### SUPRAMOLECULAR FUNCTIONALIZATION OF SINGLE-WALLED CARBON NANOTUBES WITH CONJUGATED POLYMERS

### SUPRAMOLECULAR FUNCTIONALIZATION OF SINGLE-WALLED CARBON NANOTUBES WITH CONJUGATED POLYMERS

By

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M.Sc. (Xinjiang University, P.R.China) 2004

A Thesis

Submitted to the School of Graduate Studies

In partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy

in

Chemistry

McMaster University

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DOCTOR OF PHILOSOPH	Y (2013)	McMASTER UNIVERSITY
(Chemistry)		Hamilton, Ontario
TITLE:	Supramolecula	ar Functionalization of Single Walled Carbon
	Nanotubes wit	th Conjugated Polymers
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NUMBER OF PAGES:	xxvii, 240	

Abstract

Single-walled carbon nanotubes (SWNTs) are of special interest in current research due to their extraordinary mechanical, electronic and optical properties. Their unique structure, remarkable thermal and electrical conductivity, and high mechanical strength make SWNTs viable candidates for a wide range of device applications. However, pristine CNTs are not dispersible in most solvents, the main difficulties in CNT applications are related to their purification and solution-phase processing. In recent years, the supramolecular functionalization of SWNTs with conjugated polymers has received significant attention. Research within this field has been driven by the desire to find polymer structures that can selectively disperse certain nanotubes species with high efficiency.

After a brief overview of the studies that are related to the investigation of the supramolecular interaction between various conjugated polymers and SWNTs (chapter 1), the synthesis of fluorene and thiophene-based conjugated polymers and their supramolecular complex formation properties with SWNTs are described (chapter 2, 3, 4, 5 and 6). In order to understand the effect that conjugated polymer structure has on formation of supramolecular complexes with SWNTs, various factors were investigated by: (1) altering the polymer backbone composition; (2) varying the polymer molecular weight; (3) introducing different solubilizing groups while the polymer backbone remained the same; (4) changing the polymer conformation. All of the resulting polymer-nanotube assemblies exhibit excellent solution stability in THF in the absence of excess

unbound free polymer. The spectroscopic characterization of the polymer-SWNT complex materials indicated that the interaction between the conjugated polymers and SWNTs is strongly influenced by polymer structure.

The interaction between a water soluble polythiophene derivative, poly[3-(3-N,N-diethylaminopropoxy)-thiophene] (PDAOT), and SWNTs is discussed in chapter 7. It is also demonstrated that the PDAOT-SWNT complexes form stable aqueous solutions that can be used for the fabrication of highly sensitive amperometric glucose biosensors.

### Acknowledgements

It is my greatest pleasure to express my appreciation to remarkable individuals who have been influential and extremely supportive over the course of my graduate studies at McMaster University and made my life more enjoyable in Hamilton.

First and fore most, I would like to thank my supervisor Dr. Alex Adronov for his extremely generous support, guidance, and encouragement throughout my graduate career. It has been my privilege and pleasure to work with him and I have very much enjoyed his extraordinary mentorship.

I would like to thank the members of my committee, Dr. Harald Stover and Dr. Gillian Goward, for their support, guidance and helpful suggestions throughout my work.

I would like to thank all the talented individuals whom I have had the opportunity of collaborating with: Dr. Fuyong Cheng, Dr. Xin Pang and Dr. Igor Zhitomirsky. I would also like to acknowledge all the facilities staff at McMaster, especially Dr. Steve Kornic, Frank Gibbis, Dr. Bob Berno and Dr. Kirk Green for their help with instrumentation. I want to thank Dr. Kalaichelvi Saravanamuttu, Alex Hudson and Matthew Ponte for their help with photoisomerization experiments. I would also like to thank all the wonderful staff in the Chemistry and Chemical Biology department for always being so friendly and helpful.

The members of the Adronov group have also contributed immensely to my professional and personal time at McMaster. I am very grateful to all the past and current group members for their support, suggestions and encouragement at various points of my research program. Thank you all for giving me such a friendly working environment and many valuable discussions.

To my parents, thank you for your dedication and unconditional support throughout all these years, I would not have made it this far without you. To my sisters, thank you for your encouragement and support. To my lovely daughter Munire, thank you for being such a wonderful girl always and cheering me on.

Special thanks to my husband Mokhtar for his steady support and great patience at all times. Coming to Canada after me has been a big challenge that you have accomplished successfully to bring our family together. One of the best experiences that we lived through during our Ph.D. studies was welcoming our baby girl Parida, who brought additional joys to our life. I have enjoyed wonderful times with you in the past 15 years and I am looking forward to many more of our happy and exciting years together.

Last but not least, I want to gratefully acknowledge the Ontario Ministry of Training for an Ontario Graduate Scholarship (OGS), and the Natural Science and Engineering Research Council of Canada (NSERC) for Alexander Graham Bell Canada Graduate Scholarship (NSERC CGSD).

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### List of Abbreviations

AFM	Atomic Force Microscopy
CNT	Carbon Nanotube
CPEs	Conjugated Polyelectrolytes
DCM	Dichloromethane
DGU	Density Gradient Ultracentrifugation
DMF	Dimethyl Formamide
DSC	Differential Scanning Calorimetry
EPD	Electrophoretic Deposition
GOx	Glucose Oxidase
HiPco	High-Presure Carbon Monoxide
HOPG	Highly Ordered Pyrolytic Graphite
LBL	Layer-by-Layer
MWNT	Multi-Walled Carbon Nanotube
NMR	Nuclear Magnetic Resonance
OFET	Organic Field Effect Transistors
OLED	Organic Light Emitting Diode
OPV	Organic Photovoltaic
PC	Polycarbazole
PF	Polyfluorene
PLE	Photoluminescence Excitation

### List of Abbreviations (Continued)

PMPV	Poly(m-phenylene-co-2,5-dioctoxy-p-phenylenevinylene)s
PPE	Poly(aryleneethynylene)
PPV	Poly(phenylenevinylene)
PT	Polythiophene
PTC	Phase Transfer Catalyst
RBM	Radial Breathing Mode
RRS	Resonant Raman Scattering
SDBS	Sodium Dodecyl Benzene Sulfonate
SDS	Sodium Dodecyl Sulphate
SEM	Scanning Electron Microscopy
SWNT	Single Walled Nanotubes
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
UV-Vis-NIR	Ultraviolet- visible and Near-infrared

### Chapter 1: Overview of Supramolecular Complexes between Carbon Nanotubes and Conjugated Polymers

### **1.1. Introduction**

The interactions of carbon nanotubes (CNTs) with their surroundings are of imminent importance to their incorporation within a wide range of applications. It is now clear that the mechanical, thermal, and electronic properties of both single-walled and multi-walled carbon nanotubes (SWNTs and MWNTs, respectively), on an individual tube basis, are ideal for nanoscale structural reinforcement, charge mobility through host materials, charge separation, energy storage, thermal transport, analyte sensing, and even scaffolds for tissue engineering.<sup>1-17</sup> However, in almost all of these cases, practical application of CNTs within operational devices has not been achieved to date. Although a number of limitations to CNTs exist, including cost, availability, and purity, it can be argued that the most challenging problem of CNTs, with respect to practical applications, is their lack of solubility. The inherently poor solubility of CNTs in all solvents stems from their macromolecular size (relative to small molecules), high aspect ratio, and strong tendency to form aggregates, or bundles, through  $\pi$ -stacking of their aromatic sidewalls.<sup>18-</sup> <sup>21</sup> Combined, these attributes preclude the solution-phase manipulation of CNTs, making it difficult to blend, mix, or coat other materials with them. It is therefore not surprising that the dissolution/dispersion of CNTs, especially SWNTs, through chemical functionalization has attracted a great deal of attention.

A significant body of work centered around the functionalization of CNTs has culminated in two broad strategies: covalent and non-covalent (supramolecular) functionalization.<sup>22-28</sup> Initial success was achieved by treatment with strong acids to oxidize ends and defect sites, and to liberate carboxylic acid functionalities, which were subsequently derivatized through esterification and amidation chemistry. In addition, a number of other sidewall functionalization methods have been developed, including reactions with radicals,<sup>9, 26, 29-43</sup> nitrenes,<sup>44, 45</sup> and carbenes,<sup>45, 46</sup> as well as dipolar cycloadditon chemistry,<sup>9, 35, 47-53</sup> enabling attachment of various structures to the nanotube sidewalls. Although many of these methods are highly effective at achieving a significant degree of functionalization, allowing the exfoliation of nanotube bundles and the formation of individual nanotube dispersions, covalent chemistry has the drawback of introducing defects along the nanotube sidewall, which diminish conductivity and alter the mechanical properties of CNTs (especially SWNTs).<sup>54, 55</sup>

Supramolecular functionalization of CNTs, on the other hand, involves adsorption of small molecules capable of steric or electrostatic stabilization of CNTs without any perturbation to the molecular structure or intrinsic properties of the nanotubes. Initially, this was achieved with surfactants, such as sodium dodecyl sulphate (SDS), but more recently has involved the  $\pi$ -stacking of planar aromatic molecules, most commonly pyrene.<sup>22, 56-58</sup> Although both surfactants and pyrene derivatives have resulted in nanotube dispersions, the concentrations achievable with these small molecules have been limited, and are not competitive with the concentrations achieved using covalent chemistry. In addition, a large excess of the adsorbate molecules was necessary to maintain stable dispersions of nanotubes in solution. If the surfactant or pyrene derivatives were removed from solution, the surface bound molecules would desorb and the nanotubes would reaggregate into bundles and precipitate.

Strengthening the interaction between adsorbates and the CNT surface is therefore important in achieving significant nanotube solubility without affecting the nanotube sidewall structure. This can be achieved either through the development of small molecules that exhibit higher binding affinity for the nanotube surface, or by introducing multiple sites of attachment on a macromolecule, thus achieving multivalent binding. To date, there have been no reports of new, high affinity small molecules capable of near irreversible binding to the nanotubes. Pyrene and porphyrin derivatives have dominated this area and have achieved limited success.<sup>59-61</sup> However, the development of macromolecules capable of multivalent binding to the nanotube surface has received increasing attention. The earliest examples of multivalent binding by macromolecular structures took advantage of the known binding properties of pyrene, and simple tethered pyrene molecules as side-chains on standard polymers, such as PMMA and polystyrene.<sup>62</sup>, <sup>63</sup> Although it was found that these polymers do bind to the nanotube surface and result in nanotube solubility, the achievable concentrations of nanotubes in solution were still relatively low, and could not match what was achievable with covalent functionalization.

As an alternative approach to multivalent binding, the interaction of conjugated polymers with the CNT surface has received significant recent attention. Here, rather than introducing side-chains on the polymer that interact with CNTs, it is the polymer backbone that forms the  $\pi$ -stacking interaction with the nanotube surface, and side-chains

serve to impart solubility to the polymer-nanotube complex. Since the entire polymer backbone becomes involved in the  $\pi$ -stacking interaction with the nanotube sidewall, an optimal degree of multivalent binding is achieved. Indeed, over the past decade, a number of reports have appeared detailing the formation of nanotube solutions/dispersions through supramolecular functionalization with conjugated polymers. These examples can be separated into two broad categories, wrapping and non-wrapping. The wrapping approach involves interactions with conjugated polymers that adopt helical conformations in solution. Specifically, dispersion of CNTs using poly(m-phenylene-co-2,5-dioctyloxyp-phenylenevinylene)s (PmPV)s, whose structure is a variation of the more common PPV, has been extensively explored.<sup>13, 24, 64-68</sup> Owing to the meta substitution pattern of the polymer chain, backbone dihedral angles are adopted that result in a helical structure that can therefore encircle both individual nanotubes and nanotube bundles, depending on the helical pitch of the polymer and the diameter of the nanotubes. Alternatively, other rigidrod polymers, such as poly(aryleneethynylene) (PPE) derivatives that cannot adopt helical conformations and are more likely to adhere length-wise to the nanotube surface, have been reported.<sup>69-72</sup> Supramolecular functionalization of SWNTs with thiophene, fluorene, and carbazole containing conjugated polymers has become a main focus of recent work due to their highly specific dispersing ability toward semiconducting SWNT (sc-SWNT) species.<sup>73-78</sup> To investigate the correlation between the polymer structure and its SWNT dispersing features, the vast diversity of conjugated polymers that can be prepared provides enormous potential for the formation of polymer-nanotube conjugates that are tailor-made for specific applications. Indeed, variation of the conjugated polymer

backbone allows control over conjugation length, electronic structure, and photophysical properties, while substitution of polymer side-chains enables modification of solubility, intermolecular interactions, and responsiveness to external stimuli (i.e., temperature, pH, and electric field).<sup>76, 79-83</sup> Exploration of different conjugated polymer-nanotube combinations is still in its infancy, and there exists significant potential for new discovery in this area.

This chapter will attempt to highlight the recent advances in the study and application of supramolecular interactions between conjugated polymers and carbon nanotubes. Here, emphasis will be placed on the studies that demonstrate discrete complexes between conjugated polymers and nanotubes, rather than simple combinations of the two materials via blending or extrusion techniques. While there exists a vast body of literature concerning the latter subject, the majority of this work involves small quantities of nanotubes poorly dispersed within a host polymer material. This type of composite provides little chemical information about the nature of the polymer-nanotube interaction, and is of little value for the understanding of the interface between individual polymer chains and the nanotube surface. This chapter will therefore focus on conjugated polymers that result in highly dispersed nanotubes, and is organized according to general classes of conjugated polymers.

### **1.2. Spectroscopic Characterization of SWNTs**

The structure of Carbon nanotube (CNTs) is configurationally equivalent to a two dimensional graphene sheet rolled to form a seamless cylinder that is comprised of only carbon atoms.<sup>1, 84</sup> CNTs mainly exist in one of two types: single-walled nanotubes (SWNTs), which is essentially a single layer of graphene sheet rolled into a seamless cylinder with diameters ranging from 0.2 to 2 nm, and multiwalled nanotubes (MWNTs), which contain several concentric cylinders. The way that graphene sheet is rolled up dictates whether the resulting SWNTs are metallic or semiconducting.<sup>84, 85</sup> A SWNT is identified by a pair of integers (n,m), which are coefficients of the unit vector  $a_1$  and  $a_2$  (Figure 1.1). The chiral vector  $C_h$  is written as  $C_h = na_1 + ma_2$ , which represents the circumferential direction of SWNTs or the direction to roll up the 2D graphite sheet. A chiral angle ( $\theta$ ) of a SWNT is the angle between  $a_1$  and  $C_h$ .<sup>86,87</sup>



**Figure 1.1.** Schematic showing a hexagonal graphene lattice and lattice vector used to define the chirality of SWNTs.

Each species of SWNT with specific chiral (n,m) indices exhibits unique electronic properties (Figure 1.1). If both indices are equal in value (n = m,  $\theta = 30^{\circ}$ ), the nanotubes are named as armchair nanotubes, which usually show metallic conductivity. If m = 0, the nanotubes are called zig-zag nanotubes, for which  $\theta = 0^{\circ}$ . For all other indices ( $n \neq m$ ,  $0^{\circ} < \theta < 30^{\circ}$ ), chiral SWNTs are formed. The zig-zag and chiral SWNTs are either semimetallic or semiconducting, depending on their structure.<sup>85</sup>

One of the critical advances in SWNT chemistry, characterization, and applications is the ability to differentiate individual SWNT chiralities in mixtures of SWNTs based on photophysical properties. Several spectroscopic characterization techniques including Raman spectroscopy, optical absorption, and photoluminescence spectroscopy have been widely used for the (n,m) characterization of SWNTs.<sup>85, 87-90</sup> Observation of both semiconducting and metallic SWNTs is possible by using Raman spectroscopy. The frequency and intensity of the radial breathing mode (RBM) features that have an inverse relationship with tube diameter provides the most valuable information for (n,m) characterization. Each (n,m) species exhibits a characteristic Raman signal when the Raman excitation energy matches the energy gap of the nanotube. However, only a subset of near-resonant (n,m) species can be observed when a single laser excitation is used. Therefore, obtaining a detailed analysis to identify all of the different SWNT species in the sample rather difficult since it requires a large set of spectra using different laser wavelengths.<sup>89, 91</sup>



**Figure 1.2.** Schematic density of electronic states (DOS) for a SWNT structure. Solid arrows depict the optical excitation and emission transitions of interest; dashed arrows denote nonradiative relaxation of the electron (in the conduction band) and hole (in the valence band) before emission. Reproduced with permission from ref. 86. Copyright American Association for the Advancement of Science, 2002.

UV-Vis-NIR absorption spectroscopy is another widely used technique to characterize a bulk SWNT sample, since all semiconducting and metallic (n,m) species exhibit unique absorption peaks in the visible and/or NIR wavelength. <sup>86, 92</sup> The schematic density of electronic states (DOS) diagram for a semiconducting SWNT is shown in Figure 1.2 as an illustrative example to demonstrate the basic photophysical processes.<sup>86</sup> Vis-NIR absorption in SWNTs originates from electronic transitions from the v<sub>2</sub> to c<sub>2</sub> (energy  $E_{22}$ ) or v<sub>1</sub> to c<sub>1</sub> ( $E_{11}$ ) levels, and the values of  $E_{11}$  and  $E_{22}$  vary with tube structure.<sup>86</sup> The optical transitions are relatively sharp for an individual SWNT and that can be used to identify specific (n, m) species within a sample. However, the sharpness of
the optical transition diminishes with increasing energy, and many SWNTs have very similar  $E_{22}$  or  $E_{11}$  energies, and thus resulting in significant overlap occurs in absorption spectra.<sup>86, 89</sup> In addition, SWNTs tend to form aggregates and large bundles due to strong  $\pi$ - $\pi$  interactions, and these tube-tube perturbations also significantly broadening the optical spectra of bundles, which also making detailed spectral analysis difficult. <sup>86, 88, 92</sup>

In photoluminescence excitation (PLE) measurements, the PL intensity of the sample is measured with respect to both excitation and emission wavelengths. Different chiral structures give different PLE spectra from photon absorption by sc-SWNT samples at an energy  $E_{22}$  that gives fluorescence emission at  $E_{11}$  (Figure 1.2). By matching Raman and PLE data, Weisman and coworkers successfully assigned SWNT indices to every peak of a PLE plot, and provided valuable empirical data that allows precise calculation of the E<sub>ii</sub> transition energy for each (n,m) sc-SWNTs.<sup>86, 92</sup> Research groups around the world have been using this empirical data as a reference, thus allowing easy and rapid characterization of bulk SWNTs. As an example, Figure 1.3 depicts the photoluminescence excitation (PLE) map of raw Hipco SWNTs dispersed in D<sub>2</sub>O using sodium dodecyl benzene sulfonate (SDBS), measured over a large range of excitation (500-850 nm) and emission (900-1450 nm) wavelengths. High intensities are displayed in red and low intensities are displayed in blue. The chiral indices (n,m) for the identified species are labeled on the map, where the assignment was based on the previously reported results from Weisman and coworkers.<sup>86, 92</sup>



**Figure 1.3.** PLE contour map of raw HiPco SWNTs dispersed with SDBS in  $D_2O$ , where the false colour scale represents the intensity of emission; the points represent the position of SWNT resonance using the empirical data proposed by Weisman and Bachilo (ref. 92).

## **1.3. Homopolymers**

Conjugated polymers that contain only a single type of repeat unit are known as conjugated homopolymers. In order to get optimum polymer-SWNT dispersion, aromatic groups enabling  $\pi$ - $\pi$  interactions with the nanotube surface are integrated within the polymer backbone, and desired polymer solubility is tuned via incorporation of various solubilizing side chains. Among them, the homopolymers of thiophene, fluorene, and carbazole have been mainly investigated for noncovalent functionalization of SWNTs, and poly(3-alkylthiophene) (PT), poly(9,9-dialkylfluorenyl-2,7-diyl) (PF), and poly(Nalkylcarbazole-2,7-diyl) (PC) have been found to disperse SWNTs very efficiently in a number of organic solvents, including tetrahydrofuran (THF), toluene, and chloroform. A significant number of studies have been mainly focused on the dispersion of SWNTs prepared by the high-pressure carbon monoxide (HiPco) and CoMoCat processes. Although the typical procedures for SWNT dispersion/extraction vary slightly among different research groups, most involve sonication of pristine SWNT samples in polymer solutions, and centrifugation of the mixture to remove larger bundles and residual catalyst particles. Most of these studies have used aqueous dispersions of the nanotubes as reference samples, dispersed with the surfactants sodium dodecylbenzenesulfonate (SDBS), sodium dodecylsulphate (SDS), or sodium cholate (SC). It is known that these surfactants disperse SWNTs of all lengths, diameters, and chiralities available in the commercial or synthesized samples without discrimination.<sup>86,92</sup> Optical absorbance, photoluminescence excitation mapping (PLE), Raman spectroscopy, and various microscopy techniques were used to characterize the polymer/SWNT dispersions. This section will describe the recent studies involving the use of conjugated homopolymers as a dispersing agent.

## 1.3.1. Homopolymers of 3-alkylthiophenes

The ability of PT derivatives (Figure 1.4) to disperse SWNTs has been extensively investigated, and it was found that PTs are capable of forming strong supramolecular complexes with carbon nanotubes. Composites between carbon nanotubes and PT derivatives have been widely studied due to their interesting optical and electrical properties, and their potential applications in photovoltaic cells, field-effect transistors, field emitters, and sensors.<sup>93-97</sup>



**Figure 1.4.** Chemical structures of poly(3-alkylthiophene)s that have been used to disperse carbon nanotubes.

There have been several reports detailing the interaction between CNTs and soluble PTs, and the properties of the resulting polymer-SWNT composite materials.<sup>98-106</sup> The simplest soluble PT derivative, poly(3-hexyl thiophene) (P1) has been used to disperse SWNTs in chloroform, and addition of very small amounts of SWNTs were found to induce noticeable changes to the optical properties of **P1**.<sup>101</sup> When a small amount of SWNTs was added into a dilute polymer solution (0.02 g/L), two new, redshifted absorption bands were observed for the P1-SWNT complex, which are consistent with an ordered backbone associated with a more extended and highly conjugated conformation. Significant quenching of polymer photoluminescence was also reported when less than 1 wt% of SWNTs was incorporated in the **P1** solution. Interestingly, no significant changes in optical properties of the polymer were detected when a similar experiment was repeated with other PT derivatives, such as poly(3-octylthiophene) (P2) and poly(3-dodecylthiophene) (P4).<sup>101</sup> Furthermore, removal of excess polymer by extensive washing with chloroform yielded a P1/SWNT composite that contained about 20 wt% of P1, and the resulting material was easily dispersible in chloroform without addition of extra polymer. The influence of SWNTs on crystallinity enhancement and morphology change of a polymer film was investigated by Zeng *et al.*, who used electron diffraction to show that SWNTs can enhance the crystallinity of **P1**.<sup>102</sup> Photovoltaic devices based on an active layer incorporating a small percentage of SWNTs exhibited a relatively high open-circuit voltage (V<sub>OC</sub>), though direct comparison to control devices without SWNTs was not performed.<sup>102</sup> Detailed studies of PT self-assembly and organization on SWNTs were carried out by Goh *et al.*<sup>103, 104</sup> Monolayers of regioregular poly(3-hexylthiophene) (rr**P1**) adsorbed on the SWNT surface were imaged by scanning tunneling microscopy (STM) and the results were compared with the STM image of rr**P1**on highly ordered pyrolytic graphite (HOPG). It was found that for the case of rr**P1**-SWNT composites, rr**P1** monolayers have the tendency to wrap around SWNTs, with a wrapping angle that is possibly influenced by the chiral angle of the SWNTs. In addition, the authors found that the chain-to-chain distance between rr**P1** chains is larger on the SWNTs than on HOPG, resulting from the surface curvature.<sup>103</sup>

**P1** was also studied in composite films with SWNTs, prepared by spin-coating from a 1,2-dichlorobenzene dispersion to produce samples with a thickness of 100 nm.<sup>107</sup> It was found that although the absorption spectrum of the polymer film exhibited little change upon increasing SWNT content from 0 to 30 wt%, indicating a lack of ground-state interactions between the two components, the photoluminescence was dramatically quenched, even with as little as 0.5 wt% SWNTs incorporated. This again indicates that efficient exciton transfer from the polymer to the embedded SWNTs was occurring, even in the solid state. In addition, the direct current conductivity through the nanotube-loaded

polymer films was measured using a sandwich architecture with Al electrodes above and below the films. Not surprisingly, the conductivity increased by ca. 5 orders of magnitude upon introduction of 30 wt% SWNTs, and it was reported that the percolation threshold was on the order of 2 wt%.<sup>107</sup>

Nicholas and coworkers reported the preparation of rrP1-SWNT composites by solvent extraction techniques, which yielded well-ordered nanohybrid structures consisting of SWNTs coated with a single monolayer of rrP1, and the applicability of the resulting hybrid materials in organic PVs was investigated.<sup>108, 109</sup> It was found that any free polymer could be effectively removed by a solvent extraction process, resulting in stable polymer-SWNT dispersions at high concentration. SWNTs grown by both HiPco and CoMoCat processes were dispersed with rrP1, where 5 mg of SWNTs could be dispersed with 5 mg of polymer in 10 mL of a solvent such as THF or dichlorobenzene, both of which were found to be good solvents for the polymer-nanotube complexes. Spectroscopic evidence confirmed that individual SWNTs were isolated by rrP1, and the SWNTs serve as nano-substrates for the rr**P1**, which self organizes in a highly crystalline morphology on the nanotubes.<sup>109</sup> PLE mapping studies showed an efficient energy transfer of excitons created on the rrP1 to the SWNTs via a Förster mechanism, with some evidence indicating that the efficiency of energy transfer was greater in larger diameter SWNTs.<sup>109</sup> In addition, these authors definitively showed that a diameterdependent red-shift in SWNT transition energies (both absorption and emission) occurs upon adsorption of rrP1 on the SWNT surface. This red-shift is the result of an excitonic effect, which is caused by overlap of the wavefunctions across the interface of the type II heterojunction that is formed upon nanotube complexation with low-diameter SWNTs. Based on these results, the authors suggested that high performance OPV devices can only be achieved if small diameter semiconducting SWNTs are used in combination with polymers having a high HOMO level.<sup>108</sup>

Although we have discussed the supramolecular complex formation properties of **P1** with SWNTs first, some important earlier studies focused on the supramolecular functionalization of SWNTs with structurally analogous poly(3-octylthiophene) (**P2**).<sup>98-100</sup> The interactions between SWNTs and **P2** were first investigated by Kymakis *et al.*,<sup>98</sup> similarly showing that low-level introduction of SWNTs within the polymer films (100 nm thickness) resulted in little change in absorption properties. Again, the conductivity of the films increased by 5 orders of magnitude (measured using a two-point probe) upon increasing the nanotube concentration from 0 to 20 wt%. However, the reported percolation threshold in this study was 11 wt%, much higher than that reported with **P1**,<sup>107</sup> likely due to either impure nanotube starting material or poor dispersion of nanotube bundles. It is unlikely that increasing the side-chain length by two carbons could have resulted in such a massive change in percolation threshold.

Selective dispersion of high purity semiconducting SWNTs with rrPTs was recently reported by Bao and coworkers.<sup>110</sup> A series of commercially available PT derivatives were used to disperse HiPco SWNTs in toluene. UV-Vis-NIR absorption, and resonant Raman scattering (RRS) measurements were conducted to characterize the polymer-SWNT dispersions. It was found that the rr**P4** dispersed sample exhibited the most intense SWNT absorption peaks in the NIR region, indicating that a higher

percentage of SWNTs was dispersed with this polymer in toluene. Under the same experimental conditions, the amount of dispersed SWNTs was significantly lower for the rrPT derivatives with smaller side chains, including rrP1, rrP2, and rrP3, as well as regiorandom P4 and several other substituted PT derivatives. This clearly indicates that side-chain structure and length, substitution density, substitution patterns, monomer configuration, and polymer conformation all impact the extent and selectivity of polymernanotube interactions. Interestingly, the temperature used during sonication was also found to be an important parameter for achieving high SWNT dispersion efficiency, with the highest extent of SWNT dispersion being observed when sonication was carried out at 50°C (temperatures in the range of -40 to 90°C were studied), which coincides with the melt transition for the side-chains of rrP4. RRS measurements at 3 different excitation wavelengths (532, 633, and 785 nm) demonstrated that semiconducting SWNT (sc-SWNT) species were dramatically enriched upon dispersion with rrP4, as evidenced by the disappearance of radial breathing mode (RBM) absorptions (180-280  $\text{cm}^{-1}$ ) corresponding to metallic SWNTs (m-SWNTs) after dispersion. Similarly to what was observed previously by Nicholas and co-workers,<sup>108</sup> PLE maps showed that only a subset of the original SWNTs was dispersed in toluene by **rrP4**, and a red-shift in the emission peaks was observed from polymer-decorated SWNTs relative to SWNTs dispersed with a non-selective surfactant in water. The polymer-dispersed SWNTs were then utilized for the fabrication of thin-film transistor (TFT) devices on a Si substrate. Importantly, out of 122 randomly chosen devices, none was found to exhibit shorting, as would be expected from the presence of m-SWNTs. In these devices, hole mobilities as high as  $12 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ . and on/off current ratios of  $\sim 10^6$  were observed. The authors proposed a geometrical model of the supramolecular polymer-SWNT assembly, with interdigitated side-chains, resulting in a polymer shell around the SWNT surface (Figure 1.5). Selectivity of the dispersion was explained in terms of diameter selectivity of the polymer (due to preferential polymer wrapping angle), and the potential for charge-transfer between the polymer and m-SWNTs, which would preclude optimal wrapping of metallic nanotubes.



**Figure 1.5.** Schematic diagram showing the polymer wrapping of SWNTs by rrP4, and the match between polymer shell diameter and the nanotube diameter. (b) Schematic representation of a double-stranded polymer structure that comprises the shell of the polymer-SWNT complex. Reproduced with permission from ref. 110. Copyright Nature Publishing Group 2013.

A poly(3-hexylthiophene) (P3HT) derivative bearing randomly distributed pyrene units in the side-chain (**P5**) was prepared via post-polymerization modification of the backbone by Yang and co-workers.<sup>111</sup> <sup>1</sup>H-NMR spectroscopy indicated that approximately 15% of the monomer units had been derivatized with pyrene. Interaction of this polymer with SWNTs led to stable nanotube dispersions in solution, which were characterized by UV-Vis-NIR absorption and fluorescence spectroscopy. This data indicates that exfoliation of SWNTs into individual nanotubes was not achieved in this work, as the absorption bands in the NIR were broad and poorly defined. Based on absorption data and ESR spectroelectrochemical measurements, the authors claimed that the pyrene units in the side-chain preferentially interact with the nanotube sidewall, and do not allow the P3HT backbone to form  $\pi$ - $\pi$  interactions. However, the quantitative quenching of P3HT fluorescence when complexed to SWNTs seems to contradict this hypothesis, and based on other work, it is expected that the P3HT backbone would interact more strongly with SWNTs than randomly distributed pyrene units. To definitively prove this hypothesis, one would need to carry out polymer exchange experiments between appropriate model polymers.

#### **1.3.2.** Homopolymers of Fluorene

Among all the known conjugated polymers, poly(9,9-dialkylfluorene) (PF) represents one of the most important families of electroactive polymers due to its conductivity, solubility, and stability properties, as well as its intense blue fluorescence.<sup>112-114</sup> Although PFs exhibit the extended conjugation required for  $\pi$ -stacking to the nanotube surface, interest in using PFs for non-covalent SWNT functionalization has only recently gained attention as reports of selective solubilization of certain SWNT species have begun to be published.<sup>74, 75, 78</sup> The chemical structures of the PF derivatives that have been used to disperse carbon nanotubes are depicted in Figure 1.6.



**Figure 1.6.** Chemical structures of polyfluorenes that have been used to disperse carbon nanotubes.

Nish *et al.* were the first to show that poly(9,9-dioctylfluorenyl-2,7-diyl) (**P7**) can selectively disperse certain sc-SWNT species in terms of diameter and chiral angle.<sup>74</sup> It was found that the distribution of dispersed species is strongly dependent on the solvent, and the total number of species exhibiting photoluminescence was found to be higher in THF than in Toluene. Figure 1.7 depicts the PLE maps of HiPco SWNTs dispersed with SDBS in aqueous solution (Figure 1.7, a), and with **P7** in toluene (Figure 1.7, b). The PLE map of the **P7**-SWNT dispersion exhibits 5 major peaks, which correspond to the (7,5), (7,6), (8,6), (8,7), (9,7) SWNT chiralities, with the (8,6) SWNTs emitting with highest intensity. When using CoMoCAT SWNTs with P7, dramatic selectivity for the (7,5) species was observed, with no detectable signal for the (6,5) chirality, which is present in large abundance in the as-received raw material. The greater extent of selectivity with CoMoCAT SWNTs allowed the authors to spectroscopically investigate the presence of metallic vs. semiconducting SWNTs within the dispersions. Based on UV-Vis-NIR absorption and Raman data, it was found that metallic SWNTs are not detectable in the polymer-SWNT dispersions, which is consistent with what Bao and coworkers later reported with polythiophene derivatives (vide supra).<sup>110</sup> In addition to the observed selectivity for sc-SWNTs, the discrimination between (7,5) and (6,5) CoMoCat SWNTs demonstrates a significant diameter selectivity that is achieved with **P7**, which the authors explain using molecular modeling. Molecular mechanics simulations using the MM3 force field were performed, and showed that **P7** can adopt a more favourable, higher symmetry interaction with larger SWNT diameters.<sup>74</sup> Although these simulations were idealized, comparing drastically different SWNT diameters and not including solvent effects, they nevertheless lend credence to the notion that the polymers can preferentially interact with specific tube diameters.



**Figure 1.7.** PLE contour maps of HiPco SWNTs dispersed with SDBS in aqueous solution (a), with P7 in Toluene (b), (where the false colour scale represents the intensity of emission from SWNT dispersed using SDBS, the points represent the position of SWNT resonance using the scheme proposed by Weisman and Bachilo. Reproduced with permission from ref. 74. Copyright Nature Publishing Group 2007.

Structural variations of the polymer side-chains and backbone were also investigated,<sup>74, 78</sup> and indicated that the distribution and relative emission intensity of each dispersed species is slightly different when the length of alkyl chains at the bridging

carbon atom of PF was changed. Poly(9,9-dihexylfuorenyl-2,7-diyl) (P6), with alkyl chains that are two carbon atoms shorter, resulted in much lower SWNT solubility when compared with **P7**. In addition, **P6** showed lower selectivity for specific SWNTs in toluene, predominantly solubilizing a combination of (8,6), (8,7) and (9,7) SWNT species, relative to just the (8,6) for **P7**. The corresponding **PF** structure with dodecyl side chains, P8, was investigated by Mayor and co-workers, who also found that this polymer produces stable, concentrated SWNT dispersions and exhibits good selectivity for specific SWNT chiralities, namely the (7,6) species. Interestingly, these results illustrate that there is an inverse relationship between the side chain length and the nanotube diameter that is preferentially selected by this series of **PF** derivatives.<sup>79</sup> In addition, these authors investigated a stereoisomer of P8, with 3,6 rather than 2,7 connectivity in the polymer backbone. The homopolymer of 9,9-didodecyl-3,6-fluorene (P9) was found to form very unstable dispersions with SWNTs. Clearly, P9 must adopt a conformation that is unfavourable for efficient interaction with the nanotube surface.<sup>79</sup> Kappes and coworkers also reported the near monochiral SWNT dispersion in toluene using polymers P7 and P8.<sup>115</sup> In this study, they showed that separation of specific SWNT chiralities could be achieved in organic solvent using density gradient ultracentrifugation (DGU) of polymer-wrapped SWNTs. Density gradients were achieved by using "heavy" organic molecules such as 2,4,6-tribromotoluene in chlorobenzene. It was found that (7,5), (7,6), (10,5) and (9,7) nanotubes could be isolated with respective enrichments of up to ~90% by their selective dispersion in toluene, followed by DGU.<sup>115</sup>

Berton et al. have synthesized a series of monodisperse 9,9-didodecylfluorene oligomers (from dimer to octamer) to study the effect of chain length on SWNT dispersion in toluene, and the dispersing properties of these oligomers was compared with the homologous polymer **P8** having moderate molecular weight (Mn ~ 13 kDa, PDI = 4.2).<sup>116</sup> Not surprisingly, it was found that the stability of the SWNT/oligofluorene dispersions increased with oligomer length, though none of the oligomers resulted in dispersions that could be considered stable (all precipitated within minutes to hours). Only the octamer complex remained stable long enough to enable PLE mapping, which allowed observation of its selectivity for specific nanotube chiralities. It was found that the octamer exhibits the same selectivity as **P8**, with the (7,6) SWNT species dominating the PLE map. This signifies that the polymer structure, rather than its length, dictates the selectivity for specific SWNTs. It was further demonstrated that the metastable octafluorene-SWNT complex undergoes rapid exchange when exposed to a conjugated polymer, again demonstrating that the polymer-SWNT interaction is much stronger than the oligomer-SWNT interaction (at least up to the octamer).

The effect of polymer molecular weight and solution parameters on selective dispersion of SWNT was also studied by Zaumseil and coworkers.<sup>117</sup> In this study, a commercially available **P7** structure having three different molecular weights (low, medium, and high) was used, and the authors compared the SWNT dispersion selectivity in toluene and o-xylene. In contrast to the observation by Kappes above,<sup>116</sup> it was found that selective dispersion of SWNTs depends on not only the type of solvent but also on the molecular weight of the polymer. However, the molecular weights investigated in this

work were much higher than that of the Kappes study, and the authors rationalized that the change in solvent viscosity that resulted from dissolution of different polymer molecular weights was a major factor dictating observed selectivity. Nevertheless, consideration of polymer molecular weight is extremely important when screening for new polymers for selective SWNT dispersion. Very recently, Gao *et al.* reported the preparation and optical characterization of SWNTs dispersed with **P7** in toluene, and investigated the effects of several processing parameters such as sonication time, polymer concentration, and centrifugation time and speed.<sup>118</sup> The optimal conditions for the preparation of individually dispersed semiconducting SWNTs with **P7** were found to be short sonication time (15 min), low polymer concentration (0.17 mg/mL), and high-speed centrifugation (110,000 g). SWNT selectivity was consistent with previous studies involving **P7**, with (7,5) and (7,6) species dominating the absorption and emission spectra.

## **1.3.3.** Homopolymers of Carbazole

Polycarbazoles (PCs) are structural analogues to PFs, but the para-phenylene units in carbazole are bridged by a nitrogen atom instead of carbon, and this family of polymers have been extensively investigated for a wide range of applications in optoelectronic devices, including OPVs, OFETS, and OLEDs.<sup>119, 120</sup> The chemical structures of the PC derivatives that have been used to disperse carbon nanotubes are depicted in Figure 1.8.



**Figure 1.8.** Chemical structures of polycarbazoles that have been used to disperse carbon nanotubes.

Very recently, Lemasson *et al.* reported the first example of using poly(N-decyl-2,7-carbazole) (P10) for selective SWNT dispersion, and compared their results with widely investigated PFs.<sup>77</sup> It was found that **P10** exhibits selectivity toward semiconducting SWNTs with  $(n-m) \ge 2$  in toluene, which correspond to low chiral angle  $(10^{\circ} < \theta < 20^{\circ})$  nanotubes, as opposed to the polyfluorene analog, **P7**, which prefers SWNTs with large chiral angles ( $\theta \ge 25^\circ$ ). This work seems to indicate that polycarbazoles preferentially interact with distinctly different nanotube populations than polyfluorenes, making the two polymer types complementary to one another.<sup>77</sup> In their subsequent survey of numerous polyfluorene and polycarbazole derivatives.<sup>79</sup> Lemasson et al. showed that **P10** exhibits 5 times lower dispersing efficiency when compared to **P7**. which was attributed to the single linear alkyl chain at the N atom of the carbazole unit, relative to two solubilizing chains within each fluorene unit. In order to increase the dispersing efficiency, a polymer functionalized with branched alkyl chains, poly (N-2hexyldecylcarbazole-2,7-diyl) (P11) was synthesized, and it was demonstrated that P11 exhibits relatively similar selectivity features to P10, but with twice the nanotube dispersing ability. It was noted that the nature of the alkyl chain also slightly influences the diameter selectivity of the parent polymer, where **P11** preferentially selects lower diameter (9,4), and (9,5) SWNTs while **P10** mainly disperses the higher diameter (11, 3), and (10,5) species. However, while this selectivity data gives some insight into design rules for specific polymer-nanotube interactions, one must note that the reported work comparing structures **P7**, **P10**, and **P11** was carried out with samples having drastically different molecular weight values ( $M_n$  ranging from 1.2 to 13 kDa) and relatively broad polydispersities (1.5 to 4.2). Although no discussion of molecular weight effects was provided by these authors, based on previous work (vide supra) one would expect molecular weight to have a significant influence over selectivity.<sup>117</sup> Interestingly, changing the carbazole substitution pattern within the polymer to the 3,6 positions (poly(N-decyl-3,6-carbazole), **P12**) resulted in a polymer that exhibited good interactions with SWNTs and effectively dispersed most semiconducting chiralities with little preference. This is in stark contrast to what was observed with the 3,6 substituted fluorene analog (**P9**), which produced unstable SWNT dispersions.<sup>79</sup>

More recently, a high molecular weight polycarbazole (P13,  $M_n = 61$  kDa) with large solubilizing side chains was prepared and investigated in terms of its interactions with SWNTs.<sup>121</sup> P13 exhibited excellent solubility in organic solvents, and was found to interact strongly with SWNTs. Although dramatic selectivity for specific SWNT chiralities was not observed, the large side-chains and high molecular weight seemed to dictate a preference for low-diameter SWNTs, with dominant fluorescence signals emanating from the (6,5) and (7,5) chiralities in both THF and toluene. Consistent with previous reports, this study indicated a preference for semiconducting SWNTs when using **P13**, as well as its copolymer with a fluorene monomer. Interestingly, nanotube fluorescence could be observed from films drop cast onto quartz slides, indicating that SWNTs remained debundled in the solid state as a result of the strong interaction with the polycarbazole.<sup>121</sup>

### **1.4.** Alternating Copolymers

In order to understand the correlation between a polymer's structure and its SWNT dispersing effectiveness, numerous experimental and molecular modeling studies of polymer-SWNT interactions have been conducted. Although a wide range of parameters can dictate the interaction between conjugated polymers and SWNTs, the polymer backbone structure and architecture has been found to be critically important. In particular, alternating copolymers have been extensively explored as nanotube dispersing agents, as they allow for facile variation of the polymer structure and enable identification of the most important parameters.

#### **1.4.1.** Alternating Copolymers Containing Phenylenevinylene

Much of the early work on polymer-SWNT interactions was focused on poly(phenylenevinylene) derivatives having the structures depicted in Figure 1.9. Among these, poly(m-phenylene-co-2,5-dioctoxy-p-phenylenevinylene) (PmPV) (**P14a**) was initially used with multi-walled carbon nanotubes (MWNTs), and was found to result in nanotube dispersions that did not precipitate over the course of 6 months.<sup>64, 122, 123</sup> The stability of these solutions was attributed to the helicity of PmPV, which was thought to wrap around the nanotubes, effectively suspending them on account of the solubilizing

octyloxy side chains.<sup>64</sup> PmPV-SWNT studies appeared shortly after, and also demonstrated that good nanotube dispersions could be prepared using this polymer.<sup>65, 124</sup> Dalton and co-workers specifically investigated the selectivity of the PmPV-SWNT interaction, and were the first to indicate that nanotubes were not only purified through the interaction with the conjugated polymer, but were also selectively dispersed. Careful analysis of Raman data indicated that PmPV interacts strongly and preferentially with certain nanotube diameters (1.35-1.55 nm), and differently with semiconducting vs. metallic SWNTs.<sup>65, 125, 126</sup> Computational work by Panhuis *et al.* supported these early efforts and showed that the predominant interaction between PmPV (and, presumably, most conjugated polymers) and the nanotube surface was through  $\pi$ -stacking of the polymer backbone rather than interactions of the side-chains.<sup>127</sup>

Star *et al.*<sup>128</sup> also studied the interactions of **P14a** with SWNTs, and used UV-Vis, NMR, and AFM measurements to gain a better understanding of the **P14a**-SWNT complex structure. Based on <sup>1</sup>H NMR signal broadening, it was confirmed that the conjugated backbone of PmPV is in close contact with the nanotube surface, while the octyloxy side-chains tend to dangle into solution. When mixed with SWNTs, **P14a** was found to form uniform coatings on the nanotube surface, and increasing the polymer concentration relative to SWNTs in chloroform resulted in lower diameter structures observed by AFM, indicating that the polymer is able to break up nanotube bundles into smaller diameter "ropes" as the amount of polymer present in solution was increased. Based on the photoconductivity response of single polymer-wrapped SWNT-bundles, as well as two-photon fluorescence measurements of single SWNT/ **P14a** bundles, it was

determined that the polymer is in close electrical contact with the nanotube surface, and that the polymer wraps around bundles of SWNTs rather than individual nanotubes.



**Figure 1.9.** Chemical structures of poly(phenylenevinylene) derivatives that have been used to disperse carbon nanotubes.

Investigation of the interactions between **P14a** and SWNTs produced by different methods, namely the arc discharge (which results in metallic-enriched SWNTs) and HiPco (which results in mostly semiconducting SWNTs) processes, was carried out by Keogh *et al.*<sup>129</sup> Through extensive UV-Vis-NIR and Raman spectroscopy studies, it was determined that the PmPV-SWNT interaction is more diameter selective than tube-type selective. Diameters in the range of 1.2 to 1.4 nm were selected regardless of SWNT origin, while signatures for both metallic and semiconducting SWNTs could be seen in both cases. Unfortunately, the polymer molecular weight used in this study was not

specified, and no investigation of selectivity as a function of molecular weight was performed. In a subsequent study, Keogh et al.<sup>130</sup> investigated the effect of temperature on the P14a-SWNT interaction by correlating differential scanning calorimetry (DSC) results with temperature-controlled spectroscopic (Raman, fluorescence, and IR) measurements. It was found that temperature-induced nucleation and crystallization of P14a on the nanotube surface was occurring. Based on their studies, the authors also postulated that ambient temperatures may not be best for inducing optimal polymer-SWNT interactions. The effect of temperature on the Raman spectra of P14a-wrapped SWNTs, especially on the radial breathing mode (RBM) signals, was also studied by Keogh et al.<sup>66</sup> This work showed that RBM signals for specific SWNT diameters could be damped by complexation with the polymer, and this damping is eliminated if the resulting complexes are heated above the polymer's glass transition temperature (Tg) (Figure 1.10). This highlights the pitfalls in identifying selective polymer-SWNT interactions by a single technique, such as Raman spectroscopy, as it is easy to misinterpret a lack of spectroscopic signals as signifying selectivity.



**Figure 1.10.** Tempeature-dependent Raman at excitation wavelength 514.5 nm for (a) HiPco and (b) HiPco/ **P14a** composite (0.1 wt % mass fraction of SWNT in 1 g/L of **P14a**). Reproduced with permission from ref. 66. Copyright American Chemical Society, 2006.

Selective wrapping of SWNTs using the **P14b** analog having hexyloxy instead of octyloxy side-chains was studied by Yi *et al.*<sup>131</sup> This study involved repeated sonication and centrifugation cycles in which the centrifuged sediment was collected and resuspended through subsequent sonication. Repeating this process on the sediment collected after each centrifugation step (at 7,000 g) resulted in a final supernatant that was depleted in many nanotube species while being enriched in the (11,6) and (11,7) species, corresponding to SWNT diameters of 1.19 and 1.25 nm. Sedimentation tests in which samples were allowed to settle over the course of a week, or 12 hours under UV-Vis light irradiation, indicated that the SWNT species that remained in solution were again the

(11,6) and (11,7) tubes. These results showed that **P14b** interacts more strongly with SWNTs that have diameters in the range of 1.1 to 1.3 nm. In addition, Raman data showed that, after 7 cycles of sonication and centrifugation, the collected sediment was depleted in semiconducting tubes. This indicates that **P14b** exhibits not only diameter dependent wrapping, but also prefers to wrap metallic SWNTs.<sup>131</sup> In a subsequent study, the same authors compared SWNT complexation efficiency by the *cis-* and *trans-* vinylene conformational isomers of **P14b** bearing hexyloxy side-chains ( $M_w = 24$  kDa).<sup>132</sup> Based on UV-Vis-NIR absorption and fluorescence data, it was determined that the predominantly *cis*-PmPV was twice as effective in dispersing SWNTs than the *trans*-PmPV.

Star *et al.* studied the hyperbranched analog of PmPV, **P15**, and its interactions with SWNTs.<sup>133</sup> It was found that introducing a certain degree of branching into the PmPV polymer makes it more rigid and less efficient when it comes to wrapping bundles of SWNTs, and a greater amount of **P15** was needed to obtain adequate nanotube dispersion. This polymer also resulted in the dispersion of a greater number of individual SWNTs, rather than bundles, which indicates that **P15** exhibits cavities that better match the diameter of single SWNTs.<sup>133</sup>. Star *et al.* also investigated the interaction between **P16** and SWNTs while introducing various alkoxy groups at the C-5 position on the meta-disubstituted phenylene ring.<sup>134</sup> Two different alkyl chain lengths (C2 and C6) were investigated with different end-group functionalities, and all structures were found to impart solubility to SWNT bundles in chloroform. Further elaboration of these end-groups to introduce supramolecular synthons, such as a dibenzo[24]-crown-8 (DB24C8)

macrocycle or a polyether chain incorporating a 1,5-dioxynaphthalene unit, allowed for the preparation of pseudorotaxanes on the polymer-dispersed SWNT bundles (Figure 1.11).<sup>134</sup> Unfortunately, addition of a dibenzylammonium  $PF_6$  salt to the DB24C8decorated SWNT bundles resulted in unstable dispersions that precipitated from solution within a minute, as a result of the surface charges introduced on the nanotube bundles upon threading of the macrocycles. In the case of the 1,5-dioxynaphthalene-decorated SWNTs, addition of a cyclobis(paraquat-p-phenylene) (CBPQT<sup>4+</sup>) macrocycle could not be carried out because of solvent incompatibility between the macrocycle and the SWNT bundles.<sup>134</sup> The only evidence for the interaction of the macrocycle with the nanotube surface came from tapping-mode AFM images, though these images cannot be considered conclusive.



**Figure 1.11.** Schematic representation of the formation of the pseudorotaxane-decorated SWNT bundles from 1,5-dioxynaphthalene-containing PAmPV and cyclobis(paraquat-*p*-phenylene) (CBPQT4+) macrocycles. Reproduced with permission from ref. 134. Copyright American Chemical Society, 2003.

The investigation of poly((2,6-pyridinylenevinylene)-co-((2,5-dioctyloxy-pphenylene)-vinylene)) (**P17**), which is analogous to PmPV but contains pyridine rings in the backbone, was also investigated for its ability to form interactions with SWNTs.<sup>135</sup> Of particular interest was the basicity of the pyridine rings in **P17**, which could be protonated upon addition of acid. It was found that polymer protonation became easier upon complexation with SWNT bundles in chloroform, indicating an increase in basicity resulting from adsorption onto the nanotube surface. This effect was later re-confirmed by Narizzano and Nicolini, who attempted to elucidate the mechanism of this polymer's interaction with SWNTs.<sup>136</sup> Investigation of polymer-wrapped SWNT conductivity was also performed, and it was found that dramatic optical gating of conductivity was possible, with much larger increases in conductivity for **P17**-SWNT devices than the analogous **P14-SWNT** devices. All of these results point to the potential use of such polymer-SWNT complexes for sensing applications.

Coleman *et al.* studied polymer-nanotube adsorption/desorption kinetics for poly[m-phenylenevinylene-co-(1,5-dioctyloxy-2,6-naphthylene-vinylene)] (**P18**) and poly[p-phenylenevinylene-co-(1,5-dioctyloxy-2,6-naphthylene-vinylene)] (**P19**) which had lengths averaging 6 and 12 repeat units, respectively.<sup>137</sup> Quenching of polymer fluorescence upon SWNT complexation allowed for spectroscopic (fluorescence-based) quantitation of the amount of free polymer present in a polymer-nanotube dispersion, which enabled measurement of binding energies for these polymers. Even though the two polymers were of different length, their binding energies were found to be identical, suggesting that conjugated polymers may not bind to the nanotube surface over their

entire length, but only partial segments of each polymer are bound at any one time. The spectroscopic measurements showed that a plot of free polymer present in solution vs. polymer concentration (at constant SWNT concentration) is non-linear, indicating complex adsorption/desorption kinetics, and that nanotube bundles break up into individual nanotubes as their concentration is lowered.

The photophysical properties of poly[2-methoxy-5-(2'-ethylhexyloxy)-pphenylene vinylene (MEH-PPV) (P20) and PmPV (P14) complexes with SWNTs have been described in a series of reports.<sup>138-143</sup> Most notably, Yang and co-workers showed that dramatic photoluminescence quenching of both P20 and P14 occurred when these polymers adsorbed to the surface of SWNTs.<sup>138</sup> These authors alluded to the fact that quenching was likely due to a non-radiative recombination (energy transfer) process, rather than a charge transfer from the excited state of the polymer. Direct evidence for the energy transfer process came later, in a report by Nish *et al.*,<sup>142</sup> who used PLE mapping to demonstrate enhanced SWNT emission in the NIR (1280 nm) upon excitation of P20 (and PFO, **P7**) at 500 nm. As observed by Yang and co-workers, polymer fluorescence was efficiently quenched as the excitation energy was transferred from the excited-state polymer to the nanotubes. Collison *et al.*<sup>143</sup> subsequently corroborated these results with the same polymer structure (P20), but using SWNTs produced by the CoMoCat process, as opposed to the HiPco SWNTs used by Nish et al.

Organization of SWNTs in the solid phase has also been accomplished using PPV type polymers. Kimura *et al.* showed that short, liquid crystalline PPV oligomers are able to interact with and effectively disperse SWNTs in chloroform.<sup>144</sup> The resulting PPV-

SWNT dispersions were found to precipitate rapidly upon addition of excess PPV oligomer, and the precipitate exhibited thermotropic liquid crystalline properties. Evidence for alignment and self-organization of SWNTs into micron-sized fibrous assemblies was observed through SEM. In addition, magnetic orientation of MEH-PPV complexes with SWNTs in an 8 T magnetic field was demonstrated by Yonemura *et al.*, who used atomic force microscopy to visualize nanotube alignment.<sup>145</sup>

Imahori and co-workers prepared photo-responsive polymers incorporating alternating structures of azobenzene (AZO) and phenylene (P21) or vinylene (P22) units, and applied them as dispersants for SWNTs in organic solvents.<sup>81</sup> This group found that the SWNT dispersion efficiency using P21 was better than that with P22, and also that it depended on the *cis/trans* ratio of the AZO units in the starting polymer. Photochemical isomerization of the polymer to a cis content of 9% produced higher SWNT concentrations than the all-*trans* structure, but further increasing the *cis* content (to 20, 28, and 39%) resulted in a dramatic decrease in the amount of SWNTs dispersed. The nanotube dispersions in these samples, although concentrated, showed broad absorption signals and little fluorescence, indicating that the dispersed SWNTs were bundled, and there was little selectivity in the polymer-SWNT interaction. Their experimental results showed that photochemical *trans-cis* isomerization was not possible when the polymer was adsorbed on the nanotube surface, precluding a photochemically-induced release of SWNTs. However, it was demonstrated that a significant portion of the polymer could be removed by first thermally inducing the cis-to-trans isomerization (using P21 with 9% cis content), followed by washing with THF. Using 4-point-probe measurements, it was

shown that the resistivity of SWNTs deposited on silicon decreased 3-fold upon thermal isomerization and washing, as a result of removal of the polymer coating on the SWNT surface.

#### 1.4.2. Poly(phenyleneethynylene) (PPE) Derivatives

Due to the relatively versatile synthesis of PPE, various derivatives differing in backbone or side chain structure have been prepared (Figure 1.12) and investigated for their supramolecular complexation of SWNTs.<sup>69, 146, 147</sup> Noncovalent functionalization of SWNTs with soluble PPE derivatives was first reported by Chen and co-workers.<sup>69</sup> It was demonstrated that the rigidity of the backbone of P23 prevents it from wrapping around the SWNT circumference. Instead, the  $\pi$ -stacking interaction mainly occurs such that the polymer extends along the nanotube's long axis. Evidence for a non-wrapping interaction came from absorption spectroscopy, which showed that the polymer absorption spectrum did not change significantly upon nanotube complexation. This suggests that the conjugation length remained constant, and thus the extended rigid-rod conformation of **P23** was maintained on the nanotube surface. Solubility studies supported the formation of stable, irreversibly bonded complexes between P23 and SWNTs in CHCl<sub>3</sub>, with a maximum concentration of HiPco SWNTs reaching 2.2 mg/mL (arc discharge and laser ablation tubes were dispersed with lower concentrations). As noted for other polymers, the fluorescence of **P23** was found to be efficiently quenched when it adsorbs to the nanotube surface, a result of energy transfer to the SWNT. Subsequently, it was also demonstrated that variation of PPE side-chains from a straight aliphatic to a branched aliphatic and to a ferrocenyl-group-terminated aliphatic resulted in differences in how the PPE-SWNT complexes interacted with a host polymer, parmax.<sup>146</sup> At 2% loading, there were dramatic differences in the tensile strength of the PPE-SWNT/parmax composite, with the ferrocene-containing material showing greatest strength. In addition, this same loading level increased the electrical conductivity of the host polymer by greater than 12 orders of magnitude.<sup>146</sup> It was concluded that controlling the interface between noncovalently functionalized SWNTs and a host material is crucial to achieving significant enhancement in mechanical and electrical properties of SWNT-polymer composites.



**Figure 1.12.** Chemical structures of poly(aryleneethynylene) derivatives that have been used to disperse carbon nanotubes.

Rice *et al.* synthesized 4 linear PPE derivatives (**P23**, **P24**, **P25**, **P26**), and investigated their supramolecular interaction with HiPco SWNTs.<sup>71</sup> It was found that **P25** and **P26** resulted in very stable dark-colored dispersions when mixed with SWNTs in chloroform after a short period of bath sonication (less than 5 min), while **P23** and **P24** formed less stable dispersions. The supramolecular interaction between SWNTs and

polymers **P25** and **P26** was further investigated by UV-Vis absorption, fluorescence, and Raman spectroscopy measurements and atomic force microscopy (AFM) analysis. Characteristic absorption features of SWNTs were observed in the chloroform solutions of polymer-SWNT complexes, while the fluorescence measurement revealed considerable quenching of polymer emission after complex formation with SWNTs. Raman spectroscopy studies showed that the polymers have no particular discrimination between tube types, semiconducting vs. metallic. It was concluded that the strength of  $\pi$ - $\pi$  interactions between the SWNT surface and the polymer is a key factor for SWNT dispersion and stabilization, and the long solublizing alkoxy chains are also believed to be essential as they can provide repulsive forces to prevent bundling of individual tubes.

Very recently, Pang and coworkers demonstrated that a narrow diameter range (d = 1.18-1.24 nm) of SWNTs, which includes (11,6), (12,6), and (11,7) chiralities, can be efficiently enriched by sequential treatment of the HiPco SWNT with nitric acid at reflux, followed by dispersion with a copolymer of phenyleneethynylene (PE) and phenylenevynylene (PV) (**P27**) in THF.<sup>147</sup> Raman, fluorescence spectroscopy and microscopic characterization results confirmed that the nitric acid can selectively remove the small diameter SWNTs. The subsequent treatment with copolymer **P27** led to a SWNT dispersion composed only of the (11,7) and (12,6) tubes, having diameters of 1.23 and 1.24 nm, respectively.

A novel poly(phenyl acetylene) polymer, **P28**, incorporating substituted tetrathiafulvalene vinylogues (TTFV) was prepared by Zhao and co-workers.<sup>148</sup> Although this polymer was relatively short (6 repeat units), molecular mechanics calculations

indicated that it adopts a helical conformation in solution with a cavity of 1-2 nm in diameter. Thus, it forms an ideal conformation for wrapping SWNTs, and was shown to exhibit strong interactions with both CoMoCat and HiPco nanotubes in toluene. It was found that these interactions are selective for SWNTs having diameters in the range of 0.8 to 1.2 nm, as predicted from the calculated conformation. Due to the conformational switching behaviour of TTFV,<sup>149</sup> it was possible to dramatically alter the polymer structure in solution through oxidation or protonation of the TTFV units in the polymer backbone. It was found that upon either oxidation with iodine or protonation with trifluoroacetic acid (TFA), the polymer rapidly underwent a conformational switch, and dissociated from the nanotube surface, resulting in nanotube phase separation. By carrying out several rounds of dispersion and release of the nanotubes, an enrichment of several SWNT chiralities was achieved.

# **1.4.3.** Alternating Copolymers Comprising Fluorene

Co-existence of both metallic and semi-conducting single-walled carbon nanotubes, m-SWNTs and sc-SWNTs, respectively, in as prepared SWNT samples significantly limits their applications in optical and electronic devices, since most of these applications ideally require pure samples of either m-SWNTs or sc-SWNTs. Therefore, selective dispersion and sorting of SWNTs with defined diameter or chiral angle is a major focus of current research. Since the initial report demonstrating that **P7** highly selective toward a few semiconducting chiralities, a great variety of structural modification to this polymer's backbone and side chains has been investigated, with the goal of finding the most effective polymer structures.<sup>73-76, 78-80, 82, 150, 151</sup> Figure 1.13 depicts the alternating copolymer structures comprising fluorene and other aromatic units that have been investigated so far.



Figure 1.13. Chemical structures of alternating copolymers of fluorene various comonomers.

In addition to **P7**, several commercially available polymers, poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-phenylene)] (**P29**), poly[(9,9-dioctylfluorenyl-2,7-

diyl)-co-(1,4-benzo-2,1',3-thiadiazole)] (P30), and poly[(9,9-dioctylfluorenyl-2,7-diyl)co-(N,N'-diphenyl)-N,N'-di(p-butyl-oxy-phenyl)-1,4-diaminobenzene] (P31) were also studied by Nicholas and coworkers.<sup>74, 78</sup> It was found that the dispersion efficiency and the selectivity towards certain SWNT species is strongly influenced by both the polymer structure and the solvent used. In THF solutions, polymers P29 and P30 show a preference for tube diameters in the range of 0.9-1.05 nm, which is significantly narrower than the original HiPco starting material. In toluene, P30 exhibits strong selectivity for the (10,5) species, while **P29** shows no particular preference and disperses all nanotubes well. P31 reveals strong chiral selectivity in both toluene and THF solutions. Along similar lines, **P7**, **P30**, and poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(9,10-anthracene)] (P32) were also studied by Chen et al., and it was observed that P7 and P32 have similar selectivity in wrapping high chiral angle tubes (>  $21.8^{\circ}$ ), while **P32** has a higher preference toward dispersing larger diameter tubes (0.97-1.17 nm).<sup>75</sup> In general, both groups demonstrated that selective chirality enrichment mainly depends on the structure of the polymeric repeat unit, the length of the side-chains, the ratio of polymer to nanotubes, as well as the solvent. Energy transfer from fluorene based polymers, including **P7** and poly-[(9,9-dioctylfluorene-2,7-diyl)-co-(bithiophene)] (**P33**) to SWNTs was extensively investigated using photoluminescence excitation and fluorescence lifetime studies by Chen et al.<sup>152</sup> It was again found that, in discrete polymer-SWNT complexes, polymer fluorescence is quenched and energy transfer from the polymer to the SWNT occurs. Interestingly, in the presence of excess free polymer, the authors noted that the polymer concentration impacts the optimal excitation wavelength that leads to energy transfer. For **P7**, addition of excess polymer shifted the optimal excitation wavelength from 388 to 480 nm, and a similar red-shift was observed with **P33**. By adding free polymer, it was determined that some of the excess polymer chains associate with the pre-formed polymer-SWNT complexes, extending their planarity and conjugation length. This additional polymer is then responsible for efficient energy transfer to the SWNT.<sup>152</sup> These authors also peformed a competitive binding experiment in which a polymer-SWNT complex with one polymer was exposed to the other polymer in solution. It was definitively found that the bithiophene-containing polymer, **P33**, effectively displaced the polyfluorene, **P7**, from the SWNT surface, indicating that thiophene rings form stronger nanotube interactions.<sup>152</sup> It should be noted that both polymers used in this study (available from American Dye Source), were of similar molecular weight and polydispersity.

A copolymer of fluorene and 2,7-(9,9-dioctylfluorene)-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole) (**P34**) was synthesized, and used for selective SWNT dispersion by Nakashima and co-workers.<sup>151</sup> Fluorescence maps were used to determine the chirality indices of SWNTs that were present in toluene dispersions, and it was found that **P34** selectively dispersed 5 major species, including the (6,5), (7,5), (7,6), (8,6) and (8,7) SWNTs. Molecular mechanics simulations were used to corroborate these results, and showed highest binding energies between **P34** and the nanotube chiralities observed experimentally.<sup>151</sup> Nakashima also reported that the co-polymer of 9,9-di-octylfluorenyl-2,7-diyl and bipyridine (Bpy) (PFO-BPy, **P35**) has a significantly different nanotube selectivity than the corresponding polyfluorene homopolymer (**P7**).<sup>80</sup> It was found that interaction of **P35** with CoMoCat SWNTs in p-xylene produced an SWNT dispersion that was 97% enriched in the (6,5) chirality, with no sign of metallic SWNTs in the RBM region of the Raman spectrum (excited at 633 nm). Other non-polar solvents such as toluene and m- or o-xylene also resulted in predominant dispersion of (6,5) tubes, but with slightly lower selectivity (approximately 90%). Interestingly, the same dispersion in THF led to poor selectivity, with both (6,5) and (7,5) chiralities being dispersed to similar extents. Comparison of the interaction between the same SWNTs and the PFO homopolymer (**P7**) led to predominant dispersion of the (7,5) chirality, demonstrating that the BPy units within the polymer have a significant effect on selectivity.<sup>80</sup> These results clearly show that it is possible to design and synthesize polymer structures that are selective for single chirality SWNTs.

Mayor, Kappes, and co-workers have attempted to elucidate the design rules for selective interactions between fluorene- and carbazole-based conjugated copolymers by systematically synthesizing a broad library of structures and investigating their ability to disperse SWNTs.<sup>79</sup> In these studies, the authors used DGU after dispersing nanotubes in toluene as a way of preventing high-density polymer-SWNT complexes from being sedimented during regular centrifugation. This enabled a more complete sampling of dispersed polymer-SWNT complexes, as the authors collected all of the material that was present in the centrifuge tube after DGU. Although navigating through the effects of subtle structural differences between various polydisperse polymers is extremely challenging, several general trends can be gleaned from the reported results. One of the most clear findings of these studies was that incorporation of 3,6-linked fluorene units

within a polyfluorene backbone drastically diminished the interaction stability with the nanotube surface, even when the polymer molecular weight was relatively similar.<sup>79</sup> As previously mentioned, diameter selectivity was also found to be correlated with alkyl chain length on the polymer, where larger alkyl chains induce a preference for smaller diameters.<sup>78</sup> Additionally, visualization of dispersed SWNTs by plotting nanotube chiral angle ( $\theta$ ) against diameter ( $\emptyset$ ) demonstrated that polyfluorenes prefer to select high chiral angles ( $\theta > 20^{\circ}$ ), polycarbazoles prefer lower chiral angles ( $10^{\circ} < \theta < 20^{\circ}$ ). The alternating copolymer of fluorene and carbazole (P58 in Figure 1.14) was found to combine the selectivity of both homopolymers, leading to effective dispersion of a broad range of different SWNT chiralities. This analysis was also used to determine the effect of polycyclic aromatic co-monomers that incorporated naphthalene, anthracene, and anthraquinone units (**P39-P44**).<sup>79,150</sup> Not surprisingly, the larger  $\pi$ -surface of naphthalene resulted in highest nanotube solubility, and tended to select larger diameter (d > 0.95 nm) tubes. Interestingly, changing the connectivity of the anthracene unit from 1.5 to 2,6 and 9,10 caused a large decrease in polymer dispersing ability. An additional general observation from all of these studies is that polymer solubility can be directly linked to the effectiveness of polymer-SWNT complex dispersion, where polymers that are poorly soluble on their own are not generally capable of producing good nanotube dispersions. It should again be noted that rigorous comparison of the polymer-nanotube interactions for the samples in this polymer library is difficult, as molecular weights of the different polymers were not kept constant, and molecular weight can significantly influence the polymer-SWNT interaction stability and selectivity.<sup>117</sup>
Kappes and co-workers also investigated copper-catalyzed alkyne azide cycloaddition as a polymerization protocol in the preparation of "clicked" conjugated polyfluorene-based polymers bearing aromatic 1,2,3-triazole rings as "co-monomer" units (Figure 1.13, P45-P53).<sup>153</sup> In this work, combinations of monomers were used to introduce different alkyl chain lengths and inter-fluorene linkers within the conjugated polymers. Copolymers comprised of 9,9-dihexyl and 9,9-didodecyl functionalized fluorenes and the triazole rings were found to exhibit similar selectivity and nanotube dispersion ability as regular polyfluorenes (i.e., **P7**). Interestingly, removing conjugation fluorene units by incorporating 1,4-bis(methyloxy)benzene or 1,5between bis(methyloxy)naphthalene (P52 and P53) units resulted in stable dispersions but no selectivity for specific SWNT chiralities (relative to aqueous dispersions using sodium cholate). Incorporation of meta- or para-linked phenylene units (P49-P51) resulted in a lack of SWNT dispersion. In a related study, Mayor, Kappes, and co-workers incorporated an ortho-nitrobenzylether as a co-monomer with fluorene (P54), producing a polymer that could interact with SWNTs, but was also photo-cleavable under irradiation with light.<sup>154</sup> The non-conjugated nitrobenzyl ether linker decreased the overall selectivity of the polymer for specific SWNTs, but did promote SWNT dispersion in toluene. Upon irradiation with a xenon lamp for 2 minutes, SWNT bundles were observed to precipitate as the polymer rapidly decomposed.

Along the lines of degradable polymers similar to Mayor's o-nitrophenolcontaining structures (**P54**), Chan-Park and co-workers prepared a series of novel alternating copolymers of fluorene and disilane, specifically poly[(9,9-dioctylfluorenyl2,7-diyl)-alt-co-disilane] (**P55-P57**).<sup>155</sup> These polymers were found to disperse HiPco SWNTs in toluene, and exhibited some selectivity toward semiconducting high chiral angle species, including the (8,7), (9,7) and (9,8) which have chiral angles ranging from 24.5° to 28.1° and diameters ranging from 1.0 to 1.2 nm, as major components.<sup>155</sup> Interestingly, the least sterically hindered **P55** exhibited the greatest degree of selectivity, which diminished with increasing steric hindrance (comparison of this series of polymers is valid as they are all of similar molecular weight, ca. 5,000 Da, with polydispersities close to 1.4). After isolating the samples enriched in these semiconducting SWNTs using P55, the disilane bonds in the polymer backbone were easily degraded upon stirring in dilute hydrofluoric acid (HF) solution for 10 hours, producing a sample of "clean" SWNTs that were no longer decorated with polymer. These "clean", semiconductingenriched SWNTs were then used as the active material in solution processed thin-film field-effect transistors (FETs). Comparison of "clean" vs. polymer-wrapped SWNTs within these devices showed that polymer wrapping reduced the on-current and the on/off ratio of the devices. In addition, a comparison between P55-selected semiconductingenriched "clean" SWNTs and pristine SWNTs prior to any selection showed a dramatic improvement in on/off ratios (from values in the range of 1-10 to values in the range of 1.000 to 100.000). These results indicate that the combination of polymer selection of semiconducting SWNTs and polymer removal is extremely important for improvement of mobility and on/off ratios within functional devices.<sup>155</sup>

### **1.4.4.** Alternating Copolymers Comprising Carbazole

As part of the broad investigation of the interactions between different conjugated copolymers and SWNTs, several alternating copolymers consisting of n-alkylcarbazole-2,7-diyl and selected aromatic units have been synthesized (Figure 1.14).<sup>79, 150, 151, 156</sup>



Figure 1.14. Chemical structures of alternating copolymers of carbazole and other aromatic units

As mentioned in the previous section, the alternating copolymer of carbazole and fluorene (**P58**) was found to combine the selectivity properties of both homopolymers (**P8** and **P10**), leading to effective dispersion of a broad range of different SWNT chiralities.<sup>79</sup> Polymers comprising 3,6-linked carbazole units (**P59** and **P60**) form unstable SWNT dispersions, similarly to their 3,6-fluorene homologues **P61** and **P36**. Ozawa *et al.* demonstrated that the poly(N-9'-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'benzothiadiazole) (**P62**) selectively disperses several semiconducting SWNT species, including the (6,5), (7,6), (8,6), (8,7), (6,5), (9,4), and (9,5) chiralities. Slightly different selectivity was observed with polymer **P62** when compared to the

structurally analogous polymer P34, which indicates that the difference in the fluorene and carbazole units changes the chiral selectivity of the resulting copolymers.<sup>151</sup> The analogous poly(*N*-9'-heptadecanyl-2,7-carbazole-*alt*-4,7-benzo-2,1,3-thiadiazole) (**P63**) was found to exhibit very low dispersing properties toward SWNTs.<sup>79</sup> The solubility of the polymer as well as its SWNT dispersing ability in toluene was improved when a branched alkyl chain was introduced at the N atom of the carbazole moiety (P64), though the molecular weight of this latter polymer was also much higher ( $M_w = 50$  kDa for P64 vs 2.5 kDa for P63).<sup>79</sup> It was demonstrated that P64 efficiently disperses most of the SWNT species, regardless of the diameter and chiral angle, with the (7,6) and (8,6) nanotubes dominating the distribution. Copolymers of carbazole with more rigid and flat  $\pi$ -systems such as naphthalene (P65), anthracene (P66) and anthraquinone (P67) have also been synthesized, and their dispersing ability towards SWNTs was tested by Mayor and co-workers.<sup>79, 150</sup> Surprisingly, it was found that all three of these polymers were not able to efficiently disperse SWNTs, and P66 was found to be the worst among these three, unlike the analogous fluorene-based series (P39, P42, and P44) in which the anthracenecontaining structure was the best. The difference with the carbazole analogs in this series likely results from the poor solubility of the polymers themselves, as the single decyl chain does not provide enough solubility to the structure. Conversely, the highly soluble, high molecular weight poly(carbazole-*alt*-fluorene) derivative bearing a large solubilizing group (P68) was recently reported and shown to interact strongly with SWNTs, forming concentrated and stable dispersions in various solvents (THF, chroloform, toluene). PLE

maps indicated that this polymer is not very selective for specific SWNT chiralities, though the (6,5) and (7,5) chiralities were dominant when toluene was used as the solvent.

A derivative of the alternating poly(fluorene-*alt*-carbazole) polymer (**P69**) was also prepared by Ozawa *et al.*,<sup>157</sup> who showed that this polymer is able to selectively disperse semiconducting (7,6) and (8,7) SWNTs in toluene (note that Mayor and co-workers reported dispersing (7,6) and (8,6) chiralities with a similar polymer).<sup>77</sup> Each carbazole unit in **P69** was derivatized with a butanethiol chain, which was used to complex Au and Ag nanoparticles, resulting in metal nanoparticle/SWNT hybrid composites.

### **1.5. Random Copolymers and Block Copolymers**

Although homopolymers and alternating copolymers of selected aromatic structures such as fluorene, thiophene and carbazoles have shown great promise to selectively disperse SWNTs, further improvement in narrowing the selectivity, yield, and subsequent scaling up processes are still required. A number of random copolymers comprising various aromatic structures have been synthesized (Figure 1.15), and their ability to selectively disperse certain types of SWNT species were also investigated.

Imahori and co-workers reported the synthesis of poly[(p-phenylene-1,2vinylene)-co-(p-phenylene-1,1-vinylidene)] (**P70**), which resembles a PPV derivative but contains a random distribution of 1,1-vinylidene linkages in place of the 1,2-vinylenes.<sup>158</sup> It was proposed that these structural defects increased the polymer helicity, allowing **P70** to wrap SWNTs more efficiently than the corresponding non-defective PPV structure (analogous PPV structures without 1,1-vinylidene linkages imparted much lower dispersibility to SWNTs). Based on PLE mapping results, **P70** selectively disperses several SWNT chiralities in THF, including (9,4), (8,6), (9,5), (8,7) (10,5), and (9,7). Out of these, the (10,5) species exhibited highest emission intensity, suggesting that this chirality is more efficiently exfoliated from bundles than other SWNT chiralities. Furthermore, this report was the first to show enhanced nanotube emission as a result of energy transfer upon excitation of the polymer-SWNT complexes at 400-500 nm, where the SWNTs do not absorb.<sup>158</sup>



**Figure 1.15.** The structures of the random, and block copolymers that have been used to disperse carbon nanotubes

Nakashima and co-workers synthesized 11 conjugated copolymers (**P71**) composed of different ratios of 9,9-bis(n-decyl)fluorene and the bulky, chiral 9,9-bis[(S)-(+)-2-methylbutyl]fluorene in random sequence, and investigated their selectivity for SWNT dispersion in toluene.<sup>159</sup> It was found that the composition ratio of the two monomers significantly affected the nanotube chiralities that were dispersed. Based on

Vis-NIR absorption data, the semiconducting (7,5), (7,6), (8,6), (11,3), (10,3), (8,7), and (9,7) chiralities were dispersed by the different polymers used (Figure 1.16), with practically no absorption bands associated with metallic tubes being observed.



**Figure 1.16.** Vis–NIR absorption spectra of SWNTs dispersed by PXX having different composition ratios of the monomers 9,9-bis(n-decyl)fluorene (x) and 9,9-bis[(S)-(+)-2-methylbutyl]fluorene (y). The copolymerization ratios, x:y, corresponding to each absorption spectrum are shown at the right. Reproduced with permission from ref. 159. Copyright American Chemical Society, 2011.

PLE maps showed that variation of the ratio between the two monomers led to significant differences in the chiralities contributing to emission from the sample. For instance, low incorporation of the chiral monomer resulted in predominant emission from the (7,6), (8,6) and (8,7) tubes, while high incorporation levels of the chiral monomer led to emission from the (9,7), (11,3), and (10,3) tubes. The authors suggest that these results

indicate that the chiral monomer seems to introduce selectivity according to nanotube chiral angle, as the (7,6) and (8,7) SWNTs have high chiral angles ( $\theta > 24^\circ$ ), while the (11,3) and (10,3) SWNTs have low chiral angles ( $11^\circ < \theta < 13^\circ$ ). However, the predominant selectivity of the polymer with the highest chiral monomer incorporation for the (9,7) SWNT (chiral angle ~25°) goes contrary to this conclusion. It can nevertheless be stated that the chiral monomer does not introduce diameter selectivity.<sup>159</sup>

In a follow-up study using chiral binaphthol units within the conjugated polymer backbone, Nakashima and co-workers reported the first example of one-pot separation of right- and left-handed s-SWNTs.<sup>160</sup> Using Yamamoto coupling reactions to incorporate a polymerizable (R)- or (S)-2,2'-dimethoxy-1,1'-binaphthyl-6,6'-diyl (denoted RBN and SBN, respectively), 12 copolymers having different incorporation levels of RBN or SBN were prepared (P72 and P73, respectively). Incorporation of the binaphthol units had a dramatic effect on the polymer conformation in solution, as observed by a blue-shift in the absorption spectrum with increasing amounts of RBN or SBN, indicating a less conjugated structure. Interestingly, SWNT dispersion studies indicated that the binaphthol units did not significantly affect the polymer's nanotube dispersing ability (relative to polyfluorene), but SWNT selectivity was affected by increasing the levels of RBN or SBN. Furthermore, increasing the binaphthol incorporation ratio up to approximately 40 mol% resulted in an increase in single-enantiomer SWNT dispersion, as evidenced by circular dichroism measurements. Specifically, the (6,5) and (7,5) SWNT chiralities were separated into their respective left- and right-handed enantiomers using the RBN- and SBN-containing polymers, respectively.<sup>160</sup> This study, in light of the previous work with chiral side-chains,<sup>159</sup> clearly shows that chirality in the conjugated polymer backbone has a much more dramatic effect on selectivity of nanotube enantiomers than chirality in the side chains.

Nakashima and co-workers also prepared a random copolymer composed of 9,9bis(octyl)fluorene and a Zn(II)-porphyrin monomer in a 10:1 ratio (**P74**).<sup>156</sup> This polymer was soluble in a number of organic solvents (THF, chloroform, dichloromethane, and toluene), and produced stable SWNT dispersions in all these solvents, similar to a standard polyfluorene complex. As has been observed with other polymers, use of toluene as the solvent resulted in selective dispersion of semiconducting SWNTs, whereas with the other solvents, metallic species were also observed. PLE mapping revealed that **P74** selectively disperses (8,6), (8,7), (9,7), (7,6), and (7,5) SWNTs, with (8,6), and (8,7) being the dominant species. The resulting **P74**-SWNT complexes were exposed to pyridine-decorated gold nanoparticles (py-AuNPs), allowing the pyridine rings to coordinate to the Zn-porphyrin units bound to the dispersed SWNTs. This resulted in the clear formation of AuNP-decorated SWNTs, which were characterized by AFM, TEM, SEM, and XPS.

There have been several studies investigating the supramolecular interactions of CNTs with PT containing block copolymers. Poly(3-hexylthiophene)-b-polystyrene (P3HT-b-PS) (**P75**) was prepared by Zou *et al.*, and its supramolecular complexation of both SWNT and MWNTs was investigated.<sup>161, 162</sup> The average molecular weight of the block copolymer was determined by GPC to be 23 kDa, and the mass ratio of the P3HT block relative to the PS block was measured by NMR to be 34.1% for P3HT and 65.9%

for PS. It was found that nanotubes were well dispersed in several organic solvents including chloroform, THF and toluene, and the resulting solutions were found to be stable without significant precipitation, even after a year of standing at room temperature. Using <sup>1</sup>H-NMR, it was shown that, as expected, the conjugated P3HT block interacts with the nanotube surface, leaving the PS block to extend into solution. The block copolymer was also found to produce indefinitely stable nanotube dispersions upon addition to a polystyrene solution (10 wt % in chloroform), while P3HT-dispersed SWNTs precipitated within a day. Thin films (30 μm thickness) of the nanotube-loaded polystyrene were cast from these solutions and were shown to exhibit a percolation threshold that is four times lower than that obtained when the SWNTs were dispersed with P3HT homopolymer, indicating that the dispersion in the film was more homogeneous. Subsequently, similar results were also found for both SWNT and MWNT dispersions with block copolymers of P3HT and poly(methyl methacrylate) (P3HT-b-PMMA), poly(acrylic acid) (P3HT-b-PAA), and poly(poly(ethylene glycol) methyl ether acrylate) (P3HT-b-PPEGA).<sup>162</sup>

# **1.6. Conjugated Polyelectrolytes**

Conjugated polyelectrolytes (CPEs) are an important class of conjugated polymers bearing ionic side chains, including sulfonate (SO<sub>3</sub><sup>-</sup>), carboxylate (CO<sub>2</sub><sup>-</sup>), phosphonate (PO<sub>4</sub><sup>3-</sup>) and ammonium (NR<sup>3+</sup>), which impart water solubility to the polymer. Supramolecular functionalization of CNTs with CPEs leads to the formation of stable complexes that remain dispersible in aqueous solution, which makes them useful for biomedical, as well as chemo- and biosensor applications. Figure 1.17 depicts the chemical structure of several CPEs that have been used for noncovalent functionalization of SWNTs.



**Figure 1.17.** The structures of representative conjugated polyelectrolytes that have been used to disperse carbon nanotubes

Adronov and co-workers have synthesized two anionic CPEs, poly[2,5-bis(3-sulfonatopropoxy)-1,4-phenylene-alt-1,4-phenylene) sodium salt (**P76**) and poly[2,5-bis(3-sulfonatopropoxy)-1,4-ethynylphenylene-alt-1,4-ethynylphenylene] sodium salt (**P77**), and investigated their interaction with SWNTs.<sup>72</sup> UV-Vis-NIR absorption, fluorescence, and Raman analysis supported the formation of strong supramolecular polymer-nanotube assemblies. Cryogenic high-resolution transmission electron microscopy (cryo-TEM) in vitreous ice was used to directly visualize exfoliated nanotubes that were coated with polymer (Figure 1.18).



**Figure 1.18.** Cryo-TEM images of P55–SWNT (A) before sublimation of ice, (B) during sublimation (arrows indicate location of nanotubes still tethered to sheets of ice), and (C,D) after complete sublimation. (E–G) Ultra-high-resolution TEM images of the sample after complete sublimation of ice showing individual SWNTs, small bundles, and the surface functionalization with polymers (arrows). Reproduced with permission from ref. 72. Copyright American Chemical Society, 2008.

The advantage of cryo-TEM in this analysis is that it provides a picture of nanotube morphology in solution (albeit frozen) rather than within a dried sample on a TEM grid. The CPE-decorated SWNTs were then used to produce fine conductive nanotube patterns on glass and silicon substrates via electrostatic interactions with a preformed pattern of positively charged poly-4-vinyl-*N*-methylpyridine (PVMP), which was prepared by photo-cross-linking thin films of the polymer through a photomask. This simple, inexpensive method for nanotube patterning on substrates produced features with widths as small as 10  $\mu$ m that exhibited electrical conductivity as a result of the interpenetrated network of nanotubes, confirming the continuity of SWNTs within the patterned features.

Kimura and co-workers have demonstrated that water-soluble poly(p-phenylene ethynylene) (PPE) derivatives (P78 and P79) are capable of forming strong supramolecular complexes with SWNTs in aqueous media, which allowed the formation of transparent conductive films via layer-by-layer assembly (LBL) using the anionic **P78**/SWNTs and cationic **P79** on various substrates.<sup>163</sup> It was shown that the nanotubes tend to align along the dipping and withdrawing direction, and electrical conductivity within the resulting LBL films (ten layers) is enhanced along the alignment direction. Therien and co-workers also reported that it is possible to prepare exfoliated SWNTs using the polymer **P78**.<sup>164</sup> AFM and TEM characterization confirmed that the interaction of **P78** with SWNTs leads to the dispersion of individual nanotubes that are coated with polymer in water. A high-resolution TEM image demonstrated wrapping of the polymer around a single nanotube with a helical pitch that was consistent with molecular dynamics calculations. It was also shown that CPEs can be used to disperse SWNTs in organic solvents, as long as a phase transfer catalyst (PTC) was also introduced. To demonstrate this concept, Therien and co-workers dispersed SWNTs in multiple organic solvents using poly[2,6-(1,5-bis(3-propoxy-sulfonic acid sodium salt))naphthylene]ethynylene (P80) in combination with 18-crown-6.<sup>165, 166</sup> It was found that the SWNTs were exfoliated and individualized in organic solvents, and the resulting solutions were stable for at least several months. AFM and TEM data of the organic solvent dispersed P80/SWNT composites confirm that the polymer-SWNT interaction results in a selfassembled superstructure in which a polymer monolayer helically wraps the nanotube surface with periodic and constant morphology (helix pitch length =  $10 \pm 2$  nm).<sup>165</sup> It was further demonstrated that the organic solvent solubility of P80-SWNTs enables facile fabrication of electrically active polymer-CNT composites that can be used as novel hybrid supercapacitor materials. A poly(3,4-propylenedioxythiophene) (PProDOT)containing P59-SWNT hybrid composite (PProDOT/P80/SWNT) was prepared, and its capacitive performance was compared to benchmark PProDOT-based Type I supercapacitor devices. It was found that the hybrid PProDOT/P80/SWNT materials enhanced supercapacitor charge storage and capacitance by nearly a factor of 2 when compared corresponding supercapacitors to fabricated using only pristine PProDOT.<sup>166</sup>

A polyfluorene-based CPE was prepared by Gao *et al.* by introducing quaternary ammonium ions in the side-chains of the polymer. The selectivity of SWNT complexation by the amine-functionalized (poly(9,9-di-(N,Ndimethylaminopropylfluorenyl-2,7-diyl) (PFDMA)) and its ammonium salt [(N,N,Ntrimethylammonium)-propyl]-2,7-fluorene dibromide) (**P81**) was investigated and compared to the previously studied neutral polyfluorene **P7**.<sup>167</sup> It was found that SWNT dispersions with **P81** in D<sub>2</sub>O contain similar species to the PFDMA-based dispersion in toluene, but both are different than dispersions obtained with **P7**. Poly(9,9bis(diethylaminopropyl)-2,7-fluorene-co-1,4-phenylene) (**P82**) was synthesized and employed for the supramolecular functionalization of SWNTs to create stable dispersions in organic and aqueous solvents following acid protonation of the amine side chains.<sup>168</sup> Electrophoretic deposition (EPD) was used to construct high quality, uniform films of polymer-SWNT complexes with controllable thickness. Quartz crystal microbalance data demonstrated control over the deposition rate and amount of material deposited by varying the voltage, polymer concentration, and deposition time. The EPD method described was also applicable to other CPE-SWNT complexes.<sup>169-171</sup>

A study involving a water-soluble PmPV derivative, **P83**, having propyl sulfonate groups as side-chains, was performed by Pang and coworkers.<sup>172</sup> This polymer was also found to interact with SWNTs and resulted in stable dispersions of SWNTs in water. When compared to a previously reported, organic-soluble PmPV derivative (**P14a**), it was found that the introduction of the water-soluble side-chains on **P83** dramatically improved its selectivity for specific SWNT chiralities, leading to a sample with a narrow range of diameters (d = 0.75-0.84 nm). The authors proposed that this difference in diameter selectivity results from a perpendicular alignment of benzene rings when **P83** wraps around SWNTs, as opposed to a parallel alignment that enhances  $\pi$ - $\pi$  stacking for **P14a**. It was postulated that these different conformations produce differently sized cavities for SWNTs to fit into, thus effecting diameter selectivity. However, it should be noted that comparison of **P83** and **P12a** is difficult because the two polymers had significantly different molecular weights and were studied in different solvents. Since there have been many reports detailing the dramatic impact of both molecular weight and solvent on nanotube selectivity, it is difficult to attribute the observations in this report to a single parameter.

#### **1.7.** Conclusion

The investigation of CNTs has grown dramatically in the past decade, and remarkable progress has been made toward their application, ranging from high performance composite materials to nanoelectronics. Various techniques have been developed to obtain pure and solvent dispersible carbon nanotube samples. In the past few years, the supramolecular functionalization of SWNTs by conjugated polymers has emerged as a highly promising method for dispersing and sorting SWNTs in combination with retention of their intrinsic opto-electronic and mechanical properties. The resulting supramolecular complexes have been widely investigated in the preparation of both organic and aqueous solutions to obtain highly stable dispersion of individual nanotubes. This offers the required solubility, stability, and versatility to enable formation of polymer-CNT composites that can be processed using low boiling solvents, thus allowing for low-cost film fabrication. However, the amount of purified CNTs obtained is not yet enough for large-scale applications, and also the excess polymer may alter the device performance if not removed. In addition many fundamental issues still have to be addressed before we fully understand the interaction between various conjugated polymers and SWNTs, and find the polymer structures that offer the best SWNT dispersion and selectivity.

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# Chapter 2: Soluble, Discrete Supramolecular Complexes of Single-Walled Carbon Nanotubes with Fluorene-Based Conjugated Polymers

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The work detailed in this chapter was carried out in collaboration with Dr. Fuyong Cheng and Dr. Gianluigi Botton (Canadian Centre for Electron Microscopy, McMaster University). Both Patigul Imin and Dr. Fuyong Cheng contributed equally to the experimental planning and writing of this work. Polymer synthesis, nanotubes functionalization and characterization was conducted by Patigul Imin. AFM and TEM measurements was conducted by Christian Maunders.

# Abstract

Two fluorene-based conjugated polymers, polyfluorene (PF) and poly(fluorene*co*-thiophene) (PFT) were prepared by Suzuki coupling polycondensation. It was found that these polymers strongly interact with single-walled carbon nanotubes (SWNTs) to form discrete, highly soluble supramolecular complexes. Furthermore, the electron-rich PFT was found to exhibit a stronger interaction with SWNTs than the PF. This strong non-covalent interaction resulted in a high solubility of polymer-nanotube complexes in THF, as well as efficient fluorescence quenching of the conjugated polymer by carbon nanotubes. Conductivity measurements performed on thin films produced from these materials indicated that the supramolcular polymer-SWNT complexes retain a high degree of electrical conductivity, comparable to that of pristine SWNT films.

### **2.1. Introduction**

The supramolecular functionalization of carbon nanotubes with planar aromatic structures, such as pyrene and porphyrin derivatives, has received significant attention as it allows nanotube modification without the introduction of defects.<sup>1-5</sup> In addition to small molecules with extended conjugation, conjugated polymers have recently been found to strongly interact with the carbon nanotube surface through  $\pi$ -stacking.<sup>6</sup> Indeed, it has been shown that the multivalent nature of the interaction of conjugated polymers with the nanotube surface enhances the binding strength and enables the preparation of discrete polymer-nanotube complexes.<sup>7</sup> If properly modified, these complexes can exhibit high degrees of solubility and excellent conductivity properties,<sup>8</sup> making them potentially interesting for printed electronics, supercapacitors, LEDs, photovoltaic cells, and other optoelectronic devices.

Considering that conjugated polymers prefer a relatively coplanar geometry between monomers in order to maximize  $\pi$  orbital overlap, only a small number of discrete polymer-nanotube interaction modalities can be expected. Specifically, two general methods by which conjugated polymers can supramolecularly bind to the nanotube surface include helical wrapping and non-helical adsorption along the nanotube, depending on the flexibility of the polymer backbone.<sup>6</sup> Poly(*m*-phenylenevinylene)<sup>9, 10</sup> and poly(phenylacetylene)<sup>11, 12</sup> represent two polymers that are known to adopt helical conformations in solution, and have been shown to be ideal for supramolecular nanotube wrapping. Conversely, the rigidity of poly(p-phenyleneethynylene) prevents it from adopting helical conformations, and therefore limits it to adsorption along the nanotube

length as a straight, rodlike chain.<sup>12, 13</sup> Along similar lines, we have recently reported a conjugated Zn-porphyrin polymer<sup>14</sup> and triply-fused porphyrin oligomers<sup>15</sup> that can interact with carbon nanotubes, producing soluble nanotube complexes through a non-wrapping mechanism. Although these structures undergo extremely strong binding to the nanotube surface and have interesting optoelectronic properties, the synthetic challenges associated with their preparation limit their feasibility in practical applications. It is therefore advantageous to explore the interaction of nanotubes with other, more easily accessible conjugated polymers.

Among all the known conjugated polymers, poly(9,9-dialkylfluorene)<sup>16</sup> represents one of the most important families of electroactive polymers due to its conductivity, solubility, and stability properties, as well as its intense blue fluorescence. This material has been extensively studied as a component within thin-film transistors (TFTs),<sup>17</sup> lightemitting diodes (LEDs),<sup>18</sup> and photovoltaic (PV) devices.<sup>19</sup> Fluorene-thiophene copolymers, in which the combination of electron rich thiophene units with relatively electron-deficient fluorene units allows modification of the co-polymer bandgap (and thus the maximum fluorescence wavelength), have also been investigated for their charge injection/transport properties.<sup>20</sup> Although these polymers exhibit the extended conjugation required for  $\pi$ -stacking to the nanotube surface, they have thus far attracted limited attention as supramolecular adducts for single-walled carbon nanotubes.<sup>21</sup> In this communication, we present our recent findings that poly(9,9-dialkylfluorene) (PF) and poly(9,9-dialkylfluorene-co-3-alkylthiophene) (PFT) exhibit strong supramolecular binding to the nanotube surface, and impart excellent solubility and solution-stability properties even after excess polymer is removed from solution. In addition, thin films cast from these materials were found to be several orders of magnitude more conducting than the corresponding materials where the conjugated polymers were covalently bound to the nanotube surface.

# 2.2. Results and Discussion

The PF and PFT polymers were synthesized by the Suzuki polycondensation<sup>22</sup> from diborate **1** and the corresponding dibromides **2** and **3**, as depicted in Figure 2.1. It was found that the solvent in which the polymerization was carried out dramatically influences the molecular weight of the isolated polymer. For example, the preparation of PF in DMF as the solvent resulted in a poorly soluble product having an  $M_n$  of 30 kg/mol and a polydispersity index (PDI) of 2.4. However, the same polymerization in toluene produced PF with an  $M_n$  of 9 kg/mol and a PDI of 1.6. Because of the higher solubility of the low molecular weight product, it was preferentially used in the investigation of polymer-nanotube complexes. Preparation of the PFT structure was performed in a mixture of DMF and toluene (4:1 v/v) as the solvent and yielded polymer having an  $M_n$  of 15 kg/mol and PDI of 2.7. The high polydispersities in these polymerizations are a result of the uncontrolled step-growth polymerization process, and were consistent with literature reports for similar polymers.<sup>23</sup> The <sup>1</sup>H-NMR spectra of the polymers were also in good agreement with previously reported polymers of this type.<sup>24</sup>



**Figure 2.1.** Preparation of conjugated PF and PFT polymers and a cartoon representation of their interaction with SWNTs.

The supramolecular interaction of PF (9 kg/mol) and PFT (15 kg/mol) with SWNTs was studied using our previously reported methods.<sup>7, 14</sup> In a typical experiment, a SWNT sample (10 mg) was added to a solution of polymer in THF (30 mg/20 mL) and the mixture was sonicated for 1 h. The resulting suspension was centrifuged for 20 min at 5,000 rpm, and allowed to stand overnight. The clear, dark supernatant was carefully decanted and nanotube solubility within the sample was measured without removal of the excess free polymer present in solution. Then, the isolated supernatant was filtered through a 200 nm pore diameter Teflon membrane and repeatedly washed with THF (4 × 250 mL) to remove all excess polymer. Polymer removal was monitored by measuring the fluorescence of the filtrate, which decreased dramatically with continued washing. Once no fluorescence from the filtrate was observable, it was deemed that all free polymer had been washed out of the nanotube sample. The nanotube residue was then peeled away from the Teflon membrane and added to 5 mL of THF, followed by

sonication for 5 minutes to disperse the nanotubes. After sonication, the resulting dark suspension of nanotubes was centrifuged at 5,000 rpm for 20 min and allowed to stand undisturbed overnight. Again, the supernatant was carefully transferred by pipette to a clean vial, and nanotube solubility in this solution was also measured.

It was found that, using both PF and PFT, it was possible to produce a homogeneous, dark and stable solution even after removal of the excess free polymer, as described above. This indicates that the majority of adsorbed polymer does not desorb from the nanotube surface once it is bound, and the  $\pi$ -stacking interaction between the polymer and the nanotube surface is strong enough to prevent re-aggregation of nanotubes into large bundles. All solutions remained stable for periods of at least 4 weeks, with no observable precipitation. Nanotube solubility was initially quantified using a spectrophotometric method in which a specific extinction coefficient for SWNTs at 700 nm,  $\epsilon_{700} = 2.35 \times 10^4$  cm<sup>2</sup> g<sup>-1</sup>, was utilized.<sup>25</sup> It was necessary to use this extinction coefficient rather than the more commonly used value at 500 nm<sup>26-30</sup> because of interference from the absorption of PFT, which tails off at just above 500 nm. From these measurements, it was found that all of the polymer-SWNT complexes exhibited high solubility in THF, where the solubility in the presence of free polymer (PF-SWNT, 603 mg  $L^{-1}$ ; PFT-SWNT, 718 mg  $L^{-1}$ ) was much more higher than that in the absence of free (PF-SWNT, 209 mg  $L^{-1};$ PFT-SWNT, 384 mg  $L^{-1}$ ). These polymer spectrophotometrically determined solubilities were found to be in good agreement with a more traditional gravimetric method, in which dissolved material was isolated by filtration and weighed. For the gravimetric measurements, it was necessary to subtract the

mass of polymer within the dissolved material. The polymer content was calculated by thermogravimetric analysis (TGA), which provided the weight fraction of the polymer. TGA data for the free polymers PF and PFT, as well as the corresponding polymernanotube complexes, is provided in Figure 2.2. This data indicated that it is not possible to completely decompose the conjugated polymers by heating to 800°C under Ar. Instead, the major mass loss for the polymer occurs at ca. 450°C, corresponding to the loss of alkyl side-chains within these polymers.<sup>31</sup> Indeed, the observed mass-loss values of 57 % (PF) and 60 % (PFT) are in agreement with calculated weight percentages for the alkyl side-chains of 63 % for PF and 61 % for PFT. On the basis of the observed thermograms of the free polymers, the polymer content in the two polymer-nanotube complexes could be calculated, and was found to be 38 % and 42 % for PF-SWNT and PFT-SWNT, respectively. Gravimetric measurements of solubility were done by filtering an exact volume of the saturated solution obtained after removal of excess free polymer (see above), drying the nanotube residue to constant mass, and measuring the mass of the isolated polymer-nanotube complex. The weight percentage of polymer within these complexes was then subtracted from the measured mass to determine the mass of nanotubes within the isolated sample. This method gave nanotube solubility values of 322 and 360 mgL<sup>-1</sup> for PF-SWNT and PFT-SWNT, respectively, which were in reasonable agreement with the spectrophotometrically-determined values. It should be noted that other carbonaceous material (amorphous carbon, turbostratic graphite, etc.) may be present in these solutions, augmenting our solubility values. However, the purified grade of the SWNT sample used, our TEM and AFM data (see below), and previous reports with other conjugated polymers<sup>32</sup> suggest the amount of such non-nanotube material is negligible.



**Figure 2.2.** Thermogravimetric analysis data for polymer PF (A) and PFT (B), showing thermal decomposition profiles for the free polymer and polymer-nanotube complexes.

The supramolecular interaction of the polymers with SWNTs was further investigated by UV-Vis absorption spectroscopy. Figure 2.3 depicts the spectra of the polymers, SWNTs (measured in an aqueous solution using sodium dodecyl sulphate as a surfactant)<sup>33</sup>, and the polymer-SWNT complexes in THF. In addition, by subtracting the normalized spectrum of the SWNTs alone from that of the polymer-SWNT complexes, it was possible to generate a spectrum that corresponds to just the polymer contribution to the absorption of the polymer-SWNT complexes (labeled "subtraction" in Figure 2.3). By comparing this subtraction spectrum to that of the free polymer, it was found that a bathochromic shift in the polymer absorption occurs upon nanotube complexation. This shift may arise from an increased effective conjugation length within the polymers, caused by a more planar structure of its backbone after it has interacted with the SWNT surface.<sup>7</sup> Alternatively, the bathochromic shift may also be due to the  $\pi$ -stacking
interaction, resulting in delocalization of  $\pi$  electrons onto the SWNT surface. Interestingly, a larger red-shift (18 nm) was observed for the PFT-SWNT complex, as compared to the PF-SWNT complex (4 nm). This indicates that the electronic structure of the polymers has an effect on the interaction strength with carbon nanotubes, where the relatively electron-rich PFT may exhibit stronger supramolecular complexation with SWNTs, consistent with the observed higher solubility of the PFT-SWNT complex.



**Figure 2.3.** UV-Vis absorption data from polymer-nanotube complexes, SWNTs, free polymer, and the polymer contribution to the polymer-nanotube complex spectrum (labeled "subtraction") for PF (A) and PFT (B).

The fluorescence spectra of the free polymers and polymer-SWNT complexes were also measured and quantitatively compared (Figure 2.4). By normalizing the absorption spectrum of the free polymer and the polymer contribution to the absorption of the polymer-SWNT complex (subtraction file in Figure 2.3), it was possible to determine normalization factors that could be applied to the fluorescence spectra of the two samples. From the normalized emission spectra, it is clear that highly efficient quenching of fluorescence occurs when the polymers assemble on the carbon nanotube surface. The calculated quenching efficiency was measured to be 96% and 89% for PFT-SWNT and PF-SWNT complexes, respectively, which again indicated that the PFT exhibits a stronger interaction with carbon nanotubes than PF. The fluorescence quenching is likely a result of photoinduced electron transfer from the excited conjugated polymer to the SWNTs, as previously reported for other systems.<sup>12, 34-38</sup> Interestingly, no shifts in the  $\lambda_{\text{max}}$  values of emission from the polymer-nanotube complexes, relative to the free polymer, were observed, indicating that the observed emission of the polymer-nanotube complexes is actually emanating from a small amount of free polymer that has desorbed from the nanotube surface and likely formed a dynamic equilibrium with bound polymer. This implies that the actual fluorescence quenching efficiencies for nanotube-bound polymers are likely to be higher than what were calculated from this data, most probably reaching unit efficiencies.



**Figure 2.4.** Emission spectra of free polymer and polymer-nanotube complexes using PF (A) and PFT (B) polymers, with the excitation wavelength set to the  $\lambda_{max}$  of each sample (382 nm for PF and PF-SWNT, 409 nm for PFT, and 425 nm for PFT-SWNT).

Microstructural characterization of polymer-nanotube complexes was performed using atomic force microscopy (AFM) and transmission electron microscopy (TEM). The AFM image of a PF-SWNT sample (Figure 2.5A), prepared by spin casting a dilute solution of the sample in THF onto a freshly cleaved mica disc, shows a large number of entangled "nano-fibers". Height analysis of these features indicated that most of the fibers ranged in height from ca. 2 nm to ca. 17 nm, presumably corresponding to a mixture of individual and aggregated polymer-functionalized nanotubes. Considering that, as solvent evaporates on the substrate, individual nanotubes can be pushed together into larger aggregates, the observed mixture of differently aggregated features is not surprising. Using TEM, it is also possible to observe features corresponding to nanotube fibers that are coated with polymer (Figure 2.5B). Although, from this image, it is possible to observe SWNTs as well as Fe catalyst particles underneath the polymer coating, the large amount of polymer present hinders our ability to discern individual nanotubes from nanotube bundles. The samples were therefore treated with a plasma cleaning procedure, after deposition on the TEM grid, in order to degrade the polymer coating prior to microscopy. Following plasma cleaning for 30 seconds, it was found that the majority of the polymer was removed from the sample, leaving only the underlying nanotubes exposed (Figure 2.5C). The resulting image shows an individual, bare SWNT with only small patches of polymer left on its surface. This image provides evidence that the polymer was able to exfoliate nanotube bundles and the fibers observed by AFM and TEM (prior to plasma cleaning) were composed of single SWNTs coated with polymer.



**Figure 2.5.** AFM image of a PF-SWNT sample on freshly cleaved mica (A); high-resolution TEM image of PFT-SWNT prior to plasma cleaning (B) and post plasma cleaning (C).

The conductivity properties of the polymer-SWNT complexes were evaluated by measuring the sheet resistance of thin films made from these materials. The thin films were prepared by previously reported methods involving vacuum filtration of the nanotube solutions through a 200 nm pore diameter Teflon membrane.<sup>39</sup> Briefly, the purified polymer-SWNT complexes in THF solution were carefully poured into the filtration apparatus, avoiding bubble formation on the solution surface. Each solution was filtered and washed with THF ( $4 \times 250$  mL), after which the residue was allowed to airdry while pulling vacuum on the sample for 30 min. The films were then subjected to further drying in a vacuum oven at 50°C for 24 h. Although the films could be peeled from the membrane as intact, flexible sheets, it was found that electrical contact with electrodes was easier to achieve if the films remained on the Teflon membrane, which provided extra support. Standard four-point-probe measurements were performed under

ambient conditions to determine sheet resistance values, which could be converted to conductivities after determination of film thickness according to equation (2.1):

$$S = \frac{1}{R_s \times t}$$

where  $\sigma$  is the conductivity in S cm<sup>-1</sup>, R<sub>s</sub> is the sheet resistance in ohms/square ( $\Omega$ /square), and *t* is the film thickness in cm. Based on these measurements, it was found that the supramolecular polymer-nanotube complexes can be used to produce homogeneous films having conductivities similar to those of pristine nanotubes (Table 2.1). The measured conductivity of a 240 µm thick film of the PF-SWNT complex was 34 ± 4 S cm<sup>-1</sup>, while a 180 µm thick film of the PFT-SWNT complex was 52 ± 3 S cm<sup>-1</sup>. A control film of pristine SWNTs, with a thickness of 90 µm was also measured, and exhibited a conductivity of 210 ± 40 S cm<sup>-1</sup>. The 4 to 6 fold lower conductivity for the polymer-SWNT complexes is not surprising, considering that these samples are composed of ca. 40 % polymer.

Sample	Sheet Resistance (Ω)	Film Thickness (cm)	Conductivity (S cm <sup>-1</sup> )
SWNT	0.52	$0.009 \pm 0.002$	$210 \pm 40$
PF-SWNT	1.23	$0.024 \pm 0.003$	$34 \pm 4$
PFT-SWNT	1.07	$0.018 \pm .001$	$52 \pm 3$

**Table 2.1.** Conductivity data for nanotube thin films.

## 2.3. Conclusion

In conclusion, fluorene-based conjugated polymers were synthesized and used to prepare discreet polymer-SWNT complexes. The conjugated polymers were found to form strong supramolecular complexes with SWNTs, imparting excellent solubility in organic solvents in the absence of excess free polymer. Thermogravimetric analysis indicated that the polymer-nanotube complexes were composed of approximately 40 wt % polymer. UV-Vis absorption measurements revealed a bathochromic shift in the absorption spectrum of the polymers as a result of nanotube complexation, while fluorescence measurements showed that polymer fluorescence is highly quenched in the complexes. Microstructural analysis (AFM and TEM) was used to demonstrate that the polymer chains can exfoliate SWNT bundles, resulting in individual nanotubes that are uniformly coated with polymer. Using four-point-probe measurements, it was found that the conductivity of thin films of polymer-nanotube complexes was only slightly lower than what was observed for films of pristine nanotubes. The high conductivity and solubility of the supramolecular polymer-nanotube complexes opens the door to their application in a variety of applications, such as in printed electronics.

## 2.4. Experemental

### 2.4.1. General

Purified grade single-walled carbon nanotubes (SWNTs), prepared by the HiPco method, were purchased from Carbon Nanotechnologies, Inc. (Houston, TX), and used without any further treatment. All other reagents and solvents were purchased from commercial suppliers and used as received. Atomic force microscopy was done using a Digital Instruments NanoScope IIIa Multimode AFM, with samples prepared by spincasting (4,000 rpm) sample solutions or suspensions on freshly cleaved mica substrates. The images were recorded with standard tips in tapping mode at a scan rate of 1.0 Hz. TEM analysis was performed using a JEOL 2010F operating at 200 keV. Plasma cleaning to remove the polymer coating was done using a Gatan model 950 SOLARUS Advanced Plasma System with a standard, factory set  $H_2/O_2$  gas mixture (6.4/27.5 v/v) and an exposure time of 30 sec. NMR was performed on a Bruker 200 MHz instrument in CDCl<sub>3</sub>. The chemical shifts ( $\delta$ ) are given in ppm with respect to the residual non-deuterated solvent. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 409 PC instrument under Argon with a temperature range from 20 to 800°C and a temperature gradient of 5 deg/min. Ultrasonication was done in a Branson Ultrasonics B2510 bath sonicator. Filtration was done through a 200 nm-pore Teflon membrane (Millipore). UV/vis absorption spectra were measured using a Cary 50 UV-visible spectrophotometer. Fluorescence spectra were measured using a Jobin-Yvon SPEX Fluorolog 3.22 equipped with a 450 W Xe lamp, double-excitation and double-emission monochromators, and a digital photon-counting photomultiplier. Slit widths were set to 2 nm band-pass on both excitation and emission. Correction for variations in lamp intensity over time and  $\lambda$  was achieved using a reference silicon photodiode. Conductivity measurements were performed using the four-point probe technique with a Jandel probe head having tungsten carbide tips spaced 1.00 mm apart. A Hewlett-Packard 6224B dc voltage supply provided the current source between the outer two probes; the applied current was measured with a Fluke 8000A multimeter. The voltage drop between the inner two probes was measured

with a Hewlett-Packard 34401A multimeter. The voltage-current data were corrected for sample size and shape.

#### 2.4.2. Synthesis of PF (Mn = 9.2 kg/mol)

To a 100 mL flask charged with toluene (12 mL) and aqueous potassium carbonate (8 mL, 2 M), was added 9,9-didodecyl-2,7-dibromofluorene (264 mg, 0.4 mmol) and 9,9-dioctylfluorene-2,7-bis(trimethylene)borate (223.4 mg, 0.4 mmol). The mixture was then bubbled with N<sub>2</sub> for 15 min, degassed via four freeze-pump-thaw cycles, and finally back-filled with Ar. A catalytic amount Pd(PPh<sub>3</sub>)<sub>4</sub> (1.0 mol %) was added, and the mixture was stirred at 85°C under Ar for 48 h. After cooling to room temperature, the solution was precipitated via dropwise addition to 100 mL of a methanol/de-ionized water mixture (10/1 v/v) and filtered. The residue was dissolved in a minimum amount of THF and re-precipitated in methanol (100 mL), followed by washing with methanol, water, and acetone (100 mL of each). After drying in vacuum for 20 h, a yellow solid was obtained (222.5 mg, 63 %). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.85 (br, 8 H), 7.65 (br, 4 H), 2.09 (br, 8 H), 1.13 (br, 56 H), 0.73 (br, 20 H). UV-Vis (THF):  $\lambda_{max} = 384$  nm; UV-vis (film):  $\lambda_{max} = 405$  nm; PL (THF):  $\lambda_{em} = 416$ , 440 nm. GPC: M<sub>n</sub> = 9.2 kg/ mol, M<sub>w</sub>/M<sub>n</sub> = 1.60.

## 2.4.3. Synthesis of PF (Mn = 36.7 kg/mol)

To a 100 mL flask charged with 20 mL DMF and Cs<sub>2</sub>CO<sub>3</sub> (1.5 g 4.6 mmol), was added 9,9-didodecyl-2,7-dibromofluorene (264 mg, 0.4 mmol) and 9,9-dioctylfluorene-

2,7-bis(trimethylene )borate (223.4 mg, 0.4 mmol), then the mixture was bubbled with N<sub>2</sub> for 15 min, degassed via four freeze-pump-thaw cycles, and finally back-filled with Ar. A catalytic amount Pd(PPh<sub>3</sub>)<sub>4</sub> (1.0 mol %) was added, and the resulting mixture was stirred at 100°C under Ar for 2 h. The polymer product was found to precipitate from the reaction mixture. After cooling to room temperature, the solid was isolated by filtration, then dissolved in small amount of THF, re-precipitated by addition to 100 mL of methanol, and then filtered and washed with methanol, water and acetone (100 mL of each). After drying under vacuum for 20 h, a yellow solid was obtained (320 mg, 91 %). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.71-7.57 (m, 6 H), 7.31 (s, 1 H), 2.67 (br, 2 H), 2.05 (br, 4 H), 1.68 (br, 2 H), 1.32-0.73 (m, 49 H). UV-Vis (THF):  $\lambda_{max}$  = 386 nm; UV-Vis (film):  $\lambda_{max}$  = 405 nm; PL (THF):  $\lambda_{em}$  = 416, 441nm. GPC: M<sub>n</sub> = 36.7 kg/ mol, M<sub>w</sub>/M<sub>n</sub> = 2.40.

#### 2.4.4. Synthesis of PFT

To a 100 mL flask charged with 20 mL DMF was added  $Cs_2CO_3$  (1.5 g 4.6 mmol), 9,9-dioctylfluorene-2,7-bis(trimethylene)borate (223.4 mg, 0.4 mmol), and 2,5-dibromo-3-dodecyl-thiophene (164.1 mg, 0.4 mmol) pre-dissolved in 5 mL of toluene. The mixture was then bubbled with N<sub>2</sub> for 15 min, degassed via four freeze-pump-thaw cycles, and finally back-filled with Ar. A catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> (1.0 mol %) was added, and the mixture was stirred at 100°C for 24 h under Ar. After cooling to room temperature, the solvent was evaporated, and the resulting solid was dissolved in a minimum amount of THF, followed by precipitation via addition to 100 mL of methanol. The precipitate was filtered and washed with methanol, water and acetone (100 mL of

each). After drying under vacuum for 20 h, a greenish yellow solid was obtained (240.1 mg, 94 %). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.71-7.57 (m, 6 H), 7.31 (s, 1 H), 2.67 (br, 2 H), 2.05 (br, 4 H), 1.68 (br, 2 H), 1.32-0.73 (m, 49 H). UV-Vis (THF):  $\lambda_{max}$  = 409 nm; UV-Vis (film):  $\lambda_{max}$ = 428 nm. PL (THF):  $\lambda_{em}$  = 458, 488 nm. GPC: M<sub>n</sub> = 15.7 kg/mol, M<sub>w</sub>/M<sub>n</sub> = 2.70.

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# Chapter 3: Supramolecular Complexes of Single Walled Carbon Nanotubes with Conjugated Polymers

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The work detailed in this chapter was carried out in collaboration with Dr. Fuyong Cheng (Department of Chemistry and Chemical Biology, McMaster University). Both Patigul Imin and Dr. Fuyong Cheng contributed equally to the experimental planning. All of the experimental data was collected by Patigul Imin, and paper was written by Patigul Imin.

## Abstract

We have synthesized a series of conjugated polymers, including poly[(2,7-(9,9dioctylfluorene)-alt-2,7-(9,9-didodecylfluorene)] (PF), poly[(2,7-(9,9-dioctylfluorene)alt-2,5-(3-dodecylthiophene)] (PFT), and poly(3-dodecylthiophene) (PT). Non-covalent functionalization of single walled carbon nanotubes (SWNT) with these polymers can impart good solubility to nanotubes in a number of organic solvents, including THF, dichlorobenzene, chloroform, and toluene. Solution and solid-state characterization of the resulting polymer-SWNT composites are described, including UV-Vis absorption and Raman spectroscopy. It was found that the UV-Vis absorption maximum of the polymers was red-shifted in their corresponding composites due to the planarization of the polymer backbone following adsorption upon the SWNT surface. Polymer-SWNT complexes also exhibited good solution stability at elevated temperature in THF and dichlorobenzene, with no significant SWNT sedimentation observed at elevated temperatures. Both UV-Vis absorption and Raman spectroscopy results indicated that the interaction of PT with the nanotubes was different than that of PF and PFT, suggesting that the choice of aromatic ring in the polymer structures plays an important role in the supramolecular complex formation with carbon nanotubes.

## **3.1. Introduction**

Since the seminal work of Iijima,<sup>1</sup> carbon nanotubes (CNTs) have attracted tremendous research interest due to their extraordinary mechanical, electronic, and optical properties, and have become the most extensively studied materials in the field of nanotechnology.<sup>2, 3</sup> Although the favourable properties of CNTs make them potentially useful for a number of applications, their commercial exploitation has been limited due to difficulties related to their purification, dissolution, and solution-phase processing. To overcome their inherent insolubility and improve the processability of carbon nanotubes, it is desirable to functionalize them so as to generate nanotube derivatives that are compatible with common organic solvents as well as organic matrix materials.<sup>4, 5</sup> To this end, a variety of CNT surface modification techniques have been developed during the past few years, including methods for covalent<sup>6-9</sup> and non-covalent functionalization.<sup>10-16</sup>

Although the covalent functionalization strategy has proven effective in solubilizing both single-walled and multi-walled carbon nanotubes (SWNTs and MWNTs, respectively) in various organic solvents, as well as in water, the covalent linkage of functional groups to the nanotube surface results in disruption of the sp<sup>2</sup>-hybridized carbon framework.<sup>17, 18</sup> This leads to a significant reduction in the electrical conductivity and mechanical strength of such chemically functionalized nanotubes, when compared to pristine CNTs.<sup>5, 19, 20</sup> Conversely, when non-covalent functionalization is used, the structural integrity of carbon nanotubes remains unchanged, allowing retention of the CNT properties, and enabling the use of both their conductive and mechanical properties in eventual applications. It has been shown that various conjugated structures, such as

pyrene,<sup>19, 21, 22</sup> porphyrins,<sup>12-14</sup> and  $\pi$ -conjugated polymers<sup>10, 23-42</sup> can form supramolecular complexes with nanotubes, and the resulting complex materials exhibit good solubility. In recent years, composite materials based on conjugated polymers and SWNTs have generated significant interest due to the combination of optical, electrical, and processibility properties of the conjugated polymers with the strength and conductivity properties of carbon nanotubes. A number of conjugated polymers, including poly(mphenylene vinylene) (PmPV),<sup>23-27</sup> polythiophene (PT),<sup>28-35</sup> poly(phenylene ethynylene) (PPE),<sup>10, 41, 42</sup> and polyfluorene<sup>36-40</sup> have been successfully used to modify and strongly interact with the carbon nanotube surface through  $\pi$ -stacking or helical wrapping.

Polyfluorene, polythiophene, and derivatives of these polymers are among the most widely investigated conjugated polymers due to their excellent solubility, high thermal, photochemical, and environmental stability, and ease of control over their optoelectronic properties via macromolecular engineering.<sup>43-50</sup> Recently, it has been found that fluorene-containing conjugated polymers can form stable complexes with SWNTs, and exhibit excellent solubility and solution-stability properties even after removal of excess polymer.<sup>37</sup> Interest in this class of conjugated polymers is increasing further as reports of selective solubilization of certain SWNT species have begun to be published.<sup>36, 38-40</sup> It is therefore desirable to develop a detailed understanding of how variations in the backbone of a conjugated polymer can affect the interactions between the polymer and the SWNT surface. However, few comparisons of different conjugated polymer backbones in terms of their supramolecular functionalization of CNTs have been reported.

Herein, we compare three different polymer backbones with respect to their interactions with SWNTs, including poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,7-(9,9-diddecylfluorene)] (PF), poly(3-dodecyl thiophene) (PT), and an alternating copolymer of fluorene and thiophene, poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,5-(3-dodecylthiophene)] (PFT). Specifically, the effect of changing the polymer backbone on nanotube solubility, solution stability, and photophysical properties was investigated.

### **3.2. Results and Discussion**

Scheme 3.1 illustrates the synthesis of the three polymers, PF, PFT, and PT. The preparation of both PF and PFT involved Suzuki polycondensation of commercially available diborate (1) and the corresponding dibromides (2) and (3). Synthesis of PT was accomplished by a chemical oxidation method, using 3-dodecyl thiophene as depicted in Scheme 3.1.<sup>44, 45, 49</sup> The resulting polymers were soluble in common organic solvents, such as THF, chloroform, toluene, and dichlorobenzene. The polymer molecular weight and polydispersity index (PDI) values were estimated from gel permeation chromatography (GPC), using polystyrene standards, and are listed in Table 3.1. The <sup>1</sup>H NMR spectra of the polymers were also in good agreement with the proposed polymer structures.



Scheme 3.1. Synthesis of  $\pi$ -conjugated polymers PF, PFT and PT.

 Table 3.1. Molecular weight and polydispersity index values for the synthesized polymers.

Polymer	Mn (kg/mol)	PDI
PF	9	1.6
PFT	15	2.7
PT	48	1.5

To investigate the supramolecular interactions of these polymers with SWNTs, each polymer/nanotube mixture was prepared and treated identically. In a typical experiment, 20 mL of THF was added to a vial containing 10 mg SWNT and 30 mg conjugated polymer, and the mixture was sonicated for 1 h. The vial was centrifuged at 2,576 g for 20 min, and the resulting suspension was allowed to stand overnight. The

dark-colored, clear supernatant was carefully transferred to another vial using a pipette. Then the isolated supernatant was further diluted with 50 mL of THF, sonicated for 5 min, filtered through a 200 nm pore diameter Teflon membrane, and repeatedly washed with THF until the filtrate was colorless and showed practically no fluorescence when irradiated using a UV lamp. 10 mL THF was added to the recovered SWNT residue, and the vial was further sonicated for 5 min. The resulting dark suspension was centrifuged at 2,576 g for 20 min and allowed to stand overnight undisturbed. The supernatant was carefully transferred by pipette to another vial, producing a solution of discrete polymernanotube complexes that have been separated from any unbound polymer. Figure 3.1 B-D shows photographs of the conjugated polymer-SWNT complexes in THF, along with a comparison to pristine SWNTs treated in the same way (except for initial addition of the polymer) in THF. It was found that when using these fluorene and thiophene-based conjugated polymers, it was possible to produce homogeneous solutions in THF even after removal of the excess unbound polymer, and the solutions were stable for at least four weeks without SWNT precipitation. Conversely, pristine SWNTs in the absence of polymers do not dissolve to any extent after similar treatment. Additionally, polymer-SWNT complexes exhibited good film-forming properties, easily producing uniform films by drop casting or spin coating at room temperature.



**Figure 3.1.** Photograph of four samples in THF: A) pristine SWNT; B) PF-SWNT; C) PFT-SWNT; D) PT-SWNT

Photophysical properties of the polymer and polymer-nanotube complexes were investigated by steady-state UV-Vis spectroscopy. PF, PFT, and PT were found to exhibit absorption maxima at 380 nm, 403 nm, and 435 nm in THF solution, respectively, as shown in Figure 3.2 A(i). These absorption spectra are in agreement with previously reported values for similar polymers of nearly equal molecular weight.<sup>51-53</sup> It is important to note that these three polymers represent a series in which the bandgap systematically decreases upon introduction of the electron rich and sterically less demanding thiophene units. The effect of this systematic variation to polymer composition and electronic structure on the supramolecular interaction of these fluorene and thiophene containing polymers with SWNTs in THF solution was initially evident from the UV-Vis absorption spectra of the polymer-nanotube complexes prepared as described above. From these spectra, depicted in Figure 3.2 A(ii), it is clear that the absorption characteristics of both the polymer and SWNTs are observable, even though the free polymer in solution was removed by extensive washing. In each case, it was found that the absorption maximum

of the polymer exhibited a characteristic bathochromic shift once bound to the nanotube surface. This shift arises from an increased effective conjugation length within the polymer, most likely caused by the planarization of its backbone following adsorption upon the SWNT surface. It was also found that the magnitude of the red-shift varied with polymer structure, as exhibited in Figure 3.2, A(ii). The largest absorption red-shift was observed in the PT-SWNT complex (~120 nm) in solution, while a very small red-shift (~ 4 nm) was observed when PF was used (Table 3.2).



**Figure 3.2.** UV-Vis absorption spectra of the polymers (*i*) and polymer-nanotube complexes (*ii*) in THF (A) and as films on glass (B).

polymer	polymer	polymer	polymer-SWNT	polymer-SWNT	$\Delta_1^*$	$\Delta_2^*$
	in THF (nm)	film(nm)	in THF(nm)	film (nm)	(nm)	(nm)
PF	380	380	384	384	0	4
PFT	403	416	423	423	13	20
PT	435	509	558	558	74	123

**Table 3.2.** Absorption maxima (UV<sub> $\lambda$ max</sub>) of the polymer and polymer-SWNT complexes recorded for THF solutions and in the solid state.

\*Note:  $\Delta_1 = UV_{\lambda max}$ (polymer film)-  $UV_{\lambda max}$ (polymer solution),  $\Delta_2 = UV_{\lambda max}$ (polymer-SWNT solution) -  $UV_{\lambda max}$ (polymer solution).

It is known that poly(alkylthiophene)s adopt a poorly conjugated random coil structure in good solvents, and undergo a coil-to-rod transition when transferred from solution into the solid state, producing extended chains of coplanar thiophene rings.<sup>52, 54</sup> The large shift in PT-SWNT complex absorption indicates that, in our case, the PT also adopts a random coil conformation, and transitions to a much more planar structure when adsorbed onto the nanotube surface. This may also be the result of a very strong  $\pi$ -stacking interaction between the PT backbone and the nanotube surface. The smaller red shift for PF-SWNT and PFT-SWNT composites suggests that these polymers adopt a more rigid rod conformation in THF, and only slightly planarize once adsorbed on the nanotube surface.

The preparation and characterization of high-quality, homogeneous thin films from conjugated polymers as well as nanotube composite materials is important for the fabrication of a wide variety of devices.<sup>45, 55-57</sup> Transparent and uniform films of PF, PFT,

and PT, as well as the corresponding polymer-SWNT complex materials were prepared on glass slides by drop-casting from their THF solutions at room temperature. UV-Vis absorption spectra of the conjugated polymer and polymer-SWNT complex films are provided in Figure 3.2, B(i) and B(ii). In the absorption spectra of the PF film, there was no red-shift observed relative to the corresponding solution spectrum. This indicates that there are no noticeable molecular conformation changes for PF when going from solution to solid state films. However, in PFT and PT films, significant bathochromic shifts (13 nm and 74 nm, respectively) were observed when compared to the solution-phase absorption spectra. This indicates that the polymers adopt more planar conformations when cast into thin films relative to their state in solution. Interestingly the magnitude of the red-shift for each polymer in the solid state is comparable to their corresponding complexes with the SWNTs in solution. Polymer-SWNT complex absorption spectra in the solid state exhibited absorption maxima that were similar to the corresponding polymer-SWNT complexes in solution (Figure 3.2 B(*ii*)).

Solubility and solution stability of the conjugated polymer-SWNT complexes in other organic solvents, such as CHCl<sub>3</sub>, dichlorobenzene, and toluene, were also investigated in detail. In a typical experiment, 5 mL of solvent was added to a vial containing 2.5 mg SWNT and 2.5 mg conjugated polymer, and the mixture was sonicated for 30 min. The vial was allowed to stand one week, and then the dark-colored, clear supernatant was carefully transferred to another vial using a pipette. Previous experimental and theoretical studies showed that solvents with high density and polarity are better for SWNTs.<sup>58-60</sup> Similarly, the present series of conjugated polymer-SWNT

complexes exhibited very good solubility and solution stability in CHCl<sub>3</sub> and dichlorobenzene (solvents with higher density), for periods of at least 3 months, with no observable precipitation. Quantitative flocculation and precipitation of the polymer-SWNT complexes in toluene were observed to slowly occur over several days. In addition, diluted solutions were prepared from each polymer-SWNT complex in different solvents, and the solution stability of the polymer-SWNT complexes at different temperatures was investigated by UV-Vis spectroscopy. Figure 3.3 represents variable-temperature UV-vis absorption spectra of PF-SWNT (Figure 3.3A), PFT-SWNT (Figure 3.3B), and PT-SWNT (Figure 3.3C) complexes in THF (*i*), dichlorobenzene (*ii*) and toluene (*iii*).

Upon stepwise heating from room temperature to the 65 °C in THF and up to 95 °C in dichlorobenzene, there was no visible carbon nanotube precipitation observed. However, the polymer-SWNT solution in toluene underwent significant precipitation during the course of the experiment, resulting in light scattering and a noisy UV-Vis absorption spectrum. The absorption maxima of the polymers within polymer-SWNT complexes gradually decreased in intensity and slightly blue shifted with increasing temperature. This change in the absorption is mainly due to the conformational change of the polymer from a more planar conformation to relatively disordered states at higher temperature.<sup>43</sup> The identical effect was observed for the polymers alone, in the absence of SWNTs (see Appendix I, Figure A.1).



**Figure 3.3.** UV-Vis absorption data of the polymer-nanotube complexes in THF, dichlorobenzene, and toluene at different temperatures. PF-SWNT (A), PFT-SWNT (B), and PT-SWNT (C) complexes in THF (*i*), dichlorobenzene (*ii*), and toluene (*iii*).

Raman spectroscopy was also used to further characterize the polymer-SWNT samples. Sample preparation involved drop casting the diluted polymer-SWNT solutions in THF onto a glass microscope slide, and drying in air prior to measurement. Raman spectra were collected at an excitation wavelength of 785 nm. The Raman spectra of pristine SWNTs (as received), and soluble polymer-SWNT complexes are shown in Figure 3.4A, where all the spectra are normalized to the graphitic (G) band (1590 cm<sup>-1</sup>). The position of the G band at ~1590 cm<sup>-1</sup> in polymer-SWNT complexes was almost

identical to that of pristine nanotubes. Both the disorder (D) band at  $\sim 1300$  cm<sup>-1</sup>, and the second-order G' band at 2600 cm<sup>-1</sup> did not significantly increase in intensity after supramolecular functionalization. These results indicate that noncovalent functionalization of nanotubes with these conjugated polymers does not introduce any defects in nanotube electronic structures. The frequency and intensity of radial breathing mode (RBM) features in the range of 120-350 cm<sup>-1</sup> provides the most valuable information for sample characterization.<sup>61, 62</sup> SWNT diameter distribution for the HiPcoproduced nanotubes used in this study can be estimated according to the relationship between RBM frequency and tube diameter,  $v_{RBM} = A / d_t + B$  (where  $d_t$  is the tube diameter in nm,  $v_{RBM}$  is the Raman shift of the peak in cm<sup>-1</sup>, A is 223.5 cm<sup>-1</sup> and B is 12.5 cm<sup>-1</sup> for HiPco SWNTs).<sup>63</sup> RBM profiles of the as-received HiPco sample, as well as the soluble polymer–SWNT complexes are shown in Figure 3.4B.



**Figure 3.4.** Raman spectra of the polymer-nanotube complexes, polymer-SWNT soluble fraction at 785 nm excitation, showing (A) the entire spectral range, and (B) the RBM region.

Comparing the RBM frequency and intensity, it was observed that the polymers show a preference for specific tube diameters in THF solution. In the spectrum of PF-SWNT and PFT-SWNT, the signals at  $231 \text{cm}^{-1}$  and  $224 \text{ cm}^{-1}$  (corresponding to diameters of ~1.02 and ~1.06 nm respectively) showed much higher intensity, and were significantly narrower, when compared to the original SWNT sample, while the peak at ~204 cm<sup>-1</sup> (corresponding to a nanotube diameter of ~1.17 nm) remained almost unchanged. The signal intensity at ~ 265 cm<sup>-1</sup> was decreased 2-fold for both PF-SWNT and PFT-SWNT when compared to the original pristine nanotube sample. Surprisingly, the RBM signal intensity is significantly different for the PT-SWNT sample when compared to the PF-SWNT and PFT-SWNT samples. A decrease in intensity in the signals at 231cm<sup>-1</sup> and 224 cm<sup>-1</sup> for PT-SWNT was observed, while the peak at 204 cm<sup>-1</sup> (corresponding to a nanotube diameter of ~1.17 nm) is substantially increased in intensity. It is interesting to note that the PT-SWNT sample also showed the most profound difference in the UV-Vis measurements. These results seem to indicate that the relatively electron-rich PT may interact with the SWNTs in a different manner from the other two polymers, which may be the result of complementarity with relatively electron-poor semiconducting SWNTs that dominate the nanotube sample. Further studies of this effect are needed in order to fully understand this phenomenon.

#### **3.3.** Conclusion

A series of fluorene and thiophene containing conjugated polymers was synthesized and subsequently utilized for the preparation of supramolecular polymer-SWNT composite materials. It was demonstrated that the supramolecular interaction between SWNTs and PF, PFT, and PT polymers resulted in excellent solubility of the nanotubes in THF, even after removal of the excess polymer. The resulting conjugated polymer-SWNT supramolecular complexes also exhibited solution stability in elevated temperature in several organic solvents, including THF, chloroform, and dichlorobenzene. The spectroscopic characterization of the polymer-SWNT complex materials indicated that the interaction between the conjugated polymers and SWNTs is influenced by polymer structure. Specifically, the relatively electron-rich PT sample seems to exhibit a different interaction with the SWNT surface than the PF or PFT structures.

#### 3.4. Experimental

#### 3.4.1. General

Single-walled carbon nanotubes (SWNTs) were purchased from Carbon Nanotechnologies, Inc. (Houston, TX). All reagents and solvents were purchased from commercial suppliers and used as received. UV-Vis spectra were measured by using a Cary 50 UV-visible spectrophotometer. Ultrasonication was carried out in a Banson Ultrasonics B1510, and B2500 bath sonicator. Beckman Allegra[TM] X-22R Benchtop centrifuge was used for centrifugation. Filtration was performed through a 450 nm-pore Teflon membrane (Millipore). Polymer molecular weight and polydispersity index (PDI) were estimated from gel permeation chromatography (GPC) analyses by using a Waters 2695 Separations Module equipped with a Waters 2996 photodiode array detector, a Waters 2414 refractive-index detector, a Waters 2475 Multilfluorescence detector, and four Polymer Labs PL gel individual pore-size columns. Polystyrene standards were used for calibration, and THF was used as the eluent at a flow rate of 1.0 mLmin<sup>-1</sup>. Raman

spectra from all samples were collected with a Renishaw Ramanscope at excitation laser wavelengths of 785 nm. NMR spectra were measured on Bruker Avance 200 spectrometers. Fluorescence spectra were measured using a Jobin-Yvon SPEX Fluorolog 3.22 equipped with a 450 W Xe lamp, double-excitation and double-emission monochromators, and a digital photon-counting photomultiplier. Slit widths were set to 2 nm band-pass on both excitation and emission. Correction for variations in lamp intensity over time and  $\lambda$  was achieved using a reference silicon photodiode.

## 3.4.2. Synthesis of poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,7-(9,9-didodecylfluorene)] (PF)

A 250 mL flask equipped with a magnetic stir bar charged with toluene (36 mL), aqueous potassium carbonate (24 mL, 2 M), 9,9-didodecyl-2,7-dibromofluorene (1.3212g, 2mmol), and 9,9-dioctylfluorene-2,7-bis(trimethylene) borate (1.1168g, 2 mmol), then the mixture was bubbled with N<sub>2</sub> for 15 min, degassed via three freeze- pump-thaw cycles, and the flask was then back-filled with Ar. A catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> (1.0 mol %) was added, and the resulting mixture was stirred at 85 °C under Ar for 48 h. After cooling to room temperature the solution poured into 500 mL mixture of methanol and de-ionized water (10:1), and filtered. Then the solid dissolved in small amount of THF and reprecipitated into methanol (500 mL), washed with methanol, water and acetone (300 mL each) respectively. After dried in vacuum for 20 h at 50 °C, a greenish yellow solid was obtained in 84 % yield. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.85 (br, 8 H), 7.65 (br, 4 H),

2.09 (br, 8 H), 1.13 (br, 56 H), 0.73 (br, 20 H). UV-Vis (THF):  $\lambda_{max} = 380$  nm; UV-Vis (film): PL (THF):  $\lambda_{em} = 416$ , 440 nm. GPC:  $M_n = 9$  kg/ mol,  $M_w/M_n = 1.6$ .

### 3.4.3. Synthesis of poly[(2,7-(9,9-dioctylfluorene)-alt-2,5-(3-dodecylthiophene)] (PFT)

A 250 mL flask equipped with a magnetic stir bar charged with DMF (40 mL), Cs<sub>2</sub>CO<sub>3</sub> (7.5g, 23 mmol), and 9,9-dioctylfluorene-2,7-bis(trimethylene )borate (1.117g, 2 mmol). 2,5-dibromo-3-dodecyl-thiophene (0.820 g, 2 mmol) in 10 mL of toluene was added, then the mixture was bubbled with N<sub>2</sub> for 15 min, degassed via three freeze-pump-thaw cycles, and the flask was then back-filled with Ar. A catalytic amount Pd(PPh<sub>3</sub>)<sub>4</sub> (1.0 mol %) was added, and the resulting mixture was stirred at 100 °C under Ar for 24 h. After cooling to room temperature, the solvent was evaporated, and the residue was dissolved in a minimum amount of THF and then precipitated into methanol (500 mL). The precipitate was filtered, and the solid was washed with methanol, water and acetone, (300 mL each) respectively. After drying under vacuum for 20 h at 50°C, a greenish yellow solid was obtained in 91 % yield. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.75-7.47 (m, 6 H), 7.32 (s, 1 H), 2.75 (br, 2 H), 2.04 (br, 4 H), 1.72 (br, 2 H), 1.26-0.81 (m, 49 H). UV-Vis (THF):  $\lambda_{max} = 405$  nm; PL (THF):  $\lambda_{em} = 458$ , 488 nm. GPC: M<sub>n</sub> = 15kg/mol, M<sub>w</sub>/M<sub>n</sub> = 2.7.

## 3.4.4. Synthesis of poly(3-dodecylthiophene) (PT)

A suspension of anhydrous  $\text{FeCl}_3$  (2.59 g, 16 mmol) in 100 mL of freshly distilled CHCl<sub>3</sub> was stirred for 15 min, a dark green solution with some residue  $\text{FeCl}_3$  was

obtained, and 3-dodecyl thiophene (1g, 4mmol) solution in 50 mL freshly distilled CHCl<sub>3</sub> was added dropwise over a period of 60 min. The mixture was stirred for 15 h at room temperature, and then added slowly to 600 mL MeOH. The resulting black precipitate was dissolved in 100 mL CHCl<sub>3</sub> and 5 mL of concentrated aqueous ammonia and stirred for 15 min at room temperature. Some insoluble materials was filtered, the organic phase was washed with water 3 times. Then the concentrated solution was precipitated in methanol, washed with methanol, acetone, and then dried in vacuum at 50 °C for 24 h. Dark red solid was obtained in 61 % yield. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta = 7.00$  pm( b,1H),  $\delta = 2.80$  pm( b, 2H),  $\delta = 1.66-0.87$  pm(m, b, 10H). UV-Vis (THF):  $\lambda_{max} = 435$  nm; PL (THF):  $\lambda_{em} = 564$  nm GPC: M<sub>n</sub> = 48kg/ mol, M<sub>w</sub>/M<sub>n</sub> = 1.5

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# Chapter 4: The Effect of Molecular Weight on the Supramolecular Interaction Between a Conjugated Polymer and Single-Walled Carbon Nanotubes

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The work detailed in this chapter was carried out in collaboration with Dr. Fuyong Cheng (Department of Chemistry and Chemical Biology, McMaster University). Both Patigul Imin and Fuyong Cheng contributed equally to the experimental planning of this work. All of the experimental data was collected by Patigul Imin, and paper was written by Patigul Imin.

## Abstract

The synthesis and fractionation of poly[(2,7-(9,9-dioctylfluorene)-alt-2,5-(3-dodecylthiophene)] resulted in the isolation of eight different molecular weight (M<sub>W</sub>) samples ranging from M<sub>n</sub> of 5 to 85 kg/mol. These individual polymer samples were fully characterized by Gel Permeation Chromatography, Nuclear Magnetic Resonance, as well as absorption and fluorescence spectroscopy. Each sample was separately mixed and ultrasonicated with single-walled carbon nanotubes (SWNTs) in THF, and the nanotube concentration within the resulting solutions was measured. It was found that the solubility of the polymer-SWNT complexes strongly depends on the M<sub>W</sub> of the conjugated polymer, with a maximum concentration reached when M<sub>W</sub> ranged between 10 and 35 kg/mol. Higher and lower M<sub>W</sub>s resulted in substantially reduced nanotube concentrations.

## 4.1. Introduction

Carbon nanotubes (CNTs) have attracted significant interest in both academic and industrial research due to their exceptional mechanical, optical, and electronic properties.<sup>1</sup>,  $^{2}$  The potential displayed by carbon nanotubes within a variety of applications, including photovoltaic devices, field-effect transistors, and chemical sensors, has motivated the development of functionalization and processing methods that can be applied to these remarkable nanostructures.<sup>3-6</sup> The low solubility and poor dispersability of unmodified carbon nanotubes within almost all common organic and aqueous solvents represents a significant hindrance in many of these potential applications. In attempt to solve this problem, surface modification techniques have been developed in recent years, including covalent side-wall coupling and non-covalent functionalization, that enable the effective dispersion of individual carbon nanotubes within solvents and polymeric host materials.<sup>7-</sup> <sup>12</sup> Although covalent functionalization strategies have been shown to significantly improve the solubility of CNTs in various organic and aqueous solvents, this process causes disruption of the perfectly conjugated side-wall structure of CNTs and diminishes the electronic and mechanical properties of the resulting materials.<sup>13, 14</sup> In contrast, supramolecular functionalization of carbon nanotubes with polymers or ionic surfactants provides an effective approach by which the solubility of carbon nanotubes can be enhanced while retaining all their intrinsic properties.

Recently, much attention has been paid to the use of conjugated polymers as nanotube dispersing agents, owing to their ability to strongly adsorb onto the nanotube surface via  $\pi$ - $\pi$  interactions.<sup>15-26</sup> This approach displays significant promise, allowing the

incorporation of CNTs within a conjugated polymer matrix to produce polymer-nanotube composites displaying impressive conductivity and solution-phase processability, as well as improved mechanical and optical properties. Fluorene-and thiophene-based polymers are of particular interest with respect to the preparation of CNT composites due to their good solubility, processability, and unique opto-electronic characteristics.<sup>27-30</sup> Several groups, have reported the use of commercially available polyfluorene homopolymers and copolymers for the solubilization of single walled carbon nanotubes (SWNTs). In this work, it was shown that the dispersability of the carbon nanotubes is highly influenced by the length of side chains and the precise structures of the aromatic repeat units.<sup>31-39</sup>

We recently reported that both polyfluorene and poly(fluorene-*alt*-thiophene) can form strong supramolecular complexes with SWNTs, imparting excellent solubility and solution stability in the absence of excess free polymer.<sup>40, 41</sup> In this work, it was noted that high nanotube solubility was obtained when polymers having a molecular weight of approximately 10 kg/mol were used. Although it is well established that the molecular weight of a polymer directly influences its optical and physical properties, only a limited number of studies have been carried out to determine the effect of polymer molecular weight on nanotube solubility.<sup>42, 43</sup>

In this study, poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,5-(3-dodecylthiophene)] (PFT) was employed as a model compound. Using recycling preparative GPC, a PFT sample of broad polydispersity (3.2) was fractionated to isolate eight different polymer fractions  $(M_n = 5 - 85 \text{ kg mol}^{-1})$  with relatively narrow polydispersity (~ 1.7). The structural and optical properties of each fraction were characterized by <sup>1</sup>H-NMR, UV-Vis absorption,

and fluorescence spectroscopy. Additionally, the ability of each of these polymer fractions to effectively disperse the SWNTs in THF was subsequently evaluated.

#### 4.2. Results and Discussion

The synthesis of PFT was accomplished via palladium-catalyzed Suzuki coupling starting from 9,9-dioctylfluorene-2,7-bis(trimethylene)borate and 2,5-dibromo-3-dodecylthiophene in a mixture of DMF and toluene (4:1 v/v), as depicted in Scheme 4.1.<sup>40</sup> The resulting polymer was found to be readily soluble in common organic solvents such as THF, chloroform, dichloromethane, toluene, and dichlorobenzene. The polymerization, which proceeds via an uncontrolled step-growth process, yielded polymer with high polydispersity. Gel Permeation Chromatography (GPC) analysis, using THF as the mobile phase and polystyrene standards, indicated a number average molecular weight (M<sub>n</sub>) of 14 kg/mol with a polydispersity index (PDI) of 3.2. The GPC chromatogram of as-produced PFT (Figure 4.1A) clearly shows the breadth of the molecular weight distribution. In order to separate this as-produced sample into a series of samples of different molecular weight, it was subjected to several rounds of recycling preparative GPC, resulting in the isolation of eight different fractions having M<sub>n</sub> values ranging from approximately 5 to 85 kg/mol, each having a PDI of 1.7 or lower (Table 4.1). The GPC chromatograms for each of these samples are shown in Figure 4.1B.



Scheme 4.1. Synthesis of PFT.



**Figure 4.1.** GPC chromatogram of PFT (A) and normalized GPC chromatograms of PFT fractionations (B).

Polymer Fractions (PFT)	$M_n/g mol^{-1}$	PDI	$UV_{\lambda max}/nm$
a	83 000	1.5	418
b	60 000	1.6	412
с	42 200	1.5	410
d	34 000	1.7	408
e	19 000	1.6	406
f	14 000	1.6	404
g	11 000	1.7	402
h	5 700	1.6	398

**Table 4.1.** Molecular Weight and Absorption Data (in THF as the solvent) for PFT.

The structure of the fractionated polymer samples was further investigated by <sup>1</sup>H-NMR spectroscopy. Figure 4.2 shows the <sup>1</sup>H-NMR spectra of the samples with highest (fraction **a**), intermediate (fraction **e**), and lowest (fraction **h**) molecular weight. All of the expected aliphatic and aromatic proton signals are clearly observable in these spectra. In particular, the distinct positions of the  $\alpha$ -methylene protons of the side chains on both the thiophene monomer (2.75-2.64 ppm) and the fluorene monomer (2.05 ppm) allow confirmation of the alternating copolymer structure. The integration of these signals provides the expected 1:2 molar ratio, consistent with the fact that the thiophene units exhibit a single aliphatic side chain, while the fluorene units are decorated with two. Additionally, small triplets (at 2.64 and 2.60 ppm) are observed adjacent to the  $\alpha$ methylene signal (2.75 ppm) within the thiophene units, which are attributed to the  $\alpha$ methylene protons in the terminal thiophene ring  $^{44-46}$ . The signals from the end group protons are negligible in the highest molecular weight fraction (fraction  $\mathbf{a}$ ), and the intensity of these signals increases with decreasing polymer molecular weight. The two separate triplets at different resonance frequency in the lowest molecular weight fraction (g) are likely due to the two different regiochemical isomers possible for the terminal thiophene unit. The molecular weight of the polymer can be estimated from the integration of the  $\alpha$ -methylene protons of the terminal thiophene to those present throughout the polymer main chain. Based on this <sup>1</sup>H-NMR data, the molecular weight of polymers **a**, **e** and **h** was found to be 40.0 kg/mol, 11.5 kg/mol and 5.0 kg/mol, respectively. For the lower molecular weight fractions, these NMR values are in surprisingly good agreement with the molecular weight measurements from GPC.



**Figure 4.2.** <sup>1</sup>H-NMR spectra of the PFTs, fractions a, e, and h, in CDCl<sub>3</sub>. Insets show magnified views of the aromatic (6.8-8.0 ppm) and aliphatic (2.4-3.0 ppm) regions.

Further characterization of the separated polymer fractions by UV-Vis spectroscopy shows that, as the molecular weight increases, the  $\lambda_{max}$  values shift bathochromically from 398 nm to 418 nm (Table 4.1 and Figure 4.3A). This observation is consistent with previous reports for similar conjugated polymers.<sup>46, 47</sup> The emission spectra of the separated polymer fractions, excited at their individual absorption maxima and normalized for absorption intensity, are given in Figure 4.3B. This data shows no obvious changes in the emission maxima or intensities as a function of polymer molecular weight, which is again similar to what has been observed previously with comparable polymers.<sup>48</sup>



**Figure 4.3.** UV-Vis absorption (A) and normalized emission spectra (B) of the individually fractionated PFT samples.

The supramolecular interaction of PFT with SWNTs was studied using our previously reported methods.<sup>40, 41, 49</sup> Our prior experimental results showed that PFT can form strong supramolecular complexes with SWNTs. In order to determine the effect of polymer molecular weight on carbon nanotube solubility within the present polymer-SWNT complexes, polymer-nanotube composites containing various weight percentages of PFT were prepared using bath sonication. In a typical procedure, 2.5 mg of carbon nanotubes were added to the polymer solution in 5 mL THF with varying polymer concentration. This mixture was sonicated for 30 min, and the resulting solution was centrifuged at 2576 g for 20 min. The vials were then kept undisturbed overnight. 1 mL of the supernatant was transferred to a 50 mL standard volumetric flask using a pipette, and further diluted with THF. Solubility of the nanotubes within each sample was quantified using a spectrophotometric method in which a specific extinction coefficient for SWNTs at 700 nm,  $\varepsilon_{700} = 2.35 \times 10^4$  cm<sup>2</sup>g<sup>-1</sup>, was used.<sup>22</sup> The polymer-SWNT

absorption at this wavelength originates solely from SWNTs, allowing estimation of the nanotube concentration without interference from polymer absorption, which was negligible at 700 nm.

In order to determine the optimal amount of polymer in the polymer-nanotube mixtures used to prepare solutions, the polymer:nanotube ratio was increased from 1:1 to 4:1 (wt./wt.). As expected, the concentration of nanotubes in solution increased with increasing polymer content from the 1:1 ratio to the 3:1 ratio. However, when the polymer:nanotube ratio was increased to 4:1, quantitative flocculation and gelation of the mixture was observed. At this ratio, centrifugation resulted in complete precipitation of the nanotubes, leaving a clear, colourless polymer solution in the supernatant. The exact reason for this flocculation is unknown, and will be investigated in future studies. Since the highest nanotube solubility was obtained at a polymer:nanotube weight ratio of 3:1, this ratio was used for subsequent studies of the impact of polymer molecular weight.

Interactions of SWNTs with the individual fractionated PFT samples were investigated by mixing these components in THF, as described above. For each polymer fraction, a minimum of 3 separate solutions were prepared and measured, and the average SWNT concentration for each polymer fraction was recorded. Figure 4.4 shows a plot of nanotube concentration as a function of polymer molecular weight. From this data, it is clear that the highest nanotube solubility, in the range of 500 to 800 mg/L, was obtained with polymers having intermediate  $M_n$  values of 10 to 35 kg/mol, while at higher or lower molecular weights the solubility was significantly lower. These results suggest that at low  $M_n$ , the  $\pi$ -stacking interaction between the oligomers and the nanotube surface is not strong enough to prevent re-aggregation of nanotubes into bundles. At molecular weights from 10 to 35 kg/mol, the polymers can form strong supramolecular complexes with nanotubes and enhance nanotube solubility to a significant degree. However, at polymer molecular weights greater than 35 kg/mol, a significant decrease of nanotube solubility was observed. This behaviour is attributed to the fact that the PFT polymer is itself not very soluble at high molecular weight. It is likely that aggregation of the higher molecular weight polymers with one another competes with the interaction of these polymers with the nanotube surface, leading to a decreased level of nanotube functionalization. However, further investigation of this phenomenon is required in order to fully understand the observed behaviour.



**Figure 4.4.** Plot of SWNT concentration as a function of PFT molecular weight in THF. Error bars represent the standard deviation from three separately-prepared samples.

### 4.3. Conclusion

PFT was synthesized, and the resulting polymer was successfully fractionated into eight different molecular weight fractions ranging from 5 to 85 kg/mol using recycling preparative GPC. The supramolecular interaction of these polymers with HiPco SWNTs was investigated, and it was found that the solubility of the resulting polymer-SWNT complexes strongly depends on the molecular weight of the polymer. In THF, the SWNT concentration reached a maximum when the polymer molecular weight was in the range of 10-35 kg/mol, while higher and lower molecular weights resulted in much lower solubility. Although this study focused upon the interactions of the PFTs with Hipco SWNT, we believe that these results are applicable to other conjugated polymer-SWNT systems.

#### 4.4 Experimental

#### 4.4.1. General

Single-walled carbon nanotubes (SWNTs) were purchased from Carbon Nanotechnologies, Inc. (Houston, TX). All reagents and solvents were purchased from commercial suppliers and used as received. Ultrasonication was carried out in either a Branson Ultrasonics B1510 or B2500 bath sonicator. Filtration was performed through a 450 nm-pore Teflon membrane (Millipore). Polymer molecular weight and polydispersity index (PDI) were estimated from gel permeation chromatography (GPC) analyses by using a Waters 2695 Separations Module equipped with a Waters 2996 photodiode array detector, a Waters 2414 refractive-index detector, a Waters 2475 fluorescence detector, and four Polymer Labs PL gel individual pore-size columns. Polystyrene standards were

used for calibration, and THF was used as the eluent at a flow rate of 1.0 mL/min. The concentrations of the soluble polymer-functionalized SWNTs were calculated from UV-Vis absorption spectra measured using a Cary 50 UV-Vis spectrophotometer. Fluorescence spectra were measured using a Jobin-Yvon SPEX Fluorolog 3.22 equipped with a 450 W Xe lamp, double-excitation and double-emission monochromators, and a digital photon-counting photomultiplier. Slit widths were set to 2 nm band-pass on both excitation and emission. Correction for variations in lamp intensity over time and  $\lambda$  was achieved using a reference silicon photodiode. NMR spectra were measured on Bruker AV 600 MHz spectrometer, the nondeuterated solvent signal was used as the internal standard for <sup>1</sup>H-NMR spectra.

## 4.4.2. Synthesis of poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,5-(3-dodecylthiophene)] (PFT)

A 250 mL flask equipped with a magnetic stir bar was charged with 40 mL DMF,  $Cs_2CO_3$  (7.5g, 23 mmol), and 9,9-dioctylfluorene-2,7-bis(trimethylene)borate (1.117g, 2 mmol). 2,5-dibromo-3-dodecyl-thiophene (0.820 g, 2 mmol) in 10 mL of toluene was added, then the mixture was bubbled with N<sub>2</sub> for 15 min, degassed via three freeze-pump-thaw cycles, and the flask was then back-filled with Ar. A catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> (1.0 mol %) was added, and the resulting mixture was stirred at 100°C under Ar for 24 h. After cooling to room temperature, the solvent was evaporated, and the residue was dissolved in a minimum amount of THF and then precipitated into methanol (500 mL). The precipitate was filtered, and the solid was washed with methanol, water and acetone, (300 mL each) respectively. After drying under vacuum for 20 h at 50°C, a greenish

yellow solid was obtained in 91 % yield. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 600 MHz): 1.26-0.81 (m, 49 H), 1.72 (br, 2 H), 2.04 (br, 4 H), 2.75 (br, 2 H), 7.32 (s, 1 H),  $\delta$  7.75-7.47 (m, 6 H), UV-Vis (THF):  $\lambda_{max}$  = 408 nm; PL (THF):  $\lambda_{em}$  = 458, 488 nm. GPC: M<sub>n</sub> = 14 kg/mol, M<sub>w</sub>/M<sub>n</sub> = 3.2.

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Chapter 5: Supramolecular Functionalization of Single Walled Carbon Nanotubes (SWNTs) with Dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP) Containing Conjugated Polymers

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Both Patigul Imin and Mokhtar Imit contributed equally to the experimental planning, polymer synthesis and characterization. Nanotubes functionalization and characterization was conducted by Patigul Imin.

## Abstract

Fluorene and dithieno[3,2-b:2',3'-d]pyrrole (DTP) containing conjugated polymers, {2,7-[9,9-didodecylfluorene]-*alt*-2,6-[N-dodecyldithieno(3,2-*b*:2',3'-*d*)pyrrole]} (PF-DTP1) {2,7-[9,9-didodecylfluorene]-*alt*-2,6-[N-3,4,5(nand dodecyloxy)phenyldithieno(3,2-b:2',3'-d)pyrrole]} (PF-DTP2) have been successfully synthesized using Suzuki polycondensation. These polymers possess excellent thermal stability with decomposition temperatures over 365°C under Ar. The introduction of soluble side chains on the DTP units and incorporation with soluble dialkyl substituted fluorene resulted in highly soluble polymers with novel opto-electronic properties. The supramolecular complex formation of these DTP containing polymers with single-walled carbon nanotubes (SWNTs) has been studied, and it was found that these polymers can form strong supramolecular polymer-nanotube assemblies and produce stable complexes in solution. UV-Vis-NIR absorption, photoluminescence excitation (PLE), and Raman spectroscopy were used for the characterization and identification of the nanotube species that are present in THF solution. The strong nanotube emission was observed from individual SWNTs even after removal of excess free polymer by filtration and washing. Based on these two polymers, it was found that the interactions with the SWNT surface are more strongly dictated by the polymer backbone than the side chain, though further studies may be warranted.

## **5.1 Introduction**

Single-walled carbon nanotubes (SWNTs) are of special interest in current research due to their extraordinary mechanical, electronic and optical properties.<sup>1-5</sup> Their unique structure, remarkable thermal and electrical conductivity, and high mechanical strength make SWNTs viable candidates for a wide range of device applications, including chemical sensors,<sup>6-8</sup> field-effect transistors,<sup>9</sup> nano-scale integrated radio receivers,<sup>10, 11</sup> photovoltaics,<sup>12-14</sup> and field-emission displays.<sup>3, 15</sup> However, the inherent insolubility of carbon nanotubes in most organic and aqueous solvents has hindered the widespread application of these novel nanostructures. Therefore, a great deal of research has been focused on functionalization of SWNTs, mainly to enhance their solubility and solution phase processability.<sup>5, 16, 17</sup> The supramolecular functionalization methodology has received much recent attention because this approach does not introduce any defects in the nanotube sidewall, thus preserving the electrical and mechanical properties of the resulting materials.<sup>18-20</sup>

Recently, it has been shown that various conjugated polymers form strong supramolecular complexes with SWNTs, enabling their dissolution in organic solvents, as well as water, depending on the nature of the side chain.<sup>19, 21-28</sup> Among all conjugated polymers, fluorene- and thiophene-containing conjugated polymers are of particular interest due to their good solubility, processability, and unique opto-electronic properties.<sup>14, 26, 29-36</sup> Recently, it has been found that fluorene- and thiophene-containing conjugated polymers, and exhibit excellent solubility and solution stability properties even after removal of excess free polymer.<sup>27, 29</sup>

Interest in this class of conjugated polymers has gained much recent popularity as reports of selective solubilization of certain SWNT species have begun to be published.<sup>20, 30, 31, 37, 38</sup> It is therefore desirable to develop a detailed understanding of how variations in the backbone or the side chain of a conjugated polymer can affect the interactions between the polymer and the SWNT surface. In particular, structural components that increase the strength of polymer binding to the nanotube surface are of significant interest. Although the fused-ring precursors of polythiophenes should result in stronger nanotube binding behavior when compared to the previously reported alkylthiophene-containing analogs due to the planarity of the fused thiophene rings, the noncovalent functionalization of carbon nanotubes with dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP)-containing conjugated polymers has not been reported.

Conjugated polymers containing dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP) units exhibit lower band gaps when compared to the alkylthiophene-containing analogs due to better  $\pi$ -conjugation across the fused thiophene rings.<sup>39-46</sup> In addition, the conjugated polymers having DTP units in their backbone exhibit interesting optoelectronic properties, making them potentially useful in a variety of device applications including field effect transistors,<sup>39, 47</sup> photovoltaic cells,<sup>41, 44</sup> and other optoelectronic devices.<sup>45, 46, 48</sup> Furthermore, it has been shown that the optoelectronic properties of the DTP containing polymers can be easily tailored by altering the composition of the polymer backbone and side chains.<sup>39, 46, 49</sup> In an attempt to produce a new type of functional nanostructure, we have focused our attention on supramolecular functionalization of carbon nanotubes with DTP and fluorene containing conjugated polymers. In order to improve the solubility of the resulting polymers and their supramolecular complexes with SWNTs, the polymer backbone was composed of DTP and fluorene units having long alkyl side-chains, and two copolymers were prepared that have an identical aromatic backbone, but differ in the solubilizing substituents. Here we report the full details of the monomer and polymer preparation, studies of the supramolecular complex formation properties of these polymers with SWNTs, as well as complete optoelectronic and photo physical characterization of the resulting materials. The effect of changing side chains of the polymer on the interaction between polymer and nanotubes was also investigated.

#### 5.2. Results and Discussion

Scheme 5.1 and Scheme 5.2 show the synthetic route to the target monomers. 3,3'dibromo-2,2'-bithiophene (**2**) was synthesized according to literature procedures starting from bithiophene in two steps.<sup>50, 51</sup> 3,4,5–tri(n-dodecyloxy)aniline (**7**) was prepared according to a slightly modified literature procedure starting from 1,2,3– trihydroxybenzene.<sup>52-54</sup> The N-substituted dithieno [3,2-b:2',3'-d]pyrrole precursors (compounds **3** and **8**) were prepared from primary amines and 3,3'-dibromo-2,2'bithiophene using the Buchwald-Hartwig reaction.<sup>41, 47, 55</sup> In both cases the reactions were carried out in toluene under reflux overnight, with 2,2'-bis(diphenylphosphino)-1,1'binaphthyl (BINAP) as the ligand and tris(dibenzylideneacetone)dipalladium(0) (Pd<sub>2</sub>(dba)<sub>3</sub>) as the Pd-source. The reaction products were isolated by simple column chromatography with high yields. By using a slight excess of dodecylamine, we were able to obtain N-dodecyldithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP) (compound **3**) in over 95% yield. When N-dodecyldithieno[3,2-*b*:2',3'-*d*]pyrrole was treated with N-bromosuccinimide (NBS) in CHCl<sub>3</sub>/DMF at 0°C, the target compound 2,6-dibromo-N-dodecyldithieno[3,2b:2',3'-d] pyrrole (compound **4**) was successfully synthesized in 71% yield.<sup>56</sup> However, when a similar reaction procedure was followed for compound **8**, the bromination occurred not only at the 2 and 6 positions of the DTP ring, but also on the phenyl ring due to the presence of the three activating alkoxy groups. We therefore investigated iodination as an alternative, more regioselective route to the desired monomer. The diiodo substituted N-3,4,5(n-dodecyloxy)phenyldithieno[3,2-*b*:2',3'-*d*]pyrrole was successfully synthesized using N-iodosuccinimide (NIS) in CHCl<sub>3</sub> at 0°C.<sup>52</sup>



Scheme 5.1. Synthetic routes to monomer 4



Scheme 5.2. Synthetic routes to monomer 9

The polymers PF-DTP1 and PF-DTP2 were prepared using a Suzuki polycondensation from 9,9-didodecylfluorene-2,7-bis(trimethyleneboronate) and the corresponding N-substituted-dithieno[3,2-*b*:2',3'-*d*]pyrrole monomers (compound **4** and **9** respectively) as depicted in Scheme  $5.3.^{27, 29}$  Preparation of these polymers was performed in a mixture of DMF and toluene (3:1 v/v) as the solvent and tetrakis(triphenylphosphine) palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>) as the polymerization catalyst. In both cases polymers were obtained as orange solids in yields of over 80%. The crude polymers were purified by precipitation twice in methanol. Both polymers exhibited excellent solubility in common organic solvents such as THF, chloroform, and dichlorobenzene at room temperature, which can be attributed to the bulky side-chains. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) with polystyrene standards and mixture of THF and 1% of acetonitrile as the mobile phase. The molecular weight (M<sub>n</sub>) and polydispersity index (PDI) values of the polymers are listed in Table 5.1.



Scheme 5.3. Synthetic route to the polymers

Polymer	$M_n \left( kg/mol  ight)^a$	PDI	M <sub>n</sub> (kg/mol) <sup>b</sup>
PF-DTP1	10.8	6.1 <sup>c</sup>	11.0
PF-DTP2	18.5	6.2 <sup>c</sup>	14.5

**Table 5.1.** Molecular weight and polydispersity index values for the synthesized polymers.

<sup>a</sup>Measured by GPC, <sup>b</sup>Estimated by NMR, <sup>c</sup>GPC chromatogram of the polymers showed a broad bimodal distribution.

The chemical structures of polymers (PF-DTP1 and PF-DTP2) were confirmed by <sup>1</sup>H-NMR spectroscopy (Figure 5.1). The single peak at 7.32 ppm (Figure 5.1A) corresponds to the aromatic protons from DTP, and the peaks at 7.60-7.66 ppm correspond to the aromatic protons of fluorene. On the basis of the relative areas of these peaks, the molar ratio of fluorene and DTP was determined to be 1:1 in both polymers, which is consistent with the alternating copolymer structure expected from the Suzuki polycondensation of the monomers. Phenyl groups were also successfully introduced at both ends of the polymer as end-caps, and the two sets of doublets at 7.01, 7.15 ppm for PF-DTP1 and 7.15, 7.20 for PF-DTP2 (Figure 5.1) were assigned as the end group phenyl protons.<sup>57</sup> This end group assignment was also confirmed by the 2-dimensional proton-proton correlation spectrum (<sup>1</sup>H-<sup>1</sup>H COSY), heteronuclear single quantum correlation spectrum (<sup>1</sup>H-<sup>13</sup>C HSQC), and heteronuclear multiple bond correlation spectrum (<sup>1</sup>H-<sup>13</sup>C HSQC) are proton (or DTP proton

the end-group proton signal, the average degree of polymerization (DP) and  $M_n$  were be estimated. The DP and  $M_n$  values were calculated to be 13 and 11.0 kg/mol for PF-DTP1, and 11 and 14.5 kg/mol for PF-DTP2, respectively. It should be noted that, although the two polymers have identical backbone structures, the different side-chains impart significant differences to their solubility. Not surprisingly, the larger and branched side chain of PF-DTP2 results in a more easily soluble material. Although both polymers were fully soluble in THF, chloroform, and dichloromethane, dissolution of PF-DTP2 occurred much faster relative to PF-DTP1.



**Figure 5.1.** <sup>1</sup>H-NMR spectra of the polymers in CDCl<sub>3</sub>. Insets show magnified view of the aromatic (6.5-7.9 ppm) regions.

The thermal stability of PF-DTP1 and PF-DTP2 was characterized by thermogravimetric analysis (TGA), carried out under an Ar atmosphere (Figure 5.2). These data indicate that it is not possible to completely decompose the two polymers by heating to 800°C under Ar. The major mass loss occurs at 375°C for PF-DTP1,

amounting to 48%, and 365°C for PF-DTP2, amounting to 59%. These mass losses correspond well with the loss of side chains within these polymers. Interestingly, PF-DTP2 exhibits a second decomposition, amounting to approximately 8% at 491°C, which corresponds to the loss of the benzene ring from each repeat unit.



**Figure 5.2.** Thermograms of PF-DTP1 (A) and PF-DTP2 (B) measured under Ar atmosphere.

The supramolecular interaction of PF-DTP1 and PF-DTP2 with SWNTs was studied using our previously reported methods.<sup>29</sup> In a typical experiment, a SWNT sample (5 mg) was added to a solution of polymer in THF (15 mg/20 mL), and the mixture was ultrasonicated in a bath sonicator for 1h. The resulting solution was centrifuged for 45 min at 8,300 g, and allowed to stand overnight. The supernatant was carefully transferred by pipette to another vial, producing dark colored and stable polymer-nanotube complex solutions. The isolated supernatant was further diluted with 50 mL of THF, sonicated for 5 min, filtered through a 200 nm pore diameter Teflon membrane, and repeatedly washed with THF until the filtrate was colorless, ensuring removal of all excess free polymer. 20 mL of THF was added to the recovered SWNT residue and the vial was further sonicated

for 5 min. The resulting dark suspension was centrifuged at 8,300 g for 30 min and allowed to stand overnight undisturbed. It was found that the resulting polymer-SWNT complexes exhibited very good solubility and the solutions remained stable for periods of at least 3 months with no observable precipitation.

The UV-Vis absorption properties of polymers and their corresponding SWNT complexes were measured at room temperature in THF (Figure 5.3). Due to the high solubility of the polymer-SWNT complexes, all solutions prepared in THF were diluted more than 20-fold in order to make them suitable for absorption and photoluminescence (PL) studies. For reference, the absorption spectra of just the nanotubes, measured from aqueous suspensions with sodium dodecylbenzenesulfonate (SDBS) surfactant, are also shown in Figure 5.3. PF-DTP1 and PF-DTP2 exhibited an absorption maximum ( $\lambda_{max}$ ) of 485 (with a low-energy shoulder at 516 nm), and 480 nm (with a low-energy shoulder at 509 nm) in THF, respectively. The overall absorption profiles of the PF-DTP1and PF-DTP2 were very similar.<sup>48, 49</sup>



**Figure 5.3.** UV-Vis absorption data from polymer, SDBS-SWNT, and polymer-SWNT complexes for PF-DTP1 (A) and PF-DTP2 (B).

From comparison of the polymer-SWNT absorption spectrum and that of the free polymer, it is clear that the absorption characteristics of both polymer and SWNTs are evident in the polymer-SWNT absorption spectra. To emphasize the absorption properties of the nanotube-adsorbed polymer, the nanotube component of the polymer-SWNT complex spectra was subtracted to give the subtraction curves shown in Figure 5.3 for each of the two polymers (curve labeled "Subtraction"). From these subtraction spectra, it appears that the shoulder peaks at lower-energy became much more dominant in polymer-SWNT complexes, relative to the free polymer, most likely because of increased electron delocalization.<sup>48</sup> These results indicate that the polymer backbone becomes more planar on the nanotube surface, leading to an enhanced effective conjugation length within the polymer.<sup>27, 29</sup>

The fluorescence spectra of the free polymers and polymer-SWNT complexes were also measured in THF. Both PF-DTP1 and PF-DTP2 exhibited strong emission in solution (Figure 5.4). From the normalized emission spectra it is clear that highly efficient quenching of fluorescence occurs when the polymers are adsorbed on the nanotube surface. The fluorescence quenching is likely the result of photoinduced energy or electron transfer between the excited-state conjugated polymer and the SWNT, as previously reported for other systems.<sup>18, 31, 58</sup>



**Figure 5.4.** Emission spectra of free polymer and polymer-SWNT complexes using PF-DTP1 (A) and PF-DTP2 (B) polymers, with the excitation wavelength set to the absorption maximum of each sample (485 nm for PF-DTP1 and PF-DTP1+SWNT, 480 for PF-DTP2 and PF-DTP2+SWNT respectively).

TEM analysis of the polymer-SWNT complexes revealed the presence of numerous structures resembling individual polymer-coated nanotubes. The high solubility of these complexes in THF allowed deposition and observation of large numbers of SWNT on the TEM grid. However, practically all sample preparation methods resulted in nanotubes localizing on the carbon film of the holey carbon coated TEM grids, diminishing the contrast between the nanotube features and the carbon background. Only a few regions were found with nanotubes spanning holes, where the contrast was great enough for high-resolution imaging. Such images from the PF-DTP1+SWNT sample are given in Figure 5.5. In particular, Figure 5.5C shows the presence of individual, exfoliated SWNTs that are wrapped with polymer chains. From this image, it is clear that nanotubes are separated from bundles by the interaction with the conjugated polymer,

consistent with the absorption and emission properties of the polymer-SWNT complexes presented below. For the PF-DTP2+SWNT sample, the same general features were observed (see Appendix I: Figure A.8), but regions where the sample cleanly spanned a hole could not be found. It should be noted that a large number of iron nanoparticles were also observed within the sample, which are introduced during the synthesis of the raw HiPco SWNTs that were used in this study without any purification.



**Figure 5.5.** TEM images of PF-DTP1+SWNT at different magnifications. The highmagnification image clearly shows the presence of individual polymer-wrapped SWNTs. Scale bars are 500 nm (A), 100 nm (B), and 10 nm (C).

Photoluminescence excitation maps (PLE) of the samples were measured over a large range of excitation (300-900 nm) and emission (900-1450 nm) wavelengths. As the absorption ( $E_{22}$ ) and emission ( $E_{11}$ ) properties strongly depend on the type of the carbon nanotubes, the semiconducting species that are present in solution can be easily identified.<sup>59, 60</sup> Figure 5.6 depicts the photoluminescence excitation (PLE) maps of SWNTs dispersed in THF using the DTP containing polymers (PF-DTP1 and PF-DTP2 respectively), which can be compared to the PLE maps of an aqueous dispersion using

SDBS. High intensities are displayed in red and low intensities are displayed in blue. The chiral indices (n, m) for the identified species are labeled on the maps, where the assignment was based on the previously reported results from Weisman and coworkers.<sup>59</sup>, <sup>60</sup> Figure 5.6A shows the PLE map of the pristine SWNT sample dispersed in  $D_2O$  using SDBS, where 17 different semiconducting nanotubes were detected.<sup>20, 60</sup> When the same material was mixed with polymers PF-DTP1 and PF-DTP2 in THF, entirely different results were obtained. Figures 5.6B and 5.6C depict the PLE maps of the SWNT complexes with PF-DTP1 and PF-DTP2, respectively. The observed strong nanotube emission indicates that individual SWNTs are solubilized and isolated by the polymer, and that removal of free polymer by filtration does not result in any re-bundling. It was found that both excitation and emission wavelengths of the polymer-SWNT complexes were red-shifted relative to the aqueous solution by 10-30 nm (see Appendix I: Table A.1), which is consistent with other previously reported comparable systems.<sup>14, 20, 30, 37</sup> It is obvious from the PLE map that both polymers enable solubilization and isolation of 8 major species including (7,5), (7,6), (8,6), (8,7), (9,4), (9,5), (6,5), and (8,4) in THF, and the relative emission intensity of each solubilized species is slightly different when a different polymer was used (see Appendix I: Table A.2, where the most intense signal of each dispersion was set to a value of 1, and the normalized PLE signal intensities were calculated accordingly). The dominant species within these solutions were found to be (7, 5) and (7, 6) for both polymer-SWNT complexes. Interestingly, signals for both of these nanotube types were not very intense in the PLE maps of the SDBS-SWNT sample in aqueous solution. These results indicate that both polymers may preferentially select nanotubes with a certain diameter range (0.76-1.03 nm).



**Figure 5.6.** PL contour maps of HiPco SWNTs dispersed with SDBS in  $D_2O$  (A), with PF-DTP1 in THF (B), and with PF-DTP2 in THF (C).

UV-Vis-NIR absorption studies were performed on polymer-SWNT complex solutions in THF as well as the aqueous solution of SWNTs dispersed using SDBS. The UV-Vis-NIR absorption spectra are depicted in Figure 5.7A. The absorption spectrum exhibited features that correspond to the first (E<sub>11</sub>) and second (E<sub>22</sub>) interband transitions for semiconducting tubes, which are found from 900 to 1600 nm and 600 to 900 nm, respectively.<sup>61,49</sup> The absorption peaks of the polymer-SWNT complexes become better resolved (Figure 5.7A, curves b and c), and showed relatively stronger semiconducting transitions when compared to the absorption spectrum of SWNTs dispersed in D<sub>2</sub>O using SDBS (Figure 5.7A, a). All of the transitions of polymer-SWNT complexes were found to be red-shifted more than 20 nm relative to the aqueous solution, which is consistent to what was observed in the photoluminescence maps and has been reported previously with comparable polymers.<sup>20, 30, 37</sup> The overall absorption profiles of the polymer-SWNT complexes for both polymers (PF-DTP1 and PF-DTP2) are nearly identical.



**Figure 5.7.** (A) NIR absorption spectra of SDBS/SWNT (a), PF-DTP1+SWNT (b), and PF-DTP2+SWNT (c); (B) Raman data (with excitation at 785 nm) for SDBS/SWNT (a), PF-DTP1+SWNT (b), PF-DTP2+SWNT (c), and pristine SWNT (d), showing only the Radial Breathing Modes of the nanotube samples.

Raman spectroscopy was used to further characterize the polymer-SWNT samples. Sample preparation involved drop casting dilute polymer-SWNT solutions in THF onto a glass microscope slide, and air-drying prior to measurement. Raman measurements were performed in air, using an excitation wavelength of 785 nm (see Appendix I: Figure A.9). It has been reported that the Radial Breathing Mode (RBM) profiles at this excitation wavelength can be used as a valuable tool for evaluating the extent of aggregation occurring in a sample.<sup>62, 63</sup> RBM profiles of the as-received HiPco sample, SDBS-SWNT, as well as the soluble polymer-SWNT complexes are shown in Figure 5.7B. The pristine Hipco SWNTs have five major RBM bands at Raman frequencies of ~281, 250, 243, 233, and 229 cm<sup>-1</sup> (Figure 5.7B, d), which is consistent with what has been observed previously with Hipco nanotubes.<sup>62-65</sup> Small shifts and significant changes in intensity of various bands can be observed when comparing the RBM signals of the solubilized samples to the as received SWNTs. All of the peaks of the polymer-SWNT complexes and SWNT-SDBS show a characteristic red-shift of 3~6 cm<sup>-1</sup> (284, 254, 247, 239, 230) cm<sup>-1</sup>) relative to the equivalent peaks in the spectrum of the starting material. The signal at 284 cm<sup>-1</sup> is much more dominant in spectra of pristine bundled SWNTs, and this feature nearly disappeared in the polymer functionalized samples, as well as the SDBS dispersed sample. This result indicates that the nanotubes are individually dispersed by polymers in solution, and there is no evidence of aggregation when they are drop cast onto the glass substrate. Interestingly, both polymer-SWNT complexes exhibit a strong signal at 247 cm<sup>-1</sup> (corresponding to diameters of ~0.96 nm), indicating that both

polymers selectively bring a specific nanotube species into resonance when excited at 785 nm.

#### **5.3.** Conclusion

We have successfully synthesized a new class of highly soluble alternating copolymers of fluorene and dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP). Thermogravimetric analysis indicated that both polymers exhibit excellent thermal stability under Ar. The resulting polymers were subsequently utilized for the preparation of supramolecular polymer-SWNT composite materials, and excellent nanotube solubility and solution stability was achieved. UV-vis absorption measurements revealed a bathochromic shift in the polymer absorption spectrum as a result of complex formation with nanotubes. Flourescence measurements showed that polymer emission is highly quenched in the corresponding SWNT complexes. Both TEM and Photoluminescence experiments showed that efficient and selective dispersal of SWNT is possible by using the DTP and fluorene containing copolymers. UV-Vis-NIR, photoluminescence, and Raman measurements indicated that the SWNTs were successfully debundled and isolated by polymer in solution, and removal of the free polymer by filtration did not cause further bundling.

#### 5.4. Experemental

#### 5.4.1 General

As-produced (raw) Single-walled carbon nanotubes (SWNTs) were purchased from Carbon Nanotechnologies, Inc. (CNI Lot # Ro217). All other reagents were
purchased from Aldrich Chemical Co. and Acros Organics. NMR spectra were measured on Bruker Avance 200, 500 and 600 MHz spectrometers. High resolution ES-MS measurements were done on the Micromass Ultima Global instrument (quadrupole timeof-flight). UV-Vis, and UV-Vis-NIR spectra were measured on Cary 50 and Cary 5000 spectrophotometers, respectively. Fluorescence spectra were measured using a Jobin-Yvon SPEX Fluorolog 3.22 equipped with a 450 W Xe lamp, double-excitation and double-emission monochromators, and a digital photon-counting photomultiplier. Slit widths were set to 2 nm band-pass on both excitation and emission. Correction for variations in lamp intensity over time and  $\lambda$  was achieved using a reference silicon photodiode. Photoluminescence excitation (PLE) mapping was performed using the same Jobin-Yvon SPEX Fluorolog 3.22 equipped with a 450 W Xe lamp, and fitted with a liquid-nitrogen cooled InGaAs photodiode detector. Slit widths were set to 7 nm bandpass on both excitation and emission, and samples were illuminated in a quartz cell using 5 nm wavelength steps. Polymer molecular weight and polydispersity index (PDI) were estimated from gel permeation chromatography (GPC) analyses by using a Waters 2695 Separations Module equipped with a Waters 2996 photodiode array detector, a Waters 2414 refractive-index detector, and three Polymer Labs PL gel individual pore-size columns. Polystyrene standards were used for calibration, and THF (1% acetonitrile) was used as the eluent at a flow rate of 1.0 mL/min. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 409 PC instrument under Argon. Ultrasonication was carried out in a Branson Ultrasonics a B2500 bath sonicator. A Beckman Allegra[TM] X-22R Benchtop centrifuge was used for centrifugation. Raman spectra were collected with a Renishaw InVia Laser Raman spectrometer equipped with a 25 mW argon ion laser (514 nm), a 300 mW Renishaw 785 nm laser, and 1800 L/mm and 1200 L/mm gratings for the two lasers, respectively. The Raman system is also equipped with a Leica microscope having 5×, 20×, and 50× objectives as well as a USB camera for sample viewing. The 785 nm laser was operated at 1% intensity to avoid damage to the sample. High-resolution transmission electron microscopy was performed at room temperature on an FEI Titan 80-300 Cubed TEM, operated at 80 kV. The microscope is equipped with a CEOS-designed hexapole-based aberration corrector for the image-forming lens and one for the probe-forming lens. The SuperTwin lens allows an information limit of 0.06-0.065nm.

### 5.4.2. Synthesis

### 5.4.2.1. Synthesis of 3,3',5,5'-tetrabromo-2,2'-bithiophene (1)

Bromine (9.8 g, 61.30 mmol) in 20 mL CHCl<sub>3</sub> was added dropwise over 2 h to an ice-bath cooled solution of 2,2'-bithiophene (2.78 g, 16.72 mmol) in the mixed solvent of glacial acetic acid (20 mL) and chloroform (22.5 mL). The mixture was subsequently stirred at room temperature overnight and then under reflux for 24 h. After cooling to room temperature, 50 mL of 10 % KOH aqueous solution was added, and then the mixture was extracted with CHCl<sub>3</sub> (2×300 mL). In order to remove the excess Br<sub>2</sub>, 100 mL of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10%) solution was added to the combined CHCl<sub>3</sub> layer and was stirred until the solution was light yellow or colorless. The organic layer was washed with water (3×100 mL), dried over anhydrous MgSO<sub>4</sub>, filtered, and the solvent removed by

evaporation. Recrystallization from ethanol afforded off-white crystals (7.5 g, 93% yield). <sup>1</sup>H-NMR (200 MHz) (CDCl<sub>3</sub>): 7.04 (s, 2H) ppm;

### 5.4.2.2. Synthesis of 3,3'-dibromo-2,2'-bithiophene (2)

Zn dust (0.827 g, 12.65 mmol ) was added in small portions to a refluxing solution of 3,3',5,5'-tetrabromo-2,2'-bithiophene (1) (1.1 g, 2.3 mmol) in a mixture of 27.8 mL of n-propanol, 0.6 mL of water, and 1.2 mL of glacial acetic acid over 5 min. After refluxing overnight, the mixture was cooled to room temperature, filtered, and then the solvent was removed via rotary evaporation. The residue was dissolved with ether, washed with deionized water (50 mL), saturated NaHCO<sub>3</sub> (50 mL) solution, and brine (50 mL). After drying with anhydrous MgSO<sub>4</sub>, the solvent was removed via rotary evaporation, and the solvent was removed via rotary ecaporation from hexane to give light yellow crystals (0.6 g, 81% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) (200 MHz):  $\delta$  7.41 (d, *J* = 5.2 Hz, 2H), 7.05 (d, *J* = 5.4 Hz, 2H).

# 5.4.2.3. Synthesis of N-Dodecyldithieno[3,2-b:2',3'-d]pyrrole (DTP) (3)

A flame dried 200 mL, 2 neck round bottom flask equipped with a magnetic stir bar was charged with 50 mL dry toluene, 3,3'-dibromo-2,2'-bithiophene (1.50 g, 4.65 mmol), NaOtBu (1.18 g, 12.26 mmol), and BINAP (0.3 g, 0.45 mmol). The mixture was degassed via sonication under continuous bubbling with Ar for 10 min. The Pd<sub>2</sub>dba<sub>3</sub> (catalytic amount) and dodecylamine (1 g, 5 mmol) were added to the above mixture, then the reaction mixture was stirred and heated to reflux overnight under Ar atmosphere. After cooling to room temperature, 50 mL of water was added, and the layers were separated. The aqueous phase was extracted twice with diethylether (50 mL each), and then the combined organic layers were again washed with water (30 mL). The organic layer was dried over MgSO<sub>4</sub> and concentrated via rotary evaporation. The residue was purified by silica gel column chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub>, 9:1 v/v) to give the product as a light yellow oil (1.53 g, 95% yield). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>, ppm ):  $\delta$  7.13 (d, *J* = 5.2 Hz, 2H), 7.00 (d, *J* = 5.4 Hz, 2H), 4.20 (t, *J* = 7.0 Hz, 2H), 1.86 (m, 2H), 1.24 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H).

### 5.4.2.4. Synthesis of 2,6-Dibromo-N-Dodecyldithieno[3,2-b:2',3'-d]pyrrole (DTP) (4)

A round bottom flask equipped with a magnetic stir bar was charged with N-dodecyldithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP) (0.42 g, 1.2 mmol) and 25 mL of chloroform. The solution was placed in an ice bath and stirred for 20 min. A solution of N-bromosuccinimide (0.45g 2.5 mmol) in 20 mL N,N-dimethylformamide was added dropwise to the above solution. After stirring for 1 hr at 0°C (at which point no starting material was observed by TLC), 20 mL of water was added and the layers were separated. The organic layer was evaporated and the residue was then dissolved in 50 mL of hexanes. 0.5 g of decolorizing charcoal was added, and the resulting mixture was stirred for 10 min and filtered. The solvent was removed via rotary evaporation and the crude product was purified by column chromatography with hexanes as the eluent to give the product as a light yellow solid (0.345 g, 71% yield). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>, ppm): 7.02 (s, 2H), 4.07 (t, *J* = 6.8 Hz, 2H), 1.80 (m, 2H), 1.24 (m, 18H), 0.87 (t, *J* = 6.6 Hz, 3H) (Figure A.2, Appendix I:), MS Calc'd for C<sub>20</sub>H<sub>28</sub>NS<sub>2</sub>Br<sub>2</sub> [M+H]<sup>+</sup> m/z = 504.0030, found ESMS [M+H]<sup>+</sup> m/z = 504.0061.

# 5.4.2.5. Synthesis of 1,2,3-Tri(n-dodecyloxy)benzene (5)

To a 500 mL round-bottom flask equipped with a magnetic stirrer, 1,2,3-Trihydroxybenzene (5 g, 40 mmol), K<sub>2</sub>CO<sub>3</sub> (55.28 g, 400 mmol), KI (2 g 12 mmol), 18crown-6 (0.7g, 2.65 mmol), and acetone (350 mL) were added. The mixture was stirred for 5 min, then 1-bromododecane (43 mL, 180 mmol) was added to it, and the reaction mixture was stirred at reflux for two days. The reaction mixture was cooled to room temperature and filtered. The solvent was evaporated via rotary evaporation, 300 mL of dichloromethane was added, and the resulting mixture was filtered. The filtrate was collected, the solvent was removed via rotary evaporation, and crystallization of the residue from isopropanol afforded off-white crystals (24.6 g, 98% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz, ppm)  $\delta$ : 6.90 (t, *J* = 8.2 Hz, 1H), 6.53 (d, *J* = 8.2 Hz, 2H), 3.96 (t, *J* = 6.4 Hz, 6H), 1.78 (m, 6H), 1.26 (m, 54H), 0.86 (t, *J* = 6.4 Hz, 9H).

#### 5.4.2.6. Synthesis of 1,2,3–Tri(n-dodecyloxy)nitrobenzene (6)

To a 250 mL round-bottom flask equipped with a magnetic stir bar, silica gelsupported nitric acid (20 g, 20% HNO<sub>3</sub>, 0.2 mol), and 100 mL of CH<sub>2</sub>Cl<sub>2</sub> were added. A solution of 1,2,3-tri(n-dodecyloxy)benzene (12 g, 19 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (60 mL) was added over 10 min. After stirring the resulting mixture at room temperature for 20 min, the resulting dark red mixture was filtered and the residue washed with CH<sub>2</sub>Cl<sub>2</sub>. A viscous light red oil was obtained after the solvent was removed under vacuum. A yellow precipitate formed after addition of 100 mL of cool methanol to the flask. The resulting yellow solid was collected by filtration, washed with methanol and recrystallized from isopropanol to yield **6** as a white solid (8.3 g, 65%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz, ppm)  $\delta$ : 7.46 (s, 2H), 4.03 (m, 6H), 1.82 (m, 6H), 1.26 (m, 54H), 0.86 (t, J = 6.4 Hz, 9H). MS Calc'd for C<sub>42</sub>H<sub>78</sub>NO<sub>5</sub> [M+H]<sup>+</sup> m/z = 676.5880, found ESMS [M+H]<sup>+</sup> m/z = 676.5882

#### 5.4.2.7. Synthesis of 3,4,5–Tri(n-dodecyloxy)aniline (7)

A flame dried 200 mL round-bottom flask equipped with a magnetic stirrer was charged with 60 mL of dry THF, 1,2,3-Tri(n-dodecyloxy)nitrobenzene (**6**) (8.4 g, 12.4 mmol), and 10% Pd-C (0.4 g). The reaction mixture was stirred under hydrogen atmosphere (balloon) at room temperature overnight. 50 mL of THF was added to the reaction mixture, filtered through a celite pad (3 cm thick), and then the solvent was removed via rotary evaporation. After addition of 100 mL of cool methanol to the flask, a light pink precipitate was formed. The precipitate was collected by filtration and washed with methanol (100 mL). The product was recrystallized from isopropanol to yield **7** as a light gray solid (7.5 g, 94%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz, ppm)  $\delta$ : 5.81 (s, 2H), 3.87(m, 6H), 2.92 (s, broad, 2H), 1.73 (m, 6H), 1.26 (m, 54H), 0.86 (t, *J* = 6.4 Hz, 9H). MS Calc'd for C<sub>42</sub>H<sub>80</sub>NO<sub>3</sub> [M+H]<sup>+</sup> m/z = 646.6138, found ESMS [M+H]<sup>+</sup> m/z = 646.6136 5.4.2.8. Synthesis of N-3,4,5(n-dodecyloxy)phenyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole (8).<sup>55</sup>

# 5.4.2.8. Synthesis of N-3,4,5(n-dodecyloxy)phenyl)dithieno[3,2-b:2',3'-d]pyrrole (8)

A flame dried 100 mL, 2 neck round bottom flask equipped with a magnetic stir bar was charged with 30 mL dry toluene, 3,3'-dibromo-2,2'-bithiophene (0.324 g, 1 mmol), NaOtBu (0.3 g, 4 mmol), and BINAP (0.3 g, 0.15 mmol). The mixture was degassed via sonication under continuous bubbling with Ar for 30 min. Then,  $Pd_2dba_3$ (catalytic amount) and 3,4,5–Tri(n-dodecyloxy)aniline (0.83 g, 1.3 mmol) were added to the above mixture, and the reaction mixture was stirred and heated to reflux overnight under an Ar atmosphere. After cooling to room temperature, 50 mL of water was added, and the layers were separated. The aqueous phase was extracted twice with diethylether (50 mL each), and then the combined organic layer was dried over MgSO<sub>4</sub> and concentrated via rotary evaporation. The residue was purified by silica gel column chromatography using hexanes/dichloromethane as the eluent (9:1 gradually increasing the ratio to 1:1) to give the product as a pale yellow solid (0.7 g, 87% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz, ppm)  $\delta$ : 7.17 (d, *J* = 5.0 Hz, 2H), 7.15 (d, *J* = 5.0 Hz, 2H), 6.75 (s, 2H), 4.00(m, 6H), 1.83 (m, 6H), 1.35 (m, 6H), 1.26 (m, 48H), 0.88 (m, 9H) (Appendix I: Figure A.3). MS Calc'd for C<sub>50</sub>H<sub>82</sub>NS<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> m/z = 808.5736, found ESMS [M+H]<sup>+</sup> m/z = 808.5695

# 5.4.2.9. Synthesis of 2,6-Diiodo-N-3,4,5(n-dodecyloxy)phenyl)dithieno[3,2-*b*:2',3'*d*]pyrrole (9)

A flame dried 100 mL round bottom flask equipped with a magnetic stir bar was charged with 10 mL CHCl<sub>3</sub>, and N-3,4,5(n-dodecyloxy)phenyl)[3,2-*b*:2',3'-*d*]pyrrole (0.3 g, 0.371 mmol), and the flask was placed into an ice bath and cooled for 10 min. NIS (0.183 g 0.814 mmol) was added, and stirred for 30 min, then the mixture was allowed to warm up to room temperature, and stirred for an additional 2 h. Then, 10 mL of aqueous NaHSO<sub>3</sub> (10%) solution, and 20 mL of CH<sub>2</sub>Cl<sub>2</sub> were added. The layers were separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The combined organic layers were washed twice with water (25 mL each), and dried over MgSO<sub>4</sub>. The crude product was purified by column chromatography (SiO<sub>2</sub>, hexane: CH<sub>2</sub>Cl<sub>2</sub>, 1:1), and dried under

vacuum at room temperature for 24 h. A light yellow solid was obtained (0.35 g, 88% yield). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 600 MHz, ppm)  $\delta$ : 7.21 (s, 2H), 6.57 (s, 2H), 3.89(m, 6H), 1.72 (m, 6H), 1.45 (m, 6H), 1.18 (m, 48H), 0.80 (m, 9H) (Appendix I, Figure A.4,). MS Calc'd for C<sub>50</sub>H<sub>79</sub>I<sub>2</sub>NO<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup> m/z = 1060.3669 found ESMS [M+H]<sup>+</sup> m/z = 1060.3630

# 5.4.2.10. Synthesis of poly{2,7-[9,9-didocylfluorene]-*alt*-2,6–[N-dodecyldithieno(3,2*b*:2',3'-*d*)pyrrole]} (PF-DTP1)

A 100 mL Schlenk tube equipped with a magnetic stir bar was charged with  $Cs_2CO_3$  (2.25 g, 6.9 mmol), 9,9-didoceylfluorene-2,7-bis(trimethyleneboronate) (0.402 g, 0.6 mmol), 2,6- dibromo-N-dodecyldithieno[3,2-*b*:2',3'-*d*]pyrrole (0.3 g, 0.6 mmol), 15 mL of DMF, and 5 mL of toluene. The mixture was degassed via sonication under continuous bubbling with Ar for 30 min. Then a catalytic amount of tetrakis(triphenylphosphine)palladium [Pd(PPh<sub>3</sub>)<sub>4</sub>] (~2.0 mol %) was added and stirred at 90°C under Ar atmosphere for 48 h. The resulting product was end-capped first with phenylboronic acid (0.073 g, 0.6 mmol), and the mixture was stirred for 6 h, at 90°C under Ar atmosphere. Then the second end capping agent, bromobenzene (0.094 g, 0.6 mmol), was added and the resulting mixture was stirred for an additional 6 h. After cooling to room temperature, the reaction mixture was poured into methanol (300 mL) which resulted in an orange precipitate that was collected by filtration, washed with methanol (150 mL), water (150 mL), methanol (150 mL), and acetone (300 mL). After drying under vacuum for 24 h at 50°C, an orange solid was obtained in 82% yield (0.4

g). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 600 MHz, ppm)  $\delta$ : 7.66-7.60 (m, 6H), 7.31(s, 2H), 4.26(b, 2H), 1.98 (m, 6H), 1.25-0.83 (m, 67H). UV-Vis (THF):  $\lambda_{max} = 485$  nm; PL (THF):  $\lambda_{em} = 516$  nm.

# 5.4.2.11. Synthesis of poly{2,7-[9,9-didocylfluorene]-*alt*-2,6–[N-3,4,5(n-dodecyloxy)phenyl)-dithieno[3,2-b:2',3'-d]pyrrole]} (PF-DTP2)

A 100 mL Schlenk tube equipped with a magnetic stir bar was charged with Cs<sub>2</sub>CO<sub>3</sub> (1.0 g, 3.1 mmol), 9,9-didocylfluorene-2,7-bis(trimethyleneboronate) (0.177 g, 2,6-Diiodo-N-3,4,5(n-dodecyloxy)phenyl)dithieno[3,2-b:2',3'-d]pyrrole 0.264 mmol). (0.28 g, 0.264 mmol), 15 mL of DMF, and 5 mL of toluene. The mixture was degassed via sonication under continuous bubbling with Ar for 30 min. Then a catalytic amount of tetrakis(triphenylphosphine)palladium  $[Pd(PPh_3)_4]$  (~2.0 mol %) was added and the mixture was stirred at 90°C under Ar atmosphere for 48 h. The resulting product was endcapped first by addition of phenylboronic acid (0.032 g, 0.264 mmol), allowing the mixture to stir for 6 h at 90°C under Ar. Then the second end-capping agent, bromobenzene (0.041 g, 0.264 mmol), was added and the resulting mixture was stirred for an additional 6 h. After cooling to room temperature, the reaction mixture was poured into methanol (300 mL), which resulted in an orange precipitate that was collected by filtration, washed with methanol (150 mL), water (150 mL), methanol (150 mL), and acetone (300 mL). The solid was dissolved in THF (30 mL), and re-precipitated in methanol (300 mL), filtered and washed with acetone (200 mL). The solid was dried under vacuum for 24 h at 50°C, and the resulting orange solid was obtained in 87% yield (0.3 g). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 600 MHz, ppm)  $\delta$ : 7.71 (m, 4H), 7.62 (b, 2H), 7.46(s, 2H), 6.85(s, 2H), 4.09(b, 6H), 2.07 (m, 4H), 1.88 (m, 10H), 1.53-0.90 (m, 105H). UV-Vis (THF):  $\lambda_{max} = 480$  nm; PL (THF):  $\lambda_{em} = 522$  nm.

# 5.4.3. Dispersion of SWNTs in SDBS/D<sub>2</sub>O

A SWNT sample (5 mg) was added to a solution of sodium dodecylbenzene sulfonate (SDBS) (350 mg) in 35 mL D<sub>2</sub>O. The resulting mixture was sonicated for 45 min using a bath sonicator, and centrifugation was done with an ultracentrifuge at 65,000 g for 4 h. The supernatant was carefully pipetted out of the centrifuge tube and used for subsequent studies.

# 5.5. References

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# Chapter 6: Supramolecular Functionalization of Single Walled Carbon Nanotubes (SWNTs) with Photoisomerizable Conjugated Polymer

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Both Patigul Imin and Mokhtar Imit contributed equally to the experimental planning, polymer synthesis and characterization. Nanotubes functionalization and characterization was conducted by Patigul Imin.

# Abstract

A fluorene and azobenzene containing conjugated polymer, poly[2,7-(9,9didodecylfluorene)-alt-4,4'-azobenzene] (F12AZO) has been successfully synthesized using Suzuki polycondensation. The introduction of two dodecyl chains on the fluorene unit resulted in a highly soluble polymer. F12AZO possesses excellent thermal stability, with a decomposition temperature over 400°C under Ar. The reversible photoisomerization of the azobenzene units was achieved upon alternating photoirradiation with light of wavelength less than 450 nm (cis-form), and light in the range of 450-600 nm (trans-form). The supramolecular complex formation of trans-F12AZO, and cis-F12AZO with single-walled carbon nanotubes (SWNTs) has been studied, and it was found that this polymer can form very strong supramolecular polymer-nanotube assemblies. Furthermore, the trans and cis isomers of F12AZO enable the selective dispersal of individual SWNTs in toluene or THF, and the selectivity of the SWNTs is strongly dependent on the solvent, as well as the type of isomer used. UV-Vis-NIR, and photoluminescence-excitation spectroscopy (PLE) were used for the characterization and identification of the nanotube species that are solubilized and exfoliated by this polymer.

# 6.1. Introduction

Since their discovery,<sup>1</sup> single-walled carbon nanotubes (SWNTs) have attracted significant attention due to their remarkable mechanical, thermal, optical and electronic properties.<sup>2-9</sup> Various potential applications of SWNTs, including their incorporation within chemical sensors,<sup>10-12</sup> field-effect transistors,<sup>13-16</sup> nano-scale integrated radio receivers,<sup>17, 18</sup> photovoltaics,<sup>19-21</sup> field-emission displays,<sup>22, 23</sup> and many others<sup>24, 25</sup> have been extensively explored over the past two decades. However, the inherent insolubility of carbon nanotubes in most organic and aqueous solvents and coexistence of various tube types in as-produced SWNT samples have severely limited the widespread application of these novel nanostructures. To improve their solubility and processability, various carbon nanotube surface modification techniques have been developed, including covalent and noncovalent functionalization.<sup>26-28</sup> Noncovalent functionalization of SWNTs with aromatic macromolecules or conjugated polymers is of particular interest because this approach does not introduce any defects in the nanotube sidewall, thus leaving the extended nanotube  $\pi$ -network, along with all of its consequent properties, unperturbed.<sup>29-</sup>

Recently, supramolecular functionalization of SWNTs with fluorene-containing conjugated polymers has generated significant interest due to the excellent solubility and solution stability of the resulting polymer-SWNT nano-composites.<sup>31-35</sup> Interest in this class of conjugated polymers has increased as reports of selective solubilization of certain SWNT species have begun to be published.<sup>33, 36-38</sup> It has also been shown that noncovalent functionalization of SWNTs with stimuli-responsive polymers that are

modulated by light, pH, and temperature enables reversible modification of electronic properties within the resulting CNT-based nanostructures.<sup>39-41</sup> In particular, structural components that can control the strength of polymer binding to the nanotube surface in response to external stimuli are of significant interest.

Azobenzene (AZO) is a well known photoisomerizable molecule exhibiting a reversible *trans* to *cis* isomerization that can easily be achieved upon photoirradiation, even when incorporated within polymeric structures.<sup>39, 42, 43</sup> The conformational change of the AZO unit upon photoirradiation can significantly affect the molecular shape of AZOcontaining polymers, resulting in reversible coiling/uncoiling processes.<sup>44, 45</sup> Recently, several conjugated polymers incorporating the AZO unit have been reported, and have even been shown to undergo supramolecular functionalization of SWNTs.<sup>39, 40, 43</sup> For example, Imahori and coworkers found that alternating copolymers of AZO with phenylene or vinylene units enable the dissolution of SWNTs, where the degree of dissolution depended on the *cis/trans* ratio of the AZO units in the starting polymer.<sup>43</sup> Interestingly, it was not possible to isomerize the AZO units after nanotube complexation in solution because of the strong supramolecular interaction between the AZO units in the polymer backbone and the nanotube sidewall, a result that has also been found in other studies.<sup>39, 40, 43</sup> Furthermore, the polymers reported in these studies were not found to be selective toward specific nanotube types within a mixture.

These observations inspired us to investigate the incorporation of the AZO unit within conjugated polymer backbones that have been previously found to be selective for specific nanotube chiralities, such as poly(9,9-di-n-alkylfluorene)-based polymers,<sup>33, 37</sup>

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and to determine if AZO photoisomerization can influence this selectivity. Here, we report the supramolecular functionalization of SWNTs using a photo-responsive conjugated polymer, poly[2,7-(9,9-didodecylfluorene)-*alt*-4,4'-azobenzene] (F12AZO), and describe the detailed optoelectronic and photo physical characterization of the resulting F12AZO-SWNT complexes. The effect of changing solvent, and changing the polymer conformation upon photoirradiation on the interaction between the polymer and nanotubes is also described.

### **6.2. Results and Discussion**

4,4'-diiodoazobenzene (1) was synthesized according to literature procedures starting from 4-iodoaniline.<sup>46</sup> Poly[2,7-(9,9-didodecylfluorene)-*alt*-4,4'-azobenzene] (F12AZO) was prepared using a Suzuki polycondensation from 9,9-didodecylfluorene-2,7-bis(trimethyleneboronate) and 4,4'-diiodoazobenzene as depicted in Scheme 6.1. F12AZO was obtained as an orange solid in 76% yield, and the resulting polymer exhibited excellent solubility in common organic solvents, including THF, toluene, and chloroform. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) relative to polystyrene standards, and indicated a number average molecular weight (M<sub>n</sub>) of 6.6 kg/mol with a polydispersity index (PDI) of 2.0.



Scheme 6.1. Synthetic route to the F12AZO polymer.

The chemical structure of F12AZO was confirmed by <sup>1</sup>H-NMR spectroscopy (Figure 6.1). The multiplet centered at 7.85 ppm corresponds to the aromatic protons from fluorene, and the peaks centered at 8.06 and 7.71 ppm correspond to the aromatic protons of AZO. On the basis of the relative areas of these peaks, the molar ratio of fluorene and azobenzene was determined to be 1:1, which is consistent with the alternating copolymer structure expected from the Suzuki polycondensation. Phenyl groups were also successfully introduced at both ends of the polymer as end-caps, and the two sets of small multiplets centered at 7.57 and 7.51 ppm, and the doublet at 7.97 ppm (Figure 6.1) were assigned as the end group phenyl protons.<sup>47</sup> Based on the integration ratio of the fluorene proton signals in the polymer repeat units to the end-group proton signals, the average degree of polymerization (DP) and  $M_n$  were estimated to be approximately 9 and 6.3 kg/mol, respectively. The estimated  $M_n$  value by NMR is in surprisingly good agreement with the molecular weight measurements from GPC.



**Figure 6.1.** <sup>1</sup>H-NMR spectrum of the polymer in CDCl<sub>3</sub>

The thermal stability of F12AZO was characterized by thermogravimetric analysis (TGA), carried out under an Ar atmosphere (Appendix I, Figure A.10). This data indicates that the major mass loss occurs at 400°C for F12AZO, amounting to 50%. This mass loss corresponds well with the loss of side chains within this polymer. Above this temperature, the mass decreased slowly, and levels off at ca 45% when heated to 800°C, at which point it is likely converted to char.

Optical properties of the F12AZO were characterized by UV-Vis absorption spectroscopy. F12AZO exhibits an absorption maximum ( $\lambda_{max}$ ) at 417 nm in THF (Appendix I, Figure A.11), which is in good agreement with previously reported values for similar polymers of nearly equal molecular weight.<sup>42</sup> It has been reported that all azobenzene units in the polymer backbone are most stable in the *trans* form when the polymer is kept in solution.<sup>42-45</sup> To achieve *trans*-to-*cis* isomerization, a THF solution of F12AZO (0.017 g/L) in a quartz cuvette was irradiated with light of wavelength < 450 nm

for 20 min. This resulted in a decrease in the absorption band centered at 417 nm (Appendix I, Figure A.11). The reverse isomerization (*cis*-to-*trans*) was achieved by irradiating with light in the range of 450-600 nm. In both cases the absorption spectra recorded at different irradiation times indicated that the full extent of isomerization was complete within 15 min of irradiation (Figure A.11, Appendix I). The changes of the polymer absorption in THF upon alternating photoirradiation in the two wavelength ranges (< 450 nm, and 450-600 nm) at room temperature for 15 min were also measured to confirm that F12AZO can undergo reversible *trans-cis* photoisomerization (Figure A.12, Appendix I).

The supramolecular interaction of F12AZO with SWNTs was studied using our previously reported methods.<sup>32</sup> In a typical experiment, a SWNT sample (2.5 mg) was added to a solution of polymer in THF or toluene (7.5 mg/10 mL), and the mixture was ultrasonicated in a bath sonicator for 1h. The resulting solution was centrifuged for 45 min at 8,300 g, allowed to stand overnight, and then the supernatant was carefully transferred by pipette to another vial. A dark colored, relatively concentrated polymer-nanotube complex solution was obtained in THF, while significant nanotube precipitation was observed in toluene, leaving a clear, orange solution (Figure A.13, Appendix I).

The supramolecular complexes of *trans*-F12AZO with SWNTs in THF were further investigated to determine if polymer can be released from the carbon nanotube surface upon photoirradiation. In a typical experiment, the isolated supernatant in THF was further diluted with 50 mL of THF, sonicated for 5 min, filtered through a 200 nm pore diameter Teflon membrane, and repeatedly washed with THF until the filtrate was

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colorless, ensuring removal of excess free polymer. 10 mL of THF was added to the recovered SWNT residue and the vial was further sonicated for 5 min. The resulting dark suspension was centrifuged at 8,300 g for 45 min and allowed to stand overnight undisturbed. The UV-Vis absorption properties of *trans*-F12AZO and their corresponding SWNT complexes in THF were measured (Figure A.14, Appendix I). It was found that the absorption maximum of the polymer exhibited a characteristic bathochromic shift and slight broadening once bound to the nanotube surface (Figure A.14A, Appendix I).

A diluted THF solution of *trans*-F12AZO-SWNT (after removal of excess polymer) in a quartz cuvette was irradiated to cause *trans*-to-*cis* isomerization, and the changes in the absorption spectra were recorded. Although the polymer absorption band intensity slightly decreased when irradiated below 450 nm, the change in SWNT absorption was negligible. There was no noticeable SWNT aggregation or precipitation observed after irradiation for 4h (Figure A.14B, Appendix I). It is possible that either the polymer confomation is "locked" by its interaction with the nanotube surface, or there is a rapid energy transfer that occurs from the excited state of the polymer to the SWNT, both of which would inhibit the photoisomerization. To rule out the latter possibility, we measured the emission spectrum of the F12AZO-SWNT complex when excited at the absorption maximum of the polymer ( $\lambda_{ex} = 417$  nm), in both THF and toluene. This resulted in no observable sensitized nanotube emission (Figure A.15, Appendix I), indicating that energy transfer from the excited-state polymer to the nanotube does not occur. This result is in agreement with previous studies, which found that it was not

possible to photoisomerize the AZO units once they are bound to the nanotube surface.<sup>39,</sup> 40,43

In order to confirm how the interactions between the F12AZO and the SWNTs can be affected by the conformational changes (*trans* vs. *cis*) of the F12AZO, the supramolecular complexes of F12AZO-SWNT were prepared using the above protocol with both *trans* and *cis* isomers of F12AZO (see experimental), and THF or toluene as the dispersing solvents. The UV-Vis-NIR absorption spectra of both *trans*-F12AZO-SWNT and *cis*-F12AZO complexes in THF and toluene are depicted in Figure 6.2. For reference, the absorption spectrum of just the nanotubes dispersed in D<sub>2</sub>O using sodium dodecylbenzenesulfonate (SDBS) surfactant is also shown in Figure 6.2 (curve a).



**Figure 6.2.** NIR absorption spectra of SDBS/SWNT (a), *trans*-F12AZO+SWNT in THF (b), *cis*-F12AZO+SWNT in THF (c), *trans*-F12AZO+SWNT in toluene (d), and *cis*-F12AZO+SWNT in toluene (e). Dotted lines are meant to guide the eye in comparing absorption bands from identical nanotubes.

The spectra show that the dispersing ability is affected by both the conformational state of the F12AZO polymer (trans vs. cis isomers) and the solvent. In comparison to aqueous dispersions of SWNTs using the surfactant SDBS (Figure 6.2, curve a), the absorption peaks of the F12AZO-SWNT complexes in both THF and toluene (Figure 6.2, curves b, c, d and e) are more intense, indicating efficient exfoliation into individual tubes, and exhibit relatively strong absorptions at wavelengths corresponding to semiconducting SWNTs (600-800 and 900-1500 nm). All of the transitions of F12AZO-SWNT complexes were found to be red-shifted 8-25 nm relative to the aqueous solution, which is consistent with what has been reported previously with comparable systems.<sup>33, 37, 38</sup> Upon closer examination of the each individual absorption spectrum, small shifts and changes in intensity of several signals can be observed, indicating that the *trans*- and *cis*-F12AZO show a slightly different preference for certain SWNT tube types in both THF and toluene solution. The total absorbance of several species is reduced in toluene solution when compared to THF, due to the substantial reduction in the number of different nanotube species present in F12AZO/toluene solutions. Several major absorption peak positions in the 900-1500 nm region were correlated to the corresponding chiral indices (n, m), where the assignments are based on previously reported results.<sup>48, 49</sup> It has been shown that the absorbance intensity of SWNTs is proportional to the amount of solubilized SWNTs present, independent of whether the tubes are isolated or bundled.<sup>49, 50</sup> Therefore it is difficult to attribute the changes in absorption peak intensities to individual, exfoliated tube types.

Photoluminescence spectroscopy has been used as a powerful tool to identify the solubilized species due to its sensitivity to the degree of SWNT exfoliation.<sup>37, 49</sup> Thus, photoluminescence excitation maps (PLE) of the trans- and cis-F12AZO-SWNT in toluene and THF were measured over a large range of excitation (500-900 nm) and emission (900-1450 nm) wavelengths. Figure 6.3 depicts the PLE maps of SWNTs dispersed in toluene and THF using both trans-F12AZO (maps A and B) and cis-F12AZO (maps C and D), which can be compared to the PLE map of a dispersion in D<sub>2</sub>O using the non-selective SDBS surfactant (map E). In these maps, areas of high intensity are depicted in red and areas of low intensity are depicted in blue. The chiral indices (n, m) for the identified species are labelled on the maps, where the assignments are based on previously reported results.<sup>49, 51</sup> The PLE map of the pristine SWNT sample dispersed in D<sub>2</sub>O using SDBS shows the presence of 17 different semiconducting nanotubes, a distribution that is similar to what has previously been reported.<sup>33, 51</sup> When the same material was mixed with trans-F12AZO and cis-F12AZO in toluene or THF, entirely different results were obtained. Figures 6.3A and 6.3B depict the PLE maps of the SWNT complexes with *trans*-F12AZO in THF and toluene, and Figures 6.3C and 6.3D show the PLE maps of *cis*-F12AZO complexes in THF and toluene, respectively. The observed strong nanotube emission indicates that individual SWNTs are solubilized and isolated by the polymer. It was found that both excitation and emission wavelengths of the trans-F12AZO+SWNT complex was red-shifted relative to the aqueous solution by 10-30 nm, which is consistent with previously reported comparable systems (Table A.3, Appendix I).<sup>21, 33, 37, 38</sup> It is obvious from the PLE maps (Figure 6.3, A and B) that the distribution of SWNT species depends on the solvent used, and the relative emission intensity of each solubilized species is considerably different with each solvent. When trans-F12AZO was used, 8 major carbon nanotube species were identified in THF, including (6,5), (8,4), (7,5), (7,6), (9,4), (9,5), (8,6), and (8,7), and the dominant species were found to be (6,5) and (7,5) (Figure 6.3A). Figure 6.4 depicts the normalized PLE signal intensities of 8 major SWNT species, where the most intense signal from each solution was set to a value of 1 (for numerical data, see Table A.4, Appendix I ). The nanotube species depicted in Figure 6.4 are organized by diameter, which ranges from 0.757 nm for the (6,5) tube to 1.032 nm for the (8,7) tube (for a complete list of diameters, see Table A.4, Appendix I). It is interesting to note that the nanotube diameter seems to dictate both the relative solubility in the two solvents and the selectivity of cis- or trans-F12AZO polymers for specific nanotube types. The polymer-nanotube complexes with SWNTs having diameters below 0.90 nm (consisting of the (6,5), (7,5), (8,4) and (7,6) species) all exhibit higher emission intensities in THF relative to toluene, while those with diameters above 0.92 nm (the (8.6), (9.5), and (8.7) species) exhibit higher intensities in toluene than in THF. Furthermore, as can be seen from Figure 6.4, the largest differences in emission intensities as a function of *cis/trans* polymer conformation were observed for the low diameter tubes (most notably for (6,5), (7,5), and (7,6) species), whereas *cis/trans* selectivity was weakest for the highest diameter tubes (specifically the (8,6), (9,5), and (8,7) species, especially in toluene). It is not clear why the *cis*-F12AZO polymer seems to show greater preference for solubilizing the (7,6) tube, while *trans*-F12AZO shows greater preference for the (6,5) and (7,5) species in THF. All of these results warrant further investigation. It should be noted that the above discussion implies a correlation between nanotube emission intensity and solution concentration, which assumes that SWNT fluorescence quantum yield is not affected by the polymer conformation or the surrounding solvent. This assumption will need to be tested in future studies.



**Figure 6.3.** PL contour maps of HiPco SWNTs dispersed with *trans*-F12AZO in THF (A), *trans*-F12AZO in toluene (B), *cis*-F12AZO in THF (C), *cis*-F12AZO in toluene (D), and with SDBS in  $D_2O$  (E).



**Figure 6.4.** Normalized PLE signal intensities of the major SWNT species observed in solution, in order of increasing diameter (left to right). (a), *trans*-F12AZO+SWNT in THF (b), *cis*-F12AZO+SWNT in THF (c), *trans*-F12AZO+SWNT in toluene (d), and *cis*-F12AZO+SWNT in toluene.

# 6.3. Conclusions

The photo-responsive azobenezene containing polymer, poly[2,7-(9,9didodecylfluorene)-alt-4,4'-azobenzene] (F12AZO) has been synthesized using Suzuki polycondensation, and the resulting polymer exhibited good solubility in a number of organic solvents, including THF, toluene, and chloroform. Thermogravimetric analysis indicated that F12AZO exhibits excellent thermal stability under Ar. The changes to the polymer absorption in THF upon alternating photoirradiation below 450 nm and between 450 and 600 nm, respectively, at room temperature confirmed that F12AZO can undergo reversible trans-cis photoisomerization. The trans-F12AZO and cis-F12AZO were utilized for the preparation of supramolecular polymer-SWNT composites, and excellent nanotube solubility and solution stability was achieved in THF. UV-Vis absorption measurements revealed a bathochromic shift and broadening in the polymer absorption spectrum as a result of complex formation with nanotubes. Photoirradiation of *trans*-F12AZO-SWNT complexes below 450 nm does not cause polymer isomerization on the nanotube surface, and no noticeable SWNT aggregation or precipitation was observed. Photoluminescence excitation maps showed that efficient and selective dispersal of SWNTs is possible by using *trans*-F12AZO or *cis*-F12AZO, and that both solvent and polymer conformation played a role in the selectivity. It was found that low diameter nanotubes are more strongly differentiated by the *cis*- and *trans*-F12AZO polymer conformers, and nanotube diameter also determines whether the polymer-nanotube complexes will be more soluble in THF or toluene.

# **6.4. Experimental Section**

#### 6.4.1. General

As produced Single-walled carbon nanotubes (SWNTs) were purchased from Carbon Nanotechnologies, Inc. (HiPco SWNTs-Raw, Batch #: R0-513). All other reagents were purchased from Aldrich Chemical Co. and Acros Organics. NMR spectra were measured on Bruker Avance 200, and 600 MHz spectrometers. UV-Vis, and UV-Vis-NIR spectra were measured on Varian Cary 50, and Cary 5000 spectrometer respectively. Photoluminescence excitation (PLE) mapping was performed using the Jobin-Yvon SPEX Fluorolog 3.22 equipped with a 450 W Xe lamp, and fitted with a liquid-nitrogen cooled InGaAs photodiode detector. Slit widths were set to 7 nm bandpass on both excitation and emission, and samples were illuminated in a quartz cell using 5 nm wavelength steps. Polymer molecular weight and polydispersity index (PDI) were estimated from gel permeation chromatography (GPC) analyses by using a Waters 2695 Separations Module equipped with a Waters 2996 photodiode array detector, a Waters 2414 refractive-index detector, and two Jordi Labs Jordi Gel DVB columns. Polystyrene standards were used for calibration, and THF was used as the eluent at a flow rate of 1.0 mL/min. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 409 PC instrument under Argon. Ultrasonication was carried out in a Branson Ultrasonics a B2500 bath sonicator. A Beckman Allegra[TM] X-22R Benchtop centrifuge was used for centrifugation.

#### 6.4.2. Synthesis of 4,4<sup>-</sup>-diiodoazobenzene

250 mL round bottom flask equipped with a magnetic stir bar was charged with 160 mL dichloromethane (DCM), and the DCM was degassed via bubling with Ar for 10 min, then 4-iodoaniline (6 g, 27.4 mmol) was dissolved. 10.5 g (6.26 mmol) of KMnO<sub>4</sub> and 10.5 g (40.52 mmol) of CuSO<sub>4</sub>·5H<sub>2</sub>O were added to the flask, and then the mixture was stirred at room temperature for 3 days. The mixture was filtered using 3 cm celite pad, and then the solvent was removed via rotary evaporation. The crude product was purified by column chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub>, 3:1/v:v) as the eluent to give the product as an orange solid (1.8 g, 15 % yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz, ppm)  $\delta$ : 7.84 (d, 4H, *J* = 8.6), 7.61 (d, 4H, *J* = 8.6).

# 6.4.3. Synthesis of poly{2,7-[9,9-didodecylfluorene]-*alt*-4,4'-azobenzene}

A 100 mL Schlenk tube equipped with a magnetic stir bar was charged with 9,9didoceylfluorene-2,7-bis(trimethyleneboronate) (0.436 g, 1 mmol), 4,4'- diiodoazobenzene (0.674 g, 1 mmol), and 20 mL of toluene, 6 mL of 2M K<sub>2</sub>CO<sub>3</sub>, 4 mL of ethanol, and 1 drop of aliquat 336. The mixture was then degassed via sonication under continuous bubbling with Ar for 30 min. Then a catalytic amount of tetrakis(triphenylphosphine)palladium [Pd(PPh<sub>3</sub>)<sub>4</sub>] (~2.0 mol %) was added and stirred at 80°C under Ar atmosphere for 3 days. The resulting product was end-capped first with phenylboronic acid (0.12 g, 1 mmol), and the mixture was stirred for 6 h, at 80°C under Ar atmosphere. Then the second end-capping agent, bromobenzene (0.16 g, 1 mmol), was added and the resulting mixture was stirred for an additional 6 h. After cooling to room temperature, the reaction mixture was added drop-wise into methanol (300 mL) which resulted in an orange precipitate that was collected by filtration, washed with methanol (150 mL), water (150 mL), methanol (150 mL), and acetone (300 mL). After drying under vacuum for 24 h at 50°C, an orange solid was obtained in 76% yield (0.52 g). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 600 MHz, ppm)  $\delta$ : 8.03-7.98 (m, 4H), 7.80-7.77(m, 6H), 7.64-7.57(m, 4H), 2.03 (b, 2H), 1.18-0.78 (m, 40H), 0.77 (t, 6H, *J* = 6.0). UV-Vis (THF):  $\lambda_{max} = 417$  nm.

### 6.4.4. Dispersion of SWNTs in SDBS/D<sub>2</sub>O

A SWNT sample (5 mg) was added to a solution of sodium dodecylbenzene sulfonate (SDBS) (350 mg) in 35 mL D<sub>2</sub>O. The resulting mixture was sonicated for 45 min using a bath sonicator, and centrifugation was done with an ultracentrifuge at 45,000 g for 4 h. The supernatant was carefully pipetted out of the centrifuge tube and used for subsequent studies.

# 6.4.5. Photoisomerization of F12AZO in THF

A THF solution of F12AZO (0.017 g/L) in a quartz cuvette was irradiated using a Cole Parmer Illuminator 41720-Series (tungsten-halogen lamp, emitting randomly polarized white light 400-800 nm). The appropriate UV light irradiation wavelengths were chosen with the aid of short wave pass and color glass filters (Newport). A 10SWF-450-B short wave pass filter was used for irradiation below 450 nm to cause *trans*-to-*cis* isomerization. The combination of a 10SWF-600-B short wave pass filter and an FSQ-GG455 color glass filter was used for irradiation in the 450-600 nm range to cause *cis*-to-*trans* isomerization.

# 6.4.6. Preparation of trans-F12AZO+SWNT dispersion in THF and toluene

A SWNT sample (2.5 mg) was added to a solution of polymer in THF or toluene (7.5 mg/10 mL), and the mixture was ultrasonicated in a bath sonicator for 1h. The resulting solution was centrifuged for 45 min at 8,300 g, and allowed to stand overnight, and then the supernatant was carefully transferred by pipette to another vial. A dark colored, relatively concentrated polymer-nanotube complex solution was obtained in THF, while significant nanotube precipitation was observed in toluene. THF solutions were diluted more than 20 fold for UV-Vis absorption and fluorescence measurements.

# 6.4.7. Preparation and photoirradiation of *trans*-F12AZO+SWNT dispersion in THF without free polymer

The THF dispersion of *trans*-F12AZO+SWNT was further diluted with 50 mL of THF, sonicated for 5 min, filtered through a 200 nm pore diameter Teflon membrane, and repeatedly washed with THF until the filtrate was colorless, ensuring removal of excess free polymer. 10 mL of THF was added to the recovered SWNT residue and the vial was further sonicated for 5 min. The resulting dark suspension was centrifuged at 8,300 g for 45 min and allowed to stand overnight undisturbed. A diluted THF solution of *trans*-F12AZO-SWNT in a glass cuvette was irradiated with light of wavelength less than 450 nm to cause *trans*-to-*cis* isomerization.

# 6.4.8. Preparation of cis-F12AZO+SWNT dispersion in THF and toluene

A solution of polymer in THF or toluene (7.5 mg/1.5 mL) in a glass cuvette was first irradiated with light of wavelength less than 450 nm for 1h to cause *trans*-to-*cis* isomerization. After irradiation was complete, the solution was transferred to 20 mL vial, and diluted up to 10 mL. SWNT sample (2.5 mg) was added to a solution of *cis*-F12AZO in THF or toluene, and the supramolecular complexes were prepared using the similar protocol with *trans*-F12AZO+SWNT.

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# Chapter 7: Amperometric Detection of Glucose Using a Conjugated Polyelectrolyte Complex with Single-Walled Carbon Nanotubes

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The work detailed in this chapter was carried out in collaboration with Dr. Xin Pang and Dr. Igor Zhitomirsky (Department of Material Engineering, McMaster University). Both Patigul Imin and Dr. Xin Pang contributed equally to the experimental planning, writing of this work. Polymer synthesis, nanotubes functionalization and characterization was conducted by Patigul Imin. Fabrication and characterization of the electrochemical glucose biosensor was conducted by Dr. Xin Pang.

# Abstract

The conjugated polymer, poly[3-(3-N,N-diethylaminopropoxy)thiophene] (PDAOT), was synthesized and employed in the supramolecular functionalization of single-walled carbon nanotubes (SWNTs). Highly stable aqueous solutions of PDAOT-SWNT complexes were obtained after sonication under mildly acidic conditions. UV-Vis absorption and Raman spectroscopy studies showed that the non-covalent functionalization did not change the nanotube structure and retained its inherent properties. The reactions of  $[Fe(CN_6)]^{3-/4-}$  redox couple on Au electrodes modified with PDAOT and the PDAOT-SWNT films were studied using electrochemical impedance spectroscopy and cyclic voltammetry. A lower electron-transfer resistance and higher current response were observed on the Au/PDAOT-SWNT electrode compared with the Au/PDAOT electrode. Glucose biosensors were prepared by entrapping glucose oxidase (GOx) within the PDAOT and PDAOT-SWNT films. Under optimized conditions, the Au/PDAOT-SWNT/GOx biosensor exhibited fast current response to glucose with a detection limit of 5  $\mu$ M and a sensitivity of 700 ± 26  $\mu$ A/mM·cm<sup>2</sup>. The responsiveness of the Au/PDAOT-SWNT/GOx biosensor can be attributed to the synergistic effect of the high conductivity and non-denaturing microenvironment of the PDAOT and the large active surface area and electrical conductivity provided by the SWNTs.

# 7.1. Introduction

In order to take full advantage of the unique properties of carbon nanotubes (CNTs) in practical applications, control over their dispersion and physical characteristics must be achieved.<sup>1-4</sup> In particular, the preparation of CNT-rich coatings, patterns, and deposits requires nanotube solutions in various organic and aqueous solvents. However, the inherent insolubility of both multi-walled and single-walled carbon nanotubes (MWNTs and SWNTs, respectively),<sup>5</sup> has posed a significant challenge to their solutionphase manipulation. Fortunately, it has recently been shown that both covalent and noncovalent chemical functionalization of CNTs enables their dissolution in a wide variety of solvents.<sup>5-9</sup> In particular, supramolecular functionalization has attracted significant attention because this strategy enables dissolution of CNTs without disrupting any of their original strength and conductivity properties.<sup>10</sup> To this end, the wrapping of CNTs with conjugated polymers has been investigated in recent literature as a result of the high affinity of this class of polymers for the nanotube surface.<sup>11-19</sup> In addition, a variety of properties can be introduced into the resulting supramolecular complexes through manipulation of the polymer backbone and side-chains.<sup>20, 21</sup> Recent examples include tightly-binding CNT complexes with polythiophene and polyfluorene derivatives that are not only soluble in organic and aqueous solvents, but can also enable high-resolution surface patterning, electrophoretic deposition, and separation of nanotubes according to type.<sup>22-25</sup> The high degree of solubility achievable with this approach provides an opportunity to apply homogeneously dispersed CNTs within a variety of device constructs that take advantage of the unique nanotube conductivity properties, including field effect transistors, photovoltaics, light-emitting diodes, and sensors.

In the general area of electrochemical biosensors, the use of conjugated polymers (CPs) as signal mediators has become widespread due to their remarkable stability, processability, solubility, electrical conductivity, and compatibility with biomolecules in aqueous solutions.<sup>26-29</sup> In addition to providing a suitable immobilization matrix for enzymes, antibodies, and nucleic acids, CPs have the potential to enhance stability and sensitivity of biosensors.<sup>30-33</sup> Polythiophene, along with its derivatives, represents a versatile class of conjugated polymers especially amenable for sensor applications, on account of their interesting optical and electronic properties,<sup>34</sup> as well as the facile ability to modify their structure with various side-chain functionalities that enable binding to enzymes, mediators, and compatibilizing groups.<sup>35</sup> A more important advantage of polythiophene over other conducting polymers as immobilization matrix in amperometric enzyme electrodes is its excellent stability in both air and water, making it relatively resistant to degradation by enzymatically generated oxidants, such as H<sub>2</sub>O<sub>2</sub>.<sup>36</sup>

Recently, improvements upon the CP biosensors have been realized through incorporation of nanostructures such as metal nanoparticles<sup>37</sup> and CNTs.<sup>38, 39</sup> In the case of CNTs, the high mobility of charge carriers in semiconducting tubes coupled with their large surface area makes them ideal candidates for sensor applications.<sup>40</sup> Additionally, as mentioned above, wrapping of nanotubes with conjugated polymers not only improves their solubility and general processibility, but also combines two materials having useful electrochemical properties. However, to date, nanotube complexes with only a limited

variety of CPs have been investigated in glucose biosensor applications, including Nafion,<sup>41, 42</sup> electropolymerized polypyrrole,<sup>43, 44</sup> and in-situ prepared polyaniline.<sup>45</sup> Although encouraging results have been reported with these systems, it is reasonable to assume that the CP-nanotube-biomolecule interactions can be optimized by varying the CP structure and properties. It is also advantageous to expand this CP repertoire to polymers that can easily be prepared, modified, and characterized prior to incorporation into biosensors.

In this investigation, polythiophene derivative, poly[3-(3-N,Na diethylaminopropoxy)thiophene] (PDAOT), was prepared through oxidative solution polymerization and utilized for the supramolecular functionalization of SWNTs, resulting in highly stable and concentrated aqueous solutions of PDAOT-SWNT complexes. Addition of glucose oxidase (GOx) to these solutions, followed by deposition onto gold electrodes, resulted in PDAOT-SWNT loaded polymer layers that contained entrapped GOx and formed highly sensitive glucose biosensors. The results presented here show that the PDAOT-SWNT complexes offer a versatile platform for the immobilization of enzymes within coatings that exhibit fast electron-transfer kinetics, high electrical conductivity, and excellent film quality. The obtained results pave the way for the development of other advanced biosensors based on SWNTs.

#### 7.2. Results and Discussion

# 7.2.1. Synthesis of Conjugated Polymer PDAOT

The polythiophene derivative PDAOT was prepared by oxidative polymerization of the 3-(3-N,N-diethylaminopropoxy)thiophene monomer, as depicted in Scheme 7.1. 3-(3-bromo)propoxythiophene **1** was prepared by treatment of 3-methoxythiophene with 2bromo-1-propanol in the presence of NaHSO<sub>4</sub>, as reported previously.<sup>46</sup> Subsequent treatment of **1** with diethylamine produced the amine-functionalized thiophene monomer **2.** PDAOT polymer **3** was then prepared under oxidative polymerization conditions in chloroform using ferric chloride as the oxidant. The neutral PDAOT (**3**) is readily soluble in common organic solvents such as chloroform, and THF, but insoluble in water and low-boiling alcohols (methanol and ethanol). Protonation of the amine side-chains with small amounts of acetic acid (5% vol/vol) resulted in complete and rapid dissolution of the polymer in water or ethanol, forming a blue solution (Figure 7.1A, ii).



**Scheme 7.1**. Procedure for synthesis of poly[3-(3-N,N-diethylaminopropoxy)thiophene] (PDAOT).

# 7.2.2. Investigation of the PDAOT-SWNT Supramolecular Interaction

The supramolecular functionalization of SWNTs by PDAOT was accomplished by previously published procedures<sup>23</sup> (see experemental) and resulted in a homogenous solution of PDAOT-SWNT complexes that was stable for several weeks without nanotube precipitation (Figure 7.1A, iii). The control experiment using pristine SWNTs treated identically but in the absence of PDAOT did not exhibit any observable solubility (Figure 7.1A, i). The scanning electron microscopy (SEM) images in Figure 7.1 B and C show the surface of drop-cast films of PDAOT and PDAOT-SWNT complexes. A relatively smooth and dense polymer film was formed after evaporation of the solvent (i.e. water), owing to the excellent film formation properties of PDAOT (Figure 7.1B). When mixed with SWNTs, the strong supramolecular interactions between PDAOT and the nanotubes resulted in significant debundling and homogenous dispersion of SWNTs in the polymer matrix, leading to the formation of a composite film of PDAOT-SWNT complexes upon solvent evaporation (Figure 7.1C).



**Figure 7.1.** (A) A photograph of vials containing (i) pristine SWNTs, (ii) PDAOT, and (iii) PDAOT-SWNT complexes in water after sonication for 1 hr; (B) SEM image of a drop-cast film prepared from a 6 g/L aqueous solution of PDAOT; (C) SEM image of a drop-cast film prepared from an aqueous mixture of 6 g/L PDAOT and 6 g/L SWNTs.



**Figure 7.2.** (A) Raman spectra for (a) PDAOT, (b) pristine SWNTs, and (c) PDAOT-SWNT complexes. (B) UV-Vis absorption data for aqueous solutions containing (a) GOx, (b) PDAOT, (c) PDAOT and GOx, (d) PDAOT-SWNT complexes, and (e) PDAOT-SWNT complexes with 2 g/L GOx added. Inset: Absorption data in the short wavelength region for samples a-e after two-fold dilution.

The PDAOT-SWNT supramolecular interactions were studied by Raman and UV-Vis spectroscopy. Figure 7.2A provides the Raman spectra of pristine SWNTs, and dropcast films of PDAOT alone and the PDAOT-SWNT complexes on glass slides. The spectra for samples containing SWNTs were normalized to the graphitic (G) band at 1590 cm<sup>-1</sup>. The Raman bands of PDAOT (Figure 7.2A, curve a) match with the experimental and calculated major Raman bands of poly(alkoxy thiophene)s reported in the literature<sup>47,</sup> <sup>48</sup>. The Raman spectrum of the PDAOT-SWNT complexes (Figure 7.2A, curve c) exhibits characteristic features of both the SWNTs and polymer components. The G band position (~1590 cm<sup>-1</sup>) for the PDAOT-SWNT complexes did not shift compared with that of the pristine nanotubes (Figure 7.2A, curve b). In addition, no significant increase in the intensity of the disorder (D) band at ~1300 cm<sup>-1</sup> was observed for the PDAOT-SWNT complexes compared with the pristine SWNTs, indicating that the supramolecular functionalization did not introduce any defects or structural changes into the SWNT sidewall. The radial breathing mode (RBM) profiles can be clearly observed in the Raman spectra for the pristine SWNTs and the drop-cast PDAOT-SWNT film. The decrease in intensity and small shifts of peak positions of various RBM signals after the supramolecular functionalization may be attributed to electronic interactions between PDAOT and SWNTs.

UV–Vis spectroscopy was also performed to study the PDAOT-SWNT supramolecular interactions and the possible conformational change of GOx after it was immobilized with PDAOT and the PDAOT-SWNT complexes. The spectrum of PDAOT-SWNT complexes (Figure 7.2B, curve d) revealed absorption bands corresponding to both the polymer (Figure 7.2B, curve b) at 589 nm and the SWNTs (weak van Hove singularities at 700-900 nm, along with a steady increase in absorption at shorter wavelengths). There was no shift in the absorption maximum of PDAOT upon nanotube complexation, indicating that PDAOT must adopt a relatively planar conformation in solution, and the degree of planarity (along with conjugation length) does not change appreciably upon adsorption to the SWNT surface. Figure 7.2B, curve a, shows the UV–Vis absorption spectrum of the enzyme GOx, with its characteristic absorption peaks at 278, 381, and 450 nm.<sup>49-52</sup> The absorption band at 278 nm is assigned to the characteristic peak of the polypeptide chains in the GOX structure<sup>51, 52</sup> and the peaks at 381 and 450 nm

are characteristic of the oxidized form of the flavin group.<sup>49, 50</sup> The spectrum of PDAOT/GOx (Figure 7.2B, curve c) exhibited both absorption bands corresponding to the polymer at 589 nm and the GOx (at 278, 382, and 473 nm). The spectrum of PDAOT-SWNT/GOx (Figure 7.2B, curve e) showed three additional absorption bands compared with that of PDAOT-SWNT complexes, whose position and peak shape are the same as those for pure GOx. In addition, the absorption of GOx did not change to any extent when the PDAOT-SWNT/GOx mixture was cast as a solid film on a quartz substrate (see Appendix I, Figure A.16). These results suggest that the GOx immobilized with the PDAOT and the PDAOT-SWNT complexes retains its native structure and therefore should maintain its bioactivity. The chromophoric GOx flavin groups remain embedded in the GOx polypeptide matrix and do not unfold from their hydrophobic interior domains upon immobilization.<sup>51, 52</sup>

To further corroborate these results, circular dichroism measurements were performed on the native GOx, the GOx-PDAOT mixture, and the PDAOT-SWNT/GOx material, which was re-dissolved from the surface of the electrode after drop-casting on the electrode surface. The CD spectrum of GOx in its native state exhibits strong CD signals in the visible, near-UV, and far-UV regions (Figure 7.3).<sup>53</sup> These include strong positive absorptions at ca. 380 and 270 nm from the flavin moiety and the aromatic tryptophans in the active site, respectively. The strong negative signal in the far-UV region, centered around 210 nm, results from  $n \rightarrow \pi^*$  transitions that are sensitive to the secondary structure of GOx. Comparison of the native GOx with the material that has been mixed with polymer and polymer-nanotube complexes indicates no change in the CD spectrum upon exposure to the electrode coating components, again confirming that the enzyme retains is native form even after casting within an active coating on the electrode surface.



**Figure 7.3.** Circular dichroism of (a) GOx, (b) GOx and PDAOT, and (c) a mixture of GOx, PDAOT, and SWNT in the (A) far-UV region, (B) near-UV region, and (C) visible region. The GOx concentration was (A) 0.05 g/L, (B) 5 g/L, and (C) 20 g/L in a 1 mm cuvette.

#### 7.2.3. Electrochemical Characterization of Modified Electrodes

Electrochemical impedance spectroscopy (EIS) is a highly effective method for probing the features of the surface of modified electrodes.<sup>54, 55</sup> EIS was therefore carried out to investigate the electron-transfer properties of the PDAOT and PDAOT-SWNT coatings. Figure 7.3A shows typical impedance spectra, in the form of Nyquist plots, acquired from the Au electrodes modified with films of pure polymer (Figure 7.4A, curve a) and PDAOT-SWNT complexes (Figure 7.4A, curve b). The profiles manifested a very small semicircular domain at high frequencies corresponding to the electron-transfer

limited process and a straight line at low frequencies that corresponds to the diffusion process. The Randles equivalent circuit (inset of Figure 7.4A)<sup>56-58</sup> was chosen to fit the impedance data obtained, where  $R_s$  is the solution resistance,  $R_{et}$  the electron-transfer resistance, W the Warburg impedance, and  $C_{dl}$  the double-layer capacitance. From this data, it was determined that the Au/PDAOT electrode (Figure 7.4A, curve a) exhibited a small electron-transfer resistance ( $R_{et}$ ) corresponding to 2.9  $\Omega$ ·cm<sup>2</sup>, which was calculated from the radius of the semicircular domain of the Nyquist plot. The  $R_{et}$  value may be ascribed to the conductivity of the conjugated polymer. The Au/PDAOT-SWNT electrode (Figure 7.4A, curve b) showed a lower  $R_{et}$  (0.8  $\Omega$ ·cm<sup>2</sup>), indicating that the presence of SWNTs enhanced the electron transfer from the redox probe.

Cyclic voltammetry of the ferricyanide/ferrocyanide system has also been conducted to further study the enhanced electrochemical response of the Au/PDAOT-SWNT electrode. Figure 7.4B shows cyclic voltammograms (CVs) of the Au/PDAOT and Au/PDAOT-SWNT electrodes in 5.0 mM ferricyanide/ferrocyanide solution. Welldefined oxidation and reduction peaks of  $[Fe(CN)_6]^{3-/4-}$  were observed with both electrodes. The PDAOT on the electrode surface is positively charged due to protonation and it adsorbs the negatively charged ferricyanide and ferrocyanide to the electrode, resulting in a high current response. The incorporation of SWNTs into the PDAOT film led to an increase in the oxidation and reduction peak currents of the electrode (Figure 7.4B, curve b). This can be attributed to the porous microstructure and increased specific surface area of the PDAOT-SWNT film. The peak-to-peak separation ( $\Delta E_p$ ) was 108 and 69 mV for the Au/PDAOT and Au/PDAOT-SWNT electrodes, respectively. A smaller  $\Delta E_p$  indicates faster electron-transfer kinetics for the Au/PDAOT-SWNT electrode as compared to the Au/PDAOT electrode that lacks the SWNTs.



**Figure 7.4.** (A) Nyquist plots and the equivalent electrical circuit (inset) of EIS data, and (B) CVs for (a) Au/PDAOT and (b) Au/PDAOT-SWNT electrodes prepared using 3 g/L PDAOT aqueous solution and 3 g/L PDAOT aqueous solution containing 1.5 g/L SWNTs, respectively. The electrolyte was a 0.1 mM KCl aqueous solution containing 5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]/ K<sub>4</sub>[Fe(CN)<sub>6</sub>] (1:1). In the equivalent circuit, the  $R_s$  is the solution resistance,  $R_{et}$  the electron-transfer resistance, W the Warburg impedance, and  $C_{dl}$  the double-layer capacitance.

The CVs are consistent with the EIS data. The enhanced charge transfer at the Au/PDAOT-SWNT electrode is due to the presence of well-dispersed SWNTs in the polymer matrix, which provide a conducting network facilitating charge transport through the film. Furthermore, SWNTs have shown excellent catalytic properties toward the electrochemical processes of many compounds.<sup>41, 59-61</sup> Polymer/SWNT composites have been reported to improve electrocatalytic activation of redox enzymes by enhancing

electrochemical transduction of the biochemical process.<sup>62</sup> It is expected that the film of PDAOT-SWNT complexes can act as a superior platform for the immobilization of enzymes such as GOx, with enhanced charge transport and bioelectrocatalytic properties, yielding high electrochemical responses.

#### 7.2.4. Optimization of Operation Potential of Biosensors

Glucose biosensors were constructed by modifying Au electrode coatings of PDAOT and PDAOT-SWNT films with entrapped GOx. A 6 g/L PDAOT aqueous solution containing 5 g/L GOx, and an aqueous mixture of 6 g/L PDAOT and 6 g/L SWNTs containing 5 g/L GOx were used to prepare Au/PDAOT/GOx and Au/PDAOT-SWNT/GOx glucose biosensors, respectively. The operating potential of the biosensors was optimized by amperometric response experiments. Figure 7.5 shows the current response to glucose as a function of the applied potential in the range from 0.45 to 1.0 V for Au/PDAOT/GOx (Figure 7.5, curve a) and Au/PDAOT-SWNT/GOx (Figure 7.5, curve b) biosensors. For Au/PDAOT/GOx, the current response increased with the increasing applied potential to reach a maximum at + 0.8 V, and then slightly decreased at more positive potentials. For Au/PDAOT-SWNT/GOx (Figure 7.5, curve b), the maximum current was reached at + 0.9 V. The current response increased rapidly with the increase of applied potential when the potential was lower than + 0.8 V, indicating that the current response is controlled by the electrochemical oxidation of the enzymatically generated H<sub>2</sub>O<sub>2</sub>:

Glucose + 
$$O_2 \xrightarrow{GO_x}$$
 Gluconolactone +  $H_2O_2$   
 $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ 

When the potential was higher than + 0.8 V, the current became relatively constant, which resulted from the rate-limiting process of enzyme kinetics.<sup>63, 64</sup> In subsequent experiments, a potential of + 0.8 V was selected for the operation of the Au/PDAOT/GOx and Au/PDAOT-SWNT/GOx biosensors. EIS data was also measured at the detection potential (+0.8 V) for the Au/PDAOT-SWNT electrode and resulted in a low  $R_{et}$  value of 1.1  $\Omega$ ·cm<sup>2</sup>, consistent with the measurement at open circuit potential (see Appendix I, Figure A.17).



**Figure 7.5.** Dependences of the current response to 1 mM glucose for (a) Au/PDAOT/GOx, and (b) Au/ PDAOT-SWNT/GOx on the applied potential in a 0.1 M phosphate buffered saline (pH 7.4).

#### 7.2.5. Amperometric Detection of Glucose

Figure 6 shows the current-time plots for the Au/PDAOT/GOx and Au/PDAOT-SWNT/GOx biosensors under the optimized applied potential (+0.8 V) with successive increase of glucose concentration in 0.2 mM increments. Rapid (within less than 5 s) response to glucose was observed for both electrodes, but a much higher sensitivity was observed in the presence of SWNTs (Figure 7.6, curve a) as compared to the Au/PDAOT/GOx electrode (Figure 7.6, curve b). The Au/PDAOT-SWNT/GOx biosensors exhibited linear current responses to successive increase of glucose over a range of 0.2 mM ~ 5 mM (Figure 7.6B) with a low detection limit of 5  $\mu$ M at a signal-tonoise ratio of 3. A current sensitivity of 100  $\pm$  6.0  $\mu$ A/mM·cm<sup>2</sup> was observed for Au/PDAOT/GOx, while Au/PDAOT-SWNT/GOx showed a higher sensitivity of 700  $\pm$  $26 \,\mu\text{A/mM}\cdot\text{cm}^2$ . The sensitivity of the Au/PDAOT-SWNT/GOx biosensor is much higher than what has previously been reported for glucose biosensors constructed using other polymers and carbon nanotubes.<sup>42-45</sup> The sensitivity of the Au/PDAOT-SWNT/GOx biosensor is likely the result of the synergistic effect of the high conductivity and enzymecompatible environment provided by the PDAOT-SWNT complexes, which also act as individual nano-scale electrodes providing a high effective electrode surface area.

When the glucose concentration was high, a plateau of current response was observed, showing the characteristic Michaelis-Menten kinetics for GOx. The apparent Michaelis-Menten constant ( $K_m^{app}$ ) can be calculated from the electrochemical version of the Linweaver-Burk equation<sup>65</sup>:

$$\frac{1}{i_{ss}} = \left(\frac{K_m^{app}}{i_{max}}\right) \frac{1}{C} + \frac{1}{i_{max}}$$

Where  $i_{ss}$  is the steady-state current after the addition of substrate,  $i_{max}$  is the maximum current under saturated substrate conditions, *C* is the concentration of substrate. The  $K_m^{app}$  value for the Au/PDAOT-SWNT/GOx biosensor was found to be 3.4 mM, which was much smaller than those of native GOx in solution (33 mM),<sup>49</sup> and immobilized GOx in polyaniline (31.59 mM),<sup>66</sup> polypyrrole (25.3mM),<sup>67</sup> chitosan (21 mM),<sup>68</sup> and MWCNT/Teflon composite (30 mM).<sup>69</sup> This result reveals that the GOx entrapped in the PDAOT-SWNT composite film exhibits high enzymatic activity and biological affinity to glucose.



**Figure 7.6.** (A) Amperometric responses to successive increase of 0.2 mM glucose in 0.1 M phosphate buffered saline (pH 7.4) at + 0.8 V vs. SCE, and (B) steady-state calibration curves for the (a) Au/PDAOT/GOx and (b) Au/ PDAOT-SWNT/GOx electrodes.

# **7.2.6. Detection Selectivity**

Difficulties in accurate measurement of glucose concentration can arise from electroactive interfering compounds such as ascorbic acid (AA), uric acid (UA), and acetaminophen (AP), which are commonly present within physiological samples. The selectivity of the above biosensor design was tested by adding these interfering compounds at the concentrations typically found within blood (0.1 mM, 0.3 mM, and 0.1 mM for AA, UA, and AP, respectively). Unfortunately, in the absence of any modification, the biosensor was highly sensitive to these compounds, giving signals that were on the order of 20-100% of the magnitude observed for glucose at a concentration of 5 mM. However, introduction of Nafion as an overcoat on the electrode surface dramatically reduced the sensitivity to the interfering compounds, while retaining much of the sensitivity to glucose (Figure 7.7 and Table 7.1). Under these conditions, interference from UA, AA, and AP amounted to 3.3%, 2.3%, and 13.9%, respectively, relative to the response upon introduction of a 5 mM concentration of glucose (Table 7.1). It should be noted that the second glucose addition in Figure 7.7 produced a decreased response relative to the first addition because, at that point, the glucose concentration was beyond the dynamic range for the sensor. Improvement in the selectivity of this biosensor design through variation of sensor components and glucose detection mechanism is the subject of ongoing research.



Figure 7.7. Amperometric response to sequential additions of glucose, AA, UA, and AP.

Analyte <sup>a</sup>	Current response (µA)	Relative Response <sup>b</sup>
5.0 mM alucoso	2 20	1000/ <sup>c</sup>
5.0 milli glucose	5.50	10070
0.3 mM uric acid	0.116	3.52%
0.1 mM ascorbic acid	0.078	2.36%
	01070	2.0070
0.1 mM acetaminophen	0.460	13.9%
5.0 mM glucose	2.69	81.5%

 Table 7.1. Nafion-coated sensor response to the addition of interfering compounds

<sup>a</sup> Analytes were sequentially added in the order shown. <sup>b</sup> Response relative to the initial 5.0 mM glucose addition. <sup>c</sup> The sensitivity to the initial 5.0 mM glucose addition was calculated to be  $336.2 \,\mu\text{A/mM}\cdot\text{cm}^2$ .

# 7.3. Conclusion

We have demonstrated a promising glucose biosensor by immobilizing GOx within the composite film of PDAOT-SWNT complexes. The water-soluble conjugated polymer, PDAOT, was synthesized by oxidative polymerization and utilized for the supramolecular functionalization of SWNTs. The PDAOT-SWNT complexes form stable aqueous solutions that can be used for the fabrication of highly sensitive amperometric glucose biosensor. The experimental results showed that Au electrodes modified with a film of PDAOT-SWNT complexes can provide a universal platform for the immobilization of redox enzymes, with excellent electronic conductivity and enhanced electron transfer properties. The incorporation of SWNTs into the polymer matrix increased both the electron transfer rate and total current flowing through the coating. Under optimized conditions, the Au/PDAOT-SWNT/GOx biosensor exhibited fast current response to glucose with a sensitivity of  $700 \pm 26 \ \mu\text{A/mM} \cdot \text{cm}^2$  and a detection limit of 5 µM (S/N=3). Selectivity of this sensor design was achieved by introducing a Nafion overcoat, which effectively suppressed the response to AA, UA, and AP, while maintaining much of the sensor sensitivity to glucose. The excellent performance of the biosensor can be attributed to the synergistic effect of the high conductivity and nondenaturing microenvironment of the PDAOT, as well as the large active surface area and electrical conductivity provided by the SWNTs. The results of this investigation pave the way for the fabrication of other redox-enzyme based biosensors using PDAOT-SWNT complexes.

### 7.4. Experimental Section

# 7.4.1. General

Single-walled carbon nanotubes (SWNTs) were purchased from Carbon Nanotechnologies, Inc. (Houston, TX). D-(+)-Glucose, and glucose oxidase (GOx, EC 1.1.3.4, type X-S, lyophilized powder, 130~190 units/mg, from Aspergillus niger) were purchased from Sigma-Aldrich. Glucose stock solutions were mutarotated overnight at room temperature before use. All reagents and solvents were purchased from commercial suppliers and used as received. UV-Visible spectra were measured by using a Cary 50 UV-visible spectrophotometer. Ultrasonication was carried out in a Banson Ultrasonics B1510, and B2500 bath sonicator. Beckman Allegra[TM] X-22R Benchtop centrifuge was used for centrifugation. Raman spectra from all samples were collected with a Renishaw Ramanscope at an excitation laser wavelength of 785 nm. NMR spectra were measured on Bruker Avance 200 spectrometers. SEM was performed using a JEOL JSM-7000F scanning electron microscope. The Circular dichroism (CD) measurements were performed on an AVIV Circular Dichroism Spectrophotometer Model 410 (Biomedical Inc) at 25 °C. The samples were prepared from corresponding solid films dissolved in dilute acetic acid solutions in DI H<sub>2</sub>O (pH 4.5).

All the electrochemical measurements were carried out on a PARSTAT 2273 system (Princeton Applied Research) using a conventional three-electrode cell, with a platinum gauze as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials were measured versus SCE. Deaerated 0.1 M KCl solution containing 5 mM  $K_3$ [Fe(CN)<sub>6</sub>]/ $K_4$ [Fe(CN)<sub>6</sub>] was used as supporting elecctrolyte

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for the electrochemical impedance spectroscopy (EIS) and cyclic voltammetric experiments. The EIS was performed at open circuit potential and at +0.8 V vs. SCE in the frequency range of 1 to  $10^5$  Hz. The amplitude of the applied sine wave potential was 5 mV. Cyclic voltammetry was conducted at a scan rate of 50 mV/s. Chronoamperometric experiments were conducted in 0.1 M phosphate buffered saline (PBS, pH 7.4) under gently magnetic stirring. In the steady-state amperometric experiments, the electrode was posed to a constant working potential, allowing the background current to decay to a steady-state value, and the current response of the biosensor to successive injection of glucose was recorded.

### 7.4.2. Preparation of 3-(3-bromopropoxy)thiophene (1)

A 250 mL round bottom flask equipped with a magnetic stir bar was charged with 3-methoxythiophene (5 g, 43.8 mmol), 2-bromo-1-propanol (7.7 mL, 88 mmol), NaHSO<sub>4</sub> (2.2 g, 18.32 mmol), and 100 mL of toluene. Then the mixture was heated to 100 °C, allowing a small amount of methanol to be distilled of from the reaction mixture. 20 mL of toluene was added to the reaction flask, and the temperature was raised to 120 °C, to allow approximately 50 mL of an azeotropic mixture of methanol and toluene to be distilled off. The reaction mixture was cooled and filtered. The toluene was then evaporated and the product was purified by column chromatography on silica gel using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexanes as the eluent (1:3 v/v) to give a colorless oil, which slowly turns light red over time upon standing (8.3 g, 85 % yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz, ppm)  $\delta$ : 7.20 (m, 1 H), 6.75 (d, 1 H), 6.28 (s, 1 H), 4.10 (t, 2 H), 3.60 (t, 2 H), 2.31

(m, 2 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz) δ: 30.07, 32.43, 67.54, 97.59, 119.48, 124.91, 158.04.

#### 7.4.3. Preparation of 3-(3-N,N-diethylaminopropoxy)thiophene (2)

A 500 mL round bottom flask equipped with a magnetic stir bar was charged with 3-(3-bromo)propoxythiophene (7 g, 32 mmol) (1), diethylamine (16.8 mL, 163 mmol), K<sub>2</sub>CO<sub>3</sub> (22.12 g, 160 mmol), KI (2 g, 12 mmol), and 300 mL of acetone. The reaction mixture was stirred and heated to reflux overnight. The acetone was evaporated, and the reaction mixture was dissolved in 200 mL of CH<sub>2</sub>Cl<sub>2</sub>, and then extracted with H<sub>2</sub>O (3  $\times$ 100 mL). The organic layer was dried over MgSO<sub>4</sub> and concentrated in vacuo. The residue purified by silica gel column chromatography was (ethylacetate/methanol/triethylamine 88:10:2, v/v/v) to give the product as a reddish oil (5.4 g, 80 % yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz, ppm)  $\delta$ : 7.16 (m, 1 H), 6.74 (m, 1 H), 6.24 (m, 1 H), 4.10 (t, 2 H), 2.57 (m, 6 H), 1.92 (m, 2 H), 1.02 (m, 6 H). <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 50 MHz)  $\delta$ : 11.89, 27.13, 47.08, 49.52, 68.74, 97.15, 119.60, 124.60, 158.04. MS Calc'd for  $C_{11}H_{19}NOS [M+H]^+ m/z = 214.12$ , found ESMS  $[M+H]^+ m/z =$ 214.12.

#### 7.4.4. Preparation of Poly[3-(3-N,N-diethylaminopropoxy)thiophene] (PDAOT, 3)

A flame dried, 1 L round bottom flask equipped with a magnetic stir bar was charged with FeCl<sub>3</sub> (15.2 g, 93.8 mmol), and 300 mL of freshly distilled CHCl<sub>3</sub>. The mixture was stirred for 30 min at room temperature, producing a dark green solution, with some residual FeCl<sub>3</sub> remaining. 3-(3-N,N-diethylaminopropoxy)thiophene 2 (4 g, 18.7 mmol) was dissolved in 150 mL of freshly distilled CHCl<sub>3</sub>, and this solution was added dropwise to the FeCl<sub>3</sub> solution over a period of 4 h under Ar atmosphere. The mixture was stirred for 48 h at 35 °C, and the reaction mixture was concentrated to 100 mL, and the product was then precipitated by dropwise addition to 1 L of MeOH. The precipitate was collected by filtration, and the resulting black solid was added to the mixture of 200 mL methanol, and 10 mL of hydrazine monohydrate, and resulting mixture was stirred for over night at room temperature, and then filtered again. The resulted black powder was added to 100 mL of 5 % aqueous ammonia (v/v) solution, and the precipitated polymer was collected by filtration. Then the obtained dark blue solid was washed with methanol, water, acetone, and methanol (300mL of each), and then dried under vacuum at 50 °C for 24 h. The polymer was obtained as a dark bluish solid in 90 % yield. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz, ppm)  $\delta$ : 6.87 (b, 1 H), 4.17 (b, 2 H), 2.68 (b, 6 H), 2.03 (b, 2 H), 1.07 (b, 6 H), UV-Vis (CHCl<sub>3</sub>):  $\lambda_{max, abs} = 589$  nm

# 7.4.5. Functionalization of SWNTs and Characterization of PDAOT-SWNTs complexes

The PDAOT was protonated in 5% acetic acid solutions and dissolved in water. SWNTs were functionalized in 6 g/L PDAOT aqueous solution by sonication for 1 hr, followed by centrifuge at 2576 g for 30 min. The surface morphology of drop-cast films of PDAOT and PDAOT-SWNTs complexes was investigated by SEM. To incorporate the enzyme, GOx was directly dissolved in aqueous solutions of PDAOT and PDAOT-SWNTs complexes. Aqueous solutions of PDAOT and PDAOT-SWNTs complexes in the presence and absence of 2 g/L GOx were studied by UV-Visible spectroscopy. To avoid saturating the detector, the samples had to be diluted two-fold to collect absorption data in the low wavelength range of 250 – 350 nm. Raman spectroscopy investigation was conducted on drop-cast films of PDAOT and PDAOT-SWNTs complexes.

#### 7.4.6. Preparation of Glucose Biosensors

The electrode used was a 0.5 mm diameter Au wire mounted in epoxy resin. Before modification, the Au electrode was polished to a mirror finish using 0.3  $\mu$ m alumina slurry followed by rinsing thoroughly with double-distilled water and ethanol. To form the modified Au electrode, 2  $\mu$ L of PDAOT or PDAOT-SWNTs complex solution containing 0~5 g/L GOx was dropped onto the pretreated Au electrode surface, followed by evaporation of solvent at room temperature. Au/PDAOT/GOx and Au/PDAOT-SWNTs/GOx glucose biosensors were prepared using a 6 g/L PDAOT solution containing 5 g/L GOx, and a 6 g/L PDAOT containing 6 g/L SWNTs and 5 g/L GOx, respectively. After drying, the biosensors were stored at 4°C in a refrigerator. For devices that were coated with a Nafion overcoat, 1  $\mu$ L of 0.5 wt. % Nafion solution was placed on top of the PDAOT-SWNTs/GOx coating, and allowed to air dry for at least 30 min. prior to measurement.

### 7.4.7. EIS Spectrum at the Detection Potential (+0.8 V)

The EIS spectrum obtained at +0.8 V vs. SCE exhibited a similar profile to that measured at open circuit potential (Figure 4A, curve b). A low electron-transfer resistance ( $R_{et}$ ) of 1.1  $\Omega \cdot cm^2$  for the Au/PDAOT-SWNT electrode was determined by fitting the data using the Randles equivalent circuit (see Appendix I, Figure A.17, inset). The results indicate a fast electron-transfer kinetics facilitated by the SWNTs under the operating potential of the biosensor.

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# **Chapter 8: Thesis Overall Conclusions and Recommendations for Future work**

#### **8.1. General Conclusions**

Single-walled carbon nanotubes (SWNTs) are of special interest in current research due to their extraordinary mechanical, electronic, and optical properties. Their unique structure, remarkable thermal and electrical conductivity, and high mechanical strength make SWNTs viable candidates for a wide range of device applications. However, pristine CNTs are not soluble or easily dispersible in most solvents; the main difficulties in CNT applications are related to their purification and solution-phase processing. Supramolecular functionalization of CNTs is particularly attractive as this approach allows control of CNT solubility and processability while still preserving nearly all of the CNT's intrinsic properties. Using conjugated polymers as CNT dispersing agents has received significant recent attention because these types of polymers are capable of multivalent binding to the nanotube surface, resulting in higher carbon nanotube solubility and good solution stability. In the first chapter of this thesis, the topic of supramolecular functionalization of CNTs with conjugated polymers was surveyed, and the most significant and intriguing results from the literature were reviewed and critically analyzed.

In Chapter 2 of this thesis, we outlined a simple method for the preparation of supramolecular SWNT complexes with two fluorene containing conjugated polymers. In this work, we synthesized poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,7-(9,9-diodecylfluorene)] (PF), and poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,5-(3-

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dodecylthiophene)] (PFT), and investigated their ability to form supramolecular complexes with SWNTs. In these studies, it was found that both PF and PFT can form stable complexes with SWNTs through non-covalent interactions, and the resulting polymer-nanotube assembly exhibited excellent stability properties in THF in the absence of excess unbound polymer. Thermogravimetric analysis indicated that the polymernanotube complexes were composed of approximately 40 wt % polymer. UV-Vis absorption measurements revealed a bathochromic shift in the absorption spectrum of the polymers as a result of nanotube complexation, while fluorescence measurements showed that polymer fluorescence is highly quenched in the complexes. Thin mats of the polymer-nanotube complexes were prepared by filtration through a Teflon membrane (200 nm pore diameter), and produced flexible films that could be peeled off from the membrane. The electrical conductivity of these films was determined by measuring their sheet resistance using 4-point-probe method, and it was found that the supramolecular complexes exhibited conductivities in the range of 50 S $\cdot$ cm<sup>-1</sup>, which is only slightly lower than what is found for pristine SWNT films. This work therefore demonstrated that the supramolecular functionalization of SWNTs with fluorene and thiophene containing conjugated polymers offered a means by which stable and dispersible polymer-SWNT complexes could be produced, and exploited to prepare new composite materials.

In chapter 3, we have compared three different polymer backbones with respect to their interactions with SWNTs, including poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,7-(9,9-diodecylfluorene)] (PF), poly(3-dodecyl thiophene) (PT), and an alternating copolymer of fluorene and thiophene, poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,5-(3-dodecylthiophene)]

(PFT). Specifically, we investigated the effect of changing the polymer backbone on nanotube solubility, solution stability, and photophysical properties. In this work it was shown that non-covalent functionalization of SWNTs with these three polymers can impart good solubility to nanotubes in a number of organic solvents, including THF, dichlorobenzene, chloroform, and toluene. Several spectroscopic characterization techniques involving solution and solid-state characterization of the resulting polymer-SWNT composites were also described, including UV-Vis absorption and Raman spectroscopy. It was found that the UV-Vis absorption maximum of the polymers redshifted in their corresponding composites, and the magnitude of the red-shift varied with polymer structure. The largest absorption red-shift was observed in the PT-SWNT complex (~120 nm) in solution, while a very small red-shift (~ 4 nm) was observed for PF-SWNT complex. Both UV-Vis absorption and Raman spectroscopy results indicated that the interaction of PT with the SWNTs was different than that of PF and PFT, suggesting that the choice of aromatic ring in the polymer structures plays a very important role in the supramolecular complex formation with carbon nanotubes.

In chapter 4, we have studied the effect of polymer molecular weight on the nanotube solubility in THF using PFT as a model polymer. It was found that the solubility of the resulting polymer-SWNT complex strongly depends on the molecular weight of the polymer. Eight samples having different molecular weight ranging from 5 to 85 kg/mol were used in these studies, and it was found that the SWNT concentration reached a maximum when the polymer molecular weight was in the range of 10-35 kg/mol, while higher and lower molecular weights resulted in much lower solubility. This work

suggested that the molecular weight of the polymer should be taken into account when synthesizing a new polymer for SWNT functionalization.

In Chapter 5 we further investigated the supramolecular complex formation of fluorene and dithieno[3,2-b:2',3'-d]pyrrole (DTP) containing polymers with SWNTs. Two alternating copolymers, {2,7-[9,9-didodecylfluorene]-alt-2,6-[Ndodecyldithieno(3,2-b:2',3'-d)pyrrole]} (PF-DTP1) and {2,7-[9,9-didodecylfluorene]-alt-2,6–[N-3,4,5(n-dodecyloxy)phenyldithieno(3,2-*b*:2',3'-*d*)pyrrole]} (PF-DTP2) were synthesized such that they have identical aromatic backbones, but differ in their solubilizing side-chains. UV-vis absorption measurements revealed a bathochromic shift in the polymer absorption spectrum as a result of complex formation with SWNTs. Fluorescence measurements showed that polymer emission is highly quenched in the corresponding SWNT complexes. UV-vis-NIR, photoluminescence, and Raman measurements indicated that the SWNTs were successfully debundled and isolated by the polymers in solution, and removal of the free polymer by filtration did not cause further bundling. Based on these two polymers, it was found that the interactions with the SWNT surface are more strongly dictated by the polymer backbone than the side chain.

In chapter 6, we described the supramolecular interaction between SWNTs and a photo-responsive azobenzene containing polymer, poly[2,7-(9,9-didodecylfluorene)-*alt*-4,4'-azobenzene] (F12AZO). In this study, the photo-responsive azobenzene (AZO) unit was chosen as a co-monomer with fluorene to introduce photochemical reversibility to the polymer-SWNT interaction. Unfortunately, photoirradiation of *trans*-F12AZO-SWNT complexes with absorption maximum below 450 nm does not cause noticeable SWNT

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aggregation or precipitation. Photoluminescence excitation maps showed that efficient and highly selective dispersal of SWNTs is possible by using both *trans* and *cis* isomers of F12AZO in toluene or THF, and the selectivity of the SWNTs is strongly dependent on the solvent, as well as the type of isomer used.

In chapter 7, we also investigated the interaction between water-soluble conjugated polymers (conjugated polyelectrolytes) and SWNTs. A water soluble polythiophene derivative, poly[3-(3-N,N-diethylaminopropoxy)-thiophene] (PDAOT), was synthesized and utilized for the supramolecular functionalization of SWNTs. It was found that the PDAOT-SWNT complexes form stable aqueous solutions that can be used for the fabrication of highly sensitive amperometric glucose biosensors. The glucose biosensor was prepared by immobilizing glucose oxidase (GOx) within a drop cast composite film of PDAOT-SWNT complexes, and it was found that the incorporation of SWNTs into the polymer matrix increased both the electron transfer rate and total current flowing through the coating. Under optimized conditions, the Au/PDAOT-SWNT/GOx biosensor exhibited fast current response to glucose with a detection limit of 5  $\mu$ M and a sensitivity of 700 ± 26  $\mu$ A/mM·cm<sup>2</sup>.

In summary, the most significant contribution of this thesis comes from investigating the effect that conjugated polymer structure has on the formation of supramolecular complexes with SWNTs. This thesis provides proof-of-principle examples demonstrating how the interactions between conjugated polymers with the SWNT surface are strongly dictated by the polymer backbone.

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#### 8.2. Recommendations for Future Work

SWNTs have the potential to be used for various molecular electronics including thin film transistors, photovoltaics, as well as biological and chemical sensors due to their unique combination of optical, electronic, and mechanical properties. However, there are a number of challenges associated with their practical application including lack of solubility, processability and the coexistence of metallic and semiconducting SWNTs in as-synthesized samples. With respect to these major challenges, it has been demonstrated that successful solution-phase manipulation and selective dispersion is possible by supramolecular functionalization of SWNTs with various conjugated polymers. Since each species of SWNT with specific chiral (n,m) indices exhibits unique electronic properties, strategies that focus on preparing monodisperse SWNTs with predominantly single electronic type still represent the major trend in this research area.

There are several directions in which research could carry on following the work described in this thesis. As a starting point, techniques developed for the preparation of polymer-SWNT complexes could be expanded to investigate other new conjugated polymers. A library of polymers varying in their aromatic backbone or side chains could be explored. Additionally, the study of the effect of molecular weight on the interaction between PFT and SWNTs, which was described in Chapter 4, can be extended to other polymer structures.

As mentioned in previous chapters, the interactions between conjugated polymers with the SWNT surface are strongly dictated by the polymer backbone. While most of the fluorene and thiophene containing conjugated polymers have been shown to interact strongly with SWNTs, the differences in binding strength between each polymer with SWNTs should be evaluated. A competitive binding experiment between various conjugated polymers with SWNTs should be conducted to determine how the small changes on the polymer backbone or the side chains can alter the binding strength between a polymer and the SWNT surface, as well as the selectivity preference for certain SWNT species. Furthermore, it would be useful to evaluate whether the binding strength, and preferential binding to specific SWNTs are susceptible to the incorporation of electron donating or electron withdrawing groups on the same polymer backbone.

Supramolecular functionalization of SWNTs with fluorene and thiophene containing conjugated polymers has shown great promise for enhancing SWNT solubility and processability for various applications. However, the removal of the polymer from the nanotube surface is a major bottleneck once the polymer-SWNT complex has been formed. Removing the polymer from nanotube surface after selective dispersal of certain semiconducting SWNT species was achieved offers advantages with regard to the purity of the SWNT samples. The development of new functional conjugated polymers that can be easily removable after enrichment of certain SWNT species to recover the pristine nanotubes could potentially yield SWNT materials exhibiting useful properties for practical applications.

As mentioned in Chapter 7, the water solubility of the conjugated polyelectrolyte functionalized SWNTs offers advantages over organic soluble counterparts with regard to the applicability of these materials for biological systems. We have shown that conjugated polyelectrolyte-modified SWNTs can be intimately mixed with GOx and

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coated on electrode surfaces to produce glucose sensors. Based on the results presented in this thesis, suitable design, fabrication, and testing of electrochemical sensors using lowcost technologies should be developed for sensing other analytes. Finally, methods for fabrication and characterization of conjugated polymer-SWNT based sensors should also be developed by using low-cost technologies, and tested in their application environment.

#### **Appendix I**

## Chapter 3: Supramolecular Complexes of Single Walled Carbon Nanotubes with Conjugated Polymers



**Figure A.1.** UV-Vis absorption data of the polymer in THF, dichlorobenzene, and toluene at variable temperature. PF (A), PFT (B), and PT (C) complexes in THF(i), dichlorobenzene(*ii*) and toluene(*iii*).

Chapter 5. Supramolecular Functionalization of Single Walled Carbon Nanotubes (SWNTs) with Dithieno[3,2-b:2',3'-d]pyrrole (DTP) Containing Conjugated Polymers



**Figure A.2.** <sup>1</sup>H NMR spectrum of 2,6-dibromo-N-dodecyldithieno[3,2-b:2',3'-d]pyrrole (DTP) (**4**) in CDCl<sub>3</sub>.



**Figure A.3.** <sup>1</sup>H-NMR spectrum of N-3,4,5(n-dodecyloxy)phenyl)dithieno[3,2-b:2',3'-d]pyrrole (8) in CDCl<sub>3</sub>.



**Figure A.4.** <sup>1</sup>H-NMR spectrum of 2,6-Diiodo-N-3,4,5(n-dodecyloxy)phenyl)dithieno [3,2-b:2',3'-d]pyrrole (**9**) in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure A.5.** <sup>1</sup>H-<sup>1</sup>H COSY spectrum of PF-DTP1 in CDCl<sub>3</sub>.



Figure A.6. <sup>1</sup>H-<sup>13</sup>C HSQC spectrum of PF-DTP1 in CDCl<sub>3</sub>.



Figure A.7. <sup>1</sup>H-<sup>13</sup>C HMBC spectrum of PF-DTP1 in CDCl<sub>3</sub>.



**Figure A.8.** TEM images of PF-DTP2+SWNT at different magnifications. Scale bars are 500 nm (A), 100 nm (B), and 50 nm (C).



**Figure A.9.** Raman Spectra (with excitation at 785 nm) for SDBS/SWNT (a), PF-DTP1+SWNT (b), PF-DTP2+SWNT (c), and pristine SWNT (d).

		E	<sub>411</sub> (nm)	E <sub>22</sub> (nm)					
(n,m)	Lit. <sup>12</sup>	Obs.	Obs.	Obs.	Lit. <sup>12</sup>	Obs.	Obs.	Obs.	
	SDS	SDBS	PF-DTP1	PF-DTP2	SDS	SDBS	PF-DTP1	PF-DTP2	
(6,5)	976	980	1000	1000	566	567	575	575	
(7,5)	1024	1022	1050	1045	645	645	660	655	
(7,6)	1120	1118	1155	1145	648	647	662	660	
(8,4)	1111	1115	1145	1140	589	588	600	595	
(8,6)	1173	1172	1210	1210	718	717	730	730	
(8,7)	1265	1265	1300	1295	728	729	745	745	
(9,4)	1101	1100	1133	1130	722	720	735	735	
(9,5)	1241	1241	1270	1265	672	669	685	685	

**Table A.1.** Emission peak positions of SWNT species obtained from PLE maps of

 sample prepared in SDBS aqueous solution and polymers in THF.

				normalized intensity (%)				
				D <sub>2</sub> O	THI	Ę		
(n,m)	mode	d (nm)	$\theta$ (deg)	SDBS	PF-DTP1	PF-DTP2		
(6,5)	1	0.757	27.00	0.12	0.50	0.58		
(7,5)	2	0.829	24.50	0.17	1	1		
(7,6)	1	0.895	27.46	0.47	0.80	0.94		
(8,4)	1	0.840	19.11	0.25	0.48	0.55		
(8,6)	2	0.966	25.28	1	0.42	0.42		
(8,7)	1	1.032	27.80	0.71	0.46	0.42		
(9,4)	2	0.916	17.48	0.34	0.35	0.47		
(9,5)	1	0.976	20.63	0.62	0.33	0.39		

**Table A.2.** Relative intensity of SWNT species obtained from PLE maps of sample

 prepared in SDBS aqueous solution and polymers in THF.

# Chapter 6: Supramolecular Functionalization of Single Walled Carbon Nanotubes (SWNTs) with Photoisomerizable Conjugated Polymer



Figure A.10. Thermograms of F12AZO measured under Ar atmosphere



**Figure A.11.** Changes in UV-vis spectra of the polymer in THF (c = 0.017g/L) under different irradiation times at room temperature. (A) irradiation with wavelengths < 450 nm, (B) irradiation with wavelengths in the range of 450-600 nm.



**Figure A.12.** Reversible photo-isomerization of the F12AZO in THF (c = 0.017 g/L) upon alternating irradiation at room temperature (irradiation time 15 min). (A) Changes in UV-vis spectra, (B) Absorbance at 417 nm versus irradiation cycle number.



**Figure A.13.** Photograph of *trans*-F12AZO in THF (A), the *trans*-F12AZO+SWNT complex in THF (B), and the *trans*-F12AZO+SWNT complex in toluene (C). Samples B and C are after centrifugation for 45 min at 8,300 g.



Figure A.14. UV-Vis absorption data, (A) *trans*-F12AZO, *trans*-F12AZO+SWNT complexes in THF, and SDBS+SWNT in D2O, (B) *trans*-F12AZO+SWNT complexes was irradiated with  $\lambda_{max} < 450$  nm light to cause *trans*-to-*cis* isomerization.



**Figure A.15.** Fluorescence spectra of the F12AZO-SWNT complex in THF (A) and toluene (B) excited at 417 nm (absorption maximum of the polymer) as well as 550 and 785 nm, showing that sensitized emission of the SWNTs upon polymer excitation does not occur.

	E <sub>11</sub> (nm)							E <sub>22</sub> (nm)					
		D <sub>2</sub> O	F12AZO in THF		F12AZO in toluene			D <sub>2</sub> O	F12AZO in THF		F12AZO in toluene		
(n,m)	Lit.	Obs.	Obs.	Obs.	Obs.	Obs.	Lit.	Obs.	Obs.	Obs.	Obs.	Obs.	
	SDS	SDBS	trans	cis	trans	cis	SDS	SDBS	trans	cis	trans	cis	
(6, 5)	976	975	1000	1000	1000	1000	566	565	575	575	575	575	
(7, 5)	1024	1025	1045	1045	1045	1045	645	645	655	655	655	655	
(7, 6)	1120	1120	1145	1145	1145	1140	648	645	655	655	655	655	
(8, 4)	1111	1111	1140	1140	1140	1140	589	589	595	595	595	595	
(8, 6)	1173	1172	1200	1200	1200	1200	718	715	725	725	725	725	
(8, 7)	1265	1267	1295	1295	1290	1290	728	730	735	735	740	740	
(9, 4)	1101	1100	1130	1130	1125	1125	722	720	730	730	730	730	
(9, 5)	1241	1245	1260	1260	1265	1260	672	670	680	680	685	680	

**Table A.3.** Emission peak positions of SWNT species obtained from PLE maps of sample prepared in SDBS aqueous solution and polymers in THF and toluene.

**Table A.4.** Relative intensity of SWNT species obtained from PLE maps of sample prepared in SDBS aqueous solution and polymers in THF and toluene, organized by nanotube diameter.

				Normalized Intensity (%)				
			D <sub>2</sub> O	THF		Toluen	e	
(n,m)	d (nm)	θ (deg)	SDBS	trans- F12AZO	cis- F12AZO	trans- F12AZO	cis- F12AZO	
(6,5)	0.757	27.00	0.31	1.0	0.53	0.21	0.06	
(7,5)	0.829	24.50	0.40	0.84	0.60	0.38	0.17	
(8,4)	0.840	19.11	0.44	0.33	0.38	0.17	0.1	
(7,6)	0.895	27.46	0.65	0.59	1.0	0.52	0.35	
(9,4)	0.916	17.48	0.53	0.27	0.35	0.46	0.21	
(8,6)	0.966	25.28	1.0	0.41	0.57	0.88	0.99	
(9,5)	0.976	20.63	0.55	0.51	0.46	0.74	0.74	
(8,7)	1.032	27.80	0.54	0.37	0.30	1.0	1.0	

### Chapter 7: Amperometric Detection of Glucose Using a Conjugated Polyelectrolyte Complex with Single-Walled Carbon Nanotubes



**Figure A.16.** Absorption spectra of drop-cast solid films of (a) GOx, (b) PDAOT and GOx, and (c) mixture of PDAOT, SWNTs, and GOx on quartz in the spectral ranges of 250-320 nm (A) and 320-800 nm (B).



**Figure A.17.** Nyquist plot of EIS data at 0.8 V vs. SCE for Au/PDAOT-SWNT electrode prepared using 3 g/L PDAOT aqueous solution containing 1.5 g/L SWNTs.