“Click” on Tubes: a Versatile Approach towards Multimodal Functionalization of SWCNTs


Abstract: Organic functionalization of carbon nanotube sidewalls is a tool of primary importance in material science and nanotechnology, equally from a fundamental and an applicative point of view.[1, 2] Here, an efficient and versatile approach for the organic/organometallic functionalization of single-walled carbon nanotubes (SWCNTs) capable of imparting multimodality to these fundamental nanostructures, is described. Our strategy takes advantage of well-established Cu-mediated acetylene-azide coupling (CuAAC) reactions applied to phenylazido-functionalized SWCNTs for their convenient homo-/heterodecoration with a number of organic/organometallic frameworks, or mixtures thereof, bearing terminal acetylene pendant arms. Phenylazido-decorated SWCNTs were prepared by chemoselective arylation of the CNT sidewalls with diazonium salts under mild conditions, and subsequently used for the copper-mediated cycloaddition protocol in the presence of terminal acetylenes. The latter reaction was performed in one step by using either single acetylene derivatives or equimolar mixtures of terminal alkynes bearing either similar functional groups (masked with orthogonally cleavable protecting groups) or easily distinguishable functionalities (on the basis of complementary analytical/spectroscopic techniques). All materials and intermediates were characterized with respect to their most relevant aspects/properties by TEM microscopy, thermogravimetric analysis coupled with MS analysis of volatiles (TG-MS), elemental analysis, cyclic voltammetry (CV), Raman and UV/Vis spectroscopy. The functional loading and related chemical grafting of both primary amino- and ferrocene-decorated SWCNTs were spectroscopically (UV/Vis, Kaiser test) and electrochemically (CV) determined, respectively.

Keywords: click chemistry · chemical grafting · multimodal functionalization · nanostructures · nanotubes

Introduction

Since their discovery,[3] carbon nanotubes (CNTs)[4] have received growing attention in nanotechnology because of their unique mechanical, thermal and electrical properties.[5] At present, CNTs are among the nanomaterials with the largest impact on a wide range of technological applications,[1, 2] from nanocomposite materials with improved chemophysical properties[6] to biology[7] and nanomedicine[8] for drug delivery and imaging. Due to their scarce processability and miscibility in the most common media, both covalent and noncovalent functionalization approaches at the CNT sidewall have been extensively investigated in the last few years. CNT sidewall and tip decoration with organic functional groups has allowed scientists to exploit the unique properties of these macromolecular systems more conveniently. Indeed, the development of new methodologies for the covalent functionalization of CNTs, which is aimed at integrating these nanomaterials into more complex functional structures, has recently emerged as an area of great interest.[9] Despite the chemical inertness of the CNT sidewalls, relevant examples of organic functionalization have been successfully addressed.[9] Among them, reactions with nitrines,[10] nucleophilic carbenes,[11] diazonium salts,[12] bromomalonates,[13] free radicals[14] and 1,3-dipoles[15–19a] have been widely documented on both experimental[9] and theoretical ground. In spite of this, making complex carbon nanostructures, such as SWCNTs and/or MWCNTs, flexible platforms for the efficient/facile and multiple functionalization of their sidewalls and tips, still represents a priority to be properly faced. In particular, one main challenging issue is to impart multimodality to these systems by exploiting the whole CNT surface for the anchoring of different molecules, possibly under mild reaction conditions and avoiding undesired side-
processes or conflicting side-reactions between the decorating groups.

Different synthesis approaches have been successfully applied to CNT multifunctionalization, and all of them take advantage of well-established organic strategies: from the combination of different organic protocols\(^1\) and the covalent anchoring of masked functionalities bearing orthogonally cleavable protecting groups\(^{2,3}\) to site-selective functionalization of the opposite tube ends on vertically aligned multiwall carbon nanotubes (VA-MWCNTs) exposed to different photoreactive solutions.\(^{21}\) Here, we describe a versatile and efficient organometallic approach to the (multi)functionalization of SWCNTs, starting from covalently modified nanomaterials bearing phenylazido pendant arms. Their subsequent exposure to terminal acetylenes under Cu-mediated conditions (CuAAC reaction) allows for the convenient homo- and/or heterodecoration of the CNT sidewalls with organic/organometallic fragments or mixtures thereof. Reactions described hereafter are found to be highly efficient in producing differently functionalized carbon nanomaterials, even at relatively low reaction temperatures (85 °C); this sets the way for a versatile approach towards CNT sidewall multifunctionalization. Moreover, the azide-alkyne cycloaddition reaction is compatible with various solvents and functional groups\(^{2,3}\) and the produced triazole functionality is chemically stable, with structural and functional properties similar to those of the (most common) amide bond. Accordingly, click chemistry represents a promising and original choice for boarding molecular systems on the “CNT skeleton”, thus imparting multimodality to the final nanocarbon materials.\(^ {24-26}\)

Alkynes containing either orthogonally cleavable protecting groups or chemical functional groups imparting well-defined redox properties to the final nanocarbon materials have been selected; this choice was motivated by the need for controlling the course of the functionalization process and the degree of the final functionalization loading through complementary chemical/spectroscopic and electrochemical measurements.

Such an approach for the functionalization of carbon nanostructures aims at providing chemists with “flexible platforms” (phenylazido-decorated SWCNTs) to be used for “mild” organic/organometallic (multi)decoration. In addition, the high functional group tolerance of the CuAAC protocol makes this approach highly suitable for imparting multimodality (heterodecoration) to carbon nanostructures. Indeed, a one-step cycloaddition with acetylene mixtures can be conveniently used to bring different molecules on the tube board; this minimizes the potential drawbacks that result from the application of different (and subsequent multistep) organic functionalization protocols.

All homo- and heterofunctionalized materials presented hereafter have been characterized by thermogravimetric-MS analysis, FT-IR/Raman spectroscopy and TEM microscopy. Cyclic voltammetry (CV) and ninhydrin (Kaiser) test were finally used (whenever applicable) to calculate the functional loading.

**Results and Discussion**

Our approach to the (multi)functionalization of carbon nanostructures relies on the preliminary derivatization of the CNT sidewalls and tips with 4-azidoaniline (1) under classical Tour conditions\(^{23}\) (Scheme 1).

![Scheme 1. Synthesis of the arylazido-decorated \(f_{\text{az}}\)-SWCNT (2) sample.](image)

The reaction proceeds chemoselectively in \(o\)-dichlorobenzene/acetonitrile (ODCB/CH\(_3\)CN) through the in situ generation of aryldiazonium salts to afford the arylazido-decorated \(f_{\text{az}}\)-SWCNTs (2). The 4-azidoaniline was entirely recovered with no apparent decomposition of the azido group once the reaction was carried out in the absence of the proper alkyl nitrite (blank test). Furthermore, the azido group did not show any functionalization tendency even under harsher reaction conditions (ODCB 140 °C for prolonged reaction times); this might enhance its chemical reactivity (nitrene formation after a thermally induced N\(_2\) elimination).\(^ {10,11}\)

In a typical procedure, the chemoselective arylation proceeded smoothly at 60 °C, and afforded the \(f_{\text{az}}\)-SWCNT material. Successive sonication/centrifugation/washing cycles and filtration through a 0.2 μm pore inorganic membrane (Anodisc™) were used to recover the functionalized sample; the collected solid (2) was dried under vacuum and stored under N\(_2\) atmosphere without decomposition over months. The thermal stability of the azido-functionalized material (2) was established according to the following thermal-stress test: the solid sample was maintained while being stirred at 60 °C on-air, overnight, with no apparent alteration. Furthermore, the extremely high C/N ratio of 2 makes it a relatively safe, handling and harmless, azido-containing material.\(^ {28}\)

This chemistry produces highly-functionalized samples and can be conveniently performed on a relatively large scale (up to 200 mg of SWCNTs per run). Evidence of the sidewall functionalization is firstly obtained by comparing
the TGA profiles of pristine and functionalized materials (Figure S1 in the Supporting Information); a weight loss of 6.8% is calculated in the 40–70°C temperature range.\[20\]

The N and C quantitative elemental analysis (pristine SWCNTs: N 0.26, C 63.34; fN3-SWCNTs 2: N 6.95, C 64.55) also provides evidence for the functionalization.\[29\] According to these data, it can be roughly inferred that one phenylazido group is present every 80–90 C atoms of the CNT; hence about 0.58 mmol of C6H4N3 per g of 2 are covalently tethered to the sidewalls. Additional evidence of the phenylazido decoration at the CNT sidewalls was unambiguously provided by the FT-IR spectrum of 2 (Figure S2 in the Supporting Information). A relatively intense asymmetric stretching v(N) close to 2100 cm\(^{-1}\) with its symmetric counterpart falling around 1290 cm\(^{-1}\) are indicative of azido pendant groups.\[30\]

The fN3-SWCNT sample did not show any appreciable improvement in solubility/dispersibility in either polar (DMF, EtOH) or apolar (toluene) organic solvents compared to the pristine material. On the other hand, TEM analysis of the former sample revealed a higher disaggregation degree of the CNT bundles throughout the whole scanned area (Figure S3 in the Supporting Information). Raman spectroscopy was finally used for the characterization of 2; an increased intensity of the disorder-induced mode (D-band) at 1314 cm\(^{-1}\) together with an overall reduction of the peak’s intensity of the RBMs (between 75 and 250 cm\(^{-1}\)) were unambiguously indicative of the sidewall derivatization (Figure S4a in the Supporting Information).\[18,19,31,32\] From a closer examination of the spectra reported it can be easily inferred that the functionalization increased the (I\(_D\)/I\(_G\)) intensity ratio from 0.34 (for pristine SWCNTs) to 0.66 (for 2); this suggests a substantial sp\(^2\) CNT sidewall perturbation after the functionalization (Figure S4b and c in the Supporting Information).

The as-synthesized fN3-SWCNTs (2) were exploited as a versatile starting material for convenient CNT sidewall (multi)decoration, by using organic and/or organometallic reagents bearing terminal alkyne pendant arms. Our strategy towards the (post)functionalization of 2 relied upon an efficient Cu\(^{I}\)-mediated azide-alkyne cycloaddition protocol (CuAAC).\[22a,23b,33\] A conceptually related but complementary approach has been recently proposed by Adronov and co-workers;\[34\] polymer–nanotube conjugates were prepared by successive sonication/centrifugation/washing cycles and filtration through a 0.2 mm pore inorganic membrane (Anodisc\textsuperscript{TM}) before being dried under vacuum. Afterwards, compounds 7, 9 and 10 underwent chemical deprotection to give either the hydroxy- (11) or the amine-decorated (12) nanocarbon materials (Scheme 3).

Our approach for the facile (post)functionalization of 2 is summarized in Scheme 2. According to this, a series of alkyne-terminated organic/organometallic compounds HC\(=\)C–R\(_{12}\) 3–6 were successfully coupled through CuAAC reaction by using either CuSO\(_4\)/Na-ascorbate or the organosoluble [(EtO)\(_3\)PCuI] as metal sources.\[36,37\]

In a typical procedure, terminal alkynes 3–6 and the fN3-SWCNTs were treated in degassed DMF at 85°C for two days in the presence of CuSO\(_4\)/Na-ascorbate (10 mol% Cu/alkyne ratio). Attempts to improve the functionalization degree by replacing CuSO\(_4\)/Na-ascorbate with the organosoluble [(EtO)\(_3\)PCuI] in DMF were unsuccessful for almost all the scrutinized acetylene derivatives except for the ethynylferrocene 4 (Table 1, entry 2).

All functionalized samples (7–10) were subjected to successive sonication/centrifugation/washing cycles and filtration through a 0.2 μm pore inorganic membrane (Anodisc\textsuperscript{TM}) before being dried under vacuum. Afterwards, compounds 7, 9 and 10 underwent chemical deprotection to give either the hydroxy- (11) or the amine-decorated (12) nanocarbon materials (Scheme 3).

**Table 1. Loading capacity of f-SWCNTs.**

<table>
<thead>
<tr>
<th>f-material</th>
<th>“Clicked” molecule loading [mmolg(^{-1})] (functional group)</th>
<th>Measured loading [mmolg(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>f(_{I})-SWCNT (7)</td>
<td>0.49 [85]</td>
<td>–</td>
</tr>
<tr>
<td>f(_{II})-SWCNT (8)</td>
<td>0.45 [78]</td>
<td>0.38 [80] (ferrocene)</td>
</tr>
<tr>
<td>f(_{III})-SWCNT (9)</td>
<td>0.55 [95]</td>
<td>–</td>
</tr>
<tr>
<td>f(_{IV})-SWCNT (10)</td>
<td>0.55 [95]</td>
<td>–</td>
</tr>
<tr>
<td>f(_{I(NH2)})-SWCNT (12)</td>
<td>0.49 [&gt; 99]</td>
<td>0.34 [84] (NH(_2))</td>
</tr>
<tr>
<td>f(_{II(NH2)})-SWCNT (11)</td>
<td>0.55 [&gt; 99]</td>
<td>–</td>
</tr>
<tr>
<td>f(_{IV(NH2)})-SWCNT (12)</td>
<td>n.d.</td>
<td>0.12 [43] (NH(_2))</td>
</tr>
</tbody>
</table>

[a] As calculated from the TGA profiles, assuming a phenylazido loading (–C\(_6\)H\(_4\)N\(_3\)) of 0.58 mmolg\(^{-1}\) of f\(_{Cu}\)-SWCNTs (2); [b] mol% of reacted phenylazido groups, as calculated from the TGA weight losses; [c] as calculated from cyclic voltammetric data; [d] CuSO\(_4\)/Na-ascorbate as metal source; [e] (EtO)\(_3\)PCuI as metal source; [f] as calculated from the Kaiser test.

![Scheme 2. CuAAC reaction between arylazido-decorated f\(_{Cu}\)-SWCNTs (2) and alkyne-terminated organic/organometallic compounds (3–6).](image-url)
According to Scheme 3, a complete deacetylation of the $\beta$-d-glucopyranoside 9 was achieved by refluxing the CNT tethered tetra-acetyl-sugar in acidic (H$_2$SO$_4$ cat.) ethanol, overnight, to afford the glycoconjugate derivative $f_{III(OH)}$-SWCNTs (11). Acidic conditions were also used to remove the Boc protecting group (TFA/CH$_2$Cl$_2$), whereas ethanolic hydrazine was employed to cleave the orthogonal phthalimide framework; both procedures were used to generate primary amine groups at the CNT sidewall [$f_{I–IV(NH_2)}$-SWCNT (12)].

Characterization of the $f_{I–IV}$-SWCNT samples (7–10) and their deprotected counterparts (11–12): The functionalized nanocarbon materials 7–10 and their derivatives $f_{I–IV(OH)}$ and $f_{I–IV(NH_2)}$-SWCNTs (11–12) were characterized by different chemical (Kaiser test, solubility tests, elemental analysis), spectroscopic/spectrometric (FT-IR, TGA-MS, Raman) and morphological (TEM) techniques. Evidence for the Cu-mediated azide-alkyne cycloaddition was primarily achieved by comparing the TGA profiles of the pristine SWCNTs with those of the functionalized materials.

In particular, 7 and 10 (Figure 1, top) showed a weight loss of 9.9 and 15.7 %, respectively, in the 40–700°C temperature range (calculated as the weight difference between the TGA profiles of 7/10 and the pristine sample). As a result, one may conclude that the cycloaddition reactions proceed smoothly with both alkynes under Cu-mediated conditions (ca. 85 and 95 % yield, respectively, calculated by using the $-\text{C}_3\text{H}_6\text{N}_2$ loading as reference on the $f_{I–IV}$-SWCNT sample; see also Table 1, entries 1 and 4). Similarly, 8 and 9 (Figure 1, bottom) showed a weight loss of 9.7 and 27.3 %, respectively; this is consistent with an azide–alkyne cycloaddition reaction taking place with about 78 and 95 % yield, respectively (Table 1, entries 2 and 3).

A mass analysis performed on the low molecular weight volatiles (from 25 to 125 amu) generated during the thermogravimetric tests was used to obtain further qualitative information on the composition of selected functionalized samples. In particular, the thermal decomposition and rearrangement (below 300°C) of both tert-butoxyl groups at the N-Boc protected cycloaduct 7 and the acetyl fragments at 9 were evidenced by isobutene ($m/z$ 56 [M$^+$]; $m/z$ 55 [M$^+$ – 1]; $m/z$ 57 [M$^+$ + 1]; Figure 1, top) and acetic acid ($m/z$ 60 [M$^+$].

Scheme 3. Preparation of hydroxy- (11) and primary amine-decorated (12) carbon nanostructures.

Figure 1. TGA profiles of pristine SWCNTs and $f_{I–IV}$-SWCNTs in the 40–700°C temperature range. MS analyses of selected volatiles are reported for 7 (top) and 9 (bottom).
[M]+; m/z 59 [M+–2]; Figure 1, bottom) evolution; for both samples neither additional decomposition paths nor other significant mass fragmentations are observed in the same temperature range.

FT-IR spectra of the functionalized materials show characteristic broad bands between 1740 and 1630 cm⁻¹, which can be unambiguously attributed to \( \tilde{\nu}(C=O) \) vibrational modes of carbamate, acetyl and phthalimide moieties in 7, 9 and 10, respectively. In addition, the almost complete suppression of the intense \( \tilde{\nu}(N) \) asymmetric stretching (close to 2100 cm⁻¹) for all \( \beta \)-derivatives (7–10) is additional proof that Cu-mediated azide-alkyne cycloaddition occurred (Figure S5 in the Supporting Information). Raman spectra recorded on the (post)functionalized samples 7–10 did not show any relevant modification of the \( I_s/I_G \) ratio measured for 2. This is consistent with the absence of additional perturbations at the CNT sp² network after the post-derivatization of the tethered phenylazido moieties under CuAAC conditions.

Primary amine-decorated SWCNTs (12) were prepared by successive Boc and Pht deprotection of 7 and 10, under acidic (CF₃COOH/CH₂Cl₂, room temperature) and ethanolic hydrazine (H₂NNH₂, EtOH, room temperature) conditions, respectively (Scheme 3). The primary amine loading on both samples were determined by using the colorimetric Kaiser test and the measured values are reported in Table 1, entries 5 and 7 (see also the Supporting Information). The TGA profile of the deprotected \( f_{\text{IV(NH2)}} \) sample together with the complete disappearance of the typical isobutene evolution in the 100–300°C temperature range (Figure S6 in the Supporting Information) are consistent with a complete Boc removal under acidic conditions. According to this, a complete suppression of the \( \tilde{\nu}(C=O) \) stretching mode was also evidenced on the FT-IR spectrum of the deprotected material (Figure S7 in the Supporting Information). On the contrary, the TGA profile of \( f_{\text{IV(NH2)}} \) sample as well as its FT-IR spectrum (a broad band at around 1630 cm⁻¹ still present after the hydrazine treatment) are indicative of a partial deprotection of the Pht moiety (Figure S6 and S7 in the Supporting Information).

No significant changes in the final material characterization (FT-IR, TGA profiles) were observed when harsher deprotection conditions (40°C, 96 h) were employed. As support for this (qualitative) information, the more difficult phthalimide removal from 10 was evidenced by the lower free-amine loading measured by the ninhydrin (Kaiser) test on the \( f_{\text{IV(NH2)}} \) sample (Table 1, entry 7). For both the amino-decorated samples (\( f_{\text{IV(NH2)}} \) and \( f_{\text{IV(NH2)}} \)) the Kaiser test showed a lower functionalization loading compared to that estimated from the thermogravimetric profiles. Notably, the relatively high difference in the free amine loading measured between the \( f_{\text{IV(NH2)}} \) and \( f_{\text{IV(NH2)}} \) samples (Table 1, entry 5 vs. 7) is likely due to the incomplete deprotection of 10 under alcoholic hydrazine conditions; other reasons, including detrimental π–π interactions between the CNT sidewalls and the protecting phthalimide moieties, hampering the regular efficiency of the CuAAC protocol, can be reasonably ruled out. As a matter of fact, both N-protected propargylamines (3 and 6) undergo highly efficient cycloadditions under Cu-mediated conditions (Table 1, entries 1 and 4).

Cyclic voltammetry (CV) was used to quantify the ferrocene loading on sample 8. Figure 2 shows the CV data obtained from 8 as measured in aqueous perchloric acid (1 M) solution. Well-defined redox peaks (centered at \( E^0 = +0.37 \text{ V} \), forward scan; \( E^0 = +0.32 \text{ V} \), backward scan vs. Ag/AgCl/KCl) were observed.

The peak current was found to vary linearly with the scan rate (from 20 to 400 mV s⁻¹); this is consistent with a real ferrocene surface grafting. Anodic and cathodic peaks (160 mV full-width measurements at half maximum; +76%) larger than the ideal Nernstian width suggest possible interactions between the ferrocene units. The charge measured under the reduction and oxidation peaks (as obtained from samples prepared at different concentrations of 8) is consistent with a 2.1 wt% iron content (see the Experimental Section): these data translate into 0.38 mmol of grafted ethynylferrocene (4) per gram of \( f_{g}-\text{SWCNT derivative} \) (8), in fairly good accord with the TGA outcomes (Table 1, entry 2).

Classical decacylation conditions were finally used to prepare hydroxyl decorated SWCNTs (11) from the polycrystalline material 9 and the reaction course was investigated by TGA-MS and FT-IR spectroscopy. Although only a partial decacylation of 9 was observed by heating the sugar-decorated sample 9 in acidic EtOH (EtOH, HCl cat.), a complete acetyl deprotection was obtained under harsher reaction conditions (refluxing EtOH, H₂SO₄ cat.). TGA-MS analysis and FT-IR spectroscopy of 11 are consistent with the occurrence of a complete transesterification and the subsequent generation of the hydroxyl decorated nanomaterials (Scheme 3 and Figure 3). Most importantly, 11 shows enhanced solubility in protic polar solvents (EtOH) compared to precursor 9 (Figure 3); stable inks (up to 1.5 mg mL⁻¹ of

Figure 2. Cyclic voltammetry of 8 recorded at 100 mV s⁻¹ as scan rate.
EtOH) with no apparent CNT rebundling for days were conveniently prepared upon simple sample sonication (Figure 3a). A direct comparison of TEM images recorded with 9 and 11 (from EtOH solution/suspension) clearly shows a high disaggregation degree for the latter sample (Figure 3b). No appreciable changes of either tube diameters (from 3 to 8 nm as measured in the smaller CNT bundles) or tube lengths (from 50 nm to several micrometers) were observed throughout the whole scanned area for both samples, before and after deacetylation.

**Heterodecoration of SWCNTs:** Our approach to CNT decoration through CuACC chemistry was also applied to mixtures of acetylene end-capped molecules; this imparts multimodality to the final functionalized nanomaterials. Heterodecorated SWCNTs were prepared by treatment of the arylazido fIII-SWCNTs (2) in the presence of equimolar amounts of two selected acetylenes (Scheme 4). In all the heterofunctionalization experiments the total amount [mmol] of the acetylenes in the initial mixture was kept equal to that used in the homodecoration experiments. Acetylene mixtures were selected in order to bring on the SWCNT board either the same functional groups but masked with orthogonally cleavable protecting groups, or different functional groups distinguishable on the basis of complementary analytical/spectroscopic techniques.

In a typical experiment, an equimolar mixture of 3 and 6 were treated with the arylazido fIII-SWCNTs (2) under CuAAC conditions (Scheme 4). Successive and multiple sonication/centrifugation/washing cycles were accomplished with the heterofunctionalized material 13 (fMIX-SWCNT) to remove the unreacted alkynes and physisorbed reagents. The fMIX-SWCNT material 15 was prepared similarly by treating 2 with an equimolar amount of alkynes 4 and 6 under Cu-mediated conditions, followed by identical workup procedures. Filtration/washing through a 0.2 µm pore inorganic membrane (Anodisc™) was finally used to recover both mix-decorated samples; the solids were finally dried under vacuum up to constant weight and stored in air without any apparent decomposition over months.

According to the “deprotection” procedures described above for the homodecorated samples (7, 9 and 10) all mixed functionalized materials (13 and 15) underwent sequential cleavage protocols (Boc and Pht removal) to give the free-amine decorated samples 12, 14 and 16: UV/Vis measurements (Kaiser test) and cyclic voltammetry (CV) were finally used to calculate the achieved functionalization loading. TGA and FT-IR spectra recorded on both the mixed decorated samples and their deprotected counterparts were used for qualitative investigation only. Relevant TGA spectra are reported in the Supporting Information (Figure S9).

Sample 13 was sequentially treated under “basic” (ethanolic hydrazine) and acid conditions in order to orthogonally remove both amino-protecting groups. Firstly, the Pht group was cleaved upon treatment with hydrazine in ethanol at room temperature to give the intermediate 14; subsequently, the latter material was treated under classical acidic conditions to remove the Boc framework to afford 12. For each deprotection step, the samples were submitted to workup procedures identical to those described above for
the relative homodecorated/deprotected SWCNTs. The mono- and bis-deprotected samples from 13 (\(f_{\text{monoN}N}^{\text{HT}}\)-SWCNT, 14 and \(f_{\text{Bi2D}N}^{\text{HT}}\)-SWCNT, 12) were spectroscopically characterized with respect to their amine-free loading, by using the colorimetric Kaiser test; the respective \(-\text{NH}_2\) contents are summarize in Table 2 (entry 1).

Table 2. Loading capacity of \(f_{\text{mixx}}\) and \(f_{\text{mixx}}\)-SWCNTs.\(^{[6]}\)

<table>
<thead>
<tr>
<th>(f_{\text{mixx}})-SWCNT</th>
<th>Ph[^{[6]}]</th>
<th>Boc[^{[6]}]</th>
<th>Ferrocene loading [mmol g(^{-1})][^{[6]}]</th>
<th>Total loading[^{[6]}] [mmol g(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (f_{\text{mixx}})-SWCNT</td>
<td>0.09</td>
<td>0.16[^{[6]}]</td>
<td>-</td>
<td>0.25</td>
</tr>
<tr>
<td>2 (f_{\text{mixx}})-SWCNT</td>
<td>0.08</td>
<td>–</td>
<td>0.23</td>
<td>0.31</td>
</tr>
</tbody>
</table>

[^{[6]}] Prepared by using CuSO\(_4\) (10 mol %)/Na-ascorbic as Cu\(^{[6]}\) source; [b] protecting group removed; [c] as spectroscopically determined from the colorimetric Kaiser test; [d] as calculated from CV; [e] calculated as loading difference between the total loading and the \(-\text{NH}_2\) loading measured by the only Pht deprotection.

CV and UV/Vis spectroscopy were finally used to determine the functionalization loading on the \(f_{\text{mixx}}\) sample.\(^{[6]}\) The functionalization loading of 15, as measured spectroscopically and electrochemically on the monodecorated material (\(f_{\text{HT}N}^{\text{HT}}\)-SWCNT) 16, is summarized in Table 2 (entry 2). Similar to 8, the CV profile recorded for 16 shows larger anodic and cathodic peaks (180 mV; +90 % compared to the ideal Nernstian width)\(^{[41]}\) and a peak current varying linearly with the scan rate (from 20 to 400 mV s\(^{-1}\)). The charge measured under the reduction and oxidation peaks (as obtained from samples prepared at different concentrations of 16) is consistent with a 1.3 wt % iron content (see the Experimental Section); this accounts for about 0.23 mmol of grafted ferrocene per gram of 16 (Figure S10 in the Supporting Information).

As one may infer from Table 2, equimolar alkyne mixtures result (overall) in slightly lower functionalization degrees (compared to those calculated for the homodecorated samples).\(^{[43]}\) In spite of this, the “free-amino” and “ferrocene” functional loading was found to decrease almost linearly while reducing the molar amount of the respective alkynes. This result is of crucial importance, because it allows for convenient tuning of the functional groups at the SWCNT sidewalls by just varying the molar ratio of each alkyne in the reactive mixture.

**Conclusion**

Here we have described an original approach to the convenient and facile homo- and heterodecoration of single-walled carbon nanotubes. Our methodology relies on flexible and versatile “CNT platforms” chemoselectively decorated with aryl-azido pendant arms. Joining the latter functionalities with differently substituted terminal acetylenes (or mixtures thereof), under classical CuAAC conditions, allowed for a single-step homo- and heterofunctionalization/derivatization of the CNT sidewalls. Azidated CNTs represent safe and stable substrates (high C/N ratio) for the CNT sidewall (multi)decoration, and avoid the drawbacks that result from the application of different and subsequent organic functionalization protocols. Indeed, they allow for operation under the mild and popular “click chemistry” conditions with a variety of reactive alkynes. Additionally, the biorthogonal character of the click reaction makes this approach highly desirable for conjugating CNTs and biomolecules.\(^{[45]}\)

Accordingly, examples of homo- and heterofunctionalization of SWCNTs have been presented; model acetylene reagents, featured by either the same functional groups but masked with orthogonally cleavable protecting groups or by easily distinguishable moieties (on the basis of complementary analytical/spectroscopic techniques), were employed. Free amino- and alcohol decorated SWCNTs were prepared by treating the aryl-azido functionalized CNTs with N-protected propargylamine and tetra-O-acetyl-β-D-glucopyranoside acetylene derivatives, respectively; protecting group removal (Boc, Pht or Ac) was conveniently achieved under standard deprotection conditions. The functional group loading was estimated according to the TGA-MS profile and elemental analysis; when possible, they were measured more precisely by using either UV/Vis spectroscopy (Kaiser test for primary amine groups) or electrochemical titrations (CVs) for the functionalized materials containing redox active groups.

All the functionalized materials and intermediates were characterized according to their most relevant properties by using TEM microscopy, thermogravimetric analysis coupled with MS of volatiles, elemental analysis, cyclic voltammetry, Raman and UV/Vis spectroscopy.

Finally, the established applicability of the aryldiazonium chemistry (our first step in the production of \(f_{\text{HT}N}^{\text{HT}}\) “platforms”) of the arylation of different types of CNTs\(^{2[20a,27]}\) [in terms of diameter, number of walls (SWCNTs, MWCNTs) and length (pristine and shortened CNTs)] and carbon nanostructures, widens the applicability range of our protocol. Multimodal (shortened) MWCNTs and nanohorns are currently being prepared in our laboratory with the use of the synthesis protocol described herein.

**Experimental Section**

**General:** All manipulations were carried out under dry nitrogen atmosphere by using standard Schlenk-type techniques. Nitrogen (≥ 99.999 %; Rivoira) was dried through a CaCl\(_2\) column and deoxygenated with an oxisorb cartridge from Messer Griesheim prior to use. Dry DMF (dimethylformamide) and ODCB (orthodichlorobenzene) were prepared according to the literature procedures\(^{[46]}\) and stored over 4 Å molecular sieves under a nitrogen atmosphere. Acetonitrile was obtained by means of an MBraun solvent purification system. Pristine SWCNTs were purchased from Nanocyl S.A. (Nanocyl\(^{[TM]}\) 1100, average diameter and length: 2 nm and several nm, respectively). The 4-azidoaniline (1) was prepared according to modified literature procedures\(^{[47]}\) (half gram per single batch) and stored under N\(_2\) atmosphere at 5°C without decomposition (see the Supporting Information). N-Boc-propargylamine, ethynyl-
ferrocene, 2-propynyl-tetra-O-acetyl-β-D-glucopyranoside and N-propargylthiophalimide were purchased from commercial suppliers. The phenylazide (C$_6$H$_5$N$_3$) for "model" homogeneous CuAAC screening tests (see the Supporting Information) was prepared according to literature procedures. Unless otherwise stated, all other chemicals/solvents were obtained from commercial suppliers and used as received without further purification.

Sample sonication was carried out by using an Elma S15 Elmasonic sonicator bath (37 kHz) and cooling the samples in a water/ice mixture throughout the treatment. CNT filtration was accomplished by using inorganic Anopore™ membranes/filters; Anodisc™, 47 mm, Whatman, with 0.2 μm pore size. All measurements carried out on pristine SWCNTs and functionalized materials (f-SWCNTs) were conducted on samples that underwent identical washing/sonication/filtration workup procedures.

**Material characterization and analyses conditions:** Thermogravimetric analysis (TGA) was performed under N$_2$ atmosphere (50 mL min$^{-1}$) on an EXSTAR thermogravimetric analyzer (TG/DTA) Seiko 6200 coupled with a ThermoStar™ GSD 301T (TGA-MS) for MS gas analysis of volatile tiles. Transmission electron microscopy (TEM) analysis of modified and unmodified CNTs was performed by a Philips CM12 by operating at 120 kV, on samples prepared by drop casting previously sonicated suspensions (EtOH) over copper grids coated with a Formvar film (FF200-Cu, Formvar film only). TEM images were recorded with a CCD camera (Gatan 791). Raman spectra were measured by using the 647.1 nm emission of a Kr ion laser source, accordingly to the preferential reactivity of aryldiazonium derivatives with metallic SWCNTs.[30] The scattered radiation was collected in a back scattering geometry, dispersed by using the single stage configuration of a triple Raman spectrometer (Tivista TR555) equipped with a 900 grooves/mm grating and recorded by a liquid nitrogen cooled CCD detector. The beam profile was cleaned with a spatial filter and Rayleigh scattering was filtered out by using Notch filters. The spectral resolution was 1.7 cm$^{-1}$. The incident laser power on the sample was lower than 0.4 mW and any damage to the sample due to the laser was carefully checked and excluded. The Raman spectra were collected in order to detect the presence and strength of the G and D modes.[31] According to the literature, D- and G-peak intensities were used for the calculation of the I_D/I_G ratios.

FT-IR spectroscopy was performed on a Perkin–Elmer Spectrum BX FT-IR spectrophotometer and all CNT samples were prepared by mixing spectroscopic grade KBr with pristine SWCNTs or f-SWCNTs (2:3 wt%) and analyzed in 400-4000 cm$^{-1}$ range (600-800 scans) with a resolution of 1 cm$^{-1}$. For all reported FT-IR spectra, SWCNTs (2-3 wt%)/KBr was used as background and directly subtracted from the spectra of the functionalized (f-SWCNTs) samples. Elemental analyses were performed by using a Thermo FlashEA 1112 series CHNS-O elemental analyzer with an accepted tolerance of ±0.4 units. CV experiments were conducted on a Princeton 2273A potentiostat/galvanostat, by using a three-electrode arrangement with a saturated Ag/AgCl reference electrode and a platinum wire as counter electrode. UV/Vis measurements were performed on a Cary Varian 4000 spectrometer.

**Preparation of **f$_{SWCNT}$**-SWCNTs:** In a typical procedure, f$_{SWCNT}$-SWCNTs (20 mg) were suspended in TFA/CH$_2$Cl$_2$ (1:1) solution (5 mL) and sonicated for 15 min. The mixture was maintained under stirring at room temperature for 24 h until completed, and then diluted with ethyl acetate, sonicated for 10 min and centrifuged to remove the supernatant. The collected solid was finally suspended in a NE$_2$/THF/H$_2$O 1:20:2 mixture (20 mL), sonicated for 15 min, and centrifuged to remove the supernatant. The mother solution was carefully filtered through a 0.2 μm pore filter and washed twice with EtOH (2×20 mL) and CH$_2$Cl$_2$ (2×20 mL). The resulting solid sample underwent an identical workup procedure as that described for f$_{SWCNT}$-SWCNTs. The recovered material was dried under vacuum at 50°C to constant weight. All deprotected samples were stored in air at room temperature. Amine loadings were measured spectrophotometrically (UV/Vis) by using the colorimetric Kaiser test (see the Supporting Information).

**Preparation of f$_{DOPC}$**-SWCNTs (11): Five mg f$_{DOPC}$-SWCNT sample (9): f$_{DOPC}$-SWCNT (20 mg) were weighed into a flask (15 mL), suspended in ethanol (5 mL) and sonicated for 15 min. Then 2-3 drops of sulfuric acid (97%) were added and the mixture was further sonicated for 10 min. Afterwards, the suspension was filtered at the EtOH reflux for 24 h, then diluted with a large excess of ethyl acetate (30 mL), sonicated for 10 min and centrifuged so as to remove the supernatant. The collected solid residue was then washed three times with dichloromethane, each time sonicated for 10 min and separated from the supernatant by centrifugation. The solid residue 11 was finally suspended in dichloromethane, sonicated for 15 min, filtered through a 0.2 μm pore filter and dried under vacuum at 50°C to constant weight.

**Cyclic voltammetry (CV) measurements:** CV measurements were carried out in aqueous perchloric acid solution (1 M), by using Ag/AgCl as reference electrode and a Pt wire as counter electrode. An ethanol suspension...
of carbon nanotubes (f-SWCNTs; 1 wt%) was put on a glassy-carbon electrode (area = 0.1963 cm²) and covered with 2.6 µL of a solution of nafion (0.5 wt%) in EtOH. Unless otherwise stated, samples were analyzed at 30 mV·s⁻¹. For all scrutinized samples, the peak current was found to vary linearly with the scan rate from 20 to 400 mV·s⁻¹. Each measure was repeated up to six times by using different sample loadings (from 2 to 7 mg of 1 wt%) CNT suspension deposited on the glassy-carbon electrode and the resulting peak areas were properly correlated (by means of a linear regression curve) with the relative ion loadings (see the Supporting Information).

Acknowledgements

The authors thank the FreeCats project (NMP3-SL-2012-280658) and Nanocell Project (PAR FAS Regione Toscana Linea Aria di Azione 1.1.a.3) for financial support to this work. Thanks are also due to the Ministero dell’Istruzione, dell’Università e della Ricerca (MIUR) for support. G.G. also thanks Dr. A. Rossin, Dr. M. Innocenti and Dr. A. Lavacchi for fruitful discussions.


For CuAAC reactions that use CuSO₄/Na-ascorbate as catalyst see ref. [22a] and: P. Wu, V. V. Fokin, Aldrichimica Acta 2007, 40, 7–17.


The CuI/DBU/DMF system was additionally screened as the most effective protocol reported in the literature (see ref. [25]) for “click” couplings on SWCNTs. For related Huisgen-type conditions see also: K. D. Bodine, D. Y. Gin, M. S. Gin, J. Am. Chem. Soc. 2004, 126, 1638–1639. The latter conditions did not give (in our hands) any relevant difference compared to either CuSO₄/Na-ascorbate/DMF or (EtO)₃PCuI/DMF protocol conditions.

The efficiency of each metal source (CuSO₄/Na-ascorbate vs. [(EtO)₃PCuI], 10 mol% respect to the alkyne) in the CuAAC reaction with 2 was evaluated (in DMF) for all selected acetylene derivatives (3–6). TGA profiles of cycladducts (7–10) in combination with electrochemical (CV) and spectroscopic (UV/Vis) characterizations of 8 and 11–12, respectively, were used to quantify the metal source effectiveness. Both copper sources were successfully used under homogeneous CuAAC conditions (catalytic) whereas studying with electrochemical (CV) and spectroscopic (UV/Vis) characterization with 3–6 was evaluated (in DMF) for all selected acetylene derivatives (3–6). TGA profiles of cycladducts (7–10) in combination with electrochemical (CV) and spectroscopic (UV/Vis) characterizations of 8 and 11–12, respectively, were used to quantify the metal source effectiveness. Both copper sources were successfully used under homogeneous CuAAC conditions (catalytic) whereas studying the reactivity of all selected alkynes (3–6) with the model Ph-N₃ as reagent (see Supporting Information). Homogeneous conditions did not reveal any appreciable difference between the two selected catalytic systems (in term of isolated yields).

An almost linear increases of the Δ(E°−E°') up to a maximum of 54 mV was recorded on the CVs measured at different scan rates (25–400 mV s⁻¹). Such a trend was reasonably ascribed to whatever kinetic irreversibility of the electrochemical process.

No peaks corresponding to the ferrocene redox couple were observed when f Cristiano-Moutinho et al., Nat. Chem. Biol. 2005, 1, 13–21; b) I. M. Baskin, C. R. Bertozzi, Q SAR Comb. Sci. 2007, 26, 1211–1219.


Received: February 27, 2012
Published online: May 25, 2012