

Polyglycerol-derived amphiphiles for single walled carbon nanotube suspension

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ABSTRACT

Inspired by the commercially available SDS surfactant, a new polyglycerol-derived amphiphile has been synthesized for functionalizing carbon nanotubes. SDS' sulphate group was replaced by a polyglycerol dendron. The steric hindrance offered by the dendrons makes the compound much more efficient than SDS in isolating and stabilizing nanotubes in solution. Further amphiphiles have been synthesized by adding small aromatic moieties between head and tail groups. We show that this addition leads to selective interaction between surfactants and carbon nanotubes. Excitation photoluminescence and optical absorption spectroscopy analysis confirm the change in the distribution of nanotubes' chiralities in suspension, depending on the amphiphile.

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1. Introduction

Since their discovery [1], Carbon nanotubes (CNTs) have captured strong attention because of their remarkable mechanical, electrical, and optical properties [2]. Single walled CNTs (SWNTs) are made from a graphene sheet rolled up and cut along a vector $\vec{c} = (n_1, n_2)$ that defines their chirality. SWNTs' astonishing feature is that, although they all stem from the same material, their chirality strongly affects their electronic character. Depending on n_1 and n_2 CNTs are either semiconducting or metallic [2]. Thanks to their unprecedented versatility, CNTs can be considered as a huge set of different materials, each with its own electronic properties, each offering its own performances exploitable at will.

The major technological issues preventing CNTs from the extensive exploitation they deserve are consequences of their production process. The growth techniques of CNTs result in the presence of multiple chiralities within one batch sample. Another problem is related to the presence of their extended conjugated π orbitals, which makes CNTs strongly interact with each other, and causes the formation of large strongly aggregated bundles.

In order to make practical applications of CNTs possible, it is mandatory to isolate and separate them. Typically, the isolation of SWNTs is carried out in solution and requires the use of amphiphilic surfactant molecules. The hydrophobic regions usually consist of aromatic moieties, such as pyrene [3] or one or few hydrocarbon chains [3,4], and the hydrophilic part is necessary for ensuring solubility and avoiding re-bundling of the nanotubes. There are cationic, anionic, non-ionic, and zwitterionic surfactants depending upon the nature of the hydrophilic head groups.

Over the last few years various methods have been developed to sort and separate SWNTs according to their chirality. Such techniques range from density gradient differentiation [5] to functionalization of SWNTs through molecules that enrich some nanotube families in solution according to their electronic nature, their diameter or chirality. [6–8] The latter enrichment schemes are based on the fact that there is a selectivity in the interaction of some aromatic moieties and the nanotube sidewall, as recently experimentally confirmed [9,10].

Sodium dodecylsulfate (SDS) is a well-known anionic surfactant and is one of the most extensively exploited ones for dispersing and isolating carbon nanotubes in solution [4]. The structure of this amphiphile (shown in Fig. 1a) is very simple: it consists of a tail made by an alkyl chain that interacts with the CNTs sidewall and of a head made of a sulfate group that ensures the stability of the CNTs suspension in water. The mechanism ensuring stability in dispersing and preventing CNTs from re-bundling is the Coulombic repulsion between the sulfate groups. However, SDS requires a high coverage of CNT sidewalls to be effective (typical value of SDS dispersed in water is 1% wt./vol. [11]).

In this Letter we propose, as an alternative surfactant, a compound made by attaching to the alkyl chain a polyglycerol (PG) dendron [12] (see Fig. 1c). The substitution of the sulfate group with PG makes the surfactant non-ionic. The mechanism ensuring debundling and water solubility in this case is the steric hindrance caused by the PG dendron. It will be shown that this renders the compound effective at much lower concentrations than SDS. To stress the selectivity of the process of noncovalent interaction between adsorbing molecule and CNTs, we considered variations of the morphology of the amphiphile. As SWNTs do selectively interact with some aromatic moieties [9,10], we added small aromatic groups (a triazole pentagon and a phenyl ring, see Fig. 1d and e) between the hydrophilic head and the hydrophobic tail groups to

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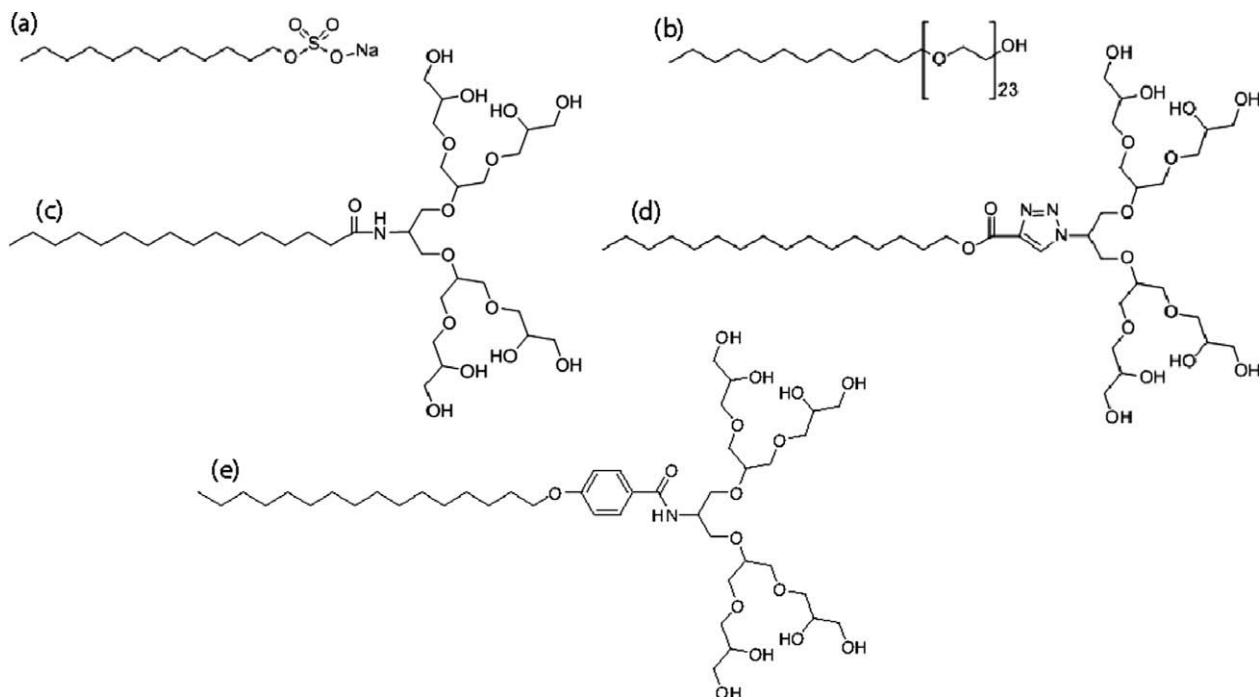


Fig. 1. Molecular structure of the commercially available SDS (a) and Brij 35 (b) surfactants. The compounds synthesized for this work are C_1 (c), C_2 (d), and C_3 (e).

induce specificity to the CNTs-surfactant interaction. We will show that the addition of the aromatic moieties causes striking changes in the population of the nanotube dispersions. This could open the way to the design of a new class of surfactants able to isolate and debundle nanotubes with the desired chirality.

2. Experimental setup and sample preparation

In Fig. 1 we show the molecular structures of the amphiphiles synthesized for this work. The experimental details of the compound synthesis are given in Supporting information file.

Compound C_1 (see Fig. 1c) is the analogue of SDS: attached to the alkyl chain there is a polyglycerol dendron (PG). Dendrons ensure efficient water solubility of the amphiphiles. An extensive treatment of PG synthesis and features can be found in Ref. [12].

As SWNTs do selectively interact with aromatic moieties, small variation of C_1 configuration have been considered in order to try and alter the chiralities of the CNTs present in the final suspensions. The moiety added in C_2 (see Fig. 1d) is a triazole pentagon while in C_3 (Fig. 1e) it is a phenyl ring¹.

In order to compare the efficiency of our amphiphiles in isolating and debundling CNTs, we chose to work at a fixed surfactant molarity and at a fixed NT concentration. For this reason, we prepared three $(1.1 \pm 0.1) \times 10^{-4}$ M water solutions containing, respectively, the surfactants C_1 , C_2 , and C_3 (whose molecular structure is shown in Fig. 1c–e). CoMoCAT nanotubes, produced by SouthWest NanoTechnologies and all belonging to the same production batch, were then dissolved in the solutions; the initial CNTs concentration was 0.01 g/L. The solutions were then tip-sonicated for an hour and finally centrifuged at 22000 g for 30 min at 15 °C.

The absorption spectra of the suspensions were taken with the UV/vis spectrophotometer Scinco S-3100 while the PLE maps were taken by the Horiba Nanolog system.

3. Measurement and discussion

3.1. Effect of the polyglycerol dendron

We first considered the two commercial surfactants, SDS (shown in Fig. 1a) and Brij 35 (Fig. 1b). SDS was introduced above; Brij 35 is a polymer-based surfactant, often used as a non-ionic alternative to SDS. The actual concentration of nanotubes in the final dispersion can be obtained from the absorption spectrum of the relative solution [4]. The initial solutions share the same surfactant molarity (1.1×10^{-4} M) and contain the same amount of nanotubes. This allows a direct comparison of the solubilizing and debundling ability of the compounds. The absorption spectra of the solutions containing SDS, Brij 35, and C_1 , shown in Fig. 2, exhibit the typical modulation due to the presence of NTs in suspension [6]. Moreover, compound C_1 ensures a higher concentration of nanotubes in solution and is thus far more efficient than SDS and Brij 35.

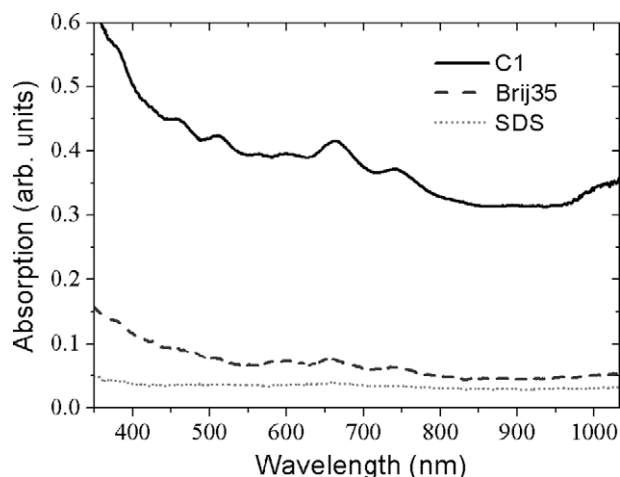


Fig. 2. Absorption spectra of SWNTs suspended with SDS (dotted line), Brij 35 (dashed line) and C_1 (continuous line).

¹ Please note that the tail part in compound C_1 is made of 15 carbon atoms while the ones in compounds C_2 and C_3 are made of 16 carbon atoms. The difference in the chain length does not significantly alter our results.

Table 1

Comparison of the absorbance values at selected wavelengths.

	462 nm	513 nm	600 nm	663 nm	745 nm
Absorbance (arb. units)					
C ₁	0.45	0.42	0.40	0.42	0.37
C ₂	0.36	0.33	0.30	0.31	0.27
C ₃	0.29	0.28	0.26	0.27	0.24
Brij 35	0.09	0.08	0.07	0.07	0.06
SDS	0.04	0.04	0.04	0.04	0.03

The substitution of the sulfate group with the polyglycerol dendron thus makes the surfactant efficient at this concentration. To make a more quantitative comparison between the different compounds, a comparison of the critical micellar concentration (CMC) of the surfactant has to be made. Details of the CMC determination are given in Supporting information file. It is worth pointing out that the CMC value of SDS is two orders of magnitude higher than the ones of our compounds.

3.2. Effect of the addition of the aromatic moieties

In Table 1 we report the absorbance values at selected wavelengths of the suspensions obtained through the compounds C₁, C₂ and C₃; we moreover added to Table 1 the absorbance values for SDS- and Brij 35-suspended CNTs solutions for comparison. All three compounds isolate and suspend nanotubes to varying degree of effectiveness. The absorbance values of the solution obtained with the compound C₁ are higher than those obtained with C₂ and C₃, meaning that C₁ is able to ensure higher concentration of SWNTs in solution. It is worth noting that this result does not imply that C₁ is better than C₂ and C₃, as C₁ is the non-specific surfactant and is thus expected to interact with a broader range of SWNT chiralities. C₂ and C₃ are expected to be more selective towards the adsorption of certain SWNT (*n*₁, *n*₂) chiralities because of the addition of the aromatic moieties.

To identify the nanotubes that are debundled in the final suspension, we measured PLE maps of the solutions [13]. Each of the peaks is uniquely due to one specific (*n*₁, *n*₂) nanotube type debundled and stable in solution. This technique is only sensitive to semiconducting nanotubes. To completely identify all the SWNTs present in solution, other experimental techniques should be exploited.

In Fig. 3a the PLE map of the C₁-stabilized SWNT suspension is shown. The peaks were labeled with the (*n*₁, *n*₂) indexes. Moreover, Fig. 3b–d show the different intensity distribution of the peaks in the PLE maps of SWNTs suspensions obtained with the C₁, C₂, and C₃ compounds. The distributions have been normalized to the intensity of the brightest peak.

A slight alteration in the surfactant morphology has profound influences on the nature of the final dispersion (Fig. 3), confirming that the addition of the aromatic moieties gives specificity to the SWNTs-surfactant interaction. The C₁, C₂, and C₃ compounds stabilize different (*n*₁, *n*₂) SWNT families.

3.3. Solvatochromic shifts

The functionalization influences the PLE maps in many ways. It not only redistributes the intensities of the different peaks, but it also shifts the position of the peaks. The shifts with respect to the air of the optical transition energies *E*₁₁ (energy of the emitted photons) and *E*₂₂ (energy of the absorbed photons) are influenced by the dielectric environment. Choi and Strano found [14] that the solvatochromic shifts can be written as:

$$E_{ii}^2 \Delta E_{ii} = \frac{c}{d^4}, \quad (1)$$

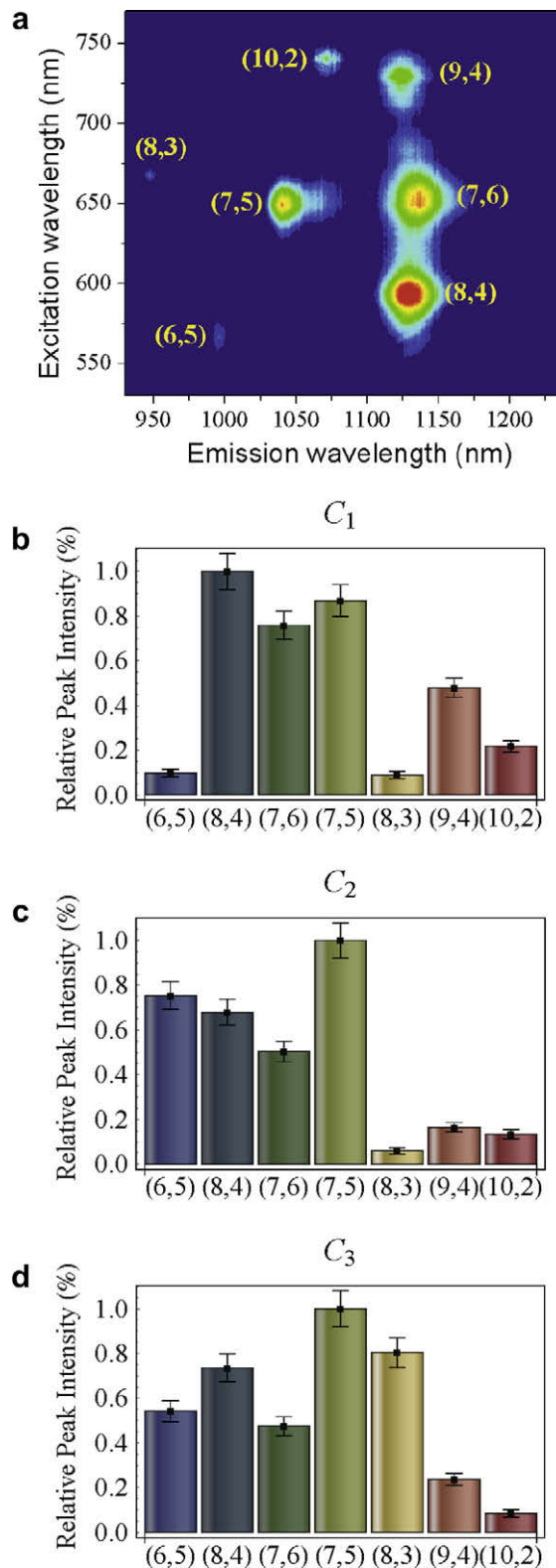


Fig. 3. PLE maps of C₁-stabilized SWNTs in water (a) and relative distribution of the peak intensities for the C₁ (b), C₂ (c) and C₃ (d) compounds.

where *d* is the SWNT diameter and *c* is a constant proportional to the dielectric constant ϵ and the refractive index η of the local environment:

$$c \propto \frac{2(\epsilon - 1)}{2\epsilon + 1} - \frac{2(\eta^2 - 1)}{2\eta + 1}. \quad (2)$$

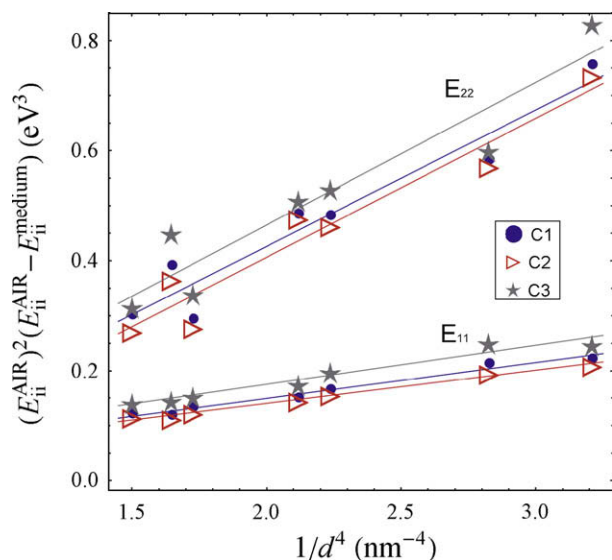


Fig. 4. Solvatochromic shifts calculated for SWNTs suspended in water by C_1 (blue circles), C_2 (red triangles), and C_3 (grey stars). (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

Table 2

Slopes of E_{11} and E_{22} versus d^4 obtained from the fit of the solvatochromic shifts (Fig. 4).

Compound	E_{11} slope ($\text{eV}^{-3} \text{nm}^4$)	E_{22} slope ($\text{eV}^{-3} \text{nm}^4$)
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
SDS ^a	0.050	0.19

^a SDS slopes values are obtained from literature [14].

In Fig. 4 we report the solvatochromic shifts obtained for the C_1 , C_2 , and C_3 compounds. The shifts follow the linear scaling behavior versus d^{-4} as predicted and observed by Choi and Strano [14].

The addition of the phenyl ring in compound C_3 and the triazole in compound C_2 produce opposite effects. The solvatochromic shifts move towards higher energies for compound C_3 while they move towards lower energies for compound C_2 . These competing effects require further analysis and investigation.

The slopes of the solvatochromic shifts shown in Fig. 4 are summarized in Table 2 and compared with the literature values for SDS. Assuming the refractive index to be approximately constant for the various solutions, the increase of the slope values of our compounds with respect to SDS suggests an increase of the dielec-

tric constant. The E_{11} slope of the compound C_2 is much smaller than the E_{22} one (21% against 34%), indicating that E_{11} is less affected by the surrounding medium. Further investigations to correlate the experimental results with the compound morphology will be performed.

4. Conclusion

In summary, we studied a non-ionic variation of SDS, a well-known commercially available ionic surfactant extensively exploited for SWNTs isolation and solubilization in water. The replacement of the SDS' sulfate group by the polyglycerol dendron makes the compound more efficient in isolating and debundling SWNTs, even at very low concentrations. The further addition of small aromatic moieties enhances the selectivity of the interaction between the compound and SWNT families, which suggests a new path towards the implementation of surfactants with morphologies designed *ad hoc* for isolating a desired target nanotube family. Further investigation on the effect of changes in the compound morphologies (e.g. addition of different aromatic moieties or effects of the chain length and so on) is planned for future work.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2010.05.052.

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