Efficient functionalization of carbon nanohorns *via* microwave irradiation†‡

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Multifunctionalization of carbon nanohorns (CNHs) is easily achieved by microwave activation. We describe an efficient strategy to produce multifunctionalized CNHs using a combination of two different addition reactions, the 1,3-dipolar cycloaddition of azomethine ylides, in solvent-free conditions, and the addition of diazonium salts in water, both *via* a simple and fast microwave-induced method. The new CNH derivatives are soluble in common solvents as well as in water. The doubly functionalized CNHs may be valuable new tools for many interesting applications.

Introduction

The mass production of new carbon nanostructures and their potential applications in many different fields have made these materials the subject of heavy investigations.[1] Carbon Nanohorns (CNHs)[2] represent a new type of nanostructured carbon-based material, which possess interesting properties for applications in clean-energy technologies as well as biology and medicine.[3] A primary CNH particle is a single graphene tube (similar in structure to single-walled carbon nanotubes) of 2–5 nm in diameter and a length of 40–50 nm, with a conically-closed tip. Around 2000 CNHs aggregate with each other to form a spherical dahlia flower-like structure with a rather narrow diameter distribution of 80–100 nm. The high purity of produced CNHs is their major advantage as compared to carbon nanotubes. They are produced without the use of any metal catalyst so that they are completely metal-free. Additionally, compared with others nanoparticles, and similar to amorphous carbon, CNHs possess high absorbability due to their large surface area and inherent micropores at interstitial sites.

Functionalization of CNHs has given scientists the ability to manipulate these structures enhancing their solubility and broadening the spectrum of applications. While different functionalization strategies have been described including covalent attachment of organic fragments[4] as well as non-covalent interactions,[5] reactions usually proceed with long times, in the presence of highly contaminating solvents and/or under harsh conditions.

Our group has recently described the multiple functionalization of carbon nanotubes using a combination of two different covalent reactions, both *via* a simple and fast microwave-induced method.[6] Microwave irradiation is an unconventional energy source, whose usefulness has been recognized in recent years.[7] The use of emerging microwave-assisted chemistry techniques in conjunction with greener reaction media dramatically reduces chemical waste and reaction times in synthetic organic chemistry.[8] Recent work has explored the use of this radiation to assist CNT purification and functionalization, and has shown that this technique is especially useful in the design of energy efficient processes, simple and easy to scale-up.[9] Surface properties of CNHs have also been modified under microwave irradiation, showing the ability of this method to enhance dispersibility.[10]

In the present work, we explore the efficiency of microwave irradiation for the covalent functionalization of CNHs. Two different reactions have been used: the 1,3-dipolar cycloaddition of azomethine ylides and the arene radical addition. Both functionalization methods allow the preparation of CNH derivatives with many functionalities, showing different solubility directly dependent on the amount of groups covalently linked. In addition, the combination of both reactions permits the double functionalization of CNHs, further broadening the variety of products that can be customized to fit into a desirable application. Finally, the microwave-assisted organic transformations here described proceed with short reaction times and involve two benign alternatives, namely solvent-free or aqueous reaction media.

Results and discussion

The first report on the covalent functionalization of CNHs was performed by Tagmatarchis *et al.*,[4a] using the 1,3-dipolar cycloaddition of azomethine ylide generated *in situ* upon the thermal condensation of aldehydes and α-amino acids, a methodology extensively applied for other materials such as fullerenes and nanotubes.[11] The reaction was reported to proceed in 100 h under reflux in DMF. Using our experience on carbon nanotubes, we changed the classical methodology to a solvent-free protocol under microwave irradiation. These conditions allow the reduction of the reaction times and avoid the use of DMF as a solvent.

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Moreover, solvent-free conditions are not only environmentally friendly but also allow to perform the reactions on a larger scale, so that the reactions can be easily performed from milligram to gram quantities.

In a typical experiment, glycines **1** and aldehydes **2** were dispersed on CNHs and irradiated for 1 h in the absence of solvent in a focused microwave reactor (Scheme 1).

To exploit the versatility of this reaction, various aldehydes have been used. In addition, α-amino acid **1b** was synthesized and employed in the cycloaddition, to produce *f*-CNHs **5** with a protected amino group, easily removable under basic conditions. The hydrophilic oligoethylene glycol chain, also part of this α-amino acid, should enhance the solubility of CNHs in polar solvents.

After work-up, the amount of organic groups in the functionalized CNHs was determined by thermogravimetric analysis (TGA).[12] The thermograms of *f*-CNHs **3**, **4** and **5**, reported in Fig. 1, present a loss of weight of 15%, 10% and 16%, respectively, at 600 °C, which corresponds to one functional group every 99, 134, and 192 carbon atoms of the nanohorn framework, respectively.

Recently Price and Tour have described a synthetic route to obtain functionalized SWNTs "on water" in the presence of a substituted aniline and an oxidizing agent, which represents a relatively "green" process.[13] Lately we have reported the same reaction with SWNTs under microwave irradiation.[6] Following the procedure described for SWNTs, we approached the functionalization of CNHs. The aniline derivative **8** was synthesized in order to prepare functionalized CNHs with a different protected group, this time removable in acidic conditions, as opposed to the phthalimido group of **5**, removed in base (Scheme 2). Therefore, CNHs were dispersed in water with derivative **8** 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 minutes at 80 °C in a focused microwave reactor (Scheme 3).

f-CNHs **9** were isolated after work-up (see Experimental). The TGA of compound **9** (Fig. 1) presents a loss of weight of 24%, at 600 ° C, which corresponds to the presence of one functional group for about 54 carbon atoms.

This value reveals that this second reaction introduces a higher number of functionalities relative to the 1,3-dipolar

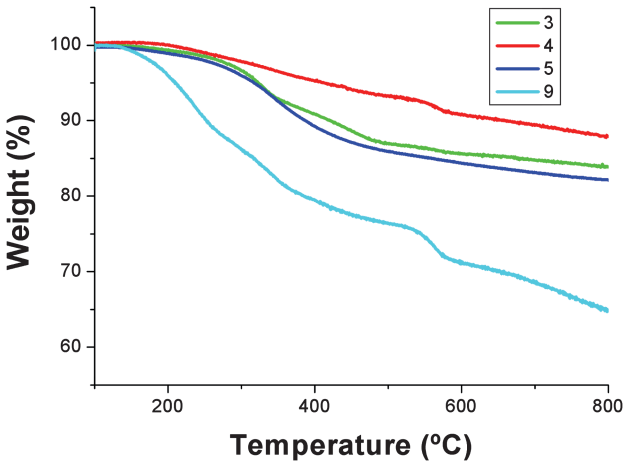
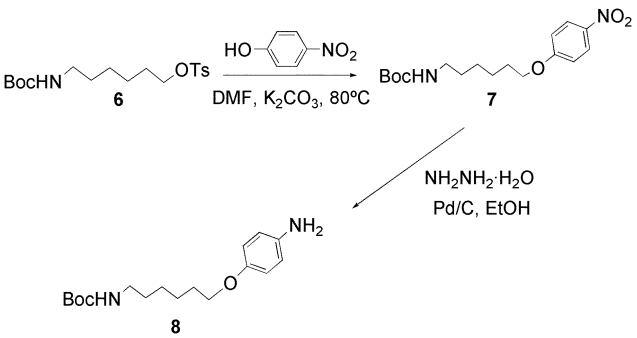


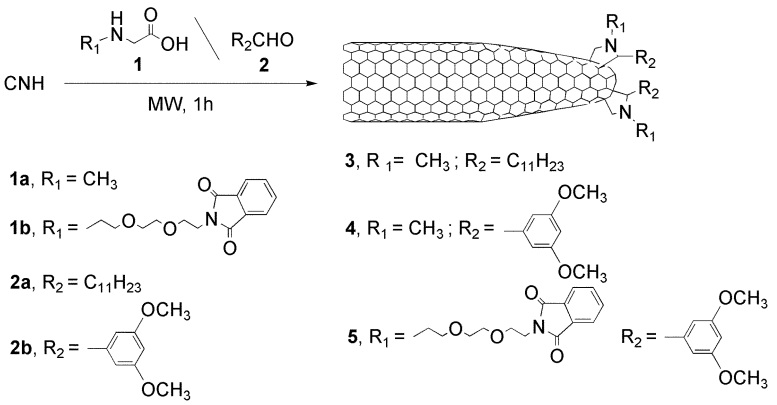
Fig. 1 TGA analysis of the *f*-CNHs **3**, **4**, **5** and **9**.



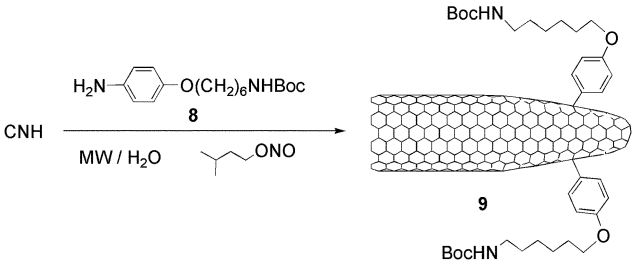
Scheme 2

cycloaddition, a result that has also been observed with carbon nanotubes.[15] It can be also noted that the loss of weight consists of two different events, the first of which being the loss of the Boc protecting group followed by degradation of the rest of the molecule. Similar behaviour has already been described.[4d]

f-CNHs, prepared by both methods, were also investigated by transmission electron microscopy (TEM). Typical images are shown in Fig. 2, indicating that the unique structures of CNHs as well as their spherical aggregates are preserved after the



Scheme 1



Scheme 3

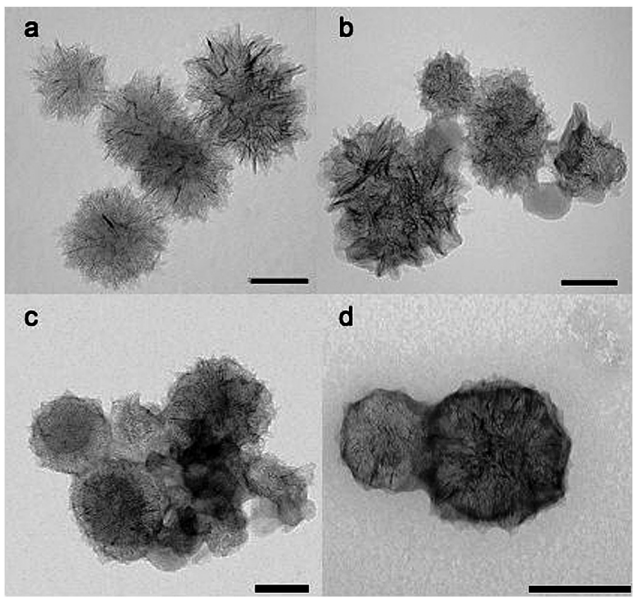


Fig. 2 TEM images of (a) *f*-CNHs **3**, (b) *f*-CNHs **4**, (c) *f*-CNHs **11**, (d) *f*-CNHs **13**. Scale bar corresponds to 100 nm.

functionalization. Furthermore, the images reveal that CNHs are well dispersed after functionalization.

Raman spectroscopy can also be used for the characterization of *f*-CNHs. Raman spectra of the pristine CNHs and their derivatives **3**, **4**, **5** and **9** are reported in Fig. 3.

The Raman spectrum of pristine CNHs exhibits two prominent bands, one at 1590 cm^{-1} (G-band) and one at 1320 (D-band). The D-band is due to a one-phonon, second-order process in which a defect site, such as an sp^3 carbon, produces an elastic scattering[14] and is commonly used for monitoring the process of functionalization (change of hybridization from sp^2 to sp^3). In the Raman spectra of CNHs functionalized *via* the 1,3-dipolar cycloaddition, the D-band is not very different from the one observed in pristine CNHs, probably because the reaction occurs where defects are already present.

However, an increase of this band can be observed after the functionalization with the radical addition (*i.e.* compound **9**) which also attacks the walls of the CNHs. We have already described that a similar trend is followed when these reactions are used to functionalize SWNTs. It seems that with the same number of groups added, the 1,3-dipolar cycloaddition produces a smaller increase in the D-band than the radical addition.[6]

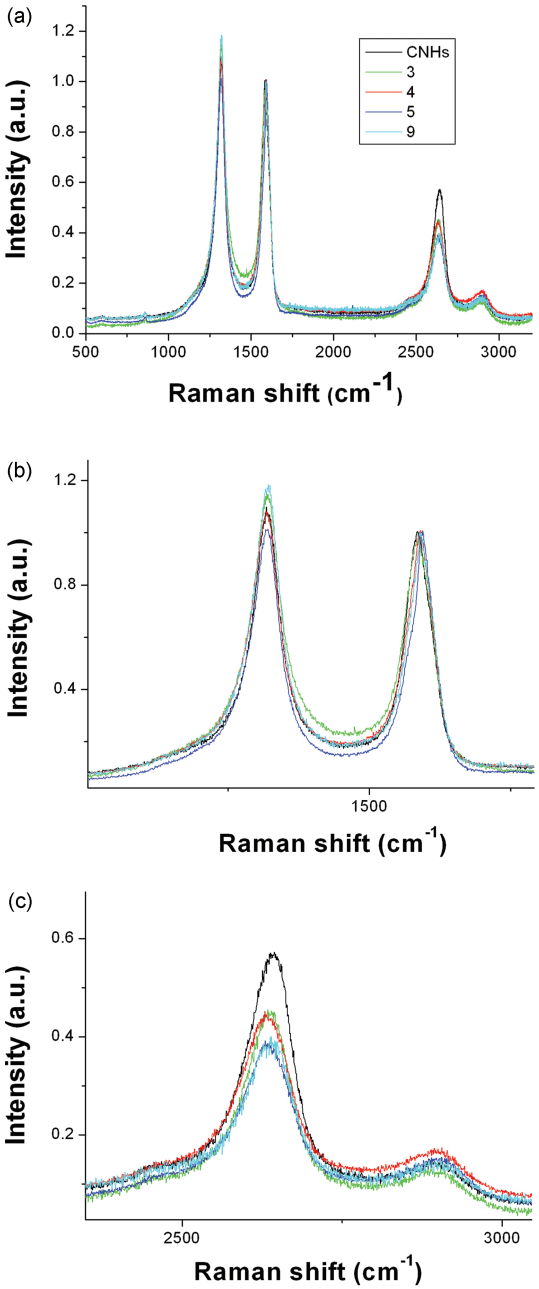


Fig. 3 (a) Raman spectra (633 nm) of pristine CNHs, *f*-CNHs **3**, **4**, **5** and **9**, (b) detailed D-region, (c) detailed G′ and D+D′ region.

Raman spectra show also another peak at 2900 cm^{-1} which can be related to the presence of defects. This peak has been recently described as a combination of the D- and D′-bands and has been shown that it is strongly defect-induced, following the same behaviour as the D-band.[15] An increase of this peak is observed for all functionalized CNHs. The ratios of the Raman D- to G-band intensities are reported in Table 1, together with the functionalization group coverage (number of CNH carbon atoms per functional group) based on weight loss from thermogravimetric analysis (TGA). Although no quantitative relationship between the D- over G-band ratio and the degree of functionalization calculated from TGA data can be deduced, a consistent trend is observed.

Table 1 Comparative study of the functionalization of compounds **3**–**5**, **9**

Product	[a]TGA weight loss (%)	[b]Functional group coverage	[c]Raman D/G ratio
3	15	99	1.19
4	10	134	1.09
5	16	192	1.09
9	24	54	1.20

[a] TGA-determined weight loss. [b] See ref. 12. [c] Calculated D/G ratios from Raman spectra.

As a result of both covalent attachments onto the skeleton of CNHs the solubility is highly enhanced in several solvents. A summary of the solubility results is presented in Table 2.

The differences observed are highly dependent on the polarity and the number of groups covalently attached to the

Table 2 Solubility (mg/mL) of *f*-CNHs in various solvents[16]

f-CNH	CH_2Cl_2	DMF	*o*-DCB
3	5	2	3.4
4	9	6	7.5
5	5	4.7	5
9	4.3	5	8.4
12	9.7	7.1	8
13	6	6	6.7

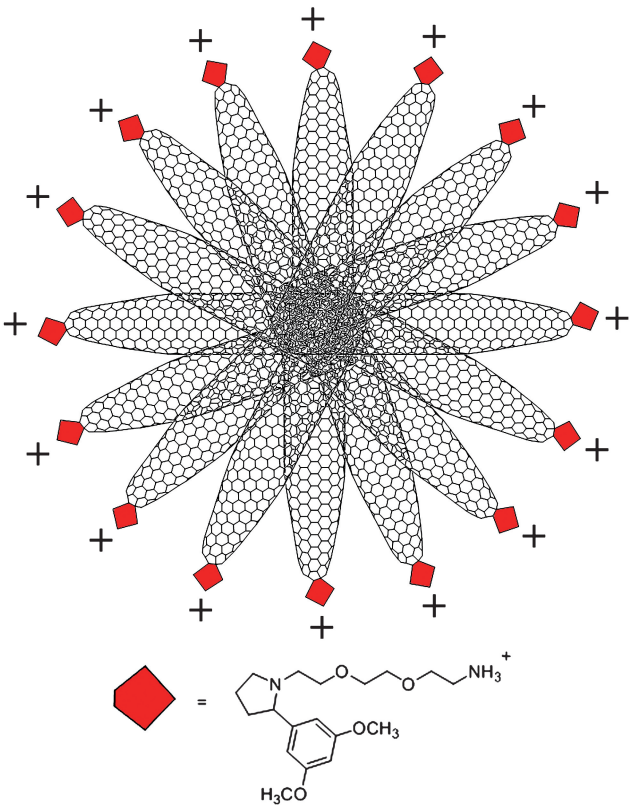


Fig. 4 *f*-CNHs **10** was prepared by stirring derivative **5** at room temperature in hydrazine/CH_2Cl_2 (see Experimental). Solubility in water: 0.38 mg/mL.

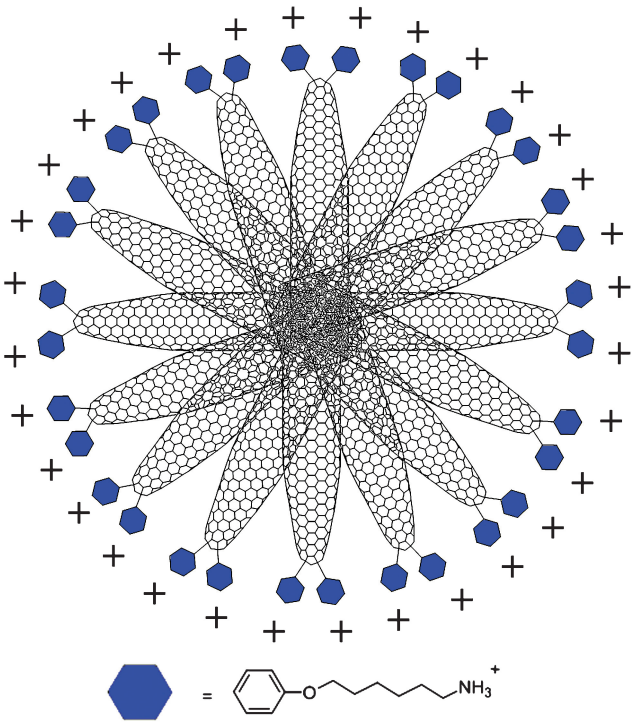


Fig. 5 *f*-CNHs **11** was prepared from derivative **9** upon treatment with gaseous HCl in DMF (see Experimental). Solubility in water: 0.75 mg/mL.

CNHs. Moreover when the phthalimido protecting group in functionalized CNHs **5** and the BOC protecting group in *f*-CNHs **9** are cleaved, **10** and **11** respectively are formed (Fig. 4 and 5).

The positively charged ammonium terminated functionalization makes these materials soluble in water (**10**: 0.38 mg/mL and **11**: 0.75 mg/mL) (Fig. 6). It seems that in this case, the different solubility depends more on the number of functionalized groups attached to the CNHs; thus, derivative **11** has a higher solubility in water compared to **10**, even though this latter possesses the more polar oligoethylene glycol chain. These water-soluble *f*-CNHs are expected to be useful in biotechnological

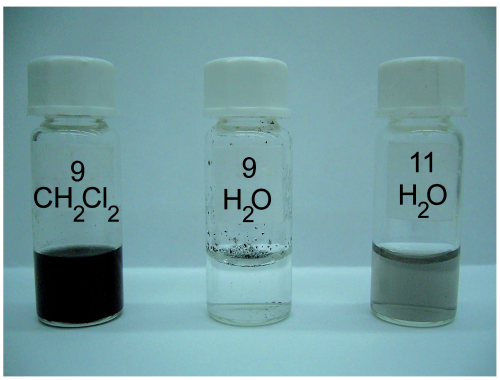


Fig. 6 Solubility test: *f*-CNHs **9** (4.3 mg) were dispersed in 1 mL of CH_2Cl_2 and 1 mL of H_2O and the corresponding deprotected *f*-CNHs **11** (0.75 mg) were dispersed in 1 mL of H_2O.

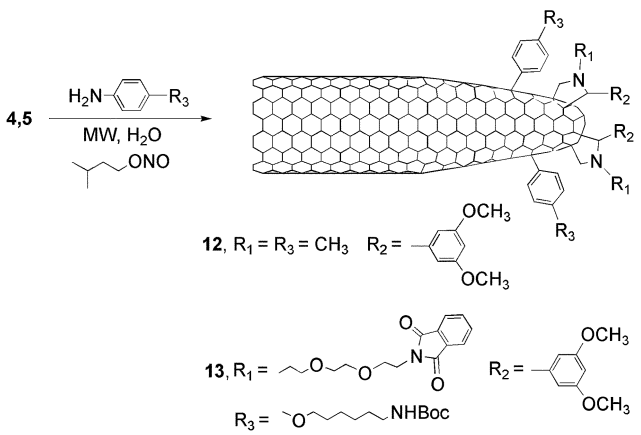
applications and work along these lines is currently under development in our laboratories.

Once the functionalization of CNHs by microwave irradiation using two different reactions was confirmed, the combination of both approaches made possible the preparation of doubly covalently functionalized CNHs. As the radical addition has proved 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*-CNHs **9**, the novel derivatives **4**, and **5** were subjected to diazonium salt reaction in order to introduce a second functional group in the same CNHs (Scheme 4).

Based on the TGA weight loss (see ESI‡) in derivative **12** we calculated one functional group every 134 CNHs carbon atoms in the 1,3-dipolar cycloaddition and one functional group every 38 carbon atoms in the arene radical addition, while in derivative **13** one functional group has been introduced every 192 CNHs carbons in the first reaction and only one functional group every 193 carbons in the second one. Therefore it seems that the steric hindrance of the group added by the 1,3-dipolar cycloaddition could influence the second reaction course, the arene radical addition being less effective than usual.

Raman spectra also confirm the double functionalization (Fig. 7). The D-band increases when the radical addition takes place and this behaviour is also observed in the (D + D′)-band.

Finally, TEM images of the doubly functionalized CNHs show the characteristic spherical superstructures of CNHs, suggesting that the unique morphology of CNHs persists (Fig. 2).



Scheme 4

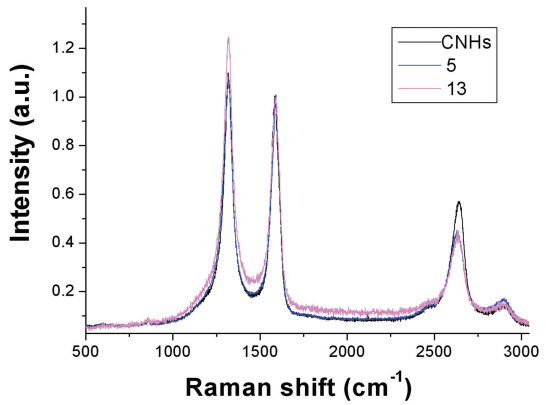


Fig. 7 Raman spectra (633 nm) of pristine CNHs, *f*-CNHs **5** and *f*-CNHs **13**.

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 under N_2. 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 CH_2Cl_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. 6-(*p*-Toluenensulfonyloxy)-*N*-(*tert*-butoxycarbonyl)hexylamine **6** was synthesized following the literature[17] procedure. CNHs were produced by Carbonium s.r.l., Padova (Italy) by direct graphite evaporation in Ar flow, according to a patented method[18] and used without purification.

Synthesis of aniline derivative 8

Synthesis of *tert*-butyl 6-(4-nitrophenoxy)hexylcarbamate 7. To an *N*,*N*′-dimethylformamide solution of **6** (10.50 g, 28.30 mmol in 40 mL), potassium carbonate (11.75 g, 85.0 mmol) and 4-nitrophenol (3.82 g, 27.50 mmol) were added. The solution was stirred at 80 °C for 16 h. After cooling to room temperature, the solution was poured into water and extracted several times with ethyl acetate and dried over magnesium sulfate. Once filtered, the solvent was removed by distillation at reduced pressure, rendering a white solid **7**, m.p. 62–63 °C (8.03 g, 74% yield).

IR-DRIFT, Nujol, cm^{-1}: 3345.91 (N–H), 1669 (C=O), 1469.09, 1341.68 (Ar–NO_2), 1255.81 (C–O–Ar, –CH_3), 848.86, 786.11 (C–C aromatics), 724.45 –$(CH_2)_6$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.20 (d, J = 9.3 Hz, 2 H), 6.94 (d, J = 9.3 Hz, 2 H), 4.57 (bs, 1 H), 4.04 (t, J = 6.6 Hz, 2H), 3.13 (m, 2 H), 1.83 (m, 2 H), 1.26–1.58 (m, 15 H).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 164.4, 140.9, 126.2, 114.6, 69.0, 31.2, 30.3, 29.1, 28.7, 26.7, 25.9.

Synthesis of *tert*-butyl 6-(4-aminophenoxy)hexylcarbamate 8. To an ethanol solution of **7** (6.22 g, 20 mmol in 40 mL),

hydrazine monohydrate (19.37 mL, 400 mmol) and a catalytic amount of 10% Pd/C were added. The mixture was stirred under reflux for 5 h. The catalyst was removed by filtration on Celite and the solvent was evaporated at reduced pressure, rendering a brown oil **8** (5.55 g, 98% yield).

IR-DRIFT, Nujol, cm^{-1}: 3367.28 (N–H, Ar–NH_2), 1694.13 (C=O), 1237.33 (C–O–Ar, –CH_3), 824.46, 778.73 (C–C aromatics), 723.18 –$(CH_2)_6$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.73 (d, J = 9.0 Hz, 2 H), 6.63 (d, J = 9.0 Hz, 2 H), 4.52 (bs, 1 H), 3.87 (t, J = 6.2 Hz, 2H), 3.12 (m, 2 H), 1.74 (m, 2 H), 1.43–1.51 (m, 13 H), 1.37 (m, 2 H).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 152.3, 139.9, 116.4, 115.7, 68.5, 40.5, 30.0, 29.3, 28.4, 26.6, 25.8

Synthesis of *f*-CNHs

***f*-CNHs 3–5.** In a typical experiment, 25 mg of pristine CNHs were suspended in 10 mL of CH_2Cl_2 with the corresponding aldehyde **2a** (0.15 mL, 0.66 mmol) or **2b** (110 mg, 0.66 mmol) and the corresponding amino acid **1a** (59 mg, 0.66 mmol) or **1b** (211.07 mg, 0.66 mmol) in a microwave quartz vessel. After sonication during 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 1 h (**1a**) or 40 min (**1b**) at different power and temperature (see ESI‡). After this period of 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 by cycles of sonication and filtration using three different mixtures of solvents: (i) 100 mL of methanol/HCl (37%) in a proportion 3 : 1, (ii) 75 mL of methanol and (iii) 75 mL of CH_2Cl_2 (sonicated and filtered) and finally dried under high vacuum affording *f*-CNHs **3**–**5** (**3**: 18.0 mg; **4**: 15.7 mg; **5**: 17.6 mg).

***f*-CNHs 9.** In a typical experiment, 20 mg of pristine CNHs were sonicated in deionized water together with **8** (2.05 g, 6.68 mmol) for 10 min in a microwave glass vessel. Finally, isoamyl nitrite (0.44 mL, 3.34 mmol) was added, and a condenser was placed. The mixture was irradiated for 90 min at 80 °C at 100 W for 30 min, and after addition of a new aliquot of isoamyl nitrite (0.44 mL, 3.34 mmol), at 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 16.2 mg of *f*-CNHs **9**.

***f*-CNHs 10.** 8 mg of functionalized CNHs **5** were suspended in 10 mL of CH_2Cl_2 with hydrazine (3 mL, 0.02 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 μm) and washed by cycles of sonication and filtration with CH_2Cl_2 (75 mL) and methanol (100 mL), and finally dried under high vacuum affording 5.6 mg of *f*-CNHs **10**.

***f*-CNHs 11.** HCl gas was bubbled for 5 min through a suspension of CNHs **9** (15.5 mg) in dry DMF (20 mL). The reaction mixture was stirred at room temperature for 14 h, filtered on a Millipore membrane (PTFE, 0.2 μm) and washed by cycles of sonication and filtration using 75 mL of three different solvents: DMF, ethanol and CH_2Cl_2. The collected black solid was finally dried under high vacuum affording 10.8 mg of *f*-CNHs **11**.

***f*-CNHs 12,13.** 15 mg of *f*-CNHs **4** and **5** were sonicated in deionized water together with *p*-toluidine (536 mg, 5.06 mmol) and **8** (1.56 g, 5.06 mmol) respectively for 10 min in a microwave glass vessel. Finally, isoamyl nitrite (0.33 mL, 2.53 mmol) was added, and a condenser was placed. The mixture was irradiated for 90 min at 80 °C at 100 W for 30 min, and after addition of a new aliquot of isoamyl nitrite (0.33 mL, 2.53 mmol), at 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 by cycles of sonication and filtration using methanol and acetone, until the filtrate was clear and finally dried under high vacuum affording *f*-CNHs **12**,**13**. (**12**: 13.3 mg; **13**: 13.8 mg).

Conclusions

We have shown that CNHs can be efficiently functionalized using microwave activation. Two covalent functionalization methods have been used: the 1,3-dipolar cycloaddition of azomethine ylides and the addition of diazonium salts, both using environmentally friendly reaction media. As a consequence of the covalent attachment, the solubility of the CNHs is highly increased. A combination of the two reactions have also permitted the preparation of doubly functionalized CNHs with orthogonally protected groups, that, in principle, can be selectively cleaved and modified with different moieties, broadening the number of derivatives that can be prepared and paving the way to new applications.

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