

Supporting Information

# Controlled Reversible Debundling of Single-Walled Carbon Nanotubes by Photo-Switchable Dendritic Surfactants

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## Experimental Section

All commercial chemicals were used as received without further purification. The synthesis of the compound G3azoC11 has been previously reported.<sup>1</sup> NMR spectra were measured by a Bruker AC 500. Mass spectra were recorded by a MAT 711 from Varian MAT. The electron energy was set to 80 eV. Single-walled carbon nanotubes were prepared by the HiPCO method and were produced by Unidym (lot no. SP0295) and all belong to the same production batch. The tubes have a diameter of 0.8–1.2 nm and a length of 100-1000 nm. A Bandelin SonoPlus HD 2070 sonicator with a maximum power of 200W was used. The samples were centrifuged using a Hettig Mikro 220R centrifuge with a 1195-A rotor. PLE measurements were taken using a Fluorlog-3 Spectrofluorometer by Horiba Jobin Yvon. The excitation was provided by a xenon lamp with an emission range of 240 nm-1000 nm and the signals were recorded using a nitrogen cooled InGaAs detector with a range of 800 nm-1600 nm. UV/Vis absorption spectra were taken by a S-3100 spectrometer from Scinco. Switching experiments were done with a 100 W mercury arc lamp from LOT Oriel with filters for 350 nm and 450 nm.

## Sample Preparation

The samples were prepared in aqueous solution using an initial nanotube concentration of 0.01 g/L and an amphiphile concentration of  $10^{-4}$  mol/L. After one hour of tip sonication with a power of 60W, they were centrifuged at 31000 g and 27 °C for 60 minutes. The supernatant was used for the experiments.

## Synthesis of G2azoG2

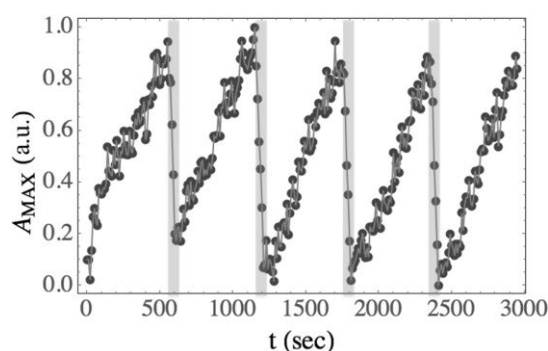
A mixture of 4,4'-dihydroxyazobenzene (22 mg, 0.10 mmol), [G2]PG-OMs (240 mg, 0.305 mmol), and cesium carbonate (102 mg, 0.306 mmol) in 3 mL of dry dimethylformamide was heated to 120 °C for 4 hours. Upon cooling, the reaction mixture was diluted with ethyl acetate (100 mL), washed twice with brine, once with water, once again with brine, then dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed *in vacuo* and the obtained residue was dissolved in methanol (20 mL). To this solution was added 0.1 mL of trifluoroacetic acid and 1 mL of water and the mixture was heated to

reflux for 3 hours. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on a CombiFlash RF automatic chromatography machine (Teledyne Isco, Lincoln, NE, USA). Purification was accomplished by elution through a RediSep RF reverse phase RP-18 column using a solvent gradient from 100% water to 70% methanol/water to afford G2AzoG2 as an orange oil (47 mg, 37%):  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  = 7.85 (d, 4H,  $J$  = 8.8 Hz), 7.15 (d, 4H,  $J$  = 8.8 Hz), 4.69-4.76 (m, 2H), 3.41-3.96 (m, 68H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  = 162.0, 148.5, 125.4, 117.4, 80.23, 80.20, 79.86, 74.02, 73.97, 72.98, 72.93, 72.90, 72.59, 72.55, 72.51, 72.47, 72.42, 72.37, 72.35, 72.25, 72.23, 72.20, 71.86, 70.6, 64.51, 64.46, 49.9. HR-MS calcd.  $[\text{C}_{54}\text{H}_{94}\text{N}_2\text{O}_{30}+\text{Na}]^+$ : 1273.5784. Found: 1273.5759.

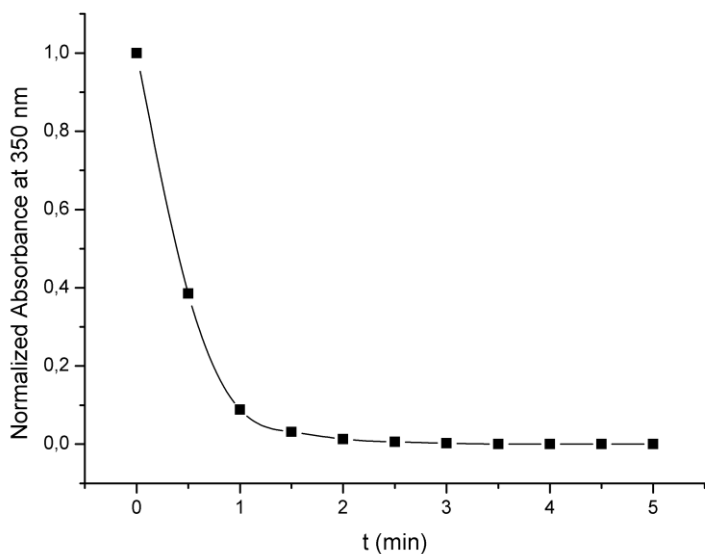
### Two-cuvettes experiment

The sample cuvette was filled with a pure G3azoC11 solution. Another cuvette with a SDS/CNT suspension was put in the light beam of 366 nm. The absorbance of the pure G3azoC11 solution at 360 nm was measured for 5 minutes irradiation time. In comparison to the G3azoC11/CNT suspension the pure surfactant solution was able to switch much faster.

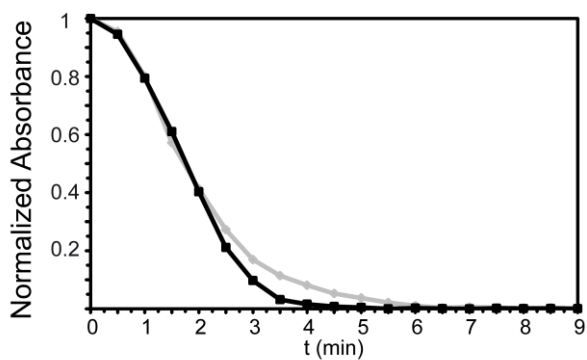
### Further investigation of the switching dynamics



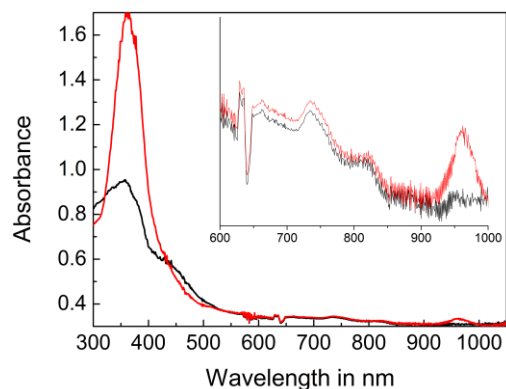
**Figure S1.** The G3azoC11/CNT suspension was irradiated with 366 nm followed by a dark cycle where thermal back-switching occurred. This was repeated 5 times.



**Figure S2.** Normalized absorbance of a pure G3azoC11 solution with a CNT suspension in the way of the light beam.



**Figure S3.** Change of the absorbance at the maximum in the 350 nm region. The black curve shows the SDS/G2azoG2 (structure shown) solution and the grey curve the SDS/CNT dispersion with G2azoG2.



**Figure S4.** Absorption spectrum of SWCNT solution showing the light-induced switching of the dendritic amphiphile from cis (black curve) to trans (red curve). The inset shows the absorption features of the tubes from switching from cis (black) to trans (red).

### **Inhibition of the photoisomerization**

Another conceivable explanation for slow switching is the deactivation of the excited azobenzenes by long-range energy transfer to the SWCNTs. To exclude this possibility we took an azobenzene substituted with two [G2] glycerol dendrons on each side, G2azoG2. The bulky glycerol group and lack of amphiphilicity should prevent a strong interaction with the nanotube surface and therefore minimize surface effects. Dispersion experiments with this compound gave no SWCNT fluorescence, indicating that G2azoG2 was not able to debundle CNTs like G3azoC11. To examine the photoisomerization in the presence of tubes, the G2azoG2 was added to a SDS dispersion of CNTs and the isomerization was triggered. The normalized intensity of the  $\pi - \pi^*$  absorbance in the region of 360 nm is plotted for G2azoG2 solutions with SDS in the presence or absence of added CNTs (Figure S3). In comparison to G3azoC11, where the switching rate is far slower, the difference can be neglected. Thus, a reduction of switching rate by long-range energy transfer from the excited azobenzenes to the SWCNTs can be ruled out.

To exclude the possibility that the inhibition of the switching process is a result of the absorption of the incident light by the SWCNTs, a two-cuvette experiment was done. A pure aqueous solution of G3azoC11 was placed into the spectrometer and a second cuvette containing a SDS/CNT suspension was put in front of the incident light beam. In this arrangement the light intensity is

reduced due to the absorption of the SWCNTs. The resulting change in absorbance (Figure S2) showed the same characteristics like the pure G3azoC11 without the nanotubes in between. The switch was not inhibited by the light absorption of the tubes.

References:

- 1 C. Kördel, C. S. Popeney and R. Haag, *ChemComm*, 2011, **DOI:** 10.1039/C1CC11673H.