Supramolecular Self-Assembly of Single Walled Carbon Nanotubes (SWNTs)

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I hereby declare that this thesis is my own work. All research was performed in the Department of Chemistry, Imperial College London; all other sources used have been completely referenced where appropriate. This work has not been submitted previously for the reward of a degree course at this or any other universities.

Hin Chun Yau

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Abstract

Applications of single walled carbon nanotubes (SWNTs) have been limited by their heterogeneity and the lack of selective assembly methodology. A selective SWNT junction formation was achieved by fullerene (C$_{60}$) end-capped linker connecting SWNTs via their open ends. The SWNT junction was demonstrated in both single solvent (N-methyl pyrrolidone, NMP) and binary solvent mixtures (NMP and toluene). Initially, bis-fullerene linker was prepared following existing literature. However, spectroscopic characterisation revealed that the reaction between azide terminated PEG and C$_{60}$ yield a novel closed ring structure rather than the linear dumbbell structure. The chain length of the PEG was found to be the key in the resulting structure of the adduct. Alternative synthetic methods were sought and the multifullerene end-capped linkers were synthesised via an one-step catalytic transesterification between polyethylene glycols (PEGs) and phenyl-C$_{61}$-butyric acid methyl ester (PCBM) with a catalytic amount of dibutyltinoxide. Polydisperse and monodisperse branched PEGs were employed in the synthesis and purification was only achieved in the latter material. Both linear and star shape linkers were employed in the assembly process and the resulting SWNT junctions were characterised by atomic force microscopy (AFM). The SWNT junctions were found to be mainly localised on the body of the SWNT to give a ‘head-to-body’ assembly rather than the desired ‘head-to-head’ assembly, due to SWNT defects. While exploring the SWNT dispersion in organic solvents, a side reaction was observed during the sonication of NMP, causing significant contamination issues in AFM sample and high temperature annealing was found to be useful in improving sample quality. IR and UV-vis absorption spectroscopy revealed that NMP might polymerise during sonication, most likely due to amide bond cleavage. In addition, the resulting polyamide originated from NMP might play an important role in the dissolution of SWNT and other nanomaterials in amide solvents.
Acknowledgements

I would like to thank Prof. Milo Shaffer for his supervision during my PhD study, without his continuous support, this thesis could not be completed. I would also like to thank my parents for supporting (both spiritually and financially) me in the past 2X years. Thank you to my girlfriend, Isabella, for loving me and organising almost everything during my write-up so I could concentrate on writing only.

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Dedication to Dr. Joachim H G Steinke

As one of my two supervisors when I started my PhD, Joachim had a massive impact on both this work and my development as a scientist. He was never one to suffer fools gladly and his exceptional insight and willingness to spare time for his students made him widely respected throughout the university. His passing is not just a loss for those who knew him and worked alongside him, but for science as a whole.


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A2 – MALDI-TOF of PEG$_{3350}$-(N$_3$)$_2$

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## Abbreviations

### General

<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>Arc</td>
<td>Arc Discharge</td>
<td>SWNT</td>
<td>SWNT Anionic Nanotube</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
<td>m-SWNT</td>
<td>Metallic SWNT</td>
</tr>
<tr>
<td>DGU</td>
<td>Density Gradient Ultracentrifugation</td>
<td>sc-SWNT</td>
<td>Semi-conducting SWNT</td>
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<tr>
<td>DWNT</td>
<td>Double Walled Carbon Nanotubes</td>
<td>MWNT</td>
<td>Multiwalled Carbon Nanotubes</td>
</tr>
<tr>
<td>FET</td>
<td>Field Effect Transistors</td>
<td>TFT</td>
<td>Thin Film Transistors</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
<td>PECVD</td>
<td>Plasma Enhanced CVD</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single Walled Carbon Nanotubes</td>
<td>RBM</td>
<td>Radial Breathing mode</td>
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<tr>
<td>VDW</td>
<td>Van der Waals</td>
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### Characterisation

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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunnelling Microscopy</td>
<td>ε</td>
<td>Extinction Coefficient</td>
</tr>
<tr>
<td>IR</td>
<td>Infra Red Spectroscopy</td>
<td>ppm</td>
<td>Part per million</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet-visible Absorption Spectroscopy</td>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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### Chemicals and Solvents

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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Tol</td>
<td>Toluene</td>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
<td>PCBM</td>
<td>PhenyC_{61}-butyric-acid-methyl-ester</td>
</tr>
<tr>
<td>o-DCB</td>
<td>Ortho-dichlorobenzene</td>
<td>DOC</td>
<td>Sodium Deoxycholate</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl pyrrolidone</td>
<td>SC</td>
<td>Sodium Cholate</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
<td>SDBS</td>
<td>Sodium Dodecylbenzenesulphonate</td>
</tr>
<tr>
<td>DBTO</td>
<td>Dibutyltinoxide</td>
<td>DCTB</td>
<td>trans-2-[3-(4-tert-Butylphenyl) -2-methyl-2-propenylidene] malononitrile</td>
</tr>
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Introduction

This research was originated from the lack of methodology in controlling the assembly of single walled carbon nanotubes (SWNTs) to produce well-defined SWNT structure which limited further development of SWNT applications. The heterogeneity issue in as-produced SWNTs have been improved by a wide variety of techniques developed in recent years. Various non-destructive exfoliations have been reported for high yield individualization of SWNTs while preserving the integrity of the SWNT structure, thus, high quality SWNTs are now widely available. Unfortunately, existing SWNT assembly methodology do not produce SWNT junctions of well-defined structure, instead, randomly aligned SWNT networks are often formed. Due to SWNT surface heterogeneity, connecting SWNTs via surface chemistry is often uncontrollable in which alternative methods must be sought. Fullerene insertion into the SWNT cavity has been studied extensively. Since there is a strong van der Waal’s interaction between fullerene and SWNTs, fullerenes insert into SWNTs readily. The concept of using covalently connected fullerene molecules to join SWNTs has not been proposed before, in which it should provide a unique route to control the formation of SWNT-SWNT junctions. By controlling the SWNT-SWNT junction formation, it is possible to produce well-defined hierarchical SWNT structures. This technology should enable the fabrication of SWNT devices which require highly ordered SWNT structures.
Aims and Objectives

The main aims of the thesis are described below;

- Prove the concept of SWNT junction formation with structural directing fullerene end-capped linkers.
- Further develop SWNT junction formation to control the geometry with different number of linkages.
- Characterise the (opto)-electrical properties of the resulting SWNT junctions.

Structure of Thesis

The thesis contains 8 chapters which include; Chapter 1 which provides an overview of the thesis including current challenges in SWNTs research. Chapter 2 details current literature on peapod and fullerene functionalisation chemistry. Characterisation techniques used in this thesis are discussed in Chapter 3. Chapter 4 focuses on the synthesis and characterisation of simple bis-fullerene end-capped linkers following exiting literature. Developed methodologies to synthesise simple fullerenes end-capped linkers are detailed in Chapter 5. SWNT dispersions preparation and contamination issues are reported in Chapter 6. Chapter 7 details SWNT junction formation with a novel solution phase filling method. Culminating with Chapter 8 conclusions and future studies.
Chapter 1 – Literature Review

1.1 Carbon Nanomaterials

$sp^2$ carbon nanomaterials namely fullerene (1985)$^1$, carbon nanotubes (CNTs) (1991)$^2$ and graphene (2004)$^3$ have raised significant interest for their superior (opto)electrical and mechanical properties attracting huge investment$^4$. A “family tree” of known carbon nanomaterials showing the relationship between these carbon nanoforms is illustrated in Figure 1.1.

![Figure 1.1 – Schematic diagram of carbon nanomaterials and their relationship to each other$^5$.](image)

All $sp^2$ carbon nanomaterials can be visualised from a single starting material – graphene. Graphene solely consists of $sp^2$ carbon arranged in a one atom thick, two dimensional sheet. A single walled carbon nanotube (SWNT) is formed when the flat graphene sheet is rolled, if multiple graphene sheets are stacked together and wrapped up concentrically, a double or multi-walled carbon nanotube
(DWNT/MWNT) is formed. SWNTs may be open ended or capped with a hemi-fullerene structure\textsuperscript{6}. Graphene and carbon nanotubes have sp\textsuperscript{2} carbons hexagonally arranged (akin to benzene); when a pentagon is introduced into the system it induces curvature, subsequently, if more pentagons are introduced, a spherical shape fullerene is formed.

Despite extensive research and development of carbon nanomaterials, limited applications have been successfully transformed from lab-scale to mass production. One of the first real-life applications of CNTs was incorporation into a tennis racket to act as a nanoreinforcement with low density\textsuperscript{7}. The major challenge of incorporating carbon nanoforms into real-life application is the lack of processability and agglomeration issues\textsuperscript{8}. Unlike conventional macro- or small- molecule system where there are standardised processing methodologies, the nanometre scale requires new processes due to significantly stronger intermolecular interactions\textsuperscript{9}. Often nano-carbon species are synthesised in a bottom-up method to form a bulk material\textsuperscript{8}, however, it is difficult to exfoliate individual nano-species from the bulk materials. Attractive intermolecular force, mainly van der Waal’s (VDW)\textsuperscript{9,10} interactions between the nano-species are sufficiently strong that destructive methodologies are routinely needed to isolate and individualise species\textsuperscript{11,12,13}.

1.2 Properties of Single Walled Carbon Nanotubes (SWNTs)

SWNTs have been found to have exceptional chemical, mechanical and (opto)electrical properties\textsuperscript{8,14}. CNTs typically have a high aspect ratio\textsuperscript{15} and have high surface area\textsuperscript{16} (on the order of 1300 \text{m}^2\text{g}^{-1}). SWNTs have a reported tensile strength of 52 GPa and Young’s modulus\textsuperscript{17} of 1470 GPa which makes it a candidate for reinforcement in composites. The SWNT family has around 2500 species which are defined by the chiral vector \((n, m)\), and the angle which the graphene sheet rolls, the chiral angle\(\theta\)\textsuperscript{8} (Figure 1.2). SWNTs exhibit both metallic \((m\text{-SWNTs})\) and semi-conducting \((sc\text{-SWNTs})\) characteristics determined by the chiral vector \((n, m)\), such that \(n-m\) is a multiple of 3, the SWNT is metallic and the
remaining combinations are semi-conducting SWNTs resulting in a 1/3 metallic species and 2/3 semi-conducting species.

Figure 1.2 – SWNT chirality map with different \((n, m)\) vector (left). Three possible SWNT structures derived from different \((n, m)\) combinations (right). Armchair SWNT \((n = m, n, m > 0, \theta = 30^\circ)\); Zig-Zag SWNT \((n > 0, m = 0, \theta = 0^\circ)\); Chiral SWNT \((n \neq m \neq 0, 0 \leq \theta \leq 30^\circ)\).13

Metallic SWNTs are excellent ballistic conductors due to quantum confinement at the nanoscale (electrical conductivity of \(m\)-SWNTs, \(1 – 3 \times 10^6\) Sm\(^{-1}\))\(^{18,19}\) with a highest reported theoretical value for SWNTs thermal conductivity of 6600 W mK\(^{-1}\). SWNTs diameters range from 0.4 nm to around 5 nm\(^{20,21}\), with the larger diameter SWNTs collapsing due to atmospheric pressure. SWNTs length can vary dramatically and can be as long as several centimetres (maximum reported SWNT length 18.5 cm)\(^{22}\).

1.3 Current Electronic and Encapsulation Applications of SWNTs

A number of applications have been developed with SWNTs including transparent and flexible electrodes, supercapacitors, field-effect transistors (FETs) and chemical sensors\(^{14,23-25}\). Majority of these applications are electronic which involve SWNT networks or individual SWNT as an electrode or conducting component. SWNTs network based transparent conducting film have been studied extensively, they are proposed as a potential replacement for indium tin oxide (ITO)\(^{22}\) which is currently
the industry standard. Flexibility is the major advantage for using SWNTs as a transparent conducting thin film to develop flexible electronic devices (ITO coating is very brittle and it is unsuitable for flexible displays). Semi-conducting SWNTs are an excellent candidate for field-effect transistor (FET) due to the small size and electron mobility\[^{27}\]. Sub-10 nm SWNT FET has been prepared and their performance exceeds traditional silicon based devices\[^{28}\]. High surface area of SWNTs have been widely exploited in chemical and biological sensors\[^{29,30}\], as they offer an ideal docking site for incoming molecules in both gaseous and solution phase. The most promising inclusion of CNTs is in their use in lithium ion batteries, as even small CNT loading in electrodes has shown to increase electrical conductivity\[^{31}\].

**Figure 1.3** – Examples of SWNTs encapsulation, from top left corner (anti-clockwise), molecular hydrogen (H\(_2\)), water, methane, fullerene C\(_{60}\) and oligothiothene.

SWNTs have been shown to encapsulate a number of molecules into their inner cavity, from simple organic molecule to inorganic compounds\[^{32-34}\] (Figure 1.3). A classic example of endohedral SWNTs is C\(_{60}@SWNT\) which is commonly known as ‘peapod’\[^{35}\]. A promising theoretical study by Maniwa *et al.* illustrated SWNTs readily uptake water into their cavity which could be applied in water purification\[^{36}\]. Examples of drug molecules encapsulated by SWNTs illustrated the use of a fullerene derivatives as a cork, which has the potential to be further developed into self-release drug carrier\[^{37}\].
1.4 SWNTs Synthesis

Synthesised SWNTs contain both metallic and semi-conducting species, but electrical application required extremely pure SWNT samples that ideally contain either metallic or semi-conducting species dependant on final use in devices. As-produced SWNTs require post-synthetic purification to separate SWNTs into different diameter, length and helicities. In a typical SWNT synthesis, a catalyst is required to grow the SWNTs which remain inside the tube. Other contaminant produced in the bulk are catalyst particles which failed to synthesis SWNTs and unwanted carbonaceous materials (amorphous carbon and graphitic carbon particles). Removal of these contaminants are essential when SWNTs are used in electrical applications. There are numerous post-synthetic purification procedures (see section 1.5) but yields are low, making the processes inefficient and unsuitable for large scale purification. Until selective SWNT synthesis is available, post-synthetic purification has to be applied.

There are three major synthetic methods for SWNT synthesis, electric arc-discharge, laser ablation and chemical vapour deposition (CVD), with each technique have their advantages and disadvantages. All SWNT synthesis methods grow SWNTs which have a distribution of diameters, lengths, helicities with varying degrees of SWNT quality. In addition, most techniques have significant batch to batch synthesis variation. Electric arc-discharge and laser ablation are the two techniques which generally give larger SWNTs diameter distributions. In the arc-discharge method SWNT synthesis is carried out by applying a high voltage across graphite electrodes which in the presence of a catalyst ejects SWNTs as well as other carbonaceous materials. In laser ablation SWNT synthesis a laser is focused onto a carbon substrate, maintained at a high temperature, which ejects carbon vapour that may form SWNTs (in the presence of suitable catalyst). In arc-discharge and laser ablation methods a huge amount of thermal energy is generated which produces SWNTs which are highly graphitic. Laser ablation method is expensive to operate and maintain and no laser ablation synthesised SWNTs are available commercially. Commercial available arc-discharged SWNTs are contaminated heavily with amorphous carbon and graphitic particles increasing the post synthesis process requirements.
Chemical vapour deposition (CVD) process has become the dominant method to produce SWNTs. CVD operates at a (relatively) lower temperature (800 – 1200 °C) when compared to arc/laser synthesis and SWNT growth may occur in the gas phase or on substrates (typically SiO₂-Si). CVD systems are dynamic, resulting in large variation of synthesis conditions which include carbon source, carrier gas, catalysts, temperature, pressure and choice of substrate all of which will have an effect on SWNTs produced. The most successful commercially available SWNT produced are HiPco (high pressure carbon monoxide) and CoMoCAT (cobalt & molybdenum bicatalyst) SWNTs. In general, both HiPco and CoMoCAT SWNTs contain lower carbonaceous and metal catalyst particle contaminants in the raw bulk synthesised material when compared to laser and arc synthesis processes. Recent development of SWNT CVD synthesis suggests that selective diameter and possibly chiral vectors can be produced.

Selective SWNT synthesis is in its infancy and subsequently there is limited availability.

1.5 Purification and Separation Techniques

Since the selective SWNTs synthesis is still in an early stage, post-synthetic sorting of SWNTs is necessary to obtain purified SWNTs with certain diameter, length, helicities and electronic properties: metallic or semi-conducting. Various methods have been proposed in the past 10 years for SWNT sorting including gel chromatography, dielectrophoresis, density gradient ultracentrifugation and covalent functionalisation. SWNTs dispersions with certain diameter range and specific electronic species have been prepared successfully using chromatography. Iterative chromatography may give a narrower diameter range and enhanced electronic selectivity. Simple dielectrophoresis separates metallic species from semi-conducting species. The relative dielectric constant of metallic species is larger than that of semi-conducting SWNTs; thus, metallic SWNTs have a stronger response to the external electric field and are preferentially separated out first. Due to the difference in dielectric constant, metallic and semi-conducting species were found to have very different reactivity in certain chemical reactions such as diazonium salt addition. The difference in reactivity between metallic and semi-conducting SWNTs offer an opportunity to separate the two species as the resultant covalently
functionalised m-SWNTs and sc-SWNTs are expected to have different solubility depending on the grafted species\textsuperscript{60,61}. The major technique in sorting SWNTs is density gradient ultracentrifuge (DGU)\textsuperscript{39} (Figure 1.4). Surfactant was found to have a preference in wrapping SWNTs with different electronic characters due to the difference in dielectric constant. Using one or more surfactants in SWNTs dispersion will then introduce a difference in surface coverage between metallic and semi-conducting SWNTs. This gives rise to a difference in density between fully covered or partially covered SWNTs. Ultracentrifugation with various density gradients can then be used in the separation of the denser species via sedimentation. Collection of the purified SWNTs (metallic and semi-conducting species) can be made easily as these highly enriched species have a distinctive colour\textsuperscript{51}. SWNTs with different diameter could also be separated out using this method as large diameter SWNT have a lower curvature which allows more surfactant coverage\textsuperscript{52}. Being able to separate electronic types and diameter in SWNTs makes DGU one of the most popular methods in SWNTs sorting. However, DGU is not scalable as only a small amount of SWNTs could be processed in each cycle and more importantly, it requires a good quality, highly individualised SWNT dispersion as a feedstock. Such dispersion is difficult to make as discussed in the next section.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(a) schematic representation of surfactant wrapped, individual and bundled SWNTs. (b) Schematic representation and photographs of SWNTs diameter separation by density gradient ultracentrifugation (DGU). Aqueous SWNT dispersion is placed between a continuous density gradient (0 hr). Fractions of SWNTs started to separated according to their density and eventually yield distinct band of SWNTs containing highly enriched SWNTs with certain diameter (12 hr)\textsuperscript{62}.}
\end{figure}
1.6 SWNT Exfoliations

Exfoliation of SWNTs into individual SWNT has always been a major bottleneck in SWNTs processing. The strong VDW intermolecular force binds individual SWNTs together to give a SWNT bundle. Various exfoliation techniques have been proposed to prepare individualised SWNT dispersions. Specific functional groups can be grafted onto the surface to introduce the desired solubility in either organic or aqueous solvents. Oxidation could also be employed to increase SWNT solubility in water. This idea was originally designed to purify SWNTs. Nitric acid is originally employed to remove transition metal catalyst and amorphous carbon, however, nitric acid treatment also oxidise the SWNTs and introduce carboxylic group on the surface. Prolonged treatment eventually leads to complete SWNTs destruction and formation of more amorphous carbonaceous materials. Other binary acid systems have also been tested such as mixtures of conc. H$_2$SO$_4$/HNO$_3$ or H$_2$SO$_4$/H$_2$O$_2$ and the results are comparable. The carboxylic groups on the surface can be attacked by nucleophiles and subsequently introduces secondary functional groups. However, these oxidised or functionalised SWNTs may not be suitable for all SWNT applications.

Sonication of SWNTs in either organic or aqueous solvent is another major approach towards exfoliation of SWNTs. Surfactants are normally introduced into the system to act as an interface between water and SWNTs. Surfactants can be divided into different categories (cationic, anionic or neutral). Typical surfactants used in SWNT dispersions are sodium dodecyl sulphate (SDS), sodium deoxycholate (NaDOC) and sodium dodecylbenzene sulphonate (SDBS). They are anionic surfactants in which the head group contains a negative charge to repel each of the surfactant wrapped SWNTs. Surfactant/SWNT dispersions are prepared by sonicating SWNT with a small loading of surfactant (ranging from 0.5 up to 2 wt%) in solution. Polymeric wrapping agent can also be incorporated into SWNT system to aid SWNT dissolution. A typical example of such polymeric surfactant system is deoxyribonucleic acid (DNA) wrapped SWNT. Similar to the simple small molecule surfactant wrapped SWNTs, the negative charge on the phosphate-deoxyribose backbone introduces a repulsive
force between the wrapped SWNTs. Up to this point, all surfactants mentioned above wrap around SWNTs via VDW intermolecular force. The surrounding surfactants form a shield around SWNTs surface and reduce direct SWNT-SWNT contact. Hence, removal of surfactant molecules is often needed in order to improve electrical conductivity of the SWNT networks. Surfactants can either be removed by dialysis in a medium with much lower surfactant concentration or simply washing with ethanol (EtOH) if SWNTs are deposited on a substrate. Extra caution should be taken when dialysing surfactant wrapped SWNTs as the SWNTs start to rebundle as the surfactants concentration drops.

Other organic polymers have been introduced onto SWNT surface to give the desired solubility in specific solvents. In this approach, the polymers are covalently attached to the SWNT surface and these polymeric species are often generated in situ polymerisation from their corresponding monomers\textsuperscript{77}. These covalently functionalised SWNTs may still require a small degree of sonication to achieve good quality dispersion.

Sonication is typically carried out in either an ultrasonic bath or a tip-horn sonicator\textsuperscript{78,79} for minutes to several hours to achieve individualised SWNT dispersions with different length distribution. Sonication of solvent results in cavitation bubble formation which is extremely important to SWNT exfoliation\textsuperscript{80}. As the cavitation bubbles collapse, a strong sheer force is exerted on any near-by SWNT bundles. Any SWNT within the bundle closer to the cavitation bubble would be pulled out from the bundle. The individualised SWNT can then be wrapped by surfactants to prevent rebundling.

Once the SWNTs are dispersed into solvents by sonication, a centrifugal force is often applied to remove large SWNT bundles and dense metal catalyst particles\textsuperscript{39}. There are various recipes for such centrifugation, varying mainly in centrifugal force (speed and rotor dependant) and time. In general, metal catalyst particles can be easily separated by centrifugation due to the significant difference in density between metal and carbon\textsuperscript{62}. Unfortunately, amorphous carbon and other graphitic carbon species have similar densities to that of individual SWNTs which limits the ability of centrifugation to
separate them. In general, there are two ways to remove amorphous carbon from SWNTs before SWNT dispersion preparation\textsuperscript{40}. The traditional approach is thermal oxidative degradation of amorphous carbon\textsuperscript{41} since amorphous carbon degrades at lower temperature (in air) than SWNTs. Nitric acid is capable of oxidising most carbon species including both amorphous carbon and SWNTs due to its strong oxidising power\textsuperscript{63}. Acid treated SWNT sample are often washed and collected by vacuum filtration; additional base washing (0.01 M NaOH) removes the oxidised amorphous carbon debris more efficiently than water\textsuperscript{81}.

Mild exfoliation techniques can involve either chemical\textsuperscript{83} or electrochemical reduction of SWNTs\textsuperscript{83,84}. Charging SWNTs (electro)chemically into SWNTs\textsuperscript{9} (nanotubides) induces SWNT-SWNT separation due to charge repulsion. However, nanotubide should be kept under inert atmosphere (typically N\textsubscript{2} or Ar), as they are quenched by moisture in ambient conditions producing hydrogenated SWNTs\textsuperscript{84}.

1.7 Current Examples of SWNTs Assembly

The concept of joining SWNTs has been discussed for the last 10 years but only limited examples of selective SWNT assembly exist in the literature and they are summarised below.

1.7.1 Direct Synthesis

As bulk SWNTs are often associated with purity and heterogeneity issues, one of the most direct methods to control individual SWNTs alignment is direct synthesis of SWNTs onto a desired substrate\textsuperscript{38}. This method is typically employed in device fabrication where only small quantities of SWNTs are needed. Although the in situ synthesis methods of SWNTs are able to produce individual SWNTs\textsuperscript{38}, example of as-grown SWNT networks are also known\textsuperscript{85,86}. In both cases, the as-grown SWNTs were selectively grown on a pre-deposited catalyst surface. This approach normally consists of three steps\textsuperscript{86}; i) lithography, patterning the surface to cover a specific area. ii) Deposition of metal catalyst particles onto the desired location. iii) Direct synthesis of SWNTs by means of a chemical vapour deposition (CVD) process. Macpherson et al. has demonstrated successful SWNT network growth and developed nitric
acid etching to remove amorphous carbon and catalyst particles to increase electrode performance\textsuperscript{85-87}. Rosenbnett and Dai et al. both reported successful individual SWNT based field effect transistor (SWNT-FET) which opened up a new phase of SWNT-FET development\textsuperscript{88}. However, the as-grown SWNTs could be either metallic or semi-conducting; metallic SWNTs contamination would greatly reduce the performance of a FET\textsuperscript{89}. Dai et al. then went on to improve the system and managed to grow highly enriched semi-conducting SWNTs using plasma enhanced chemical vapour deposition (PECVD) and enriched metallic SWNTs using laser ablation system\textsuperscript{90,91}. It has been shown that growing SWNTs in situ is possible at laboratory scale\textsuperscript{92}, however, this process is extremely unlikely to become an industrial process due to a small number of SWNT FETS could be fabricated at the same time. Although the SWNT-FET showed promising performance over conventional Si based transistors, producing a single transistor does not give any real benefit to real life applications. It is important to develop a method to produce multiple-SWNTs devices with highly ordered SWNT alignment in a single process.

**Figure 1.5** – (a) Schematic illustration of an individual SWNT based field effect transistor (SWNT-FET). (b) Optical image of an array of individual SWNT based FET. (c) Scanning electron microscope (SEM) image of a single individual SWNT-FET, inset is a zoom in image showing clear SWNT contact to the gates\textsuperscript{92}. 

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1.7.2 Electron Beam Assisted Assembly

It is well known that oxidation introduces defects onto SWNT surfaces. High energy radiation can also induce structural damage in SWNTs. It has been shown that when SWNT bundles are irradiated under an electron beam (inside a TEM), the SWNTs start to fuse together and eventually coalesce into large diameter SWNTs. In a typical dispersion drop cast SWNTs sample, SWNTs may rest on top of another SWNT. Under irradiation, the SWNTs can then fuse together at the point they touch to give a SWNT-SWNT junction. Using this method, it is even possible to create SWNT junctions between two SWNTs with very different diameter (Figure 1.6). However, there is no control on the location of where the SWNTs touch each other. Therefore, this method does not offer selective SWNT junction formation. In addition, the electron beam also induces structural defects and eventually destroys the SWNTs. Most of the previously discussed methods have been performed in a transmission electron microscope on a junction-by-junction basis, making it very difficult to scale up.

Figure 1.6 – Schematic illustration of SWNT-SWNT junctions and the corresponding TEM images. The newly formed defect sites (labelled in red) indicate where the SWNT-SWNT junctions initiated.
This method has also been employed to form junctions between multiwalled carbon nanotubes (MWNTs)\textsuperscript{87,88}. In the presence of cobalt (Co) particles embedded in a MWNT sample, strong electron beam radiation was found to fuse MWNT onto Co particles to create a heterojunction (MWNT–Co–MWNT)\textsuperscript{99}.

![Figure 1.7](image)

**Figure 1.7** – TEM images of electron beam assisted MWNTs junction formation. (a) Two MWNTs overlapped with a Co particle encapsulated in one MWNT. (b) After irradiation, the two MWNTs fused together via a Co centre to give a 4 MWNT junctions\textsuperscript{99}.

### 1.7.3 Direct Assembly of SWNTs

SWNT surface chemistry is often uncontrollable, and therefore attempt to link SWNTs via surface attachment is unlikely to be controllable. The ends of SWNTs are comparably more reactive towards chemical attack as the C-C bond located on the cap is stressed due to its local curvature\textsuperscript{8}. Thus, in a typical acid oxidation, the carboxylic group is likely to be preferentially generated at the ends. Hence, if functional groups on the surface are protected or shielded from any incoming chemical attack (leaving only the ends of the SWNTs exposed), it is possible to only perform and direct chemistry at the end of the SWNTs. Palma et al. demonstrated SWNT-SWNT junction formation using DNA strand protected SWNTs\textsuperscript{7}. Wrapping SWNTs in DNA strands has two advantages, (i) polar DNA strands aid SWNTs dissolution in water; (ii) protecting the surface functional groups. These protected SWNTs were then reacted with amine-terminated linker molecules at the unprotected ends to facilitate the junction formation. The SWNTs are connected via a covalent amide linkage. The geometry of the SWNT assembly
was controlled by the structure of amine linkers. However, it is extremely difficult to ensure that only a single amine on the linker molecule reacts with only one carboxylic group on a SWNT end. Having a protected SWNT surface still leaves multiple carboxylic groups on SWNTs. Thus, all amines on the linker molecules may react with carboxylic groups on a single SWNT, limiting the selectivity of this assembly methodology as multiple linkers may be grafted onto same SWNT.

A more advanced selective SWNT deposition from SWNT dispersion has been employed for SWNT-FET fabrication. Unlike the previous example in section 1.7.1 where individual SWNTs were synthesised in situ, similar individual SWNT based FET can be prepared from SWNT dispersions, and aligned with the aid of external electric field. When a SWNT dispersion is drop cast between two metal electrodes and an electrical current is applied, SWNTs align across the two electrodes. The number of SWNTs bridged across the electrodes can be controlled by the concentration of the SWNT dispersion and by monitoring the current. This method is important in future SWNT based FET development as it shows the potential to build a large array of individual SWNT transistors. However, this method is limited to electrical device applications where a conductive electrode is present and the electrodes are limited to lithographic scales. This assembly is unlikely to be useful in pure SWNT-SWNT assembly where no metal or other support will be present.

![Figure 1.8 – Schematic representation of electric field assisted fabrication of SWNTs array FET.](image)

Another interesting self-assembly example published is the self-assembly of multiwalled nanotubes (MWNTs) with gold nanoparticles. Although this self-assembly method has been demonstrated with
MWNTs, the methodology for the assembly is worth noting and has the potential to be applied in the self-assembly of SWNTs. In this example, MWNTs were functionalised with thiol (SH) terminated groups. The thiol functionality was then used as an anchor for the gold nanoparticles. Since the original MWNT functionalisation is very difficult to control, the thiol species were generated all over the surface of the MWNTs and thus, the gold nanoparticles could be found on the whole MWNT surface.

The importance of this publication to this project is not the materials but the method that was developed for the self-assembly. A binary solvent system was used to create a selective self-assembled 2-D network. The self-assembly was located at the interface between two solvents which contained the MWNTs and gold nanoparticles respectively. In a single solvent, a 3-D structure could be obtained as the self-assembly was no longer constrained in a 2-D environment.

![Figure 1.9 – Self-assembly of thiol-terminated MWNTs and gold nanoparticle](image)

### 1.8 Summary

The heterogeneity and purity issues in SWNT chemistry has been studied extensively. These issues can not simply be resolved by improving current synthesis methodology as all SWNTs production techniques generate SWNTs with distinct contamination (amorphous carbon, catalyst particle) and heterogeneity (length and diameter distribution, chirality). With suitable purification techniques, clean SWNTs which contain high SWNT content can be achieved. Specific enrichment of SWNTs with certain diameter and
electronic properties have been investigated extensively and it is now possible to obtain highly enriched metallic and semi-conducting SWNTs via various methods. However, yields are commonly low. In the long term, a selective SWNT synthesis method should be developed to allow synthesis of SWNTs with single chirality without contamination.

Although individual SWNTs and single SWNT junctions have excellent performance in electronic devices, the associated device fabrications are limited to lithographic which the small scale of nanotubes could not be properly utilised. In addition, SWNTs devices fabricated in laboratory are limited to a very small scale. New methods are urgently needed to rationally assemble multiple SWNTs devices which could be employed in large scale production. Simple random SWNT network also have excellent performance (like SWNT network thin film transistor, TFT). It can only be improved by controlling the network structure where each SWNTs junction is optimised to give highest conductivity.
Chapter 2 – Fullerene Chemistry Review

SWNT surface functionalisation was inefficient in linking SWNTs as there is no control in the resulting SWNTs structure. However, endohedral encapsulation of fullerene in open ends of SWNTs provides a more discrete control over surface functionalisation. Therefore, joining SWNTs via the endohedral fullerene molecule should offer a unique SWNTs structure manipulation. In order to support this hypothesis, existing peapods, fullerene chemistry and fullerene derivatives were studied and are discussed below.

2.1 Peapods

The first observation of molecules inside SWNTs was an accidental discovery. Both arc-discharge and pulse laser ablation methods are known to be able to produce both SWNTs and fullerene C\textsubscript{60}\textsuperscript{1,33,40}. In a typical SWNTs synthesis, extensive washing of the as-produced materials remove any C\textsubscript{60} present in the sample. However, when Monthioux et al. studied an as-produced laser ablated SWNTs sample under TEM, a SWNT was found to have spherical molecules trapped inside its cavity\textsuperscript{33}. The spherical molecules were found to have a diameter of 0.7 nm and have a spacing of 0.3 nm away from the inner SWNT wall. These measurements match closely with the expected value of C\textsubscript{60} and its separation from a graphitic surface\textsuperscript{40}. Beside, the contrast of the spherical molecule is similar to that of SWNTs wall under TEM which suggest the spherical molecules are also made of pure carbon atoms and not other elements (See Figure 3.3 for TEM image of peapods). All these finding confirms the encapsulated molecules are in fact, fullerene C\textsubscript{60}. Since then a vast amount of effort have been invested into selectively producing this encapsulated fullerene which is now known as ‘peapod’ (C\textsubscript{60}@SWNTs)\textsuperscript{103-105}. Shortly after the original discovery of the peapod, a gas phase insertion method was developed to prepare encapsulated C\textsubscript{60} inside SWNTs\textsuperscript{106,107}. This gas phase method has since been considered as the golden method for making peapod. This method is generally divided into two steps. Firstly, there must be holes in the SWNTs structure to allow fullerene to enter the central cavity. These holes are normally produced by either
thermal annealing of the SWNTs powder in air\textsuperscript{107} or acid treatment in solution\textsuperscript{106}. Once the holes are generated, the opened SWNTs and fullerene are then heated in a sealed capsule to 450 °C to allow fullerene to sublime and enter the SWNTs\textsuperscript{106}. Since this gas phase filling requires high temperature to allow fullerene sublimation, it is not suitable for other fullerene derivatives which may not survive at such a high temperature. Thus, a milder condition for fullerene encapsulation was developed using solution phase filling\textsuperscript{103}. Recently, Khlobystov \textit{et al.} published an in depth investigation of solution phase preparation of peapod and the associated mechanism\textsuperscript{108}. Experiments showed that solvent with relatively poor fullerene solubility generate higher yields of encapsulated fullerene\textsuperscript{108}. Further development in the field, by Khlobystov \textit{et al.}, has enabled both solid state and supercritical CO\textsubscript{2} filling\textsuperscript{109,110}. Apart from simple fullerene C\textsubscript{60}, other fullerene derivatives or small molecules have also been shown to enter SWNT to form a hybrid material with SWNTs\textsuperscript{110-112}. It has been proposed that reversible small molecule encapsulation may be an interesting candidate for a self-release drug carrier\textsuperscript{113}.

2.2 Covalent Fullerene Chemistry

From the extensive literature of peapod chemistry, a variety of fullerene derivatives have been shown to enter SWNTs. However, to fulfil the requirement of connecting SWNTs via fullerene insertion, existing fullerene derivative for peapod formation are not the ideal candidate. The difficulty is that the whole fullerene derivatives are designed to enter the SWNTs cavity to give high peapod yields. To successfully connect two SWNTs to give a simple SWNT-SWNT junction, the linker molecule must contain two fullerene molecules and only the fullerenes in the linker molecules should enter the SWNTs. Thus, a bulky spacer is required to connect the two fullerene molecules to prevent complete encapsulation.

Originally, fullerene derivatives were selectively prepared to increase the solubility of the parent fullerene molecule. Due to its strong van der Waal’s interaction within the fullerene lattice, fullerene is difficult to process/exfoliate. Thankfully, because of the versatility of fullerene surface chemistry, a
number of reactions have now become well established and are often employed in covalent functionalisation of fullerene. Carbon bonds on fullerenes surface can be classified as [5,6] and [6,6] (bond between a 5- & 6- membered ring, or between two 6- membered rings). Some of the fullerene functionalisation reactions were found to be regioselective, attacking the [6,6] site selectively. Whereas some of the reaction were found to produce mixture of products with both [5,6] and [6,6] additions. The most common examples are summarised below.

Table 2.1 – Table of solubility of fullerene in common fullerene solvents

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Solubility (mg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahydrofuran</td>
<td>0.0</td>
</tr>
<tr>
<td>n-hexane</td>
<td>0.043</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.16</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.7</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.8</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>7.0</td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>27.0</td>
</tr>
</tbody>
</table>

2.2.1  Prato Reaction – Azomethine Ylide Addition

Cycloaddition is the most frequently employed route to functionalise fullerene surfaces. It can be divided into sub-classes and one of the most famous is the Prato reaction. This method was first proposed by Maurizio Prato et al. The reaction of N-methylglycine and formaldehyde generates an azomethine ylide *in situ* which attacks the fullerene surface via 1,3-dipolar cycloaddition (Figure 2.2).
As there are multiple carbon double bonds on fullerene surface, there is a chance of having multiple additions products from the reaction. However, this tendency can be limited by using a huge excess of fullerene. Unreacted fullerene C$_{60}$ can be easily removed by column chromatography as the resultant product is more polar (due to the grafted nitrogen substituent) than the pristine C$_{60}$. Another approach to the azomethine ylide is thermal ring opening of 5-oxazolidinone$^{115}$ (Figure 2.3). Ring opening via decarboxylation to generate the azomethine ylide and it can then react with fullerene surface. Thermal ring opening of aziridine can also react with C$_{60}$$^{116}$. In both cases, the substituted heterocyclic ring is heated with C$_{60}$ in refluxing toluene and resultant substituted fullerene can be collected via column chromatography. The driving force of the reaction is the strain relief of the heterocyclic ring.

Figure 2.2 – Typical Prato reaction of azomethine ylide and fullerene C$_{60}$.

Figure 2.3 – (Top) Reaction of N-methyl-5-oxazolidinone with fullerene. (Bottom) Reaction of aziridine addition to fullerene.
2.2.2 Cycloaddition – Electron Rich Alkenes and Alkynes

Unlike the thermally activated cycloaddition of azomethine ylide, an electron rich alkene or alkyne can react photochemically with a double bond on the fullerene surface. A typical electron rich alkene used in this kind of reaction is tetraalkoxyethylene. The alkoxy group is a well known electron donating substituent and having four of the electron donating substituent on the same ethylene makes the alkene very electron rich. Since fullerene is electron withdrawing, it readily reacts with the electron rich tetraalkoxyethylene. However, due to the large number of double bonds on fullerene surface, the control of regioselectivity of the reaction becomes problematic. Multiple alkene/alkyne adducts are often generated alongside with the monoadduct from this reaction. To separate the monoadduct from the mixture, it requires repetitive column chromatography, it is time consuming and may require large amount of solvents.

Figure 2.4 – Typical photochemical reaction of electron rich tetraalkoxyalkene with fullerene. (R : any aliphatic non-electron withdrawing group)

2.2.3 Cycloaddition – Organic Azide

The zwitterionic nature of organic azides makes them ideal molecules for cycloaddition. Similar to the azomethine ylide approach, organic azides react with one of the double bonds on the fullerene surface. Depending on the substituent on the organic azide, the reacted site on the fullerene surface may be different. An aryl substituted azide preferably reacts with the [6,6] bond on fullerene where an alkyl azide attack the [5,6] bond on the surface. Again, multiple substitution patterns are a problem here
and reactions would require an excess of fullerene to yield mono-addition adducts. This reaction is the best candidate in the synthesis of the bis-fullerene linker (dumbbell) due to the ease of azide introduction into carbon framework. Azide can be introduced into a molecule by the mean of nucleophilic substitution of sodium azide (NaN₃). Since NaN₃ is not soluble in most organic solvents, the unreacted azide can be easily filtered off. Azide has a characteristic azido stretching at 2100 cm⁻¹ in infrared spectroscopy (IR). Thus the progress of the reaction can be easily followed by IR.

![Figure 2.5](image.png)

**Figure 2.5** – Typical azide addition onto fullerene surface.

### 2.2.4 Cyclopropanation

![Figure 2.6](image.png)

**Figure 2.6** – Typical Bingel reaction of fullerene with haloalkane. R : any electron withdrawing groups.

The Bingel reaction is, again, a classic example of fullerene functionalisation. Surprisingly, all three major fullerene functionalisation reactions (Prato-azomethine ylide addition, Azide addition and Bingel reaction) were all discovered in 1993. In a typical Bingel reaction, a strong base is required to remove
the methine proton to create a halocarbanion which then attacks the electron poor fullerene. Multiple electron withdrawing groups in the starting haloalkane are required to stabilise the carbanion intermediate.

A modified cyclopropanation reaction has been developed by Hirsch et al. Stirring malonate and fullerene $C_{60}$ in the present of carbon tetrabromide ($CBr_4$) and diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene yields malonate functionalised fullerene. The reaction goes via a bromomalonate intermediate which is generated in situ and reacts selectively with a [6,6] double bond via cyclopropanation. Therefore, unlike the others functionalisation which can react with either [5,6] and [6,6] bonds on fullerene, this reaction gives only [6,6] bridged fullerene. The degree of functionalisation can be controlled by varying the molar equivalent of the reagents. However, the substituent on the starting malonates was also found to affect the degree of functionalisation (Figure 2.6). The monoadduct is preferred when a simple substituent (methyl or ethyl) is used, whilst a more bulky and long substituent tends to give multi-adducts. This reaction may be useful in the synthesis of the fullerene linker molecules. Since the fullerene is functionalised with ester groups, a simple transesterification of the fullerene with a spacer molecule may be an efficient way to covalently join them together.
2.2.5 Amine Addition

Beside the cycloaddition, fullerene is also known to be attacked by alkyl amines. However, this amine insertion method received little interest in fullerene research and only limited examples are available in literature. Amine insertion could be a good methodology due to the simple starting material (primary amine) and reaction condition (stir in toluene at room temperature)\textsuperscript{123,124}. Examples of secondary amine insertion are also known but experimental data revealed mainly multi-adducts are formed\textsuperscript{125}.

![Figure 2.8 – Amine addition onto fullerene surface (R : aliphatic)](image-url)
2.2.6 Other Fullerene Functionalisations

Figure 2.9 – Alternative fullerene functionalisation reactions. Clockwise (Top) carbene reaction, Diels Alder reaction, diazo-addition, nitrene reaction.

In addition to those examples mentioned above, there are also other fullerene functionalisation that are well established\textsuperscript{126,127} (Figure 2.9). As shown in the previous examples, some fullerene functionalisation reactions are regioselective. Regioselectivity should not be a major problem in the synthesis of linker molecule. In the basic bis-fullerene linker synthesis, the most important point is to covalently connect the two fullerene molecules. The position of the linkage on fullerene surface is not important as it would not have an effect on the overall diameter of the fullerene molecule.
All the given examples are possible functionalisation strategies that could be employed in fullerene linker synthesis. Fullerene was also found to undergo various reactions (such as acid oxidation, halogenations, hydrogenation and reaction with transition metal complexes)\textsuperscript{134,135} but these reactions are unlikely to benefit the linker synthesis, therefore it will not be covered here\textsuperscript{128,129}.

2.3 Fullerene Adducts

Since the concept of self-assembly of SWNTs with structural directing fullerene linkers has not been demonstrated before, there are many questions to be answered when designing the linker molecules. The first obvious question is how to join the fullerenes together? For example, in the self-assembly of two SWNTs (simplest assembly) with a bis-fullerene linker, what is the minimum separation between the two fullerenes so the whole molecule can not enter SWNTs? Will the chemical structure of the spacer affect the insertion? These questions must be answered before designing the linker molecules. Previous ‘peapod’ examples mostly consist of single fullerene derivatives. Thus, little is known for multi-fullerene adduct in SWNTs encapsulation. However, it is believed that the separation between the two fullerenes cannot be too short (i.e. ethylene) since it is very likely that the whole molecule could enter the same SWNTs cavity. A detailed analysis of peapod formation with a mono-alkyl functionalised fullerene has been reported by Khlobystov \textit{et al}.\textsuperscript{78}. TEM studied revealed fullerene with a single C\textsubscript{17}H\textsubscript{25} long alkyl substituent is encapsulated by SWNTs. Long alkyl chains are known to coil in solution, thus long chain spacer should provide a blockage large enough to prevent complete encapsulation. This suggests the spacer must be longer than C\textsubscript{17} units to give the corresponding coiled blockage; otherwise, the whole fullerene linker molecule may be encapsulated by the same SWNTs. Alternatively, a bulky substituent can be grafted onto the spacer so that only single fullerene can enter a SWNT. On the other hand, the spacer should offer reasonable flexibility to the linker molecule. Once a single fullerene is inserted into a SWNT, enhanced flexibility may enable the other fullerenes in the linker to catch other SWNTs more easily. The spacer should also be chemically robust so the linkage between the connected fullerenes cannot be broken easily. Since fullerene has poor solubility in common organic solvents, the spacer
should also increase the overall solubility of the linked fullerenes which in turn would improve its processability.

Having considered the requirement for the fullerene linker, a flexible polymer (also being chemically inert and with high solubility in common solvent) is a good candidate for the spacer. Polymers can be found with different chain length which means the linked fullerenes can be separated with any distance. Flexible polymers are widely available commercially such as polyethylene (PE), polyvinyl chloride (PVC) and polyethylene glycol (PEG). Connecting fullerenes with these polymers would offer flexibility for the fullerenes to adopt the required conformation in self-assembly.

![Diagram of fullerene polymer adducts]

**Figure 2.10** – Summary of previously known fullerene polymer adducts. (A) Linear multiple fullerene polymer. (B) Multiple fullerenes cross linked polymer. (C) Multiple fullerene brushed polymer. (D) Fullerene end-capped polymer. (E) Fullerene polymer multiadduct.
A brief literature research has been carried out in fullerene polymer adduct examples in order to look for the most suitable candidate. Since fullerene has poor solubility in common organic solvent and insoluble in water, the first generation of fullerene polymer adduct was selectively produced to increase its solubility. A typical example of these fullerene adducts with increased solubility has been published by Prato where a water soluble polyethylene oxide chain has been grafted onto the surface.\textsuperscript{130} It has been shown that fullerene mono-adduct retains the same electronic property of the parent fullerene and thus, fullerene applications have been developed quickly due to the increased solubility\textsuperscript{131,132} but preserved electronic property. However, architecture is the main factor to be considered in designing the linker molecule. Among those fullerene polymer adducts schematically represented in Figure 2.10, the fullerene end-capped polymer is the most suitable candidate for the linker molecule. It resembles the perfect architecture of a dumbbell structure for self-assembly of two SWNTs. The covalently grafted fullerene is mono-functionalised, thus the overall diameter of the fullerene is retained and is suitable for self assembly. The polymer spacer can be easily tuned to offer different degree of flexibility which may be an advantage in fullerene insertion. The fullerene brush polymer is also an interesting candidate for connecting multiple SWNTs which may be investigated in the later stage of this project once the simple SWNT-SWNT junction has been confirmed.

2.4 Fullerene End-capped Polymers

There are only limited examples of fullerene end-capped polymers in the literature. The closest example to bis-fullerene linker is a fullerene polymer adduct published by Goh & Huang et al.\textsuperscript{133}. A single PEG (polyethylene glycol) chain is covalently grafted onto fullerene surface via azide addition.\textsuperscript{119,133} Later on, a bis-fullerene PEG monoadduct was also suggested with identical synthetic methodology but using bis-azide terminated PEG instead of mono-azide PEG\textsuperscript{23}. A similar tris-fullerene end-capped PEG adduct has also been synthesised using a commercial available tris-PEG star\textsuperscript{31}. Other fullerene end-capped polymers have also been demonstrated using other polymers such as polystyrene\textsuperscript{28} and polythiophene.\textsuperscript{26} After considering the nature of the polymer, PEG may be the best choice for the linker molecule for a number...
of reasons. (1) It offers the required flexibility to the linker molecule. (2) It gives the fullerene linker enhanced solubility in both organic and aqueous solvents. (3) The chain length of the PEG can be easily tuned as various PEG chain lengths are commercial available (can be easily longer than a C₁₇ chain). (4) PEG (or other flexible polymer) is known to coil up and form aggregate in solution. Once a single fullerene entered a SWNT, the PEG coil may prevent the other fullerene from entering the same SWNT. In addition, an associated in depth synthetic procedure is already published for this fullerene end-capped fullerene\textsuperscript{134}. Hence, it saves time for optimising reaction condition in the synthesis stage which would benefit to the project. For the above reasons, fullerene end-capped PEG dumbbell has been chosen as the first fullerene linker for self-assembly. Other than PEG dumbbell, tris-fullerene end-capped linker is also known and the synthetic procedure is similar; it can be used as the tris-fullerene linker to connect three SWNTs. By using linkers with similar properties, the optimisation of self-assembly condition should be simplified.
Chapter 3 – Characterisation Methods and Analysis

The characterisation needed in the project can be divided into two sections. Firstly, it is the characterisation of the fullerene end-capped linker molecule. Although a detailed synthesis procedure has been published in the literature, the synthesised fullerene linkers should be characterised with a range of spectroscopic techniques to confirm the true identity of the as-produced materials. These are common characterisation techniques employed in general organic synthesis including nuclear magnetic resonance spectroscopy, infra-red spectroscopy and UV-vis spectroscopy. Since the fullerene linker molecules will be synthesised with polymer as a spacer, mass spectroscopic analysis of the resultant product will be valuable in determination of the end-products masses. Thus, matrix assisted laser desorption ionisation time of flight spectrometry (MALDI-TOF) will be employed in the characterisation of the linker molecules. Additional characterisation of polymer is often supported by elemental analysis to give the atomic ratio of each element within the structure (mainly carbon, hydrogen, oxygen and nitrogen).

The second part is the characterisation of single walled carbon nanotubes (SWNTs). The spectroscopic techniques which are often applied in SWNTs characterisation are UV-vis spectroscopy, Raman spectroscopy and photoluminescence spectroscopy. These are mainly used in the determination of bulk SWNTs quality, diameter and chirality. Apart from spectroscopic characterisation, microscopic characterisation techniques are also widely used in nanotubes study. Both atomic force microscopy (AFM) and transmission electron microscopy (TEM) are the two most common methods to study SWNTs at an atomic scale. These microscopic techniques provide information on diameter and length of each individual SWNTs. More importantly, they provide vital information of the degree of exfoliation (number of individualised SWNTs) which is important in the SWNT junctions characterisation.
Apart from the spectroscopic and microscopic techniques, thermal gravimetric analysis (TGA) is also a common technique in determination of SWNTs quality. This method simply measures the weight loss over increasing temperature or time (at constant temperature). It indicates the total metal and carbonaceous material content. It is also widely used in the determination of the grafting ratio of SWNTs. As SWNTs has a relatively higher degradation temperature than most of the grafted species, the combustion of the surface functional groups would take place before SWNTs.

3.1 Spectroscopic Techniques

3.1.1 Nuclear Magnetic Resonance (NMR)

Although various nuclei can be studied by NMR spectroscopy, the most common nuclei are \(^1\)H and \(^{13}\)C which form the basis of most organic chemical structures. \(^1\)H NMR spectroscopy enable chemists to resolve protons with respect to their corresponding chemical and magnetic environment within a molecule. It is able to pick up proton-proton interactions (spin-spin coupling) which related to both distance and dihedral angle of the coupling protons. Since fullerene consists of carbon atoms only, \(^{13}\)C NMR spectroscopy is the ideal technique to characterise the fullerene structure. Pristine fullerene \(C_{60}\) is a perfectly symmetrical molecule with all the carbon atoms within the cluster being identical, therefore, only a single carbon signal is observed for \(C_{60}\). However, once a single substituent is covalently grafted onto the fullerene surface, the symmetry will be broken. Depending on the bonding environment at the functionalisation on fullerene surface, multiple signals would be observed for the fullerene carbon atoms. Therefore, \(^{13}\)C NMR spectroscopy is useful in following functionalisation of fullerene and \(^1\)H NMR spectroscopy is useful in characterising the grafted polymer.

All NMR spectra in this study were acquired using a Bruker AM 400 spectrometer operating at 9.4T. Samples were dissolved in CDCl\(_3\) and all spectra were recorded with 16 scans and \(D_1 = 1\) sec (unless specified). All chemical shifts (\(\delta\)) are given in ppm, where the residual CHCl\(_3\) peak was used as an internal reference for \(^1\)H NMR (\(\delta_H = 7.28\) ppm), and the CDCl\(_3\) peak for \(^{13}\)C NMR (\(\delta_C = 78.23\) ppm). Coupling
constants ($J$) are given in Hz, and chemical splitting patterns are abbreviated as follows: s, singlet; d, doublet; t, triplets; q, quartet; quin, quintet; sex, sextet; sep, septet and m, multiplet.

3.1.2 Infra-red (IR) Spectroscopy

Infra-red (IR) spectroscopy is widely used in the identification of specific diatomic bond stretching, bending and vibration within a molecule. Common signals correspond to C-H, C=O, C-O and O-H can be readily identified and are extremely valuable towards the initial characterisation of products. Since IR spectroscopy can only indicate the presence of the bonds and not location within the molecule, it has to be used in conjunction with other characterisation technique like NMR spectroscopy to identify the complete chemical structure. On the other hand, fullerene has distinctive absorbances at 1429, 1183, 577 and 528 cm$^{-1}$. Hence, the presence of fullerene in the products can be easily identified. All IR spectra in this study were recorded on powders or liquids (no nujol) using a Perkin-Elmer spectrometer 100 equipped with a Pike attenuated total reflectance (ATR) silicon crystal. All spectra were acquired with 16 scans and 4 cm$^{-1}$ resolution.

3.1.3 UV-vis Absorption Spectroscopy

UV-vis absorption spectroscopy measures the electronic absorbance of a molecule’s electronic structure. When UV or visible light is irradiated through a sample, certain wavelengths are absorbed by molecule to raise the ground state electron to excited state. In organic synthesis, it is widely used to probe the electronic absorbances of conjugated molecules. Since fullerene is highly conjugated, it has strong absorbance at 213, 257, 330 nm with extinction coefficient $\varepsilon_{\text{max}}$ 135,000; 175,000 and 51,000 respectively. However, absorption below 300 nm is rarely observed due to overlapping solvent bands. There is also a weak absorption at 404 nm in fullerene absorption which can be also used to identify the presence of fullerene$^{137}$. 
Figure 3.1 – Electronic absorption spectrum of fullerene $C_{60}$ in toluene. Electronic absorption below 300 nm attributed to electronic absorbance of solvent. Inset is the expanded region of 300 – 500 nm of fullerene absorption spectrum clearly showing the absorbances at 330 and 404 nm.

In the self-assembly of SWNTs with the fullerene end-capped linkers, it is very important to note the concentration of the fullerene linkers (total number of fullerene). Thus the strong absorption at 330 nm is useful for the concentration determination of the linker molecule; using the well established extinction coefficient.

SWNTs characterisation by UV-vis spectroscopy is not as straightforward as small molecules. Simple molecules dissolved in organic solvents can be used directly in UV-vis spectrometer. Due to the low solubility of SWNTs, it required lengthy sample preparation for UV-vis measurement. On the other hand, SWNTs bundle significantly absorb the incident light over a wide range of wavelength, thus, it is difficult to determine the true SWNT electronic effects. Another major issue in SWNTs UV-vis spectroscopy is the scattering issue. When the incident light wavelength is smaller or similar to the probing species, it will be scattered to a different angle (Mie scattering). Thus, any scattered incident light will not be collected up by the spectrometer and effectively increases the ‘absorbance’ by the molecules. Highly functionalised
or degraded SWNTs do not show electronic absorbance in UV-vis due to the loss of sp$^2$ configuration. To avoid these problems, SWNT dispersions must be prepared carefully with minimum damage to side walls and maximise the degree of exfoliation. SWNTs with different diameter and chirality are found to have different electronic transition. Having highly individualised SWNT dispersions allows UV-vis to resolve the individual electronic absorbance of individual SWNT species.$^{138,139}$

![Figure 3.2](image-url)  
**Figure 3.2** – UV-vis spectrum of HiPco SWNTs dispersion in NMP. The numbers on top of the curve denoted possible chiral vectors for the observed absorbances. In general, $m$-SWNTs transitions occur at around 300-700 nm whereas sc-SWNTs would be observed at around 500-1400 nm.

Similar to small molecule UV-vis spectra, SWNTs spectra can also be used in the determination of concentration. However, bulk SWNTs samples contain multiple SWNT species and it is difficult to pick each individual features and use them as a concentration reference. Luckily, a detailed analysis of SWNT concentration has been carried out by Coleman *et al.* and the absorption at 660 nm is now generally accepted as a concentration reference with a extinction coefficient$^{12}$ of 3264 ml mg$^{-1}$ m$^{-1}$. This finding is particularly relevant to this study as the concentration of SWNTs is vital in the self-assembly. All UV-vis
spectra in this study were acquired using a Lambda 950 spectrophotometer (Perkin Elmer, Waltham, MA, USA). For fullerene linker synthesis, all fullerene linkers were dissolved in toluene (unless specified) and spectra were acquired with a 1 cm path length quartz cuvette. SWNTs dispersions in this study were prepared in N-methyl pyrrolidone (NMP).

3.1.4 Raman Spectroscopy

Raman spectroscopy provides information about SWNT character, diameter and quality. There are three principle signals in Raman spectra of SWNTs\textsuperscript{140}; the graphitic band (G band) at around 1500 – 1600 cm\textsuperscript{-1} is an indication of degree of sp\textsuperscript{2} hybridisation in SWNTs. Thus, the more intense the G band, the better quality of SWNTs. Due to curvature, the G band is divided into two graphitic signals; a (G+ band) for longitudinal signal and a (G- band) for a transversal signal. In addition to the G band, a defect-induced band (D band) at around 1350 cm\textsuperscript{-1} is also present in typical SWNTs spectra. The D band is an indication of the degree of defectiveness in SWNTs. Thus the ratio between the G and D bands is a useful guide to the overall SWNT quality. Normally, all SWNT spectra are normalised to the most intense G band for ease of comparison. The last principle signal in SWNT Raman spectra is the radial breathing mode (RBM) band which appears at below 500 cm\textsuperscript{-1}. This signal corresponds to radial carbon vibration which depends on diameters. Multiple laser sources are generally applied in the full analysis of SWNTs samples as SWNT species resonate to certain wavelengths. A direct mapping of the RBM signals and the corresponding SWNT diameters as well as chirality have been constructed by Kataura and is now known as ‘Kataura plot’\textsuperscript{141}.

Raman spectroscopy has also been used to identify SWNT encapsulated fullerenes (peapods)\textsuperscript{142}. It has been shown that the signal of encapsulated fullerene is greatly reduced, and more importantly, downshifted compared to the pristine non-encapsulated fullerene molecules. Thus, Raman provides a quick and easier confirmation of the fullerene insertion into SWNTs than high resolution microscopic technique. However, in order to observed the fullerene signal inside SWNTs, a reasonable high yield of
encapsulated fullerene is needed. Considering the self-assembly experiment, only two fullerenes would enter each SWNT at each ends which may not even reach 1 % yield of these previous peapod examples. Thus, Raman spectroscopy is not suitable in the characterisation of SWNTs self-assembly.

3.1.5 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a standard measurement of SWNT electronic property. It is limited to the characterisation of semi-conducting SWNTs as metallic SWNTs do not fluoresce (no band gap in m-SWNTs). This technique is widely used in bulk characterisation of SWNTs sample as individual sc-SWNTs fluorescence is well-resolved at different excitation wavelengths. Current synthetic methodology of SWNTs often produce a mixture of both metallic and semi-conducting SWNTs, thus, PL spectroscopy can only measure a fraction of the sample. No evidence suggesting different fullerene filling rates or insertion mechanism regarding to SWNTs electronic property has been reported. Thus, the major factor to be considered in SWNTs self-assembly is the diameter of the SWNTs. Since PL measurement do not reveal a complete picture of a SWNT sample, it is not suitable for the characterisation in this study.
3.1.6 Mass Spectrometry – Matrix Assisted Laser Desorption Ionisation Time of Flight Spectrometry

Mass spectrometry (MS) is widely used in the determination of molecule masses in organic synthesis. Typical MS involves ionisation of the molecules which fly in the vacuum chamber and are sorted by mass before reaching the detector. The vacuum chamber is coupled with a magnetic field which deflects the ions according to their mass to charge ratio (m/z). The typical ionisation technique, electron impact (EI), ionises the molecule by striking it with high speed electrons. The impact often generates multiple fragmentations of the molecules. Depending on the degree of fragmentation, multiple signals are observed in the spectra. The larger the molecule, the harder the analysis of the spectra and it is often a time consuming process. This technique is therefore classified as a hard ionisation technique as it breaks up the molecule into multiple fragments. Other ionisation techniques associated with MS have been extensively reviewed.

In polymer chemistry, it is very important to study the mass of the overall polymer. However, hard ionisation techniques are only capable of resolving polymers with low molecular mass (below 400 Da). Using hard ionisation for high molecular weight polymers is unwise as it is almost impossible to construct the fragmentation pattern back into the original polymer. Therefore, the characterisation of polymers relies heavily on NMR spectroscopy and size exclusion chromatography (SEC) which only give average properties. MS is still the best technique to identify each individual polymer species with different numbers of repeating units. In 1988, matrix assisted laser desorption ionisation (MALDI) was first proposed in the field. Since then, it has revolutionised polymer science and most synthetic polymers are now characterised by MALDI. NMR spectroscopy and SEC are quick and easy to use but they are not suitable for all polymers. As polymer science has matured, more complex synthetic polymers have emerged in the field. These complex polymers are often made with sophisticated chemical structures and NMR spectroscopy and SEC may not be able to resolve them.
As illustrated in the name, MALDI uses a matrix to transfer energy from ionisation source to the polymer. Typical MALDI uses a UV light (337 nm) ionisation source. The matrix has to first absorb this short wavelength energy before it can transfer the energy to the molecule. Thus, all matrix used in MALDI are conjugated and/or aromatic and small in size. Conjugation provides the required HOMO-LUMO gap for the short wavelength UV absorption and its small size make it easier to crystallise with the polymers which make energy transfer more efficient. Typically, a metal cation (Na\(^+\)) is also added to the system along with the matrix to provide the charges for the polymer. Thus, the resulting polymer ion is often generated as \([M + Na]^+\) rather than the \([M]^+\) or \([M+H]^+\) in conventional MS. As the technique has matured, many matrices have been developed to suit various macromolecules (peptides, sugars, DNA and polymers). Some matrices are interchangeable for different macromolecules and some are more specific. More details of MALDI matrix can be found elsewhere.

3.1.6.1 Investigation of Matrixes and Sample Preparation

Since a polymer is used as the spacer to connect fullerene molecules in the linker, MALDI is used to follow the chemical transformation of the polymer (polyethylene glycol, PEG in this study). Fullerene \(\text{C}_{60}\) has a mass of 720 Da and once it is grafted onto the polymer, the significant increase in mass can be easily identified by MALDI. Many matrices have been tested for PEG and their results are well documented. However, the major issue is the fullerene. Various matrices have been tested for fullerene MALDI but mainly for relatively small fullerene derivatives. 9-nitroanthracene (9-NA) is the most commonly employed matrix in fullerene derivatives with small substituents. The only matrix which was found to be effective in short PEG chain grafted fullerene is 2,5-dihydroxybenzoic acid (DHB). However, initial trial with this DHB matrix in the MALDI did not yield promising results as it appeared that the fullerene adducts were heavily fragmented during ionisation.
Table 3.1 – MALDI matrices tested for fullerene end-capped PEG linkers (measured with positive reflectron mode).

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Structure</th>
<th>Signal Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB)</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>Good</td>
</tr>
<tr>
<td>(4-Hydroxybenzylidene) malononitrile</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>No signal</td>
</tr>
<tr>
<td>α-Cyano-4-hydroxycinnamic acid</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>very weak</td>
</tr>
<tr>
<td>4-Benzylxy-α-cyanocinnamic acid</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>No signal</td>
</tr>
<tr>
<td>Sinapic acid</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>No signal</td>
</tr>
<tr>
<td>Anthracene</td>
<td><img src="image6.png" alt="Structure" /></td>
<td>No signal</td>
</tr>
<tr>
<td>9-nitroanthracene</td>
<td><img src="image7.png" alt="Structure" /></td>
<td>No signal</td>
</tr>
<tr>
<td>Dithranol</td>
<td><img src="image8.png" alt="Structure" /></td>
<td>No signal</td>
</tr>
</tbody>
</table>
Since DHB did not work for the fullerene linkers, other matrices were tested but failed to give any signals related to the linkers. Table 3.1 summarises those MALDI matrices that were tested in the initial MALDI study. Due to the initial difficulty in running MALDI for fullerene linkers, one of the fullerene derivatives (PEG$_{3350}$-C$_{60}$ adduct) was sent to EPSRC Swansea National Mass Service for MALDI characterisation. The result was promising and the fullerene PEG adduct signal was clearly shown. The MALDI expert in the EPSRC Swansea National Mass Service suggested that using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix gives the best result for fullerene adducts with minimum fragmentation. Further research in the literature also suggests that DCTB is effective in ionising fullerene species with reduced laser intensity which limited the possibility of complete dissociation of the analyte\(^{352}\). However, sufficient MALDI signals were not observed even with DCTB matrix. The EPSRC Mass Centre only suggested the matrix but did not provide a sample preparation procedure.

Typical MALDI sample preparation involves three steps, (1) dissolve analyte, matrix and metal source (NaI) into separate solvents. (2) Mix the three solutions together. (3) Deposit the solution onto a MALDI plate for characterisation. In general, literature only gives information for solvents, concentration and/or volume of each solution. Ideally, the sample, matrix and cationic metal source should all be dissolved in one solvent as it minimises the chance of having segregation when the mixture crystallises on the MALDI plate. Tetrahydrofuran (THF) is widely used for dissolving matrix and the cationic metal salt (sodium iodide or sodium acetate), but the fullerene adduct has extremely low solubility in THF and the concentration is not sufficient for MALDI analysis. Hence, fullerene adduct was dissolved into various solvents; mixed with the matrix/metal THF solution and tested in MALDI. Among the tested solvents (toluene, carbon disulphide, chlorobenzene and dichlorobenzene), toluene (Tol) was found to give the best signal intensity in MALDI but the intensity of the signal was still weak. The remaining factor is the crystallisation process on the MALDI plate. Typical crystallisations are carried out from a single hot solvent containing saturated solutes followed by slow cooling. In the present MALDI preparation, there
are two solvents involved, THF and Tol. When the two solvent mixtures (with the dissolved matrix, fullerene adduct and metal source NaI) is dropped onto the MALDI plate, a series of process occur. Due to the difference in boiling points, THF evaporate first. With reduced volume of THF, there is not enough THF to solvate the DCTB matrix and NaI and they precipitate first. As liquid Tol remains in system, the fullerene adduct will remain solvated. Hence, it is very difficult to obtain crystals with all three components, fullerene adducts, matrix and NaI intimately mixed.

Temperature is important in crystallisation. Instead of cooling the saturated solution slowly to room temperature, cooling it in a fridge or ice-bath often produces more crystals (but smaller crystal grain size). The same theory can be applied in the MALDI preparation where the two solvents are kept at a lower temperature which allows the crystallisation to take place first. The MALDI plate is then allowed to warm up to room temperature and the solvent will slowly evaporate. To verify this theory, the MALDI plate was first cooled in a fridge for at least 2 hours before the solution mixture were drop cast onto it. After drop casting, the MALDI plate was placed in fume hood at room temperature and the solvents slowly evaporated. Luckily, MALDI sample prepared using this method gives the best signal intensity observed. All the subsequent fullerene polymer adducts were analysed using the same method.

3.1.6.2 General MALDI Preparation

All matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF) data were acquired on a Waters MICROMASS 
MALDI micro MX™ with a nitrogen laser at 333 nm in the positive reflectron mode with delayed extraction. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (>98%, Sigma-Aldrich) and sodium iodide (99.999%, Sigma-Aldrich) were used as the matrix for MALDI-TOF mass spectrometry. The instrument was calibrated in the range of 500-5000 Da using a standard poly(ethylene glycol). 10 µL samples dissolved in toluene (1-2 mg/ml) were added to the mixture of 10 µL of pre-dissolved matrix (10 mg/ml DCTB in THF) and 3 µL of NaI (3 mg/ml in THF). Small aliquots of mixture were loaded on to a cold stainless steel MALDI target plate (cool in fridge for 2 hours) and allowed to air dry at room temperature (in fume hood). The simulated
isotopic peak patterns were constructed using online software MolE - Molecular Mass Calculator v2.02 (http://rna-mdb.cas.albany.edu/RNAmods/masspec/mole.htm).

3.2 Microscopic Characterisation

Due to the small size of SWNTs, it is impossible to see individual SWNTs using conventional light microscope. Both transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are standard characterisation techniques in nanotechnology. TEM offers atomic resolution which allows direct observation of SWNT structure whereas SEM has a lower resolution and is generally used to study SWNT networks rather than individual SWNTs. Another type of high resolution microscopy is atomic force microscopy (AFM) which uses direct mechanical contact to probe the nanomaterials and it is useful to study both individual and networks of SWNT.

3.2.1 Transmission Electron Microscopy

Transmission electron microscopy (TEM) was the first method used to confirm the existence of encapsulated fullerene in SWNTs (peapod) (See Figure 1.4)\textsuperscript{33}. TEM images showing encapsulated fullerene with specific inter-fullerene distance is solid evidence of successful peapod formation. Traditionally, as-produced peapods are dispersed into solvents and drop cast onto a holey carbon grid. The only way to image encapsulated fullerene is to have the peapod over the hole on the grid. This allows direct observation of encapsulated $C_{60}$ and SWNT cavities. Since the purpose here is to observe encapsulated $C_{60}$, the SWNTs only need to be partially exfoliated. Unfortunately, imaging SWNTs self-assembly is not as straight forward as peapod. In self-assembly, a highly individualised SWNTs dispersion is intrinsically required. Similar to peapod imaging, the ideal self-assembly proof could only be observed when the SWNT-SWNT junction (with the associated fullerene linkers encapsulated) rests on top of a hole, thus, a reasonable amount of SWNTs are required. However, the concentration of self-assembled SWNTs dispersion is less than the peapod dispersion. Increasing the concentration of self-assembly dispersion would not benefit the TEM imaging as
increased SWNTs concentration would induce SWNTs rebundling which effectively reduce the chance of observing junctions.

Harsh TEM imaging conditions are known to damage SWNTs and encapsulated fullerenes via knock on damage\textsuperscript{153}. In TEM imaging, multiple encapsulated fullerenes coalesce into a more stable form, a new SWNT, which effectively produces double walled carbon nanotubes (DWNTs) (see Figure 3.2). Prolonged electron beam irradiation also induce SWNT deformation but at a slower rate than the highly curved fullerenes\textsuperscript{153}.

![Figure 3.3](image)

Figure 3.3 – TEM images of C\textsubscript{60}@SWNTs peapod (97 kV). A $\rightarrow$ H showing the effect of electron beam irradiation on the structure of encapsulated C\textsubscript{60}. It clearly shows that the fullerene eventually coalesces into a tubular structure within the parent SWNT\textsuperscript{153}.

The high energy electron in TEM is capable to damage fullerene cage. In a fullerene linker molecule, the spacer connecting the end-capped fullerenes is polyethylene glycol (PEG) which is significantly weaker than a fullerene cage. It is almost certain that the high energy electron beam will damage the PEG chain.
and cleave the fullerene linker. Thus, it is extremely difficult to observe SWNT-SWNT junctions with encapsulated fullerene at the centre of the junction.

### 3.2.2 Atomic Force Microscopy

Atomic force microscopy (AFM) involves physical contact of a scanning probe with a surface and any object deposited on it\(^{154}\). Since it is a mechanical contact, surface properties (i.e. roughness, hardness) can be obtained. AFM is widely used in SWNTs imaging as a mean to confirm the degree of exfoliation and obtain valuable information on the diameter and length distributions. Typical SWNT AFM samples are prepared on either silicon wafer or mica surfaces. Highly individualised SWNT dispersion is then either drop cast or spin coat onto the surface. The solvent has to be completely evaporated before AFM imaging as any residual solvent contaminates the scanning tip and generates an artefact in the image. This problem is easy to resolve in low boiling point solvents like water and ethanol for which drying under air overnight normally suffices. Whereas high boiling point SWNTs solvents like dimethylformamide (DMF) and N-methyl pyrrolidone (NMP) which boil at 153 °C and 202 °C respectively, means drying in atmospheric condition would be difficult to evaporate the solvents. Thus, SWNT AFM samples deposited from DMF and NMP must be dried at elevated temperature (preferably in vacuo) to ensure complete removal of residual solvents.

Due to the problems associated with SWNT self-assembly (SWNTs position on grid, concentration, electron beam damage), it is difficult to characterise the assembled SWNTs with TEM. AFM is the central method in self-assembly characterisation. Instead of electron beam in TEM, direct mechanical contact is made between the scanning tip and the surface in AFM. There is no irradiation damage in AFM imaging which mean the fullerene linkers and SWNTs structure will remain intact throughout the imaging process.
It has been demonstrated by Smalley group that AFM can be used to characterise self-assembled SWNTs. Figure 3.4 shows one of the first examples of SWNT self-assembly with gold nanoparticle. The shape of the assembled SWNTs was called ‘seven minute to three’ as the two SWNTs resemble the structure of long and short hands in a clock. In theory, SWNTs self-assembly with the structural directing fullerene end-capped linkers is similar to that of SWNTs/gold nanoparticle assembly. The main difference between the two is at the junction point. In the Smalley assembly, gold nanoparticle linkage at the centre of the junction whereas in fullerene linker’s case, only a short chain polymer (PEG) will be present (fullerenes are encapsulated inside SWNTs, will not show in AFM imaging). It is not expected to observe the polymer spacer in the middle of the junction since the chain may enter the SWNTs which can not be imaged. In SWNT/gold nanoparticle assembly, the SWNT junction could form in any direction. In the simplest case of SWNTs assembly with bis-fullerene end-capped linker, the flexible PEG chain allows SWNTs to be connected at any angle. Thus, the observed SWNT-SWNT angle (inter-SWNTs angle) should be variable (any hour, any minute). Comparing AFM micrographs before and after SWNTs self-
assembly, the degree of self-assembly could be identified (pristine SWNTs are unlikely to contain any SWNTs junctions).

AFM imaging can be carried out in either contact or tapping mode. In contact mode, the scanning tip is in constant contact with the surface and any SWNTs on the surface are likely to be pushed by the tip. Thus, all SWNTs imaging has been carried out using tapping mode. In tapping mode, the surface is divided into numerous points (depends on the required resolution) and the scanning tip only contact those designated points to map the whole surface. Therefore, any SWNTs on the surface will remain intact and the structure will not be affected. The diameter of the SWNTs were generally determined by the height profile of AFM micrographs as lateral distances on AFM micrograph are often unreliable as the SWNTs are significantly smaller than the scanning tip.

### 3.2.2.1 General Procedure of AFM Sample Preparation

SWNT dispersions / self-assembled dispersions with low concentration (less than 10 µg/ml) are required for AFM imaging. All dispersions in this study were prepared in N-methyl pyrrolidone (NMP). 3 µL of dispersion is drop cast onto a pre-cleaned (in piranha solution) silicon wafer surface (5 mm x 5 mm, Agar Scientific, UK). The wafers are then dried in vacuo (connected to Schlenk line) and heated to 200 °C overnight. AFM images were taken in tapping mode using a Digital Instruments Multimode VIII AFM with a Nanoscope IV controller. All AFM micrographs were recorded with a resolution of either 256 or 512 lines and typical scanning speed of 1 Hz. All AFM micrographs were processed using NanoScope Analysis version 1.40 (R2Sr), Bruker Corporation.
3.3 Thermal Gravimetric Analysis

As-synthesised SWNTs often contain various contaminants such as amorphous carbon, graphitic particle and metal catalysts. Although high resolution microscopy can identify these materials easily, it often requires lengthy sample preparation and it is hard to quantify. A quick analytical method to characterise these contaminants is thermal gravimetric analysis (TGA). In short, a SWNT sample is heated in a controlled environment (with controlled heating rate) in either air or inert gas (mostly nitrogen). Since SWNTs have a high thermal degradation temperature, amorphous carbon and graphitic particle are degraded at lower temperature. Whereas metal catalysts do not degrade and remain in the sample, the residual mass of the sample is, therefore, the metal content (in the form of metal oxide when carried out in air) of the SWNTs sample. As carbonaceous materials and SWNTs degrade at different temperature, the two species may be divided into two degradation features in the TGA curve (in reality, they often don’t resolve as the degradation temperatures are too close). Calculating the mass ratio between the two degradation curves gives information about the carbonaceous and SWNTs content.
Chapter 4 – Synthesis of Fullerene End-Capped PEG Linker Molecules

4.1 Justification of the Dumbbell Structure

Since the first priority of the project is to demonstrate the possibility of producing SWNT self-assembly with a structural directing fullerene end-capped linker, the first task is making the required linker molecule. To show the simplest SWNT-SWNT junction formation, a bis-fullerene end-capped linker (dumbbell) is needed. As discussed in Chapter 2, there are a number of reports in the literature of fullerene end-capped polymer with a relatively long chain spacer to separate the fullerene caps. Previous synthesis of bis-fullerene end-capped polyethylene (PEG) adduct was chosen as the initial linker molecule (See Figure 4.1). Since PEG is a common aliphatic polymer and various chain lengths are available commercially, this allows easy length modification to the fullerene linker molecule. In addition to the flexibility and widely available chain length, linear hydroxyl-terminated PEG can be easily converted into various functional groups if needed. In this case, the hydroxyl terminated PEG is converted into chloro-terminated PEG by reaction with thionyl chloride via a $S_n$ mechanism. The chloride is then substituted by azide via a $S_n2$ reaction. Then the azide attack fullerene surface via a 1,3-dipolar cycloaddition to produce the desired fullerene end-caps (See Figure 4.2 for reaction mechanism). Various publications have been reported using the same synthetic methodology to produce either mono- or bis-fullerene end-capped polymer adduct which suggests this method is reasonably well established. The main advantage of choosing this particular example is the ease of purification procedure. As shown in the literature review of fullerene functionalisation chemistry, it often takes numerous chromatography steps to separate out relatively low yield fullerene adduct. The separation of the resulting dumbbell fullerene linker molecule only required extraction in tetrahydrofuran (THF) and no lengthy column chromatography is involved.
Figure 4.1 – Proposed synthetic procedure for bis-fullerene end-capped polyethylene glycol via reaction of azido terminated linear PEG with fullerene C$_{60}$.

Figure 4.2 – Mechanism of the chemical transformation from hydroxyl-terminated PEG, OH-PEG-OH to Cl-PEG-Cl, then N$_3$-PEG-N$_3$ and eventually bis-fullerene end-capped PEG, C$_{60}$-PEG-C$_{60}$. Since bis-substituted telechelic PEG reacts in identical way for the two terminals, only one end is shown in the figure (R denoted the rest of the PEG chain with identical chemistry at the other end).

Three PEG chain lengths were chosen and employed in the synthesis of bis-fullerene end-capped linker.

The chosen PEG$_n$ are PEG$_{3350}$, PEG$_{1000}$, PEG$_{200}$ (n denoted the average molecular mass of the PEG,
manufacturer’s value). Using various PEG chain lengths generate linkers with different degree of fullerene separation which may have different effect in SWNT self-assembly.

4.2 Result and Discussion

\[
\begin{align*}
\text{HO-PEG-OH} & \xrightarrow{\text{SOCl}_2} \text{Cl-PEG-Cl} & \xrightarrow{\text{NaN}_3} \text{N}_3\text{-PEG-N}_3 & \xrightarrow{\text{C}_{60}} \left[1\right], \left[2\right] & \& \left[3\right]
\end{align*}
\]

\[\text{C}_{60}\text{-PEG}_{200}\text{-C}_{60}\]
\[\text{C}_{60}\text{-PEG}_{1000}\]
\[\text{C}_{60}\text{-PEG}_{3350}\]

45\% \quad [1]

59\% \quad [2]

86\% \quad [3]

**Figure 4.3** – Reaction scheme of the synthesis of both bis-fullerene end-capped linker (C\textsubscript{60}-PEG\textsubscript{200}-C\textsubscript{60}) and fullerene PEG diamond ring structure (C\textsubscript{60}-PEG\textsubscript{3350} \Rightarrow and C\textsubscript{60}-PEG\textsubscript{1000} \Rightarrow).

Despite the indications in the literature, the chosen synthetic methodology for the synthesis of bis-fullerene end-capped linkers resulted in an unexpected new geometry of the fullerene PEG adducts. The desired dumbbell structure was only successfully synthesised with PEG\textsubscript{200} to give C\textsubscript{60}-PEG\textsubscript{200}-C\textsubscript{60}. Unexpectedly, longer PEG chains produced closed ring structures (C\textsubscript{60}-PEG\textsubscript{3350} \Rightarrow and C\textsubscript{60}-PEG\textsubscript{1000} \Rightarrow) (diamond ring structure). The only variable in this synthesis is the chain length of the PEGs, the same
reaction condition were applied throughout the whole experiment. It suggests that the proposed synthetic procedure may not be applicable to any PEG chain length but predominantly the shorter PEG chain as the desired dumbbell was only produced with the shorter PEG<sub>200</sub>. A detailed analysis of the resultant products have been carried out in order to verify the relationship between PEG chain length and geometry of the final fullerene adducts. By understanding this reaction in more detail, modifications to the reaction condition/procedure might be applied to control the final fullerene adducts geometry.

The initial Cl–PEG<sub>3350</sub>–Cl and N<sub>3</sub>–PEG<sub>3350</sub>–N<sub>3</sub> derivatives were prepared following the procedure reported by Goh et al.<sup>158</sup>. The electronegativity difference of nitrogen compared to oxygen allows PEG-azide to be identified by <sup>1</sup>H NMR (see Figure 4.4 for <sup>1</sup>H NMR spectra of OH–PEG<sub>3350</sub>–OH, Cl–PEG<sub>3350</sub>–Cl and N<sub>3</sub>–PEG<sub>3350</sub>–N<sub>3</sub>), since the α–proton chemical shift for the N<sub>3</sub>–PEG<sub>3350</sub>–N<sub>3</sub> appears at 3.42 ppm (lit. 3.36 ppm)<sup>120</sup> compared to 3.75 ppm for OH-terminated PEG<sub>3350</sub>. The transformation of chlorides into azides is also confirmed by the presence of the azide stretching (ν<sub>asymmetric N<sub>3</sub></sub> 2095 cm<sup>−1</sup>) in FTIR (Figure 4.5)<sup>158</sup>. Further evidence for successful PEG end group transformations is provided by MALDI–TOF–MS (See Appendix for MALDI-TOF spectra of OH–PEG<sub>3350</sub>–OH, Cl–PEG<sub>3350</sub>–Cl and N<sub>3</sub>–PEG<sub>3350</sub>–N<sub>3</sub>); these data are especially helpful to monitor the transformation from hydroxyl to chloride due to the similar electronegativity of oxygen and chlorine which makes NMR assignment difficult. Isolated N<sub>3</sub>–PEG–N<sub>3</sub> was subsequently reacted with C<sub>60</sub> to afford C<sub>60</sub> end-capped PEG adducts<sup>158</sup>.
Figure 4.4 – $^1$H NMR spectra of OH–PEG$_{3350}$–OH, Cl–PEG$_{3350}$–Cl, N$_3$–PEG$_{3350}$–N$_3$ and PEG$_{3350}$–C$_{60}$ adduct (diamond ring). All spectra were recorded with $D1 = 1$ sec whereas the fullerene-C$_{60}$ adduct was recorded with $D1 = 20$sec (See Appendix A2 for $D1$).
Figure 4.5 – IR spectra of OH–PEG$_{3350}$–OH, N$_3$–PEG$_{3350}$–N$_3$ and PEG$_{3350}$–C$_{60}$ adduct (diamond ring).

With all spectroscopic analysis confirming the successful transformation from hydroxyl-terminated PEG to azido terminated PEG, the focus is now concentrated on the structural characterisation of the fullerene-PEG adduct. PEG$_{3350}$–C$_{60}$ adduct was chosen for main characterisation. As previous literature reported similar fullerene adducts prepared with PEG$_{2000}$ and PEG$_{5000}$, PEG$_{3350}$ used in this study would be an ideal candidate for the characterisation and comparison with literature. Another key factor has taken into account is the solubility of PEG$_{3350}$–C$_{60}$ adduct is significantly better than others due to the long PEG chain. Poor solubility has limited spectroscopic analysis (especially in NMR) in the case of PEG$_{1000}$ and PEG$_{200}$ fullerene adducts.
4.2.1 Characterisation of PEG$_{3350}$–C$_{60}$ Adduct, Diamond Ring or Dumbbell?

Initially, THF washing was used to isolate the PEG$_{3350}$–C$_{60}$ adduct from the crude mixture. However, weak absorption bands, characteristic for pristine C$_{60}$, at ca. 2000-2500 cm$^{-1}$ in FTIR spectrum of PEG$_{3350}$–C$_{60}$ adduct (THF washed) revealed the presence of unreacted C$_{60}$ in isolated PEG$_{3350}$–C$_{60}$ (Figure 4.5). These FTIR results suggested that THF extraction was not sufficient to isolate the PEG$_{3350}$–C$_{60}$ product, as pristine C$_{60}$ is not completely insoluble in THF (0.06 mg mL$^{-1}$). Instead, after THF extraction, the product was further extracted by water as PEG$_{3350}$–C$_{60}$ adduct is water soluble due to its long hydrophilic PEG chain. The FTIR spectrum of water extracted PEG$_{3350}$–C$_{60}$ adduct (Figure 4.5) confirmed removal of unreacted C$_{60}$. The FTIR analysis of PEG$_{3350}$–C$_{60}$ adduct (water extracted) also confirms successful azide addition by the complete loss of the characteristic azide absorption band at 2095 cm$^{-1}$ and the appearance of a medium intensity band at 1720 cm$^{-1}$ which is probably attributed to the aziridine ring (C-N) stretching (Figure 4.5). Free aziridine ring structure shows a (C-N) stretching at around 1650 cm$^{-1}$. Since the fullerene surface creates an unusual strain on the aziridine ring, the (C-N) stretching is shifted to higher wavenumber. The UV-vis spectrum of pure C$_{60}$ shows a characteristic UV-vis absorption maximum at 336 and 409 nm, whilst the PEG itself is featureless in the range measured (Figure 4.6). Once the PEG$_{3350}$–C$_{60}$ adduct is formed, the characteristic C$_{60}$ absorption band blue shifts by 8 nm to 324 nm, confirming a covalent attachment between pristine C$_{60}$ and N$_3$–PEG$_{3350}$–N$_3$. Such a shift in the UV-vis spectrum is a characteristic for fullerene bis-adduct (fullerene mono-adduct shows similar absorption profile as pristine C$_{60}$). Eight possible regioisomers (See Figure 4.7) can be formed in fullerene bis-adduct grafting reaction. Detailed UV-vis analysis has been reported for bis-fullerene adducts and only the trans-1 bis-adduct has a similar blue shift in the UV-vis spectrum. In contrast, all the other seven bis-adduct regioisomers (trans-2, trans-3, trans-4, equatorial, cis-3, cis-2, and cis-1) formed during the reaction condition were reported to display absorption maxima at around 400-700 nm which is well-above the observed 328 nm.
Figure 4.6 – UV-vis Spectra of PEG\textsubscript{3350}, pristine fullerene C\textsubscript{60}, PEG\textsubscript{3350}–C\textsubscript{60} adduct and C\textsubscript{60}–PEG\textsubscript{200}–C\textsubscript{60} (dumbbell). All spectra were recorded in toluene.

Figure 4.7 – Possible regioisomers of fullerene bis-adducts.
Further evidence for the formation of the symmetrical bis-adduct is provided by $^1$H NMR spectroscopy (Figure 4.4). Compared to the parent polymer (PEG$_{3350}$), the $^1$H NMR spectrum of the PEG$_{3350}$–C$_{60}$ diamond ring shows two new signals at 4.45 and 3.80 ppm, associated with the new bond formation. Due to the conjugated, but not superaromatic π-system, protons closer to the C$_{60}$ surface are de-shielded$^{163}$. Hence, the most de-shielded new signal, at 4.45 ppm, is assigned to α–protons and the other signal at 3.80 ppm to the β–protons (Figure 4.4). The $^1$H NMR spectroscopic results suggest that the bis-addition of N$_3$–PEG$_{3350}$–N$_3$ to C$_{60}$ is symmetrical since only one set of α– and β–protons are observed. As in the case for the bis-addition of azomethine ylides to C$_{60}$$^{162}$, the $^1$H NMR spectrum of bis-adducts formed is consistent with trans–1 addition to C$_{60}$. In theory, the integral ratio of α–protons and β–protons is expected to be 1:1. Although the observed ratio (β / α= 1.2) is close to expected value it was slightly affected by the contribution of the main PEG backbone satellite that appears at the same chemical shift as the β–proton. Unfortunately, no $^{13}$C NMR was recorded which was probably due to long relaxation times$^{164}$.

Overall, the $^1$H NMR spectroscopic data, supported by FTIR and UV-vis, indicate successful covalent bis-addition of N$_3$–PEG$_{3350}$–N$_3$ to C$_{60}$. In addition, MALDI-TOF-MS was used to confirm that the diamond ring (C$_{60}$–PEG $\supset$) geometry formed in preference to the dumbbell (C$_{60}$–PEG$_{3350}$–C$_{60}$) structure; a low laser intensity (90mW) was used to minimize any fragmentation of the polymer chain or dissociation of terminal C$_{60}$ molecules. The mass spectrum of PEG$_{3350}$–C$_{60}$ adduct shows a Gaussian distribution of positively charged ions ranging from m/z 2297 to 4720 (Figure 4.8). Assuming an average of sixty five ethylene oxide repeating units for the chain, the theoretically expected masses ([M+Na]$^+$) for diamond ring (C$_{60}$–PEG$_{3350}$ $\supset$) and dumbbell (C$_{60}$–PEG$_{3350}$–C$_{60}$) can be calculated as 3660.73 and 4380.73 Da, respectively (the signal corresponded to sixty five repeating units is the most intense signal in the starting PEG$_{3350}$ mass distribution, see Appendix for full MALDI-TOF spectrum of PEG$_{3350}$). It is clear from the mass spectrum that the reaction of N$_3$–PEG$_{3350}$–N$_3$ with excess C$_{60}$ does not yields a dumbbell structure (C$_{60}$–PEG$_{3350}$–C$_{60}$); rather, the data indicates the formation of a diamond ring structure (single
fullerene), at around 720 Da \( (C_{60} = 720\) Da) less than that of the theoretically expected mass of \( C_{60} \cdot PEG_{3350} \cdot C_{60} \). Close inspection of positively charged ions ranging from 2297 to 4720 \( m/z \) (Figure 4.9) indicate that the observed mass values are not related to fragmentation of the dumbbell structure as the molecule still contain the full chain of PEG. This finding is further supported by elemental analysis (EA) of the \( PEG_{3350} \cdot C_{60} \) adduct which shows a composition of C \( (60.23\) wt\%) and H \( (7.25\) wt\%) with a C:H ratio of 8.31; the calculated composition for the diamond ring structure (assuming 65 repeating units) is C \( (63.35\) wt\%) and H \( (7.31\) wt\%); which gives a C:H ratio of 8.67; the calculated value for the dumbbell structure is C \( (69.41\) wt\%) and H \( (6.10\) wt\%) and the C:H ratio is 11.38. Only the diamond ring C:H ratio is in good agreement with the experimental value.

**Figure 4.8** – MALDI-TOF spectrum of \( C_{60} \cdot PEG_{3350} \).
The MALDI and EA confirm the formation of a mono-fullerene substituted PEG\textsubscript{3350}–C\textsubscript{60} adduct. The simplicity of the \textsuperscript{1}H NMR spectrum indicates the adduct is a symmetrical molecule which structurally could only be explained by a diamond ring (\( \text{C}_{60}^{\text{PEG3350}} \Rightarrow \)) structure in \textit{trans}-1 conformation. Other mono-fullerene substituted linear PEG\textsubscript{3350} chains bearing azide (C\textsubscript{60} – PEG\textsubscript{3350} – N\textsubscript{3}), amine (C\textsubscript{60}–PEG\textsubscript{3350}–NH\textsubscript{2}) or hydroxyl (C\textsubscript{60}–PEG\textsubscript{3350}–OH) end-groups can also be ruled out as follows. Whilst these alternatives vary only slightly in mass, a detailed comparison of the possible masses is only consistent with a diamond ring structure (See Table 4.1 for calculated masses for C\textsubscript{60}–PEG\textsubscript{3350}–N\textsubscript{3}, C\textsubscript{60}–PEG\textsubscript{3350}–NH\textsubscript{2} and C\textsubscript{60}–PEG\textsubscript{3350}–OH). More importantly, these fullerene-PEG derivatives would show two sets of protons signal with equal intensities correspond to the two asymmetric terminals in \textsuperscript{1}H NMR spectroscopy, but only 1 set of signals was observed. The simplicity of the \textsuperscript{1}H NMR spectrum indicates the adduct is a symmetrical molecule which structurally could only be explained by a diamond ring (\( \text{C}_{60}^{\text{PEG3350}} \Rightarrow \)) structure in \textit{trans}-1 conformation. Furthermore, the experimental isotopic pattern for the sixty five ethylene oxide repeating unit peak ([M+Na]\textsuperscript{+} = 3660.73 Da) closely matches the theoretical monoisotopic peak pattern of the diamond ring (Figure 4.9). A control experiment without fullerene showed that the pure N\textsubscript{3}–PEG\textsubscript{3350}–N\textsubscript{3} did not decompose to amine when heated under identical conditions, as monitored by FTIR. Furthermore, a ninhydrin test on the C\textsubscript{60}–PEG\textsubscript{3350} adduct found no primary amine.
Table 4.1 – Comparison of calculated monoisotopic mass (with 65 repeating units) of possible derivatives to $\text{C}_6\text{O}_{\text{PEG3350}}$.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Empirical formula (65 repeating units + Na$^+$)</th>
<th>Calculated monoisotopic mass (65 repeating units + Na$^+$)</th>
<th>Mass difference to diamond ring $\text{C}<em>6\text{O}</em>{\text{PEG3350}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}<em>6\text{O}</em>{\text{PEG3350}}$</td>
<td>$\text{C}<em>{192}\text{H}</em>{264}\text{N}<em>2\text{O}</em>{65}\text{Na}$</td>
<td>3660.7310</td>
<td>-</td>
</tr>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>$\text{C}<em>{192}\text{H}</em>{265}\text{NO}_{66}\text{Na}$</td>
<td>3663.7307</td>
<td>3</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>$\text{C}<em>{192}\text{H}</em>{266}\text{N}<em>2\text{O}</em>{65}\text{Na}$</td>
<td>3662.7467</td>
<td>2</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>$\text{C}<em>{192}\text{H}</em>{264}\text{N}<em>4\text{O}</em>{65}\text{Na}$</td>
<td>3688.7372</td>
<td>28</td>
</tr>
</tbody>
</table>
4.2.2 Characterisation of PEG\textsubscript{1000}-C\textsubscript{60} and PEG\textsubscript{200}-C\textsubscript{60} Adducts

In the case of N\textsubscript{3}-PEG\textsubscript{1000}-N\textsubscript{3}, the adduct was isolated using THF extraction (×3) since it was insoluble in water probably due to shorter PEG chain length compared to PEG\textsubscript{3350}. The MALDI-TOF spectrum of the PEG\textsubscript{1000} adduct displayed a Gaussian distribution of positively charged ions in the range of 1400 – 2000 m/z, centred around the theoretically expected mass for the diamond ring PEG\textsubscript{1000} adduct ([M+Na]\textsuperscript{+}); the experimental monoisotopic peak pattern for the adduct with 20 ethylene oxide repeating units (the most intense signal in the starting PEG\textsubscript{1000} mass distribution) ([M+Na]\textsuperscript{+} = 1679.55) was consistent with the formation of diamond ring (C\textsubscript{60}\textsubscript{PEG\textsubscript{1000}} \rightarrow).
The only difference between $\text{C}_{60}$-PEG$_{1000}$ and $\text{C}_{60}$-PEG$_{3350}$ is the length of the polymer backbone. However, the longer PEG chain offers a benefit in purification. As mentioned above, THF alone was not sufficient to remove all unreacted fullerene. Having a relatively long PEG chain in the fullerene/PEG adducts (PEG$_{3350}$) makes the adduct water soluble, simplifying the complete removal of free fullerene since pristine C$_{60}$ is insoluble in water.

Unlike the longer PEG–C$_{60}$ analogues ($\text{C}_{60}$-PEG$_{1000}$ and $\text{C}_{60}$-PEG$_{3350}$), the PEG$_{200}$–C$_{60}$ adduct was not easily isolated by extracting with water or washing with THF. The short PEG$_{200}$ chain, accentuated by bis-addition of fullerene, makes the adduct insoluble in both water and THF. In contrast to the PEG$_{3350}$ and PEG$_{1000}$ products, the mass spectrum of the isolated PEG$_{200}$–C$_{60}$ adduct (Figure 4.11) showed no peaks related to diamond ring ($\text{C}_{60}$-PEG$_{200}$) formation, around the theoretically expected mass range.
(975.13 m/z for four ethylene oxide repeating units). Instead, a Gaussian mass distribution of positively charged ions ranging from 1100 to 2300 m/z was observed, consistent with the formation of dumbbell structure ($\text{C}_{60}\text{–PEG}_{200}\text{–C}_{60}$).

![MALD-TOF spectrum of C$_{60}$-PEG$_{200}$-C$_{60}$ (diamond ring). (*) indicate the expected position for the PEG$_{200}$-C$_{60}$ (diamond ring) but no signal in that region was observed.](image)

**Figure 4.11** – MALD-TOF spectrum of $\text{C}_{60}\text{–PEG}_{200}\text{–C}_{60}$ (diamond ring).(*) indicate the expected position for the PEG$_{200}$-C$_{60}$ (diamond ring) but no signal in that region was observed.

Clearly the PEG chain length determines the molecular structure of the resulting PEG–C$_{60}$ adducts. Simple space filling models of $\text{C}_{60}\text{–PEG}_{200}\text{–C}_{60}$ and $\text{C}_{60}\text{–PEG}_{200}\text{–C}_{60}$ based on four ethylene oxide repeating units show that the PEG$_{200}$ chain is insufficiently long enough to wrap around the fullerene for trans–1 addition (Figure 4.12). In this case, with diamond ring formation suppressed, dumbbells are favoured.
Previous literature suggesting selective synthesis of fullerene bis-adduct could be achieved by a huge excess of grafting species in reaction (1:10 equivalent of starting C$_{60}$ and grafting species)$^{162}$. In the preparation of both diamond rings and dumbbells, 20 equivalent of C$_{60}$ were used in the reaction in order to force the reaction to mono-adduct, dumbbell structure. Despite the large excess of C$_{60}$ available during the reaction, PEG with longer chain lengths did not react to give the dumbbell structure, but the diamond ring. Most previously reported fullerene bis-adducts were synthesised with two individual substituents, therefore, could not be classified as diamond ring since the substituents are not covalently connected$^{130}$. Recent example suggested that it is possible to get a diamond ring structure but only if specific protective groups are used during the synthesis$^{165}$. All our spectroscopic data strongly supported the trans-1 diamond ring conformation. Since previous literature of bis-adduct formation was carried out with azeomethine ylide addition$^{162}$ instead of azide click reaction, reaction outcome could be very different. In addition, previous bis-adducts did not encounter the long chain PEG substituent in the synthesis. It could be due to the highly tangled PEG chain is sterically hindered which make the second
azide addition difficult to take place on other position on the fullerene but only on the opposite position to give the trans-1 bis-adduct.

4.3 Conclusion

Both diamond ring and dumbbell structures were successfully synthesised using the click reaction of N$_3$-PEG–N$_3$ with C$_{60}$. The final structure of the polymer-fullerene adducts is determined by the polymer chain length. Previous studies had assumed a dumbbell structure would be formed for all bis-azido terminated PEG reactions with fullerene, but without sufficient spectroscopic evidence to identify the final structure fully. Experimental data shows that it is necessary to perform detailed characterisation, particularly using MALDI (and supported by EA) to establish the structure. In fact, diamond ring structures dominate, except where they are sterically frustrated by the shortness of the linking PEG chain.

Although the shorter PEG$_{200}$ produce dumbbell structure is still suitable for self-assembly purpose, this method may not be suitable to produce higher order fullerene end-capped linkers such as tris- or tetrakis- fullerene end-capped linkers for higher order SWNTs self assembly. It seems like any polymer chain grafting involves direct functionalisation of fullerene surface may result in similar problem due to both polymer chain dynamic and reactivity of fullerene issue.

4.4 Experimental

C$_{60}$ (purity > 99%) was obtained from SES Research, Houston, USA. PEG with Mn = 200, 1000, 3350 Da were purchased from Sigma Aldrich and azeotropically dried overnight using toluene. Azeotropic distillation was performed with Dean-Stark trap and reflux condenser under N$_2$. As water is denser than toluene, residual water is trapped in the bottom of the Dean-Stark trap. Thionyl chloride (≥ 99.5%) was obtained from Fluka. Thin layer chromatography (TLC) was carried out with aluminium plate covered with silica gel (silica gel 60 F254, unmodified, Merck). All other solvents were purchased from VWR and used without further purification.
Synthesis of Cl–PEG–Cl and N₃–PEG–N₃

Cl–PEG–Cl and N₃–PEG–N₃ were synthesized following the literature procedure reported by Goh et al.\textsuperscript{158}.

In brief, the bis-hydroxyl terminated PEG was first converted to bis-chloro terminated PEG (Cl–PEG–Cl) by reaction with thionyl chloride. The Cl–PEG–Cl was then reacted with sodium azide to afford bis-azido terminated PEG (N₃–PEG–N₃).

Synthesis of C₆₀ terminated PEG₃₃₅₀ diamond ring (C₆₀\textsubscript{PEG₃₃₅₀} →)

Azido terminated PEG₃₃₅₀ (0.1g, 1eq) was dissolved in 15 ml of o-dichlorobenzene in a 2-necked 50 ml round bottom flask fitted with a condenser and connected to vacuum line. C₆₀ (0.43g, 20eq) was dissolved in 20 ml of o-dichlorobenzene and transferred into a pressure equalising dropping funnel and fitted to the round bottom flask. The C₆₀ solution was then added drop wise into the stirred PEG solution. The mixture was then heated to 140°C and stirred for 24 hours. Solvent was evaporated \textit{in vacuo} and 50 ml of THF was added to the remaining solid. The THF solution was stirred at room temperature overnight and filtered under gravity to yield a dark brown solid. The solid was then dissolved in 20 ml of water to give a yellow solution and unreacted C₆₀ was filtered off under gravity. The water was evaporated \textit{in vacuo} and the solid was then freeze dried \textit{in vacuo} to yield dark brown solid C₆₀\textsubscript{PEG₃₃₅₀} (0.08g, 86%).

Characterisation Data for C₆₀\textsubscript{PEG₃₃₅₀}:

Rᵣ=0.26 toluene/methanol (9/1 v/v). \textsuperscript{1}H NMR (400 MHz, CDCl₃, D1 20 sec): δ 4.48 (t, 4H, J = 4Hz, C₆₀–CH₂–CH₂–O–), 3.80 (t, 4H, J = 4Hz, C₆₀–CH₂–CH₂–O–) ppm. FT-IR (ATR) ν/cm⁻¹: 3462, 2889, 2871, 1728, 1468, 1361, 1342, 1281, 1242, 1150, 1102, 1062, 961 and 843. MALDI-TOF m/z: C₁₉₂H₂₆₄O₆₅N₂Na [M+Na]+ Calcd. 3660.7310, found 3660.9 Da. Anal Calcd. For C₁₉₂H₂₆₄N₂O₆₅: C, 63.33; H, 7.31; N, 0.77; O, 28.58. Found: C, 60.23; H, 7.25; N, 0.90; O, 31.62. All values are given as percentages.
Synthesis of $\text{C}_{60}$ terminated PEG$_{1000}$ diamond ring ($\text{C}_{60}^{\text{}_{\text{PEG1000}}} \supseteq$)

The $\text{C}_{60}$ terminated PEG$_{1000}$ was synthesised following the same procedure described above for $\text{C}_{60}^{\text{}_{\text{PEG3350}}} \supseteq$. The resulting crude product after solvent removal was extracted by THF (3 x) since it was not water soluble. Removal of THF in vacuo afforded dark brown solid $\text{C}_{60}^{\text{}_{\text{PEG1000}}} \supseteq$ (0.056, 59%).

Characterisation Data for $\text{C}_{60}^{\text{}_{\text{PEG1000}}} \supseteq$.

\[ R_f = 0.34 \text{ toluene/methanol (9/1 v/v). } \]

FT-IR (ATR) $\nu$/cm$^{-1}$: 3391, 2972, 2877, 1729, 1463, 1431, 1384, 1353, 1292, 1249, 1184, 1105, 1044, 954, 856 and 752. MALDI-TOF $m/z$: $\text{C}_{102}\text{H}_{84}\text{O}_{20}\text{N}_2\text{Na} [\text{M+Na}]^+$ Calcd. 1679.5515, found 1679.0 Da.

Synthesis of $\text{C}_{60}^{\text{}_{\text{PEG200}}} \text{PEG} - \text{PEG} - \text{C}_{60}$

The $\text{C}_{60}$–terminated PEG$_{200}$ was synthesised following the same procedure described above for $\text{C}_{60}^{\text{}_{\text{PEG3350}}} \supseteq$. The resulting crude product was purified by silica gel column chromatography with toluene/methanol (9/1 v/v) as eluent, giving $\text{C}_{60}^{\text{}_{\text{PEG200}}} - \text{PEG} - \text{C}_{60}$ (0.04g, 45%) as dark brown solid.

Characterisation Data for $\text{C}_{60}^{\text{}_{\text{PEG200}}} - \text{PEG} - \text{C}_{60}$.

\[ R_f = 0.55 \text{ toluene/methanol (9/1 v/v). } \]

FT-IR (ATR) $\nu$/cm$^{-1}$: 3404, 2936, 2883, 1738, 1642, 1431, 1360, 1183, 101 and 729. MALDI-TOF $m/z$: $\text{C}_{130}\text{H}_{20}\text{O}_4\text{N}_2\text{Na} [\text{M+Na}]^+$ Calcd. 1607.0796, found 1605.1 Da.
Chapter 5 – Synthesis of Poly and Monodisperse Branched Fullerene End-Capped Linkers

5.1 PCBM as Starting Material

Since the previous synthetic method is only suitable for short chain length polymer, an alternative method to produce structurally well-defined fullerene end-capped linker is desperately needed. As shown in chapter 4 and various literatures, covalent functionalisation of pristine fullerene often results in bis- or multiple adducts\textsuperscript{130,162}. Direct grafting onto fullerene surface, therefore, should be avoided as separation of the desired mono-adduct from the reaction mixture could be extremely difficult. Since the discovery of fullerene\textsuperscript{1} in 1985, a number of fullerene applications have been proposed\textsuperscript{166}. One of the most studied applications is the incorporation of fullerene into materials for photovoltaic (PV) application, particularly in polymer based bulk heterojunctions (BHJ) solar cells\textsuperscript{167-170}. However, pristine fullerene C\textsubscript{60} low solubility and processability in common organic solvents has limited their direct use in solution. Thus, a wide range of chemistry of fullerene has been developed and various fullerene derivatives with enhanced solubility have been reported\textsuperscript{171-177} (also see chapter 2 for fullerene functionalisation). However, it is very important to preserve the electronic property of pristine C\textsubscript{60} while increasing the solubility. To avoid losing the electronic property of fullerene, the degree of functionalisation should be kept to minimal, single grafting to give mono-functionalised adducts. For all these reasons, Phenyl-C\textsubscript{61}-butyric-acid-methyl-ester (PCBM)\textsuperscript{80} has been developed and it can be found in almost all the BHJ solar cells. As a result, this material is now available commercially. Since an ester moiety is already grafted onto the fullerene surface to give a mono-adduct, further functionalisation could be achieved by direct modification to the ester without affecting the rest of the fullerene surface.

Since then, various fullerene derivatives have been prepared using PCBM as a starting material. In general, the PCBM ester is first hydrolysed (by acetic acid / trifluoroacetic acid, TFA) to give carboxylic
acid (phenyl-C_{61}-butyric-acid, PCBA). It is then converted to acid chloride (by reacting with SOCl\(_2\)) for further condensation via nucleophilic addition\(^{178}\).

There are various ways to incorporate a PEG chain onto a PCBM molecule. Direct condensation between hydroxy-terminated PEG with the acid chloride derivative of PCBM is one of the easiest method. Thus, a hydrolysis of PCBM has been carried out in order to produce the acid chloride derivative of the PCBM. However, the resulting PCBA was found to be almost insoluble in most organic solvents (only sparingly soluble in o-DCB and CS\(_2\)) which limit further characterisation. Thus an alternative synthetic route is needed to avoid the formation of insoluble PCBA. Since PCBM contains a simple methyl ester and PEG contains primary alcohol groups, the two could be reacted together in a simple transesterification reaction. Hence, a simple acid catalysed transesterification of PCBM and linear bis-hydroxyl terminated PEG was attempted in order to produce bis- fullerene end-capped PEG linker. Despite having excess PCBM and prolonged reflux (3 days) in toluene, the two starting materials were collected without any structural changes. Alternative transesterification route was needed in order to avoid multiple reaction steps in the synthesis. A dibutyltinoxide (DBTO) catalysed was therefore employed in the synthesis of fullerene end-capped linkers.

Unlike the azide addition to fullerene where only short chain polymer gives the desired mono-adduct, the functionalisation via ester linkage in PCBM offers a wider flexibility and control in the synthesis of multi-fullerene end-capped linkers. Since there is only one reactive ester in PCBM molecule, the geometry of the fullerene linker could be solely controlled by using linear / branched PEG core with multiple hydroxyl terminated arms. This synthetic route could be easily employed in the synthesis of a new range of fullerene linkers with various number of fullerene caps which might be useful in the self-assembly of SWNTs. A linear PEG with two hydroxyl groups would give a bis-fullerene end-capped linker. Whereas a star shape PEG with multiple arms having hydroxyl terminals could be used to make a multi-fullerene end-capped linker. This specific synthetic procedure was originally proposed by Kronholm et al. to produce cyclic PCBM necklace\(^{179}\). Unlike the PCBA route where multiple reactions are required, direct
transesterification provide a one-pot synthesis strategy for the fullerene linker molecule. Therefore, this method has a great potential to become a standardised method in fullerene linker preparation.

5.2 Synthesis of mono-, bis-, tris & tetrakis Fullerene End-capped PEG Linkers

In order to make various multiple fullerene end-capped linkers for the SWNTs self-assembly, a range of PEGs core have been selected as the core for the linkers. Mono-fullerene linker was synthesised from a simple propoxyethanol to mimic a short PEG chain for control experiment purpose. Bis-fullerene PEG linker was synthesised from linear bis-hydroxyl terminated PEG. Whereas more sophisticated tris- and tetrakis-fullerene linkers were synthesised from the corresponding three and four arms PEG stars. SWNTs supramolecular self-assembly with these four linkers should allow a complete investigation of the process. Each linker should give unique self-assembled SWNTs structure. Mono-fullerene linker should not promote any self-assembly. Bis-fullerene linker should give a linear SWNTs chain. Tris- and tetrakis-fullerene linkers should give a 2D and 3D SWNTs network respectively.
Figure 5.1 – Reaction scheme of mono-, bis-, tris- and tetrakis-fullerene end-capped linkers.

Reaction condition: 1.1 eq PCBM to -OH, 0.11 eq DBTO to -OH, o-DCB, 140°C, N₂, 5 days

2-Propoxyethanol, 1  PEG₄(OH)₂, 2  PEG₂₁(OH)₃, 3  PEG₁₅(OH)₄, 4  DBTO

\[ \text{PEG}_{4}(\text{OPCB})_2, 6 \]
\[ \text{PEG}_{21}(\text{OPCB})_3, 7a \quad \text{PEG}_{21}(\text{OPCB})_2(OH), 7b \]
\[ \text{PEG}_{15}(\text{OPCB})_4, 8a \quad \text{PEG}_{15}(\text{OPCB})_3(OH), 8b \]
5.3 Result and Discussion

5.3.1 Characterisation of mono-fullerene End-capped PEG Linker

Since the mono-fullerene linker, Phenyl-C_{61}-butyric-acid-propoxyethyl-ester, (PrOEt-OPCB [5], OPCB denote the linkage attached via oxygen in ester) was prepared from PCBM and a simple alcohol, the mono-linker was easily purified by column chromatography using Tol/MeOH 9:1 (unreacted PCBM was removed by pure toluene). The presence of the fullerene/propoxy ethyl ester linkage was confirmed by $^1$H NMR spectroscopy where newly formed methylenes (adjacent to ester) signal at 4.25 ppm (See Figure 5.3).

Figure 5.2 – $^1$H NMR spectrum of propoxyethanol
Figure 5.3 – $^1$H NMR spectrum of PrOEtOPCB. Protons (j & k) were masked by the water and vacuum grease signal between 0.87 – 1.63 ppm.

Unlike the characterisation of mono-fullerene linker, the confirmation of the other fullerene linkers is more complicated. In principle, the extent of the transesterification reaction can be determined by the ratio of the chain terminal resonances to the polymeric backbone. However, an accurate assessment of this ratio for the starting PEGs is needed as a reference. Unfortunately, the resonances corresponding to protons (alpha proton, α) adjacent to the terminal hydroxyl groups overlap with the PEG backbone as the chemical environment of the alpha position is identical to the backbone (attached to oxygen directly). To establish a suitable control and confirm the nature of starting materials, each starting PEG$_x$(OH)$_n$ was treated with highly reactive trifluoroacetic anhydride (TFFA)/CDCl$_3$ (1:19 v/v) in an NMR tube to give the corresponding per-acylated PEG$_x$(OCOCF$_3$)$_n$ derivative in situ$^{180}$. 
5.3.2 Characterisation of Starting PEGs

The electronegative trifluoroacetyl substituent deshielded the adjacent acyloxymethylene protons (alpha proton, α), $\text{F}_3\text{CCO}_2\text{CH}_2\text{CH}_2\text{O}$, giving a signal at ca. 4.51 ppm well resolved from the PEG backbone. Thus, the average number of repeating units of each PEG compound was obtained from the integral ratio of the acyloxymethylene protons to the main PEG signals (see Figure 5.4 – 5.6) and found to be 4, 21 & 15 for bis-OH, tris-OH and tetrakis-OH terminated PEGs respectively. The $^1\text{H}$ NMR spectroscopic findings for tris- and tetrakis-OH are consistent with the weight distributions in the MALDI spectra of the pure PEG cores (See Figure 5.7 – 5.8 for MALDI-TOF of PEG$_{-21}(\text{OH})_3$ and PEG$_{-15}(\text{OH})_4$).

![Figure 5.4 – $^1\text{H}$ NMR spectrum of PEG$_{-4}(\text{OCOCH}_3)_2$ (n ~ 3).](image-url)
Figure 5.5 – $^1$H NMR spectrum of PEG$_{21}$(OCOCF$_3$)$_3$ ($n_1 + n_2 + n_3 \sim 20$).

Figure 5.6 – $^1$H NMR spectrum of PEG$_{15}$(OCOCF$_3$)$_4$ ($n_4 + n_5 + n_6 + n_7 \sim 13$).
Figure 5.7 – MALDI-TOF spectrum of PEG$_{21}$(OH)$_3$.

Figure 5.8 – MALDI-TOF spectrum of PEG$_{15}$(OH)$_4$. 
However, in the $^1$H NMR spectrum of PEG$_{15}$(OCOCF$_3$)$_4$ (Figure 5.6), there is an extra signal at 4.42 ppm, adjacent to the $\alpha$ proton signal. This signal which must be generated by acylation of terminal hydroxyl with TFAA, implies that the tetrakis-OH terminated PEG contains a distinctive second species. Most likely, a fraction of the molecules contain a CH$_2$-OH stub, directly linked to the central sp$^3$ carbon, rather than through an ether linkage (Figure 5.1 in 4, one of $n_{4/5/6/7} = 0$). To confirm this hypothesis, a $^{13}$C NMR spectrum was recorded for PEG$_{15}$(OCOCF$_3$)$_4$ (Figure 5.9). Two singlets at around 45-46 ppm are in the range of the single quaternary carbon expected at the centre of the starting PEG$_{15}$(OH)$_4$; the extra signal indicates that there is a quaternary centre having a short arm. The $^{13}$C DEPT 135° (distortion enhancement by polarisation transfer) NMR spectrum of PEG$_{15}$(OCOCF$_3$)$_4$ (Figure 5.10) only showed the main PEG signals, the two singlets at around 45-46 ppm were not observed, consistent with the explanation that they correspond to two quaternary centres. Due to the similarity in the polarity of both species, it is difficult to separate them. Since PCBM is a bulky molecule, a relatively longer side chain should assist the grafting reaction; steric effects may prevent fullerene attaching onto short side chains, particularly on the CH$_2$OH stub.

![Diagram](image_url)

**Figure 5.9** – $^{13}$C NMR spectrum of PEG$_{15}$(OCOCF$_3$)$_4$.  

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5.3.3 Characterisation of Multi-Fullerene End-Capped Linkers

Similar to that of mono-fullerene linker, the $^1$H NMR spectrum of PEG$_{5}$ OPCB$_2$ (Figure 5.11) showed a new signal at 4.25 ppm corresponding to the $\alpha$ proton of the new species (adjacent to the newly formed ester linkage). Further support to this NMR finding was given by the MALDI-TOF spectrum. The mass spectrum of PEG$_{5}$ OPCB$_2$ (Figure 5.12) verified the formation of doubly transesterified PEG$_{5}$ (OH)$_2$, showing four main clusters of positively charged [M+Na]$^+$ ions ranging from 1970 to 2160 m/z ($n = 4$ to 7), where each peak region corresponds to the bis-fullerene end-capped PEG dumbbells with differing numbers of ethylene oxide repeat units. Considering the penta-ethylene oxide repeat unit cluster in detail (Figure 5.12), the experimental isotopic peak pattern of PEG$_{5}$ OPCB$_2$ was consistent with the simulated pattern across all expected masses, from $[\text{M+Na}]^+_{\text{obs}} = 2017.23$, $[\text{M+Na}]^+_{\text{calc}} = 2017.21$. 

Figure 5.10 – $^{13}$C DEPT 135° NMR spectrum of PEG$_{15}$ (OCOF$_3$)$_4$. 

![Figure 5.10](image-url)
Figure 5.11 – $^1$H NMR spectrum of PEG$_4$(OPCB)$_2$.

Figure 5.12 – MALDI-TOF spectrum of PEG$_4$(OPCB)$_2$. (Right) : Observed (top) and calculated (bottom) isotopic pattern for PEG$_4$(OPCB)$_2$. 
Purification of both tris- and tetrakis-fullerene adducts were performed by successive column chromatography. Since PEG is known to have a strong adhesion to silica gel, any unreacted PEG remains in the column and is eluted as the last fraction. The polarities of the molecules decrease with increasing number of covalently grafted non-polar fullerenes. Hence, after the removal of unreacted PCBM, the fully substituted adducts in both tris- and tetrakis-fullerene PEG stars are eluted first using Tol/MeOH 9:1 v/v mixture. The fraction of methanol was kept constant during chromatography in order to prevent possible hydrolysis of the newly formed ester linkages. All detailed analyses were carried out with these first eluted fractions from column chromatography.

Figure 5.13 – MALDI-TOF spectrum of PEG\textsubscript{21}(OPCB)\textsubscript{3}

The MALDI spectrum of PEG\textsubscript{21}(OPCB)\textsubscript{3} (figure 5.12) clearly confirmed the successful formation of the tris-fullerene linker (mean peak distribution at 3630 m/z), however, two other distributions (mean peak
distribution at around 2752 and 1741 m/z) were also observed in the spectrum. As shown in the starting PEG-21(OH)₃ MALDI spectrum (Figure 5.7), the polymer contain an average of 21 repeating units (highest intensity at 21 repeating units). In order to identify the associated mono- and bis-fullerene adduct distribution, a direct comparison of the distribution mass to the corresponding number of repeating units was constructed.

Figure 5.14 – Comparison of the observed mass distributions in PEG-21(OPCB)₃ MALDI.

As shown in Figure 5.14, the distributions centred at 3630 and 2752 m/z correspond to the tris- and bis-fullerene substituted PEG-21(OH)₃ as the number of repeating units did not change during the reaction. However, the distribution centred at 1741 m/z is within the range of a mono-fullerene substituted PEG-21(OH)₃ with 17 repeating units. The high polydispersity of 3-armed PEG triol made chromatographic purification of fullerene end-capped PEG adducts PEG-21(OPCB)₃ very difficult, compared to the PEG-5(OPCB)₂ derived from the relatively well-defined PEG-5(OH)₂. The variations in
PEG molecular weight smeared the variation in polarity associated with bis- and tris-substituted fullerene species. Thus, mono-fullerene substituted 3-arms PEG with shorter arms length could in principle be eluted out from the column as shorter chain length reduced the polarity of the molecules. However, close inspection of the monoisotopic pattern of the 1741 m/z signal was made and compared to the calculated monoisotopic pattern of PEG$_{17}$(OPCB)(OH)$_2$. Figure 5.15 clearly showed that the observed monoisotopic pattern does not match with the calculated signal which suggests the mass distribution centred at 1741 m/z does not correspond to the mono-fullerene substituted PEG$_{21}$(OH)$_3$ but the result of fragmentation of higher substituted products within the MALDI.

Figure 5.15 – Comparison of the observed (top) monoisotopic pattern 1740 m/z signal in PEG$_{21}$(OPCB)$_3$ MALDI to the calculated (bottom) monoisotopic pattern of PEG$_{17}$(OPCB)(OH)$_2$.

The MALDI spectrum of tris-fullerene polymer suggests it is a mixture of both bis- and tris-fullerene end-capped three arms PEG (the mono-fullerene distribution is the result of fragmentation). The signal intensity between the two distributions indicated there is a 86 : 14 ratio between PEG$_{21}$(OPCB)$_2$(OH) and PEG$_{21}$(OPCB)$_3$. As the MALDI signal intensity may not always reflect molecular abundance, the ratio was also determined from the integration of the signals in the $^1$H NMR spectrum.
In the $^1$H NMR spectrum of PEG-$_{21}$(OCOCF$_3$)$_3$ (Figure 5.5), the ratio of chain terminal to backbone signals was 6 : 84 (confirming 21 ethylene oxide units per dendrimer molecule). For the fullerene end-capped 3-arm PEG $^1$H NMR spectrum (Figure 5.16), the butyryl peaks of the PCB moiety and the acyloxyethylene of the chain termini are also well resolved from the polymeric PEG peak, and the corresponding ratio of chain terminal to backbone signals was 4.4 : 84.6. The MALDI suggests that the product is a mixture of only PEG-$_{21}$(OPCB)$_2$(OH) and PEG-$_{21}$(OPCB)$_3$; based on this assumption, the best fit for the $\alpha$-proton integration indicates a 90 : 10 ratio of to PEG-$_{21}$(OPCB)$_2$(OH) to PEG-$_{21}$(OPCB)$_3$(bis-fullerene product contains 4 $\alpha$-protons and tris-fullerene product contains 6 $\alpha$-protons), a value comparable to the ratio derived from the MALDI peak intensities (84 : 16).

![Figure 5.16](image)

**Figure 5.16** – $^1$H NMR spectrum of PEG-$_{21}$(OPCB)$_3$ ($n_1 + n_2 + n_3 \sim 20$).

A similar distribution pattern but with different mass regions was observed in the MALDI-TOF spectrum of PEG-$_{15}$(OPCB)$_4$ and PEG-$_{15}$(OPCB)$_3$(OH) with mean peak distributions at around 4300 and 3410 m/z,
respectively (Figure 5.17). An additional mass distribution corresponding to bis-fullerene substituted adduct was also observed at around 2240 m/z. However, comparison of the distributions (Figure 5.18) indicates that only the tris- and tetrakis-fullerene derivatives were primary signals. The tris- and tetrakis-fullerene distribution both have an average of 15 repeating units, whereas the bis-fullerene distribution was found to have an average of 6 repeating units. A true bis-substituted fullerene derivative would show a mean peak distribution centred at 2630 m/z for average 15 repeating units. The difference between the observed and ideal peak distribution suggests fragmentation of the higher substituted species within the spectrometer (similar to the previous PEG−23(OPCB)3 case).

**Figure 5.17** – MALDI-TOF spectrum of PEG−15(OPCB)4 and PEG−15(OPCB)3(OH) mixture.
Figure 5.18 – Comparison of the observed mass distributions in PEG-$15$(OPCB)$_4$ MALDI.

Figure 5.19 – $^1$H NMR spectrum of PEG-$15$(OPCB)$_4$
Whilst the MALDI-TOF indicated a 50:50 ratio between the tris- and tetrakis-fullerene signal intensities, the $^1$H NMR spectrum integral ratios provide a more reliable measure. The integral ratio of α-protons versus the main PEG backbone protons in PEG$_{15}$(OCOCF$_3$)$_4$ was 8:60 for the fully substituted product (Figure 5.6). The observed ratio in the $^1$H NMR spectrum of mixture of PEG$_{15}$(OPCB)$_4$ and PEG$_{15}$(OPCB)$_3$(OH) was 7.5:61.2 (Figure 5.19). Therefore, based on this assumption, the best fit for the α-proton integration indicates a 50:50 ratio of PEG$_{15}$(OPCB)$_4$ and PEG$_{15}$(OPCB)$_3$(OH) (tetrakis-fullerene product contains 8 α-protons and tris-fullerene product contains 6 α-protons), a value comparable to the ratio derived from the MALDI peak intensities (50:50).

Higher molecular mass species tend to be harder to ionise in MS and therefore peak intensity is not generally used in determination of natural abundance$^{146}$. However, in the current case, the values derived from both MALDI and NMR seems comparable. Although NMR integration is more reliable in determination of actual abundance, it seems that MALDI peak intensity may also be used as a quick reference in the current system.

**Figure 5.20** - Photospectrometric data for fullerenes end-capped PEG dendrimers: (Left) UV-vis spectra of PCBM, PEG$_4$(OPCB)$_2$, PEG$_{21}$(OPCB)$_3$ & PEG$_{21}$(OPCB)$_2$(OH), and PEG$_{15}$(OPCB)$_4$ & PEG$_{15}$(OPCB)$_3$(OH) recorded in toluene, each concentration was adjusted to similar value (absorbance around 0.6) for ease of comparison; (Right) FTIR spectra of PCBM, PEG$_{15}$(OH)$_4$, PEG$_4$(OPCB)$_2$, PEG$_{21}$(OPCB)$_3$ & PEG$_{21}$(OPCB)$_2$(OH), and PEG$_{15}$(OPCB)$_4$ & PEG$_{15}$(OPCB)$_3$(OH).
The UV-vis spectra of PEG$_{4}$(OPCB)$_{2}$, PEG$_{21}$(OPCB)$_{3}$ and PEG$_{15}$(OPCB)$_{4}$ products in toluene illustrated three electronic absorption bands at 330, 433 and 510 nm (Figure 5.20, Left), similar to PCBM, as expected$^{80}$. The retention of the optoelectronic properties suggests the fullerene surface remains intact during the reaction. However, in FTIR (Figure 5.20, Right), the intensity of the −OH stretching bands at around 3400 cm$^{-1}$ were significantly reduced in all products indicating successful transesterification. The stretching did not disappear completely as the non-fully substituted PEG still contains free terminal hydroxyl groups$^{182}$. As in previous reports$^{182,183}$, no spectral change was observed for the bands at 1732 cm$^{-1}$ (carbonyl stretching of PCB-PEG ester), 1180 cm$^{-1}$ and 1430 cm$^{-1}$ (C-C & C=C stretching in fullerene) and 1095 cm$^{-1}$ (C-O symmetric stretching of PEG) compared to the spectra of pure PCBM and PEG$_{15}$(OH)$_{4}$.

The MALDI-TOF results together with NMR, FTIR and UV-vis spectroscopic data confirmed the synthesis of multi-fullerene end-capped PEG dumbbells PEG$_{4}$(OPCB)$_{2}$ and stars (PEG$_{21}$(OPCB)$_{3}$ and PEG$_{15}$(OPCB)$_{4}$) through the transesterification of PCBM using polydisperse PEGs starting materials. However, the polydispersity, particularly of the tris and tetrakis products remained problematic. Fullerene end-capped PEG core with various arms length results in mixture of polarity which could not be resolved by repetitive column chromatography. As a result, both tris- and tetrakis-fullerene end-capped PEG linkers were collected as a mixture with the associated bis- and tris-fullerene end-capped counterparts. It is still possible to perform SWNTs self-assembly with these fullerene linker mixtures as a fraction of them contain the desired three-fold and four-fold fullerene linkers. However, for the ease of characterisation in SWNTs self-assembled structure, a pure multiple fullerene end-capped linker is preferred.

**5.3.4 Monodisperse Multi-Ethylene Glycol Linkers**

The polydispersity issue could be simply resolved by using a well-defined monodisperse PEG analogue. However, there is currently no multi-arms PEG with well-defined arm length available commercially.
Thankfully, a monodisperse branched PEG, [1,3,5-(25-hydroxy-2,5,8,11,14,17,20,23-octaoxapentacosan-1-yl) benzene, PEG$_{24}$(OH)$_3$] have been successfully produced by Dr. Piers Gaffney, Imperial College London and has kindly offered the material for this study$^{184}$.

**Figure 5.21** – $^1$H NMR spectrum of PEG$_{24}$(OH)$_3$.

**Figure 5.22** – $^{13}$C NMR spectrum of PEG$_{24}$(OH)$_3$. 

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A detailed characterisation of the PEG<sub>24</sub>(OH)<sub>3</sub> has been carried out using <sup>1</sup>H & <sup>13</sup>C NMR spectroscopy and MALDI-TOF mass spectrometry (Figure 5.21 – 5.23) to confirm the actual structure of this monodisperse PEG. After the initial characterisation, this three arms star-shaped PEG, PEG<sub>24</sub>(OH)<sub>3</sub> was then transesterified with PCBM using the same procedure for the polydisperse PEG<sub>x</sub>(OH)<sub>y</sub>. Due to the monodisperse character of PEG<sub>24</sub>(OH)<sub>3</sub>, it was possible to separate the resulting monodisperse tris-fullerene end-capped PEG, PEG<sub>24</sub>(OPCB)<sub>3</sub> from the mixture of mono-, bis- and tris-fullerene end-capped PEG<sub>x</sub>(OPCB)<sub>y</sub>(OH)<sub>z</sub> employing column chromatography (2 ×) followed by preparative thin layer chromatography (3 ×). Since this same purification protocol had failed to isolate the pure products from the earlier polydisperse products, it is clear that the monodispersity of the PEG star is helpful in distinguishing the products, although the separation is still lengthy.

**Figure 5.23** – MALDI-TOF spectrum of PEG<sub>24</sub>(OH)<sub>3</sub>.
Figure 5.24 – MALDI-TOF spectrum of PEG\textsubscript{24}(OPCB)\textsubscript{3}. Expanded region (represented by rectangle) shows the monoisotopic peak pattern of PEG\textsubscript{24}(OPCB)\textsubscript{3} (Bottom) and theoretically simulated monoisotopic pattern (Top).

The MALDI-TOF spectrum of isolated PEG\textsubscript{24}(OPCB)\textsubscript{3} (Figure 5.24) showed the expected monoisotopic mass at 3881.82 m/z, close to the calculated value of 3881.91 m/z, confirming the successful synthesis and isolation of individual monodisperse PEG\textsubscript{24}(OH)\textsubscript{3}. Furthermore, the simulated monoisotopic peak pattern of PEG\textsubscript{24}(OPCB)\textsubscript{3} supported the pure product formation and was in excellent agreement with the experimentally obtained isotopic peak pattern which displayed the expected nominal mass \([M+Na]^+ = 3881.82\). Mass spectrometry results were further supported by the \(^1\)H NMR spectrum which showed a shift of the -CH\textsubscript{2}OH signal from ~3.6 ppm in the starting PEG to 4.25 ppm which corresponded to methylene protons (-CH\textsubscript{2}-O-C=O) adjacent to the newly formed ester carbonyl (Figure 5.25). It was also noticed that hydroxyl protons of PEG\textsubscript{24}(OH)\textsubscript{3} at 3.15 ppm (Figure 5.21) disappeared after transesterification. The integrals of the methylene (labelled as \textbf{d} in Figure 5.25) and the PEG backbone
(labelled as $\text{CH}_2\text{CH}_2\text{O}$ in Figure 5.25) protons indicated a consistent ratio of 6.0 : 90.4, (Expected ratio 6 : 90).

**Figure 5.25** – $^1$H NMR spectrum of PEG$_{24}$(OPCB)$_3$.

### 5.3.5 Difficulty in the DBTO Catalysed Transesterification

The yields of isolated PEG$_{24}$(OPCB)$_3$ and all other adducts were low although the reaction medium was saturated with PCBM. In all cases, overall yields of the final fully substituted products were low, 4 % for PEG$_{21}$(OPCB)$_3$, 8 % for PEG$_{15}$(OPCB)$_4$ and 5 % for PEG$_{24}$(OPCB)$_3$. Due to the small yields, EA (elemental analysis) was not performed. An initial NMR integration study (Figure 5.25) of the $\alpha$-protons (adjacent to newly formed ester) revealed the reaction took a significant amount of time to initiate (about 3 days).
Figure 5.26 – Transesterification reaction of PEG-15(OH)₄ and PCBM monitored by $^1$H NMR spectroscopy: Integration of methylenic ester protons (normalized to main PEG backbone at 3.66 ppm) versus time (2h, 24 h, 48, 72 h, 96 h and 120 h).

Most likely, the reaction is limited by steric effects, related to polymer arm conformation or the geometries of the incoming PCBM molecules. Once one PCBM is attached, the second incoming PCBM molecule may be comparatively difficult to graft. Some combinations of PEG arm lengths may be impossible to fully graft for steric reasons. In addition, during this slow reaction, the catalyst may become deactivated, limiting further grafting. Although the reaction was kept under nitrogen throughout since product may be lost to oxidation during work-up. Fullerene is likely to be oxidised and polymerised in the presence of oxygen. It is well documented that fullerene is a good photo-sensitizer which could easily convert molecular oxygen into singlet oxygen which can induce fullerene polymerisation. Since the column chromatography was carried out in air, there is a distinctive coloured layer that remains in the column which is most likely cross-linked fullerene derivatives trapped in the column.
Previously reported reactions of DBTO catalysed transesterifications have been carried out with small molecules. There is a possibility that this DBTO catalyst may not be an ideal catalyst for a macromolecule, PEG, which limited the yield of the reaction. This could be explained by the fact that mono-fullerene end-capped linker (produced from propoxyethanol) was synthesised with 45 % yield which is nearly 10 times higher than the macro fullerene linkers. Organotin catalyst was originally designed for small molecule transesterification. In the case of PEG and PCBM transesterification, the fullerene on PCBM molecule is likely to collide with the adjacent substituent which may affect the formation of the reaction intermediate. Also, the incoming PEG molecule has to attack this overcrowded intermediate in order to form the new ester linkage and kick out the methanol. As more PCB unit is grafted onto the PEG, it became harder to approach the reaction intermediate which effectively reduce the yield of the fully substituted products.
5.4 Conclusion

Multiply fullerene end-capped PEGs have been synthesized using single step transesterification of PCBM with PEGs. The monodisperse nature of \( \text{PEG}_{24}(\text{OH})_3 \) allowed the isolation of pure monodisperse fullerene end-capped PEG stars \( \text{PEG}_{24}(\text{OPCB})_3 \) from the crude reaction mixture. Despite the low yield of the synthesis, the produced materials are suitable for SWNTs self-assembly as only a small amount of linkers are needed in the experiments. This transesterification of polymer and PCBM to yield structural well-defined multi-fullerene adducts could also be employed in the study of PCBM based PV application as multi-fullerene adduct has become increasing popular within the field.

5.5 Experimental

Propoxyethanol, Poly(ethylene glycol) \( [\text{PEG}_{-5}(\text{OH})_2] \), average molecular weight, \( M_n \sim 200 \), glycerol ethoxylate \( [\text{PEG}_{-21}(\text{OH})_3] \), average \( M_n \sim 1000 \), pentaerithritol ethoxylate \( [\text{PEG}_{-15}(\text{OH})_4] \), average \( M_n \sim 797 \) were bought from Sigma-Aldrich and azeotropically dried by evaporation from anhydrous acetonitrile prior to use. 1,3,5-(25-Hydroxy-2,5,8,11,14,17,20,23-octaoxapentacosan-1-yl) benzene [7, \( \text{PEG}_{24}(\text{OH})_3 \)] was provided by Dr. Piers Gaffney, Imperial College and similarly azeotropically dried.\(^{184}\) Dibutyltinoxide (DBTO, Sigma-Aldrich) was dried at 200\(^\circ\)C in vacuo prior to use. Phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM > 99.5 %, Solene BV) was vacuum dried at room temperature prior to use. Silica gel for column chromatography \( [\text{Geduran}^\text{\textregistered} \text{Si 60 (40-63µm)}, \text{Merck}] \) was neutralised using sodium bicarbonate \( (VWR) \). ortho-dichlorobenzene \( (o-\text{DCB}) \) (anhydrous, >99.8%, Sigma-Aldrich), thin layer chromatography plates \( (\text{TLC Silica gel 60 F}_{254}, \text{Merck}) \), toluene and methanol \( (\text{HPLC grade, VWR}) \) were purchased and used as received.

Synthesis of \( \text{ProOEtOPCB} \)

PCBM \( (290 \text{ mg, 0.3 mmol, 1.1 eq}) \) was dissolved in \( o-\text{DCB (10 ml)} \) under \( N_2 \) at room temperature, and was added to propoxyethanol \( (30 \text{ mg, 0.29 mmol, 1 eq}) \) and DBTO \( (8 \text{ mg, 0.03 mmol, 0.11 eq}) \) in a two-necked round-bottomed flask. The solution was then heated at 140\(^\circ\)C for 5 days under \( N_2 \), after which
the solvent was evaporated under a stream of \( \text{N}_2 \) at room temperature and further dried on rotary evaporator. The resulting dark brown residue fractionated by silica gel column chromatography. Unreacted PCBM eluted with toluene, after which fractions were collected eluting with toluene-methanol (9:1 v/v) to give PrOEtOPCB (127 mg, 45 %) as a brown solid. \( R_f \) toluene-methanol (9:1 v/v) 0.68; \( \delta \) (400 MHz, CDCl\(_3\)) 2.21 (quin, \( J = 7.6 \) Hz, 2H), 2.58 (t, \( J = 7.3 \) Hz, 2H), 2.94 (t, \( J = 8.1 \) Hz, 2H), 3.44 (t, \( J = 6.0 \) Hz, 2 H), 3.64 (t, \( J = 4.0 \) Hz, 2 H), 4.26 (t, \( J = 6.0 \) Hz, 2 H) 7.49 (t, \( J = 7.5 \) Hz, 2 H), 7.57 (t, \( J = 7.6 \) Hz, 4 H), 7.94 (d, \( J = 7.9 \) Hz, 4 H)

**Synthesis of PEG\(_4\)(OPCB)\(_2\)**

PEG\(_4\)(OH)\(_2\) (30 mg, 0.14 mmol), PCBM (280 mg, 0.31 mmol) and DBTO (8 mg, 0.03 mmol) using the same method described above, and purified by a single silica gel column chromatography step, eluting with toluene-methanol (9/1 v/v), to give PEG\(_4\)(OPCB)\(_2\) (25 mg, 9 %) as a brown solid. \( R_f \) toluene-methanol (9:1 v/v) 0.43; \( \delta \) (400 MHz, CDCl\(_3\)) 2.20 (quin, \( J = 7.6 \) Hz, 4H), 2.57 (t, \( J = 7.3 \) Hz, 4H), 2.93 (t, \( J = 8.1 \) Hz, 4 H), 3.60-3.77 (m, 17 H), 4.25 (t, \( J = 4.3 \) Hz, 4 H), 7.49 (t, \( J = 7.5 \) Hz, 2 H), 7.56 (t, \( J = 7.6 \) Hz, 4 H), 7.93 (d, \( J = 7.9 \) Hz, 4 H) ppm; \( \nu \) (FT-IR; ATR) 2917 (aliphatic C-H stretching), 2855 (aliphatic C-H stretching), 1732 (carbonyl stretching of PCBM ester), 1599, 1562, 1493, 1374, 1021 (C-O symmetric stretching of PEG), 797, 755, 695 cm\(^{-1}\); \( \lambda \) (UV-vis; toluene) 330, 433, 510 nm; \( m/z \) (MALDI-TOF) Calcd. for \([\text{C}_{152}\text{H}_{42}\text{O}_8\text{Na}]^+\) 2017.23 m/z, found [M+Na]\(^+\) 2017.21 m/z.
Synthesis of mixture of PEG-21(OPCB)₃ and PEG-21(OPCB)₂(OH)

PEG-21(OPCB)₃ (50 mg, 0.05 mmol), PCBM (150 mg, 0.16 mmol) and DBTO (4 mg, 0.01 mmol) using the general method described above, and purified by silica gel column chromatography (2 ×), followed by preparative TLC (3 ×), eluting with toluene-methanol (9:1 v/v), to give a mixture of PEG-21(OPCB)₃ and PEG-21(OPCB)₂(OH) (40 mg, 22 %, ca. 1:9 by ¹H NMR integration) as a brown solid. Rf toluene-methanol (9:1 v/v) 0.30; δH (400 MHz, CDCl₃) 2.08 (s, 5 H), 2.20 (quin, J = 7.8 Hz, 4.4H), 2.57 (t, J = 7.5 Hz, 4.4H), 2.91 (t, J = 8.1 Hz, 4.4H), 3.47-3.85 (m, 84.6H), 4.25 (t, J = 4.3 Hz, 4.4H), 7.49 (t, J = 7.5 Hz, 2.2H), 7.57 (t, J = 7.6 Hz, 4.4H), 7.94 (d, J = 7.9 Hz, 4.4H) ppm; ν (FT-IR; ATR) 2912 (aliphatic C-H stretching), 2862 (aliphatic C-H stretching), 1731 (carbonyl stretching of PCBM ester), 1600, 1446, 1428 (C=C stretching in fullerene), 1348, 1294, 1247, 1095 (C=O symmetric stretching of PEG), 944, 848, 755, 699 cm⁻¹; λ (UV-vis; toluene) 330, 433, 510 nm; m/z (MALDI-TOF) Calcd. for [C₁₅₆H₇₈O₁₆Na]⁺ 3629.78 m/z, found [M+Na]⁺ 3627.87 m/z.

Synthesis of mixture of PEG-15(OPCB)₄ and PEG-15(OPCB)₃(OH)

EG-15(OPCB)₄ (40 mg, 0.05 mmol), PCBM (200 mg, 0.22 mmol) and DBTO (5 mg, 0.02 mmol) using the same method described above, and purified by silica gel column chromatography (2 ×), followed by preparative TLC (3 ×), eluting with toluene-methanol (9:1 v/v), to give a mixture of PEG-15(OPCB)₄ and PEG-15(OPCB)₃(OH) (35 mg, 16 %, ca. 1:1 by ¹H NMR integration) as a brown solid. Rf toluene-methanol (9/1 v/v) 0.32; δH (400 MHz, CDCl₃) 2.21 (quin, J = 7.7 Hz, 8.1H), 2.58 (t, J = 7.5 Hz, 8.1H), 2.94 (t, J = 8.1 Hz, 8.1H), 3.45 (s, 5.4H), 3.53-3.67 (m, 61.2H), 4.26 (t, J = 4.3 Hz, 7.5H), 7.49 (t, J = 7.5 Hz, 4.1H), 7.58 (t, J = 7.6 Hz, 8.1H), 7.95 (d, J = 7.9 Hz, 8.1H); ν (FT-IR; ATR) 2924 (aliphatic C-H stretching), 2862 (aliphatic C-H stretching), 1731 (carbonyl stretching of PCBM ester), 1602, 1423 (C=C stretching in fullerene), 1242, 1093 (C=O symmetric stretching of PEG), 952, 796, 755, 700 cm⁻¹; λ (UV-vis; toluene) 330, 433, 510 nm; m/z (MALDI-TOF) Calcd. for [C₁₅₉H₁₁₂O₂₆Na]⁺ 4331.75 m/z, found [M+Na]⁺ 4332.85 m/z.
Synthesis of PEG$_{24}$(OPCB)$_3$

Monodisperse tris-C$_{60}$ 3-arm branched PEG linker was synthesized from PEG$_{24}$(OH)$_3$ (25 mg, 0.02 mmol), PCBM (60 mg, 0.06 mmol) and DBTO (1.6 mg, 0.007 mmol) using the same method described above, and purified by silica gel column chromatography (2 ×), followed by preparative TLC (3 ×), eluting with toluene-methanol (9:1 v/v), to give PEG$_{24}$(OPCB)$_3$ (4 mg, 5 %) as a brown solid. $R_f$ toluene-methanol (9:1 v/v) 0.35; δ$_n$ (400 MHz, CDCl$_3$) 2.21 (quin, $J$ = 8.1 Hz, 6H), 2.57 (t, $J$ = 7.5 Hz, 6H), 2.93 (t, $J$ = 8.1 Hz, 6H), 3.61-3.76 (m, 96H), 4.25 (t, $J$ = 4.3 Hz, 6H), 4.56 (s, 6H), 7.25 (s, 3H), 7.51 (t, $J$ = 7.5 Hz, 3H), 7.57 (t, $J$ = 7.6 Hz, 6H), 7.94 (d, $J$ = 7.9 Hz, 6H); ν (FT-IR; ATR) 2922 (aliphatic C-H stretching), 2852 (aliphatic C-H stretching), 1728 (carbonyl stretching of PCBM ester), 1462, 1378, 1265 (C-C stretching in fullerene), 1079 (C-O symmetric stretching of PEG), 1045, 889, 722 cm$^{-1}$; m/z (MALDI-TOF) Calcd. for [C$_{270}$H$_{138}$O$_{30}$Na]$^+$ 3881.92 m/z, found [M+Na]$^+$ 3881.83 m/z.
Chapter 6 – Preparation of SWNT Dispersions and Contamination Issues

SWNT self-assembly is different from peapod formation where the filling process can be performed with SWNT bundles. Self-assembly of SWNTs requires highly individualized SWNTs to allow junctions formation between adjacent SWNTs. Therefore, neither gas phase nor solid phase fullerene filling methods are suitable in SWNTs junction formation. Fullerene linkers with PEG (or other polymeric) spacers decompose at elevated temperature which make high temperature gas phase filling impossible as the resulting fullerene caps would not be connected anymore. On the other hands, solid fullerene linkers do not have enough kinetic energy to adopt the right conformation for self-assembly which make solid phase filling also not suitable for this study. Only solution phase is suitable for the self-assembly. It has been shown that peapods can be prepared in ethanol (EtOH), toluene (Tol), carbon disulphide (CS₂), hexane and also supercritical CO₂ with opened SWNTs. However, these filling examples were all carried out with non-exfoliated SWNTs which are not suitable for self-assembly. Therefore, in order to perform SWNTs self-assembly in solution, a highly individualised SWNTs dispersion must be prepared.
6.1 Exfoliation Techniques

When choosing the method to produce highly individualised SWNTs, there are several factors that have to be considered. (i) The method applied should not introduce excessive defect sites onto the SWNT surfaces, therefore the method should not be too aggressive. (ii) The resultant SWNT dispersion should be stable in ambient conditions (in air) so the self-assembly can be carried out easily (unlike supercritical CO₂ where a high pressure is needed). Figure 6.1 summarises the three most common methods for SWNTs exfoliation. Considering the two factors mentioned above, the most suitable method to prepare SWNT dispersions for self-assembly is by sonication and ultracentrifugation. Acid oxidised SWNTs are generally stable in aqueous solution due to the electron repulsion on the carboxylate groups and interaction with water molecules. However, prolonged treatment often degrades SWNT structure and a significant amount of defects are always introduced to SWNT surfaces. Multiple holes in SWNT might result in uncontrollable fullerene encapsulation which is undesired for selective junction formation. In addition, fullerene linkers are unlikely to be soluble in water due to the presence of non-polar fullerene end caps despite the present of PEG in the linker molecules. For all these reasons, acid treatment of SWNTs was not chosen for SWNTs exfoliation in this study. Highly exfoliated SWNT dispersion can be obtained by (electro)chemical charging. However, the charging process has to be carried out in inert
atmosphere (glove box, under N\textsubscript{2} or Ar) and the resultant dispersion also needs to be kept away from moisture to avoid quenching of the SWNT charge. Once the charge is quenched, the SWNTs are no longer stable in the solution due to the loss of electrostatic repulsion. Although the self-assembly could be performed in inert environment where the SWNTs dispersion remains stable, the charge repulsion may prevent adjacent SWNT coupling. Thus, sonication is the preferred exfoliation technique for self-assembly.

![Diagram](image)

**Figure 6.2** – Typical SWNT dispersion media, aqueous and organic solvents.

SWNT dispersions prepared by sonication have been studied extensively. It has been shown that SWNTs can be dispersed in both water and organic solvents\textsuperscript{200}. Since SWNT are hydrophobic, pristine SWNTs do not disperse in water (similar to simple oil droplet), unless small surfactants molecules or macromolecular wrapping agents (DNA, polymers) are introduced into the system to aid dissolution of SWNTs in water\textsuperscript{192} (see Chapter 1, dispersion section). Although this surfactant based SWNTs dispersion often gives a high degree of exfoliation, it is not a suitable dispersion medium for self-assembly for an
obvious reason. In order to disperse SWNTs into water, the SWNTs are required to have a high degree of surfactant coverage to give the desired stabilisation in water. Hence, the surfaces of SWNT are unlikely to be accessible to the incoming fullerene linkers and, therefore, no insertion might take place. Thus SWNT dispersions in water are not suitable for self-assembly process. This problem can be easily resolved by using organic solvent dispersion as no surfactant is generally required in organic SWNT dispersions.

In general, good SWNT organic solvents can be classified as amide and chlorinated solvents. Among the amide solvents, dimethylformamide (DMF) and N-methyl pyrrolidone (NMP) are the two best solvents for SWNT dispersions. However, not all amide solvents are suitable for SWNTs exfoliation. It has been argued that matching of the surface energy between the solvent and SWNTs is the key to SWNTs stabilisation in organic dispersions. Haloaromatic solvents have also been investigated as SWNTs solvents. Ortho-dichlorobenzene (o-DCB) was found to be a good SWNTs solvent and give highly individualised SWNTs in good yield. However, a further study has shown that the stabilisation of SWNTs in o-DCB resulted from in situ polymer formation that wrapped around the SWNTs. o-DCB was found to decompose sonochemically to form polymeric species in the system. Thus, SWNT dispersions in o-DCB are stabilised by a macromolecular wrapping agent and is not suitable for self-assembly (fullerene can not enter SWNTs). So DMF and NMP are the primary candidates for the preparation of non-protected SWNT dispersions for self-assembly. However, previous reports suggested that NMP is a better SWNTs solvent as it gives a higher SWNTs concentration in a stable dispersion and NMP was chosen as the SWNTs dispersion medium in this study.

6.2 NMP Dispersions

With the dispersion medium chosen, the process details have to be considered. In a typical SWNTs sonication, both bath and tip sonicators have been shown to be effective in SWNTs exfoliation. As well as exfoliating SWNTs, prolonged sonication was found to shorten SWNTs and an extensive
investigation of sonication time and SWNTs length (in NMP) has been reported\textsuperscript{199}. It has been shown that SWNTs are significantly shortened after 2 hours of sonication and the SWNTs structure are reasonably well preserved (confirmed by electrical conductivity). This finding is extremely important to the self-assembly study as cutting SWNTs effectively generates open ends in SWNTs which is crucial for fullerene linker encapsulation. Preserved electrical conductivity after sonication suggests that the majority of the SWNTs structure is retained (significant damage to SWNTs structure would result in loss of continuous sp\textsuperscript{2} carbon framework which reduces the electron transport property of SWNTs). Structural quality is relevant to self-assembly as fullerene linkers might be trapped in the holes along the SWNTs surface. By limiting the number of defect sites on the surface, the self-assembly should be limited to the open ends. Longer sonication times (more than 3 hours of continuous sonication) or stronger sonication power were found to have a catastrophic effect in SWNTs structure as a large number of defect sites will be generated on the surface.

Based on these findings, a dispersion of HiPco SWNTs in NMP was prepared with 2 hours sonication using a tip sonicator and studied under AFM. As expected, individualised SWNTs are observed in the AFM micrographs (Figure 6.3). However, there is a significant amount of small particles (size range from 5 – 15 nm, indicated by red arrows) which were well-dispersed and could be easily found on Si wafer surface.
In a typical SWNTs synthesis, the as-produced SWNTs normally contain amorphous carbon, graphitic particles and metal catalyst particles. Since the SWNTs dispersion has been centrifuged at 200,000 g using an ultracentrifuge, it is unlikely to have any graphitic particles and metal catalysts remains in the sample due to the huge difference in their density (metal catalysts are often trapped inside graphitic particles). The size of the particles observed in the AFM micrographs is relatively homogeneous, thus, it is unlikely to be amorphous carbon. Therefore, the particles observed in the AFM sample may hence come from the solvent – NMP.

6.3 Identifying the Contamination

In order to verify the hypothesis of NMP induced contamination, a set of experiments of sonicating pure NMP for different times was carried out in the absence of SWNTs (with identical sonication condition as dispersion preparation). Most SWNTs dispersions in literature\textsuperscript{12, 146, 200} are sonicated from 2 to 30 min and no particles formation or contamination issues are generally discussed. However, in order to ensure that the SWNTs are opened for junction formation, 2 hours sonication is preferred for short and opened
SWNTs. In addition, it is also worth investigating the effect of general sonication conditions (2 – 30 min) in the resulting AFM samples quality, as it has not been discussed before. In order to identify the effect of sonication time in AFM sample quality, a constant power output of 150 W with a tip sonicator was applied throughout the experiment.

Figure 6.4 – Sonicated NMP with increasing sonication time from 0, 5, 30 and 120 min. NMP with 120 min sonication shows a clear yellow colour.

High purity NMP (HPLC grade, Sigma Aldrich) was sonicated for 0, 5, 30 and 120 min using constant sonication power (150 W with tip sonicator) with a 3 L ice bath as a heat sink. The non-sonicated NMP (0 min) was placed in the system for 2 hours in identical condition so any external contamination issue can be ruled out with this control experiment. As the sonication time increased, a yellow colour emerged in the solvent which was most intense in the 120 min sonicated NMP (Figure 6.4). The 30 min sonicated NMP only showed a very pale yellow colour. The control experiment (NMP without sonication / 0 min) did not show any yellow colour after the experiment which suggests the yellow colour did not come from any external variable such as direct contact with glass vials and sonicator tip. Therefore, the yellow colour must result from a sonochemical process.
AFM micrographs (Figure 6.5) of these as-sonicated NMPs strongly supported the hypothesis that the observed particles were originated from NMP rather than SWNT contamination. The density of the particles observed in the AFM micrographs increases with increasing sonication time (Figure 6.5). In the case of 120 min sonicated NMP, the particles almost completely covered the whole Si surface. Considering the standard dispersion preparation procedure, centrifugation is widely used to remove large SWNTs bundles and metal catalysts. Therefore, these sonicated NMPs were centrifuged at 200,000 g for 2 hours in order to remove the observed particles. AFM micrographs (Figure 6.5) of the centrifuged samples revealed the majority of the particles can be removed by high speed centrifugation but a small amount of particles still remained in the sample. Since centrifugation can not completely remove the newly formed particles, a detailed analysis of the sonicated NMP was carried out in order to identify the nature of the particles. Understanding the chemical structure of the particles may help establishing an effectively method to remove the particles from the system.
Figure 6.5 – AFM micrographs of sonicated NMP (0, 5, 30 and 120 min sonication time). (Top) : before centrifugation. The density of the particle increasing as the sonication time increase from 5 to 120 min. (Bottom) AFM micrographs after centrifugation at 200,000 g for 2 hours clearly showing reduced particle density in 5, 30 and 120 min samples. All images were taken from the centre of the Si wafer to minimise variation between samples (scale bar 1 µm).

Figure 6.6 – UV-vis spectra of sonicated NMPs (0, 5, 30 and 120 min). (Left) before centrifugation. (Right) after centrifugation at 200,000g for 2 hours (top 50% of the supernatant collected).

As shown in the UV-vis spectra of the sonicated NMP (Figure 6.6), the 5 min sonicated NMP resembles most of the non-sonicated (0 min) NMP feature. The absorbance at 360 nm in (0 min) NMP is gradually
obscured (with increasing sonication time) by the appearance of a scattering effect (due to the present of particles) between 300 - 450 nm. As discussed in Chapter 3 – UV-vis spectroscopy section, the observed scattering effect in the UV-vis spectra can be attributed to the present of small particles in the sample. However, AFM micrographs revealed significant amount of particles were removed after centrifugation which suggested that the change in UV-vis feature did not result from scattering. Therefore, the new UV-vis feature (300 – 450 nm) was a true electronic absorbance possibly due to a newly formed species by sonochemical degradation of NMP. The absorbance in UV-vis spectra does not provide any information regarding the chemical structure of the particles. In order to analyse the structure of the particles, a reasonable amount of the sample is needed. As shown in both AFM and UV-vis spectra, 120 min sonicated NMP contains the largest quantity of the particles. Thus, the as-sonicated NMP (120 min) (10 ml) was dried under a stream of nitrogen at room temperature to evaporate the NMP solvent. Heating was avoided during the drying process to minimise any thermal degradation of the newly formed particles. A yellow oily residue (4 mg) was collected after two weeks of drying whereas drying same amount of non-sonicated NMP did not yield any oil/solid.

Figure 6.7 – IR spectra of pure NMP and the yellow residue obtained from evaporation of sonicated NMP (120 min). (Right) expended carbonyl stretching at around 1650 – 1700 cm⁻¹.

The IR spectrum of this yellow oily residue showed clear signals for both OH and NH absorptions between 3000 and 3500 cm⁻¹. In the case of pure NMP, there is only a small OH absorption at around
3500 cm\(^{-1}\) due to small amount of residual water present in the solvent. The carbonyl stretching of non-sonicated NMP was shifted to lower wavenumber which suggested the carbonyl bond in the yellow residue is lower energy than pure NMP. Since the carbonyl in NMP is situated in a 5-membered ring, the carbonyl stretching of NMP is therefore, slightly stressed compared to normal aliphatic carbonyl\(^{201}\). Since the system only contain pure NMP and no other chemicals were introduced into the system (non-sonicated NMP did not yield any oil/solid), the yellow residue must result from NMP sonication.

\[ \text{Possible Polymerisation} \]

**Figure 6.8** – Ring opening of NMP to give aliphatic carboxylic acid and a secondary amine.

The only way to obtain a non-cyclic carbonyl stretching from NMP is via ring opening of NMP 5-membered ring (Figure 6.8). This matches the observation in the IR spectrum where the new carbonyl stretch appeared at a lower wavenumber which suggest the carbonyl bond is no longer constrained by the cyclic 5-membered ring\(^{202}\) (Figure 6.7). One of the possible ring-opening mechanisms in NMP is hydrolysis of the amide bond by water. During the sonication, a large amount of energy was supplied to the sample. To avoid thermal energy accumulation in the system which may result in evaporation or thermal degradation of NMP, the solvent was cooled in an ice bath throughout the sonication. Therefore, the water vapour from the ice bath can easily condense into the NMP during sonication which may facilitate hydrolysis of the amide bond and result in NMP ring opening. In order to investigate the effect of water in NMP sonication, the sonication must be carried out in the absence of water. Apart from water vapour from ice bath, other possible water sources are moisture in air and residual water in
NMP solvent. All three water sources must be eliminated from the system in order to study the possible water hydrolysis of NMP.

**Figure 6.9** – Photograph of sonication of NMP carried out in a nitrogen bag (cooling in ice bath).

Anhydrous NMP (Anhydrous grade, >99.5 %, Sigma Aldrich) was transferred into a glass vial inside a nitrogen bag. The vial was then attached to the sonicator probe inside the nitrogen bag (as shown in Figure 6.9). The cooling ice bath and the NMP vial were separated by a nitrogen bag. The nitrogen bag was connected to a nitrogen manifold with constant nitrogen purging to maintain a positive nitrogen pressure. By doing this, the nitrogen atmosphere was maintained throughout the experiment to prevent any atmospheric moisture getting into the system. After 2 hours sonication, the NMP turned yellow and the UV-vis of the sonicated NMP (N₂) showed an electronic absorbance to the normal process (120 min, in air and ice bath) showing that the decomposition does not require water hydrolysis (Figure 6.10).
During the sonication, a 3 L ice bath was used as a heat sink to avoid continuous increase in temperature in the system. Figure 6.11 shows the temperature profile of both NMP sonication and HiPco/NMP dispersion sonication for 120 min. In the pure NMP case, temperature increase rapidly in the first 15 min of sonication but stabilised at around 28 °C until the end of the sonication. This experiment confirmed that a 3 L ice bath can maintain a constant temperature of a sonicating sample for 2 hours efficiently. Since the temperature is maintained at low temperature (28 °C), it is unlikely that any thermal
degradation of the NMP occurs. The temperature profile of HiPco/NMP dispersion was similar to the pure NMP case, although reached a slight higher temperature 30–35 °C.

More literature research was carried out in order to identify other possible NMP degradation pathways. NMP was found to decompose in the presence of titania\textsuperscript{203,204} via a radical initiated amide bond cleavage (ring opening) pathway. Once the NMP cyclic ring is opened, further complex radical reaction may initiate polymerisation of the newly formed species. Unfortunately, all commercial available sonicator tips are made of titanium alloy (Ti-6Al-4V) which is likely to have a small layer of titania built up over extensive usage. This titania may catalyse the degradation of NMP during the sonication process. Since sonication has to be applied in order to exfoliate the SWNTs, the particle formation is difficult to be completely avoided.

6.4 Polymeric Amide Species

It seems unlikely that the formation of the particles can be avoided in SWNT dispersions. As shown in AFM and UV-vis data (Figure 6.5 – 6.6), reducing sonication time can control the amount of particles being formed in the samples. IR data revealed that the particle’s formation was most likely originated from amide bond cleavage of NMP molecules. From the particle size in AFM micrographs, the degraded (opened) NMP molecules were believed to polymerise into polyamide. Luckily, centrifugation was found to be effective in removing majority of the polyamide particles. However, it should be noted that NMP SWNT dispersion prepared by sonication can be contaminated by polyamide which may be relevant to SWNT device fabrication.

The original NMP SWNTs dispersion theory stated that matching of surface energy between SWNTs and NMP is the key to stabilisation of individual SWNTs. However, there are other non-amide solvents which have similar surface energy to NMP but they do not give stable SWNTs dispersion\textsuperscript{193}. A study published by Ferrari et al. showing addition of polyvinylpyrrolidone (PVP) can increase the stability of NMP dispersions\textsuperscript{205}. PVP was found to wrap around SWNTs as a protective layer. Since PVP contains
pyrrolidone side chains, it can be easily solvated by NMP which effectively increase the solubility of the protected SWNTs. Therefore, the polyamide formed in situ during NMP sonication may have a similar effect as PVP which wrap around SWNTs to increase the stabilisation in NMP dispersions. This hypothesis would suggest that the purely physical thermodynamic model in the literature is not the complete picture for why some amides are apparently good for SWNTs. Polymerisation of solvent and possibly functionalisation of SWNT surface may play an important role in SWNTs stability.

6.5 High Temperature Annealing

Since centrifugation can not completely remove the polyamide from the dispersion, an alternative method is needed to improve the quality of AFM images. Since SWNTs are heat resistant compared other common organic molecule, high temperature annealing in inert atmosphere was employed to selectively decompose the non-SWNTs materials. Annealing the SWNTs sample in vacuo at 900 °C for 30 min was found to be effective in removing most of the non-SWNTs materials. See Chapter 7, section 7.7 for more details.
6.6 Conclusion

Experimental data suggest that NMP degrades and polymerises during sonication, contaminating SWNT dispersions. Although centrifugation was generally applied in NMP SWNT dispersions preparation, it can not completely remove the polyamide particles. Various degradation pathways of NMP are known but the polyamide species most likely originated from titania catalysed ring-opening of NMP during sonication as water hydrolysis has been ruled out by control experiment. In addition to the surface energy theory\textsuperscript{197}, the chemical nature of the solvents was also found to be crucial in stabilising SWNTs in dispersion. Amide solvents were among the best solvents for SWNTs possibly due to their ability to polymerise into polyamide and interact with SWNTs. However, further study is required to identify the actual structure of the polyamides and its contribution to the SWNT dispersion stability. Experimental data suggested that SWNTs may be wrapped by polyamide in NMP dispersion. Identical experiments were carried out with DMF and similar result was obtained (DMF also turned yellow) which suggest using DMF in SWNTs solvent do not prevent the polyamide formation.

6.7 Experimental

Semi purified HiPco SWNTs was purchased from Unidym\textsuperscript{TM} Carbon Nanotubes, CA90425, US (Lot no. P0261) and used as received. HPLC and anhydrous NMP were purchased from Sigma Aldrich. HPLC NMP was used as-received and anhydrous NMP was de-gasses by freeze-thaw in liquid nitrogen (x 5) before use. All sonication in this experiment was carried out with 20 ml of NMP in a 30 ml glass vial. The sonicator tip was placed into the NMP about 2 cm from the bottom of vial for each experiments in order minimise the variation of the power output. Sonication was carried out with 150 W power output (20% of the total output, GEX 750 ultrasonic processor with a 5 mm titanium alloy Ti-6Al-4V microtip, SONICS & MATERIALS INC, Newtown, US). A 3 L ice bath was used for each sonication. Centrifugation was performed with L-90k Optima ultracentrifuge, Beckman Coulter with a SW41 Ti rotor. Top 50 % of the supernatant collected for analysis.
HiPco SWNTs dispersion

HiPco SWNT was mixed with 20 ml of NMP (0.1 mg / ml) in a glass vial. The vial was then attached to the tip sonicator, cooled with an ice bath and sonicated for 2 hours. The SWNTs/NMP mixture turned into black dispersion within 10 second of initial sonication. After that the dispersion was allowed to stand overnight and top fraction (ca. 12 ml) was transferred into a centrifuge tube for centrifugation. After centrifuging the dispersion at 41,000 rpm; 200,000 g for 2 hours, top 50 % of the supernatant was collected as HiPco dispersion.
Chapter 7 – Supramolecular Assembly of SWNTs

From the initial synthesis and characterisation of the fullerene linkers to detailed investigation of SWNTs dispersion in N-methyl pyrrolidone (NMP), the initial preparations for the desired SWNTs self-assembly experiment seem to be ready. However, these linker molecules only make up to 50% of the materials required. The most important starting material, the SWNTs, has yet to be chosen for the experiment. As discussed in chapter 1, there are various synthetic procedures for SWNTs and each technique produces different physical parameters such as length, diameter and chirality.

7.1 Choice of SWNTs

The primary factor is the diameter of SWNTs. As shown in previous literature, SWNTs diameter for fullerene encapsulation should be at least 1.3 nm. The optimum fullerene to SWNTs inner surface distance is 0.3 nm. At this distance, the fullerene and inner tube surface have the highest van der Waal’s interaction. Together with a 0.7 nm diameter of fullerene, the total diameter required for complete fullerene encapsulation is 1.3 nm.

SWNTs length is also an issue in SWNTs self-assembly but less important than the diameter. Long SWNTs diffuse at a much slower rate than short SWNTs. Therefore, short SWNTs should be easier to assemble than long SWNTs. However, as shown in previous literature and also discussed in chapter 6, sonication can be applied to shorten the SWNTs. So length issue in as-received SWNTs should not be problematic in self-assembly. SWNTs with different chirality are often produced in SWNTs synthesis regardless of production method. In the long run, it will be important to selectively assemble SWNTs with certain chirality (m-SWNTs & sc-SWNTs) which could then be incorporated into SWNTs device fabrication. However, the primary goal of this project is to prove the concept of connecting SWNTs with fullerene end-capped linkers to give SWNTs junctions. Before establishing a standardised and effective self-
assembly methodology, this technology can not be used in any device fabrications. Therefore, SWNT chirality purification / enrichment are not considered here.

Thus, the main factor to be considered in choosing commercial SWNTs for self-assembly is SWNTs diameter distribution. Table 7.1 lists common commercially available SWNTs and their physical parameters. HiPco SWNTs are one of the most widely studied materials with a wide distribution of diameters ranging from 0.8 to 2 nm (mostly < 1 nm). Obviously, a fraction of the SWNTs with diameter less than 1.3 are not able to encapsulate any fullerene as the inner cavities do not have sufficient space. However, the rest of SWNTs which have diameter greater than 1.3 nm are possible candidates for encapsulation. Using the standard HiPco SWNTs to prove successful SWNTs junctions formation could be a good model. Since HiPco SWNTs has been studied extensively, any self-assembled SWNTs junction / network should be easily identified relative to the pristine HiPco SWNTs. However, HiPco SWNTs are synthesised with a chemical vapour deposition process (CVD) which generally produce less graphitic SWNTs. Thus, the self-assembly of HiPco SWNTs is expected to have some degree of deficiency as the SWNTs have significant defect contamination.

Both SWNT-SO (Meijo Nano Carbon) and P2-SWNT (Carbon Solutions) have an average diameter of 1.4 nm which are ideal for fullerene encapsulation. Both SWNTs are produced by arc-discharge method which suggests that these as-produced SWNTs are more graphitic than HiPco SWNTs. However, P2-SWNT from Carbon Solution contains a significant amount of amorphous carbon and metal catalyst which significantly affect the dispersion quality. Thus, a series of purifications have to be applied before the SWNTs are suitable for self-assembly experiments. However, SWNT-SO from Meijo Nano contains mainly SWNTs (> 90%) with minimal amount of metal catalyst which can be easily separated by centrifugation. No other purifications are required when handling SWNT-SO since they are pre-purified. The only drawback of SWNT-SO is the wide distribution of SWNTs length. As mentioned before, short SWNTs are more efficient in self-assembly than long SWNTs. Having such a wide range in length distribution may limit the self-assembly process as the longer SWNTs fractions diffuse at a much lower
rate. However, the dispersions are prepared by sonication which the SWNTs will be shortened during the process. Therefore, the final SWNTs length distribution in the dispersion is expected to be shorter than the original SWNTs which should increase the overall diffusion rate. Hence, for the above reasons, both HiPco and SWNT-SO were chosen for self-assembly experiments.
<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Length / nm</th>
<th>Diameter / nm</th>
<th>Process</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unidym (Hipco)</td>
<td>100 - 1000</td>
<td>0.8 – 2.0</td>
<td>HiPCo</td>
<td>&gt;80%</td>
</tr>
<tr>
<td>Meijo Nano (SWNT-SO)</td>
<td>1000 - 5000</td>
<td>1.4</td>
<td>Arc</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>Carbon Solutions (P2-SWNT)</td>
<td>1.4</td>
<td>Arc</td>
<td>60-70 %</td>
<td></td>
</tr>
<tr>
<td>nano-c</td>
<td>Up to 1000</td>
<td>1.1</td>
<td></td>
<td>70%, 95%</td>
</tr>
<tr>
<td>Hanwha (Formerly Iljin)</td>
<td>5 - 20,000</td>
<td>1.0 - 1.2</td>
<td>Arc</td>
<td>20-70wt%</td>
</tr>
<tr>
<td>nano lab</td>
<td>&gt;10,000</td>
<td>1.0 - 1.5</td>
<td>Arc</td>
<td>&gt;40% - &gt;90%</td>
</tr>
<tr>
<td>nano lab</td>
<td>1000 - 5000</td>
<td>~1.5</td>
<td>CVD</td>
<td>95%</td>
</tr>
<tr>
<td>nano-thinx</td>
<td>~ 5000</td>
<td>0.8 - 1.4</td>
<td>CVD</td>
<td>~65-85%</td>
</tr>
<tr>
<td>cheap tubes</td>
<td>3000 - 30,000</td>
<td>1.0 - 2.0</td>
<td>CVD</td>
<td>90-99wt%</td>
</tr>
<tr>
<td>cheap tubes (shorter)</td>
<td>500 - 20,000</td>
<td>0.8 - 1.6</td>
<td>CVD</td>
<td>&gt;90wt%</td>
</tr>
<tr>
<td>Nanostructured and Amporphous Materials</td>
<td>5000 - 15,000</td>
<td>1.0 - 2.0</td>
<td>CVD</td>
<td>50wt% SNWTs</td>
</tr>
<tr>
<td>Arry International</td>
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<td>1.0 - 2.0</td>
<td>CVD</td>
<td>60wt%-90wt%</td>
</tr>
<tr>
<td>Nano Powder R&amp;D Centre</td>
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<td>1.0 - 2.0</td>
<td></td>
<td>60%-90%</td>
</tr>
<tr>
<td>Chengdu Chemicals Co.</td>
<td>5000 - 30,000</td>
<td>1.0 - 2.0</td>
<td></td>
<td>60%-90%</td>
</tr>
<tr>
<td>Arknano</td>
<td>&lt; 20,000</td>
<td>&lt; 2.0</td>
<td></td>
<td>90%</td>
</tr>
<tr>
<td>Nanocyl S.A.,</td>
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<td>~ 2.0</td>
<td>CVD</td>
<td>70%</td>
</tr>
<tr>
<td>Shenzhen Nanotech Port Co. Ltd.,</td>
<td>5000 - 15,000</td>
<td>&lt; 2.0</td>
<td>CVD</td>
<td>90%</td>
</tr>
<tr>
<td>Thomas Swan</td>
<td>~900</td>
<td>~ 0.9</td>
<td>CVD</td>
<td>&gt;70%</td>
</tr>
<tr>
<td>Thomas Swan</td>
<td>~900</td>
<td>~ 0.9</td>
<td>CVD</td>
<td>99%</td>
</tr>
<tr>
<td>SouthWest NanoTechnologies Inc.(CoMoCat), High Metallic Content</td>
<td>~1000 0.7 - 1.3</td>
<td>CVD</td>
<td>&gt;90%</td>
<td></td>
</tr>
<tr>
<td>SouthWest NanoTechnologies Inc.(CoMoCat), Semiconducting (50% (6,5))</td>
<td>5000 - 15,000</td>
<td>0.5 - 1.1</td>
<td>CVD</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>SouthWest NanoTechnologies Inc.(CoMoCat), Semiconducting (50% (7,6))</td>
<td>5000 - 15,000</td>
<td>0.6 - 1.2</td>
<td>CVD</td>
<td>&gt;90%</td>
</tr>
</tbody>
</table>

Table 7.1 – Table of commercially available SWNTs and their physical parameters. All data were obtained from manufacturer’s website.
7.2 HiPco SWNT Dispersions

Opened HiPco SWNTs were prepared by sonicating SWNTs powder in NMP (0.1 mg / ml) for 2 hours as stated in previous chapter, section 6.7. The quality of the dispersion was characterised by AFM. Diameter and length distribution of the exfoliated HiPco SWNTs was measured from the micrographs.

Figure 7.1 – AFM micrographs of HiPco SWNTs dispersion in NMP (prepared by 2 hours sonication and 2 hours centrifugation at 41,000 rpm, top 50% supernatant collected). Micrograph on the left was taken from the centre of the Si wafer showing individual SWNTs. Image on the right was taken from the edge of the Si wafer surface showing SWNT networks that resulted from drying process. The small particles observed in the image are the polyamide generated in situ during NMP sonication.

As shown in Figure 7.1, 2 hours sonication in NMP yielded highly exfoliated HiPco SWNTs. The individual SWNTs were mainly observed in the centre of the Si wafer whereas SWNTs networks were found near the edge on the wafer due to Maragoni flows at the meniscus ‘coffee ring effect’.\textsuperscript{206} Since NMP has a high boiling point (202 °C), drying NMP at room temperature at atmospheric pressure take a significantly long time (3 µL NMP on Si wafer do not evaporate after one week of drying in air at room temperature). As shown in previous NMP evaporation experiment, it took two weeks of continuous nitrogen blowing to remove 10 ml of NMP. Hence, all SWNTs NMP dispersions have to be dried \textit{in vacuo} at high temperature to ensure complete removal of NMP.
The average length distribution of the HiPco dispersion was found to be around 370 nm. Some small SWNT bundles were also observed in the AFM which effectively shifted the diameter distribution to slightly higher value (average 1.56 nm). Despite having a wide diameter distribution and few SWNT bundles in the dispersion, a fraction of SWNTs have diameter larger than 1.3 nm which are suitable for fullerene encapsulation. Thus the self-assembly of HiPco SWNTs was expected to have some degree of deficiency as only a fraction of the SWNTs would be able to join together to yield SWNTs junctions.

7.3 Supramolecular Self-assembly of HiPco SWNTs

In order to fill the SWNTs cavity with the covalently attached fullerenes, a few factors have to be considered. (i) Insertion method. Since both gaseous and solid state filling have already ruled out from the system, solution state insertion is the only option. However, there is no example of fullerene encapsulation in SWNTs dispersion containing highly individualised SWNTs. As discussed before, all previous peapod samples were prepared from non-exfoliated SWNTs. The reason for having highly individualised SWNTs in self-assembly is due to diffusion of SWNTs in solution. Individualised SWNTs in
solution provide the required freedom for the SWNTs to diffuse and rotate into the right conformation for the self-assembly process. Therefore a NMP dispersion of highly individualised SWNTs was prepared instead of SWNTs bundles in solution. (ii) Solubility of fullerene. The solubility of fullerene in solution was found to be vital in the overall yield of encapsulation\textsuperscript{207}. It is important to use a solvent with poor fullerene solubility. Due to the strong hydrophobic interaction, fullerene is known to form clusters in a poor fullerene solvent. It has been shown that fullerene clusters give higher yield of encapsulated fullerene than individualised fullerene\textsuperscript{108}. However, the fullerene linkers are insoluble in NMP which is significantly different from sparingly soluble. Insoluble fullerene linkers will remain as a big cluster and may not be exfoliated into solution which may be not suitable for insertion. However, the solvents choice is limited as SWNTs can not be exfoliated in other solvents (non-amide) without addition of surfactants or other wrapping agents. Therefore the solvent system has to be modified in order to give the fullerene linker some solubility in the SWNTs dispersions.

7.3.1 Binary Solvent, NMP and Tol

Since NMP can not be replaced, the only way to provide solubility to fullerene linkers is addition of fullerene solubilising solvents into the dispersion. Considering the solubility requirement, the fullerene linkers should not be completely solubilised for high yield insertion. Therefore, good fullerene solvents such as ortho-dichlorobenzene (o-DCB) and chlorobenzene may not be suitable as they have the highest fullerene solubility (See Table 2.1 for fullerene solubility). In addition, solvents with low fullerene solubility are also not suitable. Since the additional solvents have to be mixed with NMP to give a binary solvent system, this effectively reduced the fullerene solubility in the original solvents. The main options were therefore mainly toluene and benzene. Toluene (Tol) was chosen as the fullerene linker solvent as it has a higher boiling point, it does not evaporated easily during the self-assembly process and maintains the concentration of solubilised fullerene linkers.
Adding a non-SWNTs solvent (Tol) into a NMP SWNT dispersion can easily disrupt the interaction between the NMP and SWNTs and result in destabilisation. In order to prevent SWNTs crashing out from the solvent system, but at the same time, providing some solubility for the fullerene linkers, an optimal volume ratio has to be established. Toluene was added to NMP dispersions with different volume ratios. Once the toluene was added to the dispersions, the mixtures were mixed thoroughly with a glass pipette and allowed to stand overnight at room temperature in a closed glass vial to avoid evaporation of toluene (NMP is difficult to evaporate at room temperature).

Figure 7.3 – Photographs of mixtures of NMP HiPco dispersions with various volume ratios of toluene. (Far left) Pure NMP as a control. (A) 100% HiPco SWNTs dispersion in NMP. (B) 90 : 10 v/v of HiPco dispersion and Tol. (C) 80 : 20 v/v. (D) 70 : 30 v/v. (E) 60 : 40 v/v. (F) 50 : 50 v/v. (G) 100 % Tol as a control. Image (Top) were taken just after the addition of toluene and (Bottom) 24 hours after mixing. Close inspection of C – F (labelled with ‘X’) revealed black precipitate after 24 hours which indicated SWNTs crashed out from the solvent mixtures.

Various HiPco dispersion (NMP) and toluene mixtures were prepared in different volume ratio (Figure 7.3). After 24 hours of mixing, only 90 : 10 v/v of dispersion and toluene mixture remain stable.
All other mixtures with higher toluene volume fractions were found to have black solid precipitated out after 24 hours. This result suggested high toluene ratio destabilise the NMP-SWNTs interaction which can not be used in self-assembly. Therefore, the 90 : 10 v/v ratio was chosen for the self-assembly experiment.

7.3.2 Time Required for Self-assembly

After establishing the solvent system, another important issue would be the time for the self-assembly process. A gas phase fullerene insertion can happen instantaneously at high temperature (at around 650 °C) whereas in a solution phase insertion, it can take several hours[112,209]. However, once fullerene enters the SWNTs, it requires relatively large amount of energy to remove it from the cavity (3 eV per C_{60})[209]. Therefore, the filling process should in theory be relatively irreversible and the encapsulated fullerene should remain once formed. However, little is known about the minimum time required for the initiation of fullerene insertion. Obviously, both gas and solution phase have very different filling mechanisms which suggest the kinetics are different as well. In solution phase insertion in different solvents, the kinetics must vary between solvents due to the differences in fullerene solubility, surface tension and viscosity.

In order to study the minimum time required for the insertion process using the binary solvent system (NMP/Tol), UV-vis spectroscopy was employed to monitor the insertion progress. Encapsulated fullerene should not show the corresponding π – π* absorption at 336 nm compared to free fullerene. Thus, the intensity of the 336 nm absorption could be used as an indication for the insertion / self-assembly.
Figure 7.4  –  (Top) UV-vis spectra of HiPco SWNTs dispersion with bis-fullerene end-capped PEG linkers (NMP : Tol, 9 : 1 v/v). (Bottom) Enlarged region of the original spectra showing the $\pi - \pi^*$ absorption at 336 nm (with SWNTs scattering background subtracted). The intensity of the 336 nm absorption decreased as the self-assembly proceeded and disappeared after 6 hours as the majority of the fullerene entered the SWNTs and the remaining fullerene concentration is too low to detect.

The UV-vis spectra of the HiPco SWNTs self-assembly (Figure 7.4), it clearly showed the fullerene $\pi - \pi^*$ absorption at 336 nm clearly disappeared after 6 hours which indicates that most of the fullerene was inserted into SWNTs. Therefore, the self-assembly experiment should be allowed to stand for at least 6 hours before any aliquots are taken for characterisation.
7.3.3 Self-assembly of HiPco SWNTs and bis-fullerene End-capped PEG Linker (Dumbbell)

Since there is no previous literature to follow, the optimal amount of SWNTs and linkers required for the self-assembly was not known. Therefore, a bis-fullerene end-capped PEG linker PEG-4(OPCB)_2, dumbbell solution in toluene (0.1 mg/ml) and a HiPco SWNTs dispersion in NMP (0.1mg/ml, see section 6.7) were prepared. Then 0.1 ml of the dumbbell toluene solution was added to 0.9 ml of the SWNTs dispersion in a glass vial (to keep the 9:1 v/v NMP/Tol ratio). The two solvents were mixed by a glass pipette to aid complete dissolution. 3 µL of the mixture was then taken for AFM analysis on the next day.

![AFM micrograph of SWNTs self-assembly of HiPco SWNTs with dumbbell PEG-4(OPCB)_2.](image)

**Figure 7.5** – AFM micrograph of SWNTs self-assembly of HiPco SWNTs with dumbbell PEG-4(OPCB)_2. Image was taken from the centre of the Si wafer.

From the diameter analysis of the HiPco SWNTs dispersion, only a fraction of the SWNTs are big enough to encapsulate fullerene. As expected, the AFM micrograph revealed that the self-assembled SWNTs mixture contained both individual and assembled SWNTs (Figure 7.5). The original SWNTs dispersion in NMP, mainly individual SWNTs were observed in the 10 x 10 µm AFM micrographs. Therefore, the
present of the newly formed ‘V’ shape SWNTs are a good indication of the self-assembly between SWNTs and dumbbell linkers. However, due to the flexible nature of the PEG linker, the observed inter-SWNT angles (the angle between the assembled SWNTs) were not uniform.

Figure 7.6 – Second AFM micrograph of SWNTs self-assembly of HiPco SWNTs with dumbbell PEG₄(OPCB)₂. Image was taken from the centre of the Si wafer, about 20 µm away from the previous image. Blue inset indicate a perfect SWNTs junction with ‘head-to-head’ assembly whereas the red inset showed SWNTs junctions with ‘head-to-body’ assembly.

A self-assembled SWNTs network was also found in the AFM sample (Figure 7.6) and clearly showing the SWNTs junctions within the nanotubes structure. The original hypothesis was that opened SWNTs would join together at the ends to give ‘V’ shapes SWNT junctions. This ideal assembly was observed in the sample (Figure 7.6, blue inset) where the two SWNTs were joined together via the open ends. This type of assembly can be referred as ‘head-to-head’ assembly since the body of the SWNTs does not
participate in the assembly. However, another type of assembly was also observed in the AFM micrographs. One end of SWNT was joined to the body of another SWNT to give a ‘head-to-body’ assembly (Figure 7.6, red inset). Since defects are difficult to eliminate from the HiPco SWNT structure, it is possible to have a defect site which is big enough to host fullerene and initiate junction formation.

The AFM images strongly suggested that it is possible to join SWNTs with fullerene end-capped linkers, in this case, bis-fullerene dumbbell. Comparing the original HiPco SWNTs and the self-assembled SWNTs, the observed SWNT structures in the AFM micrographs showed significant difference. In the original SWNTs dispersion, highly individualised SWNTs were observed (See Figure 7.1). However, in the case of self-assembly with bis-fullerene dumbbell (Figure 7.5), various SWNTs were observed to be connected by either ‘head-to-head’ or ‘head-to-body’ assemblies. The structure of the self-assembled SWNTs networks are different from the SWNTs network resulted from a simple drying process. The self-assembled SWNT networks showed clear nanotube structures (individual SWNTs) within the networks. Each SWNTs connection produced in the self-assembly showed a clear junction point and no sign of SWNTs overlapping (Figure 7.6).

Figure 7.7 – AFM micrographs of self-assembled HiPco SWNTs with PEG$_{3350}$(C$_{60}$) diamond ring.
A control experiment to confirm the nature of fullerene linkers in SWNTs self-assembly was carried out with the PEG\textsubscript{3350}(C\textsubscript{60}) diamond ring. Since the diamond ring molecule only contains a single fullerene connected to a PEG chain to give a closed ring structure. No junction formation is expected when mixed with SWNT dispersions. Surprisingly, AFM micrographs of this control experiment showed an unusual SWNT structure (Figure 7.7). All observed SWNTs were attached to the edge of a solid particle. Since the mixture only contains SWNTs dispersion and the PEG\textsubscript{3350}(C\textsubscript{60}) in toluene, it must be a micelle structure from aggregated PEG\textsubscript{3350}(C\textsubscript{60}). The radial attached SWNTs are mainly individual SWNTs (some SWNTs bundles containing 2 – 3 nanotubes were also found). From the shape of the self-assembled SWNT structure, the PEG\textsubscript{3350}(C\textsubscript{60}) did not fully dissolve in the solution but remained as a big aggregate/micelle. Since toluene is a better solvent for fullerene than the PEG core, the fullerenes were expected to shield the PEG chain inside the core to minimise the PEG contact to the solvent. Thus, any free SWNTs floating around the PEG\textsubscript{3350}(C\textsubscript{60}) micelle can attach onto the surface via fullerenes insertion to form a supramolecular star shaped SWNT structure ‘nano-spider’. This is the only model which explains the shape of the observed SWNTs structure. Although PEG\textsubscript{3350}(C\textsubscript{60}) diamond ring may not be the best fullerene adducts for encapsulation since there are two covalent attachments on the fullerenes, the images show that it is possible to perform the self-assembly. This control experiment strongly supports the original hypothesis that the geometry of SWNT structure can be controlled by a fullerene linker. Since only one fullerene is available in the molecule, no SWNT-SWNT junctions can form. However, the self-assembly of SWNTs with PEG\textsubscript{3350}(C\textsubscript{60}) showed a novel type of assembly which all the observed SWNTs were attached to the PEG\textsubscript{3350}(C\textsubscript{60}) core. The predominance of open ends over side wall insertion may be due to steric effects.
7.4 Supramolecular Assembly of SWNT-SO

7.4.1 Characterisation of SWNT-SO

As HiPco SWNTs do not contain many large diameter SWNTs, the yield of SWNT junctions is relatively low. In order to study the effect of fullerene linkers to the final self-assembled SWNTs structure, higher encapsulation efficiency is needed. Therefore, SWNT-SO were employed since they are mainly large diameter SWNTs which are suitable for fullerene encapsulation.

Figure 7.8 - AFM micrographs of SWNT-SO dispersion in NMP (Prepared by 2 hours sonication and 2 hours centrifugation at 41,000 rpm). Micrograph on the left was taken from the centre of the Si wafer whereas image on the right was taken from the edge of the Si wafer surface. The small particles observed in the image are the polyamide generated in situ during NMP sonication.
Figure 7.9 – Diameter (left) and length (right) distribution of a SWNT-SO dispersion prepared by 2 hours sonication in NMP. Average diameter distribution is $3.2 \pm 1.6$ nm ($N = 50$) whereas average length distribution is $890 \pm 668$ nm ($N = 50$).

Similar to the HiPco SWNT dispersions, the SWNT-SO NMP dispersion was prepared by sonicating SWNT-SO powder in NMP (0.1mg/ml) for 2 hours. Ultracentrifugation was applied to separate the metal catalyst and large SWNTS bundles. The top 50% supernatant was collected and used in self-assembly experiment. As shown in Figure 7.8, most individualised SWNTs were observed at the centre of the AFM sample and large SWNTs networks resulting from the drying process were found on the edge of the sample. Both diameter and length distribution of the SWNT-SO were measured with the SWNTs found in the centre of the sample. A number of SWNT bundles containing 2 – 8 SWNTs were also observed in the sample which effectively increased the diameter distribution of the SWNT-SO to $3.2 \pm 1.6$ nm. Despite the presence of SWNT bundles, most of the SWNTs in the dispersion are larger than that of HiPco SWNTs which suggested that a higher fullerene encapsulation can be achieved. The average length of the SWNT-SO was found to be 890 nm which is significantly longer than HiPco SWNTs.
7.4.2 Concentration of SWNT-SO

Unlike HiPco SWNTs where only a fraction of the SWNTs are suitable for encapsulation, SWNT-SO contains mostly large diameter SWNTs and thus a higher encapsulation yield was expected. It has been shown that SWNT self-assembly is controlled by the fullerene end-capped linkers. To achieve hierarchical SWNT structures with different fullerene linkers, the amount of open ends in SWNTs should be correlated to the number of fullerenes available in the system. In order to study this effect, the SWNT concentration must be determined. It has been reported that UV-vis absorption can be used to calculate the concentration of SWNT in dispersion. Typically, the 660 nm absorption is used to calculate the concentration using a standard empirical extinction coefficient $(3264 \text{ ml mg}^{-1} \text{ m}^{-1})^{12}$. The 660 nm absorption of the SWNT-SO dispersion was found to have an absorbance of 0.132, thus, the amount of the SWNTs present in the dispersion is calculated as $0.132 \div (3264 \times 0.01) = 4 \times 10^{-3} \text{ mg/ml}$. (*0.01 is the length conversion for a 1 cm path length cuvette). However, knowing the mass of the SWNTs in the dispersion does not directly give any information of the number of SWNTs (mole). To obtain the number of mole of SWNTs in the dispersion, the molecular mass of SWNTs has to be determined first.

In order to calculate the relative molecular mass of the SWNTs, the number of carbon atoms per SWNT is needed (since SWNTs are heterogeneous, only an average value can be determined). The measured diameter distribution was slightly higher than individual SWNTs due to the presence of SWNT bundles. To eliminate the errors generated by SWNT bundles in the calculation, the bundles were excluded. Therefore, the revised mean SWNT diameter (with SWNT diameter below 3 nm) was 1.42 nm which is close to the manufacture’s value 1.4 nm. Molecular modelling of the SWNTs with 1.4 nm diameter showed there are 186 carbon atoms per 1 nm segment. Therefore, a 890 nm long SWNT would contain $(890 \times 186) 165540$ carbon atoms, giving a relative molecular mass of SWNT of $(165540 \times 12 \text{ g/mol}) 1986480 \text{ g/mol}$. 

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From UV-vis, the amount of SWNTs in dispersion was found to be $4 \times 10^{-3}$ mg/ml. Thus, the number of mole of SWNTs can be calculated as $4 \times 10^{-6}$ g/ml ÷ 1986480 g/mol = $2 \times 10^{-12}$ mol/ml. If SWNTs are assumed to have two open ends, the number of mole of open ends is $4 \times 10^{-12}$ mol/ml. Since it is very difficult to estimate the number of defect sites on SWNTs surface, 2 open ends per SWNTs were assumed as a first approach.

Once the concentration of open ends of SWNTs was determined, the ratio of SWNTs and fullerene could be controlled easily. The concentration of the fullerene linkers was controlled by dilution relative to the SWNT concentration, using the 336 nm absorption for the fullerene $\pi - \pi^*$ absorption with extinction coefficient 42658 L M$^{-1}$ cm$^{-1}$ for PCBM as a reference.
7.4.3 Self-Assembly of SWNT-SO in Binary Solvent System

![Diagram of supramolecular self-assembly of SWNT-SO with corresponding fullerenes end-capped linkers.](image)

**Figure 7.10** – Schematic illustration of supramolecular self-assembly of SWNT-SO with the corresponding fullerenes end-capped linkers.

A one to one ratio of fullerenes (F) and SWNT open ends (E) was chosen as a starting point for the self-assembly study with all linkers. Mono-fullerene end-capped linkers PrOET(OPCB), was tested in the assembly as a control experiment, which was not expected to result in junction formation. Atomic force microscopy (AFM) micrographs (Figure 7.11) revealed an interesting phenomenon which some SWNTs were stuck together. This mono-fullerene derivative should, in theory, inserted into the inner cavity of SWNTs to give peapod derivative. In previous peapod literature, fullerenes are likely to ‘dock’ onto the SWNT surface and slowly diffuse along the body to find an open end/hole. The observed SWNTs networks suggested the mono-linker acted as a surfactant molecule (some mono-linker must be trapped inside the SWNTs but could not be revealed by AFM) and glued together any adjacent SWNTs.
Figure 7.11 – AFM micrographs of self-assembly of SWNT-SO with mono-fullerene linker PrOEt(OPCB) in 1 : 1 ratio of open ends of SWNTs to fullerenes.

Bis-fullerene end-capped linker, PEG$_4$(OPCB)$_2$ is expected to induce simple junction formation by joining two SWNTs at the ends. Due to the flexible (PEG) nature of the linkers, the SWNT-SWNT junctions were found to have different inter-SWNTs angle (angle between the connected SWNTs). The concentration calculation was based on two open ends per SWNT, thus, all assembly was expected to be facilitated only at the SWNT terminals to give a ‘head-to-head’ addition. However, it is unlikely to obtain perfect SWNTs with no defects along the surfaces and the reality is multiple ‘holes’ are always present on the SWNT surfaces. If the holes are large enough (> 1.3 nm), they will encapsulate any fullerene resting on the SWNT surfaces and a ‘head-to-body’ junction will be formed. From the AFM micrographs (Figure 7.12), majority of the SWNTs junctions were found to be ‘head-to-body’ assemblies. There might be ‘body-to-body’ assemblies present in the sample; however, AFM can not distinguish such assembly from simple SWNT bundles. All ‘head-to-body’ SWNT assemblies showed sharp inter-SWNT angles and minimal SWNTs overlapping were observed. This strongly suggested that the SWNTs junctions resulted from self-assembly instead of a simple partial debundling process. In an ideal self-assembly of bis-fullerene end-capped PEG linkers and perfect SWNTs (2 open ends per tube), it should result in elongated SWNTs via pure ‘head-to-head’ addition. However, this ideal assembly was not observed due
to the significant number of defects present on the SWNTs surfaces which make ‘head-to-body’ assembly predominant.

Figure 7.12 – AFM micrographs of self-assembly of SWNT-SO with bis-fullerene linker PEG₃(OPCB)₂ in 1 : 1 ratio of open ends of SWNTs and fullerenes.

In the self-assembly of SWNT-SO and polydisperse tris-fullerene end-capped PEG linker PEG₃(OPCB)₃, a three-fold junction with three SWNTs joined via ‘head-to-head’ assembly was expected. However, due to the polydispersed nature of the PEG, it was not possible to remove the corresponding bis-fullerene linkers from the reaction mixture. The majority of the junctions observed were ‘head-to-body’ additions which were similar to that of pure bis-fullerene assembly since the linkers contain mostly bis-fullerene linkers. However, a few ‘head-to-head’ SWNTs junctions (Figure 7.13, marked with red arrows) were also observed within the micrographs. Unfortunately, the observed SWNTs junctions only contain two SWNTs. This outcome can be explained by either the fullerenes on polydisperse three-fold linkers did not encapsulate completely due to steric effects or the observed junctions resulted from a bis-fullerene linkers which was inseparable from the polydisperse tris-fullerene linkers.
Figure 7.13 – AFM micrographs of self-assembly of SWNT-SO with tris-fullerene linker PEG$_2$(OPCB)$_3$ in 1 : 1 ratio of open ends of SWNTs to fullerenes. Red arrows indicate the ‘head-to-head’ assemblies.

In order to eliminate the bis-fullerene contamination issue in polydisperse tris-fullerene end-capped linkers, a novel benzene core tris-fullerene end-capped linker with monodisperse multi-ethylene oxide arms was prepared. Multi-ethylene oxide arms were again chosen to incorporate flexibility into the linker and also retain the PEG solubility so the same self-assembly system could be used. Self-assembly of this monodisperse tris-fullerene linkers with SWNT-SO revealed unusual SWNT network formation. AFM micrograph (Figure 7.14, marked with ‘*’) showed clear SWNT-SWNT assembly with two ‘head-to-head’ junctions located on the same SWNT to form an unusual ‘C’ sharp junction (similar to a football goal shape). The observed SWNT junctions appeared to have an additional SWNT attached onto the surface. Assembled SWNTs may attract other SWNTs onto their surfaces to form SWNT bundles due to reduced molecular tumbling of big SWNTs self-assembled networks. Having two nearly 90° inter-SWNT angles on the same SWNT within a SWNTs structure is a strong evidence for the self-assembly between SWNTs and fullerene end-capped linkers.
Figure 7.14 – (Left) AFM image of SWNT self-assembly with monodisperse tris-fullerene end-capped linker, PEG$_{20}$OPCB$_3$ in 1:1 ratio of open ends and fullerenes. (Right) Enlarged SWNTs self-assembly region showing a clear ‘head-to-head’ SWNT-SWNT assembly in an unusual ‘C’ shape, marked with ‘*’.

7.4.4 TEM of Self-assembled SWNT-SO with Monodisperse tris-fullerene PEG Linker

The ultimate proof of the self-assembly is a high resolution TEM image with 3 SWNTs connected by a monodisperse tris-fullerene linker and all three fullerenes are clearly shown in the cavity of the SWNTs. Since TEM is a standard method to characterise peapods, the corresponding peapod TEM sample preparation is well established. In short, SWNTs filled with fullerene are sonicated in a low boiling point solvent for a short period of time, the semi-exfoliated dispersion is then drop casted onto a TEM grid. Low power and short time sonication does not exfoliate the SWNTs completely. However, having SWNTs bundles is a benefit in peapod imaging. Since both the TEM grid and SWNTs/C$_{60}$ are made with carbon, TEM can not resolve the two clearly. In order to have a good contrast in TEM image, the SWNTs must be deposited over the holes on the carbon grid. Bundles filled with fullerenes bridges over the holes, allowing the internal structure of SWNTs to be resolved clearly.
Figure 7.15 – TEM images of SWNT-SO self-assembled networks with monodisperse tris-fullerene end-capped PEG linker PEG$_{24}$(OPCB)$_3$ in a 1:1 ratio of opened end of SWNTs to fullerene (same sample as Figure 7.14). (Left) Image showing SWNT wrap around the carbon film on copper grid (red arrow). (Right) Possible SWNTs 3-way junction with three different SWNTs. TEM images were taken by Dr. Stephen Hodge.

SWNTs self-assembly can only be carried out with individualised SWNTs in dispersion at low concentration to avoid rebundling which increase the difficulty in TEM imaging. An attempt to image junction was made by drop casting the SWNT dispersion (SWNT-SO) with monodisperse tris-fullerene end-capped PEG linker PEG$_{24}$(OPCB)$_3$ onto holey carbon grid (Figure 7.15). However, Due to the strong adhesion between SWNTs and the carbon grid and the flexibility of individual spacers, very few SWNTs were suspended over the hole. Figure 7.15 (right) shows an image of a 3-way SWNTs junction formed by self-assembly of three SWNTs with the monodisperse tris-fullerene linker. It clearly showed the SWNT structure on the carbon grid but the internal structure is not revealed due to poor contrast.
7.5  **Self-assembly of SWNT-SO in Single Solvent (NMP)**

AFM analysis of self-assemblies suggested it is possible to form junctions with fullerene end-capped linkers. Although 10% toluene does not crash out SWNTs from dispersion, it may induce a small degree of rebundling between SWNTs due to interruption of NMP solvation shell by toluene molecules. Original peapod formation mechanism suggested that fullerene should not be completely individualised in order to achieve high filling yield\[^{108}\]. Thus using pure NMP to maximise SWNT individualisation even with poor linker solubility may be an alternative route for SWNT junction formation. In addition, the ratio between number of fullerenes (F) and number of open ends on SWNTs (E) should have a significant effect of the nature of the assembled structures. In the case of monodisperse tris-fullerene linkers, it is believed that if F is equal to E, it should create large SWNT networks as each open end should encapsulate a single fullerene. If E is larger than F, it should create a smaller SWNT network should form as all fullerenes should be encapsulated and excess SWNTs remain individualised. If E is smaller than F, there will be more fullerene available in the system which should saturate each SWNT open end, thus, no assemblies are expected. Due to these two factors (solubility and ratio), a set of self-assembly experiments without the addition of toluene were carried out. Self-assembly with SWNTs and various concentrations of monodispersed tris-fullerene end-capped linkers in pure NMP were prepared and studied by AFM. All self-assembly experiments were carried out with a constant concentration of SWNTs (concentration of open ends, \(4 \times 10^{-12}\) mol/ml) for consistency.
The number of junctions observed in the AFM micrographs is an important indication of the self-assembly. The number of SWNTs present in a network can only act as a preliminary indication of the assembly, since not all SWNTs within the networks were involved in junction formation. Thus, counting the number of junctions (both ‘head-to-body’ and ‘head-to-head’) present in the samples, the degree of self-assembly can be identified. Statistical analysis of the observed junctions (Figure 7.16) showed a significantly larger number of SWNTs junctions in 1 : 0.001 (E : F, open ends of SWNTs : number of fullerenes) ratio (data point 4). Unlike assembly with other ratios where only small SWNTs networks were formed with limited number of junctions, a complete SWNTs network which covered an area of 10 µm was observed in this 1 : 0.001 ratio (Figure 7.17). Since all the self-assembly experiments have the same concentration of SWNTs, the observed network size is solely attributed to the self-assembly
process, not the effect of SWNTs concentration. This finding matches the original hypothesis that large SWNTs networks are formed when the correct ratio of linkers and SWNTs are used (1 : 1, F : E in the hypothesis). However, there is a 1000-fold difference between the observed and theoretical ratio. The calculation of the concentration of SWNTs open ends is based on the assumption of a perfect structure (no defects) with two ends per tube which give a relatively huge error in the calculation, the actual ‘holes’ concentration (including open ends and defects on surfaces) must be greater than the calculated value. Thus, the actual ratio for self-assembly must be greater than the calculated 1 : 0.001 ratio (more like 1 : <0.001). Despite the network formations (with various ratio of SWNTs and fullerenes) observed in AFM were different from the hypothetical assumption, the amount of fullerene linkers present in the system did affect the size of the SWNTs self-assembled network which suggested junction formation can be controlled by the fullerene linkers. However, due to the heterogeneity of SWNTs (wide length distribution), it is difficult to control the final geometry of the self-assembled SWNTs networks.
Figure 7.17 – AFM micrographs of SWNT-SO self-assembly with varying ratio of open ends of SWNTs to fullerenes starting from (Top left, clockwise) 1:1 ratio, 1:10\(^1\), 1:10\(^2\), 1:10\(^3\), 1:10\(^4\), 1:10\(^5\) and 1:10\(^6\). All AFM images were taken from the centre of the Si wafer to minimise variation between samples. The big SWNTs network was only observed in the 1:0.001 sample (1000 open ends of SWNTs to 1 fullerene).

7.6 Proposed Mechanism of Self-Assembly in NMP

A proposed mechanism for SWNTs supramolecular self-assembly with monodispersed tris-fullerene end-capped linkers is illustrated in Figure 7.18. The mechanism can be divided into three steps. (1) A free tris-fullerene end-capped linker approaches the surface of SWNT and eventually absorbs due to strong van der Waal’s interactions between fullerene and SWNTs surface. (2) The exohedrally absorbed fullerene linker is then free to migrate on SWNT surface in any direction. (2a) represents the linker molecule migrating towards a defect site on the surface whereas in (2b) the molecule migrates towards the open end of the SWNT. The linker then insert into either (3a) a defect site or (3b) an open end. The non-encapsulated fullerenes can then attach to other SWNTs to form SWNTs junctions as illustrated in (ii).
However, if the reaction rate of the second fullerene insertion into another individual SWNT is identical to the first insertion (i), the ratio of the SWNTs and linkers should control the final structure of the assembly. However, AFM images (Figure 7.17) showed optimal network formation was observed at a much higher SWNTs concentration than the fullerene linkers which suggest that the network formation may be governed by a kinetic effect. It is possible that at high fullerene linker concentration (1:1, E:F), the fullerene linkers should attach onto most of the SWNTs surface to form SWNT-linker complex and leaving a relatively small amount of SWNTs remain individual. The remaining SWNT may then assemble onto the SWNT-linker complex to give small SWNT networks. These small SWNT networks have to diffuse and rotate into a right conformation for further self-assembly. However, SWNT networks are believed to have a slow diffusion rate (than pristine SWNTs) and reduced molecular tumbling, thus, self-assembly of two small SWNT networks may require longer time. Whereas in the case of low fullerene concentration (1:0.001, E:F), only a fraction of SWNT may be attached with the fullerene linkers to form SWNT-linker complex and the rest of the SWNTs remain as individual SWNT. Since there are significantly more individual SWNT than the SWNT-linker complex, it may increase the probability of individual SWNT bridging the SWNT-linker complex to form large SWNT network. Since this type of assembly involves individual SWNT, the self-assembly process may be more efficient and required less time than the self-assembly of two small SWNT networks (akin 1:1, F:E). When the concentration of fullerene is too low (below 1:1000, F:E), no large SWNT network are expected as there are not enough linkers for self-assembly. However, this is only a hypothetic mechanism, more experiments are required for verification. The self-assembly should be leave for longer time and more large networks may be observed even in higher fullerene concentration. In addition to time study, the self-assembly could be carried out at higher temperature so that all SWNTs species should have higher kinetic energy which should result in faster assembly.
Figure 7.18 – Schematic representation of self-assembly mechanism between SWNTs and mono-dispersed tris-fullerene end-capped linkers, PEG$_{24}$(OPCB)$_3$. i) Sequential steps in junction formation with (a) ‘head-to-body’ assembly and (b) ‘head-to-head’ assembly. ii) Resultant SWNTs junctions with both ‘head-to-body’ and ‘head-to-head’ assembly.
7.7 Annealing the Self-assembled SWNT Networks

AFM analysis confirmed that it is possible to connect SWNTs with fullerene end-capped linkers. However, the SWNTs within the junctions are not covalently connected which make it unsuitable for fabrication of electronic devices. In order to achieve continues SWNT self-assembled structure, all SWNT must be fused together. This covalently fused SWNT structure should provide better electron transport properties than any randomly aligned SWNT network. It has been proposed that annealing SWNT at high temperature (900 °C, in vacuo) could repair the side wall damages in SWNTs\textsuperscript{133}. Given that SWNTs within the junction are very close, annealing the SWNT junctions may fuse the SWNTs together (Figure 7.19).

In addition to fusing SWNTs, high temperature annealing should remove surface contamination (polyamide from NMP sonication, fullerene linkers on surface). Since PEG and polyamide are simple organic polymers, they degrade at elevated temperature (typical degradation temperature for polymer ~ 250 – 300 °C).

![Figure 7.19 – Schematic illustration of fusion of self-assembled SWNTs at high temperature in vacuo.](image)

After high temperature annealing in vacuo, the majority of the small particles (polyamide from NMP sonication, un-encapsulated fullerene linkers) were removed. However, small amount of particles (30 - 50 nm) appeared on the surface (figure 7.20). It is most likely to be the debris remained from the thermal degradation of the polymers or contamination results from the furnace.
Figure 7.20 – AFM micrographs of SWNT-SO self-assembly with monodisperse tris-fullerene linker (1:1 ratio). Right column showing the diameter for the SWNTs in the junctions.

High resolution AFM images of SWNT-SO self-assembly with monodisperse tris-fullerene linker (1:1 ratio) in pure NMP (annealed at 900 °C) are shown in Figure 7.20. These clearly showed the diameters of the SWNTs in the junctions were different from others which suggested junction formation between three different SWNTs. All SWNTs observed within the junctions were found to have diameter from 1.3 – 1.7 nm which suggest the junction formation is produced via fullerene encapsulation. The SWNT debundling process in NMP has been studied extensively by Coleman et al.\textsuperscript{12}. It has been shown that when SWNTs peel off from a bundle, there is no sharp angle between the two SWNTs (Figure 7.21).
Close inspection of the self-assembled SWNTs junctions (figure 7.20) revealed that the observed SWNTs junction resulted from the self-assembly process since the observed inter-SWNTs angles are sharp and diameter measurement revealed each SWNTs within the junction were individual SWNTs.

Unfortunately, it has not been possible to measure electrical conductivity of the SWNT junction to verify the covalent fusing of SWNTs. Such measurement could be performed in scanning tunnelling microscopy (STM) and should be studied in the future.

Figure 7.21 – Typical debundling process of SWNTs\textsuperscript{12}.
7.8 Conclusion

Extensive AFM analysis revealed that fullerene end-capped linkers can be employed to connect SWNTs via self-assembly to give SWNTs junctions. The self-assemblies have been demonstrated in both NMP/Tol and pure NMP solvent systems. However, diameter distribution of SWNTs was found to be the key in SWNTs self-assembly as shown by HiPco and SWNT-SO. Since the open ends of SWNTs are outnumbered by the surface defects, ‘head-to-body’ assemblies were observed predominantly and only limited ‘head-to-head’ junctions were observed. The mechanism of the self-assembly was believed to proceed via a kinetic route in which the diffusion of the initially formed SWNT self-assembled structure affect the size of resultant self-assembled SWNTs networks. Higher Temperature annealing in vacuo was found to be effective in removing the polyamide (from NMP sonication) and non-encapsulated fullerene linkers from the Si surface. High resolution AFM images showed the self-assembled SWNT junction with three distinct individual SWNTs which is good evidences for this supramolecular self-assembly of SWNTs with fullerene end-capped linkers. However, further optimisation to the self-assembly system is needed in order to gain more control over the self-assembled SWNTs structure. In addition, SWNTs with narrow length distributions should produce well-defined and uniform SWNT self-assembled structures.
7.9 Methods

Self-assembly of HiPco SWNTs and fullerene end-capped linkers in Binary Solvent System

HiPco SWNTs NMP dispersion was prepared by sonication (see section 6.7). Bis-fullerene end-capped PEG linker PEG$_{5}$OPCB$_{2}$ dumbbell and PEG$_{3350}$C$_{60}$ diamond ring were dissolved in toluene (0.1 mg/ml) respectively. 0.1 ml of the corresponding dumbbell and diamond ring toluene solution was added to 0.9 ml of NMP HiPco dispersion. The mixtures were mixed thoroughly with a glass pipette and it was then allowed to stand overnight for the self-assembly to proceed. 3μL of the mixtures were taken from each mixture with an eppendorf pipette and deposited onto clean Si wafer. The Si wafers were placed in a heavy duty glass contain and connected to vacuum. The container was then heated on a hot plate at 200 °C overnight to aid complete removal of NMP and toluene.

SWNT-SO Dispersion

Arc-discharged SWNTs (SWNT-SO) were purchased from Meijo Nano Carbon Co. Anhydrous N-methyl pyrrolidone (NMP) was purchased from Sigma Aldrich and used as-received. 2 mg of SO-SWNT and 20 ml of NMP was placed into a glass vial and fitted onto a probe sonicator (GEX 750, SONICS & MATERIALS). The vial was then immersed into a 3 L ice-water bath in order to absorb any heat generated during sonication. The SWNTs was then sonicated at 20% of the 750W power (GEX 750 ultrasonic processor with a 5 mm titanium alloy Ti-6Al-4V microtip, SONICS & MATERIALS INC, Newtown, US) for 2 hrs. A 3 L ice bath was used to maintain the temperature during sonication. The dispersion was then allowed to stand overnight. Large SWNTs bundles were then removed by centrifugation at 41,000 rpm for 2 hrs with an ultracentrifuge (Optima L-90K with SW41 Ti rotor, Beckmen Coulter). 50 % of the dark supernatant was collected using a glass pipette. The supernatant was dilute with NMP prior use.
Self-Assembly of SWNT-SO and fullerene end-capped linkers in binary solvent system NMP/Tol

0.9 ml of SWNT-SO NMP dispersions (4 µg/ml, open ends concentration 4 x 10^{-12} mol/ml) were placed in a glass vial. 0.1 ml of fullerene linkers toluene solution (fullerene concentration 4 x 10^{-11} mol/ml) were then mixed with the NMP dispersion. The mixtures were mixed thoroughly with a glass pipette and it was then allowed to stand overnight for the self-assembly to proceed. 3µL of the mixtures were taken from each mixture with an eppendorf pipette and deposited onto clean Si wafer. The Si wafers were placed in a heavy duty glass container and connected to vacuum. The container was then heated on a hot plate at 200 °C overnight to aid complete removal of NMP and toluene.

Self-Assembly of SWNT-SO and monodisperse tris-fullerene end-capped linker in NMP

1 mg/ml of monodisperse tris-fullerene linker dissolved in toluene and it was then diluted by a factor of 20,000 (divided in 2 steps, 0.1 ml of the stock solution was diluted to 2 ml with fresh toluene; then 10 µl of the first diluted solution was diluted to 10 ml with fresh toluene). By now the dilution solution (stock solution) has a fullerene concentration ~4 x 10^{-11} mol/ml.

Subsequent dilution of the stock solution by a factor of 10 (0.1 ml into 1 ml) give diluted linker solutions with fullerene concentration from 4 x 10^{-12} to 4 x 10^{-17} mol/ml. 0.1 ml of each linker solutions (including the stock) were transferred into separate clean glass vials. The vials were placed in a fume hood for 3-4 hours to allow toluene to evaporate. Then 0.9 ml of the SWNT-SO NMP dispersion was added to each vials (each vials contain different amount of fullerene linkers). The mixtures were then bath sonicated for 30 seconds to aid mixing of the SWNTs and fullerene linkers. The mixtures were then allowed to stand overnight for self-assembly to proceed. 3µL of the mixtures were taken from each mixture with an eppendorf pipette and deposited onto clean Si wafer. The Si wafers were placed in a heavy duty glass container and connected to vacuum. The container was then heated on a hot plate at 200 °C overnight to aid complete removal of NMP.
High Temperature Annealing

Si wafers (containing the SWNTs) were placed in a ceramic boat and placed inside a 45 cm quartz tube (one end sealed, one end equipped with a quartz to metal joint). The quartz tube was then placed inside a furnace and with the metal joint attached to a turbo pump (Leybold PT 70F). The quartz tube was then evacuated with the pump (full speed, 1200 Hz) for 5 min. After that the quartz tube was heated to 900 °C (heating rate, 30 °C/min). The temperature was maintained at 900 °C for 30 min for annealing. After 30 min, the furnace was switch off and the quartz tube was allowed to cool overnight under vacuum and samples were collected on the next day.
Chapter 8 – Future Studies and Conclusion

8.1 Overview

This thesis outlines the initial development of SWNT junction formation via the supramolecular self-assembly of SWNTs and fullerene end-capped linkers, including the synthesis of the linker molecules and establishing suitable conditions for SWNT junction formation. Synthetic methodology reported in literature did not yield the desired bis-fullerene end-capped linker (dumbbell); a novel fullerene-PEG adduct with a diamond ring structure was subsequently discovered. Functionalisation of fullerene C_{60} to produce fullerene linkers via direct surface functionalisation was challenging and alternative routes to achieve desired linkers were sought. Commercially available PCBM (phenyl-C_{61}-butyrl-acid-methylester) was employed in the synthesis of fullerene linkers; further functionalisation was carried out on the PCBM substituents rather than direct reaction with the fullerene which avoided the multiple addition issues. Fullerene end-capped linkers with different geometries (different number of fullerene end-caps) were synthesised by dibutyltin oxide (DBTO) catalysed transesterification between PCBM and the corresponding PEG cores. Purification of branched PEGs with multiple fullerene end caps were problematic due to the polydisperse nature of the PEG cores. Monodisperse PEG cores with well-defined chain lengths resolved the separation difficulty. The resulting monodisperse fullerene linker was purified by column chromatography and employed in SWNT self-assembly. Initial SWNT junction formation was studied with HiPco SWNTs in a binary solvent system (NMP/Tol). Only a fraction of the SWNTs within the HiPco SWNTs sample have sufficient space in their inner cavities to facilitate junction formation. The bis-fullerene end-capped linker was effective in producing SWNT-SWNT junctions. However, due to the large amount of surface defects available on the SWNTs, fullerene linkers were found to insert into SWNTs via the surface defects resulting in ‘head-to-body’ junction instead of the desired ‘head-to-head’ junction. The newly discovered diamond ring fullerene adduct was found to induce selective assembly via the SWNT open ends. The diamond ring adduct with long PEG chain has a
high tendency to agglomerate into large aggregates (micelle), due to the strong interaction of PEG chains. Fullerenes localised on the surface of the micelle then inserted into SWNTs to facilitate self-assembly. Once a first SWNT is attached onto the surface, it acts as a barrier for further incoming SWNTs. The second SWNT will approach to the self-assembled surface via its ends limiting the ‘body’ addition.

Self-assembly of SWNT-SO was found to be significantly more efficient due to the larger tube diameter. Linker molecules with 1, 2 and 3 fullerene caps were employed in the assembly of SWNT-SO. ‘Head-to-body’ junctions were observed predominantly due to the surface defects. Unique SWNT junction formation was observed in the self-assembly of SWNT-SO with mono-disperse tris-fullerene end-capped linker. An unusual ‘C’ shape SWNT structure with ‘head-to-head’ self-assembled SWNTs was observed. Further investigation of the SWNT self-assembly was performed in pure NMP system. Varying the concentration of the fullerenes was found to have a significant effect on SWNT self-assembly. The size of the self-assembled SWNT networks can be controlled by the availability of fullerene linkers, probably due to a kinetic effect. High resolution AFM images of the self-assembled SWNT junctions revealed the presence of three distinct individual SWNTs which provides evidence of the intended junction formation.
8.2 Future Studies

8.2.1 Fullerene Linkers in Photovoltaics (PV)

PEG grafted PCBM has been explored as additives to control the nano- and microstructure of the active layer (PCBM/P3HT, poly-3-hexylthiophene) and was found to produce highly stable and efficient polymer solar cells\textsuperscript{182,211}. The multiply-bound fullerenes (multi-fullerene linkers) may offer additional opportunities to enhance device performance, potentially acting as more effective nuclet, inherently bringing together groups of fullerenes. At the same time, reducing the proportion of hygroscopic PEG should decrease sensitivity of the device to moisture. Thus, these multi-fullerene linkers have been sent to a polymer photovoltaic group at Imperial College in which their effect in PV device performance will be investigated.

8.2.2 Rigid Fullerene Linkers

Since all fullerenes end-capped linkers employed in this study were synthesised with flexible PEG cores, the geometry of the SWNT junctions are, therefore, difficult to control. Instead of using flexible linkers, rigid fullerene linkers with well-defined angles between the fullerene end caps would be an advantage in junction characterisation. If fullerene linkers with specific geometry are used in the self-assembly, the SWNT junction should have a constant inter-SWNT angle. A benzene core with conjugated substituents is a perfect starting material of the synthesis of rigid linkers. Grafting fullerenes onto specific position in the conjugated benzene core gives a unique geometry to the linkers so SWNT junctions can be identified easily in AFM.

8.2.3 SWNTs with Narrow Diameter and Length Distributions

Although SWNT-SO contains mostly large diameter SWNTs which are suitable for fullerene encapsulation, there is also a small fraction of small diameter SWNTs which lowered the overall encapsulation efficiency. An ideal SWNT self-assembly should be performed with SWNTs having
diameters larger than 1.3 nm to give the highest encapsulation efficiency. There are various well
documented techniques which can be applied in SWNT diameter separation. The most suitable
technique to be employed in diameter separation is density gradient ultracentrifugation (DGU) (see
section 1.4.1 for more details). Apart from selective diameters separation, DGU also separates SWNTs
according to their lengths. Therefore, SWNTs with narrow diameter and length distributions can be
achieved using a single methodology. Together with rigid fullerene end-capped linkers, it should be
possible to generate well-defined SWNT self-assembled networks.

8.2.4 Ultra Short SWNTs

The length of SWNTs is important in SWNT junction formation as short SWNTs diffuse more easily than
long SWNTs. In addition to this diffusion issue, short SWNT segments may have lower defect to open
end ratio which should promote more ‘head-to-head’ junction formation. Although the SWNTs are
shortened to hundreds of nanometers after sonication, a significant number of ‘head-to-body’ junctions
were still observed in the assembly. Therefore, the SWNTs have to be shortened further, ideally down to
10 – 20 nm which should give a high open end to defect ratio which prevents ‘head-to-body’ junction
formation. A number of SWNT cutting techniques have been reported but the reported SWNT lengths
are around 50 nm which are still longer than the desired length\textsuperscript{212,213}. A modified sonication method
reported by Dai \textit{et al.} has been shown to shorten SWNTs down to < 10 nm\textsuperscript{213}. Ultra short SWNTs can be
prepared by sonication with addition of surfactant phospholipids into the solution and the resultant
SWNTs were separated by DGU to yield highly enriched short SWNTs.

8.2.5 Measurement of Electric Conductivity of SWNT Junction

An electric conductivity measurement should be carried out on the high temperature annealed SWNT
junctions. Covalently fused SWNT junction should show increased conductivity than non-annealed
junction. The measurement would be valuable in proving covalent fusing SWNT at the stated
experimental condition. It is important to establish and characterize covalently fused SWNT structure (see section 8.3.1).

8.3 Future Applications of SWNTs Self-Assembly

8.3.1 Nanoelectronics

As shown in Chapter 1, SWNTs have been studied extensively in nanoelectronics. Existing SWNT based nanoelectronics such as TFTs (thin-film transistors) and FETs (field-effect transistors) fabricated with random SWNT networks showed excellent performance. The only way to increase the performance further is having a well-defined SWNT network instead of random SWNT percolating network. The self-assembly of individual SWNTs can be employed to produce SWNT networks with better electron transport properties than randomly formed system. In addition, the self-assembly technology is not limited to SWNT-SWNT junction formation. Fullerenes covalently grafted on a substrate can also insert into SWNTs to give heterojunctions (SWNT-substrate junction). Controlling the distance between fullerenes on the substrate, it is possible to generate multi SWNT heterojunctions in a single self-assembly process. This technology has the potential to be developed into a large scale SWNT device fabrication where large single SWNT arrays are required (e.g. FETs).

In long run, the selective self-assembly of pure m-SWNTs and sc-SWNTs should be studied to suit different electronic applications. Pure m-SWNTs network could be used to replace ITO while pure sc-SWNTs could be applied in thin film transistors (TFT).

8.3.2 SWNTs Membrane with Unique Pore Sizes

Geometry of the fullerene linkers control the structure of self-assembled SWNT networks. Planar fullerene linkers with multiple fullerene caps should produce 2D SWNT networks. Fusing the self-assembled 2D SWNT networks will give strong SWNT networks which can be used in membrane
filtration. The pore size of the membrane can be controlled by the length of the SWNTs and the planar structure of fullerene linkers.

8.3.3 High Surface Area SWNT Scaffoldings

In addition to planar SWNT networks which can be used for electronics or membrane filtration, a 3D SWNT self-assembled structure can also be produced selectively using non-planar fullerene linkers. Due to the high aspect ratio of SWNTs, it is ideal for applications which require high specific surface area. With this self-assembly technique, well-defined 3D SWNT structures might be produced with a high surface area which can be employed in hydrogen storage, electrodes, and scaffolding for hierarchal nano-composites.
8.4 Concluding Remarks

A novel supramolecular motif and concept of SWNT-SWNT junction formation with fullerene end-capped linkers was proved by extensive AFM analysis. Although the resulting junction geometry (head-to-head, head-to-body) can not be controlled with existing methods, it has opened a way for selective SWNT assemblies. Self-assembly of short SWNTs with narrow length distributions and rigid fullerene linkers with well-defined geometry should produce highly ordered SWNT structures which can be applied in real-life applications. However, the self-assembly method has not been optimised. The parameters can be investigated further are solvents, effect of temperature, SWNT lengths. In order to utilise the full potential of this self-assembly technique, perfect SWNTs without defects have to be employed. The presence of defects along the SWNT surfaces is the major disadvantage of this technique as fullerene linkers can be easily trapped into the defect sites. Unfortunately, no synthetic method producing SWNTs without defects is currently available. Since this self-assembly technique can be employed in nano-electronic device fabrication, using SWNTs without defects not only benefits the SWNT junction formation (by limiting ‘head-to-head’ junction) but will also enhance the resulting device performance.
Appendix

A4 – $^1$H NMR spectra of PEG$_{3350}$-C$_{60}$ (diamond ring) with different $D1$ delay. The spectrum with $D1 = 20$ sec was chosen for characterisation as longer $D1$ does not result in further changes in integration.
List of Publications


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