Supporting Information to the Manuscript

Non-Covalent Grafting of Carbon Nanotubes with Triblock Terpolymers: Toward Patchy 1D Hybrids

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Table S1. Specifications of the Used CNTs

Property\CNT	**Baytubes C 150P (CNT1)**	**CNT2**
Length [µm]	> 1	3 - 6
Wall number	n.a.	6 - 8
Inner diameter [nm]	~ 4	4.5 ± 0.5
Outer diameter [nm]	~ 13	10 ± 1
Carbon purity degree [%]	≥ 95	≥ 98

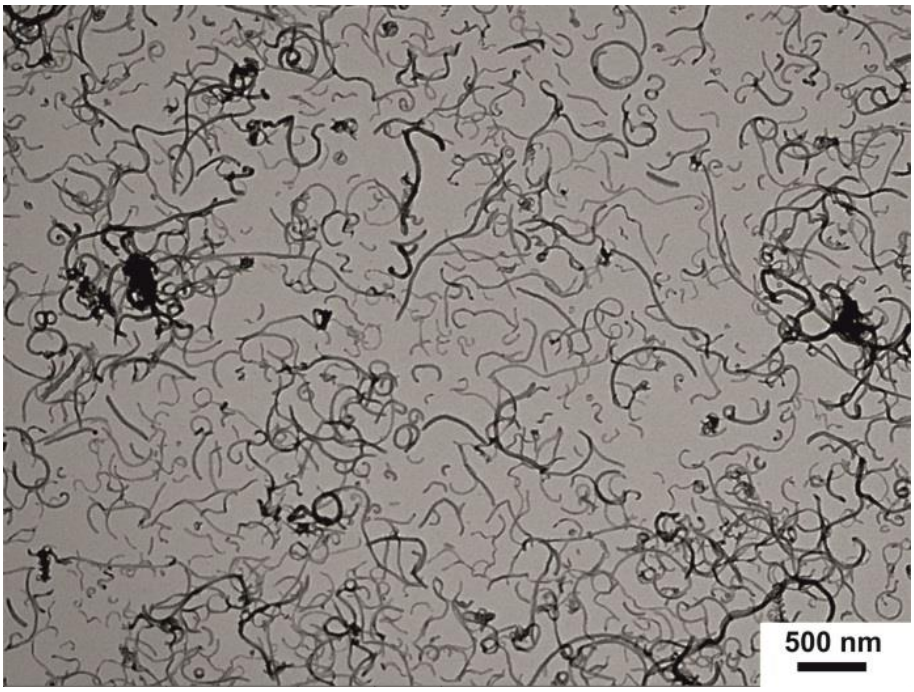


Figure S1. TEM overview image of CNT1@SEM1 prepared in toluene at a ratio of 2/1 (w/w); overall concentration of c = 30 g/L (RuO_4 staining).

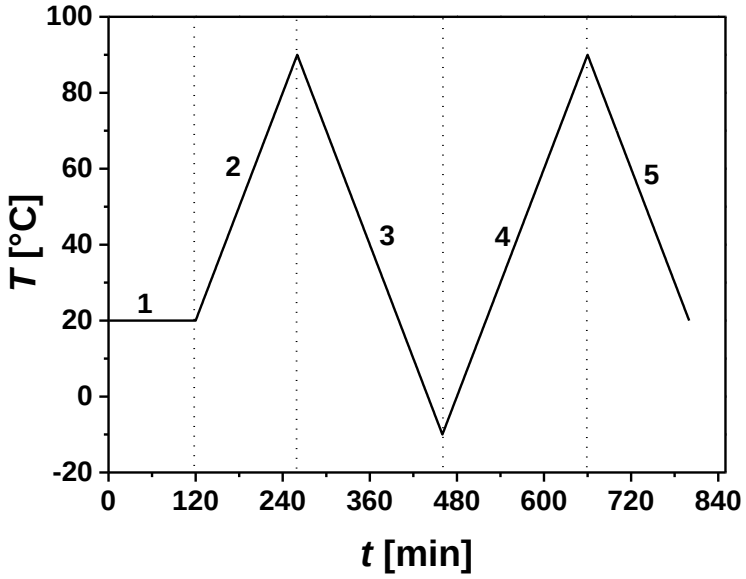


Figure S2. Typical μ-DSC temperature profile applied for SEM1 and SEM2 (scanning rate 0.5 K/min, c = 10 g/L in toluene). After an equilibration at 20 °C the samples were first heated to 90 °C, in order to completely melt all crystallites. Subsequent cooling to -10 °C was chosen, to display all crystallization transitions even below room temperature. Due to weak transitions, the concentration of SEM3 was increased to 30 g/L, and cooling in step 3 was carried out to -20 °C.

Figure S3. Digital photograph of an unsuccessful functionalization experiment with a polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) ($S_{340}B_{340}M_{360}$) triblock terpolymer (CNT1/SBM = 2/1 (w/w) in toluene, overall concentration of c = 30 g/L).

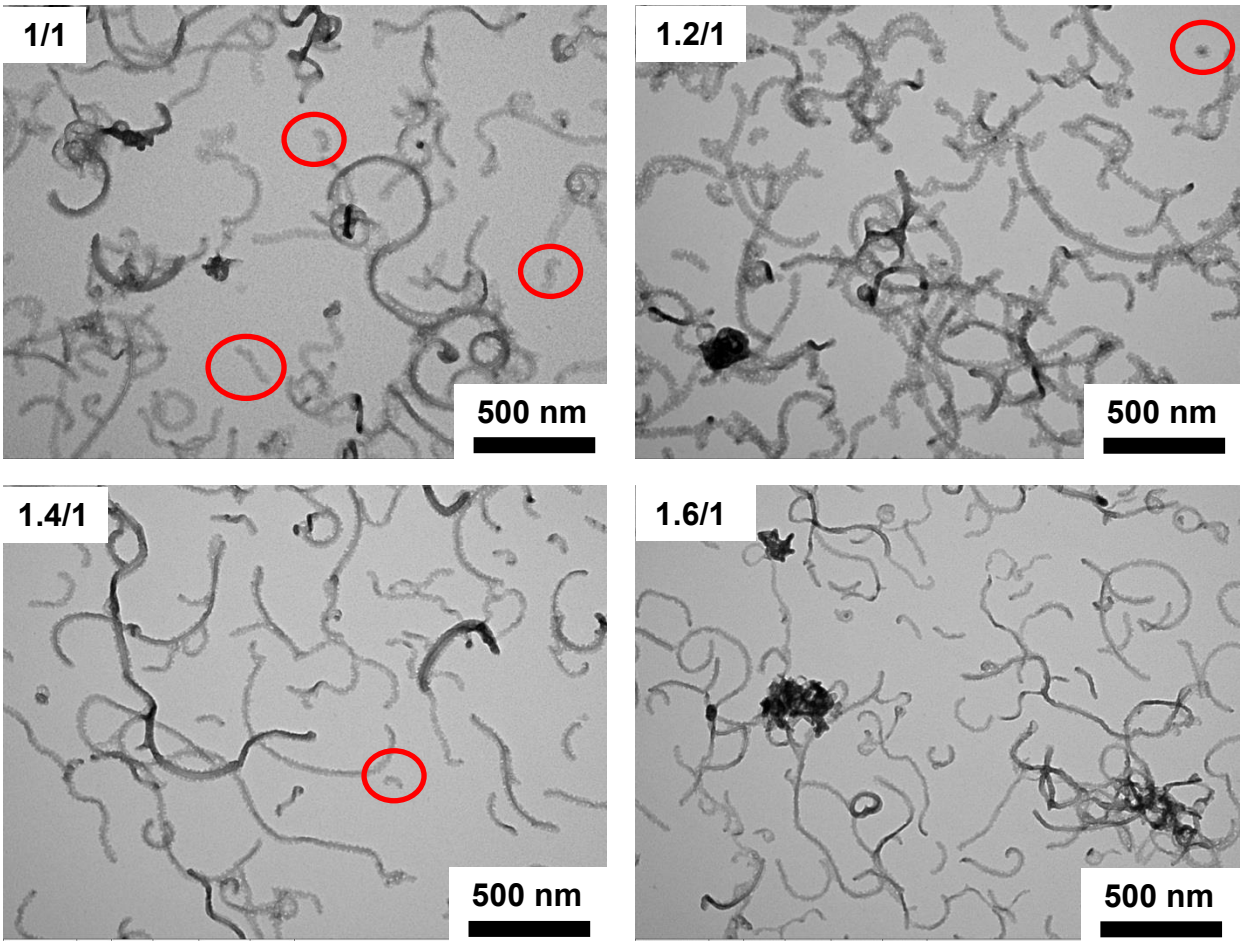
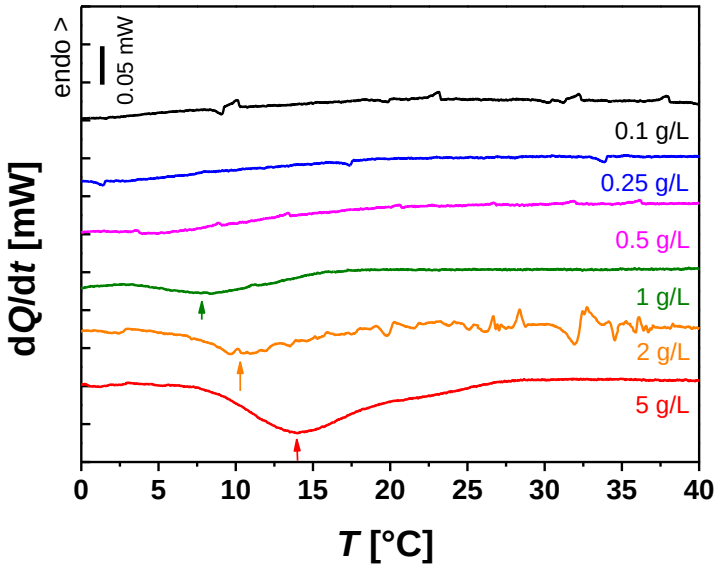


Figure S4. TEM images of CNT1@SEM1 prepared in toluene at different CNT1/SEM1 ratios (w/w) as indicated; overall concentration of c = 20, 22, 24 and 26 g/L, respectively (RuO_4 staining). Red circles indicate free SEM1 wCCMs.

A



B

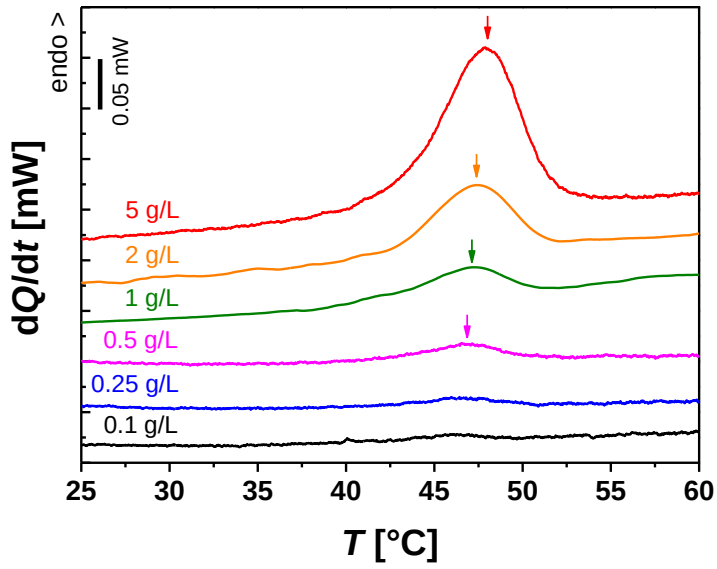


Figure S5. μ-DSC cooling (A) and 2nd heating (B) traces of neat SEM1 at different concentrations in toluene. The arrows indicate the location of the peak crystallization (T_c) and melting (T_m) temperatures, respectively. In the heating traces the area of the endothermic PE melting transition decreases with decreasing concentration and can only hardly be detected at concentrations below 0.5 g/L. Thus, the absence of thermal transitions in the corresponding heating traces of CNT1@SEM1 (Figure 2, main text) can be taken as a measure that the concentration of free SEM1 (not bound to CNT) is below 0.5 g/L, corresponding to 5 wt% of the initial SEM1 feed (10 g/L). The detection limit in the corresponding cooling traces is even higher, as below 1 g/L the crystallization exotherm is no longer detectable.

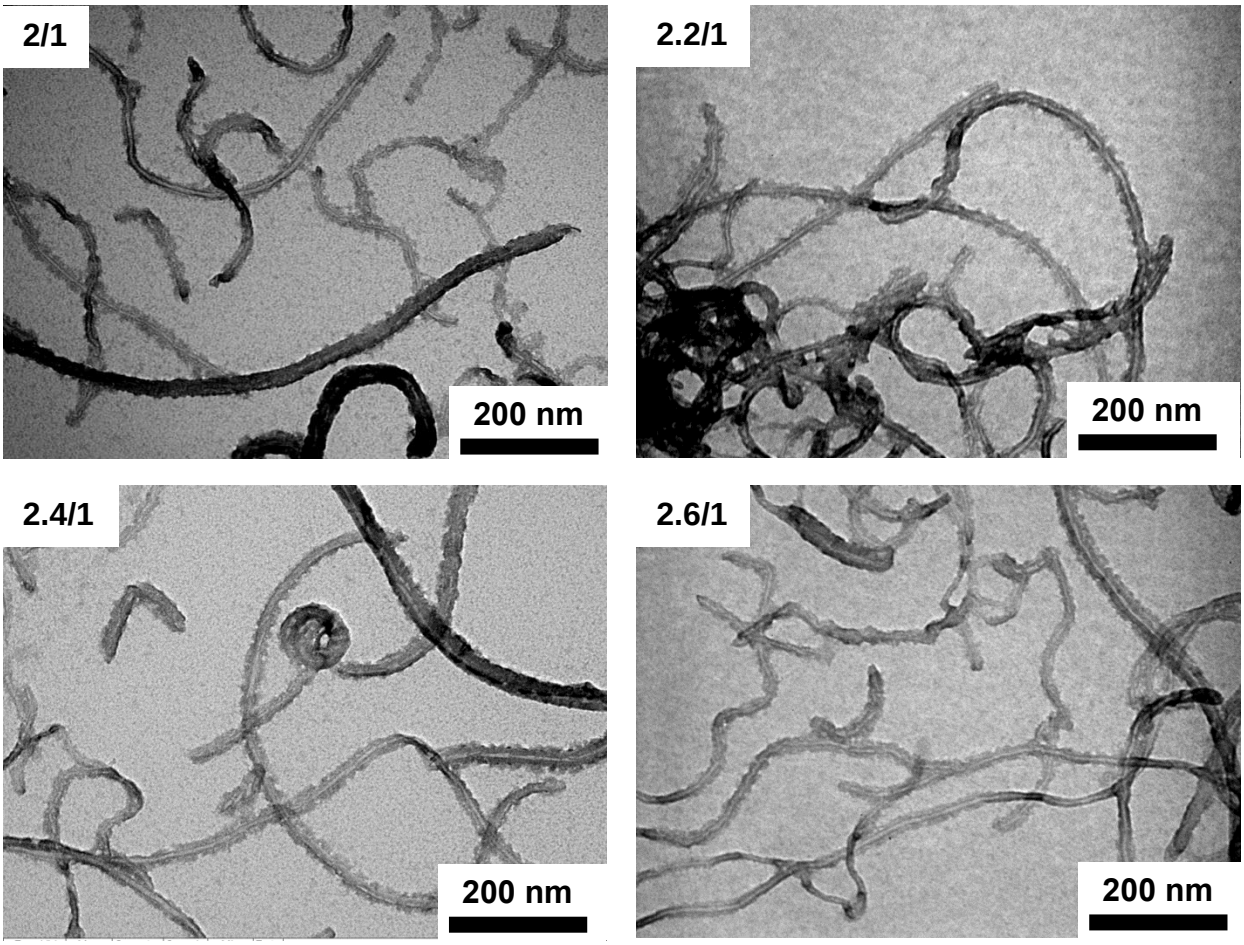


Figure S6. TEM images of CNT1@SEM1 prepared in toluene at different CNT1/SEM1 ratios (w/w) as indicated; overall concentration of c = 30, 32, 34 and 36 g/L, respectively (RuO_4 staining).

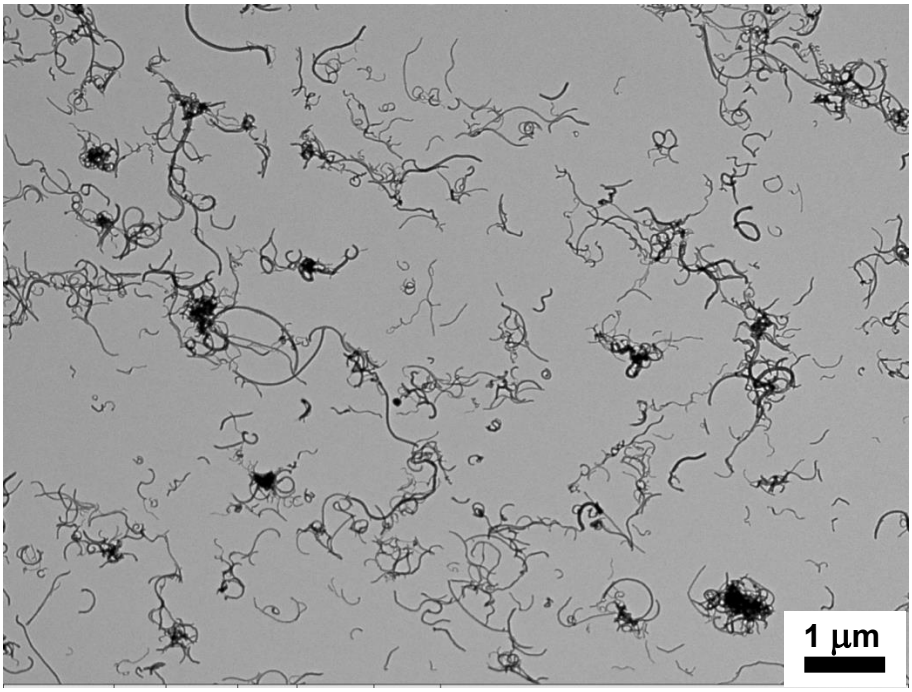


Figure S7. TEM overview image of CNT1@SEM1 prepared in 1,4-dioxane at a ratio of 2/1 (w/w); overall concentration of c = 30 g/L (RuO_4 staining).

Functionalization in 1,4-dioxane. In analogy to the functionalization experiments in toluene, we have varied systematically the CNT1/SEM1 ratio in 1,4-dioxane while keeping the SEM1 concentration constant at c = 10 g/L. From the corresponding TEM images (Figure S8, S9) a limiting CNT1/SEM1 ratio of 1.8/1 – 2/1 (w/w) can be identified at which the SEM1 is completely grafted onto CNT1, and the maximum CNT1/SEM1 ratio still resulting in stable dispersions was determined to 2.7/1 (w/w). Both values are comparable to those obtained using toluene as solvent for functionalization. A closer inspection of the corona structure of the CNT1@SEM1 formed in 1,4-dioxane (Figure 4, main text) reveals a reduced size of the dark PS patches compared to the sample from toluene (Figure 1, 3; main text). This might be attributed to the different quality of the solvents with respect to the PS and PMMA corona blocks. From the

solubility parameters (Table S2) it can be deduced that toluene is a slightly better solvent for PS compared to PMMA. Thus, the PS chains are more strongly swollen and the patch size is increased with respect to that of PMMA. In case of 1,4-dioxane a reverse situation is found, i.e., the PS patches are smaller.

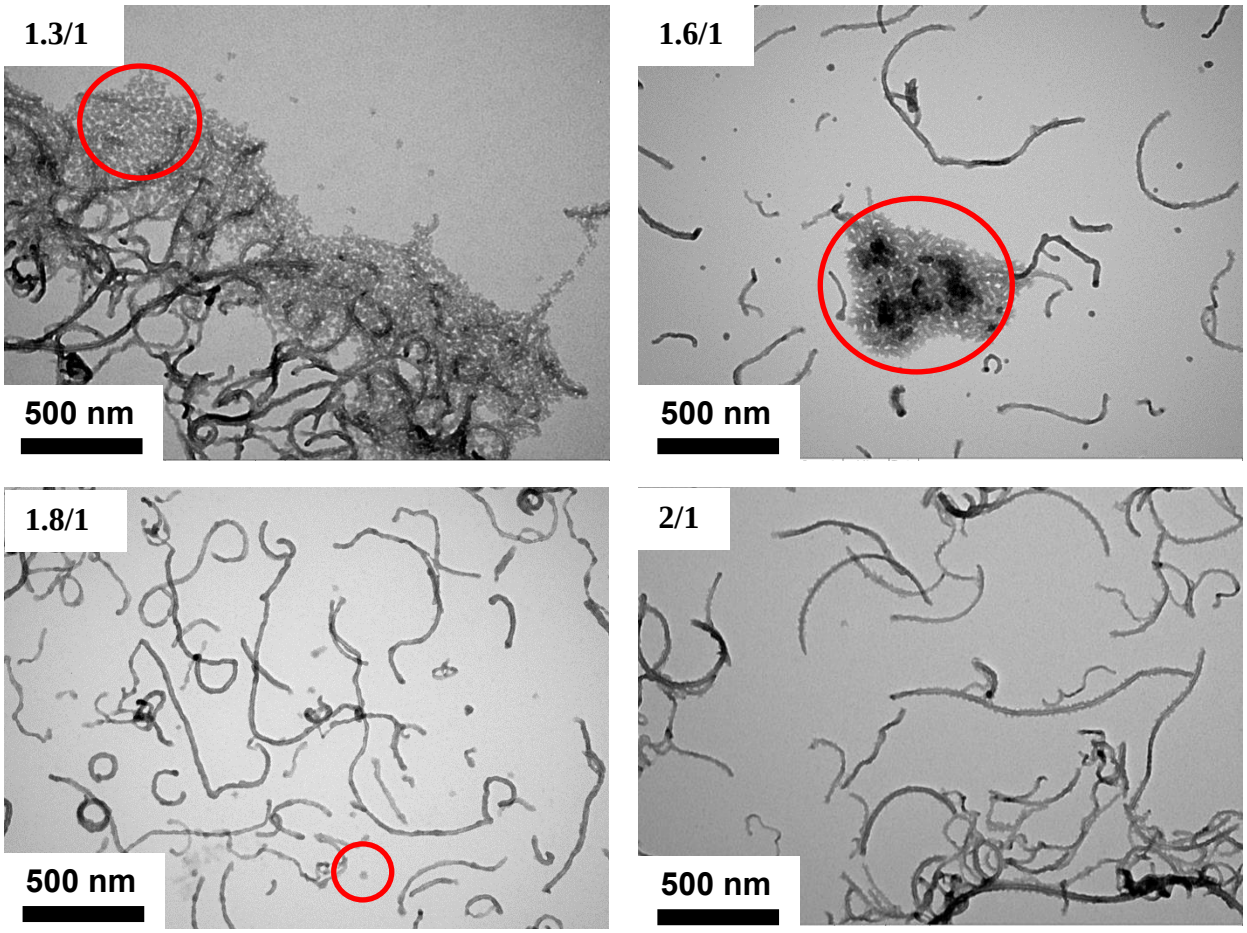


Figure S8. TEM images of CNT1@SEM1 prepared in 1,4-dioxane at different CNT1/SEM1 ratios (w/w) as indicated; overall concentration of c = 23, 26, 28 and 30 g/L, respectively (RuO_4 staining). Red circles indicate free SEM1 sCCMs. At a CNT1/SEM1 ratio of 1.8/1 (w/w) only very few sCCMs were detected and, thus, can be taken as the limiting ratio at which the SEM1 is almost completely attached to the CNT´s surface.

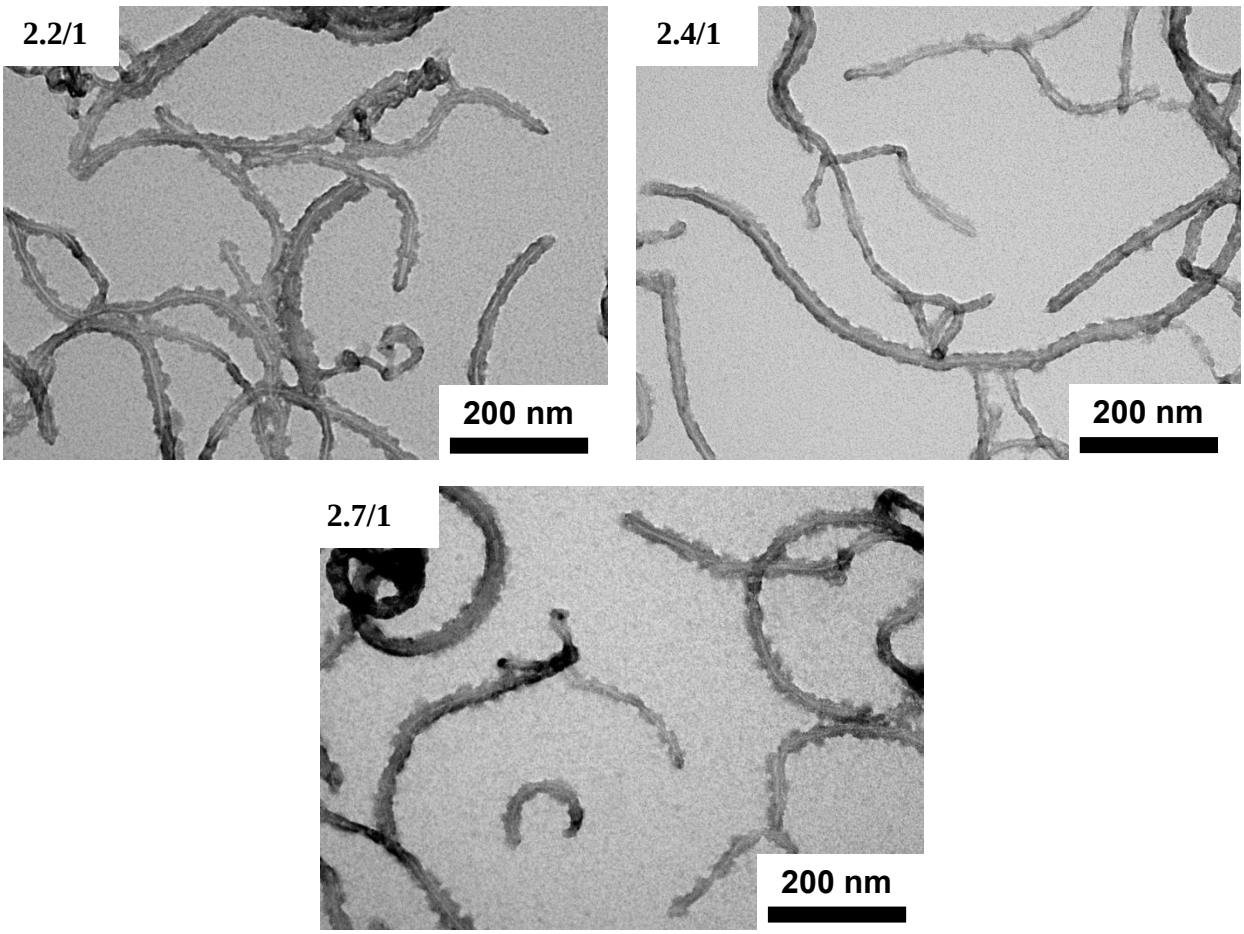


Figure S9. TEM images of CNT1@SEM1 prepared in 1,4-dioxane at different CNT1/SEM1 ratios (w/w) as indicated; overall concentration of c = 32, 34 and 37 g/L, respectively **(**RuO_4 staining**)**. Even up to a CNT1/SEM1 ratio of 2.7/1 (w/w) stable dispersions were obtained and the functionalized CNTs exhibit the typical "patchy" PS/PMMA corona.

Table S2. Solubility Parameters, δ, of the Solvents Used and the Corona Blocks[1]

	Toluene	**1,4-Dioxane**	**Polystyrene**	**Poly(methyl methacrylate)**
δ **[MPa** ^{½}**]**	18.2	20.3	18.5	19.0

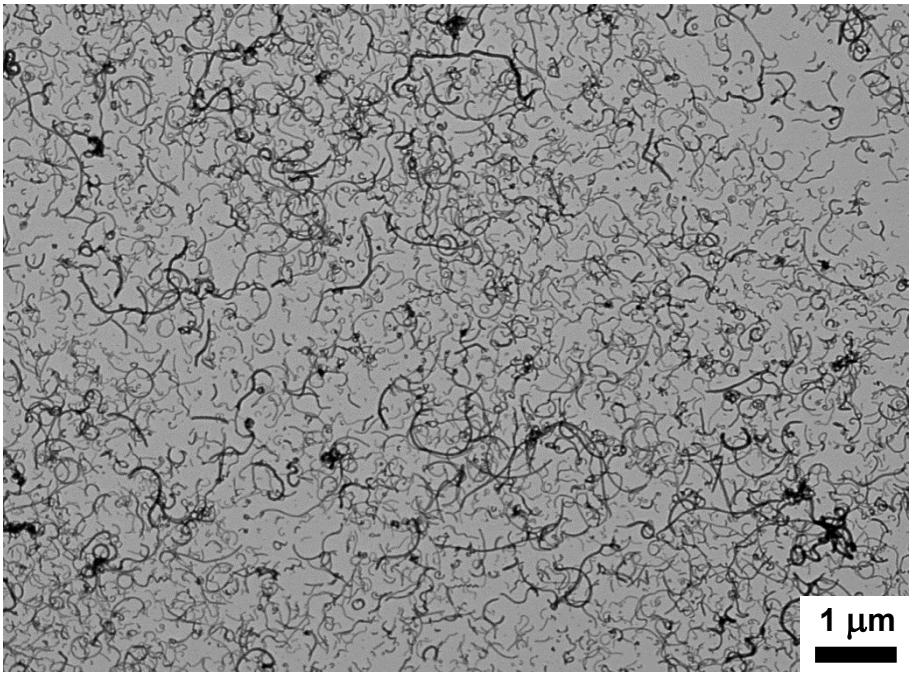


Figure S10. TEM overview image of CNT1@SEM2 prepared in toluene at a ratio of 2/1 (w/w); overall concentration of c = 30 g/L (RuO_4 staining).

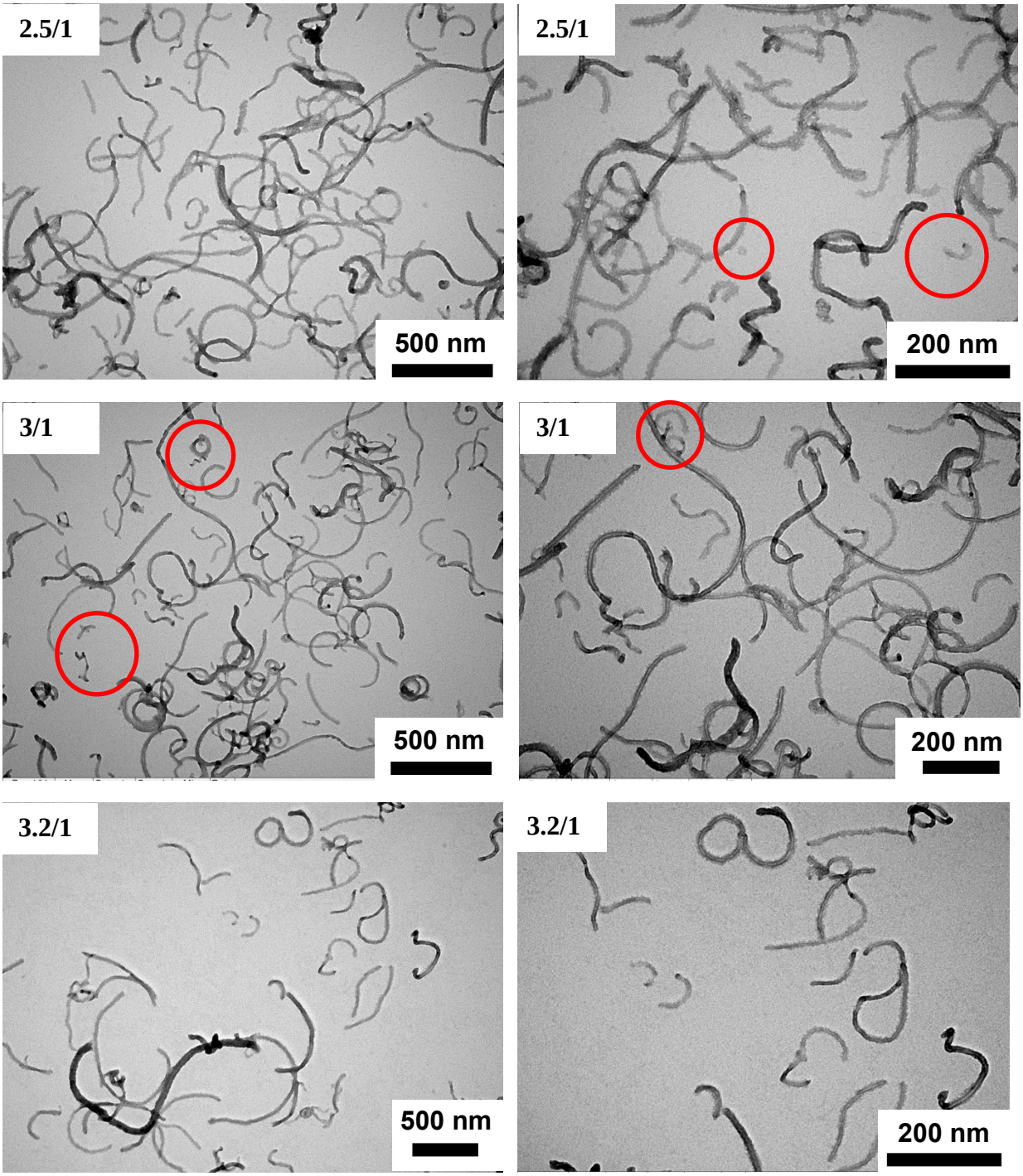


Figure S11. TEM images of CNT1@SEM2 prepared in toluene at different CNT1/SEM2 ratios (w/w) as indicated; overall concentration of c = 35, 40 and 42 g/L, respectively (RuO_4 staining). Red circles indicate free SEM1 wCCMs.

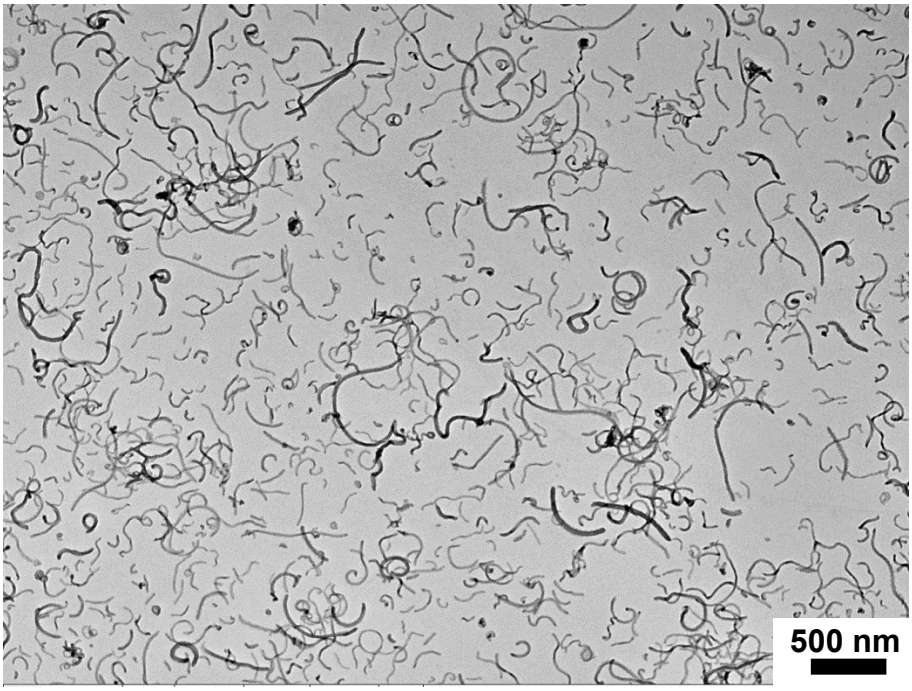


Figure S12. TEM overview image of CNT1@SEM3 prepared in toluene at a ratio of 2/1 (w/w); overall concentration of c = 30 g/L (RuO_4 staining).

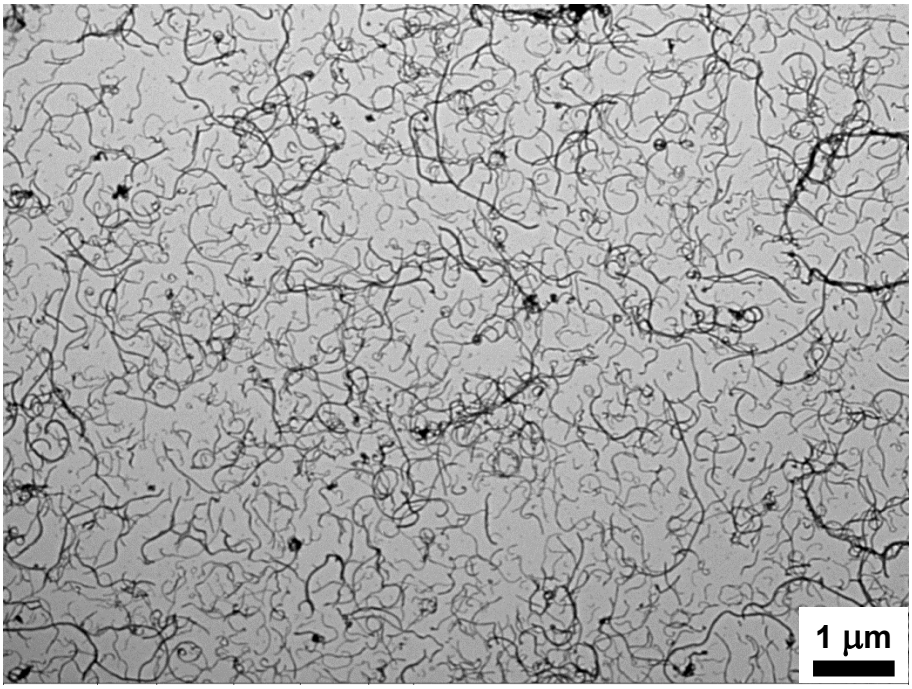


Figure S13. TEM overview image of CNT2@SEM1 prepared in toluene at a ratio of 2/1 (w/w); overall concentration of c = 1.5 g/L (RuO_4 staining).

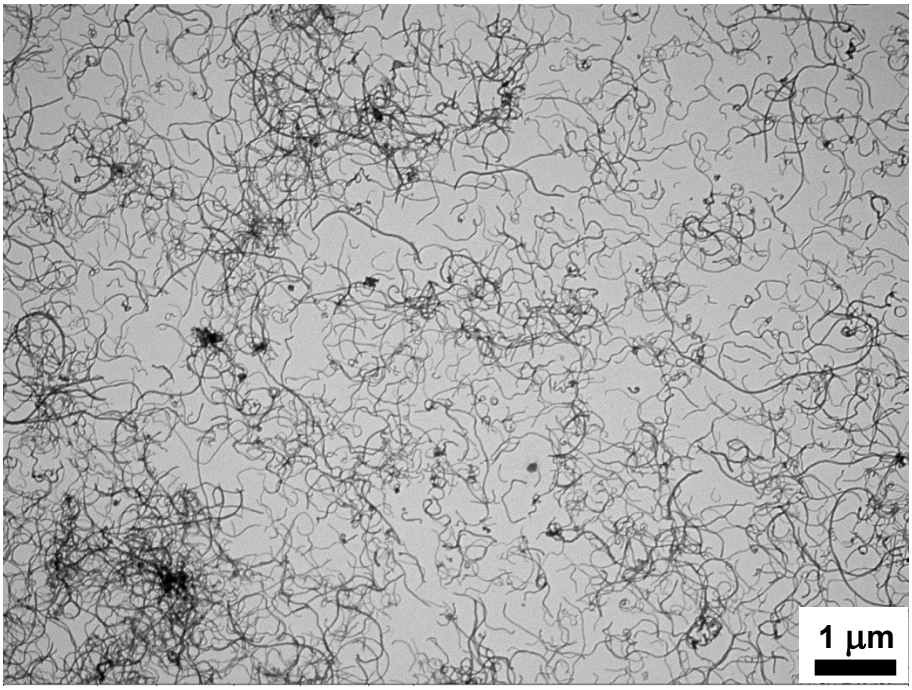


Figure S14. TEM overview image of CNT2@SEM2 prepared in toluene at a ratio of 2/1 (w/w); overall concentration of c = 9 g/L (RuO_4 staining).

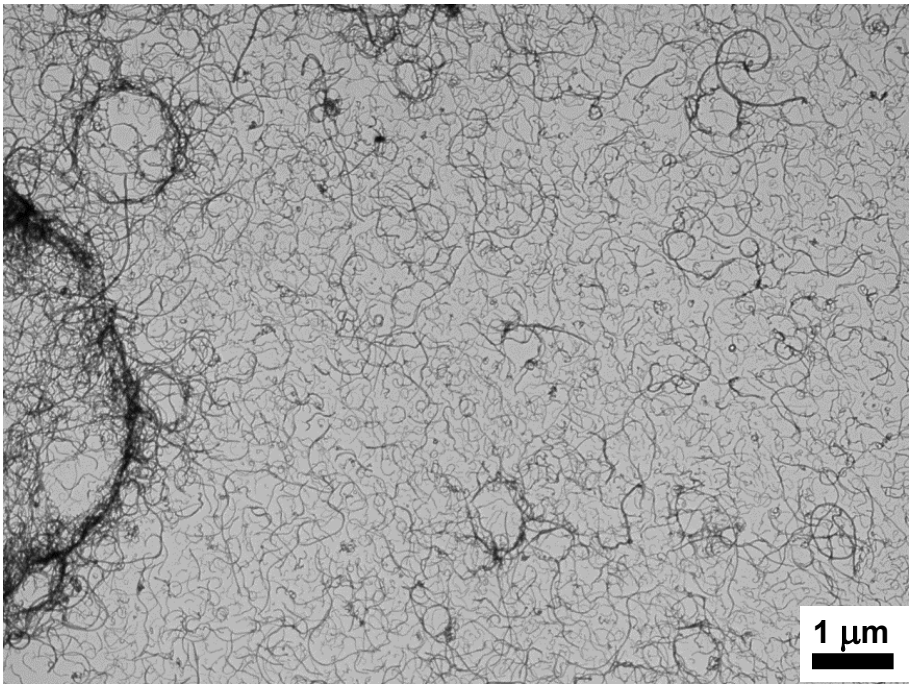


Figure S15. TEM image of CNT2@SEM2 prepared in chloroform at a CNT/SEM2 ratio of 2/1 (w/w); overall concentration of c = 6 g/L (RuO_4 staining). Circular aggregates are a result of drying artifacts during TEM sample preparation and are ascribed to the fast evaporation of chloroform.

References

(1) Barton, A. F. M. *CRC Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*, CRC Press: Boston, 1990.