg of pristine SWNTs was suspended in CH_2Cl_2 (5 mL) with 0.66 mmol of the corresponding aldehyde **1a** (121 mg), **1b** (75 mg), or **1c** (110 mg) and **2** (60 mg, 0.66 mmol) in a microwave quartz vessel. After sonication for 5 min, the solvent was evaporated under reduced pressure, the vessel was closed, and the mixture was irradiated for 1 h at different power and temperature (Table S1). After that time, the crude was resuspended in 75 mL of CH_2Cl_2 and sonicated for 5 min. The solution was filtered on a Millipore membrane (PTFE, 0.2 μm), and the collected black solid was washed with 75 mL of methanol and with 75 mL of CH_2Cl_2 (sonicated and filtered), affording f-SWNTs **3a–c** (**3a**: 26.9 mg, solubility^{33c} in CH_2Cl_2 0.20 mg mL^{-1} , in DMF 0.27 mg mL^{-1} ; **3b**: 26.0 mg, solubility in CH_2Cl_2 0.22 mg mL^{-1} , in DMF 0.27 mg mL^{-1} ; **3c**: 30 mg, solubility in CH_2Cl_2 0.33 mg mL^{-1} , in DMF 0.36 mg mL^{-1}).

SWNTs 3d. Pristine SWNTs (12.5 mg) were suspended in CH_2Cl_2 (2 mL) with **1d** (220 mg, 0.33 mmol) and **2** (30 mg, 0.33 mmol) in a microwave quartz vessel. After sonication for 5 min, the solvent was evaporated under reduced pressure, the vessel was closed, and the mixture was irradiated for 1 h at different power and temperature (Table S1a). After that time, the crude was resuspended in 35 mL of CH_2Cl_2 and sonicated for 5 min. The solution was filtered on a Millipore membrane (PTFE, 0.2 μm), and the collected black solid was washed with 35 mL of methanol and with 35 mL of CH_2Cl_2 (sonicated and filtered), affording 15 mg of f-SWNTs **3d** (solubility in CH_2Cl_2 0.22 mg mL^{-1} , in DMF 0.23 mg mL^{-1}).

SWNTs 6a–d. f-SWNTs **3a–d** (10 mg) were sonicated in deionized water together with (350 mg, 3.3 mmol) *p*-toluidine **4** for 10 min in a microwave glass vessel. Finally, isoamyl nitrite (0.22 mL, 1.6 mmol) was added, and a condenser was placed. The mixture was irradiated for 90 min at 80 °C at different power (100 W for 30 min, and after adding a new aliquot of isoamyl nitrite **5** 30 W for 60 min). After being cooled at room temperature, the crude was filtrated on a Millipore membrane (PTFE, 0.2 μm). Then the product was removed from the filter and washed with methanol

and acetone (sonicated and filtrated) until the filtrate was clear and finally washed with 40 mL of CH_2Cl_2 to yield the following functionalized SWNTs **6a–d** (11.5 mg of **6a**, solubility in CH_2Cl_2 0.26 mg mL^{-1} , in DMF 0.30 mg mL^{-1} ; 10.8 mg of **6b**, solubility in CH_2Cl_2 0.25 mg mL^{-1} , in DMF 0.35 mg mL^{-1} ; 11.1 mg of **6c**, solubility in CH_2Cl_2 0.50 mg mL^{-1} , in DMF 0.53 mg mL^{-1} ; 11.0 mg of **6d**, solubility in CH_2Cl_2 0.35 mg mL^{-1} , in DMF 0.42 mg mL^{-1}).

SWNTs 7. Pristine SWNTs (10 mg) were sonicated in deionized water together with (350 mg, 3.3 mmol) *p*-toluidine **4** for 10 min in a microwave glass vessel. Finally, isoamyl nitrite **5** (0.22 mL, 1.6 mmol) was added, and a condenser was added. The mixture was irradiated for 90 min at 80 °C at different power (100 W for 30 min, and after adding a new aliquot of isoamyl nitrite **5** 30 W for 60 min). After being cooled at room temperature, the crude was filtrated on a Millipore membrane (PTFE, 0.2 μm). The product was removed from the filter and washed with methanol and acetone (sonicated and filtrated) until the filtrate was clear and finally washed with 40 mL of CH_2Cl_2 , affording 13 mg of f-SWNTs **7** (solubility in CH_2Cl_2 0.27 mg mL^{-1} , in DMF 0.28 mg mL^{-1}).

SWNTs 8. f-SWNTs **7** (6.8 mg) were suspended in CH_2Cl_2 (2 mL) with **1c** (37 mg, 0.22 mmol) and **2** (20 mg, 0.22 mmol) in a microwave quartz vessel. After sonication for 5 min, the solvent was evaporated under reduced pressure, the vessel was closed, and the mixture was irradiated for 1 h at different power and temperature (Table S1a). After that time, the crude was resuspended in 40 mL of CH_2Cl_2 and sonicated for 5 min. The solution was filtered on a Millipore membrane (PTFE, 0.2 μm), and the collected black solid was washed with 40 mL of methanol and with 40 mL of CH_2Cl_2 (sonicated and filtered), affording 7.5 mg of f-SWNTs **8** (solubility in CH_2Cl_2 0.38 mg mL^{-1} , in DMF 0.32 mg mL^{-1}).

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Supporting Information Available: Detailed characterization data for all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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