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ABSTRACT

Since their discovery, single walled carbon nanotubes (SWNTs) have attracted much attention due to their superior mechanical and electronic properties that have led to their use in various applications. The electronic structure and optical properties of individual SWNT are uniquely dependent on the tube's chirality and diameter. In the asprepared sample, tubes are generally produced as a complex mixture containing many different chiral species. Selective enrichment and separation of SWNTs will play a vital role in the realization of the potential application of SWNTs. Separation of different types of SWNTs, however, remains one of the fundamental and challenging issues in nano science.

In this dissertation, several approaches have been examined to separate SWNTs, which are based on different molecular interaction with nanotubes, nanotube aggregation and chromatography. Among the polymers examined are water soluble poly[(*m*-phenylenevinylene)-*alt*-(p-phenylenevinylene)] (PmPV), poly[(phenyleneethynylene)-*co*-poly(phenylenevinylene)] (PPE-PPV), and water soluble poly[(*m*-phenyleneethynylene)*alt*-(*p*-phenyleneethynylene)] (PPE). Arising from the bent angle from *m*-phenylene, these polymers can form helical conformation to facilitate an intimate interaction between polymer chains and SWNTs. With unsymmetrical side groups, water soluble PmPV demonstrates that the polymer helical conformation can be controlled to sort the SWNTs by their diameters. Introduction of rotatable phenylenethynylene (PE) on the backbone allows polymer PPE-PPV quickly adjust the conformation for interaction with the SWNTs of a suitable diameter, which leads to the large diameter selectivity. The study of water soluble PPE polymer also reveals the intriguing selectivity toward tube (6,5), illustrating the impact of the carbon-carbon triple bonds on the SWNT selectivity.

The nanotubes from SWNTs/polymers dispersion tends to form aggregation. Analysis of the aggregate SWNTs shows that the sample contains enriched semiconducting SWNTs. In addition, the SWNTs are found to form aligned bundles.

Polyethylenimine (PEI) is found to exhibit selective interaction with semiconducting SWNTs. By using this property, a PEI/cellulose column chromatography can be used to separate a blue solution from the raw HiPCO SWNTs. Analysis by Raman, 2D fluorescence and UV-vis-NIR absorption spectra suggests that the isolated blue solution is pure metallic SWNTs. By changing eluent, this PEI/cellulose column chromatography appears to be capable of separating different SWNT species with single chirality.

Cationic surfactant, like benzyltrimethylammonium chloride also shows an affinity towards semiconducting SWNTs, in contrast to the little selectivity of anionic surfactant.

DEDICATION

To my parents Kezheng Chen, Lirong Wang and my fiancée Chun Gao Thank you for your love, support, encouragement and dedication throughout my life

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CHAPTER I

INTRODUCTION

1.1 Introduction to Carbon Nanotube

1.1.1 Structure of Carbon Nanotube

In 1991, the existence of carbon nanotubes was proposed by Iijima who first imaged multi-walled carbon nanotube (MWNT).¹ Two years later, Ijima and his coworker observed single walled carbon nanotubes (SWNTs). Since then, the unique structure and property of carbon nanotubes have attracted researchers around the world.² Although Iijima got the credit of discovering carbon nanotube, the observation of nanotube can go as early as 1956.³ At that time, it was called "carbon fiber" which was based on its chemical component. After several decades' research, with the excellent property and wide application, carbon nanotubes proved to be more than a fiber.

Generally, carbon nanotubes belong to the carbon material family in which carbon atom is the major component. Chemical structure of a carbon nanotube has some similarity to its allotropes: diamond, graphene and fullerene (Figure 1.1).^{4a} The difference of these carbon materials relies on the hybridized structure of carbon atom. In the diamond structure, the carbon atom is sp³-hybridized and each carbon is bonded to four other carbon atoms, forming a crystalline structure.^{4b} Due to this tetrahedral crystalline structure, diamond exhibits a great hardness and heat stability. For the structure of graphite, the carbon atoms are all sp^2 -hybridized on a planar sheet, resulting a huge hexagonal network. In this structure, each carbon atom is connected with three other carbon atoms. The electron can move freely on the delocalized bond network, exhibiting a high conductivity through the graphite layer. In fullerene, carbon atoms are hybridized as sp^2 structure. In contrast to the planar structure of graphite, fullerene is constructed as "bucky ball" in which carbon atoms bond together in pentagons and hexagons.



Figure 1.1 Structure of (a)graphite, (b)diamond (c)fullerences and (d)single-walled carbon nanotube.^[4a] (Printed from reference [4a] with permission)

Similar to graphite, the carbon atoms on carbon nanotube are also sp^2 -hybridized. The morphology of carbon nanotube can be viewed as a rolling graphite sheet, capped with fullerene hemisphere (Figure 1.2). With a large aspect ratio (ratio of length to diameter),^{5a} carbon nanotube is a perfect nano-wire in nano scale. If the tube is formed by rolling up from a single layer of graphene, this tube is called single walled carbon nanotube (SWNT). If the tube is formed by rolling up from multiple layers of graphene, this tube is called multi-walled carbon nanotube (MWNT) (Figure 1.3).



Figure 1.2 Schematic diagram of individual carbon layer rolled to form a carbon nanotube^{4c} (Printed from reference [4c] with permission)



Figure 1.3 Structure of single walled carbon nanotube (SWNT) (left) and multi-walled carbon nanotube (MWNT).^{5b} (Printed from reference [5b] with permission)

Single walled carbon nanotube (SWNT) has a small diameter around 1.0-1.5 nm. Although the length of multi-walled carbon nanotube is similar to that of single walled carbon nanotube, multi-walled carbon nanotube has a much larger diameter, for example, for a 30 coaxial tubes, the diameter of inner and outer tube is 5 and 100 nm, respectively.^{5c} Multi-walled carbon nanotubes usually have a better mechanical properties than single walled carbon nanotubes. For example, the tensile strength of multi-walled carbon nanotube is almost ten times as high as that of single walled carbon nanotube.^{6a,6d} Because of their excellent mechanical properties, multi-walled carbon nanotubes are commonly used as reinforcement filler in polymeric material,^{7a} whereas single-walled carbon nanotubes are widely researched for electronic and optical applications.

1.1.2 Classification of Single Walled Carbon Nanotube

Because the structure of single walled carbon nanotube (SWNT) originates from a single graphene layer, each SWNT can be labeled according to the rolling vector of graphene lattice.



Figure 1.4 Construction of a carbon nanotube and chiral angle.^{6b} (Printed from reference [6b] with permission)

As shown in a single layer's graphene lattice (Figure 1.4), a SWNT can be viewed as a rolled graphene following lattice vector c ($c = n a_1 + m a_2$) The assignment of each SWNT is based on the (*n*,*m*). The (*n*,*m*) is called chirality vector, which is uniquely related to a particular tube. This chirality vector (*n*,*m*), like the ID number for a particular SWNT, determines tube tube's classification and property, such as metallic property or semiconducting property. The table 1.1 shows the classification of different kinds of SWNTs according to their value of *n*-*m*.

Table 1.1 Classification of SWNTs by value of (*n*-*m*)

Value of (<i>n</i> - <i>m</i>)	Group	Example
Multiple of 3	Metallic nanotube	(12,6), (9,3)
Not multiple of 3	Semiconducting nanotube	(7,6), (7,5)
0	Armchair nanotube	(9,9), (11,11)



Figure 1.5 Chirality angle of single walled carbon nanotube^{6c} (Printed from reference [6c] with permission)

The direction of the chiral vector (n,m) is described as chiral angle (Figure 1.5). For each tube with between 0° and 30°, an equivalent tube with between 30° and 60° will be found. In order to assign each tube easily, the chiral vector restricts to the case nm 0° (or 0 30°). Based the value of , different single walled carbon tubes can be divided into three major groups: armchair nanotube, zigzag nanotube and normal chiral nanotube (Figure 1.6). The table 1.2 shows the classification of different kinds of single walled carbon nanotubes according to the chiral angle .

The value of	Group	Example
0	Zigzag nanotube	(12,0), (9,0)
30	Armchair nanotube	(7,7), (5,5)
0< <30	Chiral nanotube	(9,7), (11,5)

Table 1.2 Classification of SWNTs by chirality angle



Figure 1.6 Three types of SWNTs.^{7b} (Printed from reference [7b] with permission)

- 1.1.3 Properties of Carbon Nanotubes
- (i) Mechanical Properties:

Due to the connecting sp²-hybridized network, carbon nanotube materials exhibit a high tensile strength. As shown in the table 1.3, in comparison with stainless steel, the tensile strength of the SWNT is almost 50 times as strong as that of stainless steel.^{6a} When considering the carbon nanotubes bundle, the tensile strength and Young's modulus are even higher. Because of the fiberous nature of nanotubes, the tensile strength exhibits an orientation effect: the strength along the axis of the tube is expected to be much higher than that lateral to tube axis. Thus, the relative orientation is usually an important factor when using the carbon nanotube as reinforcement filler in polymer or rubber materials.

Material	Young's Modulus (TPa)	Tensile Strength (GPa)
SWNT	~1	13-53
Armchair SWNT	0.920	126.2
Zigzag SWNT	0.912	94.5
Chiral SWNT	0.915	
MWNT	0.8-0.9	150
Stainless Steel	~0.2	~0.65-1
Kevlar firber	~0.15	2.4-3.3

Table 1.3 Comparison of mechanical property^{6d}

(ii) Thermal Properties:

The orientation effect of carbon nanotube is found not only on the mechanical tensile strength, but also on the thermal conductivity. Along the tube axis, carbon nanotubes are expected to be very good thermal conductors, whereas they exhibit as a good insulating properties when measured along the tube's lateral direction. Researchers have reported that at room temperature, the thermal conductivity of single walled carbon nanotube is almost ten times as high as copper, which is a traditional thermal conductor.⁸ This high thermal conductivity along the axis is associated with the high aspect ratio of tube structure, because the linear tube structure limits the possible processes of thermo scattering. On the other hand, like graphene, carbon nanotube also has very good thermal stability due to the sp²-hybridized structure. For example, carbon nanotube is stable even when temperature goes up to 2800 °C in vacuum.⁹

(iii) Electric Properties:

Electron can move freely on the sp² network of carbon nanotube, which indicates a high conductivity along the axis. This conductivity of carbon nanotube is affected by several factors. As mentioned above, according to the value of *n*-*m*, carbon nanotubes can be divided into the metallic tube and semiconducting tube (Table 1.1). The metallic SWNT is expected to have a high electric current density which is over 1000 times higher than copper.¹⁰

The diameter is another factor which affects the conductivity. For example, although small diameter SWNT (5,0) is belong to semiconducting group, it exhibits some metallic property, due to the curvature effect.¹¹ In recent year, researchers are trying to

change the electric property of carbon nanotube by doping some other atoms (such as nitrogen atom) into the tube structure.¹²

1.1.4 Application of Carbon Nanotubes

The excellent mechanical, thermal and electrical property of carbon nanotubes demonstrate their unique advantages in various applications, including flexible electronics,¹³ biosensors,¹⁴ transistors,¹⁵ solar cell,^{16,17} reinforcement filler,¹⁸ antibacterial material,¹⁹ and so on. Here, we briefly discuss the antibacterial effect and reinforcement filler as two examples to illustrate the applications of carbon nanotubes.

(i) Antibacterial Effect:

Recently, carbon nanotubes have been found to be cytotoxic to bacteria, indicating their potential antibacterial application. Although most of carbon nanomaterials are cytotoxic, carbon nanotubes are expected to have the highest toxicity.²⁰ Research study implies that membrane stress raised by carbon nanotube could be the primary reason for the death of bacterial.²¹ The mechanism is believed to be consisting of three steps:²¹ (a) contact between carbon nanotube and bacterial; (b) perturbation of the bacterial membrane; (c) electronic oxidation of bacterial. Actually, this antibacterial effect is more complicated than that, because many factors can affect it, which include tube diameter and electronic structure. For example, the metallic single walled carbon nanotube is proven to have a better antibacterial effect than a normal carbon nanotube.²¹ As seen from Figure 1.7, more E. coli cells are destroyed when using the filter with a higher content of metallic SWNTs.



Figure 1.7 Representative SEM images of E. coli cell deposited on SWNT filters. E. coli cells were deposited on the SWNT filter (A,B,C), incubated for 45 min in isotonic saline (D,E,F). (A,D) is 5% metallic SWNTs, (B,E) is 30% metallic SWNTs, and (C,F) is 95% metallic SWNTs.²¹ (Printed from reference [21] with permission)

(ii) Reinforcement:

Carbon nanotubes are believed to be good reinforcing filler for improving polymer mechanical properties. One reason is the high aspect ratio. The aspect ratio of carbon nanotube can reach up to several million²² which is much higher than traditional fiber filler, such as glass wood. On the other hand, carbon nanotube has a large surface area to contract the polymer in a composite, implying a good adhesion for improved reinforcement effect. For example, the surface area of 1 g carbon nanotube can reach up to 50~1315 m².^{23a}

To realize the reinforcement application of carbon nanotube, researchers have tried to disperse carbon nanotubes in different polymer composites, such as epoxy,^{23b} polyvinyl,²⁴ natural rubber,²⁵ etc. These experiments prove that the carbon nanotubes can greatly improve the Young's modulus with small amount of loading. Zheng and coworkers further demonstrated that carbon nanotubes in natural rubber can orient itself along the stretching direction (Figure 1.8), which provides an explanation for nanotube reinforcement.²⁶



Stretching direction

Figure 1.8 Effect of strain on the alignment of SWNTs in a polymer.²⁶ In the absence of strain (a), the nanotubes (yellow lines) are randomly distributed in the polymer substrate. Under the influence of external strain (b, c), the nanotubes are partially aligned along the stretching direction. (Printed from reference [26] with permission)

On the other hand, addition of carbon nanotubes can effectively inhibit the fracture growth of polymer material. As illustrated in Figure 1.8, carbon nanotubes trend to be aligned in the polymer matrix along the stretching direction. When crack takes place during polymer stretching, those aligned carbon nanotubes are expected to form several nano "walls" between the polymer to hinder the growth of crack. As shown in Figure 1.9, existence of nano "wall" will branch off the pathway of crack growth and earn more time for polymer to response before breaking.



Figure 1.9 Reinforcement effect of SWNTs in natural rubber (Pictures is from my unpublished results)

1.2 Separation of Carbon Nanotubes

Because the physical properties of carbon nanotube is dependent on tube's chirality and diameter, obtaining the pure carbon nanotubes with a single chirality or diameter is critical for realizing the various applications of carbon nanotubes. Unfortunately, the carbon nanotubes are always produced as a mixture, which contains about 1/3 metallic nanotubes and 2/3 semiconducting nanotubes (see the classification in table 1.1). Based on our knowledge, there is no method can be used to produce carbon nanotube with pure chirality in large scale. Thus, separation of a specific tube from the carbon nanotube mixture remains a major challenge. So far, the separation of carbon nanotubes is focused on single walled carbon nanotube which has a relatively simple structure. The current separation methods can be classified as using DNA, polymers, small molecules, centrifugation and chromatography.
1.2.1 Using DNA for SWNTs separation

Zheng and coworkers found that particular DNA sequence can wrap on the surface of unique SWNT (Figure 1.10), forming a DNA/SWNT hybrid structure.²⁷ The selective interaction between specific DNA sequences and SWNTs implies the application of DNA for SWNTs recognition. They systematically explored the DNA library and found that most of the recognition DNA sequences were derived from simple pyrimidine repeats, such asTTTT...,CCCC.... andTCTC.... ²⁸ For example, 8-mer (CCG)₂CC sequences will extract tube (8,7), whereas the 12-mer (CCG)₄ will separate tube (9,4).²⁸ When interacting with SWNTs, those sequences will assembly on the surface of SWNT to form a beta sheet structure, with hydrogen bond connecting adjacent strands. Covered by the wrapped DNA beta sheet, SWNT minimizes its van der Waals and hydrophobic interactions with IEX (ion exchange resin), leading to the separation of SWNT with different chirality.²⁹

Through more than three hundred sequences tests, Zheng identified around 20 sequences for semiconducting SWNT separation. The table 1.4 shows special DNA sequences for SWNT recognition. This separation method has such high resolution that it can almost extract chirality-pure SWNT, even when two tubes have the same diameter. Unfortunately, due to the high cost of DNA sequence, this method can only separate several milligrams of SWNTs, which limits its application in large scale.



Figure 1.10 Wrapping of DNA on a SWNT²⁸ (Printed from reference [28] with permission)

Chirality (n,m)	Sequences		
(9,1)	(TCC) ₁₀ , (TGA) ₁₀ , (CCA) ₁₀		
(8,3)	(TTA)₄TT, (TTA)₃TTGTT, (TTA)₅TT		
(6,5)	(TAT) ₄ , (CGT) ₃ C		
(7,5)	(ATT) ₄ , (ATT) ₄ AT		
(10,2)	(TATT) ₂ TAT		
(8,4)	(ATTT) ₃		
(9,4)	(GTC)₂GT, (CCG)₄		
(7,6)	(GTT) ₃ G, (TGT) ₄ T		
(8,6)	(GT) ₆ (TATT) ₃ T, (TCG) ₁₀ , (GTC) ₃ , (TCG) ₂ TC,		
	(TCG) ₄ TC, (GTC) ₂		
(9,5)	(TGTT) ₂ TGT		
(10,5)	(TTTA) ₂ T		
(8,7)	(CCG)2CC		

Table 1.4 Recognition sequence for individual SWNT²⁸

(Printed from reference [28] with permission)

1.2.2 Using Polymer for SWNTs separation

In comparison with the high cost of DNA sequence, organic polymers exhibit their advantages in separating SWNTs at a lower cost. Most of the polymers used for SWNT separation are aromatic polymer and its derivatives. The rigid aromatic polymers are found to wrap SWNT by aligning the aromatic units on the tube surface to maximize the - interaction.³⁰ The aromatic units can be incorporated into the backbone or modified as pendant functional groups. Different kinds of conjugated polymers have been designed and synthesized.^{31, 32} There are some examples in Figure 1.11



Figure 1.11 Types of polymer used for SWNT separation.³¹ (Printed from reference [31] with permission)

One example is polymer poly (9,9-dioctylfluorenyl-2,7-diyl) (PFO) (Figure 1.11) which exhibits a particular selectivity of SWNT (6,5).³² Nicholas and coworkers suggest that the separation selectivity of PFO is related to the chirality angle of SWNT.³² Interestingly, this selectivity can be changed by introducing heterocyclic unit on the polymer backbone. For example, the polymer PFO-BT (Figure 1.11) exhibits a strong selectivity for nanotubes with diameter around 1.05 nm.

1.2.3 Using Small Molecules for SWNTs separation

Similar to aromatic polymers, the aim of designing small molecules is for enhancing - interaction between small molecule and SWNT.^{33,34} Considering the small molecules are easier to be synthesized and modified, their interaction with SWNTs can be manipulated more conveniently. In addition, the assembly of small molecules on SWNT surface could lead to uniquely ordered structures that facilitate the SWNT separation.

Papadimitrakopoulos and coworkers proved that flavin mononucleotide can be used for SWNT separation. They found that flavin mononucleotides on the nanotube trend to form a helical ribbon, with hydrogen bonding between adjacent flavin moieties³⁴ (Figure 1.12). Another interesting small molecule designed for SWNT separation is the nano tweezer³⁵ Because of the high affinity of porphyrin toward SWNTs, nano tweezer is designed to have two porphyrin units which are used to catch SWNTs with special chirality or diameter (Figure 1.13).



Figure 1.12 Wrapping of flavin on the surface of SWNT.³⁴ (Printed from reference [34] with permission)



Figure 1.13 Structure of nano tweezer for wrapping SWNT.³⁵ (Printed from reference [35] with permission)

1.2.4 Using centrifugation for SWNTs separation

Density-gradient ultracentrifugation is a method commonly used in biology for separating cellular components with different buoyant densities. The centrifuge tubes containing liquid mixtures are arranged to form a varying density profile before adding sample. Under strong centrifugation, sample components will migrate to different regions that match their individual densities. The separation of SWNTs by centrifugation is dependent on how surfactant molecules are organized on the surface of the carbon nanotube. DNA, sodium dodecyl sulphate and sodium cholate are common surfactants used in centrifugation separation (Figure 1.14). Hersam and coworkers demonstrated that by using density-gradient ultracentrifugation, pure semiconducting SWNTs, such as (6,5) and (7,5), can be separated.³⁶

Although a few pure SWNTs have been separated by density-gradient ultracentrifugation, it is difficult to separate nanotube with a similar density. In order to solve this problem, Weisman and coworkers introduced nonlinear density-gradient ultracentrifugation for SWNT separation.³⁷ By building a nonlinear density gradient, they successfully separated more than ten different types of pure SWNTs from raw SWNT samples which usually only yielded one or two pure SWNT species.



Figure 1.14 Separation of SWNT by centrifugation.³⁶ (Printed from reference [36] with permission)

1.2.5 Using chromatography for SWNTs separated by

Compared with the complicated procedure to build linear or nonlinear gradient density centrifuge, the simplicity of chromatography technology makes it attractive to achieve the requirement for separating SWNT in large scale. Monshammer and coworkers firstly separated metallic from semiconducting nanotubes by using allyl dextran size-exclusion gel chromatography.³⁸ Kataura and coworker further optimized this method by connecting different gel column together to achieve large-scale separation³⁹ (Figure 1.15). Although this separation mechanism is still unclear, Kataura suggested that the assembly structure of surfactant on the SWNT surface played an important role to differentiate each SWNT.³⁹



Figure 1.15 Separation of SWNTs by chromatography³⁹ (Printed from reference [39] with permission)

1.3 Analytical Techniques for Carbon Nanotube

After over ten years' development, several analytical techniques have been established to evaluate the purity and chirality of SWNTs. Those analytical techniques reflect the unique property of different SWNTs, such as diameter or absorption wavelength. Three common optical measurements will be described below. 1.3.1 Ultraviolet-Visible-Near Infrared (UV-vis-IR) Absorption Spectroscopy

Due to the one dimensional nanostructure, SWNT has one dimensional electron density of states (DOS) which result in the special optical properties of SWNT. According to Van Hove singularities, the optical absorption is from electronic transition from the V₁ to C₁ (first optical transition), or V₂ to C₂ (second optical transition) (Figure 1.16).⁴⁰ One of important optical features of SWNT is that the absorption is relatively discrete, resulting in different absorptions in UV-vis-NIR range. Thus, it is possible to assign different SWNTs according to their unique absorption peak.



Figure 1.16 Van Hove singularities of metallic (a) and semiconducting SWNT (b), where the conduction bands (C_1 and C_2) and valance bands (V_1 and V_2) are indicated along with the density of state (DOS).⁴⁰ (Printed from reference [40] with permission)

Because each SWNT has a unique interband transition energy, SWNT can be assigned and classified according to identical absorption peak.⁴⁰ For example, absorption peak from 900 nm to 1400 nm corresponds to the first optical transition (E_{11}^{S}) of semiconducting SWNT; absorption peak from 630 nm to 900 nm corresponds to the second optical transition (E_{22}^{S}) of semiconducting SWNT; absorption peaks from 450 nm to 660 nm corresponds to the first optical transition (E_{11}^{M}) of metallic SWNT (Figure 1.17). Different interband transition has special energy absorption, which resulting the different absorption intensity even in the same SWNT sample. For example, in semiconducting SWNTs, the absorption intensity of E_{22}^{S} is weaker than that of E_{11}^{S} .²⁸



Figure 1.17 A typical example of UV-vis-NIR absorption spectrum of SWNTs, which shows absorption peaks of metallic SWNT (E_{11}^{M}) and semiconducting SWNT (E_{11}^{S}, E_{22}^{S}).

1.3.2 Photoluminescence

As mentioned above, SWNT has interband transitions between its Van Hove singularities. After absorbing energy through the second interband transition, electrons will be excited from the valence band V_2 to the conduction band C_2 . During this process, an electron-hole pair (exciton) will be created. The electron and hole will relax from C_2 to C_1 and V_2 to V_1 , respectively, followed by recombination through the first transition energy S_{11} (C_1 - V_1) which leads to a photoluminescence emission (Figure 1.18). However, this photoluminescence only takes place when the tube is a semiconducting SWNT. For a metallic SWNT, although electrons can also be excited to the conduction band by absorbing energy and form electron-hole pair, the hole will not survive for interband relaxing. The electrons in metallic SWNT will immediately combine with the hole and quench the photoluminescence.



Relaxation (Phonon-assisted process)

Figure 1.18 Photoluminescence mechanism of SWNT⁴¹ (Printed from reference [41] with permission)

Due to the unique interband energy of semiconducting SWNT with different chirality, the special excitation and emission wavelength can be used to identify SWNT. As-prepared raw SWNTs are a mixture of different kinds of tubes. When the excitation wavelength is scanned in a certain range, the emission intensity can be plotted into a 2D photoluminescence map as a function of excitation and emission wavelengths (Figure 1.19). Each peak on the 2D photoluminescence represents one type of semiconducting SWNT. By using this method, one can indentify various SWNTs and detect the intensity distribution of SWNTs.



Figure 1.19 2D photoluminescence map of SWNT³⁷ (Printed from reference [37] with permission)

1.3.3 Raman Spectroscopy

Besides UV-vis-NIR and 2D photoluminescence, Raman scattering spectroscopy is another useful tool in carbon nanotube's research. Rao and coworker did some pioneering works to prove the Raman scattering phenomenon in SWNTs.⁴⁸ They found SWNTs with special diameter can be detected in Raman spectroscopy by using a laser with certain wavelengths as an excitation source. This detection depends on both excitation wavelength and diameter of SWNT. In other words, SWNTs with a particular diameter can only be excited by a laser with an energy matching its interband transition.

The displacement of a carbon atom on the carbon nanotube is Raman active, which can be detected by different modes of Raman spectroscopy. Three important modes are commonly used in nanotube study: Radial Breathing Mode (RBM), G band Mode and D band Mode (Figure 1.20).



Figure 1.20 Raman spectroscopy of SWNT⁴⁹

(i) RBM mode:

In RBM mode, carbon atoms vibrate in the radial direction of tube axis, as if the nanotube was breathing, therefore it is called Radial Breathing Mode (RBM). The RBM Raman shift is from 100 to 350 cm⁻¹, which is anti-proportional to the diameter of the detected SWNT. This relationship is described as: (RBM) = 219.3/d + 14.7, where (RBM) is the RBM Raman shift and d is the diameter of carbon nanotube. Because SWNT with special diameter can only be excited by a laser with matched wavelength, the assignment of SWNTs can be plotted into a map with functions of excitation energy of laser and tube diameter, which is known as Kataura plot (Figure 1.21).



Figure 1.21 Kataura plot of SWNTs⁴⁹

ii) G band:

G band mode consists of a couple of peaks from 1560 to 1600 cm⁻¹. Those peaks are dependent on several factors: the confinement of phonon wave vector and asymmetry effects according to SWNT curvature. Two peaks around 1570 cm⁻¹ and 1590 cm⁻¹ are identification of semiconducting and metallic SWNT, which are called G⁻ and G⁺ respectively. G⁻ band is related to the vibration of carbon atom along the circumferential direction of tube, whereas G⁺ band describes the vibration of carbon atom along the nanotube axis. Generally speaking, a broad and high G⁻ band is a sign of enrichment of metallic SWNT.

iii) D band:

D band appears around 1350 cm⁻¹, which originates from the defect on the SWNT structure. The defect usually results from the damage of sp² structure in SWNT. The intensity ratio between D band and G band is a good indicator for the purity of SWNT. If the surface of SWNT is modified with some functional groups, corresponding D band is expected to be increased, because the modification disturbed the sp² hybridization or damaged the integrity of the tube.

CHAPTER II

WATER SOLUBLE POLY(PHENYLENEVINYLENE) FOR SWNT SEPARATION

2.1 Introduction

In the simple model of aromatic - interaction, two benzene rings can be aligned in either parallel or perpendicular geometry.⁵⁰ When an aromatic dispersant interacts with a SWNT, the small molecules such as pyrene and flavin are predominantly aligned in parallel to the SWNT surface for strong intermolecular interaction. The parallel interaction is also a dominant mechanism for -conjugated polymer/SWNT complexes in the reported studies so far.⁵¹ Whereas the strong intermolecular interaction facilitates SWNT dispersion, the - interaction also makes it difficult to remove the polymer after SWNT separation. It is thus desirable to search for a SWNT sorting mechanism that uses a weaker intermolecular interaction such as van der Waals force. Poly[(*m*phenylenevinylene)-*alt*-(*p*-phenylenevinylene)] (PmPV) **2-1** represents an interesting conjugated polymer, whose backbone exhibits relative flexibility and tends to adopt a helical conformation when dispersing SWNTs.⁵¹ The *para*-phenylene units of PmPV **2-1** can be aligned either parallel or perpendicular to the SWNT surface (Scheme 2.1 conformation **2-3**) as a modeling study suggests.

In this study, we demonstrate that the polymer conformation can be tailored to favor the perpendicular alignment of the -conjugated segments to SWNT surface (see

conformation 2-4), thereby attenuating its - interaction with SWNT. The strategy is based on the synthesis of PmPV 2-2, which bears water-soluble groups to promote the helical conformation in aqueous solution. In sharp contrast to PmPV 2-1 which is known to be a good dispersing reagent but exhibits little selectivity toward metallic SWNTs,⁵² PmPV 2-2 revealed drastically improved selectivity in sorting the SWNTs on the basis of tube's diameters.⁶³



Scheme 2.1 Structure of PmPVs 2-1 and 2-2, and proposed respective helical conformations 2-3 and 2-4 when wrapping on a (7,5) SWNT. The inset shows the parallel and perpendicular alignment of two benzene rings. The $-OCH_3$ groups in 2-4 are pointing inward to provide a defined cavity size.



Scheme 2.2 Synthesis of polymer PmPV 2-2.

2.2 Experimental

2.2.1 Synthesis of Polymer PmPV 2-2

Synthesis of compound **2-7**:⁵³ 3-(4-Methoxyphenoxy)propanesulfonate (2.48 g, 0.008 mol) and poly(oxymethylene) (Sigma-Aldrich, 0.832 g, 0.028 mol) was dissolved in acetic acid (200 mL). Whereas the solution was cooled by an ice bath, HBr (45% in acetic acid, 4.8 mL, 0.028 mol) was added dropwise. The resulting mixture was stirred at room temperature for 10 min, then at 65 °C for 10 h. After cooling to the room temperature, the product mixture was poured into acetone. The white powder product (1.44 g, 42% yield) was collected by centrifugation to give 5-methoxy-2-(3-sulfonatopropoxy)-1,4-xylene- , '-bromide **2-7**. ¹H NMR (D₂O) (ppm): 2.19–2.39 (-CCH₂C-, 2H, m), 3.09–3.25 (-CH₂–SO₃, 2H, m), 3.86–4.00 (-O–CH₃, 3H, s), 4.17–4.31 (-O–CH₂–, 2H, m), 4.65–4.78 (-CH₂Br, 4H, d), 7.10–7.26 (-C₆H₂–, 2H, m).

Synthesis of monomer **2-8**: 5-Methoxy-2-(3-sulfonatopropoxy)-1,4-xylene- , 'bromide **2-7** (0.4 g, 0.88 mmol) and triphenylphosphine (Sigma-Aldrich, 0.695 g, 2.6 mmol) were dissolved in anhydrous *N*,*N*-dimethylformide (DMF) (20 mL), and the mixture was heated under reflux for 24 h. The resulting product was precipitated by dropped into ether solvent, and washed with anhydrous DMF. The product **2-8** (0.4 g, 48% yield) was obtained as a yellow powder which absorbed moisture easily. ¹H NMR (d6-DMSO) (ppm): 1.52-1.67 (-CCH₂C-, 2H, m), 2.25-2.42 (-CH₂-SO₃, 2H, m), 2.78-2.87 (-O-CH₃, 3H, s), 3.19-3.30 (-O-CH₂-, 2H, m), 4.78-4.99 (-CH₂-Ar-CH₂-, 4H, d), 6.33-6.69 (-C₆H₂-, 2H, d). 7.51-8.01 [-(C₆H₅)₃P-, 30H, m].

Synthesis of polymer PmPV 2-2: Compound 2-8 (0.37 g, 0.39 mmol) and isophthaladehyde (0.052 g, 0.39 mmol) were dissolved in anhydrous ethanol/THF (1:1) (7 mL). Sodium ethoxide (5% in ethanol, 2 mL) was added dropwise to the reactant solution. The mixture was stirred at room temperature under argon atmosphere overnight and then dropped into the mixed solvent (methanol: acetone: ethyl ether = 1: 4: 5) to precipitate the yellow polymer product (0.1 g, 70% yield, Mw = 5000). ¹H NMR (d6-DMSO) (ppm): 2.06–2.23 (–CCH₂C–, 2H), 2.64–2.79 (–CH₂–SO₃, 2H), 3.88–4.03 (–O–CH₃, 3H), 4.16–4.32 (–O–CH₂–, 2H), 7.22–7.87 (–C₆H₂–, –HC=CH–, –C₆H₄–, 10H).



Figure 2.1 (a) ¹H NMR spectrum of PmPV **2-2** in DMSO at 300 MHz. (b) ¹³C NMR spectrum of PmPV **2-2** in DMSO at 400 MHz

2.2.2 Dispersion of SWNTs with PmPV 2-2

In a typical dispersion procedure, 3 mg of raw SWNTs sample (made by the HiPCO process, Rice University) and 20 mL of polymer in deionized water solution (26.2 mg/mL) were mixed. The mixture was sonicated at 0°C for one and half hours. The supernatant solution was separated from the sediment by centrifugation at 7000 g. In order to further remove the aggregation of wrapped SWNTs, the supernatant solution was further centrifuged at 7000 g twice for thirty minutes. The resulting clear solution was used for the UV-vis-NIR (Perkin Elmer, lambda 950), Photoluminescence (Horiba, Symphony II) and AFM test. For Raman spectroscopy (Jobin Yvon, Horiba, with laser from LexeL laser Inc.), the solvent was evaporated to obtain the solid sample for analysis. For NMR spectra, the sample was dispersed in DMSO rather than deionized water.

2.3 Results and Discussion

2.3.1 Dispersion Selectivity of PmPV 2-2

(i) NMR evidence for wrapping model of PmPV 2-2

¹H NMR of PmPV **2-2** (Figure 2.1 (a)) revealed that the polymer had a regular structure as proposed. The minor aromatic singlet at 7.75 ppm was attributed to H_e , whereas the remaining aromatic and vinyl signals occurred as a broad multiple peaks at about 7.45 ppm. The protons of $-CH_2O-$ (at 4.24 ppm) and $-OCH_3$ (at 3.94 ppm) each occurred as a broad single peak, indicating that the vinylene bonds were mainly in the *trans*-configuration.⁵¹

In order to gain the insight information about the polymer wrapping, SWNTs were sonicated with PmPV 2-2, followed by centrifuging to remove the undispersed

tubes. The supernatant solution of SWNT/PmPV **2-2** was examined by ¹H NMR (Figure 2.2 B). Upon forming the complex with SWNT, the methylene protons H_c and H_d of **2-2** were shifted upfield by about 1 ppm (Figure 2.2 B). The methylene signal H_b was buried under the water peak, and addition of a drop D_2O to the NMR sample caused slight shift of water peak to make the H_b signal visible. The observed upfield shift from protons H_b-H_d was attributed to the chain assembly arising from the polymer/SWNT interaction, as the free acetone signal at 2.07 ppm was not changed in the presence of SWNTs. The signal of $-OCH_3$, however, was not detected. The signals of vinyl and phenyl protons were dramatically decreased, indicating intimate chain interaction with SWNT surface. The aromatic protons that are closely associated with SWNTs are known to become undetectable,⁵⁴ due to the presence of paramagnetic particles in the SWNT sample. Disappearance of $-OCH_3$ signals, but not H_b ($-OCH_2$ -), suggested that the former had a closer interaction with the guest SWNT than the latter, in agreement with the proposed helical wrapping model as shown in conformation **2-4** (Scheme 2.1).



Figure 2.2 ¹H NMR spectra of PmPV **2-2** (A) and its complex with SWNTs (B) in deuterated DMSO solvent. The protons are labeled by letters a-e. In the bottom spectrum (B), one drop of D_2O was added to slightly shift the water signal away from the $-OCH_2-$ signal. The starred signal at 2.07 ppm was due to trace acetone in the NMR tube. The inset is the expanded region for proton (c) of spectrum (B), showing the quintet signals.

(ii) Spectroscopic evidence for selective SWNT dispersion

Raman spectra of SWNTs/PmPV 2-2 under 647 nm laser excitation revealed that polymer 2-2 had quite high selectivity in dispersing small diameter SWNT (7,5) (Figure 2.3 a), in sharp contrast to no selectivity of PmPV 2-1.⁵² Because SWNT (7,5) is a semiconducting SWNT in which G⁻ band is expected to decrease comparing to G⁺ band (see chapter I, 1.3.3 Raman spectroscopy, G band). The G⁻ band area under 647 nm laser excitation became relatively smaller for SWNTs/PmPV 2-2 (Figure 2.4), in agreement with the enrichment of SWNT (7,5). When using 514 nm laser as excitation resource, Raman spectroscopy showed that the small diameter SWNT (9,3) was also chosen by the polymer (Figure 2.3 b). The Raman RBM peaks from polymer/SWNTs are shifted to higher frequencies than raw SWNT by 5-10 cm⁻¹, indicating that SWNTs become stiffer⁵⁵ after polymer wrapping.



Figure 2.3 Raman spectra of raw SWNTs and SWNTs/PmPV **2-2** when the samples were excited with a laser at 647 nm (a) or a laser at 514 nm (b).



Figure 2.4 Raman spectra of SWNT samples in G band mode (G band) and defect mode (D band), when excited at 647 nm

The selectivity was further observed from 2D photoluminescence spectra (Figure 2.5). The small diameter (6,5) SWNT was clearly enriched in the SWNTs/PmPV 2-2 dispersion. Although the photoluminescence intensity of (7,5) was weaker than that of (7,6) SWNT in the raw sample, the signal of (7,5) was increased to a comparable level in the SWNTs/PmPV 2-2 complex, in agreement with what was observed in Raman. It appeared that PmPV 2-2 selectively extracted the SWNTs of smaller diameter, (6,5) and (7,5) SWNTs (d = 0.76 and 0.83 nm, respectively).^{52,56} The spectra also revealed that those SWNTs with relative large diameters, such as (8,6) and (9,5) (d = 0.97 and 0.98, respectively), were effectively removed.



Figure 2.5 2D photoluminescence of SWNT samples (excitation: 500-810 nm; emission: 912-1415 nm). (a) Raw SWNTs was dispersed with addition of sodium dodecylbenzene sulfonate (SDBS) surfactant (in D₂O). (b) SWNTs were dispersed by PmPV **2-2** in D₂O

UV-vis-NIR absorption spectra of the supernatant solution provided consistent evidence that PmPV **2-2** selectively enriched the relative amounts of (7,5) and (6,5) SWNTs (Figure 2.6). Whereas those tubes with larger diameter is decreased, such as (10,3) and (8,7), in agreement with the decrease of (10,3) in Raman result (Figure 2.3). Clearly, PmPV **2-2** exhibited notable selectivity toward the SWNTs with small diameter.



Figure 2.6 UV-vis-NIR absorption spectra of SWNTs/ PmPV **2-2** in water. Raw SWNTs were dispersed in sodium dodecylbenzene sulfonate (SDBS) surfactant

Different chiral SWNTs present in the raw sample are summarized in Table 2.1, along with their respective tube diameters. On the basis of the observed selectivity toward (6,5), (7,5) and (9,3) SWNTs, PmPV **2-2** appeared to have high tendency to host the small tube with relative narrow range of diameters (d = 0.757 - 0.84 nm). Meantime, the

dispersion of SWNTs/PmPV 2-2 was depleted of the SWNTs with larger diameters such as (10,3), (9,5) and (13,4) (d > 0.936 nm). The result was in agreement with the enhanced conformation as shown in 2-4 (Scheme 2.1), as the inner alkoxy ($-OCH_3$) groups reduce the cavity size that matches the SWNTs with small diameter.

SWNTs	diameters	SWNTs structures	diameters
structures	(nm)		(nm)
$(6,5)()^{b,c}$	0.757	(8,6) () ^{b,c}	0.966
(8,3) () <i>a,b,c</i>	0.782	$(9,5) ()^{b,c}$	0.976
(9,2) () ^{b,c}	0.806	(12,1) () ^C	0.995
$(7,5)()^{a,b,c}$	0.829	$(8,7)()^{b,c}$	1.032
(9,3) () ^a	0.847	(10,5) () ^C	1.050
$(8,4) ()^{b,c}$	0.840	(12,3) () ^a	1.077
(8,5)	0.889	(9,7) () ^C	1.103
(7,6)	0.895	(10,6) () ^C	1.111
(9,4) () ^C	0.916	(14,1) () ^a	1.153
$(10, 3) ()^{a,b,c}$	0.936	(13,4) () ^a	1.206
(12,0) () ^a	0.940	(11,7) () ^a	1.231`

Table 2.1 Distribution of HiPCO SWNTs structure and diameter in the studied sample.

As shown in table 2.1, the SWNTs enriched by PmPV **2-2** are indicated by an up arrows (\uparrow), whereas those decreasing SWNTs are indicated by a down arrows (\downarrow). The superscripts^{a,b,c} denote the supporting evidence for the observed SWNT enrichment: a: Raman; b: UV-vis-NIR; c: 2D-photoluminscence.

(iii) Proposed polymer wrapping model

The remarkable difference between PmPV 2-1 and PmPV 2-2 (Scheme 2.1), in terms of SWNT selectivity, could be partially rationalized by considering the substituent impact on the polymer conformational cavity. Because both alkoxy groups in PmPV 2-1 are hydrophobic, the substituent do not have strong preference to interact with an organic solvent or SWNT surface. The *para*-phenylene in PmPV 2-1 thus can be rotated to adopt the parallel interaction with SWNT surface as shown in the polymer conformation 2-3 (Scheme 2.1).⁵⁷ A range of conformational cavity sizes, corresponding to different degrees of *para*-phenylene rotation, permit PmPV 2-1 to host SWNTs of various diameters.

In sharp contrast, PmPV 2-2 has a strong preference to adopt the conformation 2-4 (Scheme 2.1), resulting from the strong interaction between water and the hydrophilic substituent. In the conformation 2-4, the methoxy groups are forced to point inwards to confine the conformational cavity, whereas forming a hydrophobic pocket for SWNTs. The molecular modeling by using HyperChem software showed that the conformational cavity of PmPV 2-2 is slightly larger than 1 nm (Figure 2.7a). Upon inserting the (7,5) SWNT (d = 0.83 nm) through the polymer conformational cavity, the cavity became larger in the aqueous solvent (Figure 2.7b), which is partly due to the rotation of the methoxy groups. All *para*-phenylene units remain to be perpendicular to the nanotube axis, as the conformational cavity size is adjusted to host the SWNTs of small diameters.



Figure 2.7 (a) Molecular modeling of PmPV **2-2** alone by using HyperChem software, where the dotted circle indicates the approximate perimeter of (7,5) SWNT. (b) The helical conformation of PmPV **2-2** when it hosts the (7,5) SWNT in aqueous solution. The dotted circle shows the perimeter of (7,5) SWNT

An atomic force microscopy (AFM) image of the SWNT/PmPV 2-2 sample from the supernatant solution revealed that the SWNT was dispersed as single tube (Figure 2.8b). AFM profilometry (in taping mode) along the lengthwise SWNT direction gave a height profile. From the minimum height of the profile (Figure 2.8a), the diameter of the wrapped nanotube was estimated to be ~0.9 nm. High resolution TEM further confirmed that SWNT was dispersed in PmPV 2-2 (Figure 2.9), which revealed some bump areas that might be associated with the polymer chains wrapped on the carbon nanotube. The observation implies the possible existence of some specific wrapping patterns. The AFM and high resolution TEM results suggest that a nanotube is wrapped by a few polymers, whereas the average distance between the adjacent two polymers is about 100 nm (or 0.1 μ m) (Figure 2.10)



Figure 2.8 AFM images obtained in tapping mode from dispersed SWNTs/PmPV 2-2. (a)A profile along an individual SWNT, where the dashed line shows around 0.9 nm height.(b) Surface images of the SWNT, where the black line indicates the cross section direction along the tube.



Figure 2.9 High resolution TEM image of a single SWNT dispersed with PmPV **2-2** in aqueous solution. (The arrows indicate the possible polymer wrapping)



Figure 2.10 Schematic illustration of a SWNT that is wrapped by two polymer chains. The distance between the two adjacent polymer chains are at ~100 nm as observed by AFM.

2.3.2 Aggregation from Dispersion of SWNTs/PmPV 2-2

Aggregaiton which results from the strong van der Waals attraction between SWNT⁵⁸ is a common phonmenon for SWNTs. The aggregation of SWNTs indicates the poor dispersibility, which has a strong influence on the application of SWNTs.⁵⁹ Although PmPV **2-2** can disperse SWNTs, a fundamental question is how stable the dispersion of SWNTs/PmPV **2-2** would be. Because PmPV **2-2** tends to adopt the perpendicular interaction geometry (see Scheme 2.1), it would be interesting to examine the stability of the dispersion. In the study, we found that some SWNT aggregation was formed when keeping the SWNT/PmPV **2-2** solution for several weeks.

The dispersion of SWNTs with PmPV 2-2 was prepared in water under tip sonication (at 0°C for two hours). The suspension was subject to centrifugation (39000 g, 1h) twice to remove undispersed SWNT precipitation. The clear supernatant solution was collected into a small battle with cap and kept still for a week or longer. The solution sample was then used for the TEM and AFM studies. For Raman measurement, the solution underwent centrifugation to yield the solid aggregation which was used for test. For UV-vis-NIR test, aggregation solid sample was redispersed into water by SDBS.

The high resolution TEM (Figure 2.11) showed that the SWNTs were aligned along the tube axis in the aggregate. The TEM image also revealed that some tubes were in the isolated form (Figure 2.11a). There appeared to be fragments on the surface of the SWNT, which might be from the wrapping polymers. Further studies are desirable at higher magnification to confirm the polymer wrapping pattern in detail. The AFM result provides a consistent evdenice to show that formation of aligned SWNT boundles (Figure 2.12 B).


Figure 2.11 High resolution TEM image for tracing the formation of SWNT aggregation



Figure 2.12 (A) The possible process of aggregate formation when SWNTs are released from the wrapping polymer (blue wave bond). (B) AFM image of aggregated sample from SWNTs/PmPV **2-2** (distance between two red arrows is 0.216 µm).

2.3.3 Chirality Selectivity of Aggregation

In recent year, the chirality selectivity of aggregation was reported by Khan and coworkers.⁶¹ Niyogi and coworkers proved that the chirality selectivity of aggregation could be controlled by salt addition.⁶⁰ Both studies implied the possibility of chirality separation through aggregation. Therefore, we decided to examine the tube population in the SWNT aggregate. The precipitated aggregation was collected from the SWNTs/PmPV **2-2** solution by centrifugation (7700 g, 0.5 h), which was used for acquiring UV-vis-NIR and Raman spectra.

In the RBM mode of the Raman spectrum (Figure 2.13 a, excitation at 514 nm), each peak was assigned according to literature.⁶² The Raman spectrum of the aggregation from the polymer solution showed that metallic SWNTs, such as (8,5) and (9,3) were enriched in the aggregated precipitation. The Raman peaks from both SWNTs/PmPV **2-2** dispersion and its aggregation SWNT was found to be red-shifted (2~3 nm) from the corresponding SWNT in the raw SWNTs, implying that the polymer were still wrapping on the surface of SWNT.

The G band region of the Raman spectrum provides a consistent evidence to support the enrichment of metallic SWNTs. According to the literature,⁶⁴ metallic SWNT have a broader G⁻ peak than semiconducting SWNT. Thus, when comparing SWNTs/PmPV **2-2** with the aggregation sample, a little broader G⁻ peak is an indication of enrichment of metallic SWNT (Figure 2.13 b). Interestingly, after polymer dispersion and SWNT precipitations, the intensity of the D band of SWNT is decreasing (Figure 2.13 b), indicating that those SWNTs with significant defects were removed during this process. Because the dispersion of SWNTs by using PmPV **2-2** could enrich the tube of

small diameter (2.3.1), the combination of polymer dispersion with aggregation process could offer a unique approach for the SWNT purification.



Figure 2.13 Raman spectrum of SWNTs of the aggregated sample in the radial breathing mode (RBM) (a), G band and D band mode (b), when the sample was excited at 514 nm

The aggregation sample was further redispersed into an aqueous solution for UVvis-NIR absoprtion test (Figure 2.14). The UV-vis-NIR spectrum revealed higher absorbance in the region of the first metallic optical transition (E^{M}_{11}) (450-660 nm) from the aggregation sample, indicating the enrichment of metallic SWNTs.²⁸ In the UV-vis-NIR spectrum, the absorption peaks of aggregate sample was slightly red-shifted from that of raw SWNTs, which indicates the existence of polymer wrapping on SWNTs.



Figure 2.14 UV-vis-NIR absorption spectra of dispersed SWNTs in water, where the metallic SWNT area is marked with light purple color

The Raman spectrum of the SWNT aggregate sample revealed another interesting trend, when the SWNT sample was irradiated continuously by the laser (514 nm). The peak intensities of metallic SWNTs at ~249 & 264 cm⁻¹ were gradually decreased in a very short time, whereas no change was observed from the semiconducting SWNTs (Figure 2.15 a), The result clearly indicated that the metallic SWNTs were less stable than the semiconducting ones, which is in agreement with the high reactivity of metallic

SWNT reported in literature.⁶⁵ The G band mode provided consistent evidence (Figure 2.15 b), as the G^- band became narrower (a sign of decease of metallic SWNT). The increase of the intensity of D band also indicated that the laser beam used in Raman excitation can damage the sp² structure of metallic SWNT, which could have potential use for laser etching applications. In addition, the laser-induced damage on the metallic SWNTs appeared to occur easier than that on the semiconducting SWNTs.



Figure 2.15 Raman spectrum show the laser etch of SWNT under 514 nm excitation in both radial breathing mode (RBM) (a) and G band mode (b). The energy of the laser is 0.419 (mW)

When the solution of SWNTs/PmPV **2-2** was left in a vial at room temperature, we accidently found that small SWNT ribbons with regular shape were formed during aggregation (Figure 2.16 a and b). The AFM image (Figure 2.16 c) showed that the surface of the specimen was very similar to the cross scetion of grown SWNT forest⁶⁶. The AFM 3D picture in Figure 2.16 d further showed that the ribbon was composed of many SWNTs tubes bundles, which proves the existence of aligned SWNT bundles in a small area. SEM shows this SWNT bar has a smoother surface than both raw SWNT and normal SWNT precipitation (Figure 2.17), due to the alignment of SWNT ribbon which are parpendicular to surface.



Figure 2.16 The photograph of a small SWNT ribbon obtained from from SWNTs/PmPV **2-2** dispersion in water (a and b). The AFM image of the SWNT ribbon's top surface by using tapping mode (c) and 3D picture (d).



Figure 2.17 SEM images of surface on raw SWNT (a), normal aggregation (b) and SWNT aggregation ribbon (c)

Interestingly, the G band of this SWNT ribbon has a very high peak around 1503 cm^{-1} at G⁻ band range (Figure 2.18 b). When the sample was irradiated with laser, the G⁻ peak intensity decreased significantly within 25 s, whereas the peak intensity in the RBM region did not show the corresponding decrease (Figure 2.18 b). The observation suggests

that the peak at 1503 cm⁻¹ might also be associated with other structural feature of metallic-enriched SWNT boundles.

Because this SWNT ribbon is consisting of aligned SWNTs which are parpendicular to surface, the high peak of 1503 cm⁻¹ could be due to the signal of nanotube cap (carbon nanotube can be viewed as rolling one layer graphene with a hemisphere fullerene ball). Theoretical reaserch reported that the Cg(6) mode of vibrational frequency of fullerene would be observed around 1497 and 1505 cm⁻¹, which matches the peak of 1503 cm⁻¹ in our Raman spectroscopy.⁶⁷ That suggests that the Raman peak at 1503 cm⁻¹ is from the cap of the metallic nanotube, because all the nanotube is aligned perpendicualr to the surface of SWNT bar. The assumption is consistent with a reported study which shows that the cap of a metallic SWNT would be much more reactive than the cap of a semicondcuting SWNT, therefore only the cap of semiconducting SWNT can survive from UV radiation.²² (shown in scheme 2.3). This result is mtached with the phenomenon of decreased peak at 1503 cm⁻¹ burned by Raman laser.



Figure 2.18 Raman spectra of SWNT ribbon sample under 514 nm excitation in RBM (a) and G band mode (b). The energy of laser is 0.419 (mW)



Scheme 2.3 Illustration of metallic SWNT's cap burned by laser beam.

2.4 Conclusion

A water-soluble poly[(*m*-phenylenevinylene)-*alt*-(*p*-phenylenevinylene)] (PmPV) **2-2** has been synthesized, which exhibits an unsymmetrical substitution pattern on the *para*-phenylene unit. With one substituent being hydrophilic and the other being hydrophobic, the polymer chain has a higher tendency to fold as a helical conformation in aqueous solution. The polymer is found to selectively disperse the SWNTs of small diameters. This small diameter selectivity is proved by the results from Raman, UV-vis-NIR and photoluminescence. According to the NMR of SWNTs/polymer, the diameterbased selectivity is believed to be associated with the confined helical conformation, which forms a suitable cavity to host the SWNT with proper diameter. The dispersion of SWNT/PmPV 2-2 solution is also found to slowly form SWNT aggregation. The Raman and UV-vis-NIR results show that this aggregation has a high selectivity for metallic SWNT. Over an extended period (e.g. over one week), a ribbon-like object was found to be formed. Based on the evidence from TEM and AFM studies, SWNTs in the ribbon-like sample appear to be aligned in bundles along the tube axis. We assume that polymer may play an important role in tube's alignment, as the SWNTs could be slowly released from the polymer/SWNTs dispersion. Interesting, those metallic SWNT bundles are sensitive to laser due to the high reactivity of metallic SWNT. That implies the possibility of using laser to etch the surface of metallic SWNT material.

Both studies provide a useful demonstration that the polymer conformation of PmPV **2-2** can have a profound impact on the SWNT sorting. By using this aggregation method, it can even harvest aligned metallic SWNT bundles in a small area, which provides a potential separation method of SWNT boundless for nano electric application.

CHAPTER III

POLY(PHENYLENEETHYNYLENE)-CO-POLY(PHENYLENEVINYLENE) FOR SWNT SEPARATION

3.1 Introduction

Comparing with the high cost of using DNA polymer for SWNT separation, π conjugated polymers are emerging as an attractive alternative to achieve the SWNT
separation. Currently, polyfluorene has exhibited the potential to differentiate various
nanotube species, and is capable of enriching the semiconducting (10,5) SWNT to
~60%³² and (7,5) SWNT to ~75% purity.^{30,31} The fluorene-based copolymers have shown
improved characteristics in isolating semiconducting SWNTs, achieving enriched (11,3),
(9,7), and (10,3) SWNTs with proper chiral side chains,⁶⁸ and leading to near pure (6,5)
SWNTs (~90%) with 2,2'-bipyridinyl group on the main chain.⁶⁹ Although several
polymers have shown potential for isolation of SWNTs of single chirality, their
applications are currently limited to small scale (e.g., < 1 mg). The search continues in
the development of methods that have the potential to isolate SWNTs in a large scale.

In this chapter, we demonstrate that poly(phenyleneethynylene)-co-poly(phenylenevinylene) (PPE-PPV) **3-1**⁷⁰ (Scheme 3.1 a) exhibits some selectivity towards certain SWNT species. Molecular modeling (Scheme 3.1 b) showed that the helical conformation of PPE-PPV **3-1** had a slightly larger cavity in comparison with that

of PmPV 2-1 which is a well known dispersion agent for SWNTs.⁷¹ In comparison with the phenylene in PmPV 2-1, the phenylene in the phenyleneethynylene (PE) units can rotate easily around the carbon-carbon triple bonds, whose cylindrical orbital shapes lead to a low rotational barrier (0.64-3.3 kcal/mol).^{72,73} These factors allow the molecule to quickly adjust the polymer conformation for intimate interaction with SWNTs of a suitable diameter. As a consequence of introducing the C=C bond along the polymer chain, PPE-PPV 3-1 exhibits notable selectivity toward some SWNT of larger diameters such as (11,7), in sharp contrast to PmPV 2-1 which exhibits no selectivity. The result indicates that incorporation of C=C bonds along the chain microstructure improves the SWNT selectivity. We further demonstrate that a simple treatment with nitric acid leads to unexpected chemical reactivity that selectively removes SWNTs of smaller diameter, thereby simplifying the SWNTs isolation by having fewer SWNT species. Subsequent treatment of the sample with PPE-PPV 3-1⁷⁰ (Figure 3.4 a and b), finally provides a SWNT sample with very narrow diameter distribution.

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Scheme 3.1 (a) Chemical structures of PmPV **2-1** and PPE-PPV **3-1**. (b) Overlay of PmPV **2-1** (back, grey color) and PPE-PPV **3-1** (front, blue color) oligomers in helical conformations, showing that the PPE-PPV **3-1** has a slightly larger conformation cavity. The thick arrows point to the phenyl groups that can rotate to vertical position.



Scheme 3.2 Synthesis of polymer PPE-PPV 3-1

3.2 Experimental

3.2.1 Synthesis of PPE-PPV 3-1

1,4-Bis(3-formylphenyl-1-ethynyl)-2,5-dihexyloxybenzene (**3-3**): 2,5-Diiodo-1,4dihexyloxybenzene (2.651 g, 5 mmol) and 3-ethynylbenzaldehyde **3-2** (Sigma-Aldrich , 1.302 g, 10 mmol) were dissolved in a solvent mixture consisting of 5 mL of triethylamine and 50 mL of toluene. The solution was degassed under vacuum and subsequently filled with argon to remove oxygen. After addition of Pd(PPh₃)₂Cl₂ (Sigma-Aldrich, 35 mg, 1 mol%) and CuI (20 mg, 2 mol %), the reaction mixture was stirred overnight at room temperature under a positive argon atmosphere. After removing the precipitate via filtration, further purification on a silica gel column (hexanes/ethyl acetate = 10:1) afforded the product (1.1 g, 41%) as yellowish crystals. ¹H NMR (CDCl₃, 300MHz,): 0.87 (t, J = 6.8 Hz, 6H, -CH₃), 1.32-1.55 (m, 12H, -CH₂-), 1.85 (m, 4H, - CH₂-), 4.04 (t, J = 6.8 Hz, 4H, -OCH₂-), 7.02 (s, 2H, Ar'-H), 7.52 (t, J = 7.8 Hz, 2H, Ar-H), 8.02 (s, 2H, Ar-H), 10.01 (s, 2H, -CHO).

Polymer **PPE-PPV** 3-1: Monomer 3-3 2,5-dihexoxy-*p*-xylylenebis and (diethylphosphonate) (0.2673 g, 0.5 mmol) were dissolved in 10 mL of dry THF. Whereas the solution was cooled by an ice/water bath, potassium tert-butoxide (Sigma-Aldrich, 1.0 M in THF, 1.2 mL, 1.2 mmol) was added dropwise via a syringe over a period of 1 h under an argon atmosphere. During the initial reaction period, a pink-red color was formed and quickly disappeared upon addition of potassium *tert*-butoxide. A steady orange color was formed at the end of addition. The reaction mixture was then further stirred overnight at room temperature. The polymer was precipitated out by dropwise addition of its THF solution in methanol (150 mL). After drying at 40 °C under vacuum for 24 h, the polymer was obtained as orange powder in 56% yield (Mw = 170000). ¹H NMR (CDCl₃, 300 MHz,): 0.89 (12H, -CH₃), 1.35 (12H, -CH₂-), 1.56(8H, -CH₂-), 1.86 (8H, -CH₂-), 4.05 (8H, trans –OCH₂-), 7.01-7.14 (6H, Ar-H), 7.34-7.51 (8H, Ar-H), 7.69 (2H, Ar-H)



Figure 3.1 (a)¹H NMR spectrum of PPE-PPV **3-1** in CDCl₃ at 300 MHz (b)¹³C NMR spectrum of PPE-PPV **3-1** in CDCl₃ at 500 MHz

3.2.2 Dispersion of SWNT with nitric acid and PPE-PPV 3-1

Nitric acid treatment: in the first purification step, the raw SWNTs (about 0.5-1 g) prepared from HiPCO process were treated with aqueous HNO₃ (2.6 M, 300 mL) under reflux conditions for 48 h to afford SWNTs I in ~30% yield.⁷¹ (Nitirc acid treatment was done by our coworkers Dr. Marisabel Lebron-Colon, Structures and Materials Divison, NASA Glenn Research Center, Cleveland, Ohio)

Polymer wrapping (Scheme 3.3): 3 mg of SWNTs and 17 mL of THF was sonicated for 3 hours; then 50 μ L of PPE-PPV **3-1** in THF solution (26.2 mg/mL) was added to the SWNTs suspension, and the mixture was sonicated for an additional 1 hour while it was cooled in an ice-water bath. The obtained suspension (Sus1) was subject to centrifugation at 7000 g for 1 hour to remove the non-dispersible SWNTs. The resulting supernatant solution and sediment of SWNTs were designated as Sup-1 and Sed-1, respectively. Sed-1 was collected and re-dispersed in PPE-PPV **3-1** solution (50 μ L) and THF (20 mL), followed by sonication and centrifugation. The resulting suspension, supernatant, and sediment were designated as Sus-2, Sup-2 and Sed-2, respectively. After repeating this process several times, all the supernatants were collected together.



conditions: (i) PPE-PPV **3-1**/THF (0.65 mg/mL), sonication 3 h at 0°C; (ii) centrifugation, 1 h at 7000 g.



3.3 Results and Discussion

3.3.1 Dispersion Selectivity of PPE-PPV 3-1

When using PPE-PPV **3-1** to disperse raw SWNTs, SWNTs with larger diameter were enriched, such as (11,6) and (11,7) with diameters of 1.18 nm and 1.24 nm, respectively (Figure 3.2). The Raman spectroscopy excited with laser of 514 nm shows a consistent evidence to prove this diameter selectivity (Figure 3.3 a), in which the intensity of larger diameter SWNT (11,7) are increased. However, this selectivity is not effective enough. Although small diameter SWNT will be extracted out during PPE-PPV **3-1** dispersion, it can not remove all of the small-diameter SWNTs. Furthermore, the

Raman spectroscopy excited with laser of 647 nm shows that PPE-PPV **3-1** has a special affinity towards SWNT (7,5) (Figure 3.3 b).



Figure 3.2 UV-vis-NIR spectrum of raw SWNTs and SWNTs/PPE-PPV 3-1 solution



Figure 3.3 RBM mode of Raman spectrum excited at 514 nm (a) and 647 nm (b). The diameter of SWNT is anti-proportional to the Raman shift, which means SWNT with smaller Raman shift have a larger diameter.

3.3.2 Treatment with Nitric Acid

In order to fully achieve the larger diameter selectivity, it is necessary to "prescreen" those small diameter SWNTs out before dispersed with PPE-PPV **3-1**. Raw SWNTs from the HiPCO process were purified by using nitric acid, in order to remove the iron catalyst particles and amorphous carbon species that exist in the as-prepared sample. Interestingly, a majority of small diameter SWNTs, including (10,3), (7,5) and (8,3) (with diameter of 0.936, 0.829, and 0.782 nm, respectively) species, were also removed during the nitric acid treatment, as observed from the Raman spectra at 647 nm laser excitation (Figure 3.4 a). Raman analysis of the nitric acid treated sample with green laser excitation at 514 nm displayed a consistent pattern (Figure 3.4 b), showing that the nitric acid removed the small diameter (9,3) and (8,5) SWNTs (with diameter of 0.84 nm and 0.89 nm, respectively). UV-vis-NIR absorption spectra (Figure 3.5) further confirmed the Raman observations, when the nitric acid treated sample SWNTs **I** revealed much lower absorption between 1050-1350 nm which is associated with the semiconducting (7,5) and (7,6) and (8,7) SWNTs.²⁸

The nitric acid treatment, therefore, selectively removed the SWNTs of smaller diameter: (8,3), (7,5) and (10,3) SWNTs (d = 0.78, 0.83 and 0.93 nm, respectively).^{56,71} The metallic (12,3) and (13,4) SWNTs with respective tube diameter 1.08 and 1.21 nm, however, were not affected (Figure 3.4 a).



Figure 3.4 Raman spectra of SWNT samples in radial breathing mode (RBM) region at 647 nm (a) 514 nm excitation (b). The as-prepared raw SWNTs are subsequently treated with HNO₃ (SWNTs **I**) and wrapped by PPE-PPV **3-1** polymer (SWNTs **II**).



Figure 3.5 UV-vis-NIR absorption spectra of dispersed SWNTs in THF. The as-prepared raw SWNTs are subsequently treated with HNO₃ (SWNTs I) and wrapped by PPE-PPV **3-1** polymer (SWNTs II)

High resolution TEM (Figure 3.6) further revealed that nanotubes with small diameters in SWNTs I were bundled. The tube diameters were found between 1-1.2 nm. The result is in agreement with the results of using concentrated H_2SO_4/HNO_3 (ratio 1:9, with 97% H_2SO_4 and 60% HNO_3) at room temperature, which is reported to selectively react with metallic SWNTs of smaller diameter (less than 1.1 nm).⁴⁷ A possible explanation is that the dilute HNO_3 can generate low concentration of NO_2^+ , which will

selectively react with the small-diameter SWNTs. The observed higher reactivity of the small-diameter SWNTs are attributed to their increased curvature strain,^{74,75,76} in comparison with the relative lower reactivity of larger diameter nanotubes.



Figure 3.6 High resolution TEM images of SWNTs **I.** The sample contains bundled SWNTs (left image), and the tube (right image).

The intriguing chemical selectivity of HNO₃ toward different (*n*,*m*) SWNT was further examined by photoluminescence spectroscopy. Figure 3.7 (a) and (b) shows the 2D photoluminescence mapping of raw SWNTs and nitric acid treated SWNTs, where each SWNT is assigned according to the literature.⁵⁶ Clearly, nitric acid treatment removed most SWNTs with small diameter(d<0.9 nm, see table 3.1), including the major semiconducting species SWNT (8,4) and (7,6). The result complements the finding from UV-vis-NIR and Raman spectra (Figure 3.4 and 3.5), demonstrating that the nitric acid



Figure 3.7 2D photoluminescence of SWNTs samples in THF (excitation: 500-840 nm; emission: 912-1415 nm). SWNT I is raw SWNT treated with nitric acid. SWNT II is raw SWNT treated with both nitric acid and PPE-PPV **3-1**. Raw SWNTs was dispersed with addition of sodium dodecylbenzene sulfonate (SDBS) surfactant (65% in water).

3.3.3 Combination of Nitric Acid and PPE-PPV 3-1

The nitric acid treated SWNTs I were then dispersed with PPE-PPV 3-1 which was synthesized as described in scheme 3.2^{70} In a typical dispersion procedure (Scheme 3.3),⁷¹ SWNTs I sample was sonicated with PPE-PPV 3-1 in THF solution. The supernatant solution was separated from the sediment by centrifugation. Raman analysis of the resulting supernatant solution showed that the (13,4) and (11,7) in SWNTs I were separated from the (12,3) SWNT (Figure 3.4 a and b). The enriched (11,7) SWNT was also observable from the absorption spectrum (λ_{max} at ~1525 nm, Figure 3.5), where the absorption peak is assigned according to the literature.^{56,77} The absorption band at ~1397 nm, which was assigned to (11,6) SWNT (d = 1.186 nm),⁵⁶ was less affected. 2D photoluminescence spectra (Figure 3.7 b and c) revealed that PPE-PPV 3-1 treatment further purified the sample by selectively removing SWNT (8,6) and other SWNTs. The results revealed a striking pattern that the reported approach led to SWNTs sample with very narrow distribution of diameter, which is 1.23 nm and 1.21 nm for (11,7) and (13,4) SWNTs, respectively. The *co*-polymer PPE-PPV **3-1** thus exhibited good selectivity toward certain SWNT species, in contrast to PmPV 2-1 which exhibits little selectivity to specific SWNTs.⁷¹

Raman analysis further revealed that nitric acid treatment increased the intensity of the D band due to the damage of the sp² structure of the nanotubes. Polymer treatment by using PPE-PPV **3-1**, however, removed those defective tubes (Figure 3.8 light yellow area). The result showed that the polymer wrapping was a necessary step in achieving the desirable separation and removing those defective tubes.



Figure 3.8 Raman spectra of SWNT samples in G band mode (G band) and defect mode (D band) at 647 nm excitation. The as-prepared raw SWNTs are subsequently treated with HNO₃ (SWNTs I) and wrapped by PPE-PPV **3-1** polymer (SWNTs II).

Table 3.1 Diameter of different SWNT ((<i>n,m</i>) i	in the	studied sa	ample.
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SWNTs	Tube	SWN	Ts	Tube
structures	diameters	struct	ures	diameters
	(nm)			(nm)
(6,5)- <i>sc</i> ^a	0.757	(10, 3	3)- <i>sc</i>	0.936
(8,3)- <i>sc</i>	0.782	(8,6)-	-SC	0.966
(7,5)- <i>sc</i>	0.829	(9,5)-	-SC	0.976
(9,3)-met ^b	0.84	(8,7)-	SC	1.032
(8,4)- <i>sc</i>	0.840	(12,3)-met	1.077
(8,5)- <i>met</i>	0.89	(9,7)-	·SC	1.103
(10,2)- <i>sc</i>	0.884	(12,4)-sc	1.145
(7,6)- <i>sc</i>	0.895	(11,6)-sc	1.186
(9,4)- <i>sc</i>	0.916	(13,4)-sc	1.206
		(11,7)-sc	1.248

^{a,b} the "sc" and "met" stand for semiconducting and metallic tubes, respectively.



Figure 3.9 AFM images obtained in tapping mode. (a) A profile along an individual SWNT, where the dashed line shows ~ 1.3 nm height. (b) Surface images of the SWNT, where the black line indicates the cross-section direction along the tube. The inset image shows the dimension of the same SWNT.

An atomic force microscopy (AFM) image of the SWNTs/PPE-PPV **3-1** sample from the supernatant solution revealed that the SWNT sample was dispersed as a single tube (Figure 3.9 b). AFM profilometry in tapping mode (Figure 3.9 a) along the lengthwise SWNT direction gave a height profile of regular pattern, indicating that the nanotube was wrapped section by section with multiple polymers chains. From the minimum height of the profile, the diameter of the wrapped nanotube was estimated to be ~1.3 nm, which is in agreement with the diameter of 1.21~1.24 nm for (13,4) and (11,7) SWNTs.

The observed narrow selectivity toward the (13,4) and (11,7) SWNTs could be related to the polymer's ability to adopt a suitable helical conformation for intimate polymer interaction with larger-diameter nanotubes. Molecular modeling studies showed that a set of the substituents are pointing inward with the natural helical conformation of PmPV **2-1** (Scheme 3.1 b), which could shield the π -conjugated polymer backbone from intimate contact with the surface of SWNTs. The configuration can be altered in PPE-PPV **3-1**, because the phenyl rings in the phenyleneethynylene (PE) segments could be rotated easily around the -C C- bond due to its low rotational energy barrier.^{72,73} As a consequence, the phenyl rings in the PE segments can adopt the parallel alignment along the nanotube surface (Figure 3.10 a), thereby resulting in a more favorable π - π interaction.

The modeling results also showed that the natural conformational cavity from PPE-PPV **3-1** was sufficiently large to match the size of (13,4). The results were consistent with the observations that the PPE-PPV **3-1** had favorable interaction with the large diameter tubes (13,4) and (11,7) (Figure 3.3), because those tubes with smaller

diameters (d < 1.14 nm) would be too loosely fitted into the conformational cavity. The ability of PPE-PPV **3-1** to adopt a natural helical conformation with enhanced parallel π - π interaction for SWNTs, in addition to proper diameter match, was thought to play a crucial role in the observed selectivity.



Figure 3.10 Molecular modeling of PPE-PPV **3-1** tetramer (n = 4) in front (a) and side view (b), showing a helical conformation with proper cavity size (~2.0 nm) to host (13,4) SWNT. (CNT: carbon nanotube)



Figure 3.11 Chirality map of SWNTs after nitric acid treat and PPE-PPV **3-1** wrapping. SWNTs in raw SWNT sample are printed in bold character. Enriched SWNTs are labeled with circle

3.4 Conclusion

In summary, we have demonstrated that a narrow diameter range of SWNTs. SWNT (13,4) and (11,7) (d = 1.21-1.24 nm), can be isolated by sequential treatment with nitric acid, followed by PPE-PPV **3-1** polymer wrapping (summarized in Figure 3.11). The nitric acid selectively removed the tubes with small diameters. Free rotation along a carbon-carbon triple bond allows part of the conjugated backbone to have parallel interaction with SWNT surfaces, while retaining the polymer's natural helical conformation. The helical conformation cavity of PPE-PPV **3-1** appears to match the diameter of (13,4) (d = 1.21 nm) and (11,7) (d = 1.23 nm), leading to favorable interaction with SWNTs of specific diameter.

CHAPTER IV

WATER SOLUBLE POLY(PHENYLENEETHYLENE) FOR SWNT SEPARATION

4.1 Introduction

Poly(p-phenyleneethylene) (PPE) exhibits a rigid linear structure whose high luminescence has led to applications in chemical sensors.⁷⁸ Although an earlier study suggests the linear π - π interaction between the rigid PPE and SWNTs,^{37,79} a helical wrapping interaction has been demonstrated recently by water-soluble PPE derivative 4-1.⁸⁰ (Scheme 4.1) No selective dispersion of SWNTs has been observed by using PPE derivatives 4-1.^{80,81} In comparison with its linear rigid isomer PPE, poly[(mphenyleneethynylene)-*alt*-(*p*-phenyleneethynylene)] (P*m*PE*p*PE) **4-2** (Scheme 4.1) exhibits improved chain flexibility.^{82,83} Our recent study shows that the polymer helical conformation could be used to sort SWNTs of small diameter, as observed from a vinylene analogue, poly[(m-phenylenevinylene)-alt-(p-phenylenevinylene)] (PmPV) 2-2 (Scheme 4.1).⁶³ On the basis of the structural similarity, polymer (PmPEpPE) 4-2 is assumed to be water-soluble, where the low rotation barrier⁸⁴ of C=C bond could facilitate the helical conformation. Because the helical conformation of polymer (PmPEpPE) 4-2 (Scheme 4.1) prefers to host the SWNTs of comparable sizes, the polymer could have a build-in mechanism to separate SWNTs by their diameters. In addition, the freely rotating C=C bond ⁸⁴ allows the *para*-phenylene to be aligned in
parallel to the SWNT surface, which provides a unique platform for - interaction with SWNTs (Scheme 4.1 structure 4-4). All these factors could be translated into a desirable selectivity for a specific nanotube. In order to prove the hypothesis, we synthesized water soluble PmPEpPE 4-2



Scheme 4.1 Polymer structures of **2-2** and **4-1**, and synthesis of PmPEpPE **4-2**. The inset **4-4** illustrates the helical wrapping of **4-2** on a SWNT.



Scheme 4.2 Synthesis of PmPEpPE 4-2

4.2 Experimental

4.2.1 Synthesis of Polymer PmPEpPE 4-2

Synthesis of diiodobenzene monomer **4-3**: In a three-necked round bottom flask equipped with a flux condenser was charged with dialkoxybenzene compound (4.42 g), KIO₃ (1.06 g) and iodine (6.33 g). To this reaction mixture was added acetic acid (29 mL), deionized water (35 mL), and concentrated sulfuric acid (2 mL). The resulting mixture was heated to reflux for 6 h with constant stirring. The residual iodine was consumed by the addition of 20% sodium hydrosulfite. A fine solid precipitate was collected by filtration and recrystallized twice from deionized water to yield large needle-like crystal, yield 12.5%. ¹H NMR (D₂O, 300 MHz, ppm): 7.47 (s, 2H), 4.15 (t, 4H), 3.22-3.17 (m, 4H), 2.25-2.21 (m, 4H).

Synthesis of PmPEpPE **4-2**: Monomer **4-3** (0.9 g, 1.4 mmol) and 1,3diethynylbenzene (0.17 g, 1.4 mmol) were dissolved in a mixture of water (20 mL) and DMF (20 mL) at 60 °C in a Schlenk flask with a gentle flow of argon and with magnetic stirring. The resulting clear solution was deoxygenated by several cycles of vacuumargon cycling. Another solution comprised of 52.0 mg (45.0 µmol) of Pd(PPh₃)₄ and 10.0 mg (45 µmol) of CuI in a mixture of 10 mL of triethylamine and 10 mL of DMF was likewise deoxygenated and was subsequently added to the former solution by means of a cannula. The final mixture was again deoxygenated by vacuum, followed by argon filling. The reaction mixture was then warmed to 50-55° C and stirred under a positive pressure of argon for 14 h. The resulting solution was viscous, brown in color and exhibited an intense blue photoluminescence when illuminated with a UV lamp. The solution was cooled and then slowly added to a solvent mixture (1 L) of methanol/acetone/ether (ratio = 10:40:50 by volume). The polymer precipitate was collected by filtration, redissolved in 20 mL of water/methanol 70:30, and precipitated by addition to a large volume of methanol/acetone/ether (10:40:50). After drying under vacuum, the product was obtained as brown solid (0.31 g; yield: 47%, Mw = 9500). ¹H-NMR (D₂O; δ_{ppm}): 2.28 (m, 4H); 3.23 (m, 4H); 4.18 (m, 4H); 6.94-7.56 (m, 6H).



Figure 4.1 (a)¹H NMR spectrum of PmPEpPE **4-2** in deuterated water at 300 MHz. (b)¹³C NMR spectrum of PmPEpPE **4-2** in deuterated water at 300 MHz

4.2.2 Dispersion of SWNTs with PmPEpPE 4-2

In a typical procedure for nanotube dispersion, 3 mg of raw SWNTs (produced by HiPCO process, Rice University) sample were dispersed by using 5 mg of *PmPEpPE* **4-2** in 20 mL deionized water. The solution was sonicated at 0 °C for one and half hours, followed by centrifugation at 7000 g for two hours to remove the sediment of the undispersed SWNTs. In order to further remove the catalyst metal and the aggregation of wrapped SWNTs, the supernatant solution was further centrifuged at 48000 g twice for two hours. The resulting clear solution was used for the UV-vis-NIR, Photoluminescence and AFM spectrascopy. For Raman spectroscopy, the solvent was evaporated to get the solid test sample.

4.3 Results and Discussion:

4.3.1 Characterization of SWNTs/ PmPEpPE 4-2 Solution

In ¹H NMR of P*m*PE*p*PE **4-2**, the signal at 7.08 ppm was assigned to phenyl proton H_d on the basis of PmPEpPE polymer; in ¹³C NMR spectrum of P*m*PE*p*PE **4-2** in deuterated water. The aromatic carbons are at 150.5 ppm; the acetylenic carbons are at 92.7 and 83.7 ppm; the alkyl chain are at 65.8, 46.1, and 22.5 ppm.

SWNT dispersion characterization: the AFM image revealed that the SWNTs in the dispersion were single tubes (Figure 4.2 a), indicating that PmPEpPE 4-2 was an effective dispersing reagent. 2D photoluminescence maps of SWNT samples were acquired (Figure 4.3), where the chirality of SWNTs was assigned according to the literature.⁵⁶ The intensities of the photoluminescence peaks for small diameter nanotubes (6,5) and (8,3) (d = 0.757 and 0.782 nm, respectively) were increased after dispersion

with PmPEpPE 4-2 (Figure 4.3 b). Meanwhile, the peaks of large nanotubes, such as (8,6), (9,5), and (8,7) (d = 0.966-1.032 nm) were removed. The SWNT (7,5), (8,4), and (7,6) (d = 0.829, 0.840, and 0.895 nm, respectively) were found with lower intensity. The changes in photoluminescence intensity clearly indicate diameter selectivity when using PmPEpPE 4-2 in dispersing SWNTs.



Figure 4.2 AFM image of SWNTs dispersed with PmPEpPE 4-2 in water (a) and distribution of tube diameters based on the measurement by using tapping mode (b).



Figure 4.3 2D photoluminescence map of SWNTs, where each SWNT is indicated by its chiral indices (n,m). (a) Raw SWNTs were dispersed with sodium dodecylbenzenesulfonate (SDBS) surfactant in D₂O. (b) SWNTs were dispersed by using PmPEpPE **4-2** in D₂O. Chiral indices (n,m) of each SWNTs are shown.

The UV-vis-NIR absorption spectra of the supernatant solution provided consistent evidence for small diameter selectivity (Figure 4.4). According to UV-vis-NIR, SWNT dispersion by PmPEpPE **4-2** enriched small diameter SWNTs (8,3) and (6,5), whereas discarding larger diameter (8,4) and (7,6) SWNTs (Figure 4.4). The population of (7,5) tube became relatively low, in agreement with the observation from the 2D photoluminescence. The absorption peaks of SWNTs appeared to be broad, as a consequence of interaction between the SWNT and the wrapping polymer.



Figure 4.4 UV-vis-NIR absorption spectra of SWNTs dispersed in surfactant SDBS and *PmPEpPE* **4-2**. The supernatant solution of SWNTs/*PmPEpPE* **4-2** is obtained after subjecting high speed centrifugation to remove undispersed SWNTs.

The absorption λ_{max} of the polymer backbone was blue-shifted by about 5 nm (Figure 4.5), after its interaction with SWNTs. This is consistent with the helical model proposed in **4-4**, where the *para*-phenylene is rotated away from *co*-planarity with the adjacent *meta*-phenylene (Scheme 4.1).



Figure 4.5 UV-Vis (300-460 nm) absorption spectra in water.

The RBM and G band regions of the Raman spectra further confirmed the nanotube's population changes before and after dispersing by PmPEpPE **4-2** (Figure 4.6). The (7,5) SWNT was chosen as a reference for the tube population change, because the (6,5) SWNT was not observable under the laser frequency used in the Raman.⁸⁶ The result indicated that the content of (8,3) was slightly increased in comparison with (7,5), whereas that of (7,6) and (10,3) were decreased. The relative content of each peak in the Raman spectra was measured by comparing the ratio of their Lorentzian integration to (7,5). The result clearly indicated that the PmPEpPE **4-2** selectively enriches small

diameter nanotube (8,3) (0.782 nm),⁸⁷ whereas the nanotubes with larger diameter (d > 0.829 nm)⁵⁶ were deselected. In addition, the Raman G band (inset in Figure 4.6) indicated the enrichment of semiconducting nanotube, which is in agreement with rejection of large diameter metallic (13,4) and (12,3) tubes in RBM region. In other words, dispersion by using PmPEpPE **4-2** offers an effective strategy to purify the small diameter semiconducting SWNTs in aqueous solution.



Figure 4.6 Raman spectra of raw nanotube and SWNTs/P*m*PE*p*PE **4-2** dispersion in the radial breathing mode (RBM) region (excitation at 647 nm). The inset is G band region.

4.3.2 Dispersion Selectivity of PmPEpPE 4-2

In order to calculate the content change for each nanotube, we used a Lorentzian curve fitting for each peak in the Raman RBM mode and calculated the integration area C for every SWNT (n,m) (Figure 4.7 and Table 4.1). For comparison, the relative content of SWNT (7,5) in each sample is used as the relative standard. R (n,m) is the relative content, which is defined as R(n, m) = C (n,m)/C(7,5). The change of relative content is estimated with the change percentage of relative content before and after polymer wrapping, which was defined as the value of [R(SWNT/ PmPEpPE 4-2)-R(raw SWNT)]/R(raw SWNT)

According to Figure 4.8, as the diameter gets smaller, change of relative content gets larger. When the SWNT's diameter is larger than 0.89 nm, all the change of relative content is negative, which means the content of those SWNTs was decreased, such as (12,3) and (10,3). Whereas SWNTs with diameters smaller than 0.82 nm had a positive relative change, which means those SWNTs get enriched, such as (8,3).



Figure 4.7 Lorentzian peak fit of Raman for raw SWNTs and SWNTs/PmPEpPE 4-2

Table 4.1 Relative content of eac	N SWNT in different nanotube samples.
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(<i>n</i> , <i>m</i>)	diameter of	relative content in	relative content in	change of
	nanotubes	raw nanotubes ^a	SWNTs/PmPEpPE 4-2 ^a	relative content
(13,4)	1.206	5.477698	0.993738	-0.81858
(12,3)	1.077	0.505755	0.049468	-0.90219
(10,3)	0.936	1.264388	0.19975	-0.84202
(7,6)	0.895	0.491367	0.292423	-0.40488
(7,5)	0.829	1	1	0
(8,3)	0.782	0.248561	0.422041	0.697938

^aRelative content is calculated by using peak area from the lorentzian-fitted Raman



Figure 4.8 Relative peak area change after dispersion by using PmPEpPE 4-2

All spectroscopic evidence consistently points to the fact that PmPEpPE 4-2 exhibits good selectivity toward the small diameter SWNT (6,5). The conclusion of enriching SWNT (6,5) (d = 0.757 nm) is consistent with the tube population observed in AFM (Figure 4.2 b), where most tubes have diameters between 0.7–0.8 nm. whereas the helical conformational cavity of PmPEpPE 4-2 could play some role, the diameterselection mechanism by using the polymer conformation alone can not fully explain the differentiation of SWNTs with very close diameters. The polymer's ability to differentiate SWNTs with close diameter, such as the (6,5) (d = 0.757) and (8,3) (d =

0.782 nm), (9,2) (d = 0.806 nm) and (7,5) (d = 0.829 nm), strongly suggests that the observed selectivity involves the electronic interaction between the wrapping polymer and SWNTs.



Figure 4.9 Chirality maps of SWNTs showing that small-diameter nanotubes (red bold circle) were enriched by PmPEpPE **4-2** wrapping, and the large-diameter nanotubes (dotted blue circle) were removed.

4.4 Conclusion:

In conclusion, a water soluble polymer PmPEpPE 4-2 has been synthesized, in which the *meta*-phenylene unit introduces a bent angle along the polymer backbone to facilitate the helical conformation. In aqueous solution, the polymer is found to disperse SWNTs with good selectivity toward the (6,5) SWNT and some selectivity toward (8,3) SWNT (Figure 4.9), which have the small diameters (d = 0.757 and 0.782 nm, respectively). The intriguing selectivity is partly due to the helical conformation of the polymer backbone, whose cavity size could act as a pre-sort mechanism to select the tubes of small diameters (Structure 4-4 in Scheme 4.1). The SWNTs of similar diameters are further differentiated by interaction with the local phenyleneethynylene (PE) chromophores, whose assembly is guided by the helical conformation and assisted by the low rotational barrier of the carbon carbon triple bonds. Selective dispersion of small-diameter SWNT (6,5) illustrates that dispersion with PmPEpPE can be an effective tool to aid the SWNTs sorting separation.

CHAPTER V

POLYETHYLENIMINE AND ITS CHROMATOGRAPHY FOR SWNT SEPARATATION

5.1 Introduction

Previous studies have shown that amines could be absorbed onto the surface of SWNT.⁸⁸ A few studies also demonstrated that the amines could interact selectively with either semiconducting SWNT⁸⁹ or metallic SWNT.⁸⁸ In an organic solvent (THF), propylamine exhibits a stronger affinity toward the metallic SWNT.⁸⁹ The octadecylamine (n- $C_{18}H_{37}NH_2$ in THF) or amine-terminated monolayer, however, show a high affinity for semiconducting SWNTs,⁸⁸ which is useful for selective extraction of semiconducting SWNTs. In addition, octadecylamine and amine-terminated monolayer have been used to selectively adsorb and extract semiconducting SWNTs.^{90,15} Herein, we report a new polyamine dispersion agent: polyethylenimine (PEI) (Scheme 5.1) which not only shows good selectivity for choosing semiconducting SWNTs, but also exhibits a pH-dependent property for dispersing SWNTs.

Chromatography is one of traditional separation methods, which is widely used in the laboratory and drug industry for purification. Few studies have been reported in developing the chromatographic methods for SWNT purification. Recently, Moshammer and coworkers⁹¹ successfully separated metallic and semiconducting SWNTs by using an allyl dextran-based size-exclusion gel. Kataura and coworkers³⁹ further demonstrated that single-chirality separation of SWNTs can be achieved by using an allyl dextran-based gel. This gel chromatography technology, however, does not differentiate metallic SWNTs.³⁹ Herein, based on the SWNT selectivity of polyethylenimine (PEI), we built a novel affinity chromatography, which is packed with the PEI modified cellulose, can be used to separate the metallic SWNTs from the semiconducting ones. Remarkably, the PEI-based affinity chromatography can be used to achieve the single chirality isolation of SWNT, leading to the isolation of metallic (10,10) and (9,9) SWNT.



Scheme 5.1 Chemical structure of PEI **5-1** (purchased from Sigma Aldrich). The Mn and Mw of PEI **5-1** is around 60,000 and 750,000, respectively. The ratio of primary amine: secondary amine: tertiary amine is 1:2:1, with a branching site every 3-3.5 nitrogen atoms.

5.2 Experimental

5.2.1 Dispersion of SWNT with PEI 5-1

PEI 5-1 solution (10 g, 50% in water) was added to the 900 mL of deionized water. The pH value of this solution was adjusted to 7 by addition of 6 N hydrochloric acid solution with stirring. After that, more water is added to make the final solution volume of 1 liter. The PEI 5-1 is clear, viscous solution at the bottom of the bottle, as the pH of the solution decreases, PEI 5-1 will be dissolved into the solution.

A 3 mg sample of SWNTs sample was dispersed in 20 mL water by using 1 mL prepared PEI **5-1** solution. This SWNTs/PEI solution was sonicated at 0 °C for two hours, followed by centrifugation at 7000 g for two hours to remove the sediment of undispersed SWNTs. In order to further remove the catalyst metal and the undispersed SWNTs, the supernatant solution was further centrifuged at 48000 g twice for two hours. The resulting clear solution was used for the UV-vis-NIR, photoluminescence and AFM spectroscopy. For Raman spectroscopy, it requires to evaporate the solvent to measure the solid test sample.

5.2.2 Preparation of Chromatographic Packing Material

Phosphorylation of cellulose: Cellulose (5.0 g Sigma-Aldrich, S5504) was put into a 250 mL round-bottomed flask with a magnetic stirrer, followed by adding 20.0 g of urea (Acros), 100 mL of dimethylformamide (GR, ACS), and 34.0 g of 85% H_3PO_4 (Aldrich). The mixture was heated to reflux for 3 hours. The resulting grey suspension was cooled to room temperature, and the DMF solvent was decanted off. The light yellow product was washed with a large amount of water four times and separated by centrifugation.

Adsorption of PEI **5-1**: The phosphorylated cellulose (light yellow solid) was then soaked for 15 min in a 0.5 % solution of polyethylenimine (pH = 7, the polyethylenimine solution was neutralized with hydrochloric acid solution). The resulting cellulose was separated by filtration, and dried at room temperature for storage. Before use, the cellulose was immersed in water for 2 h to swell at room temperature.

5.2.3 Separation of SWNTs with PEI Chromatography

A sample of raw SWNTs (~3 mg) from HiPCO process was dispersed in sodium dodecylbenzene sulfonate (SDBS) (20 mL aqueous solution; concentration: 2.8 mg/mL) by sonication at 0 °C for 1.5 h. The resulting suspension (3 mL) was then loaded onto a short column packed with the PEI resin on a glass pipette. When deionized water was used as an eluent, a band of SDBS was flowing out first (within a few minutes as observed on a UV-vis-NIR spectrometer). After eluting with deionized water for 12~24 h, the blue band containing metallic SWNTs will be achieved.

5.3 Results and Discussion

5.3.1 Dispersion Selectivity of PEI 5-1

When using Raman spectroscopy to test the SWNTs/PEI **5-1** dispersion solution, (Figure 5.1 a and c) it is found that metallic SWNT (12,0), (8,5), (9,3), (12,3) and (13,4) were decreased, whereas semiconducting nanotube (11,7), (7,5), (7,6) and (8,3) was increased. That indicates during dispersion metallic SWNTs were been removed. However, not all the semiconducting SWNTs can survive after dispersion, for example, the peak of (14,1) is also decreased (Figure 5.1 a), which implies that PEI **5-1** has a different selectivity between semiconducting SWNTs. Because the G⁻ band is the characteristic peak for metallic SWNT, the narrow and small G⁻ band (Figure 5.1 b and d) provide a consistent evidence to confirm the decrease of metallic SWNTs.⁹²



Figure 5.1 Raman spectra of raw SWNTs and SWNTs/PEI **5-1** dispersion. RBM mode (a) and G band (b) are from Raman spectroscopy excited with 514 nm laser. RBM mode (c) and G band (d) are from Raman spectroscopy excited with 647 nm laser. The peaks are assigned according to the Kataura plot and literature⁶²



Figure 5.2 UV-vis-NIR absorbance spectra of SWNTs dispersed in surfactant SDBS and PEI **5-1**. The supernatant solution of SWNTs/PEI **5-1** is obtained by removing undispersed sediment after centrifugation.

In agreement with the Raman results, the decrease of E^{M}_{11} from 450 to 660 nm (absorption peaks of metallic SWNTs) in UV-vis-NIR (Figure 5.2) implies reduction of metallic SWNTs. This evidence further confirms the semiconducting SWNT selectivity of PEI **5-1** proved by Raman spectra. In UV-vis-NIR, the first transition absorption of

metallic tube (E_{11}^{M}) is between 450~660 nm, which have some overlap with second transition absorption of semiconducting tube E_{22}^{S} (630~900 nm).³⁶ However, the intensity of E_{22}^{S} is much weaker compared with E_{11}^{S} or E_{11}^{M} , ¹² thus, the lower absorption between 450~660 is dominantly contributed to the decrease of metallic nanotube (E_{11}^{M}). Similar to the Raman result, the absorbance intensity of semiconducting tube have changed after dispersion (Figure 5.2), for example, in contrast to (7,6), the intensity of (9,5) and (8,7) shows a decrease, which indicates that PEI **5-1** has unique selectivity for different semiconducting tubes.





Figure 5.3 2D photoluminescence map of SWNTs dispersed with SDBS (a) and PEI 5-1(b). Those major SWNTs are labeled with bold or dash circle in chirality map (c).

The dispersion selectivity for different semiconducting SWNTs was further proved by 2D photoluminescence results (Figure 5.3). In raw SWNTs, the are five major types of tubes: (8,4), (7,6), (8,6), (9,5) and (8,7). After dispersion with PEI **5-1**, only (7,6) and (8,6) became the dominating species in the sample (Figure 5.3 c). The change of major semiconducting nanotubes distribution indicates that PEI **5-1** has a unique selectivity affinity towards different semiconducting nanotubes. In the other case, when comparing (9,5) and (8,6), although both SWNTs have similar diameter (0.976 nm for (9,5) and 0.966 nm for (8,6) respectively), only (8,6) was enriched in SWNTs/PEI **5-1** solution, which indirectly excluded the possible diameter selectivity of **5-1**.



Scheme 5.2 PEI 5-1 is absorbed on the surface of a SWNT

5.3.2 pH-dependent SWNT dispersion

From the structure of PEI (Scheme 5.1), there are three kinds of amine (primary, secondary and tertiary (ratio is 1:2:1), according to the product description from Sigma-Aldrich). It is necessary to find out which kind amine is playing a dominating role in SWNT dispersion. Linear PEI (secondary amine) and triethylene amine (tertiary amine) were used for SWNT dispersion, however, both show poor dispersion property. That implies that primary amine is the effective group for dispersing SWNTs, as shown in Scheme 5.2



SWNT/PEI 5-1 \implies after 3 weeks \implies pH below 3 dispersion

Figure 5.4 Photo picture of SWNTs/PEI **5-1** dispersed solution. (a) SWNTs/PEI **5-1** dispersion; (b) SWNTs/PEI **5-1** kept for three weeks; (c) adjust the pH value of SWNTs/PEI **5-1** solution below 3.

After keeping the dispersion solution of SWNTs/PEI **5-1** for 3 weeks, there is almost no aggregation of SWNTs (Figure 5.4 a and b). However, when the solution's pH value was decreased to 3 by adding HCl solution, SWNTs aggregation took place immediately and they precipitated out (Figure 5.4 c). That means the dispersed SWNTs were released out from the PEI **5-1** solution under acid condition, which may be due to the weakening of adsorption between primary amine and SWNT. Several researches reported that isolated SWNT would exhibit molecular-like behavior,^{93,94} and also implied

that reversible oxidation/reduction could take place at the surface of SWNT.⁸⁸ (Shown in reaction (I)).

$$SWNT + nH^+ + (n/4)O_2 \implies SWNT^{n+} + (n/2)H_2O \qquad (I)$$

In the presence of acid (H⁺), SWNT will lose electrons to produce oxidized, pdoped SWNT (SWNTⁿ⁺), meanwhile primary amine in PEI **5-1** will be protonized. The resulting Coulomb Force between PEI **5-1** and SWNTⁿ⁺ weakened the adsorption of PEI **5-1** on SWNT's surface, leading to the release of SWNTs from PEI **5-1** solution. Considering the semiconducting SWNT selectivity of PEI **5-1** (Figure 5.1 and 5.2), it can separate semiconducting SWNTs by PEI **5-1** dispersion and adjustment of solution's pH value.

5.3.3 Design of PEI Chromatography for SWNT Separation

Inspired by the semiconducting SWNT selectivity of PEI **5-1**, we combined PEI **5-1** and chromatography technology to build a novel affinity chromatography. In the design of chromatography packing material, PEI **5-1** was fixed by adsorbing onto the phosphorylated cellulose backbone (Scheme 5.3). Previous study (see section 5.3.2) showed that the primary amine play an important role to interact with SWNTs and exhibit a higher affinity toward semiconducting SWNT than metallic SWNT. Thus, this PEI chromatography is expected to separate semiconducting SWNTs from the metallic ones.



Scheme 5.3 Simplified chemical structure of the support used in PEI chromatography. PEI **5-1** supported on the phosphorylated cellulose

In order to test the selectivity of this novel chromatography, PEI/cellulose was packed into around 1 cm length chromatography column. Surfactant dispersed SNWTs were loaded on the top of column, followed by elution with deionized water. A blue band was gradually developed and moved very slowly when water was flowing continuously through the column. Once the blue band was fully developed (as shown in Figure 5.5 a), the water flow was stopped. The separated blue nanotube sample can be collected by using either methods: 1) the column was eluted with aqueous ammonium solution (7 wt%), following by concentrating the eluent or 2) the blue section on PEI packing material could be cut out, and the separated SWNTs were released by adding several

drops of HCl solution (0.01mol/L), followed by neutralizing with $NH_4(OH)$ or NaOH. We suggest that the method (2) is the best way to harvest metallic SWNTs.



Figure 5.5 (a) A sample of SWNTs being separated on a column packed with PEIcellulose, where a blue band is eluted by water. (b) The blue SWNT solution was collected by washing the separated SWNTs.

5.3.4 Characterization of Separated Metallic SWNT

The AFM image of the blue sample solution confirmed the presence of carbon nanotube (Figure 5.6). Because UV-vis-NIR absorption at 450 ~ 660 nm is characterization for metallic SWNTs, the major absorption band at ~630 nm of the blue SWNT solution indicates that the isolated blue solution was metallic SWNTs (Figure 5.7). Because there is only a low absorption between 1100-1300 nm (semiconducting SWNT region) in blue sample solution, it implies that majority semiconducting SWNTs had been removed by simple passing through a short column of PEI/cellulose. The purity of metallic SWNTs is as high as 92.2% on the basis of Lorentzian peak fitting (Figure 5.8).



Figure 5.6 AFM image of metallic SWNTs.



Figure 5.7 UV-vis-NIR absorption of isolated metallic SWNTs



Figure 5.8 Peak fitting of UV-vis-NIR absorption spectrum of isolated blue metallic SWNT fraction

Use of 2D photoluminescence spectroscopy of the blue solution detected no signal from the blue SWNTs solution (inset of Figure 5.9), in sharp contrast to the strong signals from the raw SWNTs sample under the same concentration and instrument conditions (Figure 5.9). Because only semiconducting SWNTs shows the photoluminescence, whereas metallic SWNTs doesn't (chapter 1.3.2), this result further confirmed the resulting blue solution is metallic SWNTs.



Figure 5.9 2D photoluminescence spectroscopy of raw SWNTs, where the inset shows the photoluminescence of the blue SWNT solution.

Separation of metallic SWNTs from the semiconducting SWNTs was also supported by the Raman spectra (Figure 5.10). The Raman spectral results showed that the blue eluent contained metallic SWNTs, such as (13,4) and (11,8), whereas the nanotubes on PEI resin were enriched with semiconducting SWNTs, such as (7,6) and (7,5). From the Raman spectra, the metallic SWNTs were the major component in that blue eluent solution, in agreement with the purity from the UV-vis-NIR absorption.



Figure 5.10 Raman spectra in the radial breathing mode (RBM) for raw SWNTs, metallic SWNTs from eluent, and residual SWNTs on PEI, with excitation at 647 nm

In order to figure out the enrichment of specific metallic SWNT, each SWNT peak must be assigned by Raman RBM mode (Chapter 1.3.3). The assignment of individual metallic SWNT is based on excited laser wavelength (energy) and the diameters of nanotube.⁹⁵ Shown in Figure 5.11, when using 647 nm laser as excitation source (red dash line), the observed Raman RBM peaks from the blue metallic SWNT sample (black dotted line) matched the positions for (11,8), (13,4), (10,7) and (12,3). The assigned SWNTs are circled. The content of metallic SWNTs were further identified by peak fitting (Figure 5.12), which shows (13,4) SWNT takes up 70% of the sample.



Figure 5.11 Plot of energy versus Raman RBM peak shift for metallic SWNTs

Raman intensity (a.u.) ഗ		(13,4) metallic SWNTs stimulation of SWNTs stimulation (11,8) (10,7) (12,3) (12,3) (170 180 190 200 210 220 230 Demon objit (cm ⁻¹)			
_	Raman shift of metallic SWNTs (cm ⁻¹)	(n , m)	Content in metallic SWNTs(%)		
-	182.6	(11,8)	12		
-	195.7	(13,4)	70		
_	208.6	(10,7)	15		
_	223.1	(12,3)	3		

Figure 5.12 Peak fitting of Raman spectrum (Figure 5.10) of blue metallic SWNT fraction on the basis of Raman peak positions.⁹⁵

Clearly, the PEI chromatography has a high efficiency in separating the specific metallic SWNTs from the semiconducting SWNTs, as the nanotube sample had only passed a short column (about 1 cm long). By converting the UV-vis absorption intensity at 273 nm to mass concentration,⁹⁶ the separation yield for the blue metallic SWNTs was calculated to be about 10% based on the raw SWNTs. The isolation yield obtained by using PEI chromatography is about 100 times higher than the yield by using DNA
separation.²⁸ This simplicity in operation, in addition to its high isolation yield, indicates the great potential of PEI chromatography for large-scale separation.

5.3.5 Separation Mechanism of PEI Chromatography

Previous studies of SWNT/PEI **5-1** dispersion shed a light on the separation mechanism of PEI chromatography. As seen in Scheme 5.4, the PEI was absorbed on the surface of phosphorylated cellulose, which built a PEI polymer network for nanotube's separation. During the dispersion, the surfactant SDBS was absorbed to a SWNT surface to solubilize the nanotube (Scheme 5.4 a). Under the water elution, the solubilized SWNTs were expected to move with the aqueous phase. Some of the SDBS might be replaced from SWNT surface, due to the interaction between nanotube and amine. The observation that metallic SWNTs were eluted faster suggests that the PEI chromatography might have a higher affinity toward semiconducting SWNTs (Scheme 5.4 b), which in agreement with semiconducting SWNT selectivity of PEI **5-1** dispersion (5.3.1). The cationic charge on PEI could also play a positive role in the observed separation, which can interact with the negative charge accumulated on SWNT via SDBS adsorption.



"semi" and "met" represent semiconducting and metallic, respectively.

Scheme 5.4 Schematic illustration of SWNT separation. First, SWNTs dispersed in SDBS surfactant are loaded on the front of PEI column (a). Second, under the water flow, metallic SWNTs are moving with the mobile phase whereas semiconducting SWNTs were holding relatively tight on the column (b).

5.3.6 Potential for Separation of individual metallic SWNTs

By using water alone as eluent, the collected blue solution exhibits an absorption peak at 633 nm (Figure 5.7). The retention time of the SWNTs was assumed to be dependent on the tube's interaction/affinity with the amino groups on PEI chromatography. In order to further examine the scope of PEI's column in separation, we increased the elution strength by addition of a small amount of amine, as the presence of the amine in the mobile phase would weaken the interaction of SWNTs with the PEI's amino group.

Interestingly, the elution with amine aqueous solution gave several fractions that showed different absorption λ_{max} (633 nm \rightarrow 660 nm \rightarrow 605 nm) (Figure 5.13 a), when using 1.5%, 7.5% and 10.5% of protonated amine aqueous solution as eluent (Figure 5.13 b), respectively. The result indicates the separation of different metallic SWNT species. The observation supports the hypothesis that the PEI-amine groups have different affinity to SWNTs of different chirality, as the increasing amount of NH₄⁺/NH₃ in the mobile phase would weaken the PEI-amine/SWNT interaction.



Figure 5.13 UV-vis-NIR absorption spectra of different fractions by using different concentration of NH_3 aqueous solution as eluent.

Although the absorption bands appeared are broad, Raman analysis showed that the first fraction was predominantly SWNT (13,4) and (10,7), whereas the second fraction ($\lambda_{max} = 660$ nm), and third fraction ($\lambda_{max} = 605$ nm) were nearly pure (10,10) and (9,9) SWNTs, respectively (Figure 5.14). The isolated pure armchair (10,10) and (9,9) exhibited only G⁻ band at ~1600 cm⁻¹, which is matched with the result from the armchair SWNTs separated by using DNA sequence⁹⁷ and centrifugation.⁹⁸ The Raman of fraction 1 revealed a large gap between G⁺ and G⁻, which agrees with the literature prediction for metallic SWNTs.⁶⁵ The results thus clearly demonstrated that the PEI chromatography could provide a simple and effective method to isolate metallic SWNTs of different chirality. The availability of pure metallic SWNTs would lead to broad investigation of their properties.



Figure 5.14 Raman spectra (RBM) for fractions 1-3, where the inset shows the G band

5.4 Conclusion:

Polyethyleneamine (PEI) **5-1** has been proved to be used for dispersing SWNTs, in which primary amine plays a dominant role for adsorbing SWNTs. The dispersion selectivity for semiconducting SWNTs is supported with Raman and UV-vis-NIR evidence. According to 2D photoluminescence, the PEI **5-1** dispersion solution is majorly enriched with (7,6) and (8,6). Furthermore, this dispersion is found to be pH-dependent. According to the selectivity of PEI, a novel affinity chromatography was built, in which the PEI chromatography exhibited a stronger affinity toward the semiconducting SWNTs, thereby allowing the purification of metallic SWNTs with high efficiency. Moreover, the metallic SWNTs can be further separated into different fractions, providing SWNT sample of near single chirality. Its potential for large scale could have significant impact on the nano-science involving SWNTs.

CHAPTER VI

BENZYLTRIMETHYLAMMONIUM CHLORIDE FOR SWNT SEPARATION

6.1 Introduction:

Although few cationic surfactants have been known to disperse SWNTs, their applications could lead to different nanostructure assemblies or properties in comparison with the samples by using anionic surfactant. For example, in scheme 6.1, when the cetyltrimethylammonium bromide (CTAB) 6-1a is used, the resulting film from the dispersion SWNTs/6-1a exhibits a number of alignment features in the solid state.⁹⁹ Comparison has shown that the SWNTs dispersion by using CTAB 6-1a could exhibit different property from those obtained by SDBS.¹⁰⁰ By using cetyltrimethylammonium 4vinylbenzoate (CTVB) 6-1b to disperse SWNTs, the vinyl groups on the surrounding counter-anions can be polymerized to provide a stable SWNTs dispersion.¹⁰¹ In addition, the electronic device fabricated from SWNT is shown to be more sensitive to the presence of a cationic surfactant (such as CTAB 6-1a) than to an anionic surfactant.¹⁰² such as SDS 6-3. Clearly, a cationic surfactant could exhibit a diverse interaction with the dispersed SWNTs. Herein, we report the cationic surfactant (benzyltrimethylammonium chloride 6-2) can selectively disperse SWNTs, in sharp contrast to the anionic surfactant SDBS 6-4.



Scheme 6.1 Cationic and anionic surfactant used for SWNT dispersion

6.2 Experimental

Raw SWNTs (2 mg, from HiPCO process) was dispersed in 7 mL benzyltrimethylammonium chloride **6-2** solution (0.4 g/mL) under tip sonication in an ice-bath for 5 h. The dispersed SWNTs solution is easy to form aggregation, thus the resulting solution needs to be filtered with glass wool shortly. In order to remove all the aggregation, repeat the filtering process two times, which finally results a clear solution. The resulting solution was heated in hot water bath at ~90°C for an hour. During heating, SWNTs gradually precipitated out from the clear solution. The solution was cooled to room temperature, followed by centrifugation at 7000 g for 30 min. After centrifugation, the SWNTs sediment was collected for Raman test. In the other case, SWNTs sediment

was redispersed in 5 mL H₂O under tip sonication at ice-bath for 30 mins. The resulting solution is for AFM, UV-vis-NIR and photoluminescence test.

6.3 Results and Discussion:

6.3.1 Dispersion Selectivity of Benzyltrimethylammonium Chloride 6-2

Photoluminescence spectra showed that the supernatant SWNTs/6-2 (Figure 6.1 b) contained fewer nanotubes than SWNTs/SDBS (Figure 6.1 a), with (8,4), (7,5) and (7,6) tubes being predominant. Comparison of the tube's photoluminescence intensity in the same environment showed that the cationic surfactant 6-2 exhibited good selectivity in dispersing SWNTs.



Figure 6.1 2D photoluminescence of SWNTs dispersed in SDBS (a) and benzyltrimethylammonium chloride **6-2** (b), respectively.

The UV-vis-NIR absorption (Figure 6.2) showed that the absorbance of (8,4) and (7,6) tubes became higher in SWNTs/6-2 dispersion, in agreement with their increasing population observed in the 2D photoluminescence spectra (Figure 6.1). Interestingly, the absorption of metallic tubes (E_{11}^{M} region in about 450-660 nm¹⁰³) decreased, indicating selective elimination of metallic SWNTs during dispersion with benzyltrimethylammonium chloride 6-2.



Figure 6.2 UV-vis-NIR absorption spectra of dispersed SWNTs in SDBS and benzyltrimethylammonium chloride **6-2**

The dispersion selectivity was further confirmed in Raman spectrum. After dispersion with benzyltrimethylammonium chloride **6-2**, all the metallic SWNTs peaks were notably decreased, whereas the content of semiconducting SWNTs was increased (Figure 6.3 a).³¹ The G⁻ band, the characteristics of the metallic SWNT, decreased notably for SWNTs/**6-2** (Figure 6.3 b), further supporting that the assumption that dispersion by **6-2** enriched the semiconducting SWNTs.¹⁰⁴ Moreover, similar D band for SWNTs/**6-2** and raw SWNTs indicated that dispersion with the cationic surfactant did not introduce any defect on the surface of SWNTs.



Figure 6.3 Raman spectra of SWNTs in the radial breathing mode (RBM) (a) and G band mode (b) with excitation at 647 nm.

Atomic force microscopy (AFM) images of the supernatant solution further revealed that SWNTs were dispersed very well as single tubes by the cationic surfactant **6-2** (Figure 6.4 b). AFM profilometry (in tapping mode) provided SWNT diameter distribution with SDBS and surfactant **6-2** (Figure 6.4 c). The sample from the SWNTs/**6-2** exhibited a narrower distribution, in comparison with that from the original raw SWNTs (sample SWNTs/SDBS). The tube population curve reached maximum when the diameter d 0.7 - 0.9 nm, which was consistent with diameter of the enriched SWNTs (7,6) (d = 0.89 nm), (7,5) (d = 0.83 nm), and (8,4) (d = 0.84 nm). The results provided additional evidence to support the observation from the optical measurements: the cationic surfactant selectively dispersed the SWNTs (7,6), (7,5), and (8,4), leading to enriched semiconducting tubes.





Figure 6.4 AFM images are obtained in AFM tapping mode. SWNTs are dispersed by SDBS (a) and surfactant benzyltrimethylammonium chloride **6-2** (b). The chart (c) is plotted with percentage of SWNTs based the diameter of SWNTs.

The selective enrichment is summarized into the chirality map (Figure 6.5). Clearly the selectivity is not solely based on the tube diameters, as SWNT (7,6) (d = 0.89 nm) was selected whereas SWNT (10,2) (d = 0.884 nm) was deselected. It appears that the selectivity of SWNT (n,m) is related to the value of 2n+m. When 2n+m = 19 or 20, the SWNT (n,m) was enriched. On the other hand, when 2n+m = 22, 23, 25 or 26, the corresponding SWNT (n,m) was decreased.



Figure 6.5 Chirality map showing the enriched and depleted SWNTs. The tubes present in the raw SWNTs are indicated by the bold number

6.3.2 Computer Modeling for Selectivity Study

(Computer modeling work was done by Dr. Rosi N. Gunasinghe and Dr. Xiao-Qian Wang at Department of Physics and Center for Functional Nanoscale Materials,

Clark Atlanta University, Atlanta, GA)

Computer modeling studies were carried out, in order to shed some light on the interaction of specific tube to the cationic surfactant. Because the π - π interaction would be important between the surfactant and SWNT surface, there are two possible

alignments, depending on whether the ammonium group is pointing away (interaction **I**) or toward the SWNT surface (interaction **II**, Scheme 6.2).



Scheme 6.2 Possible interactions of the cationic surfactant 6-2 with the SWNT surface

Interaction of the cationic surfactant benzyltrimethylammonium chloride **6-2** with SWNTs was examined by using dispersion-corrected DFTB method. The binding energy of the cationic surfactant with SWNTs was calculated from DFTB for optimized composite and separate structures of nanotube and benzyltrimethylammonium chloride **6-2**: $E_B = E_{bc/SWNT} - E_{SWNT} - E_{bc}$, where $E_{bc/SWNT}$ is the total energy of the composite, E_{SWNT} is the energy of the nanotube without surfactant **6-2**, and E_{bc} is the energy of surfactant **6-2** without the nanotube. In order to reveal further details for the tube-surfactant interaction, we compared the energy difference between the modes **I** and **II**, $\Delta E = E_{(II)} - E_{(I)}$. When $\Delta E > 0$, the interaction mode **I** is preferred; when E< 0, the interaction mode **II** is preferred. Interestingly, the calculated energy difference was negative ($\Delta E < 0$) for most tubes (Figure 6.6). The result suggests that the interaction mode **II** is preferred over the mode **I**, although the steric hindrance of trimethylammonium group could weaken the π - π interaction. It appears that the interaction mode is dependent on the chirality of SWNTs, as metallic tubes such as (8,2), (8,5) and (11,2) were shown to favor the interaction mode **I** (ΔE >0). This observation is in accordance with the finding that the metallic tubes are in general not favored with donor-acceptor dispersing agents.¹⁰⁵

Among those semiconducting SWNTs, the tubes (8,4) and (7,6) exhibited the large energy difference ΔE , pointing to that their enrichment was likely achieved via the interaction mode **II**. The interaction mode **II**, however, was not always predominant, as the tube (7,5), whose $\Delta E \sim 0$, did not show any preference. The enrichment of (7,5) could be partially attributed to its relatively higher binding energy with the surfactant **6-2**.



Figure 6.6 Energy difference U*E* between interaction modes \mathbf{I} and \mathbf{II} for various SWNTs. Semiconducting SWNTs are labeled with"+", whereas metallic SWNTs are not

The driving force for adopting the interaction mode **II** could be related to the electronic interaction between the tube and the surfactant **6-2**. The calculated interaction for SWNT complexes (8,4)/**6-2** and (7,6)/**6-2** (Figure 6.7) showed that a stronger charge transfer interaction was observed from the interaction mode **II** (in comparison with the corresponding interaction mode **I**). In the interaction mode **II**, both phenyl and ammonium groups are near the SWNT surface. During the charge transfer interaction, the phenyl ring acts as charge donor (giving electron to SWNT), whereas the ammonium group acts as charge acceptor (receiving electron from SWNT). Such charge transfer interaction could play an important role in the observed selectivity, as a semiconducting tube of small diameter favors such interaction with π -conjugated molecules (or segments).¹⁰⁶



Figure 6.7 The corresponding charge density of LUMO-derived bands for SWNT (8,4) and (7,6), in interaction modes **I** and **II**, respectively

6.4 Conclusion:

In summary, we demonstrated a convenient approach to achieve selective dispersion of semiconducting SWNTs by using surfactant benzyltrimethylammonium chloride **6-2**. The simple dispersion by using the cationic surfactant leads to significant enrichment of semiconducting SWNT (8,4), (7,6) and (7,5), in sharp contrast to no selectivity by using the anionic surfactant SDBS. By combining all the test result into the chirality map (Figure 6.5), it appears that the selectivity of SWNT (*n*,*m*) by surfactant **6-2** is related to the value of 2n+m. With the aid of computational study, the result reveals that the observed intriguing selectivity from **6-2** is related to the synergistic interaction of phenyl (for π - π interaction) and the ammonium group (for charge transport) with SWNTs.

CHAPTER VII

SUMMARY

In this dissertation, several methods have been explored for separating SWNTs by using different polymers. A water soluble poly[(*m*-phenylenevinylene)-*alt*-(*p*-phenylenevinylene)] (PmPV) derivative **2-2** has been synthesized, where the *p*-phenylene unit is attached with both hydrophilic and hydrophobic substituents. Such unsymmetrical substitution pattern is found to play an important role to provide a hydrophobic cavity to enhance the interaction with SWNTs of small diameters (d 0.8 nm). Although PmPV **2- 2** can disperse SWNTs in aqueous solution, the SWNT aggregation trends to be formed from the dispersion of SWNTs/PmPV **2-2**. The aggregation process shows some selectivity for metallic SWNTs. In one occasion, a ribbon-shaped SWNT sample is formed slowly from the aggregation process, which might be associated with the slow release of SWNTs from the polymer-wrapped tubes. Spectroscopic analysis of the ribbon-shaped SWNT sample suggests that the SWNTs might be in an ordered assembly.

Poly(phenyleneethynylene)-*co*-poly(phenylenevinylene) (PPE-PPV) **3-1** containing carbon-carbon triple bond have been synthesized to examine the impact of C=C bond linkage on the SWNT selectivity. PPE-PPV **3-1** is found to selectively disperse SWNTs with a larger diameter. Combination of nitric acid treatment and dispersion with PPE-PPV **3-1** leads to separate SWNTs with a narrow diameter distribution. In the main chain of PPE-PPV **3-1**, the bonds that link phenylene groups are consisting of both vinylene (-CH=CH-, ~ 50%) and ethylene ($-C\equiv C-$, ~ 50%). Further increasing the population of the C=C linkage leads to poly[(*m*-phenyleneethynylene)-*alt-*(*p*-phenyleneethynylene)] (P*m*PE*p*PE) **4-2**, which shows an excellent selectivity to choose SWNT (6,5) when dispersing SWNTs.

Polyethylenimine (PEI) **5-1** in aqueous solution shows a higher affinity towards semiconducting SWNTs. The dispersion of SWNTs/PEI **5-1** solution is found to be pH dependent. Attaching PEI to cellulose provides a column packing material, which can be used to build a PEI affinity chromatography. When loading the HiPCO SWNTs on a PEI column, a blue solution containing metallic SWNTs can be harvested by using water as eluent. By changing the eluent, metallic SWNTs of near single chirality can be separated out. Further study indicates the isolation mechanism is related to the selectivity of PEI which is absorbed on the cellulose.

One cationic surfactant (benzyltrimethylammonium chloride **6-2**) is also examined for its potential selectivity for SWNTs. When used to disperse SWNTs, the cationic surfactant **6-2** exhibits a good selectivity towards semiconducting SWNTs, in which the selectivity of SWNT (n,m) is related to the value of 2n+m.

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APPENDIX

PUBLICATIONS

- 1. Guangzhuo Rong, **Yusheng Chen**, Lei Wang, Joanne Li, Junfeng Wang, Matthew J. Panzer, Yi Pang "A benzoxazole sulfonamide accelerator: synthesis, structure, property and implication in rubber vulcanization mechanism" *Journal of Applied Polymer Science* **2013** (accepted).
- 2. Tengfei, Xiang; Xiumin, Liu; Ping, Yi; Mingming, Guo; **Yusheng, Chen**; Chrys, Wesdemiotis; Jie, Xu and Yi, Pang "Schiff base polymers derived from 2,5-diformylfuran" *Polymer International* **2013**, January 24th (online).
- 3. **Yusheng Chen**, Yongqian Xu, Qiuming Wang, Rosi N. Gunasinghe, Xiao-Qian Wang, Yi Pang "Highly Selective Dispersion of Carbon Nanotubes by Using Poly(phenyleneethynylene)-Guided Supermolecular Assembly" *Small* **2013**, *9*, 870-875.
- 4. **Yusheng, Chen**; Yongqian, Xu; Kelly, Perry; Alexei, P. Sokolov; Karren, More and Yi, Pang "Achieving Diameter-Selective Separation of Single-Walled Carbon Nanotubes by Using Polymer Conformation-Confined Helical Cavity" *ACS Macro Lett.* **2012**, *1*, 701–705.
- 5. **Yusheng, Chen**; Andrey, Malkovskiy; Xiaoqian, Wang; Marisabel, Lebron-Colon; Alexei, P. Sokolov; Kelly, Perry; Karren, More and Yi, Pang "Selection of Single-Walled Carbon Nanotube with Narrow Diameter Distribution by Using a PPE–PPV Copolymer" *ACS Macro Lett.* **2012**, *1*, 246–251.
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