Versatile microwave-induced reactions for the multiple functionalization of carbon nanotubes†

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Carbon nanotubes (CNTs) have been readily functionalized by microwave activation using two different reactions affording functional derivatives characterized by two orthogonally protected amino groups. The doubly functionalized CNTs can serve as multipurpose, versatile synthons in materials science and biological applications.

Introduction

High-speed treatment with microwaves has considerably improved our lives. Microwave (MW) heating is a widely accepted procedure not only for domestic uses but also for the industrial processing of foods and manufactured goods. MW heating has also become an established procedure in synthetic chemistry. There are many examples of MW-assisted organic synthesis (MAOS) leading to shorter reaction times, reduction of side reactions and higher yields.[1] Combination of solvent-free conditions or benign reaction media with MW irradiation is also an interesting and approved approach within the growing field of green chemistry.[2]

Among the many fields in which MAOS can afford remarkable results, the activation of carbon nanotubes (CNTs) represents one of the more interesting possibilities.[3] Since their discovery, CNTs have generated great expectations for their high potential in practical applications. However, their difficult manipulation has raised serious obstacles to many technological developments. One of the more powerful approaches to improve CNT handling is the covalent functionalization of their sidewalls and tips. Although carbon nanotube functionalization has been deeply investigated in recent years, their integration into organic, inorganic or biological systems is still a formidable challenge. In fact, it is not yet easy to achieve sufficient functionalization of the CNT surface to ensure an easy processing or to facilitate the attachment of functional moieties, while avoiding significant degradation of the structure. In addition, most of the described protocols require long periods of time and use of aggressive reagents that cause CNTs shortening and damage.[4]

When subjected to microwave treatment, CNTs absorb the radiations very strongly, while heating and light emission are produced. This strong absorption can be used to assist CNT functionalization.[5] In general, the reaction conditions applied under microwaves have been transposed from the ones used under classical heating. Instead, our group has developed a solvent-free technique combined with MW irradiation, which provides a fundamentally different approach.[6,7] In the absence of solvents, it is possible to take full advantage of the strong microwave absorption typical of pristine nanotubes. Moreover, the solvent-free conditions open the door to green protocols and large-scale functionalization.

In this paper we extend the scope of these MW-assisted reactions and show the versatility of this functionalization methodology. We have performed a comparative study of both cycloaddition and arylation reactions using classical heating and MW activation. We have also explored two different environmentally friendly reaction media, solvent-free conditions and the use of water as solvent, in order to better evaluate the use of microwaves for CNT functionalization. MW conditions offer the advantage of being energy saving, while differences in the reactivity of some type of tubes can be observed under solvent-free conditions. Moreover, we have prepared doubly functionalized CNTs with orthogonally protected amino functions that can be selectively deprotected and subsequently modified, therefore enhancing the number of possible functional CNT derivatives. Characterization of the reaction products is performed using several spectroscopic, analytical and microscopic techniques.

Results and discussion

In a first approach, pristine HiPco single-walled carbon nanotubes (SWNTs) were functionalized by 1,3-dipolar cycloaddition using α-aminoacid **1** and aldehyde **2** in solvent-free conditions under MW irradiation or using DMF as solvent in a classical heating protocol (Scheme 1). Aminoacid **1** was synthesized and employed in the cycloaddition, to produce functionalized SWNTs (f-SWNTs) **3** with an amino group protected as phthalimide. This protecting group is particularly useful as it is highly stable to harsh acidic conditions but it is easily removed under mild basic conditions. The hydrophilic oligoethylene glycol chain, also part of α-aminoacid **1**, will enhance the solubility of f-SWNTs in polar solvents.

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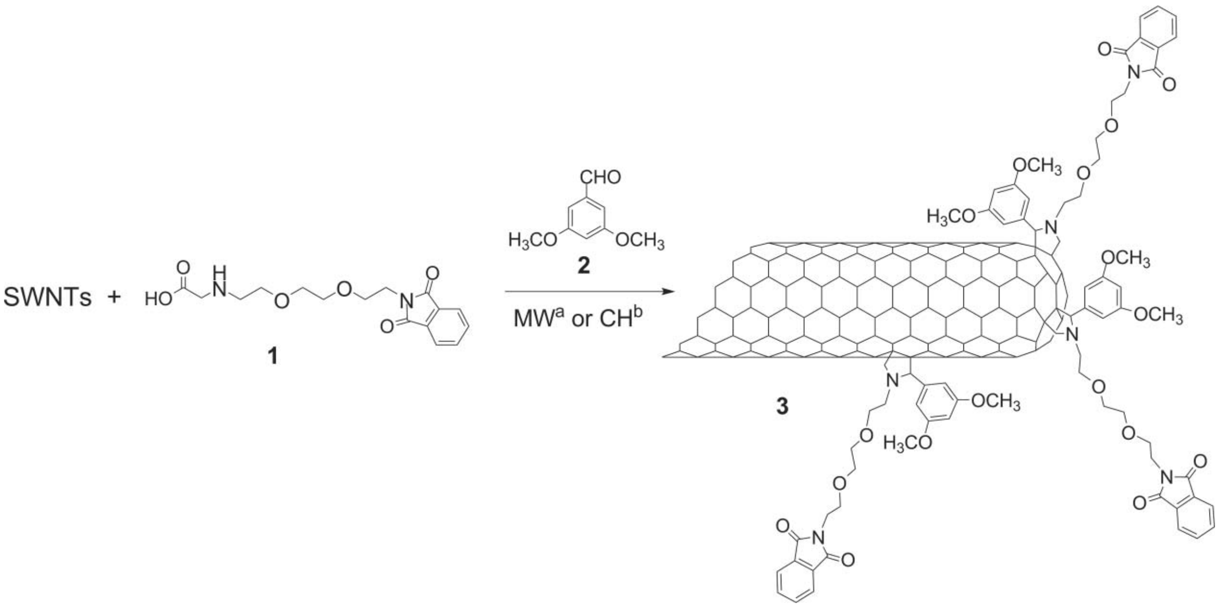


Scheme 1 ^{a}MW: 1 h under microwave irradiation in solvent-free conditions. ^{b}CH: 5 days of reaction under DMF reflux using classical heating.

To prepare *f*-SWNTs using MW activation in the absence of solvent, a careful control of the reaction conditions was performed. The functionalization was carried out in a CEM focused microwave reactor, model Discover, in a closed quartz tube with control of pressure. Different power and ramp times were used to control the temperature (for details see ESI†), because in solvent-free conditions, nanotubes display an extremely high microwave absorption. After 40 min of irradiation the reaction was stopped, and subsequent work-up was performed. When using classical heating, the reaction proceeded for 5 days under DMF reflux, while the aminoacid and the aldehyde were added portionwise every 24 h (see Experimental Section).

The amount of organic groups in the *f*-SWNTs was determined by thermogravimetric analysis (TGA).[8] The thermograms of *f*-SWNTs **3**, reported in Fig. 1, show a higher loss of weight for SWNTs functionalized with microwaves (**3MW**), indicating one functional group every 128 carbon atoms of the nanotube skeleton, while *f*-SWNTs **3** prepared under classical heating (**3CH**) presents a loss of weight of 12% at 600 °C, which corresponds to one functional group every 270 carbon atoms of the nanotube framework. In addition, MW conditions allow to avoid the use of DMF, a highly toxic solvent and reduce the reaction time to just 1 h.

Raman spectroscopy was also used for the characterization of *f*-SWNTs. 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}. The spectrum of the functionalized material exhibits an increased intensity of the D band, indicating covalent functionalization of the SWNTs since the new functional groups introduce sp^3 sites on the sp^2 network of the nanotube[9,10] (Fig. 2, exciting line = 632.8 nm). This increase is higher for carbon nanotubes functionalized using microwave activation (red line) in comparison with the same *f*-SWNTs functionalized under classical heating (green line), in agreement with the results

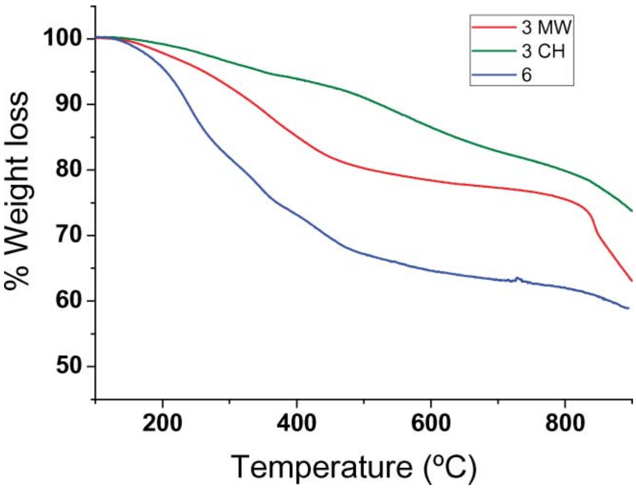


Fig. 1 TGA analysis of the *f*-SWNTs **3MW**, **3CH** and **6**.

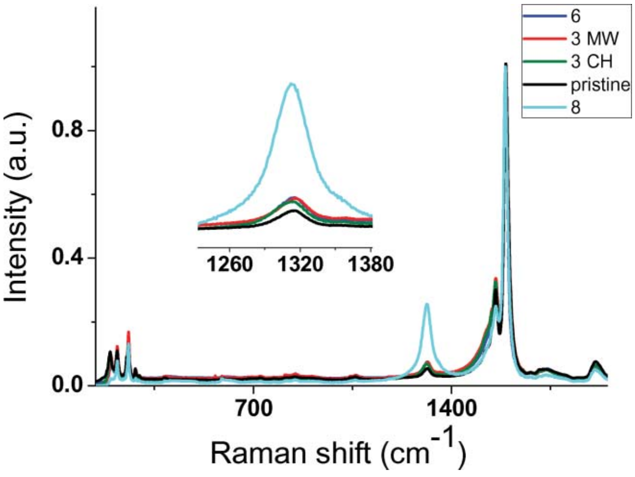


Fig. 2 Raman spectra (633 nm) of pristine SWNTs, *f*-SWNTs **3MW**, **3CH**, **6** and **8**.

observed with TGA. Control reactions were carried out using the same microwave conditions but using (i) only SWNTs in air, (ii) SWNTs in the presence of the aromatic aldehyde **2** and (iii) SWNTs in the presence of the aminoacid **1**. No increase in the intensity of the D-band is observed (see ESI, figure S3 and S4†).

The radial breathing mode (RBM) can provide important information relative to nanotube characteristics.[11] In fact, the RBM spectral region below 400 cm^{-1} shows that the spectra of the pristine SWNTs and those functionalized under microwaves or under classical heating, **3MW** and **3CH**, respectively, have the same bands for both semiconducting nanotubes, above 230 cm^{-1}, and metallic nanotubes, below this frequency (Fig. 3).[12] Notwithstanding this, it is possible to observe some intensity variations for metallic nanotubes, when the reaction takes place with microwave activation. For instance, it can be seen from the Raman spectrum of **3MW**, that the intensity of the metallic peak at around 200 cm^{-1} has reduced significantly relative to that of the semiconducting peak at 255 cm^{-1}.

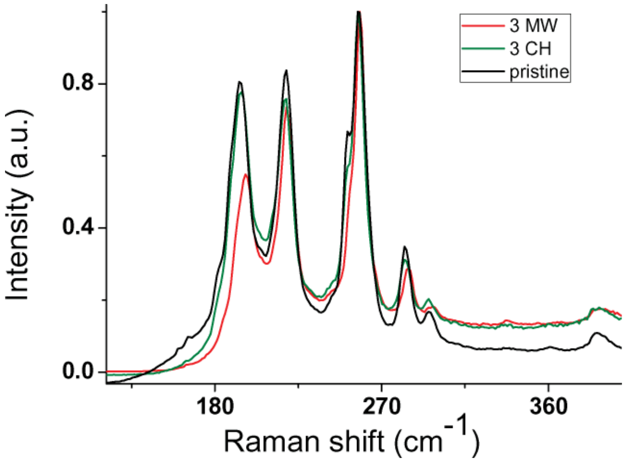


Fig. 3 Detailed normalized RBM region of the Raman spectra (633 nm) of pristine SWNTs, and *f*-SWNTs **3MW** and **3CH**.

Due to the difference in their electronic structures, metallic and semiconducting tubes may have different responses when subjected to MW irradiation.[3] This could lead to a preferential functionalization of metallic tubes under MW conditions in the absent of solvents, which could explain the lower intensity of the RBM bands related to these tubes.[13] However, the selective destruction of metallic nanotubes, based on different MW treatments, has recently been described, and this circumstance was also explained with the suppression of the RBM intensity.[14] To better elucidate if our microwave conditions were producing a preferential functionalization or a selective nanotube destruction of metallic tubes, pristine SWNTs were subjected, in air, to MW heating under the same conditions and time as those used for the preparation of **3MW**. Raman spectrum of these microwave treated SWNTs presents no differences with respect to the one of the pristine tubes (see ESI, figure S3†), which seems to exclude the possibility of selective destruction of tubes under our MW treatment.

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 is described when strong oxidation is used, since in this latter case small diameter nanotubes, which are more reactive due to their increased curvature, are destroyed.[15]

To extend the scope of this functionalization, we removed the phthalimido group of **3MW** using a solution of hydrazine in ethanol and the resulting free amino group was then coupled with fluorescein isothiocyanate (Scheme 2). The number of free amino groups in compounds **4** and **6** was measured using a quantitative Kaiser test.[16] Compound **4** resulted in 0.142 mmol g^{-1} of $-NH_2$, while compound **6** gave a negative Kaiser test which confirmed the exhaustive transformation of all the amino groups of the reaction. Moreover, the TGA of compound **6** (Fig. 1) presents a loss of weight of 36% which corresponds to one functional group every 104 carbon atoms of the nanotube, which confirms that every free amino group has been coupled with fluorescein. Moreover, it is interesting to note that the D-band for this derivative does not change during the coupling (Fig. 2, blue line). This excludes further reactions at the nanotube sidewalls.

Recently Tour and co-workers have described a synthetic route to obtain functionalized SWNTs “on water” in the presence of a substituted aniline and an oxidizing agent.[17] This method represents a relatively “green” process and gives a good opportunity to study the microwave activation of CNTs in an intermediate microwave absorbing solvent such as water. Aniline derivative **7**, possessing a differently protected amino group, removable in acidic conditions, as opposed to the phthalimido group of **5**, was synthesized. Therefore, pristine SWNTs were dispersed in water with derivative **7** in a microwave glass vessel. After sonicating for a few minutes, isoamyl nitrite was added and a condenser was attached. The mixture was irradiated for 90 min at 80 °C in a focused microwave reactor (Scheme 3).

f-SWNTs **8** were isolated after work-up (see Experimental). The TGA of compound **8** (Fig. 4), exhibits a loss of weight of 24%, at 600° C, which corresponds to the presence of one functional group for about 68 carbon atoms. This value reveals that this reaction introduces a higher number of functionalities relative to the 1,3-dipolar cycloaddition, a result that is also confirmed by the high D band observed in the Raman spectrum (Fig. 2, light blue line), in agreement with previous results.[7] It can be also noted that the loss of weight is consistent with two different events, the first of which being the loss of the Boc protecting group followed

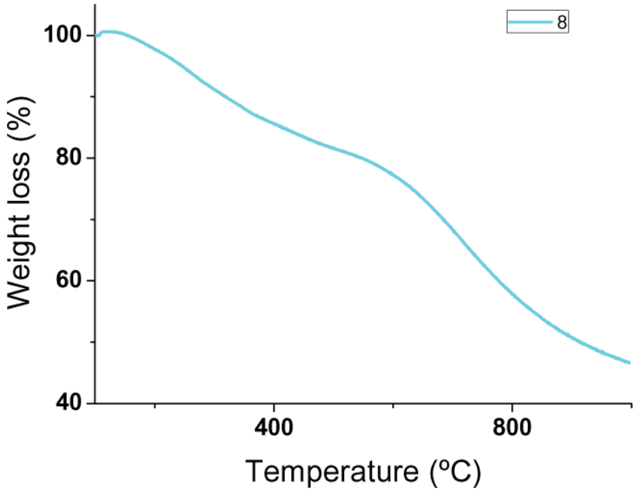
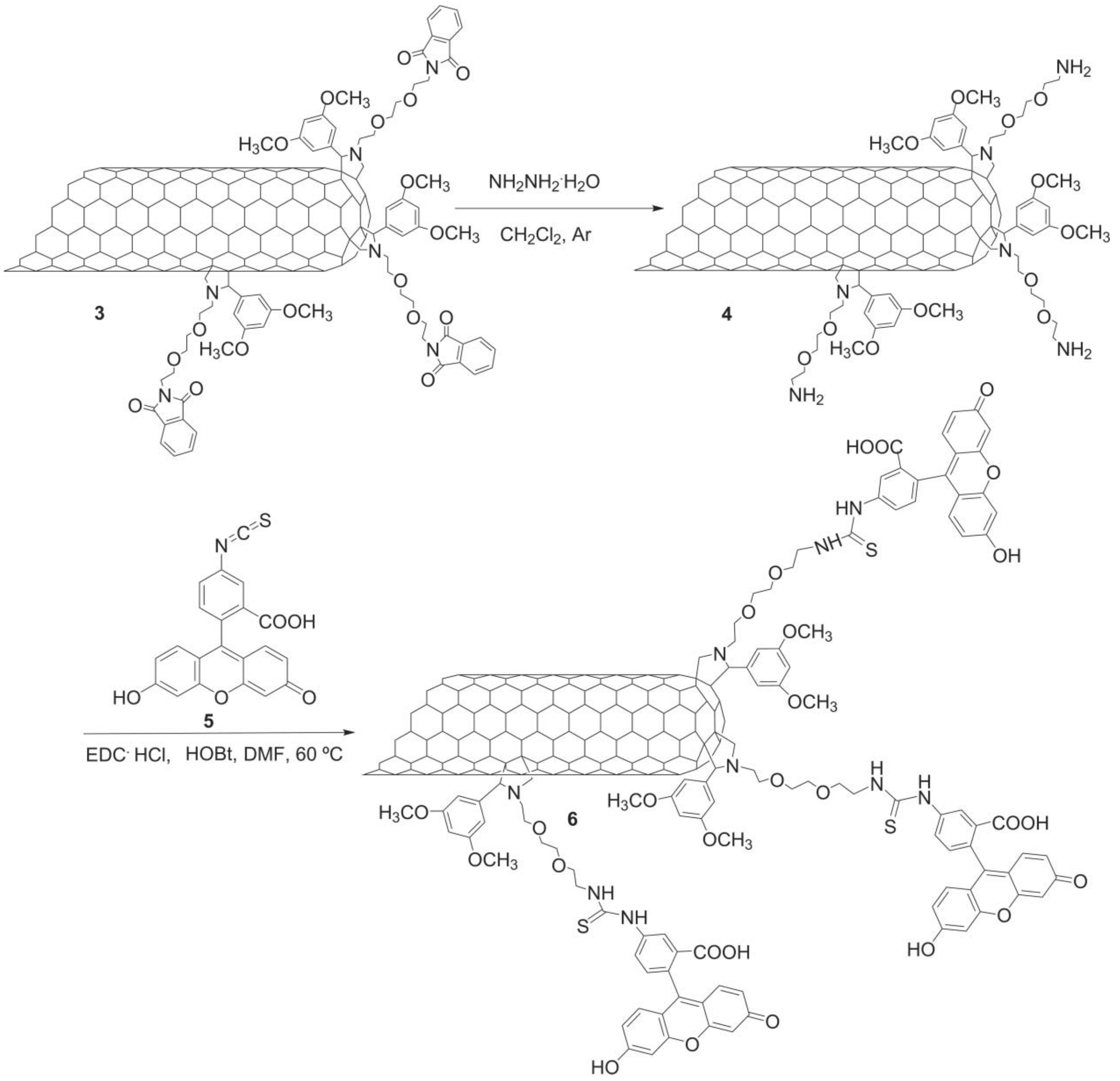
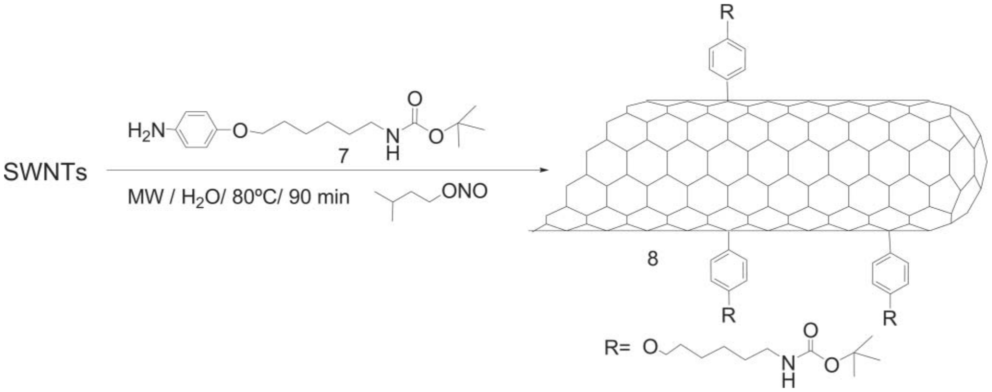


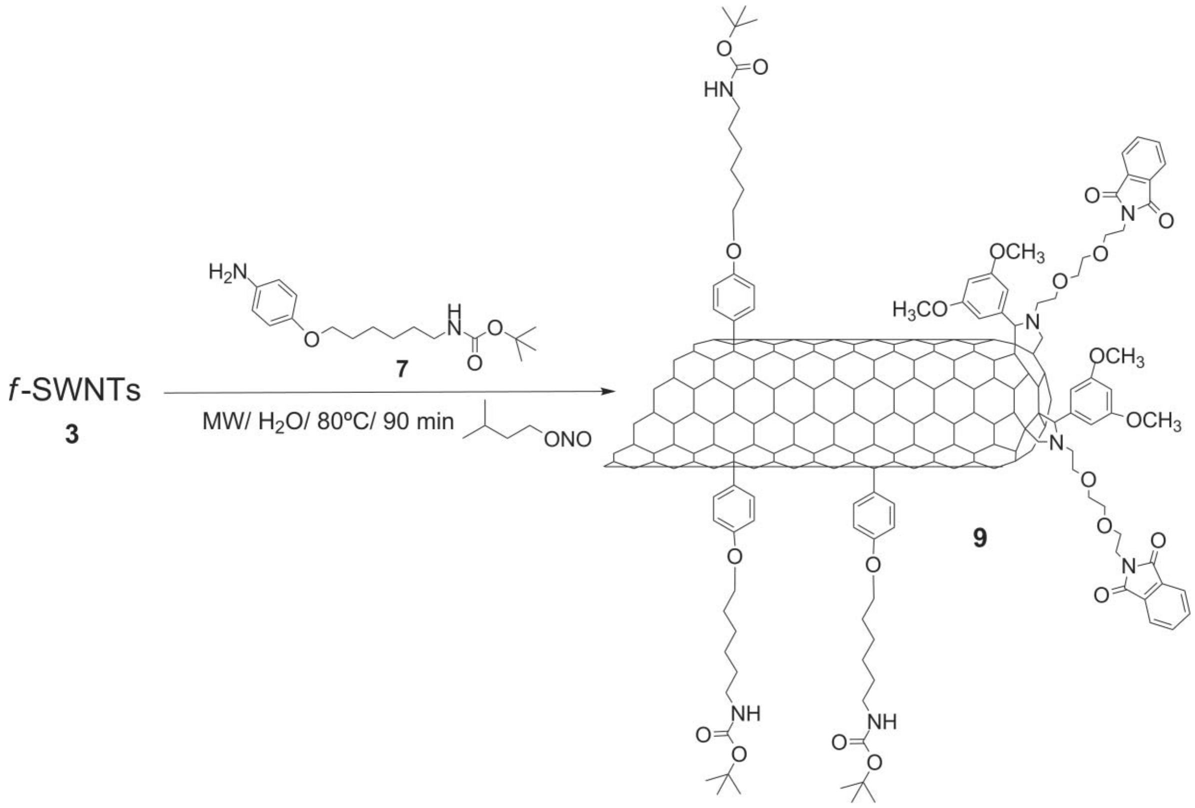
Fig. 4 TGA of *f*-SWNTs **8**.



Scheme 2



Scheme 3



Scheme 4

by degradation of the rest of the molecule. Similar behavior has already been described.[18]

In this case, MW conditions show similar results than classical heating (data not shown) with comparable degrees of functionalization in the same reaction times. CNTs functionalized by radical addition using classical heating or MW heating present also similar RBM spectral regions. This may be attributed to the use of water as solvent. Water can convert efficiently microwave irradiation into heat, but under these reaction conditions the medium can become viscous. It has been proposed that this environment can affect the microwave absorptions of CNTs, avoiding the intense local heating observed in the absence of solvent, thus probably reducing the differences between the two types of heating.[19]

The combination of the two reactions makes possible the preparation of doubly covalently functionalized SWNTs with orthogonally protected amino groups. As the radical addition has proven to be more effective than the 1,3-dipolar cycloaddition, we decided to perform the more selective cycloaddition first and then the arene addition. Consequently, following the same procedure described for the synthesis of *f*-SWNTs **8**, the novel derivative **3** was subjected to diazonium salt reaction (Scheme 4).

Fig. 5 reports representative Raman spectra showing an increase in the D-band of **9** relative to **3** and to pristine nanotubes, which supports further functionalization after the arene radical addition. This result is consistent with the increase in the TGA loss observed for derivative **9** in comparison to derivative **3**. Table 1 summarizes the functional group coverage, obtained by TGA, along with the D/G ratio for all the described compounds, showing a qualitative and consistent trend between the D over G ratio and the degree of functionalization calculated by TGA data.

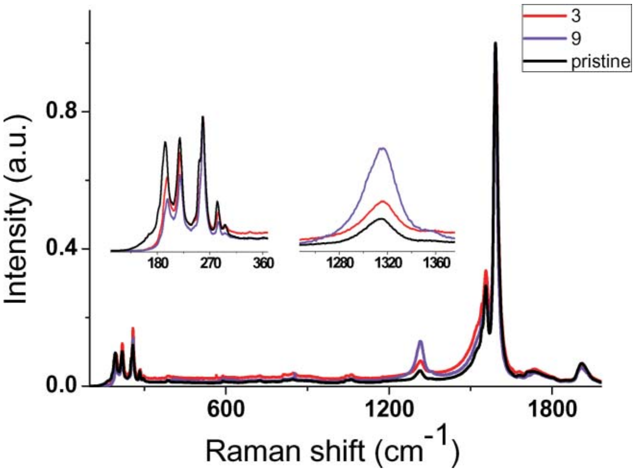


Fig. 5 Normalized Raman spectra (633 nm) of pristine SWNTs, *f*-SWNTs **3MW** and **9**.

Analysis of the RBM spectral region shows that all the bands observed for *f*-SWNT **3** are present in *f*-SWNTs **9**, but one also observes that metallic nanotubes (bands below 230 cm^{-1}) reacted more quickly than semiconducting ones.

Finally, *f*-SWNTs were also studied by transmission electron microscopy (TEM). Images reveal that compound **3** forms thin bundles of *f*-SWNTs while, in *f*-SWNT **9**, the average thickness of the bundles is reduced as a result of further functionalization after the arene radical reaction (Fig. 6).

Table 1 Comparative study of the functionalization of products **3MW**, **3CH**, **8** and **9**

Product	[a]TGA wt loss (%)	[b]Functional group coverage (1,3-Dipolar Cycloaddition)	Functional group coverage (Arene Radical Addition)	[d]Raman D/G ratio
3MW	22	128	—	0.08
3CH	12	270	—	0.07
8	26	—	68[b]	0.26
9	30	128	281[c]	0.14

[a] TGA results show total weight loss. [b] Number of carbons of the nanotube skeleton for every functional group, see ref. 8. [c] The different between the total weight loss and the weight loss after the 1,3-Dipolar Cycloaddition, gives the functional group coverage of the arene radical addition. [d] Calculated D/G ratios from Raman spectra.

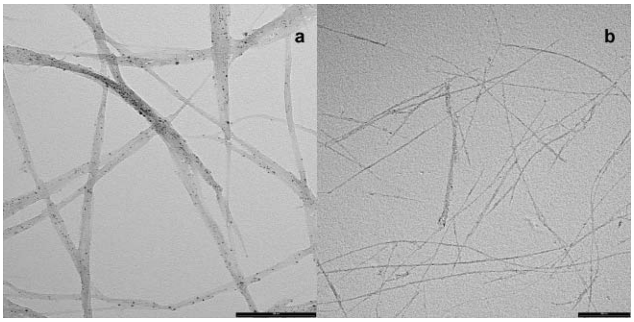


Fig. 6 TEM photographs of a) *f*-SWNTs **3MW**, b) *f*-SWNTs **9**. Scale bar corresponds to 200 nm.

Experimental

Techniques

Microwave irradiations were carried out in a CEM DISCOVER S-Class reactor, with infrared pyrometer, pressure control system, stirring and air-cooling option. The thermogravimetric analyses were performed with a TGA Q50 (TA Instruments) at 10 °C min^{-1} under N$_2$. Raman spectra were recorder 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 CH$_2$Cl$_2$ and a drop of the suspension was placed on a copper grid (3.00 mm, 200 mesh, coated with carbon film). After air-drying the sample was investigated by TEM Philips EM 208, accelerating voltage of 100 kV.

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 Acros Organics and used as received without further purification. α-aminoacid **1**[20] and aniline derivative **7**[18b] were synthesized following the literature procedure. HiPCO SWNTs were purchased from Carbon Nanotechnologies Inc. lot # R0496 (www.cnanotech.com) and used without purification.

Synthesis of *f*-SWNTs

***f*-SWNTs 3MW.** 25 mg of pristine SWNTs were suspended in 15 mL of CH$_2$Cl$_2$ with the aldehyde **3** (110 mg, 0.66 mmol) and the amino acid **1** (211 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 introduced into a monomode microwave where the mixture was irradiated for 40 min at different power and temperature (see ESI, table S1†). After this period of time, the crude was re-suspended in 75 mL of CH$_2$Cl$_2$ and sonicated for 5 min. The solution was filtered on a Millipore membrane (PTFE 0.2 μm) and the collected black solid was washed by cycles of sonication and filtration with 75 mL of methanol and with 75 mL of CH$_2$Cl$_2$, affording 24.3 mg of *f*-SWNTs **3MW**.

***f*-SWNTs 3CH.** 25 mg of pristine SWNTs were suspended in DMF (30 mL) after sonication for 30 min, the aminoacid **1** (140 mg, 0.84 mmol) and the aldehyde **3** (140 mg, 0. 44 mmol) were added portion wise (35 mg every 24 h), and the reaction mixture was heated at 115 °C for 5 days. After being cooled to room temperature, unreacted CNTs were separated by centrifugation, and *f*-SWNTs were collected in the supernatant. Unreacted CNTs were centrifugated several times using fresh DMF. The supernatant was filtered on a Millipore membrane (PTFE 0.2 μm) and the collected black solid was washed with 100 mL of methanol and with 75 mL of CH$_2$Cl$_2$ (sonicated and filtered) affording 11 mg of *f*-SWNTs **3CH**.

***f*-SWNTs 4.** 11.4 mg of functionalized *f*-SWNTs **3** were suspended in 10 mL of CH$_2$Cl$_2$ with hydrazine (4.3 mL, 0.03 mol) and the mixture was stirred for 16 h at room temperature under argon. The crude was filtered on a Millipore membrane (PTFE, 0.2 mm) and washed by cycles of sonication and filtration with CH$_2$Cl$_2$ (75 mL) and methanol (100 mL), and finally dried under high vacuum affording 10.8 mg of *f*-SWNTs **4**.

***f*-SWNTs 6.** A suspension of *f*-SWNTs **4** (20 mg) in DMF (20 mL) was sonicated for 30 min. Simultaneously, to a solution of fluorescein isothiocyanate (2.64 mg, 6.76 μmol) in DMF, 1-ethyl-3-(3-dimethyllaminopropyl)carbodiimide hydrochloride (1.25 mg, 6.76 μmol) and *N*-hydroxybenzotriazole (1.26 mg, 6.76 μmol) were added followed by stirring at room temperature for one hour under argon. Both solutions were mixed and stirred at 60 °C during 16 h under argon. After that time the reaction mixture was filtered on a Millipore membrane (PTFE, 0.22 μm), and the collected black solid was washed using cycles of sonication and filtration with DMF (75 mL), methanol (100 mL) and CH$_2$Cl$_2$ (75 mL), affording 19.8 mg of *f*-SWNTs **6**.

***f*-SWNTs 8.** 15 mg of pristine SWNTs were sonicated in 25 mL of deionized water together with aniline **7** (1.54 g, 5 mmol) for 10 min in a microwave glass vessel. Finally, isoamyl nitrite (0.33 mL, 2.5 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 30 W for 60 min). After cooling at room temperature, the crude was filtered on a Millipore membrane (PTFE 0.2 μm). The collected black solid was washed using cycles of sonication and filtration with methanol and acetone until the filtrate was clear and finally dried under high vacuum affording 14.5 mg of *f*-SWNTs **8**.

***f*-SWNTs 9.** 15 mg of *f*-SWNTs **3MW** were sonicated in 25 mL deionized water together with aniline **7** (1.54 g, 5 mmol) for 10 min in a microwave glass vessel. Finally isoamyl nitrite

(0.33 mL, 2.5 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 30 W for 60 min). After cooling at room temperature, the crude was filtered on a Millipore membrane (PTFE 0.2 μm). The collected black solid was washed using cycles of sonication and filtration with methanol and acetone until the filtrate was clear and finally dried under high vacuum affording 14.4 mg of *f*-SWNTs **9**.

Conclusions

The synthetic approach to *f*-SWNTs using microwave heating has been successfully applied to different and very useful reactions. The 1,3-dipolar cycloaddition, performed in absence of solvent, followed by the radical arylation, have been carried out in series, affording doubly functionalized *f*-SWNTs with two orthogonally protected amino groups.

In conclusion, the new SWNT derivatives described herein can serve as multipurpose, versatile synthons in materials science and biological applications.

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8 Total mass loss was attributed to functional groups covalently attached to the sidewalls. The number of functional groups was calculated considering the mass loss and the molecular weight of the organic fragment. The residual mass was attributed to pristine SWNTs, which was used to determine the mequiv of SWNT carbons present.

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