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Brominated Single Walled Carbon Nanotubes as Versatile Precursors for Covalent Sidewall Functionalization

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1. Materials

Purified HiPco SWCNTs (grade: pure; lot number P0261, TGA residue 13.3 wt) were purchased from Unidym Inc. (Sunnyvale, CA). SWCNTs were used without further treatment. Chemicals and solvents were purchased from Sigma-Aldrich Co. (Germany) and were used as-received if not stated otherwise. Argon was received from Rießner Gase, purity 5.0.

THF was distilled three times in an argon inert gas atmosphere: 1.) over CaH_2, 2.) over sodium and 3.) over sodium-potassium alloy. Afterwards, the remaining traces of oxygen were removed by pump freeze technique (3 iterative steps). The resulting absolute $THF_{(abs)}$ was used for all reactions.

2,2,2-Trifluoro ethanolate – sodium salt:

50 mg 2,2,2, trifluoro ethanol (0.5 mmol) was dissolved in 10 ml of $THF_{(abs)}$ and 46 mg cleaned sodium metal (2 mmol) was added. Afterwards the solution is refluxed for 6 h and was filtered subsequently under inert gas conditions, yielding the corresponding sodium 2,2,2-trifluoro ethanolate in THF.

2. Equipment and Characterization

Glove Box: Sample functionalization and preparation was carried out in an argon filled Labmaster sp glove box (MBraun), equipped with a gas filter to remove solvents and an argon cooling systems, with an oxygen content <0.1 ppm and a water content <0.1 ppm.

Raman Spectroscopy: Raman spectroscopic characterization was carried out on a HoribaLabRAM Aramis confocal Raman microscope (λ_{exc}: 532, 633 and 785 nm) with a laser spot size of about 1 µm (Olympus LMPlanFI 100x, NA 0.80). The incident laser power was kept as low as possible to avoid structural sample damage: 210 µW (532 nm), 110 µW (633 nm) and 2.2 mW (785nm). Spectra were obtained by a CCD array at -70°C and a 600 grooves/mm (523 & 633 nm) or 300 grooves/mm (785 nm) grating from a 50 µm 50 µm area with 2 µm step size in SWIFT mode for low integration times. Sample movement was obtained by an automated XY-scanning table.

Thermogravimetric Analysis (TGA) combined with Mass Spectrometry (TGA-MS): Mass spectrometer coupled thermogravimetric analysis (TGA-MS) was carried out on a Netzsch STA 409 CD instrument equipped with a Skimmer QMS 422 mass spectrometer (MS/EI) with the following programmed time-dependent temperature profile: 20-700 °C with 10 K/min gradient. The initial sample weights were 6.5 mg, and the experiments were performed under inert gas atmosphere with a He gas flow of 80 mL/min.

3. Synthesis

*Potassium Carbon Nanotubides **1a***:

In an argon filled glove box (<0.1 ppm oxygen; <0.1 ppm H_2O), 12 mg HiPco (1.00 mmol) SWCNTs and 9.77 mg potassium (0.25 mmol) were heated under occasional stirring at 150 °C for 6 hours. Afterwards a brown salt is yielded. The salt is allowed to cool to room temperature and is dispersed in a subsequent step in a flame dried 250 mL round bottom flask with 100 mL of $THF_{(abs)}$. Afterwards, the airtight sealed flask is unloaded from the glove box.

*Potassium Carbon Nanotubides **1b***:

In a 250 mL flamed dried 3 necked round bottom flask, 12 mg HiPco SWCNTs (1 mmol) and 100 mL of $THF_{(abs)}$ were added under an argon atmosphere. Afterwards, the solution is cooled to -78 °C (dry ice/acetone) and 100 mL of liquid ammonia is condensed. 9.77 mg of potassium (0.25 mmol) is added and the dispersion immediately turns into dark blue. The dispersion is now allowed to warm to room temperature and the ammonia is evaporated overnight under constant stirring of the dispersion.

*Brominated Carbon Nanotubes **2a** and **2b**:*

The respective dispersions were purged with argon for 10 minutes. Afterwards, the charged SWCNT intermediates were homogeneously dispersed by the aid of a tip sonicator (Bandelin UW 3200 – 100 J / 5 min). After cooling to 0 °C, 2.5 mL (0.5 mmol) of liquid bromine was added carefully *via* a syringe under safety precautions (exothermic reaction). The dispersions were now allowed to cool to room temperature and stirred overnight. Afterwards, the sample was filtered through a 0.2 μm reinforced cellulose membrane filter (Sartorius) and washed 5 times with $THF_{(abs)}$, 10 mL each. Afterwards, the material is dispersed in 50 mL $THF_{(abs)}$.

Bromide substitution with sodium 2,2,2-trifluoro ethanolate *yielding SWCNT derivatives **3a** and **3b**:*

The respective dispersions were purged with argon for 10 minutes. Afterwards, (0.5 mmol) of sodium 2,2,2-trifluoro ethanolate dissolved in $THF_{(abs)}$ was added to the dispersion (preparation see materials section). The dispersion was stirred for 4 hours and the reaction mixture was carefully transferred to a separation funnel with cyclohexane and water (50 mL each). The organic cyclohexane phase was discarded and the water/THF layer with the functionalized nanotubes was purged three times with cyclohexane. Afterwards, the aqueous layer was filtered through a 0.2 μm reinforced cellulose membrane filter (Sartorius) and washed with 100 mL of water (three times) and subsequently with 100 mL of THF. The functionalized SWCNT derivatives are scraped off the filter paper and the resulting black powder is dried at RT in vacuum.

Bromide substitution with water *yielding SWCNT derivatives **4b**.*

The dispersion of **2b** was purged with argon for 10 minutes. Afterwards, 9 mg (0.5 mmol) of water dissolved in 5 mL THF was added to the dispersion. The dispersion was stirred for 4 hours and the reaction mixture was carefully transferred to a separation funnel with cyclohexane and water (50 mL each). The organic cyclohexane phase was discarded and the water/THF layer with the functionalized nanotubes was purged three times with cyclohexane. Afterwards, the aqueous layer was filtered through a 0.2 μm reinforced cellulose membrane filter (Sartorius) and washed with 100 mL of water (three times) and subsequently with 100 mL of THF. The functionalized SWCNT derivatives were scraped off the filter paper and the resulting black powder was dried at RT in vacuum.

Precipitation of the Bromide ions in the water phase.

The aqueous layer, after separation and filtration of the hydrolyzed SWCNT derivatives **4b**, was collected. Remaining organic residues were removed by distillation yielding a slightly colored yellow water solution. 0.1 M of $AgNO_3$ was added drop wise to the dispersion, leading to an instant formation of a white / beige residue. The addition was carried out until no further precipitation was achieved.

Attempts to get a gravimetric determination of the amount of resulting silver bromide were not successful because of co-precipitated amorphous carbon by the silver bromide particles. This amorphous carbon could not be remove completely from the residue.

4. Raman Spectroscopic Characterization of Brominated SWCNT Derivatives 2a, 2b

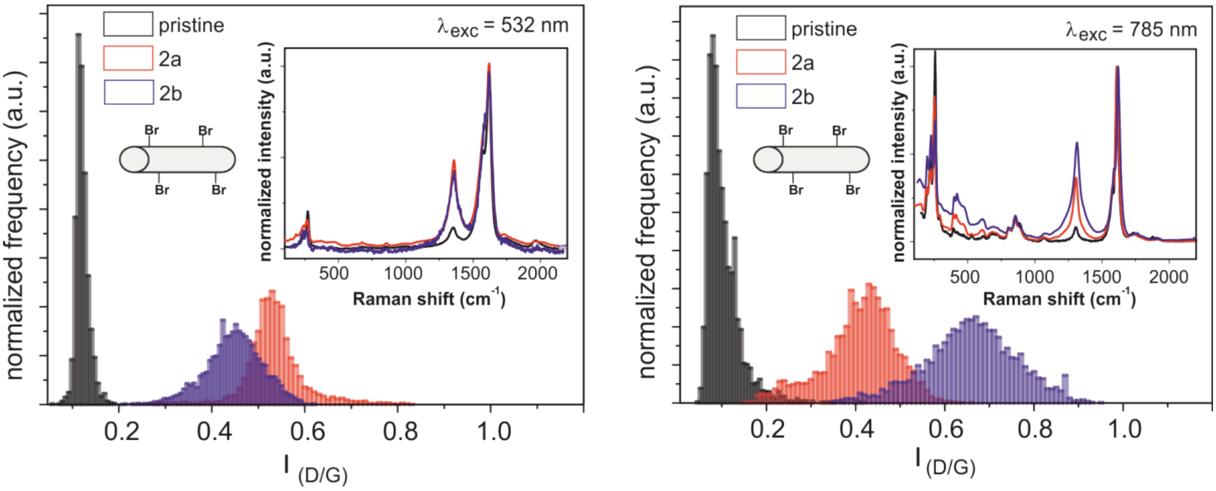


Figure S1: Statistical Raman analysis of the pristine starting material and of the brominated SWCNT derivatives **2a**, **2b** derived by a direct bromination of reductively charged carbon nanotubide intermediates **1a** (molten potassium) and **1b** (Birch type reduction with potassium). Samples were analyzed under inert gas conditions (argon). Left: Histograms of the $I_{(D/G)}$ distribution functions with λ_{exc} = 532 nm – Inset: mean spectra; data basis: 625 individual spectra. Right: Histograms of the $I_{(D/G)}$ distribution functions with λ_{exc} = 785 nm – Inset: mean spectra; data basis: 625 individual spectra.

5. Raman Spectroscopic Characterization of Final Substitution Products in Comparison to Brominated Intermediates

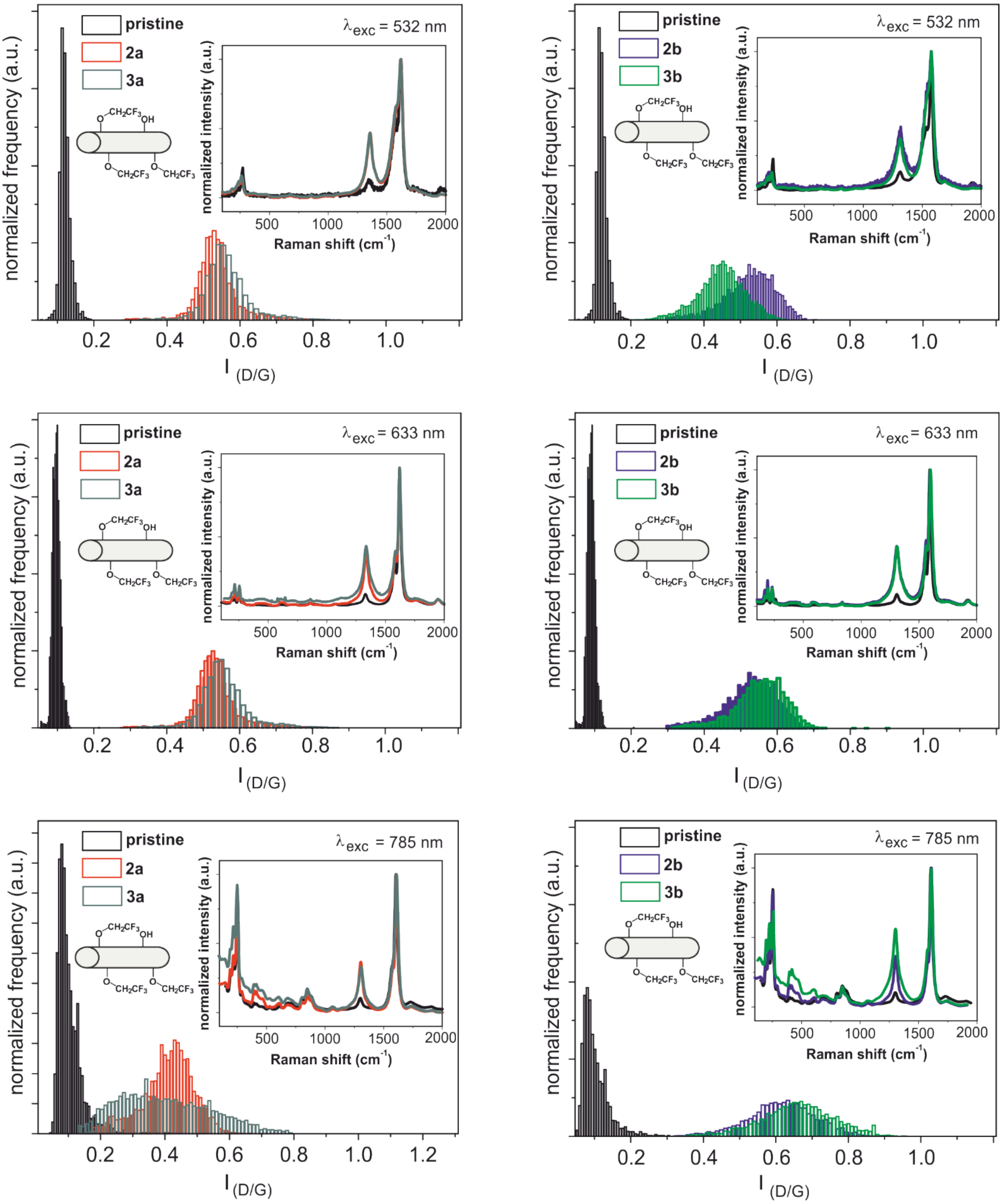


Figure S2: Statistical Raman analysis of the pristine starting material, brominated SWCNT intermediates and final substitution product with different excitation wavelengths λ_{exc} = 532 nm, 633 nm, 785 – from top to bottom. Left column: Reductive SWCNT functionalization *via* molten potassium route (derivatives **2a**, **3a**). Right column: Reductive SWCNT functionalization *via* Birch type reduction (derivatives **2b**, **3b**).

6. 2D-Raman Index Plot Data

Sample	RDI	RHI	RSI [°]
2a	0.69	108	1.9
3a	0.68	41.7	3.2
2b	0.85	52.7	12.3
3b	0.77	44.8	10.5

Table T1: 2D-Raman index plot data for SWCNT derivatives synthesized *via* reaction pathway (a) (solid state reduction) and pathway (b) (Birch type reduction) after bromine addition (**2a**, **2b**) and subsequent nucleophilic substitution of sidewall bromine atoms by 2,2,2-trifluoro ethanolate – **3a**, **3b**. The respective Raman indices – Raman Defect Index (RDI), Raman Homogeneity Index (RHI) and Raman Selectivity Index (RSI) – can be used for a quantitative comparison of different sidewall addition reactions.

For further details see: F. Hof, S. Bosch, J. M. Englert, F. Hauke and A. Hirsch, "Statistical Raman Spectroscopy: A Method for the Characterization of Covalently Functionalized Single-Walled Carbon Nanotubes" *Angew. Chem. Int. Ed.*, **2012**, *51*, 11727-11730.

*Bromination of intermediates **1a** and **1b**:*

In contrast to pathway (a), exhibiting a RDI of 0.69, a RHI of 108 and a RSI of 1.9, the Birch type based functionalization sequence (b) yields a functionalized material with a slightly higher degree of functionalization (RDI = 0.85) but a clearly decreased bulk homogeneity (RHI = 52.7). Moreover, as discussed in the main part of the manuscript, the sidewall addition of bromine is electronic type selective in respect to semiconducting carbon nanotubes in the case of pathway (b).

*Nucleophilic substitution of bromine atoms by alcoholates yielding **3a** and **3b**:*

In both pathways, the degree of functionalization (expressed by RDI) remains unchanged after the addition of 2,2,2-trifluoro ethanolate. The respective final bulk homogeneity is decreased in both cases and the respective RSI indices remain roughly constant.

7. TG/MS Analysis of Pristine Starting Material

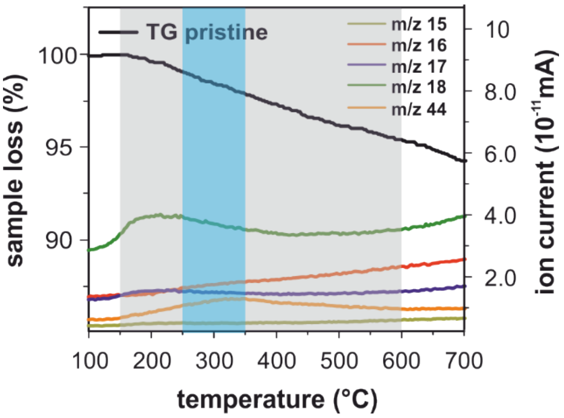


Figure S3: TG/MS profile of the pristine starting material (100 – 700 °C). For the whole temperature region a total mass loss of 6 % is detected. Mass fragments: m/z 15 (-CH_3); m/z 16 (CH_4), (O); m/z 17 (OH); m/z 18 (H_2O); m/z 44 (CO_2).

The detected mass loss for the brominated SWCNT derivative **2b** (250 – 350 °C – blue shaded region) was corrected by the respective mass loss of the pristine starting material in the same temperature range (1 %). Based on this data the amount of substance for detached bromine can be calculated: 28.4 µmol.

The detected mass loss for the hydroxylated SWCNT **4b** (150 – 600 °C – grey shaded region) was corrected by the respective mass loss of the pristine starting material in the same temperature range (4 %). Based on this data the amount of substance for detached hydroxyl-groups can be calculated: 28.9 µmol.

8. TG/MS Mass Traces of Hydroxylated SWCNT Derivative

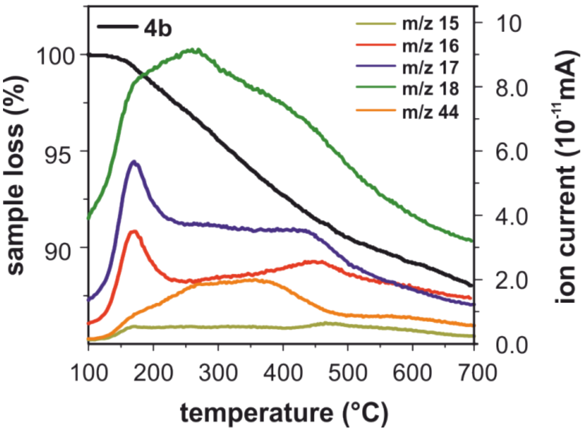
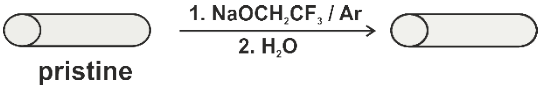


Figure S4: TG/MS profile of **4b** (100 – 700 °C) with additional mass traces. Mass fragments: m/z 15 (-CH_3); m/z 16 (CH_4), (O); m/z 17 (OH); m/z 18 (H_2O); m/z 44 (CO_2).

9. Reference Experiment: Direct Nucleophilic Addition



Scheme S1: Reaction of pristine HiPco SWCNTs with 2,2,2-trifluoro ethanolate under the same reaction conditions as used for the bromo substitution sequence.

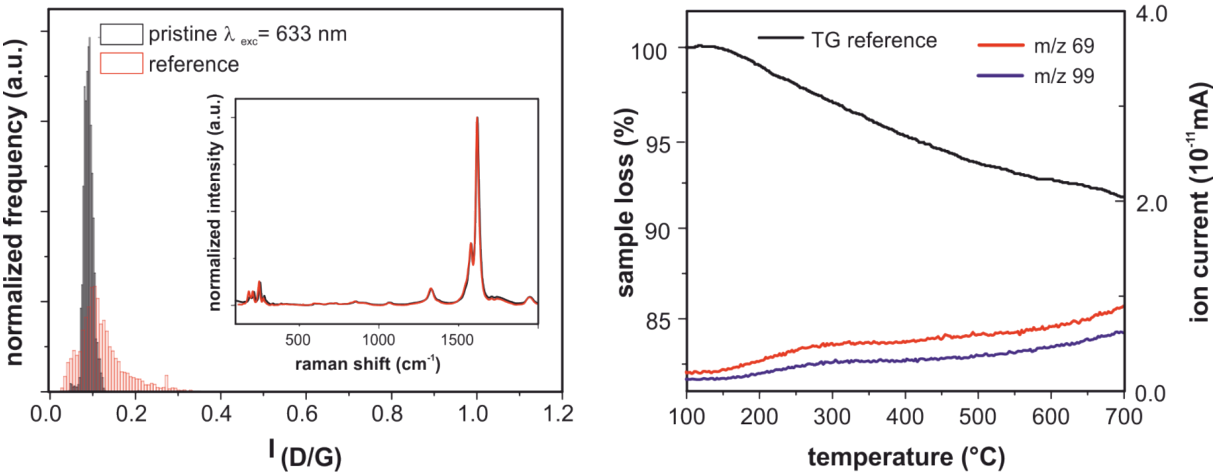


Figure S5: Left: Statistical Raman analysis of the reference sample; λ_{exc} = 633 nm. Right: TG/MS profile of the reference sample. Mass fragments: m/z 69 $-CF_3$, m/z 99 F_3CCH_2O.