Separation of Single-Walled Carbon Nanotubes By Electronic Type Using Conjugated Polymers
TITLE: Separation of Single-Walled Carbon Nanotubes By Electronic Type Using Conjugated Polymers

AUTHOR: Nicole A. Rice
B.Sc., (Chemistry)
Memorial University, St. John’s, Canada

SUPERVISOR: Professor Alex Adronov

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Abstract

Since their discovery over two decades ago, single-walled carbon nanotubes (SWNTs) have become one of the most investigated nanomaterials in materials science. Their exotic optical, electrical, thermal and mechanical properties afford them amazing potential in a variety of different fields. Current SWNT synthetic processes produce heterogeneous mixtures of both semiconducting and metallic SWNTs. The mixed electronic nature of these materials, combined with their limited solubility, has significantly hampered the realization of many applications and necessitates the development of post-synthetic purification techniques. Conjugated polymers offer a significant advantage over other proposed strategies in that not only do they provide a cheaper and scalable route towards the isolation of SWNTs, but they also allow for the preparation of materials with novel properties. Polyfluorenes have been extensively investigated in the literature due to their preference towards dispersing semiconducting SWNTs; however, these dispersions are often quite dilute, and the polyfluorene structure is incompatible with certain device applications for SWNTs. Poly(2,7-carbazole)s offer a viable alternative to polyfluorenes for the purification of bulk SWNT material. At the time of this thesis, there have been relatively few reports investigating the interactions of poly(2,7-carbazole)s with SWNTs, and the majority of examples in the literature have suffered from poor stability and complex dispersal procedures due to the inherent insolubility of the 2,7-carbazole structure.

The work presented in this thesis involved the preparation and characterization of a novel poly(2,7-carbazole) structure that displayed excellent solubility in a variety of organic solvents, allowing for the preparation of extremely stable and relatively concentrated dispersions of SWNTs. Thorough characterization of the supramolecular complexes through absorbance, photoluminescence and Raman spectroscopies
determined that this polymer preferentially disperses semiconducting SWNTs.

A second objective of this work was to investigate how modification of various parameters (including polymer structure, molecular weight and the type of SWNTs) can influence the quality of the resultant composite dispersions. One important study performed was to investigate how the electronic nature of the polymer backbone can affect the separation of SWNTs by electronic type. We demonstrate for the first time that by incorporating an electron-poor functionality into a polyfluorene it is possible to change from dispersing only semiconducting SWNTs to solubilizing both electronic types. This investigation highlights the potential importance of incorporating electron-poor functionalities in the development of polymeric systems that can selectively discriminate metallic SWNTs, which remains a challenging endeavor at the time of this thesis publication.
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>anpHiPCO</td>
<td>Annealed Purified HiPCO</td>
</tr>
<tr>
<td>BWF</td>
<td>Briet-Wigner-Fano</td>
</tr>
<tr>
<td>$C_h$</td>
<td>Chiral Vector</td>
</tr>
<tr>
<td>CoMoCAT</td>
<td>Cobalt Molybdenum Catalyst</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DGU</td>
<td>Density Gradient Ultracentrifugation</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DOC</td>
<td>Sodium Deoxycholate</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of Polymerization</td>
</tr>
<tr>
<td>d_t</td>
<td>Diameter</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>EtOAc</td>
<td>Ethyl Acetate</td>
</tr>
<tr>
<td>FET</td>
<td>Field Effect Transistor</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
</tr>
<tr>
<td>HiPCO</td>
<td>High Pressure Carbon Monoxide</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>HRMS</td>
<td>High-Resolution Mass Spectrometry</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>IEX</td>
<td>Ion Exchange Chromatography</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Number-Average Molecular Weight</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight-Average Molecular Weight</td>
</tr>
<tr>
<td>MWNT</td>
<td>Multiwalled Carbon Nanotube</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>m-SWNT</td>
<td>Metallic Single-Walled Carbon Nanotube</td>
</tr>
<tr>
<td>$(n,m)$</td>
<td>Integer Lattice Translations Indices for SWNTs</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>ns</td>
<td>Nanosecond</td>
</tr>
<tr>
<td>NT</td>
<td>Nanotube</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic Photovoltaic</td>
</tr>
<tr>
<td>P3AT</td>
<td>Poly(3-alkylthiophene)</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity Index</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene Glycol</td>
</tr>
<tr>
<td>PFO</td>
<td>Poly(9,9-dioctylfluorenyl-2,7-diyl)</td>
</tr>
<tr>
<td>pHIPCO</td>
<td>Purified HiPCO</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PC</td>
<td>Poly(2,7-carbazole)</td>
</tr>
<tr>
<td>PC-PF</td>
<td>Poly(carbazole-co-fluorene)</td>
</tr>
<tr>
<td>PPE</td>
<td>Poly(phenylene ethynylene)</td>
</tr>
<tr>
<td>PPV</td>
<td>Polyphenylene Vinylene</td>
</tr>
<tr>
<td>ps</td>
<td>Picosecond</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>RBM</td>
<td>Radial Breathing Mode</td>
</tr>
<tr>
<td>SCh</td>
<td>Sodium Cholate</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>sc-SWNT</td>
<td>Semiconducting Single-Walled Carbon Nanotube</td>
</tr>
<tr>
<td>SDBS</td>
<td>Sodium Dodecylbenzenesulfonate</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium Dodecyl Sulfate</td>
</tr>
<tr>
<td>SEC</td>
<td>Size Exclusion Chromatography</td>
</tr>
<tr>
<td>ssDNA</td>
<td>Single-Stranded Deoxyribonucleic Acid</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single-Walled Carbon Nanotube</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TFA</td>
<td>Trifluoroacetic Acid</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>UV-Vis-NIR</td>
<td>Ultraviolet Visible-Near-Infrared</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
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<tr>
<td>$\omega_{RBM}$</td>
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Chapter 1

Dispersal Methodologies and Characterization of Carbon Nanotube Composites

1.1 Introduction to Carbon Nanotubes

Carbon nanotubes (NTs) are hollow, tubular allotropes of carbon that are only nanometers in diameter but can be up to centimeters in length.\(^1\) Their quasi-1D shape affords these nanomaterials unique chemical, thermal, mechanical, optical and electrical properties and tremendous application potential across many disciplines.\(^2\)–\(^4\) NTs can consist of one layer of carbon atoms to form a single-walled carbon nanotube (SWNT), or they can have several layers of SWNTs of different diameters nested inside one another to form a multi-walled carbon nanotube (MWNT), as is shown in Figure 1.1. SWNTs are only approximately 0.4 – 3 nm in diameter, while the diameters for MWNTs vary greatly depending on the number of layers in the structure, ranging from at least 2 nm to upwards of 50 nm.\(^5\)

![Figure 1.1. Examples of allotropes of carbon: (a) fullerene (b) graphene (c) SWNT and (d) MWNT.](image)

SWNTs are often described using the “rolled graphene sheet” analogy, where
A NT is a seamless cylinder rolled from a 2D graphene sheet, as shown in Figure 1.2. The chiral vector \( C_h \), blue arrow, connects two crystallographically equivalent carbon atoms on the graphene sheet, which is “rolled” such that the two endpoints of the chiral vector are superimposed on each other. As there are many different permutations in how the graphene sheet can be rolled, it is possible to form a variety of different SWNT species. The simplest way to identify a tube is using the chiral vector equation, which is given by:

\[
C_h = n a_1 + m a_2 = d_t \pi \tag{1.1}
\]

where \( n \) and \( m \) are integers corresponding to the lattice translational indices, and \( a_1 \) and \( a_2 \) are unit vectors for the graphene lattice. Unique SWNT structures are often specified by the pair of integer indices \((n,m)\). Since the chiral vector is in the circumferential direction of the rolled up NT, it can also be related to the diameter \((d_t)\) of the SWNT, as shown in Equation 1.1.

![Figure 1.2. (a) Graphene lattice showing the chiral vector \((C_h, \text{blue arrow})\), chiral angle \((\theta, \text{green arrow})\) and unit vectors \(a_1\) and \(a_2\) (grey arrows). Armchair and zigzag SWNT directions have also been labeled in red and purple, respectively. (b) A graphene map with \((n,m)\) chirality labels. Red labels correspond to armchair metallic (MOD0) SWNTs, blue labels are non-armchair metallic (MOD0) SWNTs and black labels are semiconducting SWNTs (MOD1 or MOD2).]
Another important property used to describe a SWNT is the chiral angle, $\theta$, which is defined as the angle between the vectors $C_h$ and $a_1$:

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

(1.2)

Due to hexagonal symmetry in the graphene lattice, the chiral angle is confined to the values of $0 - 30^\circ$. The two extreme chiral angle values both represent tubes that are achiral; if $\theta = 0^\circ$ ($m = 0$), the tube is referred to as a zigzag NT, while if $\theta = 30^\circ$ ($n = m$) the SWNT is called an armchair NT. All other SWNTs are chiral tubes and lack mirror symmetry.

### 1.2 Electronic Properties of SWNTs

SWNTs are composed entirely of covalently bonded carbon atoms. Each carbon atom is bound to three other carbon atoms by $\sigma$-bonds, with the remaining p electrons contributing to a delocalized $\pi$-electron system. SWNTs are formed as a variety of discrete structures with distinct diameters and chiralities, which correspondingly allows for a variety of $\pi$-electron band structures and excitations. A key feature of NTs is the strong dependence of their electronic properties on the physical structure of the tube.

The electronic structures of NTs originate from graphene, which is a semimetal, or zero-band gap semiconductor. In 2D graphene, the $\pi$-bands are closer to the Fermi level than the $\sigma$-bands, therefore electrons are optically excited from the valance $\pi$ (HOMO) to the conducting $\pi^*$ (LUMO). Electronic energy surfaces of 2D graphene can be calculated with the nearest neighbor tight binding method, which finds that the $\pi/\pi^*$ bands touch each other at so-called K points, corresponding to the six corners
of the hexagonal first Brillouin zone, and Fermi level of intrinsic graphene. Upon “rolling” the 2D graphene sheet to form a 1D SWNT only certain quantized wave vectors are allowed (“cutting lines” on the 2D graphene electronic surfaces) due to the 1D quantum confinement, resulting in a tiny subset of allowed states when the sheet is rolled into a cylinder. When the 1D cutting lines are superimposed onto the 2D graphene electronic energy surface (Figure 1.3a), it is possible to obtain the electronic band structure and calculate the electronic density of states (DOS) for specific \( (n,m) \) chiralities. If the cutting lines for a particular \( (n,m) \) NT pass through a K point, where the \( \pi \) and \( \pi^* \) levels are degenerate, then there is an allowed state in the Fermi level and the resulting SWNT is metallic in nature. If the K point is located between two cutting lines (one third the distance between two adjacent K points, Figure 1.3b), then the DOS at the Fermi level equals zero, and there is a band gap between the valance and conduction bands resulting in a semiconducting NT. Statistically, it is expected that one third of all possible SWNT structures combine with the right diameter and twist to include the Fermi point and form a metallic SWNT, while the remaining two thirds of possible structures are semiconducting SWNTs.

Since the electronic and optical properties of a SWNT depend on the physical structure of that particular tube (such as diameter and chirality), if the indices \( (n,m) \) are known, then it is possible to determine the electronic nature of the tube. A metallic SWNT (m-SWNT) is any \( (n,m) \) species that satisfies \( |n - m| = 3q \), where \( q = 0, 1, 2, 3... \); metallic SWNTs are also referred to as MOD0 SWNTs since \( v \equiv (n - m) \text{mod} 3 = 0 \). m-SWNTs can be further subdivided into armchair, \( n = m \) \( (\theta = 30^\circ) \), and non-armchair \( n \neq m \) species. Armchair \( (n,n) \) SWNTs are distinguishable from all other SWNT species because they are the only truly gapless tubes with a
finite electronic DOS at the Fermi energy. For MOD0 SWNTs where $n \neq m$, the NTs are referred to as semimetallic because they possess a small curvature-induced band gap, making them narrow-gap ($1 - 100$ meV) semiconductors.\footnote{13} All other nanotubes are medium band gap ($\sim 0.5 - 1.0$ eV) semiconducting SWNTs (sc-SWNTs), where $\nu \equiv (n - m) \mod 3 = 1$ or 2 (for MOD1 and MOD2 nanotubes, respectively).\footnote{14} sc-SWNTs have different band gaps because every tube has a unique set of allowed valance and conduction states, with the magnitude of the band gap having an inverse relationship with tube diameter, resulting in smaller diameter NTs having less states that are spread further apart. Figure 1.2 depicts a graphene map with color-coded $(n,m)$ values showing armchair m-SWNT (red), non-armchair m-SWNT (blue) and sc-SWNT (black).

![Graphene map with color-coded $(n,m)$ values](image)

Figure 1.3. (a) The calculated constant energy contours for the $\pi$ and $\pi^*$ of 2D graphene in the first Brillouin zone, with the cutting lines shown as solid curves. (b) Kataura plot showing the $E_{ii}$ values for MOD0 (stars), MOD1 (open circles) and MOD2 (closed circles). Reproduced with permission.\footnote{8} Copyright Elsevier, 2005.

In a calculated DOS diagram for a SWNT, sharp maxima with significant DOS values appear (Figure 1.4). These peaks are referred to as van Hove singularities, and arise due to the 1D character of the tubes. The van Hove singularities in the valance and conduction bands are labeled with index numbers ($i = 1, 2, 3, ...$), counting away
from the Fermi level. The corresponding electronic transitions are labeled $E_{ii}^M$ (for m-SWNTs) and $E_{ii}^S$ (for sc-SWNTs), where the $i$ values correspond to particular van Hove singularity peaks in the valance and conduction bands. In most cases, the only symmetry-allowed electronic transitions are those with the same symmetry (index numbers). For certain special experiments, such as polarization experiments, different symmetry rules are applied such that $E_{i'i'}$ ($i' = i \pm 1$) transitions are allowed.$^{15}$

![Figure 1.4. Representations of density of states (DOS) plots for (a) metallic and (b) semiconducting SWNTs. The line labeled $E_f$ represents the location of the Fermi level.](image)

For 1D systems like SWNTs, the electron-hole distance is short enough that Coulombic interactions become much larger, resulting in excited states that are excitonic in nature. An exciton is a bound electron-hole pair, and the exciton binding energy is the energy difference between the ground state exciton and the band gap between continuum of states. For sc-SWNTs, the exciton binding energy has a value of $0.3 – 0.4$ eV, while for m-SWNTs the electron-hole interaction is much weaker because of screening effects by conduction band electrons, resulting in a binding energy of $\sim 50$ meV.$^{16}$

Since each $(n,m)$ tube exhibits a unique set of van Hove singularities in the valance and conduction bands, it is possible to use $E_{ii}$ electronic transitions to characterize
SWNT structures. In 1999, Kataura et al. used the tight-binding approximation to calculate the transition energies for various SWNTs and produced a plot which organizes chirality assignments to an energy ($E_{ii}$) versus diameter distribution. Later named a Kataura plot after the author, these graphs provide a way to correlate experimental data from various spectroscopic methodologies to both $E_{ii}$ values and diameters, allowing for $(n,m)$ chiralities to be discerned. An example of a Kataura plot is shown in Figure 1.3b, with the $E_{ii}$ for optically-allowed transitions broken into first ($E_{11}$), second ($E_{22}$), third ($E_{33}$), etc. transitions for both semiconducting and metallic SWNTs. As each specific $(n,m)$ SWNT has several different electronic transitions, multiple $E_{ii}$ values are possible for each diameter.

Points on a Kataura plot can be further placed into groups, with broken lines that spread out from the center of each $E_{ii}$ main branch. These groupings are referred to as families, with the chiralities in each branch sharing the same $2n + m$ value. In each family the chiral angle becomes larger with increasing tube diameter. For non-armchair metallic (MOD0) SWNTs, the $E_{ii}^{M}$ always splits into a lower energy ($E_{ii}^{M-}$) and higher energy ($E_{ii}^{M+}$) transition, giving rise to a V-shaped pattern. The energy difference in $E_{11}^{S}$ and $E_{22}^{S}$ is less for MOD1 compared to MOD2 NTs, leading to a closer packing pattern for MOD1 tubes and a more spread out pattern for MOD2.

1.3 Synthesis of Carbon Nanotubes

The first successful synthesis of carbon NTs was achieved by Sumio Iijima in 1991, who prepared MWNTs using an arc discharge method; however, carbon NT structures had been observed by TEM prior to this first reported synthesis. It would be an additional two years before SWNTs would be created (independently by Iijima and Ichihashi and Bethune et al.). Significant progress has been made in the past
two decades towards understanding the growth processes for these nanomaterials. Several synthetic techniques are now employed for synthesizing NTs on a commercial scale, including: arc discharge, laser ablation, chemical vapor deposition (CVD), high-pressure carbon monoxide disproportionation (HiPCO), and CoMoCAT. The ultimate objective of SWNT synthesis is to produce samples consisting of a single chirality, however this has proven to be incredibly difficult to achieve. At the time of this thesis, all methodologies produce heterogeneous mixtures of tubes with varying sizes and electronic properties, as well as impurities including amorphous carbon and residual metal catalysts.

The arc-discharge method is one of the oldest ways to produce macroscopic amounts of SWNTs. Carbon electrodes are placed in a pressurized chamber filled with gases (like CH$_4$ and argon), and the cathode is impregnated with small metal (such as iron) catalyst particles. When a current is applied across the electrodes, the carbon soot produced can settle onto the catalyst particles allowing for the growth of NTs. NTs produced from the arc-discharge method typically have diameters of 1.2 – 1.4 nm, with few structural defects; however, these tubes tend to be shorter than those produced using other methodologies.

The laser ablation process was first used to produce SWNTs in 1995. A pulsed laser is used to strike a graphite target (that contains small amounts of a metal like nickel or cobalt) in a high-temperature reactor filled with an inert gas. This causes the carbon to vaporize, and when it reaches the chilled surface of the reactor walls the carbon condenses to form NTs. This methodology is very efficient (producing yields of up to 70%), with the SWNT material obtained as mats of ropes. Variations in temperature and catalyst conditions allows for control over the diameters synthesized.
CVD is a highly-tunable process for preparing large-scale batches of SWNTs. First reported in 1996, CVD involves a hydrocarbon gas (for example CH$_4$, C$_2$H$_4$ or C$_2$H$_2$), a process gas (like ammonia, nitrogen or hydrogen) and a solid substrate, which are heated together to a high temperature (700–900°C) in a reaction chamber. The hydrocarbon gas decomposes, allowing the formation of NTs on metal catalyst nanoparticles (like iron, cobalt or nickel) which are present in the substrate. The size of the catalyst particles is critical for controlling the diameter of the SWNTs made.

The HiPCO process is a variation of the CVD method. Developed at Rice University in 1999, this method involves introducing the metal catalyst particles in the gas phase rather than the solid phase. This method is suitable for large-scale production because the NTs are formed free of a catalyst support and the reaction can be operated continuously. The HiPCO process normally involves the use of carbon monoxide gas as the carbon source and iron pentacarbonyl (Fe(CO)$_5$) as the catalyst, producing tubes with smaller diameters (0.7–1.3 nm). HiPCO SWNTs are commonly reported in the literature and have been investigated extensively with conjugated polymers.

CoMoCAT is also a variation of the CVD process involving the disproportionation of carbon monoxide, but this time in the presence of a special cobalt-molybdenum catalyst (referred to as CoMo). The carbon monoxide is heated between 700–950°C in the presence of the CoMo catalyst to yield significant amounts of NT material, with greater than 80% SWNT content. CoMoCAT SWNTs have narrow diameter distributions (∼0.8±0.1 nm), and further refinement of the technique and purification process has allowed for the production of materials that are highly enriched (>98%) in sc-SWNTs; they can even be enriched in a particular chirality (∼41% (6,5)).

The 1D electronic nature of SWNTs, combined with their high mobility, makes
them promising candidates for applications in biotechnology, electronics, sensors, and energy conversion and storage devices. SWNTs can in principle play the same role as silicon in electronic circuits, but at a molecular level where silicon and other semiconducting materials cease to work, allowing for the potential to yield both smaller and better versions of existing devices, as well as completely novel ones. The heterogeneity of as-synthesized SWNTs (in terms of diameter, length and electronic type), combined with their tendency to bundle together strongly due to van der Waals interactions, affords them poor processibility and dispersibility, hampering commercial applications of these nanomaterials. Post-processing purification of all crude SWNT material is required to remove non-SWNT impurities and to circumvent the limited solubility and processibility of the tubes. Separation by electronic type or isolation of individual chiralities is also required for certain applications.

1.4 Solubilization Techniques for SWNT Bundles

Strong intermolecular forces, such as van der Waals and π-π stacking, exist between NT walls, resulting in SWNTs having a natural tendency to aggregate into large bundles or ropes as soon as they are synthesized. These bundles have poor processibility and dispersibility, and contain NTs with different diameters, chiralities and electronic properties. Post-synthetic processing of crude SWNT material is required to enhance processibility and to create sufficiently stable dispersions that will not reaggregate. It is also highly desirable to develop efficient methodologies that can purify SWNT mixtures in terms of electronic nature, diameter or even to extract specific \((n,m)\) chiralities from an ensemble.

A significant volume of work is currently being devoted towards searching for suitable solubilizing and sorting techniques for SWNTs. Methodologies for dispersing
and discriminating SWNTs can be broadly classified into two categories: covalent and non-covalent functionalizations. Both small molecules and polymers have been employed in these processes, and in recent years impressive progress has been made towards the separation of SWNTs by type, diameter and chirality.

1.4.1 Covalent Functionalization of SWNTs

The first successful covalent chemistries performed on SWNTs involved strong oxidizing conditions. Sonicating raw tubes in mixtures of either sulfuric acid and nitric acid or sulfuric acid and hydrogen peroxide was found to purify the raw NT material of carbonaceous impurities, and simultaneously create a variety of oxygenated functional groups (such as carboxylic acids, esters, quinones and anhydrides) at tube ends or at highly reactive defect sites along the NT sidewall. These functional groups can be further reacted to make the SWNTs water or organic soluble, and have the advantage of creating permanent linkages which can anchor the NTs in polymer matrices. While it is possible to achieve good solubility using covalent chemistry, the intrinsic electrical, mechanical and optical properties of the tubes are altered. This is due to the destruction the regular graphene-type network of the SWNT by the conversion of sp²-hybridized carbons into sp³. Additionally, these processes also reduce the lengths of the tubes. Thermal treatment can be used in some cases to remove the covalently-bonded functional groups and restore some (but not all) of the electronic and optical properties of the NTs. Covalent functionalizations are also not selective towards one specific chirality, however in many cases m-SWNTs are found to be more susceptible to covalent reactions compared to sc-SWNTs.
1.4.2 Non-covalent Functionalization of SWNTs

Non-covalent functionalization of NTs is often considered to be superior over covalent functionalization because it leaves the physical, optical and electrical properties of the NTs unmodified. In non-covalent functionalization, SWNTs are added to a dispersant and the mixture is agitated (normally via sonication) to mechanically de-bundle the tubes. Dispersant molecules stabilize the exfoliated NTs via non-covalent interactions without significantly altering the chemical structure of the tubes, therefore leaving the electronic and mechanical properties of the NTs intact. A variety of dispersants, including surfactants, biomolecules and conjugated polymers, have all been used with great success for the non-covalent modification of SWNTs, allowing for solubilization and, in some cases, purification of raw SWNT material.

1.4.3 Surfactant-Assisted Dispersion of SWNTs

![Surfactant Structures](image)

Figure 1.5. Structures of common surfactants and bile acid salts used to disperse SWNTs.

A 2002 Science paper by researchers at Rice University describing aqueous surfactant suspensions of SWNTs represented a significant breakthrough in the development of solubilization techniques for NTs. An anionic surfactant, sodium dodecyl sulfate (SDS), was used to disperse HiPCO SWNTs into aqueous media. Ultrasonication
is used to break apart the SWNT bundles, after which the surfactant molecules orient themselves so that the hydrophobic tails point towards the NT wall and the hydrophilic heads form a shell around the tube. The formation of the surfactant micelle around the tube surface prevents reaggregation, allowing for stable suspensions of isolated SWNTs to be obtained. Other surfactants, such as sodium dodecylbenzenesulfonate (SDBS) and bile salts such as sodium cholate (SCh) and sodium deoxycholate (DOC) (Figure 1.5) have also been found to be effective at individualizing SWNTs. Due to the nature of the interaction between the surfactant molecules and walls of the tubes, there is no differentiation between different types of SWNTs and the surfactants listed in Figure 1.5 are assumed to disperse all SWNT chiralities indiscriminately.\textsuperscript{56,57}

An important advancement in the post-processing of SWNT materials came in the mid-2000s with the development of density gradient ultracentrifugation (DGU) techniques. DGU is commonly used in biochemistry to separate biological macromolecules like DNA and proteins based on molecular mass and chemical moiety. The first DGU separations of SWNTs were reported in 2006 by Arnold et al.\textsuperscript{58} Aqueous dispersions of surfactant-suspended SWNTs were placed in a mass density gradient and ultracentrifuged ($\sim$200,000$g$) for several (often upwards of 18) hours. The surfactant-coated SWNTs travel through the density gradient under the applied force of centrifugation, allowing the different density NT species to migrate through the solvent gradient until they reach an equilibrium position.\textsuperscript{59,60} At this point, the aqueous-suspended SWNTs are sufficiently separated in vertical distance, as shown in Figure 1.6,\textsuperscript{61} to create multiple colored bands containing specific subsets of SWNTs separated based on diameter or chirality, which can be extracted using simple fractionation techniques. Using the
DGU method it is also possible to produce samples separated by electronic type, allowing for the isolation of m-SWNT or sc-SWNTs.\textsuperscript{62,63} Modification of experimental conditions, such as the addition of electrolytes (like alkali and alkaline earth metals)\textsuperscript{64} and the development of two or three surfactant systems has led to finer fractionation and the ability to produce samples with narrow SWNT diameter distributions ($\pm 0.1 \text{Å}$).\textsuperscript{65} Further refinement of techniques and the combination of multiple iterations of DGU has allowed for fractions composed of single chiralities to be obtained, and even the resolution of SWNT enantiomers.\textsuperscript{66}

In addition to DGU, other secondary separation techniques have also been used to successfully sort surfactant-suspended SWNTs. Agarose gel columns have been used to separate SDS-SWNT mixtures; m-SWNT fractions were found to elute from the column first, and by modifying the eluent it was possible to obtain fractions of sc-SWNTs with narrow diameter distributions.\textsuperscript{67} A variation of the agarose gel method exploits the selective adsorption of sc-SWNTs, and utilized a simple gel-squeezing technique to obtain samples consisting of 70% m-SWNTs.\textsuperscript{68} Sephacryl (a cross-linked copolymer of allyl dextran and $N,N'$-methylene bisacrylamide) size exclusion chromatography (SEC) has also been used to purify SWNTs.\textsuperscript{69} Using a single surfactant (SDS), combined with multiple filtrations, it is possible to achieve relatively pure single-chirality SWNTs.\textsuperscript{70}

Surfactant-suspended SWNTs have also been purified using aqueous two-phase systems. Two water-soluble polymers, polyethylene glycol (PEG) and dextran, form separate phases when mixed at certain concentrations, leading to a biphasic system with a hydrophobic PEG-rich system on top of a more hydrophilic dextran-rich layer. Dispersions of SCh-SWNTs have been observed to spontaneously partition based on diameter or electronic nature, depending on the types of SWNTs (CoMoCAT or arc
Modification of separation conditions has allowed for the rapid isolation of several single-chirality SWNT samples.

Dielectrophoresis was used by Kurke et al. to discriminate m-SWNTs from sc-SWNTs in a mixture of SDS-dispersed SWNTs. When the SDS-SWNT dispersion was subjected to an electric field gradient (generated by a microelectrode array), the metallic tubes migrated towards the electrodes, while the sc-SWNTs remained in the stationary position, allowing for separation of SWNTs by electronic type.

Although DGU and gel-based separations are currently being used to prepared commercial samples of highly-enriched aqueous suspensions of SWNTs, only sub-microgram (up to as much as a single milligram) quantities of purified material can be produced, and usually only after combining multiple iterations of these techniques.
This is not a consequence of the parent SWNT material before separation, but a symptom of the low overall efficiency of these separation techniques. As a result, the samples produced by these methods are very expensive and not suitable for large-scale commercial applications.

1.4.4 DNA Dispersion of SWNTs

Figure 1.7. UV-Vis-NIR absorption spectra of raw HiPCO SWNTs (top black spectrum) and 12 isolated sc-SWNT chiralities obtained using DNA and IEX. Reproduced with permission. Copyright Nature Publishing Group, 2009.

DNA can also be used to disperse and individualize SWNTs, and is capable of producing highly enriched samples of single-chirality species. In DNA dispersions
of SWNTs, $\pi-\pi$ stacking of the nucleobases with the $\pi$-surface of the NT allow the DNA molecules to helically wrap around the tubes, with the hydrophilic charged functional groups of the DNA molecules supporting the dispersion.\textsuperscript{75} In contrast to surfactant-based dispersions, single-stranded DNA (ssDNA) wrapping of SWNTs can be highly selective, demonstrating preferential interactions with specific electronic types and chiralities.\textsuperscript{76} The resulting hybrids of ssDNA-SWNTs are negatively charged, so ion exchange chromatography (IEX) can be used to purify the supramolecular complexes. When the aqueous ssDNA-SWNT dispersions are injected into the anionic exchange column and eluted with a salt gradient, differential adsorption and desorption of DNA-wrapped NTs on the IEX column allows for separation of SWNTs by electronic types.\textsuperscript{77} The identity of the ssDNA sequence plays a key role in the separation process, as the wrapping structure of the ssDNA may be ordered or disordered depending on the ssDNA sequence and the chirality of the NT, resulting in differential retention between different types of SWNTs. A significant amount of work has been performed to find the proper ssDNA sequences required for the purification of several different chiralities of SWNTs. As shown in Figure 1.7, Zheng and coworkers were able to use several highly-specific DNA sequences (consisting of short 9 – 14mers) to separate and isolate twelve different sc-SWNT chiralities.\textsuperscript{74} DNA-SWNT hybrids can also be sorted using DGU techniques,\textsuperscript{78} or using the aqueous two-phase system described previously if a PEG/polyacrylamide biphasic system is used.\textsuperscript{79}

As with DGU, DNA-based chromatography techniques are capable of producing highly-enriched single-chirality dispersions of SWNTs, but this process also suffers from low yields due to the low overall efficiency of this technique; additionally, the DNA material is expensive to prepare, and is therefore not suitable for large-scale separation (gram or kilogram quantities) of as-prepared SWNT material.
1.5 Non-Covalent Functionalization of SWNTs with Conjugated Polymers

Non-covalent functionalization of SWNTs by semiflexible polymers offers a convenient, selective and scalable alternative to the time-consuming processes outlined in Section 1.4. Polymers have been used for over a decade to solubilize SWNTs, but the possibility of selective discrimination of SWNTs has only been recently realized. Of the various types of polymer-SWNT interactions studied, π-π stacking with conjugated polymers represents a powerful and promising purification and discrimination strategy for NTs. Conjugated polymers are multifunctional in that they can exfoliate SWNTs, allowing for processibility, while potentially purifying and extracting specific SWNTs at the same time. The possibility of synergistic effects, like good thermal and photostability, high mechanical strength, high electrical conductivity and excellent optoelectronic properties allows for the possibility to form composites with novel properties and potential applications in chemical sensors, photovoltaic devices, FETs and transparent electrodes.

Conjugated polymers disperse NTs by exploiting the interaction of the long-chain π-conjugated polymer backbone with the π-electron surface of the NT. This disrupts the van der Waals attractive forces between the tubes and prevents reaggregation. Supramolecular complexes can be formed by helical wrapping or non-helical adsorption of the polymer, depending on the flexibility of the polymer backbone. The wide library of potential monomer structures and modular nature of polymers (in terms of molecular weight and side chain composition and length), combined with extrinsic variables (including choice of solvent and concentration), allows for the possibility to customize and tune polymer systems for selective interactions with specific chiralities.
of SWNTs.\textsuperscript{5,89}

Most supramolecular complexes between conjugated polymers and SWNTs are prepared using a relatively facile sample protocol, consisting of a simple sonication followed by a low-speed centrifugation. Homopolymers, alternating copolymers, random copolymers, as well as block copolymers have all been demonstrated to be suitable polymer architectures for the solubilization of SWNTs in both organic and aqueous solvents. Among the possible of polymer families, polyfluorenes and their copolymers have been the most extensively explored for the discrimination of SWNTs by electronic type, and have shown unique selectivity towards specific kinds of sc-SWNTs. Other polymer architectures that have demonstrated selective interactions with SWNTs include polycarbazoles, polythiophenes, polyphenylene vinylenes (PPVs), and polyphenylene ethynlenes (PPEs), among others.\textsuperscript{80} Various parameters, including the identity of the polymer backbone, polymer molecular weight, length and nature of side chains, and solvents employed, have all been found to have a drastic effect on the selectively of the polymer-SWNT interactions.\textsuperscript{9}

### 1.5.1 Polyfluorenes

One of the first reported examples of selective interactions of conjugated polymers with SWNTs was a paper by the Nicholas group in 2007 that investigated supramolecular complexes of HiPCO and CoMoCAT SWNTs with four polyfluorene derivatives (Figure 1.8): poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO), poly(9,9-dihexylfluorenyl-2,7-diyl) (PFH), poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-phenylene)] (PFO-P) and poly [(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(1,4-benzo-2,1’,3-thiadiazole)] (PFO-BT).\textsuperscript{90} While all four polymers were capable of dispersing SWNTs, both PFO and PFO-BT
Figure 1.8. Examples of polyfluorenes that have been used to prepare supramolecular complexes with SWNTs.

displayed remarkable selectivity towards sc-SWNTs in toluene; this selectivity represented a marked improvement compared to bile acid salts. Absorbance and Raman spectra proved the absence of m-SWNTs, and the photoluminescence quantum yields of the sc-SWNTs was found to be increased, reaching a value ten times higher than that obtained with surfactants. The PFO structure in particular was found to be exceptionally efficient at exfoliating sc-SWNTs with small diameters ($\sim 0.8 - 1.2$ nm) and large chiral angles ($\theta > 24^\circ$).

Selective sorting of SWNTs is determined not only by the physical structure of the conjugated polymer, but also by the conformation it adopts, so the choice of solvent is crucial for effective discrimination. A variety of solvents including chloroform, THF, toluene, $o$-xylene and $p$-xylene have all been investigated with polyfluorene systems.\textsuperscript{91,92} Good solvents like chloroform and THF yield highly concentrated, dark
suspensions of PFO-SWNTs that disperse all chiralities indiscriminately.\textsuperscript{91} Poor solvents like toluene and \textit{p}-xylene produce much more dilute, but highly specialized SWNT dispersions. This is attributed to a combination of the polymer conformation and solution viscosity,\textsuperscript{92} and highlights the importance of optimizing all variables when designing polymeric dispersants for SWNTs.

Many subsequent studies have confirmed the selectivity of PFO with HiPCO and CoMoCAT SWNTs.\textsuperscript{93–95} Other polyfluorene copolymers have also been prepared, such as: poly\{[(9,9-dihexylfluorenyl-2,7-diyl)-co-(9,10-anthracene)] (PFH-A),\textsuperscript{96} cis/trans isomers of poly [2,7-(9,9-didodecylfluorene)-\textit{alt}-4,4'-azobenzene] (F12AZO)\textsuperscript{97} and a family of “clicked” polymers comprised of alternating 9,9-dialkylfluorene and 1,2,3-triazole units (such as the PF-Az structure in Figure 1.8).\textsuperscript{98,99} Many of these structures are effective at dispersing HiPCO SWNTs, with some showing preferential interactions with sc-SWNTs. However, unlike PFO, none of them show the
same selectivity towards a smaller range of chiralities or the ability to completely remove all metallic NTs. Water-soluble polyfluorene derivatives, such as \([(N,N,N\text{-trimethylammonium})\text{-propyl}]\text{-}2,7\text{-fluorene dibromide}\) (PFAB) have also been prepared and used to solubilize SWNTs, however these polymers tend to be less selective compared to PFO and other organic-soluble polymers.\(^{100}\)

Several of the polymers in Figure 1.8, including PFO, PFH, PFH-A, PFO-BT and poly\([\text{9,9-dioctylfluorenyle} -\text{diyl}]\text{-}alt\text{-}co\text{-}(6,6\text{-}(2,2\text{-bipyridine}))\] (PFO-BPy) were used to purify larger diameter SWNTs prepared using either the laser ablation or arc discharge methodology. The best results with these larger diameter SWNTs were obtained with PFH-A and PFO-BPy, both of which selectively dispersed sc-SWNTs with excellent yields; additionally, PFH-A was found to preferentially solubilize near-armchair SWNTs over a narrow range of tube diameters.\(^{101}\)

Nakashima and coworkers have prepared polyfluorene derivatives with bulky side chains that have not only allowed for selective dispersion of sc-SWNTs, but have also been able to discriminate different enantiomers of sc-SWNTs. The first iteration of these polymers was a random copolymer \((\text{F10})_x(\text{F5})_y\), composed of 9,9-bis\((n\text{-decyl})\text{fluorene}\) and 9,9-bis\([\text{S\text{-}(+)-2-methylbutyl}]\text{fluorene}\) blocks (Figure 1.9).\(^{102}\) By varying the ratios of the two monomer components the authors were able to tune the sc-SWNT chiralities dispersed, and by increasing the amount of the F5 monomer they were also able to see better separation of enantiomers. A subsequent paper utilized a chiral binapthol moiety to synthesize different copolymers of \([\text{9,9-dioctylfluorenyle}\text{-diyl}]\text{-}x\text{[}(\text{R})\text{- or (S)}\text{-2,2\text{-dimethoxy-1,1\text{-binaphthalen}-6,6-diyl}]y}\) (Figure 1.9, \((\text{PFO})_x(\text{R-BN})_y\) or \((\text{PFO})_x(\text{SBN})_y\)) allowing for a “one-pot” separation of specific chiralities of sc-SWNTs with enhanced enantiomeric selection.\(^{103}\)
Polyfluorene-SWNT composites have also been used to prepare field effect transistor (FET) devices\textsuperscript{86,87,104} One of the challenges with preparing high-performance FETs from polymer-dispersed SWNTs is the presence of excess polymer that is not wrapped around the tubes. The polymer chains can be deposited into the channel, hampering electronic transport and resulting in lower charge carrier mobilities. The wide band gap of PFO can also sometimes be detrimental for certain devices. One way to overcome these issues is to remove unbound residual polymer with multiple filtrations\textsuperscript{97,105} or through double-step ultracentrifugations.\textsuperscript{106} Another route is through the design of polymers which can be removed from the NT walls, either through a degradation process or by a stimuli-triggered switching mechanism such as light or acid. A 2011 paper reported the synthesis of disilane-containing polymers, such as the poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(1,1,2,2-tetramethyldisilane) (PFO-Si) shown in Figure 1.9. This polymer was able to disperse sc-SWNTs, and upon the addition of HF the disilane bonds were cleaved and the polymer could be washed away.\textsuperscript{107} A photocleavable polymer containing an o-nitrobenzylether linkage interspersed between blocks of PDDF (PDDF-oNBE) has also been reported. Precipitation of SWNTs was induced by exposing the samples to light, and the time it took for the SWNTs to be released could be controlled by varying the ratio of the monomers.\textsuperscript{108} Metal-coordination polymers composed of a fluorene-bridged \textit{bis}-phenanthroline ligand (PhenFO) and metal ions have been shown to be able to selectively discriminate sc-SWNTs. The metal-ligand complexes can then be removed from the tubes using trifluoroacetic acid (TFA).\textsuperscript{109} In our own group, an alternating copolymer containing fluorene and tetrathiafulvalene (TTFV) units (PF-TTFV) has been synthesized and used to disperse both HiPCO and CoMoCAT SWNTs.\textsuperscript{110} When TFA was added to
the PF-TTFV-SWNT supramolecular complexes, the polymer underwent a conformational change and released the tubes. The advantage of these last two methodologies (PhenFO and PF-TTFV) is that both the polymer and the SWNTs can be recovered, allowing the polymer material to be recycled. While all of these removable polymer systems represent interesting routes towards the isolation of sc-SWNTs free of polymer coatings, all the polymeric structures (with the exception of PhenFO) still dispersed a significant amount of metallic SWNTs. Further work is required to develop polymers that display the same selectivity as PFO, but can also be removed from the surface of the NTs.

1.5.2 Polycarbazoles

![Polycarbazole structures](image)

Figure 1.10. Examples of polycarbazole structures that have been used to prepare supramolecular complexes with SWNTs.
Polycarbazoles are an interesting class of conjugated polymers, with potential applications in organic photovoltaics, light emitting diodes and electrochromic devices. While poly(3,6-carbazole)-SWNT composites have been investigated for over a decade, the first report of poly(2,7-carbazole)s being used as a dispersant for SWNTs did not occur until 2011. This is due to the more challenging synthesis that is required for the preparation of poly(2,7-carbazole)s, combined with the fact they typically suffer from low molecular weights and poor solubility. In the initial report by Mayor and Kappes, HiPCO SWNT dispersions were prepared in toluene using both PFO and poly(\(N\)-decyl-2,7-carbazole) (PC1, Figure 1.10). Despite the relatively low molecular weight (\(M_n \sim 3.5\) kDa) of PC1 and its poor solubility, preferential interactions with sc-SWNTs were observed, with a “complementary” selectivity when compared to the PFO analogue. In a subsequent investigation, the Kappes and Mayor groups prepared a library of different homopolymers and copolymers containing fluorene, 2,7-carbazole or 3,6-carbazole monomer units and investigated their interactions with SWNTs. Several of the polymers, such as PC9 and PC10 (Figure 1.10), did not produce stable suspensions with SWNTs. Other polymers, like PC6, PC7 and PC8, were able to produce SWNT suspensions, however these dispersions were described as “poor” by the authors; PC5 produced a dispersion described as “medium.” PC2, PC3 and PC4 were all able to produce stable suspensions of sc-SWNTs, however selectivity was only observed if a large excess of polymer (50 mg of polymer to 1 mg SWNT) and a DGU step were used, making these polymers impractical for large scale purification of sc-SWNTs.

The Nakashimi group has also prepared several poly(2,7-carbazole) derivatives, including a copolymer with thiophene and benzothiadiazole (PC11, Figure 1.10). The dispersal procedure to produce polymer-SWNT complexes did not require DGU
and the authors claimed to see preferential interactions with sc-SWNT chiralities; however Raman spectroscopy was not performed so the removal of metallic SWNTs was not confirmed. This same research group also prepared 2,7-carbazole copolymers with functionalized side chains containing either a thiol functionality to allow for the formation of metal nanoparticle/conjugated polymer/SWNT hybrids, or a fullerene derivative to allow for more efficient energy transfer between $C_{60}$ moieties and SWNTs.

### 1.5.3 Polythiophenes

![Polythiophenes](image)

Figure 1.11. Examples of poly(3-alkylthiophene) derivatives that have been used to prepare supramolecular complexes with SWNTs.

Poly(3-alkylthiophene)s (P3ATs, Figure 1.11) are an important family of conjugated polymers that have been studied extensively for applications in organic photovoltaic (OPV) devices. Regioregular poly(3-hexylthiophene) (rrP3HT) in particular has demonstrated good performance in OPVs due to its ability to self-assemble into highly-ordered structures in thin films. As a consequence, P3ATs are a natural choice for dispersing SWNTs, with several studies investigating the performance of P3AT-SWNT composites in OPV devices.

Many of the P3AT-SWNT investigations have involved P3HT and have focused on
parameters that are important for optimization of OPV device performance, such as the regioregularity of the polymers,\textsuperscript{126} morphology of the thin films formed from these supramolecular complexes\textsuperscript{106,127} and characterizing energy transfer between P3HT and SWNTs.\textsuperscript{128–130} P3HT binds very strongly to the surface of NTs, but it is unable to discriminate between semiconducting and metallic tubes in small diameter (HiPCO and CoMoCAT) samples, leading to a mixture of electronic properties in the composites which can negatively impact device performance.\textsuperscript{131} One potential solution to this problem is to use a two-step process that exploits the fact that different polymers bind to SWNTs with different strengths.\textsuperscript{132} PFO is first used to suspend NTs to produce a sample containing a small subset of sc-SWNTs, after which P3HT is added. P3HT has a stronger affinity to the SWNT surface and can displace the PFO, resulting in P3HT-SWNT composites that are almost entirely (>99%) sc-SWNTs.\textsuperscript{133}

Other polythiophene derivatives that have also been used to prepare supramolecular complexes with SWNTs include poly(3-octylthiophene) (P3OT),\textsuperscript{134} poly(3-dodecylthiophene) (P3DDT),\textsuperscript{135,136} poly[2,7-(9,9-dioctylfluorene)-alt-2,5-(3-dodecylthiophene)] (PFT),\textsuperscript{137,138} and poly(3,3′′-didodecylquaterthiophene) (PQT-12).\textsuperscript{135,139,140} The polymer backbone rigidity and shape has a strong influence on how the polymer can assemble around the tubes. In a paper by Liu et al., rrP3HT, PQT-12, poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBT TT-14), and poly(2,5-bis(3-tetradecylthiophen-2-yl)thiophen-2-yl)thiophen-2-ylthiazolo[5,4-d]thiazole) (PTzQT-14) self-assembly on SWNTs was investigated, and the polymers were able to produce nanowire structures that branched off the SWNT backbone.\textsuperscript{139}

Bao and coworkers investigated several P3ATs, including rrP3HT, rrP3DDT, PQT-12 and regioregular poly(3-methyl-4-decyl-thiophene-2,5-diyl) (rrP3MDT).\textsuperscript{135} They were able to produce excellent dispersions of HiPCO sc-SWNTs using rrP3DDT
by varying the sample preparation conditions; a ratio of 2:1 polymer to SWNT (wt/wt) was used, and the sample was heated to \(\sim 50^\circ C\) (which coincides with the side chain melting temperature) during sonication, after which the sample was centrifuged for 150 min at 42,000 \(g\). No metallic SWNTs were observed in the Raman spectra of this sample, or in the absorbance spectrum after removal of the polymer.

### 1.5.4 Poly(phenylene vinylene)s (PPVs)

![Poly(phenylene vinylene)s (PPVs)](image)

Figure 1.12. Examples of poly(phenylene vinylene)s (PPVs) that have been used to prepare supramolecular complexes with SWNTs.

Some of the earliest investigations of the interactions between conjugated polymers and carbon NTs involved poly(\(p\)-phenylene vinylene)s (PPVs).\(^{141-143}\) PPVs have been investigated for incorporation into light emitting diodes (LEDs) and organic photovoltaic (OPV) devices, and were initially considered to be a promising option for the dispersion of SWNTs due to the ability of the flexible PPV backbone to form a helical structure, which could hypothetically form a shell around the wall of
the SWNT to impart solubility and stability.\textsuperscript{144} While many studies have been performed using PPV derivatives like poly[(\textit{m}-phenylenevinylene)-\textit{co}-((2,5-dioctyloxy-\textit{p}-phenylene)vinylene)] (\textit{PmPV}),\textsuperscript{145} poly[(2,6-pyridinylenevinylene)-\textit{co}-((2,5-dioctyloxy-\textit{p}-phenylene)vinylene)] (\textit{PPyPV}),\textsuperscript{143,146} poly[(5-alkoxy-\textit{m}-phenylenevinylene)-\textit{co}-[(2,5-dioctyloxy-\textit{p}-phenylene)vinylene)] (\textit{PAmPV}) derivatives\textsuperscript{143} and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV),\textsuperscript{147-149} (Figure 1.12) it has since been demonstrated that PPV derivatives do not adhere to the surface of NTs as well as other conjugated polymers.\textsuperscript{146}

Two papers by Yi et al. have proposed that \textit{PmPV} can have selective interactions with SWNTs based on electronic nature and diameter. In one paper the authors did sequential extractions on a sample of HiPCO SWNTs using \textit{PmPV}; the SWNTs were suspended by sonication and centrifugation, after which the residue from centrifugation was collected, additional \textit{PmPV} was added, and a subsequent sonication and centrifugation step was performed for a total of ten extractions.\textsuperscript{144} The authors monitored the extractions using UV-Vis-NIR and Raman spectroscopy (using a single excitation wavelength of 647.1 nm), and claimed that the (12,6) and (8,8) metallic SWNTs were being selectively extracted based on a slight increase in the intensity of the semiconducting features in the radial breathing mode (RBM) in the final sediment. However, the authors only used one excitation wavelength which cannot account for changes in the SWNT resonance conditions, which could arise due to polymer coating or the proximity of solvent molecules. Additionally, the UV-Vis-NIR results show a significant amount of sc-SWNTs present for all extractions, which contradicts the statement of selective interactions with metallic tubes. Further studies by this group looking at polymer conformation using trans-\textit{PmPV} (\textgreater{} 95\% trans linkages) and cis-\textit{PmPV} (\textasciitilde{}70\% cis bonds) found that the cis-\textit{PmPV} dispersed
all SWNTs indiscriminately, and was capable of producing more concentrated and more stable suspensions compared to trans-$Pm$PV.\textsuperscript{150}

A copolymer composed of poly(phenyleneethynylene)-$co$-poly(phenylenevinylene) (PPE-PPV) has also been reported to have selective interactions with SWNTs.\textsuperscript{151} Raw HiPCO SWNTs were first covalently functionalized with acid as a “purification” step (which selectively removed many of the smaller-diameter species) before being mixed with PPE-PPV. The authors claimed that following this procedure a sample containing SWNTs with a narrow diameter range ($1.18 - 1.24$ nm) was obtained.

### 1.5.5 Poly(phenylene ethynylene)s (PPEs)

![Poly(phenylene ethynylene)s](image)

Figure 1.13. Examples of poly(phenylene ethynylene)s (PPEs) that have been used to prepare supramolecular complexes with SWNTs.

Less flexible rigid-rod like polymers have also been investigated for dispersing
SWNTs.\textsuperscript{152,153} Of these, poly(phenylene ethynylene)s (PPEs) have been shown to be promising structures for the dispersal of SWNTs into organic and aqueous solvents.\textsuperscript{154} The first reported use of PPEs to disperse SWNTs was in 2002,\textsuperscript{155} and it was initially hypothesized that the linear nature of the polymer would force it to coat the NT surface in a non-helical (linear) fashion. More recent theoretical studies have suggested that this interaction may be better described as helical, especially for water-soluble structures.\textsuperscript{156}

Most of the organic-soluble polymers, such as structures PPE1-PPE4 (Figure 1.13) suffer from lower solubility compared to polyfluorenes and polythiophenes, requiring that many of the supramolecular complexes be prepared in chloroform.\textsuperscript{155,157} The density of chloroform makes it challenging to remove all the SWNT bundles, and therefore difficult to evaluate the selectivity of these polymers. Water-soluble supramolecular complexes with SWNTs have also been prepared using both anionic\textsuperscript{158} and neutral\textsuperscript{159} PPEs. Some of the reported structures like poly[p-(2,5-bis(3- propoxy-sulfonic acid sodium salt))phenylene]ethynylene (PPES) are able to individualize HiPCO SWNTs in water at much higher concentrations than surfactants,\textsuperscript{160} with a derivative of this polymer, poly[(m-phenyleneethylene)-alt-\(p\)-phenylene- ethynylene)] (PmPEpPE) showing some selectivity towards smaller diameter (\(\sim0.7\) nm) SWNTs, such as the (6,5) and (8,3) chiralities.\textsuperscript{161} Poly[2,6-(1,5-bis(3-propoxy-sulfonic acid sodium salt))naphthylene]ethynylene (PNES) has been found to be very efficient at exfoliating SWNTs in a variety of solvents (including water, DMSO, DMF and methanol) in the presence of a phase transfer catalyst like 18-crown-6, with the supramolecular complexes remaining stable in solution upwards of months.\textsuperscript{162,163} Water-soluble PPE-SWNT derivatives have been investigated for incorporation into devices, such as glucose sensors which have demonstrated enhanced sensitivity.\textsuperscript{164}
Chiral polyanionic PPEs based on 1,1'-bi-2-naphthol derivatives have been synthesized, such as the S-PBN(b)-Ph$_5$ structure shown in Figure 1.13.$^{165,166}$ These molecules are able to align themselves along the wall of a SWNT, resulting in highly-individualized tubes; HRTEM showed single-polymer coating on individual tubes, as well as enantioselective control of the helical screw axis of the polymer.$^{165}$

1.5.6 Side Chains

The ability of a conjugated polymer to wrap and select for specific SWNTs is dictated not only by the nature of the polymer backbone but also by the length and identity of the aliphatic side chains, which play a key role stabilizing the supramolecular complexes. Describing how the side chain can influence selectivity is not trivial, with the exact outcome also depending on the nature of the polymer backbone, molecular weight and solvent used. In some cases, drastic changes in the size and shape of the side chain result in very little difference in what types of SWNTs are dispersed.$^{167}$ In other polymeric systems, the addition of an extra two carbons to an $n$-alkyl side chain can result in drastically enhanced selectivity in the SWNT dispersions.$^{104,168}$

Several studies have demonstrated the importance of the length of the side chain on the ability of polyfluorenes to selectively disperse sc-SWNTs. As mentioned previously, PFO (octyl side chain) interacts with HiPCO and CoMoCAT SWNTs to produce stable suspensions of sc-SWNTs with a small population of chiralities, while PFH (hexyl side chain) shows no discrimination.$^{91}$ If larger diameter SWNTs ($> 1.2$ nm) are used, PFO does not demonstrate the same selectivity for sc-SWNTs, but polyfluorenes with longer alkyl side chains can.$^{104}$ Polyfluorenes with decyl, dodecyl (PDDF in Figure 1.8), tetradecyl and pentadecyl alkyl side chains all exhibit an affinity for larger-diameter NTs, with several papers proposing that PDDF exhibits
the best selectivity towards larger diameter (> 1.2 nm) sc-SWNTs.\textsuperscript{104,168} Molecular dynamic simulations suggest that polyfluorenes with longer aliphatic side chains can wrap larger-diameter SWNTs more effectively to provide stronger binding to the NT wall and prevent bundling. However, the effectiveness of the polymer to selectively sort sc-SWNTs decreases above a certain chain length. One explanation for this is that a larger variety of wrapping geometries are possible for polymers with longer aliphatic chains, making the polymers more efficient at suspending tubes at the consequent selectivity.\textsuperscript{168}

It is important to control for other variables (such as the identity of the polymer backbone and molecular weight) when evaluating the effect that the length or nature of a side chain has on the ability of a polymer to discriminate SWNTs. If there are drastic changes to more than one variables it can be challenging to apply any conclusions in the design of future materials.\textsuperscript{169}

\section*{1.5.7 Molecular Weight}

Many of the conjugated polymers used to disperse SWNTs are prepared through step-growth polymerization techniques,\textsuperscript{170} leading to a wide variety of molecular weights ($M_n$) and degrees of polymerization (DP). The molecular weight of a polymer has been shown to have a significant effect on the concentration of SWNTs that can be dispersed, as well as the selectivity of the resulting hybrids.

Analogous to investigations on the nature of the side chain, many of the molecular weight studies in the literature have focused on polyfluorene derivatives. A previous paper from our group in 2011 looked at different molecular weights of a fluorene-thiophene copolymer (PFT, Figure 1.11).\textsuperscript{171} The polymer was synthesized via Suzuki polycondensation and then fractionated using recycling preparative Gel Permeation
Chromatography (GPC) to yield eight different molecular weight fractions, with $M_n$ values ranging from 5.7 – 83 kDa and low polydispersities (PDIs) of 1.5 – 1.7. Each polymer fraction was used to prepare supramolecular complexes with SWNTs in THF, and the overall concentration of SWNTs was estimated using absorption spectroscopy. The highest and lowest molecular weight fractions yielded the lowest concentrations, while the intermediate $M_n$ values (11 – 34 kDa) produced the most concentrated dispersions. Polymer selectivity towards different $(n,m)$ chiralities was not investigated in this study.

Ding and coworkers investigated the influence of molecular weight on the ability of PDDF (Figure 1.8) to selectively solubilize sc-SWNTs prepared using a laser ablation method. PDDF samples with $M_n < 8$ kDa were unable to disperse SWNTs; for molecular weights in the range of 10 – 30 kDa there was no apparent difference in the ability of the polymer to disperse or selectively discriminate sc-SWNTs. When the molecular weight was increased to above 45 kDa, the viscosity of the polymer-SWNT dispersions increased to a level that hindered sample preparation. Similar observations were made by the Zaumseil group, who looked at PFO and F8BT hybrids with HiPCO SWNTs. Low ($M_n = 7.4$ or 6.7 kDa for F8BT and PFO respectively) and medium molecular weight ($M_n = 36.2$ or 14.4 kDa) polymers were found to have better selectivity at lower concentrations, with selectivity decreasing for higher molecular weight polymers ($M_n = 62.8$ or 98.1 kDa) and with increasing concentration of the dispersions. The authors proposed that the solution viscosity was one of the most prominent factors influencing this apparent selectivity as the viscosity could affect the reaggregation rate of the NTs.

Short-chain oligomers have also been investigated, including a study by the Kappes and Mayor groups which looked at oligomers of PDDF (Figure 1.8) comprised of
2 – 8 monomer units.\textsuperscript{172} Due to the very short nature of the oligomer chains, all of the suspensions were unstable, however the authors claim that based on PL results, the longest oligomer (8 monomer units) showed the same selectivity as the parent polymer PDDF. However, the UV-Vis-NIR absorption spectrum for the oligomer-SWNT suspension indicated the presence of bundles, which complicates the PL analysis for this material. Mayo and coworkers reported a theoretical investigation involving oligomers of polycarbazoles and SWNTs.\textsuperscript{173} Both poly($N$-(2-ethylhexyl)-2,7-carbazole)s and poly($N$-(2-ethylhexyl)-3,6-carbazole)s comprised of 6 – 15 monomer units were modeled with SWNTs. The poly(2,7-carbazole)s were found to form more energetically-favorable hybrids with the NTs, and the authors claimed that based on their calculations, the shorter the oligomer chain the stronger the interaction between the carbazole and the SWNT. It should be noted that this stronger interaction does not necessarily translate into better dispersions, as incomplete coverage of the NT walls by the shorter oligomer chains could allow for the SWNTs to reform bundles and crash out.

\subsection*{1.6 Characterization of SWNTs}

Spectroscopy is a powerful tool for characterizing SWNTs, resulting in significant progress being made in the understanding of the optical and optoelectronic properties of these nanomaterials over the past decade. Absorbance, photoluminescence (PL), Raman, Rayleigh, and magneto-optical spectroscopy have all been used to investigate and characterize samples of SWNTs.\textsuperscript{15} In particular, absorbance, PL and resonant Raman spectroscopy have become essential tools for characterizing macroscopic heterogeneous samples of SWNTs.

When NTs are electronically excited by thermal, optical or electrical means they
can relax back to the ground state via emission of a photon through several different processes. An absorbance process (Figure 1.14a) occurs in a SWNT when the incident photon matches a corresponding excitonic energy difference (E_{ii}), resulting in the production of an exciton. If light is emitted without the exciton gaining or losing energy, the process is elastic and is referred to as Rayleigh scattering (Figure 1.14b). When the exciton decays to the lowest lying excited state (c1) by relaxation, and then recombines to emit a photon with much lower energy (E_{11}) than the incident photon, a photoluminescence (PL) process occurs (Figure 1.14c). If the exciton loses or gains energy by emitting or absorbing a phonon in a scattering process to an intermediate state, the electron and hole will recombine by emitting a photon with slightly lower (E_{22}-E_{ph}) or higher (E_{22}+E_{ph}) energy for Stokes (Figure 1.14d) and Anti-Stokes Raman processes, respectively. Since the optical transition energies (E_{ii}) of a SWNT depend on the (n,m) identity of the tube, it is possible to determine the (n,m) chiralities present in a sample using various spectroscopic techniques. It should be noted that E_{ii} values obtained from different spectroscopic methods (such as resonant Raman or PL spectroscopy) can differ due to the different states of the
excitons. For example, in the Raman process free excitons are probed whereas in PL spectroscopy excitons are localized, yielding lower $E_{\text{ii}}$ values.\textsuperscript{174}

When using optical spectroscopy to characterize a SWNT dispersion, it is essential to account for various environmental factors and the effects they have on the optical properties of the tubes.\textsuperscript{175} The optical properties of SWNTs (and therefore the observed $E_{\text{ii}}$ values) are sensitive to environmental conditions due to the fact that excitons exist on the surface of a SWNT. Changing the dispersant or solvent used can have a significant impact on the observed optical properties, which must be accounted for when evaluating the effectiveness of a purification process. Additionally, the optical spectra of macroscopic heterogeneous samples of SWNTs typically exhibit severe inhomogeneous broadening due to the presence of bundles and overlap between the energy states of different NTs. If the sample is processed to overcome the strong tendency of SWNTs to aggregate into bundles, then more distinct features can be observed.

1.7 Absorbance Spectroscopy

Optical absorbance spectroscopy is one of the most fundamental and (in many cases) experimentally simple measurements that can be performed on a nanomaterial. The optical absorbance spectrum of a SWNT sample can provide fundamental quantities like optical transition energies, and is therefore potentially capable of elucidating the $(n,m)$ chirality distribution of a sample.\textsuperscript{176} It can also provide information on the efficiency (and electronic purity) of a separation protocol, but this is only possible when the optical features are well defined.

As all current SWNT production methodologies generate a mixture of different $(n,m)$ species, it is expected that the optical spectra for bulk raw NT materials will
show multiple transitions at various wavelengths. Some of the first reported optical absorbance experiments on SWNTs were performed by Kataura et al. on thin films, prepared from ethanol dispersions of SWNTs synthesized via the electric-arc discharge method.\textsuperscript{17} The films were measured from $\sim 200 - 2500$ nm, and a relatively diffuse absorption spectrum was obtained, with no fine features observed. Three distinct, broad absorbance features corresponding to the first and second optical transitions of sc-SWNTs ($E_{11}^S$ and $E_{22}^S$) and the first optical transition of m-SWNTs ($E_{11}^M$) were present. It was not until 2002, when O’Connell and coworkers succeeded in suspending SWNTs in H$_2$O with the surfactant SDS that fine features arising from different chiralities of SWNTs could be observed (Figure 1.15A and B).\textsuperscript{55} The individualization of SWNT bundles allowed for the optical absorption spectrum to reveal multiple sharp absorbance bands, corresponding to distinct optical transitions of both sc-SWNTs and m-SWNTs. For small diameter ($<1.2$ nm) HiPCO SWNTs, the metallic $E_{11}^M$ region is located between $\sim 440 - 650$ nm, the semiconducting $E_{22}^S$ absorbance occurs from $\sim 570 - 850$ nm and the $E_{11}^S$ features occur between $\sim 850 - 1600$ nm.\textsuperscript{55} For mixed samples of metallic and semiconducting NTs, a broad featureless exponential background arising from $\pi$ and plasmon absorbance is often observed.\textsuperscript{177} The better the exfoliation of the NTs, the weaker this background absorbance will be.\textsuperscript{178} Therefore, a characteristic of a well-exfoliated sample enriched in sc-SWNTs is the presence of sharp highly symmetrical Lorentzian lineshapes in the $E_{11}^S$ and $E_{22}^S$ absorbance ranges combined with low background absorbance.

As the metallic and semiconducting features occur in different regions of the UV-Vis-NIR spectrum it is possible to identify the electronic nature of the tubes present in a particular sample; in some cases the electronic purity of an enriched sample can
Figure 1.15. (A) and (B) UV-Vis-NIR absorption spectra for SDS-suspended SWNTs prepared using two different variations of the HiPCO process, (C) SDS-SWNTs coated in poly(vinylpyrrolidone) and (D) surfactant-suspended HiPCO SWNTs before ultracentrifugation. Reproduced with permission.\(^5\) Copyright AAAS, 2002.

be estimated by integrating the area under the peaks in both the metallic and semiconducting regions.\(^{179}\) Obtaining quantitative amounts of metallic or semiconducting tubes in a mixture using this method can be tricky due to the overlap between spectral excitation regions, which leads to uncertainty in the boundaries for the integration areas. Spectral overlap also prevents \((n,m)\) specific assignments in the spectrum of a heterogeneous mixture because a single “sharp” absorbance feature may actually arise from the overlap of transitions from several chiralities.\(^{180}\) This is especially true for m-SWNTs, as the overlap in optical transitions from members of the same family can be as small as 60 meV, which is comparable to the line width of the absorbance peak.\(^{12}\) Calculations using Beer’s Law to determine the concentration of SWNTs (either in bulk or for individual \((n,m)\) chiralities) is also made challenging by spectral congestion. Several investigations have been performed to try to find ways to account
to for background absorbance or to calculate the molar extinction coefficients for various \((n,m)\) chiralities,\(^{181}\) but these values are specific to the particular environment the tube is in and cannot be applied on a general basis.

For many polymer-SWNT systems the polymer maximum absorbance peak falls in the same range as the metallic SWNT transitions, making analysis of the efficiency of electronic separation challenging. Additionally, assigning \((n,m)\) chiralities is complicated by a red-shift in the location of all the peak maxima, with theoretical experiments suggesting that the magnitude of the red-shift varies depending both on chirality and the identity of the polymer.\(^{182}\) It is possible to make qualitative assumptions based on the removal of the broad exponential background, but other characterization methodologies, such as PL mapping or Raman spectroscopy, are required for a more comprehensive characterization of the sample.

1.8 Photoluminescence (PL) Mapping

Photoluminescence (PL) excitation spectroscopy measures the fluorescence intensity of sc-SWNTs with respect to both excitation and emission wavelengths. It can provide a sensitive qualitative (and in certain cases quantitative) evaluation of the \((n,m)\) composition of a complex mixture of SWNTs.\(^{11}\) NT fluorescence can be detected at far lower concentrations than those required for absorbance spectroscopy and the PL map for a heterogeneous sample is more structured than its corresponding absorbance profile; however, this technique is only suitable for sc-SWNTs that are sufficiently debundled and are efficient emitters with detectable PL.

During a PL excitation experiment, the \(E_2^{S}\) state of a sc-SWNT is resonantly excited by the incident photon to generate an exciton. The exciton relaxes via a phonon to the lowest-lying excitonic state \((c_1)\) on a short time scale \((\sim 0.1 \text{ ps})\) before
Figure 1.16. (a) 2D PL map for SDS-SWNTs in D$_2$O. The white oval represents the locations of fluorescence maxima from different chiralities that are explored in figures (b) and (c). (b) Locations of the peak maxima from the PL map in (a), with lines denoting possible patterns in the data. (c) Ratios of excitation ($E_{22}^S$) and emission ($E_{11}^S$) frequencies (from (b)), plotted against excitation wavelength; lines again denote perceived patterns. (d) $E_{22}^S/E_{11}^S$ ratios calculated from the tight binding model, where blue symbols represent MOD1 NTs and red symbols represent MOD2 NTs. Reproduced with permission.$^{183}$ Copyright AAAS, 2002.

Radiative or non-radiative recombination occurs (Figure 1.14c).$^{184}$ The lifetime for radiative recombination in a SWNT is theoretically expected to be $\sim 1$ ns, but has been shown experimentally to be much shorter, on the order of tens of picoseconds. This short recombination lifetime suggests that the dominant recombination process is non-radiative, and luminescence quantum efficiencies for SWNTs are estimated experimentally to be on the order of several percent.$^{185}$ As fluorescence only occurs in any appreciable yield from the lowest energy excited state (Kasha’s Rule), the
emission always corresponds to the $E^{S}_{11}$ transition.\textsuperscript{186} A 2D “PL map” consisting of a rich pattern of peaks can be generated by scanning multiple $E^{S}_{22}$ and $E^{S}_{11}$ ranges, where each peak originates from a different $(n,m)$ structural species as is shown in Figure 1.16a. PL does not occur in m-SWNT (MOD0) materials because they have a continuous DOS at the Fermi level, resulting in rapid non-radiative recombination of the exciton.

The first PL map was reported by O’Connell and coworkers in 2002 for HiPCO SWNTs dispersed by SDS in an aqueous solvent.\textsuperscript{183} Due to the limited transparency of H$_2$O, which blocks most light beyond 1350 nm, aqueous dispersions of SWNTs need to be prepared in D$_2$O to extend the useful range of mapping out to 1850 nm. It is essential for the SWNTs to be debundled and individualized as the presence of bundles in a sample may cause the fluorescence intensity to decrease significantly or even be quenched completely.\textsuperscript{187} NTs in bundles may undergo at least two types of electronic perturbations. They can experience increasing polarizability (that varies with position in the bundle), which causes a redshift and broadening of observed electronic transitions; additionally, electronic couplings can occur within the bundle, enabling a rapid energy transfer from an optically excited SWNT to a smaller-band gap neighbor.\textsuperscript{188} If the accepting species is a m-SWNT, the PL emission is quenched; if the accepting tube is a sc-SWNT with a smaller band gap, the PL emission is shifted to an unexpectedly long wavelength. This exciton energy transfer can lead to additional peaks in the PL map, some of which may be beyond the limit of the detector response or solvent transparency. As $\sim$ 33% of SWNTs are metallic in nature, any bundles comprised of three or more tubes could contain at least one m-SWNT, implying that bundles are essentially non-emissive. Disruption of the $\pi$-electron system of the NT sidewall through damage like covalent chemistries, chemical derivatization,
or harsh sonication conditions can also significantly suppress fluorescence quantum yields.\textsuperscript{189,190} The best PL is obtained from pristine NTs that have not undergone any chemical processing. PL quenching can also occur in some surfactant suspensions when the sample is acidified. Unlike chemical functionalization, this process is fully reversible and the PL intensity can be restored to previous values by adding base to increase the pH.\textsuperscript{191} Different SWNTs vary in their susceptibility towards acid quenching, with longer wavelength PL features vanishing before shorter wavelength features.

The various peak maxima in a 2D PL map obtained from individualized SWNTs can be assigned \((n,m)\) values using a Kataura plot. As discussed in Section 1.2, the Kataura plot relates chirality assignments to transition energies and diameters of NTs, using a tight-binding approximation to describe the electronic structure of the tubes. However, a real NT is more complex than this approximation suggests, making a direct comparison between theoretical and experimental results complicated. Additionally, extrinsic environmental factors, such as other tubes, solvents, dispersants and substrates all cause a red-shift in the experimentally-obtained \(E_{\text{gi}}\) values, as well as a broadening of optical features. Free-standing SWNTs in air have optical transitions that are red-shifted (lower energy) compared to PL from free-standing SWNTs in a vacuum. Surfactant-suspended SWNTs and tubes that are lying on a substrate have PL values that are red-shifted compared to free-standing tubes in air;\textsuperscript{192} in some cases, the fluorescence intensity for SWNTs deposited on a substrate (like silicon or sapphire) is decreased or even quenched. PL values for polymer-dispersed SWNTs are red-shifted even further than those for surfactant-suspended samples.\textsuperscript{148} One explanation for these variations in optical transitional energies is changes in the dielectric
screening caused by various environmental factors, such as small molecules and solvents. The exact energy shift depends on the \((n,m)\) identity of the SWNT and if the tube is MOD1 or MOD2 in nature, as well as the identities of the dispersant molecule and solvent.

![Semiempirical Kataura plot of \(E_{11}^S\) (black circles), \(E_{22}^S\) (blue circles) and \(E_{11}^M\) (red stars). Data for sc-SWNTs and m-SWNTs electronic transitions were obtained from literature sources. The orange box shows the expected diameter range for HiPCO SWNTs (\(\sim 0.7 - 1.3\) nm) while the horizontal lines denote the three laser excitation wavelengths used for Raman studies in this thesis.]

In an effort to overcome the limitations of the theoretical Kataura plot, semiempirical Kataura plots have been created for surfactant-dispersed SWNT samples. Such plots can be calculated using \((n,m)\)-resolved spectral data from PL mapping (for sc-SWNTs only) or resonance Raman maps (for both m-SWNTs and sc-SWNTs). These semiempirical descriptions of NT transition energies show considerable deviations from conventional Kataura plots, but agree quite well with experimental results.
Assignment of \((n,m)\) values for any NT sample can be achieved by choosing the correct Kataura plot, with \(E_{ii}\) values obtained under identical (or at least similar) environmental conditions as the sample being investigated. There are currently no Kataura plots available for conjugated polymer dispersions of SWNTs, but it is still relatively easy to make chirality assignments for these samples. The x-y coordinates from a Kataura plot created for a surfactant-dispersed sample (Figure 1.17) can be overlaid onto the 2D PL map obtained for the polymer-SWNT sample, allowing for \((n,m)\) assignments to be made. The distinctive family \((2n+m)\) patterns make chirality assignments possible even for samples that display significant red-shifts in excitation and emission values.

While it is relatively facile to make qualitative descriptions of the \((n,m)\) composition of a NT sample, obtaining quantitative results from PL maps is much more challenging. The observed PL intensity for a \((n,m)\) tube is dependent not only on mass concentration, but also on \((n,m)\)-specific quantum efficiencies of light absorbance and emission.\(^{198}\) Precise measurements of the PL quantum efficiency for each sc-SWNT is hampered by the scarcity of reference standards in the NIR and by overlapping SWNT transitions. There are reports that different \((n,m)\) tubes exhibit different quantum yields, with near armchair SWNTs \((\theta \sim 30^\circ)\) having higher PL quantum yields compared to zigzag tubes \((\theta \sim 0^\circ)\), but it is still not known how values vary with diameter, chiral angle and modulus. There are also reports that quantum yields can vary with tube quality and length.\(^{199,200}\) Complicating this issue, molecular dynamics and quantum chemical calculations, along with experimental spectroscopic studies, have shown that after removal of excess polymer it is possible to observe modified PL from polymer-wrapped SWNT solutions. Polyfluorene-SWNT suspensions have exhibited superior quantum yields (as high as 1.5%) compared to surfactant-suspended SWNTs

\(^{45}\)
(\sim 0.1\%); additionally, the PL lifetime of excitons for polymer-wrapped SWNTs have a longer decay time (38 ps) compared to NTs separated by surfactants (22 ps).  

1.9 Resonant Raman Spectroscopy  

Raman spectroscopy is a versatile, non-destructive type of vibrational spectroscopy commonly used to characterize diameter and \((n,m)\) distributions for both metallic and sc-SWNTs.  

As Raman spectroscopy can be performed on both individualized or unsorted samples, this technique is a valuable tool for monitoring separation methodologies and for characterizing the purity (in terms of both electronic separation and defect density) of the tubes.  

In the Raman process a photon is absorbed and one (or more) phonon scatterings occur before a photon is emitted (Figure 1.14d). Raman spectroscopy measures the intensity of the scattered photon with respect to the Raman shift, which is defined as the frequency difference (in cm\(^{-1}\)) between the incident and scattered photon.  

A resonant Raman process gives significantly enhanced signals over non-resonance Raman, and can allow for the detection of SWNTs even on a single-tube level.  

The optical selection rules for a resonant Raman process are similar to those for optical absorbance, with the added consideration that either the incident or scattered light can be in resonance with an electronic transition (\(E_{\text{ii}}\)). Strong resonance enhancement of SWNTs is achieved by tuning the excitation wavelength to overlap with the van Hove singularities present in the 1D DOS for SWNTs.  

Since every SWNT chirality has a unique set of van Hove singularities, only a subset of the total NT population is accessed by any given excitation wavelength. For complete analysis of all the chiralities present in a sample it is necessary to have a tunable excitation source. The
(n,m) identities of the tubes present can be assigned by matching both the experimental optical transition energy (E\text{ii}, corresponding to the excitation wavelength) and diameter value (calculated from the \( \omega_{RBM} \)) with a point on the Kataura plot.\(^{205}\)

![Raman Spectrum Diagram](image)

Figure 1.18. Example of a typical Raman spectrum for HiPCO SWNTs showing the locations of the RBM (red box), D-band (blue box), G-band (purple box) and G’-band (green box).

The first resonant Raman experiments on NTs were performed by Rao and coworkers on SWNT powders prepared using a laser ablation process.\(^{206}\) These early experiments observed four dominant sets of peaks in the Raman spectrum (Figure 1.18), which were later assigned as: the radial breathing mode (RBM) from \( \sim 100 - 400 \) cm\(^{-1}\), the D-band from \( \sim 1250 - 1450 \) cm\(^{-1}\), the G-band from \( \sim 1550 - 1595 \) cm\(^{-1}\), and the G’ (or D*) mode at \( \sim 2500 - 2900 \) cm\(^{-1}\).\(^{8}\) Several other weak bands occurring between the G and G’ are assigned as combinational bands, including: the RBM+G (1700 - 1900 cm\(^{-1}\)) and the iTO+LA (\( \sim 1950 \) cm\(^{-1}\)), while the weak intermediate frequency modes (IFM) are located from 600 - 1100 cm\(^{-1}\).\(^{207}\) Of the four dominant sets of peaks, the RBM and G-band are often the most intense due to the fact they
are first order Raman processes. In a first order single resonance (Stokes) Raman process, the phonon-scatter electron recombines with the hole by emitting a scattered photon with one phonon energy lower than the incident photon as only one resonance process (photon absorption) occurs. The Stokes Raman intensity for first order modes is a function of the phonon frequency ($\hbar \omega$) and incident laser energy ($E_L$). Resonance is maximized for the incident resonant condition, $E_L = E_{ii}$, or at the scattered response condition, $E_L = E_{ii} + \hbar \omega$. The phonon energies ($\hbar \omega$) for the RBM and G-band are $\sim 0.02$ and $0.2$ eV respectively, and represent the width of the resonance windows for these modes. The larger resonance window for the G-band means that it is possible to see contributions from SWNTs in the G-band region that are not observed in the RBM. Contributions from the incident and scattered resonances for RBM phonons cannot be distinguished and a single maximum profile is observed. Both the D- and G'-bands are double resonance processes, because they involve an additional resonance scattering.

1.9.1 G-Band

The G-band (also known as the tangential mode) is a Raman active optical phonon feature present in all graphitic structures with sp$^2$-hybridized carbons, originating from in-plane carbon-carbon bond stretches. The G-band is a single feature in graphene but due to curvature-induced inequality of the two-bond displacement directions it splits into two modes for SWNTs: a lower-frequency peak call the $G^-$ and a higher frequency peak referred to as the $G^+$. The $G^-$ is normally centered between $1550 - 1585$ cm$^{-1}$, and arises due to tangential carbon vibrations along the circumferential direction of the tube. The $G^+$ is at $\sim 1590$ cm$^{-1}$, and is a result of tangential vibrations along the tube axis. The exact locations of the $G^-$ and $G^+$
depend on the diameter of the SWNT, and the shape of the $G^-$ mode is widely used to distinguish m-SWNTs from sc-SWNTs.

![Graph showing comparison of G-band regions for sc-SWNT (black) and m-SWNT (red) HiPCO SWNTs using 785 and 514 nm excitation wavelengths respectively.](image)

Figure 1.19. Comparison of the G-band regions for sc-SWNT (black) and m-SWNT (red) HiPCO SWNTs using 785 and 514 nm excitation wavelengths respectively.

For sc-SWNTs, both the $G^+$ and $G^-$ features are narrow, symmetrical Lorentzian peaks (Figure 1.19). For m-SWNTs (MOD0), the $G^+$ is also a narrow Lorentzian peak but the lower-frequency $G^-$ is an extremely broad, asymmetric peak. Early theoretical studies found that the broad $G^-$ feature can be treated through a Briet-Wigner-Fano (BWF) lineshape, and was originally ascribed to the coupling of phonons with the electronic continuum. The $G^-$ feature is now believed to be due to a frequency-softened and broadened longitudinal optical (LO) phonon feature, a hallmark of Kohn anomalies. Although a broad $G^-$ feature is considered to be a characteristic feature of m-SWNTs, this peak only appears for non-armchair MOD0 tubes and is absent for armchair ($n = m$) SWNTs. The G-band region for armchair NTs consists of a single, narrow peak from the $G^+$. Therefore, the shape of the $G^-$ peak alone cannot be used to describe the electronic nature of a mixture of SWNTs, and the
analysis of the G-band must be confirmed with a corresponding investigation of the RBM.

The location of the G-bands has been demonstrated to have some dependence on tube diameter. Attempts have been made to correlate the G$^+$ and G$^-$ band lineshapes and locations with specific ($n,m$) identities, with some studies showing that the location of the peak maxima for the G$^-$ can vary more than the G$^+$. However, such shifts are only visible for isolated SWNTs and are not applicable for bulk samples dispersed by polymers. The larger resonance window for the G-band (compared to that of the RBM) means that many different chiralities can be in resonance at the same time, and also lowers the accuracy of calculated diameters when compared to values obtained from the RBM. The G-band frequency can also be affected significantly by strain, charge-transfer, or the nature of the substrate. These frequency shifts are again more important for experiments involving single tubes, and arise due to the sensitivity of the G-band phonons to doping and charge-transfer from environmental effects, which can induce localization of electron density in NT the π-electron cloud, ultimately modifying the NT band structure. The BWF is also affected by pH, and can shift or become indistinguishable from the Lorentzian component with decreasing pH.

1.9.2 Radial Breathing Mode (RBM)

The strongest low-frequency Raman mode is the Radial Breathing Mode (RBM), which is unique to SWNTs. The RBM arises from in-phase radial movements of carbon atoms (as if the tube is “breathing”) meaning that the frequency of the peaks in the RBM ($\omega_{RBM}$) are diameter-dependent. The diameter and $\omega_{RBM}$ are related by
the equations:

$$\omega_{RBM} = \frac{A}{d_t} + B = \frac{227}{d_t} \sqrt{1 + C \cdot d_t^2}$$  \hspace{1cm} (1.3)$$

where A, B and C are empirical constants; B is related to environmental effects, such as the surfactant and solvent used, and C is the influence of the van der Waals interactions between the NT and its environment.\(^{211}\) The most common form of the equation involves the A and B variables, with several values of A and B reported in the literature for different types of SWNTs in a variety of different environments. Covalent chemistries disrupt the symmetry of the RBM, resulting in a decay of features that is correlated to reaction times.\(^{222}\)

Raman maps of SDS-dispersed HiPCO SWNTs have been obtained by incrementally varying the excitation wavelength from 457 – 821 nm (2.71 – 1.51 eV) to generate 3D plots (Figures 1.20a and 1.20b).\(^{223}\) From these spectra, 22 individual sc-SWNTs were identified with Raman RBM frequencies ranging from 183 – 373 cm\(^{-1}\), corresponding to diameters between 1.3 – 0.6 nm. The resolution of a large number of SWNT chiralities (including those with identical \(\omega_{RBM}\) but different resonant energies) allowed for the observation of four periodic groupings, labeled I–IV in Figure 1.20. These groupings result as a natural consequence of NT chiralities being described as families with \(2n + m\) relationships. When this Raman data was fit to Equation 1.3 values of \(A = 223.5\) and \(B = 12.5\) were calculated for the surfactant-suspended HiPCO SWNTs.

When SWNTs are in close proximity in bundles, intertube interactions arise that can affect the electronic and vibrational structures of the NTs. The intimate relationship between \(E_{ii}\) and the tube environment means the RBM region for bundled tubes will show drastically different features, making it a valuable tool for evaluating SWNT aggregation.\(^{224}\) Figures 1.20c and 1.20d show 3D plots for bundled HiPCO SWNTs,
obtained using the same excitation wavelengths as the SDS-dispersed HiPCO sample. A direct comparison between the maps in Figure 1.20 clearly shows the same groupings of SWNTs in both the individualized and roped spectra, but occurring at different excitation wavelengths. A pronounced red-shift (~ 54 – 157 meV) in the excitation wavelengths (and therefore the $E_{ii}$ transition energies) occurs for all chiralities in the spectra for bundled tubes. The red-shifting of transitions has the consequence of bringing into resonance new chiralities, resulting in a marked difference in the RBM spectra between samples of individualized and bundled tubes when observed at the exact same excitation wavelength. Additionally, the peaks appear “blurred” together with individual RBM features appearing less resolved due to the broadening of electronic transitions, leading to transition widths that are double or triple upon bundling for all chiralities.
The excitation wavelength of 785 nm has been found to be especially useful for comparing isolated versus bundled HiPCO SWNT samples. As shown in Figures 1.21a and 1.21b, substantial enhancement of the peak at 267 cm\(^{-1}\) (corresponding to the (10,2) chirality) compared to the peak at 234 cm\(^{-1}\) ((12,1) chirality) can be observed for a sample that contains a significant amount of bundled NTs. This is because the 785 nm excitation wavelength is near the peak of the enhancement profile (resonance window) for individualized (12,1) SWNTs (Figure 1.21c), but not individualized (10,2) SWNTs (Figure 1.21d). After the bundling-induced red-shift, the 785 nm excitation is near the peak maximum for the (10,2) chirality when it is bundled, but still significantly in the resonance window for the bundled (12,1) chirality as well. Therefore, an excitation wavelength of 785 nm offers a qualitative means for probing the extent of SWNT aggregation, and the peak at 267 cm\(^{-1}\) is often referred to as the “roping” or “bundling” peak.\(^{227}\) This also means that, unlike conventional optical spectroscopies, Raman spectroscopy can be used to characterize samples of bundled SWNTs, allowing for chirality assignments to be made. Environmental effects other than bundling can also affect the resonance window widths and locations for SWNTs; environmental interactions (such as substrates, solvents or polymer wrapping) can result in different degrees of stabilization of NT electronic structures, resulting in varying shifts in transition energies that may mask the total magnitude of bundling.\(^{227}\) Attempts have been made to create a semi-quantitative description of the extent of aggregation using the bundling peak, however these equations can vary greatly in the literature and none have been found to be applicable for all systems.

It is important to stress that no significant changes in the locations of the RBM frequencies (\(\omega_{RBM}\)) occur when the tubes are bundled or individualized. The actual location of a peak for any given chirality remains the same, regardless of \((n,m)\)
species electronic type, environment, doping, or aggregation state (as all these factors mainly affect the optical transition energy). Therefore, resonant Raman scattering is ideal for determining the \((n,m)\) chirality distribution of SWNTs that have been non-covalently functionalized with conjugated polymers. Caution must be used when drawing conclusions from results obtained at a single excitation wavelength, as a decrease in the relative size of a peak may be incorrectly attributed to changes in the relative concentrations when it could be caused by a shift in the electronic transition energies due to the polymer wrapping changing the resonance conditions for that tube. The more excitation wavelengths used to characterize a sample, the more accurate
the assignments become.

As many labs are not equipped with tunable lasers, several studies have been performed focusing on the chirality assignments for common Raman excitation wavelengths, including 830, 785, 633, 532 and 514 nm. For HiPCO SWNTs, the 785, 633 and 514 nm excitation wavelengths in particular have been found to be especially useful. The 785 nm (1.579 eV, 12,739 cm\(^{-1}\)) excitation wavelength is mostly in resonance with \(v_2-c_2\) sc-SWNT transitions (Figure 1.17), and as previously discussed the peak at 267 cm\(^{-1}\) can be used to evaluate the ability of a dispersant to exfoliate HiPCO SWNTs. The 633 nm (1.959 eV, 15,798 cm\(^{-1}\)) excitation wavelength offers a unique view for experiments investigating the separation of metallic and semiconducting species as both larger diameter m-SWNTs and smaller diameter sc-SWNTs are in resonance.\(^{229}\) Mostly metallic \(v_1-c_1\) transitions are in resonance at 514 nm (2.412 eV, 19,455 cm\(^{-1}\)), however some small diameter sc-SWNTs can also be seen.\(^{230}\)

### 1.9.3 D-Band and G’-Band

The D-band, located between 1250–1350 cm\(^{-1}\), is often referred to as the disorder mode, and is present in other carbonaceous materials. In the mechanism responsible for the D-band, electrons are scattered elastically by structural defects (such as vacancies, impurities or sp\(^3\)-hybridized carbons), and as such this peak can be used to probe the chemical purity of the tubes.\(^{22,231}\) It is especially useful for monitoring covalent modification of the NT sidewall as an increase in the D-band (relative to the G-band) corresponds to the conversion of sp\(^2\)-hybridized carbons into sp\(^3\)-hybridized carbons. Conversely, if the D-band is nearly absent it means that the SWNTs have a low defect concentration. The intensity of the D-band does not increase with surfactant, polymer or hydronium ion adsorption onto the NT surface.
The G’ (also known as the 2D or D*) feature at $2600 - 2700 \text{ cm}^{-1}$ is a disorder-based overtone of the D-mode that appears at approximately twice the Raman shift of the D-band. As with the D-band, the G’-band is not specific to SWNTs and is found in other carbonaceous materials. Most SWNTs have a symmetric G’, but a few have been found experimentally to exhibit asymmetric G’ features, which can be fitted with two Lorentzian peaks. This splitting is only observed for MOD1 sc-SWNTs and non-armchair m-SWNTs, and arises due to the laser being in resonance with related $E_{ii}$ values (either incident or scattered resonances), like an $E_{33}^S$ and $E_{44}^S$ or $E_{ii}^{M+}$ and $E_{ii}^{M-}$. If the $E_{ii}$ values are close to each other and are all within the resonance window of a certain excitation wavelength, two features (one with incident resonance, the other with scattered resonance) can be observed at slightly different frequencies due to the dispersive behavior of the double-resonance process.

1.10 Summary

The heterogeneity inherent in all SWNT production methodologies results in samples with a variety of lengths, diameters, chiralities and electronic types. The development of surfactant-based dispersion and purification techniques like DGU and agarose gel filtration over the past decade have allowed for the realization of highly specialized samples of SWNTs; however, many of these methodologies require long, complicated procedures and suffer from low yields, precluding them from large-scale commercial applications. Conjugated polymers are a viable alternative to these processes due to their lower cost and potential to be applied on a larger scale. The tunable nature of polymeric systems allows for the possibility to design selective dispersal agents, as well as the production of novel hybrid materials. Of all the conjugated polymer families investigated for dispersing SWNTs, polyfluorenes have received the most attention.
and have demonstrated great promise for selectively dispersing sc-SWNTs. However, the presence of a wide band-gap polymer like polyfluorene on the surface of a NT could be detrimental for device (such as FET) performance. Additionally, selectivity for sc-SWNTs is only observed in “poor” solvents, meaning that the dispersions are relatively dilute.

In theory, poly(2,7-carbazole)s offer a viable alternative to polyfluorenes, and there are a limited number of examples in the literature of poly(2,7-carbazole)s being used to prepare supramolecular complexes with SWNTs. These experiments seem to suggest that this class of polymers can also selectively disperse sc-SWNTs, but many of the composites formed possessed limited stability and required arduous dispersal protocols (such as excessive amounts of polymer and DGU). One of the major goals of this work was to design a novel poly(2,7-carbazole) that would possess excellent solubility to allow for the formation of supramolecular complexes with SWNTs using a more facile methodology. Taking into account the complexities that can arise once the polymer coats the NT walls, significant effort was also put towards characterizing the polymer-SWNT supramolecular complexes through multiple techniques (including absorbance, photoluminescence and resonant Raman spectroscopy, as well as atomic force microscopy) to obtain an accurate description of the composites formed and to confirm that the poly(2,7-carbazole) unit preferentially interacts with sc-SWNTs.

A secondary goal of this thesis was to use optical spectroscopy to elucidate what effect changing certain polymer parameters has on the quality of the dispersions obtained. The ability of a polymer to selectively solubilize SWNTs by electronic type arises from a complex interplay between the identity of the polymer backbone, molecular weight, solvent and the density and structure of any side groups. As such, developing reliable design rules for polymer-SWNT supramolecular complexes remains
a challenging field. An example of this is that although there are now several polymer structures that can selectively disperse sc-SWNTs, there are still no polymeric systems that can selectively discriminate m-SWNTs. The selectivity of a poly(2,7-carbazole) towards sc-SWNTs was monitored while the molecular weight, concentration or type of SWNT was varied to evaluate the robustness of this polymer. Other polymer structures were also investigated, including polyfluorene derivatives that incorporated either an electron rich or electron poor co-monomer, with the goal of establishing relationships between the chemical structure of the conjugated polymer and its ability to effectively and selectively sort SWNTs. This involved controlling for several variables (such as molecular weight and relative size of the side chains) so that the relationship between the nature of the polymer backbone and the types of SWNTs dispersed could be elucidated. It was found that the introduction of an electron-poor co-monomer had a drastic impact on the types of SWNTs dispersed, with the results of these experiments offering a viable route towards the development of polymeric systems that can selectively solubilize m-SWNTs.

1.11 References


Chapter 2

Supramolecular Interactions of High Molecular Weight Poly(2,7-carbazole)s with Single-Walled Carbon Nanotubes

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Abstract

A novel 2,7-carbazole monomer unit was synthesized and used to prepare two poly(2,7-carbazole)s, both of which were obtained in relatively high molecular weight and display excellent solubility in common organic solvents. The polymers were able to effectively disperse carbon nanotube bundles in both THF and toluene using a relatively simple procedure to yield concentrated polymer-carbon nanotube samples that were stable for months. The polymer-coated carbon nanotube samples were characterized by thermogravimetric analysis, atomic force microscopy, absorption spectroscopy, photoluminescence mapping, and Raman spectroscopy. It was found that the polymers used in this study preferentially interact with carbon nanotubes having diameters of 1.15 nm or less. Additionally, it was observed that the carbon nanotubes remained effectively debundled by the polymers after removal of solvent, as was demonstrated by Raman and photoluminescence mapping of solid films of the polymer-carbon nanotube composites.
2.1 Introduction

Polymer composites of single-walled carbon nanotubes (SWNTs) are promising materials as a result of the outstanding mechanical, optical, and electronic properties that SWNTs can impart.\textsuperscript{1-7} The electronic structure of a SWNT depends on the length and chiral angle of the roll-up vector on a graphene sheet.\textsuperscript{8,9} Considering that most synthetic procedures for the production of SWNTs result in polydisperse samples that consist of a distribution of chiralities, the purification of raw SWNT samples into batches that consist of only a single chirality has received tremendous recent attention.\textsuperscript{10} In particular, density gradient ultracentrifugation and agarose gel filtration have been the most successful SWNT purification techniques reported thus far.\textsuperscript{11,12} In addition to these physical techniques, noncovalent chemical functionalization of SWNTs to enable their selective dispersion in a variety of solvents has also received a great deal of interest.\textsuperscript{13-17} Specifically, mixing conjugated polymers with SWNTs has been demonstrated to result in strong polymer-nanotube interactions.\textsuperscript{18-20} Recent work on SWNT functionalization with polyfluorene\textsuperscript{21-23} and polythiophene\textsuperscript{24-26} derivatives has begun to uncover the possibility for selective interactions, where the polymer only interacts with a subset of SWNT chiralities. This chemical approach to SWNT purification is attractive as access to a large variety of conjugated polymer backbone structures is synthetically feasible, and it may be possible to enable the polymer-nanotube interaction to be extremely selective through the introduction of appropriate functionality on the polymer. Yet the diversity of conjugated polymer structures that have been investigated for nanotube functionalization thus far has been limited.
Relative to polyfluorenes and polythiophenes, polycarbazoles have received significantly less attention as nanotube decorating agents. However, polycarbazoles have a number of advantageous properties that make them uniquely interesting for nanotube functionalization work. In particular, the monomer is fully conjugated, highly stable, and easily derivatized through reaction at the nitrogen atom, allowing the preparation of various polycarbazole derivatives with tunable bandgaps.\textsuperscript{27-29} Since the first complete synthesis of a poly(2,7-carbazole) was reported in 2001,\textsuperscript{30} a wide range of carbazole homopolymers and copolymers have been investigated. Poly(2,7-carbazole)s have potential applications in organic light-emitting diodes,\textsuperscript{31} organic field effect transistors,\textsuperscript{32} and photovoltaic devices.\textsuperscript{33,34} In general, poly(2,7-carbazole)s tend to suffer from lower molecular weights and solubilities compared to poly(2,7-fluorene)s. Modification of side chains to include bulky alkyl and aryl substituents, as well as inclusion of more soluble comonomers, has been found to help increase the solubility and molecular weight of the polymers, but many high molecular weight poly(2,7-carbazole)s still suffer from poor solubility and high polydispersities.\textsuperscript{35}

Despite the advantages of poly(carbazole)s, very few studies have been performed using this class of polymer to prepare polymer-carbon nanotube complexes. Several studies involving covalent grafting of poly(\textit{N}-vinylcarbazole) to the sidewalls of carbon nanotubes though various mechanisms have been performed,\textsuperscript{36-38} and a solution of poly(9-vinylcarbazole) has been used to noncovalently disperse carbon nanotubes.\textsuperscript{39} Recently, the potential of poly(2,7-carbazole)s to solubilize SWNTs has been reported.\textsuperscript{40-44} The initial work with poly(\textit{N}-decyl-2,7-carbazole) indicated that it was selective for semi-conducting SWNTs with specific chiralities, and it was suggested that poly(2,7-carbazole)s and poly(2,7-fluorene)s could have complementary selectivity.\textsuperscript{40} However, upon further study of other poly(2,7-carbazole) structures,
it was noted that the majority of polymers studied formed “poor” or “unstable” SWNT solutions, likely owing to the low molecular weight and poor solubility of the polymers/oligomers that were used. While this work revealed the potential of poly(2,7-carbazole)s as a template for preparing selective complexes with SWNTs, the problems of low molecular weight and poor solubility of polycarbazoles used in nanotube functionalization still need to be addressed.

Here, we present the preparation of two novel, highly soluble, and high molecular weight polymers containing the 2,7-carbazole unit and investigate their noncovalent interactions with SWNTs. Because of the necessity that the polymer-SWNT composites be highly soluble, coupled with the fact that most poly(2,7-carbazole)s suffer from low molecular weights and poor solubility, it was necessary to first design a novel carbazole monomer unit that exhibits an effective solubilizing group. We found that introduction of a 3,4,5-tris(hexadecyloxy)phenyl moiety, separated from the polymer backbone by \( n \)-hexyl spacer, was able to yield extremely soluble polymers with high molecular weights using common polymerization techniques. Additionally, these polymers were very effective in dispersing carbon nanotube bundles within organic solvents and represent a new and interesting class of polymers that can be used to form nanotube composites.
2.2 Results and Discussion

2.2.1 Monomer and Polymer Synthesis

Preparation of a highly soluble 2,7-dibromocarbazole derivative involved the incorporation of a 3,4,5-tris(hexadecyloxy)phenyl moiety as a solubilizing group, tethered by an \( n \)-hexyl linker. This solubilizing moiety was prepared from methyl-3,4,5-tris(hydroxy)benzoate (1), which was alkylated via Williamson ether synthesis with hexadecyl bromide, followed by reduction to the benzyl alcohol 3.\(^{45}\) Subsequent deprotonation with NaH and stoichiometric substitution of 1,6-dibromohexane produced side-chain 4 in 71% yield over three steps (Scheme 2.1).

The synthesis of the 2,7-carbazole monomer unit (8) is outlined in Scheme 2.2. 2,7-Dibromocarbazole (7) was prepared in two steps from 4,4'-dibromobiphenyl (5) following literature procedures.\(^{46,47}\) This involved nitration of 5 followed by a triethylphosphite-mediated Cadogan ring closure to yield carbazole 7 (Scheme 2.2). Coupling of the side chain involved deprotonation of 7 with NaH followed by addition of 4 to yield the desired monomer in 96% yield.
Monomer 8 was then used to prepare a poly(2,7-carbazole) homopolymer (PC) as well as a poly(2,7-carbazole-alt-2,7-fluorene) alternating copolymer (PC-PF), as shown in Scheme 2.3. The homopolymer was prepared using a Ni(COD)$_2$-mediated Yamamoto coupling, following a previously reported procedure, while PC-PF was prepared using a commercially available 2,7-bis(boronic ester) of fluorene via Suzuki polycondensation. After precipitation in MeOH, both polymers were obtained as yellow solids in excellent yields. Characterization of the two polymers was carried out by $^1$H NMR and size exclusion chromatography (SEC, relative to PS standards) as well as UV-vis absorption and fluorescence spectroscopy. The NMR data for the two polymers are shown in Figure 2.1. For PC, two small signals at 7.4 and 7.5 ppm were attributed to the phenyl end-groups, and integration of these signals relative to well-resolved aromatic protons in the polymer side-chain at $\sim$6.5 ppm indicated a number-average ($M_n$) molecular weight of ca. 66 kDa, corresponding to a degree of polymerization in the range of 61. Since PC-PF does not exhibit any distinct end-groups, molecular weight calculation based on NMR analysis was not possible. SEC analysis of PC and PC-PF also indicated that high molecular weights were achieved in both cases, with $M_n$ values of 61 and 70 kDa relative to polystyrene standards,
Scheme 2.3. Synthetic Route to the 2,7-Carbazole Homopolymer (PC) and the Copolymer with Fluorene (PC-PF).

respectively (Table 2.1). For PC, the close agreement between calculated molecular weights from NMR and SEC indicates that SEC is a good measure of molecular weight for this class of polymer, even though polystyrene standards were used to create the calibration curve. Polydispersities of the two polymers were in the expected range (Table 2.1), indicating that both polymerizations proceeded smoothly by a step-growth mechanism. Despite the high molecular weight of these two polymers, they exhibited good solubility in common organic solvents, including THF, chloroform, and toluene. This allowed facile measurement of absorption and emission spectra of both polymers (Figure 2.2). The absorption and emission spectra of PC and PC-PF in THF are very similar, with both polymers having a maximum absorbance of 393 nm and a maximum fluorescence emission at 417 nm. Identical results were obtained in toluene solutions (Figure 2.14, Supporting Information).
Figure 2.1. NMR spectra of PC (top) and PC-PF (bottom) polymers (in CDCl$_3$). Inset shows the aromatic region of the spectrum for PC.

2.2.2 Polymer Complexes with Carbon Nanotubes

Complexes of the two conjugated polymers with SWNTs were prepared following previously published protocols. Briefly, 10 mg of raw HiPCO SWNT powder was added to a polymer solution containing 15 mg of polymer dissolved in 20 mL of solvent. The polymer-SWNT mixtures were sonicated for 45 min in a bath sonicator chilled with ice, followed by 20 min of centrifugation at 8346g. The supernatant was
Table 2.1. Molecular Weight, Polydispersity Index (PDI), and Approximate Degree of Polymerization (DP) for the Synthesized Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Yield(%)</th>
<th>NMR (kDa)</th>
<th>SEC (kDa)</th>
<th>PDI</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>86</td>
<td>66</td>
<td>61</td>
<td>61</td>
<td>106</td>
</tr>
<tr>
<td>PC-PF</td>
<td>82</td>
<td>70</td>
<td>128</td>
<td>1.8</td>
<td>47</td>
</tr>
</tbody>
</table>

Figure 2.2. UV-Vis absorption (solid lines) and emission (dashed lines) spectra for PC (red) and PC-PF (blue) in THF.

carefully removed from the centrifuge tubes to obtain stable dispersions of polymer-SWNT complexes. These dispersions were then subjected to ultrafiltration (using a Teflon filtration membrane having 0.2 μm diameter pores) and rigorous washing with solvent until the filtrate was no longer fluorescent when irradiated with UV light (365 nm), indicating that all excess free polymer had been removed. Both THF and toluene were found to be excellent solvents for the resulting polymer-SWNT complexes, and the dispersions were all very stable with no observable flocculation over the course of a year. Both polymers formed clear, colorless solutions in THF and toluene before addition of SWNTs, while the polymer-SWNT complexes were
extremely dark. Interestingly, upon dilution, it was observed that the PC-SWNT dispersion exhibited a dark green color, while the PC-PF-SWNT dispersion was a darker green-blue color (Figure 2.15). A dispersion of the same batch of raw HiPCO SWNTs in SDBS was also prepared in D$_2$O, following a published procedure.$^{50}$

![Figure 2.3. TGA data showing mass loss upon heating for PC, PC-PF, PC-SWNT, and PC-PF-SWNT samples.](image)

The polymer-SWNT composites were initially characterized by thermogravimetric analysis (TGA), with results depicted in Figure 2.3. The thermograms for the PC and PC-PF polymers show a mass loss of 84.1% and 78.5%, respectively, which corresponds exactly to the expected mass loss upon thermal decomposition of the side chains. For the PC-SWNT and PC-PF-SWNT samples, the observed mass loss was 60.3% and 59.0%, respectively. These values were used to calculate the percent SWNT composition within the polymer-SWNT complexes, which amounted to 28.3% and 24.8%, for PC-SWNT and PC-PF-SWNT, respectively. These values likely overestimate the actual SWNT composition, as some amount of metal nanoparticles and
amorphous carbon from the raw HiPCO SWNTs may be present in the polymer-wrapped material.

2.2.3 AFM Analysis

![AFM images](image)

Figure 2.4. AFM images of PC-SWNT (left) and PC-PF-SWNT (right) samples spin-cast onto a freshly cleaved mica substrate. Dashed lines represent location of the height profile given below each of the two images. Scale bars correspond to 200 nm.

Sample preparation for tapping-mode atomic force microscopy (AFM) analysis involved spin-coating the polymer-SWNT solutions onto freshly cleaved mica substrates. The resulting images clearly showed the presence of long filamentous structures, resembling polymer-coated SWNTs. The PC-SWNT sample (Figure 2.4) was more concentrated than the PC-PF-SWNT sample, and consequently the corresponding image shows a larger number of features. Interestingly, even in this concentrated sample, the image shows an interwoven mesh of individual SWNT fibers. Height analysis in different regions (indicated by white dashed lines in the images) produced values for the smallest features of \( \sim 1 \) nm, while larger features exhibited heights ranging from...
2 to 15 nm, likely corresponding to small bundles of polymer-coated SWNTs. These AFM images are consistent with the expectation that both PC and PC-PF polymers strongly interact with SWNTs and are able to exfoliate them into individual tubes or very small bundles of tubes in solution. It is reasonable to expect that some of the larger features observed in Figure 2.4 are the result of aggregation upon sample drying.

2.2.4 Absorbance

Figure 2.5. UV-Vis-NIR absorbance data for PC-SWNT and PC-PF-SWNT in THF (a) and toluene (b). The SDBS-SWNT dispersion in both plots was measured in D$_2$O. Absorbance traces have been vertically offset for clarity.

UV-Vis-NIR absorption spectra for PC-SWNT, PC-PF-SWNT, and SDBS stabilized SWNT dispersions in both THF and toluene are shown in Figures 2.5a and 2.5b, respectively. The absorption spectra were not normalized but have been vertically offset for clarity. The sharp rise in absorbance intensity around 400 nm in the polymer-SWNT spectra is due to the absorbance of the significant amount of polymer bound to the SWNT surface. Well-resolved absorbance peaks in the S$_{11}$ (approximately 830 – 1600 nm) and S$_{22}$ (approximately 600 – 830 nm) ranges can
be observed for all the samples. Although there are clearly metallic nanotubes suspended in the SDBS D$_2$O solution (found in the range of 440 – 645 nm), it is difficult to determine if metallic nanotubes are dispersed by the polymers due to the presence of strong polymer absorbance for the PC-SWNT and PC-PF-SWNT samples overlapping in this wavelength range. Additional differences can be observed in the absorbance data when comparing the SDBS-SWNT spectrum to the PC- and PC-PF-SWNT spectra. In particular, a significant red-shift in the position of absorption peaks associated with both polymer-SWNT samples is observed, relative to the SDBS-dispersed SWNT sample. This red-shift has previously been observed for SWNT composites with conjugated polymers and complicates exact assignment of chiralities corresponding to each peak in the four polymer-SWNT absorption spectra depicted in Figure 2.5. Considering that our sample contains multiple chiralities of SWNTs, a dense array of peaks overlap to cause spectral congestion, making the exact assignment of chiralities difficult.

While there may be some metallic SWNT species present in both PC-SWNT and PC-PF-SWNT, the UV-Vis-NIR results suggest that our samples are enriched in semiconducting SWNTs.

When comparing polymer-SWNT absorbance data measured in the two different solvents, only minor differences in the relative intensity of the various peaks are noticeable. There is a notable lack of background absorbance in all four polymer-SWNT absorption spectra, possibly indicating that these samples do not contain significant amounts of amorphous carbon and SWNT aggregates. This suggests that our sample preparation protocol removes most of the impurities present in the commercial SWNT sample and efficiently disperses SWNT bundles.
2.2.5 Fluorescence

Photoluminescence (PL) mapping is a powerful tool for studying bulk samples of SWNTs. It allows for the characterization of semiconducting SWNTs in solutions, provided that the tubes are effectively debundled and there is not an overabundance of metallic SWNT species, as both of these can dramatically reduce the observed PL intensity. The PL map for SDBS dispersed SWNTs is shown in Figure 2.6. From this plot, 22 unique semiconducting SWNT species can be observed and are labeled according to their \((n,m)\) indices, where integers \(n\) and \(m\) represent the number of unit vectors needed to make up the SWNTs roll-up vector (listed in Table 2.2). These results agree with previously reported PL maps for raw HiPCO SWNTs; however, it should be noted that the relative concentration of each SWNT species can vary between commercial samples. The expected locations of emission maxima for the SWNTs that emit in this part of the NIR spectrum are also plotted as dots (Figure 2.6), using literature values.
Figure 2.7. Photoluminescence contour maps for HiPCO SWNTs dispersed by PC (a) and PC-PF (b) in THF.

PL maps for PC-SWNT and PC-PF-SWNT dispersions in THF are depicted in Figures 2.7a and 2.7b, and dispersions in toluene are depicted in Figures 2.8a and 2.8b, respectively. A stark difference is noticeable between the polymer-SWNT dispersions and the SDBS dispersed HiPCO SWNTs. There are fewer SWNT species present in the polymer-SWNT dispersions compared to the SDBS-SWNT dispersion, and for those SWNTs that remain, there is a difference in the relative distribution of intensities. For PC-SWNT, there were 18 unique chiralities observed in THF and 18 in toluene. For PC-PF-SWNT, 15 species were detected in THF and 16 in toluene. In general, both conjugated polymers seem to preferentially select SWNTs of low diameter in both THF and toluene, with all of the observed chiralities having diameters lower than 1.15 nm and 1.10 nm for PC-SWNT and PC-PF-SWNT, respectively.

In the SDBS-SWNT dispersion, the (8,6) chirality was the most dominant fluorescent species, while for the PC-SWNT dispersion, the (6,5) chirality was the most dominant in both THF and toluene. For the PC-PF-SWNT dispersions, the (6,5) nanotube is also the dominant species in toluene, while the (9,4) SWNT gave rise to
the most intense fluorescence band in THF. These results are interesting as the (6,5) SWNT fluorescence in the SDBS map is quite weak compared to the other chiralities. This again indicates that the conjugated polymers are selective for a subset of the original SWNT population, particularly those with low diameter.

The relative abundance of each SWNT species was estimated by finding the maximum intensity of each peak in the PL maps and then dividing by the maximum intensity of the most intense peak for that particular plot; the most intense peak was then set to a value of 100 (Table 2.2). This methodology does not take into account any difference in fluorescence quantum yield among different SWNT species. Previous reports have attempted to determine the quantum efficiency for each individual SWNT, and the protocol was applied to various SWNT dispersions.\textsuperscript{57-60} These studies suggest that the quantum efficiency of a SWNT is complex and can be affected by factors including diameter, chirality, modulus, length, and presence of defects. Additionally, most of the reported quantum yield values have been determined for SWNTs...
dispersed by surfactants or DNA in aqueous solvents using various sample preparation procedures, which could also affect the observed quantum yields. Thus, no other correction or normalization factors were applied to our data, and we recognize that the values given in Table 2.2 are only rough estimates. Using these estimates, a plot of the relative abundance of each nanotube type as a function of diameter is given in Figure 2.9. Again, this data shows that there is a preference for dispersion of low-diameter SWNTs using the PC and PC-PF polymers in both THF and toluene. Plots of the relative abundance of each SWNT as a function of chiral angle (θ) are provided in the Supporting Information (Figure 2.17) and show no obvious selectivity for θ by either polymer.

An additional feature observed in the polymer-SWNT PL maps is that the location of the peak maxima of all chiralities of SWNTs have been red-shifted in both excitation and emission, similarly to what was observed in the UV-Vis-NIR absorption data. This phenomenon has been previously reported for conjugated polymer-SWNT complexes. The magnitude of the red-shift varies between the PC and PC-PF polymers and with the chirality of the SWNTs in question, with no clear trend. Observed red-shifts varied from 10 − 28 nm and 10 − 60 nm for E_{22} and E_{11} transitions for PC-SWNT and 5 − 17 and 16 − 33 nm for the E_{22} and E_{11} transitions for PC-PF-SWNT samples, respectively (Tables 2.3 and 2.4). It has been suggested that bundles of SWNTs can show significant broadening and red-shifting of PL values, but we do not believe this is the case here as the presence of SWNT bundles would also be expected to decrease the intensity of fluorescence in the PL map, which we do not see. Additionally, the lack of a broad background in the absorbance data, discussed previously, suggests most nanotube bundles have been removed.

The PL maps also indicate that an energy transfer occurs from the polymer to the
Table 2.2: Relative Intensities of SWNT Species from SDBS and Polymer Dispersions, in Order of Nanotube Diameter

<table>
<thead>
<tr>
<th>(n, m)</th>
<th>Diam (nm)</th>
<th>Chiral Angle (deg)</th>
<th>SDBS ( (\text{D}_2\text{O}) )</th>
<th>PC ( (\text{THF}) )</th>
<th>PC-PF ( (\text{toluene}) )</th>
<th>PC-PF ( (\text{THF}) )</th>
<th>PC-PF ( (\text{toluene}) )</th>
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Figure 2.9. Relative PL signal intensities of the major SWNT species as a function of nanotube diameter in THF (a) and toluene (b). For reference, the signal intensities of the sample dispersed using SDBS is also plotted (c).

nanotubes when the polymer is directly excited. With the excitation wavelength ($\lambda_{ex}$) set to 420 nm, the observed SWNT emission in the polymer-decorated samples was significantly more intense for most (but not all) chiralities, relative to what was found for the SDBS-SWNT sample (Figure 2.10). Since this $\lambda_{ex}$ value corresponds well with the absorption maximum of the polymer, it is likely that the increased emission results from polymer-to-nanotube energy transfer. It is interesting that only some of the emission bands are increased in intensity, suggesting that energy transfer occurs preferentially with some nanotube chiralities over others. In addition, the emission intensity of the polymer-SWNT composites was higher in toluene than in THF, with some differences in relative intensity of the various peaks (Figure 2.10). The exact
origin of these differences will require further investigation. Complete maps showing emission intensities upon UV excitation are given in the Supporting Information (Figure 2.16). It should also be noted that similar energy transfer phenomena have been shown previously for conjugated polymer-SWNT dispersions.\textsuperscript{61,62}

Figure 2.10. Comparison of PL signal intensity using an excitation wavelength of 420 nm for SDBS-SWNT in D$_2$O and PC-SWNT and PC-PF-SWNT in THF (a) and toluene (b), showing increased PL intensity due to energy transfer from the polymer to the SWNTs.

\subsection*{2.2.6 Raman}

Raman spectroscopy was performed on solid film samples of all five SWNT dispersions. The films were prepared by drop-casting the dispersions onto silicon wafers, and a laser excitation wavelength of 785 nm was used to characterize the samples. Raman spectra for PC-SWNT and PC-PF-SWNT cast from THF are shown in Figure 2.11, along with the Raman spectrum of the SDBS-SWNT sample cast from D$_2$O. All spectra have been normalized to the G band (at ~1590 cm$^{-1}$) and offset for clarity. The expanded RBM region for each of the samples is given in Figure 2.11b. Similar data were observed for samples cast from toluene (see Figure 2.18).
Figure 2.11. Raman spectra of solid films of PC-SWNT and PC-PF-SWNT cast from THF solutions as well as SDBS-SWNT cast from D$_2$O recorded using an excitation wavelength of 785 nm (a). The expanded RBM region from the same data is given in (b).

The most striking feature of the Raman results at this excitation wavelength is the presence of broad transitions stretching from the region of the D band (~1300 cm$^{-1}$) to the G’band (~2600 cm$^{-1}$). Multiple attempts were made to obtain Raman spectra without these features, including changing the film thickness, using different substrates and film preparation techniques, and solution Raman experiments. However, these features remained consistently present in all experiments. Upon converting the Raman spectra such that intensity is plotted as a function of the Raman shift on a wavelength scale (nm) and comparing them to fluorescence spectra from PL maps (taken at an excitation wavelength of 786 nm), it was found that some of these Raman features match well with fluorescence traces, as shown in Figure 2.12. These peaks thus appear to be fluorescence from SWNTs in the solid state. Fluorescence in Raman data has been observed before for samples enriched in (6,5) SWNTs using a laser excitation wavelength of 740 nm.$^{53}$ The NIR emission upon excitation at ca. 785 nm can be attributed to fluorescence tails for (8,3), (6,5), and (7,5) chiralities.
Figure 2.12. Comparison between Raman results (excitation wavelength of 785 nm) with emission data (excitation wavelength of 786 nm) in both solution and solid state for (a) PC-SWNT and (b) PC-PF-SWNT THF samples.

(approximately 952, 976, and 1024 nm, respectively). The peaks in the Raman data at approximately 930 and 880 nm are at the limits of the PL detector but could be due to (6,4) and (9,1) chiralities. These results seem to indicate that our polycarbazole polymers are capable of keeping SWNTs debundled enough in the solid state to allow for efficient SWNT fluorescence.

To further investigate SWNT fluorescence in the solid state, thin films were prepared on quartz slides by drop-casting dispersions of PC-SWNT and PC-PF-SWNT from THF. PL maps were obtained using a solid sample holder, with the sample positioned at an angle of 35° relative to the incident light. The solid films were mapped in an identical manner to their solution samples, and the results can be seen in Figure 2.13. While there is still clearly SWNT fluorescence from the sample, it is not as intense as the solution sample from which it was prepared. Interestingly, the PL intensity of several species of SWNTs decreased, while it remained high for other chiralities. Most notably, the PL from (8,7), (9,5), (10,3), and (11,1) SWNTs was quenched in the solid state, while chiralities (6,5), (7,5), (7,6), and (8,3) all remain...
Figure 2.13. Photoluminescence map of PC-SWNT drop-cast onto a quartz slide from THF.

clearly defined. Although the exact reason for the differential quenching is not clear, it is interesting to note that low-diameter SWNTs seem to retain their fluorescence, while higher-diameter SWNTs become quenched in the solid state.

2.3 Conclusions

We have reported the synthesis of a 2,7-carbazole monomer unit that is capable of forming high molecular weight poly(2,7-carbazole)s that possess excellent solubility in common organic solvents. These polymers form strong supramolecular interactions with HiPCO SWNTs, resulting in relatively concentrated dispersions. It was found that polymers PC and PC-PF successfully debundled SWNTs. After removal of solvent to form thin films, the SWNTs remained effectively debundled to allow for observation of SWNT fluorescence by both Raman spectroscopy and PL mapping of
a solid film. While the polymers reported in this paper do not seem to show dramatic selectivity for specific chiralities of SWNTs, there was a diameter dependence noted. By combining the 2,7-carbazole monomer with other comonomer species, it could be possible to design conjugated polymer systems that combine the excellent dispersal properties of this carbazole with selective interactions for specific chiralities of SWNTs.

2.4 Supporting Information

2.4.1 General

Raw HiPCO single-walled carbon nanotubes were purchased from Carbon Nanotechnologies, Inc (Houston, TX, lot #RO217) and used without further purification. Dry DMF for the preparation of the polycarbazole was prepared by distilling the DMF off of P$_2$O$_5$ and storing it over molecular sieves before distilling the required amount of solvent into the reaction flask. All other reagents and solvents were purchased from commercial suppliers and used as received. NMR spectroscopy was performed on a Bruker 500 or 600 MHz instrument. Polymer molecular weight and polydispersity index (PDI) were estimated from gel permeation chromatography (GPC) using a Waters 2695 Separations Module equipped with a Waters 2996 photodiode array detector, a Waters 2414 refractive-index detector, and three Polymer Labs PL gel individual pore-size columns. Polystyrene standards were used for calibration, and a 0.1% TBAB in THF solution was used as the eluent. Sonication was carried out in a Banson Ultrasonics B1510 bath sonicator. UV-Visible spectroscopy was performed using either a Cary 50 or a Cary 5000 spectrophotometer using a 10 mm quartz cuvette. Fluorescence spectra were measured with a Jobin-Yvon SPEX Fluorolog 3.22
equipped with 450 W Xe lamp and an InGaAs detector. Slit widths were set to 10 nm band-pass on both excitation and emission, and correction factor files were applied to account for instrument variations. Raman spectra were collected with a Renishaw InVia Laser Raman spectrometer, equipped with a 25 mW argon ion laser (514 nm, grating 1800 L/mm), a 300 mW Renishaw laser (785 nm, grating 1200 L/mm). The lasers were set at less than 1% power to avoid damaging the samples. Thermogravimetric analysis (TGA) was carried out on a S3 TA Instruments Q50 thermogravimetric analyzer. All measurements were done under Ar, with sample masses ranging from 1.4 to 2.0 mg.

2.4.2 Synthesis

The synthetic procedures for preparing 3,4,5-tris(hexadecyloxy)benzyl alcohol (3) and 2,7-dibromocarbazole (7) have been previously reported.

5-(((6-bromohexyl)oxy)methyl)-1,2,3-trihexadecyloxybenzene (4)

A 250 mL flame-dried flask was charged with NaH (2.41 g, 60.2 mmol) and 3,4,5-tris(hexadecyloxy)benzyl alcohol (2.57 g, 3.01 mmol), predissolved in 120 mL anhydrous THF. The mixture was allowed to stir at room temperature for 20 min before 1,6-dibromo-hexane (4.63 mL, 30.1 mmol) was added to the reaction flask slowly and rinsed with 20 mL of THF. The mixture was then heated to 70 °C and left to stir for 2 days. The NaH was quenched with 50 mL of H₂O, and the THF was removed before the product was extracted into DCM (3 x 75 mL). The organic layer was rinsed with H₂O (80 mL) and brine (100 mL) before being dried over Na₂SO₄. After filtration, the solvent was evaporated in vacuo, and the product was purified by column chromatography (1 − 2% EtOAc:Hex eluent) to yield a white solid (2.63 g, 88%). ¹H NMR
(CDCl$_3$, 600 MHz): $\delta = 0.88$ (t, $J = 6.92$ Hz, 9H), 1.21-1.49 (m, 82H), 1.60-1.65 (m, 2H), 1.70-1.75 (m, 2H), 1.76-1.81 (m, 4H), 1.84-1.89 (m, 2H), 3.40 (t, $J = 6.82$ Hz, 2H), 3.45 (t, $J = 6.53$ Hz, 2H), 3.92 (t, $J = 6.62$ Hz, 2H), 3.96 (t, $J = 6.52$ Hz, 4H), 4.39 (s, 2H), 6.52 (s, 2H); $^{13}$C NMR (CDCl$_3$, 600 MHz): $\delta = 14.2, 22.8, 25.5, 26.2, 28.1, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 30.0, 30.4, 32.0, 32.9, 33.9, 69.2, 70.2, 73.2, 73.5, 106.2, 133.6, 137.7, 153.2; HRMS (EI): $m/z$ calcd for C$_{61}$H$_{115}$BrO$_4$H [M+H]$^+$: 991.8057; found: 991.8071.

**Carbazole Monomer (8)**

A flame-dried 50 mL flask was charged with NaH (0.160 g, 4.00 mmol) and purged with argon. 2,7-Dibromocarbazole (0.650 g, 2.00 mmol) was dissolved in 5 mL of anhydrous THF and transferred drop wise to the flask containing NaH. The mixture was allowed to stir at room temperature for 30 min. 4 (2.58 g, 2.60 mmol) was dissolved in 12 mL of THF and added to the reaction mixture slowly. The flask was then heated to 50 °C and allowed to stir for 5 days before the unreacted NaH was quenched with H$_2$O. The THF was removed from the mixture, and the product was extracted with DCM (4 x 40 mL), and the organic layer rinsed with H$_2$O (80 mL) and brine (100 mL) and then dried over Na$_2$SO$_4$. After filtration, the solvent was evaporated in vacuo, and the resulting solid was purified by column chromatography (a gradient of 0.5–2% EtOAc in hexanes was used as the eluent) to yield an off-white solid (2.48 g, 96%). $^1$H NMR (CDCl$_3$, 600 MHz): $\delta = 0.88$ (t, $J = 6.90$ Hz, 9H), 1.21-1.49 (m, 82H), 1.57-1.64 (m, 2H), 1.69-1.80 (m, 6H), 1.82-1.88 (m, 2H), 3.43 (t, $J = 6.52$ Hz, 2H), 3.93 (m, 6H), 4.20 (t, $J = 7.31$ Hz, 2H), 4.37 (s, 2H), 6.51 (s, 2H), 7.33 (dd, $J = 1.56$ and 8.25 Hz, 2H), 7.52 (d, $J = 1.40$ Hz, 2H), 7.89 (d, $J = 8.26$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 600 MHz): $\delta = 14.3, 22.8, 26.1, 26.3, 27.2, 28.9, 29.5,
29.6, 29.7, 29.8, 29.9, 30.5, 32.1, 43.4, 69.2, 70.3, 73.3, 73.5, 106.3, 112.1, 119.9, 121.4, 121.6, 122.7, 133.7, 137.8, 141.5, 153.3; MS (EI): m/z calcd for C$_{73}$H$_{121}$Br$_2$NO$_4$Na $[M + Na]^+$: 1258.75; found: 1258.8. HRMS (ESI+): m/z calcd for C$_{73}$H$_{122}$Br$_2$NO$_4$H $[M+H]^+$: 1234.7741; found: 1234.7773.

Polycarbazole (PC)

Ni(COD)$_2$ (0.211 g, 0.768 mmol) was added to a Schlenk flask and dissolved in 1.5 mL of dry toluene. 2,2'-bipyridyl (0.120 g, 0.768 mmol) was dissolved in a small amount of toluene and transferred to the reaction flask. Dry cyclooctadiene (0.094 mL, 0.768 mmol) and dry DMF (1.5 mL) were also added to the Schlenk flask, and the mixture was allowed to stir at 80 °C for 1 hour. Carbazole monomer 8 (0.500 g, 0.404 mmol) and bromobenzene (0.001 mL, 0.0101 mmol), previously dissolved in 4 mL of dry toluene, were then added to the Ni(COD)$_2$ solution and the mixture was left stirring at 80 °C for 4 days. The polymer mixture was precipitated into 400 mL of MeOH and the solid was collected over a 0.2 µm membrane. The solid polymer was rinsed with 300 mL of 0.2 M HCl solution, 250 mL of saturated EDTA/H$_2$O solution, 100 mL of H$_2$O and finally with 100 mL of MeOH to yield a bright yellow solid (0.381, 87.5%).

Poly(carbazole-co-fluorene (PC-PF)

To a Schlenk tube equipped with a stir bar was added 9,9-dioctylfluorene-2,7-bis(trimeth-yylene)borate (0.051 g, 0.091 mmol) and Cs$_2$CO$_3$ (0.578 g, 1.77 mmol). 8 was dissolved in a DMF-toluene mixture (9:1, 10 mL) and added to the Schlenk flask. The mixture was then bubbled with N$_2$ gas for 10 min, and further de-gassed with three freeze-pump-thaw cycles before back-filling the flask with Ar. A catalytic amount of Pd(PPh$_3$)$_4$ (0.0352 g, 0.0183 mmol) was added to the flask. The reaction
mixture was stirred at room temperature for 2 hours before being heated to 90 °C and allowed to stir for 24 hours. The solvent was removed and the resulting solid was dissolved in the minimum amount of THF and precipitated into MeOH. This mixture was filtered and rinsed with H₂O and MeOH. The residue was then re-dissolved in THF and centrifuged (5,000 rpm for 20 min) and the solution decanted. The polymer was precipitated into a 5% acetone-MeOH mixture and dried in a vacuum oven (50 °C) for 24 hours to yield a pale yellow solid (0.098 g, 72.4%).

Figure 2.14. UV-Vis absorption (solid lines) and emission (dashed lines) spectra for PC (red) and PC-PF (blue) in toluene.
Figure 2.15. Photograph of diluted PC-SWNT (left) and PC-PF-SWNT (right) dispersions in THF. The solutions in this photo were prepared from stock solutions that have been standing on the benchtop for over a month.
Figure 2.16. (a) SDBS-SWNT, (b) PC-SWNT in THF, (c) PC-PF-SWNT in THF, (d) PC-SWNT in toluene and (e) PC-PF-SWNT in toluene
Figure 2.17. Plots of photoluminescence intensity as a function of SWNT chiral angle for PC-SWNT and PC-PF-SWNT samples in THF (a) and toluene (b). For reference, the photoluminescence intensity as a function of SWNT chiral angle for SWNTs dispersed using SDBS is also provided (c).
Figure 2.18. Raman spectra of solid films of PC-SWNT and PC-PF-SWNT cast from toluene solutions, as well as SDBS-SWNT cast from D₂O recorded using an excitation wavelength of 785 nm (a). The RBM region of the same data is given in (b).
Figure 2.19. $^1$H (top) and $^{13}$C DEPT-q (bottom, CH$_2$ up) NMR spectra for side-chain compound 4.
Figure 2.20. $^1$H (top) and $^{13}$C (bottom) NMR spectra for monomer 8.
Table 2.3. Location of peak maxima for PC-SWNT.

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Table 2.4. Peak maxima for PC-PF-SWNT.

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2.5 References


Chapter 3

Selective Interactions of a High-Molecular-Weight Polycarbazole with Different Commercial Nanotube Samples

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Abstract

The ability of a poly(2,7-carbazole) to disperse three samples of commercially available single-walled carbon nanotubes (raw HiPCO, purified HiPCO, and CoMoCAT nanotubes) has been investigated. UV-Vis-NIR absorption spectroscopy, photoluminescence mapping, Raman spectroscopy, and atomic force microscopy were used to characterize the dispersions obtained. It was found that the polycarbazole preferentially interacted with semiconducting nanotubes and was efficient at dispersing smaller diameter (under 1.1 nm) carbon nanotubes. Larger diameter nanotubes could be dispersed to form stable suspensions in THF; however, it appeared that there were some small bundles present. It was found that annealing the purified HiPCO nanotubes at high temperature under an inert atmosphere greatly enhanced the ability of the polycarbazole to disperse the nanotubes and remove metallic species.
3.1 Introduction

Single-walled carbon nanotubes (SWNTs) are an important allotrope of carbon, possessing unique optical, electrical and mechanical properties. SWNTs have been proposed for potential applications in disparate fields, particularly in organic photovoltaics, thin-film transistors, and energy storage. Despite their advantageous properties, many problems still exist with commercially available samples. SWNT samples are generally polydisperse, containing tubes with varying lengths and diameters. Additionally, the presence of metal catalysts, amorphous carbon, and fullerene derivatives preclude widespread application of commercial SWNTs. While there are purification techniques that can be utilized to help remove some of these impurities, they contribute to the cost of preparing the bulk material, and can introduce defects or dopants on the nanotube surface, dramatically affecting their inherent optical and electrical properties. Thus, nondestructive purification of SWNTs is an area of intense research. In particular, conjugated polymers have shown great promise in their ability to not only disperse SWNTs in various aqueous and organic solvents via noncovalent interactions, but also to purify them. A wide variety of conjugated polymer structures have been studied, including derivatives of polyphenylene vinylenes, polyphenylene ethynlenes, polyfluorenes, and polythiophenes. Variations of the polymer backbone, sidechains, polymer molecular weight, and the solvent used have all been shown to significantly impact the quality of nanotube dispersions. Previous work has shown the potential of polyfluorenes, such as poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO), to selectively disperse a subset of semiconducting SWNTs.
Recent studies in our group as well as others have shown the ability of poly(2,7-carbazole)s to disperse SWNTs in organic solvents.\textsuperscript{28-31} Interest in polycarbazoles\textsuperscript{32,33} stems from their potential applications in organic photovoltaics,\textsuperscript{34,35} light-emitting diodes,\textsuperscript{36} thin-film transistors,\textsuperscript{37} and electrochromic cells.\textsuperscript{38} Thus, composite materials combining the properties of both polycarbazoles and SWNTs represent a potentially interesting class of materials.

Some of the polycarbazole-SWNT complexes previously reported have suffered from poor solubility or complicated dispersion procedures.\textsuperscript{39} We have previously demonstrated that a poly(2,7-carbazole) possessing a solubilizing group consisting of a 3,4,5-tris(hexadecyl-oxy) phenyl moiety, separated from the polymer backbone by an alkyl spacer chain, is effective in dispersing raw HiPCO SWNTs within organic solvents using a relatively facile procedure.\textsuperscript{28} We found that the solutions formed were very stable, and that changing the solvent did not have a significant effect on the chiralities of SWNTs dispersed.

In this work we further investigate the ability of this poly(2,7-carbazole) to disperse raw HiPCO SWNTs, as well as with two other commercially available SWNT samples: purified HiPCO and CoMoCAT. These three SWNT samples were chosen as they are among the most common SWNT samples investigated in the literature. We demonstrate that this polymer preferentially interacts with low-diameter semiconducting SWNTs when mixed with raw HiPCO or CoMoCAT SWNTs. Although it is also able to form stable dispersions with larger-diameter purified HiPCO SWNTs, these dispersions contain bundles in which metallic species could be trapped. Interestingly, a simple annealing process allowed for a much more efficient dispersal of the purified HiPCO nanotubes by the polymer, facilitating a more effective removal of the metallic species. Annealing of the purified HiPCO sample also restored some of
the optical properties of the nanotubes in the polymer-SWNT dispersions.

3.2 Results and Discussion

3.2.1 Preparation of Complexes

Figure 3.1. Structure of the poly(2,7-carbazole) (PC) used in this study.

The full procedure for preparing polymer-SWNT dispersions can be found in the Supporting Information. Briefly, 15 mg of the polycarbazole (PC, Figure 3.1) was dissolved in 20 mL of THF, to which 10 mg of SWNT powder was added. The polymer-SWNT mixtures were sonicated in a bath sonicator at 0 °C for 45 min, followed by centrifugation at 8346g for 15 min. The soluble supernatant was removed and filtered through a 0.2-μm PTFE membrane to remove excess polymer. The black polymer-SWNT buckypaper was peeled away from the membrane and re-suspended in 15 mL of THF by sonication, followed by a second centrifugation step (8346g for 10 min) to ensure that the polymer-SWNT material was successfully re-suspended. The dispersions with excess polymer removed were stable on the benchtop for months with no observable precipitation of SWNTs. Dispersions of all three SWNT samples were also prepared using SDBS in D$_2$O following previously reported methodologies.25
3.2.2 Absorbance

Figure 3.2. UV-Vis-NIR absorption spectra for PC (red) and SDBS (black) dispersions of (a) raw HiPCO, (b) CoMoCAT and (c) purified HiPCO SWNTs. The SDBS-rHiPCO spectrum has been multiplied by a factor of 2, while the SDBS-CoMoCAT and SDBS-pHiPCO spectra have been multiplied by a factor of 3.

UV-Vis-NIR absorbance measurements for all three polymer-SWNT supramolecular complexes, as well as for the three corresponding SDBS dispersions, can be found in Figure 3.2. All three polymer dispersions gave rise to absorbance features that were more intense than those observed with the corresponding SDBS samples. The absorption spectrum for PC-rHiPCO (Figure 3.2a) displays multiple strong, well-resolved fine features from the van Hove transitions of various chiralities of SWNTs. Sharp absorbance peaks are seen in the semiconducting E_{11} and E_{22} regions from approximately 830 to 1600 and 600 to 800 nm, respectively.\(^{40}\) Analysis of the metallic E_{11} region from 440 to 645 nm is made difficult by the presence of PC (which has a maximum absorbance at 393 nm); however, it appears that there are fewer peaks present in this range relative to the SDBS-rHiPCO dispersion, suggesting removal of metallic SWNTs. In addition, very little background absorption is observed with PC-rHiPCO. Broad background absorbance in SWNT absorption spectra arises from a complex combination of effects, including spectral congestion due to the presence of multiple chiralities, different nanotube lengths, plasmonic absorption of SWNTs and
carbonaceous impurities, bundling of tubes, defects in the nanotube structure, and the presence of metallic SWNTs. Due to the significant lack of broad, exponential absorbance in the PC-rHiPCO sample we can further deduce that we are removing a large amount of the impurities, bundles, and metallic species through the interaction with PC. The small amount of remaining background absorption arises from spectral congestion due to the presence of multiple semiconducting chiralities. This spectral overlap, combined with a red-shift in the locations of peak maxima that arises in conjugated polymer-SWNT systems, makes exact determination of the various chiralities complicated.

The absorption spectra for the CoMoCAT samples (Figure 3.2b) are much less congested as the CoMoCAT material contains fewer species of SWNTs compared to raw HiPCO samples. In correlation with PC-rHiPCO, strong, sharp transitions are present in the PC-CoMoCAT absorption spectrum and the lack of a broad, exponential absorbance background for PC-CoMoCAT also seems to imply that the polymer is again preferentially exfoliating semiconducting SWNTs, while removing bundles and impurities.

Unlike the PC-rHiPCO and PC-CoMoCAT samples, the PC-pHiPCO SWNT dispersion did not show any intense fine features, despite visually appearing to be the most concentrated of the samples (see Supporting Information Figure 3.11). Only low-intensity features were observed in the polymer-nanotube absorption spectrum, along with an intense, broad background, indicating the presence of bundles. Similar features are also present in the SDBS-pHiPCO spectrum, suggesting an inherent problem with dispersing the purified HiPCO SWNTs. Modifications in the ratio of polymer (or SDBS) to SWNTs and variations in the sonication and centrifugation times did not yield better results.
While the exact purification procedures for pHiPCO SWNTs are not available, they likely involved treatment with concentrated acids at elevated temperatures. Previous studies have shown that this type of nanotube purification can result in degradation of optical properties compared to raw starting materials by the introduction of small defects along the tube surface.\textsuperscript{42,43} Acid treatments also have the potential to shorten SWNTs, which can have a significant effect on the observed optical properties.\textsuperscript{44}

### 3.2.3 Photoluminescence

Photoluminescence (PL) mapping is a powerful technique that allows for the characterization of semiconducting SWNT species that are present in a mixture.\textsuperscript{45} The presence of SWNT bundles and metallic SWNTs both cause a severe reduction in the observed fluorescence by quenching through nonradiative pathways.\textsuperscript{46} The identity of the various semiconducting chiralities present can be determined by overlaying the expected excitation and emission energies from experimental Kataura plots\textsuperscript{47} on the 2D contour fluorescence plots.

The PL maps for PC-rHiPCO, PC-CoMoCAT, and PC-pHiPCO are given in Figure 3.3(a-c), respectively. The presence of multiple fluorescence peaks in Figure 3.3a from several semiconducting SWNT species confirms that the PC-rHiPCO SWNT sample contains a variety of semiconducting chiralities. The relative intensity of each emission maximum can be found and divided by the most intense peak for each individual map to give an estimate of the relative amount of each semiconducting chirality present. Such an analysis does not consider the PL efficiency for individual chiralities, which may be affected by tube diameter, chirality, modulus, length, and the presence of defects.\textsuperscript{41,48–50} No correction factors were applied to the data, providing a broad
Figure 3.3. PL maps of (a) PC-rHiPCO, (b) PC-CoMoCAT, and (c) PC-pHiPCO. Expected locations of semiconducting chiralities have been plotted from literature values. 47
estimate of the true distribution of semiconducting species. Specifically, the (6,5) chirality was found to give rise to the most intense fluorescence peak for the PC-rHiPCO dispersion (Figure 3.2a). Similar analysis was also performed on SDBS suspensions of the three SWNT samples (Supporting Information Figure 3.12) to allow comparison with the polymer samples. Tables of the relative intensities of the peak maxima can be found in the Supporting Information, and are depicted in bar graphs with relation to nanotube diameter in Figure 3.4. As can be seen in Figure 3.4(a,b), fewer semiconducting chiralities are present in PC-rHiPCO compared to SDBS-rHiPCO, and it appears that smaller diameter SWNTs are preferentially dispersed by the polymer.

Figure 3.4. Bar graphs depicting the relative intensities of fluorescence of various semiconducting SWNT chiralities as determined from PL maps, in relation to nanotube diameter for (a) PC-rHiPCO, (b) SDBS-rHiPCO, (c) PC-CoMoCAT, and (d) SDBS-CoMoCAT.

Strong fluorescence signals were also observed for the PC dispersion of CoMoCAT SWNTs, shown in Figure 3.3b. The CoMoCAT sample was already enriched in the (6,5) chirality, so very little difference can be noted between the PC and SDBS dispersions, and the bar graphs in Figure 3.4(c,d), corresponding to these two samples, show the same trend.
Neither the SDBS nor the polymer dispersion of purified HiPCO SWNTs produced a clean PL map, as can be observed in Supporting Information Figure 3.12 and Figure 3.3c, respectively. Although few larger diameter chiralities can be seen in the SDBS dispersion, most notably the (9,7) and (10,5) SWNTs, the intensity of fluorescence was so low that background noise made analysis of the plots difficult. Results with PC-pHiPCO were worse, making it impossible to identify any semiconducting chiralities. These maps are consistent with the presence of bundles, metallic species, or defects in the nanotube structure, agreeing with what was observed in the UV-Vis-NIR absorption spectra for these samples.

### 3.2.4 Raman

![Raman spectra](image)

Figure 3.5. Raman spectra for samples containing raw HiPCO SWNTs excited at (a) 785 nm and (b) 514 nm. Insets in (a) and (b) show the expanded RBM regions. Residue refers to the nanotube material left in the bottom of the centrifuge tube after decantation of the polymer-SWNT dispersion.

Raman spectroscopy was performed on solid film samples using 785 and 514 nm excitation wavelengths. Although more than two laser excitation energies are required
to generate an accurate picture of all the chiralities present in the samples, experiments with these two wavelengths can indicate the presence of metallic nanotubes, as well as the relative degree of bundling. Raman samples of the three polymer-SWNT dispersions were prepared by drop-casting the THF solutions onto silicon wafers. Solid films of the three nanotube samples before functionalization with polymer were obtained by short sonication of each nanotube powder in CHCl₃, followed by depositing a few drops onto a silicon wafer. To corroborate our analysis of the polymer-SWNT dispersions, the residue left over from centrifugation of the polymer-SWNT samples was also studied. After washing this residue to remove any free polymer, the remaining impure nanotube material was suspended in THF and drop-cast onto silicon wafers. Raman spectra for the polymer-SWNT samples with 514 nm excitation could only be obtained after removal of excess polymer, as the polycarbazole exhibits intense fluorescence when excited at this wavelength. All spectra were normalized to the G-band and offset for clarity.

Figure 3.6. Raman spectra for samples containing CoMoCAT SWNTs excited at (a) 785 nm and (b) 514 nm. Insets in (a) and (b) show the expanded RBM regions; PC-CoMoCAT and residue spectra have both been multiplied by a factor of 3 in the inset in (b).
The Raman data for the raw HiPCO SWNT sample is given in Figure 3.5. Intense, broad fluorescence peaks from the SWNTs were observed from approximately 1200 to 3000 cm\(^{-1}\) in the PC-rHiPCO sample excited at 785 nm, suggesting that the SWNTs remain effectively debundled by the polymer even after removal of the solvent. Strong SWNT fluorescence was also observed in the PC-CoMoCAT Raman spectrum when the sample was excited at 785 nm (Figure 3.6a), but not for PC-pHiPCO (Figure 3.7a). The lack of fluorescence for PC-pHiPCO could be due to bundling of the nanotubes, the presence of metallic species, or chemical damage, but it is also possible that the chiralities of SWNTs that give rise to the fluorescence bands in the raw HiPCO and CoMoCAT samples are not present in the PC-pHiPCO dispersion.

Figure 3.7. Raman spectra for samples containing purified HiPCO SWNTs excited at (a) 785 nm and (b) 514 nm. Insets in (a) and (b) show the expanded RBM regions.

The G-band, located around 1600 cm\(^{-1}\), can be used to identify the electronic nature of the SWNTs present in a sample. The G-band arises in all graphitic structures, but in carbon nanotubes it splits into two modes, a \(G^+\) mode at higher frequency and a \(G^-\) mode at lower frequency.\(^{51}\) In semiconducting SWNTs, both the \(G^+\) and \(G^-\) modes have Lorentzian line shapes, while in metallic SWNTs, the \(G^+\) has a Lorentzian
shape, but the G\(^-\) is broadened with a Breit-Wigner-Fano (BWF) line shape.\(^{52}\) Analysis of the G\(^-\) frequency in our polymer-SWNT samples relative to the as-received SWNT material can give an estimate of the amount of metallic SWNT material that has been removed from the polymer-SWNT samples. At 514 nm excitation, changes in the G\(^-\) line shape can be observed in the PC-SWNT Raman spectra compared to the spectra of as-received SWNTs. As can be seen in Figure 3.5b, the broad peak centered at 1545 cm\(^{-1}\) in the raw HiPCO SWNT spectrum is completely removed in the PC-rHiPCO spectrum, but is still present in the spectrum of the residue left over from centrifugation. These data confirm our hypothesis from the UV-vis-NIR absorption data and PL maps that PC preferentially interacts with semiconducting SWNTs over metallic SWNTs. A similar trend can be observed in the polymer-CoMoCAT sample excited at 514 nm (Figure 3.6b). Interestingly, the G\(^-\) band has been almost completely removed in both of these polymer-nanotube samples at both excitation wavelengths. The Raman spectrum for PC-pHiPCO at 514 nm (Figure 3.7b) still shows a slight broadening of the G\(^-\) peak, although it is much less intense compared to the starting material and residue left after centrifugation. This indicates that some metallic SWNTs are still present in the polymer mixture, possibly stuck in bundles.

The PC-SWNT Raman scans at 514 nm all appear to have a high-frequency shoulder on the G\(^+\) band, located at 1620 cm\(^{-1}\). This peak does not appear in any of the SWNT spectra, but its presence in all the polymer samples leads us to believe it arises from the polycarbazole. However, this could not be confirmed by measuring the Raman spectrum of free PC because of the strong fluorescence it exhibits when excited at this wavelength.

Another region of interest in the Raman spectra is the radial breathing mode (RBM), from 100 – 400 cm\(^{-1}\).\(^{53}\) The frequency of the peaks in the RBM region
have an inverse dependence on SWNT diameter, and allow for identification of the various SWNT species present. The tube environment can have a significant impact on which nanotubes are in resonance with a particular excitation wavelength, making analysis of polymer-coated SWNTs challenging. However, several informative features can be discerned. In particular, the peak located at 265 cm$^{-1}$ in the raw HiPCO spectrum, excited at 785 nm, arises from the (10,2) SWNT. The (10,2) nanotube is not in resonance at 785 nm, and only appears in the RBM at this excitation wavelength if it is bundled. The intensity of this bundling peak can be used as a qualitative measure of the extent of bundling in our PC-SWNT samples. The inset in Figure 3.5a shows a significant decrease in the bundling peak for the PC-SWNT sample compared to the raw HiPCO powder and the residue from centrifugation. This indicates that, even in the solid state, there are very few bundles of SWNTs present in the PC-rHiPCO sample.

For the purified HiPCO sample (Figure 3.7), the RBM region for PC-pHiPCO at 785 nm excitation (inset, Figure 3.7a) shows the presence of a small peak at 265 cm$^{-1}$. Comparing the relative heights of the peak at 265 cm$^{-1}$ with the peak at approximately 214 cm$^{-1}$ for the PC-pHiPCO and purified HiPCO spectra shows only a slight depression of the bundling peak in the polymer-functionalized sample, indicating that a significant degree of bundling is still present.

Further information can be obtained by considering the other peaks present in the RBM region, particularly for the spectra obtained with 514 nm excitation. The raw HiPCO SWNT powder (inset, Figure 3.5b) shows the presence of multiple metallic chiralities at this excitation wavelength, such as the (8,5), (9,3) and (12,0) at approximately 260, 272, and 247 cm$^{-1}$, respectively. These peaks are not present in the PC-rHiPCO spectrum, but are still present in the residue after centrifugation,
further confirming the removal of metallic species from our polymer sample. Similarly, the features at 270 cm$^{-1}$ in the CoMoCAT SWNT spectra (inset, Figure 3.6b) that correspond to the (8,5) and (9,3) metallic SWNTs, are not present in the PC-CoMoCAT dispersion, but remain in the residue from centrifugation. Intense features are observed in all three RBM spectra at 514 nm for the purified HiPCO samples (inset, Figure 3.7b), such as metallic (8,5) and (12,0) species (at 264 and 246 cm$^{-1}$, respectively),\textsuperscript{54} validating the analysis of the G$^-$ band for this sample.

### 3.2.5 Atomic Force Microscopy

![AFM images](image)

Figure 3.8. Representative AFM images of (a) PC-rHiPCO, (b) PC-CoMoCAT, and (c) PC-pHiPCO. Dashed lines represent the location of the height profile given below each image. Black scale bars correspond to 500 nm.

Tapping-mode atomic force microscopy (AFM) analysis was performed on thin films of each PC-SWNT sample, prepared by spin-coating dilute polymer-nanotube dispersions onto mica. Representative images from these studies can be found in Figure 3.8. The PC-rHiPCO and PC-CoMoCAT images show the presence of long, filamentous structures with diameters ranging from approximately 1 – 4 nm and...
1–6 nm, respectively. The smallest features correspond to individual polymer-coated SWNTs, confirming results from absorbance, fluorescence and Raman spectroscopy. The larger features arise from small bundles of polymer-coated SWNTs, which can form after removal of solvent.

The AFM image for PC-pHiPCO in Figure 3.8c displays much larger features compared to PC-rHiPCO and PC-CoMoCAT. The heights of polymer-SWNT features for PC-pHiPCO are in the range of 2–10 nm. Combined with the results from absorbance, fluorescence, and Raman experiments, we believe these features arise from bundles of SWNTs that are coated in polymer. Such features would explain the loss of fine structure in the optical spectra.

3.2.6 Annealing Studies

We hypothesize that the lack of optical features for the purified HiPCO SWNT samples could be due to the presence of defects introduced during the purification process, including carboxylic acid and hydroxyl functional groups or small molecule dopants along the surface of the SWNTs. To determine if this is the case, we annealed a sample of the purified HiPCO material by heating it to 600 °C for 90 minutes under an atmosphere of argon. This treatment is known to remove defects and allow nanotubes to re-form their pristine structures.

Dispersions of annealed purified HiPCO (anpHiPCO) SWNTs with PC and SDBS were prepared following the protocols previously discussed with minor modifications (see Supporting Information), and excess polymer was removed by filtration. The UV-Vis-NIR absorption spectrum of SDBS-anpHiPCO (Figure 3.9a) roughly resembles the absorption spectrum of SDBS-pHiPCO (Figure 3.2c). However, upon interaction with PC, a dramatic difference can be observed for PC-anpHiPCO compared to
PC-pHiPCO. After annealing, the van Hove transitions have been partially restored for the purified HiPCO sample, as indicated by the more defined features in the semiconducting $E_{11}$ and $E_{22}$ regions for PC-anpHiPCO (Figure 3.9a). Although there is an improvement in the absorption features, some broad background absorbance is still present in the PC-anpHiPCO spectrum, indicating that bundles and/or metallic SWNTs remain.

Interestingly, the PL map of PC-anpHiPCO (Figure 3.9b) is much more defined than the PL map for PC-pHiPCO (Figure 3.3c). The signal-to-noise for PC-anpHiPCO is enhanced compared to PC-pHiPCO, allowing for determination of the chiralities of semiconducting SWNTs present. The ability to obtain a PL map indicates that the SWNTs were sufficiently debundled and/or the majority of the metallic species were removed. The intensity for the PC-anpHiPCO map is still low compared to the other polymer-SWNT PL maps, and there is a noticeable broadening of a few of the peaks, again indicating that not all the bundles have been completely exfoliated. A map of SDBS-anpHiPCO was also attempted (Supporting Information...
Figure 3.10. Raman spectra for samples containing annealed purified HiPCO SWNTs excited at (a) 785 nm and (b) 514 nm. Insets in (a) and (b) show the expanded RBM regions.

Figure 3.12), and while we were able to identify a few more species of semiconducting SWNTs compared to SDBS-pHiPCO, we did not see the same improvement in the signal-to-noise as we did for PC-anpHiPCO.

Figure 3.10 depicts Raman results for the annealed purified HiPCO material and PC-anpHiPCO, as well as the residue left over from centrifugation. The RBM region of the samples excited at 785 nm (inset, Figure 3.10a) is similar to that of Figure 3.7a; however, the peak at approximately 265 cm$^{-1}$ is of lower intensity for PC-anpHiPCO. This indicates that fewer bundles are present in the PC-anpHiPCO sample. However, it should be noted that the (10,2) chirality does not have a significant fluorescence peak in Figure 3.9b, so the peak depression could also be due to a lower concentration of the (10,2) chirality in the polymer dispersion. AFM analysis of the PC-anpHiPCO sample (Supporting Information Figure 3.14) showed that, although features with heights in the range of 10 nm are still observable, there was an increase in the number of structures with heights lower than 5 nm, relative to the corresponding sample.
Table 3.1. XPS Data Acquired for the Original Purified HiPCO SWNTs and the Annealed Sample

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<tr>
<td>anpHiPCo</td>
<td>93.8±4.7</td>
<td>6.2±0.3</td>
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before annealing. This indicates an increase in polymer-induced debundling of the nanotubes after annealing, in agreement with the Raman data. Notable changes can also be observed in the RBM regions of the Raman spectra excited at 514 nm when comparing samples before and after annealing. The broad peaks, corresponding to metallic SWNTs, present in the RBM at this excitation wavelength disappear after annealing, corroborating what was observed with the raw HiPCO and CoMoCAT SWNT samples.

Removal of metallic species from PC-anpHiPCO is further confirmed from analysis of the G− peak in the spectrum obtained at 514 nm (Figure 3.10b). The annealed, purified HiPCO SWNT spectrum shows a slight increase in the intensity of the G− band when compared to the nanotubes before annealing. Despite this, a significant decrease in the BWF line shape was found with the PC-anpHiPCO sample. However, the ratio of D to G band heights ($I_D/I_G$) before and after annealing remained constant, with a value of 0.04. This indicates that the significant changes observed in our polymer-functionalized annealed SWNT samples do not result from removal of sp³-carbon defects on the surface of the nanotube.

From these studies, it is clear that thermal annealing of purified HiPCO SWNTs is important for improvement of their dispersability using the PC polymer (and, possibly, other conjugated polymers). After annealing, the interaction between PC
and the purified HiPCO SWNTs seems to be more selective, allowing for better removal of metallic species. This allowed spectroscopic analysis of dispersed SWNTs to be carried out. The observed selectivity occurred despite the polymers preference for low-diameter SWNTs, and demonstrates the remarkable selectivity of the polycarbazole structure for semiconducting SWNTs. However, the exact origin of the improved dispersability and selectivity in the presence of PC is unclear. The initial hypothesis that surface defects are removed by annealing was not borne out in the Raman data, where a decrease of $I_D/I_G$ would be expected if defects are being removed. Alternatively, nanotube bundling in the purified SWNTs could be promoted by strongly interacting functional groups introduced on the nanotube surface, such as carboxylate or nitro-functionalities. To investigate this possibility, we performed X-ray photoelectron spectroscopy (XPS) to gain quantitative analysis of the elemental composition of the pHiPCO sample before and after annealing. The XPS data show that, upon annealing, the O1s signal decreases from 8.1 to 6.2%, while the C1s signal does not change appreciably (Table 3.1 and Supporting Information Figure 3.15). The observed small increase in the C1s signal is lower than the experimental error in the measurement. This suggests that oxygen-containing defects, such as hydroxyl and carboxylate groups, are being eliminated to some extent by the annealing process. No trace of nitrogen could be observed in either sample, indicating that nitrogen-containing defects (such as nitro functionalities) were not present in the purified SWNTs sample. We therefore speculate that the oxygen-containing functional groups present on the pHiPCO SWNTs impede the supramolecular interaction of this material with PC, preventing efficient exfoliation of the nanotubes. Upon removal of these groups through the annealing process, the polymer-SWNT interaction is enabled, allowing efficient dispersion of individual polymer-wrapped SWNTs. However,
the exact nature of these processes remains unclear.

This study has important implications on the characterization of polymer-SWNT samples, as commercial purified SWNTs are often investigated. Recent reports have studied the use of a combination of acid-purification followed by dispersion of the purified SWNT materials with conjugated polymers.\textsuperscript{60} If optical absorbance spectroscopy and PL mapping are to be used as methods to characterize the resulting materials, care must be taken to ensure that the true representation of chiralities of SWNTs present can still be determined. We suggest that thermal annealing is an important step in the analysis of such materials.

### 3.3 Conclusions

This study demonstrates the efficacy of PC to solubilize semiconducting SWNTs from three commercial samples consisting of a mixture of chiralities, tube diameters and lengths. The interaction between PC and the different SWNT samples is strong, and produces stable dispersions after a relatively mild dispersion protocol. UV-Vis-NIR, PL, and Raman spectroscopy all indicate that metallic SWNT species can be removed from both raw HiPCO and CoMoCAT nanotube samples after dispersion with PC. Additionally, dispersions appeared to favor exfoliation of smaller diameter SWNTs. Although it formed a stable suspension, the PC-pHiPCO SWNT sample contained small bundles of SWNTs in which some metallic nanotubes were trapped. Interestingly, a simple annealing of the purified HiPCO SWNT sample before mixing with the polymer allowed for more efficient interaction of PC with the nanotubes, resulting in more effective removal of the metallic species. The incomplete removal of bundles of SWNTs seems to suggest that PC is not as efficient at dispersing large diameter SWNTs. Our results indicate that care must be taken in using purified
SWNT samples in polymer dispersions to guarantee that the true composition of polymer-SWNT systems can be determined.

3.4 Supporting Information

3.4.1 General

The synthesis of the poly(2,7-carbazole) (PC; $M_n = 61$ kDa, $M_w = 106$ kDa, PDI = 1.7) used in this study has been reported previously. Three commercially available samples of SWNTs were used: Raw HiPCO SWNTs (NanoIntegris, batch RO-513, 12.3 wt% solid), Purified HiPCO SWNTs (Carbon Nanotechnologies Inc., batch P0347) and CoMoCAT SWNTs (SWeNT, SG65, batch 000-0035). THF was purchased from Caledon Laboratories, and $D_2O$ was purchased from Cambridge Isotope Laboratories Inc., and both were used without further purification. SDBS was purchased from Sigma Aldrich.

Sonication was performed using a Banson Ultrasonics B1510 bath sonicator or QSonica Ultrasonic Processor cup horn sonicator (average power 100 W). Centrifugation of the polymer samples was performed using a Beckman Coulter Allegra X-22 centrifuge, while the SDBS dispersions were centrifuged on a Beckman Coulter OptimaMax 130K centrifuge. Absorbance measurements were performed on a Cary 6000 spectrometer in dual beam mode, using matched 10 mm quartz cuvettes. Fluorescence spectra were obtained with a Jobin-Yvon SPEX Fluorolog 3.22 equipped with 450 W Xe lamp and an InGaAs detector, also using a 10 mm quartz cuvette. Slit widths for both excitation and emission were set to 10 nm band-pass, and correction factor files were applied to account to instrument variations. Photoluminescence maps were obtained at 25 °C. Raman spectra were collected with a Renishaw InVia...
Laser Raman spectrometer, equipped with a 25 mW argon ion laser (514 nm, grating 1200 L/mm), a 300 mW Renishaw laser (785 nm, grating 1200 L/mm). Laser intensity at 514 nm was set to 50% for CHCl$_3$ solutions and residue samples, and 10% for polymer-SWNT samples. For spectra obtained at 785 nm, laser intensity was set to 1% for CHCl$_3$ solutions and residue samples from centrifugation, and 0.5% for polymer-SWNT samples. Tapping mode atomic force microscopy was performed using a Digital Instruments NanoScope IIIa Multimode AFM using standard tips, with a scan rate of 1.5 Hz. AFM samples were prepared by spin coating (3500 rpm for 30 sec) a few drops of dilute polymer-SWNT dispersions on freshly cleaved mica. Thermal annealing of purified HiPCO SWNTs was performed using a TA Instruments Q50 thermogravimetric analyzer under Ar atmosphere. Multiple annealings were done to ensure reproducibility of results. X-ray photoluminescence spectroscopy was performed using a Physical Electronics (PHI) Quantera II spectrometer equipped with an Al anode source for X-ray generation and a quartz crystal monochromator for focusing the generated X-rays. A monochromatic Al K-α X-ray (1486.7 eV) source was operated at 50 W 15 kV. The system base pressure was no higher than 1.0 x 10$^{-9}$ Torr, with an operating pressure that did not exceed 2.0 x 10$^{-8}$ Torr. A pass energy of 280 eV was used to obtain survey spectra and 26 eV pass energy was used for the high resolution C1s and 55 eV pass energy was used for the O1s high resolution scans. All spectra were obtained at 45° take off angles, and used a dual beam charge compensation system for neutralization of all samples. The instrument was calibrated using a sputter-cleaned piece of Ag, where the Ag 3d$_{5/2}$ peak had a binding energy of 368.3 ± 0.1 eV and full width at half maximum for the Ag 3d$_{5/2}$ peak was at least 0.52 eV. Data manipulation was performed using PHI MultiPak Version 9.4.0.7 software.
3.4.2 Preparation of Composites

Polymer-SWNT composites were prepared by first dissolving approximately 15 mg of dry polymer powder in 20 mL of THF. Around 10 mg of SWNT powder was then added and the mixture was sonicated in a bath sonicator chilled with ice for 45 min, followed by immediate centrifugation at 8,346 g for 15 min. The resulting supernatant was carefully removed from the centrifuge tubes and filtered through a 0.2 μm polytetrafluoroethylene (PTFE) membrane to remove excess polymer. The polymer-SWNT samples were washed with solvent until there was no observable fluorescence from the filtrate, as determined using a UV lamp (365 nm). The residue left on the membrane was then re-dispersed in 15 mL of THF by sonication for 20 min in a bath sonicator chilled with ice. To ensure the stability of the excess-polymer removed samples, centrifugation was performed again at 8,346 g for 10 min. No flocculation was observed after this second centrifugation for the PC-rHiPCO and PC-CoMoCAT dispersions, while a small amount of precipitation occurred with PC-pHiPCO and PC-anpHiPCO. All polymer-SWNT solutions were stable for months on the benchtop after removal of excess polymer.

The residues left over from the first centrifugation were also collected and filtered over 0.2 μm Teflon membranes to remove excess polymer. The SWNT residues were then dispersed in THF by sonication for 20 min in a bath sonicator chilled with ice and used to prepare solid films for Raman studies. It should be noted these residues could also contain small amounts of the solubilized polymer-SWNT complexes as complete removal of the supernatant was not always possible.

Dispersions of all four SWNT samples were also prepared in sodium dodecylbenzenesulfonate (SDBS) following previously reported procedures, with a few minor modifications. SDBS dispersions were prepared using a ratio of 5 mg of SWNTs to 350
mg of SDBS in 35 mL of D$_2$O. The solutions were all sonicated using a cuphorn sonicator for 20 minutes, followed by bath sonication (chilled with ice) for 1 hour except for SDBS-anpHiPCO which required cup horn sonication for 3.5 hours, followed by bath sonication for 2 hours. The SDBS dispersions of the three commercial samples required centrifugation at 45,000$g$ for 4 hours at 15 °C, while the SDBS dispersion of annealed purified HiPCO SWNTs required a shorter (2.5 hour) centrifugation time.

Figure 3.11. Photograph of polymer solutions in THF. From left to right: PC (no SWNTs), PC-rHiPCO, PC-CoMoCAT, PC-pHiPCO, and PC-anpHiPCO.
Figure 3.12. PL maps for (a) SDBS-rHiPCO, (b) SDBS-CoMoCAT, (c) SDBS-pHiPCO and (d) SDBS-anpHiPCO dispersions. Expected locations of semiconducting chiralities have been plotted from literature.47
Figure 3.13. Bar graph depicting the relative intensities of semiconducting SWNT species in PC-anpHiPCO in relation to nanotube diameter (as determined from PL map).

Figure 3.14. AFM image of PC-anpHiPCO. The dashed lines represent the location of the height profiles, and the black scale bar corresponds to 500 nm.
Figure 3.15. XPS data for (a) the original purified HiPCO SWNTs (pHiPCO); and (b) the annealed purified HiPCO SWNTs (anpHiPCO).
Table 3.2. Percent relative abundance of the semiconducting chiralities present in SDBS-rHiPCO and PC-rHiPCO, arranged in order of increasing diameter.

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<th>$(n,m)$</th>
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Table 3.3. Percent relative abundance of the semiconducting chiralties present in SDBS-CoMoCAT and PC-CoMoCAT, arranged in order of increasing diameter.

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Table 3.4. Percent relative abundance of the semiconducting chiralties present in PC-anpHiPCO in THF, arranged in order of increasing diameter.

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3.5 References


Chapter 4

The Effect of Molecular Weight on the Separation of Semiconducting Single Walled Carbon Nanotubes using Poly(2,7-carbazole)s

This chapter has been reprinted with permission from Journal of Polymer Science Part A: Polymer Chemistry. Submission date: April 27th, 2015. Accepted for publication on May 23rd, 2015; published online on June 19th, 2015. Nicole A. Rice, Ayyagari V. Subrahmanyam, Scott E. Laengert, and Alex Adronov. DOI: 10.1002/pola.27715. Copyright (2015) Wiley Periodicals, Inc.

Nicole Rice and Ayyagari Subrahmanyam were both involved in the planning of this study. Nicole Rice, Ayyagari Subrahmanyam and Scott Laengert all synthesized the poly(2,7-carbazole) monomers, and Ayyagari Subrahmanyam prepared all the polymers except the PC₅ polymer which was synthesized by Nicole Rice. All polymer-SWNT composites were prepared and characterized by Nicole Rice.
Abstract

The use of selective interactions between conjugated polymers and single-walled carbon nanotubes (SWNTs) has emerged as a promising method for the separation of nanotubes by electronic type. Poly(2,7-carbazole)s have been shown to preferentially interact with semiconducting SWNTs, however a detailed investigation of polymer parameters, such as molecular weight, has not been performed. We have prepared seven different molecular weights of a poly(2,7-carbazole), from short chain oligomers to high molecular weight polymers, and have investigated their effectiveness for dispersion of semiconducting SWNTs. While all polymer chain lengths were able to efficiently exfoliate carbon nanotube bundles using a mild dispersion protocol, only polymers above a certain threshold molecular weight ($M_n \sim 30$ kDa) were found to exhibit complete selectivity for semiconducting nanotubes. Additionally, we found the quality of separation to be strongly dependent on the ratio of polymer to SWNT. Contrary to previous reports, we have found that an excess of poly(2,7-carbazole) leads to incomplete removal of metallic carbon nanotubes.
4.1 Introduction

Single-walled carbon nanotubes (SWNTs) are unique, one-dimensional nano-materials that have attracted significant attention over the past two decades. Their structural and opto-electronic properties afford them tremendous potential for a variety of applications, including molecular electronic devices, thin-film transistors, sensors, organic photovoltaics and electrodes for flexible electronics. Despite significant progress in the synthesis and understanding of the fundamental intrinsic properties of SWNTs, all current SWNT synthesis methods produce a mixture of metallic and semiconducting SWNTs, presenting a major hurdle to large-scale industrial applications of these nano-materials. Several purification techniques, including density-gradient ultracentrifugation (DGU), agarose gel filtration, and DNA-assisted dispersion have all been shown to be extremely effective at purifying and isolating small distributions of SWNT chiralities, but are limited in their scalability.

Conjugated polymers have gained appreciable attention recently as a viable option for the purification of raw SWNTs on a bulk scale. The diverse synthetic methodologies and monomers available for the preparation of conjugated polymers allows for control over polymer backbone and side-chain composition, which modifies the three dimensional shape, conformation, and electronic properties of the final macromolecule. By modifying these properties, it is possible to design structures that exhibit some degree of selectivity in their interactions with specific SWNT chiralities. Several conjugated polymer families, including polyfluorenes, polythiophenes, polycarbazoles and poly(phenyl acetylenes) have been exploited
to purify SWNTs, with a preference in many cases toward the dispersion of semiconducting species.\textsuperscript{36} A significant challenge with using conjugated polymers is that the majority of these polymers are prepared through step-growth polymerization techniques, which can lead to significant batch-to-batch variability in terms of molecular weight and polydispersity index (PDI).\textsuperscript{37} Previous studies involving polyfluorenes and polythiophenes have demonstrated that molecular weight can have a significant impact on the quality and stability of the SWNT dispersion.\textsuperscript{38-41} In order to compare the effect of changing conjugated polymer structure on the selectivity for dispersing specific SWNT chiralities, it is important to consider the effect of polymer length, as one cannot assume that the observed selectivity is independent of this parameter. It is therefore worthwhile to investigate the stability, quality, and selectivity of nanotube dispersions that are achieved with different conjugated polymer types when polymer length is varied.

Poly(2,7-carbazole)s have been demonstrated to have applications in organic photovoltaics,\textsuperscript{42,43} as well as electrochromic\textsuperscript{44} and light-emitting devices.\textsuperscript{45,46} Poly(2,7-carbazole) homopolymers typically suffer from low molecular weights and poor solubility compared to their fluorene analogs, due to the poor inherent solubility of the carbazole monomer.\textsuperscript{47,48} We have previously demonstrated that a poly(2,7-carbazole) containing side-chains composed of the 3,4,5-tris(hexadecyloxy)phenyl structure, separated from the polymer backbone by an alkyl spacer chain, can be prepared in relatively high molecular weight ($M_n = 61$ kDa), while retaining excellent solubility in organic solvents.\textsuperscript{49} This polymer structure interacts strongly with SWNTs and was shown to preferentially disperse semiconducting SWNTs.\textsuperscript{50} However, a detailed analysis of the effect that this polymer’s molecular weight has on its ability to disperse SWNTs has not been reported. Here, we investigate the ability of a series of different
molecular weight poly(2,7-carbazole)s, ranging from short oligomers to high molecular weight polymers, at dispersing SWNTs. We found that, although all the poly(2,7-carbazole)s were very efficient at exfoliating SWNT bundles using a relatively mild dispersion protocol, complete removal of metallic SWNTs was not achieved at very low molecular weights. Additionally, we found that the polymer/nanotube ratio can have a significant impact on the dispersion quality obtained, with excess polymer leading to incomplete separation of SWNTs by electronic type.

4.2 Results and Discussion

![Structure of the poly(2,7-carbazole) (PC) used to prepare complexes with SWNTs.](image)

Figure 4.1. Structure of the poly(2,7-carbazole) (PC) used to prepare complexes with SWNTs.

The structure of the poly(2,7-carbazole) (PC) used in this work is shown in Figure 4.1. The synthesis of the 2,7-carbazole monomer has been reported previously.\textsuperscript{49} Seven different homopolymers were prepared using either Yamamoto or Suzuki polycondensation conditions,\textsuperscript{51,52} with molecular weights ranging from 4.6 kDa (a short chain oligomer comprised of 4 monomer units) to 91.7 kDa (corresponding to a degree of polymerization of 85). All polymers were highly soluble in a variety of organic
Table 4.1. Yields, molecular weights, polydispersity (PDI) and degree of polymerization (DP) for synthesized polymers.

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<th>$M_w$ (kDa)</th>
<th>PDI</th>
<th>DP$^a$</th>
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<tr>
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<td>PC$_{92}$</td>
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<td>91.7</td>
<td>203.0</td>
<td>2.22</td>
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</tbody>
</table>

$^a$Calculated from $M_n$ values

solvents, including THF, toluene, xylenes, dichloromethane, and chloroform.

Polymer-SWNT complexes were prepared in THF with raw HiPCO SWNTs using a relatively mild dispersion protocol, similar to previously published methods.$^{50}$ Three different ratios of polymer:SWNT were investigated, including 1:2, 1:1 and 2:1 (wt/wt). Samples were prepared by dissolving polymer (5, 10 or 20 mg) in THF, to which 10 mg of SWNTs was added. The polymer-SWNT samples were sonicated in a bath sonicator (chilled with ice) for 1 hour before being centrifuged for 30 min at 8,346$g$. The supernatant was carefully removed from the tubes and filtered over a 0.2 $\mu$m Teflon membrane to remove excess polymer, after which the polymer-SWNT mat was scraped from the membrane and re-dispersed in 10 mL of THF by a second sonication and centrifugation step.

All the PC samples, with the exception of the lowest molecular weight PC$_5$, were capable of producing stable supramolecular complexes with raw HiPCO SWNTs after removal of excess polymer at the 1:1 polymer:SWNT ratio. A stable, dilute SWNT dispersion was only obtained for PC$_5$ at this ratio when excess polymer was still present. All seven PC polymers were capable of producing stable SWNT suspensions
after removal of excess polymer at the 2:1 polymer:SWNT ratio. Surprisingly, when a polymer:SWNT ratio of 1:2 was used, none of the polymer samples were capable of producing stable supramolecular complexes after removal of excess polymer. This indicates that, at this ratio, sub-optimal coverage of the nanotube surface is achieved, allowing the partially polymer-coated SWNTs to still π-stack with one another and flocculate. These unstable dispersions were therefore not characterized. The lowest (PC$_5$) and highest (PC$_{92}$) molecular weight polymers produced relatively dilute SWNT dispersions, consistent with previously reported results. PC$_9$ and PC$_{15}$ both yielded black SWNT dispersions after removal of excess polymer at both the 2:1 and 1:1 polymer:SWNT ratios, while the rest of the polymers (PC$_{27}$, PC$_{30}$ and PC$_{43}$) all produced clear, olive-green SWNT dispersions (see Figure 4.8 in Supporting Information).

![AFM images](image)

Figure 4.2. Representative AFM images from (a) PC$_{92}$-SWNT (1:1, wt/wt) and (b) PC$_9$-SWNT (1:1, wt/wt) samples, with the corresponding height profiles shown below. The black scale bar represents 500 nm, and the dashed white line is the location of the height trace.

To determine if nanotube bundles are present in the samples, tapping-mode AFM
analysis was performed on diluted dispersions of the polymer-SWNT complexes, which were spin-coated onto freshly cleaved mica surfaces. Representative AFM images for PC$_{92}$-SWNT (1:1) and PC$_9$-SWNT (1:1) can be found in Figure 4.2. Both samples showed long, filamentous features consistent with polymer-coated SWNTs. Height-trace analysis showed that all tubular features were less than 5 nm tall. The smallest features ($\sim 1 - 2$ nm) correspond to isolated polymer-coated SWNTs, while the larger features most likely arise from small bundles of polymer-coated SWNTs, possibly the result of sample drying. AFM images from other molecular weight samples (see Figure 4.10 in Supporting Information) were all consistent in height, and no major differences in features or height profiles were observed with samples produced from the 2:1 polymer:nanotube ratio. This indicates that even the short-chain PC oligomers are very effective at exfoliating SWNT bundles.

![Graph](image1)

**Figure 4.3.** UV-Vis-NIR absorption spectra for polymers at (a) 1:1 and (b) 2:1 polymer:SWNT ratio. All spectra have been normalized to the polymer absorbance peaks at approximately 400 nm.

UV-Vis-NIR absorption spectra for several polymer-SWNT dispersions are illustrated in Figure 4.3 for both 1:1 and 2:1 polymer:SWNT ratios (spectra for the remaining samples can be found in Figure 4.11 in the Supporting Information). All
absorption spectra have been normalized to the polymer maximum absorbance peak at $\sim 400$ nm. The PC$_{92}$-SWNT, PC$_{43}$-SWNT, PC$_{30}$-SWNT and PC$_{27}$-SWNT spectra all show intense, sharp, well-resolved absorbance features in both the $S_{11}$ ($830 - 1600$ nm) and $S_{22}$ ($600 - 800$ nm) regions for the 1:1 polymer:SWNT ratio. These spectra indicate that the higher molecular weight polymers are very efficient at exfoliating semiconducting SWNTs, and at molecular weights above 27 kDa, changing polymer length resulted in little difference in the distribution of chiralities being dispersed. Analysis of the $M_{11}$ region ($440 - 645$ nm) is challenging with these polymer-SWNT complexes as the polymer absorbance overlaps in this region, however the significant depression of absorbance features in this region for the higher molecular weights suggests extensive removal of metallic SWNTs. Upon changing the polymer:SWNT ratio to 2:1 (wt/wt), the absorption features for these four higher molecular weight polymers again show a number of peaks in the $S_{11}$ and $S_{22}$ regions, however the peaks are not as well resolved, possibly indicating that increasing the amount of polymer used for dispersion increases the likelihood of dispersing metallic SWNTs.

Figure 4.3 also depicts the absorption spectra for the lower molecular weight polymer-nanotube dispersions, PC$_{9}$-SWNT and PC$_{15}$-SWNT, at both the 1:1 and 2:1 ratio (data for the PC$_{5}$-SWNT dispersion at the 2:1 ratio is provided in the Supporting Information, Figure 4.11). These samples show multiple absorbance features in both the $S_{11}$ and $S_{22}$ regions, again indicating the presence of multiple semiconducting SWNT chiralities, however the peaks are not as well resolved. These spectra also contain a broad, exponential background, indicative of incomplete removal of metallic SWNTs. This data gives the first indication that the polymer selectivity for wrapping semiconducting SWNTs is diminished at molecular weights below 20 kDa.
Photoluminescence (PL) mapping was performed on the polymer-SWNT complexes in THF to further characterize the identity of semiconducting nanotube species dispersed by the different polymer lengths. The PL maps for PC$_{92}$-SWNT (1:1) and PC$_{9}$-SWNT (1:1) are provided in Figure 4.4 (PL maps for PC$_{43}$-SWNT, PC$_{30}$-SWNT, PC$_{27}$-SWNT and PC$_{15}$-SWNT are available in Figures 4.12 and 4.13 of the Supporting Information). PC$_{92}$-SWNT (1:1) exhibits intense fluorescence peaks from several semiconducting SWNT species, confirming the presence of multiple chiralities observed in the absorption trace. The most intense PL signal arises from the (9,4) chirality, with the (7,5), (7,6) (8,3) and (10,2) chiralities also exhibiting significant fluorescence intensity. In comparison, the lower molecular weight polymer dispersions, PC$_{9}$-SWNT (1:1) and PC$_{15}$-SWNT (1:1), also show PL peaks from various semiconducting SWNTs, but the fluorescence intensity of these maps is an order of magnitude lower than what is observed with the higher molecular weight samples. This was attributed to the presence of metallic SWNTs, which are known to quench nanotube fluorescence,$^{17,57}$ within the dispersions obtained with the lower molecular
weight polymers. This observation is consistent with the UV-Vis-NIR absorption data presented above.

Similar trends were noted for the 2:1 polymer:SWNT samples, with all samples showing very similar distributions of semiconducting SWNTs. Again, the PL intensity decreased dramatically upon changing from higher to lower molecular weight polymers for the dispersions. Additionally, the fluorescence intensity observed from dispersions prepared with all of the polymer molecular weights at the 2:1 polymer:nanotube ratio were slightly lower than those obtained with the 1:1 ratio, again indicating that an excess of polymer during the dispersion may increase the amount of metallic SWNTs dispersed.

To further investigate the selectivity differences upon changing polymer molecular weight, resonance Raman spectroscopy was used to identify both metallic and semiconducting SWNT species present in the dispersions. The radial breathing mode (RBM) region from 100 – 400 cm\(^{-1}\) is especially useful as the location of peaks can be used to determine the electronic nature of the SWNTs present in a mixture. It has been previously demonstrated that using a combination of three excitation wavelengths (514, 633 and 785 nm) is sufficient to detect the majority of metallic and semiconducting HiPCO SWNTs within a sample.

Thin films of the polymer-SWNT samples were prepared by drop casting the solutions onto a silicon wafer. A sample of the raw HiPCO SWNT powder was dispersed in CHCl\(_3\) via sonication and also drop cast onto silicon to determine the composition of the original mixture. All Raman spectra were normalized to the G band at \(\sim 1590\) cm\(^{-1}\) and offset for clarity. RBM data for all three excitation wavelengths can be found in Figure 4.5 for 1:1 dispersions and Figure 4.6 for 2:1 dispersions (full Raman spectra can be found in the Supporting Information).
Figure 4.5. Raman RBM spectra at (a) 514, (b) 633 and (c) 785 nm for 1:1 polymer:SWNT samples. Grey boxes represent location of semiconducting SWNT peaks, while pink regions are metallic SWNT features.
At an excitation wavelength of 514 nm it is possible to observe peaks from both metallic ($\sim 220 - 300 \text{ cm}^{-1}$) and semiconducting ($\sim 160 - 220 \text{ cm}^{-1}$) SWNTs in the raw HiPCO SWNT spectrum.\textsuperscript{61,62} Strong semiconducting and metallic SWNT peaks can also be observed in the PC$_9$-SWNT (1:1) dispersion, confirming the presence of metallic SWNTs in this sample. Metallic SWNT features can also be observed in the PC$_{15}$-SWNT (1:1) sample, however the intensity of these peaks is drastically reduced. Very faint peaks from metallic SWNTs can be observed in both the PC$_{27}$-SWNT (1:1) and PC$_{30}$-SWNT (1:1) samples, suggesting incomplete removal of metallic SWNTs. No metallic SWNT peaks were observed in the dispersions prepared from the highest molecular weight polymers, PC$_{43}$-SWNT (1:1) and PC$_{92}$-SWNT (1:1). These results confirm analysis from UV-Vis-NIR and PL mapping suggesting that selectivity towards semiconducting SWNTs increases with increasing molecular weight.

Using 633 nm excitation, both metallic ($\sim 175 - 240 \text{ cm}^{-1}$) and semiconducting ($\sim 240 - 310 \text{ cm}^{-1}$) SWNTs can be observed in the SWNT spectrum.\textsuperscript{53,62,63} The PC$_9$-SWNT (1:1) spectrum still shows a significant amount of metallic SWNTs, however no metallic SWNT features were observed in any of the other polymer-SWNT samples. With 785 nm excitation, mainly semiconducting SWNTs are in resonance.\textsuperscript{63} All six samples at the 1:1 polymer:SWNT (wt/wt) ratio showed intense peaks in the RBM region at this excitation wavelength, confirming the presence of semiconducting SWNTs for all samples. The intense peak at 265 cm$^{-1}$ in the SWNT spectrum arises from the (10,2) chirality that comes into resonance at 785 nm when present in bundles.\textsuperscript{64} It is often referred to as the “bundling peak” as it can be a useful indicator of the extent to which SWNTs are bundled in a sample.\textsuperscript{65} All six samples showed the presence of the (10,2) chirality in the PL maps, ensuring that qualitative analysis of this peak in the Raman data is possible. In all six samples, at the 1:1 polymer:SWNT
Figure 4.6. Raman RBM spectra at (a) 514, (b) 633 and (c) 785 nm for 2:1 polymer:SWNT samples. Grey boxes represent location of semiconducting SWNT peaks, while pink regions are metallic SWNT features.
ratio, a significant depression in the intensity of the bundling peak can be observed, indicating that the nanotubes are largely exfoliated in these samples, consistent with the AFM results.

For the 2:1 polymer:SWNT (wt/wt) samples, low-intensity peaks were observed between 220 – 300 cm$^{-1}$ in the RBM region at 514 nm excitation for all samples, indicating incomplete removal of metallic SWNTs for all molecular weights. The presence of metallic SWNTs is substantiated by broader UV-Vis-NIR absorption features and the lower PL map intensity for these samples. This demonstrates that selective dispersion of semiconducting SWNTs not only requires high polymer molecular weight, but is also affected by the polymer:SWNT ratio that is used. Using 633 and 785 nm excitation, the RBM signals were very similar to what was observed with dispersions obtained using a 1:1 polymer:SWNT ratio. Again, with 785 nm excitation, the bundling peak at 265 cm$^{-1}$ shows a significant decrease in intensity, confirming the exfoliation of SWNTs in these samples.

4.3 Conclusions

We have shown that a poly(2,7-carbazole) structure that possesses excellent solubility is able to efficiently exfoliate SWNT bundles in organic solvent at a variety of different molecular weights using a relatively facile and mild dispersion protocol. The supramolecular complexes formed are stable after removal of excess polymer and, consistent with earlier studies, we have found that poly(2,7-carbazole)s preferentially interact with semiconducting SWNTs over metallic SWNTs. Despite the lower molecular weight PC polymers being able to efficiently individualize SWNT bundles, they are unable to completely remove metallic SWNTs, which is consistent with other
reports involving polyfluorenes. Molecular weights above 30 kDa are effective at removing metallic SWNTs completely; however, if too much excess polymer is present in the sample, incomplete removal of metallic SWNTs is observed, indicating an intimate relationship between molecular weight and ratio of polymer:SWNT required for optimal separation of SWNTs by electronic type.

4.4 Supporting Information

4.4.1 General

Raw HiPCO SWNTs were purchased from NanoIntegris (batch R1-901, 9.9 wt% solid). All other reagents and solvents were purchased from commercial suppliers and used without further purification. Polymer solutions were sonicated in a Branson Ultrasonics B2800 bath sonicator and centrifuged using a Beckman Coulter Allegra X-22 centrifuge. The SDBS dispersion was sonicated using a QSonica Ultrasonic Processor cup horn sonicator (average power 100 W) and then centrifuged on a Beckman Coulter OptimaMax 130K centrifuge. Absorbance measurements were performed on a Cary 5000 spectrometer in dual beam mode, using matched 10 mm quartz cuvettes. SWNT fluorescence spectra were obtained with a Jobin-Yvon SPEX Fluorolog 3.22 equipped with 450 W Xe lamp and an InGaAs detector, using a 10 mm quartz cuvette. Slit widths for both excitation and emission were set to 10 nm band-pass, and correction factor files were applied to account to instrument variations. Photoluminescence maps were obtained at 25 °C, with 5 nm intervals for both the excitation and emission. Samples were diluted (if necessary) until maximum fluorescence was observed. Argon gas was bubbled through the solutions for 10 minutes before the start of the fluorescence maps, and the cuvette was sealed with parafilm. Raman
spectra were collected with a Renishaw InVia Laser Raman spectrometer, using three different lasers: 25 mW argon ion laser (514 nm, 1800 L/mm grating) at 10% power for polymer-SWNT samples; a 500 mW HeNe Renishaw laser (633 nm, 1800 L/mm grating) at 1% power; and a 300 mW Renishaw laser (785 nm, 1200 L/mm grating) at 0.1% power. Tapping mode atomic force microscopy was performed using a Digital Instruments NanoScope IIIa Multimode AFM using standard tips, with a scan rate of 1.1 Hz. AFM samples were prepared by spin coating (3500 rpm for 45 sec) a few drops of dilute polymer-SWNT dispersions on freshly cleaved mica.

4.4.2 Synthesis

The synthetic procedure for preparing the carbazole monomer has been previously reported. Polymers were prepared by Yamamoto coupling following a procedure published previously, or using a Suzuki polycondensation procedure outlined below.

Carbazole Diboronate Ester (2)

![Scheme 4.1. Synthesis of carbazole bis(boronate ester) (2).](image)

Under argon atmosphere, dibromocarbazole (1) (0.57 g, 0.46 mmol), B$_2$pin$_2$ (0.42 g, 1.65 mmol), potassium acetate (0.265 g, 2.76 mmol) and Pd(dppf)Cl$_2$ (0.019 g,
6 mol%) were dissolved in DMF (10 mL) and heated to 60 °C and stirred for 12 h. After the reaction mixture was cooled to room temperature, water (50 mL) and diethyl ether (100 mL) were added. The aqueous layer was extracted with diethyl ether (50 mL) and the combined organic layers were dried over MgSO₄ and concentrated under vacuum. The crude product was purified on silica gel column chromatography by eluting with 5% hexanes in ethyl acetate to yield a pale yellow solid (0.6 g, 98%). ¹H NMR (CDCl$_3$, 600 MHz): δ 8.14 (dd, $J = 7.8, 0.6$ Hz, 2H), 7.89 (s, 2H), 7.70 (dd, $J = 7.8, 0.6$ Hz, 2H), 6.52 (s, 2H), 4.41 (t, $J = 7.2$ Hz, 2H), 4.38 (s, 2H), 3.96 (t, $J = 6.6$ Hz, 4 H), 3.93 (t, $J = 6.6$ Hz, 2H), 3.45 (t, $J = 6.6$ Hz, 2H), 1.96-1.92 (m, 2H), 1.82-1.73 (m, 6H), 1.64-1.62 (m, 2H), 1.49-1.44 (m, 6H), 1.41 (s, 24H), 1.36-1.24 (m, 76H), 0.90 (t, $J = 7.2$ Hz, 9H).

**General Procedure for Synthesis of Poly(2,7-carbazole) via Suzuki Polycondensation**

![Scheme 4.2. General procedure for preparing poly(2,7-carbazole) using Suzuki polycondensation.](image)

To a solution of 2 (0.15 mmol) and Cs₂CO₃ (1.80 mmol) in a mixture of DMF (2 mL) and toluene (3 mL) was added 1 (0.15 mmol). The mixture was degassed for 30 min by bubbling with argon. A catalytic amount of Pd(PPh₃)$_4$ (5 mol%) was
added to the flask. The reaction mixture was heated to 95 °C and allowed to stir for 72 h. The reaction mixture was concentrated under vacuum. After cooling to room temperature, water was added to the reaction mixture and the product was extracted with chloroform (3 x 50 mL). The combined organic extracts were washed with excess water, dried over Na$_2$SO$_4$, and concentrated under vacuum. The crude compound was dissolved in a minimum amount of chloroform (2 mL) and added slowly into methanol (250 mL). The precipitate was filtered and dried under vacuum.

Figure 4.7. $^1$H NMR spectrum of carbazole diboronate ester monomer (2) in CDCl$_3$.

4.4.3 Preparation of SWNT Dispersions

Polymer solutions were prepared by dissolving the appropriate amount of polymer (20, 10 or 5 mg for the 2:1, 1:1 and 1:2 dispersions respectively) in 20 mL of THF before 10 mg of raw HiPCO SWNT material was added. The polymer-SWNT mixture
was sonicated for 1 h in a bath sonicator (chilled with ice), followed by centrifugation at 8,346\,g for 30 min. The supernatant was carefully removed from the centrifuge tube and filtered over a PTFE membrane (0.2 \,\mu m) to remove excess polymer. The resulting polymer-SWNT film was rinsed repeatedly with THF until there was no observable fluorescence from the filtrate. The polymer-SWNT material was then scraped off the membrane and re-suspended in 10 mL of solvent by sonication for an hour followed by a second centrifugation (30 min at 8,346\,g) to ensure that the samples were stable.

Figure 4.8. Photographs of polymer-SWNT dispersions in THF. Top photograph is of 1:1 polymer:SWNT dispersions. From left to right: PC$_9$-SWNT, PC$_{15}$-SWNT, PC$_{27}$-SWNT, PC$_{30}$-SWNT, PC$_{43}$-SWNT and PC$_{92}$-SWNT. Bottom photograph is of 2:1 polymer:SWNT dispersions. From left to right: PC$_5$-SWNT, PC$_9$-SWNT, PC$_{15}$-SWNT, PC$_{27}$-SWNT, PC$_{30}$-SWNT, PC$_{43}$-SWNT and PC$_{92}$-SWNT.
Figure 4.9. (a) UV-Vis-NIR absorption and (b) PL map of SDBS-SWNT dispersion.
Figure 4.10. Representative AFM images for: PC$_{92}$-SWNT (2:1), PC$_9$-SWNT (2:1), PC$_{43}$-SWNT (1:1) and PC$_{15}$-SWNT (1:1), with corresponding height profiles shown below. The black scale bar represents 500 nm, and the dashed white line is the location of the height trace.
Figure 4.11. UV-Vis-NIR absorption spectra for PC$_5$-SWNT and PC$_{27}$-SWNT at (a) 1:1 and (b) 2:1 polymer:SWNT ratios. The PC$_5$-SWNT (1:1) still has excess polymer present and has not been normalized.
Figure 4.12. PL maps for PC$_{43}$-SWNT, PC$_{30}$-SWNT and PC$_{15}$-SWNT, all at 1:1 ratio of polymer:SWNT.
Figure 4.13. PL maps for PC$_{92}$-SWNT, PC$_{43}$-SWNT, PC$_{15}$-SWNT, PC$_{9}$-SWNT and PC$_{5}$-SWNT, all at 2:1 ratio of polymer:SWNT.
Figure 4.14. Full Raman spectra for the six PC samples at a 1:1 ratio of polymer:SWNT at (a) 514, (b) 633 and (c) 785 nm excitation wavelengths.
Figure 4.15. Full Raman spectra for the seven PC samples at a 2:1 ratio of polymer:SWNT at (a) 514, (b) 633 and (c) 785 nm excitation wavelengths.
4.5 References


Chapter 5

The Effect of Induction on the Dispersion of Semiconducting and Metallic Single-Walled Carbon Nanotubes Using Conjugated Polymers

This chapter has been reprinted with permission from Macromolecules. Nicole A. Rice, Ayyagari V. Subrahmanyam, Brian R. Coleman, and Alex Adronov, 2015, 48 (15), pp 5155–5161, DOI: 10.1021/acs.macromol.5b00631. Copyright (2015) American Chemical Society.

Nicole Rice was involved in the planning of this study, and prepared and characterized all polymer-SWNT composites. Ayyagari Subrahmanyam synthesized the monomers and polymers. Nicole Rice and Ayyagari Subrahmanyam were both involved in polymer characterization. Brian Coleman was involved in the initial planning of the study and preparation of monomers and polymers.
Abstract

Despite significant advances in single-walled carbon nanotube (SWNT) synthesis and purification strategies, the separation of metallic and semiconducting SWNTs on a large scale remains a barrier to the realization of many commercial applications. Selective extraction of specific SWNT types by wrapping and dispersion with conjugated polymers has been found effective for semiconducting SWNTs, but structural parameters that dictate selectivity are poorly understood. Here, we report nanotube dispersions with two structurally similar conjugated copolymers, both being poly(fluorene-co-phenylene) derivatives, having comparable degrees of polymerization but differing in the extent of electron donation from functional groups on the phenylene comonomers. It is found that copolymers decorated with electron donating methoxy functionalities lead to predominant dispersion of semiconducting SWNTs, while copolymers decorated with electron withdrawing nitro functionalities bias the dispersion toward metallic SWNTs. Differentiation of semiconducting and metallic SWNT populations was carried out by a combination of UV-Vis-NIR absorption spectroscopy, Raman spectroscopy using multiple excitation wavelengths, and fluorescence spectroscopy. These results provide new insight into polymer design features that dictate preferential dispersion of specific SWNT types.
5.1 Introduction

Amongst the known nano-scale materials, single-walled carbon nanotubes (SWNTs) have attracted a tremendous amount of research attention since their discovery.\(^1\)\(^-\)\(^5\) Their unique properties, including high tensile strength,\(^6\) high aspect ratio,\(^7\) thermal and electrical conductivity,\(^8\)-\(^11\) and extraordinary optical characteristics,\(^12\)-\(^14\) make them potentially valuable components of advanced materials with a wide range of applications. Indeed, SWNTs have been incorporated in field-effect transistors (FETs),\(^7\),\(^15\) sensors,\(^16\)-\(^19\) photodetectors,\(^20\) photovoltaics,\(^21\)-\(^23\) flexible printed circuits,\(^24\) electrode materials for flexible electronics,\(^25\) touch screens,\(^26\) and microelectronic interconnects,\(^27\) amongst other devices.\(^28\) In these applications, the molecular nature, resilience, and amenity to chemical modification of SWNTs make them decisively advantageous over many other nano-scale materials. However, despite recent progress in nanotube commercialization,\(^27\) applications that require controlled electrical and optical properties have not kept pace with expectations. This lag is a consequence of the inability to industrially prepare SWNTs that are pure in terms of their electrical properties. All known SWNT synthesis methods, such as high-pressure carbon monoxide disproportionation (HiPCO),\(^29\) carbon vapor deposition (CVD),\(^30\) arc-discharge,\(^31\) laser ablation,\(^32\) and plasma torch growth,\(^33\) result in the production of mixtures of metallic SWNTs (m-SWNTs) and semiconducting SWNTs (sc-SWNTs).\(^34\) Since components of electronic devices require either m-SWNTs (electrodes, interconnects, etc.) or sc-SWNTs (transistors, sensors, etc.), their separation into pure samples is imperative. Several methods for separating and purifying SWNTs have recently been developed, including density-gradient ultracentrifugation (DGU),\(^35\) agarose gel filtration,\(^36\) electrophoresis,\(^37\) and selective dispersion using conjugated polymers.\(^38\) Of
these, selective dispersion with conjugated polymers is the most promising as, unlike the other techniques, it is a low-cost and scalable process. While it has recently been shown that some conjugated polymers, such as commercially available polyfluorenes, can selectively disperse sc-SWNTs in toluene, the resulting dispersions are extremely dilute, precluding isolation of bulk quantities of purified SWNTs. More importantly, selectivity for m-SWNTs has not been reported, and remains an elusive goal.

The selectivity of the interaction between conjugated polymers and SWNTs arises from a complex mixture of polymer features, including polymer structure, conformation, molecular weight, and the nature of the side-chains. Modification of some or all of these parameters has been demonstrated to have significant impact on the stability and selectivity of SWNT dispersions. In addition to the polyfluorenes mentioned above, interactions of SWNTs with polythiophenes, polycarbazoles, poly(phenylene vinylene)s, poly(phenyl acetylenes), and a number of other structures and derivatives have been investigated. Some of these structures have shown significant selectivity in their interactions with specific chiralities, diameters, and conductivity types, rivaling that of polyfluorenes. Despite this progress, a fundamental understanding of the interaction selectivity, from the perspective of controllable polymer characteristics such as backbone structure, side-chain structure, and electronic properties, has been elusive. One of the difficulties in determining the effect of structural variability on interaction selectivity is the fact that changing monomer structure often affects polymerization kinetics, solubility, and overall reactivity toward polymerization catalysts, which results in significant variability in the polymer chain length. It has been well documented that chain length, in addition to other structural elements, can have a significant impact on the types of SWNTs being dispersed by a particular polymer. Thus, maintaining constant chain length is imperative when
comparing polymers of different structure in their ability to disperse SWNTs, as this decreases the chance of inaccurate interpretation of observations.

In this report, we investigate how inductive effects of polymer side chains impact the electronic types of SWNTs that are dispersed by conjugated polymers composed of fluorene and phenylene units. We demonstrate that when other variables (such as molecular weight and size of side chains) are kept constant, the electronic nature of the polymer backbone has a significant effect on which species of SWNTs are dispersed. In particular, we observe that by changing from a simple electron rich co-monomer (para-dimethoxyphenyl) to an electron poor co-monomer (para-dinitrophenyl) it is possible to switch from dispersing solely sc-SWNTs to dispersing a mixture that contains significant amounts of m-SWNTs.

5.2 Results and Discussion

5.2.1 Polymer Design and Synthesis

The polymer structures were carefully designed in an effort to minimize the various parameters that can affect the nature of the polymer-SWNT interaction and prevent unambiguous investigation of the effect of changing the electronic character of the conjugated polymer backbone on the polymer’s ability to disperse SWNTs. In particular, polymer architecture has been shown to play an important role in the types of SWNTs that are dispersed, as well as on the stability of the polymer-SWNT complexes obtained. Drastic changes in the size of the functionalities on the polymer backbone could change how the polymer wraps the SWNT surface, potentially interfering with the polymer-nanotube interaction. It was therefore desirable to keep side-chain size identical between different polymer structures. It was also
important to obtain polymers with the same degree of polymerization, as polymer length has been previously demonstrated to significantly affect the quality of SWNTs dispersions.\textsuperscript{48,49}

\begin{center}
\includegraphics[width=\textwidth]{scheme51.png}
\end{center}

Scheme 5.1. Synthesis of monomers.

A fluorene-containing polymer backbone was chosen because polyfluorenes have been shown to interact well with SWNTs and can exhibit selectivity towards small subsets of SWNTs under appropriate solvent conditions.\textsuperscript{54} 1,4-Dibromo-2,5-dinitrobenzene and 1,4-diiodo-2,5-dimethoxybenzene were chosen as co-monomers to produce the electron poor and electron rich polymer structures, respectively. The nitro and methoxy functionalities are comparable in size, allowing the two polymers to adopt similar conformations on the surface of SWNTs. The choice of small electronically inductive functionalities also avoids any negative steric interactions that could arise from the presence of bulky or drastically different side chains. Synthesis of the 9,9-bis(dodecyl) fluorene-2,7-diboronate ester monomer\textsuperscript{55} (3) and the two co-monomers, 1,4-dibromo-2,5-dinitrobenzene\textsuperscript{56} (5) and 1,4-diiodo-2,5-dimethoxybenzene\textsuperscript{57} (7), was accomplished according to literature procedures (Scheme 5.1).
Scheme 5.2. Synthesis of PFdNB and PFdOMB copolymers by Suzuki polycondensation.

The two poly(fluorene-co-phenylene) copolymers were prepared using Suzuki polycondensation conditions by reacting the 9,9-bis(dodecyl)fluorene-2,7-diborionate ester (3) with the corresponding electron deficient and electron rich monomers (5 and 7, respectively), as shown in Scheme 5.2. The nitro-containing polymer (PFdNB) was prepared using PEPPSI-IPr as the catalyst in a toluene/K$_2$CO$_3$ (aq) (2.5:1 v/v) co-solvent mixture. The crude polymer was purified by precipitation in methanol, followed by soxhlet extraction in hexanes and acetone to yield a yellow solid in 81% yield. Gel permeation chromatography (GPC) indicated that the polymer had a number average molecular weight ($M_n$) of 26.0 kDa, corresponding to a degree of polymerization (DP) of 39 repeat units (Table 5.1). The electron-rich methoxy-containing polymer (PFdOMB) was prepared using a Pd(PPh$_3$)$_4$ catalyst in a DMF/toluene (3:1 v/v) co-solvent mixture. The PFdOMB polymer was also precipitated into methanol and purified using soxhlet extraction with hexanes and acetone and was isolated as a pale yellow solid. Several polymerization attempts were necessary to produce a polymer with $M_n$ similar enough to PFdNB to allow for a valid comparison. The polymer fraction with the closest molecular weight to PFdNB had an $M_n$ of 26.9 kDa.
Table 5.1. Yield and molecular weight data for dinitro (PFdNB) and dimethoxy (PFdOMB) copolymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Yield (%)</th>
<th>$M_n$ (kDa)</th>
<th>$M_w$ (kDa)</th>
<th>PDI</th>
<th>DP*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFdNB</td>
<td>81</td>
<td>26.0</td>
<td>49.8</td>
<td>1.92</td>
<td>39</td>
</tr>
<tr>
<td>PFdOMB$_{21}$</td>
<td>74</td>
<td>20.7</td>
<td>54.5</td>
<td>2.64</td>
<td>32</td>
</tr>
<tr>
<td>PFdOMB$_{27}$</td>
<td>55</td>
<td>26.9</td>
<td>59.2</td>
<td>2.20</td>
<td>42</td>
</tr>
<tr>
<td>PFdOMB$_{60}$</td>
<td>62</td>
<td>59.8</td>
<td>196.6</td>
<td>3.29</td>
<td>94</td>
</tr>
</tbody>
</table>

*Calculated from $M_n$ values

(PFdOMB$_{27}$), which corresponds to a DP of 42 (Table 5.1). Two other polymerizations yielded significant amounts of the dimethoxy polymer, one with a slightly lower molecular weight (PFdOMB$_{21}$, $M_n = 20.7$ kDa) and one with a much higher molecular weight (PFdOMB$_{60}$, $M_n = 59.8$ kDa). These polymers were also used to prepare complexes with SWNTs (see Supporting Information) to investigate the effect of molecular weight on selectivity toward specific SWNTs. All the polymers used in this study exhibited excellent solubility in various organic solvents at room temperature, including THF, toluene, dichloromethane, and chloroform.

5.2.2 Polymer-SWNT Complexes

Supramolecular polymer-SWNT complexes were prepared using the different copolymers and raw HiPCO SWNTs following previously reported procedures. Briefly, 5 mg of SWNTs was added to a polymer solution consisting of 10 mg of polymer dissolved in 20 mL of solvent. The mixture was sonicated for one hour in a bath sonicator chilled with ice, followed by centrifugation at $8,346g$ for 30 minutes. The supernatant was carefully removed from the centrifuge tube, filtered, and continuously washed with solvent to remove excess polymer. After removal of excess polymer, the polymer-SWNT buckypaper was re-dispersed in 15 mL of solvent by sonication,
followed by a second centrifugation. A SWNT suspension using sodium dodecyl benzene sulfonate (SDBS) as the surfactant for nanotube dispersion was also prepared following literature procedures and used for comparison.

Two different solvents, THF and toluene, were used in the initial studies. Consistent with previous results using poly(9,9-dioctylfluorene) (PFO), we obtained relatively concentrated SWNT suspensions in THF using PFdNB-SWNT and the three PFdOMB-SWNT samples, however, with the exception of PFdOMB_{60}, these samples showed very little selectivity in the chiralities dispersed. In toluene, superior selectivity toward a smaller subset of chiralities (in particular sc-SWNTs for the PFdOMB samples) was obtained, but this occurred at the expense of overall SWNT concentration. A convenient compromise was found with a 1:1 THF/toluene (v/v) co-solvent mixture. This solvent system displayed almost identical selectivity results to those obtained in neat toluene, but with a concentration of SWNTs that was comparable to what is achieved in THF. This co-solvent mixture was used for all polymer-SWNT samples except PFdOMB_{60}-SWNT, for which THF was found to yield the best results. The PFdOMB_{27}-SWNT, PFdOMB_{21}-SWNT and PFdOMB_{60}-SWNT samples were all clear, green dispersions, while the PFdNB-SWNT suspension exhibited an orange-brown color (see Supporting Information, Figure 5.8).

5.2.3 Polymer-SWNT Complex Characterization

To investigate the degree of nanotube bundling that is present in samples of the polymer-dispersed SWNTs, atomic force microscopy (AFM) studies were performed. Polymer-SWNT complex samples were prepared by spin-coating dilute dispersions on mica. Tapping-mode AFM analysis was performed on these samples, and representative images from these studies are shown in Figure 5.1. Long, filamentous structures
Figure 5.1. Representative AFM images for (a) PFdOMB$_{27}$-SWNT and (b) PFdNB-SWNT, with corresponding height profiles shown below. The dashed white lines represent the location of the height profile, and the black scale bars correspond to 500 nm.

were observed in both samples, with average heights of 1-5 nm. The smallest diameter features correspond to individual polymer-coated SWNTs, while the larger diameter features could arise from small polymer-SWNT bundles, which were either present in the dispersions or formed upon removal of the solvent during the spin-coating process. These observed height profiles indicate that significant exfoliation of nanotube bundles occurred upon sonication with both polymer types, and there was no appreciable difference in the degree of nanotube exfoliation by PFdOMB and PFdNB.

UV-Vis-NIR absorption spectroscopy was performed on the polymer-SWNT supramolecular complexes (Figure 5.2). The absorption features for SWNTs arise from the inter-band transitions of the van Hove singularities, with different chiralities of SWNTs having different transition energies between the various allowed levels, enabling the electronic transitions to be organized as a function of diameter and chirality. The absorbance features can be grouped into three categories in the observed
Figure 5.2. UV-Vis-NIR absorption spectra for PFdOMB$_{27}$-SWNT (blue) and PFdNB-SWNT (red) in a 1:1 mixture of THF/toluene.

absorbance range: two semiconducting regions, $S_{11}$ (830–1600 nm) and $S_{22}$ (600–800 nm), and a metallic $M_{11}$ (440–645 nm) region. Despite spectral congestion in these regions, qualitative assignment based on peak location and shape can be made for the PFdOMB$_{27}$-SWNT complex in the $S_{11}$ region (see Supporting Information, Table 5.2).

The absorption spectrum for PFdOMB$_{27}$-SWNT displays multiple intense, sharp features in both the $S_{11}$ and $S_{22}$ regions. This absorption spectrum suggests that the electron-rich PFdOMB effectively exfoliates sc-SWNTs in the THF/toluene co-solvent mixture. The location of the various peak maxima is red-shifted compared to a reference SDBS-SWNT dispersion (see Supporting Information, Figure 5.11), consistent with previous observations for conjugated polymer-SWNT supramolecular dispersions. The PFdNB-SWNT absorption spectrum also contains multiple red-shifted peaks in the $S_{11}$ and $S_{22}$ regions, however the peaks are much broader and lack the fine features displayed by the PFdOMB$_{27}$-SWNT sample. The relatively intense,
featureless absorption background of the PFdNB-SWNT spectrum is indicative of the presence of m-SWNTs. However, detailed analysis of the $M_{11}$ region is complicated for these samples as the polymer absorption overlaps in this region.

To further investigate the differences in nanotube populations dispersed by the two different polymers, resonance Raman spectroscopy was performed. This technique allows for identification of different SWNT species within a given sample as both metallic and semiconducting SWNTs can be examined. Resonance enhancement occurs when the excitation wavelength is tuned to overlap with the van Hove singularities present in the 1D density of states for a particular nanotube. As these electronic transitions depend on nanotube diameter and chirality, only a subset of the total nanotube population will be enhanced and detected for any given excitation wavelength. The low-frequency radial breathing mode (RBM, $100 - 400 \text{ cm}^{-1}$) is a particularly useful region for study as the peak locations have an inverse dependence on SWNT diameter.

Thin film samples were prepared from the polymer-SWNT complexes by drop casting the solutions onto silicon wafers and allowing the solvent to evaporate. A reference SWNT sample was also prepared by sonicating a small amount of the SWNT material in CHCl$_3$ and using this suspension to prepare a solid film using the same drop casting method. Raman scans were obtained at three excitation wavelengths, including 514, 633, and 785 nm. It has previously been shown that these three excitation wavelengths are adequate for characterizing the electronic nature of a HiPCO SWNT sample, as both metallic and semiconducting species can be separately probed.

Figure 5.3 shows the RBM regions from the three samples at each excitation wavelength (full-scale Raman scans are provided in the Supporting Information, Figure 5.10). All Raman spectra were normalized to the G band at approximately $1590 \text{ cm}^{-1}$
Figure 5.3. RBM regions of the Raman spectra using (a) 514 (b) 633 and (c) 785 nm excitation wavelengths. The gray regions represent locations of signals arising from semiconducting nanotubes, while the pink regions represent the locations of signals from metallic nanotubes. The inset in (a) shows the G-band region, located at \( \sim 1590 \) cm\(^{-1} \), upon excitation at 514 nm.
and offset for clarity. Upon excitation at 514 nm, two dominant RBM features are observed in the SWNT spectrum (Figure 5.3a, black curve): a broad feature arising from sc-SWNTs centered at 180 cm\(^{-1}\), and several sharp peaks from 225 – 290 cm\(^{-1}\) which are attributed to m-SWNTs.\(^{70}\) Both the semiconducting and metallic features remain present in the PFdNB-SWNT sample (Figure 5.3a, red curve), while PFdOMB\(_{27}\)-SWNT only shows a single peak in the sc-SWNT region (Figure 5.3a, blue curve), suggesting that m-SWNTs are not present in this sample. This fact is corroborated by analysis of the G band region at this excitation wavelength, which is shown in the inset in Figure 5.3a. The G band is comprised of two peaks: a lower frequency G\(^{-}\) and a higher frequency G\(^{+}\). For sc-SWNTs, both the G\(^{-}\) and G\(^{+}\) have Lorentzian lineshapes, but in m-SWNTs the G\(^{-}\) displays a broader Breit-Wigner-Fano (BWF) lineshape.\(^{71}\) A very broad G\(^{-}\) band is observed for both the SWNT and PFdNB-SWNT samples but not for PFdOMB\(_{27}\)-SWNT, confirming that m-SWNTs are largely absent in the latter sample.

Both metallic and semiconducting SWNTs are also in resonance when the 633 nm excitation wavelength is used. For HiPCO nanotube samples at this excitation wavelength, m-SWNT features are found at approximately 175 – 230 cm\(^{-1}\), while sc-SWNTs give rise to peaks at approximately 230 – 300 cm\(^{-1}\).\(^{62,69}\) Both metallic and semiconducting SWNT features are observed in the SWNT and PFdNB-SWNT samples, while only sc-SWNT features are observed for PFdOMB\(_{27}\)-SWNT, confirming the interpretation of results from 514 nm excitation.

While mainly semiconducting HiPCO SWNTs are in resonance with the 785 nm excitation wavelength, it has been reported that a few large diameter metallic species, most notably the (16,7) and (12,9) chiralities, may be observed in the low frequency
region.\textsuperscript{68,70} Several small peaks were observed in the SWNT and PFdNB-SWNT spectra from 149 – 168 cm\textsuperscript{-1} and were assigned to m-SWNTs, while no features were observed below 200 cm\textsuperscript{-1} for the PFdOMB\textsubscript{27}-SWNT sample. The most intense peak in the SWNT spectrum occurs at 265 cm\textsuperscript{-1}, which arises from (10,2) SWNTs that come into resonance with this excitation wavelength when they are bundled.\textsuperscript{72} This peak is often referred to as the “bundling peak”, and can be a useful handle to qualitatively identify the presence of bundling in a SWNT sample treated with various dispersants.\textsuperscript{73} Figure 5.3c shows that a significant decrease in the bundling peak occurs when SWNTs are dispersed with PFdNB, suggesting that nanotube bundles are being efficiently exfoliated by this polymer. Furthermore, there is no peak present at 265 cm\textsuperscript{-1} for the PFdOMB\textsubscript{27}-SWNT sample, which indicates that the SWNTs are either completely debundled, or that the (10,2) chirality is not dispersed by PFdOMB\textsubscript{27} (see Figure 5.4a). Based on these results, it is clear that PFdOMB\textsubscript{27} disperses only sc-SWNTs, while PFdNB disperses a higher proportion of m-SWNTs, along with some amount of sc-SWNTs. In addition, we found that the two higher molecular-weight electron-rich polymers, PFdOMB\textsubscript{27} and PFdOMB\textsubscript{60} exhibit higher selectivity for sc-SWNTs relative to the lower molecular weight PFdOMB\textsubscript{21} (complete Raman analysis of these samples is provided in the Supporting Information, Figure 5.15 and preceding paragraphs).

### 5.2.4 Photoluminescence (PL) Mapping

PL maps were recorded for the polymer-SWNT samples (Figure 5.4), as well as for the SDBS-SWNT suspension (Supporting Information, Figure 5.11). The locations of the various SWNT fluorescence maxima were assigned according to previously published data.\textsuperscript{13} High intensity PL signals were observed for the PFdOMB\textsubscript{27}-SWNT
Figure 5.4. Photoluminescence maps for (a) PFdOMB\textsubscript{27}-SWNT and (b) PFdNB-SWNT at a similar concentration to the PFdOMB\textsubscript{27}-SWNT sample, and plotted on the same scale. Figure (c) is a more concentrated sample of PFdNB-SWNT, with the scale adjusted to show weak fluorescence.
sample, with the most intense peak arising from the (8,7) chirality (consistent with the major UV-Vis-NIR absorption peak at 1287 nm, Figure 5.2). Both the PL map and absorption spectrum for PFdOMB$_{27}$-SWNT also show removal of some smaller-diameter semiconducting species, such as the (6,5) and (7,5) chiralities. Additionally, intense PL signals were observed for the PFdOMB$_{21}$-SWNT and PFdOMB$_{60}$-SWNT dispersions (Supporting Information, Figure 5.16), but a slightly different distribution of chiralities was found. Overall, the PL and absorption spectra for all three PFdOMB-SWNT dispersions showed intense signals that can be attributed to the (8,7) chirality, but they also contain significant amounts of the (9,4) and (7,6) nanotube species.

The PL map for the PFdNB-SWNT sample is strikingly different. We initially recorded the map with a sample concentration that was very similar to that of PFdOMB$_{27}$-SWNT, by matching the absorption intensity for the (8,7) chirality at 1287 nm (see Figure 5.2). Despite evidence from the absorption and Raman spectra of the presence of sc-SWNTs in the PFdNB-SWNT sample, the PL map did not display any fluorescence peaks of significant intensity (Figure 5.4b). After repeated attempts at various concentrations, a low-intensity PL map (Figure 5.4c) was recorded, with weak fluorescence from some low-diameter SWNTs, such as (6,5), (7,5) and (7,6), and very weak PL intensity from the (8,7) chirality. Since m-SWNTs do not exhibit fluorescence, and are known to quench the fluorescence of sc-SWNTs, this result, in combination with the Raman data, indicates that PFdNB is much more selective for m-SWNTs than PFdOMB.

To further support the selectivity of PFdNB for m-SWNTs, it is necessary to rule out the possibility that the electron-poor polymer itself is responsible for quenching nanotube fluorescence. We therefore performed a polymer exchange experiment to
ascertain whether quenching by the polymer was possible. A 2 mg/mL solution of 
PFdNB in the THF/toluene co-solvent mixture was prepared and added to a dilute
sample of the PFdOMB\textsubscript{27}-SWNT dispersion in small aliquots (50 \( \mu \)L increments, corresponding to 0.1 mg of PFdNB). The sample was sonicated for 10 min after each addition, and an absorption and two PL spectra (at \( \lambda_{ex} = 650 \) and 725 nm) were recorded. The results of this experiment (Figure 5.5a-c) show an increase in the absorption intensity from 600 – 1100 nm, attributed to the tail end of the PFdNB polymer absorbance (which is present in a large excess). Initially as the PFdNB polymer was added there was no change in the SWNT PL intensity. However, upon the sixth addition a slight decrease in the PL intensity was noticed for both excitation wavelengths. A continual decrease in PL intensity was observed upon addition of subsequent aliquots. However, this decrease is attributed to the dilution of SWNTs, rather than to quenching, as a similar decrease in SWNT PL intensity was observed in a control experiment where identical volumes of pure solvent were added to the same starting concentration of PFdOMB\textsubscript{27}-SWNT (see Supporting Information, Figure 5.12).

5.3 Conclusions

In the design of next-generation polymers for selective dispersion and purification of SWNTs, it is imperative to understand the key parameters that dictate polymer selectivity toward specific SWNT types. We have demonstrated that modification of the poly(fluorene-\textit{co}-phenylene) backbone with electron donating or electron withdrawing functionalities can have a significant impact on the electronic nature of the SWNTs dispersed by the polymer. The copolymer bearing electron donating methoxy functional groups interacts preferentially with semiconducting SWNTs, while the nearly
identical copolymer bearing electron withdrawing nitro functionalities produces dis-
persions that are much more enriched in metallic SWNTs (though some semiconduct-
ing SWNTs are still present). Considering that the fluorene unit is relatively electron
rich itself, and preferentially interacts with semiconducting SWNTs, it is not surpris-
ing that exclusive dispersion of metallic SWNTs was not achieved. Nevertheless, the
electron rich copolymer shows a clear preference for semiconducting SWNTs, while
the electron poor copolymer shows a bias toward metallic SWNTs. This work justifies
further investigation of more electron poor conjugated polymers for their ability to
exhibit greater selectivity for metallic SWNTs.
5.4 Supporting Information

5.4.1 General

Raw HiPCO SWNTs were purchased from NanoIntegris (batch R0-513, 12.5 wt% solid; and R1-901, 9.9 wt% solid). All other reagents and solvents were purchased from commercial suppliers and used without further purification. Sonication of polymer solutions was performed using a Branson Ultrasonics B2800 bath sonicator; an QSonica Ultrasonic Processor cup horn sonicator (average power 100 W) was used to prepare the SDBS suspension. Centrifugation of the polymer samples was performed using a Beckman Coulter Allegra X-22 centrifuge, while the SDBS dispersions were centrifuged on a Beckman Coulter OptimaMax 130K centrifuge. Absorbance measurements were performed on a Cary 5000 spectrometer in dual beam mode, using matched 10 mm quartz cuvettes. SWNT fluorescence spectra were obtained with a Jobin-Yvon SPEX Fluorolog 3.22 equipped with 450 W Xe lamp and an InGaAs detector, also using a 10 mm quartz cuvette. Slit widths for both excitation and emission were set to 10 nm band-pass, and correction factor files were applied to account to instrument variations. Photoluminescence maps were obtained at 25 °C, with 5 nm intervals for both the excitation and emission. Argon gas was bubbled through the solutions for 5 minutes before the start of the fluorescence maps, and the cuvettes were sealed with parafilm. Raman spectra were collected with a Renishaw InVia Laser Raman spectrometer, using three different lasers: 25 mW argon ion laser (514 nm, 1800 L/mm grating); a 500 mW HeNe Renishaw laser (633 nm, 1800 L/mm grating); and a 300 mW Renishaw laser (785 nm, 1200 L/mm grating). Laser intensity for both 514 and 633 nm excitations was set to 5% for the SWNT sample dispersed in CHCl₃.
and 1% for polymer-SWNT samples. For spectra obtained at 785 nm, laser intensity was set to 0.1% for the CHCl$_3$ sample, and 0.05% for polymer-SWNT samples. Tapping mode atomic force microscopy was performed using a Digital Instruments NanoScope IIIa Multimode AFM using standard tips, with a scan rate of 1.5 Hz. AFM samples were prepared by spin coating (3500 rpm for 45 sec) a few drops of dilute polymer-SWNT dispersions on freshly cleaved mica.

5.4.2 Synthesis

The synthetic procedures for preparing the 9,9-bis(dodecyl)fluorene-2,7-diboronate ester (3),\textsuperscript{55} 1,4-dibromo-2,5-dinitrobenzene (5),\textsuperscript{56} and 1,4-diiodo-2,5-dimethoxybenzene (7)\textsuperscript{57} monomers have all been previously reported.

**PFdNB**

A mixture of 9,9-bis(dodecyl)fluorene-2,7-diboronate ester (3) (0.3 g, 0.396 mmol), 1,4-dibromo-2,5-dinitrobenzene (5) (0.13 g, 0.396 mmol), PEPPSI-IPr catalyst (0.014 g, 0.02 mmol) and potassium carbonate (0.328 g, 2.38 mmol) in toluene (5 mL) and distilled water (2 mL) was degassed for 30 min and stirred at 95 °C for 48 h. The mixture was extracted in chloroform (3 x 10 mL) and the combined organic extracts were washed with water, brine and dried over MgSO$_4$. The salts were filtered off and the solution was concentrated to a small volume. The crude product was filtered through Celite and then precipitated in methanol. The precipitate was filtered and purified by soxhlet extraction using hexanes and acetone. The product was then taken up in chloroform and re-precipitated in methanol, yielding a light yellow solid (217 mg, 81%). $M_n = 26.0$ kDa, PDI = 1.92, DP = 39. For $^1$H NMR data, see Figure 5.6, below.
### General Procedure for PFdOMB

To a solution of 9,9-bis(dodecyl)fluorene-2,7-diboronate ester (3) (0.6 mmol) and Cs₂CO₃ (4.76 mmol) in a mixture of DMF (5 mL) and toluene (3 mL) was added 1,4-dibromo-2,5-dimethoxybenzene (7) (0.6 mmol). The mixture was degassed for 30 min under argon. A catalytic amount of Pd(PPh₃)₄ (0.03 mmol) was added to the flask. The reaction mixture was heated to 95 °C and allowed to stir for 48 h. After cooling to room temperature, water was added to the reaction mixture and the product was extracted with chloroform (3 x 50 mL). The combined organic extracts were washed with excess water, dried over Na₂SO₄, and concentrated under vacuum. The crude compound was dissolved in minimum amount of THF (2 mL) and precipitated slowly into methanol solution (250 mL). The precipitate was filtered and purified by soxhlet extraction using hexanes and acetone. The product was taken up in chloroform and re-precipitated in methanol to yield a yellow solid. Yields and GPC data are given above. For ¹H NMR data, see Figure 5.6.

### 5.4.3 Characterization of Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Yield (%)</th>
<th>Mₙ (kDa)</th>
<th>Mₘ (kDa)</th>
<th>PDI</th>
<th>DP*</th>
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<tbody>
<tr>
<td>PFdOMB₂₁</td>
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<td>20.7</td>
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<tr>
<td>PFdOMB₆₀</td>
<td>62</td>
<td>59.8</td>
<td>196.6</td>
<td>3.29</td>
<td>94</td>
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</table>

*Calculated from Mₙ values
Figure 5.6. $^1$H NMR of PFdOMB (top) and PFdNB (bottom) polymers in CDCl$_3$. 
Figure 5.7. Absorption (solid lines) and fluorescence (dash lines) spectra for the four polymers used. All the PFdOMB polymers had maximum absorbance around 368 nm and a maximum emission at 413 nm. PFdNB had a maximum absorbance at 329 nm and a weak fluorescence profile that had a maximum emission at 364 nm.
5.4.4 Preparation and Characterization of SWNT Dispersions

Polymer solutions were prepared by dissolving 10 mg of polymer in 20 mL of solvent. 5 mg of raw HiPCO SWNT material was then added and the mixture was sonicated for 1 h in a bath sonicator (chilled with ice), followed by centrifugation at 8,346 \text{g} for 30 min. The supernatant was carefully removed from the centrifuge tube and filtered over a PTFE membrane (0.4 \text{m}) to remove excess polymer. The resulting polymer-SWNT residue, which formed a uniform film, was rinsed repeatedly until there was no observable fluorescence from the filtrate; as PFdNB did not fluoresce strongly, the filtrate was monitored by UV-Vis absorption spectroscopy for the loss of the polymer absorbance peak. The polymer-SWNT material was then scraped off the membrane and re-suspended in 15 mL of solvent by sonicating the sample for an additional hour. A second centrifugation (30 min at 8,346 \text{g}) was performed to ensure that the samples were stable.

![Figure 5.8. Photo of dilute polymer-SWNT suspensions investigated in this work. From left to right: PFdOMB_{21}-SWNT (1:1 THF/toluene), PFdOMB_{27}-SWNT (1:1 THF/toluene), PFdOMB_{60}-SWNT (THF) and PFdNB-SWNT (1:1 THF/toluene).](image)

Three different solvents were investigated initially: THF, toluene and a co-solvent...
mixture of 1:1 THF/toluene (v/v). THF was found to yield the most concentrated dis-
persions for all four polymer-SWNT complexes. Dispersions prepared in toluene were
quite dilute, but it was observed that the absorbance features for PFdOMB$_{27}$-SWNT
and PFdOMB$_{21}$-SWNT were much sharper and more defined in toluene compared to
THF. No difference beyond concentration was observed for the PFdNB-SWNT and
PFdOMB$_{60}$-SWNT samples. The broadening of features in the PFdOMB$_{27}$-SWNT
and PFdOMB$_{21}$-SWNT THF suspensions was attributed to the presence of metallic
SWNTs trapped in bundles.

A cosolvent mixture of 1:1 THF/toluene was found to be an optimal compromise
between the concentrated results obtained in THF and the selectivity observed in
toluene, as shown in Figure 5.9. This co-solvent mixture was used for PFdOMB$_{27}$-
SWNT, PFdOMB$_{21}$-SWNT and PFdNB-SWNT suspensions. The PFdOMB$_{60}$-SWNT
sample displayed sharp, fine features when THF was used as the solvent, indicating
that bundles and metallic SWNTs were effectively removed, so the co-solvent system
was not required (see Figure 5.13).

Qualitative Chirality Assignments

The $S_{11}$ absorption region for PFdOMB$_{27}$-SWNT was fit between 950 – 1500
nm with Lorentzian lineshapes to find the locations of the peak maxima from the
various semiconducting SWNTs. As absorption maxima for polymer-coated SWNTs
can be significantly red-shifted from their expected locations, emission maxima from
the photoluminescence map of PFdOMB$_{27}$-SWNT were used to help with chirality
assignments.
Figure 5.9. UV-Vis-NIR absorption for PFdOMB$_{21}$-SWNT in the three different solvent systems studied: 1:1 THF/toluene (blue), THF (magenta), and toluene (red). The PFdOMB$_{21}$-SWNT THF sample needed to be diluted before measurement, and the toluene absorption spectrum has been multiplied by a factor of 7. Similar trends were noted for PFdOMB$_{27}$-SWNT and PFdNB-SWNT suspensions.

Figure 5.10. Raman spectra of PFdOMB$_{27}$-SWNT (blue), PFdNB-SWNT (red) and SWNT material (black) obtained at (a) 514 (b) 633 and (c) 785 nm.

5.4.5 Quenching Experiment

A 2 mg/mL solution of PFdNB was prepared by dissolving 5 mg of polymer in 2.5 mL of 1:1 THF/toluene. The starting volume of PFdOMB$_{27}$-SWNT was 2.25 mL. The polymer-SWNT dispersion was sonicated for 10 minutes (bath sonicator, chilled) and
Table 5.2. Qualitative chirality assignments based on peak locations in the absorption and emission spectra of PFdOMB\textsubscript{27}-SWNT dispersion.

<table>
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<th>Chirality</th>
<th>Reference E\textsuperscript{11} (nm)</th>
<th>E\textsubscript{11,Absorbance} (nm)</th>
<th>E\textsubscript{11,Fluorescence} (nm)</th>
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<tbody>
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<td>(6,5)</td>
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<td>984</td>
<td>995</td>
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\textsuperscript{†}Values from previously reported data.\textsuperscript{13}

\textsuperscript{‡}A single peak was observed and attributed to a combination of overlapping signals from two chiralities.

Figure 5.11. (a) UV-Vis-NIR and (b) PL map for SDBS-SWNT sample.
an absorption and two emission scans (using excitation wavelengths of 650 and 725 nm) were obtained before the first addition of PFdNB. For each sequential addition of polymer, a 50 µL aliquot of the PFdNB stock solution (corresponding to 0.1 mg of PFdNB) was added to the PFdOMB\textsubscript{27}-SWNT dispersion. The mixture was sonicated for 10 minutes before obtaining the absorption and photoluminescence spectra. By the 12\textsuperscript{th} addition of PFdNB it was not possible to fit the entire volume of solution in the cuvette.

**Dilution Study**

To confirm that the observed decrease in the fluorescence features of the solution where PFdNB was added to PFdOMB\textsubscript{27}-SWNT was due to dilution rather than quenching from the presence of excess polymer, a dilution study was performed. The same volume (2.25 mL) of the PFdOMB\textsubscript{27}-SWNT stock solution was used and an identical procedure was used; 50 µL additions of 1:1 THF/toluene were made sequentially and the sample was sonicated for 10 minutes after each addition. The absorption and emission data are plotted in Figure 5.12 for every second dilution. A more pronounced depression of the fluorescence features was observed during the dilution study, confirming that the slight increase in the volume of this solution was enough to significantly affect the fluorescence intensity observed.

**5.4.6 Molecular Weight Study**

Three different molecular weights of the PFdOMB polymer were synthesized. PFdOMB\textsubscript{27} was the closest in molecular weight to the PFdNB polymer and was used for a direct comparison; the slightly lower molecular weight PFdOMB\textsubscript{21} and the higher molecular PFdOMB\textsubscript{60} were also used to prepare polymer-SWNT complexes.
following the same procedure used for PFdOMB$_{27}$.

The UV-Vis-NIR absorption for PFdOMB$_{21}$-SWNT and PFdOMB$_{60}$-SWNT are shown in Figure 5.13. The PFdOMB$_{60}$-SWNT and PFdOMB$_{27}$-SWNT (Figure 5.2) absorption spectra look quite similar with strong, sharp features in the S$_{11}$ and S$_{22}$
regions and a lack of a broad exponential absorbance background. This suggests that both polymers preferentially interact with semiconducting SWNTs. While the PFdOMB$_{21}$-SWNT absorption spectra does display strong, sharp semiconducting absorbance features, the presence of a slight exponential absorbance background suggests incomplete removal of metallic SWNTs.

AFM analysis of PFdOMB$_{21}$-SWNT and PFdOMB$_{60}$-SWNT (Figure 5.14) show that they also contained long, filamentous features with heights of between 1 – 4 nm, corresponding to polymer-coated SWNTs.

Raman spectra from PFdOMB$_{60}$-SWNT and PFdOMB$_{21}$-SWNT are shown in Figure 5.15; all spectra have been normalized to the G band at $\sim$1590 cm$^{-1}$ and offset for clarity. Raman analysis confirms that only semiconducting SWNTs were dispersed by the PFdOMB$_{60}$ polymer. At both 514 and 633 nm excitation wavelengths, there are no metallic SWNT features in the RBM region for the PFdOMB$_{60}$-SWNT sample; additionally, the G$^-$ peak in the PFdOMB$_{60}$-SWNT spectrum at 514 nm has
Figure 5.14. AFM images for (a) PFdOMB$_{21}$-SWNT and (b) PFdOMB$_{60}$-SWNT samples, with corresponding height profiles shown below. The dashed white lines represent the location of the height profile, and the black scale bars correspond to 500 nm.

been significantly depressed and does not display any broadening, further confirming removal of metallic SWNTs.

The PFdOMB$_{21}$-SWNT sample also shows a lack of peaks in the RBM region at 514 nm, however the G$^-$ band is does appear to be slightly broadened, suggesting incomplete removal of metallic SWNTs. This was confirmed by analysis of the RBM region at 633 nm, where faint peaks were observed for the PFdOMB$_{21}$-SWNT sample in the metallic region ($175 - 230$ cm$^{-1}$). This suggests that a certain molecular weight of PFdOMB is required before complete removal of metallic SWNTs can occur, further highlighting the importance of controlling for molecular weight when comparing conjugated polymers with different molecular weights.

Exfoliation of nanotubes in both PFdOMB$_{60}$-SWNT and PFdOMB$_{21}$-SWNT is confirmed by strong, intense peaks in the Raman RBM spectra at 785 nm. Both nanotube dispersions show the presence of the (10,2) chirality in the fluorescence
Figure 5.15. Raman spectra at (a) 514, (b) 633 and (c) 785 nm for PFdOMB\textsubscript{60}-SWNT (green) and PFdOMB\textsubscript{21}-SWNT (purple) samples. The HiPCO SWNT spectra are also shown for comparison. Inserts in the figures show the RBM region.
maps (Figure 5.16), so analysis of the bundling peak at 265 cm\(^{-1}\) is applicable. The bundling peak has been completely removed in the PFdOMB\(_{60}\)-SWNT spectrum, and is almost completely depressed in the PFdOMB\(_{21}\)-SWNT sample, confirming AFM results that both of these polymers are efficient at exfoliating SWNT bundles.

Figure 5.16. PL maps for (a) PFdOMB\(_{60}\)-SWNT in THF and (b) PFdOMB\(_{21}\)-SWNT in 1:1 THF/toluene.

The PL maps for PFdOMB\(_{21}\)-SWNT and PFdOMB\(_{60}\)-SWNT both exhibit intense, distinct fluorescence signals from a variety of semiconducting species (similar to PFdOMB\(_{27}\)-SWNT) indicating that these molecular weights were also capable of creating high quality dispersions of semiconducting SWNTs with efficient debundling. The PFdOMB\(_{21}\)-SWNT and PFdOMB\(_{60}\)-SWNT PL maps show a similar distribution of semiconducting chiralities, with the (9,4) and (7,6) chiralities giving rise to the most intense peaks. Minor differences in the relative intensities between the three different molecular weights could be due to slight variations in which semiconducting SWNTs are dispersed most efficiently, but could also be influence by the fact that a different batch of raw HiPCO SWNTs was used for the PFdOMB\(_{27}\)-SWNT dispersion.
5.5 References


8. Han, Z.; Fina, A. Progress in Polymer Science 2011, 36, 914 – 944, Special Issue on Composites.


Chapter 6

Thesis Overall Conclusions and Recommendations for Future Work

6.1 General Conclusions

SWNTs are a fascinating allotrope of carbon with unique mechanical, electrical and optical properties. The current status of our understanding and control over SWNT synthesis is unfortunately inadequate for the direct incorporation of these nanomaterials into most applications. The heterogeneity of SWNT samples (in terms of lengths, diameters, chirality and electronic nature), as well as impurities (such as amorphous carbon and metal catalyst residues), combined with the inherent insolubility of SWNT bundles hinder the realization of many potential device applications. While methodologies have been developed to allow for the creation of highly-pure samples of SWNTs, such as DGU and agarose gel filtration, these processes are inherently inefficient and are only capable of producing sub-microgram quantities of materials. Conjugated polymers represent a viable alternative for designing procedures that can solubilize and purify SWNTs on a larger scale. Many conjugated polymer families have been investigated successfully for preparing supramolecular complexes with SWNTs, with some structures demonstrating selective isolation of small subsets of SWNTs based on diameter, electronic type or chirality. In particular the polyfluorene PFO has displayed excellent discrimination of sc-SWNTs; however, PFO is incompatible with many potential device applications and this selectivity can
only be achieved using a “poor” solvent. Poly(2,7-carbazole)s offer a viable alternative to polyfluorenes because they are fully conjugated and highly stable, but it is essential to first overcome the inherent low solubility and low-molecular weights that are often reported for these polymers before their full potential can be reached.

The low molecular weight and poor solubility of poly(2,7-carbazole)s, combined with the necessity that the polymer-SWNT composites be highly soluble, necessitates careful design of the monomer structure. In Chapter 2 of this thesis I discussed the design and synthesis of a novel carbazole monomer unit comprised of a 3,4,5-tris(hexadecyloxy)phenyl moiety separated from the polymer backbone by an n-alkyl spacer chain. This design was chosen to impart solubility to the polymer-SWNT composites without hindering the ability of the polymer backbone to interact with the tubes. With this monomer I was able to prepare two high molecular weight, highly soluble polymers: a poly(2,7-carbazole) and poly(2,7-carbazole-co-2,7-fluorene). Both polymers were capable of dispersing raw HiPCO SWNTs and represented a significant improvement over previously-reported poly(2,7-carbazole)-SWNT systems due to the fact they did not require excessive amounts of polymer or laborious DGU steps. UV-Vis-NIR spectroscopy, AFM, and PL mapping confirmed the ability of these polymers to exfoliate SWNT bundles. Additionally, relatively concentrated samples of polymer-coated SWNTs could be obtained, which have exhibited extraordinary stability in solution, remaining dispersed for years.

The versatility and selectivity of the poly(2,7-carbazole) (PC) homopolymer prepared in Chapter 2 was confirmed in Chapter 3 by preparing supramolecular complexes from multiple NT sources. In this investigation I also addressed the difficulty that can arise when working with nanotubes that have undergone a purification process, such as oxidative treatments. Raman analysis at an excitation wavelength of 514
nm proved that when PC was mixed with either raw HiPCO or CoMoCAT SWNTs (in THF) the PC polymer selectively discriminates sc-SWNTs. This was an interesting result when viewed in the context of “good” versus “poor” solvents; THF is considered to be a good solvent for PC, meaning that a relatively high concentration of polymer-coated sc-SWNTs can be obtained. While PFO selectively disperses a smaller subset of sc-SWNTs, this selectivity is only possible when a “poor” solvent like toluene is used so the purity is achieved at the expense of concentration. When purified HiPCO SWNTs were used as the NT source, incomplete removal of the m-SWNTs and less-resolved optical features (in terms of absorbance peaks and PL intensity) were observed. This was attributed to the presence of oxygen-containing functionalities adsorbed onto the surface of the tubes, which interfered with the polymer coating and prevented the polymer from completely exfoliating all the small bundles of NTs. A simple annealing of the NT material before mixing with the polymer allowed for better interaction between the polymer backbone with the walls of the tubes, resulting in more efficient dispersal of the SWNTs and complete removal of m-SWNTs. This improved discrimination is an important result for applications that require purified SWNTs as their NT source.

The robustness of the PC polymer structure was confirmed in Chapter 4, and the boundary conditions for selective dispersion of sc-SWNTs was investigated in terms of the molecular weight and ratio of polymer to SWNT. Seven different molecular weight fractions of PC, ranging from 5 – 92 kDa, were prepared and used to disperse raw HiPCO SWNTs. Three different ratios of polymer to SWNT (by weight) were considered - 1:2, 1:1 and 2:1. Samples prepared using a 1:2 polymer:SWNT ratio were unstable, while all polymers (except the lowest weight 5 kDa) were capable of preparing stable supramolecular complexes at the 1:1 ratio. If excess polymer (2:1 ratio)
was used, all seven polymers were found to be capable of preparing stable SWNT dispersions. Through thorough analysis of Raman data at 633 and 514 nm it was determined that selective dispersion of sc-SWNTs was only achieved for polymers with molecular weights above 30 kDa, and only at the 1:1 polymer:SWNT ratio. A significant depression of the m-SWNT features was observed for the polymer-SWNT samples prepared from polymers with molecular weights between 15 – 30 kDa at the 1:1 ratio, and for all polymers above 15 kDa at the 2:1 polymer:SWNT ratio. This study represented the first comprehensive investigation of the effect of the molecular weight of a poly(2,7-carbazole) on its ability to selectively discriminated sc-SWNTs. Additionally, the suitable molecular weight range is different compared to PFO systems and highlights the need to optimize all parameters when considering different polymer structures for supramolecular complexes with SWNTs.

The work performed in Chapter 5 involved a novel study that focused on investigating the influence of the electronic nature of the polymer backbone on the electronic types of SWNTs dispersed. Two polyfluorene copolymers were prepared, one containing an electron withdrawing nitro functionality (PFdNB), the other having electron donating methoxy groups (PFdOMB). These functional groups were chosen for their small size in the hope that potential contributions from steric effects would be minimized. The results from Chapter 4 highlighted the importance of how even small changes in molecular weight can have drastic effects on the ability of a polymer to selectively discriminate SWNTs, so significant effort was devoted towards obtaining polymers with the same degree of polymerization. This had a secondary effect of allowing for a molecular weight investigation of PFdOMB, which allowed for the determination of the minimum molecular weight required to see selectivity. In an effort to overcome the limitations of the dilute nature of polyfluorene-SWNT
composites, I proposed using a co-solvent system of THF and toluene; this allowed for the preparation of relatively concentrated samples that still displayed the same selectivity observed in toluene. Through analysis of absorbance, PL and Raman data I found that the electron-rich PFdOMB selectively discriminated sc-SWNTs, while the electron-poor PFdNB dispersed both sc-SWNTs and m-SWNTs. As the only major difference between the two structures was the identity of a small functional group attached to the backbone of the polymer, this study allowed us to definitively demonstrate the intimate relationship between the electronic nature of the polymer and it’s ability to select for SWNTs of a certain electronic type.

The most significant contribution from this thesis comes from the investigation and determination of potential design rules for polymers that can selectively interact with SWNTs, particularly with my experiments involving the modification of the electronic nature of the polymer backbone. At this time, there are no conjugated polymer structures that can selectively disperse m-SWNTs. By carefully controlling for other variables (such as molecular weight and size of functional groups) I have been able to demonstrate for the first time the significant impact that the electronic nature of the polymer backbone can have on the types of SWNTs dispersed. The ability to switch from dispersing solely sc-SWNTs to a mixture of sc-SWNTs and m-SWNTs was achieved simply by changing from an electron-rich to an electron-poor functional group. Although I was unable to disperse only m-SWNTs with the particular polymer structure used, this work creates the foundation upon which new polymeric systems can be designed to allow for the realization of polymers that can selectively discriminate m-SWNTs.
6.2 Recommendations for Future Work

The work performed in this thesis mostly focused on using smaller-diameter SWNT materials like HiPCO and CoMoCAT SWNTs. HiPCO SWNTs can suffer from significant batch-to-batch variability, and it is currently challenging to obtain high-quality samples of HiPCO SWNTs; additionally, it has been suggested in several recent literature studies that larger-diameter SWNTs would be better suited for several proposed device applications. It would therefore be advantageous to switch to larger diameter NTs, such as those prepared using the plasma-torch methodology. Future work involving the conjugated polymer structures discussed in this thesis will require the optimization of dispersal methodologies for these new SWNT materials. In particular, it may be necessary to adjust the ratios of polymer and SWNT materials used, and for any polyfluorene derivatives it may also require redesigning the monomer structures, especially in terms of the lengths of the alkyl chains.

The selectivity and incredible stability of the poly(2,7-carbazole)-SWNT dispersions described in this thesis affords these materials excellent potential for device applications that require stable solutions of individualized SWNTs. Ongoing projects are currently investigating the use of these supramolecular complexes for the production of sensors (via inkjet printing), as well as the incorporation of these materials into electrospun nanofibers. Additionally, incorporating our 2,7-carbazole monomer structure into other polymer architectures that currently suffer from poor solubility (such as polymers that incorporate alkyne functionalities in the polymer backbone) could afford a way to investigate novel polymer structures capable of dispersing SWNTs to yield highly stable and concentrated samples.
As discussed in Section 6.1, our results from the study involving electron-withdrawing and electron-donating co-monomers opens up a fascinating avenue of investigation with potential for the realization of selective discrimination of m-SWNTs. We hypothesize that one of the reasons why both sc-SWNTs and m-SWNTs were dispersed by PFdNB was due to the presence of the fluorene monomer unit, which has been demonstrated to preferentially interact with sc-SWNTs. By changing the co-monomer to a structure that does not show selectivity for sc-SWNTs it could be possible to decrease amount of sc-SWNTs dispersed. Ongoing projects in the Adronov group are investigating incorporating phenylene, thiophene and benzothiadiazole co-monomers into electron-poor conjugated polymers to see if this will help improve the isolation of m-SWNTs from sc-SWNTs. Other interesting avenues of investigation would be to functionalize “traditional” electron-rich monomers that have been demonstrated to interact well with SWNTs (for example, fluorenes and carbazoles) with electron-withdrawing functional groups (such as trifluoromethyl or cyano functionalities) and investigate their ability to discriminate m-SWNTs. A combination of both experimental routes would be an important follow up to the work presented in this thesis, potentially allowing for the preparation of a polymer containing only electron-poor monomer units.