

Amphiphile replacement on carbon nanotube surfaces: Effect of aromatic groups on the interaction strength

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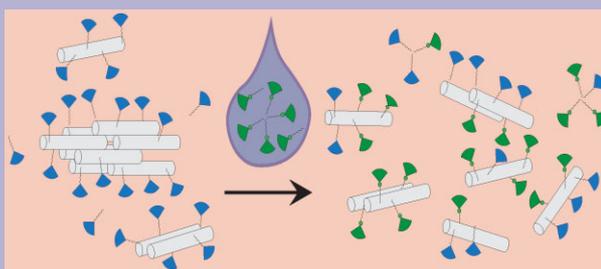
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Carbon nanotubes (CNTs) were solubilized using alkyl/polyglycerol amphiphiles. Similar cosurfactants, bearing different aromatic moieties between head and tail, were added to these samples. The interaction strength between these amphiphiles and CNTs changes depending on the inserted aromatic moieties. The insertion of a phenyl ring allows the amphiphile to replace the starting one indicating a higher interaction strength, while the insertion of a triazol pentagon does not, suggesting that the interaction strength is lower. The replacement was monitored via PLE mapping.



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1 Introduction The optical and electronic properties of carbon nanotubes (CNTs) highly depend on the tubes' chirality. A tube's unit cell (and thus Brillouin zone) denoted by its (n, m) value determines its electronic, dynamic, and optical properties. Among these are the tube's electron and phonon band structure and therefore, whether the tube is semiconducting or metallic, as well as its optical transitions, the surface curvature and thus pyramidalization and chemical reactivity [1, 2].

Since CNTs are quasi one dimensional, their electronic density of states consist of a series of sharp peaks (van-Hove singularities) arranged symmetrically around the Fermi level. Transitions between states of equal distance to the Fermi level ($E_{xx}, x = 1, 2, \dots, n$) are strongly enhanced. Thus, photoluminescence excitation (PLE) maps of a typical CNT sample consist of a series of distinct spots. The spectral location of these spots depends unequivocally on the distance of the van Hove singularities and thus the tube chirality. Therefore, the presence of a certain tube chirality in a sample can be confirmed via PLE mapping [3, 4].

As a consequence of their production process, however, a CNT sample consists of many different chiralities. As CNTs have a very rich π -network, they tend to form bundles subsequently quenching their luminescence due to the presence of metallic tubes within the bundles. To build devices from CNTs or investigate them, it is often necessary to break up these bundles, suspend the tubes and prevent them from rebundling.

Amphiphilic surfactants have been exploited intensively to serve this purpose [1, 4]. Aromatic groups such as pyrene [9], porphyrin [10], and other aromatic moieties [5] as well as alkyl chains [1, 7, 8] have been exploited to attach on to the nanotube surface and prevent rebundling of the tubes. Specialized amphiphiles are used to enrich CNT samples exploiting the fact that interaction between tubes and amphiphiles depends on the electronic properties of the amphiphile, as well as the tubes chirality and diameter [11, 12]. However, many details of these interactions have not yet been understood.

The change of the amphiphiles' aromaticity has been shown to drastically alter the composition of a nanotube

sample [7, 8]. However, the interaction between nanotubes and adsorbed amphiphiles alter the tubes' optical and electronic properties. This alteration is easily visible in the PLE maps as a shift of the peaks and gives a measure of the interaction strength. While weakly interacting surfactants may be able to attach to nanotubes bundles and bring them in solution, amphiphiles interacting more strongly are able to replace the weakly interacting ones.

Here we study the effect of the interaction strength on the surfactant replacement on CNTs.

2 Experimental setup and sample preparation

2.1 Compounds Figure 1 depicts the amphiphiles used in this work [6]. Similar to established surfactants like sodium dodecyl sulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS) [1, 3, 4], the amphiphiles consist of an alkyl chain to adsorb onto the CNT surface. Attached to the chain are polyglycerol (PG) dendrons to ensure efficient water solubility.

As the interaction between CNTs and aromatic moieties varies for different tube chiralities, we used three molecule designs, with different parts connecting the alkyl chain and PG dendron. In an earlier work, we found that an aromatic linker group can influence the intensity of the interaction of the surfactants with some laola families of nanotubes ($q = 2n + m = \text{fixed}$) drastically [7]. While compound C_1 has the head and tail directly connected, in C_2 a triazole pentagon is used as a linker. In C_3 , a phenyl ring is used (see Fig. 1).

2.2 Sample preparation The samples were prepared in aqueous solution using an initial nanotube concentration of 0.01 g/L and amphiphile (C_1 – C_3) concentration of $(1.1 \pm 0.1)10^{-4}$ mol/L. After 1 h of tip sonication with a power of 60 W, they were centrifuged at $22\,000 \times g$ and 15°C for 30 min. The supernatant was used for the experiments.

To investigate the relative interaction strength, we prepared a sample using C_1 and added C_2 and C_3 , respectively. From Table 1 we expect the interaction of C_2 with CNTs to be weaker, the interaction of C_3 to be stronger

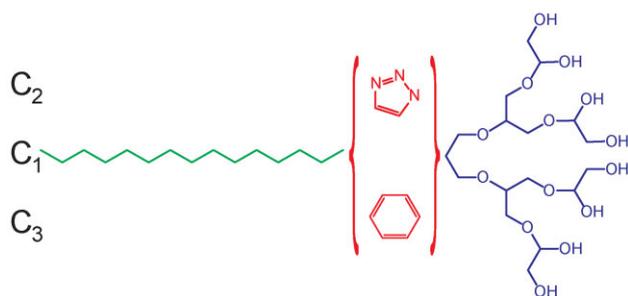


Figure 1 (online color at: www.pss-b.com) Schematic representation of the three amphiphiles used in this article (for the exact structures see Ref. [7]). While C_1 only consists of an alkyl chain and PG dendrons, C_2 and C_3 have aromatic moieties (a triazole pentagon and a phenyl ring, respectively), inserted between these two parts.

Table 1 Solvatochromic shifts of SWNTs calculated for C_1 – C_3 [7].

compound	E_{11} slope ((eV) $^{-3}$ (nm) 4)	E_{22} slope ((eV) $^{-3}$ (nm) 4)
C_1	0.065 ± 0.005	0.25 ± 0.03
C_2	0.060 ± 0.003	0.25 ± 0.03
C_3	0.071 ± 0.003	0.26 ± 0.04

than for C_1 . Thus C_3 addition is supposed to lead to surfactant replacement and maybe even further debundling, significantly affecting the PLE signal. C_2 addition, however, is not expected to alter the PLE signal.

We used a *Bandelin SonoPuls HD 2070* with a maximum power of 200 W. The samples were centrifuged using a *Hettig Mikro 220R* centrifuge with a *1195-A rotor*.

For these experiments we used HiPCO CNTs from *Unidym* (lot no. SP0295) and all belonging to the same production batch. The tubes have a diameter of (0.9 ± 0.3) nm and a high aspect ratio.

3 Measurements PLE measurements were taken using a Fluorlog-3 Spectrofluometer by Horiba Jobin Yvon. The excitation was provided by a Xenon lamp with a range of 240–1000 nm, the signals were recorded using a nitrogen cooled InGaAs detector with a range of 800–1600 nm.

The spectral position of the tubes' characteristic PLE signal highly depends on environmental effects like the surfactant used in nanotube suspension [13, 14]. The peak intensity, however, is related to the amount of individual tubes of a certain chirality in the sample, bundles hardly contributing as luminescence is quenched by metallic tubes. We monitored the change in relative PLE intensities when increasing the cosurfactant concentration as indicator of efficient replacement of one surfactant by the other.

4 Results and discussion From the solvatochromic shifts in Table 1 we expect the interaction strength between amphiphiles and nanotubes to differ for C_1 – C_3 . We expect the weakest interaction for C_2 , while C_3 will probably exhibit the strongest interaction.

Furthermore, the sample composition for CNTs dispersed in aqueous solution using C_{1-3} varies. When using the amphiphile without aromatic linker (C_1), the dominant species in PLE map is the (8,4) tube. In samples prepared using the amphiphiles bearing an aromatic group in between alkyl chain and anchor, the (7,5) tube is the dominant one.

We can use this to test the hypothesis that the interaction strength will be strongest between tubes and the C_3 amphiphile and weakest between tubes and C_2 . Starting from presolubilized nanotubes using the intermediate C_1 compound, C_2 and C_3 , respectively, are added to the sample. As C_2 interacts weaker than C_1 it is not expected to replace C_1 on the nanotube sidewall and, thus, to produce any differences in the PLE maps. C_3 , however, interacting

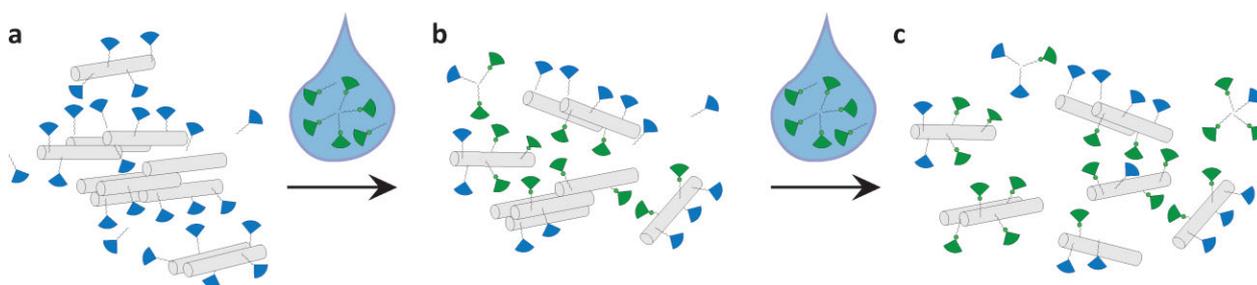


Figure 2 (online color at: www.pss-b.com) A schematic of CNTs solubilized with C_1 (blue) is shown in (a). The sample consists of single tube as well as small bundles. After addition of C_3 surfactant (green), C_1 molecules are replaced on the tube surface and even more bundles are broken up (b). Further addition even splits more bundles (c).

stronger than C_1 , will be able to adsorb onto the CNTs either replacing C_1 molecules or maybe even expanding the surface by promoting further debundling (Fig. 2). Thus C_3 addition is expected to lead to changes in the PLE intensity as well as the peak positions.

Indeed, the addition of C_3 to the samples can be monitored in the PLE maps, while this is not the case for C_2 . Figure 3 shows a fraction of the PLE maps after the addition of C_2 and C_3 , respectively. In the C_3 sample the (7,5)

signal is enhanced drastically, as in a sample of nanotubes dispersed using only C_3 as a surfactant. The C_2 sample, however, does not exhibit an equal behavior. Furthermore, Fig. 3 shows the peak positions of the (7,5) and (7,6) tube. As with the intensities, the positions hardly change after the addition of C_2 , but are strongly affected by the addition of C_3 (see Table 2).

The quantitative change in the PLE intensity is shown in Fig. 4. A direct comparison of the measured intensities confirms that adding C_3 induces drastic changes to the PLE intensity (gray circles). A C_3 concentration 5 $\mu\text{mol/L}$ almost

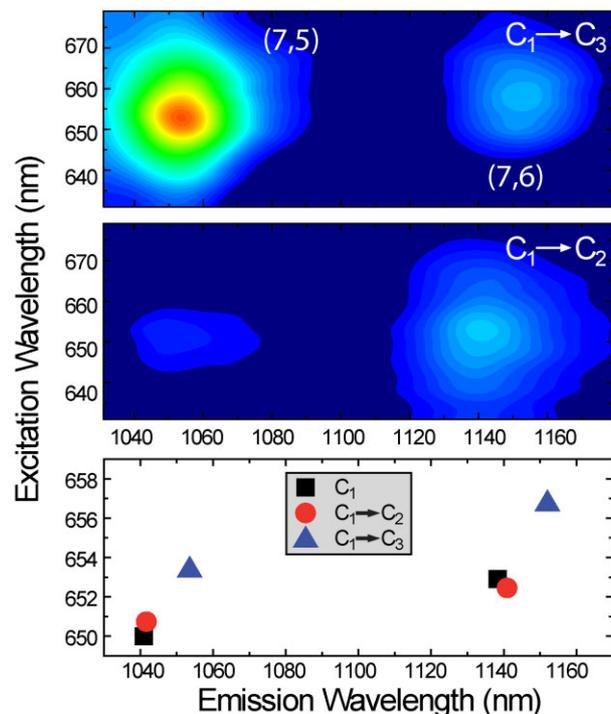


Figure 3 (online color at: www.pss-b.com) Fraction of the PLE maps after addition of C_2 and C_3 , respectively. The image shows the PLE peaks of the (7,5) and (7,6) tube. After addition of C_3 the (7,5) peak is much stronger than the (7,6) peak. Addition of C_2 , however, does not enhance the (7,5) tubes' signal. The lower image shows the peak positions for the C_1 sample without any cosurfactant and after C_2 and C_3 addition, respectively. While the addition of C_2 only induces mild changes, the addition of C_3 moves the peak positions considerably. The maps are normalized to the (7,6) peak intensity.

Table 2 Peak shifts from the PLE maps in Fig. 3.

tube		C_2 (meV)	C_3 (meV)
(7,6)	excitation	1.307 ± 0.003	-11.07 ± 0.03
	emission	-2.513 ± 0.004	-12.95 ± 0.02
(7,5)	excitation	-2.140 ± 0.005	-9.79 ± 0.03
	emission	-0.789 ± 0.002	-14.22 ± 0.02

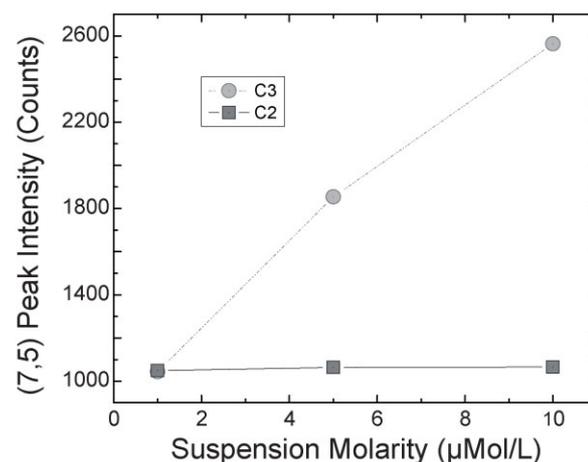


Figure 4 PLE Intensity of the (7,5) tube after the addition of C_2 and C_3 , respectively. It is evident that the addition of C_3 drastically enhances the PLE signal, while the addition of C_2 does not affect the PLE intensity.

doubles the signal. This effect is even enhanced when the concentration is heightened to 10 $\mu\text{mol/L}$. The addition of C_2 on the other hand does not induce an intensity change (dark gray squares).

5 Conclusion We have attempted to replace an alkyl-/PG surfactant (C_1) adsorbed onto CNTs by two cosurfactants (C_2 and C_3). Both cosurfactants were very similar to C_1 , bearing additional aromatic moieties inbetween the alkyl head and the PG tail group. The solvatochromic shifts predict a successful replacement in the case of a phenyl linker inbetween head and tail (C_3), but not for the case of a triazol pentagon (C_2). In our experiments this was confirmed by monitoring the replacement using PLE mapping. While the addition of C_2 hardly induced changes in the peak positions and intensities, C_3 addition altered both considerably.

We have shown that the addition of cosurfactants can be used to alter the composition of a CNT sample. Thus, by selecting the proper surfactants it is possible to gain a certain degree of control over the chiral distribution inside a sample.

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