Photophysics of Individual
Single-Walled Carbon Nanotubes

by

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Dedication

For my family and Adam

Curriculum Vitae

The author was born in Gowanda, New York on October 18, 1982. She attended the State University of New York College at Fredonia from 2000 to 2004, where she graduated *summa cum laude* with a Bachelor of Science degree in Chemistry with Adolescence Education and Honors in Liberal Arts in 2004. During her undergraduate studies, she received the Chemistry Department Dingley Scholar Award in 2001, the Thumm Analytical Chemistry Award in 2003, and the Gilbert and Ruth Moos Outstanding Senior Award in 2004. She came to the University of Rochester in the Fall of 2004 and began graduate studies in chemistry. During her tenure at the University of Rochester, she received the Hugh Alan Ewart Research Fellowship in 2004 and 2005, the Robert and Marian DeRight Research Fellowship in 2006, the Elon Huntington Hooker Research Fellowship in 2007, and the Agnes M. and George Messersmith Research Fellowship in 2008. She pursued her research in physical chemistry under the direction of Professor Todd D. Krauss and received the Master of Science degree in Chemistry from the University of Rochester in 2006.

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“Turns out not where, but who you’re with, that really matters.”

—*Dave Matthews*

Abstract

Single-walled carbon nanotubes (SWNTs) are hollow cylinders of graphene with unique mechanical, electrical, and optical properties that are directly influenced by their exact diameter and chirality. Stable near-infrared fluorescence from semiconducting SWNTs could generate significant advances in the fields of biological imaging, single molecule sensing, telecommunications, and quantum optics. Still, one factor potentially limiting the development of applications based on SWNT fluorescence is their extremely low fluorescence quantum yield (QY), which is typically $<0.1\%$. Surprisingly, the fluorescence from individual SWNTs can be detected with relatively high signal-to-noise, making it unclear if the low luminescence efficiency is an intrinsic property of all nanotubes. Further, elucidating the intrinsic QY of carbon nanotubes could provide important insights into their fundamental photophysics.

SWNTs were suspended in a suite of surfactants and biomolecules using an ultrasonic technique, and the procedure was optimized for subsequent single molecule investigations. Epifluorescence microscopy revealed important features of individual SWNT fluorescence such as Lorentzian line shapes, narrow line widths, and the absence of blinking at room temperature. To determine the luminescence efficiency of individual SWNTs, the fluorescence from individual nanotubes was compared to single CdTe/ZnS quantum dots with a well-defined QY. For the brightest SWNTs, the QY was $\sim 3 \pm 1\%$, suggesting that the intrinsic nanotube QY is much higher than previously believed.

To quantify the population of emissive particles and further clarify the role of extrinsic factors on the QY, correlated measurements of fluorescence and topography

were performed for individual SWNTs. These studies elucidated that only ~6% of all isolated SWNTs are emissive and that approximately one-third of SWNTs are bundled, suggesting that the QY is low because only a small population of SWNTs is bright. Further, SWNT photoluminescence exhibited a strong dependence on the local environment. Thus, with appropriate tailoring of the SWNT surroundings, it may be possible to engineer carbon nanotubes that have brighter luminescence than current samples. In the future, the availability of higher-quality SWNT starting materials will enable further clarification of the intrinsic photophysical properties of carbon nanotubes and will inform the rational development of applications based on these fluorophores.

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by curve A and the data points between 950 and 1800 nm were empirically fit by a third order polynomial given by curve B.

$$\begin{aligned}\eta_A &= 1.7778 \times 10^{-8} \lambda^3 - 5.5048 \times 10^{-5} \lambda^2 \\ &\quad + 5.6594 \times 10^{-2} \lambda - 18.507 \\ \eta_B &= 1.4915 \times 10^{-9} \lambda^3 - 6.1261 \times 10^{-6} \lambda^2 \\ &\quad + 7.6383 \times 10^{-3} \lambda - 2.1891\end{aligned}$$

Figure was adapted from the published source.²⁴²

Figure A-2 Spectral response (R) as a function of wavelength (λ) for a 180 germanium detector (Northcoast Scientific, EO-8175) cooled to -196°C with liquid nitrogen. The data points represent an average between curves provided by two published sources.^{243,244} Data points between 800 and 1549 nm were empirically fit by a third order polynomial given by curve A and the data points between 1550 and 1800 nm were empirically fit by a third order polynomial given by curve B.

$$\begin{aligned}R_A &= -2.2719 \times 10^{-10} \lambda^3 + 2.3766 \times 10^{-7} \lambda^2 \\ &\quad + 1.0946 \times 10^{-3} \lambda - 0.55901\end{aligned}$$

$$R_B = -7.3162 \times 10^{-9} \lambda^3 + 4.1944 \times 10^{-5} \lambda^2 \\ - 8.1871 \times 10^{-2} \lambda + 54.246$$

Figure was adapted from the published sources.^{243,244} An additional published source is also available.²⁴⁵

Figure A-3 Relative efficiency (η) as a function of wavelength (λ) for a 181
300 groove/mm, 1.0- μ m blaze grating in the emission
monochromator (SpectraPro 2300i) used in epifluorescence
microscope studies. The data points between 800 and 899
nm were empirically fit by a third order polynomial given
by curve A and the data points between 900 and 1800 nm
were empirically fit by a third order polynomial given by
curve B.

$$\eta_A = 5.3333 \times 10^{-8} \lambda^3 - 1.4514 \times 10^{-4} \lambda^2 \\ + 1.3231 \times 10^{-1} \lambda - 39.483 \\ \eta_B = -7.5127 \times 10^{-10} \lambda^3 + 2.8951 \times 10^{-6} \lambda^2 \\ - 4.2008 \times 10^{-3} \lambda + 2.9060$$

Figure was adapted from the published source.²⁴²

Figure A-4 Spectral response (R) as a function of wavelength (λ) for 182
the CCD used in epifluorescence microscope studies
(Princeton Instruments, XTE 400R deep depletion Spec-
10). Data points between 400 and 762 nm were empirically
fit by a fourth order polynomial given by curve A and the
data points between 763 and 1100 nm were empirically fit
by a fourth order polynomial given by curve B.

$$\begin{aligned}
 R_A &= 1.9720 \times 10^{-10} \lambda^4 - 4.6287 \times 10^{-7} \lambda^3 \\
 &+ 3.9726 \times 10^{-4} \lambda^2 - 1.4617 \times 10^{-1} \lambda + 19.483 \\
 R_B &= 1.2108 \times 10^{-12} \lambda^4 + 1.3279 \times 10^{-8} \lambda^3 \\
 &- 4.5188 \times 10^{-5} \lambda^2 + 4.3858 \times 10^{-2} \lambda - 13.016
 \end{aligned}$$

Figure was adapted from the published source.²⁴⁶

List of Abbreviations

ADF	annular darkfield
AFM	atomic force microscopy
AMP	amplitude
CAS	sodium cholate hydrate
CoMoCAT	cobalt–molybdenum catalyst
CCD	charge coupled device
CVD	chemical vapor deposition
DCE	dichloroethane
DNA	deoxyribonucleic acid
DOS	density of electronic states
EELS	electron energy loss spectroscopy
FET	field effect transistor
FWHM	full width at half maximum
G	guanine
HiPco	high-pressure carbon monoxide
HOMO	highest occupied molecular orbital
HPLC	high-performance liquid chromatography
JDOS	joint density of electronic states
LUMO	lowest unoccupied molecular orbital
MW	molecular weight
MWNT	multi-walled carbon nanotube

NA	numerical aperture
NDC	negative differential conductance
NIR	near-infrared
PC	polycarbonate
PL	photoluminescence
PLE	photoluminescence excitation
PMMA	poly(methyl methacrylate)
QD	quantum dot
QY	fluorescence quantum yield
RBM	radial breathing mode
SDBS	sodium dodecylbenzene sulfonate
SDS	sodium dodecyl sulfate
SEM	scanning electron microscope
STEM	scanning transmission electron microscope
SWNT	single-walled carbon nanotube
T	thiamine
TB	tight binding
TEM	transmission electron microscope
VLS	vapor–liquid–solid mechanism

Foreword

For Chapter 1, Kathryn Leach, formerly of the University of Rochester Chemistry Department and presently of ACT I Corporation, provided the SEM image presented in Figure 1-2.

For Chapter 2, Todd Krauss of the University of Rochester Chemistry Department performed the band structure and DOS calculations presented in Figure 2-8. Megan Hahn, formerly of the University of Rochester Chemistry Department, synthesized CdSe quantum dots and provided their spectra for Figure 2-13. Joaquin Calcines of the University of Rochester Chemistry Department supplied a digital photograph of CdSe quantum dots presented in Figure 2-13.

For Chapters 4–6, Achim Hartschuh, formerly of the University of Rochester Optics Department and presently of the University of Munich Department of Chemistry and Biochemistry, and Jeffrey Peterson, formerly of the University of Rochester Chemistry Department and presently of the State University of New York College at Geneseo, developed the Labview and Visual Basic codes used to control the piezoelectric scanning stage and generate images for single molecule fluorescence measurements.

For Chapter 5, Sara Maccagnano–Zacher and John Silcox of the Cornell University Department of Applied and Engineering Physics performed STEM and EELS measurements for CdTe/ZnS quantum dots. Ming Zheng of DuPont Corporation provided the sample of (6,5) DNA–SWNTs that were used to perform the calculation of SWNT absorption cross sections.

For Chapter 6, Ming Zheng of DuPont Corporation provided the sample of (6,5) DNA–SWNTs that were used for studies of correlated fluorescence and topography. Kathryn Leach, formerly of the University of Rochester Chemistry Department and presently of ACT I Corporation, prepared patterned quartz substrates. She also compiled optical light microscope images of the substrates and conducted preliminary AFM measurements as presented in Figure 6-2. Julie Smyder of the University of Rochester Chemistry Department collected AFM data presented in Figures 6-5 and 6-6 for the correlated measurements.

CHAPTER 1

Introduction

Carbon is an abundant element that takes many forms, one of which is the hollow, cylindrical fullerene molecule known as a carbon nanotube. These materials have an intriguing history and alluring mechanical, electronic, and optical properties. Advances in nanotube synthesis and purification have enabled studies of their fundamental properties. Characteristics including incredible strength, ballistic charge transport, and near-infrared fluorescence make carbon nanotubes excellent candidates for incorporation into innovative applications, especially as researchers continue to better understand and control their unique properties.

1.1 Carbon Phases

Of all the elements, the special nature of carbon has long been noted, largely due to the variety and quantity of structures that it forms. Carbon is the fourth most abundant element in the universe by mass, the second most abundant element in the human body, and the basis for all known life.¹ Carbon can form over 10 million different compounds, more than any other atom; this striking diversity results from its ability to form extremely strong bonds with nearly every known element.

1.1.1 Carbon Atoms

Inside each carbon nucleus are six protons and six neutrons that contribute most of the element's mass, while six electrons orbit the nucleus and are responsible for forming chemical bonds. Two core electrons occupy the first spherically-shaped $1s$ orbital; although they do not generally affect the solid-state properties of carbon, these electrons are important because they partially screen the positive charge of the nucleus from valence electrons in the outer shell.² As a result, valence electrons can participate in bonding because they are more weakly bound to the nucleus than are core electrons. In carbon, four valence electrons partially fill the atomic $2s$ and $2p$ orbitals of the second shell. The wave functions of the electrons in these atomic orbitals can hybridize, or mix, to form molecular orbitals (i.e., sp^3 , sp^2 , or sp) that have an enhanced ability to bond with neighboring atoms.

In general, when the molecular orbitals of neighboring atoms overlap, two electrons with opposite spin share the space between the nuclei, forming a covalent bond.¹ In particular, sp^3 -hybridized atoms can form up to four σ -bonds (i.e., single

bonds), sp^2 -hybridized atoms can form up to three σ -bonds and one π -bond, and sp -hybridized atoms can form up to two σ -bonds and two π -bonds. A double bond is composed of one σ -bond and one π -bond, and a triple bond is composed of one σ -bond and two π -bonds. Unlike many other atoms that cannot create multiple bonds, such as silicon, the ability of carbon to configure its electrons in so many ways helps to explain the natural diversity of carbon compounds.¹

1.1.2 Carbon Allotropes

In nature, carbon adopts many forms even when bonded only to other carbon atoms. The four major carbon allotropes are amorphous carbon, diamond, graphite, and fullerene; each carbon phase has physical properties that depend on differences in how the atoms are arranged. Amorphous carbon has no crystalline structure, but is a disordered mix of sp^3 - and sp^2 -hybridized carbon that exists as carbon black, charcoal, or coke.³ The other three allotropes are crystalline, though their physical properties vary widely (Figure 1-1). For example, diamond is hard, colorless, and insulating. In contrast, graphite is slick, black, and conductive.

The first crystalline carbon allotrope is diamond, a highly organized network of sp^3 -hybridized carbon atoms covalently bound in a tetrahedral arrangement (Figure 1-1a). Each carbon atom forms four σ -bonds to surrounding carbons, with bond angles of 109.5° . Coupled with the immense strength of the carbon–carbon single bond (348 kJ/mol),¹ this stable tetrahedral arrangement makes diamond the hardest substance that occurs naturally and also accounts for its excellent thermal conductivity. Conversely, diamond is an insulator because its electrons are strongly localized in covalent bonds.¹

(a) Diamond

(b) Graphite

(c) Fullerenes

Figure 1-1. Three crystalline phases of carbon. (a) Diamond is a tetrahedral arrangement of carbon atoms (represented by circles), (b) graphite is composed of stacked layers of sp^2 -hybridized carbon, and (c) the carbon fullerenes include 0D buckyballs (top), 1D nanotubes (middle), and 2D graphene (bottom).

Interestingly, diamond at ambient conditions is a metastable state of carbon that slowly transforms into graphite, its thermodynamic standard state.

Graphite is the second crystalline carbon phase, and its 3D structure appears as stacked layers of carbon atoms arranged in fused six-membered rings resembling chicken wire (Figure 1-1b).¹ A single sheet of graphite is called graphene, and in this trigonal planar arrangement of molecules, each sp^2 -hybridized carbon atom forms three σ -bonds to neighboring atoms, with bond angles of 120° . One remaining $2p$ atomic orbital from each carbon atom lays perpendicular to the plane of the graphene sheet; when these $2p$ orbitals overlap with one another, they form closely spaced π -bonds that are important for stabilizing the sheet and delocalizing electrons.¹ This arrangement of π -electrons contributes to the electrical conductivity of graphite, which has metallic features because

the Fermi level resides within the electronic bands. Importantly, graphite is the parent structure for all carbon fullerenes.

The carbon fullerenes are a family of low-dimensional, cage-like structures. Fullerenes are made up of hexagonal or pentagonal groups of carbon atoms assembled into 0D spheres (buckyballs), 1D cylinders (nanotubes), or 2D planes (graphene), as depicted in Figure 1-1c. Similar to graphite, the carbon atoms in fullerenes are sp^2 -hybridized and their π -electrons are delocalized. As a result of these similarities, many characteristics of the fullerenes are closely related to those of graphite (Chapter 2). On the other hand, the electronic and optical properties of fullerenes diverge from those of graphite because their small physical dimensions impose stringent restrictions on which energy levels are available for electrons to occupy.

At physical dimensions approaching one-billionth of a meter, carbon nanotubes are classified as nanoscale materials due to the extremely small size of their diameters (~ 1 nm). Carbon nanotubes samples are powdery soot, composed of individual particles with extremely high aspect ratios (i.e., length to diameter ratios), as illustrated in Figure 1-2. These molecules come in two varieties: hollow cylinders with only one wall are single-walled carbon nanotubes (SWNTs) and those with many nested shells of SWNTs are multi-walled carbon nanotubes (MWNTs). SWNTs are perhaps the best example of a system that experiences one-dimensional quantum confinement. Nanotubes are composed of hundreds to thousands of atoms; therefore, they are larger than a simple molecule governed by quantum mechanics, but smaller than a particle described by Newton's laws of motion.⁴ This feature accounts for many of their remarkable properties.

Figure 1-2. Scanning electron microscope (SEM) image of carbon nanotubes (white lines). SEM image is courtesy of Kathryn Leach. Inset: Digital photograph of carbon nanotube soot.

1.1.3 *Discovery of Carbon Nanotubes*

Although carbon nanotubes are often regarded as modern materials, they have a fascinating history that is centuries old. For example, transmission electron microscopy (TEM) recently revealed the presence of MWNTs in the ultrahigh-carbon steel of a seventeenth century Damascus sabre, similar to those originally produced for the Crusades.⁵ The presence of carbon nanotubes in the blade gave these Middle Eastern swords unique properties, including exceptional strength, not typical of European steels, and an unusually sharp cutting edge.

The first active interest in developing carbon fibers was sparked in 1889, when Thomas Edison suggested their use as filaments for incandescent light bulbs. By 1892, a patent had been secured for growing carbon filaments via thermal decomposition of

gaseous methane, a method that is still used to produce carbon nanotubes. Studies of carbon filaments continued through the early 1900s, as materials scientists worked to prevent their formation during processing in coal and steel plants, and later in the coolant channels of nuclear reactors.⁶

Advances in understanding the growth mechanisms for carbon filaments soon made it possible to grow extremely thin fibers. Consequently, a Russian group reported the first nanometer-sized hollow carbon filaments in 1952. The authors generated the nanotubes by flowing carbon monoxide over iron at 600 °C and then imaged the fibers (~50-nm-thick) in these carbon deposits, noting that “the majority of the C particles are of an elongated wormlike shape.”⁷ Many accounts reporting the synthesis of hollow nanoscale carbon fibers soon followed, including the growth of MWNTs using chemical vapor deposition by Oberlin, Endo, and Koyama in 1976.⁸

Carbon nanotube research took off in 1991 when Sumio Iijima serendipitously observed MWNTs in carbon soot that he had produced while exploring new methods to produce fullerenes.⁹ In 1993, several small-scale methods were elucidated to produce carbon nanotubes with only one sidewall,^{10,11} and the first method for the large-scale production of SWNTs was presented in 1996.¹² Since the appearance of SWNTs, the number of scientific publications involving nanotubes has grown exponentially and totals well over 19,000 papers, with research activity currently doubling every 2 to 3 years.¹³

1.2 Production and Purification of SWNTs

Two years after MWNTs were grown in 1991, SWNTs were produced nearly simultaneously by two independent teams (i.e., Iijima and Ichihashi¹⁰ and Bethune et

al.¹¹). However, early nanotube studies focused on MWNTs because they could be generated in large quantities, whereas SWNTs were present only in small amounts and were intermixed with other forms of carbon.² Thus, it was not until 1996 that a scaled-up synthesis of SWNTs catalyzed vigorous fundamental research of nanotubes with only one sidewall.¹² In general, a high-quality SWNT synthesis is hallmarked by minimal amounts of MWNTs, fullerenes, carbon nanoparticles, and amorphous carbon. Because single-walled carbon nanotubes are the centerpiece of this dissertation, the emphasis for carbon nanotube synthesis in this chapter is placed solely on the production of SWNTs.

1.2.1 *Synthesis of SWNTs*

Three major methods have been used to produce SWNTs and are depicted in Figure 1-3: arc discharge, laser vaporization (i.e., ablation), and chemical vapor deposition (CVD). Arc discharge and laser vaporization were initially developed to produce fullerenes, whereas CVD had been used for decades to synthesize carbon filaments. These methods were originally configured to produce MWNTs, but were subsequently modified to generate SWNTs. To produce carbon nanotubes, each synthesis method requires a carbon source, a catalyst material (in general, MWNTs do not require a catalyst for growth but SWNTs do), and a high temperature necessary to evaporate the carbon source.

Arc discharge was used by Iijima to generate MWNTs in 1991⁹ and holds significance because it was the first method scaled up to produce gram quantities of SWNTs.¹⁴ In arc discharge, the carbon source is composed of two rod-shaped graphite electrodes that are separated by about a millimeter (Figure 1-3a).² SWNT synthesis is

Figure 1-3. Illustration of three common apparatuses used for SWNT synthesis. (a) In arc discharge, SWNTs form on the graphite cathode;² (b) in laser vaporization, SWNTs accumulate on the copper collector as a felt;¹² and (c) in chemical vapor deposition, SWNTs grow from metal catalyst particles loaded onto a substrate.²

achieved by drilling holes into the anode, which is subsequently filled with a powdered mix of graphite and metal catalyst (e.g., Fe, Ni, or Co). Current of ~ 100 A is passed through the electrodes at 30 V to generate a >3000 °C plasma that evaporates the carbon, thereby shrinking the length of the anode. Nanotubes collect on the negative electrode once helium gas is flowed through the chamber to cool and condense the carbon. Overall, this method can convert ~ 70 – 90% of the graphite target into SWNT ropes of approximately 5–20 nanotubes, with an average nanotube diameter of ~ 1.4 nm.¹⁴

In 1996, Smalley and co-workers developed laser ablation as a second technique to produce nanotubes (Figure 1-3b).¹² The process is carried out inside a quartz tube heated to 1200 °C. To create gas phase carbon, two sequenced Nd:YAG laser pulses are focused onto a graphite target that is doped with Co and Ni catalyst particles. As the carbon condenses to form SWNTs, argon gas is flowed in to carry the SWNTs from the target to a water-cooled copper condenser at the end of the quartz tube. Laser vaporization results in $>70\%$ conversion of graphite to SWNT aggregates (i.e., bundles) that are 5–20 nm in width and tens to hundreds of micrometers in length.

Chemical vapor deposition synthesis of MWNTs was reported by Yacaman et al. in 1993.¹⁵ For CVD growth of SWNTs, a quartz substrate is loaded with a metal catalyst and is placed inside a furnace; a carbon feedstock flows over the sample to produce nanotubes (Figure 1-3c).² The diameter distribution of SWNTs can be tuned by varying the carbon source, catalyst composition and size, growth temperature, and growth time. The carbon source is typically a gas or volatile compound such as methane,^{16,17} ethanol,^{18,19} carbon monoxide,²⁰ or a combination of these. Methane is the most commonly used hydrocarbon due to its kinetic stability at high temperatures and limited

production of amorphous carbon.²¹ Further, use of a carbon monoxide feedstock can completely prevent the deposition of amorphous carbon.²¹ The catalysts used for CVD are usually metal nanoparticles (i.e., Fe, Ni, Co, or Mo).²²⁻²⁴ Growth temperatures usually range between 500 and 1000 °C,² but lower temperatures have been used to grow SWNTs on flexible or glass substrates.^{25,26} Synthesis times vary from a few minutes to several hours, and SWNT growth ceases when the feedstock is discontinued or the catalyst becomes poisoned by amorphous carbon.^{27,28} The catalyst lifetime can be extended by using carbon sources containing oxygen^{18,24,28} or by introducing water, oxygen, or hydrogen gas during the synthesis.^{29,30}

Chemical vapor deposition offers a number of advantages over the arc discharge and laser vaporization methods for SWNT synthesis. For example, although both arc discharge and laser vaporization convert >70% of the carbon source to SWNTs, they unfortunately produce nanotubes as tangled bundles in a powdery soot. Additional steps are also required to separate the nanotubes from the carbon target. Both of these synthesis techniques require specialized equipment to evaporate targets at extremely high temperatures, a process that consumes huge amounts of energy. On the other hand, CVD uses simple equipment and facilitates controlled growth of SWNTs (i.e., horizontal or vertical direction)²⁷ that are intrinsically isolated from the gas-phase carbon source. Because CVD is used to produce the two commercially available SWNTs that were used in this work, HiPco (high-pressure carbon monoxide) and CoMoCAT (cobalt–molybdenum catalyst) SWNTs, only the CVD growth mechanism is considered here.

1.2.2 Growth Mechanism for SWNTs

The vapor–liquid–solid mechanism (VLS) underlies the growth of many 1D crystals that are grown by CVD, including whiskers, nanorods, and nanotubes. Growth of a crystal by direct adsorption of a gas-phase molecule onto a solid surface is very slow; VLS instead makes use of a solid-state carbon–metal solution to nucleate SWNT crystal growth.³¹⁻³³ Specifically, the catalyst decomposes and adsorbs the gas-phase carbon molecule. Once the solution is supersaturated, the carbon atoms diffuse to the catalyst surface and precipitate as sp^2 -hybridized carbon in the form of a cylinder, a configuration that is favored because of its high structural stability and lack of dangling bonds.²⁷ Because the structural energy of a nanotube depends only weakly on its chirality, it is not currently possible to synthesize one SWNT structure selectively. However, it was recently elucidated that SWNTs grow by an axial screw dislocation that determines the rate of growth as well as the chirality of the SWNT that is produced.³⁴

Two categories of VLS that are relevant to nanotube synthesis are tip growth and base growth (Figure 1-4).³¹ Specifically, if the catalyst particle is weakly attached to the substrate, it will ride along the developing tip of the SWNT during synthesis (tip growth);^{19,35,36} on the other hand, growth will proceed from the SWNT base if the catalyst is strongly associated with the substrate (base growth).^{37,38} Atomic force microscopy (AFM) or TEM can elucidate whether the catalyst particle is situated at the tip or base of the SWNT during synthesis (Figure 1-4).

Figure 1-4. Depiction of carbon nanotube growth mechanisms.³¹ (a) In the tip-growth mechanism, the nanotube grows away from the substrate after the catalyst separates from the surface. Inset: TEM image of CVD carbon nanotubes synthesized at 550 °C from an ethylene feedstock (dark spots are nickel catalyst particles).³⁹ (b) In the base-growth mechanism, the nanotube grows from the substrate because the catalyst is strongly bound to the surface. Inset: TEM image of CVD carbon nanotubes synthesized at 900 °C from a methane feedstock (the black arrow indicates iron oxide catalyst particles).³⁸ Figure was adapted from ref 40.

1.2.3 Purification of SWNTs

Advanced measurements as well as practical applications require highly purified SWNTs.²⁷ Nanotube purity is usually defined as the “isolation of carbon nanotubes from other entities”, opposed to separating SWNTs that have different structures (*vide infra*).² To allow studies of intrinsic SWNT properties, it is essential to remove metal catalyst particles, support systems, and sp^3 -hybridized carbon after synthesis. Because each of these impurities requires different treatments for removal, nanotube purification is a multistep process; care must be taken to minimize additional contamination or structural damage to the nanotube sidewall at each step.²⁷ One further challenge is that most traditional chemical purification methods such as filtering, chromatography, and centrifugation have shown limited effectiveness for isolating nanotubes from impurities.²

A combination of dry and wet methods is used to purify SWNTs from unwanted forms of carbon and metal catalyst particles. One efficient dry purification technique is oxygen burning, or annealing, in which oxygen gas preferentially oxidizes both amorphous carbon and sp^3 -hybridized carbon nanoparticles, which are more reactive than sp^2 -hybridized SWNTs.^{41,42} Wet techniques such as liquid or size-exclusion chromatography^{43,44} and high-speed centrifugation⁴⁵ provide limited SWNT separation from other forms of carbon. Still, the primary obstacle for nanotube purification is removal of residual metal catalyst particles that embed between the SWNTs; these particles are more stable than nanotubes and are therefore difficult to remove.²⁷ Removal of the catalyst is usually accomplished with a nitric acid reflux, which also eradicates any remaining superfluous carbon.^{41,46-48} Although dry and wet purification methods remove

the majority of residual carbon and metal catalysts, it is important to note that some residual impurities remain in all current SWNT samples.

As mentioned, defect sites can be introduced to the nanotube sidewall during synthesis, purification, and subsequent processing.⁴⁹ The role of defects is not well understood in terms of their impact on the mechanical, electronic, and optical behavior of SWNTs. For some applications, defect sites advantageously provide a reactive site for covalent attachment of particles to the SWNT sidewall. However, because sidewall functionalization of a pristine nanotube significantly alters its electronic and optical properties, only non-covalent attachment strategies are considered in this dissertation (Chapter 3).

1.3 Technological Applications

The production of high-quality SWNT samples has enabled sophisticated studies of their fundamental properties. Indeed, a wealth of recent experiments has verified many of the remarkable mechanical, electronic, and optical characteristics theoretically predicted before the onset of large-scale SWNT production. As such, nanotubes are now enticing particles for development into an array of novel applications (Figure 1-5). Especially salient for device fabrication is the ability to tune the properties of an SWNT not by altering its composition, but simply by changing its size.⁴

1.3.1 Mechanical Properties and Applications

The unique structural properties of single-walled carbon nanotubes include their small diameter and density, high strength and elasticity, and robust thermal behavior.⁵⁰

The diameter of a carbon nanotube is ~ 1 nm and its density is 1.4 g/cm^3 , about half that of aluminum.⁵⁰ The cylindrical arrangement of carbon atoms, coupled with the immense energy of the carbon–carbon bond, is responsible for the superlative strength and flexibility of carbon nanotubes. SWNTs have an incredible tensile strength of 45 billion Pa, at least 20 times greater than that of steel.⁵⁰ These flexible particles can be deformed, flattened, or bent at large angles and restraightened without damage owing to their extremely high Young's modulus (970 billion Pa).⁵¹ SWNTs are predicted to exceed the heat transmission of pure diamond by nearly a factor of 2 ($6000 \text{ W/m}\cdot\text{K}$) and can withstand temperatures up to 2800°C in vacuum or 750°C in air.⁵⁰

As expected, each of these remarkable traits has led to unique innovations (Figure 1-5). One of the areas most immediately accessible for developing applications is the use of nanotubes as components of resilient, lightweight, and high-strength composites. For example, carbon nanotubes have already been used as composite materials for sporting equipment like bicycles and hockey sticks. Their resilience to deformation has inspired their integration as sharp, highly sensitive AFM probes that facilitate the imaging of deep substrate features with very high resolution,⁵² as well as their development as artificial muscles that could eventually find use in robotics.⁵³ Carbon nanotubes have also been touted as the only material strong enough to comprise the cable of a space elevator intended to transport materials between Earth and space without need of rockets.⁵⁴

The small size of SWNTs has enabled other unique innovations. For example, because they are able to penetrate the cell membrane without any noticeable cytotoxicity, SWNTs have been suggested as vehicles for drug delivery.^{55,56} Further, when functionalized with a folate moiety, SWNTs selectively bind to cancer cells with

corresponding folate receptors; subsequent heating of the nanotubes in vivo triggers selective cell death, making SWNTs potentially attractive as cancer therapy agents.⁵⁷ Finally, SWNTs show great promise for electronics applications, as the thinnest metal wires currently available by lithography are at least 25 times wider than a nanotube and melt at one-third of the temperature that an SWNT can withstand.⁵⁰

1.3.2 *Electronic Properties and Applications*

Single-walled carbon nanotubes derive many features from their structural similarity to graphene, and their electronic properties strongly reflect this influence (Chapter 2). SWNTs are a hybrid mix of metallic and semiconducting structures. The source of this diversity is the quantum confinement of electrons around the nanotube circumference, which permits only a few of the electron wavelengths, or quantum states, of graphene to remain when the sheet is hypothetically rolled into a nanotube. Consider that an electron can behave as both a particle and a wave; electron waves can add either constructively or destructively around the SWNT circumference, and only electrons with the right wavelength, or quantum state, are not cancelled out by destructive interference.⁵⁰ Depending on the particular diameter and chirality of the SWNT, the nanotube is either metallic (~33% of structures) or semiconducting (~67% of structures).⁵⁸

SWNTs display fascinating electrical properties such as enormous current carrying capacity, ballistic charge transport,⁵⁹ negative differential conductance (NDC),⁶⁰ and field emission.^{32,61} Metal SWNTs carry 1000 times more current density than copper wires⁵⁰ and transport charges down the nanotube without significant scattering.⁵⁹

Interestingly, when a voltage is applied to metallic nanotubes, they deviate from Ohm's law after a certain voltage threshold is reached; specifically, the current at the threshold voltage surprisingly decreases rather than increases, an effect known as NDC.^{60,62,63} SWNTs are also exceptional field emitters due to their small diameters. In particular, when an electric field passes through a nanotube that is stood on its end, the sharp nanotube tip concentrates the electrons and rapidly projects them onto a target.⁵⁰

As circuit miniaturization progresses, SWNTs offer the attractive advantage that they can act as metallic nanowires that have the potential to significantly impact the fields of energy storage⁶⁴ and molecular electronics⁶⁵⁻⁶⁹ (Figure 1-5). NDC is observed for metallic nanotubes at low electric fields, which is significant for electronic applications and holds general implications for high-current applications based on 1D materials.⁶⁰ In addition, semiconducting SWNTs have already been incorporated into field effect transistors (FETs) that transport electrons between two metal electrodes while a voltage is applied to a third gate electrode that switches the device on and off.^{62,66} Processors that integrate SWNT FET switches could operate 1000 times faster than current silicon-based devices.⁵⁰ Because they are excellent field emitters, SWNTs have also been integrated as components of flat panel displays that can activate phosphor targets at very low voltages (1–3 V with 1- μm spacing).^{50,70}

1.3.3 *Optical Properties and Applications*

Both metallic and semiconducting SWNTs can transport charge; however, only semiconducting SWNTs display fluorescence.⁷¹ SWNTs fluoresce in the near-infrared (NIR) region of the electromagnetic spectrum and exhibit narrow line widths.⁷²⁻⁷⁴ The

particular wavelength of fluorescence emission varies for each nanotube structure, and so the desired emission energy can be selected by simply tuning the nanotube diameter and chirality. Most known fluorophores suffer from photoinduced bleaching and fluorescence intermittency on the single particle level (i.e., blinking), but strikingly, emission from nanotubes remains steady and uninterrupted over hours of continuous excitation at room temperature.^{72,75,76} Still, the luminescence efficiency, or fluorescence quantum yield (QY), for ensembles of SWNTs is extremely poor, typically <0.1%.⁷⁷

Due to their unique optical properties, SWNTs may satisfy a long-standing need for superior fluorophores required for *in vivo* single biomolecule imaging and single particle tracking (Figure 1-5). Coupled with their relative ease of uptake into cells and infrared emission at wavelengths most transparent to biological tissue, SWNTs hold great promise in this area because NIR radiation passes through tissue without causing significant heating, scattering, or damage to live cells.^{57,75,76,78,79} The development of single molecule sensors based on SWNT fluorescence is particularly promising because all SWNT carbon atoms are situated on the surface of the molecule, making their response extremely sensitive to changes in the local environment. In fact, the ability of SWNTs to perform as glucose⁷⁸ and biological sensors^{76,79} has already been demonstrated.

Stable NIR fluorescence also makes carbon nanotubes exciting candidates for development as single-photon sources.⁸⁰ Specifically, quantum cryptography requires a source of single photons, as sources that emit two or more photons provide opportunities for a compromised transmission.⁸¹ SWNTs could be an exceptional source of single photons because they do not show fluorescence intermittency at room temperature, nor

Figure 1-5. (a) AFM cantilever with nanotube tip (scale bar is 1 μm). Reprinted from ref 52. Copyright 1998 American Chemical Society. (b) Artificial nanotube muscle before (left) and after (right) applying a voltage. Reprinted from ref 53. Copyright 2009 AAAS. (c) Nanotube cables envisioned for a space elevator. Reprinted from ref 54. Copyright 2004 Nature Publishing Group. (d) Diagram (top) and AFM image (bottom) of a nanotube FET. Reprinted from ref 82. Copyright 2007 Wiley-VCH. (e) Nanotube field emission display. Reprinted from ref 83. Copyright 2002 AAAS. (f) Implanted nanotube glucose sensor. Reprinted from ref 78. Copyright 2005 American Chemical Society. (g) Fibroblast cells incubated with nanotubes. Reprinted from ref 56. Copyright 2004 The Royal Society of Chemistry. (h) Normal cells were unharmed by laser irradiation (top), but cancer cells tagged with nanotubes were selectively killed (bottom). Reprinted from ref 57. Copyright 2005 The National Academy of Sciences of the USA.

do they photobleach.^{80,84} However, the extremely low luminescence efficiency for SWNTs remains a major concern for all potential fluorescence-based applications.⁷⁷

1.3.4 Outlook

Since the 1990s, carbon nanotube research has been fueled by a desire to discover, understand, and harness the unique properties of these materials. The recent discovery of carbon nanotubes spurred fast-paced research that has resulted in an impressive body of literature: experimental validation of theoretical predictions for one-dimensional systems;⁸⁵ development of commercially attractive nanotube synthesis methods;^{28,86} and the assignment of optical features to specific nanotube structures⁸⁷ are examples of such advances. Already, from strong composites and nanoscale electronics to biological tags, these molecules are beginning to find application in commercially relevant avenues.

The range of technological applications based on carbon nanotubes is rapidly evolving. However, research on carbon nanotubes is still a young field, and the high cost of producing these particles remains a substantial factor limiting their use. For example, the price of carbon nanotubes has decreased significantly in recent years, but high-quality commercial samples still sell for approximately \$500 per gram.⁸⁸ Further, before any material can be integrated into devices and applications, a thorough understanding of its fundamental properties must first be achieved, and many aspects of SWNT behavior require further study. Nevertheless, current advances in the production of high-quality carbon nanotube samples should promote vigorous study of their fundamental properties,

thereby facilitating the rational integration of these particles as components of consumer products, electronic devices, and optical systems.

1.4 Organization of this Dissertation

The research presented in this dissertation spotlights the central theme of carbon nanotube photophysics. This work begins with the preparation of high-quality, optically-active SWNT suspensions, moves to spectroscopic measurements of ensemble samples, and extends to single molecule measurements that aim to clarify how light interacts with individual carbon nanotubes. This work is motivated by the quest to understand how the macroscopic behavior of nanoscale materials arises from the fundamental contributions of single molecules. Further, this research seeks to quantify the value of critical photophysical parameters for SWNTs, such as their luminescence efficiency and absorption cross sections, which will assist in the design of innovative applications based on these materials.

Chapter 2 provides background information regarding the structural, electronic, and optical properties of SWNTs, as well as semiconductor quantum dots that are used as a reference particle in subsequent single molecule fluorescence studies. Chapter 3 provides a summary of sample preparation techniques used to create high-quality aqueous dispersions of carbon nanotubes intended for use in single molecule spectroscopic studies. Chapter 4 summarizes the fundamental principles of single molecule spectroscopy as well as results of single molecule fluorescence measurements performed on a suite of SWNT samples. Chapter 5 presents measurements of the relative single molecule fluorescence quantum yield and absorption cross section for bright

individual carbon nanotubes. Chapter 6 discusses studies of correlated fluorescence and topography performed on individual SWNTs. Finally, Chapter 7 provides an outlook on the major questions guiding the current and future directions of carbon nanotube research.

CHAPTER 2

Structure and Optical Properties

The structural design and electronic properties of carbon nanotubes are intimately tied to those of graphene, and this chapter serves as a guide for understanding how the geometric structure of the SWNT influences both its electronic and optical properties. Interestingly, carbon nanotubes are either metallic or semiconducting depending on their structure, which strongly influences their optical properties. The nature of the SWNT excited state and brief reviews of absorption, fluorescence, and Raman spectroscopies for SWNTs are presented.

2.1 Structural Design

Single-walled carbon nanotubes have a unique one-dimensional architecture that influences nearly all of their physical properties. SWNTs are hollow cylinders constructed entirely from one atomic layer of sp^2 -bonded carbon (Figure 2-1), and so the physical structures of these molecules can be described in terms of a graphene sheet. Unlike conventional molecules, carbon nanotubes are synthesized as heterogeneous samples, composed of molecules with different diameters, chiralities, and lengths.⁸⁹ SWNT diameters range from ~ 0.4 to 2 nm ^{90,91} and their lengths vary from $\sim 10\text{ nm}$ to 1 cm ,⁵⁸ which gives them an extremely high aspect ratio.

2.1.1 Graphene Unit Cell

In general, the unit cell for a crystal is defined as an area containing one or more lattice points that, when translated, will reconstruct the entire structure.⁹² The unit cell

Figure 2-1. Construction of a carbon nanotube from a graphene sheet, where the white region represents the area used to form the nanotube. Two corresponding lattice points overlap (open or filled circles) to form a (6,6) nanotube with a chiral angle of 30° .

Figure 2-2. Illustration of unit cells for graphene and a (4,2) SWNT. (a) The graphene unit cell is shaded violet and two carbon atoms are represented by A and B. The coordinate axes are given by x and y , and the graphene lattice vectors are given by $\mathbf{a}_1$ and $\mathbf{a}_2$. (b) The SWNT unit cell is shaded violet and is bounded by the chiral vector and the translational vector. The graphene lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are shown for reference. Figure was adapted from ref 2.

for graphene is a parallelogram that contains two carbon atoms, A and B (Figure 2-2a).

In a hexagonal arrangement of carbon atoms, the lattice spacing is given by $a = \sqrt{3}d = 2.46 \text{ \AA}$, where d is the C–C bond length ($d = 1.44 \text{ \AA}$).⁵⁴ The lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ can be used to translate a carbon atom to any other lattice point and are related to both the spacing interval of the lattice (a) and the standard unit vectors $\hat{x}$ and $\hat{y}$.⁸⁵

$$\mathbf{a}_1 = \left(\frac{\sqrt{3}a}{2} \right) \hat{x} + \left(\frac{a}{2} \right) \hat{y} \quad (2-1)$$

$$\mathbf{a}_2 = \left(\frac{\sqrt{3}a}{2} \right) \hat{x} - \left(\frac{a}{2} \right) \hat{y} \quad (2-2)$$

2.1.2 SWNT Unit Cell

The primitive cell of graphene provides a convenient framework for describing the structure of a carbon nanotube. As illustrated in Figure 2-2b, the SWNT unit cell is

shaped like a rectangle bounded by the chiral vector ($\mathbf{C}_h$) and the translational vector ($\mathbf{T}$). Because of differences in the diameter of each SWNT, as well as the angle at which it is rolled up, the size of the unit cell varies for each nanotube structure.² One important boundary condition for constructing a nanotube from a graphene sheet is that two lattice points must coincide to connect the edges of the cylinder.⁸⁵

The chiral vector $\mathbf{C}_h$ is the imaginary line that connects these starting and ending lattice points, and its magnitude provides the circumference (L) of the SWNT. $\mathbf{C}_h$ is expressed in terms of the graphene lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, where n and m are integers.

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \equiv (n,m) \quad (2-3)$$

As depicted in Figure 2-3, each nanotube structure is uniquely defined by its (n,m) index, which is also related to the SWNT diameter (d_t) and chiral angle (θ).²

$$d_t = \frac{L}{\pi} = \frac{a}{\pi} \sqrt{n^2 + m^2 + nm} \quad (2-4)$$

$$\theta = \tan^{-1} \left(\frac{\sqrt{3}n}{2m+n} \right) \quad (2-5)$$

The chiral angle specifies the tilt between the hexagonal lattice and the radial axis of the nanotube.⁸⁹

SWNT structures can be classified according to symmetry, which varies according to the chiral angle. Due to the sixfold rotational symmetry of graphene, an irreducible wedge of $0^\circ \leq \theta \leq 30^\circ$ fully describes all nonrepetitive SWNT structures (Figure 2-3).⁹³ Highly symmetric structures are achiral (i.e., when $\theta = 0^\circ$ or 30°) because the SWNT and its mirror image are identical. These structures are termed zigzag $(n,0)$ and armchair (n,n) nanotubes, respectively, and are named for the pattern that can be

Figure 2-3. Depiction of possible SWNT (n,m) structures represented on a single graphene sheet. Semiconducting SWNTs are white and metallic SWNTs are shaded. Illustration of three classes of SWNTs: zigzag, chiral, and armchair, as presented in ref 94.

traced around the radial axis (Figure 2-3). All other SWNT structures are chiral. Although chiral SWNTs exhibit no symmetry when reflected through a horizontal or vertical mirror plane, they do exhibit a spiral symmetry that gives them a left or right handedness,⁹⁵ corresponding to nanotubes that are hypothetically rolled up either above or below the plane of the graphene sheet.²

The translational vector $\mathbf{T}$ is orthogonal to $\mathbf{C}_h$, and extends from the starting lattice point to the first carbon atom through which it passes (Figure 2-2b). The translational vector is expressed in terms of the graphene lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, where t_1 and t_2 are integers and d_r is the greatest common divisor of $(2m+n)$ and $(2n+m)$.²

$$\mathbf{T} = t_1 \mathbf{a}_1 + t_2 \mathbf{a}_2 \equiv (t_1, t_2) \quad (2-6)$$

$$t_1 = \frac{2m+n}{d_r} \quad (2-7)$$

$$t_2 = \frac{2n + m}{d_r} \quad (2-8)$$

The magnitude of $\mathbf{T}$ is related to the SWNT circumference by

$$|\mathbf{T}| = \frac{\sqrt{3}L}{d_r} \quad (2-9)$$

Finally, the number of carbon atoms in a given nanotube can be deduced from its unit cell. For instance, the area of the unit cell is available from the magnitude of the vector product of $\mathbf{C}_h$ and $\mathbf{T}$, which contains N hexagons. Each hexagon contains only two carbon atoms, as every atom in a honeycomb lattice is shared between three hexagons (Figure 2-2a). Altogether, $2N$ carbon atoms are present per unit cell. The number of carbon atoms per unit cell (N_A) is given by²

$$N_A = 2N = \frac{4(m^2 + n^2 + nm)}{d_r} = \frac{4L^2}{a^2 d_r} \quad (2-10)$$

2.2 Electronic Properties

Solids are often classified in terms of their electronic properties, and they typically fall into one of the following groups: metals, semiconductors, or insulators. However, carbon nanotubes have the intriguing ability to exhibit either metallic or semiconducting behavior depending on the particular (n,m) structure, which results from the quantum confinement of π -electrons around the nanotube circumference.² Calculating the electronic band structure for SWNTs is useful for understanding both the electronic and optical behavior of these materials.

In a free-electron approximation, the electrons are treated as free particles that move throughout a crystal, feeling the potential from nuclei and interacting with all other electrons. On the other hand, electrons can be modeled as being restricted to atoms that interact only with their neighbors. This second approach is known as tight binding (i.e., a linear combination of atomic orbitals), and works exceptionally well for calculating the band structure of graphene.² The energy dispersion for SWNTs can be found by restricting the allowed electron wave vectors for graphene based on periodic boundary conditions around the nanotube circumference, an approach known as zone folding.⁹³

2.2.1 *Graphene Electronic Band Structure*

Tight binding (TB) refers to the assumption that atomic orbitals at each lattice point can be treated independently because the electrons are tightly bound to an individual atom. Thus, the overall strategy for a TB calculation is to select a set of relevant atomic orbitals, define the atoms of interest, and generate electron wave functions for this specific set of atomic orbitals. The electron wave functions are eventually summed over the entire molecule in a linear combination to obtain a solution to the Schrödinger equation, which provides the energy band structure.

Accordingly, the first step for determining the energy dispersion of graphene is to select the atomic orbitals that will be considered in the calculation. As described in Chapter 1, each sp^2 -hybridized carbon atom in graphene has three valence electrons that form σ -bonds with neighboring carbon atoms, and one valence electron that participates in π -bonding.⁸⁵ Although it may appear that in-plane σ -bonds influence the electronic properties of graphene, they lie too far below the Fermi level to participate in either

electron transport or optical transitions.⁹³ Further, the π -electron separates from the three σ -bonding electrons by symmetry, as the s , p_x , and p_y wave functions are symmetric above and below the graphene layer, but the p_z orbital changes sign because it is perpendicular to the plane of the graphene sheet.⁹³ Thus, the Hamiltonian ($\hat{H}$) and overlap ($\hat{S}$) integrals between the σ -electrons and the π -electrons vanish, and the only electron considered in the TB calculation is the π -electron.^{85,93}

Next, the atoms considered for the calculation are selected; these are usually the atoms encompassed in the primitive cell (because they are repeated throughout the crystal). The geometric structure of graphene has already been described in terms of a repeating unit cell encompassing atoms A and B (Figure 2-2a); thus, these atoms are selected for the TB calculation. In addition, the calculation is simplified significantly by considering the π -electrons for A and B in terms of their momentum instead of position. The momentum ($\mathbf{p}$) of an electron in a crystal is related to its plane wave vector ($\mathbf{k}$) by $\mathbf{p} = \hbar\mathbf{k}$. Because the wave vector is a more fundamental quantity than $\mathbf{p}$, the energy of a quasiparticle (like an electron) is usually expressed in terms of $\mathbf{k}$.⁹²

Every real lattice has a unique reciprocal lattice that expresses the position of each atom in terms of its wave vector (Figure 2-4). The primitive cell in reciprocal space is known as the Brillouin zone. It is the only region considered for energy dispersion calculations because it contains solutions for all of the electron wave functions that are repeated throughout the crystal. For graphene, the reciprocal lattice is a hexagonal network of carbon atoms, and so the Brillouin zone is a hexagon with lattice vectors $\mathbf{b}_1$ and $\mathbf{b}_2$, and a lattice constant equal to $\frac{4\pi}{\sqrt{3}a}$, as presented in Figure 2-4a.

Figure 2-4. Illustration of the first Brillouin zone for graphene and a (4,2) SWNT. (a) The graphene unit cell in reciprocal space is shaded violet. The coordinate axes are given by k_x and k_y , and the graphene reciprocal lattice vectors are given by $\mathbf{b}_1$ and $\mathbf{b}_2$. The high-symmetry points Γ , K, and M are labeled. (b) The SWNT unit cell in reciprocal space is shaded violet. The graphene reciprocal lattice vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ are shown for reference, and $\mathbf{K}_1$ and $\mathbf{K}_2$ are the SWNT reciprocal lattice vectors. Figure was adapted from ref 2.

$$\mathbf{b}_1 = \left(\frac{2\pi}{\sqrt{3}a} \right) \hat{x} + \left(\frac{2\pi}{a} \right) \hat{y} \quad (2-11)$$

$$\mathbf{b}_2 = \left(\frac{2\pi}{\sqrt{3}a} \right) \hat{x} - \left(\frac{2\pi}{a} \right) \hat{y} \quad (2-12)$$

Every hexagon has three high-symmetry points, and in the graphene Brillouin zone these are labeled Γ (center), K (each corner), and M (each edge center).²

After selecting the $2p_z$ atomic orbitals for A and B, and defining the primitive cell in reciprocal space, the third step in a TB calculation is to characterize the electron wave function $\psi(\mathbf{k})$. The wave function is later substituted into the time-independent Schrödinger equation to solve for the energy bands $E(\mathbf{k})$ of the electron.

$$\hat{H}\psi(\mathbf{k}) = E(\mathbf{k})\psi(\mathbf{k}) \quad (2-13)$$

$\hat{H}$ is the Hamiltonian, $E(\mathbf{k})$ are the eigenvalues, and $\psi(\mathbf{k})$ are the eigenfunctions of the electron. The overall wave function $\psi(\mathbf{k})$ can be expressed as a linear combination of

individual Bloch functions $\Phi_l(\mathbf{k})$, which describe the movement of electrons in a periodic potential like a crystal (l is the atom under consideration).

$$\psi(\mathbf{k}) = \sum_l C_l \Phi_l(\mathbf{k}) \quad (2-14)$$

Further, the Bloch functions in graphene can be expressed as a linear combination of atomic wave functions, $\phi(\mathbf{r})$, for the carbon atoms A and B, which are multiplied by a phase factor with lattice periodicity.

$$\Phi_A(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_A} e^{i\mathbf{k} \cdot \mathbf{R}_A} \phi(\mathbf{r} - \mathbf{R}_A) \quad (2-15)$$

$$\Phi_B(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_B} e^{i\mathbf{k} \cdot \mathbf{R}_B} \phi(\mathbf{r} - \mathbf{R}_B) \quad (2-16)$$

The Bloch functions are normalized by the total number of unit cells (N) in the solid; $\mathbf{R}_l$ is the vector between neighboring lattice points and $\mathbf{r}$ is a position vector.⁹³

With $\psi(\mathbf{k})$ defined in terms of the Bloch functions for each carbon atom, the Schrödinger equation can be solved. For graphene, the Hamiltonian is a 2×2 matrix because the basis functions are supplied by two carbon atoms.

$$\hat{H} = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \quad (2-17)$$

Substituting this Hamiltonian into eq 2-13 and operating on the electron wave function in eq 2-14, a system of two linear equations is obtained.⁹³

$$C_A [H_{AA}(\mathbf{k}) - E(\mathbf{k})S_{AA}(\mathbf{k})] + C_B [H_{AB}(\mathbf{k}) - E(\mathbf{k})S_{AB}(\mathbf{k})] = 0 \quad (2-18)$$

$$C_A [H_{BA}(\mathbf{k}) - E(\mathbf{k})S_{BA}(\mathbf{k})] + C_B [H_{BB}(\mathbf{k}) - E(\mathbf{k})S_{BB}(\mathbf{k})] = 0 \quad (2-19)$$

The transfer matrix element for the Hamiltonian (H_{lj}) and the overlap between Bloch functions (S_{lj}) are given by the following expressions.

$$H_{IJ} = \langle \Phi_I(\mathbf{k}) | \hat{H} | \Phi_J(\mathbf{k}) \rangle \quad (2-20)$$

$$S_{IJ} = \langle \Phi_I(\mathbf{k}) | \Phi_J(\mathbf{k}) \rangle \quad (2-21)$$

The Hamiltonian and overlap matrix elements can be simplified before calculating the solution to the Schrödinger equation. First, because A and B are identical atoms in graphene, $H_{AA} = H_{BB}$. Second, the Hamiltonian is a Hermitian operator, and so the complex conjugate of H_{AB} is equal to H_{BA} .² Altogether, the most general form of the secular equation for the π -orbitals of graphene is⁹³

$$\begin{vmatrix} H_{AA}(\mathbf{k}) - E(\mathbf{k})S_{AA}(\mathbf{k}) & H_{AB}(\mathbf{k}) - E(\mathbf{k})S_{AB}(\mathbf{k}) \\ H_{AB}^*(\mathbf{k}) - E(\mathbf{k})S_{AB}^*(\mathbf{k}) & H_{AA}(\mathbf{k}) - E(\mathbf{k})S_{AA}(\mathbf{k}) \end{vmatrix} = 0 \quad (2-22)$$

The final step in tight binding is to diagonalize the simplified 2×2 secular equation to obtain the energy dispersion. For the diagonal term in eq 2-22, one integral must be solved for a single carbon atom. For the off-diagonal element, H_{AB} , the interaction of A over the three nearest-neighbor B atoms must be considered (Figure 2-2a); γ_0 is the nearest-neighbor hopping integral for graphite ($\gamma_0 = 2.7$ eV).²

$$H_{AB} = \gamma_0 \sum_{l=1}^3 e^{i\mathbf{k} \cdot \mathbf{R}_l} \quad (2-23)$$

The energy eigenvalues and coefficients are determined by solving the determinant (i.e., $\det[H - ES] = 0$) to obtain the energy dispersion for 2D graphene (E_{g2D}).

$$E_{g2D}(k_x, k_y) = \pm \gamma_0 \left[1 + 4 \cos\left(\frac{\sqrt{3}k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right) \right]^{1/2} \quad (2-24)$$

Figure 2-5. (a) Calculation of the 3D graphene energy band structure. A 2D contour shadow is projected onto the xy plane in reciprocal space. (b) Allowed electron states for nanotubes (solid black lines) pass through the K -point for metallic SWNTs, but lie on either side of the K -point for semiconducting SWNTs.

A three-dimensional view of the resulting graphene valence and conduction bands is depicted in Figure 2-5. The symmetric combination of atomic wave functions provides the energies of the π -bonding valence band (indicated by the positive sign); the antisymmetric combination supplies energies for the π^* antibonding energy bands in the conduction band (indicated by the negative sign). There are $2N$ carbon atoms per unit cell, and molecular orbital theory therefore predicts N bonding (π) and N antibonding (π^*) electronic energy bands.² The valence and conduction bands are degenerate at the six K -points in the Brillouin zone (Figure 2-5a); in conjunction with the quantum confinement of π -electrons around the circumference of a nanotube, these K -points play a major role in the discussion of SWNT electronic properties.

2.2.2 SWNT Electronic Band Structure

As introduced earlier, the nanotube energy band structure is derived from graphene. Graphene is a semimetal because occupied π and unoccupied π^* energy bands overlap at the Fermi energy for six quantum states called K -points; electrons in these states are free to conduct. As illustrated in Figure 2-5b, the allowed electron states for an SWNT are a small subset of those in graphene, determined by the nanotube's diameter and twist (i.e., (n,m)).⁹⁶ One-third of SWNTs are metallic because some of the allowed electron states intersect the conductive K -point $[(n - m) \bmod 3 \equiv 0]$. The rest are semiconducting because allowed electron states lie on either side of the K -point, creating an energy gap $[(n - m) \bmod 3 \equiv 1 \text{ or } 2]$.⁸⁹

To identify the wave functions that are allowed for electrons in a carbon nanotube, one must consider the two boundary conditions that arise from hypothetically rolling the graphene sheet into a hollow cylinder. First, the wave function must satisfy the periodical boundary condition around the SWNT circumference.⁹⁷

$$\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{C}_h) \quad (2-25)$$

A second requirement is that the wave function must satisfy Bloch's theorem for a crystal lattice, which states that the wave function must be the product of a modulating plane wave and a function $u(\mathbf{r})$ that has the periodicity of the lattice.

$$\psi(\mathbf{r}) = e^{(i\mathbf{k} \cdot \mathbf{r})} \cdot u(\mathbf{r}) \quad (2-26)$$

Hence, the boundary condition only affects the plane wave, which does not already follow the periodicity of the lattice.⁹⁷ Altogether, the boundary conditions for an SWNT are the circumferential confinement and lattice periodicity requirements for the electron wave vector.

$$\psi(\mathbf{r} + \mathbf{C}_h) = e^{(i\mathbf{k} \cdot (\mathbf{r} + \mathbf{C}_h))} \cdot u(\mathbf{r}) = \psi(\mathbf{r}) \cdot e^{(i\mathbf{k} \cdot \mathbf{C}_h)} \cdot u(\mathbf{r}) = \psi(\mathbf{r}) \quad (2-27)$$

Thus, the electron wave vector becomes quantized.

$$k_x = \frac{2\pi n}{|\mathbf{C}_h|} = \frac{2n}{d_t} \quad (2-28)$$

$$n = 0, 1, 2, \dots N$$

k_x is the component of the momentum in the circumferential direction and n is an integer that indexes the electron energy subband under consideration. The component of the electron wave vector that is associated with the long axis of the nanotube remains quasicontinuous (Δk_y is small) and is bounded within $\pm \pi/|\mathbf{T}|$.

After restricting the allowed electron wave functions, the SWNT energy bands appear as a set of 1D slices across the 2D energy landscape of graphene (Figure 2-4b).² For each of these 1D Brillouin zones, the π -electron energy band dispersion for the SWNT valence (v) and conduction (c) bands is given by⁹⁸

$$\begin{aligned} E^{c,v}(k_x, k_y) = & \pm \gamma_0 \left[1 + 4 \cos \left(\left(\frac{\sqrt{3}a}{2} \right) (k_y \cos \theta + k_x \sin \theta) \right) \right. \\ & \times \cos \left(\left(\frac{a}{2} \right) (k_y \sin \theta - k_x \cos \theta) \right) \\ & \left. + 4 \cos^2 \left(\left(\frac{a}{2} \right) (k_y \sin \theta - k_x \cos \theta) \right) \right]^{1/2} \end{aligned} \quad (2-29)$$

Interestingly, electronic transport and optical transitions involve only the low-lying energy states that are situated near the corners of the Brillouin zone (Figure 2-5).⁹³ The energy for these wave functions is obtained by expanding eq 2-29 around the K -point, and an excellent derivation is provided in ref 98.

The first SWNT Brillouin zone is a line segment centered at the Γ -point and is represented by the line segment $\overline{WW'}$. Simple unit vectors for the SWNT reciprocal lattice can be expressed in terms of those for graphene.²

$$\mathbf{K}_1 = \frac{1}{N}(-t_2\mathbf{b}_1 + t_1\mathbf{b}_2) \quad (2-30)$$

$$\mathbf{K}_2 = \frac{1}{N}(m\mathbf{b}_1 - n\mathbf{b}_2) \quad (2-31)$$

N line segments run parallel to $\mathbf{K}_2$, with a length of $2\pi/|\mathbf{T}|$ and a spacing of $|\mathbf{K}_1| = 2\pi/|\mathbf{C}_h|$. As expected, the length, number, and orientation of the SWNT energy bands depend on the (n,m) structure of the SWNT.

With a clear picture of the allowed wave functions and energy levels of the first Brillouin zone for an SWNT, it is possible to predict which nanotubes are metals and which are semiconductors. As mentioned, the condition for a metallic SWNT is that an allowed wave vector must pass through one of the six K -points. Figure 2-6 illustrates that the vector $\mathbf{YK}$ lies orthogonal to $\overline{WW'}$ and extends from the SWNT Brillouin zone to one of the K -points. If the ratio of $|\mathbf{YK}|$ to $|\mathbf{K}_1|$ is an integer, then the wave vector will

Figure 2-6. Representation of the first SWNT Brillouin zone (violet), showing the condition for metallic energy bands (i.e., if $|\mathbf{YK}|/|\mathbf{K}_1|$ is an integer, then the SWNT is metallic). The coordinate axes are given by k_x and k_y , and the SWNT reciprocal lattice vectors are given by $\mathbf{K}_1$ and $\mathbf{K}_2$. Figure was adapted from ref 2.

intersect one of the K -points and the SWNT is metallic.²

$$\frac{|\mathbf{YK}|}{|\mathbf{K}_1|} = \frac{2n+m}{3} \quad (2-32)$$

Hence, $(2n + m)$, or equivalently $(n - m)$, is a multiple of 3 for metallic nanotubes.² The remaining SWNTs do not intersect the K -point, making them semiconductors with a band gap.

In closing, the tight binding method provides an excellent framework for calculating and understanding the electronic properties of carbon nanotubes. To further refine the results, the calculation can be modified to include additional nearest neighbor carbon atoms and overlap integrals,⁹⁹ the effects of curvature,¹⁰⁰ and exciton influences (vide infra).^{101,102} For example, because tight binding does not account for the curvature of the SWNT, it is only a good approximation for large diameter nanotubes ($d_t > 1.5$ nm).⁹³ Yet even without additional corrections, tight binding has successfully predicted the metallic and semiconducting behavior of SWNTs, ballistic transport through metallic SWNTs, and the indirect relationship between the semiconducting SWNT band gap and nanotube diameter.⁸⁵

2.2.3 SWNT Density of Electronic States

The density of electronic states (DOS) indicates the number of electron states available in a particular energy band, which is useful for understanding optical transitions. As illustrated in Figure 2-7, the 0D DOS is discrete for small molecules with well-defined energy levels. Similar to molecular energy levels, one-dimensional materials like carbon nanotubes display sharp peaks in the 1D DOS called van Hove singularities.⁸⁹ In general, the DOS $\rho(E)$ for a one-dimensional material is given by⁹⁷

Figure 2-7. Diagram showing energy versus density of states for materials of various dimensions. The first two dipole-allowed absorption transitions (E_{11} and E_{22}) from the valence band (gray) to the conduction band (white) are labeled for the 0D and 1D densities of states.

$$\rho(E) = \frac{\Delta n}{\Delta E} = \frac{2}{\pi} \left| \frac{\partial E}{\partial k} \right|^{-1} \quad (2-33)$$

where n represents the number of available states. For SWNTs, the DOS is¹⁰³

$$\rho(E) = \frac{4a}{\pi^2 d_t \gamma_0} \sum_{i=-\infty}^{\infty} g(E, E_i) \quad (2-34)$$

$$g(E, E_i) = \begin{cases} |E| / \sqrt{E^2 - E_i^2} & |E| > |E_i| \\ 0 & |E| < |E_i| \end{cases} \quad (2-35)$$

where i denotes an integer index. As expected, the denominator approaches zero at the band edge (i.e., where $E = E_i$) and produces sharp discontinuities in the 1D DOS. Figure 2-8 provides calculations of the band structures and corresponding densities of state for a metallic and semiconducting SWNT using the program YAeHMOP.^{104,105}

Quantifying the density of states that can be populated by carriers is fundamentally important for understanding optical absorption and emission. In general, Fermi's Golden Rule predicts that the transition probability per unit time (W_{if}) from an

Figure 2-8. Calculations of the band structure and density of electronic states for (a) a (10,10) metallic SWNT and (b) an (8,4) semiconducting SWNT using the program YAcHMOP.^{104,105} The Fermi energy is indicated by the dotted line. For the metallic SWNT in (a), no energy gap exists between the valence and conduction bands (also indicated by the existence of a finite DOS at the Fermi energy). For the semiconducting SWNT in (b), the energy gap is visible between the valence and conduction bands and the DOS is equal to zero in this region. Insets: Ball and stick models of the SWNT structures.

initial to final quantum state is¹⁰⁶

$$W_{if} = \frac{\pi}{2\hbar^2} \left| \langle f | \boldsymbol{\mu} \cdot \mathbf{E}_0 | i \rangle \right|^2 \rho_J(E) \quad (2-36)$$

The density of states ρ_J that appears in Fermi's Golden Rule is the joint density of electronic states (JDOS), which provides the number of available electron and hole (i.e., valence and conduction) states per unit bandwidth (the JDOS for SWNTs is calculated in ref 98). The intensity of a transition is related to the oscillator strength, which is the product of the JDOS and the square of the transition dipole ($\boldsymbol{\mu}$).¹⁰⁶

As a free electron moves from an initial to final quantum state, it must conserve energy and momentum, giving rise to a set of optical selection rules. Thus, only vertical transitions are allowed because $\Delta \mathbf{k}$ must equal zero. Further, the selection rules depend on the orientation of the exciting electric field ($\mathbf{E}$) in relation to the long axis (z) of the nanotube. The angular momentum quantum number (Δm) for an energy band must remain unchanged when the SWNT absorbs a photon with angular momentum ± 1 , and so symmetry dictates that $\Delta m = 0$ for $\mathbf{E} \parallel z$ and $\Delta m = \pm 1$ for $\mathbf{E} \perp z$.⁹³ As a result, in the simplest picture, optical transitions for SWNTs take place between mirror image peaks (i.e., van Hove singularities) in the 1D DOS because $\Delta m = 0$. Each allowed transition is abbreviated as E_{nm} (E_{11} , E_{22} , etc.),¹⁰⁷ where n is an integer, and the energy varies inversely with nanotube diameter according to^{87,107}

$$E_{nm} = \frac{2na_{c-c}\gamma_0}{d_t} \quad (2-37)$$

The 1D DOS provides a simple picture for understanding optical transitions in SWNTs; however, accurate transition energies also depend on the (n,m) structure of the nanotube, partially due to the effects of sidewall curvature.⁸⁷ This dependence of

transition energy on chirality arises because some of the SWNT wave vectors cut through graphene near the K -point, where the energy contours deviate from linearity (Figure 2-5). This effect is known as trigonal warping.¹⁰⁸

2.3 Optical Properties

Modern ideas about atomic and molecular electronic structure originate from the study of optical properties.¹⁰⁹ SWNT photophysics describes the interaction of carbon nanotubes with light by absorption, emission, and scattering processes. In particular, optical absorption and emission spectra supply information about the electronic band structure and the symmetry of electronic states. Further, time-resolved optical measurements elucidate the dynamics of electrons and holes in the excited state; identifying the exact nature of the excited state (i.e., free electrons or excitons) is an important consideration for interpreting SWNT optical spectra, as many-body effects become pronounced for low-dimensional materials. Finally, the behavior of phonons in vibrational processes are elucidated by inelastic (Raman) or elastic (Rayleigh) scattering.⁹³

2.3.1 *Free-Electron vs. Exciton Models*

A simple free-electron picture of an SWNT excited state explains several qualitative features of nanotube optical spectra, but this model fails to represent many experimental observations accurately. For example, the free-electron picture underestimates the energetic separation of the experimentally observed E_{11} electron states while it both overestimates and underestimates E_{22} values.^{91,110} Free-electron models also

predict that the ratio $E_{22}:E_{11}$ should be 2 for large-diameter SWNTs, but its observed value is closer to 1.7 (i.e., the ratio problem).^{96,111,112} These dissimilarities imply that electron–electron and electron–hole interactions strongly influence the physics underlying optical transitions in SWNTs.⁸⁹

Electrostatically bound electron–hole (e – h) pairs are known as excitons. When a negatively charged electron is excited from the valence band, it leaves behind a pocket of positive charge called a hole; for most bulk systems, these quasiparticles move around the molecule independently before the electron radiatively recombines with the hole to emit a photon or relax nonradiatively. However, due to strong 1D confinement in SWNTs, the electrostatic electron–hole interaction energy (i.e., exciton binding energy) is very large, on the order of 300–500 meV, relative to an energy gap of ~ 1 eV.^{111–114} As a result of this strong e – h attraction, it is generally accepted that the photoexcited state of an SWNT is excitonic. In SWNTs, the electron orbits the heavier hole at a characteristic e – h separation (Bohr radius) of approximately 2.5 nm.^{111,113,115} The exciton is a mobile quasiparticle that travels along the SWNT with an average diffusion length of ~ 90 nm before relaxing to the ground state.¹¹⁶

Both the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels of SWNTs are doubly degenerate, which gives rise to four singlet excitonic states and twelve triplet excitonic states (Figure 2-9). The singlet excitonic states lead to fluorescence, but Coulomb interactions break their degeneracy, resulting in one allowed and three optically forbidden singlet transitions.^{112,117} Therefore, because there is one optically active exciton per pair of matching peaks in the DOS, the linear absorptions and emissions of SWNTs approximate what would be observed from a

simple free-electron picture. This behavior may account for the original misconception that free electrons arise from SWNT optical transitions.

Figure 2-9. Calculation of the four lowest-energy exciton bands for a (19,0) SWNT. When an electron with spin $\uparrow$ absorbs a photon, the excited state is either (a) a singlet exciton ($S = 0$) or (b) a triplet exciton ($S = 1$). The green circle indicates the positively charged hole that is left behind following photon absorption. For the exciton energy bands, the position of the band in relation to the E_{11} energy is plotted as a function of momentum for the photoexcited state (k). The solid black curves are doubly degenerate exciton bands with nonzero angular momentum. The dashed blue curves are even parity (dipole forbidden) exciton bands with zero angular momentum. The dotted red curves are odd parity (dipole allowed) exciton bands with zero angular momentum. (a) The red dotted curve thus corresponds to the only bright exciton associated with the SWNT. The partial DOS for this band is indicated by the red dotted curve in the DOS. Interestingly, the dashed blue line corresponds to a dark singlet exciton with a lower energy than the bright exciton. (b) All triplet excitons are considered dark. The change in scale of 1/3 is for triplet degeneracy. Figure was adapted from refs 117 and 118.

2.3.2 Absorption and Fluorescence Spectroscopy

Nanotubes aggregate during synthesis, thus limiting early optical studies to bundles of SWNTs. For bundles, the absorption spectrum exhibits severe inhomogeneous broadening as the result of mixing between the energy states of different nanotube structures; it is possible only to observe broadened transitions corresponding to E_{11} and E_{22} for semiconducting SWNTs and E_{11} for metallic SWNTs.⁸⁴ Fluorescence is not observed from nanotube bundles because photoexcited carriers that are generated in semiconducting SWNTs relax along the efficient nonradiative channels provided by any metallic SWNTs in the bundle.⁸⁹

Isolating individual nanotubes was a major advancement toward their optical characterization. O'Connell et al. pioneered a method to encapsulate SWNTs in a variety of surfactants including micelles,^{71,119} polymers,¹²⁰ and DNA.¹²¹ Isolated semiconducting

Figure 2-10. Spectra showing normalized absorbance (orange solid line) and fluorescence (blue dotted line) from an ensemble of HiPco-manufactured SWNTs suspended in SDS/D₂O. Resolved peaks correspond to various (n,m) structures.

SWNTs fluoresce, revealing resolved optical transitions for distinct nanotube (n,m) structures (Figure 2-10).⁷¹ To assign a specific (n,m) structure to each optical feature, the fluorescence energy and the diameter-dependent radial breathing mode (RBM) energy in the resonant Raman spectrum were correlated (vide infra);^{87,96} complicated fitting procedures were necessary, as several assignments are plausible.^{87,96} Single molecule studies directly confirmed spectral assignments.⁷²

The fluorescence quantum yield provides a measure of the luminescence efficiency for a fluorescent molecule. Importantly, the fluorescence quantum yield offers insight into the rates of radiative and nonradiative relaxation processes (k_r and k_{nr} , respectively), which are related to the lifetime (τ) of a molecule in an excited state.

$$\Phi_{SWNT} = \frac{k_r}{k_r + k_{nr}} = \frac{1}{1 + (\tau_r / \tau_{nr})} \quad (2-38)$$

Typically, the ensemble QY for an aqueous suspension of single-walled carbon nanotubes is only 0.05%,⁸⁹ which is a major concern for the development of fluorescence-based applications that would incorporate SWNTs. Relatively little is known about why the ensemble QY is so poor for nanotubes, which presents an exciting opportunity to clarify the yet incomplete description of SWNT photophysics.

Two methods can be used to determine fluorescence QYs. Absolute QY measurements count all photons absorbed by the sample as well as all emitted photons captured by the detector; however, these values are extremely difficult to quantify. On the other hand, a more straightforward approach is to measure a relative QY by comparing the fluorescence efficiency of the unknown molecule (X) to a standard (S) with a well-defined QY (Φ). In this case, both dilute samples are excited at the same wavelength and resulting fluorescence spectra are integrated over the same wavelength

range (F). The absorbance (A) is measured at the excitation energy for each sample and a simple correction accounts for differences in the refractive index of the solvents (η).

$$\Phi_x = \Phi_s \left(\frac{F_x}{F_s} \right) \left(\frac{A_s}{A_x} \right) \left(\frac{\eta_s}{\eta_x} \right)^2 \quad (2-39)$$

2.3.3 Raman Spectroscopy

If a photon of light is not absorbed by a molecule, it can scatter elastically or inelastically. Elastic scattering conserves the energy of the incoming photon but changes its direction, and is called Rayleigh spectroscopy. Rayleigh scattering has been used to confirm the family behavior of optical transitions in semiconducting SWNTs as well as predictions for the splitting of optical transitions in metallic SWNTs that arise from trigonal warping.¹⁰⁸ On the other hand, inelastic light scattering involves an exchange of energy between the incoming photon and the molecule. Thus, Raman spectroscopy is a simple and sensitive probe of electron–phonon coupling that provides a wealth of information about the diameter, orientation, and metallic or semiconducting identity of a carbon nanotube.

Raman scattering is a three-step process that conserves energy and momentum. First, an incoming photon with frequency ω_1 creates a resonant electron–hole pair. Second, the quasiparticle scatters inelastically by the emission (Stokes) or annihilation (anti-Stokes) of a phonon with frequency ω_{ph} . Finally, the electron and hole recombine and emit a scattered photon of frequency ω_2 .⁹³

$$\hbar\omega_1 = \hbar\omega_2 \pm \hbar\omega_{ph} \quad (2-40)$$

In other words, Raman scattering is a change in a molecule's polarizability caused by interaction with light, and group theory predicts three Raman-active modes for nanotubes with symmetry of A , E_1 , or E_2 .¹²²

A Raman spectrum for carbon nanotubes exhibits four major peaks, which are presented in Figure 2-11. These modes are the G-band, D-band, G'-band, and RBM.¹²² An unusual feature of Raman spectroscopy for SWNTs is that spectra can be observed for individual nanotubes when they are excited on-resonance. Resonant Raman spectroscopy results in a huge enhancement of the SWNT scattering signal because the DOS is high near van Hove singularities.¹²²

The G-band is named for its relationship to graphite and arises from the symmetric stretch of sp^2 -hybridized carbon in the honeycomb lattice network. The G-band is located between 1550 and 1605 cm^{-1} and its line shape can be used to discern the presence of semiconducting or metallic SWNTs. For example, semiconducting SWNTs

Figure 2-11. Spectrum showing Raman scattering from an ensemble of micelle-encapsulated CoMoCAT-manufactured SWNTs in D_2O . The RBM, D-band, G-band, and G'-band are indicated.

exhibit two Lorentzian features with full width at half maximum (FWHM) approximately equal to 6–15 cm^{-1} ; the low-frequency component (ω_{G-}) is associated with vibrations in the circumferential direction and the high-frequency component (ω_{G+}) is assigned to vibrations along the length of the SWNT. For metallic SWNTs, ω_{G+} has a similar line width to that of semiconducting SWNTs, but ω_{G-} has a broad Breit–Wigner–Fano line shape reflecting strong coupling to a continuum of surface plasmons.¹²²

Second, the D-band, or disorder band, is caused by scattering from a defect that breaks the basic symmetry of the crystalline SWNT. Defects in carbon nanotubes arise from the presence of sp^3 -hybridized carbon atoms associated with structural imperfections including pentagon–heptagon pairs, kinks, open SWNT ends, or impurities. The D-band is situated at $\sim 1350 \text{ cm}^{-1}$ and, interestingly, shifts in response to changes in excitation energy, in contrast to the other Raman modes.¹²² The ratio of the G- and D-band intensities is often used to qualitatively assess the presence or absence of defects along the SWNT. The G'-band is the overtone of the D-band.

The RBM arises from the in-phase expansion and contraction of the nanotube as all of the carbon atoms move in the radial direction.¹²² Thus, the frequency of the RBM correlates well with the diameter of the SWNT as empirically deduced by Bachilo et al.⁸⁷

$$\omega_{RBM} = \frac{223.5 \text{ cm}^{-1}}{d_t} + 12.5 \text{ cm}^{-1} \quad (2-41)$$

where ω_{RBM} (cm^{-1}) is the frequency of the RBM and d_t (nm) is the diameter of the SWNT. The RBM is usually located near $\sim 200 \text{ cm}^{-1}$ and is often used to identify the particular (n, m) structure of the SWNT.¹²² A summary of vibrational modes observed for Raman scattering in SWNTs is presented in Table 2-1.

Table 2-1. Vibrational Modes Observed for Raman Scattering in SWNTs¹²²

notation	frequency (cm ⁻¹)	symmetry	type of mode	SWNT information
G-band	1550–1605	A, E_1, E_2	graphite-related optical mode	metallic or semiconducting
D-band	~1350	–	defect-induced, dispersive mode	presence of sidewall defects
RBM ⁸⁷	$(223.5/d_t) + 12.5$	A	in-phase radial displacements	diameter and (n,m) structure

In summary, SWNTs experience quantum confinement due to their narrow circumference, creating unique electronic features that make nanotubes either metallic or semiconducting. Optical transitions take place between singularities in the DOS, but a more complete picture of the excited state must involve excitons. Oriented SWNTs facilitate a detailed comparison of absorption and emission properties predicted by calculations of the electronic band structure. Importantly, the isolation of SWNTs enables observation of NIR SWNT luminescence. Raman spectroscopy is a powerful tool for extracting the diameter, orientation, and identity of a particular SWNT, as well as assessing its overall structural quality.

2.4 Quantum Dot Structure and Optical Properties

Quantum dots (QDs) are zero-dimensional semiconducting nanocrystals.¹²³ CdSe and CdTe nanoparticles are used in this work as a reference molecule for obtaining single molecule relative QY measurements for SWNTs (Chapter 5). These particular moieties are made up of a few hundred to a few thousand atoms that are arranged in a wurtzite crystal structure. Because its surface to volume ratio is large, the quality of the electronic properties for a QD is highly dependent upon the absence of defect sites on the surface

Figure 2-12. (a) Spectra presenting absorbance (solid) and fluorescence (dotted) for CdSe QDs ranging in diameter from 2.0 nm to 4.4 nm. Data are courtesy of Megan Hahn. (b) Digital photograph of CdSe QD fluorescence generated upon illumination with a handheld UV lamp with approximate QD diameters indicated. Image is courtesy of Joaquin Calcines.

that can trap electrons and holes. To passivate the surface, shelling techniques are routinely used to encase the core of the crystal with a material possessing both a larger band gap (to avoid leaking of carriers into the shell) and a similar lattice constant (to minimize the lattice mismatch between the core and shell).¹²³ Therefore, ZnS and CdS are often used to shell CdSe and CdTe quantum dots.¹²⁴

The photophysical properties of quantum dots are dictated by their size. As described, an absorbed photon in a bulk material creates a bound electron-hole pair that can easily maintain a spatial separation equal to the exciton Bohr radius. The physical dimensions of a quantum dot are smaller than this distance, and so the exciton is confined in nanocrystals. The energy of the exciton can be modeled simply by the three-dimensional particle in a box model, where transitions occur at discrete energy levels.¹²³

$$E \approx E_g + \frac{n^2 h^2}{8R^2 m_e} + \frac{n^2 h^2}{8R^2 m_h} \quad (2-42)$$

E is the lowest optical transition, E_g is the band gap of the bulk semiconducting material (i.e., CdSe), n is the principle quantum number, h is Planck's constant, R is the radius of the nanocrystal, and m_e and m_h are the effective masses of the electron and hole, respectively. As the size of a QD increases, its band edge energy shifts to the red,¹²³ as demonstrated in Figure 2-12. As fluorophores, QDs offer numerous advantages over traditional organic dyes, including a continuous range of absorption energies, good photostability, and emission that is brighter, narrower, and has a more symmetric line shape.¹²⁵

CHAPTER 3

Sample Preparation

Carbon nanotubes are insoluble in water and most organic solvents, and so dispersing agents are used to produce aqueous suspensions of isolated SWNTs. Nanotubes were suspended in a suite of surfactants and biomolecules using ultrasonic dispersion followed by high-speed centrifugation. The choice of SWNT starting material, dispersing agent, and processing conditions were varied to determine an optimized dispersion protocol for single molecule studies. The quality of SWNT suspensions was assessed by absorption and fluorescence spectroscopies, with calculation of fluorescence quantum yields.

3.1 Introduction

3.1.1 Motivation

As introduced in Chapter 2, carbon nanotubes are produced as inhomogeneous mixtures of molecules with different diameters, chiralities, lengths, and aggregation states.⁷¹ Although this diversity provides access to a profusion of SWNT structures, it also complicates the research and development of unique features displayed by each moiety. For optical studies, the primary obstacle in sample preparation is the aggregation caused by strong van der Waals interactions between SWNT sidewalls (~ 500 eV/ μm of sidewall contact),⁷¹ which obscures resolved absorption features and quenches fluorescence.

Further, their propensity to form complex networks of aggregates and their lack of surface functional groups make carbon nanotubes highly resistant to wetting.¹²⁶ As a result, SWNTs are insoluble in water and nearly all common organic solvents, with the exception of N-methylpyrrolidone.^{127,128} It is desirable to solubilize SWNTs in aqueous environments to accommodate both ease of sample processing and compatibility for biological applications. Although the nanotube sidewall can be functionalized to provide an appropriate interface between the solute and solvent, non-covalent functionalization retains the pristine electronic properties of the SWNT and is the preferred solubilization method for optical studies.

Both aggregation and insolubility can be overcome by suspending SWNTs in dispersing agents that noncovalently attach to their sidewalls by hydrophobic interactions or π -stacking.^{129,130} To isolate SWNTs from aggregated bundles, an ultrasonic dispersion process is used to induce gaps at the bundle ends, allowing surfactant adsorption to

Figure 3-1. (a) Cartoon depicting bundled (left) and isolated (right) SWNTs encapsulated in SDS surfactant, viewed along the face of the SWNTs. Figure adapted from ref 71. (b) Digital photograph of bundled (left) and isolated (right) SWNTs encapsulated in a surfactant.

propagate along the length of the bundle.¹³¹ Since the seminal work of O’Connell et al. in 2002,⁷¹ ultrasonic processing has been used to isolate SWNTs in an extensive library of dispersing agents including surfactants,^{119,130} polymers,¹²⁰ single-stranded DNA,^{19,132,133} peptides,¹³⁴ and cage-like molecules such as Sarkosyl.¹³⁵ Figure 3-1 contrasts the appearance of an aqueous suspension containing mostly bundles and an aqueous sample enriched in isolated SWNTs. Recent work has also demonstrated that it is possible to achieve limited separation of exfoliated SWNTs according to (n,m) structure,^{58,121,136} left- or right-handed chirality,⁹⁵ length,^{137,138} and electronic character (i.e., metallic or semiconducting).¹³⁹⁻¹⁴⁵

SWNT surfactants are classified in terms of their ionic character (i.e., anionic, cationic, or nonionic). Ionic surfactants have a positively or negatively charged head group that interacts with the solvent and a nonpolar tail that associates with the nanotube

sidewall; SWNT aggregation is hindered by charge repulsion between the polar head groups that extend into the solvent.¹¹⁹ On the other hand, nonionic surfactants have long side chains that impede nanotube aggregation sterically, and so effective dispersion depends strongly upon the size and solubility of these dispersing agents.¹¹⁹ Nonionic surfactants are particularly salient for preparing SWNT samples that are compatible with biological media, as they do not interact with charged cell membranes.

In contrast to surfactants that pack onto the SWNT sidewalls, DNA is a biological dispersing agent that wraps helically around SWNTs to suspend them.¹³² Recent evidence even suggests that wrapping becomes more organized as the sample ages.¹⁴⁶ The DNA bases associate with the nanotube sidewall while the charged phosphate backbone interacts with the solvent (i.e., water).¹²¹ Importantly, DNA can be functionalized with a linker molecule such as biotin, which facilitates attachment to a substrate by specific binding to a target molecule like avidin.

3.1.2 Purpose of this Study

The main goal of this SWNT solubilization study is to optimize the protocol for producing high-quality nanotube samples intended for use in ensemble and single molecule spectroscopic experiments in this dissertation (Chapters 4–6). In this work, we preserved the main features of a typical sample preparation outlined in the literature,⁷¹ but incorporated slight modifications to optimize our results. We used identical processing equipment and characterization techniques to evaluate how the choice of SWNT starting material (i.e., HiPco or CoMoCAT), dispersing agent, and processing conditions influenced the overall quality of the suspension. This analysis was required because

dispersion methods have been developed across laboratories that use different SWNT sources and processing equipment, thereby convoluting quantitative comparisons of suspension techniques presented in the literature.

Here we prepare aqueous dispersions of SWNTs isolated in surfactants and biomolecules; the chemical structures for each of these molecules are provided in Figure 3-2. SWNTs were suspended in three ionic surfactants, three nonionic surfactants, and two sequences of DNA, and resulting samples were evaluated in terms of their suitability for use in single molecule measurements. An optimized dispersion protocol for producing high-quality aqueous SWNT samples was achieved by quantitatively monitoring the optical properties of each sample using absorption and fluorescence spectroscopies.

3.2 Experimental Procedure

3.2.1 *Suspension of SWNTs in Dispersing Agents*

Carbon nanotube suspensions were prepared by ultrasonic dispersion following the general method described by O'Connell et al.⁷¹ First, three anionic surfactants were used to suspend SWNTs: sodium dodecyl sulfate (SDS; Aldrich, 99%), sodium dodecylbenzene sulfonate (SDBS; Acros Organics, 88%), and sodium cholate hydrate (CAS; Alfa Aesar, 99%). The surfactants were typically dissolved in ten milliliters of D₂O in a 15-mL plastic centrifuge tube, resulting in 1.0 wt % SDS, 0.5 wt % SDBS, or 1.5 wt % CAS solutions. SWNT starting materials were used as-received, and approximately 2 mg of nanotube soot was added to each surfactant solution. For consistency, the same two stock samples of HiPco (Carbon Nanotechnologies, Inc.)²⁸ and

CoMoCAT (SouthWest Nanotechnologies, Inc.)⁸⁶ SWNTs were used for all studies in this dissertation. The resulting mixtures were vortexed for 30 s using a VWR Mini Vortexer, followed by 1 h of high-shear agitation (~15 000 rpm) with an Ultra-Turrax T8 homogenizer to break up large nanotube flakes.

To exfoliate nanotube bundles, intense high frequency pulses were applied to each mixture using a Branson 450 probe ultrasonicator. The probe ultrasonicator was usually fitted with a ¼” microtip, but could also accommodate a ½” tip that delivered half the power of the ¼” microtip at each amplitude setting. The probe was submerged as far as possible into the SWNT mixture and samples were chilled in an ice–water bath to prevent excessive heating during ultrasonication. The duty cycle (i.e., fraction of pulse duration) was set to 20–25% of a second and the duration of ultrasonication ranged from 1 to 75 min. The pulse amplitude controlled the output power and could be tuned between 1 (minimum) and 10 (maximum), which correlated with power of approximately 12–68 W.

Following ultrasonic dispersion, isolated nanotubes were separated from bundled and unencapsulated nanotubes by ultracentrifugation. Suspensions were divided into ~1.2-mL aliquots that were placed into open Beckman polycarbonate (PC) centrifuge tubes. The PC centrifuge tubes were housed in a TLA 100.2 rotor and loaded into a Beckman-100 ultracentrifuge. The sample was spun under vacuum at 65 000 rpm (150 477g) for 4.5 hrs at a constant temperature of 20.0 °C. The top ~2/3 of the supernatant was withdrawn from the pellet and was reserved for analysis. Some samples also underwent a second round of ultracentrifugation or were disrupted for an additional 30 min in a VWR 250D bath sonicator.¹⁴⁷

Three nonionic Tween surfactants (Tween 60, 80, and 85; Sigma) were also used to suspend SWNTs. Approximately 1 mg of SWNT starting material was added to Tween solutions with concentrations of 1 wt % prepared in 900 mM NaCl/H₂O. The samples were vortexed, homogenized, and probe ultrasonicated using parallel processing procedures to those described above. Suspensions were divided into 1-mL aliquots that were placed into capped 1.5-mL Eppendorf tubes. The Eppendorf tubes were loaded into a Heraeus Instruments Biofuge Pico centrifuge and were spun in air at 13 000 rpm (16 080g) for 90 min. The top ~2/3 of the supernatant was withdrawn from the pellet and was recentrifuged a total of 4 times (i.e., 6 h of centrifugation). The final supernatant was reserved for analysis.

Finally, SWNTs were dispersed in DNA following a procedure similar to that outlined for the surfactant systems. Slight modifications were incorporated according to the protocol suggested by Zheng et al.^{121,132} Two custom oligonucleotides, single-stranded DNA (GT)₃₀ and DNA (GT)₁₅ with a 5'-labeled Biotin linker, were ordered with standard desalting purification and used as-received (IDT DNA Technologies, Inc.). Approximately 1 mg of SWNT starting material was added to solutions of 1 mg/mL DNA in 100 mM NaCl/D₂O. The samples were vortexed, homogenized, and probe ultrasonicated using parallel processing procedures to those described above, except that the small sample volumes (i.e., 1–3 mL) necessitated a slower homogenization speed (~11 000 rpm) and a lower probe sonication amplitude (setting 3; ~30 W) to prevent loss of sample by aerosoling. Suspensions were divided into ~1-mL aliquots that were placed into capped 1.5-mL Eppendorf tubes. The Eppendorf tubes were loaded into a Heraeus Instruments Biofuge Pico centrifuge and were spun in air at 13 000 rpm (16 080g) for 1

h. The top $\sim 2/3$ of the supernatant was withdrawn from the pellet and was reserved for analysis.

3.2.2 *Optical Characterization Methods*

Absorption spectra were collected with a UV/vis/NIR spectrophotometer (Perkin–Elmer Lambda-19, Lambda-900, or Lambda-950) and emission spectra were captured with a modular Acton Research Corporation fluorometer. Samples were loaded into a four-walled 1-cm quartz cuvette for all absorption and fluorescence measurements. Absorption data were collected at 0.5-nm intervals with a typical scan range of 400–1400 nm. For fluorescence measurements, samples were excited with an ~ 5 -mW (~ 100 mW/cm²) helium–neon laser ($\lambda_{\text{ex}} = 632.8$ nm) with a beam diameter of ~ 0.25 cm. An 850-nm longpass filter was positioned at the entrance of the emission monochromator to block the laser line while allowing SWNT fluorescence to pass. The emission monochromator was equipped with a 1.0- μm blaze grating with 600 grooves/mm, and slits both into and out of the emission monochromator were set to 3 mm. SWNT fluorescence was detected at a right angle with a liquid nitrogen-cooled germanium detector. Data were collected at 1.0-nm intervals with 200-ms integration at each point over a typical scan range of 900–1700 nm. All fluorescence spectra were corrected by the relative efficiency of the grating in the emission monochromator (Figure A-1) and the spectral response of the germanium detector (Figure A-2), which are provided in Appendix A.

Figure 3-3. Normalized absorption and emission spectra for the standard dye IR-26, with its chemical structure shown in the inset.

3.2.3 Ensemble Fluorescence Quantum Yields

The relative fluorescence quantum yields of suspended HiPco and CoMoCAT samples were calculated by comparing their absorption and excitation profiles to those of the standard infrared dye IR-26 (Exciton), which has a fluorescence QY $\sim 1 \times 10^{-3}$.¹⁴⁸ The absorption and fluorescence spectra for IR-26, as well as its chemical structure, are shown in Figure 3-3. IR-26 solutions were prepared by adding a few grains of the powdered dye to ~ 5 mL of dichloroethane (DCE).

For absorption measurements, both the SWNT and IR-26 samples were diluted until their absorbance was <0.05 at the desired fluorescence excitation wavelength (i.e., 960 nm for HiPco and 900 nm for CoMoCAT samples). For fluorescence measurements,

the samples were excited using a 29-mW (38 mW/cm^2) Ti:sapphire laser, pumped by a 532-nm Nd:YAG laser, that had a beam diameter of $\sim 0.5 \text{ cm}$. The excitation energy was tuned to the desired wavelength with the aid of a spectrometer (Ocean Optics, Inc. S2000), and an appropriate bandpass filter removed unwanted light from the excitation beam. Fluorescence spectra were integrated for 600 ms per point. Values of 1.328 and 1.444 were used for the refractive indices of D_2O and DCE, respectively. The QYs for HiPco and CoMoCAT samples were calculated using eq 2-39.

3.3 Results

3.3.1 SWNT Starting Materials

Figure 3-4 presents ensemble absorption and emission spectra of micelle-encapsulated HiPco and CoMoCAT nanotubes suspended in 0.5 wt % SDBS. In agreement with the literature, HiPco nanotubes exhibited more peaks than CoMoCAT SWNTs at the expected transition wavelengths due to the larger distribution of (n,m)

Figure 3-4. Optical absorption (orange solid line) and fluorescence spectra (blue dotted line) comparing the relative diameter distributions of (a) CoMoCAT and (b) HiPco SWNTs dispersed in SDBS/ D_2O . Spectra were normalized to the peak at $\sim 980 \text{ nm}$ in CoMoCAT and the peak at $\sim 1250 \text{ nm}$ in HiPco.

structures in this starting material.⁸⁶ HiPco SWNTs have a diameter distribution of 0.62–1.31 nm and an average diameter of 0.93 nm.^{87,91} CoMoCAT SWNTs, in contrast, have a much smaller diameter distribution (0.62–1.05 nm) and a lower average diameter of 0.81 nm.⁸⁶ CoMoCAT nanotubes are naturally enriched in (6,5) and (7,5) SWNTs; based on fractional fluorescence intensities, each of these structures comprises ~28% of the semiconducting species, for a combined total of ~38% of all CoMoCAT structures.⁸⁶ We did not systematically vary the amount of SWNT starting material during these studies, as during ultracentrifugation, most of the solid starting material collected as a solid pellet.

3.3.2 SWNT Dispersing Agents

SWNTs were successfully dispersed in SDS, SDBS, CAS, Tween 80, and DNA. Using similar processing conditions to those used to disperse other surfactants, Tween 60 and Tween 85 did not suspend SWNTs. Table 3-1 provides the molecular weight (MW) of the surfactants and summarizes the E_{11} transition energies for SWNT absorption and fluorescence, the associated Stokes shift, and the fluorescence line width of the (7,5) E_{11} peak. The (7,5) feature was used as a reference between optical measurements because this strong peak displayed minimal overlap with other structures, enabling more accurate measurements of line widths. SDS was the surfactant system selected as a reference, as it has been examined extensively in the literature.

In agreement with the results of Moore et al.,¹¹⁹ the choice of surfactant influenced the exact energy of the SWNT absorption and fluorescence transitions,¹¹⁹ which is demonstrated in Figure 3-5. In comparison to the SDS standard, each of the surfactants generally shifted optical transitions to lower energies; one notable exception

Table 3-1. Spectral Properties of CoMoCAT SWNTs in Dispersing Agents

	SDS	SDBS	CAS	Tween 80 ^a	DNA
MW (g/mol)	288.4	348.5	430.6	1 308.0	18 940.2 (GT) ₃₀ 9833.5 (GT) ₁₅ -Biotin
(9,1) SWNTs					
$\lambda_{11, \text{ABS}}$ (nm)	912	915	911	-	932
$\lambda_{11, \text{PL}}$ (nm)	914	917	922	-	933
Stokes shift (cm ⁻¹)	24	24	133	-	12
Stokes shift (meV)	3	3	17	-	1
(8,3) SWNTs					
$\lambda_{11, \text{ABS}}$ (nm)	954	956	953	957	972
$\lambda_{11, \text{PL}}$ (nm)	957	959	964	960	978
Stokes shift (cm ⁻¹)	33	33	122	33	64
Stokes shift (meV)	4	4	15	4	8
(6,5) SWNTs					
$\lambda_{11, \text{ABS}}$ (nm)	979	979	974	986	989
$\lambda_{11, \text{PL}}$ (nm)	982	986	984	987	995
Stokes shift (cm ⁻¹)	31	73	106	10	62
Stokes shift (meV)	4	9	13	1	8
(7,5) SWNTs					
$\lambda_{11, \text{ABS}}$ (nm)	1021	1024	1021	1038	1034
$\lambda_{11, \text{PL}}$ (nm)	1027	1028	1035	1041	1045
Stokes shift (cm ⁻¹)	58	39	140	33	103
Stokes shift (meV)	7	5	17	4	13
PL line width (cm ⁻¹)	323 ± 73	323	262	500	349
PL line width (meV)	40 ± 9	40	32	62	43

^a The (9,1) transitions were not resolved in Tween 80 optical spectra.

Figure 3-5. Spectra presenting optical absorbance (solid lines) and emission (dotted lines) for CoMoCAT SWNTs in five dispersing agents. All spectra were normalized to the (6,5) SWNT absorbance or emission peak and are offset for clarity. Dotted gray lines highlight the shifting of spectral peaks with respect to SDS-encapsulated SWNTs.

is the blue shift of CAS absorption relative to SDS. The surfactants can be listed in order of increasing average red shift of E_{11} absorption energies compared with SDS-encapsulated SWNTs: CAS ($\Delta\lambda_{11, \text{ABS}} = -1.9$ nm), SDBS ($\Delta\lambda_{11, \text{ABS}} = 2.0$ nm), Tween 80 ($\Delta\lambda_{11, \text{ABS}} = 8.8$ nm), and DNA ($\Delta\lambda_{11, \text{ABS}} = 15.3$ nm). The surfactants can also be listed in order of increasing average red shift of E_{11} fluorescence energies: SDBS ($\Delta\lambda_{11, \text{PL}} = 2.5$ nm), CAS ($\Delta\lambda_{11, \text{PL}} = 6.3$ nm), Tween 80 ($\Delta\lambda_{11, \text{PL}} = 7.3$ nm), and DNA ($\Delta\lambda_{11, \text{PL}} = 17.8$ nm).

The Stokes shift was obtained by subtracting the position of the E_{11} peak in the fluorescence spectrum from its position in the absorption spectrum (Figure 3-5). In order of increasing average Stokes shift, the surfactants are: Tween 80 ($\Delta\lambda_{11} = 25$ nm), SDS

($\Delta\lambda_{11} = 37 \text{ cm}^{-1}$), SDBS ($\Delta\lambda_{11} = 42 \text{ cm}^{-1}$), DNA ($\Delta\lambda_{11} = 60 \text{ cm}^{-1}$), and CAS ($\Delta\lambda_{11} = 125 \text{ cm}^{-1}$). O'Connell et al. observed an average Stokes shift of $\sim 45 \text{ cm}^{-1}$ for SWNTs dispersed in SDS,⁷¹ in good agreement with our value; however, the value of the CAS Stokes shift observed here is nearly 4 times larger than value provided in ref 149 for the same surfactant (32 cm^{-1}).

Finally, the fluorescence line widths were measured for the (7,5) SWNT peak in each surfactant system (Figure 3-5). The smallest fluorescence line widths were measured for CAS ($\Delta E = 262 \text{ cm}^{-1}$), followed by SDS and SDBS ($\Delta E = 323 \text{ cm}^{-1}$), DNA ($\Delta E = 349 \text{ cm}^{-1}$), and Tween 80 ($\Delta E = 500 \text{ cm}^{-1}$). For SWNTs dispersed in SDS, the literature value for fluorescence line widths is typically $\sim 200 \text{ cm}^{-1}$, which agrees relatively well with the values obtained here, although our fluorescence line widths are broader.⁷¹ These broader line widths may indicate that, in comparison, fewer residual bundles were removed from our samples during ultracentrifugation. In addition, spectral overlap between different SWNT structures sometimes impeded measurement of fluorescence line widths, which could account for some differences.

3.3.3 Sample Preparation Conditions

Figures 3-6a and 3-6b display the effect of varying the surfactant concentration for a representative series of CoMoCAT samples dispersed in CAS using identical sonication conditions (i.e., 25% duty cycle, amplitude 7 ($\sim 55 \text{ W}$), 75 min). Absorption spectra indicate that the concentration of suspended SWNTs increased with surfactant concentrations between 1.0 and 2.0 wt % CAS, but decreased at a higher concentration of 2.6 wt % CAS. In corresponding fluorescence spectra for the same samples, the intensity

Figure 3-6. Comparison of sample preparation parameters and their influence on corresponding absorption and fluorescence spectra for CoMoCAT SWNTs dispersed in various surfactants. Spectra indicate the changes in the optical spectra resulting from variations in (a) and (b) surfactant concentration, (c) and (d) amplitude (AMP) of tip sonication power, and (e) and (f) duration of tip sonication. For each comparison, sample preparation conditions were held constant except for the parameter under consideration (see text for details).

for 1.0 wt % CAS was the lowest, as expected. However, the fluorescence intensity increased dramatically for 1.5 wt % CAS and then continued to decrease with increasing surfactant concentration.

Figures 3-6c and 3-6d present the effects of varying sonication settings for a series of CoMoCAT SWNTs dispersed in 0.5 wt % SDBS using similar sonication conditions (i.e., 20 or 25% duty cycle, 60 min). Three different ultrasonication

amplitudes were used for this comparison: 5.0 (~42 W), 6.0 (~48 W), and 9.5 (~68 W). Increasing the sonication power did not cause a direct increase in the quantity of suspended SWNTs as evidenced by either absorption or fluorescence spectroscopies. Instead, the absorbance decreased between amplitude 5.0 and 6.0, and then increased dramatically at amplitude 9.5; the fluorescence intensity decreased significantly between amplitude 5.0 and 6.0, and then increased dramatically at amplitude 9.5.

Figures 3-6e and 3-6f present the impact of sonication duration on a series of CoMoCAT SWNTs dispersed in 0.5 wt % SDBS using similar sonication conditions (i.e., 20 or 25% duty cycle, amplitude 5 (~42 W)). Three different ultrasonication durations were used for this comparison: 4, 30, and 60 min. The absorbance and fluorescence intensities both increased with increasing length of sonication time.

After typical sample preparation, two post-processing studies were carried out. First, an additional round of ultracentrifugation was applied to a sample of CoMoCAT SWNTs dispersed in 1 wt % SDS. The intensity of the (6,5) absorption peak displayed a 47.7% decrease for the suspension that was centrifuged twice compared to the suspension that was centrifuged once. Second, the influence of additional bath sonication was assessed for two samples of CoMoCAT SWNTs dispersed in 0.5 wt % SDBS (sonication conditions varied between samples). The intensity of the (6,5) absorption peak displayed an average increase of 0.5% upon 30 min of bath sonication.

3.3.4 Ensemble Fluorescence Quantum Yields

Ensemble fluorescence quantum yields were calculated for five SWNT samples relative to the standard dye IR-26. The calculated QY values are presented in Table 3-2.

Table 3-2. Measured Ensemble QYs for SWNT Dispersions

SWNT dispersion	QY (%)
HiPco in 1% SDBS	0.042
CoMoCAT in 0.5% SDBS	0.054
CoMoCAT in 1.5 wt % CAS	0.029
CoMoCAT in 1.5 wt % CAS	0.015
(6,5) CoMoCAT SWNTs in DNA (GT) ₃₀ ^a	0.14

^a Sample was kindly provided by Ming Zheng (DuPont Corporation).

In agreement with literature values, the typical fluorescence QY was ~0.04% for micelle-encapsulated SWNTs.^{71,150} Interestingly, the purified sample of DNA-wrapped (6,5) semiconducting SWNTs displayed a QY that was nearly three times greater than that of the heterogeneous, surfactant-wrapped samples.¹⁵¹

3.4 Discussion

The choice of SWNT starting material, surfactant, and processing conditions were assessed in terms of the quality of sample that was produced for use in single molecule spectroscopic measurements. Immediately following sample preparation, visual inspection served as an immediate qualitative indicator of whether or not SWNTs were suspended successfully, as solubilized samples appeared gray and were devoid of aggregates in the solvent (Figure 3-1). Detailed analysis was provided by interpretation of optical absorption and fluorescence spectra and determination of fluorescence QYs. Based on a thorough analysis of optical data, a standard protocol was outlined for the production of high-quality SWNT samples in surfactants and wrapping agents.

3.4.1 *Recommended SWNT Starting Material*

Because of their small average diameter, CoMoCAT SWNTs exhibit E_{11} transition energies that are centered at higher energies than are HiPco SWNTs. This feature is amenable for accessing the high-energy spectral region at which NIR detectors generally have lower noise, such as read noise and dark current (Chapter 4). In addition, the narrower distribution of diameters for CoMoCAT SWNTs leads to less complicated ensemble spectra and also benefits statistical analysis of single molecule measurements (i.e., for the same number of measurements, more data is collected for each SWNT type).

3.4.2 *Recommended SWNT Dispersing Agents*

The surfactants were dissolved in one of three solvent systems. Specifically, all ionic surfactants were dissolved in D_2O , Tween surfactants were dissolved in 900 mM NaCl/ H_2O , and DNA was dissolved in 100 mM NaCl/ D_2O . Although the influence of solvent environment was not studied here, differences in the choice of solvent system may complicate direct comparison between the ionic surfactants and Tween or DNA. The rationale for using D_2O as a solvent is that water shows an intense absorption peak in the NIR that is caused by the O–H stretch; the band largely obscures SWNT absorption transitions for $\lambda > 900$ nm (Figure 3-7). In contrast, the more massive D atom in D_2O shifts the stretch to lower energies. As a result, D_2O exhibits only a modest absorption band in this region, which can be compensated easily by background subtraction. Saline solutions were used for Tween surfactants and DNA, which denatures below a 100 mM threshold of counterions.¹⁵² High salt concentrations have been shown to initiate SWNT

Figure 3-7. Absorption spectrum for H₂O (dotted line) and D₂O (solid line), indicating the low absorbance for deuterated water in the spectral region where SWNT absorption occurs.

flocculation, and could further impede direct comparison between suspensions produced using the ionic surfactants and Tween or DNA.⁷¹

All tested ionic surfactants and DNA successfully suspended SWNTs, but the nonionic Tween series showed less predictable results. Conflicting results have been noted in the literature, as Moore et al.¹¹⁹ observed SWNT suspension only in Tween 85 whereas Wenseleers et al.¹³⁰ observed SWNT suspension only in Tween 60 or Tween 80. In our experiments, Tween 80 was the only nonionic surfactant that successfully suspended SWNTs. The direct link between the molecular weight of a nonionic surfactant and its ability to suspend SWNTs has been well-studied and likely explains the superior dispersing ability of Tween 80 (1308 g/mol) relative to Tween 60 (439 g/mol).¹¹⁹ On the other hand, although Tween 80 has a lower molecular weight than Tween 85

(1839 g/mol), the solubility of Tween 85 is reduced in water because it has three nonpolar chains and only one freestanding polar branch (i.e., a poly(ethylene glycol) chain), making molecular packing more difficult and limiting the stability of micellar structures.¹³⁰

The presence of water at the SWNT surface increases the strength of the local dielectric environment, which shifts the fluorescence peak and lowers its intensity.¹¹⁹ Based on this idea, the shifts in our fluorescence spectra indicate that SDS packs most densely on the SWNT (i.e., resulting in the lowest exposure to solvent), followed by SDBS, CAS, Tween 80, and DNA. It has been well established that when SWNTs are wrapped non-uniformly with DNA of finite length, a large percentage of the SWNT sidewall remains exposed to the solvent.¹⁵³

The local environment influences nearly all aspects of SWNT fluorescence. For example, transition energies for surfactant-coated nanotubes are red shifted by an average of ~28 meV compared with unprocessed SWNTs suspended across pillars¹⁵⁴ or ~50 meV compared with as-grown SWNTs.¹²⁹ These shifts may result from screening of electron–hole interactions by the surrounding dielectric medium.¹⁵⁵ The peak position can depend upon defects in the nanotube sidewalls introduced during their suspension¹⁵⁶ and upon the choice of surfactant used for solubilization.^{119,129} SWNT fluorescence is also affected by other environmental factors such as temperature,^{157,158} mechanical strain,¹⁵⁹ surrounding dielectric constant,¹⁵⁵ or the presence of a magnetic field.¹⁶⁰

In particular, the large variation in Stokes shifts highlights the importance of the local environment surrounding the SWNT.¹⁴⁹ For most surfactants, the relatively small Stokes shift was well within the range of accepted literature values (~45 cm⁻¹);⁸⁷ the

Stokes shift observed for CAS was larger than expected (125.1 cm^{-1}). In all spectra, corresponding peaks in the absorption and fluorescence spectra (i.e., that arose from the same SWNT structures) exhibited only small Stokes shifts, indicating a set of chromophores with minimal differences in the amount of electron–phonon coupling occurring in the ground and excited states.¹⁶¹ In other words, small Stokes shifts indicate that the SWNT, surfactant, and solvent undergo little geometric reorganization upon photoexcitation.⁷¹ Although it is unclear how the Stokes shift is influenced by the surfactant,¹⁶¹ these observed energy shifts provide validation that the local dielectric environment also influences the magnitude of the exciton binding energy.¹¹¹

Fluorescence line widths are strong indicators of the degree of bundling present in a sample. Specifically, isolating SWNTs in dispersing agents reduces the electronic coupling between SWNTs and resolves fine structure in their optical spectra. The fluorescence line width for CAS was only 262 cm^{-1} , indicating a very high percentage of isolated SWNTs. The narrow line widths for SDS (323 cm^{-1}), SDBS (323 cm^{-1}), and DNA (349 cm^{-1}) also indicate high-quality dispersions with limited bundling. Yet our line widths were broader than those reported in ref 71 (200 cm^{-1}), suggesting that in our studies, a smaller fraction of residual bundles was extracted during ultracentrifugation. An extremely broad line width was observed for Tween 80 (500 cm^{-1}), indicating severe bundling in this sample. In addition, the fluorescence intensity for Tween 80 samples was disproportionately high at long wavelengths, arising from transfer of excited carriers in high energy (small-diameter) SWNTs to low energy (large-diameter) SWNTs. The abundance of residual aggregates in Tween 80 samples likely resulted from a combination of low centrifugation processing speeds and high salt concentrations.⁴⁴

The nature of the suspension (i.e., micellar packing onto or helical wrapping around the SWNT) did not produce markedly different spectral characteristics between surfactant systems and DNA. However, the stability of prepared samples was much greater when using dispersing molecules that wrapped the SWNT instead of packing onto its surface. For example, the ionic surfactants could generally be used within three to six months of production before significant rebundling occurred, and the Tween suspensions had a very short shelf life, on the order of 1–2 weeks before the onset of aggregation. In contrast, DNA debundled a very high percentage of nanotubes that was stable for over one year, indicated by resolved optical features.

Altogether, SDS, SDBS, and CAS all provided high-quality SWNT samples and were used in subsequent single molecule studies (Chapters 4–6). SDS and SDBS both serve as excellent standard suspensions, especially for ensemble measurements; however, one concern for using SDBS-encapsulated samples is the limited purity of the starting material (88%). Of the ionic surfactants, CAS samples were used most extensively for single molecule studies because they provided the narrowest fluorescence line widths of all the dispersing agents tested, indicating an excellent degree of debundling. In addition, the natural curvature of the CAS molecule leads to enhanced suspension of (6,5) and (7,5) SWNTs.¹²⁹ Tween 80 did not suspend or isolate SWNTs as efficiently as the other surfactants or DNA, and its use is not generally recommended. On the other hand, DNA-wrapped samples displayed high dispersing concentrations and long-term stability, and are more amenable to biological applications than Tween 80. Further, for applications requiring attachment to a surface or target molecule, biotinylated DNA wrapping agents provide a convenient route to specific binding.

3.4.3 *Recommended Sample Preparation Conditions*

An optimal concentration was determined for each surfactant; no analogous concentration was determined for DNA, as it does not form micellar structures. If the amount of surfactant is too low, Grossiord et al. note that bundled SWNTs remain in the suspension because there is not enough material to adsorb onto the SWNT sidewalls. However, too much surfactant produces surfactant micelles in the solution; bundles are formed by attractive interactions between remaining nanotube molecules (i.e., the depletion effect).¹⁶² Our observations of low absorption and fluorescence intensities at both low and high surfactant concentrations can be understood in the context of this interpretation. For example, the fluorescence decrease at high surfactant concentrations most likely results from the presence of residual bundles, which quench fluorescence, in the suspensions. Although Rickard et al. reported that the fluorescence intensity decreases at higher SWNT concentrations due to the reabsorption of emitted photons, the absorbance values for our samples were <0.15 , and so this effect cannot account for our observations.¹⁶³

Ultrasonic disruption conditions (i.e., power and duration) are perhaps the most influential parameters that can be adjusted to control SWNT sample quality and dispersion efficiency. Unfortunately, a significant tradeoff is associated with the intensity and duration of sonication and the resulting sample quality. Harsh ultrasonic processing damages the sidewalls and severs the nanotubes (wide SWNTs are shortened more than are narrow SWNTs).¹³⁷ The ideal sonication time depends upon the final desired application for which the SWNTs will be used. For example, high SWNT concentrations are not usually required for single molecule measurements. For

consistency and to reduce sample heating, all prepared suspensions were chilled in an ice–water bath during sonication, as the temperature at which sonication occurs can also influence their optical spectra.¹⁵⁶

The large increase in absorption observed at high sonication intensities likely reflects the increased generation of graphitic particles, a byproduct of the harsh ultrasonication process, which elevates the baseline. Nair et al. have provided a fitting curve that can be used to subtract the contributions to absorption spectra caused by these graphitic impurities and resonant π -plasmons.¹⁶⁴ The fluorescence intensities did not directly scale with absorption intensities, which reinforces the idea that sample quality generally degrades with increasing sonication power.

The intensity of absorption and fluorescence increased with increasing duration of sonication, as expected. Thus, the efficiency of SWNT suspension increased for longer sonication times. The length of nanotubes in an ultrasonicated sample scales as $t^{-0.5}$, as demonstrated in ref 165, and so shorter SWNTs were most likely produced with longer ultrasonication times. The estimated lengths of the SWNTs used in single molecule studies in this dissertation were 100–500 nm, and the average length measured for DNA-wrapped samples used in Chapter 5 was ~ 380 nm.⁷⁷

Ultracentrifugation is required because complete separation of bundled and isolated SWNTs is never achieved by the sonication procedure, as a dynamic equilibrium is established between these species during the process.¹³¹ After centrifugation, it was extremely important not to extract too much supernatant liquid from the centrifuge tube. Recent studies have demonstrated that the number of bundles increases with distance into the centrifuge tube,¹⁶⁶ and so it is advisable to attain a smaller final sample volume than

to withdraw the supernatant immediately surrounding the solid pellet. Still, as evidenced by the decreased absorption intensity for the sample subjected to a second round of ultracentrifugation, it is highly likely that residual bundles are present in both the SWNT samples prepared here and those described elsewhere in the literature. Although corresponding fluorescence spectra were not collected for the recentrifuged sample, it is possible that some improvement to the QY would accompany the removal of any residual bundles; on the other hand, if this additional processing extracted SWNTs that originally had been isolated in the surfactant, then no improvement to the QY would be expected.

One final sample preparation parameter that was tested was postcentrifugation bath sonication. It has been suggested that 30 min of gentle bath sonication enhances the yield of suspended SWNTs while maintaining their lengths, when gentle sonication is applied to already-dispersed bundles instead of entangled mats in the raw soot.¹⁴⁷ However, only a 0.5% improvement in absorption intensity was observed in our study; because this enhancement was so small (and actually decreased the absorption intensity for one sample), the bath sonication method was not incorporated as part of the standard protocol for SWNT sample preparation.

Reproducibility for sample preparation was fairly consistent; however, identical sample preparation trials usually did not produce absorption and fluorescence spectra with identical intensities. Three factors that were not studied here, but may account for some differences in reproducibility, are discussed. First, the probe ultrasonicator tip continuously erodes over time, which alters the actual power delivered to the sample. Second, the duty percent was not systematically varied, but influences the rate of sample heating, which we nominally controlled by completing this step in an ice–water bath.

Finally, the sample pH was not monitored during these studies, but could be adjusted by simple addition of acid or base; variations in pH have been shown to influence the intensity of optical transitions due to reversible hole doping of the SWNT sidewall.^{167,168}

In summary, a high-quality sample is considered to have (i) a high concentration of exfoliated SWNTs, (ii) minimal amounts of residual bundles or unwrapped SWNTs, (iii) highly resolved optical features in absorption and fluorescence spectra, and (iv) a high fluorescence quantum yield. Table 3-3 summarizes the recommended protocol for producing high-quality SWNT dispersions in SDS, SDBS, CAS, Tween 80, and DNA. Parameters can be modified according to the intended application.

Table 3-3. Recommended Protocol for Production of SWNT Dispersions

	SDS ^a	SDBS ^a	CAS ^a	Tween 80 ^b	DNA ^b
surfactant concentration	1.0 wt %	0.5 wt %	1.5 wt %	1.0 wt %	1.0 mg/mL
vortexer speed (setting)	7	7	7	7	7
vortexer time (s)	30	30	30	30	30
homogenizer speed (×1000 rpm)	15	15	15	15	11
homogenizer time (h)	1	1	1	1	1
sonicator probe size (in)	0.25	0.25	0.25	0.25	0.25
sonicator duty percent (%)	25	25	25	25	25
sonicator power (amplitude; W)	5; ~42	5; ~42	5; ~42	5; ~42	3; ~30
sonicator time (min)	60	60	60	60	45
centrifuge speed (×1000 rpm)	65	65	65	13	13
centrifuge time (h)	4.5	4.5	4.5	6	1

^a Samples were processed using a Beckman-100 ultracentrifuge. ^b Samples were processed using a Heraeus Instruments Biofuge Pico centrifuge.

3.4.4 Ensemble Fluorescence Quantum Yields

The ensemble QY was slightly larger for SWNTs dispersed in SDBS than in CAS, but purified (6,5) SWNTs displayed at least a threefold increase in QY ($\sim 0.14\%$) compared with surfactant-processed SWNTs ($\sim 0.04\%$). This large enhancement likely resulted from the removal of metallic SWNTs and other impurities during separations, using strong anion-exchange high-performance liquid chromatography (HPLC). In general, the extremely low fluorescence QY for SWNT samples has been attributed to the presence of metallic SWNTs that absorb but do not fluoresce, the presence of residual bundles in the suspension, defect sites along the SWNT sidewall that are introduced during ultrasonication, and the influence of nonradiative dark states, which are examined in detail in this dissertation in Chapters 5 and 6. Sources of error in all ensemble SWNT QY measurements include not accounting for contributions from π -plasmons and graphitic impurities in SWNT absorption spectra, exciting the sample with only one wavelength (i.e., that is not resonant with E_{11} for all structures), and integrating the fluorescence intensity over a limited number of SWNT structures (i.e., due to overlap between SWNT fluorescence and the laser line).

3.5 Conclusions

In summary, SWNTs were dispersed in a variety of surfactant systems and wrapping agents, which enabled the study of resolved optical transitions for different nanotube structures. The choice of dispersing agent strongly influenced absorption and fluorescence spectra, which were used to monitor the success of efficient suspension and debundling for each sample. For each dispersing agent, variation of surfactant

concentration and processing conditions enabled optimization of the protocol used to prepare high-quality dispersions. Of the tested dispersing agents, CoMoCAT SWNTs suspended in SDS, SDBS, CAS, and DNA gave the most favorable results for subsequent single molecule studies.

CHAPTER 4

Single Molecule Spectroscopy of SWNTs

Single molecule spectroscopy supplies a detailed and fundamental representation of the photophysical behavior of SWNTs, unencumbered by ensemble averaging effects. Single molecule measurements were performed for SWNTs using epifluorescence microscopy. Important features of single molecule SWNT emission include their Lorentzian line shapes, narrow line widths, and the absence of blinking at room temperature. The local environment strongly influences the fluorescence behavior of individual SWNTs.

4.1 Introduction

4.1.1 *Principles of Single Molecule Spectroscopy*

Optical spectroscopy is a powerful tool for examining the photophysical properties of fluorescent particles, and the ultimate resolution is achieved by microscopic measurements performed on single molecules. Although ensemble fluorescence studies initially revealed the important relationship between nanotube (n,m) structure and emission energy,¹⁶ some key features remained obscured by inhomogeneous line broadening and spectral overlap between fluorescence from different nanotube structures (e.g., fluorescence emission maxima, intrinsic line shapes, and line widths). In addition, ensemble studies mask time-dependent dynamics that are relevant for understanding the temporal evolution of fluorescence behavior. In studies of single molecules, it is possible to determine these fundamental features directly and without the need to synchronize many single molecules undergoing a time-dependent process, such as intersystem crossing.¹⁶⁹ It is also possible to observe additional unique behavior such as fluorescence intermittency (i.e., blinking) that cannot be observed for bulk samples.¹⁷⁰

Ensemble studies benefit significantly from the clarification of fundamental photophysical behavior that is exposed on the single particle level, which has catalyzed single molecule studies for many fluorescent systems including dyes,¹⁷¹⁻¹⁷⁴ polymer chains,^{175,176} proteins,¹⁷⁷⁻¹⁷⁹ semiconductor quantum dots,^{170,180,181} and single-walled carbon nanotubes.^{72,77,182} The observation of fluorescence from individual SWNTs was first reported in 2003 and, importantly, confirmed spectral assignments of (n,m) made on the ensemble level.⁷² Importantly, single molecule spectroscopy intrinsically avoids the

need for difficult separation techniques by enabling the examination of one molecule at a time, which is particularly useful for studying non-uniform SWNT samples.

The basic configuration of the modern fluorescence microscope, which can detect emission from single molecules, is based on nearly one hundred years of research and development.¹⁸³ The most notable advance accompanied the development of episcopic illumination (i.e., when light is reflected onto the sample rather than transmitted through it). Epifluorescence microscopes are now the most common type of fluorescence microscopes because they require that only this backscattered excitation light (i.e., from the sample or substrate) be removed from the emission. The two major types of epifluorescence microscopes are wide-field and confocal setups, in which the illuminating light is either defocused to excite the full field of view or focused to a diffraction-limited spot in the sample plane, respectively.

It may seem surprising that fluorescence from individual particles can be observed using magnification of 100× or less; however, the real key to performing successful single molecule measurements is overcoming the substantial challenges associated with noise and background. Noise is inherently present in all fluorescence measurements and arises, for example, from fluctuations in the number of photons emitted from the molecule. In contrast, background refers to photons arriving at the detector from any source other than the fluorescent molecule. One can appreciate the importance of removing background by considering the simple example of a candle burning in a field. On a sunny day, it is difficult to discriminate the burning candle from its surroundings, but at night, when all other sources of light are removed, its location becomes immediately apparent.

Three major sources of noise are thermal, shot, and environmental noise.¹⁸⁴ Thermal noise plagues NIR measurements, as Planck's Law of Blackbody Radiation predicts that this increases approximately exponentially at low energies.¹⁸⁵ Therefore, it is necessary to use cameras that are cryogenically or thermoelectrically cooled for efficient NIR detection, as dark electric current fluctuations are a major source of noise for CCD (charge coupled device) detectors. One source of shot noise is Poisson distributions of photons reaching the detector (i.e., individual fluctuations of the average) from either the excitation source or the fluorescent molecule. Finally, the surroundings can contribute some sources of environmental noise (e.g., ac power lines, radio and TV stations, and lightning).

Oppositely, a number of strategies can be used to minimize background, such as performing single molecule experiments in a darkroom to eliminate stray room light. In addition, backscattered excitation light can be reduced by use of optical filters and high-quality oil-immersion objectives, which can limit the intensity of backscattered light to <0.001% of its original level.¹⁸³ Simple background subtraction can address autofluorescence from optical components or the substrate, as these contributions are relatively small and cannot be removed with optical filters (i.e., autofluorescence often appears in the spectral region where the fluorophores emits).

Upon successful minimization of noise and background, it is also necessary to evaluate the brightness of the fluorescent molecule. The intensity of fluorescence from a single molecule is based on its absorption cross section (σ) and fluorescence quantum yield. The absorption cross section is related to the extinction coefficient (ϵ), and therefore indicates how efficiently light is absorbed at a certain wavelength.

$$\sigma = \frac{2303\varepsilon}{N_A} \quad (4-1)$$

The fluorescence quantum yield indicates how much of the absorbed light is converted to luminescence and can be used to predict whether a particular fluorophore is bright enough to be detected above noise and background levels. It is also important to consider the effects of fluorescence quenching during single molecule measurements; for example, photochemical reactions can photobleach the molecule and decrease its QY over time.

A simple calculation can predict the excitation intensity (power per area) that will produce SWNT fluorescence using 633-nm excitation. First, the power is the product of the excitation energy (i.e., $\sim 3 \times 10^{-19}$ J) and the excitation rate. The excitation rate should be, at minimum, a factor of ten or more slower than the excited state lifetime of the molecule to prevent formation of multiple excitons; taking a fluorescence lifetime of 100 ps for SWNTs,¹⁸⁶ the excitation rate should thus be $\sim 10^9$ photons/s. Second, for excitation at 633 nm, one (6,5) SWNT has an absorption cross section of 7×10^{-15} cm² (vide infra). Thus, the excitation intensity should fall below 40 kW/cm², which is easily obtainable with our system. Using the excitation rate above, SWNTs should emit $\sim 5,000$ photons/s based on a QY $\sim 0.05\%$. However, most of the emitted photons will not reach the detector (much greater than 99% loss) due to losses through the objective ($\sim 10\%$ transmission) and associated optics ($\sim 50\%$ transmission), as well as the grating efficiency ($\sim 80\%$; Figure A-3, Appendix A) and low NIR efficiencies for the CCD ($\sim 20\%$; Figure A-4, Appendix A). Nevertheless, fluorescence from individual nanotubes was routinely observed in this work, indicating that the QY for these moieties likely exceeds a 0.05% QY.

4.1.2 *Purpose of this Study*

Here we present measurements of fluorescence and Raman spectroscopy for individual single-walled carbon nanotubes suspended in three different surfactant systems, preparations of which are detailed in Chapter 3. Studies of single molecule fluorescence for SWNTs reveal variations in emission maxima, intrinsic line widths and line shapes, and the absence of blinking behavior. The local environment strongly influences both the optical transition energy of individual SWNTs and their resistance to fluorescence quenching. Comparison of fluorescence quenching behavior enabled the selection of a dispersing agent that is most amenable to single molecule studies of the SWNT QY (Chapter 5).

4.2 **Experimental Procedure**

4.2.1 *Preparation of Substrates and Samples*

Single molecule measurements were performed on thin films of SWNTs spun cast onto 1" round quartz (ESCO Products) or 1" square glass (VWR) coverslips that, prior to use, were subjected to a rigorous cleaning procedure to remove any contaminants. During cleaning, coverslips were loaded into a Teflon holder nested in a 1-L glass beaker, and were subjected to sonication and heating in a Branson 250D bath sonifier. First, acetone was added until the Teflon holder was immersed in solvent, and the beaker was sonicated for 10 min. Second, coverslips were soaked in 1% Hellmanex II (Hellma) in nanopure water at 35 °C for 30 min and were subsequently sonicated in nanopure water for 10 min to rinse. Third, coverslips were immersed in 6 M HCl for 1 h and were subsequently sonicated in nanopure water for 10 min to rinse. Fourth, coverslips were

sonicated in methanol for 15 min and were dried in air for 1 h. The dry coverslips were stored in Fluoroware holders (Entegris) that had been swabbed with a methanol-soaked wipe and were blown free of dust under a stream of nitrogen.

For single molecule measurements, CoMoCAT nanotubes were dispersed in aqueous suspensions using SDS, SDBS, and CAS according to the procedures outlined in Chapter 3. The samples were diluted to low concentrations with nanopure water until a single molecule density was achieved (i.e., isolated bright spots were observed in raster scans with no additional fluorescence detected in the field). Typically, one drop of the as-prepared or diluted sample was placed onto a bare substrate and was dispersed at 2000 rpm for 3 min using a spin coater (Speedline Technologies, P6204). To insulate the SWNTs from direct contact with the substrate, some samples were dispersed onto substrates coated with a thin layer of poly(methyl methacrylate) (PMMA; Aldrich, <5% toluene), prepared by spin-casting two drops of 0.1 wt % PMMA onto the substrate at 2000 rpm for 3 min.

4.2.2 *Single Molecule Fluorescence Measurements*

Confocal epifluorescence microscopy enabled imaging of the emission from single nanotubes and was accomplished using an inverted TE300 Nikon Eclipse microscope, as depicted in Figure 4-1. A helium–neon laser (Coherent or Melles–Griot) was used for excitation at 632.8 nm with a typical diffraction-limited spot size of ~600 nm and an excitation intensity of ~30 kW/cm². Illumination passed through a Nikon PlanFluor 100× oil immersion objective with a high numerical aperture (NA = 1.3) to excite the sample, which was positioned on a piezoelectric stage (Mad City Labs, Nano

Figure 4-1. Schematic diagram for the epifluorescence confocal microscope used for all single molecule spectroscopic studies. The beam was expanded by a factor of 6 to overfill the back aperture of the 100 $\times$ objective.

H70). Emission was collected by the same objective and was passed through two holographic notch filters before reaching a thermoelectrically-cooled Si:CCD detector (Princeton Instruments, Spec-10).

A piezoelectric raster scanning stage was used to create a 2D image representative of the fluorescence from the sample, as shown in Figure 4-2. Isolated bright spots in the scan corresponded to fluorescence from individual SWNTs. The stage could be repositioned to place a single nanoparticle in the excitation beam, allowing collection of fluorescence or Raman spectra and time traces (temporal changes in intensity under continuous excitation) with typical integration times of 1 min and 100 ms, respectively. Altogether, fluorescence and Raman spectra, intensity time traces, and polarization

Figure 4-2. False color image of fluorescence from individual SWNTs in a $20 \times 20 \mu\text{m}^2$ raster scanned image. Circled bright pixels indicate the positions of isolated nanotubes. Scale bar: black pixels are low intensity and white pixels are high intensity.

curves were recorded for 255 individual CoMoCAT SWNTs. Spectra were rejected if bright spots corresponded to fluorescence from more than one SWNT or scattering from trace impurities on the substrate; for each scan, four spectra were typically collected at dark field positions to ensure that single molecules were being studied.

4.3 Results

4.3.1 Preparation of Substrates

First, autofluorescence levels from glass and quartz substrates were measured to determine which substrate is more amenable to single molecule measurements. Glass substrates are less expensive than quartz coverslips (i.e., \$0.05 per glass coverslip versus \$13 per quartz coverslip). However, as illustrated in Figure 4-3, glass shows a very large autofluorescence background that is suppressed for quartz. Therefore, all single molecule measurements in this thesis were performed on quartz substrates. Second, the advantages of using bare or PMMA-coated substrates were assessed. No noticeable differences in fluorescence quenching behavior were observed when SWNTs were cast directly onto

Figure 4-3. Comparison of autofluorescence signal from quartz (solid green line) and glass (dotted blue line) substrates using $\lambda_{\text{ex}} = 633$ nm, indicating the superior optical properties of quartz coverslips for NIR measurements.

quartz versus PMMA-coated substrates, perhaps due to the intrinsic insulating behavior of the dispersing agent surrounding the SWNT. Further, PMMA-coated substrates showed higher background levels that made it difficult to discern the location of individual SWNTs in raster scans. As such, SWNTs were dispersed onto bare quartz substrates for all single molecule measurements in this dissertation.

4.3.2 Fluorescence Spectra for Individual SWNTs

It is expected that the SWNT ensemble fluorescence spectrum can be reconstructed from a collection of single nanotube spectra, much like that observed for other single molecules such as CdSe quantum dots.¹⁷⁰ Figure 4-4a displays such a histogram for CoMoCAT-manufactured SWNTs, where the ensemble spectrum is completely recovered. Fluorescence spectra for individual nanotubes are displayed in Figure 4-4b. Individual SWNTs exhibited only one emission peak with an energy that approximately matched the corresponding (n,m) wavelength from the ensemble spectrum.⁷²

The observed fluorescence line shape was Lorentzian. Interestingly, the full width at half maximum was ~ 23 meV, nearly equivalent to $k_B T$ at room temperature. Thermal broadening accounts for most of the line width (>20 meV),^{72,73} and at low temperatures, studies have revealed line widths as narrow as 200 μ eV for individual nanotubes.⁷³ Phonon sidebands were not observed in our measurements, indicating weak coupling to phonons.⁷² SWNTs are expected to have multiple emission centers, each with a slightly different local environment, and the corresponding shifts in these emission maxima contribute to inhomogeneous broadening.^{182,187} Indeed, variations in peak

Figure 4-4. (a) Histogram of 77 single nanotubes overlaid with emission from an ensemble of CoMoCAT SWNTs. (b) Single molecule fluorescence observed for four nanotube (n,m) structures. Spectra were integrated over 1 minute, normalized, and fitted with Lorentzian functions. (c) Fluorescence spectra for different single (6,5) nanotubes, showing variations in peak positions and line widths.

position and line width were observed for nanotubes with the same (n,m),⁷² as shown for (6,5) nanotubes in Figure 4-4c. The energy of the emission maxima varied within the measured ensemble line widths that were presented in Chapter 3. The position of the each peak remained constant over time (spectral wandering was not observed) because the fluorescence line width at room temperature was greater than any energy shift.⁸⁴

We tested three techniques commonly used to confirm that single molecules are being studied. First, fluorescence intermittency, also known as on/off intensity blinking, is usually used as the definitive indication that observed emission arises from an

Figure 4-5. Single nanotube time trace. To show the contrast between on and off states for emission, the laser was physically blocked at 90 s.

individual molecule. For example, under continuous excitation, the fluorescence from CdSe quantum dots cycles on and off at all times like a telegraph signal.¹⁷⁰ Although blinking has been observed for SWNTs at low temperatures (*vide infra*),⁷³ their fluorescence emission at room temperature surprisingly showed no indication of blinking on time scales ranging from 0.1 to 100 s (Figure 4-5). Second, as the incident electric field (polarization) is rotated, SWNTs are expected to exhibit an angular dependence of fluorescence intensity that agrees very well with a $\cos^2\theta$ dependence, as anticipated for a 1D molecule.^{72,188} Using our setup, polarization studies for individual SWNTs were complicated by a depolarization effect that was displayed by optics within the setup, which caused the intensity of incoming light to vary as the polarization was rotated. To circumvent these problems, it is also possible to rotate the polarized emission from individual SWNTs; however, this method cannot distinguish isolated nanotubes from bundles consisting of the same (n,m) structures, nor can it definitively identify individual nanotubes that lie curved or kinked on the substrate. Therefore, an alternate strategy,

based on the presence of isolated bright spots in raster scans and the observation of extremely narrow SWNT emission line widths, was used to validate that single molecules were being studied.

All SWNT carbon atoms lie on the molecule's surface,¹⁸⁹ and the local environment significantly impacted nanotubes' optical spectra. Figure 4-6 shows the

Figure 4-6. Fluorescence intensity for CoMoCAT SWNTs suspended in (a) SDS, (b) SDBS, and (c) CAS. All spectra were integrated for 1 min and were taken in succession. For CAS, the small peak near 965 nm corresponds to an artifact from the CCD.

typical temporal evolution of fluorescence spectra for SWNTs suspended in SDS, SDBS, and CAS. Significant fluorescence quenching was detected for SWNTs suspended in SDS and SDBS surfactants, perhaps due to some interaction with the quartz substrate or the aromatic rings of the SDBS surfactant. Although this behavior was also observed for some SWNTs suspended in CAS, the original fluorescence intensity was only slightly attenuated over several minutes of continuous excitation.

4.3.3 Raman Spectra for Individual SWNTs

It was also possible to observe Raman scattering for individual SWNTs, as resonant excitation causes an enormous enhancement of the signal, as described in Chapter 2. As expected, the G- and D-bands occurred at the expected energies (Figure 4-7) and the relative ratio of these peak intensities was used as a rough qualitative indicator

Figure 4-7. Raman spectrum for an individual SWNT showing the D-band, G-band, and G'-band. The low relative intensity of the G-band:D-band indicates a high quality SWNT with limited sidewall damage. Inset: Corresponding Raman spectrum for an ensemble of SWNTs, shown for comparison.

of whether the SWNT sidewall had sustained significant damage during synthesis, purification, and processing. In our individual SWNT Raman studies, the RBM was not observed because the laser energy was not exactly resonant with any of the CoMoCAT structures and because RBMs occur very close to the laser line. In other words, the notch filter transmission cut-on was not sharp enough to enable observation of these transitions.

4.4 Discussion

It is expected that the SWNTs sampled in these measurements were representative of the ensemble population, which is evident in the histogram provided in Figure 4-4a. Table 4-1 presents the E_{22} and E_{11} energies and the measured population distributions for the five CoMoCAT SWNT structures that could be observed with our setup (shaded). It is likely that detection of some species at higher energies may have been favored because the collection efficiency of the CCD decreases at lower emission energies. For example, based on their small ensemble populations, far more (6,4), (9,1), and (8,3) SWNTs were observed than expected; similarly, very few (7,5) SWNTs were observed despite their large ensemble population. One additional consideration that may account for high observation rates for structures like (8,3) SWNTs is that their E_{22} values are more resonant with the excitation energy ($\lambda_{\text{ex}} = 633 \text{ nm}$) than other moieties.

A spectral line is characterized by its shape, intensity, position, and width. The observed fluorescence line shape was Lorentzian, also known as the intrinsic or natural line shape, and represents the power spectrum for a damped harmonic oscillation. Lorentzian functions were used to fit the spectra presented in Figure 4-4b. The intensities of the fluorescence lines varied widely for SWNTs and detailed studies are

Table 4-1. Population Distribution for Observed CoMoCAT SWNTs

(n,m)	E_{11} (nm) ^a	E_{22} (nm) ^a	percent of all SWNTs (%) ^b	percent of observable SWNTs (%) ^c	number of SWNTs observed ^d	percent of observed SWNTs (%) ^d
(6,4)	873	578	2.8	4.0	48	18.8
(9,1)	912	691	0.8	1.1	41	16.1
(8,3)	952	665	11.0	15.6	69	27.1
(6,5)	976	566	28.0	39.7	94	36.9
(7,5)	1024	645	28.0	39.7	3	1.2
(9,4)	1101	722	2.3	-	-	-
(8,4)	1111	589	14.0	-	-	-
(7,6)	1120	648	8.5	-	-	-
(9,2)	1138	551	1.7	-	-	-
(8,6)	1173	718	0.8	-	-	-

^a Literature values.⁹¹ ^b Literature values are the integrated fluorescence intensities from a PLE map of CoMoCAT SWNTs.⁸⁶ Additional SWNT structures collectively contribute <3% of the population and are not included here. ^c The percent of the SWNT population that were imaged with our Si:CCD are indicated by shaded lines. ^d Spectral overlap complicates fluorescence-based (n,m) assignments, and some small variation in the distribution is likely present.

presented in Chapter 5. Variations in emission energy maxima were observed for all SWNT structures (Figure 4-4c); these fluctuations illustrate the origin of inhomogeneous broadening in the ensemble spectrum, which arises from structural or chemical defect sites⁸⁴ and the particular interaction of each SWNT with the surfactant or substrate. Further, the strong dependence of FWHM on the local environment has indicated that one SWNT may have multiple emission centers.¹⁸² The measured FWHM for individual SWNTs was ~23 meV, much narrower than that reported for other fluorescent systems like quantum dots (~30–40 meV for CdSe at 300 K),¹⁹⁰ and in excellent agreement with reported literature values.⁷² At room temperature, spectral wandering was not observed

because any shift was smaller than the observed line width, although energy shifts up to 20 meV have been reported at low temperature (4 K) for individual SWNTs.⁷³

Careful examination of fluorescence line widths can also elucidate excited state dynamics. Homogeneous broadening of Lorentzian lines results from both the excited state relaxation time (τ) and the dephasing time (T_2); the observed line width is proportional to $1/\tau + 1/T_2$. Based on the Heisenberg uncertainty principle, the intrinsic fluorescence line width is inversely proportional to the excited state lifetime of a molecule. However, because the excited state lifetime is only a few hundred picoseconds for nanotubes, dephasing is the dominant mechanism for spectral broadening. For SWNTs with structural defects, very fast exciton dephasing times (i.e., on the order of femtoseconds) have been both predicted¹⁹¹ and observed.⁷⁴ Rapid dephasing may promote fast nonradiative decay to triplet or dark excitonic states, effectively lowering the QY. In contrast with the small width of the emission lines observed here, photoluminescence excitation (PLE) profiles exhibit spectral line widths nearly a factor of three larger,¹⁸⁷ which suggests that electron–phonon scattering is efficient in nanotubes.⁷⁴ The Lorentzian line shape itself is indicative of the exciton coupling to surrounding molecules, suggesting a dominant intra-nanotube dephasing mechanism.¹⁵⁰

The absence of fluorescence blinking for single nanotubes is astonishing and distinguishes them from almost all other known emitters (Figure 4-5).¹⁹² Because ~50% of emissive SWNTs exhibit blinking at low temperature (~1.8 K),⁷³ it is unclear whether this behavior slows to an observable rate at low temperatures or if blinking mechanisms become disabled at higher temperatures. For example, the trap and release of excitons at defect sites has been suggested as a plausible temperature-dependent blinking mechanism

that could slow to observable rates at low temperatures.⁸⁴ In addition, Georgi et al. suggested that the presence of holes along the sidewall of the nanotube can cause localized quenching of mobile excitons via non-radiative recombination, which turns off fluorescence in that particular segment and results in the observed blinking behavior.¹⁹³

In general, the absence of fluctuations in fluorescence intensity at room temperature is attractive for applications in quantum optics that require a steady and uninterrupted source of single photons. Recent studies of fluorescence antibunching have confirmed that SWNTs are single-photon emitters at low temperatures.⁸⁰ For example, the probability that an SWNT will simultaneously emit more than one photon is only 3% up to 10 K, and increases only to 15% at 25 K. Antibunching behavior is more pronounced at low temperatures due to strong localization of excitons, which diminishes the strength of nonlinear interactions between different sites along the nanotube sidewall.⁸⁰ Although SWNT antibunching has not yet been observed at room temperature, if single photon emission could be demonstrated under these conditions, nanotubes would be leading candidates for development as quantum optical components.

As presented in Chapter 3, the local environment strongly influences SWNT emission, and Figure 4-6 depicts the evolution of SWNT fluorescence spectra when associated with SDS, SDBS, and CAS surfactant systems. Fluorescence bleaching can be caused by protonation of adsorbed oxygen on the SWNT sidewall, the presence of an electron-accepting surfactant, or a photoinduced oxidation of the nanotube caused by chemisorption of initially adsorbed oxygen.¹⁹³ Protonation occurs at $\text{pH} < 7$, and could account for some small reduction in the observed fluorescence signal.¹⁹³ The presence of sulfate groups on SDS and SDBS make these surfactants slightly more electron-accepting

than CAS, and so the former may be able to trap photoexcited charges from the nanotube. Further, chemisorption of oxygen is weak for molecules in the ground state, but is extremely favorable for molecules in the excited singlet state.¹⁹³ Therefore, some chemisorption of oxygen likely occurs for all SWNT–surfactant systems upon excitation. It is also possible that the surfactants do not sufficiently coat the SWNT to fully insulate it from the quartz surface, which could possibly influence its fluorescence behavior.¹⁹⁴ The presence of impurities in the SDBS starting material may also account for some quenching. For these reasons, CAS was selected as the surfactant system to be used for measurements of the single molecule SWNT QY in Chapter 5.

Raman spectra were observed for individual SWNTs. For our samples, the large G-band:D-band ratio provides qualitative evidence that the sp^2 -hybridized system is largely intact, although some sidewall damage occurred during synthesis, purification, and processing. The position of the emission maximum usually indicates the (n,m) structure of the SWNT under study, and the RBM provides additional verification of the nanotube identity. Use of more efficient optical filters near the laser line, such as a dichroic beam splitters and razor edge filters, could enable the observation of RBMs using our setup. Also, the intensity of all Raman transitions increases with resonant laser excitation.

One final consideration for single molecule measurements is that they tend to be extremely resistant to reproducibility. This is true in the sense that reproductions of SWNT samples for which single molecules were observed were prepared with the same stock sample, and meticulous attention was paid to using identical preparation conditions and techniques. However, the density of SWNTs on the coverslip was rarely uniform and the particular location studied on the coverslip also influenced the number of particles

that were observed. In addition, rebundling of the sample over time presented an additional challenge because the concentration of the stock sample was continuously evolving. Therefore, although every precaution was taken to carry out the experiments using identical preparation and measurement conditions, it was found that sample concentrations had to be adjusted nearly every time a sample was prepared, which limited the efficiency of using single molecule microscopy for these studies. Still, the wealth of information afforded by single molecule measurements outweighed the challenges associated with these experiments and warranted its use in subsequent studies.

4.5 Conclusions

Studies of fluorescence from individual SWNTs were accomplished by epifluorescence confocal microscopy for nanotubes suspended in three surfactant systems, with CAS providing the most stable emission spectra. Narrow Lorentzian line shapes for individual (n,m) structures were observed, which reconstructed the ensemble spectrum. In addition, constant fluorescence emission and Raman scattering were observed for individual SWNTs. Further, the important effects of the local environment were manifested by variations in emission maxima, line widths, and fluorescence quenching behavior for SWNTs suspended in different dispersing agents. Providing a detailed and fundamental approach to measuring the fluorescence intensities of individual molecules in homogeneous samples, additional single molecule measurements can inform our understanding of the low ensemble QY for SWNTs, which is the focus of Chapters 5 and 6.

CHAPTER 5

Fluorescence Efficiency of Individual SWNTs

The luminescence efficiency of individual single-walled carbon nanotubes was determined by comparing the fluorescence from individual nanotubes to single CdTe/ZnS quantum dots with a well-defined fluorescence quantum yield. The single carbon nanotube QY was determined to be $3 \pm 1\%$, nearly 100 times greater than values previously reported for ensembles. The intrinsic nanotube QY is potentially much higher than previously believed and appears lower in ensembles due to defective nanotubes and residual bundles.

5.1 Introduction

5.1.1 Motivation

Single-walled carbon nanotubes possess an impressive array of optical properties, including size-tunable emission,⁸⁷ near-infrared fluorescence,⁷¹ and high photostability.^{72,76} These qualities are extremely desirable for fluorescence-based applications such as biological imaging^{76,79} and biological sensing,⁷⁵ which rely heavily upon the availability of fluorophores with high brightness and stable emission. Nanotubes may also fulfill the long-standing need for a single-photon source in the near-infrared, which is necessary for applications in quantum optics.⁸⁴

Because they experience strong van der Waals attractions, nanotubes form aggregated bundles when synthesized. This interaction quenches SWNT fluorescence by allowing nonradiative transfer from semiconductor SWNTs to any metallic nanotubes within the bundle.⁷¹ A major milestone in the optical characterization of SWNTs was the development of an ultrasonic dispersion method to wrap surfactants around nanotubes, thereby isolating them.⁷¹ Fluorescence spectra of isolated SWNTs exhibit a series of well-resolved peaks that correspond to optical transitions from various (n,m) structures present within an ensemble,^{87,91} as displayed in the inset to Figure 5-1a.

Toward the realization of applications based on nanotube fluorescence, one important consideration is their relative fluorescence efficiency, or fluorescence quantum yield. Based on a ratio of radiative and nonradiative rate constants, a molecule's QY is also one of its most fundamentally important photophysical parameters.¹⁹⁵ For an ensemble of nanotubes, the fluorescence QY is $<0.05\%$,^{71,150,186} which is extremely poor and would likely preclude their use in fluorescence-based applications. However, recent

Figure 5-1. (a) Absorption spectrum from a DNA-solubilized SWNT sample, highly enriched in (6,5) nanotubes (1 cm path length). The first, second, and third excited excitonic states are labeled in the figure. Inset: Absorption and fluorescence spectra ($\lambda_{\text{ex}} = 632.8$ nm, excitation intensity ~ 28 mW/cm², 500 ms integration time at each data point) from an ensemble of isolated CoMoCAT carbon nanotubes. (b) Absorption spectrum for 705 ITK CdTe/ZnS QDs. Inset: Absorption spectrum with the excitation wavelength ($\lambda_{\text{ex}} = 632.8$ nm) and first exciton absorption peak ($\lambda_{\text{ex1}} \sim 677$ nm) indicated.

experiments suggest that the QY of SWNTs is potentially much higher than previously reported. For example, unusually fast excited-state recovery times suggest that a significant fraction of suspended nanotubes are bundled and, therefore, nonemissive.¹⁹⁶ In addition, the fluorescence from single nanotubes can be detected with high signal-to-noise, suggesting a higher QY for individual nanotubes.⁷² In another study, when SWNTs were suspended with a density gradient and subsequently fractionated,¹³⁶ the

least dense fractions showed QYs of $\sim 1\%$.¹⁶⁶ Finally, the absolute QY for nanotubes suspended across pillars was recently estimated to be $\sim 7\%$,¹⁹⁴ but the accuracy of such measurements is limited by difficulties in knowing the exact number of photons absorbed by the sample and received by the detector, which are extremely challenging to quantify.¹⁶⁷

5.1.2 Purpose of this Study

Here we present measurements of the fluorescence QY of isolated SWNTs obtained using single molecule spectroscopy. Comparisons between the relative fluorescence intensities of individual SWNTs and CdTe quantum dots allowed for a direct determination of the QY for bright nanotubes ($\text{QY} \sim 3 \pm 1\%$), which is 2 orders of magnitude higher than the value for ensembles. This approach offers the first relative fluorescence QY measurement on the single particle level and allows us to report on whether the measured ensemble SWNT QY represents an intrinsic property of all nanotubes. Our measurements can also determine the influence of inter-tube interactions (i.e., residual bundles), processing defects, or interactions with the local environment on the QY.

5.2 Experimental Procedure

For fluorescence measurements, CoMoCAT-manufactured SWNTs (SouthWest Nanotechnologies, Inc.) were dispersed with sodium cholate in D_2O using methods similar to O'Connell et al.⁷¹ Carboxyl-coated ITK 705 CdTe/ZnS quantum dot samples (Invitrogen Corporation) were diluted with water to ~ 0.1 nM. SWNTs and QDs were

then spun cast consecutively onto a quartz cover slip. Fluorescence from SWNTs and QDs was collected by epifluorescence microscopy on an inverted microscope, as described in Chapter 4, using a helium–neon laser for excitation ($\lambda_{\text{ex}} = 632.8 \text{ nm}$). Typical fluorescence images are shown in the insets of Figure 5-2. The excitation intensity was $\sim 1.5 \text{ kW/cm}^2$ ($\sim 30 \text{ kW/cm}^2$) for QDs (SWNTs). The stage could be positioned to place a single nanoparticle in the excitation beam, allowing collection of fluorescence spectra and time traces (temporal changes in intensity under continuous excitation) with typical integration times of 1 min and 100 ms, respectively.

Scanning transmission electron microscopy (STEM) with electron energy loss spectroscopy (EELS) was used to determine the chemical distribution of core and shell atoms in the CdTe/ZnS QDs¹⁹⁷ (705 ITK organic quantum dots, Invitrogen Corporation). STEM images were collected using the Cornell VG HB501 100 kV UHV STEM, and EELS data were obtained as described previously.¹⁹⁷ The SWNT cross section was calculated from the absorption spectrum of a sample highly enriched in (6,5) SWNTs, shown in Figure 5-1a.¹²¹

5.3 Results

A molecule's relative QY is typically determined by comparing the spectrally integrated fluorescence intensity of the unknown to a molecule with a known QY. For example, for the CoMoCAT SWNTs in sodium cholate, an ensemble fluorescence QY of $\sim 0.03\%$ was determined via direct comparison with the standard infrared dye IR-26 ($\lambda_{\text{ex}} = 900 \text{ nm}$, intensity $\sim 37 \text{ mW/cm}^2$, 600 ms integration time at each data point). However, there is no well-established procedure that has been used to determine the relative

fluorescence QY for a single molecule. We have defined the single nanotube relative QY by eq 5-1, which is comparable to an expression given by Lakowicz.¹⁹⁸

$$\Phi_{SWNT} = \Phi_{QD} \left(\frac{F_{SWNT}}{F_{QD}} \right) \left(\frac{\sigma_{QD}}{\sigma_{SWNT}} \right) \left(\frac{I_{QD}}{I_{SWNT}} \right) \left(\frac{\eta_{QD}}{\eta_{SWNT}} \right) \quad (5-1)$$

Φ is the fluorescence quantum yield, F is the fluorescence intensity, σ is the molecular absorption cross section, I is the excitation intensity, and η is the efficiency of the detector at the emission wavelength, provided in Appendix A (Figure A-4). In an ensemble QY measurement, the fluorescence intensities are corrected by the absorbance at the excitation wavelength for each sample.¹⁹⁸ Here, we correct the fluorescence counts for the relative excitation rate of the two nanoparticles using the product of absorption cross section and excitation intensity.¹⁹⁸

5.3.1 Single Molecule Fluorescence Quantum Yield of QDs

CdTe QDs are an ideal reference molecule for our measurement for several reasons. First, the single molecule fluorescence QY is very well defined for CdSe QDs (closely related to CdTe QDs). Indeed, correlated AFM and fluorescence imaging,¹⁹⁹ fluorescence correlation spectroscopy,²⁰⁰ and dielectric-dependent photoluminescence studies²⁰¹ have all demonstrated that the fluorescence QY approaches unity for individual bright QDs. Therefore, although the ensemble CdTe QD QY is ~70%, we can assume that the maximum fluorescence counts in a given time trace correspond to a single CdTe QD QY of ~100%. Second, the fluorescence from individual QDs is very robust, and thus there exists little chance that the QD will irreversibly photobleach during the course of the measurement. Finally, these CdTe QDs absorb and fluoresce at wavelengths in the near infrared, and so they can be excited by the same laser source used for the SWNTs.

Figure 5-2. (a) Single CdTe/ZnS QD fluorescence spectrum. Inset: Fluorescence image of a $20 \times 20 \mu\text{m}^2$ area scanned with an $\sim 1.5 \text{ kW/cm}^2$ intensity. Circled pixels indicate fluorescence from individual nanoparticles (top two circles correspond to SWNTs and bottom two circles correspond to QDs). The spectrum corresponds to the circled pixels indicated with an arrow. (b) Time trace for the same QD showing the characteristic on/off blinking behavior, which confirms that the spectrum corresponds to a single molecule. (c) A typical fluorescence spectrum from an (8,3) SWNT. Inset: Fluorescence image of the same $20 \times 20 \mu\text{m}^2$ area in (a), scanned with an $\sim 30 \text{ kW/cm}^2$ intensity. Emission from a single (8,3) SWNT corresponds to the circled pixels indicated with an arrow. (d) Time trace for the same SWNT showing stable and uninterrupted emission over 95 s. The laser was physically blocked to artificially produce the off level of fluorescence near the end of the scan.

5.3.2 Fluorescence Intensities of Single Molecules

A fluorescence spectrum from a single CdTe/ZnS QD with emission centered at $\sim 705 \text{ nm}$ and a FWHM of $\sim 40 \text{ nm}$ is displayed in Figure 5-2a, with a typical fluorescence image shown in the inset. The characteristic fluorescence intermittency, or on/off blinking behavior, for emission from a single quantum dot is shown in Figure 5-2b. Blinking is considered to be a definitive hallmark of fluorescence from a single QD,¹⁷⁰ and time traces were collected for each nanoparticle to confirm that individual QDs were being studied.

The corresponding image and spectrum of the fluorescence from a single nanotube are shown in Figure 5-2c. For single SWNTs, the emission follows a Lorentzian line shape with energies corresponding to E_{11} transitions of particular nanotube (n,m) structures, and also exhibits a narrow line width limited by $\sim k_B T$ at room temperature.⁷² A time trace collected for this same nanotube is presented in Figure 5-2d and illustrates the continuous, photostable emission of SWNTs, in stark contrast to what is observed for single QDs. Because light absorption is not strongly allowed for nanotubes that lie perpendicular to the polarization axis of the excitation source,^{72,188,189,202} the nanotubes we observe are oriented nearly parallel to the exciting electric field. The raw fluorescence intensities collected for QDs (Table B-1) and SWNTs (Table B-2) are presented in detail in Appendix B and average values are summarized in Table 5-1.

Table 5-1. Raw Fluorescence Intensities and Absorption Cross Sections for SWNTs and QDs

	(6,4) SWNTs	(9,1) SWNTs	(8,3) SWNTs	(6,5) SWNTs	CdTe/ZnS QDs
E_{22} (nm) ^a	581	693	663	567	-
E_{11} (nm) ^a	873	912	952	975	-
average fluorescence intensity (counts) ^b	196	188	203	183	263
counts/power (counts/mW)	153	147	159	143	2023
average QY (%)	3.1	2.9	3.0	2.9	-
estimated $\sigma_{633 \text{ nm}}$ (cm ²) ^c	7×10^{-15}	7×10^{-15}	7.5×10^{-15}	7×10^{-15}	2.6×10^{-15}
σ_{E11} (cm ²) ^c	-	-	-	1×10^{-13}	-

^a Literature values.⁸⁷ ^b Fluorescence intensities were later corrected by the excitation intensity and detection efficiency at the peak emission wavelength. ^c The absorption cross section was measured for enriched (6,5) SWNTs and was used to estimate approximate values for all other chiralities in this study.

5.3.3 Absorption Cross Section of QDs

Determining an accurate absorption cross section for QDs and SWNTs is critical to determining their excitation rates. For II–VI QDs, the absorption cross section can be related to the size of the QD.^{203,204} From the first exciton absorption wavelength, the diameter of the CdTe QD can be calculated using an empirical fitting function,²⁰⁴ which can then be used to calculate the absorption cross section at the first exciton absorption peak.^{203,204} For the CdTe/ZnS QDs, the first exciton absorption peak resides at ~677 nm (Figure 5-1b), corresponding to a CdTe core diameter of ~55 Å and a cross section of $\sim 1.43 \times 10^{-15} \text{ cm}^2$. However, large red shifts by as much as 130 nm have been observed upon capping CdTe QDs with a semiconductor shell²⁰⁵ and, therefore, it is unclear whether the position of the absorption peak can be used to determine the cross section reliably. Further, these QDs are highly anisotropic and exhibit a characteristic bullet shape,²⁰⁶ which complicates the direct determination of the QD diameter based on simple empirical formulas.

Therefore, for high accuracy, STEM with EELS imaging was employed to accurately quantify the dimensions of the emissive CdTe core. Figure 5-3 displays an annular darkfield (ADF) scattering image for a typical CdTe/ZnS QD acquired by STEM. The ADF signal is proportional to the sample thickness and the atomic number of the imaged material (to the power of ~1.7).²⁰⁷ Conversely, the integrated EELS signal for sulfur (a component of the shell material) is proportional to the amount of sulfur in the direction of electron beam propagation.¹⁹⁷ For a well-shaped QD, the integrated sulfur EELS signal generally displays a maximum at the edges of the core, where the total cross-sectional shell thickness (i.e., sulfur content) is greatest, and a minimum at the

Figure 5-3. (a) Annular darkfield STEM image for a typical single CdTe/ZnS QD. The red horizontal and vertical dots correspond to the data points in (b) and (c), respectively, and indicate the positions along the dot for which ADF and sulfur EELS data were collected. (b) ADF (dashed red line, squares) and integrated sulfur EELS (solid black line, circles) data were acquired by scanning across the QD horizontally. The length of this CdTe QD core is approximately 61 Å. (c) ADF (dashed red line, squares) and integrated sulfur EELS (solid black line, circles) data were acquired by scanning across the QD vertically. The width of this CdTe core is approximately 51 Å.

center of the core, where the total shell thickness is smallest.

Atomic EELS imaging is very difficult, and data were collected for 7 QDs. From theoretical modeling of the EELS signals, we determined the distribution of the shell around the core, and thus could determine an average core length of 67.5 ± 2.9 Å and a core diameter of 47.9 ± 1.7 Å. Using a weighted average to obtain an effective QD diameter (to insert into the empirical expressions), these values translate to an absorption cross section at the first exciton absorbance of $1.4 \times 10^{-15} \text{ cm}^2$, in excellent agreement with our optical measurement. At the excitation wavelength, the QD absorbance is nearly two times greater than at the first exciton peak (Figure 5-1b). Hence, the absorption cross section (σ_{QD}) at 633 nm is $\sim 2.6 \times 10^{-15} \text{ cm}^2$ (Table 5-1).

5.3.4 Absorption Cross Section of SWNTs

The SWNT cross section was calculated from the absorption spectrum of a sample of highly enriched (6,5) DNA-SWNTs, shown in Figure 5-1a. In order to

determine the mass of SWNTs present in a 1-mL solution containing ~ 20 μg of combined DNA and SWNTs, the mass of DNA was determined by subtracting the SWNT contribution under the DNA absorption peak ($\lambda \sim 270$ nm) according to Nair et al.¹⁶⁴ We determined that ~ 12 μg of (6,5) SWNTs are present, in good agreement with the molecular modeling predictions of a DNA:SWNT mass ratio of 1:1.²⁰⁸ The SWNT concentration was converted to a molarity ($\sim 2.5 \times 10^{-8}$ M) by quantifying the number of moles of carbon present in a 380-nm long SWNT.² This SWNT length, as measured by AFM, is typical of our samples and agrees with length distributions for other samples prepared by ultrasonic dispersion methods.^{43,209} In general, Beer's law can be used to extract the density of SWNTs from the absorption spectrum of a single (*n,m*) SWNT species if its absorption cross section is known. Assuming a negligible difference in cross section among different SWNT structures, the concentration distribution for an ensemble of SWNTs can be extracted by a deconvolution algorithm that breaks an SWNT absorption spectrum into its (*n,m*) components¹⁶⁴ or by using experimentally determined calibration curves for a given surfactant.²¹⁰

It is possible that some of the absorbance at 633 nm (Figure 5-1a) corresponds to impurities and not to the (6,5) nanotube. To quantify the fraction of absorbance that was contributed only by SWNTs, we performed photoluminescence excitation spectroscopy, in which a library of fluorescence spectra are acquired as a tunable source changes the excitation wavelength; PLE and absorption spectroscopy provide similar information, but only species that emit can contribute to the PLE intensity. Therefore, when detecting fluorescence from only the (6,5) SWNT (at ~ 990 nm), the relative ratio of the PLE intensities at E_{22} and 633 nm serves to quantify the fraction of the sample that absorbs at

633 nm and also contributes to (6,5) nanotube fluorescence (assuming the absorption at E_{22} is all from (6,5) SWNTs). From the absorption spectrum, E_{22} :633 nm is ~ 2.5 and from the PLE spectrum, E_{22} :633 nm is ~ 4.9 . Therefore, nearly half of the material absorbing at 633 nm is not contributing to the fluorescence at E_{11} , making the value of the SWNT cross section at 633 nm $\sigma_{\text{SWNT}} \sim 7 \times 10^{-15} \text{ cm}^2$, compared to a value of $\sigma_{\text{SWNT}} \sim 1 \times 10^{-13} \text{ cm}^2$ at E_{11} (Table 5-1). Detailed calculations of the SWNT absorption cross sections are presented in Appendix B (Table B-3).

5.3.5 *Single Molecule Fluorescence Quantum Yield of SWNTs*

Combining the measured absorption cross sections and the fluorescence intensities from individual SWNTs and QDs, we determined the average QY of individual isolated SWNTs to be $\sim 3 \pm 1\%$, nearly 100 $\times$ greater than the ensemble value. This QY value represents an average over all SWNTs, including several different (n,m) structures that compose the CoMoCAT ensemble; the fluorescence intensity can vary by a factor of 2 from one individual SWNT to another. The value of the (6,5) SWNT cross section was assumed to be similar to other structures and, therefore, was used to calculate all QYs (Table 5-1). The author emphasizes that the QY represents the measured value for the brightest SWNTs in a sample, as single molecule fluorescence measurements are naturally biased toward molecules that exhibit the strongest fluorescence. In fact, recent single molecule photothermal absorption studies suggest that luminescent SWNTs comprise only a small fraction of all nanotubes in such a sample.²¹¹

The primary sources of error in the QY value arise from the variability in counts for each SWNT ($\sim 50\%$), as well as the determination of QD diameter (8%) and SWNT

length (10–15%) in the respective calculated absorption cross sections. It is also unclear how the QY varies with SWNT length, which is a subject of current debate. For example, Fagan et al. have observed a strong dependence of fluorescence intensity on nanotube length²¹² that is supported by another study showing an exciton diffusion length of ~90 nm along the SWNT.¹¹⁶ These studies imply that the fluorescence efficiency for short SWNTs may be lowered by efficient quenching of bound excitons at the cut ends of nanotubes. However, since the average length of the nanotubes used here is over 350 nm, it is unlikely that pure length effects could change the QY value by more than a factor of 2. Differences in the SWNT QY may arise for different lengths because shorter nanotubes likely have a higher percentage of defect sites per nanotube, as a result of the sonication process used to isolate them.

5.4 Discussion

In principle, measurements of the QY relative to a known standard are much more straightforward than absolute QY measurements. In particular, it is extremely difficult to quantify, with a high degree of accuracy, the exact amount of light absorbed by the sample and received by the detector in an absolute QY measurement, especially on the single molecule level. The significance of our approach lies in the simplicity of correcting easily measured relative fluorescence intensities (between the reference molecule and the unknown) for the molecular absorption cross sections, excitation intensities, and detection efficiencies, all of which can be determined in a relatively simple manner with fairly high accuracy.

Because the individual SWNT QY is nearly two orders of magnitude greater than the ensemble value, the majority of nanotubes in an ensemble are either quenched in bundles or are not optically active (i.e., dark). Indeed, strong evidence that bundling is a major contributor to the low QY comes from ensemble fluorescence measurements on isolated SWNTs, which had a QY approaching 1% when separated from small bundles.¹⁶⁶ On the other hand, AFM studies of the dispersed SWNT sample find largely individual SWNTs,¹⁴⁷ suggesting that a significant fraction of the suspended individual nanotubes are dark. As noted, defects to SWNT sidewalls²¹³ and at the SWNT ends¹³⁷ that are introduced during the harsh sonication process can efficiently quench fluorescence and may explain the low percentage of bright nanotubes in an ensemble. However, the overall effect of structural imperfections on SWNT fluorescence efficiencies remains an important question in nanotube photophysics.

It is well-known that the local environment can affect the fluorescence energy and efficiency of SWNTs,⁷² and it has been shown that SWNT fluorescence is quenched when the nanotube lies on a surface.¹⁸⁹ Interestingly, we have discovered that nanotubes deposited onto a quartz substrate are emissive, with a QY similar to that of purely suspended SWNTs.¹⁹⁴ Although it is possible that the micelle layer encapsulating the SWNT insulates it from the quartz surface, it is clear that surface-bound SWNTs do exhibit strong fluorescence, which should encourage further single nanotube optical studies using this relatively simple sample preparation method.

The maximum possible QY for SWNTs is still very much unknown, as a pristine SWNT free of the defects caused by harsh sonication and acidic purification processes may have a significantly higher QY than what we have measured. On the other hand,

suspended SWNTs that are not subject to harsh sonication treatments seem to have QYs similar to the processed SWNTs we have measured.¹⁹⁴ This finding suggests that a perfect SWNT may have a QY only on the order of a few percent, limited by intrinsic nonradiative decay mechanisms such as phonon emission, or intersystem crossing to a triplet state or a low-lying nonradiative electronic state (e.g., dark exciton).^{113,117}

Theory predicts that an optically forbidden exciton state, known as the dark exciton, lies just below the energy of the optically active exciton that is responsible for fluorescence.^{112,113,117} However, the energetic separation of the bright (i.e., emissive) and dark exciton was recently determined to be only 5–10 meV, well within $k_B T$ at room temperature.²¹⁴ The existence of the dark exciton may explain the low fluorescence efficiency of SWNTs relative to more efficient nanoparticles like single QDs. Indeed, recent studies show that the SWNT fluorescence lifetime decreases at low temperatures, suggesting that the dark exciton state may influence the radiative decay kinetics.²¹⁵ However, the role of the dark exciton in SWNT fluorescence remains an open question, and it certainly cannot account for the extremely low ensemble nanotube fluorescence QY relative to the single SWNT.

5.5 Conclusions

In conclusion, using an original single molecule method, we have determined that the QY for an individual SWNT is a few percent, which indicates that nanotubes' emissive efficiencies may not be as low as previously thought. Carbon nanotubes remain promising candidates for biological imaging, single molecule sensing, and quantum optics, and each of these applications would benefit greatly from the incorporation of

SWNTs with a luminescence efficiency that is not impractically small. It is unclear just what limits the QY of individual SWNTs to a few percent, but further improvements in sample preparation and purification should allow for the eventual mitigation of fluorescence quenching due to defects, thereby allowing for further insights into intrinsic nanotube photophysics.

CHAPTER 6

Correlated Fluorescence and Topography

Correlated measurements of fluorescence and topography were performed for individual SWNTs using epifluorescence microscopy and AFM. In correlated images, only ~6% of all SWNTs were emissive, which is a strong indicator that the ensemble QY is low because only a small population of SWNTs is bright. To accommodate AFM measurements, a rinsing technique was used to remove excess surfactant from the substrate; individual SWNTs on non-rinsed and rinsed surfaces displayed notable differences in fluorescence intensities, line widths, and photostability, highlighting the important influence of the local environment for optical measurements performed on individual SWNTs.

6.1 Introduction

6.1.1 Motivation

The quantum yield for bright individual SWNTs is $\sim 3\%$, and will impact how carbon nanotubes could be developed as biological labels, single molecule sensors, and components of quantum optical systems.⁷⁷ Still, the heterogeneous nature of samples poses considerable challenges for measuring the intrinsic luminescence efficiency of a pristine nanotube, and the nonradiative pathways that dominate exciton relaxation processes in carbon nanotubes still are not well understood. Correlated measurements of fluorescence and topography can distinguish whether intrinsic single molecule properties or small populations of very bright emitters limit the QY, and can provide a framework in which to interpret the extremely low ensemble luminescence efficiencies observed for SWNTs.

Single molecule measurements offer exciting opportunities to view individual components of ensemble spectra, uninhibited by inhomogeneous broadening and averaging, and can enable observation of additional unique behavior such as blinking and spectral wandering.^{72,170,216} However, fluorescence measurements for single molecules are naturally biased toward detection of the brightest particles, often overlooking fluorophores that are less efficient. For example, photothermal absorption measurements indicate that luminescent SWNTs represent only a small fraction of all those typically present on a coverslip.²¹¹ Therefore, single molecule studies of carbon nanotube fluorescence would benefit significantly from topographic measurements that indicate the number of SWNTs that are emissive compared to the total number of particles present,

and elucidate the relationship between fluorescence intensity and the SWNT structure, length, and orientation on the substrate.

Previously, Credo and co-workers performed measurements of fluorescence and shear force topography for luminescent porous silicon, and clarified that the 1–10% ensemble QY was caused by a small population of bright emitters instead of a large population of weak emitters.²¹⁷ Similarly, Banin and co-workers used simultaneous measurements of fluorescence and AFM topography to examine single molecule versus ensemble QYs of CdSe/ZnS semiconductor nanocrystals.¹⁹⁹ By counting bright particles in fluorescence scans and measuring the total population of particles in topography scans, these researchers used simple statistical analysis to deduce that samples with a higher fraction of bright emitters also had higher ensemble QYs. Unlike earlier reports, AFM was used during these studies to identify multiple or aggregated particles, which were excluded from analysis.

SWNTs are composed entirely of surface atoms, and are thus incredibly sensitive to variations in their local environment, which can alter their intrinsic luminescence behavior. For example, complete luminescence quenching has been observed when SWNTs directly contact metallic nanotubes in bundles⁷¹ and when they touch some substrates such as silicon; however, it is important to note that these substrates were also coated with catalyst particles and residual carbon deposits from SWNT CVD syntheses.^{154,189} Attenuation of nanotube fluorescence also accompanies dispersal in polar solvents,²¹⁸ encapsulation in certain surfactant systems,¹⁴⁹ protonation at low pH,¹⁶⁷ and shortening of the nanotube length.²¹² In addition, the presence of defect sites, impurities, and oxygen is expected to decrease the QY via hole doping, which effectively

removes an electron from the valence band and provides a trap for the excited state.^{213,219}

Another conjecture is that these processes may accelerate intersystem crossing to triplet states, which sequesters excited state carriers and lowers the observed QY.²²⁰

Promisingly, SWNT sample quality is continuing to improve, and tailoring the environment immediately surrounding SWNTs could make it possible to suppress competing processes that arise from extrinsic factors, enabling more carriers to decay by radiative relaxation pathways.

To determine what fraction of SWNTs in a typical sample is emissive and to understand better how the local environment influences their photophysical behavior, we performed measurements of correlated fluorescence and topography for individual SWNTs, including studies of fluorescence behavior in different local environments. SWNTs were wrapped in DNA and subsequently enriched in the (6,5) moiety via strong anion-exchange chromatography. This processing technique removes unwanted metallic nanotubes as well as some residual bundles and impurities. Nominally, only one semiconducting SWNT structure is isolated from the ensemble, which reduces the total number of variables under study. Importantly, use of a sample that excludes metallic nanotubes simplifies quantitative measurements that seek to elucidate the fraction of bright emitters among semiconducting species. In addition, studying only one SWNT type naturally eliminates bias in fluorescence measurements toward structures that are more resonant with the excitation source or more efficiently detected by the CCD, as discussed in Chapter 4.

6.1.2 *Purpose of this Study*

Here we present measurements of fluorescence from two samples that were correlated with topography, thereby enabling comparison between the measurements. By measuring fluorescence from bright SWNTs compared with topographic information obtained using AFM, we determined that only ~6% of all SWNTs were emissive. Overall, these measurements strongly suggest that the ensemble QY is low for SWNTs because only a small fraction of the total population is composed of bright emitters. We also examined single molecule fluorescence obtained from SWNTs dispersed onto quartz with varying levels of surfactant coverage, which effected huge variations in the observed photoluminescence behavior from individual SWNTs, again emphasizing the importance of controlling the local environment for optical measurements.

6.2 Experimental Procedure

6.2.1 *Preparation of Samples*

Clean quartz coverslips were subjected to a lithographic patterning procedure to create markers for correlated measurements of fluorescence and topography obtained on two separate instruments. Figure 6-1 depicts the procedure used to pattern the quartz coverslips. First, a layer of photoresist was deposited onto the substrate, a photomask with $20 \times 20\text{-}\mu\text{m}^2$ square openings was placed above the coverslip, and the exposed areas of photoresist were removed following brief exposure to UV light. Second, the coverslips were immersed in hydrofluoric acid to etch the exposed quartz squares, producing a grid of $400\text{-}\mu\text{m}^2$ wells. Third, gold was evaporated onto select areas of the coverslip to fill some of the wells and provide alignment markers. The photomask was

Figure 6-1. Diagram outlining the procedure used to pattern quartz substrates. Figure was adapted from ref 40.

subsequently removed, revealing patterned quartz substrates with etched wells that were surrounded by gold alignment markers. Overall, ~15,000 open wells (i.e., not filled with gold) were etched onto each 1" quartz coverslip. The location of each well was identified using a coordinate system of letters and numbers (Figure 6-2).

CoMoCAT SWNTs were wrapped with (GT)₂₀ single-stranded DNA and subsequently enriched in (6,5) structures by HPLC purification (samples were kindly provided by Ming Zheng of DuPont Corp.). Figure 6-3 presents absorption and fluorescence spectra for this sample, confirming that the ensemble sample contains mostly (6,5) SWNTs. However, these spectra also indicate that (6,4), (9,1), (8,3), and (7,5) SWNTs were present in small amounts.

For single molecule measurements, SWNTs were deposited onto quartz substrates and three types of films were prepared. To remove excess surfactant (needed to

Figure 6-2. Optical microscope image depicting the patterned quartz substrate used to facilitate correlated fluorescence and topography measurements. The dark squares were used as alignment markers and were filled with gold. The open squares (i.e., inside the black box) were used as holders for film samples. A unique letter and number index identified each square. Inset: AFM image of wells inside the red circle. Reprinted from ref 40. Copyright 2009 UMI.

accommodate AFM measurements), soft-rinsed and hard-rinsed films were prepared using a procedure adapted from ref 221. First, for soft-rinsed samples, equal volumes of SWNTs (32-fold dilution from the stock) and 20 mM MgSO_4 were combined and allowed to stand for 30 min. Next, 5 μL of sample were deposited on the coverslip and allowed to incubate for 10 min; the film was rinsed with 2 drops of water from a Pasteur

Figure 6-3. Spectra showing normalized absorbance (orange solid line) and fluorescence (blue dotted line) from an ensemble of CoMoCAT-manufactured SWNTs suspended in DNA/H₂O. The sample was enriched in (6,5) SWNTs, as indicated by the prominent peaks near ~1000 nm.

pipette and was dried under a gentle stream of nitrogen for ~1 min until no water was visible on the coverslip. Second, for hard-rinsed samples, equal volumes of SWNTs (128-fold dilution from the stock) and 20 mM MgSO₄ were combined and allowed to stand for 2 h. Next, 5 μ L of sample were deposited on the coverslip and allowed to incubate for 20 min; the film was rinsed with 5 drops of water from a Pasteur pipette and was dried under a gentle stream of nitrogen for ~1 min until no water was visible on the coverslip. Finally, as a control for fluorescence measurements, non-rinsed films were prepared; the stock sample was diluted 32 000-fold with water, 5 μ L of sample was deposited on the coverslip, and the film was dried in air for at least one hour before fluorescence and topography measurements were performed.

6.2.2 *Single Molecule Fluorescence Measurements*

Epifluorescence microscopy for individual SWNTs was accomplished using the equipment and procedures outlined in Chapter 4. Two notable differences were the use of a yellow helium–neon laser for excitation at 594.1 nm, replacement of the beam splitter with a high-transmission dichroic beam splitter with cut-on at 633 nm, and replacement of the two holographic notch filters with a razor-edge longpass filter with cut-on at 633 nm. The excitation intensity was $\sim 40 \text{ kW/cm}^2$. On the patterned quartz, one etched well was selected and, with the aid of a surveillance camera that was mounted onto the inverted microscope, was aligned over the tightly focused excitation beam. Individual $20 \times 20\text{-}\mu\text{m}^2$ raster scans with a resolution of 500-nm/pixel were stitched together, generating large images of the fluorescence from individual SWNTs located in and around the etched well. For each isolated bright spot in the scan, a fluorescence spectrum and time trace were captured with collection times of 1 min and 100 ms, respectively.

6.2.3 *Single Molecule Topography Measurements*

Topographic measurements for individual SWNTs located in and around the etched wells selected in fluorescence measurements were accomplished using a Bioscope AFM (Dimension IIIa controller) operated in TappingMode. Height and amplitude data were recorded for each scanned area. Images were typically acquired at 0.75 Hz with a resolution of 512 samples/line and individual SWNTs could be identified in the images using a resolution of $\sim 10 \text{ nm/pixel}$. Individual $5 \times 5\text{-}\mu\text{m}^2$ AFM scans were stitched

together to create large images representing the topography of the quartz substrate, which were then used to identify the location and morphology of the SWNTs.

6.3 Results

6.3.1 *Preparation of Samples*

SWNT samples were prepared on quartz with no rinsing, soft rinsing, and hard rinsing; for each sample preparation, representative topography images of $5 \times 5\text{-}\mu\text{m}^2$ areas are provided in Figure 6-4a. As the level of rinsing increased, more of the surfactant layer was removed, as indicated by the increasing visibility of the pitted quartz surface and the disappearance of surfactant spheres in the image. For all rinsed samples, Mg^{2+} was used to tether the SWNTs, wrapped in DNA with a negatively charged phosphate backbone, to the negatively charged quartz surface. Taking advantage of Coulomb interactions, the cation passivated these negative charges. As expected, in control experiments, rinsing SWNT films that were not treated with magnesium resulted in complete removal of the nanotubes (i.e., no SWNTs were observed in either fluorescence or topography scans).

6.3.2 *Correlated Fluorescence and Topography*

Fluorescence and topography were correlated for one soft-rinsed and one hard-rinsed sample; correlated images are presented in Figures 6-5 and 6-6, respectively. In fluorescence scans, the diffraction-limited luminescence features for individual particles appear much larger than those in the topography scan because the resolution is ~ 500 nm/pixel for fluorescence images versus ~ 10 nm/pixel for topography images.

Figure 6-4. Effect of rinsing on substrate coating and fluorescence spectra. Topography shown for (a) non-rinsed, (b) soft-rinsed, and (c) hard-rinsed samples. Representative fluorescence spectra corresponding to each of the substrates presented in (a)–(c) are displayed in (d)–(f), and illustrate the differences in spectral characteristics and intensity between non-rinsed and rinsed substrates.

Therefore, each fluorescent nanotube in the topography scan occupied only 1 or 2 pixels in the fluorescence scan, as the average length of the SWNTs was $\sim 311 \pm 80$ nm. Table 6-1 indicates the total population of nanotubes, the fraction of bright emitters, the fraction of bright emitters that were bundles, the average fluorescence intensities and line widths for individual SWNTs, and their average diameters and lengths. Appendix C presents raw data for all SWNTs used to compile Table 6-1 (Table C-1 and Table C-2).

Figure 6-5 presents correlated fluorescence and topography data for a soft-rinsed film. In a $755\text{-}\mu\text{m}^2$ area, the average particle density was ~ 1 particle/ $6\text{ }\mu\text{m}^2$ ($n = 124$

Table 6-1. Summary of Fluorescence and Topography Measurements for Correlated Samples

	soft-rinsed	hard-rinsed
total area correlated (μm^2)	755	325
total number of particles present	124	16
total number of bright fluorescent particles ^a	8	3
total number of weak fluorescent particles ^b	45	6
total percentage of bright emitters (%) ^a	6	19
total number of weak emitters (%) ^b	36	38
number of individual bright fluorescent SWNTs ^a	6	3
number of bundled fluorescent SWNTs ^a	1	0
number of closely neighboring fluorescent SWNTs ^{a,c}	1	0
average fluorescence intensity of individual SWNTs (counts) ^d	1687 ± 375	1479 ± 641
average FWHM (meV) ^e	90 ± 17	80 ± 14
fluorescence intensity of bundled SWNTs (counts) ^{a,d}	2758	-
fluorescence intensity of closely neighboring SWNTs (counts) ^{a,c,d}	4223	-
average individual SWNT diameter (nm)	1.8 ± 0.3	1.6 ± 0.4
average individual SWNT length (nm)	345 ± 55	242 ± 150

^a Bright fluorescent particles are those for which bright pixels were observed in the fluorescence image with a corresponding fluorescence spectrum. ^b Weak fluorescent particles are those for which bright pixels were observed in the fluorescence image, but with no corresponding fluorescence spectrum. ^c Closely neighboring fluorescent particles indicate more than one nanotube occupying the same excitation volume that are not bundled (i.e., isolated SWNTs in the topography scan occupied the same pixel in the fluorescence scan). ^d Spectra were corrected by the grating and CCD efficiencies given in Appendix A, and were integrated from 815–1050 nm. ^e Fluorescence line widths were calculated for individual nanotubes only (bundles were excluded).

particles imaged) in topography images and the average particle density was ~ 1 particle/ $94 \mu\text{m}^2$ ($n = 8$ particles imaged) in fluorescence images. Thus, despite the high density of SWNTs on the substrate, only $\sim 6\%$ of all particles displayed bright luminescence at detectable levels (i.e., bright pixels observed in the fluorescence image with a corresponding fluorescence spectrum). Approximately 36% of all particles

Figure 6-5. Top: (a) Overlaid topography (tan) and fluorescence (blue) scans for a soft-rinsed sample of SWNTs on patterned quartz. Blue lines represent the location of nanotubes and green circles indicate areas for which fluorescence spectra were observed. $\vec{E}$ is the direction of polarization for the incident excitation. Bottom: Zoom-in of (b) topography and (c) fluorescence for the red, boxed area in (a).

Figure 6-6. Top: (a) Overlaid topography (tan) and fluorescence (blue) scans for a hard-rinsed sample of SWNTs on patterned quartz. Blue lines represent the location of nanotubes and green circles indicate areas for which fluorescence spectra were observed. $\vec{E}$ is the direction of polarization for the incident excitation. Bottom: Zoom-in of (b) topography and (c) fluorescence for the red, boxed area in (a).

displayed weak luminescence (i.e., weak pixels observed in the fluorescence image, but with no corresponding fluorescence spectrum). Figure 6-6 presents correlated fluorescence and topography data for a hard-rinsed film. In a $325\text{-}\mu\text{m}^2$ area, the average particle density was 1 particle/ $20\text{ }\mu\text{m}^2$ ($n = 16$ particles imaged) in topography images and the average particle density was ~ 1 particle/ $122\text{ }\mu\text{m}^2$ ($n = 3$ particles imaged) in

fluorescence images. The percentage of bright SWNTs in this area was ~19% and the percentage of weak emitters was ~38%.

For both scans, no additional correction factor was necessary to account for intrinsically dark metallic SWNTs, as these particles were mostly removed during HPLC purification. This claim is supported by the absence of peaks in the metallic region of the absorption spectrum, except for two small peaks at 460 nm and 510 nm (Figure 6-3). As such, our sample contained almost purely semiconducting species that, nominally, could exhibit fluorescence. Most structures that were observed were (6,5) SWNTs, but other nanotube moieties were occasionally detected due to the presence of residual semiconducting species that were not completely removed during HPLC purification.

In correlated measurements, the location of bright pixels in the fluorescence scans corresponded with the location of nanotubes in the topography scans. Only one fluorescence spectrum did not line up with the location of a nanotube in the topography image, perhaps due to movement of the SWNT as the substrate was transferred between instruments, and the spectrum was assigned to the nearest nanotube in the topography image. Correlated measurements reveal that fluorescence spectra for 25% of the bright SWNTs in Figure 6-5 arose from two or more nanotubes, which were either bundles (12.5%) or closely neighboring SWNTs occupying the same excitation volume (12.5%). As presented in Table 6-1, the average fluorescence intensity observed for nanotube bundles was higher than that measured for individual SWNTs, as expected. Importantly, based solely on fluorescence data, spectra from closely neighboring nanotubes originally would have been attributed to individual SWNTs.

On the other hand, some bright pixels in the fluorescence scan (~36%) also aligned with nanotubes for which fluorescence spectra were not observed. Interestingly, it is possible that fluorescence from these weak emitters was quenched upon initial exposure to the photoexcitation, that their fluorescence intensity was too low to be detected with the laser power and integration time used here, or that these were (7,5) SWNTs that emitted too far to the red to be detected efficiently with the CCD. Additional bright spots in fluorescence scans that did not exhibit spectra and did not align with the location of carbon nanotubes in the topography scans were attributed to scattering, for example, from the edges of the well.

The position of each fluorescent SWNT with respect to the orientation of the incident electric field was also considered. The fluorescence intensity is expected to follow a $\cos^2\theta$ curve for individual SWNTs that are oriented linearly on the surface,^{72,182} but interestingly, fluorescence was observed from SWNTs regardless of their relative orientation with respect to the laser polarization. For instance, the two SWNTs depicted in Figure 6-6b were aligned at 71° and 83° with respect to the incident electric field and displayed higher fluorescence intensities than the third nanotube in Figure 6-6a, oriented 7.6° with respect to the incident electric field. Similar to the SWNTs observed by Cognet et al.,²²² fluorescence spectra were acquired for straight, bent, and C-shaped SWNTs, complicating analysis of the fluorescence dependence on incident laser polarization.

Three different nanotube structures were observed in our correlated measurements: (9,1), (8,3), and (6,5) SWNTs. The average fluorescence intensities observed for these particles were 1692 counts (n = 1 particle observed), 2168 ± 860 counts (n = 2 particles observed), and 1422 ± 411 counts (n = 6 particles observed), as

Figure 6-7. Fluorescence intensity (blue circles) and SWNT length (red triangles) as a function of SWNT structure.

presented in Figure 6-7. Although recent studies suggest that the luminescence intensity varies inversely with the nanotube diameter,²²³ our data did not follow this trend, perhaps due to variations in length and orientation with respect to the polarization of the incident electric field. In addition, only a small population of structures with different diameters was available for study in our (6,5)-enriched sample.

The average length of all fluorescent SWNTs was $\sim 311 \pm 80$ nm, and agrees well with other samples prepared using ultrasonic processing techniques.¹³⁷ The average lengths of individual (9,1), (8,3), and (6,5) SWNTs were ~ 136 nm, 303 ± 4 nm, and 343 ± 144 nm (Figure 6-7), which correspond to diameters of 0.757 nm, 0.782 nm, and 0.757 nm, respectively.⁹¹ Samples that have endured ultrasonic processing are expected to display shorter average lengths for large-diameter species, which we did not observe here, likely due to limited statistical data for (9,1) and (8,3) SWNTs.^{137,156} In addition, unlike previous measurements performed for ensembles of nanotubes,²¹² longer SWNT

lengths did not correlate with brighter luminescence intensities, although direct comparison was again complicated by variations in the orientation of the SWNTs on the substrate with respect to the excitation polarization.

6.3.3 Influence of Local Environment on SWNT Fluorescence

Single molecules were observed in fluorescence scans using each of the three sample preparation protocols. In Table 6-2, a summary of fluorescence measurements (not correlated with topography) is presented, indicating the total number of individual and bundled SWNTs for which fluorescence spectra were observed, as well as characteristics of their fluorescence spectra. Appendix C presents raw data for all SWNTs used to compile Table 6-2 (Table C-1, Table C-2, and Table C-3).

Table 6-2. Summary of Fluorescence for Uncorrelated Samples

	non-rinsed	soft-rinsed	hard-rinsed
number of particles observed	42	27	5
number of individual nanotubes	29	18	5
number of bundled nanotubes ^a	13	9	0
fraction of individual nanotubes (%)	69	67	100
fraction of bundled nanotubes (%) ^a	31	33	0
photostability	fair	poor	poor
average fluorescence intensity (counts) ^b	6934 ± 8254	2567 ± 1896	1356 ± 322
average FWHM (meV)	34 ± 5	88 ± 25	83 ± 15

^a Bundled nanotubes were classified as those with more than one peak in the fluorescence spectrum (for all samples) or FWHM greater than or equal to 45 meV (for non-rinsed samples only, as the fluorescence intensity for rinsed samples was too low to discriminate bundles from individual SWNTs). ^b Fluorescence intensities were calculated for individual nanotubes only (bundles were excluded). Spectra were corrected by the grating and CCD efficiencies given in Appendix A, and were integrated from 815–1050 nm.

Figure 6-8. Consecutive fluorescence spectra from an SWNT on a non-rinsed quartz substrate over five minutes of continuous excitation.

The characteristics of fluorescence spectra were strongly dependent upon the local environment. For example, the average fluorescence intensity was nearly three times greater for SWNTs in non-rinsed versus rinsed environments, displayed much larger variations in intensity, and exhibited much narrower line widths. Huge differences in the stability of fluorescence were also observed for the three sample preparations. For example, as displayed in Figure 6-4d–f, typical fluorescence intensities for non-rinsed samples were much greater than those measured for rinsed samples. In addition, fluorescence from non-rinsed samples initially decreased but then remained stable over several minutes (Figure 6-8); in contrast, fluorescence from rinsed samples was completely quenched after the first minute of photoexcitation.

Usually, it is not possible to observe fluorescence from bundles due to the likely presence of metallic species that completely quench fluorescence from bundles in

unsorted nanotubes samples. However, our study used a (6,5)-enriched sample, and fluorescence from bundles composed entirely of semiconducting structures was frequently observed. Bundles composed nearly one-third of all fluorescence spectra for non-rinsed and soft-rinsed samples; no bundles were observed for hard-rinsed samples, perhaps due to their removal during rinsing or use of a smaller data set. Based solely on fluorescence data, it is unclear whether all other SWNTs classified as individual nanotubes are truly isolated, especially those with very large fluorescence intensities. In light of correlated measurements, it is possible that some spectra ascribed to individual SWNTs may actually arise from bundles or multiple nanotubes with identical (n,m) structures that occupied the same $0.25\text{-}\mu\text{m}^2$ area corresponding to one pixel in the fluorescence scan.

6.4 Discussion

6.4.1 *Preparation of Samples*

First, careful attention was paid to the selection of substrates and preparation of SWNT films intended for single molecule studies. AFM measurements for SWNTs are typically performed on silicon or mica because they are extremely smooth substrates, and the quality of AFM images improves as the surface roughness decreases; however, neither substrate satisfies the requirement for transparency needed to accommodate fluorescence measurements. As discussed in Chapter 4, glass or quartz substrates can be used for optical measurements, but glass surfaces exhibit much higher levels of background fluorescence. Although quartz surfaces are not as smooth as glass (i.e., quartz surfaces are pitted with tiny microcracks), it was still possible to discern SWNTs

clearly on these substrates. Therefore, quartz coverslips were selected for all measurements.

An appropriate protocol was developed for depositing SWNT samples onto the substrate. To prepare films intended for single molecule studies, spin coating is often the preferred method, as consistent single-particle densities can be achieved. However, spin-coating particles onto patterned substrates could push the SWNTs toward the edges of the wells, making it difficult to attain uniform densities of isolated nanotubes. Instead, we used a stain technique in which 5 μL of sample was deposited onto the substrate and allowed either to incubate on the coverslip for a brief period before rinsing or, for non-rinsed samples, to dry completely.

Rinsing procedures were optimized such that clean single molecule images were obtained for both fluorescence and topography scans. For rinsed samples, which were mixed with a magnesium salt solution prior to incubation on the coverslip, water was used to rinse away excess surfactant. Although some nanotubes remained on the substrate, it is likely that a significant portion of SWNTs were washed away during this rinsing procedure. For example, single molecules were observed for rinsed films using a sample nearly 300 times more concentrated than that used to prepare non-rinsed films. For non-rinsed samples, the quartz surface was covered in a layer of surfactant, attributed to excess DNA from the stock suspension. Even at ultralow sample concentrations, this layer completely coated the quartz surface; thus, SWNTs could not be discerned in AFM scans for non-rinsed samples (Figure 6-4a).

6.4.2 *Correlated Fluorescence and Topography*

Overall, only ~6% of all particles displayed luminescence at detectable levels in correlated measurements, despite high densities of SWNTs on the substrates. Therefore, low ensemble QYs for carbon nanotubes can be definitively attributed to a small percentage of bright SWNTs in the ensemble, and not to a large population of weakly emitting SWNTs. Weak emitters composed ~36% of all observed SWNTs and the remaining SWNTs were considered dark. As noted in Chapter 5, the QY for each bright individual SWNT is ~3%. Considering that only ~6% of all semiconducting SWNTs are emissive, the estimated QY for an ensemble of semiconducting SWNTs should be ~0.18%. This value is in excellent agreement with our measurement of the ensemble QY for a similar (6,5)-enriched sample of DNA-SWNTs, which was ~0.14% (Chapter 3). Our correlated measurements also enable us to make projections about typical heterogeneous samples that include metallic SWNTs and bundles. Viewed in the context that approximately one-third of CoMoCAT nanotubes are metallic,⁸⁶ our measurements indicate that ~96% of all nanotubes are dark in typical unsorted samples. The remaining ~4% of bright emitters are isolated semiconducting nanotubes.

Our measurement of the fraction of bright emitters is in reasonable agreement with recent photothermal absorption measurements that estimate ~10% of all SWNTs dispersed onto a coverslip are emissive.²¹¹ Importantly, our approach eradicates many of the correction factors that were used to calculate the fraction of emissive SWNTs in the previous study. For example, Berciaud and co-workers studied HiPco SWNTs; therefore, fluorescence from only ~20% of structures was detected, and further corrections were necessary to account for the presence of non-emissive metallic SWNTs that comprised

approximately one-third of the sample.²¹¹ Alternatively, CoMoCAT SWNTs were examined in our study, nearly all of which could be detected with a silicon CCD, and this sample consisted entirely of semiconducting species.

In addition to quantifying the number of emissive particles in a sample, correlated measurements also determined the fraction of aggregated particles. In correlated images, 25% of all emissive particles were either bundles or neighboring SWNTs that occupied the same pixel in fluorescence measurements. For our control measurement of non-rinsed samples, 31% of all emissive particles were assigned to bundles, based solely on characteristics of the fluorescence spectra. This high fraction of bundles corroborates previous studies suggesting that residual bundles are present in typical samples and significantly lower the ensemble QY, as typical samples contain metallic SWNTs that quench fluorescence from semiconducting species in bundles.⁷⁷ Also, it is expected that the percentage of aggregated SWNTs in this (6,5)-enriched sample was lower than that for a typical surfactant-suspended ensemble, as the HPLC purification process removes some aggregates; thus, the fraction of residual bundles in a typical sample likely exceeds ~30%. Finally, correlated measurements indicate that some spectra usually assigned to individual SWNTs may actually result from bundles or nanotubes that are situated too close together to be resolved with most optical microscopes.

The diameter of a (6,5) SWNT is ~ 0.757 nm,⁹¹ but the average SWNT diameter measured by AFM was $\sim 1.7 \pm 0.3$ nm, over two times larger than the expected literature value. The nanotubes observed in correlated measurements were considered to be individual particles based on characteristics of the fluorescence spectra; therefore, it is likely that the additional height arises from the layer of DNA that wraps around the

SWNT. Our measurements are consistent with the AFM heights of 1–2 nm reported by Zheng and co-workers for a similar sample of DNA-wrapped SWNTs,¹³² and with recent calculations of ~2 nm width for (6,5) SWNTs wrapped with DNA.^{224,225} Using scanning transmission microscopy, Yarotski and co-workers found that multiple DNA strands sometimes stack upon the nanotube, and we observed similar variations in the height measured at different locations along the same nanotube.^{224,225} As expected, bundles had higher fluorescence intensities and broader fluorescence line widths than individual SWNTs. Specifically, the fluorescence intensity of bundled SWNTs was approximately two times greater than individual nanotubes; given that each bundle contained ~3 SWNTs, the combined fluorescence intensity nearly equaled the sum of the contribution from each individual nanotube.

As presented in Chapter 5, the fluorescence intensity varies for individual SWNTs,⁷⁷ and we are now able to connect how these variations may be related to the morphology, structure, or length of the SWNT under study. Importantly, the orientation of the nanotube with respect to a polarized laser directly influences the intensity of the observed fluorescence.^{72,182} Although it is possible that fluorescence from some SWNTs was not be observed due to misalignment with the excitation, many SWNTs were observed that were not closely aligned with the polarization.^{182,187} Interestingly, our measurements indicate that there is a gradient of fluorescence intensity associated with variations in the polarization of the incident electric field, but that the luminescence intensity from the SWNT does not fall to zero when the excitation is aligned perpendicular to the long axis of the nanotube. To account for this behavior, one possibility is that incoming photons excited a perpendicular transition (i.e., E_{12} or E_{21}),

when $\Delta m = \pm 1$ (Chapter 2). For example, despite predictions that the perpendicular transition will be mostly suppressed, cross-polarized PLE studies for an ensemble of SWNTs indicate that the E_{12} energy is close to the E_{22} excitation energy, and these transitions can be readily observed.^{102,226} Other factors that could account for the observation of fluorescence from misaligned SWNTs include the possibility of imperfect laser polarization or depolarization effects associated with other optics in our setup such as the high NA objective.

In our measurements, the photophysical behavior displayed by SWNTs with different (n,m) structures was directly accessed. As displayed in Figure 6-7, the fluorescence intensity did follow the structure-dependent trends observed by Tsyboulski and co-workers (i.e., that mod 2 species should be brighter than mod 1 species). However, the fluorescence intensity did not increase for smaller-diameter SWNTs;²²³ considering that (9,1) SWNTs are least resonant with the excitation energy, followed by (8,3) and (6,5) SWNTs (Chapter 4), one might expect the smallest-diameter species to be least intense because of variations in the absorption cross section at the excitation energy. Altogether, (n,m) -dependent effects are intertwined with variations in how the SWNT is oriented with respect to the polarization, as well as its length and interactions with the surface of the substrate, which could account for some differences.

As illustrated in Figure 6-7, the SWNT length increased for larger-diameter SWNTs, as expected. However, our data did not follow the trend presented by Heller et al., who estimated that the intrinsic QY increases non-linearly for longer SWNTs.¹³⁷ In addition, it is worthwhile to note that all SWNTs in our correlated measurements were longer than ~ 122 nm. Importantly, for nanotubes with lengths shorter than the exciton

diffusion length (i.e., ~90 nm), it is expected that any exciton produced within half the distance of the exciton diffusion length will be dark due to quenching at the nanotube ends. On the other hand, fluorescence was surprisingly observed from individual species that are shorter than 100 nm in other studies.^{116,222} It is important to reiterate that the fluorescence intensity and QY are separate entities, and that the QY may be equivalent for short (dim) and long (bright) SWNTs.

Given the number of variables that can influence nanotube emission, it is instructive to consider the characteristics that an optimal SWNT emitter might have. First, the SWNT should be a mod 2 semiconducting structure, as these moieties tend to be brighter than mod 1 species. Second, the length of the ideal emitter should exceed the exciton diffusion length (~90 nm) to prevent quenching of excitons at the open ends of the SWNT. Third, the SWNT must be isolated from neighboring nanotubes, and the local environment surrounding the nanotube should be uniform. In solution, the ideal emitter would be suspended in a nonpolar solvent; SWNTs exhibit higher QYs in nonpolar than in polar solvents.²¹⁸ On a substrate, it is desirable that SWNTs be straight (i.e., not bent or kinked) and perfectly aligned with the incident electric field to facilitate maximum absorption and emission of photons. Finally, for an ideal SWNT, defect sites would be passivated or completely absent from the nanotube sidewall.

6.4.3 *Influence of Local Environment on SWNT Fluorescence*

As photoexcited excitons relax to the ground state, the relative rates of competing radiative and nonradiative processes are given by the fluorescence quantum yield. Understanding a molecule's interactions with the local environment is important for

distinguishing fundamental photophysical behavior from extrinsic factors. Intrinsic relaxation events are influenced by the distribution of the excited state energy levels, dictated by the diameter and chirality of a particular nanotube, as well as quantum mechanical selection rules that determine which states will be bright or dark. In addition, intersystem crossing to triplet states can lead to sequestering of excited-state carriers. On the other hand, extrinsic variables include residual bundles, defect sites, adsorbed oxygen, and interactions with the solvent or substrate.

As presented in Figure 6-4, the local environment played an important role in the photoluminescence (PL) behavior of individual the SWNTs studied here, and could account for the poor photostability observed for all emitters in rinsed samples compared to more photostable non-rinsed samples (Figure 6-4). For example, fluorescence from an SWNT varies with surfactant system,^{119,129,155,227} solvent,²¹⁸ atmosphere,¹⁵⁵ temperature,¹⁵⁷ and pressure,¹⁵⁸ and quenches when in direct contact with some substrates like silicon.¹⁸⁹ Indeed, the fluorescence spectra of SWNTs changed dramatically upon rinsing, displaying greatly reduced intensities and broader line widths (Figure 6-4). Removal of the insulating surfactant layer or contact with the quartz substrate could contribute to this effect.¹⁵⁵ For example, it is possible that upon photoexcitation, charges build up on the quartz surface, which creates a localized population of negative charge near the SWNT.

A second possibility is that the magnesium sulfate electrolyte added to rinsed samples could play a significant role in their observed luminescence behavior. Niyogi and co-workers found that addition of MgSO_4 to SWNT suspensions resulted in slightly decreased absorption intensities and broadening of absorption features.²²⁸ Also, the

addition of electrolytes to SWNTs suspended in surfactants has been shown to increase luminescence intensities and narrow line widths up to a certain concentration threshold, upon which SWNT rebundling occurred.²²⁹ Our 20 mM Mg^{2+} concentration exceeded the rebundling threshold reported in ref 229, which may account for the presence of some bundles observed in correlated measurements. Addition of electrolytes in previous studies enhanced the luminescence intensity due to reorganization of surfactant molecules on the surface of the SWNT, such that they projected into the solvent instead of lying flat along the nanotube.²²⁹ It is unclear whether this effect is also observed for SWNTs wrapped with DNA. On the other hand, SO_4^{2-} and Cl^- can also slightly quench SWNT fluorescence,^{230,231} it is possible that sulfate anions contribute oxygen to the solution, which, when adsorbed to the nanotube sidewall, can extract photoexcited carriers.²³¹ However, sulfate groups are present in common SWNT surfactants like SDS and SDBS and are not expected to account fully for fluorescence quenching (Chapter 3).

Studies of correlated fluorescence and topography have clarified some important features of SWNT photophysics including the fraction of emissive particles in a typical sample, the fraction of bundles that are present, and the important influence of the local environment on fluorescence behavior. Single molecule fluorescence could be collected for a sample of DNA–SWNTs to which Mg^{2+} has been added, but without rinsing the substrate after depositing the sample; this approach would distinguish whether the quenching results from interactions with the electrolyte or with the underlying substrate. If no effect is observed, an alternate salt, such as MgCl_2 , could be added to assess how the identity of the ion influences the fluorescence behavior of SWNTs.

Our measurements indicate that with careful control of the local environment, it may be possible to achieve SWNT QYs that exceed 3% for individual SWNTs. Determining what factors cause some SWNTs to be dark and others bright is a question of paramount importance in nanotube photophysics. If structural defects or other physical factors cause some SWNTs to be non-emissive, then it may be possible to sort bright from dark SWNTs, an accomplishment that would hold major significance for applications based on carbon nanotube fluorescence.

6.5 Conclusions

Correlated measurements of fluorescence and topography were performed for a sample of (6,5)-enriched DNA-wrapped SWNTs. By measuring fluorescence from bright SWNTs compared with topographic information obtained using AFM, we determined that only ~6% of all SWNTs in an ensemble are bright, caused by a combination of intrinsic (e.g., scattering to dark exciton states) and extrinsic factors (e.g., (n,m) structure, length, orientation with respect to polarization, and interactions with the substrate). Therefore, the low ensemble SWNT QY is low because only a small fraction of the total population is composed of bright emitters. Variations in the local environment, including surfactant coverage and the presence of electrolytes added to the suspensions, effected extreme variations in the observed photoluminescence behavior from individual SWNTs, emphasizing the importance of controlling the local environment for optical measurements. Altogether, these studies signify a substantial advance in our understanding of the source of low ensemble SWNT QYs, and should aid researchers seeking to prepare brighter NIR fluorescence labels incorporating carbon nanotubes.

CHAPTER 7

Future Directions

The work presented in this dissertation has clarified some aspects of the luminescence behavior of individual SWNTs, which is particularly salient for understanding the ensemble behavior of heterogeneous samples. Still, many areas of nanotube photophysics pose important questions that merit further investigation and development. Closing this dissertation, this chapter outlines current challenges in the field and experiments that could further interrogate the photophysical properties of individual SWNTs.

7.1 Current Challenges in SWNT Photophysics

Nearly two decades after their discovery,⁹ carbon nanotubes continue to fascinate the scientific community. As described in this dissertation, SWNTs possess several unique photophysical features that arise from their interesting molecular structure and small radial dimensions. By investigating the photophysical properties of individual SWNTs, our work has lent meaning to ensemble measurements and offered insight into the excited state dynamics of these unique molecules.

Overall, the low ensemble QY for SWNTs is influenced by the presence of metallic nanotubes, residual bundles, defect sites, fast scattering into nonradiative dark states, and intersystem crossing to triplet states. Therefore, the luminescence efficiency of ensemble samples is affected by a heterogeneity that extends far beyond simple differences in diameter and chirality. Here, we review four of the most important questions in nanotube photophysics that would provide a helpful context in which to understand the seemingly low SWNT QY. We also put forward experiments that could be used to interrogate these topics.

One area of nanotube photophysics that merits further investigation concerns the need for refined models that accurately describe SWNT energy levels and optical transition energies. For example, for most (n,m) structures, the tight binding model predicts optical transition energies that are so much smaller than observed energies that it is unclear why this model works at all.^{111-113,232} As explained in Chapter 2, the basic tight binding model is calculated for electrons; however, recent inclusion of additional nearest-neighbor atoms, curvature effects, trigonal warping, and excitonic effects have resulted in significant improvements. For example, a recent tight-binding calculation that included

all four carbon valence electrons, accounted for orbital overlap, and included nanotube curvature displayed exceptional agreement between theory and experiment when a 0.3-meV upward energy shift was applied to the calculated transition energies.²³³ Still, a detailed understanding of self-energy and excitonic effects that may account for the necessary shift remain to be explored, and should lead to more accurate models.²³³

Second, the local environment strongly influences the measured line widths and photoluminescent lifetimes of SWNTs in an unknown manner.^{209,234} As presented in Chapter 3, fluorescence peaks shift and line widths sharpen or broaden according to the dispersing agent associated with the SWNT. The local environment also encompasses defect trap sites along the sidewall that alter the excited state lifetimes for individual nanotubes.²³⁴ To better understand these effects, single molecule fluorescence and photoluminescence lifetime measurements could be conducted for SWNTs suspended in a range of surfactants. In particular, near-field optical techniques could enable the study of tiny areas of the SWNT with a uniform micellar environment (i.e., molecules typically adsorb nonuniformly onto the SWNT sidewall, and far-field measurements average over this distribution of local dielectric environments). Alternatively, optical measurements could be performed for SWNTs immobilized in cage-like molecules such as Sarkosyl, which supply a constant dielectric environment around each SWNT.

Third, the recent prediction of a forbidden exciton state, with an energy below that of the allowed exciton, may play a large role in SWNT optical properties.^{112,235} Under an applied magnetic field, low-temperature photoluminescence measurements not only confirm the existence of the dark singlet exciton, but also reveal a very small 1–4 meV energy splitting between the lowest-lying bright and dark singlet excitons (for

SWNTs with diameters ranging from 1.0 to 1.3 nm).²³⁶ Some loss of fluorescence intensity can be attributed to fast scattering of excited carriers to the dark exciton state by electron–phonon coupling.^{111,237} Still, the existence of the low-lying dark excitonic state cannot completely account for the low fluorescence QY observed for SWNTs. The percentage of carriers that are transferred to the dark exciton from the singlet exciton could be quantified by evaluating the relative increase in integrated fluorescence intensity of the dark state relative to the bright state using cryogenic micromagnetic photoluminescence measurements;²³⁶ however, it is unclear how this measurement could be performed at room temperature due to significant thermal broadening of fluorescence line widths.

Fourth, although much attention has centered on singlet excitons, the role of triplet states in SWNT photoluminescence behavior has received less attention. Specifically, many triplet states exist at energies below the bright singlet exciton.¹¹⁷ Therefore, it is likely that intersystem crossing to long-lived triplet states competes with radiative relaxation. Although the energy of the triplet state has been predicted for SWNTs, this transition has never been observed experimentally for ensemble samples.²²⁰ At low temperatures, it may be possible to observe phosphorescence from the triplet state and to quantify the fraction of excited-state carriers involved in intersystem crossing. Further, triplet quenching of the singlet exciton in SWNTs can be monitored by addition of triplet-quenching molecules like β -mercaptoethanol, DDT, and Trolox, which could potentially increase the fluorescence response. Measurement of long fluorescence decay components upon addition of triplet quenchers would reveal how these additives affect quenching of the triplet state, and are ongoing in the Krauss laboratory.

7.2 Current Challenges for SWNT Applications

Each of these research areas holds important implications for SWNT photophysics. Still, these investigations have been hindered by the absence of chirality-sorted, pristine SWNT starting materials for use in spectroscopic measurements that could be compared to available models. Advances in sample preparation would significantly progress photophysical studies, and current challenges in synthesis, purification, and processing are considered. In general, as the photophysical properties of carbon nanotubes continue to become better understood, emphasis will shift toward whether these properties can enable groundbreaking applications; therefore, it is also important to consider the potential impact that carbon nanotubes could have on human health and the environment.

Significant effort has been devoted to developing the selective growth of one nanotube structure at a time (i.e., with control over the diameter, chirality, and length of the species); although the relationship between the structure of the SWNT and its physical properties is not well understood, selective growth could be achieved by accessing some property that varies sensitively according to SWNT type.²³⁸ Toward the production of homogenous starting materials, more success has been achieved by selection of one SWNT structure from a heterogeneous sample using specially tailored dispersion agents and innovative processing techniques. Still, only limited separation can be achieved using current approaches. Therefore, it is highly desirable to develop a surfactant system that would selectively associate with or wrap one SWNT structure. For example, altering DNA and peptide sequences to selectively associate with SWNTs that have different diameters and sidewall curvature presents one option.

Photophysical studies are also strongly influenced by the limited purity of starting materials. As mentioned in Chapter 1, all currently available SWNT samples, including those having undergone purification, contain extraneous carbonaceous material, residual catalyst particles, defective SWNTs with sidewall damage, and adsorbed oxygen. Therefore, it is often unclear whether observed photophysical behavior results solely from the nanotube itself or if it reflects the strong influence of impurities associated with the SWNT. Ongoing progress toward establishing standards for sample purity should assist with reproducibility between different laboratories, even if the starting materials are not completely pristine at this time.²³⁹ Addition of antioxidants like ascorbic acid could provide some removal of adsorbed oxygen species; these studies are ongoing in the Krauss laboratory.

During all synthetic, purification, and post-processing methods, defect sites are incorporated onto the SWNT sidewall, as mentioned in Chapter 1. It is important to differentiate between the optoelectronic properties of defect-free and damaged nanotubes, as the behavior of SWNTs is influenced in an unknown way by disruption of the pristine sp^2 -bonding along the nanotube axis. The prevention of defect site formation during synthesis and multiple purification steps would be extremely difficult; however, repairing the defects may present a more practical approach to addressing this challenge. Detailed studies that explain how defect sites influence optical spectra are largely absent from the literature, but thermal annealing or removal of bound surface oxygen by de-epoxidation chemistry could provide some repair to the SWNT sidewall.^{213,240} Ju et al. also recently demonstrated that flavin mononucleotide molecules exclude oxygen from the SWNT

surface, resulting in improvements for measured ensemble QYs (11% in toluene and 0.08% in D₂O, used here).²¹⁸

On a final note, any evaluation of future directions would be remiss without considering the potential environmental impacts, health effects, and toxicology of carbon nanotubes in living organisms. Indeed, significant attention should be given to the development of protocols that will assist the safe and responsible handling of these materials before SWNTs become ubiquitous in consumer products. On one hand, optical spectroscopy has been used to track suspended SWNTs that were intravenously administered to both rabbits and *Drosophila melanogaster* fruit flies, revealing promising circulation persistence but no acute toxicity.^{79,164} On the other hand, research has indicated that the long, fibrous nature of nanotube soot mimics asbestos particles; lesions known as granulomas formed when MWNTs were administered to the mesothelial lining of the body cavity in mice.²⁴¹ Clearly, further investigation is required to establish a firm understanding of the risks that SWNTs pose to both humans and the environment.

7.3 Conclusions

Continuing efforts to understand the remarkable photophysical properties of carbon nanotubes are essential to the realization and success of applications incorporating these materials. In particular, the availability of pristine, structure-sorted starting materials would significantly advance both theoretical and experimental studies of the physical, electronic, and optical characteristics of SWNTs. With developments in all of these arenas, our understanding of the photophysical properties of single-walled carbon nanotube should continue to advance rapidly. Ultimately, the production of innovative

devices will be made possible by fundamental research that has undertaken great challenges, and yielded even greater rewards.

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APPENDIX A

Spectral Response Curves for Gratings and Detectors

Figure A-1. Relative efficiency (η) as a function of wavelength (λ) for a 600 groove/mm, 1.0- μm blaze grating in the emission monochromator (SpectraPro 300i) used in epifluorescence microscope studies. The data points between 800 and 949 nm were empirically fit by a third order polynomial given by curve A and the data points between 950 and 1800 nm were empirically fit by a third order polynomial given by curve B.

$$\eta_A = 1.7778 \times 10^{-8} \lambda^3 - 5.5048 \times 10^{-5} \lambda^2 + 5.6594 \times 10^{-2} \lambda - 18.507$$

$$\eta_B = 1.4915 \times 10^{-9} \lambda^3 - 6.1261 \times 10^{-6} \lambda^2 + 7.6383 \times 10^{-3} \lambda - 2.1891$$

Figure was adapted from the published source.²⁴²

Figure A-2. Spectral response (R) as a function of wavelength (λ) for a germanium detector (Northcoast Scientific, EO-8175) cooled to -196°C with liquid nitrogen. The data points represent an average between curves provided by two published sources.^{243,244} Data points between 800 and 1549 nm were empirically fit by a third order polynomial given by curve A and the data points between 1550 and 1800 nm were empirically fit by a third order polynomial given by curve B.

$$R_A = -2.2719 \times 10^{-10} \lambda^3 + 2.3766 \times 10^{-7} \lambda^2 + 1.0946 \times 10^{-3} \lambda - 0.55901$$

$$R_B = -7.3162 \times 10^{-9} \lambda^3 + 4.1944 \times 10^{-5} \lambda^2 - 8.1871 \times 10^{-2} \lambda + 54.246$$

Figure was adapted from the published sources.^{243,244} An additional published source is also available.²⁴⁵

Figure A-3. Relative efficiency (η) as a function of wavelength (λ) for a 300 groove/mm, 1.0- μm blaze grating in the emission monochromator (SpectraPro 2300i) used in epifluorescence microscope studies. The data points between 800 and 899 nm were empirically fit by a third order polynomial given by curve A and the data points between 900 and 1800 nm were empirically fit by a third order polynomial given by curve B.

$$\eta_A = 5.3333 \times 10^{-8} \lambda^3 - 1.4514 \times 10^{-4} \lambda^2 + 1.3231 \times 10^{-1} \lambda - 39.483$$

$$\eta_B = -7.5127 \times 10^{-10} \lambda^3 + 2.8951 \times 10^{-6} \lambda^2 - 4.2008 \times 10^{-3} \lambda + 2.9060$$

Figure was adapted from the published source.²⁴²

Figure A-4. Spectral response (R) as a function of wavelength (λ) for the CCD used in epifluorescence microscope studies (Princeton Instruments, XTE 400R deep depletion Spec-10). Data points between 400 and 762 nm were empirically fit by a fourth order polynomial given by curve A and the data points between 763 and 1100 nm were empirically fit by a fourth order polynomial given by curve B.

$$R_A = 1.9720 \times 10^{-10} \lambda^4 - 4.6287 \times 10^{-7} \lambda^3 + 3.9726 \times 10^{-4} \lambda^2 - 1.4617 \times 10^{-1} \lambda + 19.483$$

$$R_B = 1.2108 \times 10^{-12} \lambda^4 + 1.3279 \times 10^{-8} \lambda^3 - 4.5188 \times 10^{-5} \lambda^2 + 4.3858 \times 10^{-2} \lambda - 13.016$$

Figure was adapted from the published source.²⁴⁶

APPENDIX B

Microscopy Data and Calculations for Chapter 5

Table B-1. Raw Fluorescence Intensities for Individual SWNTs

Number	(<i>n,m</i>)	Fluorescence Peak (nm)	Fluorescence Intensity (counts)	Uncertainty
1	(6,4)	884	181.89	7.22
2	(6,4)	891	210.14	8.11
(6,4) average			196.02	5.43
3	(9,1)	918	168.29	7.10
4	(9,1)	924	191.31	7.49
5	(9,1)	926	205.33	7.42
(9,1) average			188.31	4.24
6	(8,3)	960	199.99	7.62
7	(8,3)	962	200.65	7.47
8	(8,3)	964	199.59	7.09
9	(8,3)	964	212.87	8.47
10	(8,3)	965	49.55	9.58
(8,3) average			203.28	3.84
11	(6,5)	969	224.20	8.05
12	(6,5)	978	29.47	74.70
13	(6,5)	979	200.63	10.00
14	(6,5)	980	224.13	7.67
15	(6,5)	982	35.58	12.05
16	(6,5)	994	238.86	8.73
(6,5) average			183.46	15.34
weighted average^b			192.89	8.62

^a The average represents the average of the fluorescence from all four SWNT structures. ^b The weighted average represents the average of all SWNT structures.

Table B-2. Raw Fluorescence Intensities for Individual QDs^a

Number	Coverslip	Fluorescence Peak (nm)	Fluorescence Intensity (counts)	Uncertainty
1	A	712	371.01	49.26
<i>A average</i>			371.01	49.26
2	B	704	328.62	125.03
3	B	710	19.45	8.49
<i>B average</i>			174.04	125.31
4	C	684	1189.10	137.48
5	C	710	609.84	108.61
<i>C average</i>			899.47	175.20
6	D	708	45.45	10.72
7	D	713	50.58	9.64
<i>D average</i>			48.02	14.41
8	E	696	66.09	12.89
9	E	709	16.41	7.022
<i>E average</i>			41.25	14.67
10	F	677	241.38	55.69
11	F	703	528.23	88.68
<i>F average</i>			384.81	104.72
12	G	704	24.68	9.39
13	G	713	15.49	5.41
<i>G average</i>			20.09	10.83
<i>weighted average^b</i>			263.50	30.87

^a QD fluorescence intensities were captured from the same coverslips for which single molecule SWNT fluorescence was observed (Table B-1). ^b The weighted average represents the average from each coverslip (i.e., A–G).

Table B-3. Calculation of (6,5) DNA–SWNT Absorption Cross Section^a

Parameter	Quantity
d_t (nm) ^b	0.7579
l_{SWNT} (nm)	380
$ T $ (nm) ^c	4.124
Unit cells per SWNT	92
Atoms of carbon per unit cell ^d	364
Atoms of carbon per SWNT	33,488
Moles of carbon per SWNT (mol)	5.6×10^{-20}
Mass of carbon (μg) ^e	10
SWNT concentration (M)	2.5×10^{-8}
Extinction coefficient ($\text{M}^{-1}\text{cm}^{-1}$) ^f	5.2×10^7
σ_{E11} (cm^2) ^g	1×10^{-13}
$A_{\lambda_{\text{ex}}}$ (AU)	0.17475
A_{E11} (AU)	1.2934
$A_{\lambda_{\text{ex}}}/A_{\text{E11}}$	0.1351
$\sigma_{\lambda_{\text{ex}}}$ (cm^2) ^h	1.35×10^{-14}
A_{E22} (AU)	0.52869
PLE_{E22} (counts) ⁱ	67,076
$\text{PLE}_{\lambda_{\text{ex}}}$ (counts) ⁱ	13,217
$A_{\text{E22}}/A_{\lambda_{\text{ex}}}$	3.0254
$\text{PLE}_{\text{E22}}/\text{PLE}_{\lambda_{\text{ex}}}$	5.0750
Correction Factor ^j	0.5961
Corrected $\sigma_{\lambda_{\text{ex}}}$ (cm^2)^k	7×10^{-15}

^a All values were calculated for a 1-mL sample of (6,5) DNA-wrapped SWNTs with $\lambda_{\text{ex}} = 632.8$ nm, $\lambda_{\text{E11}} = 985$ nm, and $\lambda_{\text{E22}} = 574$ nm. ^b Literature value.⁹¹ ^c Calculated with eq 2-9. ^d Calculated with eq 2-10. ^e Estimated from molecular modeling indicating 1:1 mass ratio of DNA:SWNT.¹³² ^f Obtained by Beer's law using A_{E11} . ^g Calculated using $\sigma = ((2303)(\epsilon)/N_A)$. ^h Obtained by scaling σ_{E11} by the absorbance at λ_{ex} and λ_{E11} . ⁱ PLE was monitored at 998 nm. ^j The correction factor is the quotient of $A_{\text{E22}}/A_{\lambda_{\text{ex}}}$ and $\text{PLE}_{\text{E22}}/\text{PLE}_{\lambda_{\text{ex}}}$ and assumes that all material absorbing light at E22 also emits. ^k Corrected $\sigma_{\lambda_{\text{ex}}}$ is the product of $\sigma_{\lambda_{\text{ex}}}$ and the correction factor.

APPENDIX C

Microscopy Data for Chapter 6

Table C-1. Summary of PL Measurements for Non-Rinsed Samples

Number	$(n,m)^a$	PL Intensity (counts) ^b	Fluorescence Peak (nm)	FWHM (meV)
<i>Sample A</i>				
1	(8,3)	4154	968	28
2	(8,3)	5753	970	28
3	(6,5)	462	990	36
4	(6,5)	579	993	32
5	(6,5)	978	995	33
6	(6,5)	1281	1002	35
7	(6,5)	1607	988	42
8	(6,5)	1640	999	34
9	(6,5)	2021	991	30
10	(6,5)	2948	992	38
11	(6,5)	3309	992	33
12	(6,5)	4553	990	32
13	(6,5)	7792	1001	30
14	(6,5)	16 287	994	43
15	(6,5)	22 922	991	39
16	(6,5)	33 709	990	34
17	B	6366	-	-
18	B	6767	-	-
19	B	9029	-	-
20	B	68 787	-	-
<i>Sample B</i>				
21	(6,5)	694	1003	22
22	(6,5)	18 394	990	30
23	B	1655	995	45
24	B	9191	867	48

Number	$(n,m)^a$	PL Intensity (counts) ^b	Fluorescence Peak (nm)	FWHM (meV)
25	B	16 046	972	46
<i>Sample C</i>				
26	(9,1)	8563	922	34
27	(8,3)	1032	963	32
28	(6,5)	546	1001	36
29	(6,5)	1254	997	38
30	(6,5)	1303	1002	31
31	(6,5)	4112	996	28
32	(6,5)	9103	888	38
33	(6,5)	16 038	984	42
34	B	4179	-	-
35	B	7182	996	46
36	B	7695	996	74
37	B	10 466	-	-
<i>Sample D</i>				
38	(9,1)	15 144	930	26
39	(6,5)	486	998	35
40	(6,5)	14 407	973	43
41	B	13 485	-	-

^a Bundled nanotubes are indicated by *B* and were classified as having more than one peak in the fluorescence spectrum or a line width greater than or equal to 45 meV. ^b Fluorescence intensities were calculated for individual nanotubes and bundles with only one emission peak. Spectra were corrected by the grating and CCD efficiencies, given in Appendix A (Figures A-3 and A-4, respectively), and were integrated from 815–1050 nm.

Table C-2. Summary of PL and AFM Measurements for Soft-Rinsed Samples^a

Number	(<i>n,m</i>) ^b	PL Intensity (counts) ^c	PL Peak (nm)	FWHM (meV)	Diameter (nm)	Length (nm)	Orientation ^d
<i>Sample E</i>							
1	(8,3)	1060	972	94	-	-	-
2	(6,5)	1595	995	74	-	-	-
3	(6,5)	3582	995	57	-	-	-
4	B	1961	-	-	-	-	-
5	B	2205	-	-	-	-	-
6	B	2881	-	-	-	-	-
7	B	3231	-	-	-	-	-
8	B	3820	-	-	-	-	-
9	B	9377	-	-	-	-	-
10	B	12 342	-	-	-	-	-
11	B	23 355	-	-	-	-	-
<i>Sample F</i>							
12	(6,4)	6046	884	70	-	-	-
13	(8,3)	2309	946	113	-	-	-
14	(6,5)	1109	978	86	-	-	-
15	(6,5)	1845	972	137	-	-	-
16	(6,5)	7284	981	136	-	-	-
<i>Sample G</i>							
17	(9,1)	1692	934	96	1.4	136	41.3°
18	(8,3)	1560	943	76	1.3	300	30.2°
19	(8,3)	2776	945	88	1.5	305	62.5°
20	(6,5)	929	988	111	2.3	560	curved
21	(6,5)	1224	996	73	2.1	475	bent
22	(6,5)	1944	1000	96	2.1	295	51.7°
23	(6,5)	2000	1014	75	-	-	-

Number	$(n,m)^b$	PL Intensity (counts) ^c	PL Peak (nm)	FWHM (meV)	Diameter (nm)	Length (nm)	Orientation ^d
24	B	2758	991	87	-	-	bundled
25	N	4223	-	-	-	-	neighboring
Sample H							
26	(6,5)	818	982	44	-	-	-
27	(6,5)	5682	1002	68	-	-	-

^a Shaded lines represent nanotubes that were located in correlated scans. ^b Bundled nanotubes are indicated by *B* and were classified as having more than one peak in the fluorescence spectrum and closely neighboring nanotubes in the topography scan that occupied the same pixel in the fluorescence scan are indicated by *N*. ^c Fluorescence intensities were calculated for individual nanotubes only (bundles were excluded). Spectra were corrected by the grating and CCD efficiencies, given in Appendix A (Figures A-3 and A-4, respectively), and were integrated from 815–1050 nm. ^d Orientation refers to the position of the SWNT with respect to the laser polarization as indicated in Figure 6-5. Orientations are provided for nanotubes that were straight, and those that were curved, bent, bundled, or neighboring are noted as such.

Table C-3. Summary of PL and AFM Measurements for Hard-Rinsed Samples^a

Number	(<i>n,m</i>)	PL Intensity (counts) ^b	PL Peak (nm)	FWHM (meV)	Diameter (nm)	Length (nm)	Orientation ^c
<i>Sample I</i>							
1	(6,5)	1081	969	61	1.2	283	7.6°
2	(6,5)	1277	992	91	-	-	-
3	(6,5)	1529	1012	89	1.8	179	71.2°
4	(6,5)	1826	997	73	1.7	265	83.0°
<i>Sample J</i>							
5	(6,4)	1067	890	31	-	-	-

^a Shaded lines represent nanotubes that were located in correlated scans. ^b Fluorescence intensities were calculated for individual nanotubes only (bundles were excluded). Spectra were corrected by the grating and CCD efficiencies, given in Appendix A (Figures A-3 and A-4, respectively), and were integrated from 815–1050 nm. ^c Orientation refers to the position of the SWNT with respect to the laser polarization as indicated in Figure 6-6.