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Reproducibility and Efficiency of Carbon Nanotube End-Group Generation and Functionalization

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In a systematic fashion, several methods for esterification and amidation of single-walled carbon nanotubes have been evaluated with focus on efficiency and reproducibility in forming covalently functionalized products soluble in organic media. The outcome of transformations was determined using IR, Raman and NMR spectroscopy and by thermogravimetric analysis (TGA). Amidation proceeding via a SWNT-$(COCl)_n$ intermediate yielded the expected covalent product, whereas carboxylate salt formation dominated with other attempted methods. Esterification was achieved via the acyl chloride method and via alkylation of SWNT-$(COO^-)_n$, the latter being the more efficient method. A non-covalent solubilizing interaction was obtained for RNH_2 but not for ROH (R = octadecyl), proving that the most important non-covalent interaction between oxidatively cleaned SWNTs and octadecylamine is a salt formation. The outcome of the secondary functionalization of carboxyl units is highly reproducible for experiments carried out on the same batch of SWNT-$(COOH)_n$. Normalization of the outcome of the secondary functionalization to the composition of the different batches of starting materials reveals an overall high reproducibility of the secondary functionalizations. The differences in outcome related to different commercial SWNT batches from the same synthetic procedure is negligible compared to that resulting from differences in overall carboxyl content after the primary HNO_3 oxidative cleaning step. Hence, the composition of purified SWNT starting materials always needs to be assessed, in particular before drawing any conclusions concerning differences in outcome from reaction systems involving different sources of SWNT material.

Introduction

From a materials perspective, carbon nanotubes (CNTs) are 1-dimensional entities with a high aspect ratio that may or may not exhibit metallic conductance. From a molecular perspective, CNTs are carbon structures with poor solubility that by chemical treatment can be transformed into giant macromolecules with at least some solubility and other interesting properties. Synthetic chemists have been both optimistic and quite successful in translating the chemistry of small and well-defined molecules, and the field has during the past decade exhibited a tremendous development,[1] with chemically modified CNTs currently finding applications in solar cells,[2] biosensors,[3] drug delivery systems[4] and various electronic devices.[5] Despite this, chemical modification of CNTs is far from being a fully developed field. As none of the methods for CNT preparation give homogeneous "one-product" CNTs, synthetic chemists has to cope with the fact that already the CNT starting material is a mixture of compounds,[6] that moreover vary between different methods for preparation and even between batches from the same method. This means that literature procedures for CNT functionalization are not automatically comparable. A further challenge is the characterization of products, in particular assessing the product purity (in regard to excess reagent) and which functional groups that are present. In general, IR spectroscopy gives important qualitative information concerning the identity of functional groups present in a sample. Over-interpretations are however not uncommon, in particular in the early CNT functionalization literature. A more complete picture of organic functionalization is obtained from critical evaluation of data from several qualitative standard methods (IR, Raman and NMR spectroscopy) in combination with quantitative data from TGA analysis.

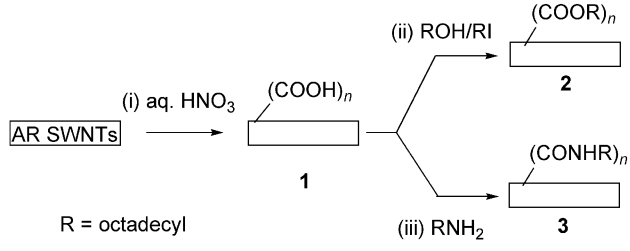

Figure 1. Generalized transformation of as-received (AR) SWNT material to SWNT-esters **2** or SWNT-amides **3** via SWNT-$(COOH)_n$ **1**, using reactions that involve (i) aq. HNO_3, (ii) ROH/RI (R = octadecyl) and (iii) RNH_2.

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In the present study we have evaluated several procedures that according to literature should yield amides or esters from oxidatively treated CNTs (Figure 1), using HiPco SWNT from several cleaning/oxidation preparations and from different commercial batches in order to find conditions for cleaning and further functionalization that are both generally applicable and with acceptable reproducibility.

2. Results and Discussion

2.1 Purification and Primary Functionalization

A major problem with current production methods for carbon nanotubes is the impurities that are formed together with the CNTs. These impurities may be in the form of amorphous carbon, fullerenes, metal particles or multishell nanocapsules encapsulating iron particles.[7] Purification is most commonly carried out using liquid-phase acidic and oxidizing conditions capable of removing various types of impurities from a relatively large amount of material using simple procedures.[7–9] Furthermore, besides the removal of impurities, these methods introduce a substantial amount of oxygen-containing functional groups such as carboxylic acids at the side- and end-walls of the carbon nanotubes (Figure 2).[10,11] These functional groups can then be utilized for further derivatization of CNTs. In the present study, purification protocols based on 2.6 M and 8 M HNO_3 have been evaluated using commercially available post-synthesis processed HiPco SWNT materials. As our main intention is to use the acid-oxidized SWNTs for further covalent derivatization, it is imperative to know how these methods differ in their ability to introduce functional groups into the material and to determine to what extent the tubes are damaged by the two procedures. Also, it is important to consider the reproducibility and scalability of the methods.

Both treatments involve refluxing the SWNTs in aqueous HNO_3. Method A employs 2.6 M acid and a reaction time of 4 days, whereas in method B, the acid concentration is 8 M and the reaction time only two hours.[10,12] Both purification methods include a subsequent work-up procedure in which the SWNT-$(COOH)_n$ are separated from the acidic solution and washed neutral. Starting from two commercial batches of SWNTs, several sets of SWNT-$(COOH)_n$ (**1**) were prepared by each method in small scale (10 mg of SWNT material) and on a large scale (100 mg of SWNT material). As each batch of SWNT-$(COOH)_n$ might be different from the other, no pooling of products was carried out at any stage.

Thermogravimetric analysis (TGA) of the as-received HiPco SWNT material (in air) showed a residual mass of 11% after 650 °C, consistent with the reported purity (≈ 90%). From the TGA of the SWNT-$(COOH)_n$ products it was evident that both methods decrease the metal content of the SWNTs in small-scale as well as large-scale experiments (Table 1 and Figure 3), with slightly better results for the small-scale reactions.

Table 1. TGA results for the two methods in small scale and on a large scale. The remaining mass after 650 °C is related to residual metal oxides.

SWNT compound[a]	Method/ scale	TGA (in air) residual mass (%) after 650 °C
As-received SWNTs	–	11%
1j	A/100 mg	1.9%
1g	A/10 mg	0%
1e	B/100 mg	6.3%
1b	B/10 mg	0%

[a] Referred to the SWNT-$(COOH)_n$ compounds in Figure 5.

Raman spectra of the acid-treated products showed a significantly higher D-band intensity as compared to the as-received HiPco SWNT material (Figure 4). The D/G band ratio increased from ca. 0.2 in the as-received SWNTs to approximately 0.5 in the acid-oxidized compounds. These results suggest that the treatment introduces a substantial amount of defects like carboxylic groups at the SWNT sidewalls. The increase in D-band intensity could also be due to amorphous carbon, formed in degradation of small-diameter SWNT degradation.[13] Analysis of the radial breathing modes for the acid-oxidized products confirms this, as the signals in the high-frequency RBM region that are visible in the as-received SWNT material are missing in the acid-oxidized SWNT samples.

A relative measure of the amount of carboxylic acid groups in a SWNT sample can be obtained from the intensity of characteristic bands in the IR spectra (see supplementary material). The most important ones are O–H stretch at about 3530 cm^{-1}, the C=O stretch at 1710–1732 cm^{-1}, the 1st order E_1 tangential SWNT mode[14] at 1548–1586 cm^{-1} and the C–O stretch at 1147–1191 cm^{-1}. Assuming that the carbonylic band mainly is associated with carboxylic acid groups in the SWNTs and not with any other functional group such as ketone or aldehyde

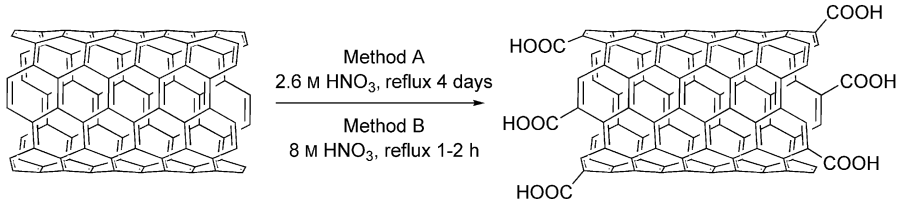


Figure 2. Oxidation of HiPco SWNTs during purification.

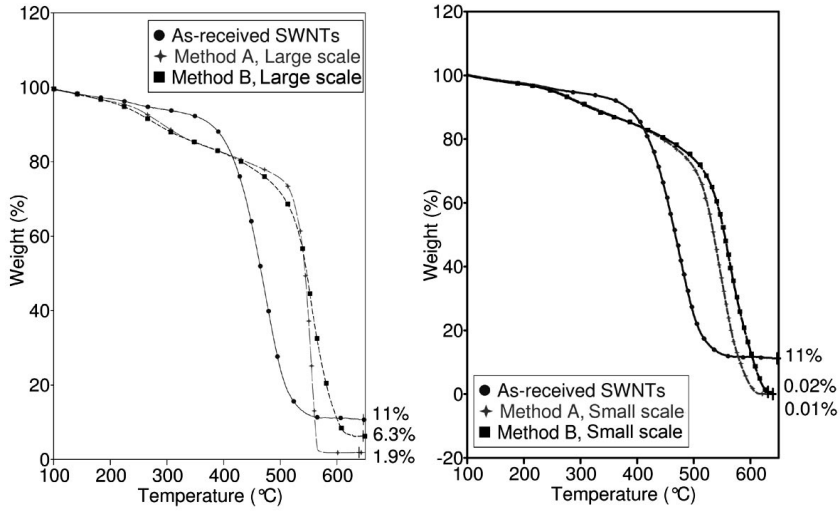


Figure 3. TGA (in air) of as-received SWNTs, SWNTs treated by method A in large/small scale, and SWNTs treated with method B in large/small scale.

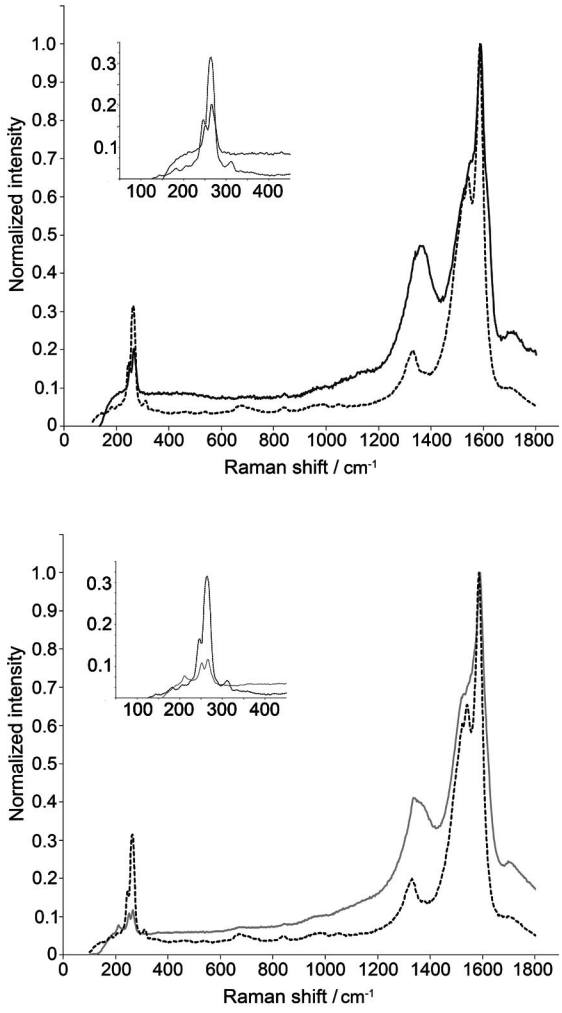


Figure 4. Raman spectra of (upper): as-received HiPco SWNTs (dashed) and SWNT-(COOH)$_n$ **1l** (solid) prepared by method A on a large scale and (lower): Raman spectra of as-received HiPco SWNTs (dashed) and SWNT-(COOH)$_n$ **1d** (solid) prepared by method B on a large scale. Insets show expansions of the RBM area.

groups, and that the intensity of the tangential nanotube mode does not differ significantly between products from the two methods, the ratio of the intensity of the 1st order E_1 band relative to the carbonylic band can be used to compare the outcome of the primary purification for different batches. Figure 5 summarizes the IR analysis of 15 batches prepared at four different conditions and starting from two commercial SWNT batches. First of all, we can conclude that the differences between the two commercial batches of SWNTs are essentially negligible as the choice of oxidation method and scale are significantly more important parameters. Other general observations are that method B is more efficient in introducing COOH groups than method A, and that both method A and B introduces lower amount of COOH groups when the scale of the reaction is increased. Furthermore, it is evident that **1** prepared by identical protocols from the same batch of starting material can be quite different from each other.

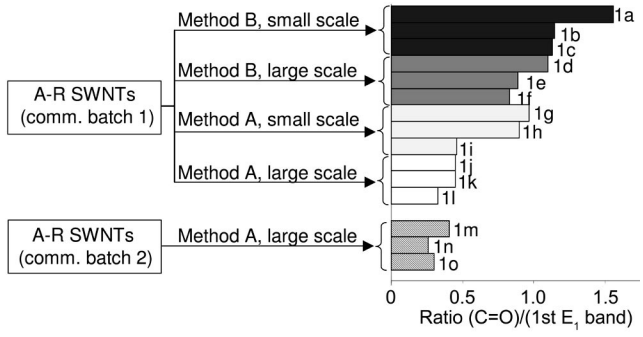


Figure 5. Relative amount of carboxylic acid groups in SWNT-(COOH)$_n$ compounds prepared by method A and B on a large scale and in small scale (based on the ratio of the intensity of the IR carbonylic band relative to the 1st order E_1 IR band).

The small-scale experiments were carried out in 25 mL flasks with very efficient stirring. The larger-scale reactions were carried out in 100 mL flasks with comparably less efficient stirring. A likely explanation for the observed differ-

ences when changing the scale is that the more extensive surface contact between the SWNTs and the acid in the small-scale experiments leads to a higher frequency of reactions, resulting in more functionalization and more efficient removal of metal catalyst particles. The differences within a set of products prepared by the same protocols are also attributed to small differences in stirring efficiency and temperature between individual experiments.

The conclusion of this study is that SWNT-$(COOH)_n$ from different experiments are not necessarily of the same composition, thus each synthetic batch need to be treated as a unique SWNT-$(COOH)_n$ compound and characterized prior to subsequent treatments.

2.2 Secondary Functionalization of SWNT-$(COOH)_n$

The main objective was to evaluate various published methods for secondary functionalization of SWNT-$(COOH)_n$ (**1**), reactions that may give SWNT-esters **2**, SWNT-amides **3** or SWNT-alkylammonium carboxylate salts **4** (Scheme 1). We have investigated several general approaches towards **2** and **3**, with introduction of the same octadecyl chain R in all cases in order to achieve fair comparisons. The products were characterized by IR, TGA and Raman spectroscopy as well as ^{1}H NMR analysis in solution, possible since the octadecyl chain induces solubility. As a low amount of COOH in **1** will result in a low amount of introduced R compared to the outcome from a reaction using a SWNT-$(COOH)_n$ with higher COOH content, correlation of the outcome to the relative amount of carboxylic acid groups of the starting material **1** was necessary in order to fully establish what methods are the most appropriate in terms of efficiency and reproducibility.

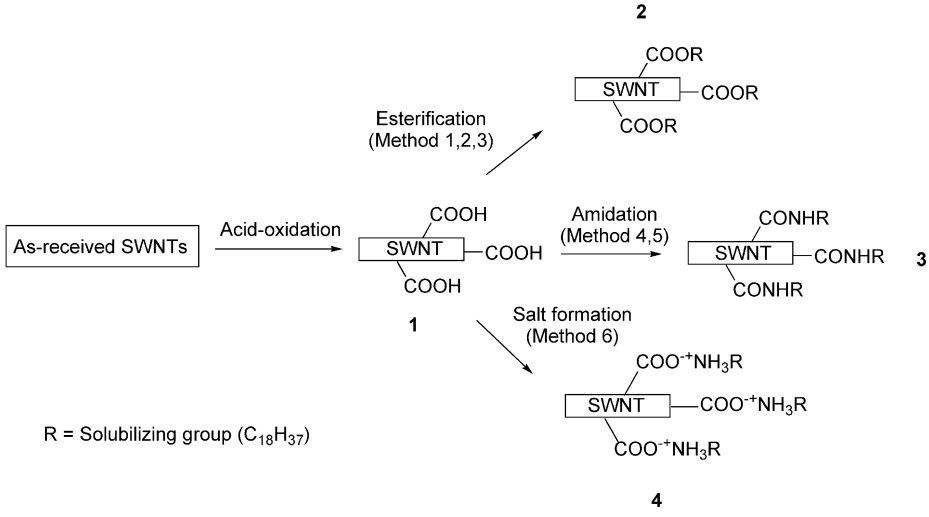
2.2.1 Esterification

Treatment of SWNT-$(COOH)_n$ (**1**) by $SOCl_2$ followed by octadecyl alcohol (method 1)[15] gave soluble products **2a**–**c** that according to ^{1}H NMR, IR and Raman spectroscopy were SWNT-esters. In particular, the frequency of the carbonylic stretch vibration in the IR spectrum for **2a**–**c** was blue-shifted with regard to that of the corresponding starting material **1**, indicating the presence of ester carbonyl units (Table 2). The products could form dispersions in $CHCl_3$ that were quite stable over a period of a few hours at room temp. Alkylation of SWNT-$(COO^-)_n$ with octadecyl bromide (method 2)[16] was also successful, with SWNT-octadecyl ester derivatives **2d**–**f** that stayed dispersed in $CHCl_3$ for several weeks. In contrast, Steglich esterification (method 3) did not result in any dispersible SWNT derivatives despite careful modulations of the parameters of the published procedure.[17,18]

Table 2. IR and TGA data of the SWNT-octadecyl ester derivatives prepared by methods 1 and 2 and IR of material recovered after treatment by method 3.

Method	Prod.	SWNT-$(COOH)_n$[a]	ν(C–H) (stretch) [cm^{-1}]	Δ ν(C=O)[b]	TGA[c]
1	**2a**	**1n**	2916, 2846	+14 cm^{-1}	13%
1	**2b**	**1o**	2916, 2846	+3 cm^{-1}	17%
1	**2c**	**1m**	2915, 2846	+7 cm^{-1}	19%
2	**2d**	**1n**	2917, 2847	+7 cm^{-1}	32%
2	**2e**	**1o**	2917, 2848	+7 cm^{-1}	34%
2	**2f**	**1m**	2917, 2847	+3 cm^{-1}	37%
3	**2g**[d]	**1m**	–	±0 cm^{-1}	0%

[a] **1m**–**1o** refers to the different batches of SWNT-$(COOH)_n$ that was used for the secondary functionalization (see Figure 5). [b] Δ ν(C=O) of product as compared to the starting material **1m**–**o**. [c] [TGA mass loss (< 500 °C in N_2) of product] – [TGA mass loss (< 500 °C in N_2) of starting material **1m**–**1o**]. [d] No ester product was detected.



Scheme 1. Synthetic approach to covalent SWNT derivatives using carboxyl chemistry. *Esterification procedures*: Method 1. *i*) Thionyl chloride, reflux 24 h. *ii*) SWNT-$(COCl)_n$, octadecanol, 100 °C. Method 2. aq. NaOH, hexadecyltrimethylammonium bromide, octadecyl bromide, reflux 8 h. Method 3. DCC/DMAP, octadecanol, stirring in room temp. or MW heating. *Amidation procedures:* Method 4. *i*) Thionyl chloride, reflux 24 h *ii*) SWNT-$(COCl)_n$, octadecylamine, 100 °C. Method 5. DCC/DMAP, octadecylamine, MW-heating or conventional heating. *Salt formation:* Method 6. DMF, octadecylamine, 100 °C.

The two successful protocols were applied to SWNT-$(COOH)_n$ from three different batches and the products were analyzed by TGA in order to quantify the degree of derivatization (Table 2 and Figure 6). When the outcome of the secondary functionalization is correlated to the carboxylic content of the batch of starting material **1**, it is evident that method 2 is both more efficient with regard to the amount of alkyl chain introduced, and more reproducible. A further advantage with the alkylation route is that it does not involve use of the corrosive $SOCl_2$, and moreover, being a two-step one-pot process with no need for removal of excess reagents between steps, it is less time-consuming than the route via the acid chloride.

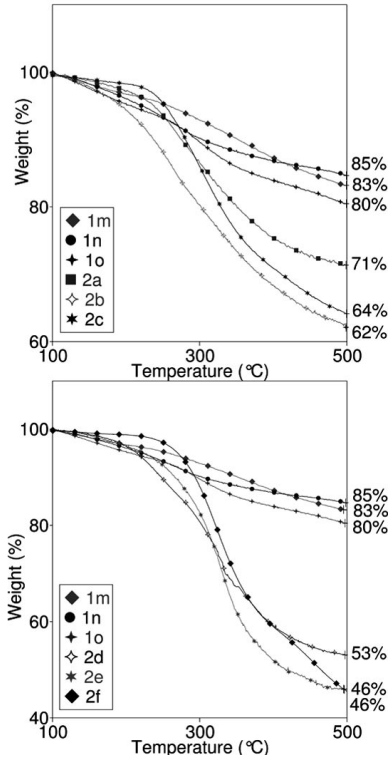


Figure 6. TGA curves (N_2 atmosphere) of the SWNT-octadecyl ester derivatives and starting materials [SWNT-$(COOH)_n$] prepared by method 1 (upper) and method 2 (lower).

2.2.2 Amidation and Carboxylate Salt Formation

Treatment of **1** with $SOCl_2$ to give a SWNT-acid chloride intermediate that is allowed to react with octadecylamine (method 4)[19] gave SWNT-octadecylamide derivatives **3a**–**b** that formed stable dispersions in $CHCl_3$. IR and ^1H NMR of the reaction products provided convincing evidence for successful covalent derivatization (Figure 7 and Figure 8). TGA showed a mass loss of 23–36% between 100–500 °C as compared with the corresponding SWNT-$(COOH)_n$ starting material (Table 3 and Figure 7). Interestingly, esterification via the acid chloride (method 1) was considerably less efficient. This can be due to the higher nucleophilicity of amines as compared to alcohols but may also be a result of additional adsorption of excess octadecylamine to the SWNTs.[20]

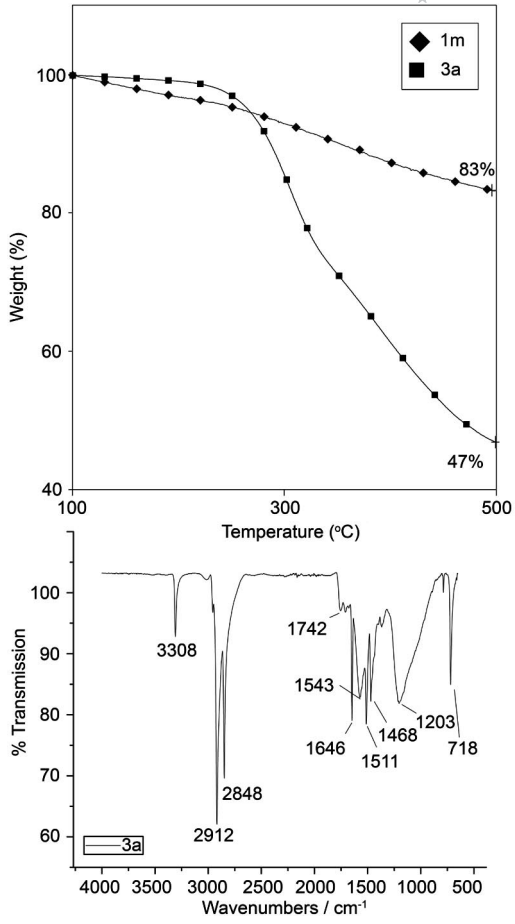


Figure 7. TGA and IR results for SWNT-octadecylamide derivative **3a** prepared by method 4. (Upper): TGA curves (N_2 atmosphere) of SWNT-octadecylamide **3a** and SWNT-$(COOH)_n$ (compound **1m**). (Lower): IR spectrum (with baseline-correction) of compound **3a**.

Attempts to carry out the amidation in the presence of DCC/DMAP (method 5)[21] gave products that initially could be dispersed in $CHCl_3$. However, the solubility was lost after the work-up procedure indicating that only non-covalent derivatization had taken place. IR and ^1H NMR analysis confirmed this and gave no evidence for covalent derivatization. This result is analogous to the failure of the Steglich esterification of **1**.

The simplest approach to solubilize acid-oxidized SWNTs is to convert the carboxylic acid groups on the SWNTs to carboxylate salts of for example octadecylamine. When **1** was heated with an excess of octadecylamine (method 6),[22] the product obtained after a workup analogous to that of methods 4 and 5 was soluble in dichloromethane and in chloroform. This is in contrast to the product obtained from method 5. This indicates that a large excess of octadecylamine together with high temperature probably is important for successful salt formation. However, only the aliphatic signals at 2918 and 2848 cm^{-1} and a carbonylic band at 1742 cm^{-1} are clearly distinguishable in the IR spectra, whereas the signals around 1610–1550 and 1420–1300 cm^{-1} expected for carboxylate salts[23] are not observed. The ^1H NMR spectrum of the material showed

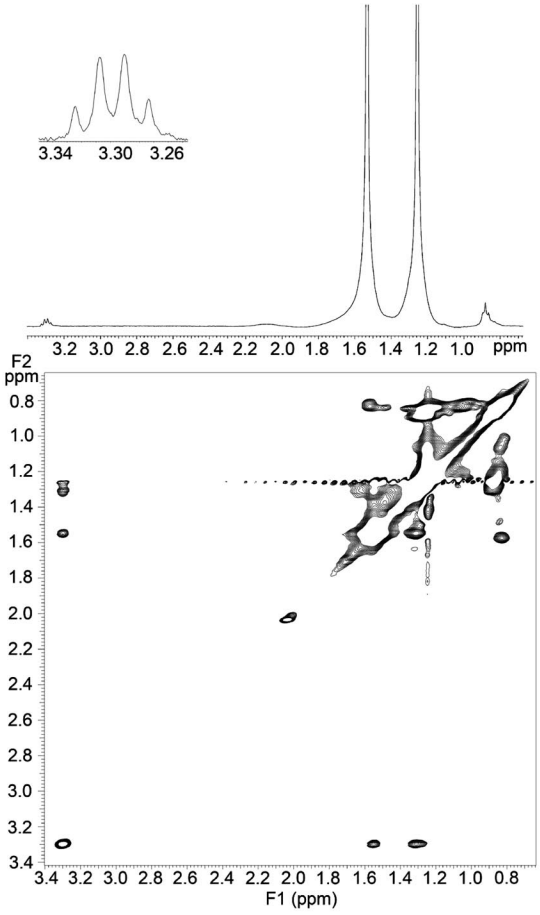


Figure 8. NMR results for SWNT-octadecylamide derivative **3a** prepared by method 4. (Upper): ^{1}H NMR spectrum ($CDCl_3$, 25 °C). (Lower): TOCSY spectrum ($CDCl_3$, 25 °C).

aliphatic signals together with a very broad water signal, indicating proton exchange. Despite the lack of the expected carboxylate signals in the IR spectrum we argue that salt formation between SWNT-$(COOH)_n$ and octadecylamine is the primary reason for the solubility of the product, with secondary van der Waals adsorption of further octadecylamine onto the SWNTs,[20] the latter interaction being much weaker than the ionic interaction between the –COOH and $–NH_2$ groups. In any case, TGA analysis was consistent with efficient derivatization and showed a mass loss of 26–46% as compared with the starting material (Table 3).

Table 3. IR and TGA data of the SWNT-octadecylamide and SWNT-$(COO^{-+}NH_3C_{18}H_{37})_n$ derivatives prepared by methods 4–6.

Method	Prod.	SWNT-$(COOH)_n$[a]	ν(C–H) (stretch) [cm^{-1}]	ν(C=O) [cm^{-1}]	TGA[b]
4	**3a**	**1m**	2917, 2848	1646, 1511	36%
4	**3b**	**1n**	2917, 2846	1709, 1668, 1516	23%
5	**3c**[c]	**1m**	2920, 2849	1708	n.d.
5	**3d**[c]	**1n**	2915, 2847	1725	n.d.
6	**4a**	**1m**	2916, 2846	1709	46%
6	**4b**	**1o**	2916, 2846	1750, 1712	26%

[a] **1m**–**1o** refers to the different batches of SWNT-$(COOH)_n$ that was used for the secondary functionalization (see Figure 5). [b] [TGA mass loss (<500 °C in N_2) of product] – [TGA mass loss (<500 °C in N_2) of starting material **1m**–**o**]; n.d.: not determined. [c] These products did not show any characteristic amide IR signals.

2.2.3 NMR Evidence for Covalent Interaction in SWNT-Octadecylamide 3

The ^{1}H NMR spectrum of SWNT-octadecylamide derivative **3a** in $CDCl_3$ (Figure 8) contains all expected features for an octadecyl-chain, with signals at δ = 7.40 (br., NH), 3.30 (dt), 1.25 (m) and 0.89 (m) ppm. Additionally, a 2D TOCSY spectrum confirmed that these signals indeed belonged to the same spin-system and furthermore revealed an additional cross-peak to a signal buried under the water signal at δ = 1.56 ppm. (Figure 8). To further verify that these proton resonances originated from hydrocarbon entities associated with SWNTs in the sample, a series of NMR diffusion experiments were carried out using the LED-PGSE (Longitudinal Eddy current Delay-Pulsed field Gradient Spin Echo) sequence.[24] The octadecyl signals of the SWNT amide has a diffusion coefficient in $CDCl_3$ at 25 °C of 1.3×10^{-6} cm^2/s, whereas the coefficient for free octadecylamine under the same conditions was determined to 2.6×10^{-6} cm^2/s (see supplementary material). This significantly slower diffusion rate for the SWNT-octadecylamide derivative compared to free octadecylamine suggest that the octadecyl units are associated with the SWNTs.

Conclusions

Functional groups such as carboxylic acid groups introduced by oxidative purification of SWNTs can be efficiently utilized to prepare soluble SWNT derivatives. Thionyl chloride-mediated activation of the -COOH groups followed by esterification or amidation with alcohol or amine respectively, produces covalent SWNT derivatives that are soluble in chloroform and in dichloromethane, whereas activation of the carboxylic groups using Steglich conditions (DCC/DMAP) do not result in formation of any covalent SWNT derivatives. Covalent SWNT-octadecyl ester derivatives can also be prepared by alkylation of SWNT-$(COO^-)_n$ with octadecyl bromide in the presence of a phase-transfer reagent. This route to form covalent SWNT-octadecyl ester derivatives is more efficient and less time-consuming than the thionyl chloride-mediated procedure. Dispersions of SWNT-octadecyl ester prepared by this method are also more stable than the ones prepared by the thionyl chloride-mediated esterification. Non-covalent derivatization of SWNTs with octadecylamine by treating SWNT-$(COOH)_n$ with excess octadecylamine at high temperature yield SWNT derivatives that can be well dispersed in $CHCl_3$ and in dichloromethane.

SWNT-$(COOH)_n$ from different batches do not have the same COOH content. Thus, each synthetic batch needs to be treated as a unique SWNT-$(COOH)_n$ compound. Both esterifications and amidations have been carried out using SWNT-$(COOH)_n$ from batches with different ratios for the C=O/1st order E_1 band (Figure 5). The outcome was as expected from the assumption that a starting material with more carboxylic acid groups will give a product with a relatively higher mass of added groups (in this study octadecyl groups). The TGA results were in agreement with this assumption (Tables 2 and 3). When the outcome of the secondary functionalization was normalized to the relative carboxyl content of the corresponding starting material, is was clear that the differences observed were mainly due to the different COOH content of the SWNT-$(COOH)_n$ batches produced in the purification/primary functionalization step.

Experimental Section

General: HiPco SWNTs was used as received (claimed less than 15 wt.-% ash content, purchased from Carbon Nanotechnologies Inc.). ^1H and ^{13}C NMR spectra were recorded on a Varian 400 MHz or 500 MHz spectrometer and chemical shifts are given in ppm (δ) using $CDCl_3$ as internal standard. Centrifugation-assisted filtration was performed using an Eppendorf minispin centrifuge together with Vectaspin microvials equipped with a 0.45 μm polypropylene filter-membrane (Whatman Schleicher & Schuell). Raman spectra were recorded on a Renishaw Raman spectrometer using a 514 nm Argon laser, with a 50× lens and a laser power of 10 mW. IR spectra were recorded on a Perkin–Elmer Spectrum-100 FT-IR spectrometer with an ATR accessory. Neat samples were analyzed by placing them directly onto the ATR crystal. Sonication was carried out in a bath using Vibro Cell Sonics equipment. Thermogravimetric analysis was performed on a Q500 TGA (TA instruments) in air or in N_2 atmosphere (gas flow: 60 mL/min). Samples (1–1.5 mg) were placed on a platinum plate and heated in the TGA at a rate of 20 °C/min up to 600 or 800 °C.

Preparation of Acid-Oxidized SWNTs According to Method A on Large/Small Scale: SWNT material (CNI HiPco) (100/10 mg) was added to a 100/25 mL round bottomed flask together with HNO_3 (2.6 M, 50/5 mL). The mixture was ultrasonicated for 10 min and then refluxed for 4 d. The mixture was then allowed to cool and the acidic solution was diluted, neutralized and separated from the SWNTs by centrifugation. The solid SWNT material was washed with H_2O and acetone on a 0.45 μm polypropylene filter membrane and the SWNT material was then dried in a vacuum oven at 160 °C for 24 h. Typical yield: 50%.

Preparation of Acid-Oxidized SWNTs According to Method B on Large/Small Scale: SWNT material (CNI HiPco) (100/10 mg) was added to a 100/25 mL round bottomed flask together with HNO_3 (8 M, 50/5 mL). The mixture was ultrasonicated for 10 min and then refluxed for 2 h. The mixture was allowed to cool and the acidic solution was diluted, neutralized and then separated from the SWNTs by centrifugation. The solid SWNT material was washed with H_2O and acetone on a 0.45 μm polypropylene filter membrane and the SWNT material was dried in a vacuum oven at 160 °C for 24 h. Typical yield: 70–80%.

Preparation of SWNT-octadecyl Esters 2a–c According to Method 1:[15] SWNT-$(COOH)_n$ (**1**) (5 mg) was dispersed in DMF (2 mL) using ultrasound for 10 min. Thionyl chloride (5 mL, 68 mmol) was added and the mixture was refluxed for 24 h. The black dispersion was centrifuged and the acidic supernatant was decanted and separated from the SWNT material. The formed SWNT-$(COCl)_n$ was then washed with dry THF (5 × 5 mL) and dried in vacuo. The SWNT-$(COCl)_n$ was stirred in a large excess of 1-octadecanol for 4 d at 100 °C in inert atmosphere. Dichloromethane (20 mL) was added to the reaction flask and the resulting black solution was transferred to a separatory funnel and washed with water (3 × 10 mL). The organic phase was subsequently added to EtOH (25 mL) whereas precipitation occurred. Centrifugation-assisted filtration of the dispersion through a Vectaspin microvial equipped with a 0.45 μm polypropylene filter membrane and washing of the SWNT material with EtOH (5 mL) resulted in a black product that was dried in a vacuum oven at 160 °C for 24 h.

Preparation of SWNT-octadecyl Esters 2d–f According to Method 2:[16] SWNT-$(COOH)_n$ (**1**) (5 mg) was sonicated in NaOH (1 M, 2 mL) for 10 min. The resulting dispersion was filtered and the solid SWNT material was added to water (10 mL). Hexadecyltrimethylammonium bromide (15 mg, 41 μmol), octadecyl bromide (25 mg, 75 μmol) was added to the reaction flask and the mixture was refluxed for 8 h. Dichloromethane (10 mL) was added to the flask, resulting in solvation of the SWNT material and formation of a black organic phase. The organic phase was washed with water (3 × 10 mL) and EtOH was then added to the organic phase, resulting in precipitation of the SWNT material. The SWNT material was then collected by centrifugation-assisted filtration. The solid SWNT material was washed with EtOH (3 × 5 mL) and water (3 × 5 mL). The product was dried in a vacuum oven at 160 °C for 24 h.

Preparation of SWNT-octadecylamides 3a–b According to Method 4:[19] SWNT-$(COOH)_n$ (**1**) (5 mg) was dispersed in DMF (2 mL) using ultrasound for 10 min. Thionyl chloride (5 mL, 68 mmol) was added and the mixture was refluxed for 24 h. The black dispersion was centrifuged and the acidic supernatant was decanted and separated from the SWNT material. The SWNT-$(COCl)_n$ was washed with dry THF (5 × 5 mL) and then dried in vacuo. The SWNT-$(COCl)_n$ was stirred in a large excess of 1-octadecylamine for 4 d at 100 °C under inert atmosphere. Dichloromethane (20 mL) was added to the reaction flask and the resulting black solution was transferred to a separatory funnel and washed with aqueous HCl (3 × 20 mL) and then with water (3 × 10 mL). The organic phase was added to EtOH (25 mL) whereas precipitation occurred. Centrifugation-assisted filtration through a Vectaspin microvial equipped with a 0.45 μm polypropylene filter membrane and washing of the solid SWNT material with EtOH (5 mL) resulted in a black product that was dried in a vacuum oven at 160 °C for 24 h.

Preparation of SWNT-octadecylammonium Carboxylate Salts 4a–b According to Method 6:[22] SWNT-$(COOH)_n$ (**1**) (2.5 mg) was sonicated in DMF (1.5 mL) for 10 min. 1-Octadecylamine (500 mg, 1.9 mmol) was added to the dispersion and the resulting mixture was stirred at 100 °C for 4 d. Dichloromethane (10 mL) was added and the black solution was transferred to a separatory funnel and washed with water (3 × 15 mL). The volume of the black organic phase was reduced and the solution was then added to EtOH whereas precipitation occurred. The SWNT material was collected by centrifugation-assisted filtration of the suspension through a Vectaspin microvial equipped with a 0.45 μm polypropylene filter membrane. The solid material was then washed with EtOH (5 mL) and dried in a vacuum oven at 160 °C for 24 h.

Supporting Information (see also the footnote on the first page of this article): IR spectra of acid-oxidized SWNTs (compounds **1c**, **1f**, **1g**, **1k**) and of ester derivatives **2c**–**2e**. Raman spectra (com-

pounds **2c**, **2d**, **3a**). ^{1}H NMR spectra of compounds **2a**, **2e**, **4a** and experimental details of NMR diffusion measurements.

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