

Alkane Encapsulation Induces Strain in Small Diameter Single-Wall Carbon Nanotubes

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ABSTRACT

Encapsulation of linear alkane molecules in the endohedral volumes of small diameter single-wall carbon nanotubes (SWCNTs) is shown to induce diameter dependent strain on the hexagonal lattice of carbon atoms composing the tubular structure. For the smallest diameter nanotubes, such as the (6,5), (9,1), (8,3) and (10,0), encapsulation leads to expansive radial strain. This effect is demonstrated through precision measurements of induced shifts in the energy of the intrinsic optical transitions of single-chirality nanotube populations. The effect on the optical transitions

from strain is found to exceed that of the effective dielectric medium change when comparing the same SWCNT population filled with an alkane versus those filled with water. This differs from encapsulation of alkanes into larger diameter nanotubes for which dielectric effects dominate due to the relative sizes of the guest molecules and the SWCNT cavity. For the SWCNT species examined in this work, the interior cavity diameters are smaller than the smallest unstrained cross-section of an alkane molecule. These results imply that SWCNT species-dependent strain is likely to be encountered when encapsulating any molecule into a SWCNT, with particular complexity to be expected for filling by molecules close to the sieving size of the endohedral cavity.

INTRODUCTION

Encapsulation of molecules within the interior, endohedral, volume of single-wall carbon nanotubes (SWCNTs) from the liquid phase is an area of significant active research for a variety of scientific and application driven reasons. These include the study of the effect of confinement on material phase diagrams,¹⁻³ the generation of novel material structures,⁴⁻⁸ and the use of the SWCNT as protective carriers for active molecules.⁹ Liquid-phase filling is preferred for enabling a greater range of potential fillers and the simplicity of the approach, however, high temperature sublimation can alternatively be utilized to encapsulate robust molecules such as C₆₀.¹⁰⁻¹²

Recently, authors of this study demonstrated that the optical properties of dispersed populations of liquid phase filled guest@SWCNT hybrids are generally substantially improved over SWCNTs not subjected to controlled filling.¹³ In particular, improvement was noted for alkane-filled SWCNTs in aqueous dispersion, for which the SWCNTs would otherwise fill with water. The primary effect driving improvement was identified as a reduction in the effective dielectric constant of the environment felt by the SWCNT, along with additional benefits due to the

(generally) lower reactivity and presumed homogeneous nature of the specified fillers within the SWCNTs relative to water.

The key considerations for whether a SWCNT would fill with a particular molecule were found to be whether the ends of the nanotubes were sufficiently open and whether the cross-sectional size of the potential guest was small enough, *i.e.* could the molecule fit. In previous literature on isolating empty *versus* water-filled SWCNTs,¹⁴⁻¹⁶ it has been reported that the interior volumes of commercial SWCNTs subjected to chemical purification by their manufacturer are all readily accessible. This observation was confirmed for larger diameter SWCNTs by successful controlled filling with various alkane and alkane-like fillers.¹³ However, small-diameter SWCNT materials were found to require high temperature oxidation or annealing in an inert gas to ensure a significant fraction of alkane-filled hybrids. Consistent with results published in nanofluidics studies,^{2,17,18} it was hypothesized that dangling functional groups at the end of the nanotube were likely blocking the entry of molecules larger than water in the absence of applied oxidation and annealing. Unfortunately, this observation prevented measurement and analysis of the effects of filling highly-constrained guest molecules into SWCNTs near their sieving size limit.

In this contribution, we partake to fully open the ends of SWCNTs as small as the (6,5) and (9,1) chiralities, using a furnace oxidation and annealing procedure, to enable filling of their entire populations with a linear alkane. The optical properties of diameter-similar pairs of highly-purified single-chirality alkane-filled SWCNTs are then measured in the small-diameter nanotube limit and compared against the optical properties of identically processed SWCNTs from the same parent material filled with water. In this limit, the primary effect on the optical properties of these nanotubes from filling by the alkane is found to be from endohedrally-generated strain, with a

smaller, diameter dependent, effect due to the change in the effective dielectric environment sensed by each SWCNT.

EXPERIMENTAL

Current commercially available SWCNT powders each contain a substantial number of SWCNT species, colloquially termed “chiralities” and described by the chiral vectors n and m and the chiral angle, θ , indicating the way in which the graphene structure is “rolled up” to form that nanotube. For the cobalt-molybdenum catalyst (CoMoCat)¹⁹ synthesis SWCNTs (Chasm Technologies SG65i) utilized herein, the observed number of species is ≈ 25 ; each chiral species of SWCNT (*i.e.*, not armchair: $n = m$, $\theta = 30^\circ$, nor zigzag: $m = 0$, $\theta = 0^\circ$) in the population additionally has both left and right-handed enantiomeric structures. Although much of the SWCNT mass is in < 10 species, including several of the species desired for this study, separation of the polydisperse nanotube sample into single (n,m) and enantiomer populations is required to enable precise measurement of the specific optical properties for each given alkane or water-filled hybrid structure.

To enable total filling of the target small-diameter SWCNTs while in the powder form with the linear alkane, an oxidation and annealing procedure was developed to fully open the nanotube ends. For oxidation, SWCNT powder was placed in a ceramic boat at the center of a 2.5 cm (1 ") diameter quartz tube inside a furnace (Lindberg Blue M, ThermoScientific) and heated to a set temperature for a fixed time with one furnace tube end open to the atmosphere. For annealing, argon gas was regulated to flow through the quartz furnace tube at a rate of several mL/s before the furnace was brought to elevated temperature for a fixed time; the volume of the tube is such that volumetric exchange of the atmosphere occurred in ≈ 30 s. The samples presented in the figures below were oxidized at 355 °C for 30 min, and then annealed at 425 °C under argon flow

for 1 h. Optimization of the procedure was informed by isothermal thermogravimetry experiments shown in the Supporting Information (SI). A single powder subjected to both the oxidation and annealing procedure was then separated into two vials and used to generate the alkane-filled and water-filled samples reported below.

Alkane filling was performed as previously reported¹³ through incubation of the SWCNT powder in the liquid alkane followed by filtration and washing steps; individualized dispersion of the SWCNTs in a surfactant solution of sodium deoxycholate (DOC) was achieved through ultrasonic processing (SI). For this contribution, the alkane utilized was tetracosane ($C_{24}H_{50}$, 99 %, Aldrich), and was incubated with the soot at 70 °C. Tetracosane was chosen as it balances an empirical preference towards longer alkane chain length for robust filling with the increasing difficulties in processing due to the greater melting points of even longer alkanes.¹³ Filling of the non-alkane filled SWCNTs by water occurs spontaneously during the dispersion procedure.^{15,16}

Post-dispersion, the resulting SWCNT populations were centrifuged at 1885 rad/s (18 kRPM) in a JA-20 rotor for 2 h for a rough purification, and then were separated by a series of previously reported methods to isolate a set of highly purified individual (n,m) SWCNT dispersions. Details and spectra after each step of the sequential process are reported in the SI. In brief, dispersions were first purified by rate-zonal ultracentrifugation to remove defective nanotubes, bundles, and remaining impurities.^{13,16} The resulting populations were then concentrated and separated through surfactant gradient aqueous two-phase extraction (ATPE) to generate highly enriched (approximately 50 % to 80 %) single (n,m) populations.²⁰⁻²² Finally, a surfactant to DNA dispersant exchange procedure²³ was used to enable DNA-sequence based recognition extraction *via* ATPE to select for single (n,m) and enantiomer populations.^{24,25} For some measurements, such

as fluorescence spectroscopy, it was additionally beneficial to re-exchange the DNA coating for 10 g/L DOC after the recognition extraction.

Absorbance spectroscopy was performed on a Cary 5000 UV-visible-near infrared (UV-vis-NIR) absorbance spectrometer through a 1 mm path length cuvette at room temperature. Samples and reference solutions were measured in separate runs, with the reference spectra subtracted during data analysis. Measurements were conducted for the range of 200 nm to 1880 nm with a 1 nm step, a 2 nm bandpass, and an integration time of 0.1 s/step for low resolution measurements. Separated SWCNT samples were measured over the range of 200 nm to 1450 nm with a 0.25 nm step, a 1 nm bandpass, and an integration time of 0.1 s/step.

Fluorescence measurements were performed on a Horiba Jobin-Yvon Nanolog NIR fluorescence spectrophotometer. Excitation-emission measurements were used to determine the excitation wavelength with maximum emission intensity. Highly diluted SWCNT samples were measured in a 5 mm by 5 mm cuvette in a right-angle geometry, with the emitted light passing through a 750 nm longpass filter to reject Rayleigh scattered light. Slits were set to yield bandpass values of 5 nm for both excitation and emission. Typical acquisition time was 45 s with 8 acquisitions per sample. Presented data are corrected for the efficiency of the detector train including the longpass filter, and for small differences in sample concentration as determined by UV-vis absorbance measurements.

Resonant Raman scattering measurements were performed in a collinear 180° backscattering configuration on a Horiba Jobin-Yvon T64000 with a liquid nitrogen cooled CCD detector. Excitation at 573 nm (25 mW) was provided by a dye laser using Rhodamine 590 (Exciton) dye pumped by an Ar⁺ laser (Coherent Innova Sabre with multiline head). Three sets of 60 s collections were averaged per grating position. Benzonitrile was used as a reference.

Where reported, uncertainty values are equal to one standard deviation.

RESULTS AND DISCUSSION

UV-vis-NIR absorbance spectra of alkane-filled and water-filled parent SWCNT populations, purified by rate-zonal ultracentrifugation, are shown in Figure 1. For small diameter SWCNTs, the lowest order optical transition, E11, is located at NIR wavelengths (830 nm – 1400 nm), the second order, E22, transitions in the visible (430 nm – 800 nm), and higher order E33, E44, E55, etc., plus absorbance due to π and σ electrons in the UV. These dispersions were prepared from the same opened SWCNT soot, and so the clear shifts in the peak wavelength and changes in linewidths of the optical transitions are attributable to the differential effects of the two fillers, H₂O and C₂₄H₅₀, rather than differences in (n,m) distribution of the SWCNTs. Spectra demonstrating reproducibility of the alkane-induced peak shifts for four additional soot oxidation and annealing preparation variations are reported in the SI.

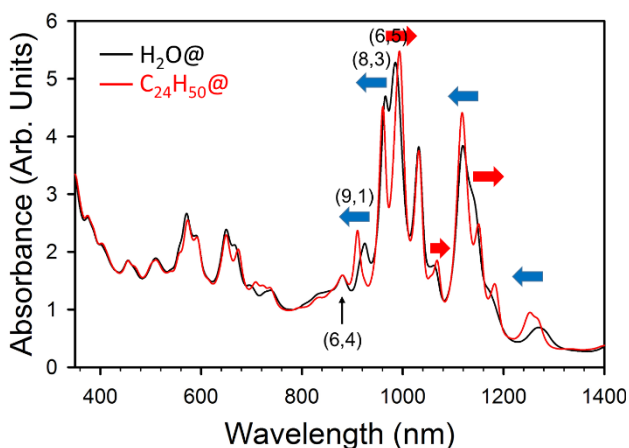


Figure 1. Absorbance spectra of rate-zonal ultracentrifugation purified dispersions of water (black line) and C₂₄H₅₀ (red line) filled SWCNTs. Peak features are due to the intrinsic optical transitions of the SWCNTs. The difference in the endohedral environment of the SWCNTs due to H₂O or C₂₄H₅₀ filling are responsible for the differences in position of the optical transitions; arrows

highlight the observed peak shift directions for going from water to alkane filling for selected E11 peaks. Clearly, the (n,m) distributions of the two dispersions are very similar.

In the absorbance spectra shown in Figure 1, several trends in peak position shifts are observed. At wavelengths > 1200 nm the alkane-filled sample displays strongly blue-shifted (towards higher energy) and sharpened peaks consistent with those observed previously for larger diameter SWCNTs with alkane filling.¹³ For smaller diameter nanotubes, however, with E11 peaks between 900 nm and 1050 nm, both blue and red-shifts of peaks are observed, as well as peak sharpening for the alkane-filled sample. For the smallest diameter SWCNT observed, the (6,4) with its E11 peak at ≈ 880 nm, no shift or sharpening is observed. As a blue-shift of peak transitions is expected with a reduction in the effective dielectric environment experienced by the SWCNTs, this implies that, similar to yet larger diameter nanotubes, the largest diameter SWCNTs in this population experience only the bulk effect. The (6,4) shows no effect because it is too small to be filled by the alkane molecule (hence it gets water-filled).²⁶ Intermediate to these behaviors, the small diameter nanotubes show a complicated response of both red and blue shifts to filling when the size of the molecule approximates the size of the inner pore of the nanotube.

The primary question arising from the data in Figure 1 is the source of the varied spectral response observed for the small diameter, but large enough to fill, (≈ 0.757 nm to < 1 nm diameter) SWCNT species. Hypotheses for the varied response include the breakdown of the continuum (bulk) dielectric effect for highly confined molecules, non-bulk arrangement of the filler molecules within the SWCNTs leading to an effective dielectric environment very different from the bulk value, and application of strain to the nanotube lattice. The first two of these effects are likely to be primarily dependent on the degree of confinement and should thus be the same for two SWCNTs of the same diameter. Dielectric-like effects should also affect all optical transitions for the same SWCNT in one direction. The last should also depend on confinement, but will

additionally be modified by the enveloping SWCNT's mechanical properties and electronic band structure, and thus would apply different effects to two SWCNTs of the same diameter but different chiral structure. This is particularly the case for SWCNTs of different mod index, defined as $\text{mod}(n-m,3)$, for which optical transitions should shift in opposite directions for mod1 and mod2 structures.²⁷

Due to this difference between the scaling of the hypothesized effects, SWCNT species of special interest (labelled in Figure 1) are the (9,1), (6,5), and (8,3) species, which respectively contribute the three large E11 features at ≈ 910 nm, ≈ 985 nm, and ≈ 960 nm. These species have carbon-center to carbon-center diameters²⁸ calculated to be 0.757 nm for both the (6,5) and (9,1) and to be 0.782 nm for the (8,3). If a standard approximation for the thickness of a single layer of carbon is subtracted, 0.34 nm, that then implies pore size diameters of ≈ 0.42 nm and ≈ 0.44 nm respectively. For reference, the approximate head-on cross section size of the undistorted C₂₄H₅₀ linear alkane in all anti-conformation is ≈ 0.453 nm.²⁹ The (6,5), (9,1) and (8,3) species are further useful, because they allow testing of the hypothesis for the root cause of the complex behavior using pairs of similar diameter SWCNT species, with different characteristics, at multiple pore diameters in the non-bulk behavior limit. The diameter equivalence of the (6,5) and (9,1) pair is long known; to make a pair with the (8,3) we use the isolatable *via* processing (10,0) species. The (10,0) has the closest diameter, 0.794 nm, to the (8,3), but is much less prevalent in the parent population and so does not contribute prominently to the peak features in Figure 1.

To analyze the source of the more complex behavior it is critical to utilize (n,m) purified SWCNT samples, as they enable more accurate identification of peak positions,³⁰ and in some cases can eliminate additional complexity such as differential interaction of the chiral DOC or DNA dispersants with the two enantiomers of chiral (n,m) structures. As noted in the Methods section,

the dispersions of Figure 1 were separated using a combination of ATPE techniques^{21,23,25} to yield paired populations of identically processed single (n,m) and single enantiomer water- and alkane-filled SWCNTs.

Absorbance spectra for several single (n,m) species pairs, produced from the parent dispersions shown in Figure 1, are shown in Figure 2. In each panel, the spectra for a single SWCNT species pair, alkane and water-filled of the same (n,m) , are shown. In contrast to prior results for alkane-filling of the smallest diameter SWCNT,¹³ each population (alkane or water filled) is approximately pure, *i.e.*, fully filled, as indicated by the presence of single, narrow, optical transition peaks. Surprisingly, the difference in peak positions between alkane- and water-filled samples is somewhat reduced after the purification to single (n,m) SWCNT populations relative to the larger shifts apparent in Figure 1. However, both E11 (900 nm to 1200 nm) and E22 peaks (550 nm to 750 nm) retain measurable shifts on the order of several nm in peak position. Fluorescence spectra (*vide infra*) and Raman scattering in the radial breathing mode (RBM) region (SI) support the conclusion that the SWCNTs under study remain filled. Several possibilities may account for the reduction in observed shift. Most likely is that a small number of alkane molecules leak from the ends during processing, slightly reducing the fraction of the tube length that is strained from the initial level. Externally adsorbed alkane can be disregarded as a possibility, as it would significantly affect both the rate-zonal separation and ATPE purification, which is not observed. Further discussion is included in the SI. Verification of the source of this effect, and the degree to which it may be prevented by modification of processes, are the object of future investigation.

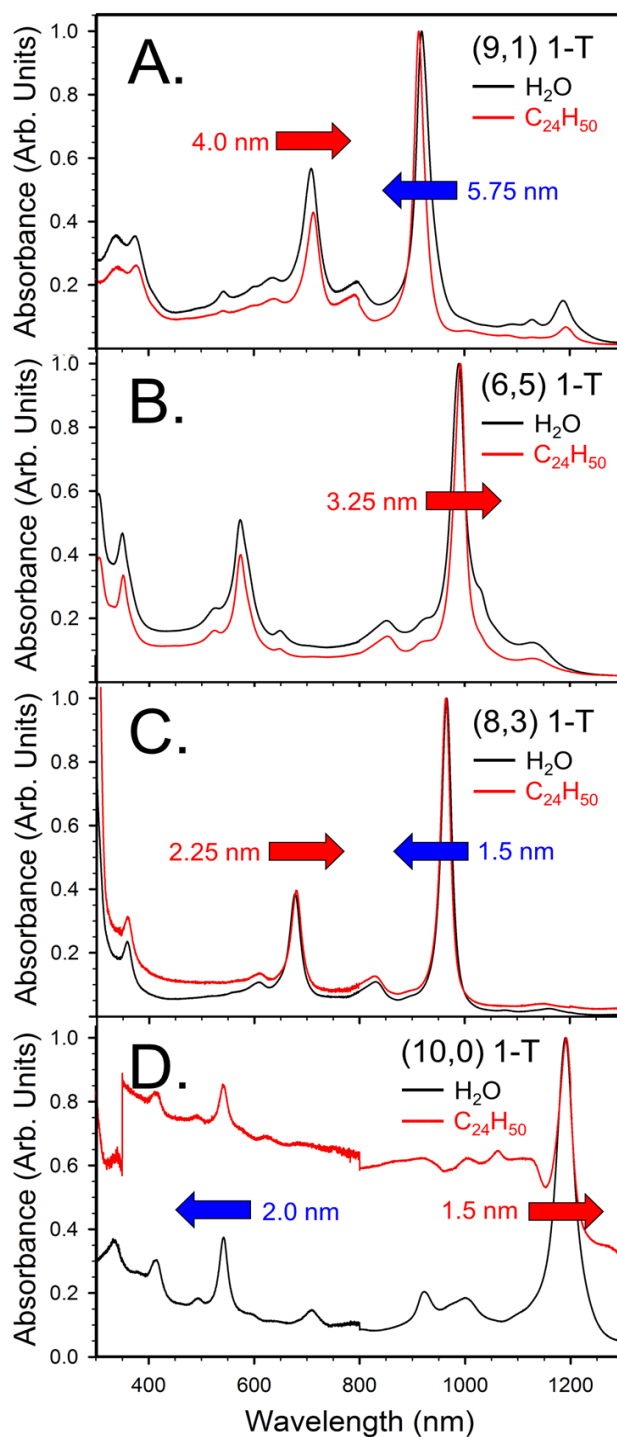


Figure 2. Absorbance spectra of pairwise identically processed single (n,m) structure SWCNT dispersions of water (black lines) and C₂₄H₅₀ (red lines) filled SWCNTs. Pairs of spectra are shown for the A. (9,1); B. (6,5); C. (8,3) and D. (10,0) SWCNT species. The separation by ATPE reduces the apparent amount of peak shift between the water and alkane-filled samples, however several nm-scale shifts are measured for the E11 and E22 transitions. For the E11 these are red-

shifts for (6,5) and (10,0) and blue-shifts for the (9,1) and (8,3); arrows indicate the direction of peak shift from water to alkane-filling. Effective dielectric effects would cause all peak features to shift in the same direction, indicating a different source (strain) of the observed behavior.

Inspection of the spectral shifts indicate that the direction of the peak shift is correlated with the mod index of the nanotube. The mod index is equal to 1 for the (6,5) and (10,0) samples, and equal to 2 for the (9,1) and (8,3) samples. Metallic and semi-metallic nanotubes are mod = 0. In both cases for the semiconducting SWCNTs analyzed in this contribution, the mod 1 SWCNTs display a red-shift in E₁₁, and mod 2 SWCNTs display a blue-shift in E₁₁. E₂₂ feature shifts are small, or in the opposite direction of E₁₁ shifts. The values for the measured shifts from absorbance spectroscopy are reported in Table 1. These observations are consistent with the effects caused by strain on a nanotube,^{27,31} and not with either of the solely diameter dependent alternative mechanisms.

Table 1. Measured shift in optical transition peak values from absorbance spectra.

Chiral Index (<i>n,m</i>)	(6,5) (1-T)	(6,5) (3-B) ^a	(9,1)	(8,3)	(10,0)	(8,4) ^a
Diameter ^b (nm)	0.757	0.757	0.757	0.782	0.794	0.840
mod index	1	1	2	2	1	1
θ (deg)	27	27	5.21	15.3	0	19.11
ΔE_{11} (nm) ^{c,d}	-3.25	-3.75	5.75	1.50	-1.50	0.75
ΔE_{22} (nm) ^{c,d}	-0.5	0	-4.0	-2.25	2.0	0
ΔE_{11} (meV) ^d	-4.1 ± 0.45	-4.7 ± 0.44	8.5 ± 0.52	2.0 ± 0.47	-1.3 ± 0.31	0.73 ± 0.35
ΔE_{22} (meV) ^d	-1.9 ± 1.3	0 ± 1.3	-9.8 ± 0.87	-6.1 ± 0.95	8.5 ± 1.5	0 ± 1.2

^a Shifts measured for additional separated fractions shown in SI, (6,5) 1-T and 3-B are opposite enantiomers of (6,5).

^b carbon center – carbon center definition diameter from ref. 28

^c Shifts are reported relative to the peak positions of water-filled SWCNTs in the same dispersant and aqueous chemical environment. A blue-shift of the alkane-filled relative to the water-filled is defined as being positive.

^d The uncertainty in each peak position is estimated as ± 0.25 nm, and is thus $\approx \pm 0.35$ nm for all ΔE_{11} and ΔE_{22} values. The uncertainty in meV units varies due to the differing wavelengths of the optical transition features and the inverse relationship between wavelength and energy.

Fluorescence emission was also measured for several of the samples. Figure 3 shows an emission intensity comparison for each pair of the (6,5) and (8,3) water and alkane-filled samples. The experiments show a marked increase in the fluorescence emission intensity of the alkane-filled populations relative to the water-filled SWCNTs as in previous results.¹³ The magnitude of this enhancement is stronger for the $C_{24}H_{50}@{(8,3)}$ sample than for the $C_{24}H_{50}@{(6,5)}$ sample, also consistent with previous observations. In addition to the intensity enhancement, the peak emission wavelength also shifts with alkane-filling for both pairs. These shifts are consistent with the observed shifts in E11 absorbance peaks measured for the same samples, but are measured at lower spectral resolution due to instrumental limitations.

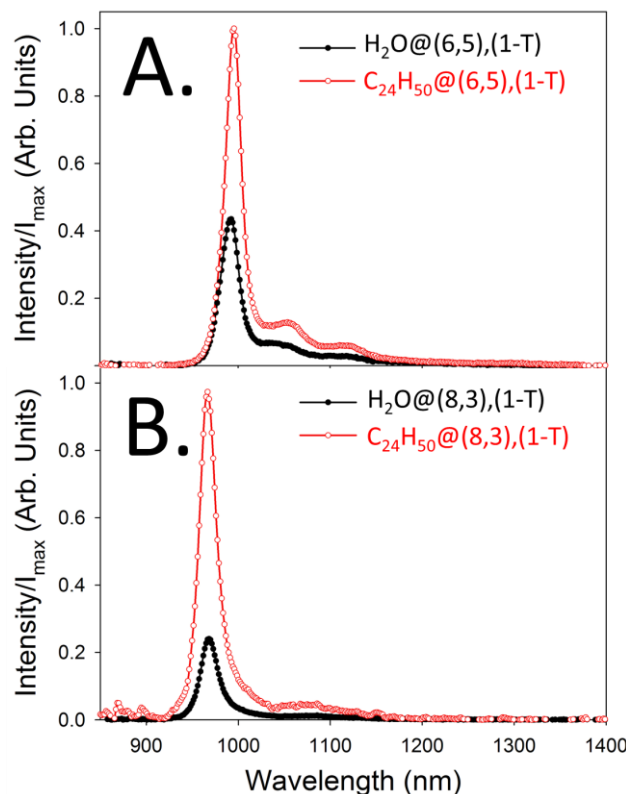


Figure 3. NIR fluorescence emission spectra for A. water and alkane-filled (6,5) SWCNTs, 1-T DNA-ATPE separated fractions, in 10 g/L DOC; B. water and alkane-filled (8,3) SWCNTs, 1-T

DNA-ATPE separated fractions, in DNA dispersion. Emission is compared after scaling for SWCNT concentration, followed by normalization to the maximum intensity in the panel. Each sample was measured at its independently determined E22 peak. Alkane-filling results in increased emission intensity in both sample pairs in line with prior results, as well as shifts in the emission peaks similar to those measured for E11 absorbance peaks for the same samples.

Unfortunately, the emission intensity in Figure 3 is not entirely from a single peak feature. In particular, in Figure 3A several side bands at lower emission energies are observed. These features are consistent with spectra observed for mildly oxygen-doped SWCNTs,³² indicating that the oxidation and annealing methodology used to fully open the SWCNT ends in this contribution is likely somewhat damaging to the nanotubes in a manner that is not recovered through the annealing step. Thermogravimetric measurements (SI) also indicate that significant mass loss of the SWCNT soot occurs at the conditions utilized in this work, and that this mass loss is not easily decoupled from the full opening of the ends. Research into optimizing oxidation and annealing conditions and other potentially milder methods for fully opening the SWCNT ends is ongoing.

Evaluating the observed phenomenon as strain, we follow Leeuw *et al.*³¹ and plot the E11 and E22 energy shifts versus the value of $(-1)^{i+1}(-1)^{k+1}\cos(3\theta)$ for each SWCNT pair in Figure 4, in which k is the mod index, i is the order of the optical transition E_{ii} , and θ is the chiral angle of the nanotube. As each pair of samples is composed of the same SWCNT (n,m) from the same and identically processed SWCNT soot and in the same solution environment, contributions to the peak shifts from the arrangement on exohedral environmental factors or from differences in defect density can be neglected. Differences can be attributed instead to factors resulting in a difference in the bulk endohedral dielectric, which should be approximately identical for SWCNTs of the same diameter, and strain derived effects. The former should appear as an offset from zero on the vertical axis intercept in Figure 4, whereas the slope will reflect strain.

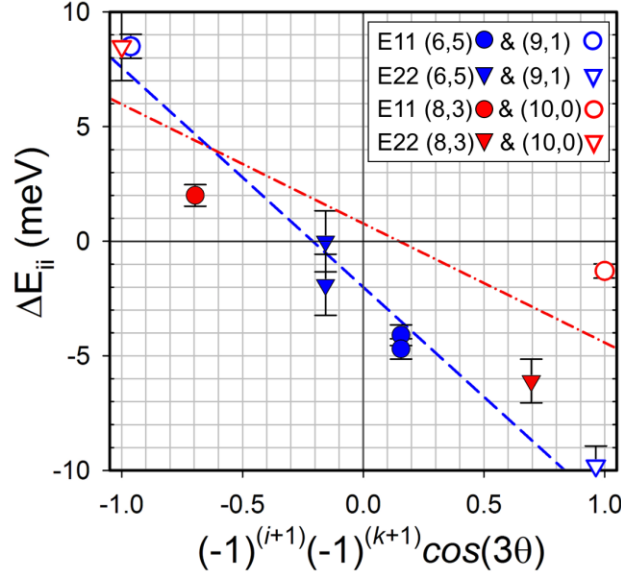


Figure 4. Energy shifts measured for the (6,5), (9,1), (8,3) and (10,0) SWCNT species water and alkane-filled pairs from Table 1 plotted versus the nanotube structural factor $(-1)^{i+1}(-1)^{k+1}\cos(3\theta)$. Since both E11 and E22 energy shifts are measured from absorbance peak positions we use the multiplicative factor $(-1)^{i+1}$, not used in ref. 31, to reflect the E22 points relative to the E11. The lines are the best linear fit through the two sets of values corresponding to the two different SWCNT diameter pairs. The slope of the line through the peak shifts for the (9,1) and the two (6,5) enantiomers is significantly steeper than the slope for the larger diameter (8,3) and (10,0) peak shifts, indicating a greater applied strain in the smaller diameter SWCNTs from the alkane-filling. For reference, at constant SWCNT diameter, a solely dielectric effect would appear as a horizontal line on such a plot.

In Figure 4, the data for the (6,5) and (9,1) are best fit by an appreciably steeper line, indicating a greater degree of applied strain, than the data points for the larger diameter (8,3) and (10,0) pair. This is exactly what is expected for filling with a mechanically compressible molecule that is inserted into a smaller, (6,5) and (9,1), or larger, (8,3) and (10,0), cavity respectively. Interestingly, the linear fit to the (6,5) and (9,1) pair data also shows a non-zero/negative y-intercept at zero value of the structural parameter indicative of an effective dielectric constant increase with the replacement of water with the linear alkane in the interior volume. This surprising observation

may, however, be due to the fact that the water in the comparison sample is known to adopt highly non-bulk configurations in these SWCNTs,³³⁻³⁵ and thus may not exhibit the expected large value for its effective dielectric. This unexpected feature is also absent for the larger (8,3) and (10,0) pair, for which the apparent dielectric driven change, albeit in a poorer fit attributable to the slightly mismatched diameters of the two structures, is seen to be in the expected direction.

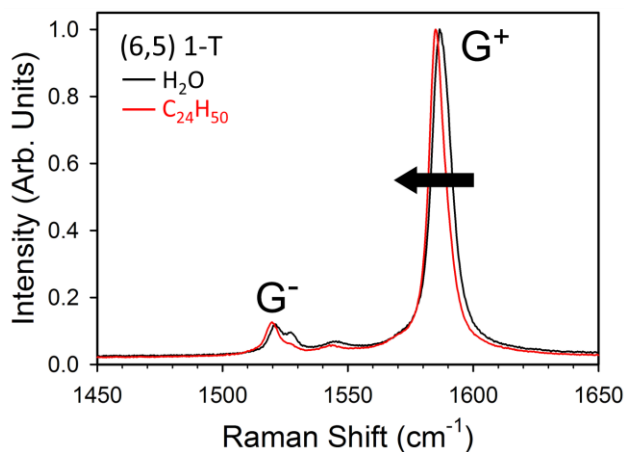


Figure 5. Resonant Raman scattering spectra observed for the water (black curve) and alkane-filled (red curve) (6,5) SWCNTs in the G-band region with 573 nm (resonant) excitation. Both the G⁻, and G⁺ peak features are shifted to ≈ 2 cm⁻¹ lesser values in the alkane-filled SWCNT relative to the water-filled peak positions.

The observation that the peak shifts from alkane filling are consistent with applied strain leads to the question of the nature of the strain and its direction. Because the samples are dispersed in liquid and composed of the same SWCNTs, it is unlikely that the strain is due to either torsional or bending deformation of the SWCNT lattice. Instead, the source must be either uniaxial or radial lattice deformation. To distinguish amongst the strain sources and directions on the nanotube lattice, resonant Raman spectroscopy was measured for the (6,5) alkane and water-filled pair. Figure 5 shows that the alkane-filled SWCNT G-band modes peak at lower Raman shifts

frequencies (lower energies) than the modes in the corresponding water-filled sample. This softening of the modes implies that the type and direction of the strain from alkane filling is radially expansive. This is schematically illustrated in Figure 6, in which the expected direction of peak shifts for each of the four possible strain modes are presented. This direction of the strain is reasonable, as pressure from the encapsulated alkane should push radially outwards on the inner cavity surface. Another possibility is that the water-filled SWCNTs are strained in radial compression, and thus are not a neutral reference point for comparison to the alkane-filled samples. Unfortunately, literature data for the G-band shift from empty to water-filled (6,5) SWCNTs, or the other species utilized here, are not available. The observation that the E11 peak features for the similarly dispersed (6,5) SWCNTs populations occurs in the order of empty, water-filled and then alkane-filled from bluest to reddest, however, makes this possibility unlikely.

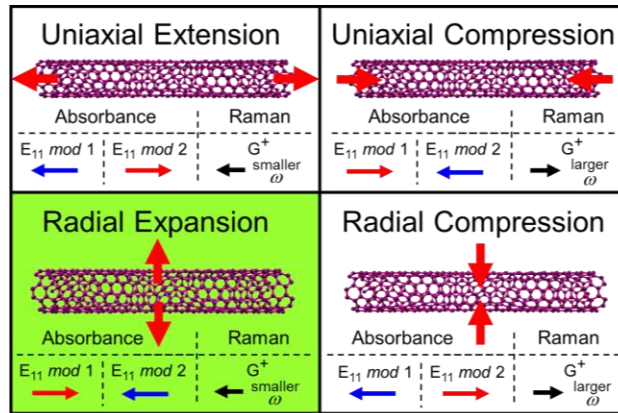


Figure 6. Diagram of the potential strain types and their respective directions for optical property shifts. Shifts in absorbance and fluorescence observed here imply either radial expansion or uniaxial compression as the source of the strain. Of the two, however, only radial expansion is consistent with the observed shift in the Raman G-band.

Interpreting the slopes of the lines in Figure 4 as strain, we can estimate the degree of strain applied to the nanotubes using theoretical or empirical relations. Peak shifts in the optical

transition wavelengths have been predicted as a function of uniaxial strain,²⁷ and applied to calculate radial strain from fullerene encapsulation for ≈ 1.3 nm diameter SWCNTs.^{11,12} For the smaller diameter SWCNTs used in this work, we instead compare to an empirical relation extracted from the data of Leeuw *et al.*³¹ for uniaxial strain on ≈ 1 nm diameter SWCNTs; they report their values to match well with those theoretically expected for realistic values of both the electron-phonon coupling and Poisson ratio,³¹ or the updated theory of Huang *et al.*³⁶ For the (6,5) and (9,1) SWCNTs, the slope in Figure 4 is $\approx 78 \text{ cm}^{-1}$. In ref. 31 the best fit slope through 10 SWCNT species was found to be $710 \pm 30 \text{ cm}^{-1}/(\% \text{ strain})$. Using these values, we estimate the applied strain for the (6,5) and (9,1) to be $\approx 0.1 \%$ if the modulus and response of the SWCNTs are assumed to be similar for radial and uniaxial strain. For the larger (8,3) and (10,0) pair, the slope $\approx 42 \text{ cm}^{-1}$ and the estimated strain is subsequently less, at $\approx 0.06 \%$. If we make a similar assumption for strain effects on the Raman G-band, the degree of strain estimated for the (6,5) pair also matches extremely well with the value of $\approx 0.1 \%$ strain that can be calculated independently using the $\approx 1.7 \text{ cm}^{-1}$ peak shifts in the G-band modes³⁷⁻³⁹ shown in Figure 5. Both of these strain estimates are also significantly less than the 0.6% strain calculated for C₆₀ inserted at high temperature in its sieving limit,¹² consistent with the low energy route of alkane insertion and its lower modulus.

An estimation of the degree of strain can alternatively be approached by comparison to literature reports on SWCNT properties under radial compression. Lebedkin *et al.*⁴⁰ report G-band shifts for hydrostatic radial compression with positive slopes of $(8.0 \pm 0.2, 6.5 \pm 0.6, \text{ and } 8.0 \pm 0.5) \text{ cm}^{-1}/\text{GPa}$ for small diameter semiconducting nanotubes dispersed in an aqueous sodium cholate solution at excitations wavelengths of 514 nm, 633 nm, and 785 nm respectively. G-band shifts for hydrostatic compression have also been reported for dispersed ≈ 1.4 nm diameter SWCNTs in DOC of $10 \pm 0.2 \text{ cm}^{-1}/\text{GPa}$ and $7.0 \pm 0.2 \text{ cm}^{-1}/\text{GPa}$ for empty and water-filled SWCNTs,

respectively,⁴¹ and for SWCNT powders of ≈ 1.4 nm diameter in varying pressure transmitting media of approximately (6 to 10) cm⁻¹/GPa.⁴²⁻⁴⁵ The similarity of these results across diameter ranges and pressure transmitting media imply an apparent expansive pressure on the order of 0.2 GPa from alkane filling. This value allows for estimation of the strain through the Young's modulus (Y). For $Y \approx 1$ TPa,⁴⁶ the projected strain, σ , is thus $\sigma = \frac{0.2 \text{ GPa}}{Y} = 0.02 \%$, which is within reason given the rough manner of the estimation. Unfortunately, more precise estimation, or similar calculations of the filling strain from comparison of the E11 and E22 positions to those observed for radial compression, are limited by the lack of appropriate data to compare against, and, more importantly, by convoluting phenomena driven by applied pressure. For instance, Torres-Dias *et al.*³⁸ observed mod-independent red-shifts of both E11 and E22 optical transitions under applied compression and attributed it to condensation of additional surfactant altering the local dielectric constant. Such phenomena preclude comparison to the current data set.

Implications of strain as a measurable contributor to the optical properties of nanotubes after filling are manifold. At the highest level, it highlights that the packing of individual molecules into nanoporous structures is likely to be highly molecule specific, and especially complex as a function of the SWCNT diameter near the sieving threshold of fitting the filler into the nanopore. For nanotube applications, it suggests that complex factors beyond a bulk dielectric constant effect may be expected to complicate studies examining the effects of filler choice. This is particularly important, because this work demonstrates that strain can be generated even from liquid molecules at or near room temperature, and is not limited to high temperature sublimation in which molecules such as C₆₀ might be inserted despite energetic barriers.^{47,48} In contrast, the continued existence of the interior applied strain from alkane filling indicates either a kinetic barrier to the ejection of the filler molecules, and/or a significant enthalpy of adsorption for alkane ingestion as compared to

water in these SWCNTs. This agrees with simulations and experiments that report substantial energy of absorption for alkanes into SWCNTs,⁴⁹⁻⁵¹ although no results are available for SWCNTs as small as the (6,5). The conformation of any filling molecule and the amount of strain applied may even be modifiable by factors such as the temperature of the material,^{52,53} similar to evidence of phase changes in water-structure observed previously,^{2,31} and will likely engender further investigations.

The continued observation of increased emission intensity of the alkane-filled samples in Figure 3 is also significant due to the desire for NIR emitters below 1000 nm. This is consistent with our previous reports,¹³ but further confirmatory, in that uniformly-filled populations of alkane or water-filled SWCNTs were achieved and compared using the same parent soot material. This experimental methodology, including multiple ATPE separation exchanges, removes potential alternate explanations for the increased fluorescence, such as potential differences in defect density or remaining alkane on the exohedral surface. Alkane filling is also shown to be possible at near 100 % efficiency for accessible SWCNTs, vastly increasing the mass throughput over the separation of bright empty nanotubes from water-filled SWCNTs.⁵⁴ These results further imply that alkane filling is scalable and may be compatible with other methods such as specific defect addition to additively increase SWCNT fluorescence efficiencies beyond the roughly 20 % maximum reported.⁵⁵

CONCLUSIONS

The filling of linear alkanes into the endohedral volume of small-diameter SWCNTs (< 1 nm) is shown to result in the application of radial strain on the nanotube's graphene lattice, causing shifts in optical properties in addition to effects from the dielectric constant of the nanotube interior. This effect is dominant for the smallest diameter SWCNTs filled by the linear alkane tetracosane,

leading to opposite directions of optical transition peak shifts for the equal diameter, but opposite mod, (6,5) and (9,1) SWCNTs. By extension, the potential effects of strain to the nanotube properties should be evaluated for SWCNTs near the sieving diameter of larger molecules of interest for specified filling. Future work to determine optimal nanotube opening procedures and the achievable variation in SWCNT optical properties through non-water filling is advocated.

Supporting Information. The supporting information contains UV-vis-NIR absorbance spectra documenting stages of the purified single (n,m) sample preparation, additional fluorescence and Raman spectra, and thermogravimetric measurements.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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