

Effective Solubilization of Single-Walled Carbon Nanotubes in THF Using PEGylated Corannulene Dispersant

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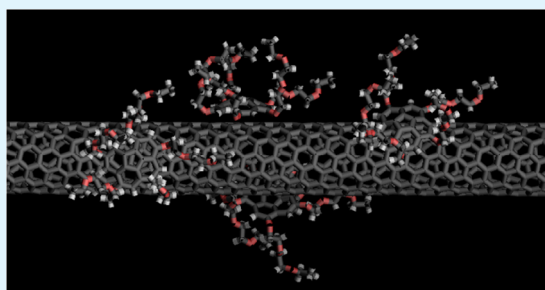
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S Supporting Information

ABSTRACT: PEG-derivatized corannulene compound has been found to be very effective in solubilizing single-walled carbon nanotubes in tetrahydrofuran. Solubilizing efficiency is close to the commonly used anionic surfactant, sodium dodecyl sulfate (SDS). Corannulene derivative has also been found to have a tendency to disperse metallic nanotubes more effectively than the SDS counterpart. Theoretical calculations predict higher dispersion interactions of corannulene backbone with the convex surface of nanotubes in comparison to those calculated with other commonly used polyaromatic hydrocarbon derivatives.

KEYWORDS: carbon nanotubes, corannulene, photoluminescence, Raman spectroscopy, density functional theory



Because of superior physical and chemical properties of single-walled carbon nanotubes (SWNTs),¹ they can be potentially used for high-performance electronics, sensors, and optoelectronic devices. SWNTs are 30–100 times stronger than steel at a sixth the weight.² In addition, SWNTs exhibit anisotropic thermal conductivity that can make them multifunctional materials.³ Specifically, they are promising materials for future thin-film transistors,⁴ field-effect transistors,⁵ organic photovoltaic devices,⁶ saturable absorbers,⁷ light detectors,⁸ and biosensors.⁹ However, the synthesis of carbon nanotubes leads to coexistence of various tubular configurations and this has been a severe setback for large-scale applications and fundamental studies.¹⁰ SWNTs also form bundles because of strong π - π interactions that inhibit their solubility in common organic solvents. In essence, SWNTs are graphene sheets wrapped into tubes which are commonly expressed as indices (n,m) for different chiralities. Most production methods for SWNTs yield a mixture of metallic ($|m - n| = 3k$, where k is an integer) and semiconducting nanotubes ($|m - n| = 3k \pm 1$) with the metallic component representing the minority fraction in the mixture at a ratio of 1:2. Thus, chirality of SWNT sample defines the electronic and optical properties of nanotubes. As a result, chirality specific SWNTs are needed if these promising materials are to be used in laboratory research or in technological applications.

There are several techniques utilized in separation of carbon nanotubes by chirality. Density gradient centrifugation,¹¹ dielectrophoresis,¹² and DNA wrapping followed by anion-exchange chromatography^{13,14} can be used to obtain highly enriched semiconducting SWNTs. Gel-based separation of semiconducting and metallic nanotubes,^{15,16} microfluidic separation¹⁷ as well as selective destruction of semiconducting

nanotubes¹⁸ have been shown as viable techniques in the literature. Polymer wrapping has also been shown to be effective in chirality-selective nanotube enrichment.¹⁹ Most of the dispersants, however, are difficult to remove after solubilization and therefore inhibits the use of such nanotubes in electronic applications where high purity is a prerequisite.

Selective dispersion SWNTs can be obtained via noncovalent interactions in the presence of polyaromatic hydrocarbons (PAHs),^{20,21} conjugated oligomers,²² or nanotweezers.²³ The solubilization of SWNTs has been achieved with planar aromatic molecules, such as derivatized free-base porphyrin and pyrene with long alkyl chains.^{24–26} The advantage of these dispersants lie in the possibility of removal after solubilization.²⁴ However, these molecules selectively disperse mostly semiconducting nanotubes without any chirality specific separation. Nonetheless, these studies also show the potential of SWNT separation by polyaromatic hydrocarbon derivatives.

Corannulene is a polycyclic aromatic hydrocarbon, consisting of cyclopentane ring fused with five benzene rings (Figure 1, top). It is of scientific interest because it has nonplanar polyarene structure and can be considered as a fragment of buckminsterfullerene.²⁷ Because of its slightly bowl shape, corannulene is also known as bucky bowl.²⁸ It is anticipated that this bowl structure along with the extended arene geometry will enable better dispersion of SWNTs because of improved adsorption interactions with the convex surface of nanotubes compared to fully planar pyrene or porphyrin derivatives.

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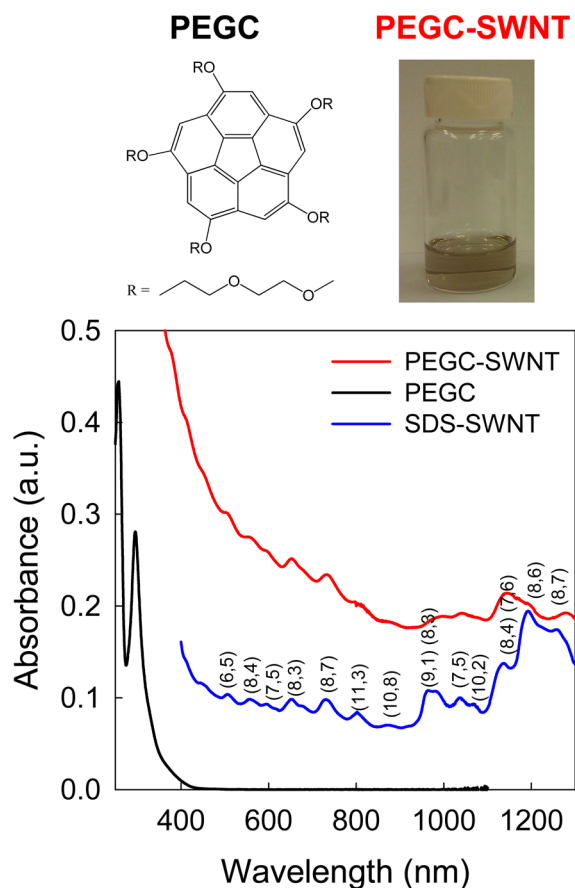


Figure 1. Optical absorption spectra of PEGC and PEGC-SWNT in THF. Optical absorption profile for SDS-SWNT sample in aqueous media is also given for comparison.

Because the solubilization technique does not rely on functionalization/covalent modification of SWNTs, it is expected that the electronic properties of nanotubes will be preserved and this is the driving factor as to why noncovalent modification is crucial to SWNT separation.

In this letter, we report the ability of polyethylene glycol (PEG) functionalized corannulene (PEGC) in solubilizing SWNTs (HiPco, Unidym, Inc., Lot#P2150). The synthesis of this dispersant has been reported elsewhere.²⁹ PEG groups facilitate solubility both in aqueous and organic media. SWNT dispersion with PEGC has been studied using a previously reported method.³⁰ In a typical experiment, a SWNT sample (1.6 mg) was added to a solution of PEGC in THF (75 mg/15 mL), and subjected to 15 min of ultrasonication using an Omni Raptor 450 Homogenizer (tip sonication, 20% power), followed by bath sonication for 3 h. The resulting solution was centrifuged for 45 min at 3000 rpm (Beckman SW40Ti Swing bucket). The supernatant was carefully transferred to another vial, producing dark colored and stable nanotube-dispersant complex solution. The isolated supernatant was filtered through a 200 nm pore diameter Nalgene Teflon membrane, and continuously washed with THF until the filtrate was colorless and no photoluminescence is observed from washing solution. Approximately 6 mL of THF was then added to recover the SWNT residue. The resulting relatively dark solution was further sonicated for 15 min and remained stable for at least 2 months without any precipitation. Similar

experiments in other solvents (e.g., water, toluene) were less successful.

The optical absorption of spectrum of PEGC dispersed SWNT solution is shown in Figure 1. The absorption peaks from individually dispersed carbon nanotube species is clearly discernible (see Figure S1 in the Supporting Information). Optical density of PEGC-SWNT sample increases as wavelength decreases between 400 and 600 nm. This is probably due to M_{11} absorption of metallic nanotubes and in part due to presence of PEGC absorption tail states. Most of the peaks match those observed in SDS dispersed sample.³¹ This is much more evident in the 2D excitation–emission map of solubilized nanotubes (Figure 2). The major SWNTs found in SDS sample

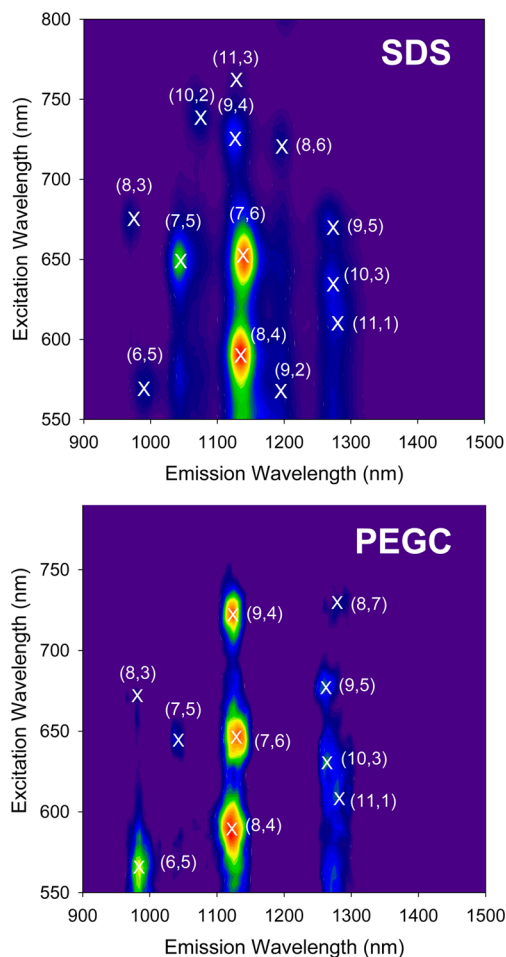


Figure 2. 2D excitation–emission map for samples solubilized by SDS and PEGC dispersants.

are (8,4), (7,6), and (7,5); whereas (8,4), (7,6), (9,4), and (6,5) are dispersed efficiently with PEGC.³² Both maps reveal similar dispersion characteristics by SDS and PEGC dispersants. The major difference is in the relative amount of nanotubes dispersed by each dispersant. Transmission electron microscopy (TEM) images prove individualized nature of nanotubes obtained with PEGC (see Figure S2 in the Supporting Information).

Figure 3 shows the resonant Raman modes of SWNT samples excited with a laser line of 532 nm (785 nm excitation data is given in the Supporting Information). At the excitation wavelength of 532 nm, mostly metallic nanotube species are in resonance with the laser beam.^{20,33} The PEGC-SWNT sample

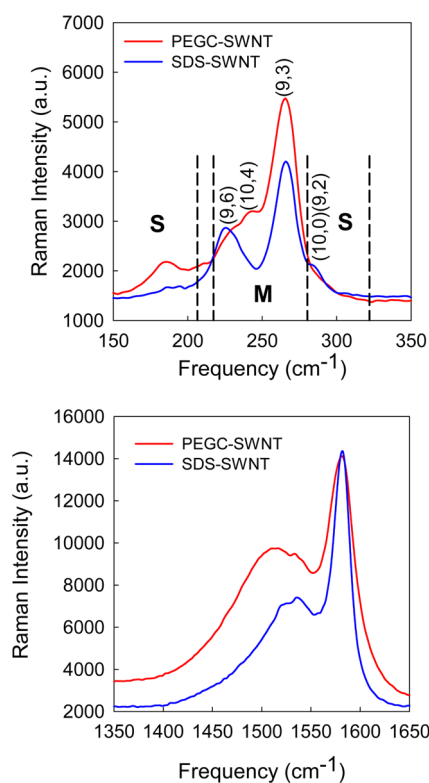


Figure 3. Solid-state Raman spectra of samples excited at 532 nm. M and S denotes metallic and semiconducting regions for RBM modes, respectively.

shows more metallic nanotube species than the nanotubes dispersed with SDS. The ratio of G^- band to G^+ band is a good indicator for the extent of metallic content in a dispersed sample. The G^- band is broadened due to presence of metallic nanotubes, possessing Breit–Wigner–Fano line shape instead of Lorentzian broadening seen in semiconducting nanotubes.¹⁷ Although both PEGC and SDS dissolve similar semiconducting species, the G^- band of PEGC-SWNTs is greater in magnitude than that of SDS-SWNTs, indicating metallic enrichment using PEGC. Further, the shift of the G^- band maxima (1512 cm^{-1} vs 1535 cm^{-1} in SDS) also supports the notion of metallic enrichment with PEGC. Most of the bands for radial-breathing-modes (RBM) are identified as metallic nanotubes (Figure 3, top). Laser excitation at 785 nm is mostly in resonance with semiconducting nanotubes (see Figure S3 in the Supporting Information). Overall, PEGC disperses similar nanotube types as SDS. Again, the ratio of G^- band to G^+ band is 0.14 and 0.10 for PEGC-SWNT and SDS-SWNT samples, respectively. The same measurement with a pristine sample is 0.21. These results suggest PEGC disperses more metallic SWNTs than SDS, supporting the results obtained at 532 nm excitation. However,

the results also suggest—but do not prove—that the metallic/semiconducting ratio does not reach the levels to that of pristine sample for PEGC-dispersed SWNT sample.

We have also performed ab initio and semiempirical calculations to reveal the robustness of solubility with PEGC dispersant in comparison to other PAHs used in the literature (Table 1). The calculations were performed using the SWNT geometries generated by TubeGen³⁴ (C–C bond length of 1.421 Å) and B3LYP/6-31G* optimized geometries of dispersants. Energy minimization was carried out using ω -B97X-D functional and the MM3 force field while holding the internal geometries of the nanotube and dispersant fixed (see the Supporting Information for details). The binding energy was calculated from the difference in total energy of isolated components and minimized energy structure of the complex. The magnitudes of binding energy are different yet the same trend is predicted by both methods (Table 1). The binding energies are highest for corannulene among all the other PAHs calculated in this work. We speculate that the concave surface of corannulene has better dispersion interaction with the convex surface of SWNTs. Therefore, PEGC works quite efficiently in dispersing carbon nanotubes. Calculations also indicate there is no significant chiral angle or diameter dependence based on the results obtained for three different nanotube species. This, partially, explains the lack of chiral selectivity of PEGC in solubilizing carbon nanotubes. Recently, kilogram scale synthesis of corannulene has been reported by Siegel and co-workers.³⁵ PEG functionalization reaction of corannulene has moderate yield, though it can be accomplished with ease. Thus, we believe PEGC and related derivatives have strong potential in solubilizing carbon nanotubes in organic solvents.

■ ASSOCIATED CONTENT

Supporting Information

Details of theoretical calculations, PEGC-SWNT absorption spectrum, TEM images recorded for PEGC-SWNT sample, and Raman spectra with ex: 785 nm. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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Table 1. Binding Energies of Several SWNT-PAH Complexes Calculated at DFT and MM3 (in parentheses) Levels of Theory

	chirality (n,m), diameter, chiral angle		
	(6,5), 0.75 nm, 27.0	(8,4), 0.83 nm, 19.1	(10,3), 0.92 nm, 12.7
	binding energies (kcal mol ⁻¹)		
anthracene ³⁶	-28.3 (-15.6)	-38.1 (-15.9)	-26.1 (-16.2)
pyrene ²⁵	-30.1 (-16.8)	-39.2 (-17.1)	-37.3 (-17.5)
coronene ²⁰	-36.3 (-22.3)	-46.8 (-22.9)	-45.6 (-23.6)
corannulene	-50.5 (-23.8)	-61.2 (-24.5)	-49.6 (-25.2)

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