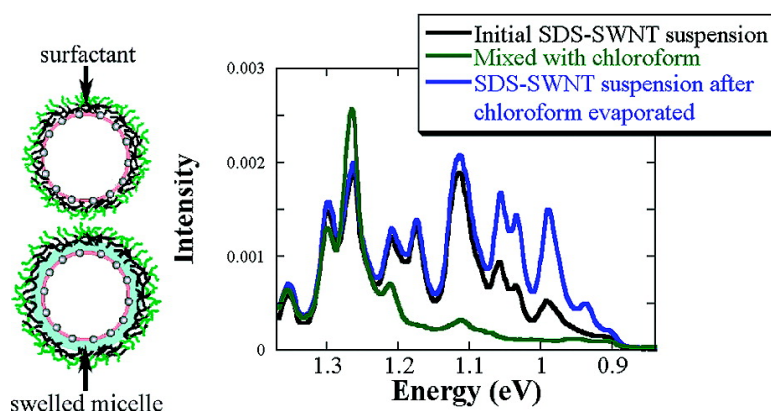


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Swelling the Micelle Core Surrounding Single-Walled Carbon Nanotubes with Water-Immiscible Organic Solvents

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Abstract: Solvatochromic shifts in the absorbance and fluorescence spectra are observed when surfactant-stabilized aqueous single-walled carbon nanotube (SWNT) suspensions are mixed with immiscible organic solvents. When aqueous surfactant-suspended SWNTs are mixed with *o*-dichlorobenzene, the spectra closely match the peaks for SWNTs dispersed in only pure *o*-dichlorobenzene. These spectral changes suggest that the hydrophobic region of the micelle surrounding SWNTs swells with the organic solvent when mixed. The solvatochromic shifts of the aqueous SWNT suspensions are reversible once the solvent evaporates. However, some surfactant-solvent systems show permanent changes to the fluorescence emission intensity after exposure to the organic solvent. The intensity of some large diameter SWNT (*n*, *m*) types increase by more than 175%. These differences are attributed to surfactant reorganization, which can improve nanotube coverage, resulting in decreased exposure to quenching mechanisms from the aqueous phase.

Introduction

Single-walled carbon nanotubes (SWNTs) are tubular structures of carbon with several unique physical and chemical properties.^{1,2} Dispersing SWNTs in a solvent is required for many applications, but common organic solvents offer insufficient solvation forces to suspend SWNTs.³ Surfactants or polymers are often used to stabilize aqueous SWNT suspensions. The hydrophobic part of the surfactant noncovalently attaches to the sidewall of the nanotubes while the hydrophilic end extends into the water phase. The resulting surfactant shell creates a repulsive barrier that overcomes the strong van der Waals attractive forces needed to disperse the SWNTs.⁴ The anionic surfactants sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS) are frequently used because of the high dispersion quality of the resulting SWNT suspensions.^{5,6}

The ability to individually disperse SWNTs in solution enabled the discovery of near-infrared (NIR) fluorescence of semiconducting nanotubes,⁵ which correspond to the specific (*n*, *m*) type of each nanotube.⁷ The fluorescence emission

energies of SWNTs are sensitive to the surrounding environment with suspended SWNTs being red-shifted in comparison to SWNTs in air.^{8–10} The extent of the shift is dependent on the surfactant,⁶ protein,^{11–14} or polymer that encases the nanotube.^{15,16} The first measurements of the photoluminescence quantum yields for dispersed SWNTs were on the order of 0.1% or less.^{5,17} The optically excited electronic states of SWNTs are highly mobile,¹⁸ making them sensitive to extrinsic effects that can reduce the quantum yield, including sidewall defects,^{10,18–21} protonation,^{18,22–24} surfactant inhomogeneities,^{19–21,25} bundles,^{20,26–28} and nanotube ends (i.e., lengths).^{29,30} Indeed,

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single-molecule spectroscopy in both aqueous solutions¹⁹ and air¹⁰ have observed spots along the length of a nanotube, which have reduced fluorescence emission intensity. These dark spots allowed Cognet et al.¹⁸ to estimate the exciton diffusion length to be ~ 90 nm. When the quantum yields are calculated on single nanotubes that have no dark spots, the quantum yields improve dramatically to values approaching 10%.^{10,18,19}

The observation of these extrinsic factors has raised questions regarding the capability of fluorescence spectroscopy to quantify relative (n , m) ratios.^{10,19} The difference in quantum yield measurements seen for bulk-scale suspensions and single-molecule analysis points to the importance in understanding how SWNT dispersion affects fluorescence intensities. For example, different quantum yields are observed for different surfactants.²⁵ Differences in fluorescence intensity between different surfactant suspensions also led to the conclusion that some surfactants, such as SDS, preferably disperse small diameter SWNTs.⁸ The ultimate objective is to learn how to compensate for these differences.¹⁹ Recently, the elimination of small bundles was shown to improve the quantum yields of bulk SWNT suspensions to ~ 1 –1.5%.²⁶

Understanding the importance of these extrinsic factors to the quantum yields of SWNTs may be compounded by an incomplete understanding of the surfactant structure surrounding the nanotube. In general, three models of surfactant structure have been suggested: (a) hemisphere,³¹ (b) cylindrical,³² and (c) randomly adsorbed surfactant structures surrounding the nanotubes.³³ However, there is no accepted structure for the surfactant surrounding the nanotubes. Recently, Wallace et al.³⁴ showed through coarse-grained molecular dynamics (MD) calculations that the surfactant structure around SWNTs was concentration dependent. At low concentrations, the surfactant molecules tend to orient themselves along the length of the nanotube. However, the surfactant extends out into the aqueous phase at higher concentrations. These simulations combined with the previously observed extrinsic factors suggest that processing

conditions may play an important role in the photophysical properties of SWNT suspensions.

In this paper, we describe the swelling of the hydrophobic core of the micelle surrounding the SWNTs. Mixing aqueous suspensions of SWNTs with various immiscible organic solvents results in solvatochromic shifts indicative of a coating surrounding the nanotubes. The solvatochromic shifts and changes in the fluorescence intensity are dependent on the surfactant coating the nanotube, allowing the spectral changes to be used to probe the surfactant structure around SWNTs. While the solvatochromic shifts are reversible once the solvent is removed, the fluorescence intensity depends on the surfactant–solvent combination used to swell the micelle. For SDS-coated SWNTs, the largest diameter nanotubes show significant increases in fluorescence intensity after some organic solvents are removed. In addition, these SWNTs are better protected from the fluorescence quenching effect of acid. The spectral changes suggest that the organic solvent is capable of reorganizing the surfactant surrounding the SWNT.

Experimental Section

SWNT suspensions (Rice HPR 145.1) were prepared in both 1 wt% SDS and SDBS solutions followed by ultracentrifugation.⁵ Aqueous nanotube suspensions were prepared by mixing 20 mg of raw SWNTs with 200 mL of an aqueous SDS or SDBS surfactant solution (1 wt. %). High-shear homogenization (IKA T-25 Ultra-Turrax) for 1.5–2.0 h and ultrasonication (Misonix S3000) for 10 min were used to aid dispersion. After ultrasonication, the mixture was ultracentrifuged at 20 000 rpm for 5 h (Beckman Coulter Optima L-80 K). Immiscible solvents, such as *o*-dichlorobenzene (ODCB), were added to each SWNT suspension (solvent:water volume ratio of 0.5) and mixed. The mixture was shaken vigorously for 30 s with a vortex stirrer. After shaking, a white emulsion phase immediately started to phase separate. The characterization of aqueous SWNT suspensions was done after waiting for 1.5–2 h to reach steady state. The excess organic solvent was then carefully removed from the aqueous SWNT suspension to prevent further emulsification. SWNT suspensions prepared in pure ODCB were ultrasonicated and then filtered through coarse filter paper to remove the large visible aggregates in the suspension prior to characterization.⁵

The aqueous phase was characterized by vis-NIR absorbance and NIR-fluorescence spectra using an Applied NanoFluorescence Nanospectrolyzer (Houston, TX) with excitation from 662 and 784 nm diode lasers. Raman spectra were recorded with a Renishaw Invia Bio Raman with excitation from a 785 nm diode laser.

Results

Figure 1 shows the NIR fluorescence spectra for the initial aqueous SWNT suspension and the aqueous suspension after mixing with ODCB. In both the SDBS- and SDS-SWNT suspensions, the peaks have red-shifted by 0.01–0.1 eV (9–17 nm), indicating a change to the environment surrounding the nanotubes. The fluorescence intensity has also significantly decreased in both suspensions. In SDS suspensions, the fluorescence emission from the largest diameter SWNTs has almost completely disappeared.

Nanotubes have limited solubility in pure ODCB without using surfactants,³ allowing direct comparison to aqueous suspensions mixed with ODCB. Figure 2 compares the normalized fluorescence spectra of ODCB-suspended nanotubes to aqueous SDS- and SDBS-suspended nanotubes after mixing with ODCB. Once the SDBS- and SDS-coated aqueous SWNT suspensions are mixed with ODCB, the suspensions show similar emission spectra to SWNTs dispersed in pure ODCB.

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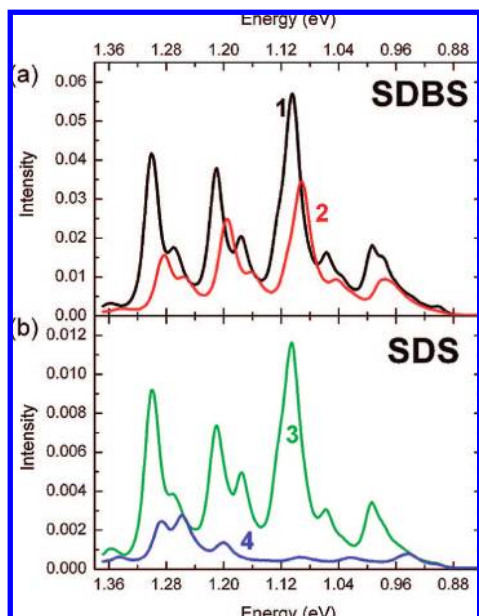


Figure 1. Comparison of NIR fluorescence spectra (ex = 662 nm) of surfactant-coated SWNT suspensions before (1 and 3) and after mixing with ODCB (2 and 4). (a) SDBS-suspended SWNTs and (b) SDS-suspended SWNTs.

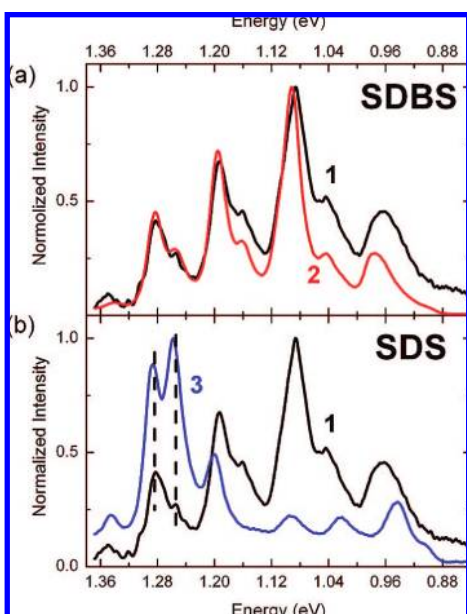


Figure 2. Comparison of normalized NIR fluorescence spectra (ex = 662 nm) of surfactant-coated SWNT suspensions to SWNTs dispersed in only ODCB (1). (a) SDBS-SWNTs (2) and (b) SDS-SWNTs (3) after mixing with ODCB.

The smallest diameter nanotubes (larger emission energy) have very good agreement in peak position with nanotubes in ODCB, especially for SDBS-coated SWNTs. The similarity in the spectra implies that ODCB molecules are in close proximity to the nanotubes.

The organic solvent was removed from the surfactant-coated SWNT suspensions by room temperature evaporation for 24 h. Figure 3a shows the fluorescence spectra for SDS-coated SWNT suspensions during evaporation of ODCB. The time dependent changes to the intensity of the (7, 6) and (8, 3) nanotubes are shown in Figure 3b. The smallest diameter nanotubes (e.g.,

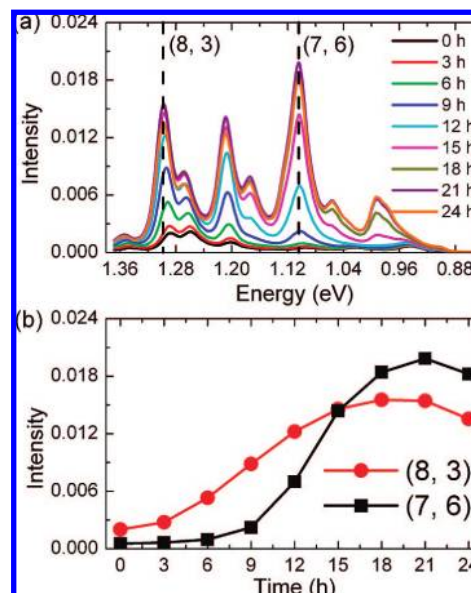


Figure 3. (a) NIR fluorescence spectra (ex = 662 nm) of SDS-coated SWNT suspensions mixed with ODCB during solvent evaporation. (b) Time-dependent recovery of (7, 6) and (8, 3) peak intensities of SDS-SWNTs mixed with ODCB.

(8, 3) SWNTs) recover their fluorescence intensity faster than the larger diameter nanotubes (e.g., (7, 6) SWNTs). All nanotube fluorescence intensities have reached equilibrium after ~20 h. The spectra for both SDS- and SDBS-suspended SWNTs return to their original peak positions and have intensities close to their initial values (compare Figure 1b for SDS-suspended SWNTs, discussed further below).

Spectral changes were also observed for aqueous SWNT suspensions mixed with other organic solvents. Figure 4 plots the fluorescence spectra of SDBS- and SDS-suspended SWNTs mixed with various organic solvents. Once again, the solvatochromic shifts and changes to fluorescence emission intensity were dependent on the surfactant used to suspend the SWNTs. For each solvent, the SDBS-suspended SWNTs in Figures 4a and 4c showed similar changes to both the solvatochromic shifts and fluorescence intensity for each (*n*, *m*) SWNT type. SDBS-SWNT mixtures with hexane showed a slight increase in fluorescence emission and blue-shifts. On the other hand, mixtures of benzene with SDBS-SWNTs showed red-shifts and both slight increases and decreases in fluorescence intensity. Finally, chloroform mixtures with SDBS-coated SWNTs had similar decreases in intensity and red-shifts as the ODCB mixtures. In contrast to the SDBS-coated SWNT suspensions, the SDS-SWNTs in Figures 4b and 4d showed changes to the fluorescence intensity, which was dependent on the SWNT (*n*, *m*) type. The emission spectra for SDS-SWNTs red-shift and significantly decrease in intensity for hexane mixtures while benzene mixtures have small blue-shifts of the emission and significant increases in fluorescence intensity. The response of SDS-SWNTs mixed with chloroform was diameter dependent and varied slightly between different suspensions. In general, the small diameter nanotubes (e.g., (8, 3) SWNTs) have minor changes to both emission energy and intensity while large diameter nanotubes show no shifts but large decreases in intensity. Similar to mixtures with ODCB, the intensity of the largest diameters (e.g., (9, 5) SWNTs) almost completely disappeared.

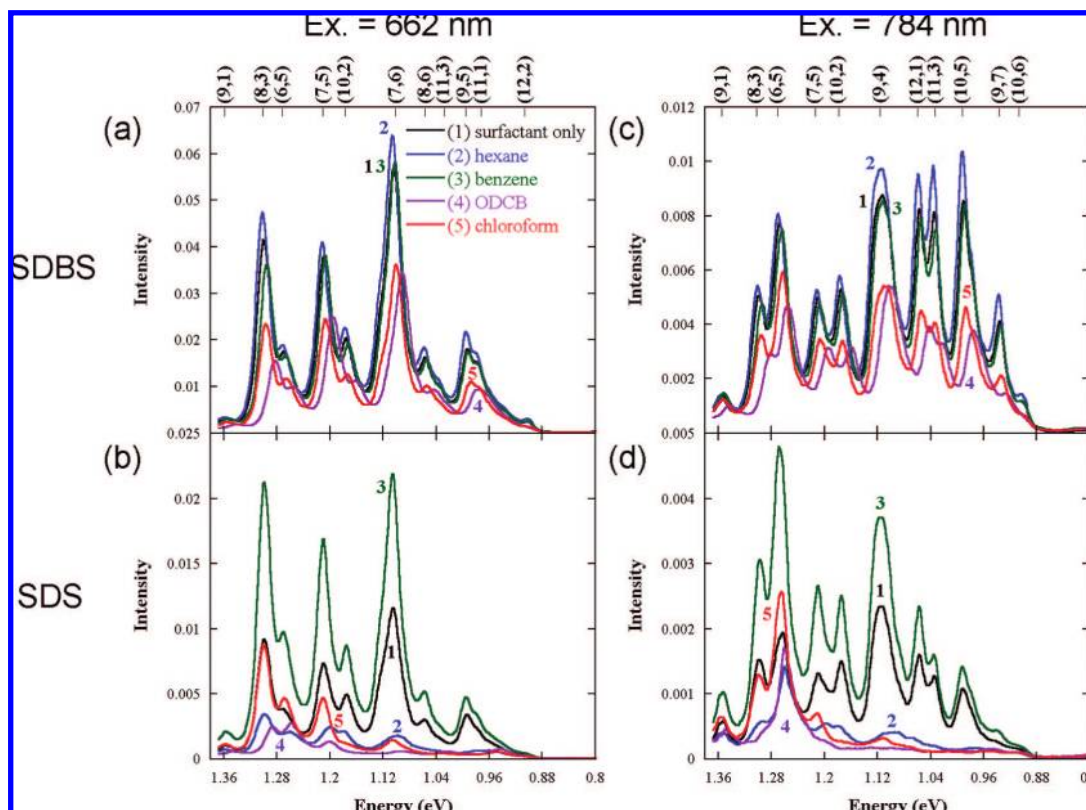


Figure 4. NIR fluorescence spectra of SDBS- and SDS-coated SWNT suspensions after being mixed with the immiscible organic solvents: hexane (2), benzene (3), ODCB (4), or chloroform (5). The initial surfactant–SWNT suspension (1) is plotted for comparison. Excitation from 662 and 784 nm lasers.

Table 1. Spectral Changes of Surfactant-Coated SWNTs Mixed with Organic Solvents

organic solvent	dielectric constant ^a	dipole moment (D) ^a	SDBS–SWNTs		SDS–SWNTs	
			fluorescence intensity change	solvatochromic shift change	fluorescence intensity change	solvatochromic shift change
hexane	1.89	0	small increase	blue	large decrease	red
benzene	2.28	0	varied	red	large increase	slight blue
chloroform	4.81	1.04	decrease	red	varied	varied
ODCB	10.12	2.50	decrease	red	large decrease	red
water	80.1	1.85	—	—	—	—

^a Values taken from the CRC Handbook of Chemistry and Physics.

Table 1 summarizes the fluorescence emission of SWNT suspensions after being mixed with each solvent. In general, all systems that red-shift show decreases in fluorescence intensity. Figure 4 also shows that the largest diameter SWNTs have the most significant decreases in fluorescence emission intensity. The spectral shifts for SDBS-coated SWNTs closely mirror the differences in dielectric constant and polarity of the organic solvent. However, there is no apparent trend of the spectral changes of the SDS-coated SWNT suspensions with the solvent. The largest decreases in fluorescence intensity occurred when mixed with the solvent that has the highest dielectric constant (ODCB) and the lowest dielectric constant (hexane). The polarity also seems to have no influence on the fluorescence intensity since the two nonpolar species showed the ability to either decrease (hexane) or increase (benzene) the intensity after mixing with the aqueous SWNT suspensions.

The spectra for both SDBS- and SDS-suspended SWNTs exposed to immiscible solvents return to their original peak positions after the solvent is evaporated from the aqueous suspension and have intensities close to the surfactant only SWNT suspensions, as shown in Figure 5. This is somewhat

surprising for SDS-suspended nanotubes since the peaks had nearly disappeared in Figures 4b and 4d after mixing with ODCB, chloroform, and hexane. For example, the fluorescence spectra for SWNTs mixed with ODCB in Figures 4b and 4d shows the fluorescence of only the (8, 3), (7, 5), and (6, 5) SWNT types. After the evaporation of ODCB, the fluorescence emission from all SWNT (*n, m*) types return, as shown in Figures 5b and 5d. There are some minor differences in the intensity of SDBS-coated SWNTs after exposure to the organic solvents, which may be attributed to removal of nanotubes or impurities at the interface.^{35,36} On the other hand, substantial increases to the fluorescence intensity for SDS-suspended SWNTs are observed after ODCB and chloroform have evaporated. For example, the large diameter SWNTs in Figures 5b and 5d have considerable increases in fluorescence emission intensity after the organic solvent is removed.

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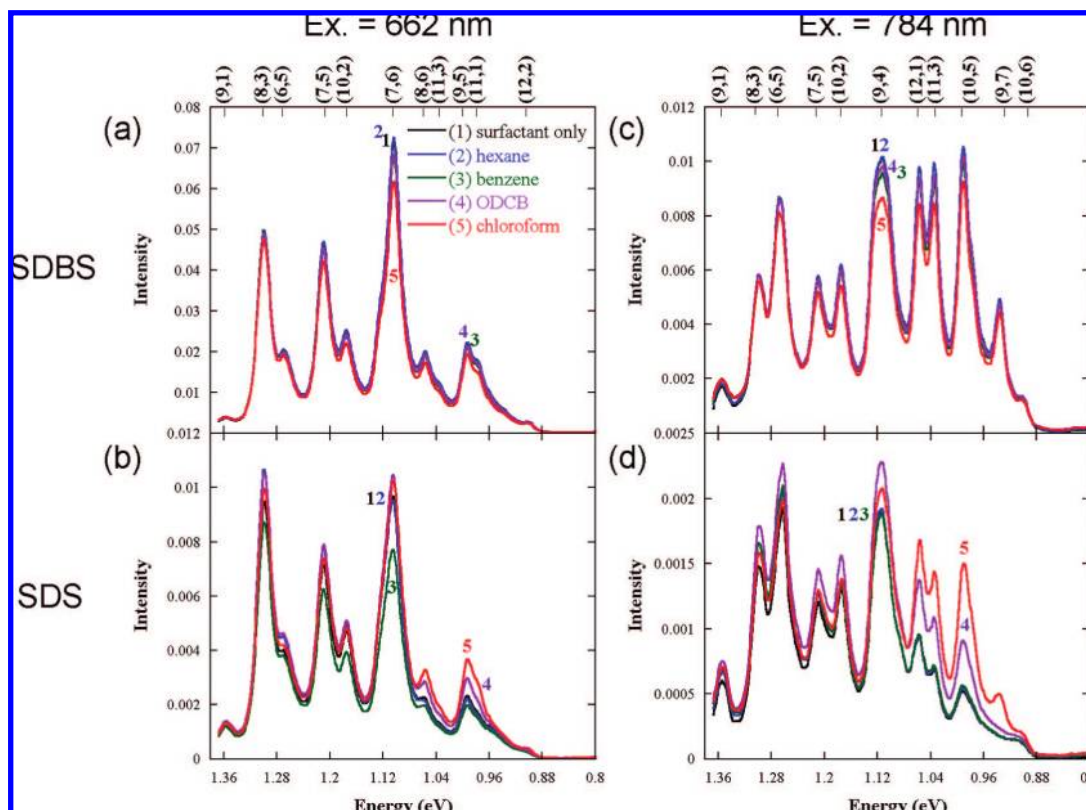


Figure 5. NIR fluorescence spectra of SDBS- and SDS-coated SWNT suspensions after evaporation of the immiscible organic solvents: hexane (2), benzene (3), ODCB (4), or chloroform (5). The surfactant–SWNT suspension exposed to air for 24 h (1) is plotted for comparison. Note that both SDS- and SDBS-coated SWNT suspensions showed minor changes to the emission spectra after being open to air for 24 h. Excitation from 662 and 784 nm lasers.

These changes in fluorescence intensity occur without any differences to the relative ratios between (n, m) types in either the absorbance or Raman spectra. The absorbance spectra after the solvent is removed from the aqueous suspension in Figure 6a show that, in general, the spectra are similar to the initial SWNT suspension. Although the SDS–SWNT suspensions exposed to ODCB and chloroform have minor changes to the absorbance baseline, there are no changes to the ratio of peak heights. The decrease in absorbance observed with chloroform would indicate further proof that impurities were removed from the system.^{35,36} Most importantly, there is no broadening or red-shifting of the peaks for any of the spectra. The radial breathing modes (RBMs) of the Raman spectra are dependent on the diameter of the nanotubes and can also indicate changes to the (n, m) types. As seen in Figure 6b, the intensity of the Raman RBMs for each peak is nearly identical to that observed for the initial SDS–SWNT suspension. Note that the (10, 5) SWNT has the largest intensity increase in Figure 5d. In addition, there are no changes to the so-called aggregation peak ($\sim 270 \text{ cm}^{-1}$) after the organic solvents are removed. These results indicate that the suspension has no significant changes to the relative concentration of nanotube (n, m) types or bundling, which could cause the changes in fluorescence emission seen in Figures 5b and 5d.^{19,25,28,35,37}

Discussion

The solvatochromic shift in fluorescence emission spectra of SWNTs mixed with organic solvents indicates a change to the environment surrounding the nanotubes. When compared to SWNTs suspended in pure organic solvents, these spectra show

nearly identical peak positions (see Figure 2), suggesting that organic solvents are forming a layer or a shell around the sidewall. Since the fluorescence, absorbance, and Raman spectra return to the initial values after the solvent has evaporated, the surfactant must still be present. Otherwise, there would be substantial bundling of the nanotubes resulting in broadened and red-shifted absorbance as well as quenching of the fluorescence emission.^{5,19,25} The reversibility of both the spectral shifts and intensities is good evidence that the presence of the organic solvent molecules rather than aggregation or surfactant removal is responsible for the observed changes. Therefore, the data suggest that the organic solvent is swelling the hydrophobic region of the surfactant micelle surrounding the SWNTs, similar to the swelling of micelle cores in block copolymers,³⁸ as shown in Figure 7a. This conclusion is also supported by the consistent trend of the solvatochromic shift of SDBS-coated SWNT suspensions with solvent polarity (see Figures 4a, 4c, and Table 1), indicating that the environment around the nanotubes is systematically changing when mixed with different solvents.

The spectral changes observed for SDS-coated SWNT suspensions when mixed with organic solvents are more complex. In hexane mixtures, the fluorescence intensity of SWNTs increases significantly in Figures 4b and 4d. On the other hand, fluorescence emission decreases considerably for other solvents. The presence of the organic solvents can affect the fluorescence intensity;³⁹ however, the solvatochromic shifts

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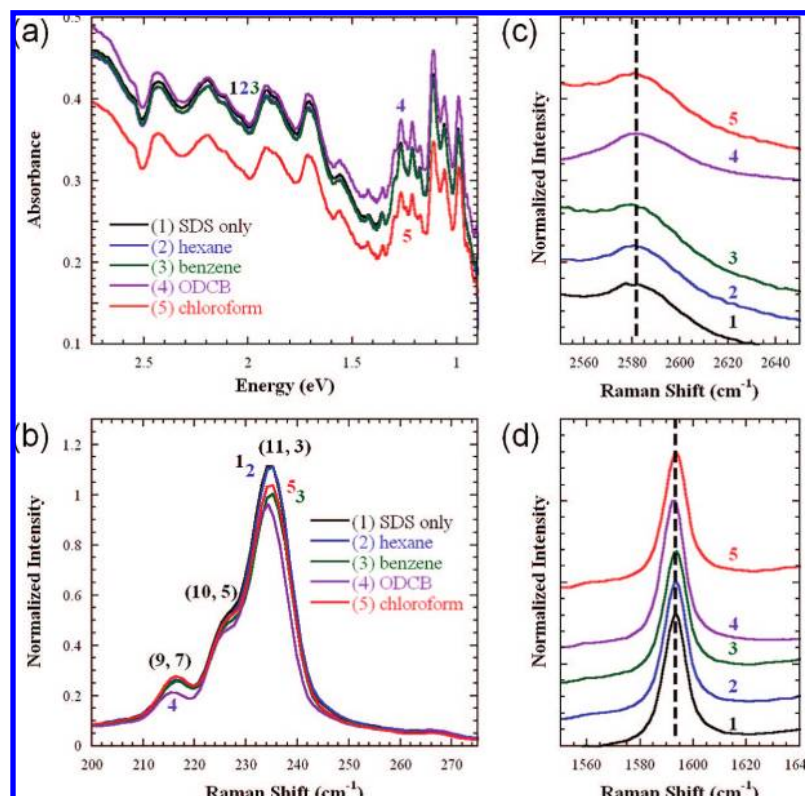


Figure 6. (a) Absorbance and (b–d) Raman spectra (ex = 785 nm) of SDS-coated SWNT suspensions after evaporation of the organic solvent: hexane (2), benzene (3), ODCB (4), or chloroform (5). The surfactant–SWNT suspension exposed to air for 24 h (1) is plotted for comparison. The radial breathing modes (RBMs) for specific (n, m) SWNT types are shown in b while c and d show the Raman spectrum of the G' and G band of the SDS-coated SWNTs suspensions, respectively. The dashed lines indicate the positions of the surfactant suspensions prior to mixing with organic solvents. All spectra in c and d are offset for clarity.

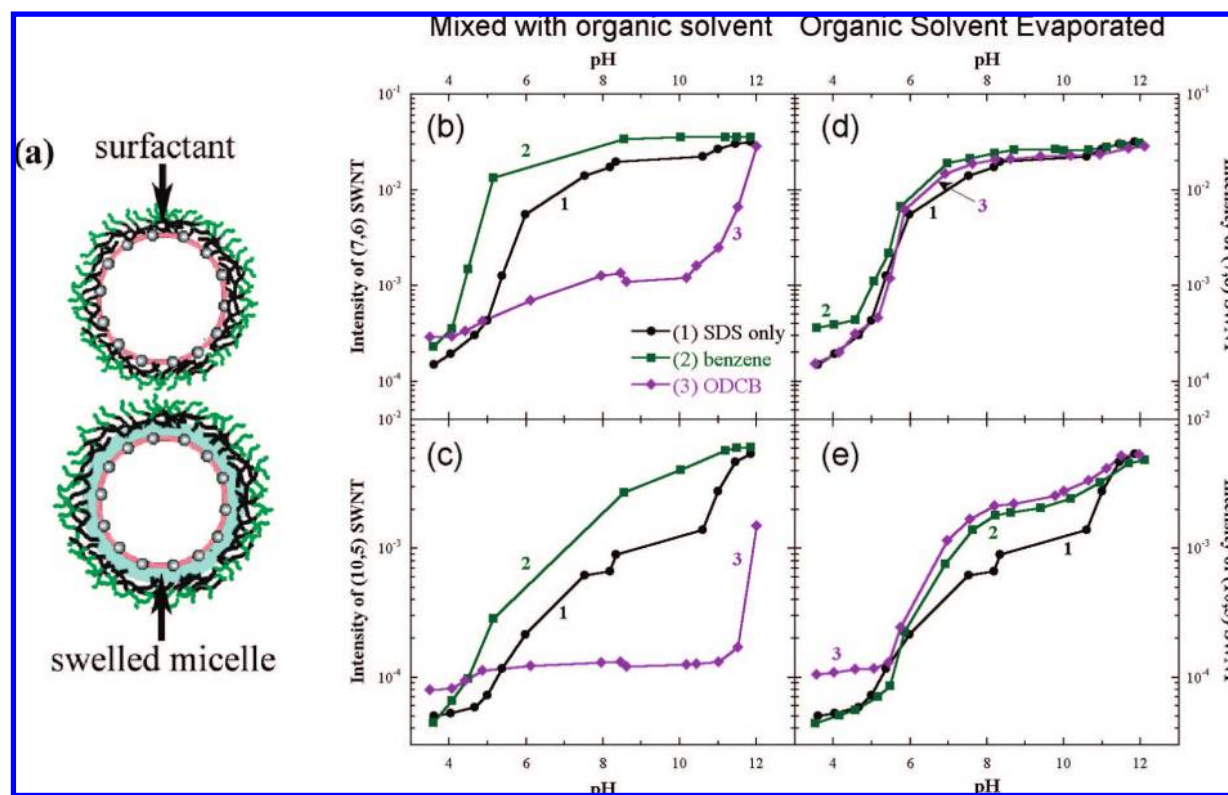


Figure 7. (a) Swelling of the hydrophobic core of the micelle surrounding SWNTs. (b–e) The effect of pH on the fluorescence intensity of the (7, 6) SWNT (ex = 662 nm) and (10, 5) SWNT (ex = 784 nm) in SDS-suspensions after being mixed with the immiscible organic solvents benzene and ODCB and after evaporation of the solvent.

and intensity changes should tend to follow polarity changes as observed with SDBS–SWNT suspensions. The effect of each solvent should also yield consistent changes to the SWNT emission spectra. In other words, if a solvent (e.g., ODCB) is inducing changes to the emission spectra in Figures 4b and 4d, similar changes to the emission spectra should be observed in the spectra in Figures 4a and 4c. The lack of a consistent trend for SDS-coated SWNTs (see Figure 4b, 4d, and Table 1) and the different response for each surfactant suggest that another phenomenon is responsible for the changes in SDS-coated SWNT suspensions.

Recently, researchers have observed increased fluorescence intensity due to Förster energy transfer between individual SWNTs.^{9,20,27,28} For example, the emission of large diameter SWNTs (smaller band gap energy) was enhanced during nanotube bundling by excitation and energy transfer from the larger band gap, smaller diameter SWNTs.²⁷ If energy transfer is responsible for the increased fluorescence emission of large diameter SWNTs after solvent evaporation, then a decrease in fluorescence intensity would be expected for the smaller diameter SWNTs. However, the increases in nanotube emission intensity observed after chloroform and ODCB exposure occur without a simultaneous decrease in intensity from other SWNTs. The lack of any significant changes to the Raman aggregation peak also seems to rule out Förster energy transfer as the cause for increased fluorescence emission of some (n, m) types. The fact that a new peak corresponding to the (9, 7) SWNT appears in the emission spectra in Figure 5d strongly suggests that this species is present in the initial suspension but is not fluorescing. This behavior often is indicative of exciton energy transfer^{9,20,27,28} but this SWNT type is already observed in the spectra for SDBS-suspended SWNTs in Figure 5c and the Raman spectra in Figure 6b. In fact, the spectra in Figures 5b and 5d after exposure to chloroform are strikingly similar in shape and relative intensity when compared to all of the spectra in Figures 5a and 5c.

SWNTs are also susceptible to doping when the solvent is in close proximity to the surface. If solvent doping were responsible for the observed intensity changes after evaporation, then both SDS- and SDBS-coated SWNTs should have similar changes. As shown in Figure 1, both systems have a solvatochromic shift that indicates that ODCB is surrounding the SWNTs. However, only the SDS–SWNT suspensions show improvements to the fluorescence intensity in Figure 5. In addition, the nanotube (n, m) types which show decreases in intensity when the solvent is present are the same nanotube types that have increased emission after exposure to the solvents. For example, the fluorescence emission from the (7,6), (12,1), (11,3), and (10,5) SDS–SWNT suspensions in Figures 4b and 4d are completely quenched but then show the largest increases in intensity after evaporation in Figures 5b and 5d. Without changes to the chemical structure of the solvent during evaporation, it is unlikely that solvent doping can cause this behavior. Recently, researchers showed that decomposition products of ODCB generated during ultrasonication could dope SWNTs.⁴⁰ However, the authors observed that mixing with solvents, similar to the approach in this study, does not cause decomposition or doping. To determine if photochemistry could initiate ODCB decomposition and doping during evaporation, SWNTs were also processed under natural light and dark conditions. The fluorescence spectra of the light and dark suspensions were

identical (not shown) eliminating decomposition-induced changes. Finally, Raman spectra after solvent evaporation show that the G' and G band do not have any shifts or width changes associated with doping.^{40,41} The G' band in Figure 6c is partially obscured by the background fluorescence but clearly shows that there are no shifts after solvent evaporation. Similarly, the G band in Figure 6d has no major changes to the shifts or width after evaporation.^{40,41} It does appear that ODCB may have a slight red-shift ($\sim 1 \text{ cm}^{-1}$); however, this would indicate a small amount of n-type doping rather than p-type doping observed previously.⁴⁰ The lack of significant changes to the G, G', and RBM modes of the Raman spectra suggests that solvent doping is not responsible for the changes to fluorescence emission intensity observed in Figures 5b and 5d.^{40–42}

One plausible explanation is that the fluorescence of the large diameter SWNTs in SDS-suspended SWNTs was quenched in the initial suspension. It is generally accepted that exposure of the nanotube to protons in the aqueous phase quenches the exciton.^{18,22–25} The surfactant shell surrounding the nanotube, therefore, provides the needed protection to prevent nonradiative recombination of the exciton. Okazaki et al.⁸ observed different ratios of the fluorescence emission intensities of SWNTs suspended in SDS to SWNTs in air, leading them to conclude that SDS did not suspend larger diameter nanotubes. This conclusion is supported by the fact that smaller diameter SWNTs have stronger binding energies to SDS.⁴³ More recently, researchers have observed that larger diameter SWNTs coated with SDS have a higher sensitivity to quenching.²⁵ Indeed, the initial SDS-suspensions have lower fluorescence intensities for larger diameter SWNTs in comparison to the initial SDBS-suspensions, as seen in Figures 4c and 4d. Therefore, these intensity differences could mean that the largest diameter nanotubes have either (1) inadequate surfactant shells to aid dispersion and are truly not present or (2) incomplete or nonuniform surfactant structures surrounding the nanotubes, which quench the emission fluorescence.

Wallace and Sansom³⁴ showed through MD simulations that surfactant coverage was nonuniform and the thickness varied along the length of the nanotube. In other words, the surfactant permeability to protons from the water could potentially be altered as the surfactant concentration is changed, affecting fluorescence intensity. Others have also speculated similar 'holes' in the surfactant layer to help explain fluorescence behavior.^{23,25} If the permeability of the surfactant structure were altered, then these potential quenching spots could be removed, resulting in increased emission intensity. These alterations could occur by introducing solvents to protect the nanotube or by reorganization or redistribution of the surfactant surrounding SWNTs. These changes to the SDS surfactant structure should be most sensitive to the largest diameter SWNTs.

To test if solvents can improve the ability of the surfactant to protect the SWNT from quenching protons, the pH of the aqueous phase was adjusted to control the concentration of protons (fluorescence quenchers) while the organic solvent was still present and after the solvent is evaporated. As shown in Figures 7b and 7c, the fluorescence intensity from the (7, 6) and (10, 5) SWNT types in a pure SDS–SWNT suspension decrease by 2 orders of magnitude at acidic pH similar to

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Table 2. Fluorescence Intensity Changes for Various SWNT (*n*, *m*) Types after Exposure to ODCB or Chloroform

SWNT	diameter (nm)	intensity increase (%)	
		ODCB	chloroform
(7, 6) ^a	0.895	8.3	6.0
(9, 4) ^b	0.916	20.6	10.1
(8, 6) ^a	0.966	24.9	42.4
(9, 5) ^a	0.976	27.9	57.5
(12, 1) ^b	0.995	46.0	75.9
(11, 3) ^b	1.014	56.8	107.1
(10, 5) ^b	1.050	72.4	179.3
(9, 7) ^b	1.103	34.6	177.6

^a Excitation from 662 nm laser. ^b Excitation from 784 nm laser.

previous observations.^{23,25} However, the aqueous SWNT suspensions with the organic solvents forming a shell around the nanotubes have different trends from the pure SDS–SWNTs. The aqueous suspension mixed with benzene shows that the SWNTs are more resistant to pH changes. This resistance suggests that benzene offers another protective layer around the nanotube, providing further support for a swelled micelle state surrounding the SWNTs. On the other hand, suspensions mixed with ODCB showed more susceptibility to pH quenching effects across the entire pH range. Only at pH values above 10 does the fluorescence intensity start to recover. These results suggest that the surfactant structure has become more permeable to quenching by protons or water,^{23,25} indicating that the nanotube surfactant structure has been altered or reorganized. Once again, the trends of all SWNT suspensions after solvent evaporation are similar to that of pure SDS as shown in Figures 7d and 7e, which indicates that the surfactant structure has been recovered to a state similar to the initial state. However, there are some noticeable differences in the pH response. For the (7, 6) nanotube, ODCB provides some improvement to quenching in pH values near neutrality while benzene also shows improvements with slightly better fluorescence intensity at acidic pH values. In contrast, the larger diameter (10, 5) nanotube in Figure 7e shows significant improvement in fluorescence emission intensity. SDS–SWNT suspensions exposed to benzene show significant improvement at pH values between 5 and 10. ODCB exposed nanotube suspensions show even better protection to the quenching effects of acid. This organic solvent improves the fluorescence intensity across the entire pH range but most notably for the acidic pH values.

The physisorption of surfactant molecules on nanotubes is a dynamic process, continuously being interchanged with free surfactant in solution. The introduction of an organic phase may alter this process. Indeed, surfactant molecules have slower desorption kinetics in emulsions than in micelles.⁴⁴ The organic

phase may also enable increased mobility of the surfactant around the nanotubes. Depending on the interactions and their strengths, the surfactant reorganization may result in beneficial or detrimental effects to the fluorescence emission. These differences in surfactant–solvent–SWNT interactions help explain the difference in spectra seen for SDS suspensions in Figure 4. While benzene appears to swell the micelle, the other solvents open holes, enabling quenching from the aqueous phase. Upon evaporation of the solvent, the surfactant structure can also be altered, which can improve the resistance to quenching and the fluorescence emission intensity. Table 2 summarizes these increases in intensity, which is also directly related to increases in their quantum yield since absorbance changes are relatively minor. The intensity increases are most significant for the largest diameter nanotubes. Chloroform tends to improve the fluorescence emission intensity more than ODCB. The largest emission increases are observed for the (11, 3), (10, 5), and (9, 7) SWNT types, which have a 107.1%, 179.3%, and 177.6% increase in intensity, respectively.

Conclusion

The hydrophobic core of the surfactant structure surrounding SWNTs can be swelled with immiscible organic solvents. These swelled states could be either a continuous or a discontinuous organic layer that results in significant changes to the fluorescence and absorbance spectra. The spectral shifts are reversible, disappearing once the solvent is removed. However, some surfactant–solvent systems show permanent increases to fluorescence emission intensity, which cannot be attributed to changes in concentration, dispersion, or doping. These permanent changes to emission intensity are attributed to surfactant reorganization, which helps eliminate fluorescence quenching from the aqueous phase. These results may have important implications in processing SWNT suspensions and analyzing the fluorescence of SWNT suspensions. For example, the exposure of SWNTs to small amounts of organic solvents may give the illusion that separation has occurred as seen in Figures 1b, 4b, and 4d. Finally, the changes in fluorescence attributed to surfactant reorganization suggest that changes to processing conditions may yield improved fluorescence intensity (quantum yields) of bulk SWNT suspensions.

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