Raman Study of Electronic Properties of Propylamin-functionalized Single-walled Carbon Nanotubes

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Covalent sidewall functionalization of carbon nanotubes has become a keystone to a variety of nanotube applications and therefore the chemical reaction sequences have been reviewed in many related articles. To attack the tubes framework, quite harsh reaction conditions are necessary [1]. A major task of synthesis and characterization is a well-defined increase of the solubility of carbon nanotubes in certain media.

The understanding of how a functional group influences the tube framework and its electronic structure is an important topic on the road to versatile application. Raman spectroscopy is a very powerful and non-destructive technique for both the investigation of structural changes in the tube lattice and changes of the electronic structure of nanotubes [2].

In our work a direct nucleophilic addition reaction based on *in situ* generated primary amides which are used for attaching *n*-propylamine addends to the sidewalls of single-walled carbon nanotubes (SWCNTs) is introduced. A reoxidation by air of a negatively charged $(n\text{PrNH})_n$-SWCNT^{n-} intermediate leads to a covalently bound amino functionality. From the chemist's view this causes a drastic increase of the solubility of the SWCNT-derivative in organic solvents [3]. The influence of the amino functionalities on the electronic structure of the nanotubes is investigated by means of resonant Raman scattering. From the extracted resonance profiles of the radial breathing modes (RBMs) the chiral indices of the corresponding tubes are assigned following the procedure of Ref. [4]. We observe significant changes in the transition energies and the widths of the resonance windows due to chemical modification of SWCNTs. The relative Raman intensities of the decorated samples indicate a diameter dependence of the reactivity as it has been observed for other moieties [5]. From analysis of the defect-induced *D* mode in combination with thermogravimetric analysis (TGA) we observe a considerable degree of functionalization accompanied by an almost unharmed tube structure, which ensures that the observed effects are mainly driven by changes of the electronic structure. We discuss our findings in the context of a possible selectivity of certain tube species to the chemical reaction.

References:

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Figures:

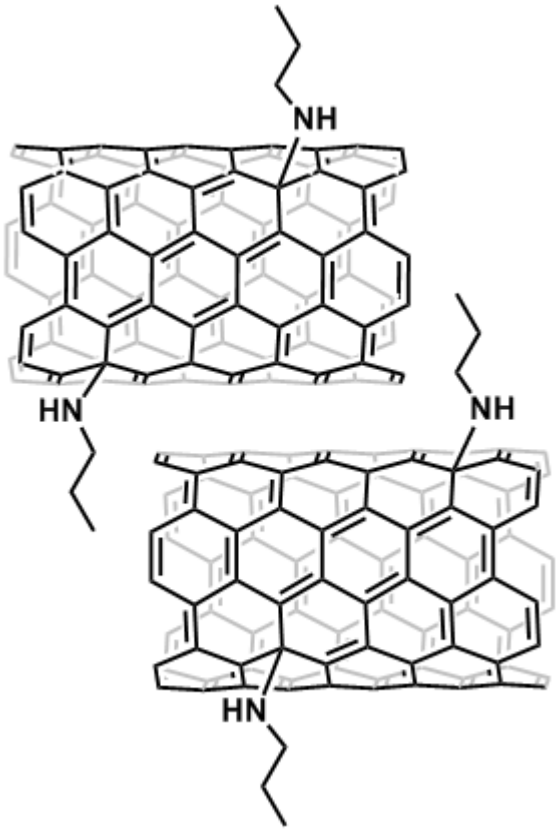

Figure 1: $(nPrNH)_n$-SWCNT