



( $\text{NLi}_2$ )<sub>x</sub> intermediate **6** by reaction of **1** with  $\text{Li}_3\text{N}$  and then subsequent reaction of **6** with  $\text{RCl}$  ( $\text{R} = \text{n-butyl, benzyl, H}$ ) reagents (Scheme 3).

## 2 EXPERIMENT

The fluoronanotubes were prepared by direct fluorination of purified HiPco-SWNTs [17] at 150 °C to approximately  $\text{C}_2\text{F}$  stoichiometry according to a procedure described elsewhere [18]. Fluoronanotubes **1** were reacted with diamines **2a-d**, such as ethylene **2a**, propylene **2b**, butylene **2c**, and hexamethylene diamine **2d** (Scheme 1), or diethanolamine **4** (Scheme 2) in solution phase by stirring the reactants at elevated temperatures (70-170 °C) in the presence of pyridine (Py) as a catalyst. The intermolecular elimination of HF in the reaction of **1** with **2** or **4** resulted in the formation of corresponding aminoalkylated or aminoalkyl-hydroxylated SWNTs **3a-d** and **5**, respectively.

In these experiments a milligram quantity (normally 10-20 mg) of precursor **1** was placed into the reaction vessel and 5-20 ml of amine **2** or **4** added. The subsequent ultrasonication for three minutes caused almost complete dispersion of fluoronanotubes to form a black colored solution; thereafter five drops of Py were added and the reaction mixture stirred under nitrogen atmosphere for three hours at ~150-170 °C. After completion of the reaction and cooling to room temperature the work-up involved centrifugation to separate insoluble black material. The decanted solution was filtered onto 0.2  $\mu\text{m}$  pore size Teflon membrane (Cole Palmer) and the precipitated functionalized SWNTs **3** and **5** were washed with ethanol and dried overnight in a vacuum oven at 70 °C.

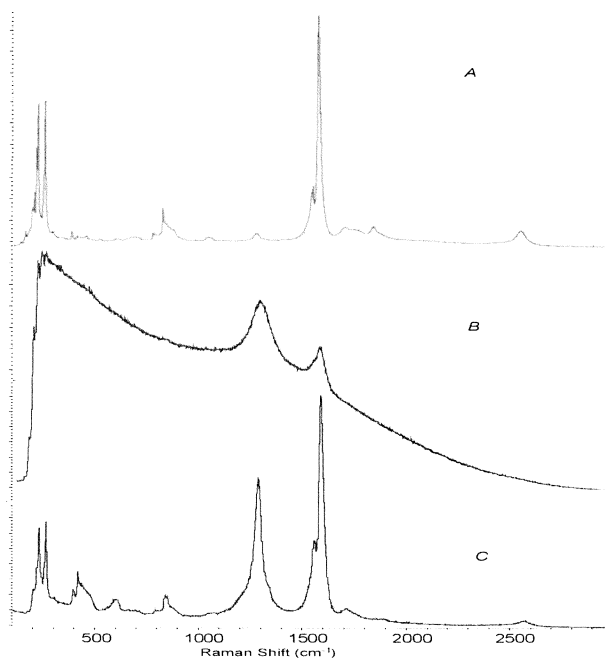
In the typical two-step functionalization procedure 40-50 mg of **1** were added to the solution of 20-30 mg  $\text{Li}_3\text{N}$  in 50-70 ml of dry diglyme and then refluxed at 120 °C for 12 h under nitrogen. Thereafter, the reaction mixture was quenched either by 2 ml of n-butyl or benzyl chlorides or 10% HCl and stirred for 1 h. The functionalized SWNTs **7a-c** were isolated after washing the precipitate formed on a filtering membrane with ethanol and water and subsequent drying in vacuum oven.

FTIR, RAMAN, UV-Vis-NIR, SEM/EDAX, TEM, variable temperature-mass spectrometry (VTP-MS), and TGA analyses were used to determine the sidewall attachment of the aminoalkyl functional groups.

## 3 RESULTS AND DISCUSSION

Evidence for the significant alteration of the electronic state of **3**, **5**, and **7** due to sidewall functionalization was obtained by Raman and UV-Vis-NIR spectroscopy. In the Raman spectra (Fig. 1) the typical for purified HiPco-SWNTs breathing and tangential mode peaks at 200-263 and 1591  $\text{cm}^{-1}$ , respectively (Fig. 1A), were observed to decrease in fluoronanotubes **1** and the peak at 1291  $\text{cm}^{-1}$  to increase of dramatically (Fig. 1B) owing to large presence (nearly 50%) the  $\text{sp}^3$  hybridized carbons in the  $\text{C}_2\text{F}$  composition structure

of **1**. The substantial relative intensity of the  $\text{sp}^3$  carbon peak at 1291  $\text{cm}^{-1}$ , observed in **3a** (Fig. 1C) and the other samples **3b-d**, **5**, and **7a-c** provide a diagnostic indication of disruption of the graphene  $\pi$ -bonded electronic structure of the side walls, suggesting their covalent functionalization.



**Figure 1.** Raman spectra of purified HiPco-SWNTs (A), fluoronanotubes **1** (B), and functionalized SWNTs **3a** (C).

This was further confirmed by the solution-phase UV-Vis-NIR spectra of nanotube-derivatives **3**, **5**, and **7** which have shown typical for functionalized SWNTs [9,13,18] complete loss of the van Hove absorption band structures, routinely observed in purified HiPco-SWNTs [17].

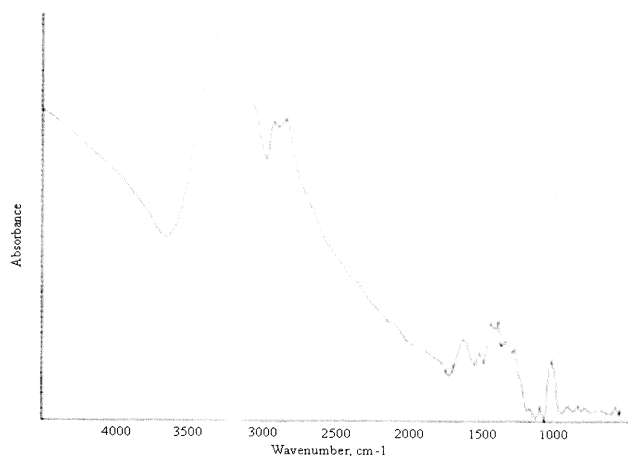
The ATR-FTIR spectra allow the identification of aminoalkyl functionalities on the SWNTs. The two intense peaks at 1214 and 1102  $\text{cm}^{-1}$ , characteristic for the C-F bond stretches in fluoronanotubes **1** (Fig. 2A), disappear after the reaction with diamines **2** (Fig. 2B-E) or diethanolamine **4** (Fig. 3) or after  $\text{Li}_3\text{N}/\text{RCl}$  treatment as a result of fluorine displacement. The appearance of new peaks in the 3100-3400 and 2800-3000  $\text{cm}^{-1}$  regions, attributed to the O-H, N-H and C-H stretches, respectively, give a strong indication of the aminoalkyl group attachment to the side walls in **3a-d** and **7a-c** and aminoalkyl hydroxyl groups in **5**. The intensities of the  $\text{NH}_2$  and C-H peaks were observed to be weaker in **3b-c** relative to **3a**, which is probably due to the possibility of partial dual buckling of **2b-c** to the side wall or crosslinking of the SWNTs by longer chain alkyldenediamino groups.

The elemental analyses of **3**, **5** and **7** by SEM/EDAX yielded for all samples significant nitrogen content (within 12-17 at. %) as well as a very low (1-2 at. %) fluorine content, validating efficient displacement of F by the amino functionalities. The thermal degradation studies have

provided further evidence for covalent functionalization.



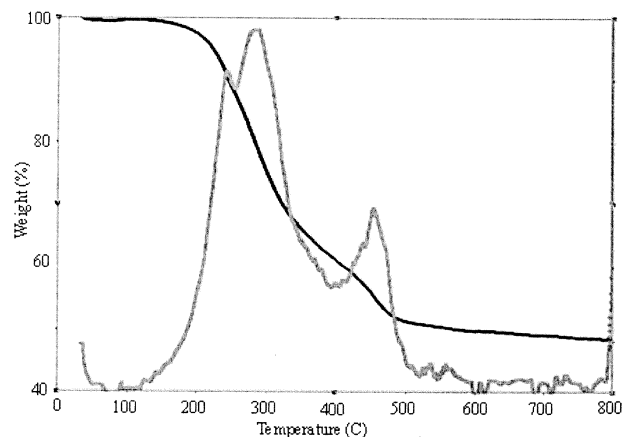
**Figure 2.** ATR-FTIR spectra of fluoronanotubes **1** (A), and functionalized SWNTs: **3a** (B), **3b**(C), **3c**(D), **3d**(E).



**Figure 3.** ATR-FTIR spectrum of **5**.

As an examples, the TGA analysis of **3a** (Fig. 4) shows on a derivative plot a major peak at 300 °C and a minor peak at 450 °C which correspond to the two-step loss of ethylene diamine **2a** evolving at temperatures obviously too high to be due to physisorbed species. The same analysis for **3d** also yielded a two-step degradation mechanism with the loss of hexamethylene diamine **2d** in the 400-550 °C temperature range. The VTP-MS analyses of **3a-d** show a major loss of corresponding attached groups under vacuum conditions at ~ 350-500 °C, which were detected in mass spectra by a peak

at  $m/z=59$  ( $\text{HNCH}_2\text{CH}_2\text{NH}_2$ ) in case of **3a**, and by peak at  $m/z=73$  ( $\text{HNCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ) in case of **3b**. The peak at 85  $m/z$ , detected for **3c**, is probably indicative of formation of  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}$  fragments from diamine **2c** units, each attached by a single or two C-N linkages to the side wall in **3c**. The observed peaks in VTP-MS spectrum of **3d** at  $m/z$  100 and 99 due to  $(\text{CH}_2)_6\text{NH}_2$  and  $(\text{CH}_2)_6\text{NH}$  fragments, respectively, evolving at ~ 450 °C, imply that the N-alkylidene bond cleavage is likely preferred over the side wall C-N bond. The presence of C-N covalent attachment in **5** causes appearance of a major peak ( $m/z$  105) of detaching amine **4** at a temperature as high as 350 °C. In **7a** the detachment of  $\text{N}(\text{C}_4\text{H}_9)_2$  groups, monitored by peaks at  $m/z$  114 ( $\text{C}_8\text{H}_{18}$ ) and 28 ( $\text{N}_2$ ), has been observed at about 500 °C, while in **7b** the peaks at  $m/z$  119  $\{(\text{C}_6\text{H}_5)_2\text{CH}_2\text{NHCH}\}$  and 105  $\{(\text{C}_6\text{H}_5)\text{CHNH}\}$  indicated the fragmentation of the side wall di- and mono benzylamino moieties at about 450 °C; in **7c** the evolution of detaching  $\text{NH}_3$  ( $m/z$  17) was taking place at ~ 350 °C.



**Figure 4.** TGA/DTA data plot for **3a**.

The TEM studies have revealed in addition to the individual functionalized SWNTs, which were successfully imaged in case of **3a** specimen, a large number of the cross-linked nanotubes, abundant in the case of the larger chain aminoalkyl functionalized SWNTs, e. g., **3d**. Nevertheless, all terminal amino-functionalized samples **3a-d** have been tested positively by Kaiser testing procedure [19] for the free  $\text{NH}_2$  groups. Their availability help to improve the solubility of nanotubes in primary amines, alcohols, water, and dilute acids and also give access to various solution phase reactions involving functional group interchange, for example, with the adipyl chloride to form new “nylon-nanotube” materials or to attach the DNA base to the SWNTs or to bind nanotubes to polymer organic and inorganic matrixes. Work on these very exciting modifications of the SWNTs is in progress.

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