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Investigating Charge Generation and Mobility in Type-Separated Single-Walled Carbon Nanotube Ensembles for Solar Photovoltaics

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Investigating Charge Generation and Mobility in Type-Separated Single-Walled Carbon Nanotube Ensembles for Solar Photovoltaics

by

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B.S., Harvey Mudd College, 2007
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A dissertation submitted to the Faculty of the Graduate School of the University of Colorado in the partial fulfillment of the requirement for the degree of Doctor of Philosophy
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Investigating Charge Generation and Mobility in Type-Separated Single-Walled Carbon Nanotube Ensembles for Solar Photovoltaics
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The final copy of this dissertation has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Mistry, Kevin Sharad (Ph.D., Physics)

Investigating Charge Generation and Mobility in Type-Separated Single-Walled Carbon Nanotube Ensembles for Solar Photovoltaics

Dissertation directed by Dr. Jeffrey L. Blackburn

Single-walled carbon nanotubes (SWCNTs) have a number of unique and remarkable properties, including high electrical conductivity and tunable optical absorption. Due to their optoelectronic properties, considerable interest has been expressed in incorporating them into organic photovoltaic devices. Several challenges, as well as opportunities, have arisen in recent years as SWCNTs have been investigated for photovoltaic applications. This dissertation covers both main roles for SWCNTs in solar cells: as charge collecting transparent electrodes and as charge generating light absorbers in the active layer.

Typical SWCNT synthesis methods produce both metallic and semiconducting species with a wide range of diameters, electron affinities, and ionization potentials. To overcome this polydispersity, I employ post-synthetic separation techniques to extract purely semiconducting species and even narrow chiral distributions. To incorporate SWCNTs as electrodes in solar cells, chemical doping can be used to improve both conductivity as well as transparency. While p-type doping has been more common and typically environmentally stable, I investigated n-type doping as a means for increasing flexibility in device architecture as well as for use in nanoelectronics. A full spectroscopic characterization of and comparison of transport properties between n- and p-type films is presented.

Thus far, SWCNTs have not produced highly efficient photovoltaic devices. In part, this has been due to a poor understanding of how multichiral distributions with widely varying band-gaps and energetic offsets affect photoinduced charge generation and separation in the active layer. By taking into account differences in electron affinity, exciton binding energy, thermodynamic driving force, and
charge transfer reorganization energy, I systematically investigate how to improve exciton dissociation in two widely differing SWCNT samples using a large range of fullerene acceptors. Finally, using a similar experimental technique, I report on progress towards a fundamental understanding of nanotube mobility and how it is affected by nanotube length, diameter, and environment.
What is that feeling when you’re driving away from people and they recede on the plain till you see their specks dispersing? – it’s the too-huge world vaulting us, and it’s good-by. But we lean forward to the next crazy venture beneath the skies.

--Jack Kerouac, On the Road
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Chapter 1

Introduction

As global power consumption reaches tens of terawatts, the need for cheap, clean, reliable energy sources grows along with it.\textsuperscript{1} With over 165,000 terawatts of solar power hitting the earth, photovoltaics (PV) can be a solution to our energy needs if the technology can deliver power at a few cents per kilowatt-hour.\textsuperscript{1} The promise of low-cost, thin-film solar cells made from earth-abundant materials has been a driving force for progress in the field of organic photovoltaics (OPV). The incorporation of single-walled carbon nanotubes (SWCNTs) into OPV devices has been a field of considerable interest due to their unique and remarkable optoelectronic properties. Unfortunately, SWCNTs have not yet produced significant improvements to OPV devices due to insufficient understanding and control of their properties. In this dissertation, I will discuss some of the advancements in understanding charge generation and mobility within SWCNTs and controlling their electronic type and energetic levels.

Single-walled carbon nanotubes are $sp^2$ hybridized allotropes of carbon, which form hollow cylinders only a single atom thick.\textsuperscript{2} Different species, or chiralities as they are referred to by the nanotube community, of SWCNTs are denoted by two indicies $(n,m)$, which are visualized in Figure 1.1 showing how a graphene sheet can be rolled up to form a SWCNT by varying the two unit vectors. Left and right handedness are referred to as enantiomers, but are outside the scope of this dissertation. SWCNTs have extraordinary properties including high electrical and thermal conductivity, extraordinary mechanical strength, and tunable optical and electrical properties. While they can be used in a myriad of
applications, here I focus on their optoelectronic properties and the ways in which they can be beneficial to photovoltaics.

Figure 1.1. A graphene sheet diagram of the different \((n,m)\) SWCNT chiralities. Each SWCNT chirality is named by the coefficients on the unit vectors, \(i.e. n \cdot a_1 + m \cdot a_2\). When \(\text{mod}(n - m, 3) = 0\), the chirality refers to a metallic species, while for \(\text{mod}(n - m, 3) = \pm 1\) the chirality is semiconducting.

By rolling up the graphene sheet at different angles and diameters, SWCNTs can have a wide range of electrical and optical properties. Due to their nearly one-dimensional structure, the density of states (DOS) in carbon nanotubes has sharp peaks called van Hove singularities (Figure 1.2a).\(^3\)\(^4\) While this “single-particle” picture is valid for SWCNTs containing one type of excess carrier (\(e.g.\) hole- or electron-doped), photon absorption produces excitons, tightly bound electron-hole pairs, due to strong Coulomb interactions.\(^5\) The Coulomb interaction in SWCNTs is particularly strong in SWCNTs due to reduced screening, and hence lowers the optical band gap (exciton energy) relative to the electrical band gap (defined by the single-particle DOS) by as much as \(~1/4\) of the electrical band gap in
semiconducting (s-)SWCNTs (Figure 1.2). The single-particle DOS in metallic (m-)SWCNTs is also
dominated by van Hove singularities, but in contrast to s-SWCNTs, there is a non-zero DOS in between
the lowest two singularities. In contrast to most metals, and despite the appreciable ground state free
carrier concentration, the optical transitions of m-SWCNTs are excitonic, albeit with much lower exciton
binding energies than found in s-SWCNTs.

![Image of density of states for m- and s-SWCNTs]

**Figure 1.2.** (a) Density of states for m- and s-SWCNTs. Metallic SWCNTs have a non-zero DOS between
the lowest two van Hove singularities, while semiconducting species have a true gap. (b) Optical and
electrical band-gaps in s-SWCNTs as a function of diameter. The optical transitions in SWCNTs are
excitonic in nature and the binding energy is the difference between the exciton energy and electrical
band-gap.

Electronic properties of polydisperse SWCNT samples are complex, since since both metallic and
semiconducting species are formed in most production techniques. Semiconducting SWCNTs are highly
insulating in their intrinsic state due to finite band gaps with energies much larger than $k_B T$ at room
temperature. In contrast, intrinsic m-SWCNTs are conducting, due to the presence of carriers at the
Fermi level (Figure 1.2a). Both optical and transport properties can be modified by chemical/redox
doping. For example, injection of charge density into s-SWCNTs, either electrons or holes, leads to
quenching of optical transitions and an increase in conductivity by pushing the Fermi level into one of
the bands. Several theoretical and experimental studies have reported ballistic electronic transport,
*i.e.* negligible resistivity from electron scattering, along single s-SWCNTs, with FET mobility ranging from
$10^3$ to $10^5$ cm$^2$/Vs, resulting in mean free path lengths on the order of half to several microns.
(assuming an effective mass of 1 and Fermi velocity of $8 \times 10^5$ m/s). In fact, FETs comprised of single isolated semiconducting SWCNTs have been demonstrated to yield mobility values in excess of 100,000 cm$^2$/Vs, larger than the best known inorganic semiconductor InSb (~70,000 cm$^2$/Vs). In nanotube networks, the tunnel barrier formed at the intertube junctions$^{12}$ reduces charge mobility, with the extent of reduction highly dependent on the properties of the network, e.g. SWCNT length, semiconducting/metallic content, and residual polymer/surfactant.

### 1.1 SWCNT Synthesis Methods

Single-walled carbon nanotubes can be synthesized in a variety of different methods such as chemical vapor deposition (CVD), combustion, arc-discharge, or laser vaporization (LV). At NREL we mainly synthesize SWCNTs using laser vaporization, but also utilize a number of commercially available sources: CVD – CoMoCat from SWeNT and HiPco from Unidym, combustion – Nano-C, and arc-discharge – NanoLab.

SWCNTs are prepared in-house at NREL by laser vaporization (LV) of a graphite target containing 3% (by weight) each of nickel and cobalt catalysts. Nitrogen is used as the carrier gas for all syntheses, regulated at a flow rate of 150 standard cubic centimeters per minute (sccm) and constant pressure of 500 Torr. All syntheses employ a Nd:YAG laser, operating in “free run” mode (i.e. not Q-switched) at 1064 nm. The power density for all runs is ~100 W/cm$^2$. An external furnace surrounding the quartz tube reactor allows for the regulation of synthesis temperature. The synthesis temperature for typical runs is 1125 °C, but can be adjusted to several temperatures over the range of 800 – 1175 °C for diameter tuning as in Section 2.4.1. For a schematic of the LV synthesis set-up, see Figure 1.3 below.
1.2 Standard Sample Preparation

For a number of applications, including different types of optical spectroscopy, a dispersion of well-isolated SWCNTs may be desired. Typically these are aqueous and make use of some type of surfactant as carbon nanotubes are not readily soluble in water on their own. A typical surfactant solution would be a 1% concentration of sodium dodecyl sulfate (SDS), sodium cholate (SC), or sodium dodecylbenzenesulfonate (SDBS). The SWCNTs can be added in powder form to this solution and then tip-sonicated (typically 1/4” tip for 30 minutes at 30% on the Cole-Parmer CPX 750) to debundle and allow surfactant access to the nanotube surface. Sonication is known to shorten the average length of the nanotubes, however, and should be taken into account when preparing a solution. Finally, the dispersion must be centrifuged (typically on the SW32 rotor at 28,000 RPM for 4 hours at 20°C) to pellet out remaining bundles and metal catalysts. The remaining supernatant will have SWCNTs of all electronic types and diameters that are well isolated in solution.
Often it is useful to form a so-called ‘buckypaper’ (i.e. a filtered mat of nanotubes) instead of working with nanotubes in solution. In order to prepare a buckypaper, we start with raw LV soot from the in-house LV synthesis method. Taking about 80-100 mg of this material, we reflux with 4 M nitric acid for 16 hours at 220°C. Afterwards, this mixture is filtered through a 90 mm PTFE filter (throughout the next steps, the filter always remains wet) and washed copiously with DI water. The acid filtrate waste is discarded appropriately and then the filter is washed alternatively with acetone and DI water about 3-4 times. These steps help to wash out amorphous carbon. Next about 20 ml of 1 M NaOH is sent through the filter. After washing with DI water, another couple of rounds of acetone/DI rinse are run. The added base, wash and rinse steps are repeated once more, but is ended with acetone. To remove the buckypaper from the PTFE filter, it is placed in an oven to help it peel off. A typical yield is around 36 mg. An additional ‘air burn’ step can be done to remove the remaining amorphous carbon and defective nanotubes. A furnace tube is heated to 525°C and about 10 mg of buckypaper is inserted in one end. The buckypaper is slowly pushed inside the tube until it ignites and burns away the unwanted material. After removing the remainder, we are left with 3-5 mg of fairly matte material that is highly enriched (~97%) in SWCNTs. The final yield of highly purified SWCNTs is ~15 – 20%.

1.3 Opportunities and Challenges in Using SWCNTs for PV

This dissertation covers a range of topics related to the incorporation of SWCNTs into thin-film photovoltaic devices. Two primary roles that SWCNTs can play in PV are (1) charge collection in transparent conducting electrodes, and (2) charge generation in PV active layers. While the technological inspiration for this work is PV, the results are relevant to the ways in which SWCNTs can potentially enable or enhance a number of other devices. Below are some important scientific challenges that I have considered for the incorporation of SWCNTs into PV.
One of the main hurdles to be overcome before SWCNTs can be successfully integrated into devices is that of polydispersity, *i.e.* all current SWCNT synthesis methods produce both semiconducting and metallic species as well as a wide range of chiralities. While nanotube cloning is an impressive technique to control the growth of particular chiralities,\(^{14}\) it has a yield much too low for use in commercial applications. After synthesis, the next best approach is post-synthetic processing to extract the desired SWCNTs in high concentrations. Importantly, highly enriched semiconducting SWCNTs, likely with a narrow diameter (band-gap) range, are needed for PV since metallic SWCNTs are recombination centers. In Chapter 2, I discuss several methods employed in our lab to extract s-SWCNTs and narrow chiral distributions. Most current separation techniques become less selective for larger diameter SWCNTs. To this end, Chapter 2 highlights a study in which I developed a robust, high-yield method for extracting narrow chiral distributions of s-SWCNTs over a wide range of diameters, with particular success for large-diameter SWCNTs. These types of SWCNT samples are critical for tuning the electrical and optical properties needed for successful incorporation into PV devices, and are also desirable for other high-performance devices such as field-effect transistors.

Because of their unique properties, SWCNTs offer a promising route to producing flexible, solution-processed transparent conducting electrodes, which can be used in applications such as solar cells, touch screens, and light emitting diodes. In Chapter 3, I discuss how chemical doping can tune the ground-state carrier density to enhance the optical and transport properties of SWCNT networks. Furthermore, while p-type doping has been prevalent, n-type films are needed for flexibility in PV device architecture or for use in nanoelectronics which require both p- and n-type components (*e.g.* p-n junction solar cells, thermoelectrics, and logic circuits). Thus, Chapter 3 highlights my detailed study on n-type doping, which includes a full spectroscopic characterization of and comparison of transport properties between n- and p-type films.
Successful integration of SWCNTs into PV active layers requires a careful understanding of how varying SWCNT diameters, band-gaps, and energetic offsets affect the formation of a type II heterojunction. Such a heterojunction produces a staggered, but overlapping gap between donor and acceptor that can dissociate excitons to produce separated charges. In particular, for a SWCNT:fullerene donor:acceptor system we need to understand how differences in electron affinities, ionization potentials, driving force, exciton binding energy, and charge transfer reorganization energy play a role in exciton dissociation and charge recombination. In Chapter 4, I address these concerns using widely differing separated SWCNT samples along with a wide range of fullerene acceptors.

Charge transport in SWCNTs is of critical importance to device performance. In Chapter 5, I discuss how we can inject a known dose of carriers into SWCNTs, either through chemical doping or directly via pulse-radiolysis, to measure and compare the mobility of charge carriers in isolated nanotubes or coupled SWCNT networks. These studies can provide insight into the origins and recombination mechanisms of photo-induced charges in SWCNTs.

References


Chapter 2

Separation Techniques and Nanotube Sorting

For many applications and studies, we desire only one electronic type of SWCNTs, a narrow diameter range, or even a single chiral species. Because single-walled carbon nanotube synthesis cannot yet produce purely a single chirality, we are forced to find methods to sort nanotubes by diameter, band gap, or electronic type. In my doctoral research, I have explored and expanded on three main nanotube separation techniques: density gradient ultracentrifugation, gel column chromatography, and polymer extraction.

Separating semiconducting (s-) and metallic (m-) SWCNTs may offer the possibility of increasing the conductivity or transparency of SWCNT films as well as improving performance of PV active layers. Furthermore, producing samples with narrow or even single-chirality distributions may prove even more beneficial. In Sections 3.2 and 4.1, covering the use of SWCNTs in either transparent conducting thin films (TCFs) or in PV active layers, I discuss in detail the potential advantages of using highly enriched semiconducting or metallic SWCNTs. Briefly, for TCFs we have found that m-SWCNTs out-perform s-SWCNTs in the intrinsic state, while s-SWCNTs out-perform m-SWCNTs when doped (p- or n-type).\(^1,2\) For PV active layers, m-SWCNTs serve as recombination centers, hindering the realization of a long-lived charge-separated state that is needed for efficient generation of photocurrent in a device.\(^3,4\) Thus, it is imperative to use highly enriched s-SWCNTs for bilayer or bulk heterojunction OPV devices, and near-complete m-SWCNT removal is desirable. Additionally, excitons and charges may become trapped in small bandgap SWCNTs in OPV active layers containing multiple SWCNT species, so there may also be
advantages to using s-SWCNT samples with primarily a single chirality of SWCNT.\textsuperscript{5} Finally, SWCNT energetics (\textit{i.e.} band-gap, electron affinity, ionization potential) play an important role in optimizing a donor/acceptor system with nanotubes. Beyond simply requiring a type II heterojunction with sufficient driving force for charge separation from the absorber material, additional concerns must be satisfied when choosing an appropriate donor/acceptor material to pair with a specific SWCNT species. In particular, Marcus electron transfer theory may determine the charge transfer rate as a function of driving force and hence a narrow chiral distribution is required to understand and optimize such a system.\textsuperscript{6-8} These considerations will be explored in detail in Chapter 4.

\subsection{Density Gradient Ultracentrifugation}

Taking advantage of differences in buoyant densities of SWCNTs encapsulated by surfactants, density gradient ultracentrifugation (DGU) can be used to sort nanotubes by electronic type or by diameter.\textsuperscript{9} Essentially, DGU entails injecting a nanotube solution into a density gradient column and centrifuging at high speeds for several hours (sometimes up to \textasciitilde 24 hours). If done correctly, bands of different nanotube species will form at their isopycnic points, \textit{i.e.} the point in the centrifuge tube where the density of the gradient matches that of the particular nanotubes. The density gradient medium (iodixanol for our studies, but several others can be used) can be diluted to different densities. We fill the column using two layers that define the minimum and maximum starting density to be used and rotate the column at an angle to create a linear gradient between these two densities.

For our applications, we initially explored sorting metallic and semiconducting species. As discussed in Section 1.2, we can make an aqueous solution of LV SWCNTs using sodium dodecyl sulfate (SDS) and sodium cholate (SC) surfactants. By using both competing surfactants at different ratios, we can primarily select for the desired electronic type. For extracting a well-defined band of SWCNTs enriched in metallic species, we use a 2\% by weight solution of 3:2 SDS:SC. The density gradient is
prepared to range from ~1.07 mg/ml to ~1.11 mg/ml. To extract primarily semiconducting SWCNTs, the ratio changes to 4:1 SC:SDS at 2% total loading. The density gradient column is also prepared to match this ratio of surfactants so that this surfactant ratio is found throughout the centrifuge tube. For extracting m-SWCNTs, we used the SW41 rotor run at 41,000 RPM at 12°C for 12 hours, while the s-SWCNTs were run at 25°C for 16 hours, but also 41,000 RPM. After removing the centrifuge tubes, distinct bands can be seen and these can be extracted using a flat tipped needle. Altogether, DGU can be a time-consuming and low-yield process, but can produce high purity samples in a few iterations.9,10 One novel application of DGU that we demonstrated was the separation of highly enriched s- and m-SWCNTs that were labeled with 20% 13C.11 These 13C-labeled SWCNTs enabled the first determination of the unique NMR chemical shifts of s- and m-SWCNTs.

2.2 Gel Column Chromatography

Previously, separating m- and s-SWCNTs was time consuming or low yielding.9,12 Recent advances in separation techniques have sought to drastically improved yield, purity and throughput. Gel column chromatography uses differences in surfactant morphology on the surface of m- and s-SWCNTs to modify the extent to which certain SWCNT species adsorb to an ion exchange column. SWCNTs dispersed in sodium dodecyl sulfate (SDS) were added to columns of agarose gel beads, after which metallic species were found to pass through and s-SWCNTs adsorbed to the column.13 The s-SWCNTs were eluted from the gel using a solution of sodium deoxycholate (DOC); in this case, the high affinity of DOC for the surface of s-SWCNTs disrupts the affinity of the SDS/s-SWCNT with the agarose surface. This dual surfactant method can be easily scaled up by using larger columns, but only reaches purities of 90-95% for m- and s-SWCNTs respectively.13 A single surfactant method was developed to allow for multiple iterations of purification and in fact led to near single chiral distributions of s-SWCNTs.14 This method uses SDS as the surfactant, but requires Sephacryl (allyl dextran-based size exclusion gel)
instead of agarose gel. Liu et al. started with HiPco (commercial, high-pressure disproportionation of carbon monoxide) SWCNTs in low concentration (2%) SDS solution by applying it to a stack of small columns and then following this step with washing 2% SDS through the stack of columns. Each column was then eluted separately with high concentration (5%) SDS yielding a narrow chiral distribution of s-SWCNTs that roughly increased in diameter with successive columns. This process could be repeated to increase purity toward near single chiral distributions. While still scalable, this method required a large number of columns (>30) to run. A more efficient way to reach single-chirality samples has been demonstrated by controlling the temperature of the gel column. Below room temperature the affinity of SDS-wrapped SWCNTs for the Sephacryl column decreases and can be tuned to sort a range of small-diameter s-SWCNT chiralities.

![Figure 2.1](image_url)

Figure 2.1. (left) absorption spectra of semiconducting and metallic enriched small-diameter HiPco SWCNTs separated using the dual surfactant method. (right) a similar s-/m-SWCNT enrichment using large-diameter LV SWCNTs.

We reproduced semi/metal separations using the two surfactant method and agarose gel on smaller diameter HiPco CVD SWCNTs as well as LV SWCNTs produced in-house (see Figure 2.1). This method works over a wide range of diameters, but because the second surfactant elutes the SWCNTs, it does not lend itself easily to multiple iterations. The single surfactant method using Sephacryl had more success and we were able to expand this method to extracting narrow chirality distributions of s-SWCNTs as well. Although we initially used the multi-column method, we found that similar fractions
could be obtained from a single large column by varying the SDS concentration in finer increments. We prepared our initial inks using 1 mg/ml HiPco SWCNTs in 1% SDS. These were sonicated for 30 minutes instead of the 20 hours used in previous literature reports,\(^\text{14}\) which should allow us to have longer, lower-defect density nanotubes.\(^\text{16,17}\) As described in Section 1.2, they are then centrifuged for 4 hours to remove impurities and bundles. The inks can have SDS added to increase the concentration or diluted with DI water to reduce the concentration of surfactant, depending on the experiment. To prepare a gel column, a syringe was plugged with cotton. Next the syringe was partially filled with Sephacryl S100-HR and then washed with DI water. A solution of SDS at a selected concentration was used to wash the column and equilibrate it. Finally the nanotube ink was added to the column where it would begin to separate out into an absorbed fraction and a fraction that passes through. The same concentration of SDS is then added to the column to wash out the unbound fraction. To elute the bound fraction, a higher concentration of SDS solution is used. This can be done in incremental steps to elute out different chirality ranges. For example, at 1% SDS most s-SWCNTs in the HiPco distribution absorb to the gel, but will slowly elute out as the SDS concentration is increased. By about 4-5% SDS, all of the s-SWCNTs that can be recovered will have been eluted. There is always some small fraction of material permanently bound to the column. The order in which the SWCNTs are eluted is described in more detail below, but is opposite the order of the multi-column method (\textit{i.e.} roughly from larger to smaller diameter). Our method benefits from the ease of scaling up a single column, as well as being able to quickly elute a specific chiral species by selecting an appropriate SDS concentration range. The column is sensitive to changes in parameters such as initial gel volume, SWCNT ink volume and concentration, SDS concentration, and length of the column. The most sensitive parameter is always the SDS concentration, but the other factors can influence reproducibility and cutoffs for different chiralities.

As a concrete example, 4 ml of 1% SDS ink (1 mg/ml HiPco loading) was sent through a column with 1.4 ml of gel. Incrementally increasing the SDS concentration by 0.5% led to new fractions being
eluted from the column. The absorption spectra of these aliquots are shown in Figure 2.2a. Each of these fractions can be further sorted by using finer increments of SDS. To understand the sorting order, I ran a number of gel columns at varying concentrations and measured PLE maps to identify when each semiconducting chirality began to elute. In the PLE map shown in Figure 2.2b, different 2n+m families are circled and familial and chiral angle dependence to their locations can be observed on the map. I found that as the concentration of SDS is increased, the circled nanotube families eluted from largest diameter to smallest diameter, and within a given family from higher chiral angle to lower chiral angle. This is similar to the order found by Liu et al. based on bond curvature radius. Unfortunately, overlap between consecutively eluting species prevents us from isolating single-chirality samples with this technique.

Figure 2.2. (a) Absorption spectra of eluted column fractions taken at increasing SDS concentration and (b) PLE map showing familial dependence. As SDS concentration is increased, smaller diameter SWCNT families begin to elute from high chiral angle to low.

To further isolate individual chiralities, we investigated whether a longer column length could reduce overlap between species with similar elution concentrations. While a typical syringe column length is 4-5 cm, our thinner, longer glass column is 25-30 cm. Appreciable spread occurred in the eluted fraction, whereas previously the fractions eluted nearly as a band. While there were differences
between the initial and final aliquots, they were not significant enough to allow for single iteration
single-chirality samples. Additionally, due to the spreading, the aliquots were dilute as compared to the
shorter column.

While the gel column chromatography method works well for isolating narrow chirality or \((n,m)\)
family distributions of small-diameter (~0.7 – 1.2 nm) SWCNTs, it becomes less effective as the diameter
increases and other techniques need to be developed as well. With larger diameter SWCNTs, the gel
column chromatography method (similar to DGU) is primarily useful for rapid separation of metallic and
semiconducting populations (at 90-95% purity) without easy selection of narrow chirality/family
populations of SWCNTs.

2.3 Polymer Extraction

Another recent technique to separate s-SWCNTs uses fluorene-based polymers to enrich
different semiconducting chiralities. Unlike aqueous separations, these dispersions are made in organic
solvents such as toluene. Additionally, this method can often have high throughput and scalability since
the selective extraction of s-SWCNTs occurs in the first application of sonication and centrifugation
(minutes), and does not require hours of additional centrifugation or running columns. There are several
different polyfluorene derivatives that have been successful in separating particular s-SWCNTs. By
choosing appropriate starting SWCNT material and polymer, one can specifically select a wide range of
semiconducting nanotubes or a narrow to even single-chirality sample (see Figure 2.3). Differences in
the polymer side-chain or co-units can dramatically change the selectivity of the polymer for specific
diameter or chiral ranges.\(^{18,19}\) Similar to aqueous dispersions with surfactants, these polymer dispersions
involve sonicating the nanotubes in solution with the polymer and then centrifuging briefly to remove
bundles and impurities. Unlike the aqueous dispersions, however, there are typically many chiralities
within a particular SWCNT diameter distribution that a given polymer will not wrap or isolate well. These
poorly isolated chiralities will thus crash out during centrifugation, leaving behind a narrow chiral
distribution in the supernatant.

![Graph showing absorbance vs. wavelength for different polymer dispersions of SWCNTs.]

Figure 2.3. Examples of narrow chirality distributions of small-diameter s-SWCNTs using polyfluorene polymers. By tuning the polymer and the starting nanotube distribution, several near-single chirality dispersions can be made.

One of the first successful demonstrations of this technique utilized the polymer poly[9,9-
dioctylfluorenyl-2,7-diyl] (PFO) to disperse five chiralities from the HiPco distribution. These five chiralities are all near arm-chair s-SWCNTs (i.e. they have a high chiral angle). By starting with a more narrow diameter distribution of SWCNTs, such as CoMoCat, PFO can be used to primarily select the (7,5) chirality. Another polymer, poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-{6,6’-{2,2’-bipyridine}}] (PFO-BPy), has been successfully used with CoMoCat SWCNTs to produce dispersions highly enriched in the (6,5) chirality. There are numerous other reports of polyfluorene derivatives used to select certain small-
diameter s-SWCNTs at varying yields. However, as with other techniques, dispersions with narrow chiral distributions of larger diameter (d > 1.3 nm) s-SWCNTs have been elusive. Thus, we set out to find polyfluorene derivatives that enabled the successful extraction of large diameter s-SWCNTs with high yield.
2.4 Polymer Separations of Large-Diameter SWCNTs

In section 2.4, I focus on my detailed study aimed at extracting large-diameter s-SWCNTs with high yields, using polyfluorene polymers. Adapted with permission from ACS Nano, 2013, 7, 2231. Copyright 2013 American Chemical Society.

All current synthesis methods for SWCNTs produce both metallic (m-) and semiconducting (s-) species, typically with ~33% metallic content, but as low as ~8% for the small-diameter (d ≈ 0.8 nm) CoMoCat process.22 A number of applications envisioned for SWCNTs, such as photovoltaic (PV) active layers,3-5 field-effect transistors (FETs),23-25 and logic circuits,26 specifically require s-SWCNTs with minimal m-SWCNT impurities. To further enrich samples in semiconducting species, researchers have developed several post-synthetic strategies, including density gradient ultracentrifugation (DGU),10 column chromatography,13 and selective dispersion using aromatic polymers.19 DGU and column chromatography have been applied to a wide range of SWCNT diameters, but tend to suffer from low throughput for reaching purities and yields necessary for large-scale production of devices. Selective dispersion using polymers, polyfluorene derivatives in particular, has emerged as a powerful and scalable strategy for enriching small diameter s-SWCNTs,19,21,27 but has been minimally explored for larger diameter (d > 1.2 nm) SWCNTs.28,29

Scalable purification and enrichment processes are required for a number of applications that may benefit specifically from larger diameter s-SWCNTs. For example, thin film SWCNT FETs require metallic content less than ~2%, while the ultimate goal for digital logic is in the range of parts-per-million to parts-per-billion m-SWCNT impurities. FET performance is enhanced by using nanotubes with d > 1.2 nm, which reduce current-limiting Schottky barriers and dramatically improve the on/off ratio relative to small-diameter SWCNTs.23 Increased carrier mobility, which scales quadratically with nanotube diameter,31 may also improve FETs and PV devices that incorporate large-diameter SWCNTs. In PV devices, large-diameter s-SWCNTs cover a larger range of the solar spectrum by absorbing deeper
into the infrared (IR) and may also form type II heterojunctions with low band gap polymers or high electron affinity fullerenes, potentially increasing efficiencies of SWCNT PV active layers. SWCNT PV active layers based on large-diameter SWCNTs may also realize enhanced efficiencies by exploiting multiple exciton generation (MEG) in the visible and near-IR, as opposed to small-diameter SWCNTs which exhibit MEG primarily in the ultraviolet region. Lastly, enriched s-SWCNTs that absorb around 1530 nm – 1565 nm (1.3 nm < d < 1.4 nm) would be useful as photonic elements in telecommunications applications.

In this study, we examine the ability of nine separate fluorene-based semiconducting polymers to selectively wrap large-diameter SWCNTs produced by laser vaporization (LV). Two polymers in particular, poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(6,6’-{2,2’-bipyridine})] (PFO-BPy) and poly[(9,9-dihexylfluorenyl-2,7-diyl)-co-(9,10-anthracene)] (PFH-A), demonstrate the ability to exclusively select large-diameter semiconducting species with high yields critical to scalable device fabrication and higher luminescence intensities than typical aqueous dispersions. While PFO-BPy shows no selectivity for particular large-diameter s-SWCNTs, PFH-A disperses narrow chirality distributions comprised primarily of near-armchair s-SWCNTs and interacts uniquely with particular chiral indices. The results obtained here enable a better fundamental understanding of how aromatic polymers select particular SWCNTs to produce the highly enriched samples needed to move toward commercial applications requiring semiconducting SWCNTs. Additionally, the high-yield/high-purity s-SWCNT samples demonstrated here can be easily integrated into high-efficiency field-effect transistors and solar cells, and should immediately impact the fields of SWCNT digital logic and photovoltaics.
2.4 Results and Discussion

We first tested the ability of fluorene-based polymers to disperse LV SWCNTs produced at our typical synthesis temperature of 1125 °C (<d> = 1.3 nm). Figure 2.4a demonstrates that two polymers in particular, both PFO-BPy and PFH-A, disperse high concentrations of these large-diameter SWCNTs with undetectable contributions from metallic SWCNTs. The optical density (O.D.) for the PFO-BPy wrapped LV SWCNTs in a 5 mm path length cuvette is greater than 1.0 for most of the third (S33) and second (S22) semiconducting exciton peaks. With a peak S22 O.D. > 1.4 at 935 nm, these concentrations are significantly higher than any other reports using fluorene-based polymers on large-diameter arc discharge (S22 O.D. = 0.01) or LV SWCNTs (S22 O.D. < 0.2 in 10 mm cuvette). Furthermore, these results can be produced rapidly (< 1 hour), in contrast to methods such as DGU that typically require steps of 18 – 24 hours, produce relatively small quantities, and often require multiple iterations to
produce high s-SWCNT enrichment (e.g. > 99%). Interestingly, Berton et al. recently reported on a fluorene-based polymer with anthracene subunits (similar to PFH-A) that dispersed large-diameter LV SWCNTs, but required an additional DGU step to remove m-SWCNTs that lowered the yield (S_{22} O.D. ≈ 0.1). Using thermogravimetric analysis (TGA) and absorbance spectroscopy (detailed description in Section 2.4.4, Figures 2.12 – 2.13), we found that, for the sample shown in Figure 2.4a, PFO-BPy dispersed ~1/3 of the s-SWCNTs present in the raw SWCNT material without any other purification or centrifugation steps required prior to dispersion. Since device cost is intimately tied to raw material yield, our high-yield dispersions lend themselves naturally to commercial-scale production that will be necessary for future electronics applications. As demonstrated in Figure 2.4b, the highly concentrated SWCNT inks enabled by these polymers are easily integrated into roll-to-roll solution deposition strategies (e.g. ultrasonic spraying) for thin-film transistors or PV materials. The 3 x 3 inch film shown in Figure 2.4b required only a few milliliters of solution to fabricate and was sprayed in minutes.

In addition to commercially relevant yields, both absorbance and Raman spectroscopy demonstrate undetectable m-SWCNT impurities. The first metallic excitonic transitions (M_{11}), visible in Figure 2.4a for (non-selective) sodium cholate (SC) dispersed LV SWCNTs, are completely absent for the same SWCNTs dispersed with PFO-BPy and PFH-A. In Figure 2.4a, asterisks mark the positions of vibronic optical transitions for the s-SWCNTs, arising from coupling of A_{1g} phonons to momentum-forbidden dark excitons. These peaks also appear in the excitation scans extracted from PLE maps (Section 2.4.6, Figures 2.15 – 2.16). It is important to differentiate the s-SWCNT vibronic peaks from optical transitions of m-SWCNTs since they appear in a range (~700 – 800 nm) similar to that expected for the excitonic transitions of the largest diameter m-SWCNTs within this diameter distribution. For a more detailed discussion, we refer the reader to Section 2.4.6. To further verify the selectivity of these polymers, we looked for signatures of m-SWCNTs using Raman spectroscopy with a probe wavelength of 632.8 nm (1.96 eV), resonant with the M_{11} transitions of our LV m-SWCNTs (<d> ≈ 1.3 nm). In our control sample
of SC-dispersed SWCNTs (Figure 2.4c), we observe clear signatures assigned to the D, G, and M bands of m-SWCNTs. In contrast, for the PFO-BPy and PFH-A wrapped LV samples, we observe only peaks that match those from a polymer/toluene control sample (all peaks assignable to toluene), but no signs of m-SWCNT peaks. Polymer:SWCNT concentrations can be intentionally tuned to reduce the selectivity of PFO-BPy for s-SWCNTs. In this case, we are able to see signatures such as the G band that match those seen in the SC/LV sample (see Section 2.4.3, Figure 2.10), demonstrating that the characteristic m-SWCNTs appear identical in both samples. Other methods such as DGU can enrich large-diameter s-SWCNTs to 99%, while gel electrophoresis and column chromatography typically reach up to 95%. While not a quantitative comparison, we note that typically published absorbance spectra for large-diameter s-SWCNT samples produced by these methods have some small, but visible contributions to the absorbance spectra from m-SWCNTs. In contrast, for our PFO-BPy and PFH-A SWCNTs, we find no evidence of m-SWCNTs in the absorbance spectra or the more sensitive Raman measurements. From an analysis of the absorbance spectrum, and a comparison to a commercially available s-SWCNT material (Section 2.4.5, Figure 2.14), we estimate the s-SWCNT purity at > 99.0%.

![Figure 2.5. PLE maps of (a) PFO-BPy/LV, (b) SC/LV, and (c) PFH-A/LV. The inset shows a PL slice of PFO-BPy/LV (blue) and SC/LV (black) at 935 nm when both solutions had the same optical density. The PL intensity for the PFO-BPy/LV solution is ~3 times higher than the SC/LV solution. Circles indicate positions of s-SWCNT chiralities as reported by Weisman et al. Circles in red are near-armchair chiralities, with q = mod(n – m, 3) = 2 species filled in black. LV synthesis temperature for all three panels was 1125 °C. Full chirality assignments are omitted in (a) and (b) to avoid congestion, but are given in Section 2.4.7 (Figures 2.19 – 2.21).](image-url)
To determine the chiralities wrapped by each polymer, we obtained photoluminescence excitation (PLE) maps, shown in Figure 2.5. Most semiconducting species with $S_{11}$ from 1400 nm – 1750 nm and $S_{22}$ from 820 nm – 1010 nm are present in the PFO-BPy/LV PLE map. A similar chirality distribution is found in the PLE map of SC-dispersed SWCNTs in D$_2$O (Figure 2.5b), suggesting that PFO-BPy does not select particular chiral indices. When compared with the same LV SWCNTs dispersed in SC (Figure 2.5b inset), the PFO-BPy/LV peaks are significantly narrower and the PL intensity is a factor of ~3 higher for a sample with similar O.D. Increased PL intensity is consistent with recent reports that solvents with lower dielectric constants lead to higher PL quantum yields due to the reduction of excitonic screening and charge transfer-induced exciton dissociation sites.\textsuperscript{43,44} Water-filled SWCNTs have also been shown to produce broader peaks with lower PL quantum yield.\textsuperscript{45} The sharper and brighter peaks of the PFO-BPy/LV sample in toluene demonstrate that large-diameter LV SWCNTs can be bright near-IR fluorophores when dispersed in low dielectric media. Additionally, these samples should facilitate future quantitative PL studies of larger diameter SWCNTs that have not previously been dispersed by organic polymers.
Figure 2.6. (a) Raman spectra of LV SWCNTs synthesized at different furnace temperatures, highlighting the region of the diameter-dependent radial breathing modes (RBM). All spectra were taken of raw SWCNT powders with an excitation wavelength of 488 nm and a power of 7 mW. (b) Normalized absorbance spectra of PFH-A dispersed LV SWCNTs synthesized at different furnace temperatures. (c) and (d) PLE maps of PFH-A/LV using SWCNTs synthesized at 900 °C and 1175 °C, respectively.

The absorbance spectrum of PFH-A clearly contains a reduced number of peaks in the S_{11}, S_{22}, and S_{33} regions, indicating that it selects specific chiral species of s-SWCNTs. Accordingly, the PLE map for PFH-A (Figure 2.5c) is dominated by near-armchair SWCNTs, in particular the (10,8) SWCNT (d = 1.24 nm), demonstrating the ability of this polymer to disperse narrow chirality distributions of large diameter SWCNTs. In an attempt to probe the scope of PFH-A selectivity, we systematically manipulated the diameter distribution of the LV SWCNTs by tuning the temperature of LV synthesis away from our standard 1125 °C. Figure 2.6a displays the radial breathing modes of the raw SWCNTs produced by LV at different synthesis temperatures, and demonstrates a systematic progression to smaller average diameter (larger RBM ω) as the furnace temperature decreases, in agreement with absorbance spectra (Section 2.4.7, Figures 2.17 – 2.18). The PLE maps shown in Figures 2.6c-d (and others in Section 2.4.7,
Figures 2.19 – 2.21) demonstrate that PFH-A primarily selects near armchair SWCNTs regardless of diameter. For example, samples synthesized at 1175 °C (Figure 2.6d) are enriched primarily in the (11,9) SWCNT, while 900 °C synthesis (Figure 2.6c) leads to enrichment primarily in (9,7). Figure 2.7a summarizes the semiconducting species dispersed by PFH-A at all synthesis temperatures, demonstrating a universal preference of PFH-A for near-armchair SWCNTs over a large diameter range of ~0.8 – 1.4 nm. As the diameter increases, a small amount of SWCNTs with smaller chiral angles are observed in the PLE spectra, but these minority species only represent a small fraction of the population. These results demonstrate that the exertion of synthetic control over SWCNT diameter distribution, coupled with careful selection of wrapping polymer, can be used to rationally tune narrow chirality distributions for applications.

Figure 2.7. (a) Section of the graphene sheet near the arm-chair edge (θ = 30°). Semiconducting LV SWCNTs dispersed by PFH-A are denoted by red hexagons. Thick hexagons represent majority species, while thin hexagons represent minority species. (b) Shifts of S11 and S22 peak positions in PFH-A dispersions relative to PFO-BPy. Near-armchair q = 2 SWCNTs (red circles) reveal distinct trends, while other chiralities (blue diamonds) do not.

To better understand the underlying mechanism driving the selectivity of PFH-A for near-armchair SWCNTs, we compared the excitation (S22) and emission (S11) peak positions for the PFH-A and PFO-BPy dispersions. SWCNT exciton transition energies are known to be sensitive to the surrounding...
environment and undergo what are generally referred to as solvatochromic shifts when the surrounding dielectric medium is changed significantly.\(^{43}\) Thus, we expected to potentially observe different trends for the \(S_{11}\) and \(S_{22}\) solvatochromic shifts of PFH-A dispersed near-armchair SWCNTs when compared to minority species with smaller chiral angles. Figure 2.7b displays the shifts in \(S_{11}\) and \(S_{22}\) exciton energies (\(\Delta S_{11}\) and \(\Delta S_{22}\)) of SWCNTs dispersed with PFH-A relative to the energies observed in PFO-BPy. We chose the PFO-BPy exciton energies for normalization since PFO-BPy does not exhibit any chiral selectivity for large-diameter SWCNTs. Surprisingly, we found significant differences in shifts only for the near armchair SWCNTs in the \(q = \mod(n - m, 3) = 2\) family, as compared to all other SWCNTs dispersed with PFH-A (Section 2.4.7, Table 2.2). As shown in Figure 2.7b, the \(S_{22}\) energies for the \((7,5)\), \((8,6)\), \((9,7)\), \((10,8)\), and \((11,9)\) SWCNTs exhibit large blue-shifts (~ 4 – 9 meV) in the PFH-A sample (relative to PFO-BPy). In contrast, all other chiralities, including \(q = 1\) near-armchair SWCNTs, display either no shift or very small shifts, with most of these species exhibiting red-shifts. Additionally, the \(S_{11}\) energies for these five SWCNTs have red-shifts of 3.7 – 8.0 meV in the PFH-A sample compared to PFO-BPy (inversely correlated with diameter), while all other chiralities display a blue-shift. These marked differences suggest a change in the local dielectric environment around PFH-A dispersed \(q = 2\) near-armchair nanotubes\(^{43}\) that is not experienced by other SWCNTs dispersed by this polymer. This remarkable difference suggests that PFH-A may have different adsorption geometries based on chirality, similar to what has been predicted by molecular dynamics modeling for poly[9,9-dioctylfluorenyl-2,7-diyl] (PFO).\(^{47}\) These molecular dynamics models suggest that the selectivity of PFO is driven by a combination of SWCNT diameter and chiral angle that enables helical wrapping of the polymer around the nanotube. Another recent study suggests that in some cases, selectivity may be driven by the electronic overlap between polymer and SWCNT energy levels.\(^{29}\) Importantly, in the current study we dramatically vary both the diameter and the diameter-dependent positions of SWCNT orbital energy levels, so the unique shifts observed for \(q = 2\) near-armchair SWCNTs cannot be explained by these mechanisms.\(^{29,47}\) Instead,
we suggest that the adsorption geometry of PFH-A may be sensitive to subtle changes in chiral angle, given that the q = 2 near-armchair SWCNTs fall within a narrow chiral angle range (24.5 ° < θ < 26.7 °).

While these intriguing results do not allow us to speculate on the particular geometries adopted by PFH-A, they encourage the future use of molecular dynamics modeling to observe the potentially unique adsorption of PFH-A on near-armchair q = 2 SWCNTs.

Figure 2.8. (a) Structures of the polymers used in this study. Full names are given in text. We also studied the terpyridine and monopyridine analogues of PFO-BPy (Section 2.4.7, Figure 2.23). (b) Absorbance spectra for five other polyfluorene polymer/LV dispersions. LV synthesis temperature was 1125 °C. Spectra were taken in a 5 mm cuvette.

Besides PFO-BPy and PFH-A, we tested several other fluorene-based polymers with our standard LV synthesis (T = 1125 °C) SWCNTs: PFO, poly[9,9-dihexylfluorenyl-2,7-diyl] (PFH), poly[9,9-di-(2-ethylhexyl)-fluorenyl-2,7-diyl] (PF2/6), poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(9-hexyl-3,6-carbazole)] (PFO-C), and poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co{(1,4-benzo-[2,1′,3]-thiadiazole)}] (PFO-BT or F8BT). These five polymers showed minute or no extraction of large-diameter SWCNTs (Figure 2.8). We note, however, that the absorbance spectrum for PFO-BT wrapped LV SWCNTs is similar to that reported by Tange et al., who found enrichment in the (15,4) chirality.29 The very low SWCNT concentrations dispersed by PFO-BT make it difficult to assess the presence or absence of m-SWCNTs via absorbance and Raman, and also suggest this polymer is less useful for commercial SWCNT device applications.
Homopolymers of fluorene monomers with various alkyl chains (PFO, PFH, and PF2/6) did not exhibit any significant ability to disperse large-diameter SWCNTs. As has been observed for HiPco and CoMoCat SWCNTs, PFO was successful in dispersing smaller diameter LV SWCNTs synthesized at lower temperatures (Section 2.4.7, Figure 2.22), with dispersion ability rapidly falling off at a SWCNT diameter of ~1.1 nm (e.g. (9,7) SWCNT). It is likely that this inability for the homopolymers to effectively disperse large-diameter SWCNTs is primarily a structural effect related to the steric packing efficiency of the polymers around the SWCNT. Copolymers of fluorene and another subunit showed mixed results. While anthracene and bipyridine copolymers (e.g. PFH-A and PFO-BPy) are effective, PFO copolymers with benzothiadiazole and carbazole (PFO-BT and PFO-C) as the alternating subunit do not disperse large-diameter SWCNTs effectively. We also investigated the effect of modifying the copolymer subunit for PFO-BPy to one with a single pyridine and one with a terpyridine group (Section 2.4.7, Figure 2.23). Both of these polymers selected a similar range of s-SWCNT chiralities (partially reduced chirality distribution for the mono-pyridine subunit), but did not offer yields as high as PFO-BPy. Although our empirical results do not allow for a great deal of speculation on why certain subunits are particularly effective for dispersing large-diameter SWCNTs, we hope that they serve as a basis for future molecular dynamics studies aimed at exploring both steric and electronic effects. Such modeling efforts, when coupled with the synthetic control over SWCNT starting material demonstrated here, could aid in developing predictive models for polymers designed to select specific SWCNT species across a wide diameter range.

We conclude with a brief discussion of the relevance of these results to commercial processes and devices. For large-scale applications, it may be desired to use commercially available SWCNTs, and it has been suggested that arc SWCNTs may be less expensive to produce than LV SWCNTs. Figure 2.9a demonstrates the ability of PFO-BPy and PFH-A to disperse high concentrations of large-diameter s-SWCNTs synthesized via arc-discharge (purchased from NanoLab). These arc-discharge SWCNTs provide
a larger range of diameters to continue testing and indicate that PFO-BPy and PFH-A are effective regardless of synthesis method.

Figure 2.9. (a) Absorbance spectra of commercial arc-discharge SWCNTs (NanoLab D1L110-J) dispersed by PFO-BPy and PFH-A. Spectra were taken in a 5 mm path length cuvette. (b) and (c) PLE maps of PFO-BPy/arc-discharge and PFH-A/arc-discharge dispersions.

We further evaluate four key metrics that influence the scalability of our process:

- Impurity concentrations – percentage of m-SWCNTs in this case
- Dispersion concentration – mass of SWCNTs per volume of solution
- Yield – percentage of the SWCNTs in the raw material that end up dispersed
- Throughput – amount of desired SWCNT material that can be produced in a given amount of time

The importance of these metrics is fairly straightforward. Lower m-SWCNT impurity levels lead to devices with better performance and reproducibility, such as PV devices with minimized recombination centers and fewer short-circuited devices and FETs with larger on/off ratios and higher on-currents. Higher dispersion concentrations allow for rapid roll-to-roll deposition of SWCNT films over large areas. Higher yields minimize raw material costs, and higher throughput ensures that SWCNT ink production does not constitute a rate-limiting step in a particular fabrication process.

Our earlier analysis demonstrated that m-SWCNT impurity concentrations are kept well below 1% in our polyfluorene LV dispersions. From a TGA/spectroscopy analysis (Section 2.4.4, Figures 2.12 – 2.13), we found that ~1/3 of all s-SWCNTs present in the raw SWCNT material were dispersed by PFO-
Briefly, this analysis revealed that our raw LV SWCNT soot contains ~33% SWCNTs by mass and that the centrifuged dispersion in Figure 2.4a contains $0.081 \pm 0.002 \text{ mg/ml}$, or ~0.81 mg total, of > 99.0% s-SWCNTs. Combining this concentration with the SWCNT mass percentage of the raw soot (33%) demonstrates that 33 ± 4% of the semiconducting SWCNTs originally present in the raw SWCNT soot (or ~22% of all SWCNTs) are dispersed by PFO-BPy to yield the dark ink demonstrated in Figure 2.4. Using a conservative estimate of the amount of SWCNT solution we can produce and centrifuge in our lab, this translates to a lab-scale throughput of several milligrams (up to ~10 mg) of > 99% pure s-SWCNTs ($<d> \approx 1.3 \text{ nm}$) in under one hour.

To put this throughput in perspective, it is useful to compare to other separation methods. Although the quantitative yield and throughput are not routinely discussed for DGU and column chromatography studies, one recent study provides a useful benchmark. Feng et al. estimated a 27.2% yield of s-SWCNTs for their DGU separation, with a total retrieval of approximately 1 mg after DGU, or ~20 μg of SWCNTs per hour when considering the full 48 hours required to generate the sample. In addition to the significantly lower throughput relative to our polyfluorene dispersions, an important consideration to account for in this comparison is the fact that this DGU study required sonication for 24 hours. Several studies have demonstrated that key SWCNT performance metrics for electronics applications, such as conductivity in transparent conducting films or PL quantum yield, are significantly degraded by sonication-induced nanotube shortening, even for sonication times as low as one hour. We note that column chromatography should have significantly higher throughput than DGU, but we are unaware of detailed reports on the yield and throughput of this technique for large-diameter SWCNTs, so we cannot comment directly on how our process compares. The metrics addressed in our analysis of the PFO-BPY dispersions are summarized in Table 2.1.
For certain applications, it may be required to remove or replace excess polymer in solution. For example, films sprayed from these dispersions may need to have reliable nanotube-nanotube connections and hence minimizing the amount of polymer is needed. Excess polymer can be removed using a solvent extraction technique that involves pelleting out the SWCNTs with additional centrifugation and removing polymer rich supernatant. Neat solvent can be added to the precipitate to re-disperse nanotubes using mild bath sonication. Further polymer removal can be achieved by repeating this process. Another process by which we can remove excess polymer involves filtering solutions through a 0.2 μm Teflon filter, originally developed for removing PFO. Excess polymer washes through, while SWCNTs and bound polymer aggregates into a filter cake, which can be further washed and then re-dispersed under mild bath sonication. Furthermore, in both of these techniques the polymer rich supernatant can be reused to disperse new SWCNTs in order to reduce costs, although we have not yet explored the number of cycles for which the polymer selectivity is retained. Recent work has also been reported on exchanging PFO-BT for the photoactive polymer poly(3-hexylthiophene). This technique requires an initial solvent extraction step followed by adding an excess of the desired polymer to displace the fluorene polymer. Another solvent extraction step can then be performed. Polymer exchange could potentially be used to replace PFO-BPy or PFH-A for a number of other polymers relevant to a particular study or device.
2.4.2 Conclusions

In conclusion, both PFO-BPy and PFH-A demonstrate the ability to select and disperse large-diameter s-SWCNTs with excellent yield, throughput, and purity. PFH-A selectively disperses narrow chirality distributions comprised primarily of near-armchair SWCNTs, with $q = 2$ near-armchair SWCNTs displaying unique solvatochromic shifts. These results indicate that PFH-A has a universal preference for near-armchair SWCNTs over a large diameter range ($\sim 0.8 \text{ nm} < d < 1.4 \text{ nm}$), and also exerts a unique family dependence even within this narrow subset of large chiral angle SWCNTs. The concentrated dispersions enabled by these polymers will allow for semiconducting LV nanotubes to be used in commercially scalable solution-processed devices including FETs and photovoltaics. The bright and narrow PLE spectra permit further studies into individual chiralities whose diameter range can be tuned by careful selection of starting material. Finally, we demonstrate that synthetic control over the SWCNT diameter distribution within a particular synthetic protocol facilitates a better mechanistic understanding of how polyfluorene polymers wrap particular SWCNTs, and can also be used to rationally tune chirality distributions for applications.

2.4.3 Methods

Materials Synthesis

All of the polymers used in this study were purchased from American Dye Source, Inc. and were used without any further purification. Arc-discharge SWCNTs were purchased from NanoLab (D1L110-J), and were also used without further purification. LV SWCNT synthesis is described earlier in Section 1.2.

SWCNT/Polymer Dispersions

Polymer loadings for Figures 2.4, 2.8, and 2.9 were 2 – 2.5 mg/ml, while polymer loadings for Figures 2.5 and 2.6 were $\sim 1 \text{ mg/ml}$. All solutions were made in 10 ml toluene and heated to $\sim 80 \text{ °C}$ for a few minutes to dissolve the polymer. LV SWCNT loading for all samples was approximately 1 mg/ml of raw LV soot. NanoLab arc-discharge loading was higher at $\sim 4.5 \text{ mg/ml}$ because lower loadings led to m-
SWCNT impurities (See below for a detailed discussion on experimental conditions). Solutions were sonicated with a ½” probe tip for 30 minutes at 300 Watts (Cole-Parmer CPX 750) in a bath of cool (18 °C) flowing water to dissipate heat. Following sonication, solutions were centrifuged at 30,000 g for 5 minutes using a SW32Ti rotor (Beckman).

The SC solution was 1% SC in D2O with ~1 mg/ml raw LV soot. It was sonicated for 30 minutes with a ¼” probe tip at 225 Watts (Cole-Parmer CPX 750) in a bath of cool (18 °C) flowing water to dissipate heat and centrifuged for 4 hours at 134,000 g using a SW32Ti rotor (Beckman).

To intentionally disperse m-SWCNTs in PFO-BPy (Figure 2.10), we decreased the amount of nanotube material used to 1.4 mg in 10 ml toluene and kept the PFO-BPy concentration above 0.1%. Additionally, we used a purified buckypaper instead of raw soot. The buckypaper was produced by refluxing raw LV SWCNTs in 4 M nitric acid for 16 hours, and then filtering and washing with water, acetone, and 1 M NaOH to remove impurities generated by the reflux. Following this procedure, the buckypaper was burned rapidly in air at 525 °C to remove amorphous carbon.

Figure 2.10. (a) Absorbance spectrum of PFO-BPy/LV prepared to intentionally include m-SWCNTs (green). The absorbance spectra for SC/LV and PFO-BPy from Figure 2.4 are included for comparison. (b) Raman spectra showing metallic signatures in a solution of PFO-BPy/LV in toluene. Spectra have been offset for visibility. The concentration of PFO-BPy was higher than typical solutions and the LV SWCNTs were treated to remove metal catalyst and amorphous carbon impurities before being dispersed into solution in order to get m-SWCNTs to disperse as well. The D, G, and M bands become visible in this solution as well as the signatures from PFO-BPy/toluene.
Yield and Purity Dependence on Experimental Conditions

Expanding our results to disperse large-diameter s-SWCNTs from any source may play an important role in future applications using these polymers. We explored a number of different experimental factors to determine which ones are important for producing concentrated type-pure semiconducting SWCNTs, namely polymer loading, SWCNT loading, polymer:SWCNT ratio, sonication time, centrifugation time, and SWCNT source.

Higher polymer loading (in our raw LV case, ~2.5 mg/ml) led to more concentrated and higher yield dispersions. If the initial SWCNT loading is too low, having a high polymer loading can lead to m-SWCNTs being dispersed as well. This loading, however, depends on starting SWCNT material (LV vs. arc-discharge, raw vs. purified, and fraction of SWCNTs in material). Thus, it is the polymer:SWCNT ratio that must be tuned based on the starting material. Too high a ratio and metals can begin being dispersed, while too low a ratio leads to lower yields and concentrations. Interestingly, our raw LV SWCNTs could be pushed to a higher polymer loading without acquiring metals than our purified LV (buckypaper) material. The reason for this difference is still unknown, but allows us to skip purification steps that lower yield and are time intensive, while obtaining higher yield, higher throughput results. As seen in Figure 2.18, we also dispersed raw commercial arc-discharge SWCNTs (NanoLab D1L110-J) as well as our own raw in-house arc-discharge SWCNTs using loadings of about 1:1 polymer:raw SWCNT material.

Sonication and centrifugation considerations were also made. We found that increasing sonication time from 30 minutes to 1 hour led to higher yields, and behaved similarly to adding extra polymer, i.e. it could lead to m-SWCNTs starting to disperse. This allows a tradeoff between throughput (shorter sonication time) and starting material (less polymer). Longer centrifugation did not have a strong effect on our dispersions, but did lead to minor modifications in the chiral distribution. Other minor modifications were observed for lower polymer loadings, but neither of these removed any individual chirality to the point of higher selectivity.
Lastly, we were later able to test the effects of molecular weight (Mw) on yield and selectivity. For the above study, the Mw of PFH-A was 83,000 g/mol (83 kDa). In Figure 2.11 below, dispersions were made with five different molecular weights of PFH-A: 112 kDa, 83 kDa, 57 kDa, 51 kDa, and 14 kDa. The yield of dispersed SWCNTs increased with higher Mw, but the selectivity of the 112 kDa sample was lower than the other four, indicating that there is an upper limit for yield if one desires a narrow chiral distribution.

![Figure 2.11. Mw comparison of PFH-A. Higher Mw leads to higher yield, but can begin to reduce selectivity for very high Mw.](image)

**Spectroscopy Characterization**

All spectroscopic measurements (absorbance, Raman, and PLE) were taken in a 5 mm path length cuvette, except for the SC/LV absorbance, which was taken in a 2 mm path length cuvette to prevent saturation of the detector. Some absorbance spectra in the sections below were taken in 1 mm path length cuvettes, and are labeled as such. Absorbance measurements were performed on a Varian Cary 500 spectrophotometer. Raman spectroscopy was performed using a Jobin Yvon 270 M spectrometer with a HeNe excitation laser at 1.96 eV (632.8 nm) in a backscattering configuration. Photoluminescence excitation (PLE) maps were acquired using a home-built Fourier transform spectrometer as previously described.\(^5^1\)
For Figure 2.5, the dispersions were diluted to have the same O.D. at 935 nm (peak S_22 O.D. of the PFO-BPy/LV sample). PL slices were then taken in 5 mm cuvettes to be able to quantitatively compare PL intensity across different samples, as seen in the inset.

### 2.4.4 Calculation of Dispersion Concentration and Yield for PFO-BPy

We calculated the concentration and yield of SWCNTs dispersed by PFO-BPy through a detailed gravimetric and spectroscopic approach. We define the dispersion concentration as the mass of nanotubes contained per milliliter of total solution (mg/ml) and the dispersion yield as the mass of dispersed semiconducting SWCNTs following centrifugation relative to the total mass of semiconducting SWCNTs found in the raw material before dispersion (% yield of s-SWCNTs). The yield can also be expressed as a total yield, which is defined as the mass of s-SWCNTs dispersed by PFO-BPy relative to the total mass of SWCNTs present in the raw material before dispersion.

Ideally, calculating the yield and concentrations of these dispersions could be made by simply comparing the absorbance of a sonicated dispersion before and after centrifugation. However, it is important to realize that the raw SWCNT soot that we use to make these dispersions contains much less than 100% SWCNTs by mass. There is a significant amount of amorphous carbon present in the raw soot, as well as the Ni and Co catalyst particles. Figure 2.12a compares the absorbance spectra for raw and highly purified SWCNTs at identical concentrations (0.12 mg/ml). To prepare the purified SWCNTs, 100 mg of SWCNTs are first refluxed for 16 hours in 4 M nitric acid, and then rigorously washed in a filtration apparatus (Teflon filter) with acetone, water, and 1 M sodium hydroxide to flush out non-nanotube carbon. Finally, the resulting nanotube paper is burned in air at 525 °C for ~30 seconds to thoroughly remove any remaining amorphous carbon. Thermogravimetric analysis (TGA) indicates that the resulting SWCNT paper is 97 ± 1% SWCNTs, with the remainder being Ni and Co catalyst particles.
In Figure 2.12a, each sample is sonicated in PFO-BPy/toluene for 30 minutes and is not centrifuged following sonication. It is immediately apparent that the absorbance spectrum for the raw soot dispersion contains a significant background that rises into the UV that is absent for the purified dispersion. This background has been demonstrated in numerous studies to arise from amorphous carbon impurities, and can be roughly approximated by a power law fit (red dashed line). When this background is subtracted from the raw soot dispersion (Figure 2.12b), the resulting spectrum is dominated by the strong excitonic SWCNT transitions, and overlays well on top of the purified spectrum when appropriately normalized. There are slight deviations between the corrected raw spectrum and the purified spectrum that arise from:

1. The power law fit not being a perfect representation of the absorbance for the amorphous carbon
2. A slight reduction in the contribution of small diameter SWCNTs to the purified dispersion, due to the increased reactivity (and loss) of smaller diameter SWCNTs in the purification process.

Regardless of these minor deviations, we can use the ratio of the optical densities (or the integrated peak areas) of the two samples to determine that the SWCNTs contribute to ~31% of the optical density observed for the purified SWCNT sample. Correcting for the weight % of SWCNTs in the purified dispersion (97%), and running this analysis on five separate raw SWCNT dispersions, we calculate an average value of 30 ± 3% by mass of SWCNTs in the raw soot.

To further validate the analysis described above, and as a second check on this analysis, we used TGA to determine the mass of SWCNTs relative to the total mass of raw soot, as shown in Figure 2.12c. Several groups, including ours, have demonstrated that when raw SWCNT soot is burned in air, both amorphous carbon impurities and SWCNTs decompose at the same time due to the exothermic oxidation of metal catalyst impurities that leads to thermal runaway. Thermal runaway can be avoided by performing the TGA in a flowing CO₂ atmosphere, in which the decomposition/oxidation of all phases becomes endothermic. Figure 2.12c demonstrates that in flowing CO₂, two distinct thermal
decompositions appear that are well separated by nearly 500 °C. Our extensive previous work, combining TGA and transmission electron microscopy, demonstrated that the first thermal decomposition can be assigned to amorphous carbon and the second decomposition can be assigned to SWCNTs. In the raw SWCNTs, the amorphous phase constitutes ~49% of the total mass loss, while the SWCNT phase constitutes ~38%. The residual mass observed above 1200 °C results from the oxidized Ni and Co catalyst particles. Previous X-ray diffraction (XRD) measurements in our group demonstrated that this phase consists primarily of NiO and CoO, but can also oxidize farther to Ni$_2$O$_3$ and Co$_2$O$_3$ at higher temperatures, resulting in mass increases of the catalyst phase of 127 – 136%. The residual mass of 9.9% yields a Ni/Co catalyst content of 7.5 ± 0.3%, close to the value of 6% utilized for the LV target material. Multiple TGA decompositions were measured to arrive at an average value of 36 ± 2% by mass of SWCNTs in the raw soot, a value slightly larger than the 30 ± 3% value estimated by absorbance. This discrepancy is understandable, since there could be amorphous carbon trapped within/between SWCNT bundles that isn’t burned away within the first decomposition. Regardless, including an artificially high value obtained by TGA should only cause us to underestimate the ultimate dispersion yield that we calculate. With this in mind, we calculate an average value for the SWCNT content of the raw soot of 33 ± 4% by mass, based on the average values of the absorbance and TGA measurements.

We next set out to calculate an absorbance coefficient for the second semiconducting excitonic transitions ($S_{22}$). For this measurement, we first dispersed six different aliquots of the highly purified (97%) SWCNT material into 10 ml of PFO-BPy solution, using the same sonication regime described for the samples in Section 2.4.3. The samples were weighed on a Mettler-Toledo microbalance, and masses ranged from 0.139 mg to 1.165 mg. The resulting dispersions were not centrifuged following sonication, so that the mass of SWCNTs in each dispersion was accurately known. Absorbance spectra of three of these samples are shown in Figure 2.13a. The optical density at 937 nm ($OD_{937}$ the peak of the $S_{22}$ transition envelope) was used to generate an absorbance coefficient, $\epsilon$, via Beers law: $A = OD_{937} = \epsilon \ell c$
where $\varepsilon$ is the absorbance coefficient with units of (ml mg$^{-1}$ cm$^{-1}$), $\ell$ is the path length in centimeters and $c$ is the concentration in mg/ml. Figure 2.13b plots $OD_{937}$, normalized to path length, versus the concentration of purified SWCNTs. The slope of the plot yields an absorbance coefficient, $\varepsilon = 39.86 \pm 0.69$ (ml mg$^{-1}$ cm$^{-1}$). Taking into account that the sample is not 100% SWCNTs, normalizing this value to the SWCNT content of $97 \pm 1\%$ yields $\varepsilon = 41.10 \pm 0.83$ (ml mg$^{-1}$ cm$^{-1}$).

The value of $\varepsilon = 41.10 \pm 0.83$ (ml mg$^{-1}$ cm$^{-1}$) is a valid absorbance coefficient for SWCNT dispersions containing the statistical ratio of s- and m-SWCNTs. Thus, this value must be adjusted for samples such as the PFO-BPy LV dispersions demonstrated in Section 2.4.1 that contain only s-SWCNTs. To adjust the absorbance coefficient accordingly, the absorbance spectrum was deconvoluted into the separate contributions of s- and m-SWCNTs. The s-SWCNT contribution was simply modeled by the PFO-BPY LV absorbance spectrum shown in Figure 2.4a. To model the m-SWCNT contribution, we utilized the spectrum of a highly pure (> 99%) m-SWCNT sample produced in our lab by density gradient ultracentrifugation (DGU). Figure 2.13c shows the result of this deconvolution, and demonstrates that for a sample containing only s-SWCNTs, $OD_{937}$ is $\sim 85\%$ of the value found for a sample containing the statistical ratio of s- and m-SWCNTs. This analysis adjusts the absorbance coefficient to $34.94 \pm 0.70$ (ml mg$^{-1}$ cm$^{-1}$) at the peak of the S$_{22}$ transitions, $\varepsilon_{937}$, for dispersions containing only s-SWCNTs.

We now have all of the numbers we need to calculate the concentration and yield of our PFO-BPy LV dispersions. First, we use the value for the absorbance coefficient determined above to estimate the concentration of the dark PFO-BPy dispersion displayed in Figure 2.4a-b, noting that the $OD_{937} = 1.41$ and $\ell = 0.5$ cm. This analysis yields a concentration of $0.081 \pm 0.002$ mg/ml for the PFO-BPy dispersion shown in Figure 2.4a. Next, using our estimation that the raw soot is comprised of $33 \pm 4\%$ SWCNTs, we can calculate the yield of s-SWCNTs dispersed by PFO-BPy. We start with the fact that our initial SWCNT loading for the sample in Figure 2.4a is $1.1$ mg/ml, meaning that $0.363$ mg/ml of SWCNTs are initially present in solution before processing, and only $2/3$ of these SWCNTs ($0.242$ mg/ml) are semiconducting.
Using the final concentration of the sample after centrifugation of 0.081 mg/ml, calculated above, we arrive at a yield of 33 ± 1%. This analysis suggests that PFO-BPy selectively disperses ~33% of the s-SWCNTs initially present in the raw SWCNT soot, or ~22% of all SWCNTs initially present in the raw soot.

To translate these numbers to a throughput, we consider that the high ink concentrations and material yields demonstrated above only require 30 minutes of sonication and 5 minutes of centrifugation. We have performed batch dispersions as large as 100 ml without observing any loss of selectivity. The centrifuge rotor used here (Beckman SW-31) has capacity for six tubes, with each tube holding a maximum of 39 ml, for a maximum capacity of 234 ml. If we consider a conservative estimate of performing two separate 100 ml batch sonications simultaneously (i.e. with two sonicators) and leaving 2 ml of solution in the bottom of every centrifuge tube following centrifugation, we arrive at 188 ml of retrieved solution. Using the concentration of 0.08 mg/ml calculated above, this translates to a lab-scale throughput of ~15 mg of > 99% pure s-SWCNTs (<d> ≈1.3 nm) in under one hour.
Figure 2.12. (a) Comparison of the absorbance spectra for raw and highly purified SWCNTs (97 ± 1 % SWCNTs) at identical concentrations. Each sample is sonicated in PFO-BPy/toluene for 30 minutes and is not centrifuged following sonication. The red dashed line illustrates a power law fit used to approximate the contribution of amorphous carbon impurities to the spectrum of the raw SWCNTs. (b) Comparison of the corrected absorbance spectrum for the raw soot (amorphous phase removed via subtraction of power law fit) to the spectrum of the purified material. Both samples are total mass loadings of 0.12 mg/ml. The dashed green spectrum is the corrected raw spectrum multiplied by 3.2 to overlay with the purified spectrum, indicating a ~32% SWCNT content in the raw soot (when correcting for the fact that the purified material is 97% SWCNTs). (c) Thermogravimetric analysis (TGA) of raw LV SWCNTs in CO₂. The 5 mg sample was ramped at 10 °C per minute to 1440 °C and held for 10 minutes. The weight loss axis is normalized to a 1 mg sample for clarity. The weight losses associated with each separate component are labeled in the plot, demonstrating that the SWCNTs comprise ~38% of the total sample weight. Two TGAs of separate aliquots of the raw material returned an average value of 36 ± 2% SWCNTs by weight in the raw material. Combining the values obtained through spectroscopic and gravimetric analysis produces an average value of 33 ± 4% SWCNTs by weight in the raw soot.
Figure 2.13. (a) Absorbance spectra of highly purified LV SWCNTs (~97% SWCNTs) dispersed in PFO-BPy/toluene and *not subjected to centrifugation*. (b) Absorbance (normalized to a 1 cm pathlength) at the peak of the S_{22} peaks (937 nm) for six different samples prepared in the same manner, as a function of sample concentration (mg/ml). The linear regression, shown in red, yields an absorbance coefficient at 937 nm of 39.86 ± 0.69 (ml mg\(^{-1}\) cm\(^{-1}\)). Correcting this number for the actual SWCNT mass (97 ± 1% of sample mass) yields a corrected value of 41.10 ± 0.83 (ml mg\(^{-1}\) cm\(^{-1}\)). (c) De-convolution of the absorbance spectrum of the purified SWCNT material into the contributions from s-SWCNTs and m-SWCNTs. The blue spectrum is a PFO-BPy LV dispersion containing only s-SWCNTs (semis) and the yellow spectrum is a > 99% m-SWCNT sample obtained via DGU (metals). The green spectrum is the sum of these spectra, which overlays well on top of the spectrum obtained from the purified SWCNTs dispersed in PFO-BPy and not centrifuged (black trace). This analysis allows us to correct the absorbance coefficient by multiplying by 85% to reach a final corrected value of 34.94 ± 0.70 (ml mg\(^{-1}\) cm\(^{-1}\)).

2.4.5 Qualitative Evaluation of s-SWCNT Enrichment

It is an important, but difficult, task to quantitatively evaluate the enrichment level of semiconducting or metallic SWCNTs produced by a given separation or dispersion procedure. Such information guides the expectations for a given material in device applications and also influences the interpretation of fundamental measurements that can be influenced by impurities with undesired
electronic structure. We typically estimate the enrichment level of our LV SWCNTs by absorbance spectroscopy. Specifically, a comparison of the integrated areas underneath the $S_{22}$ and $M_{11}$ peak envelopes can afford an estimate of the semiconducting or metallic SWCNT percentages. Using this analysis on our LV SWCNTs dispersed with PFO-BPy and PFH-A, we estimate s-SWCNT enrichment levels of at least 99%. A more quantitative analysis becomes difficult, especially for s-SWCNTs, at high levels of enrichment, e.g. > 99%, due to spectral overlap of the $M_{11}$ peaks with the $S_{22}$ and $S_{33}$ peak envelopes. Thus, absorbance cannot be used to assess whether or not a s-SWCNT enriched sample has the ppm-level m-SWCNT impurities required for applications such as digital logic.

In an attempt to qualitatively benchmark our polyfluorene dispersed LV s-SWCNTs, we compare our absorbance spectrum to that of (to our knowledge) the only commercially available large-diameter SWCNT product enriched in semiconducting nanotubes. This comparison is shown below in Figure 2.14. The spectrum of a sample that is sold as 99% s-SWCNTs, produced by Nanointegris via DGU of arc-discharge SWCNTs, was obtained directly from the Nanointegris Technical Data Sheet for their IsoNanotubes-S product: (http://www.nanointegris.com/en/downloads). The IsoNanotubes-S spectrum is shown in purple, while our PFO-BPy/LV sample is shown in green. We adjusted the absorbance and wavelength ranges of our spectrum to match those used by Nanointegris (the wavelength tick marks are included in our plot and overlay directly over the tick marks in the other plot). The absorbance axis is adjusted so that the peak intensity of the $S_{22}$ envelope is equivalent for each spectrum, and the axis range is adjusted so that each axis covers the same fractional change in absorbance (i.e. a factor of 12 absorbance change over the displayed range). This normalization ensures that valid comparisons, free of artificial baseline manipulation, can be made between the spectra. The primary qualitative observation that can be made from this comparison is that the spectrum for our PFO-BPy dispersed LV SWCNTs has less structure, and a deeper valley, between the $S_{22}$ and $S_{33}$ peak envelopes where the $M_{11}$ peaks are observed in mixed samples. This observation suggests that our PFO-BPy dispersed LV SWCNTs have an s-
SWCNT enrichment level at least equivalent to, and likely higher than, this commercially available IsoNanotubes-S product that is quoted at a 99% s-SWCNT purity level. From this comparison, and our own analysis of the integrated S_{22}/M_{11} areas, we conclude that our polyfluorene-dispersed LV SWCNTs have s-SWCNT enrichment levels greater than 99.0%. Work to rigorously quantify the purity beyond this level is ongoing.

Figure 2.14. Overlay of PFO-BPy/LV absorbance in toluene with the absorbance of the commercially available IsoNanotubes-S product from Nanointegris. The range for the absorbance axis for the PFO-BPy/LV sample is 0.14 to 1.68.

2.4.6 Vibronic Sidebands of s-SWCNTs in Absorbance Spectra (e.g. Figure 2.4a)

The peaks labeled with asterisks in Figure 2.4a are vibronic absorbance features related to optical transitions of dark (optically forbidden) excitons (center of mass momentum at the K point, thus momentum-forbidden) that are coupled to in-plane transverse optical (iTO) phonons, also known as the D band. We discussed this vibronic feature in detail for the (6,5) SWCNT in a recent Nano Letters publication. These features are easy to distinguish in nearly-monochiral samples (Figure 2.15), but show
up as broad peak envelopes in samples with multiple chiralities and may overlap with optically allowed transitions. The peaks in question arise from the second K-momentum dark exciton vibronic transitions. The energy of this feature always appears ~180 – 200 meV above the energy of the optically allowed transitions in question, since the dark exciton lies ~25 – 40 meV above the bright exciton. The peaks arising from the first (lowest energy) K-momentum dark exciton vibronic transitions are easily visible in the region of ~1200 to 1350 nm in the absorbance spectrum in Figure 2.4a, and those arising from the second dark exciton vibronic transitions are visible in the range of ~700 – 800 nm. The correlation of two shoulders in Figure 2.4a at 750 nm and 800 nm with semiconducting SWCNTs can be most easily seen by turning the 2D PLE map of Figure 2.5a into a 3D map and turning it on its side (Figure 2.16a). This produces a structured excitation profile of the semiconducting SWCNTs that demonstrates distinct peaks at ~750 nm and ~790 nm. Excitation slices also reveal these features very clearly (Figure 2.16b). For example, the excitation slice at 1555 nm emission wavelength reveals a prominent feature at 750 nm, due to the vibronic excitation of the second dark (K-momentum) exciton of the (11,7) SWCNT.

Figure 2.15. (a) PLE map of PFO-dispersed CoMoCAT SWCNTs (SG65 material). The sample is highly enriched in the (7,5) SWCNT, with small contributions from the (7,6), (8,6), and (6,5) SWCNTs. (b) Absorbance spectrum (green) and PL excitation spectrum (orange) of the same sample. Labels mark the first and second bright excitonic transitions (S_{11} and S_{22}) of the (7,5) SWCNT, as well as the first and second phonon-assisted dark excitonic transitions (X_{11} + D and X_{22} + D, where D is the iTO “D-band” phonon).
Figure 2.16. (a) Three-dimensional PLE map of PFO-BPy dispersed LV SWCNTs (synthesis T = 1125 °C) turned on its side to display the excitation spectra of all SWCNTs. The arrows point out two vibronic peaks due to phonon-assisted absorbance of the optically forbidden K-momentum exciton ($\chi_2$) via coupling to the D band phonon. (b) Excitation slices at 1555 nm and 1592 nm to highlight the vibronic sidebands of the (11,7) and (10,9) SWCNTs, at 750 nm and 790 nm, respectively.

2.4.7 Spectroscopic Characterization of the Full-Range of SWCNT Synthesis

In the figures below, the full absorption spectra and PLE maps are shown for SWCNTs synthesized by laser vaporization at 800°C, 900°C, 1000°C, 1125°C, 1175°C, and commercial arc discharge when dispersed by SC, PFO-BPy and PFH-A. These data give a broad overview of the selective capabilities of the two main polymers studied here.
Figure 2.17. Normalized absorbance spectra of SWCNT starting materials dispersed by SC in D$_2$O. LV SWCNT diameters increase with higher synthesis temperatures. Commercial arc discharge SWCNTs (NanoLab D1L110-J) provide larger diameter SWCNTs to increase our diameter range.

Figure 2.18. Normalized absorbance spectra for (a) PFH-A dispersions of LV SWCNTs synthesized at different temperatures and two different sources for arc-discharge SWCNTs and (b) the same spectra, but dispersed with PFO-BPy.
Figure 2.19. PLE maps for LV SWCNTs synthesized at (left column) 800 °C and (right column) 900 °C. The rows correspond to SWCNTs dispersed in (top row) SC/D$_2$O, (middle row) PFO-BPy/toluene, and (bottom row) PFH-A/toluene. The bottom left distribution, observed for the 800 °C sample, is consistent with that of PFH-A/HiPco. Diagonal features in the upper left corners correspond to excitation light entering the detector.
Figure 2.20. PLE maps for LV SWCNTs synthesized at (left column) 1000 °C and (right column) 1125 °C. The rows correspond to SWCNTs dispersed in (top row) SC/D$_2$O, (middle row) PFO-BPy/toluene, and (bottom row) PFH-A/toluene. Diagonal features in the upper left corners correspond to excitation light entering the detector.
Figure 2.21. PLE maps for (left column) LV SWCNTs synthesized at 1175 °C and (right column) commercial arc-discharge SWCNTs (NanoLab D1L110-I). The rows correspond to SWCNTs dispersed in (top row) SC/D_{2}O, (middle row) PFO-BPy/toluene, and (bottom row) PFH-A/toluene. Diagonal features in the upper left corners correspond to excitation light entering the detector.
Figure 2.22. Absorbance spectra for PFO dispersions of LV SWCNTs synthesized at temperatures varying from 800 °C to 1125 °C. At lower synthesis temperatures, the spectra are similar to those from HiPco SWCNTs, but for higher synthesis temperatures, PFO is no longer efficient at selecting near armchair SWCNTs.

Figure 2.23. (a) Absorbance spectra of PFO-BPy derivatives with a single pyridine (PFO-MPy, red) and a terpyridine group (PFO-TPy, purple). While not as effective as PFO-BPy, these other two polymers also disperse only s-SWCNTs. (b) PLE map of PFO-MPy/LV. SWCNT dispersions using PFO-MPy are
significantly lower yield, but show a preference for (13, 5) nanotubes as recently reported.\(^3\) (c) PLE map of PFO-BPy/LV. (d) PLE map of PFO-TPy. LV synthesis temperature for all three samples was 1125 °C. Polymer and SWCNT loading was the same as in Figures 2.4 and 2.8.

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Table 2.2. PLE peak positions in PFO-BPy/LV and PFH-A/LV dispersions. The shifts in PFH-A relative to PFO-BPy are also given. The near-armchair SWCNTs are in red. Clear trends are seen in the mod(n – m, 3) = 2 subset of these as explained in the main text. Larger diameter chiralities may be present in some dispersions, but are beyond our current PLE capabilities to quantify.

### 2.5 Solvent Extraction and Advanced Separation Methods

In most stable SWCNT solutions, there is often an excess of surfactant or polymer in solution that remains in equilibrium between the adsorbed and desorbed solution phases. In Section 3.1, I will discuss film preparation where the surfactants and polymers are no longer desired. Briefly, aqueous surfactants can be filtered out or polymers such as CMC can be removed with acid treatment. Fluorene-based polymers in organic solvents such as chlorobenzene or toluene require a bit more care.

Two main methods have been developed to remove excess polymer from polyfluorene-based SWCNT dispersions: filtration\(^{25,52}\) and solvent extraction.\(^{50}\) In filtration, the dispersion is run through a 0.1 or 0.2 µm pore size PTFE filter that allows free polymer through, but aggregates nanotubes and
bound polymer.\textsuperscript{25,53} This mat of nanotubes can be washed and redispersed in a different organic solvent with mild sonication. With the solvent extraction method, dispersions of nanotubes are centrifuged until they precipitate out into a pellet.\textsuperscript{49,50} The supernatant, which contains free (unbound) polymer, is removed, while the pellet is redispersed into fresh solvent with mild bath sonication. For the three main polymers we use for extractions – PFO, PFO-BPy, and PFH-A – we generally make dispersions in toluene. In this case, to form the SWCNT pellet, we centrifuge the dispersion in the SW32 rotor at 24,100 RPM (100,000 g) for 20 hours at 0°C. This step can be repeated as necessary and varies with polymer and starting concentration. Removing excess polymer from solution becomes critical for fabricating well-coupled films as discussed in later sections.

Further characterization of these dispersions after polymer removal offers insight into the quantity of polymer removed in each step, yield of nanotubes retained, polymer to nanotube ratio, etc. To quantify the concentrations of the polymer and nanotubes, the extinction coefficients or absorption cross sections are needed. Finding the extinction coefficient of each polymer is a straightforward measurement where a known mass of polymer is dispersed in a fixed volume of solvent and the absorption spectrum is taken. From a series of these measurements, an extinction coefficient can be extracted. For example, in Figure 2.24, a series of PFO-BPy solutions are made and the peak OD at 360 nm is measured. According to the Beer-Lambert Law,

\[
A = \varepsilon lc
\]

where \(A\) is the optical density of the solution in a cuvette with path length \(l\) at a concentration \(c\), the extinction coefficient (\(\varepsilon\)) is about 108 ml/(mg*cm). Likewise, for PFO an extinction coefficient of approximately 90 ml/(mg*cm) is obtained (in agreement with previously reported values)\textsuperscript{54} and for PFH-A it is around 100 ml/(mg*cm). For carbon nanotubes, a few extinction coefficients exist in the literature, including one shown in detail in Section 2.4.4, and these can form the basis for estimating values for other species.\textsuperscript{55,56}
In Figure 2.25a below, the absorption spectra are given for PFO/(7,5) before and after polymer removal steps. In the sample with polymer removal, the residual polymer to nanotube ratio is about 1:1. The polymer peak is greatly reduced and the onset of absorption is blue-shifted in the samples with polymer removal. Furthermore, interesting features can be seen in photoluminescence maps. In Figure 2.25b-c, an energy transfer peak from the polymer to the nanotubes can be seen in both samples. The energy transfer peak positions blue-shift as the polymer concentration is reduced, in agreement with previous studies.\textsuperscript{53,57} The aggregated \(\beta\)-phase polymer has absorption features which are red-shifted compared to the free polymer in solution and this phase is more prevalent in the dispersion before removing polymer.\textsuperscript{53} Furthermore, the energy transfer is apparently weaker when there is excess polymer in solution, indicating that not all polymer in solution is in close proximity to the nanotubes.
In the process of separating and purifying SWCNTs, one may also find the surfactant or solvent of the desired end product to differ from those used in the intermediary steps. Changing solvents can include going from an aqueous dispersion to an organic one or switching between two organic solvents, while unwanted surfactants can arise from earlier DGU runs or in polyfluorene polymer separations.

Starting from the solvent extraction procedure, it is also possible to exchange surfactants or polymers. One such approach based on solvent extraction was recently used to disperse nanotubes into poly(3-hexylthiophene) (P3HT) after a DGU step that produced an aqueous solution of s-SWCNTs. After DGU, there were two surfactants as well as the density gradient material, iodixanol, which needed to be removed. The SWCNTs were precipitated out by adding methanol (with a volume equal to that of the aqueous dispersion) and then centrifuging. Further steps of centrifuging and washing in water, acetone

Figure 2.25. (a) Absorption spectra of PFO/(7,5) before and after polymer removal steps. PLE maps of PFO/(7,5) (b) before and (c) after polymer removal. The energy transfer peaks blue shift as the polymer concentration is reduced.
and toluene removed the surfactants and prepared the SWCNTs for redispersion into a P3HT/toluene solution.³ Alternatively, poly(9,9'-dioctylfluorene-co-benzothiadiazole) (F8BT) was exchanged in favor of P3HT by removing excess F8BT via solvent extraction and then adding in excess P3HT, which displaced F8BT around the nanotubes.⁵⁰ This method can also be used to make coaxial coatings of two different polymers.⁵⁰ Furthermore, this technique was found to preferentially allow unselective polymers to replace more selective ones.⁵⁸ In this way, PFO bound to single-chirality (7,5) SWCNTs could be replaced by F8BT or P3HT.⁵⁸ This method can potentially be expanded to make several different single-chirality samples in a desired polymer.

Another method to move from an aqueous solution to an organic solvent is based on filtration. To acquire a near single-chirality sample, we combined the separation techniques of column chromatography and polyfluorene polymers. As discussed earlier, narrow diameter ranges of SWCNTs can be obtained from column chromatography by tuning the SDS concentration used to elute the nanotubes from the column. After eluting the larger diameter HiPco SWCNTs (i.e., those that contain (9,7) but no other smaller diameter near arm-char species), we added an equal volume of methanol to aggregate the nanotubes and then vacuum filtered the solution through a 200 nm pore size alumina filter. The SWCNTs formed a loose mat that was washed with deionized water until the SDS all washed through. The filter was then dissolved in 4M NaOH leaving only the mat of nanotubes that were subsequently washed with water, acetone and then toluene before redispersing the SWCNTs in a solution of PFO in toluene. The PFO primarily selects the (9,7) from this distribution, producing a near single-chirality sample. In this way, combining both column chromatography and polymer extraction can improve chiral selectivity.

Finally, I explored another technique of improving selectivity by combining polymer extraction and DGU. Starting with a concentrated sample of PFH-A wrapped 1125°C LV SWCNTs yields a dispersion with three main chiral species and about six minor ones. To further narrow the chiral distribution, I
sought to run this sample in a density gradient ultracentrifugation step. Since the polymer-wrapped SWCNTs have a higher density than surfactant encapsulated ones and the solvent is now toluene instead of water, this procedure required moving from aqueous iodixanol as the density gradient medium to 2,4,6-tribromotoluene (TBT) in chlorobenzene (CB) as had been tested previously.\textsuperscript{28,59} To prepare the DGU tube, two fractions of TBT in CB are made: one at 1.3 g/ml and one at 1.4 g/ml. The PFH-A dispersion is then added to the top of these two layers (see Figure 2.26a). Unlike the aqueous DGU, here the gradient forms on its own instead of being prepared beforehand. The SW32 rotor is used and run at 28,500 RPM for 17 hours at 20°C and a visible gradient is seen with a band below it, which is highly enriched in the (10,8) chirality as seen in Figure 2.26b-c. Obtaining such narrow chiral samples, especially at larger diameters, can be quite challenging. However, combining multiple separation techniques as shown may allow us to achieve near single chiral distributions required for sensitive optical experiments that cannot be otherwise attained in large enough quantities.

Figure 2.26. TBT DGU centrifuge tubes (a) before and (b) after running DGU step. (c) PLE map of enriched (10,8) sample made \textit{via} polymer extraction combined with DGU.

References


Chapter 3

Chemical Doping for Transparent Conducting SWCNT Films

In typical photovoltaic device architectures, the electrodes are on the front and back surfaces of the solar cell. In order for light to reach the photoactive region, the front contact must be transparent to the solar spectral region. Traditional transparent conducting oxides (TCOs) such as In$_2$O$_3$:Sn (ITO) and SnO$_2$:Fe (FTO) have provided low sheet resistances with high optical transmission, however they are brittle and not suitable for solution processing. Transparent conducting films (TCFs) of carbon nanotubes or graphene have the potential for reduced costs, use in flexible thin-film architectures, and offer a wider range of processing/deposition strategies. Furthermore, through chemical doping the conductivity of these films can be increased and the work function can be tuned appropriately for different device architectures making SWCNTs a versatile option. For optimal performance as TCFs, SWCNTs may need to exceed 90% transmittance with sheet resistance below 100 Ω/sq.\(^1\)

Before SWCNTs can be successfully used in photovoltaic devices, appropriate methods of film preparation are required. This may involve tuning the thickness, roughness, SWCNT type, and other parameters. In the next section, I will discuss the most suitable techniques for film deposition. Beyond simply fabricating films, the next steps involve understanding and manipulating SWCNT film properties to maximize transparency and conductivity (Sections 3.2-3.3).

3.1 Preparing Films of Single-Walled Carbon Nanotubes

Incorporation of SWCNTs into PV devices relies heavily upon developing methods to produce uniform thin films with properties suitable for a given device architecture. Transparent conducting
electrodes must be uniform over large areas and preferably be prepared by high-throughput methods to ultimately minimize cost. In the following section, some methods for deposition of thin SWCNT films are discussed, with an emphasis on films for transparent conducting electrodes.

Early methods of preparing SWCNT films involved vacuum filtering a suspension of nanotubes over an alumina or mixed cellulose ester filter membrane.\(^2\)\(^3\) These films could then be transferred by dissolving the filter membrane or by a wet transfer process.\(^4\) While this process is quite versatile, and produces films with good transparency and conductivity, it suffers from some drawbacks with regards to the incorporation of SWCNT films into finished devices. For example, vacuum filtered films often suffer from high surface roughness, \textit{i.e.} nanotubes do not necessarily all lie in the plane of the film.\(^5\) This high surface roughness can be especially problematic for organic photovoltaic devices, since it can lead to SWCNTs penetrating through the thin active layer and short-circuiting devices. Similarly, the process is not particularly well-suited to high-throughput deposition for large-area devices.

In an effort to address the need for high-throughput deposition of uniform SWCNT films, we use a technique developed at NREL based on ultrasonic spraying.\(^5\) In this method, a syringe pump is used to feed a SWCNT ink through an ultrasonic spray nozzle, which atomizes the solution into a fine mist. These microdroplets are then directed down towards a heated substrate on a motion control stage. Ultrasonic spraying is a scalable, precise, and controllable technique to reproducibly fabricate large-area films. In one adaptation of this technique, SWCNTs are dispersed in an aqueous carboxymethyl cellulose (CMC) solution before using the ultrasonic sprayer to deposit a film of nanotubes. The SWCNTs are suspended in a matrix of CMC, which is subsequently removed in an acid bath to create a thin, smooth film consisting only of nanotubes. The film is comprised of a dense percolation network of interconnected SWCNTs, with many junctions between individual SWCNTs and/or SWCNT bundles. The majority of SWCNTs lie in the plane of the film, implying transport in the lateral direction should be much preferred over transport perpendicular to the plane of the film. These film properties – high nanotube/nanotube
junction density and preferential alignment in the plane of the film – play important roles in both charge carrier and exciton transport and will be discussed in more detail below.

The method described above relied upon an acid treatment to remove the CMC polymer matrix from the SWCNT film to form robust nanotube/nanotube junctions. Such aggressive post-deposition treatments are incompatible with applications requiring SWCNT TC deposition directly onto PV active layers. Recent techniques have been developed to avoid the use of surfactants in preparing SWCNT inks. For example, certain solvents disperse SWCNTs effectively in the absence of a surfactant or wrapping polymer, due to the matching of the surface energy of SWCNTs with that of the solvent. In particular, n-methyl pyrrolidone (NMP) and cyclohexyl pyrrolidone (CHP) produce stable SWCNT solutions, albeit at relatively low concentrations.6 These inks can be used to prepare films without requiring an additional step such as treating with harsh acids. In a recent study, it was demonstrated that transparent conducting SWCNT films prepared by ultrasonic spraying from CHP had identical sheet resistance versus transmittance compared to films prepared by CMC, once each set of films was doped.6 This comparison demonstrates that the ultimate performance of thin films prepared by true SWCNT solutions can match that of films prepared by SWCNTs dispersed with surfactants. Note, however, that a final acid doping step was used to ensure that each set of films was doped strongly p-type, ostensibly negating the lack of an acid-based polymer removal step in the CHP process. However, there are several other less chemically aggressive p-type dopants to choose from that are as effective as nitric acid, such as triethyloxonium hexachloroantimonate,7 which would enable a fully acid-free doped SWCNT thin film deposition process for thin-film PV. Additionally, for device applications, where it may be desirable to maintain a low defect density and long nanotube length, a method of dispersing SWCNTs without sonication has been developed. SWCNTs were observed to spontaneously disperse in a dimethylformamide solution of alkali metal-ammonia or under the application of an electrochemical potential.8,9
Finally, this ultrasonic spraying technique can be applied to other SWCNT inks such as highly enriched s-SWCNTs dispersed in organic solvents with polyfluorene polymers. Although this is primarily used for preparing films used in active layers, it can also be used to make transparent conducting films. This technique uses inks from the polymer extraction described in Sections 2.3-2.4 and is explained in more detail in the following section.

3.1.1 Ultrasonic Spraying of SWCNT Films from Organic Solvents

As discussed in Chapter 1, many applications such as FETs and photovoltaic devices require highly enriched s-SWCNTs are desired for optimal performance.10,11 Dispersions such as those from Sections 2.3-2.4, can be easily used in the preparation of films for these devices. Previously for these dispersions, film deposition methods included drop-casting,11 spin-coating,12 and doctor-blading.13 Ultrasonic spray deposition, however, overcomes certain deficiencies in these techniques to provide a scalable, reproducible method for depositing uniform nanotube networks (see Figure 3.1).

Figure 3.1. (a) AFM image of a nanotube film sprayed from a polymer extraction dispersion. (b) Examples of inks used to spray a large-area thin-film such as the one shown here.
Since the solvent used in these inks differs from that of the aqueous CMC inks, some parameters of the ultrasonic sprayer need to be adjusted. These account for differences in solvent boiling point, volatility, and viscosity. The nozzle power used was approximately 0.8 W, the syringe dispensing rate was set to 0.25 ml/min, and the flow rate of nitrogen gas was set to 7.0 SLPM. Initially, we sought to heat the substrate such that the vapor pressure of toluene would match that of water at 80°C. Our first films sprayed at this temperature, 86°C, showed significant signs of scattering and high surface roughness. Increasing the temperature to 130°C, however, helped to create smoother films. Although the surface roughness is improved, we found that additional post-treatment steps can further improve the quality of the film. Further details on these treatments are described in Section 3.5.

![Figure 3.2](image)

**Figure 3.2.** (a) Absorbance spectra of transparent thin films prepared by ultrasonic spraying of LV SWCNTs dispersed in toluene with either PFO-BPy or PFH-A. The PFH-A film suffers from more haze than the PFO-BPy, most likely due to scattering from excess PFH-A, producing a sloping background for the PFH-A absorbance spectrum. However, the comparison clearly demonstrates the narrower chirality distribution for PFH-A, in agreement with the PLE maps shown in the main manuscript. (b) Absorbance spectra of PFO-BPy and PFH-A dispersions of LV SWCNTs taken in a 1 mm path length cuvette to allow toluene background subtraction. Excitonic transitions in solution are clearly narrower than in films because SWCNTs are well isolated.

As seen in Figure 3.2, the absorption spectra from sprayed films differ from that of the parent solution. In toluene, the nanotubes are well-isolated, but in the films they are in close contact with polymer and other SWCNTs which leads to broadening of optical transitions. These broader peaks lead to additional spectral congestion and smoother features.
3.2 Improving Transparency and Conductivity of SWCNT Films

Conductivity ($\sigma$) is defined as the product of the carrier density ($n$) and the carrier mobility ($\mu$): $\sigma = ne\mu$. Thus, any conducting film requires two important things: appreciable carrier density at/near the Fermi level, and appreciable mobility for those carriers. For SWCNT thin films, the carrier density is a function of both electronic structure and the Fermi level ($E_F$). As mentioned above, m-SWCNTs are semi-metals and have carriers at $E_F$ even when intrinsic. However, it should be noted that the actual carrier density at $E_F$ is fairly small, since the DOS vanishes in the vicinity of the Dirac point. Thus, the potentially excellent conductivity of m-SWCNTs relies heavily upon the presence of high carrier mobility when in the intrinsic state. Semiconducting SWCNTs have no carriers at $E_F$, and are thus highly insulating, in their intrinsic state. Thus, s-SWCNTs must be doped either p- or n-type to shift $E_F$ positive or negative in order to increase the carrier density. Doping SWCNTs can be done in three main ways: (1) substitutional doping where C atoms are replaced with electron-rich or electron-deficient atoms (e.g. N or B), (2) electrochemical doping where SWCNTs are held at a potential difference relative to another electrode, and (3) chemical doping where ions or small molecules adsorbed to the nanotube surface inject or remove some local charge. Chemical doping is the main focus of this section as it does not disrupt the SWCNT pi electron cloud by $sp^2$-$sp^3$ rehybridization or rely on supplying an external voltage.

Most commonly, SWCNT films tend to be slightly p-type due to atmospheric oxygen adsorption. Furthermore, most p-type chemical dopants show some degree of environmental stability, since oxygen and water have been shown to be p-type dopants of SWCNTs themselves. Typically, Brønsted acids, SOCl$_2$, or halogens have been used to intentionally dope SWCNT films p-type, however halogens are corrosive and acid processing can damage sensitive devices. Triethyloxonium hexachloroantimonate (OA) has been shown to be an alternative to harsh acids and further benefits from longer term stability than dopants such as nitric acid. After just a few days, nitric acid doped films
showed a decrease in conductivity, as well as decreased transmission in the $S_{22}$ regions, while OA remained stable.\textsuperscript{7} Another organic p-type dopant, bis(trifluoromethanesulfonylimide) (TFSI), has been shown to reduce SWCNT film sheet resistance.\textsuperscript{15}

Environmental stability has been a problem for n-type SWCNTs and most previous work has been with individual nanotubes. One such chemical dopant that has been employed in a limited number of nanotube studies is polyethylenimine (PEI).\textsuperscript{16} Additionally, alkali metals can be used to dope individual SWCNTs n-type.\textsuperscript{17} We have shown that amines, most notably hydrazine, work as chemical n-type dopants for entire SWCNT films,\textsuperscript{18} as discussed in detail below. While these films still need to remain in an inert environment, progress has been made towards air-stability by encapsulating the films with polymers such as PEI, but devices may also be closed to environment to enhance lifetime and thus negate the need for such encapsulation.

Another method of improving transparency of films is to exclude SWCNT chiralities that strongly absorb in the visible region. The $M_{11}$ transitions in m-SWCNTs with diameters between 0.7 – 1.4 nm overlap with the brightest region of the solar spectrum, so having a film of only s-SWCNTs can improve transparency. Furthermore, type-pure semiconducting SWCNTs lack the $\pi$-plasmon resonance that gives a rising absorption background starting in the near-UV or blue-edge of the visible spectrum.\textsuperscript{19} Even s-SWCNTs, however, have significant spectral congestion due to overlapping excitonic transitions,\textsuperscript{19} so narrow or single-chirality s-SWCNT films may provide the best transparency for SWCNT TCFs.

There remains some uncertainty over what type of electronic properties are best in SWCNT films to reach the best device performance. Chemical doping studies on nanotube films with tunable s-/m-SWCNT ratios have shown that films with a higher ratio of s-SWCNTs exhibit lower sheet resistance and would thus be expected to perform better in a PV device.\textsuperscript{20} Since m-SWCNTs have a non-zero density of states at $E_f$ even when intrinsic, they tend to outperform s-SWCNTs that have not been strongly doped. Upon chemical doping, however, the Fermi level can be shifted up or down into the first van Hove
singularity in s-SWCNTs to dramatically increase the DOS available. In another study, however, PV devices made with electronic type controlled SWCNT films doped with HNO₃ were found to have a larger PCE with a higher ratio of m-SWCNTs. This difference was attributed to de-doping of the films during processing. To resolve this issue, a potential experiment could be done using a more stable dopant such as OA to maintain doping levels during device processing.

3.3 N-Type Doping of SWCNTs

In Section 3.3, I focus on my detailed study aimed at controllably doping SWCNT thin films n-type, and understanding the fundamental optical and electrical properties of both n- and p-type SWCNT thin films. Adapted with permission from ACS Nano, 2011, 5, 3714. Copyright 2011 American Chemical Society.

N-type chemical doping of SWCNTs has been performed by two general approaches – treatment with alkali metals and adsorption/intercalation of small molecules or polymers. Alkali metal doping relies on either vapor transport of the metal into a SWCNT network or intercalation of metal ions in aprotic solvents such as THF or DMSO. In some cases, doping by alkali metals has been observed to introduce irreversible structural defects as observed by an increased D band in Raman spectra. The majority of molecular n-type SWCNT dopants consist of amine-containing molecules or polymers, although other organic dopants have been utilized. Small molecule amines, such as hydrazine, and amine-containing polymers, such as polyethylenimine (PEI), have been used to create n-type single-tube or sparse-network field effect transistors. Other work has used hydrazine to disperse nanotubes through electrostatic repulsions, similar to the case of alkali-metal saturated organic solvents mentioned above. To our knowledge, no groups have applied n-type doping strategies to thin, optically transparent SWCNT networks. Furthermore, fundamental spectroscopic studies of n-type SWCNTs are relatively scarce in the literature, motivating the need for more detailed investigations.
In this study, we investigate the effects of several amines on thin SWCNT films to find an effective n-type dopant for SWCNT TCFs. Based on conductivity and optical transparency, we determine hydrazine (N₂H₄) to be more effective than methylamine, ethylenediamine, and polyethyleneimine. Then, using hydrazine as a case study, we use a combination of Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), and nuclear magnetic resonance (NMR) to investigate the mechanisms underlying the interactions of amines with SWCNT networks. Using a range of macroscopic samples, from transparent films to opaque buckypapers, allows us to correlate a variety of doping-induced spectroscopic modifications to the excellent transport properties obtained by hydrazine doping. Previous work on the doping effects of hydrazine on SWCNTs has focused on single-tube field effect transistors (FETs).²⁷,³⁰ In contrast to studies of single-tube FETs where it is difficult to decouple the carrier density injected into the nanotube from modification of the nanotube/contact junction by the dopant,²⁷,³¹ we unambiguously find physi-sorbed hydrazine to be an effective n-type dopant of SWCNTs when used in an inert environment. Moreover, we find that N₂H₄ can produce films with nearly the same sheet resistance (at a given transparency) as p-doped HNO₃ treated films due to the injection of extremely high electron densities into both semiconducting and metallic SWCNTs. These results serve both to increase the knowledge base in the community regarding the fundamental properties and spectroscopic signatures of n-type doped SWCNTs and to expand the versatility of functional SWCNT network electrodes that have typically been resigned to high work function p-type SWCNTs.

3.3.1 Results and Discussions

Amine-Doped Transparent Conducting Films

We produced thin nanotube films by ultrasonic spraying of SWCNTs dispersed in sodium carboxymethyl cellulose (CMC). An inter-connected SWCNT network was formed by removal of CMC in a nitric acid treatment as previously described.⁵ After CMC removal, the film is doped heavily p-type from
the nitric acid soak. The film may be made intrinsic by soaking in 4M hydrazine overnight in a helium
glovebox and then exposing the film to air.\textsuperscript{32} Further details are provided in the Methods section. We
further treated these intrinsic films with four different amines (hydrazine, methylamine,
ethylenediamine, and polyethylenimine) and compared their sheet resistances and transmittance
spectra (Figure 3.3a) for insights into the relative doping abilities of the different amines. Injection of
carriers by dopants, whether holes or electrons, quenches the optical transitions of SWCNTs by
emptying initial states or filling final states involved in these transitions.\textsuperscript{33,34} Due to the one dimensional
density of states of SWCNTS, optical transitions are excitons that acquire their oscillator strength from
pairs of van Hove singularities and are labeled, for example, $S_{11}$ for the first transition in semiconducting
SWCNTS or $M_{11}$ for the first transition in metallic ones.\textsuperscript{33,34} The amine-treated samples each have
significantly quenched intensity for the semiconducting $S_{11}$ optical transition (Figure 3.3a), which is a
clear sign of a doping-induced Fermi level shift. Of the four amines, hydrazine had the lowest sheet
resistance and most significant $S_{11}$ quenching. It is well documented that nitric acid lowers the Fermi
level of SWCNT networks by removal of π electron density,\textsuperscript{20,34} and conversely the data in Figure 3.3a
suggest that adsorbed amine molecules and polymers increase the Fermi level by electron injection (\textit{vide infra}).

Figure 3.3. (a) Transmittance spectra of thin SWCNT films of similar thickness treated with different
dopants. The sheet resistance for each sample is noted and a spectrum for the uncoated glass substrate

![Figure 3.3](image_url)
is shown for comparison. Four different amines were tested with hydrazine showing the best quenching of the \( S_{11} \) transition and having the lowest sheet resistance. (b) Sheet resistance vs. transmittance at 550 nm (\( T_{550} \), with the glass substrate subtracted out) for a series of SWCNT films. The films were sprayed at four different thicknesses and treated with either nitric acid or hydrazine. Sheet resistance for hydrazine films was measured in an inert-atmosphere glovebox where they were prepared, while nitric acid treated samples were measured in air.

For many device applications such as solar cells, touch screens, and LEDs\(^5,35,36\) it is important for SWCNT thin films to have low sheet resistances while maintaining high visible light transmittance. Previous work has found that doping SWCNT films p-type using nitric acid or thionyl chloride will drastically lower sheet resistance for films with relatively high transmittance,\(^20,32\) allowing these films to be incorporated as hole-collecting electrodes in PV devices. To investigate how hydrazine compares to nitric acid, several films were sprayed with varying thicknesses and were doped either p-type with nitric acid or n-type with hydrazine. Figure 3.3b shows a plot of sheet resistance vs. transmittance at 550 nm for these two series of films. We note that these transmittance values have been adjusted for the transmittance of the glass substrate, shown in Figure 3.3a, so that the values represent the percentage of light transmitted through the SWCNT films only. This correction was done in order to provide values for useful comparison to other literature values, since this is the most common method of comparison found in the literature. Figure 3.3b demonstrates that hydrazine can be used to produce SWCNT films with comparable sheet resistances, at a given transmittance, to those treated with HNO\(_3\). This reduction in sheet resistance, along with bleaching of the \( S_{11} \) transition, is strong evidence that hydrazine acts as a chemical dopant. Furthermore, the performance demonstrated by Figure 3.3b is among the best ever obtained for p-type SWCNT TCFs\(^37-39\) (~50 \( \Omega/\text{sq} \) at 75% \( T_{550} \)) and is the first result we are aware of demonstrating highly conductive n-type SWCNT TCFs (~70 \( \Omega/\text{sq} \) at 75% \( T_{550} \)).

The absorbance and transport measurements shown in Figure 3.3 demonstrate that small molecule and polymeric amines act as strong chemical dopants on single-walled carbon nanotubes, enabling highly conductive TCFs. However, these results cannot confirm that the amines are acting as n-type dopants, since absorbance quenching can result from state-filling by holes or electrons.
Furthermore, the M\(_{11}\) transitions are not affected in Figure 3.3, making it unclear to what extent the amines interact with metallic SWCNTs. Finally, Figure 3.3 yields no information on the mechanism of amine interaction with the SWCNT surface, i.e. whether or not the amine molecules form covalent bonds with the SWCNT or are simply physisorbed to the SWCNT surface. To investigate these questions in more detail, we performed a variety of spectroscopic characterizations, including x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy.

**X-Ray Photoelectron Spectroscopy (XPS)**

Photoelectron spectroscopy is a useful tool for understanding molecular adsorption and charge transfer on SWCNT surfaces. Since XPS probes the binding energy of core electrons, it is sensitive to changes in the Fermi level and can also be used to reveal the specific bonding environment(s) of carbon atoms in the doped SWCNTs. Moreover, by comparing the intensities of different atomic core levels, the overall atomic composition can be determined, which can yield information on the coverage of dopants on the SWCNT surface. Figure 3.4 displays core-level XPS spectra for intrinsic, hydrazine-doped, and nitric-doped SWCNT buckypapers in the C 1s and N 1s regions. Significant doping induced changes were observed in both the C 1s and N 1s core levels. Previously reported results for C 1s peak position in nitric acid treated samples were found to be shifted 0 eV, 0.1 eV, and 0.2 eV toward lower binding energy compared to as-prepared samples. Since the binding energy is measured with respect to the Fermi level, a change in binding energy of spectral features directly corresponds to a change in the Fermi level. As shown in Figure 3.4a, we find a downshift of 0.1 eV, in good agreement with the previous results, and consistent with a shift in the Fermi level towards the valence band edge due to p-type doping by HNO\(_3\). For the hydrazine-treated sample, we find an upshift of 0.7 eV in the C 1s binding energy, which is consistent with a sizable Fermi level shift towards the vacuum level. Importantly, the magnitude of this shift, 0.7 eV, is larger than the expected energy difference (ΔE\(_{\text{LUMO}}\)) between the Fermi level for intrinsic SWCNTs and the first van Hove singularities for ~1.35 nm diameter semiconducting SWCNTs. Taking the
S_{11} energy of ~0.73 eV (S_{11} peak in Figure 3.3a of 1700 nm) as the energy of the first excitonic transition, and an estimate of 0.25 eV as the approximate binding energy for this transition for 1.35 nm diameter SWCNTs, we approximate ΔE\text{LUMO} to be 0.48 eV. Thus, the Fermi level shift of 0.7 eV demonstrates that N_2H_4 injects a sufficient electron density into the SWCNT network to raise the Fermi level well into the conduction band of the semiconducting SWCNTs.

The N 1s spectra were examined to determine the nitrogen bonding configurations present in nitric acid and hydrazine treated samples. The as-prepared and nitric-doped samples both have peaks in the 406 – 407 eV range, consistent with HNO\textsubscript{3} and NO\textsubscript{2}. The presence of this signal in the intrinsic sample indicates an incomplete removal of nitrate in the washing procedure used for SWCNT purification. The N 1s spectrum of the hydrazine treated sample shows a peak at 400.9 eV, which we attribute to hydrazine since it falls within the expected range for amines of 399-401 eV. Two other small peaks appear between 404.5 and 407 eV, which could be residual nitrites and nitrates. The relative area of the 400.9 eV N peak for the hydrazine doped sample indicates that approximately 79% of the nitrogen comes from hydrazine. Based on this value and the atomic composition found via XPS, we can approximate a coverage of ~1.84 hydrazine molecules for every 100 carbon atoms and accordingly a density of 6.92 x \text{10}^{20} hydrazine molecules/cm\textsuperscript{3}. Taking the number of carbon atoms per nm of SWCNT to be 119.7·d_{(n,m)}, where d_{(n,m)} is the diameter of the SWCNT in nanometers, we find a coverage of approximately three hydrazine molecules per nm of SWCNT.

Based on the higher conductivity and stronger quenching of optical transitions in HNO_3 doped films, we expected the downshift in the C 1s core level for nitric acid treated films (Figure 3.4a) to be similar in magnitude to, or higher than, the upshift in hydrazine treated films. Furthermore, we would expect to see a higher nitrogen concentration for the nitric-treated film than is observed. We attribute this discrepancy to desorption of nitric acid while under vacuum during XPS measurements, as has been seen before. Further evidence of HNO_3 desorption was found when measuring sheet resistance. When
samples were brought into a glovebox, they were exposed to vacuum (<100 mTorr) in an antechamber. For nitric-treated samples exposed to vacuum in the antechamber, even for a matter of 3-5 minutes, we observed a significant increase in the sheet resistance relative to samples kept in air and not exposed to vacuum. After ~5 minutes in vacuum the resistance had increased by around 20%, while after one hour the resistance had doubled. In contrast, when N$_2$H$_4$ treated samples were exposed to vacuum, there was no noticeable change in sheet resistance, even for samples kept under vacuum for an hour. Collectively, these experiments demonstrate that adsorbed hydrazine is significantly more stable on the SWCNT than nitric acid in a vacuum environment, explaining why we are able to observe a much larger Fermi level shift in the high-vacuum XPS experiment for the hydrazine-doped sample. However, we note that the XPS spectra for both hydrazine- and nitric-doped SWCNTs do not show evidence of additional peaks (relative to the undoped sample) associated with $sp^3$ carbon, which are expected in the range of 285 – 290 eV. Thus, it appears that the mechanism for SWCNT doping is based on charge transfer from physically adsorbed dopant molecules without covalent bond formation, as we confirm by NMR measurements below.

![Figure 3.4. XPS spectra of (a) C 1s (normalized) and (b) N 1s (normalized to C 1s peak) core levels for as-prepared, nitric acid treated, and hydrazine treated buckypapers.](image-url)
Raman Spectroscopy

Raman spectroscopy provides further insight into the effects of doping on SWCNT samples. For chemical dopants, charge transfer from electron donors into the SWCNT π system softens the C-C bonds, dampening vibrations and leading to a redshift of Raman peaks, while charge transfer from the SWCNT π system into electron acceptors stiffens the bonds and blueshifts Raman peaks. The G band is often used to investigate charge transfer in doped SWCNTs, while the G’ peak has been found to be more sensitive to changes in π electron density. For example, studies using Li, K, and Rb as electron donors have found doping-induced redshifts of up to 8 cm⁻¹ in the G band due to electron transfer into the nanotubes. In contrast, for electron acceptors like HNO₃ and Br₂, blueshifts are observed for both the G and G’ peaks. Shin et al. investigated p-doped arc discharge nanotubes treated with HNO₃ and report blueshifts of 9.9 cm⁻¹ in the G’ band when excited with a 1.96 eV laser, which mainly probes the metallic SWCNTs and blueshifts of 21.6 cm⁻¹ for the G’ band with a 1.58 eV laser, which primarily excites semiconducting SWCNTs.

While photoabsorption and XPS measurements demonstrate that hydrazine raises the Fermi level into the conduction band of the semiconducting SWCNTs, these measurements do not address the scope of interaction with metallic SWCNTs. To probe metallic nanotubes, we took Raman spectra using an excitation laser of 1.96 eV (632.8 nm), which is resonant with the M₁₁ transition of 1.35 nm diameter SWCNTs. In Figure 3.5a, the G bands for three samples of different doping (intrinsic, n-type with hydrazine, and p-type with nitric acid) are shown. We observe a significant reduction of the asymmetric Breit-Wigner-Fano (BWF) lineshape of the G band for metallic SWCNTs in the hydrazine and nitric treated samples, which is consistent with previous work on HNO₃ and SOCl₂ treated SWCNTs that attribute this decrease to a loss of continuum states due to chemical modification. We further find that both the D (~1320 cm⁻¹) and M (~1745 cm⁻¹) bands in the two doped samples are greatly reduced as compared to the intrinsic film (Figure 3.5a). The complexity of the G band at this excitation wavelength
makes the determination of absolute doping-induced shift ($\Delta G$) difficult. However, we note that the G band for the hydrazine-doped sample is redshifted 8.8 cm$^{-1}$ relative to the nitric-doped sample, as expected for samples that are relatively electron-rich and electron-poor, respectively. The structure of the G’ band at ~2630 cm$^{-1}$ is less complex than that of the G band, and the G’ position has been shown to be very sensitive to charge transfer doping of SWCNTs. Figure 3.5b shows the G’ band for the same three samples, showing dramatic quenching of the G’ for both N$_2$H$_4$ and HNO$_3$. Furthermore, Figure 3.5b demonstrates a redshift for the hydrazine-doped sample of approximately 11.8 cm$^{-1}$ and a blueshift of 10.4 cm$^{-1}$ for the nitric-doped sample. Since shifts in opposite directions are expected for the injection of holes and electrons, these results confirm the conclusion reached through XPS measurements that hydrazine dopes the SWCNTs strongly n-type by injecting electrons and raising the Fermi level towards vacuum.

Figure 1.5. (a) Raman spectra of G bands for thin SWCNT films of different doping types: intrinsic (black), nitric-doped (blue), and hydrazine-doped (red). The hydrazine and nitric treated films have a doping-induced reduction of the BWF line shape as compared to the intrinsic film, as well as a significant reduction in D and M bands. (b) Raman spectra of G’ band for the same films show doping-induced shifts. The asterisk indicates background from the substrate and sample holder. Excitation is at 1.96 eV (632.8 nm), primarily resonant with metallic SWCNTs.

**Nuclear Magnetic Resonance (NMR)**

Solid-state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy with magic-angle spinning (MAS) is a powerful tool for probing the local chemical and electronic environment of carbon nuclei in
SWCNTs. While the benefits of NMR for studying functionalized SWCNTs\textsuperscript{43,48} are widely appreciated due to the obvious tie to traditional aromatic substitution reactions, NMR is also particularly useful for studying charge-transfer induced changes in the Fermi level.\textsuperscript{49} The observed chemical shift ($\delta$) for $^{13}$C nuclei can be separated into two parts, the chemical shift ($\sigma$) and the Knight shift ($K$):

$$\delta = \sigma + K$$  \hspace{1cm} \text{Equation 3.1}

In Equation 3.1, $\sigma$ and $K$ are second-rank tensors and consist of an isotropic and anisotropic part. The chemical shift $\sigma$ arises from two primary contributions – so-called London ring-currents due to delocalized inter-atomic currents in the aromatic ring structure, and the intra-atomic “Pople” contribution arising from the hybridization of the carbon atom. The Knight shift $K$ arises from short-(isotropic) or long-distance (anisotropic) coupling of nuclear spins to the spins of conduction electrons. The isotropic Knight shift ($K_{iso}$) is paramagnetic (causing a shift to higher frequency) and is related to the Fermi contact between nuclei and conduction electrons in orbitals with non-negligible s character. Thus, $K_{iso}$ is proportional to the probability density of conduction electrons at the nucleus $\psi_F(0)^2$ and the density of states at the Fermi level $n(E_F)$:

$$K_{iso} = \frac{\alpha}{3} \psi_F(0)^2 \mu_B^2 n(E_F)$$  \hspace{1cm} \text{Equation 3.2}

where $\mu_B$ is the Bohr magneton. In graphite, $\psi_F(0)^2$ is negligible because conduction electrons only occupy orbitals with p character. However, curvature-induced $sp^2$-$sp^3$ rehybridization in SWCNTs and fullerenes leads to a non-negligible s character for conduction electrons, meaning Fermi level changes due to charge transfer should induce an isotropic Knight shift.\textsuperscript{49,50}

Figure 3.6a shows solid-state MAS $^{13}$C NMR spectra for the same SWCNT sample either in an intrinsic, n-type, or p-type state. For each doped sample, the $^1$H-$^{13}$C cross-polarization (CP-MAS) NMR spectrum is also shown. In each case (n- and p-type state) the transfer of magnetization from protons of the dopant species to adjacent $^{13}$C nuclei on the SWCNT was observed. The series of spectra in Figure 3.6a demonstrates several interesting trends. The isotropic chemical shift for the intrinsic SWCNT
sample, directly after degassing, is 121 ppm, the characteristic chemical shift expected for undoped, highly pure SWCNTs. Upon n-type doping the SWCNT sample with hydrazine, the peak shifts to higher frequency by 8 ppm and broadens significantly relative to the undoped SWCNT sample. The CP-MAS spectrum for the same n-type SWCNT sample shows a similar broad and shifted peak at 128 ppm. After exposing the n-type sample to air for several hours, the peak narrows and shifts back to its original position at 121 ppm. Finally, when the sample is doped p-type by soaking in concentrated nitric acid, the peak again shifts to higher frequency (128 – 129 ppm) and broadens significantly, a strikingly similar behavior to the n-type doped SWCNT sample. Figure 3.6b compares the CP-MAS spectra for the hydrazine- and nitric-doped SWCNTs. The isotropic chemical shift of SWCNTs, in the range of 121 ppm (128 ppm for the doped samples), is due to \( sp^2 \)-hybridized carbon atoms. When aromatic \( sp^2 \) systems such as fullerenes or nanotubes are converted to \( sp^3 \) through the formation of covalent bonds, new peak(s) appear at lower frequency for the \( sp^3 \) carbon nuclei, typically in the range of 50 – 90 ppm. Figure 3.6b shows a complete lack of \( sp^3 \)-related peaks in the spectra for both hydrazine- and nitric-doped SWCNTs. This result clearly demonstrates that the mechanism for doping involves physically adsorbed dopant molecules and no covalent bond formation, in agreement with the conclusions reached from XPS analysis.
Figure 3.6. (a) Solid-state MAS $^{13}$C NMR spectra of 20% $^{13}$C-enriched SWCNT sample with 66% s-SWCNTs after various treatments (listed above/below the corresponding spectra). $^1$H-$^{13}$C CP-MAS spectra are labeled accordingly. The asterisk indicates the $^{13}$C resonance from the polyethylene plugs used to balance the rotor. (b) Comparison of CP-MAS NMR spectra for hydrazine- and nitric-doped samples, highlighting the area where peaks are expected for $sp^3$ carbon. Spinning side bands are labeled with asterisks.

Returning to Equation 3.2, the significant paramagnetic shifts observed for the $^{13}$C resonance in doped SWCNT samples are consistent with Knight shifts arising from a substantial increase in the density of states at the Fermi level due to injection of electrons or holes from the physically sorbed dopants. This conclusion is consistent with the absorbance, Raman, and XPS measurements discussed above, and lends further support to strong charge transfer interactions of SWCNTs with amines such as hydrazine that result in injection of electrons into the SWCNTs. The 7 – 8 ppm paramagnetic shift observed for the nitric acid-doped SWCNTs is also consistent with our previous work on SWCNTs doped strongly p-type with sulfuric acid. The efficiency of the spin polarization transfer process utilized in the CP-MAS experiment is distance-dependent, with a $1/r^6$ dependence. Thus, CP-MAS NMR can selectively probe SWCNT $^{13}$C nuclei in direct proximity of absorbed dopant molecules. In both cases, for hydrazine and nitric acid-doped samples, the CP-MAS spectra are similar in chemical shift and line width to the equivalent MAS $^{13}$C NMR spectra, implying a rather complete intercalation and coverage of the dopant.
molecules into the SWCNT buckypapers. Finally, the spectrum of the hydrazine-treated air-exposed sample confirms that reaction of the hydrazine sample in air over the course of several hours returns the doped SWCNTs to its intrinsic state and is completely reversible.

It is interesting to compare these results to previous results on other charge-transfer doped graphite-based systems. Significant Knight shifts have been consistently observed for electron-doped graphitic systems such as alkali-doped graphite intercalation compounds (GIC), C_{60} compounds, and SWCNTs. However, these shifts (Knight) have not been observed in hole-doped GICs, a phenomenon that has spawned much discussion in the GIC community. NMR measurements on both oxidized and reduced C_{60} have demonstrated doping-induced paramagnetic shifts that are accompanied by broadening, although the observed shifts for the oxidized fullerene are smaller than their reduced counterparts. Importantly, our results demonstrate that the coupling of $^{13}$C nuclear spins to the spins of both free electrons in n-type SWCNTs or free holes in p-type SWCNTs induces a paramagnetic shift (of similar magnitude) in the aromatic $^{13}$C NMR resonance for intrinsic SWCNTs. To equate the magnitude of the NMR shift to a density of injected carriers, a rigorous treatment would take into account the temperature-dependent spin-lattice relaxation time, which can be related directly to $n(E_F)$ via the Korringa relation, but this is beyond the scope of this dissertation.

**Air Stability of Amine n-Type Doping**

Now that we have rigorously characterized the n-type doping effects of amine molecules on SWCNT networks, we return to a practical consideration for device applications. A shortcoming of nearly all strategies for producing n-type SWCNTs is the lack of air stability. In an attempt to probe the air stability of our amine-doped n-type SWCNT TCFs, we monitored the doping-induced $S_{11}$ absorbance quenching for several different films. As shown in Figure 3.8a, we find that the doping effects of hydrazine are not stable in air for prolonged periods of time. By monitoring the strength of the $S_{11}$ optical transition over time as the sample sits in air, we can see that the peak increases in strength with
time as in Figure 3.8a, indicating a time-dependent de-doping of the film. This change in absorption is accompanied by an increase in sheet resistance, which is another indication that the doping level has decreased. This change in doping may be a result of hydrazine reacting in air,\textsuperscript{60} compensation by a p-type dopant such as oxygen, desorption of hydrazine, or a combination of some of these processes. From our testing of samples in vacuum, described above, it appears unlikely that hydrazine desorption is the cause. We further find that returning a sample to an inert atmosphere after brief exposure to air partially quenches the $S_{11}$ transition again and reduces the sheet resistance (see Figure 3.7). As there is no additional dopant added by allowing a sample to sit in the helium glovebox, this apparent “re-doping” is consistent with a decrease in compensation via oxygen desorption from the SWCNT film while remaining in a glovebox or when in vacuum as the sample is brought inside. However, after prolonged exposure to air, recovery of n-type conductivity is no longer possible.

![Absorbance vs Photon Energy](image)

Figure 3.7. A hydrazine-treated thin SWNT film was exposed to air briefly and then returned to an inert atmosphere. After air exposure, the $S_{11}$ transition returns, but is partially reduced upon sitting in a glovebox.

To address stability issues, several groups have explored the use of the amine-containing polymer polyethylenimine (PEI), which has been noted to produce relatively air stable FETs.\textsuperscript{16,28} We performed a series of experiments to probe and compare the air stability of our hydrazine and PEI
doped SWCNT TCFs. Films treated with PEI were found to partially quench the $S_{11}$ optical transition with sheet resistances several times higher than comparable hydrazine treated films (Figure 3.3). After exposure to air, we found that the PEI treated films also showed signs of decreased doping, indicated by a time-dependent increase in sheet resistance and the return of the $S_{11}$ (Figure 3.8b). We speculate that part of the reason that PEI has shown air stable results in FETs is due to its ability to keep oxygen away from the nanotubes. To investigate this further, we immersed a SWCNT film, which had already been treated with hydrazine, in PEI. This film had a sheet resistance around half that of a sample treated solely with PEI. In Figure 3.8c, we show that the $S_{11}$ transition returns much more slowly than for the other films treated with only hydrazine or PEI. In fact, the degree of $S_{11}$ quenching after 90 minutes of air exposure is nearly equivalent to the quenching observed for the hydrazine-treated sample immediately after air exposure. It should be noted, however, that the results in Figure 3.8 are indicative of the best air stability achieved and that there can be significant variability between samples, as well as variations depending on the type of PEI used (see supporting information). This demonstration of improved air stability is promising, and could be improved upon by optimization of the PEI over-coating, suggesting potential strategies to further develop air stable n-type SWCNT networks. Ultimately, for n-type SWCNT networks to be adopted in technological applications such as photovoltaics, significantly improved stability over what is presented here will be necessary.
3.3.2 Conclusions

In conclusion, four different amines (hydrazine, methylamine, ethylenediamine, and polyethylenimine) were used to treat thin conducting carbon nanotube networks. We found that all four amines induced a reduction in sheet resistance and partially quenched the $S_{11}$ optical transition, as compared to intrinsic films, showing signs of n-type doping. N-type TCFs, prepared from hydrazine-doped SWCNT networks, performed nearly as well as their p-type counterparts with $R_s$ values of 75 $\Omega$/sq at $T_{550}$ of 75%. Hydrazine doped SWCNTs were studied in depth to ascertain the fundamental
spectroscopic signatures of n-type SWCNTs and compare them to those of a well-characterized p-type dopant. Hydrazine induced spectroscopic changes clearly demonstrate the n-type doping behavior, as deduced by an upshift in the XPS-measured C 1s core level binding energies, indicating an increase in the Fermi level towards the vacuum level. Furthermore, we observed redshifts in Raman bands due to injected charge from the hydrazine electron donor, an opposite shift to that observed for p-type SWCNTs doped by nitric acid. NMR results demonstrate that both n- and p-type doping of SWCNTs leads to significant paramagnetic shifts in the isotropic $^{13}$C chemical shift. Because n-type SWCNTs generally lack the air stability of their p-type counterparts, we investigated the use of a polymer amine for our macroscopic thin film networks that has seen some success for FETs and single tube studies. Although PEI did not display doping characteristics as favorable as hydrazine, it was successful at prolonging the stability of our hydrazine-doped n-type film in air, suggesting potential strategies for the further development of air-stable n-type SWCNT networks. N-type SWCNT TCFs, such as the ones developed here, offer the ability to create efficient photovoltaic devices and LEDs with transparent SWCNTs as both hole and electron collecting electrodes, and could potentially enable tandem devices which require transparent electrodes for both contacts. Furthermore, spatially controlled coating of SWCNT networks (or forests) with amines as n-type dopants, in conjunction with molecular p-type dopants, opens up the possibility for macro-scale p-n junction photovoltaics.

3.3.3 Methods

Synthesis, purification, and ultrasonic spraying of CMC dispersed SWCNTs techniques employed in this paper have been described previously. CMC was removed by overnight soaking of the films in 4M nitric acid, which collapses the isolated SWCNTs into an interconnected conducting network as well as serves to dope them p-type. These TCFs were used in absorption, four-point probe, and Raman measurements.
To remove the doping effects of the nitric acid treatment and create intrinsic films, the sample was immersed in either 1 or 4M hydrazine in a helium environment and then exposed to air. Doping the films n-type involved a two-step process from the nitric doped samples. First, the films were immersed in 4M hydrazine and then exposed briefly to air (<10 minutes). Next, the films were immersed in neat hydrazine and kept in an inert environment. Soaking times for 1M and 4M hydrazine lasted from 4 to 24 hours, while neat hydrazine was only used for about 4 hours.

For the small molecule amine comparison, we started with intrinsic samples and soaked the films overnight in a glovebox in either hydrazine (neat), ethylenediamine (neat), or methylamine (33% wt. in ethanol). For PEI treated samples shown, intrinsic films were immersed in 10% w/v PEI (Aldrich, \( M_n = 10,000 \)) in methanol overnight, followed by rinsing in methanol to match previous work on PEI.\(^{61}\) For PEI used to overcoat hydrazine in Figure 3.8, we used 27% w/v PEI (Aldrich, \( M_n = 600 \)) in methanol overnight with rinsing.

Sheet resistance measurements were taken on a linear four-point probe.\(^{62}\) Hydrazine (and other amine) treated films were tested with a probe in the glovebox where they were prepared, while nitric treated samples were tested in air. Nitric treated samples that were brought into the glovebox had higher sheet resistances because of significant desorption of the dopant during the vacuum exposure. Raman spectroscopy was performed using a Jobin Yvon 270M spectrometer with a HeNe excitation laser at 1.96 eV (632.8 nm) in a backscattering configuration. The optical absorption spectra were taken on a Varian Cary 500 spectrometer.

For XPS and NMR measurements, thicker ‘bucky papers’ were used instead of sprayed films. The SWCNTs for NMR were synthesized via laser vaporization as above, but used a 20% \(^{13}\)C enriched graphite target. The \(^{13}\)C-enriched SWCNTs were subjected to density gradient ultracentrifugation to separate SWCNTs by electronic structure and remove residual catalyst metal (Co, Ni) impurities for the NMR measurements. Several samples were combined to produce a sample with ~66% semiconducting
SWCNTs, as measured by absorbance spectroscopy, after which a bucky paper was produced by vacuum filtration. This sample was degassed by heating to 200°C on a temperature programmed desorption apparatus to remove adsorbed impurities before doping. The bucky paper for XPS measurements was formed from un-enriched (i.e. no $^{13}$C) laser vaporization SWCNT sample that was subjected to our typical purification. This involves refluxing in nitric acid for 18 hours and then filtering and washing with water, acetone, and NaOH remove impurities generated by the reflux. This bucky paper was then burned rapidly (30 seconds) in air at 525 °C to remove amorphous carbon.

NMR samples were prepared in a glove-box under a helium atmosphere. The SWCNT materials (~0.8 mg) were loaded into zirconia rotors (7 mm outer diameter) and packed between two plugs of either polyethylene or Teflon to balance the rotor, center the small amount of SWCNT sample in the NMR coil, and provide a barrier against exposure to ambient conditions. Polyethylene plugs were used in single pulse experiments (35000 scans) and Teflon plugs in CP experiments (150000 scans) in order to minimize background signals. Samples were transferred in a helium bag directly to the NMR spectrometer. High-resolution, solid-state $^{13}$C NMR spectra were collected on a Bruker Avance 200 MHz spectrometer (4.7 T) operating at 50.13 MHz for $^{13}$C at room temperature, with a MAS rotation rate of 7 kHz under a nitrogen atmosphere. The spectra were acquired under high-power proton decoupling using a $\pi/2$ pulse length of 5.3 µs and a recycle delay of 10 s and were referenced to adamantane. The features at 115 and 139 ppm are due to unsaturated impurities in the polyethylene plugs. Ramped-amplitude CP experiments were carried out at room temperature using a 5 ms contact time, spinning rate of 7 kHz, and a pulse repetition rate of 1.0 s.

### 3.4 SWCNT Network p-n Junctions

Now that n-type doping of SWCNT networks was demonstrated, a logical next step would be to show that macroscopic SWCNT networks can form p-n junctions as well. This capability unlocks great
potential for nanotube electronic devices, such as a nanotube p-n junction diode that was produced using benzyl viologen as the n-type dopant.\textsuperscript{63} To fabricate our p-n junctions, either a p-type SWCNT film was partially immersed in an n-type dopant or vice versa. First a p-type film formed by doping with nitric acid was tested. Approximately one third of the film was submerged in the 10\% w/v PEI solution. For the n-type film, a hydrazine doped film was used and one third of it was submerged in OA. As has been shown in Section 3.3.1, Raman spectroscopy is a sensitive tool for detecting doping type and concentration in single-walled carbon nanotubes and has been characterized for both p-type and n-type doping. Using this technique, I investigated the change in doping to the macroscopic films and how it varied across these films. The hydrazine/OA film showed more success than the nitric/PEI film in terms of changes to sheet resistance and Raman characteristics. Figure 3.9 shows the G’ peak position as a function of distance across the hydrazine/OA film. The transition from n-type to p-type can be seen over 11.5 mm in the film with neat hydrazine and OA films displayed for reference. For typical device architectures, one usually desires a stacking of p-type and n-type films, rather than a change across the film, however, this method still demonstrates the feasibility of macroscopic p-n junctions. It should also be noted that these films were prepared using bulk LV SWCNTs sprayed from a CMC dispersion, as in Section 3.1, and thus do not make a true p-n junction, which requires purely s-SWCNTs. In Section 3.5, I discuss how we can dope films made by spraying polymer extracted s-SWCNTs.
Figure 3.9. Raman spectrum of an n-type SWCNT film partially soaked in OA to dope one side p-type. The G’ peak position is blue-shifted as the probe moves from the n-type side to the p-type side over 11.5 mm. Spectra of neat hydrazine doped (n-type) and OA doped (p-type) films are shown for reference.

3.5 Comparison with Separated SWCNT Films

As discussed in Section 3.1.1, we can spray films of type-separated SWCNTs by using the dispersions made via polymer extraction. Due to the increased transparency of the films from reduced spectral congestion and removal of metallic species, they may be suitable for use as transparent conducting films in PV or other applications. However, these films still have some amount of residual polymer which may inhibit charge transport and thus we sought to investigate the differences between these films and those made from bulk SWCNTs dispersed in CMC. 

With samples made from CMC dispersed SWCNTs, the CMC can be fully removed by treating the film with dilute nitric acid, which digests the cellulose polymer. The fluorene-based polymers are not digested by nitric acid, and are also adsorbed relatively strongly to the SWCNT surface, so it is important to probe the extent to which remaining polymer within the SWCNT/Polymer film perturbs charge
transport. Already, more than 99% of free polymer in solution is removed prior to spraying the films by the solvent extraction method described in Section 2.5. After spraying, the film is soaked in warm (70°C) toluene for between 2 minutes and an hour. For PFO, the soaking time does not seem to change the resultant film.

Figure 3.10. (a) Absorption spectra of a PFO/(7,5) film before and after soaking in toluene. PLE spectra of a PFO/(7,5) film (b) before and (c) after soaking. Photoluminescence from the (7,5) is quenched after soaking, indicating that the nanotubes may be highly coupled.

In Figure 3.10a, the absorption spectra of a PFO/(7,5) film is shown before and after the soaking step. Several changes are observed. The integrated absorbance of the soaked film ($S_{22}$) is lower, indicating that some nanotubes are lost due to soaking the film in toluene. The $S_{11}$ transition broadens and slightly red-shifts, potentially signaling a better coupled network. The $S_{22}$ transition also broadens slightly, and undergoes a minor blue-shift. Finally, the PFO peak loses some structure on the red edge of the main absorption band, and also loses the β-phase shoulder at ~420 nm, indicating that aggregated
polymer is removed. Some of these changes can be verified by PLE maps and scanning electron microscope (SEM) images as shown in Figure 3.11. Before soaking, photoluminescence from the (7,5) nanotubes is observed from the film, while after the soaking step, the emission peak corresponding to the (7,5) is quenched. At low resolution, the ‘coffee’ ring formation can be seen in the pre-soaked film, while after soaking, the film has become uniform. At higher resolution, the pre-soaked film appears to have large amorphous domains, but after soaking, individual nanotubes can be observed.

Figure 3.11. Low resolution SEM images of a PFO/(7,5) film (a) before and (b) after soaking in toluene. Characteristic ‘coffee’ ring formation can be seen in (a) before soaking. High resolution SEM images of a PFO/(7,5) film (c) before and (d) after soaking in toluene. A network of nanotubes is clearly seen in (d) after soaking.
After producing well-coupled films of s-SWCNTs, the next step is doping them to decrease sheet resistance. Initial attempts with nitric acid either led to the films detaching from the substrate or to films whose sheet resistance increased over time. For more stable (and less aggressive) doping, we turned to OA. We soaked the films for 1 hour at 70°C in a solution of 100 mg OA in 10 mL dichloroethane (DCE). Figure 3.12a shows the full quenching of the $S_{11}$ transition and partial quenching of the $S_{22}$ transition as expected for a strongly doped film. Furthermore, four-point probe measurements of sheet resistance show that these OA doped LV/polymer films are comparable to the earlier n-type and p-type films made by doping bulk LV SWCNT films sprayed from CMC. This promising result shows that the residual polymer in the film does not significantly hinder the transport properties of the nanotube network and that these films can be incorporated into devices that require type-pure s-SWCNTs.

Figure 3.12. (a) Transmittance spectra of a film made by polymer extraction of LV SWCNTs using PFH-A. The nanotube exciton peaks become broader and less structured after toluene soaking and the $S_{11}$ becomes fully quenched after doping with OA. (b) Sheet resistance vs. transmittance for films made from PFO-BPy/LV and PFH-A/LV along with the data for bulk SWCNTs from Figure 3.3.

References


Chapter 4

Understanding and Controlling Charge Generation in SWCNT Active Layers

Organic photovoltaics (OPVs) are a class of second-generation photovoltaics with photo-absorbing active layers comprised primarily of $\pi$-conjugated polymers and fullerenes. OPVs operate on substantially different physical principles than their traditional inorganic (e.g., silicon) counterparts. Due to a lower dielectric constant than inorganic materials, and hence lower Coulombic-screening, the primary photoexcitations in organic media are excitonic in nature. Accordingly, OPVs are often referred to as excitonic solar cells.

Single-walled carbon nanotubes hold great potential for use in photoactive layers of solar cells. Particularly, they are strong optical absorbers at tunable wavelengths due to their wide range of chirality-dependent excitonic transitions. Furthermore, they exhibit high electrical conductivity, which may help to efficiently shuttle charge away from the interface (where exciton dissociation occurs) to the electrode for charge collection. The mobilities for both holes and electrons are comparable, due to rough equivalent effective masses for both carriers, so SWCNTs can be used as either the electron accepting or donating material. In this chapter, I briefly examine the progress made on incorporating SWCNTs into OPV active layers and discuss experiments that allow us to understand why SWCNTs have not yet lived up to their potential. I will investigate how electron affinity, exciton binding energy, thermodynamic driving force, and charge transfer reorganization energy all must be taken into account in order to improve exciton dissociation yields.
4.1 Flash-Photolysis Time-Resolved Microwave Conductivity

In order to better understand the nature of charge generation and separation in carbon nanotube photoactive layers, we need an effective tool to detect charge carriers. Microwaves can be a valuable contactless probe to investigate the conductance of a system through both the attenuation and phase shift of a microwave probe beam. This section discusses how microwaves can be used to directly measure the conductivity of mobile charge carriers and how we can characterize the mobility and yield of photo-generated charges in single-walled carbon nanotubes.

By measuring the time-resolved change in microwave power absorbed after photoexcitation, we can directly measure the change in conductance of our sample. An iris can also be used as shown in Figure 4.1 to couple microwaves into a cavity, which allows us to measure a microwave resonance curve similar to the one shown in Figure 4.2. The benefits of using a cavity include a more sensitive probe for low conductance samples as well as the ability to measure a shift in the resonance frequency to access information about the imaginary component. For time-resolved microwave conductivity (TRMC) measurements, however, we lose some time resolution for fast initial processes. To calculate the change...
in photo-conductance when using the iris, we use parameters from the resonance curve as shown in
Equation 4.1:\(^1,2\)

\[
\frac{\Delta P_r}{P_r} = \frac{2Q_L(1+1/\sqrt{R_0})}{\pi f_0\epsilon_0\epsilon_r a/b} \Delta G = -K\Delta G
\]

Equation 4.1

where \(P_r\) is the reflected microwave power, \(Q_L\) is the quality factor given by \(2\pi f_0/\text{FWHM}\), \(a\) and \(b\) correspond to the long and short axis of the X-band waveguide,\(^3\) and \(d\) is the length of the cavity. We then relate the change in photo-conductance (\(\Delta G\)) to the yield mobility product with Equation 4.2:

\[
\varphi \sum \mu_i = \frac{\Delta G_{\text{max}}}{\beta \epsilon_0 F_A}
\]

Equation 4.2

where \(\Delta G_{\text{max}}\) is the maximum change in conductance, \(\beta\) is the ratio of \(a\) and \(b\), and \(I_0\) is the incident intensity of the laser, and \(F_A\) is the fraction of light absorbed by the sample. In this equation, we assume that yield \(\varphi\) of each carrier type is the same as they are created by dissociation of excitons. The mobility \(\mu\), however, may be different for each carrier type. The microwave mobility is measured at a frequency of \(\sim 8.9\) GHz.

---

Figure 4.2. A typical resonance curve extracted from the microwave setup when using the iris. We can fit parameters such as FWHM (full-width at half-maximum), \(R_0\) (resonance depth), and \(f_0\) (resonance frequency). These are used in equation 4.1 above.

Flash-photolysis time-resolved microwave conductivity (FP-TRMC), measures microwave transients as a function of time in photo-excited films and probes sub-nanosecond scale changes to the
photoconductance within a film. Figure 4.3 shows the experimental setup. The 4 ns laser pulse is generated by a tripled Nd:YAG laser that pumps a tunable OPO with a range from 420 nm – 2200 nm. For most samples, the yield of mobile charges generated by the laser pulse is unknown, but the product of yield and mobility can still be measured. If yield or 9 GHz mobility can be measured in another way as in Chapter 5, then this product can be separated. In other cases, the relative changes to the yield mobility product can provide a wealth of information on their own.

Figure 4.3. The FP-TRMC experimental setup. A tunable microwave source generates the ~8.9 GHz microwave signal. A microwave circulator directs the microwaves towards the sample and the reflected radiation is sent to a microwave detector which records the change in microwave power over time.

The TRMC technique has been used to successfully study photo-induced charge generation and separation in nanotube blends with polymers and fullerenes. Due to impressive charge transport mobilities, SWCNTs were seen as an ideal acceptor to blend with the photoactive polymer poly(3-hexylthiophene) (P3HT), which had previously been used successfully in blends with fullerenes. Unfortunately, solar cells made with SWCNT/P3HT blends had poor performance/conversion efficiency. These early PV devices used bulk SWCNTs with roughly one-third m-SWCNTS and two-thirds s-SWCNTs. To understand the effects of electronic type on the performance of these devices, TRMC was used to probe the charge separation and lifetime of blends of P3HT with type-separated SWCNTs at
varying s-SWCNT content. These results showed the detrimental effects of m-SWCNT content on both charge generation as well as recombination rates.

As separation techniques improved, the effects of multi-chiral distributions could be investigated in greater detail. As discussed in Section 2.3, near single-chirality distributions of (6,5) or (7,5) SWCNTs can be attained in sufficient quantities to fabricate devices. A recent study found that a device that utilized absorbance in only the S_{11} and S_{22} transitions of the (7,5) SWCNT has a theoretical power conversion efficiency (PCE) of 7.58%, although this would be in an ideal case. A (7,5)/C_{60} bilayer device was found to have a PCE of 0.95%, although the nanotube absorbing layer was <5 nm. In this device, ~60% of the photocurrent arises from photons absorbed by the SWCNTs. Although high IQEs have been reported, the IQE falls off for thicker films due to a low diffusion length in the direction perpendicular to the nanotube plane. A (7,5)/C_{60} bulk heterojunction aerogel was found to have a PCE of 1.7% and further gains will likely be possible through additional morphological control.

In a device with an active layer composed of a C_{60} and primarily (6,5) SWCNTs, it was found that even small quantities of other chiralities can lead to trapping sites forming, especially with smaller band-gap SWCNTs. Furthermore, since the electron affinity varies with SWCNT chirality and diameter, the driving force for charge separation is unique for each species of SWCNT that is paired with a particular acceptor (e.g. C_{60}). In another study, an active layer composed of C_{60} deposited on a film of five different near arm-chair chiralities wrapped by PFO was fabricated in order to explore differences in charge separation yield and recombination kinetics for different chiralities. TRMC measurements showed that the larger diameter, smaller band-gap (9,7) chirality had insufficient driving force to separate charges across the interface, while smaller diameter, larger band-gap SWCNTs produced long-lived charge separation. These significant studies highlight the importance of rationally tuning the driving force in SWCNT active layers by controlling the chirality distribution desired.
Although the previous approach showed that specific SWCNT chiralities can be used as donors with C\textsubscript{60} as the acceptor, it only considered the thermodynamic driving force for charge transfer. In choosing an appropriate donor/acceptor system, we need to consider that both the driving force and the reorganization energy determine the electron transfer rate and hence yield. In Section 4.4, I will discuss how we can rationally tune the thermodynamic driving force between donor and acceptor over a wide range in order to probe the changes in yield and determine the validity of Marcus electron transfer theory in these systems.

### 4.2 Charge Generation and Separation in (7,5)/C\textsubscript{60} Heterojunctions

A follow-up study to the multi-chiral PFO study uses primarily the (7,5) species with C\textsubscript{60}.\textsuperscript{13} In the initial multi-chiral and single-chiral studies, the nanotube films were produced via doctor-blading (by collaborators at the University of Wisconsin) to varying thicknesses and then a \~{}90 nm C\textsubscript{60} layer is thermally evaporated on top.\textsuperscript{6,13} Before moving on the large-diameter LV s-SWCNTs and other fullerene acceptors (Sections 4.3-4.4), I first needed to reproduce these results on films prepared in our own laboratory. For my (7,5)/C\textsubscript{60} bilayers, I use ultrasonic spray deposition (as in Section 3.1.1) to produce the nanotube film and similarly deposit C\textsubscript{60} using a thermal evaporator. Morphological differences can be observed in microscopy of the nanotube films. To optimize the bilayer production, I modified a number of parameters including film thickness, post-spray toluene soaking (see Section 3.5), and C\textsubscript{60} deposition rate. Each of these parameters had a noticeable effect on the TRMC end of pulse (EOP) yield mobility product (\(\phi\Sigma\mu\)). In Figure 4.4, a \(\phi\Sigma\mu\) plot is given as a function of absorbed fluence for several different films. A few trends began to emerge from these data. The EOP values increase with increasing film thickness and saturate above a certain thickness as is seen in the doctor-bladed films.\textsuperscript{13} For the samples in which the nanotube film was not soaked in toluene following spray deposition, the \(\phi\Sigma\mu\) signal is higher and longer lived than in the samples with the post-deposition treatment. The increase in
signal is partially due to the soak removing some nanotubes and thus having a thinner film, but there are also morphological differences that lead to an increase in charge carrier lifetime. This can be partially explained by recognizing the degree of interfacial contact between the nanotube layer and the C₆₀.

![Graph](image)

Figure 4.4. Yield mobility product vs absorbed fluence for several films. By changing parameters such as thickness, post-spray treatment, and C₆₀ evaporation rate, I was able to fabricate bilayers that closely matched the doctor-bladed ones made by our collaborators.

When C₆₀ is deposited on a nanotube film prepared in any method, there is a slight red-shift of the S₁₁ peak position due to a change in the local dielectric environment. Trends in the red-shift can be observed in the differently prepared films (Figure 4.5). In both the unsoaked sprayed films and the doctor-bladed films, the red-shift is much lower for thicker films, whereas for the soaked sprayed films, the red-shift is still considerable for thicker films. This is likely due to the fact that the soaked films have higher porosity since the excess polymer is removed and the bundle size may be lower allowing a more intimate contact between the nanotubes and C₆₀. Regardless, this change in S₁₁ peak position can be a helpful marker in understanding the degree to which nanotubes and fullerenes form an interface in a given film.
Figure 4.5. Red-shifts of the S_{11} peak position in different films. Before C_60 deposition, the S_{11} peak position is around 1043 nm. Both doctor-bladed and sprayed films follow a similar trend, while sprayed films that are post treated with a toluene soak show a greater red-shift. The magnitude of shift seems to be independent of C_60 evaporation rate (either 0.5 Å/s or 2 Å/s).

Since the data in Figure 4.4 showed that sprayed nanotube layers can match or beat doctor-bladed ones, we can move on to new experiments using the sprayed nanotube layers. Our goal is to understand how nanotube chirality and thermodynamic driving force affect the yield and lifetime of free charge carrier generation to maximize the efficiency of a photovoltaic active layer. One strategy involves tuning both the donor and acceptor band levels, in this case that involves using different SWCNT chiralities for the donor and a series of tunable fullerene derivatives as the acceptor. Common functionalized derivatives of C_60 include PCBM or adding indene groups (e.g. ICBA), but another class of derivatives with the structure C_{60}(CF_3)_n have been developed and characterized by collaborators at Colorado State University (CSU). These perfluoroalkyl fullerenes (PFAFs) have a wide range of HOMO/LUMO levels available by tuning the number of CF_3 groups and their positions on the fullerene cage. Due to the high electronegativity of fluorine, most (though not all) PFAFs have a deeper electron affinity than C_60 and span a range of ~160 meV above to ~570 meV below that of C_60. Notationally, PFAFs are labeled by two indices: the first number denotes the number of CF_3 groups and the second is the
isomer label, \( \textit{e.g.} \ C_{60}-10-5 \) has ten \( \text{CF}_3 \) groups on the \( C_{60} \) cage and is the fifth such isomer and can alternatively be denoted \( C_{60}(\text{CF}_3)_{10}-5 \) or simply \( 10-5 \) as all the fullerenes in this study are derivatives of \( C_{60} \). In our thermal evaporator, we found that approximately 100 mg of \( C_{60} \) were needed per deposition of 90 nm. This presented us with a problem as few of these PFAFs are available in such quantities, especially if multiple depositions become necessary. To overcome this issue, I explored the feasibility of spraying films of fullerenes as this technique works well for SWCNTs and allows us to use small quantities of material.

![Figure 4.6](image)

Figure 4.6. Optical microscope images of \( C_{60} \) spray deposited on glass in different regimes: (a) Droplets merge before drying and form domains of \( C_{60} \) leaving some areas uncovered, (b) droplets dry before merging and show typical ‘coffee’ ring formations, but can cover most of the substrate, (c) the narrow intermediate regime where some droplets may merge, and (d) wet regime where many droplets merge and dry slowly allowing crystalline growth to occur. Microscope images are approximately 370 µm across.
Ultrasonic spray deposition has a number of parameters that affect the ultimate film morphology. I explored changes to fullerene film morphologies due to substrate temperature, ink flow rate, ink concentration/number of coats, and nozzle power. While concentration and number of coats does change the film surface roughness and appearance, the fundamental morphology remains similar even over an order of magnitude of change (e.g. a 10x dilute ink sprayed with 10x more coats). Changing substrate temperature and ink flow rate were much more instrumental in shifting the regime in which the film forms. I found three distinct regimes when spraying C$_{60}$: a fast-drying regime where individual microdroplets dry quickly, a slow-drying regime in which individual microdroplets merge on the surface before drying out, and a wet regime that allows layers of droplets to merge and form three-dimensional crystallites. These regimes are shown in Figure 4.6 and very clear differences can be observed at the micron scale. The intermediate regime is quite narrow in terms of temperature or flow rate settings. An increase or decrease of just 10°C can make a large change in surface morphology if it crosses into a different regime. For films studied below, the fast-drying regime corresponds to a flow rate of 0.700 ml/min and a substrate temperature of 70°C, while the merging droplet regime is done with a flow rate of 0.500 ml/min and a substrate temperature of 50°C. Both films are sprayed from a 1 mM solution of C$_{60}$ in toluene with 11 coats for the lower flow rate and 8 coats for the higher flow rate. One could also fix either the temperature or flow rate and vary the other parameter as well to reach the desired regime. All of these sprayed films are in stark contrast to those made via thermal evaporation which forms uniform films with low surface roughness. Critically, however, well-controlled fullerene layer thickness and uniformity may only be required for devices. In TRMC studies, there is no additional layer deposited on top of fullerenes and we are not interested in extracting photogenerated charges, but simply understanding and controlling charge generation and separation across the interface. To probe the validity of this hypothesis, I fabricated several different (7,5)/C$_{60}$ heterojunctions. The nanotube films were all sprayed as before, but half were post-treated with a toluene soak. Each set of films then
has C$_{60}$ deposited by different methods: thermal evaporation, spraying in the merging droplets regime, and spraying in the fast-drying regime. In Figure 4.7, the EOP $\phi \Sigma \mu$ values for these samples are plotted vs absorbed fluence. The film with C$_{60}$ sprayed in the fast-drying regime shows the highest EOP value, nearly a factor of two above that of the one sprayed in the merging regime. This difference can be accounted for by the poor surface coverage of the latter film since it forms domains of fullerenes with some areas remaining uncovered and hence not forming a proper interface. Additionally, the kinetics in Figure 4.8 (taken at an absorbed fluence of $\sim$2e12 photons/cm$^2$) show a long-lived component in all of the films. We can fit the transients to tri-exponentials convolved with a Gaussian (4 ns FWHM) representing the pump pulse.$^{13}$ This allows us to extrapolate back to $t=0$ by using the sum of the pre-exponential factors as some photogenerated charges decay within the pulse. When taking this into account, the sprayed film (merged droplets regime) still outperforms the thermally evaporated film.

![Yield x Mobility ($\phi \Sigma \mu$)](image)

Figure 4.7. The red and green traces correspond to sprayed C$_{60}$ layers and the black trace is thermally evaporated. The jump in data was caused by poor calibration of the neutral density filters, but the relative values can be compared. Later data uses a pulse energy meter to obtain the correct fluence at each filter combination.
Now we are able to fabricate nanotube/fullerene bilayers with adequate interfacial contact using ultrasonic spray deposition for both layers. This enables the following study of alternative electron acceptors such as PFAFs that are currently only produced in small quantities. In the following section, a study using one of these fullerenes together with both (7,5) and narrow diameter LV SWCNTs explores the possibility of using this class of fullerenes. Section 4.4 follows up with an extensive investigation into the relationship between thermodynamic driving force, reorganization energy, and charge separation yield.

4.3 A New Acceptor for (7,5) and LV SWCNT Donors

While C\textsubscript{60} has been successfully used as an electron acceptor in blends with small-diameter SWCNTs like the (7,5), it was shown to be a poor acceptor for larger diameter SWCNTs such as the (9,7).\textsuperscript{6} Large-diameter SWCNTs may be desired as they should have higher mobility\textsuperscript{17} and lower binding energies.\textsuperscript{18,19} Furthermore, they may be more suitable for exploiting effects such as multiple exciton generation (MEG) since photons with energies three or four times the band-gap will still fall within the visible part of the solar spectrum.\textsuperscript{20} More importantly, it is crucial to understand the fundamental interplay between the thermodynamics of the donor:acceptor (SWCNT:fullerene) interface and the kinetics/yield of interfacial charge separation. The PFAFs from our CSU collaborators provide a unique opportunity to dramatically vary the EA of the acceptor fullerene. Additionally, our SWCNT synthesis and
selective dispersion expertise allows us to simultaneously tune the ionization potential and electron affinity of the SWCNT donor. The result is a donor:acceptor system with widely varying thermodynamic driving force that can be used as a probe for the validity of Marcus electron transfer theory in explaining charge transfer in such excitonic systems.

In this experiment, we use PFH-A wrapped 1125°C LV s-SWCNTs (see Section 2.4.1 and Figures 2.4-2.5) and (7,5) s-SWCNTs dispersed by PFO. These dispersions have a narrow chirality range of s-SWCNTs with diameter 1.24 – 1.38 nm for the LV and 0.83 nm for the (7,5). We can spray these LV SWCNTs to make films in the same way we made the (7,5) samples. The polymer removal step, spray parameters, and toluene-soak treatment are identical for both sets of nanotubes. On top of this nanotube layer, fullerenes are spray deposited. Before we decide on fullerene acceptors to investigate for the LV s-SWCNTs, we need to determine the energetics and driving forces. In a previous study, the driving force for charge separation from the (9,7) to C₆₀ was taken as 0 eV. Using an electron affinity (EA) of 4.28 eV for C₆₀ and a binding energy of 0.2 eV for the (9,7) in a medium with a relative dielectric constant of 4, the EA of the (9,7) is estimated to be 4.08 eV. From this value and assuming that the Fermi levels of different chiralities are the same, we can calculate the EA and hence driving force for other species. The calculations for a few near-armchair chiralities are given in Table 4.1. These particular SWCNTS were chosen because of their experimental relevance: the (6,5) and (7,5) are easily isolated from CoMoCat commercial SWCNT samples (SG65i material, using PFO-BPy or PFO respectively) and the (10,8), (10,9), and (11,9) are the main chiralities in the PFH-A/LV (1125°C) distribution shown in Figure 4.9. The (11,9) is the dominant species at the peak of the S_11 envelope for these LV films and two shoulders appear at the positions of the (10,8) and (10,9). For these experiments we excite at the peak of the S_11 in each film respectively.
Table 4.1. Nanotube energetics. The binding energies are calculated assuming a dielectric environment of $\varepsilon=4$. $\Delta G < 0$ corresponds to an exergonic thermodynamic driving force, while $\Delta G > 0$ corresponds to an endergonic thermodynamic driving force.

To begin, we note that $C_{60}$ has a large endergonic $\Delta G$ (Gibbs energy) when paired with our 1.24 – 1.38 nm LV SWCNTs, suggesting inefficient photoinduced electron transfer from SWCNT to $C_{60}$ for these SWCNT diameters. Thus, we first used TRMC to confirm the lack of charge generation and separation in LV/$C_{60}$ bilayers by comparing the kinetics of a neat LV film to a heterojunction LV/$C_{60}$ film. In Figure 4.10, the EOP $\Delta G$ (photo-conductance) signals for both the neat LV and LV/$C_{60}$ films are nearly identical showing the same baseline charge generation seen in other neat SWCNT films. Furthermore, neither film exhibits a long-lived signal indicative of charge separation. As predicted above, the driving force is insufficient for charge injection in this blend.
Since the driving force of the (11,9) is approximately ~0.17 eV less than that of the (7,5), a reasonable first attempt at choosing a new acceptor is the C60-4-1, which has an EA approximately 0.17 eV below that of C60, which is known to induce spontaneous exciton dissociation in the photoexcited (7,5)/C60 heterojunction (see Table 4.2). We started with a fullerene sample that was about 85% enriched in the C60-4-1 as a proof of principle experiment. This fullerene also demonstrates adequate coverage of the nanotube layer or substrate in spray deposited films. Indeed, when we excite the peak of the S11 in the LV/4-1 sample we find both a significant increase in the EOP signal as well as a long-lived component in our photoconductance transients. In Figure 4.11, these signatures of charge generation and long-lived separation are incredibly clear. These results showing enhanced yield and lifetime of mobile charge carriers indicates a path forward for the integration of larger diameter SWCNTs into photoactive layers. Furthermore, we are now able to explore the LV SWCNTs with a wide range of fullerene acceptors.
Table 4.2. Energetics of fullerenes and estimated driving forces. Fullerenes in italics correspond to experiments that are planned in the near future.

<table>
<thead>
<tr>
<th>Fullerene</th>
<th>$E_{1/2}$ relative to $C_{60}$ (eV)</th>
<th>(7,5) Driving Force (eV)</th>
<th>(11,9) Driving Force (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICBA</td>
<td>0.25</td>
<td>0.14</td>
<td>0.31</td>
</tr>
<tr>
<td>PCBM</td>
<td>0.09</td>
<td>-0.02</td>
<td>0.15</td>
</tr>
<tr>
<td>C60-6-2</td>
<td>-0.07</td>
<td>-0.04</td>
<td>0.13</td>
</tr>
<tr>
<td>C60</td>
<td>0</td>
<td>-0.11</td>
<td>0.06</td>
</tr>
<tr>
<td>C60-8-4</td>
<td>0.06</td>
<td>-0.17</td>
<td>0</td>
</tr>
<tr>
<td>C60-2-1</td>
<td>0.11</td>
<td>-0.22</td>
<td>-0.05</td>
</tr>
<tr>
<td>C60-4-1</td>
<td>0.17</td>
<td>-0.28</td>
<td>-0.11</td>
</tr>
<tr>
<td>C60-6-1</td>
<td>0.26</td>
<td>-0.37</td>
<td>-0.2</td>
</tr>
<tr>
<td>C60-8-1</td>
<td>0.33</td>
<td>-0.44</td>
<td>-0.27</td>
</tr>
</tbody>
</table>

The end-of-pulse yield mobility products (EOP $\phi \Sigma \mu$) as a function of absorbed fluence can be fit to the empirical expression in Equation 4.3:

$$\phi \Sigma \mu = A \left/ \left(1 + \sqrt{B I_0 F_A} + C I_0 F_A \right) \right.$$  

Equation 4.3

where $A$, $B$, and $C$ are fitting parameters and $I_0 F_A$ is the absorbed photon fluence. The parameter $A$ gives a measure of the maximum $\phi \Sigma \mu$ reached at low fluences, such as that of solar irradiance. It is safest to make quantitative comparisons between yield mobility products in this low-fluence regime, since bimolecular (e.g. exciton-exciton and exciton-charge) processes are minimized at fluences producing low exciton densities. Importantly, the high-frequency microwave mobility of each fullerene type is at least two orders of magnitude lower than that of the nanotubes. Thus, we assume that the yield mobility product is dominated by the mobility of free charges in the nanotubes. Furthermore, for a given SWCNT type, either (7,5) or LV, the nanotube mobility is the same for each bilayer (to which a range of fullerene acceptors is applied). Hence, we can use the $A$ parameter as a measure of the relative yield of charge separation for this range of fullerene acceptors. While Equation 4.3 was empirically determined, the $B$ and $C$ terms can be attributed to second-order loss processes at high absorbed fluences.
As a comparison, we also made a (7,5)/4-1 bilayer. As compared to the neat (7,5) film, both bilayers showed a large increase in photoconductance. The (7,5)/4-1 blend, however, showed an enhanced long-lived photoconductance signal as compared to even the (7,5)/C\textsubscript{60} sample (Figure 4.12). This difference may enhance the efficiency of a solar cell by allowing more time to extract charges even if both blends generate a comparable number of free charges. As before, we can fit the photoconductance transients with tri-exponential fits. Extracting to the t=0 signal for the (7,5) films, we find that although the EOP signal is higher for the (7,5)/4-1 heterojunction, the t=0 signal is higher in the (7,5)/C\textsubscript{60} heterojunction, but faster recombination rates cause it to appear lower. Previous work has shown that the extrapolated low fluence A value is comparable whether the EOP signals or the t=0 values are used.\textsuperscript{13} Further experiments in the next section will examine trends in yield and lifetime of free carrier generation as a function of driving force.
4.4 Tuning Charge Transfer Yield by Varying Driving Force

Now that we have proven that LV SWCNTs as well as (7,5) SWCNTs can act as an electron donor in a SWCNT/fullerene heterojunction, we can use two different s-SWCNT films with widely differing electron affinities and band-gaps. With a host of acceptors and an effective probe, we can systematically investigate the role of thermodynamic driving force on the relative yield of photo-induced charge carriers and their lifetimes.

Initially, we chose to investigate PFAFs with only a few CF₃ groups and chose ones that would provide a driving force higher and lower than the 4-1. In Table 4.2, the estimated Gibbs energy changes for SWCNT electron transfer to different fullerene acceptors are given for the 2-1, 4-1, and 6-1 and all three are exergonic (unlike C₆₀), indicating that we should expect to observe spontaneous charge transfer and separation in these systems. Indeed, all three PFAFs show an enhanced EOP φΣµ and a long-lived signal (see Figure 4.13). We must be careful in comparing the magnitude of the EOP φΣµ for each sample as there are several components that can contribute to this signal. We are exciting the peak $S_{11}$ transition in the LV film, which we assign primarily to the (11,9). The residual PFH-A polymer should not be energetically favorable to accept either the electron or hole, but these three fullerenes can
accept the electron as established earlier. Additionally, as explained earlier the electron mobility in C\textsubscript{60} is at least two orders of magnitude lower than that of the holes in SWCNTs\textsuperscript{6} and we expect the mobility in PFAFs to be even lower than C\textsubscript{60}. Therefore, our EOP $\phi \Sigma \mu$ signal is dominated by the charges in the nanotube film and we can compare the relative yields directly.

In Figure 4.13b, the relative yields for all four fullerenes are plotted vs their respective driving force. Although the thermodynamic driving force for the LV/6-1 heterojunction is the most exergonic, it has a lower yield than that of the LV/4-1 system. To probe this intriguing result further, we looked to the (7,5)/fullerene system where we have access to other fullerenes with EA above C\textsubscript{60} in addition to the three fullerenes tested with LV films.

![Graph](image)

Figure 4.13. (left) The $\phi \Sigma \mu$ vs $I_0 F_\text{a}$ plots for the LV heterojunctions. These data are fit using Equation 4.3 with a C parameter set to 0. (right) The extracted relative yields vs thermodynamic driving force.

We chose PCBM and ICBA as additional fullerenes to study in the (7,5) system and their respective Gibbs energies are given in Table 4.2, along with the 2-1, 4-1, and 6-1. The EOP $\phi \Sigma \mu$ and corresponding fits using Equation 3 are shown in Figure 4.14 below and when we plot the relative yield vs Gibbs energy for these six heterojunctions, we very clearly see a maximum in charge transfer yield where systems with more negative Gibbs energy produce an inverted region with lower relative yields.
A potential model for free carrier generation in these systems that describes the inverted region is Marcus Theory.\textsuperscript{24} While predicted in 1956, the Marcus inverted region was not experimentally confirmed until the mid-1980s.\textsuperscript{25,26} In this theory, photo-induced electron transfer (PET) from an initial state to a final state depends not only on the Gibbs energy we calculated, but also the reorganization energy ($\lambda$) which represents the energy required to reorganize the configuration of nuclear states and charge distribution of the initial state into the final state. The PET rate ($k_{PET}$) is given by the following equation:

$$k_{PET} = A_{PET} e^{-\frac{(\Delta G - \lambda)^2}{4\lambda k_BT}}$$  \hspace{1cm} \text{Equation 4.4}

where $A_{PET}$ is a constant and $\lambda$ is the reorganization energy of the system. Equation 4.4 indeed predicts a maximum rate of charge transfer when $|\Delta G|$ equals $\lambda$ and an inverted region when $|\Delta G|$ is larger. Additionally, both the position of the maximum and the width of the Marcus curve depend on the reorganization energy.

Equation 4.4 relates the rate constant to driving force, but we are extracting relative yields from the TRMC data. To relate yield and rate, we need to use

$$\phi = \frac{k_{PET}}{k_{PET} + k_{loss}}$$  \hspace{1cm} \text{Equation 4.5}
where $\phi$ is the absolute yield and $k_{\text{loss}}$ is the sum of loss rate constants. We make the assumption that $k_{\text{loss}}$ is constant for a given SWCNT film type as we are exciting the nanotubes themselves. From recent transient absorption measurements, we can estimate the absolute yield of the (7,5)/C$_{60}$ bilayer to be $\sim 40\%$. Using this value, we set $k_{\text{loss}} = 1.5 A_{\text{PET}}$ such that the yield approaches 40% at the peak of the Marcus curve. This allows us to fit the relative yield vs driving force data in order to extract the reorganization energy. For the LV films, we can scale the mobility as the square of the nanotube diameter. From the (7,5) data, we can then scale the absolute yield of the LV data to estimate a maximum yield of 3-4%, although this does not take into account differences in defect density or length distribution. In Figure 4.13, I have plotted fits to the data assuming several different yields, but there is not a significant change to the reorganization energy obtained.

Fitting the data in Figures 4.13b and 4.14b to Equation 4.4, we can extract a reorganization energy for both systems of $\sim 130$-135 meV. Previous estimates for the reorganization energy of fullerenes is estimated at 0.11-0.23 eV, which would seem to indicate that the contribution to the reorganization energy from the SWCNTs is extremely small. In a recent FP-TRMC study using similar fullerenes, but in a blend with fluorene-based polymers, reorganization energies of 0.4-0.8 eV were found. It is important to note that the low reorganization energies predicted and observed for fullerene acceptors is typically attributed to efficient delocalization of the electron wave function over the pi network of the fullerene cages. The low reorganization energies we observe for SWCNT/fullerene heterojunctions can be rationalized similarly, by considering that both species (donor and acceptor) in this case have extended pi networks that should enable efficient delocalization of each charge in the separate phases.

For a given OPV system, a smaller reorganization energy leads to a smaller Gibbs energy required to maximize the PET rate and thus an improved efficiency. In the (7,5)/C$_{60}$ system, it was perhaps fortuitous that the most widely available fullerene and one of the most readily isolated single-
chirality SWCNT species produced a donor/acceptor blend with a near optimization of the balance between $\Delta G$ and $\lambda$. With a fuller understanding of the reasons behind this, we now expect that larger diameter SWCNTs can likewise be optimized by choosing an appropriate acceptor, such as in the LV/4-1 blend. Ultimately, our results suggest that particular SWCNT chiralities can be paired with fullerenes having appropriate electron affinities to carefully tune the solar capture of SWCNT/fullerene solar cells.

References


Chapter 5

Time-Resolved Microwave Conductivity and Mobility Measurements

As we saw in the previous chapter, time-resolved microwave conductivity (TRMC) can be a powerful technique for probing charge generation and lifetime. Although the product of charge carrier yield and mobility ($\phi \Sigma \mu$) can provide a wealth of information, it can sometimes be more useful to have the absolute yield or mobility. If one of these values is known, the other can be calculated. In this chapter, I focus on experiments that use microwave conductivity measurements to directly probe the mobility of charges in SWCNTs. In addition to allowing us to calculate the yield in comparable systems, the absolute mobility can be important to study on its own in order to learn how mobility scales with nanotube diameter, length, or carrier density as well as the differences in mobility between isolated SWCNTs and highly coupled films.

5.1 Dark Carrier Mobility

As discussed in Section 4.1, by measuring the change in conductance, we can extract the yield of free carriers multiplied by the sum of their mobilities ($\phi \Sigma \mu$). In this section, I describe how we measure steady-state differences in the microwave resonance curves of a film with different known quantities of charges added via chemical doping. In Chapter 3, we showed how chemical doping is an effective way to increase the conductivity of SWCNT films by injecting charge density into the nanotubes. By calculating the change in carrier density between films, we can measure the microwave mobility of these charges in SWCNT films.
The SWCNTs used in this study were prepared by polymer extraction as explained in Sections 2.3-2.4. PFO wrapped SWCNTs (either CoMoCat SG65 to extract (7,5) SWCNTs or HiPco to extract a multichiral distribution) were prepared in solution, followed by removing the excess polymer. Films of ~9 nm thickness were then doped with triethyloxonium hexachloroantimonate (OA). The $S_{11}$ transitions for both types of films showed significant quenching (~70%) due to the removal of electron density within the nanotube as OA is a p-type dopant. This change in $S_{11}$ quenching ($\Delta A/A$) can be quantified as an increase in hole density by Equation 5.1 taking into account state-filling and charge screening of the exciton binding energy.\(^1\) The term $\delta/E_{bin}(0)$ in Equation 5.1 represents the dependence of charge-induced screening of the exciton binding energy on the hole density and can be estimated to be approximately 0.88.\(^1,2\) The terms $N_0$ and $N_h$ represent the hole density required to fully bleach the $S_{11}$ transition and the estimated hole density in the film respectively.

$$\frac{\Delta A}{A} = \left(1 - \sqrt{1 - \frac{\delta}{E_{bin}(0)} \sqrt{N_h}}\right) + \frac{N_h}{N_0}$$

Equation 5.1

To calculate the term $N_0$, we use Equation 5.2 which takes into account the density of states for holes up to an energy $E_{bin}(0)$ from the band-edge.\(^1,3\) The term $m_h$ is the effective mass of the hole and can be estimated as $\sim 0.14 m_e$.\(^4\) Finally, we estimate the binding energy, $E_{bin}(0)$, to be approximately 0.26
eV by taking into account the local dielectric environment with $\varepsilon = 4$. Combining these, we calculate $N_0 \approx 1.24$ hole/nm to fully quench the $S_{11}$ transition.

$$N_0 = \frac{4}{\pi\hbar} \sqrt{2m_eE_{bin}(0)}$$

Equation 5.2

Thus in the doped films, we calculate a hole density ($N_h$) of approximately 0.44 holes/nm compared to the intrinsic film. Using this value as our yield of charges due to doping, we can decouple the yield mobility product found in microwave resonance experiments. Measuring these microwave resonance curves requires the use of the iris to create a cavity as explained in Section 4.1. In Figure 5.1, the microwave cavity resonance can be seen to deepen, broaden and shift due to the increase in hole density within the SWCNT film. The change in conductance of the sample can then be estimated by modeling the response of the cavity using the COM-SOL software package. This modeling is in progress and will be compared to the mobility estimates obtained for the multichiral film in a prior study.6,7

Similarly, we have measured the resonance curves of PFH-A extracted LV SWCNTs and found that films similar in thickness to those used in Sections 4.3-4.4 are already quite deep. This means that the films are highly conductive already. After doping, the films pass through critical coupling (the point at which the full microwave radiation is absorbed by the sample and the resonance curve depth reaches 0) and become overcoupled. In this regime, the mobility may still be modeled, but the analysis becomes much more complex. A simpler solution involves measuring the mobility on even thinner samples.

5.2 Pulse-Radiolysis TRMC

As discussed earlier, by measuring the attenuation of a microwave probe beam by mobile charges (either steady-state between samples or time-resolved after excitation), we can directly measure the change in conductance of our sample. A third microwave experiment, pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) investigates charge mobility after the sample is irradiated by a short pulse of high-energy electrons from a Van de Graaff accelerator. The method of creating
charges differs in each of the three microwave experiments, but the underlying physics remain the same. PR-TRMC is a pump-probe measurement similar to FP-TRMC, but allows us to extract the mobility directly, similar to the dark conductivity measurements, by injecting a known dose. Unlike the films used in the other two methods, this experiment uses a solution of SWCNTs in benzene. A non-polar solvent, such as benzene, is used because polar liquids can have a dipole relaxation time on the order of the oscillation period of the microwaves. Benzene is also used because the ionization chemistry of benzene is well-characterized, allowing for the possibility of injecting well-known densities of carriers from ionized benzene radicals into analytes (such as polymers or in our case SWCNTs).

This experiment is done in collaboration with Brookhaven National Laboratory (BNL). The 2 MeV Van de Graff accelerator source seen in Figure 5.2, has a tunable pulse length from 50 ns to 400 ns. An iris is used with a window to allow microwaves through, but hold the solution inside the cavity. Akin to the previous measurements, this setup is also in reflection mode. The microwave source is a Hittite T-2240 that can be controlled via LabVIEW instead of manually adjusted, allowing us to quickly sweep out resonance curves without breaking the interlock to the room with the Van de Graff accelerator. The microwave mobility is still measured at a frequency of ~8.9 GHz in this setup.
Some adjustments to Equations 4.1 and 4.2 from Section 4.1 that dealt with flash-photolysis TRMC need to be made for this PR-TRMC experiment. We extract the yield mobility product in a slightly modified fashion: \[ \Delta P_r = \frac{\Delta \sigma}{P_r} \]

Equation 5.3

where $F$ is the overlap function and $\Delta \sigma$ is given by:

$\Delta \sigma = e \sum_i N_i \mu_i$

Equation 5.4
and $N_i$ is the concentration of a particular charge species.

We initially sought to study two series of samples: one with varying length, but a single chirality and the other with similar lengths, but different diameter distributions. Since benzene is already a well-characterized non-polar solvent, we attempted to make solution of SWCNTs in benzene directly. Polymer extraction lends itself well to a number of organic solvents, so I made solutions of PFO/(7,5), PFO-BPy/(6,5) and PFH-A/LV. The yield of the PFO samples was very poor so we only used the other two polymers. While PFH-A had a high yield and good solubility, the PFO-BPy had lesser solubility than in toluene. To make three different length distributions of (6,5) SWCNTs, samples were sonicated for either 30 minutes, 1 hour or 2 hours, with longer sonication times leading to shorter nanotubes.\textsuperscript{12} For different diameter distributions, four different LV synthesis temperatures were used for the starting material: 950°C, 1000°C, 1040°C, and 1125°C. The absorption spectra of these samples are shown in Figure 5.3. The goal of this experiment is to quantify the mobility as a function of length and diameter, with the expectation that it should increase with increasing length or diameter.\textsuperscript{13}

![Figure 5.3. Absorption spectra of the different solutions made to study. (left) Three samples of (6,5) SWCNTs whose length distribution decreases with sonication time. (right) Four samples of PFH-A extracted LV SWCNTs of increasing diameter distribution.](image)

When the incident electron pulse from the Van de Graff generator hits the sample cavity, a number of benzene molecules are ionized creating benzene cations and electrons. Geminate ion pairs quickly recombine, but a fraction of these electron-hole pairs can separate and transfer to other species.
Ideally, one charge should be rapidly captured (e.g. electrons by dissolved oxygen) so the other charge can make it to the analyte (e.g. holes to the nanotubes). As our system still has some polymer in solution as well, the energetics of each species must be considered and estimates of the EA/IP levels are shown in Figure 5.4. From relative concentrations, we estimate that the oxygen rapidly captures electrons and the polymer captures holes. Ideally only the polymer would then transfer charge to the nanotubes. To add certainty to the charge density on the nanotubes, we turn to another technique available at BNL – the laser-electron accelerator facility (LEAF). The LEAF setup at BNL is a similar pump-probe technique to PR-TRMC, but uses a laser pulse to probe the sample, akin to transient absorption. The Van de Graff accelerator used for LEAF has a >7 ps pulse of 8.7 meV electrons. With this technique, we can probe the creation and decay of triplets or polarons in polymers, cations in benzene, or bleaches in the nanotube $S_{11}$ transition. Each of these distinct features can appear as a bleach or induced absorption and by comparing the rates of decay and growth, we hope to learn about the mechanisms of charge transfer.

Figure 5.4. Estimates of EA/IP levels for several polyfluorene polymers, molecular oxygen, and (6,5) SWCNTs. Ideally the oxygen captures electrons in benzene, but our nanotube EA might be low enough to accept electrons from oxygen.
In our initial PR-TRMC experiment, we decided to start with the 1125°C LV sample to maximize our chance of seeing a signal, as we expected it to show the highest mobility. The microwave transients showed that the signal actually increased over some time scales. This would nominally be a decrease in conductance, but can actually show up if the conductance increases enough for the cavity to move past critical coupling. Alternatively, a shift in the frequency of the resonance curve caused by a large imaginary component could also cause an increase or decrease in the apparent signal. Thus, the high mobility of carriers in the large-diameter SWCNTs (as observed in dark conductivity measurements above) may actually be detrimental to this study, since it adds a level of complexity to interpreting the microwave transients.

To simplify the experiment, we looked at the near-single chirality (6,5) samples and took microwave transients at many different frequencies, thus allowing us to map out the change in the resonance curve over time. Figure 5.5 clearly shows an asymmetric change to the resonance curve, indicating a shift in frequency and change in resonance depth due to a change in both the real and imaginary components of conductivity.

Figure 5.5. The change in microwave resonance after excitation by electron pulse in the 30 minute sonicated (6,5) sample. The asymmetric shape is indicative of a shift in resonance frequency.
From these shifts, we can recreate the resonance curve at different times and separate the change in depth from the change in frequency in order to analyze the real and imaginary components separately. Figure 5.6 shows an example of this process.

![Figure 5.6](image)

Figure 5.6. (top) Change in resonance depth and (bottom) change in frequency as a function of time. From these two components, we can begin to analyze the changes to the real and imaginary components of conductivity.

For the shortest length (6,5) sample (sonicated for 2 hours), we found that the change in the resonance curve was asymmetric on the microsecond time scale, but symmetric on the millisecond time scale. Figures 5.7 a-b show the differences for the two time scales. The transient taken at 8.942 GHz is shown in Figure 5.7c and a distinct oscillation is observed as the signal decays. A closer analysis, in Figures 5.7d-e, shows that the real component is contributing to the decay, while the imaginary component mostly contains the oscillation alone, hence the symmetric change to the resonance curve. To probe the source of this oscillation, we looked at the FFT power spectrum of the imaginary part and found that the oscillations may be acoustic vibrations from the pulse hitting the thinned out wall of the cavity.
Figure 5.7. The 2 hour sonicated (6,5) sample. (a) shows the change in the resonance curve at early times (1 µs), while (b) is at later times (8 ms). (c) is a sample transient taken away from the resonance frequency and has distinct oscillatory behavior over long time scales. The change in (d) depth and (e) frequency of the resonance curve can be separated. At long time scale, the change in frequency is simply oscillatory and from a FFT power spectrum analysis, appears to be acoustic in nature.

Our goal for the (6,5) samples is to measure the mobility of each SWCNT sample, sonicated for different lengths of time, in order to determine the dependence on nanotube length. To quantify the mobility, we need a known quantity of charges on the SWCNTs, which can be found through measurements on LEAF. Figure 5.8a shows the LEAF bleach of the $S_{11}$ transition of each sample following irradiation by the Van de Graaff. We can follow the calculation of the dark carrier mobility in Section 5.1
using the bleach as our degree of $S_{11}$ quenching. For the 30 minute sample the bleach is approximately 0.166% of the original $S_{11}$ peak, which we can use as $\Delta A/A$ in Equation 5.1. We estimate of the effective mass of the hole $= 0.138 \, m_0$. The binding energy of the (6,5) is estimated at 0.287 eV using a local dielectric constant of 4 since the excess polymer has not been removed. Thus we calculate $N_0 \approx 1.30$ holes/nm per Equation 5.2. Combining the two equations, we find $N_h \approx 1.40 \times 10^{-5}$ holes/nm.

![Figure 5.8. (left) A bleach in the LEAF data around 1000 nm corresponds to the $S_{11}$ of the (6,5). From this bleach, we can calculate the charge density on the nanotubes. (right) Microwave transients of the three (6,5) samples. While the bleach is highest for the 2 hour sonicated samples, it has the lowest microwave signal indicating that it has the lowest mobility.

While the microwave detector needs to be re-calibrated in order to convert $\Delta V/V$ to $\Delta P/P$, we can still qualitatively compare the relative mobility of the three samples. Figure 5.8 shows that while the shorter, 2 hour sonicated sample has a deeper bleach (indicating more charges on the nanotubes), it has the lowest TRMC signal. This confirms our expectation of the shorter SWCNTs having lower mobility. Additionally, we can calculate the dosage of charges from the Van de Graaff to understand the fraction of charges captured by the nanotubes. In LEAF, the dose is about 10 Gray/shot in water, but for benzene it should be lower as it scales with density (0.88 g/cm$^3$). The G value in benzene is approximately 0.05-0.08 ions/100 eV for homogeneous ions. The lower bound on this is equivalently $5.2 \times 10^{-9}$ moles/J. Since 1 Gray = 1 J/kg, we can estimate about 2.5 nM ($1.5 \times 10^{12}$ ml$^{-1}$) homogeneous ion pairs created per shot. Using $N_h$ above along with the OD of the sample and an absorption cross section of 4400 M$^{-1}$ cm$^{-1}$ for
we can calculate the SWCNT charge density to be \( \sim 2.4 \times 10^{10} \text{ ml}^{-1} \). It is possible that this value is lower than expected due to charge capture by the free polymer in solution. In order reduce the effect of the excess polymer in solution, we decided to make a set of samples with most of the PFO-BPy removed.

For the next round of samples, a new source of PFO-BPy was used as it was more readily available. The old source was from American Dye Source and had a Mw of 68k and Pd of 3.2, while the new source was from Solaris with a Mw of 130k and Pd of 2.14. Since they did not appear to have a major difference in yield, we assumed they behaved similarly. To better understand the effects that the polymer may have in capturing charges, we sought to make another set of samples with the excess polymer removed. This step is normally done before spraying films, as in Section 2.5, but differs here since the solvent used is benzene. Excess polymer in toluene solution is successfully removed by centrifuging the solution in the SW32 rotor at 24,100 RPM (100,000 g) for 20 hours at 0°C. Unfortunately, the benzene freezes at this temperature and the SWCNTs cannot pellet out anymore. Furthermore, I found that since the PFO-BPy is less soluble in benzene than in toluene, polymer can start to pellet out with the SWCNTs as well. Increasing temperature improved solubility and reducing centrifuge time aided in optimizing the yield of nanotubes in pellet vs polymer in supernatant. Thus, I found that PFO-BPy is successfully removed in benzene by using the SW32 rotor at 24,100 RPM (100,000 g) for 16 hours at 20°C. This new method was not without issues, however, and the pellet became difficult to re-disperse into benzene without long bath sonication times. Furthermore, it required a higher final polymer:nanotube ratio than in toluene in order to keep the SWCNTs from flocculating out too quickly. In the future, samples may be prepared in toluene and only re-dispersed into benzene for the final step.

Since questions remain regarding the energetic offsets between molecular oxygen dissolved in benzene and the EA of the (6,5) in solution, we are investigating the addition of small molecule charge acceptors (Figure 5.9). In particular, we believe that tetrafluorobenzoquinone (TFBQ) should be an
excellent electron acceptor and N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) should work well as a hole acceptor. By adding these molecules to the nanotube solutions, we should be able to measure LEAF transients while only observing the effects from one type of charge. In this way, we hope to better understand which charges are present in the nanotube and possible pathways for them to reach there.

Figure 5.9. The molecular structure of (left) TFBQ and (right) TMPD, the electron and hole acceptors we have chosen to test.

Future Directions

The main goal of these experiments is to extract the 9 GHz mobility of different SWCNT samples in order to understand how mobility scales with length or diameter and how isolated SWCNTs and film ensembles differ. Although the dark mobility measurements on films in Section 5.1 are more relevant to experiments such as those in Chapter 4, the PR-TRMC experiments are more significant to our fundamental knowledge of SWCNT mobility.

There remain some issues with reproducibility between sample sets due to differences in polymer used and concentrations. We hope to limit problems such as polymer aggregation that can lead to different behavior at longer time scales by probing samples with limited free polymer in solution. Additionally, this should aid in capturing more charges and hence having a deeper bleach on LEAF for more accurate measurements. With the addition of these small molecule acceptors, we will hopefully be able to study a single charge carrier type to limit further complications. With those changes, we can then
determine the type of charge carrier on the nanotubes, as well as the concentration. Using that information, along with the PR-TRMC data, we hope to extract the mobility as desired.

References


7. Ferguson, A. J.; Bindl, D. J.; Mistry, K. S.; Dowgiallo, A.-M.; Reid, O. G.; Arnold, M. S.; Blackburn, J. L. Interfacial Charge Generation, Mobility, and Recombination in Near-Monochiral Single-Walled Carbon Nanotube Heterojunctions with Fullerene Acceptor Layers. (*In Preparation*).


12. Tenent, R. C.; Barnes, T. M.; Bergeson, J. D.; Ferguson, A. J.; To, B.; Gedvilas, L. M.; Heben, M. J.; Blackburn, J. L. Ultrasmooth, Large-Area, High-Uniformity, Conductive Transparent Single-Walled-


Bibliography


### Glossary of Abbreviated Terms

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>BNL</td>
<td>Brookhaven National Laboratory</td>
</tr>
<tr>
<td>CB</td>
<td>Chlorobenzene</td>
</tr>
<tr>
<td>CoMoCat®</td>
<td>Cobalt Molybdenum Catalyst</td>
</tr>
<tr>
<td>CP-MAS</td>
<td>Cross-Polarization Magic-Angle Spinning</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DCE</td>
<td>Dichloroethane</td>
</tr>
<tr>
<td>DGU</td>
<td>Density Gradient Ultracentrifugation</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DOC</td>
<td>Sodium Deoxycholate</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>EA</td>
<td>Electron Affinity</td>
</tr>
<tr>
<td>E_F</td>
<td>Fermi Energy</td>
</tr>
<tr>
<td>EOP</td>
<td>End of Pulse</td>
</tr>
<tr>
<td>FET</td>
<td>Field-Effect Transistor</td>
</tr>
<tr>
<td>FP-TRMC</td>
<td>Flash Photolysis Time-Resolved Microwave Conductivity</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine Doped Tin Oxide</td>
</tr>
<tr>
<td>GIC</td>
<td>Graphite Intercalation Compounds</td>
</tr>
<tr>
<td>HiPco</td>
<td>High-Pressure CO Conversion</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>ICBA</td>
<td>Indene-C_{60} Bis-Adduct</td>
</tr>
<tr>
<td>IP</td>
<td>Ionization Potential</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>LEAF</td>
<td>Laser Electron Accelerator Facility</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>LV</td>
<td>Laser Vaporization</td>
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<tr>
<td>MAS</td>
<td>Magic-Angle Spinning</td>
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<tr>
<td>MEG</td>
<td>Multiple Exciton Generation</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>m-SWCNT</td>
<td>Metallic Single-Walled Carbon Nanotube</td>
</tr>
<tr>
<td>Mn</td>
<td>Number Average Molecular Weight</td>
</tr>
<tr>
<td>Mw</td>
<td>Weight Average Molecular Weight</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NREL</td>
<td>National Renewable Energy Laboratory</td>
</tr>
<tr>
<td>OA</td>
<td>Triethylloxonium Hexachloroantimonate</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic Photovoltaics</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>PCBM</td>
<td>[6,6]-phenyl-C_{61}-butyric Acid Methyl Ester</td>
</tr>
<tr>
<td>PCE</td>
<td>Power Conversion Efficiency</td>
</tr>
<tr>
<td>Pd</td>
<td>Polydispersity</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyethyleneimine</td>
</tr>
<tr>
<td>PEM</td>
<td>Pulse Energy Meter</td>
</tr>
<tr>
<td>PET</td>
<td>Photoinduced Electron Transfer</td>
</tr>
<tr>
<td>PF2/6</td>
<td>Poly[9,9-di(2-ethylhexyl)fluorenyl-2,7-diyl]</td>
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</table>
PFAF  Perfluoroalkyl Fullerene
PFH  Poly[9,9-dihexylfluorenyl-2,7-diyl]
PFH-A  Poly[(9,9-dihexylfluorenyl-2,7-diy1)-co-(9,10-anthracene)]
PFO  Poly[9,9-dioctylfluorenyl-2,7-diyl]
PFO-BPy  Poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(6,6'-2,2'-bipyridine)]
PFO-BT  Poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(1,4-benzo-2,10,3-thiadiazole)]
PFO-C  Poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(9-hexyl-3,6-carbazole)]
PFO-MPy  Poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(2,6-pyridine)]
PFO-TPy  Poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(6,6'-2,2':6',2''-terpyridine)]
PLE  Photoluminescence Excitation
PR-TRMC  Pulse-Radiolysis Time-Resolved Microwave Conductivity
PV  Photovoltaic
SC  Sodium Cholate
SDBS  Sodium Dodecylbenzenesulfonate
SDS  Sodium Dodecyl Sulfate
SLPM  Standard Liters Per Minute
s-SWCNT  Semiconducting Single-Walled Carbon Nanotube
SWCNT  Single-Walled Carbon Nanotube
SWeNT  SouthWest NanoTechnologies Inc.
TBT  2,4,6-Tribromotoluene
TCF  Transparent Conducting Film
TCO  Transparent Conducting Oxide
TGA  Thermogravimetric Analysis
TRMC  Time-Resolved Microwave Conductivity
XPS  X-ray Photoelectron Spectroscopy
φΣµ  Yield Mobility Product