

## Carbon Nanotubes

# Covalent Grafting of BPin functions on Carbon Nanotubes and Chan–Lam–Evans Post-Functionalization

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Abstract: The chemical functionalization of carbon nanotubes is often a prerequisite prior to their use in various applications. The covalent grafting of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (BPin) functional groups directly on the surface of multi- and single-walled carbon nanotubes, activated by nucleophilic addition of nBuLi, was carried out. Thermogravimetric analysis (TGA) coupled with mass spectrometry, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ions mass spectrometry (ToF-SIMS) confirmed the efficiency of this methodology and proved the integrity and covalent grafting of the BPin functional groups. These groups were further reacted with various nucleophiles in the presence of a copper(II) source in the conditions of the aerobic Chan-Lam-Evans coupling. The resulting materials were characterized by TGA, XPS and ToF-SIMS. This route is efficient, reliable and among the scarce reactions that enable the direct grafting of heteroatoms at carbonaceous material surfaces.

Carbon nanotubes (CNTs) and, in general, nanocarbons (NCs) have proven to be of great interest thanks to their outstanding properties. Nonetheless, their chemical modification with desired functionalities<sup>[1-6]</sup> is often required for applications, such as in nanomedicine<sup>[7,8]</sup> or in the preparation of nanocomposite materials,<sup>[9,10]</sup> energy devices<sup>[11,12]</sup> or heterogeneous catalysts.<sup>[13]</sup> In their pristine state, CNTs tend to stack together due to  $\pi$ - $\pi$  interactions of their sidewalls. The stacking results in a very low dispersibility, an unfriendly manipulation and bad processability. Different synthetic ways have been developed to transform NCs into chemical platforms for further post-functionalization reactions. Among these reactions, the Suzuki–Miyaura cross-coupling has often been used and requires the presence of either a halogenated group (Cl, Br or I) or a boronic moiety on the carbonaceous surface.<sup>[14-17]</sup> Following Tour's seminal

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report, the addition of different phenyl groups has been described (including iodophenyl or phenyl boronic acid) starting from the diazo derivative (Scheme 1).<sup>[15,18,19]</sup> An alternative to this method is the direct grafting of halogens. The grafting of fluorine,<sup>[21]</sup> bromine<sup>[22-24]</sup> and iodine<sup>[25,26]</sup> through different reactions has been reported. Complementary to those reactions, to the best of our knowledge, there is currently no way to graft boronic groups directly on carbon nanotube or another carbon allotrope surfaces. This feature is of major interest as boronic acid derivatives have risen among the most useful tools in chemical transformations and have also found wide applications in materials, analytical chemistry and nanomedicine.<sup>[27-34]</sup>

Among the different methodologies available in the literature, we focused on the two-steps nucleophilic addition of organolithium reagents and electrophile capture.[35-37] We have recently reported the successful grafting of propargylic moieties on NCs surface using this method, which was later used for click post-functionalization.<sup>[38]</sup> We propose hereafter the use of boron derivatives as a new set of electrophiles for introducing boron atoms under soft conditions directly linked to the surface of single- and multi-walled carbon nanotubes (S-/MWNTs). We investigated thereafter the reactivity of the grafted boronic moieties. Complementary to the well-known Suzuki reaction that has already been exploited in the field of CNT functionalization, we decided to tackle the challenging task of grafting Oand N-based nucleophiles on the surface of CNTs using the Chan-Lam-Evans transformation.<sup>[39,40]</sup> This copper-catalyzed oxidative coupling between a boronic species and different nucleophiles has never been used in NC functionalization and brings very interesting features. First, this coupling is very easy to handle as the reaction occurs under aerobic atmosphere and does not require any precaution, contrary to palladium catalyzed cross-coupling. Moreover it enables the versatile grafting of heteroatoms (e.g., O, N, S) directly on the surface. The only other reactions to our knowledge with this specificity are through the use of hazardous nitrene, pre-synthesized halogenated supports or aliphatic lithium amides.<sup>[23,41,42]</sup> Contrary to materials doped during their synthesis, this approach enables the formation of new single-site characterized supports.

We screened different boron-based reagents for the immobilization of either boronic acid or boronic acid pinacol ester (BPin) groups. The addition of *n*BuLi to SWNTs or MWNTs at -78 °C led to the formation of the anionic intermediate **1** (Scheme 2). Nanotubides **1** were then able to trap one of the 4

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## **Previous work**



Scheme 1. Covalent functionalization of CNTs for the immobilization of anchors used for post-functionalization.



Scheme 2. Chemical functionalization through nucleophilic addition and boron moieties capture.

electrophiles envisaged. The capture of trichloroborane resulted in the grafting of boronic acid groups on the surface to yield the material 2a. The use of trimethylborate or triisopropylborate led to 2b and 2c, respectively. Finally, 2d was generated when 2isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (iPrOBPin) was employed. The grafting efficiency was evaluated by means of thermogravimetric analysis (TGA). When pristine nanotubes (p-MWNTs) were submitted to increasing temperature under an inert atmosphere, no degradation of the material was observed until 750 °C (Figure 1). However, a weight loss was observed with materials 2a-d around 400°C and resulted from the decomposition of the grafted functions on the nanotube surface. This loss was relatively low in the case of 2a-c, approximatively

tunctions on the nanotube surface. This loss was relatively low in the case of 2a-c, approximatively 3.0 wt.% (Table 1). However, when *i*PrOBPin was used, we observed a consequential loss of 11.22 wt.% for **2d**. The weight losses were then converted into a functionalization degree (C/R), which takes into account the relative weight of the func-



Figure 1. TGA-MS graph obtained by performing the measurement under  $N_{\rm 2}$  atmosphere.

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	Table 1. Weight loss around 400 $^\circ\text{C}$ and calculated degree of functionali-				
zation (C/R) determined by TGA.					

Entry	Electrophile	Weight loss [wt.%]	C/R
2a	R = Z = CI, R' = OH	3.00	137
2b	R = Z = OMe, R' = OH	2.98	138
2 c	R = Z = OiPr, R' = OH	2.95	140
2 d	$R_2 = Pin = R'_{2'} Z = OiPr$	11.22	57

tional groups. More details on the calculation can be found in the Supporting Information. Similar degrees were obtained for **2a-c**. The best result was obtained with BPin-functionalized **2d** and the external functionalization degree, considering the ten concentric layers composing our MWNTs, was evaluated as one in seven carbon atoms.

To endorse our hypotheses, TGA was coupled with a mass spectrometer (MS) (Figure 1). A first peak was observed for m/ z=45 below 100 °C and was due to residual solvent. A second peak was obtained around 400 °C when the surface functions decomposed. This signal can be linked to the function B(OH)<sub>2</sub>. A third signal was recorded for m/z = 57 which corresponds to the *n*-butyl groups. The presence of pinacol moiety was confirmed by two signals at m/z = 101 and 59. The first one is due to the releasing of a molecule of water from pinacol and the second one is the consequence of the cleavage between the two guaternary carbons. The identity of the BPin group was ultimately verified with time-of-flight secondary ion mass spectrometry (ToF-SIMS). Indeed, a peak at 127.09 u (positive ions), corresponding to BPin group, could be observed. In addition, a peak at 139.09 u (positive ions) was detected as well (see Supporting Information). This peak can be attributed to BPin moieties plus one carbon atom. This supplementary carbon can only come from the carbonaceous surface and strongly indicates a covalent functionalization of the boron-based group. All this evidence put together confirm that both butyl and BPin functions are successfully grafted on the carbon support.

The covalent nature of NC functionalization is most commonly established by Raman spectroscopy. The intensity of the defect (D) band (ca. 1300 cm<sup>-1</sup>) and graphitic (G) band (ca. 1590 cm<sup>-1</sup>) were compared. The intensity ratio  $I_D/I_G$  raises alongside the anchoring of external groups as the sp<sup>3</sup> C contribution increases. Indeed, we noticed the increasing of  $I_D/I_G$  from 0.13 up to 0.38, confirming the covalent nature of the grafting (Figure 2). We submitted **2d**–MWNTs to X-Ray photoelectron spectroscopy (XPS) to reveal the presence of boron. We could successfully observe a peak at 192 eV corresponding to B<sub>1s</sub> with atomic concentration of 0.22 at.% (see Supporting Information).

We then took advantage of the grafted BPin functions. The Chan–Lam–Evans reaction is unique in its type and enables the coupling of two nucleophiles: an aryl organoboron (2 d) and various oxygenated or aminated partners (3 a–n) under mild oxidative conditions. Through a detailed mechanistic investigation, Watson and co-workers have recently reported modified reaction conditions that greatly improve the coupling of BPin reagents instead of boronic acid derivatives.<sup>[40]</sup> Such conditions



Figure 2. Raman spectra ( $\lambda = 1064$  nm) of p-SWNTs and 2 d–SWNTs.

consist in 10 mol% of Cu(OAc)<sub>2</sub>, an inverted organoboron/ amine stoichiometry, in which the organoboron species is the limiting reagent, and the replacement of the commonly used organic base (NEt<sub>3</sub>) with B(OH)<sub>3</sub>. This coupling was performed starting from **2d** with different nucleophiles **3a–o** in acetonitrile at 80 °C for 24 h under air leading to the formation of post-functionalized products **4a–o** (Scheme 3).

Compounds **4a–n** were submitted to TGA and XPS investigations (Table 2). When TGA was performed on products **4a–n**, a significant weight loss could be observed, as in the starting materials. We observed that the conversion was not complete and part of the starting material was subject to protodeboronation. Nonetheless, the presence of expected heteroatoms in appreciable quantity was observed by XPS. We were pleased to see that a large variety of nucleophiles could be employed: phenols (**4a–c**), alcohols (**4d**), sulfonamides (**4e,f**), pyrazoles (**4g,h**), anilines (**4i–k**), primary and secondary amines (**41–o**) were grafted. The presence of heteroatoms (F, Cl, Br, S or N) bore witness to the success of the coupling. The atomic ratios

Table 2. Compilation of TGA and XPS data of products 4a-o.								
Entry	Weight loss [wt.%] <sup>[a]</sup>	N <sub>1s</sub> <sup>[b]</sup>	$F_{1s}^{[b]}$	$S_{2p}^{\ \ [b]}$	$X^{[b]}$	Experimental at. ratio vs. theoretical at. ratio <sup>[c]</sup>		
4a 4b 4c 4d 4e 4f 4g 4h 4i	4.53 6.60 11.90 6.80 5.47 10.58 5.26 5.86 4.92	- 2.31 2.40 0.11 0.28 0.75 0.27 0.20	0.44 0.27 - 1.09 - 1.64 0.49	- - 0.08 0.38 - - -	0.11 <sup>[d]</sup> - - - 0.17 <sup>[e]</sup> - -	F/Br = 4.0  vs.  3 - - N/S = 1.4 vs. 1 S/CI = 2.2  vs.  2 - F/N = 2.5 vs. 3		
4j 4k 4l 4m 4n 4o	6.01 6.67 5.98 5.05 5.50 7.62	0.38 0.68 0.37 0.47 1.22 0.40	- 0.64 0.26 0.31 -	0.18 - 0.10 - -	- - - 0.32 <sup>[f]</sup> 0.22 <sup>[g]</sup>	N/S = 2.1 vs. 2 N/F = 1.1 vs. 1 N/F = 1.4 vs. 1 F/S = 3.0 vs. 3 - P/Pd = 1.5 vs. 2		

[a] Determined by IGA. [b] Determined by XPS, expressed as at.%. X=generic heteroatom. [c] Experimental value obtained from XPS data, theoretical one calculated from the substrate structure. [d]  $X = Br_{3d}$ . [e]  $X = Cl_{2p}$ . [f]  $X = P_{2p}$ . [g]  $X = Pd_{3d}$ .



Scheme 3. Catalytic Chan–Lam–Evans post-functionalization of boron-grafted MWNTs.

between heteroatoms were compared to give an insight of the grafted molecule. An experimental value close to the theoretical one suggest the maintenance of the molecular structure. The most pertinent ratios are reported hereafter (Table 2). In most cases, the experimental values corresponded tightly with the theoretical values. Therefore, we concluded that the integrity of the coupled species was preserved.

Complementary analysis was achieved with ToF-SIMS. The mass spectra of **4i** as model substrate allowed us to completely reconstruct the molecule grafted on the carbonaceous surface (Figure 3). A first peak at 68.99 u corresponded to the moiety  $[CF_3]^+$  (Figure 3 a). A second one at 145.03 u was linked to the fragment  $[C_6H_4CF_3]^+$  (Figure 3 b) and a third one at 160.04 u (negative ions) was in agreement with the whole grafted molecule  $[NHC_6H_4CF_3]^-$  (Figure 3 c). Finally a last peak distinguished himself at 172.04 u and was ascribed to the grafted compound plus one additional carbon atom, coming from the support (Figure 3 d). These results further corroborated the existence of covalently bound nucleophiles on CNT surface, validating thus the methodology we propose.



Figure 3. Portions of ToF-SIMS spectra of 4i for positive (a, b, c) and negative ions (d).

In conclusion, we presented the efficient functionalization of carbon nanotubes with boron-based groups grafted directly on the surface. This grafting was quantified by TGA and the nature of the immobilized moieties was confirmed by TGA-MS and ToF-SIMS. Both ToF-SIMS and Raman spectroscopy supported the covalent nature of this functionalization. Various nucleophilic functionalities were then covalently linked to CNTs through Chan–Lam–Evans coupling. This post-functionalization was confirmed by TGA and XPS, whereas ToF-SIMS supported the integrity of the covalently grafted nucleophiles. The present work provides a new approach towards the covalent functionalization of CNTs.

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#### **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** carbon nanotubes · Chan–Lam–Evans coupling · materials science · organoboron compounds · ToF-SIMS

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