Nanotube Chemistry

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Reductive Retrofunctionalization of Single-Walled Carbon Nanotubes**

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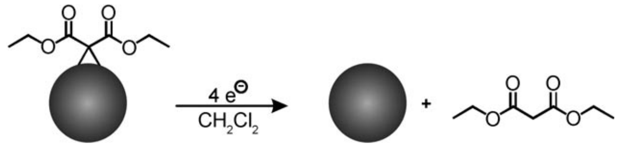
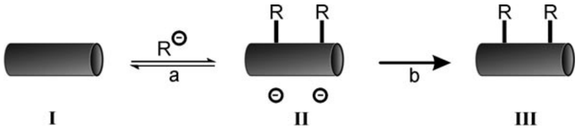
The chemical functionalization of fullerenes,[1] carbon nanotubes,[2] and graphene[3] is a prerequisite for the use of these synthetic carbon allotropes in high-performance applications. For this reason, addition reactions to the conjugated π system of fullerenes and single-walled carbon nanotubes (SWCNTs) have been intensively investigated.[1,2] The intrinsic chemical properties of these carbon allotropes can be determined by cage functionalization, but the new derivatives also offer new perspectives such as: 1) increased solubility, processability, and functionality; and 2) properties combined with those of other compound classes. Addition reactions to the sp^2-hybridized carbon framework are always accompanied by the generation of sp^3-hybridized atoms in the cages and, as a consequence, by changes of properties, in particular the electronic structure. This might be considered a drawback because the electronic properties of the parent sp^2 allotropes are in many regards outstanding and unprecedented.[4] However, once the attached addends have completed their assignment in a given process chain, they may be removed such that the structure and function of the SWCNTs are recovered. Cleavage of covalently bound addends,[5] however, often requires high temperatures, conditions that might not be compatible with many applications. In fullerene chemistry mild retrofunctionalization methods have already been discovered such as retro-Diels–Alder reactions[6] and retro-cyclopropanations[7] induced by cage reduction with at least two electrons (retro-Bingel reaction, Scheme 1). In the case of the retro-Prato reaction the removal of the pyrrolidine ring from the sp^2-hybridized carbon sphere is supported by Lewis acid catalysis or microwave irradiation.[8]



Scheme 1. Retrocyclopropanation of fullerene malonates.[7b]

We have recently developed a very versatile method for the functionalization of the sidewalls of SWCNTs, namely, the nucleophilic addition of metal alkylides and amides followed by reoxidation of the negatively charged intermediates $R_n SWCNT^{n-}$ to give the neutral derivatives $R_n SWCNT$ (Scheme 2).[9] Like the Billups alkylation of carbon nanotubes,[10] which is promoted by initial Birch reduction of SWCNTs with sodium and liquid ammonia followed by quenching with alkyl iodides, this method offers the advantage of efficient exfoliation of the parent SWCNT bundles; the electrostatic repulsion of the negatively charged intermediates allows for an even and homogeneous functionalization of individualized tubes. We have demonstrated that both methods are selective for the functionalization of small-diameter carbon nanotubes.[9b,11]



Scheme 2. Nucleophilic addition to SWCNTs: a) addition of R^- to the sidewall of the SWCNT, b) oxidation of the charged intermediate by oxygen.

We report herein on a fundamental discovery that demonstrates the close relationship between fullerene and SWCNT chemistry, namely, the reversibility[12] of addition reactions on SWCNT sidewalls. The reaction is analogous to the retrofunctionalization of C_{60} depicted in Scheme 1. Our rationale for the defunctionalization of alkylated SWCNTs is based on the assumption that the initial addition to SWCNTs is reversible (reaction (a), Scheme 2).

This proposal is supported by the observation that the degree of functionalization for nucleophilic addition reactions increases with the amount of addition reagent, even when a large excess of RLi is used. The results of a series of independent experiments—Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA)—support this conclusion. Figure 1 shows the

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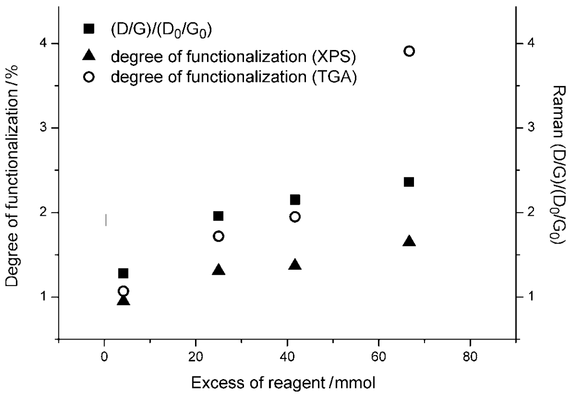
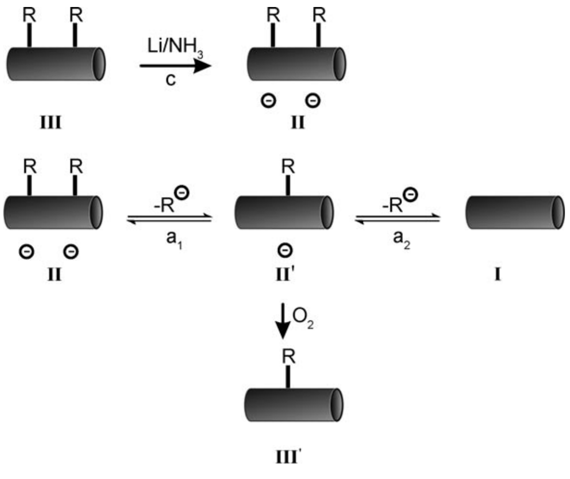


Figure 1. Comparison of the degree of functionalization for the reaction of SWCNTs with lithium *n*-propylamide. Raman (Figure S1), XPS (Figure S2), and TGA data (Figure S3).

results for the addition of lithium *n*-propylamide to HiPco SWCNTs (for details, see the Supporting Information), where even after a 40-fold excess of added amide, the still-moderate degree of functionalization continues to increase.

This finding prompted us to set up a series of further experiments to prove the presence of an equilibrium as well as possibly promote retrofunctionalization. If reaction (a) is an equilibrium, then retrofunctionalization should be observable starting from the negatively charged species **II** in the absence of LiR.

Therefore, we generated **II** by treatment of f-(*n*PrNH)$_n$SWCNT and f-(*n*Bu)$_n$SWCNT with lithium in liquid ammonia (reaction (c), Scheme 3) and subsequently oxidized the charged intermediates with oxygen. The Raman spectra (Figure 2) clearly show a considerable decrease of the D-band intensities of the retrofunctionalized tubes rf-R$_n$SWCNTs (**III′**) compared with their functionalized precursors f-R$_n$SWCNTs (**III**). This proves the proposed reduction induced defunctionalization of the tube sidewalls.



Scheme 3. Reductive retrofunctionalization of single-walled carbon nanotubes (R = *n*Bu, *n*PrNH).

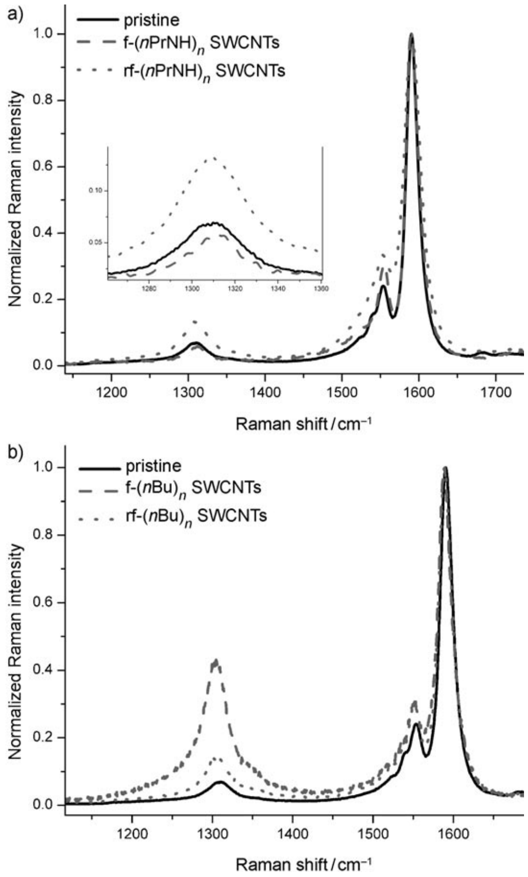
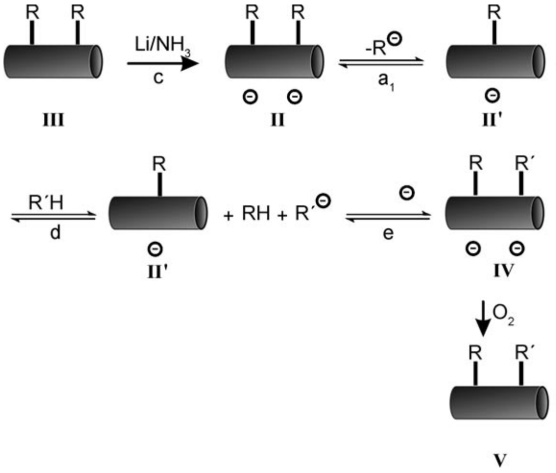


Figure 2. a) D- and G-bands of pristine material, *n*PrNH-functionalized SWCNTs (f-(*n*PrNH)$_n$SWCNTs), and charged *n*PrNH-functionalized tubes after oxidation with oxygen (rf-(*n*PrNH)$_n$SWCNTs). b) D- and G-bands of pristine material, *n*BuLi-functionalized SWCNTs (f-(*n*Bu)$_n$SWCNTs), and charged *n*BuLi-functionalized tubes after oxidation with oxygen (rf-(*n*Bu)$_n$SWCNTs). Excitation wavelength: 633 nm.

The next experiment was set up to find out whether an addend R can be exchanged for another addend R′. This substitution would be possible only if reaction (a) in Schemes 2–4 is reversible. For this purpose we used f-(*n*Bu)$_n$SWCNTs (**III**) as the starting material and converted them by means of a Birch reduction into the corresponding negatively charged species **II** (Scheme 4). Then we added *n*-propylamine with the expectation that *n*BuLi, generated by reaction (a$_1$), as the stronger base would deprotonate the primary amine. The resulting lithium *n*-propylamide would then be part of the new equilibrium reaction (d) and undergo nucleophilic addition to the SWCNT sidewall, yielding mixed SWCNT derivatives mf-(RR′)$_n$SWCNT^{n-} (**IV**).

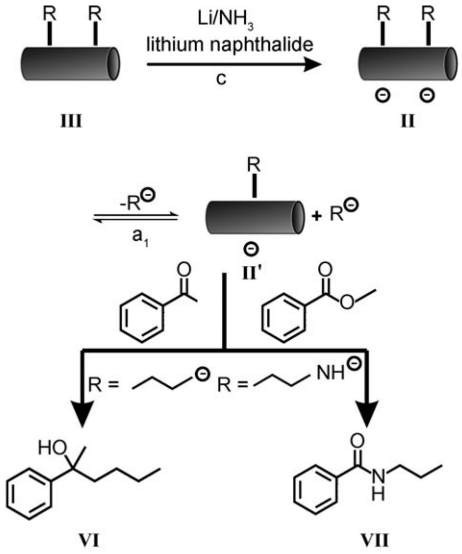
After reoxidation of **IV** with oxygen we analyzed the sample (mf-(RR′)$_n$SWCNT–**V**) by XPS and coupled thermogravimetric mass spectrometry (TGA–MS). The characteristic N 1s signal corresponding to the nitrogen atom of the amine substituent was clearly detected in the XPS spectra (Figure S4 in the Supporting Information). In TGA–MS analysis the signal of the *n*PrNH fragment at m/z 58, which detached in the temperature range between 300–500 °C, was evident (Figure S5 in the Supporting Information). Both methods unambiguously prove the presence of covalently attached *n*-propylamino moieties within the mixed adduct **V** and therefore confirm the existence of the equilibrium reaction (a$_1$).



Scheme 4. Exchange of functional groups R→R′ (R = *n*Bu; R′ = *n*PrNH) based on the deprotonation of *n*PrNH$_2$ by *n*Bu$^-$, which is generated by reduction of *n*Bu-functionalized SWCNTs.

It should be mentioned that in a control experiment the negatively charged tubes generated by the Birch reduction of parent SWCNTs did not deprotonate *n*-propylamine, since no *n*-propylamine-functionalized SWCNTs were detected. Apparently negatively charged SWCNTs are relatively weak bases. This observation is in line with the weak basisity of fullerenides (e.g. *t*Bu-C$_{60}^-$ pK_a = 5.7).[13] The basisity of SWCNTs should be even considerably lower because of 1) the lower degree of pyramidalization of SWCNTs and 2) the much more pronounced delocalization of the negative charges.[14]

The final proof of the proposed retrofunctionalization of SWCNTs was obtained from trapping experiments (for detailed information see the Supporting Information) with different electrophiles (Scheme 5). f-(*n*Bu)$_n$SWCNTs and f-(*n*PrNH)$_n$SWCNTs were reduced with lithium naphthalenide or Li/NH$_3$ and subsequently acetophenone, in the case of f-(*n*Bu)$_n$SWCNTs, or methyl benzoate, in the case of f-(*n*PrNH)$_n$SWCNTs, was added. The respective trapping products **VI** and **VII** formed, as unambiguously demonstrated by NMR spectroscopy and mass spectrometry after isolation from the reaction mixture.



Scheme 5. Trapping sequence: Charged SWCNT intermediates **II** and **II′** in equilibrium (a$_1$) with the free organolithium species R$^-$ and subsequent reaction with acetophenone (for R$^-$ = *n*Bu$^-$) and methyl benzoate (for R$^-$ = *n*PrNH$^-$).

In conclusion, we showed that the nucleophilic additions to the sidewalls of carbon nanotubes are reversible as long as there is excess of negative charge on the tubes. As a consequence retrofunctionalization of SWCNT derivatives can be achieved under mild conditions simply by reduction. The underlying equilibrium can also be used in transfunctionalization reactions, where one functional entity is partly exchanged for another, giving access to mixed SWCNT derivatives with an extended functionality profile. The retrofunctionalization of carbon nanotubes described here is closely related to known reactions in fullerene chemistry such as the retro-Bingel reaction. Here, retrofunctionalization is also initiated upon charging of the carbon cage. Analyzing the structure of the synthetic carbon allotropes shows that the degree of pyramidalization of the C atoms decreases in the series fullerenes to SWNCTs to planar graphene.[14] The expectation is that the ease of reductive retrofunctionalization increases in the opposite direction, with graphene being the least reactive allotrope for addition reactions but the most reactive for reduction-induced retrofunctionalization. The exploration of addition and retroaddition reactions to the flat π surface of graphene is currently under way in our laboratory.

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