

Interaction between single-walled carbon nanotubes and alkyl-polyglycerol derivatives

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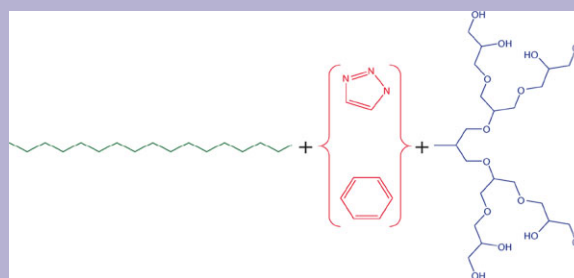
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We use three alkyl-polyglycerol derivatives to suspend single-walled carbon nanotubes. The molecules differ by the aromatic moieties between the alkyl tail and the polyglycerol head. The suspended nanotubes are analysed by photoluminescence spectroscopy. We observe a dependence of the luminescence intensity and hence nanotube abundance on the aromatic moieties. Interestingly, the strength of interaction depends on the nanotube families.



Molecular sketch of the studied surfactants.

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1 Introduction Among the various carbon allotropes, carbon nanotubes (CNTs) are incomparably versatile, since between one tube and another substantial changes in physical properties occur [1]; particularly interesting are single-walled carbon nanotubes (SWCNTs) as, depending upon their chirality $c = (n_1, n_2)$, they show either a metallic or a semiconducting character [1]. Even the value of the band-gap of the semiconducting tubes changes with n_1 and n_2 , making them a versatile candidate material for a wide range of applications. This big advantage doubles as a drawback, as the synthesis process provides, within the same batch, CNTs with different chiralities, which are strongly aggregated into big bundles. The isolation of a single variety of nanotubes with a specific chirality is thus of big technological relevance. Approaches to tackling this problem can be classed into two categories, depending on whether the selection of the single (n_1, n_2) chirality is performed during or after the de-bundling process that ends up with the dispersion of isolated tubes.

In the ‘after-isolation’ approach, SWNTs first pass through the de-bundling process; the surfactants exploited in

this scheme are commercially available surfactants – mostly sodium dodecyl sulphate (SDS) and sodium cholate (SC). Subsequently, the individual chiralities are separated in a second step, usually by density gradient ultracentrifugation (DGU) [2] or gel electrophoresis [3], exploiting, respectively, the distinct density or mobility of different nanotube species. This allows for example the selection of SWNTs according to their electronic nature [4, 5].

The second approach exploits the selectivity occurring in the interaction between aromatic moieties and SWNTs of certain chiralities. Alteration of the (n_1, n_2) distribution in suspensions has been achieved by synthesizing *ad hoc* surfactants [6, 7]. Naturally occurring molecules may be exploited for these purposes: for instance, using DNA fragments, Zheng and co-workers [8] have been able to select 12 different semiconducting SWNT single-chirality species.

In a recent work, we synthesized, in the framework of the second approach, a non-ionic surfactant capable of solubilizing SWNTs [9]; its morphology resembles the SDS one. By adding small aromatic moieties between the head and the tail group of such a surfactant, we were moreover

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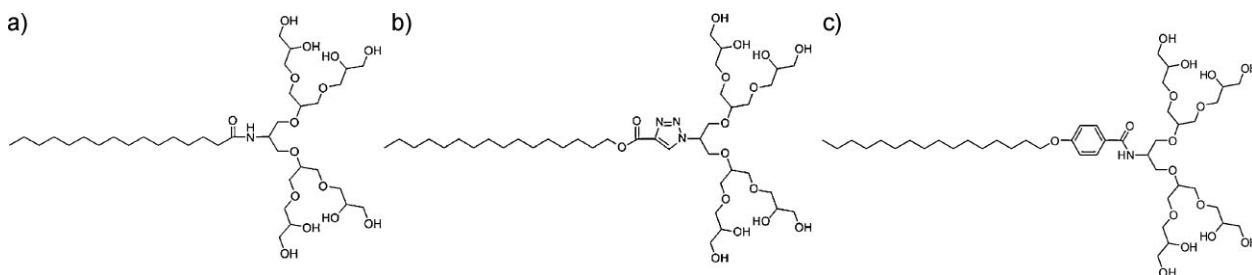


Figure 1 Molecular structure of the compound C_1 (a), C_2 (b) and C_3 (c).

able to modify the population of the dispersions, altering the chirality distribution within the obtained samples. Here we analyse the selectivity in the interaction between SWNTs and such new composites, showing the emergence of a clear-cut, systematic trend in the behaviour of each $2n_1 + n_2$ *laola* family.¹

2 Sample preparation and experimental setup In Fig. 1 we show the molecular scheme of the amphiphiles exploited for this work. For the experimental details of the amphiphile synthesis, please refer to Ref. [9] and its Supporting Information.

We prepared our mixture by working at both a fixed surfactant molarity and at a fixed NT density. For comparison with the results of Ref. [9], we prepared three $1.1 \pm 0.1 \times 10^{-4}$ M water solutions containing the surfactants C_1 , C_2 and C_3 , respectively (their molecular structure is shown, respectively, in Fig. 1a–c). CoMoCAT nanotubes SG76 – with tube diameter of 0.9 ± 0.3 nm and high aspect ratio (1000) – produced by SouthWest NanoTechnologies and all belonging to the same production batch, were then dissolved in the solutions; the initial NTs density was 0.01 g/L. The solutions were then tip-sonicated for 1 h and finally centrifuged at $22\,000 \times g$ for 30 min at 15 °C.

Excitation photoluminescence (PLE) maps were taken through the Horiba Nanolog system, whose excitation source is a Xe short arc lamp, emitting continuously from UV up to NIR. Selection of single excitation wavelengths is performed through a monochromating system equipped with two mechanically coupled gratings (1200 lines/mm). Emitted spectra were dispersed through a single grating monochromator (with the choice, for optimal selection of the appropriate resolution, between three gratings, namely 150, 600 and 1200 lines/mm) and then analysed through a liquid nitrogen-cooled InGaAs detector.

3 Measurements and discussion PLE is a very powerful technique that allows to optically investigate the interaction between the adsorbed molecules and nanotubes.

By analysing the emission features contained within our PLE charts, it is possible to recognize systematic shifts of

the positions of the PLE peaks. The spectral positions of the peaks of the nanotubes dispersed, respectively, with the C_1 , C_2 and C_3 surfactants are shown in Fig. 2. The addition of small aromatic moieties such as the triazole pentagon or the phenyl ring between the hydrophilic head group and the hydrophobic tail strongly influences the way the surfactant interacts with CNTs, even if it does not significantly alter in percentage the mass of the surfactant.

As is possible to see in Fig. 2, there is no rigid shift of the whole PLE map by passing from one surfactant to the other, suggesting each of the nanotubes interacts distinctly with each of the surfactants.

The adsorption of C_3 causes a red shift (whose amount changes from tube to tube) of the absorbed and emitted photon lines with respect to the ones observed for compound

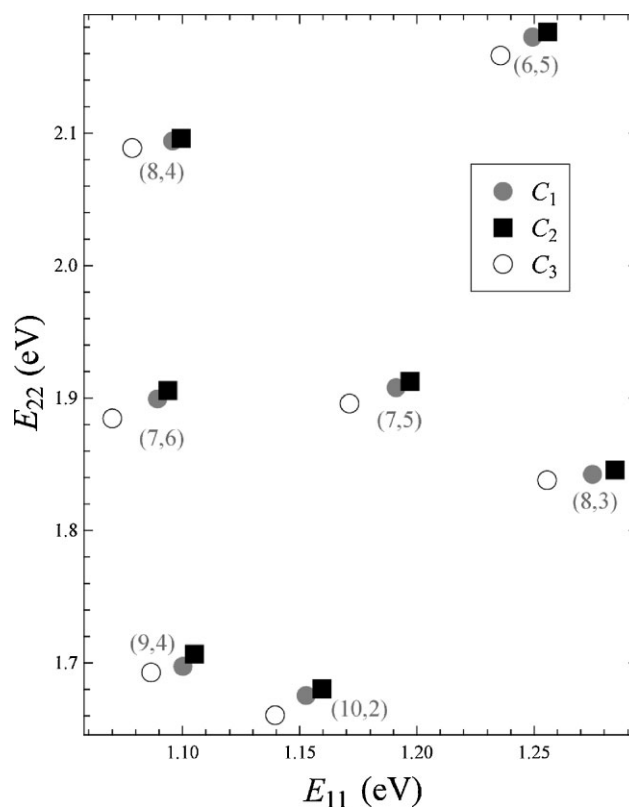


Figure 2 Spectral positions of the photons absorbed (E_{22}) and emitted (E_{11}) by the nanotubes suspended by C_1 , C_2 and C_3 .

¹ A *laola* family consists in a set of nanotubes possessing different (n_1, n_2) chiralities but the same $2n_1 + n_2$ value.

C_1 . On the contrary, C_2 -SWNTs complexes show blue-shifted peaks with respect to the C_1 ones.

Those observations, together with considerations on the long term stability of the suspensions (after 1 month the C_2 -suspension starts precipitating while the C_3 and C_1 ones remain stable over months) may suggest that the binding of compound C_2 on SWNT sidewalls is weaker than for compound C_1 and C_3 .

An important consideration that can be drawn out of the PLE charts pertains the global trend of both E_{11} and E_{22} shifts. The fact that those shifts are in the same direction suggests that the effect of the surfactants arises from dielectric screening of excitons [10] and not from a strain-induced band-shift, which would cause opposite shifts for E_{11} and E_{22} [11].

It is worth noting that no sideband features can be discerned within our charts, suggesting that a significant presence of big bundles can be ruled out in our samples [12] and that our observations can thus be mostly attributed to the effects of the different surfactant morphologies.

Another interesting effect coming out of the PLE chart analysis concerns the changes of the intensity distribution of the PLE peaks for the different surfactants (Fig. 3). The brightness of such peaks is related to the abundance of a certain (n_1, n_2) species in solution [13]; changes in brightness of these peaks thus imply changes of the composition of SWNT populations within the suspensions.

By comparing in Fig. 3a the intensities of the peaks in the C_1 -suspended SWNT sample with the one of the C_2 -suspended one (whose difference is the addition of the triazole pentagon) and by comparing in Fig. 3b the C_1 with the C_3 sample (whose difference is the addition of the phenyl ring), a systematic trend can be made out. As a matter of fact, the behaviour of SWNTs belonging to a $2n_1 + n_2$ laola family is the same for all family members. An increase in the intensity of the peaks for the $2n_1 + n_2 = 17$ and 19 families is observed, implying that the presence of the aromatic moieties in the C_2 and C_3 surfactants induces an accretion of the relative abundance of tubes belonging to these families, with respect to the C_1 -suspended population. For the $2n_1 + n_2 = 20$ and 22 families, on the contrary, a decrease in the intensity is observed, suggesting a lower occurrence of tubes belonging to these families in the C_2 and C_3 suspensions with respect to the C_1 suspension. It is worth noting that the most striking difference between the behaviour of the C_2 and the C_3 compound arises for the (8,3) nanotube, whose abundance strongly increases when suspended with compound C_3 (Fig. 3c).

Those results indicate that there is a relationship between the nanotube's morphology and the way it interacts with a different surfactant configuration. From this point of view, the C_1 , C_2 and C_3 compounds, whose morphological difference lies only in the addition of a small aromatic moiety between head and tail group, offer a good case-study context for isolating the effect of the selectivity of the surfactant-nanotube interaction and can thus lead the way to the engineering of smart

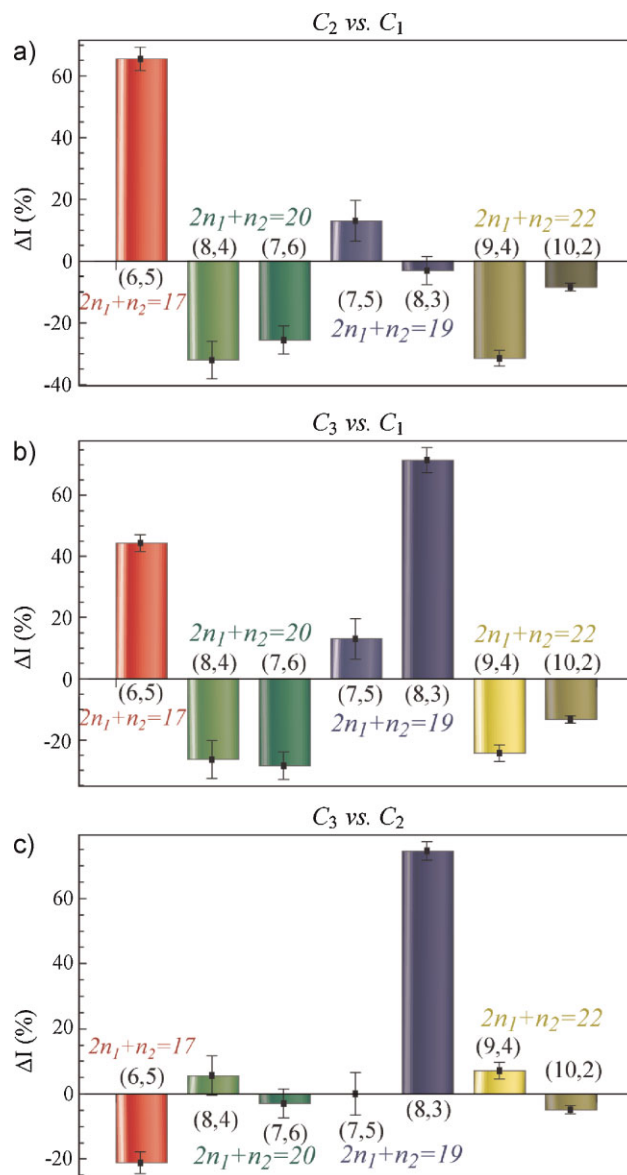


Figure 3 (online colour at: www.pss-b.com) Percentage change of the intensities of PLE peaks from the C_1 map to the C_2 one (a), from the C_1 to the C_3 (b) and from the C_3 to the C_2 (c).

surfactants able to selectively disperse a desired kind of SWNTs.

4 Conclusions We have considered the interaction between some polyglycerol-derived surfactants and single-walled CNTs. PLE acquisitions suggest that each (n_1, n_2) nanotube interacts differently with different surfactants. Hence it is possible, by varying the surfactant morphology, to alter the population of the suspension. This could herald the synthesis of a new class of surfactants able to selectively debundle and suspend desired kinds of SWNTs.

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