Supporting Information

for

A facile one-pot route to poly(carboxybetaine acrylamide) functionalized SWCNTs

Basit Yameen,[a] Cesar Rodriguez-Emmenegger,[a,d] Ishtiaq Ahmed,[b] Corinna M. Preuss,[a] Christoph J. Dürr,[a] Nicolas Zydziak,[a] Vanessa Trouillet,[c] Ljiljana Fruk,*[b] and Christopher Barner-Kowollik*[a]

[a]*Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe, Germany and Institut für Biologische Grenzflächen, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. Email: christopher.barner-kowollik@kit.edu, http://www.macroarc.de*

[b]*DFG-Centre for Functional Nanostructures, Karlsruhe Institute of Technology (KIT), Wolfgang Gaede Str. 1a, 76131 Karlsruhe, Germany. E-mail: ljiljana.fruk@kit.edu*

[c]*Institute for Applied Materials (IAM) and Karlsruhe Nano Micro Facility (KNMF), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.*

[d] *Zoologisches Institut, Zell- und Neurobiologie, Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany.*

Experimental Details

Materials and methods

N-Methylpyrrolidone (NMP, 99%) was obtained from Acros Organics. SWCNTs were purchased from Carbon Solutions Inc. and used as received. 2-(dodecylthiocarbonothioylthio)propionic acid (DoPAT) was obtained from Orica Pty Ltd., Melbourne, Australia. Amine functionalized ss-DNA (5´-amine-GTGGAAAGTGGCAATCGTGAAG), Cy5 functionalized complimentary DNA strand (5´-Cy5-CTTCACGATTGCCACTTTCCAC), *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC·HCl, 98%) and *N*-hydroxysuccinimide (NHS, 98%) were obtained from Sigma-Aldrich. Cp functionalized RAFT agent **1** was synthesized according to a reported procedure.[1] The CBAA monomer **2** was synthesized according to a previously reported procedure.[2] 4,4´-Azobis(4-cyanopentanoic acid) (V-501) **3** was purchased from Sigma–Aldrich and was recrystallized from methanol.

The ATR-FTIR spectra were recorded on a Bruker ALPHA. The samples were measured as pure substances.

The TEM images were obtained on a Philips CM200 FEG/ST electron microscope. The p-SWCNTs based samples were dispersed in toluene (10 $\mu g \cdot mL^{-1}$) via ultrasonic bath for 5 minutes. The poly(CBAA) functionalized SWCNTs based samples were prepared in the similar fashion, except ethanol was used instead of toluene. One drop of the dispersion was applied onto a copper grid with polymer coverage and allowed to dry under ambient conditions prior to TEM imaging.

The molecular weight of the polymer samples was determined via absolute size exclusion chromatography (SEC) using an HPLC Shimadzu with a Superose 6 column equipped with UV, differential refractometer Optilab rEX and multi-angle light scattering detector DAWN 8 (Wyatt Technology Corp., USA). 0.3 M sodium acetate buffer (pH 6.5) containing 0.5 g L^{-1} sodium azide was used as the mobile phase. The flow rate was 0.5 $mL \cdot min^{-1}$.[3]

XPS measurements were performed using a K-Alpha XPS spectrometer (ThermoFisher Scientific, East Grinstead, UK). Data acquisition and processing using the Thermo Avantage software is described elsewhere.[1] All SWCNTs were deposited on Au substrates and analyzed using a microfocused, monochromated Al Kα X-ray source (30-400 μm spot size). The K-Alpha charge compensation system was employed during analysis, using electrons of 8 eV energy and low-energy argon ions to prevent any localized charge build-up. The spectra were fitted with one or more Voigt profiles (BE uncertainty: $\pm$0.2 eV).

Fluorescence imaging was performed using a Till iMIC digital microscope, equipped with a CCD camera IMAGO Type QE, from TILL Photonics. The water dispersions of the samples were deposited on the glass slide sample holder and allowed to dry under ambient conditions. All the images were taken at 60× magnification. ImageJ software was used to analyze the images.

One-pot functionalization of p-SWCNTs with poly(CBAA) (4)

5 mg of p-SWCNTs were dispersed in 50 mL of NMP. After 1 h of sonication, 60 mg (0.111 mmol) of Cp functionalized RAFT CTA **1** was added (dissolved in a minimum volume of NMP). The mixture was sonicated for 1 h under N_2(g) bubbling. The resulting dispersion was stirred overnight at ambient temperature, purged with N_2(g) for 1.5 h, and a degassed solution of CBAA monomer **2** (1.14 g, 5 mmol) and the initiator **3** (8.1 mg, 0.029 mmol) in 5.5 mL of water was added. The dispersion was degassed for 1 h with N_2(g) bubbling at 10 °C and polymerization was carried out at 70 °C for 24 h. The poly(CBAA) functionalized SWCNTs sample **4** was obtained by filtration using a PTFE-membrane (0.2 µm pore size, Sartorius). The residue was washed with copious amounts of water, re-dispersed in water and subjected to lyophilization to afford **4**. The filtrate was subjected to dialysis against deionized water for 10 days using a SpectraPor 3 membrane (MWCO: 3500 Da) and subsequently lyophilized. The resulting polymer was characterized via absolute SEC, which gave an M_n of 46000 g·mol^{-1} with a broad $Đ$ (2.4). The corresponding negative control **5** was prepared employing a process analogous to the preparation of **4**, except Cp functionalized RAFT CTA **1** was replaced with the DoPAT. The ATR-IR spectrum of the negative control **5** is depicted in Fig. S1, which did not show any absorption characteristic of the poly(CBAA). Furthermore, **5** was not dispersible in water, underpinning the necessity of the Cp group of **1** towards the surface functionalization of SWCNTs with poly(CBAA).

Functionalization of 4 with amine functionalized (ss)-DNA (6) and subsequent hybridization with complimentary DNA strand (8)

0.3 mg of poly(CBAA) functionalized SWCNTs **4** were dispersed in 100 µL of H_2O (from a Milli-Q purifier). To this dispersion, NHS (0.05 M, 100 µL) and EDC·HCl (0.2 M, 100 µL) were added. After the dispersion was incubated for 10 min at 25 °C, amino functionalized ss-DNA (aD1, 100 µM, 100 µL) was added. The dispersion was again incubated at 25 °C for 4 h. The SWCNTs-DNA conjugate **6** was obtained by subjecting the dispersion to centrifugation and washing with H_2O (from Milli-Q purifier, 3×100 µL) to remove the excess of DNA. To exclude the contribution from the electrostatic interactions, the negative control sample **7** was prepared in an analogous manner except the addition of NHS and EDC·HCl. Sample **6** and the corresponding negative control **7** were subjected to hybridization with the complimentary DNA

strand. A dispersion of SWCNTs-DNA conjugate **6** in H_2O (from Milli-Q purifier, 100 µL) was incubated with the complimentary DNA strand (cD1-Cy5) functionalized with the Cy5 dye (100 µM, 5µL) at 25 °C for 50 min. The dispersion was centrifuged, washed with MQ H_2O (from Milli-Q purifier, 3×100 µL) and with PBS buffer (300 mM NaCl, 3×100 µL) to remove the excess of cD1-Cy5.

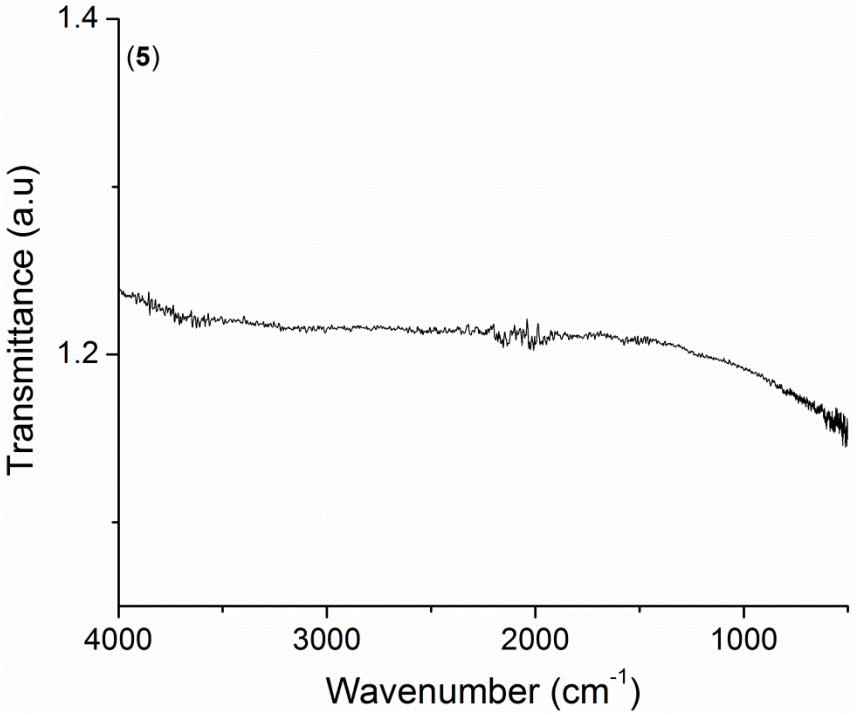

Fig. S1 ATR-FTIR spectrum of the negative control **5**

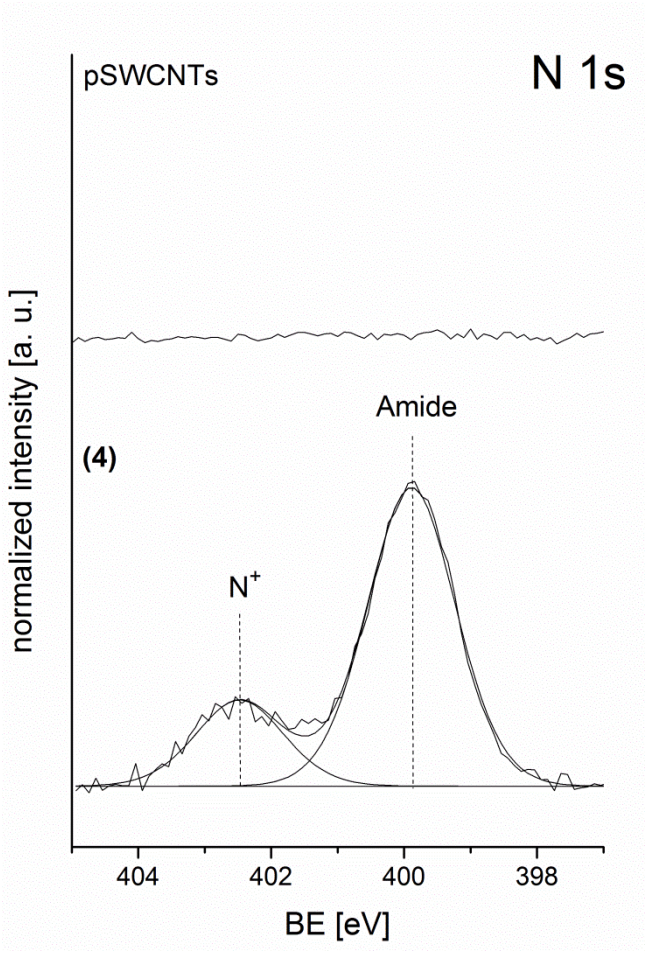

Fig. S2 N 1s high resolution XPS scans of pristine SWCNTs and SWCNTs functionalized with poly(CBAA) (**4**).

The pristine SWCNTs do not show any signal in the N 1s high resolution spectrum, whilst **4** depicts a signal for N^+ at 402.5 eV and a signal for the amide at 399.9 eV.[4]

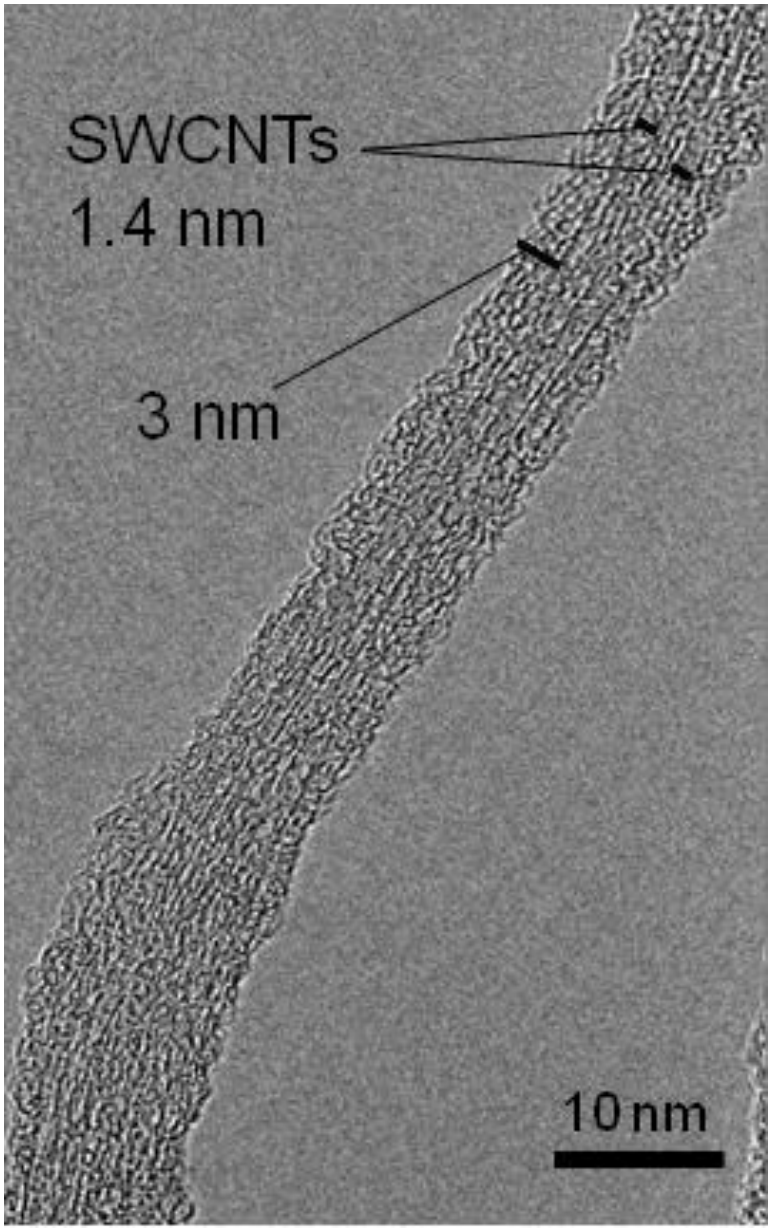

Fig. S3 TEM image of poly(CBAA) functionalized **4**. The image shows two functional SWCNTs lying next to each other, with an outer amorphous layer of approximately 3 nm. Using this number, one can estimate the grafting density of polymer chains on the surface as explained in the main text. A critical factor in estimating the grafting density is the length of the formed polymer chain. As an approximation, the number average molecular weight of the polymer formed in solution is employed. As the sequential one pot sequence leads to an almost quantitative attachment of the Cp-functional RAFT agent on the SWCNTs, the entire polymerization is controlled from the surface of the SWCNTs, leading to a limited control of the molecular weights in solution. Thus, the employed molecular weight is arguably larger than the polymer grafted from the surface, making the provided grafting density a lower limit (as lower number average molecular weights lead to higher grafting densities).

Reference and Notes

[1] C. J. Dürr, L. Hlalele, A. Kaiser, S. Brandau and C. Barner-Kowollik, *Macromolecules*, 2013, **46**, 49.

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[4] Y. Jiang, B. Rongbing, T. Ling, S. Jian, and L. Sicong, *Colloids and Surfaces B: Biointerfaces*, 2004, **36**, 27.