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May 2010

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### Recommended Citation

Aromin, Jourdan T.; Dolash, Bridget D.; and Sooter, Letha J. (2010) "Tunable Single-Walled Carbon Nanotube Fluorescence Emission Via Associated DNA Sequence," *Mountaineer Undergraduate Research Review*. Vol. 2 , Article 7.

Available at: <https://researchrepository.wvu.edu/murr/vol2/iss1/7>

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# TUNABLE SINGLE-WALLED CARBON NANOTUBE FLUORESCENCE EMISSION VIA ASSOCIATED DNA SEQUENCE

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## Abstract

Single-walled carbon nanotubes, or SWCNTs, are nanomaterials that possess unique characteristics, most importantly their differing structural arrangement in terms of chirality. Each single-walled carbon nanotube exhibits a unique fluorescence spectra that is dependent upon its chirality. The association of single-stranded DNA (ssDNA) with SWCNTs is monitored by near-infrared fluorescence spectroscopy. The DNA:SWCNT hybrid exhibits fluorescence spectra dependence upon both the selected sequence and the selected chirality.

## Introduction

Single-walled carbon nanotubes (SWCNTs) are a type of carbon-based nanomaterial that show unique optical, electrical, and thermal properties. These properties can be manipulated for molecular detection. SWCNTs normally vary in their physical structure in terms of chirality (Saito, Dresselhaus, and Dresselhaus 1998). Variations in chiralities correlate with variations in properties such as diameter and conductivity. Each chirality appears at different wavelengths in optical spectra. This allows the use of optical spectroscopy to differentiate between each chirality. This can be accomplished by analyzing the absorbance and fluorescence emission spectra from SWCNTs. When specific sequences of single-stranded DNA are bound to the SWCNT, changes from the native spectra may also be observed using this method. Comparisons and characterizations of different SWCNT suspensions are therefore straightforward.

SWCNTs are composed of 1-carbon thick walls and are cylindrical in shape. Diameters of SWCNTs typically range from 1 to 2 nm, but vary depending on chirality. The chirality associated with the SWCNT is denoted by a (n,m) system, where n and m represent the number of vector units along their corresponding directions. These units in each direction dictate how the SWCNT will wrap around itself, which in turn alters

the interactive properties of the SWCNT. SWCNTs can be synthesized using chemical vapor deposition (CVD). CVD is a process in which gaseous molecules are decomposed into their reactive species, eventually resulting in new particle growth (Che et al. 1998). CVD allows the production of these SWCNT and provides control over the synthesized structure.

A major challenge in the characterization of carbon nanotubes is their extreme hydrophobicity. In order to overcome poor aqueous solubility, SWCNTs must be dispersed using a surfactant such as sodium dodecyl sulfate (SDS) or sodium cholate. Aqueous dispersion of SWCNTs can also be achieved by using DNA, which has a stronger association than other surfactants (Sánchez-Pomales, Santiago-Rodríguez, and Cabrera 2009). It is hypothesized in the literature that the DNA interacts with SWCNTs through non-covalent interactions, in particular through  $\pi$ -stacking between the nucleotide bases of the DNA and the highly  $\pi$ -conjugated sidewalls of the SWCNTs (Yang et al. 2008; Zheng et al. 2003). Efficient dispersal depends on the sequence of DNA used—most effective short sequence identified being a 30-nucleotide alternating thymine-guanine nucleotides (TG15) (Zheng et al. 2003).

Here, SWCNTs were dispersed by SDS or varied DNA sequences. The SWCNTs are sonicated with the surfactant to produce DNA/SWCNT or SDS/SWCNT conjugates. The conjugates were characterized by ultraviolet-visible (UV-VIS) and near-infrared (NIR) absorbance spectroscopies and NIR fluorescence spectroscopy. UV-VIS spectroscopy allows a method of quantifying the concentration of DNA attached to SWCNTs by comparing it to the SDS sample, void of DNA, attached to the same chirality. The SDS/SWCNT spectra serve as a background spectra allowing quantification of DNA. SWCNTs have spectral features in the NIR region using fluorescence spectroscopy. DNA is void of spectral characteristics in this region. By monitoring changes in the NIR-fluorescence region as the DNA sequence is varied, conclusions can be drawn as to how different DNA sequences interact with individual chiralities of SWCNTs.

## Results

Three different chemically synthesized DNA oligonucleotide sequences (IDT, Coralville, IA) were individually sonicated with a mixed SWCNT sample (Sigma-Aldrich, St. Louis, MO). Table 1 lists the three sequences used.

Table 1. Oligonucleotide sequences used with each corresponding name.

T30	5'-TTT TTT TTT TTT TTT TTT TTT TTT TTT-3'
TG15	5'-TGT GTG TGT GTG TGT GTG TGT GTG TGT GTG-3'
R.LS.N52	5'-ACG TCT CGT CAA GTC TGC AAT GTA-3'

NIR fluorescence spectroscopy (using excitation wavelengths of 638 nm, 690 nm, and 784 nm) showed peak shifts between each of the DNA sequences used. At the 638nm excitation, peak emissions between 1035nm and 1050nm correspond to the (7,5) chirality for CVD synthesized single-walled carbon nanotubes. The wavelength of the peak maxima differ between all three DNA sequences. At the 638 nm excitation, peaks corresponding to the (7,5) chirality, R.LS.N52 yields a peak position at 1046.11 nm, while T30 and TG15 peaked at 1043.449 nm. Another peak can be seen for T30 prior to its characteristic (7,5) peak. This represents an additional SWCNT hybrid, but there is insufficient data to determine what chirality has caused the peak to occur (see Figure 1). Spectra intensities varied according to DNA sequence with T30 being the least intense and R.LS.N52 being the most intense.

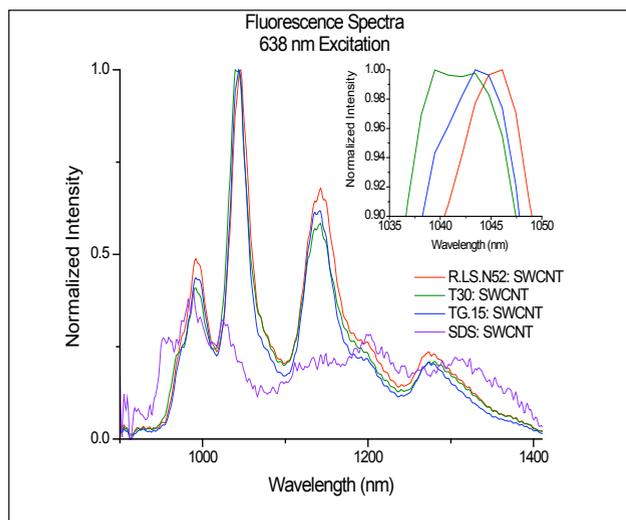


Figure 1. Near-infrared fluorescence emission spectra at an excitation wavelength of 638 nm. Emission spectra are shown for each DNA sequence and SDS hybridized to SWCNTs.

At an excitation of 690 nm, fluorescence spectra also show shifted peaks at wavelengths that correspond to different chiralities when the DNA sequence is varied. Peaks corresponding to the (6,5) chirality were positioned at 991.7304 nm for both the R.LS.N52 and TG15, but the T30 peaked at 990.4086 nm. The peaks corresponding to the (7,5) chirality at an excitation of 690 nm shifted with sequences similarly to the shifts seen at 638 nm. R.LS.N52 peaked at 1044.78 nm, whereas the T30 and TG15 were shifted at 1043.449nm. See Figure 2. Peak intensities varied according to DNA sequence as they did with the 638nm excitation.

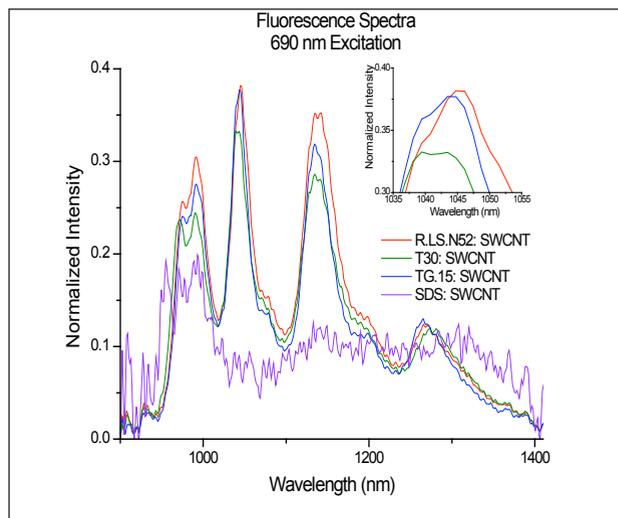


Figure 2. Near-infrared fluorescence emission spectra at an excitation wavelength of 690 nm. Emission spectra are shown for each DNA sequence and SDS hybridized to SWCNTs.

At a 784 nm excitation, the fluorescence spectra show shifts between all three sequences can be found in the wavelength that corresponds to the (7,5) chirality. The R.LS.N52 sequence shifts the peak to 1046.11 nm, while the T30 shifted peak is at 1039.459 nm. The TG15 sequence yields a shifted peak at 1043.449 nm (see Figure 3, next page). Again, peak intensities are weakest for the T30 sequence and greatest for the R.LS.N52 sequence.

Data from the NIR fluorescence spectra were also used to determine the relative soluble abundance of chiralities present when dispersed with differing DNA sequences. This is an indicator of how well the individual DNA sequences associate with the SWCNT. The (6,5) chirality was the predominate chirality for each of the three sequences. Other chiralities exhibited varied numerical data that varied when the sequence of DNA was changed (see Table 2).

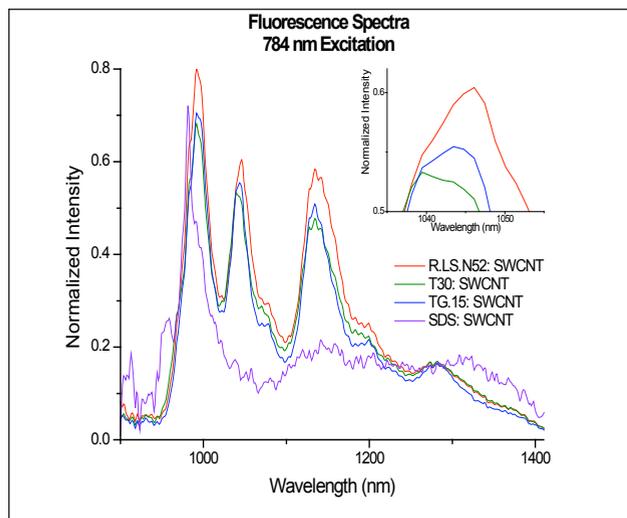


Figure 3. Near-infrared fluorescence emission spectra at an excitation wavelength of 784 nm. Emission spectra are shown for each DNA sequence and SDS bound to SWCNTs.

Table 2. Relative abundance percentage of chiralities in each mixture containing different DNA sequences.

(n,m)	R.LS.N52	T30	TG15
(6,5)	24.2823	20.7167	23.7913
(9,4)	11.536	6.2637	0
(8,4)	0.2697	7.3453	18.00823
(7,6)	8.537	6.633	7.13
(13,2)	0.0233	0.2033	0.06074
(12,7)	0.4247	0.4953	0

## Discussion

The results at all three excitations (638nm, 690nm, and 784nm) exhibited fluorescence emission peak shifts when the DNA oligonucleotide sequence was changed. This data indicates that the optical properties of SWCNTs are indeed altered in respect to SDS-dispersed SWCNTs and the shifts are dependent on the sequence selected. However, not all peaks corresponding to chiralities within the spectra were shifted with sequence variation. This provides further support that chiralities interact with different DNA sequences at differing levels of strength. A previous study has shown that the wrap-

ping of carbon nanotubes by single-stranded DNA is sequence dependent (Zheng et al. 2003). Our data expands upon this observation, showing that the electronic and optical properties of the SWCNT are affected by the sequence of the associated DNA. These properties account for the highly specific and sensitive spectra of a DNA:SWCNT hybrid.

The relative abundance of each chirality found in Table 1 reiterates the importance of the DNA sequence for the SWCNT hybrid. While some chiralities like (6,5) may interact extremely well with all three of the tested sequences, other chiralities such as (9,4) exhibit a wide variation. It can easily be bound to form a hybrid with R.LS.N52, but when TG15 is used this chirality is absent in the mixture.

Due to the sensitivity of the spectra, optical spectroscopy of SWCNTs can be utilized for many different applications. Unique electrical and optical properties provide the opportunity for biosensor development in conjunction with DNA aptamers. Aptamers, which can be generated through *in vitro* selection, are biomolecules that bind with high affinity and specificity to a target. The sensitivity of the spectra based on sequence variation and interactions with different chiralities supports the further use of *in vitro* selection using ssDNA. This preliminary experimental data on DNA/SWCNT hybrids collected during characterization supports that the chiralities present in a mixture is dependent on the DNA sequence.

## Methods

### Preparation of DNA/SWCNTs.

Single-walled carbon nanotubes (2 mg) are measured in the aluminum weigh boat and then transferred into a 5-mL round-bottom culture tube. Phosphate buffered saline (PBS, pH 7.4) (2 mL) are then also added to the round-bottom culture tube. The selected DNA sequence is added to the SWCNT solution at a 1:1 weight ratio. After the DNA is added, the 5-mL round-bottom culture tube is placed into a test tube holder contained in an ice bath to reduce heat during sonication. The mixture is then sonicated using a probe sonicator at approximately 8 watts for 120 minutes.

The sonicated DNA/SWCNT sample is aliquoted into two separate 1 mL samples and centrifuged for 90 minutes at 16,000 g. Centrifuged samples are separately placed in Amicon Ultra-4 Centrifugal Filter Devices and diluted with double-distilled water (ddH<sub>2</sub>O) to a total volume of 4 mL. The samples were then filtered according to the manufacturer's protocol. Briefly the devices were centrifuged for 15 minutes at 4,000 RPM, the fil-

trate collected, and the sample diluted to 4mL. These steps were repeated two times, including the collection of filtrate between rounds of centrifugation. The filtered sample is collected and placed into two separate eppendorf tubes containing PBS (500  $\mu$ L) for storage. The DNA/SWCNT hybrids are stored at room temperature and are stable for several weeks.

#### Preparation of SDS/SWCNTs

SWCNTs (2 mg) were weighed and placed into a 5-mL round-bottom culture tube. A 1% SDS solution (2 mL) was added. The tube was placed into a test tube holder contained in an ice bath to reduce heat during sonication. The mixture is sonicated using a probe sonicator at approximately 8 watts for 90 minutes. The sonicated SDS/SWCNT solution is still aliquoted into two separate 1 mL portions and centrifuged for 90 minutes at 16,000 g. The samples are collected and stored at room temperature.

#### *Optical Spectroscopy*

NIR fluorescence spectroscopy was obtained using using a NanoSpectralyzer (NS1) from Applied NanoScience. Dilutions of each DNA/SWCNT were made to be 1:50 and the SDS/SWCNT to 1:10. The diluted samples were placed in a quartz crystal cuvette. The NIR fluorescence emission spectra were measured using excitation wavelengths of 638 nm, 690 nm, and 784 nm.

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