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Covalent Sidewall Functionalization of SWNTs by Nucleophilic Addition of Lithium Amides

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The synthesis and characterization of sidewall-functionalized SWNT derivatives $(n\text{PrNH})_n$-SWNTs containing *n*-propylamine addends is reported. The nucleophilic addition of in situ generated lithium *n*-propylamide to the sidewall of SWNTs and the subsequent reoxidation of charged intermediates of the type $(n\text{PrNH})_n\text{-SWNT}^{n-}$ leads to carbon nanotube derivatives with covalently attached amino groups. Based on the reaction sequence, a homogeneous dispersion of the carbon nanotube material is achieved as a result of the electrostatic repulsion of negatively charged intermediates. The solubility of the resulting propylamine-functionalized $(n\text{PrNH})_n$-SWNT material in organic solvents is drastically increased. The functionalized tubes were characterized in detail by Raman spectroscopy, thermogravimetric analysis (TGA/MS), X-ray photoelectron spectroscopy (XPS) and UV/Vis/NIR spectroscopy.

Introduction

Soon after SWNTs[1] became available in macroscopic amounts[2] scientists started to exploit the remarkable potential of this extraordinary new carbon allotrope. Their unique one-dimensional structure and therefore their outstanding electronic, thermal and mechanical properties are unrivalled by any other substance class.[3] In order to pave the road for CNT applications in various molecular-based devices[4] a multitude of hurdles have to be overcome related to the intrinsic poor solubility of SWNTs in organic and aqueous solvents.[5] It was quickly recognized that chemical functionalization was the keystone to achieving this[6] and would also help to solve another problem relating to the production of SWNTs, that is, the separation of metallic and semiconducting tubes. Up to now, all the techniques used for the production of SWNTs yield a mixture of carbon nanotubes in terms of length, diameter and chirality, and, directly related to this, a mixture of metallic and semiconducting tubes which hampers their entry into nanoworld devices. Therefore the chemical functionalization and structural alteration of carbon nanotubes has flourished in the last half decade and has been documented in a series of review articles related to this topic.[7]

The structural alteration by functionalization turned out to be a more complicated task than was first anticipated. One reason for this is the low inherent reactivity of the graphitic sidewalls of the SWNTs.[8] Nevertheless, progress was made, for example, by the use of very reactive compounds, such as fluorine,[9] azomethine ylides,[10] diazonium compounds,[11] radicals,[12] carbenes,[12a,13] nitrenes,[12a,13a,14] alkali metals[15] and organometallic reagents.[16] This allowed direct functionalization of the sidewall of SWNTs leading to the generation of sufficiently soluble material.

Some of these addition reactions also exhibit a preference for metallic over semiconducting nanotubes.[11c,15f,16d,16e] In a recent detailed study we showed that this is also true for the nucleophilic addition of organometallic compounds to the sidewalls of SWNTs followed by the reoxidation of the intermediates by air.[16e]

Herein we report that in situ generated *n*-propylamide can covalently be attached to the sidewalls of HiPco® SWNTs[3b] by a direct nucleophilic addition reaction. This reaction sequence based on primary organic amines is in contrast to well-established defect functionalizations,[17] non-covalent interaction procedures[18] and nucleophilic substitution reactions.[19] The direct addition of amines to the end-caps and defect sites of MWNTs has been reported by Basiuk et al.,[20] but to the best of our knowledge, the direct sidewall functionalization of intermediately generated amides has not been investigated up to now. In our reaction sequence, the negatively charged $(n\text{PrNH})_n\text{-SWNT}^{n-}$ intermediates are reoxidized by air leading to SWNT derivatives with covalently bound amino functionalities. The functionalized tubes exhibit a drastically improved solubility in organic solvents, most clearly pronounced in THF. A system-

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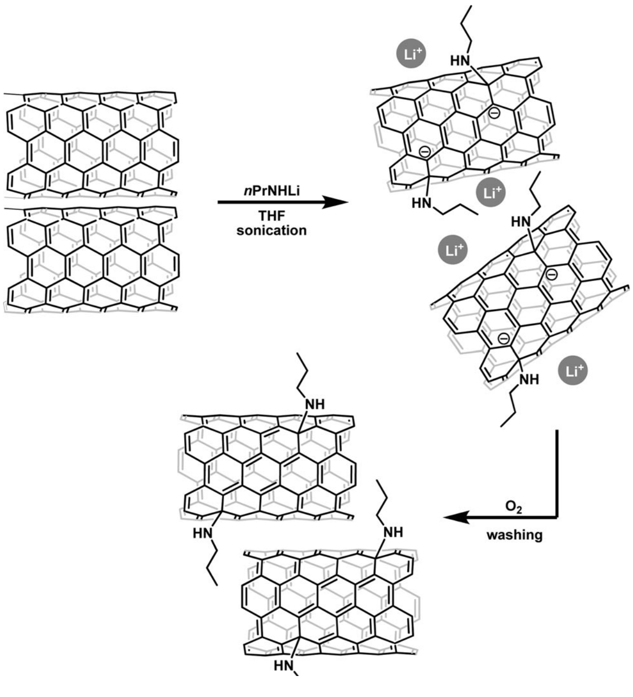
atic study of the concentration dependence of the reaction shows that there is a direct correlation between the amount of the lithium amide used and the functionalization-induced disorder in the SWNT derivatives.

Results and Discussion

In order to answer the question as to whether the nucleophilicity of lithium amides is high enough to attack SWNT sidewalls and to establish a covalent bond between the generated sp^3 carbon atom of the tube framework and the nitrogen atom of the amide functionality, we used in-situ-generated lithium *n*-propylamide in a similar reaction to one performed earlier for the generation of alkyl-functionalized SWNT derivatives.[16d,16e] The whole reaction sequence is outlined in Scheme 1.



Scheme 1. Amidation sequence of SWNTs with lithium *n*-propylamide followed by reoxidation.

By nucleophilic addition of the in situ generated *n*-propylamide in THF to the SWNT sidewall one negative charge is transferred per addend to the nanotube π system. This leads to the intermediate formation of negatively charged SWNT derivatives of the type $(n\mathrm{PrNH})_n$-SWNT^{n-}. Owing to the electrostatic repulsion, the SWNTs are individualized and very effectively solubilized, which is clearly demonstrated by the formation of a black homogeneous solution. The subsequent reoxidation of the $(n\mathrm{PrNH})_n$-SWNT^{n-} intermediates leads to the formation of the neutral derivatives $(n\mathrm{PrNH})_n$-SWNT. This uncharged material still exhibits a high degree of solubility due to the *n*-propylamine addends.

In order to elaborate the effect of lithium amide concentration on the degree of functionalization or on the metallic versus semiconducting selectivity, we performed this nucleophilic addition reaction with varying amide/nanotube ratios. The different amounts of *n*-propylamine used for the functionalization of 20 mg SWNTs are summarized in Table 1.

Table 1. Assignment of the functionalized SWNT derivatives obtained after treatment with varying amounts of *n*-propylamide.

Product	Millimolar carbon ratio SWNT[a]/amine
f0-$(n\mathrm{PrNH})_n$-SWNT	1:1
f1-$(n\mathrm{PrNH})_n$-SWNT	1:2.5
f2-$(n\mathrm{PrNH})_n$-SWNT	1:5
f3-$(n\mathrm{PrNH})_n$-SWNT	1:25
f4-$(n\mathrm{PrNH})_n$-SWNT	1:50

[a] This number is derived from the weight of the SWNT material divided by the molar weight of carbon.

We immediately realized that after functionalization the material was considerably more soluble in all organic solvents, with THF leading the way, than the pristine starting material. This is nicely illustrated in Figure 1. The stability of a THF solution of the functionalized material is directly related to the amount of amine used for the derivatization sequence. Samples with fewer *n*-propylamine side-chains are stable for several hours, whereas *f4*-$(n\mathrm{PrNH})_n$-SWNT, which has the highest number of attached functional groups, is stable for several days. The solubility of this material in THF is in the order of about 1 mg/mL.

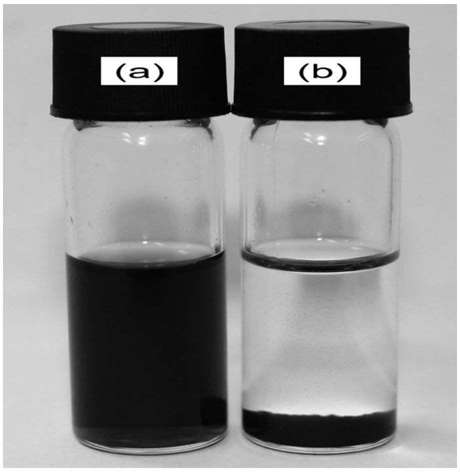


Figure 1. Photograph of *f4*-$(n\mathrm{PrNH})_n$-SWNT (a) and pristine SWNTs (b) in THF.

For the chemical modification of SWNTs the unravelling of the SWNTs bundles,[24] and therefore the individualization of the nanotubes in solution, is a fundamental key step. One common approach to achieving this individualization is the use of aqueous solutions of ionic detergents like sodium dodecylsulfate (SDS) or sodium dodecylbenzenesulfonate (SDBS).[21,22]

The rebundling of the tubes after rope separation by ultrasonication is prevented by charged detergent molecules. The disadvantages of this method are the relatively high concentrations of surfactants required and the instant rebundling after the removal of the detergents. Methods that transfer charge and an organic moiety at the same time have the advantage of achieving the debundling and the functionalization of the SWNTs in one step.

This is the case in our addition sequence and represents an elegant approach to the covalent sidewall functionalization of SWNTs. The dramatic solubility enhancement of the derivatized material is a first hint of the covalent binding of the *n*-propylamine addends.

Further evidence is provided by thermogravimetric analysis (TGA) of the alkylated material *f4*-(*n*PrNH)$_n$-SWNT in the temperature range 100–700 °C; the analysis was performed in conjunction with online-monitoring of the volatile products by mass spectrometry (MS). In Figure 2 (A) the TGA/MS curves of the functionalization product *f4*-(*n*PrNH)$_n$-SWNT (bottom) and of a reference system (top) are depicted. The reference sample was treated exactly the same way as those leading to the functionalized derivatives *fx*-(*n*PrNH)$_n$-SWNT, except for the addition of *n*-buthyllithium to the *n*-propylamine solution with the consequence that no lithium *n*-propylamide was generated. The functionalized sample shows a pronounced weight loss starting at temperatures above 170 °C which is not observed in the reference sample. Based on that a mass loss induced by the desorption of non-covalently attached organic molecules can be ruled out in the functionalized material. We therefore attribute the observed mass loss to the detachment of covalently linked amino groups. Similar temperature-dependent behaviour of covalently connected functional groups has been reported by other groups.[15b,18,26a] Assuming that the difference in weight loss between *f4*-(*n*PrNH)$_n$-SWNT and the reference sample at 700 °C is the weight of the detached functional groups and that the residual weight can be attributed to the defunctionalized SWNTs, a degree of functionalization in the order of 3%, which can be directly translated into one *n*-propylamino group per approximately 35 carbon atoms of the CNT framework, can be calculated.

The ion currents of the characteristic fragments of the covalently attached *n*-propylamino groups are depicted in Figure 2 (B). Curve *(a)* shows the evolution of ethyl radical fragments at m/z = 29 at 220 °C and in the range between 395 and 523 °C for the amino-functionalized material *f4*-(*n*PrNH)$_n$-SWNT. In addition, all other fragmentation products of the *n*-propyl side-chains can also be detected in the temperature range of 200–540 °C, namely: $CH_3CH_2CH_2$ [m/z = 43 *(b)*], CH_3 [m/z = 15 *(c)*] and $CH_3CH_2CH_2NH_2$ [m/z = 59 *(d)*]. It is important to note that no volatile products based on the thermal degradation of *n*-propylamine could be detected with the reference sample. As an example, in the inset in Figure 2 (B) the ion current for the CH_2CH_3 fragment (m/z = 29) in the reference material [*ref-(a)*] and in the amino-functionalized material [*f4-(a)*] are depicted. This leads to the conclusion that the solubilization enhancement detected is not based on a non-covalent interaction of *n*-alkylamines with SWNTs, which was investigated earlier.[18]

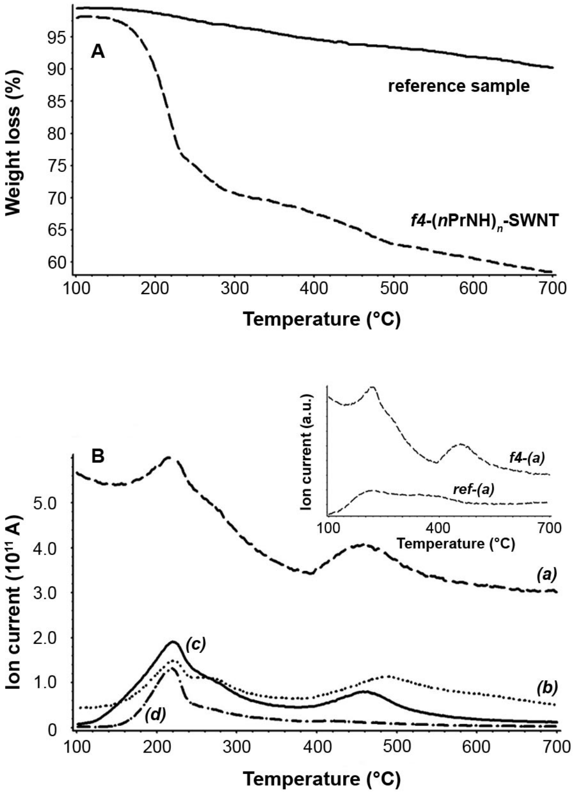


Figure 2. (A) Weight loss plot for *f4*-(*n*PrNH)$_n$-SWNT (bottom) and the SWNT reference material (top). (B) TGA/MS analysis of the evolution products from *f4*-(*n*PrNH)$_n$-SWNT: Ion current vs. temperature for m/z = 29 [CH_2CH_3 *(a)*], 43 [$CH_2CH_2CH_3$ *(b)*], 15 [CH_3 *(c)*] and 59 [$NH_2CH_2CH_2CH_3$ *(d)*]. Inset B: ion current plot of m/z = 29 [CH_2CH_3] for *f4*-(*n*PrNH)$_n$-SWNT [*f4-(a)*] and for the reference material [*ref-(a)*].

The covalent attachment of a substituent containing a heteroatom allows photoelectron spectroscopy (XPS) to be used as a characterization tool. XPS survey spectra of the functionalization product *f4*-(*n*PrNH)$_n$-SWNT and the reference material are depicted in Figure 3. The emission by the nitrogen-containing functional groups is clearly visible owing to the characteristic N 1s core level emission of the functionalized SWNT material *f4*-(*n*PrNH)$_n$-SWNT which is absent in our reference sample. It is important to note that the oxygen content does not increase during the functionalization sequence (a small increase in the oxygen content is induced by the introduction of SiO_2, probably due to glass particles produced by ultrasonication). This indicates that nitrogen, carbon and probably hydrogen are the only elements present in the sample and that the nitrogen content can directly be traced back to the introduction of the *n*-propylamino group.

The N/C ratio measured from the survey spectrum of the functionalized *f4*-(*n*PrNH)$_n$-SWNT derivative corresponds to a degree of functionalization of 2.4%. This is in good agreement with the values obtained by the TGA measurements. A close-up of the N 1s core level spectra is depicted in Figure 4. Only trace amounts of nitrogen are present in the reference SWNT material, in contrast to the functionalized SWNTs for which a large component with a binding

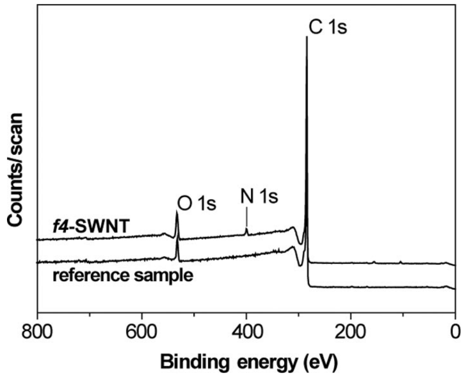


Figure 3. XPS survey spectrum of the functionalized SWNT sample *f4*-(nPrNH)$_n$-SWNT (top) in comparison with the spectrum of the reference material (bottom). The appearance of the N 1s core level emission is directly related to the introduction of the functional *n*-propylamino groups. The two survey spectra are vertically offset for clarity.

energy of 399.9 eV is observed. This binding energy is slightly higher than the binding energy measured for nitrogen in poly(ethyleneimine) (PEI) for which a binding energy of 399.1 eV is reported.[23]

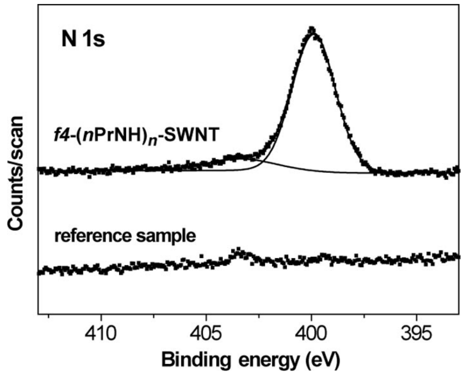


Figure 4. N 1s core level spectrum of the functionalized SWNT sample *f4*-(nPrNH)$_n$-SWNT (top) in comparison with the spectrum of the reference SWNT material (bottom) The two survey spectra are vertically offset for clarity.

In the XPS spectra of nitrogen-containing functional groups on activated carbon, components with a binding energy of 399.9 eV are attributed to amide, alkylamide and amine functionalities,[24] in accord with the functional groups in our experiments.

One of the most important tools for investigating structural changes in the sp^2-bonded SWNT network, induced by the local transformation of a sidewall carbon atom into an sp^3 configuration, is resonant Raman spectroscopy.[25] In Figure 5 the D and G bands of sample *f4*-(nPrNH)$_n$-SWNT are presented and compared with the reference material (see above). For both excitation wavelengths, which are sensitive to semiconducting (λ = 740 nm) and metallic SWNTs (λ = 532 nm), an increase in the D/G ratio is evident.

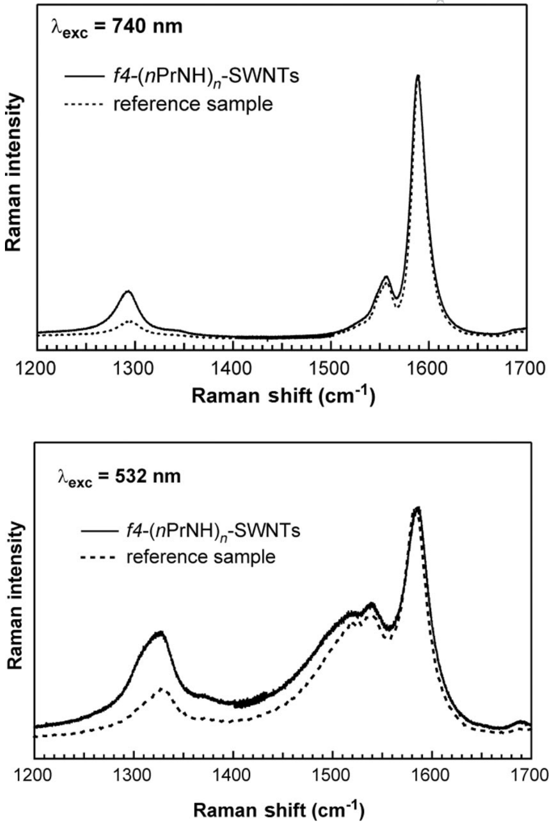


Figure 5. D and G band Raman spectra of *f4*-(nPrNH)$_n$-SWNT and the reference sample recorded at λ = 740 (top) and 532 nm (bottom).

The increase in the D-band intensity, which is caused by functionalization-induced disorder, is summarized in Figure 6. The results imply a dependence of the D/G ratio on the concentration of lithium amide. The fact that the sample *f1*-(nPrNH)$_n$-SWNT does not follow the general trend prevents a clear functional relationship between the D/G

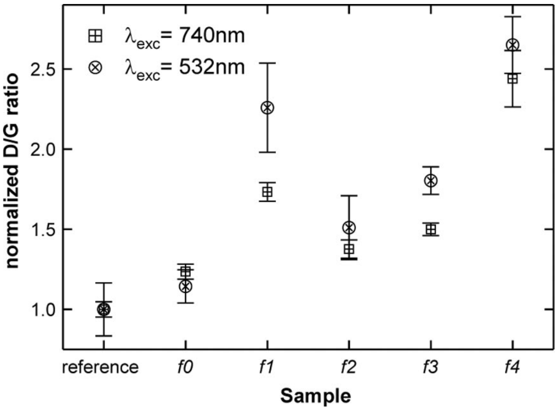


Figure 6. D/G ratio of the functionalized SWNT derivatives *fx*-(nPrNH)$_n$-SWNT normalized to that of the reference sample at two excitation wavelengths. The arrow bars represent the scatter in intensity of the respective sample (spectra were taken from at least three different sample locations of the bucky paper).

ratio and the concentration of the amide from being established. Further investigations on this topic are underway to clarify this point.

Nevertheless, the data obtained show unambiguously that covalent sidewall functionalization took place by the addition of *n*-propylamino groups. Defect group functionalization can be ruled out as this would functionalize only pre-existing defects and therefore no increase in the D/G ratio would be expected.

Owing to the high solubility of the functionalized SWNT derivatives in organic solvents, their UV/Vis/NIR spectra were recorded in THF. In contrast, the UV/Vis/NIR spectrum of the pristine SWNT (*p*-SWNT) starting material was recorded in D$_2$O/SDC as unfunctionalized carbon nanotubes are completely insoluble in THF. In Figure 7, the spectrum of *f4*-(*n*PrNH)$_n$-SWNT is compared with the spectrum of *p*-SWNT. The pristine material exhibits characteristic peaks arising from transitions between van Hove singularities in the density of states (DOS) of metallic (M) and semiconducting (S) SWNTs: M$_{11}$ (350–800 nm), S$_{22}$ (600–1000 nm) and S$_{11}$ (1100–1600 nm).

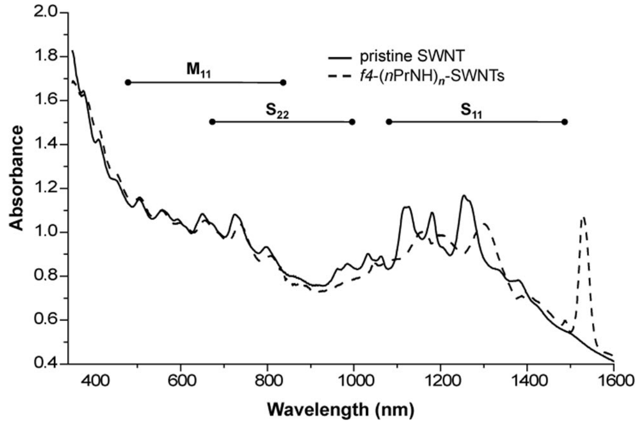


Figure 7. UV/Vis/NIR absorption spectra of pristine SWNT in D$_2$O/SDC and amino-functionalized SWNT derivative *f4*-(*n*PrNH)$_n$-SWNT in THF.

Sidewall functionalization of SWNTs is usually coupled with a loss of van Hove transitions due to alteration of the π system by the introduction of sp^3 defects which results in an unstructured absorption spectrum.[9–16] The spectrum observed for the functionalized SWNTs investigated here is in marked contrast to the spectra usually obtained. As can be clearly seen in Figure 7, the functionalized material *f4*-(*n*PrNH)$_n$-SWNT exhibits well-resolved absorption peaks in the Vis/NIR spectrum due to the good individualization provided by the propylamine substituents. The peak-position shifts in the long wavelength region can probably be attributed to solvent effects. The phenomenon of preserved van Hove transitions after direct sidewall functionalization has also been observed recently by other authors.[26] In our opinion, this is related to the fact that in THF the functionalized SWNTs are completely individualized and that the amount of defects introduced by the functionalization is comparably low. The observation that the maxima in the absorption spectra are still preserved may therefore be caused by the fact that the degradation of the electronic structure of the SWNTs by functionalization is compensated by an improved solubility of individual tubes.

Conclusions

Nucleophilic addition to the sidewalls of SWNTs has so far only been carried out by using very strong nucleophiles such as alkyllithium reagents.[16] Herein we have demonstrated that nucleophilic sidewall addition is also possible by using amine-based nucleophiles, namely in situ generated lithium amides. The negatively charged (*n*PrNH)$_n$-SWNT^{n-} intermediates are reoxidized by air leading to (*n*PrNH)$_n$-SWNT derivatives with covalently bound amino functionalities. Such adducts exhibit a drastically improved solubility in organic solvents, most clearly pronounced in THF. We have unambiguously shown by a variety of spectroscopic tools, namely, Raman spectroscopy, TGA, XPS and UV/Vis/NIR absorption spectroscopy, that the functional *n*-propylamino group is covalently attached to the carbon nanotube framework. As our functionalization sequence is based on amines, this will open the door to a broad variety of SWNT derivatives with different functional groups. Up to now, no selectivity between metallic and semiconducting SWNTs has been observed in our experiments.

Experimental Section

Instruments and Measurement: Raman spectra were obtained with a Jobin Yvon T64000 triple-grating spectrometer with tunable excitation laser. Thermogravimetric analysis (TGA) was accomplished with a Netzsch STA = 409 CD instrument equipped with a Skimmer QMS 422 mass spectrometer (MS) using the following programmed time-dependent temperature course: 24–100 °C at 100 K/min, 100 °C for 1 h, 100–1000 °C at 10 K/min, 1000 °C for 1 h and cooling to 400 °C. The initial weights were about 5–10 mg. Sonication was performed with a Bandelin Sonorex RK 106 or Hielscher UP400S Ultrasonic Processor. UV/Vis/NIR spectra were obtained with a SHIMADZU UV-3102pc spectrophotometer. Solubilization of the pristine material was achieved in a 1% solution of sodium deoxycholate (SDC) (Acros) in deuterium dioxide. The functionalized material *f4*-(*n*PrNH)$_n$-SWNT was dissolved directly in dry THF. The spectra were measured from the supernatant after sonication (5 min) and precipitation (1 d) of the insoluble SWNTs or after centrifugation at 15000 g for 30 min. X-ray-induced photoelectron spectra were measured on bucky-papers of the respective materials. As the photon source a monochromatized Al-K_α small-spot X-ray source was used ($\eta\omega$ = 1486.6 eV). All binding energies refer to the Fermi level, which was regularly calibrated using the Au 4f 7/2 core level at 84.00 eV.

Materials: SWNTs were obtained from Carbon Nanotechnologies Inc. (purified HiPco® Single-Wall Carbon Nanotubes, Lot number P0335) and further purified by sonication and boiling in hydrochloric acid (37%).[16e] Chemicals and solvents were purchased from Acros (Geel, Belgium) and used as received.

Preparation of Amide-Functionalized SWNTs: The lithium amide solution was prepared as follows. In a nitrogen-purged and heat-dried four-necked round-bottomed flask (250 mL) equipped with two gas inlets and pressure compensation *n*-propylamine (*f0* =

0.2 mmol, *f1* = 0.5 mmol, *f2* = 1.0 mmol, *f3* = 5.0, *f4* = 10.0 mmol) was dissolved in dry THF. The solution was cooled to 0 °C for 15 min. The respective amount of *n*-butyllithium (90% of the *n*-propylamine amount) was added dropwise to this solution over a period of 10 min. Then the solution was stirred at room temperature for 1 h. In another 250 mL nitrogen-purged and heat-dried three-necked round-bottomed flask equipped with two gas inlets, purified HiPco SWNTs (5 mg) were dispersed in anhydrous solvent (100 mL; benzene or THF) by sonication (15 min). This dispersion was added to the first flask through a heat-dried dropping funnel. After completion of the addition, the resulting suspension was stirred for 30 min at room temperature and sonicated for 30 min which resulted in a stable, black, homogeneous dispersion. The reaction mixture was stirred for 20 h (room temp.) and subsequently quenched by bubbling oxygen for 1 h through the solution. The resulting dispersion was diluted with cyclohexane (100 mL), transferred to a separating funnel and purged with water and diluted hydrochloric acid until the pH value remained neutral. The organic layer with the nanotubes was filtered through a 0.2 µm PP membrane filter and washed with cyclohexane, methanol, ethanol and water. The resulting black solid was dried in a vacuum oven at 50 °C overnight.

Preparation of the SWNT Reference Sample: In a nitrogen-purged and heat-dried four-necked round-bottomed flask (100 mL) equipped with two gas inlets and pressure compensation, *n*-propylamine (10 mmol) was dissolved in dry THF. SWNTs (5 mg) were added to the solution followed by sonication for 30 min and stirring for 2 h. The resulting dispersion was diluted with cyclohexane (100 mL), transferred to a separation funnel and purged with water and diluted hydrochloric acid until the pH value remained neutral. The organic layer with the nanotubes was filtered through a 0.2 µm PP membrane filter and washed with cyclohexane, methanol, ethanol and water. The resulting black solid was dried in a vacuum oven at 50 °C overnight.

Acknowledgments

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