Highly Efficient Hyperbranched CNT Surfactants: Influence of Molar Mass and Functionalization

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Supporting Information

Degree of Functionalization

NMR spectra (in DMSO) for unfunctionalized PG10000 (Figure S1, S2 and S3) and 3.7% PG10000 (Figure S4, S5 and S6). Spectra of unfunctionalized PG10000 (^{1}H, ^{13}C and ^{13}C DEPT-135) are added for comparison. ^{1}H NMR (Figure S4) reveals the degree of functionalization. By taking the integrated area between 3.9 and 2.8 ppm (-CH- and -CH_2- from the PG core) as a reference, the functionalization can be calculated from the integrated area in between 7.8 and 6.8 ppm (-C_6H_5 from trityl). The signal in between 4.9 and 4.3 is caused by the hydroxyl groups of the PG core. ^{13}C NMR spectra (Figure S5) of purified material provide prove for successful functionalization, with the quaternary carbon adjacent to the trityl phenyl groups giving rise to a signal at 85.7 ppm. The peak at 143.9 ppm originates from the quaternary carbon from the phenyl groups, whereas the other 5 phenyl carbons produce peaks at 128.3 ppm, 127.8 ppm and 126.9 ppm. The signals from the hyperbranched

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PG structure can be found between 81 and 60 ppm. DEPT-135 spectra (Figure S6) confirm this analysis.

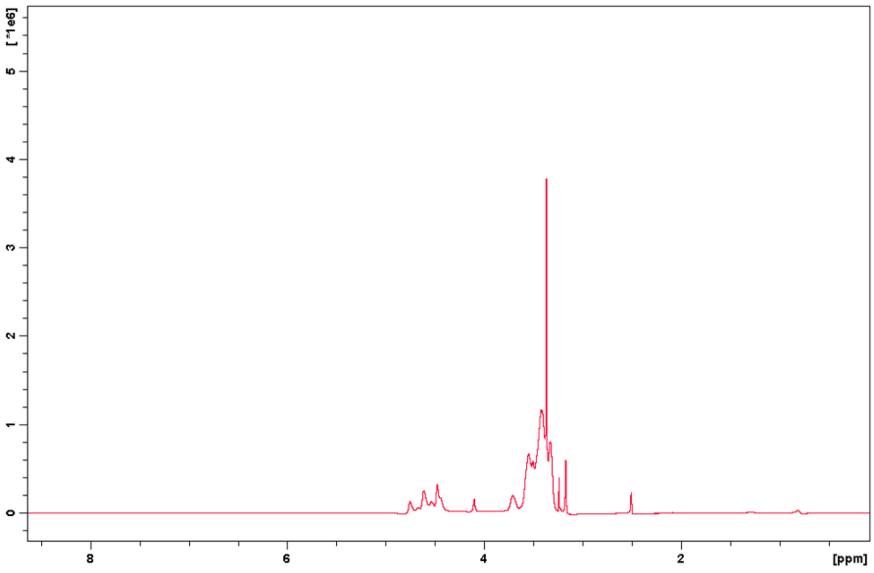

Figure S1: ^{1}H NMR spectrum for unfunctionalized PG10000.

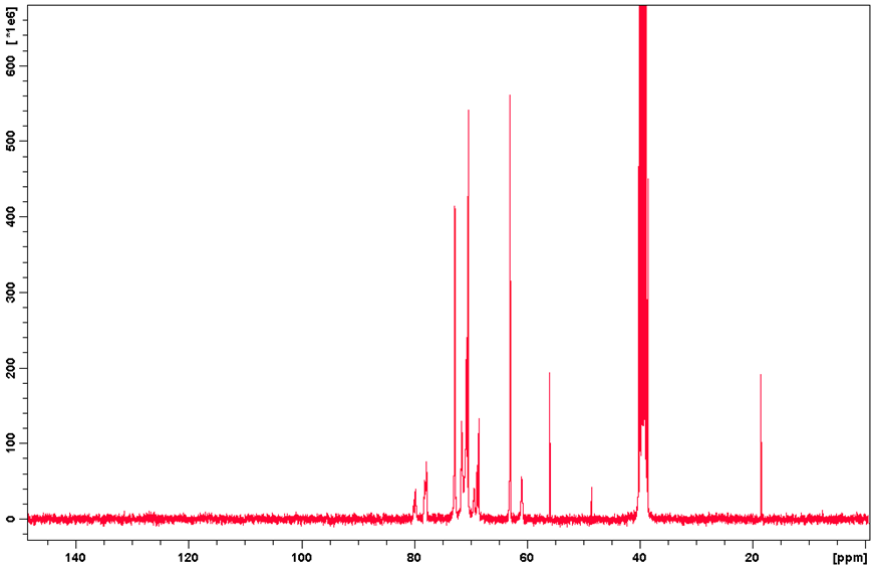

Figure S2: ^{13}C NMR spectrum for unfunctionalized PG10000.

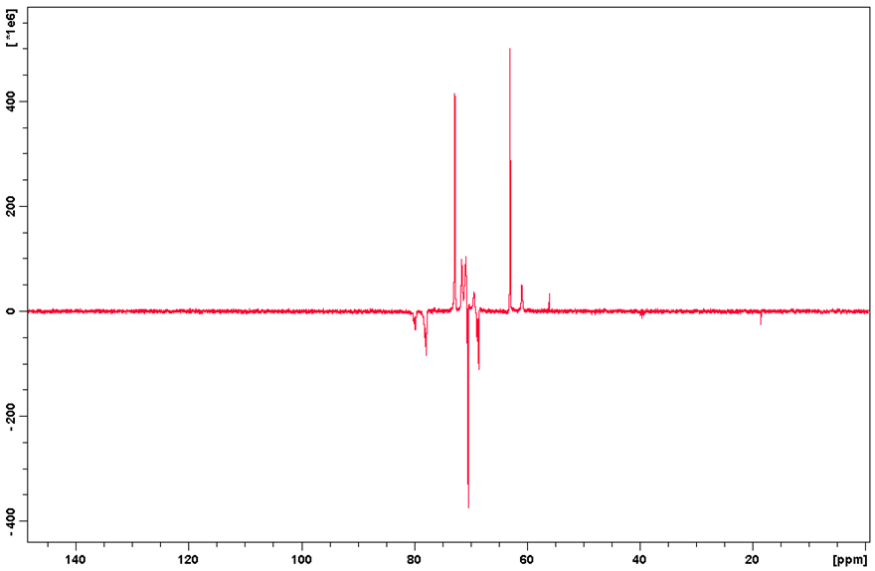

Figure S3: ^{13}C DEPT-135 NMR spectrum for unfunctionalized PG10000.

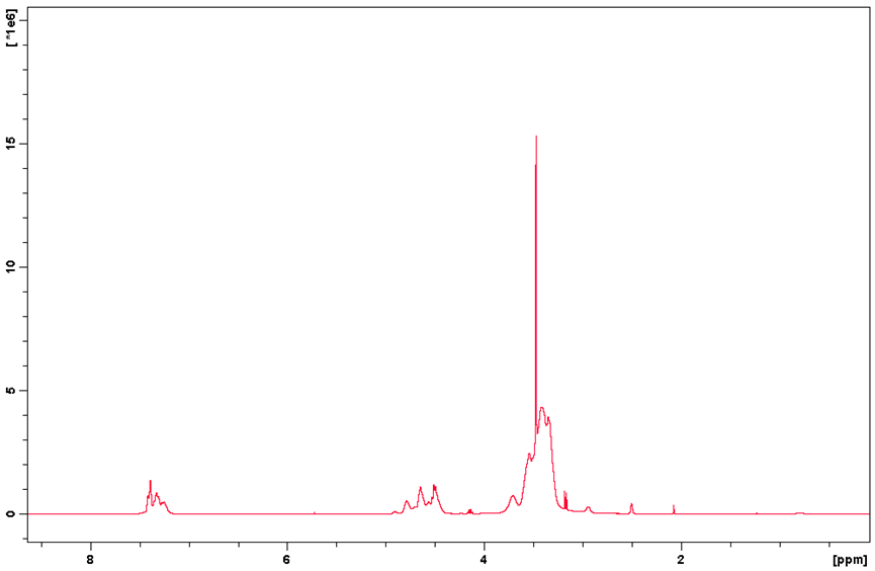

Figure S4: ^{1}H NMR spectrum for 3.7% PG10000.

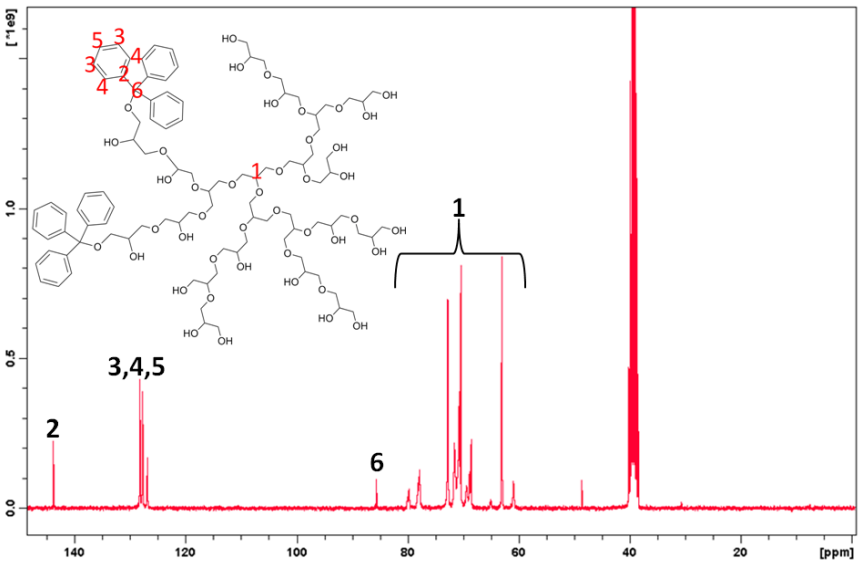

Figure S5: ^{13}C NMR spectrum of 3.7% PG10000.

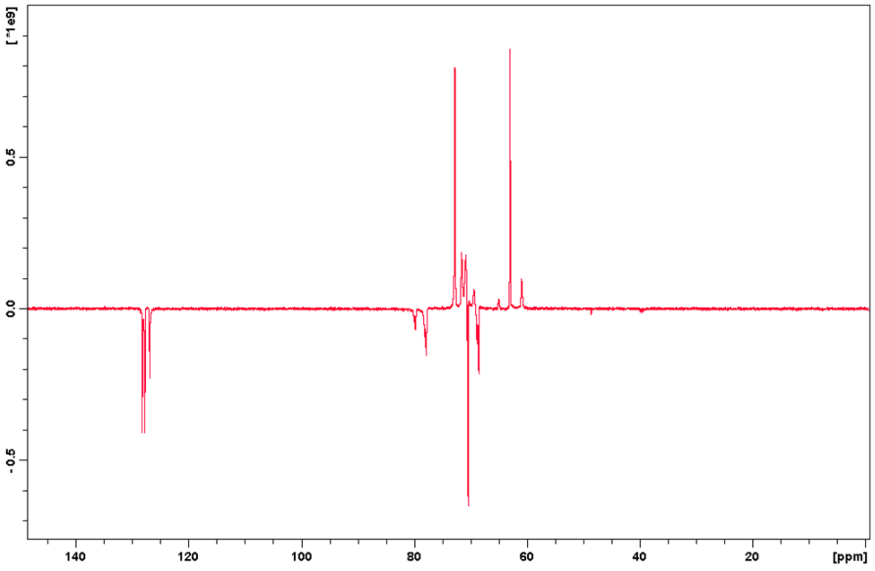

Figure S6: ^{13}C DEPT-135 NMR spectrum for 3.7% PG10000.

Surfactant(trityl)-CNT Interaction

The aromatic part of the ^{1}H NMR spectrum of an aqueous surfactant solution (3 mg 2.7% PG10000 in 1 mL of D_2O, referenced to the water peak) (Figure S7A) and of this solution

after addition of pristine MWCNTs and ultrasonication (Figure S7B), both with chemical shifts referenced to the water peak. As shown in this figure, the signals assigned to the aromatic trityl groups (6.63-7.59 ppm) in the aqueous solution shift downfield after addition of nanotubes and ultrasonication (6.79-7.67 ppm), similar to what was found by Chen et al.[1] This confirms (the suggested π-π stacking) interactions between the trityl groups and the carbon nanotubes.

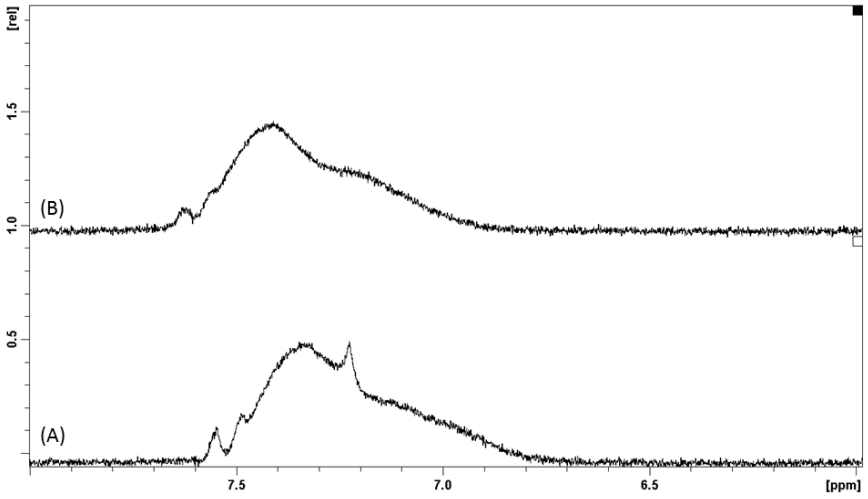

Figure S7: Aromatic part of the ^{1}H NMR spectrum of a 2.7% PG10000/MWCNT aqueous solution before (A) and after addition of MWCNT and ultrasonication (B).

(Intramolecular)Trityl Group Interactions

The aromatic region of the ^{1}H NMR spectrum of PG5000 surfactants with a different degree of functionalization in DMSO-d_6, referenced to the DMSO peak (Figure S8). For the lowest degree of functionalization a more detailed fine structure can be seen. Higher degrees of functionalization cause a downfield shift, as well as the disappearance of the fine structure. This confirms trityl-group interactions, and supports the hypothesis of intramolecular interactions between trityl groups at higher degrees of functionalization. It must be kept in mind that Figure S8 concerns DMSO as a solvent,rather than water. However, as DMSO is a better solvent for the trityl (functionalized) molecules compared to water, mutual trityl interactions probably will even increase when using water. The same phenomena can be

seen for the PG2000 (Figure S9) and PG10000 (Figure S10) series.

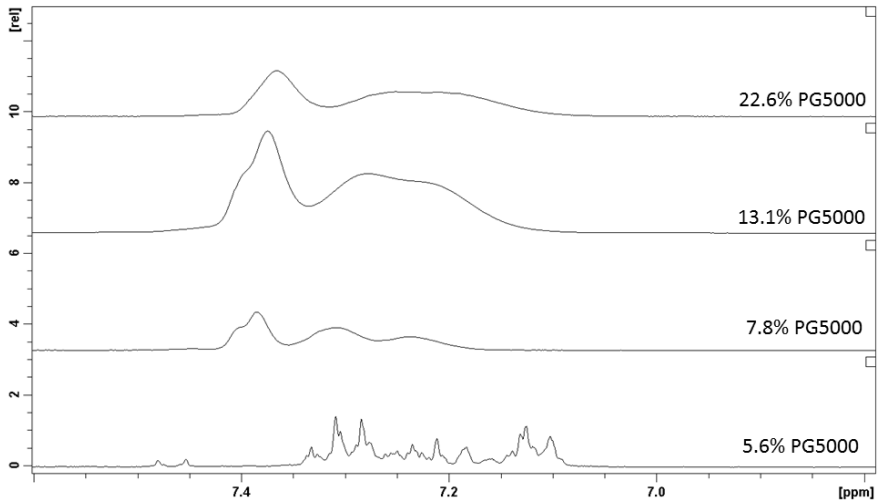

Figure S8: Aromatic part of the ^{1}H NMR spectrum of the PG5000 series dissolved in DMSO-d_6.

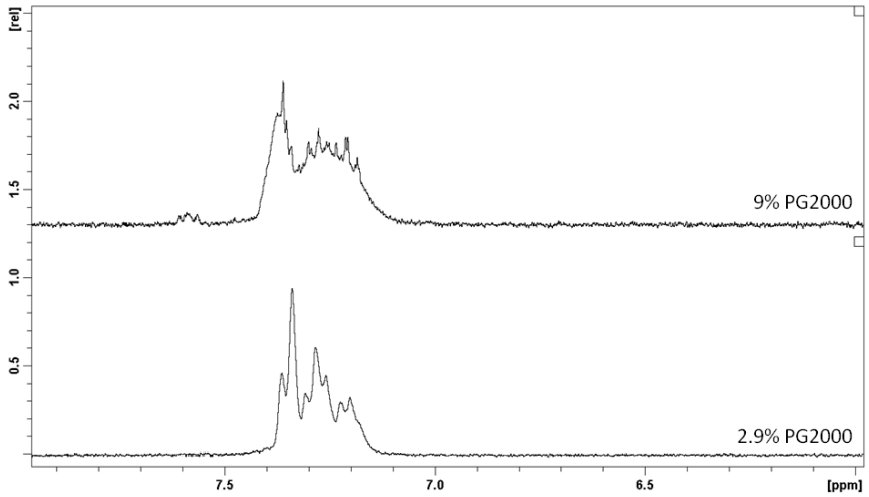

Figure S9: Aromatic part of the ^{1}H NMR spectrum of the PG2000 series dissolved in DMSO-d_6.

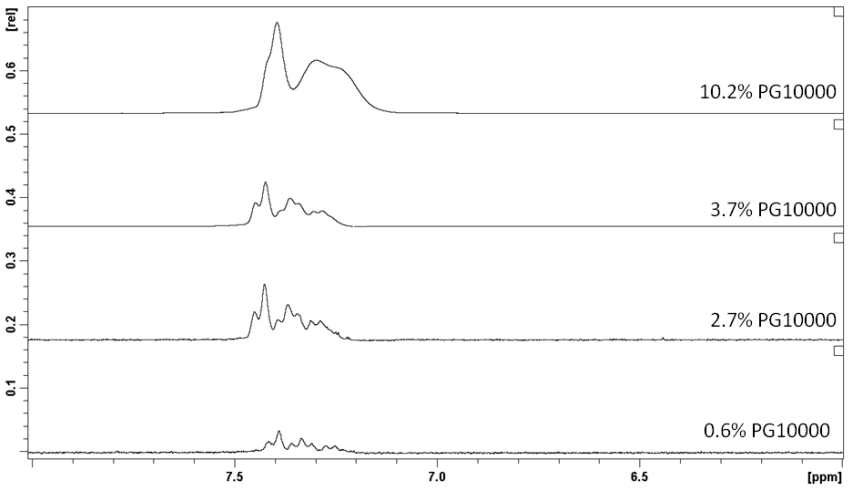

Figure S10: Aromatic part of the ^{1}H NMR spectrum of the PG10000 series dissolved in DMSO-d_6.

UV-vis spectra

UV-vis spectrum of a 20 mL aqueous surfactant (2.9% PG2000) solution in the absence of carbon nanotubes (Figure S11A) and UV-Vis spectrum of this solution after addition of nanotubes and different ultrasonication times (Figure S11). Especially in the region in between 200 nm and 280 nm a relatively strong (surfactant) absorption can be seen.

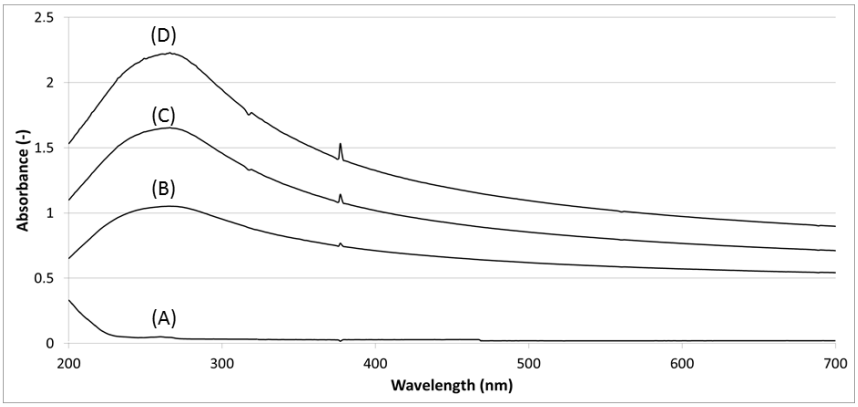

Figure S11: UV-vis spectrum of an aqueous solution containing 2.5 mg of 2.9% PG2000 (A). UV-Vis spectrum of an aqueous solution containing 5 mg MWCNT and 2.5 mg of 2.9% PG2000 after 20 min (B), 40 min (C) and 60 min (D) of ultrasonication.

References

(1) Chen, S.; Jiang, Y.; Wang, Z.; Zhang, X.; Dai, L.; Smet, M. Light-controlled single-walled carbon nanotube dispersions in aqueous solution. *Langmuir* **2008**, *24*, 9233–9236.