Selective Solubilisation of Single Walled Carbon Nanotubes Using Polycyclic Aromatic Hydrocarbons

by

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B. Sc. (Hons.), M. Sc.

A thesis submitted to the Dublin Institute of Technology for the degree of Doctor of Philosophy (Ph.D.)

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August 2010
Abstract

Single-walled carbon nanotubes (SWCNTs) are proposed to be one of the most promising nanomaterials, with unique electronic and mechanical properties which lend themselves to a variety of applications. In all cases the quality of the SWCNT material is important, and for some applications it is paramount. Despite sustained efforts, all currently known SWCNT synthetic techniques generate significant quantities of impurities. They also grow in bundles or ropes and are largely insoluble in common organic solvents. SWCNTs can have a range of structures and their electronic properties (metallic or semiconducting) depend on their structure and as well as their diameters. Currently there is no production process that can produce only one particular type of SWCNTs. For these reasons, carbon nanotubes have been slow to reach maximum potential applications. To speed up the potential applications of SWCNTs it has now become mandatory to purify, increase the solubility, disperse and separate SWCNTs according to their electronic properties in a simplified and economical way. In this project polycyclic aromatic hydrocarbons (PAHs) of two oligomer series, namely the polyacene series and polyphenyl series, of systematically varied length, were used to selectively solubilise, disperse and separate SWCNTs produced by the high pressure decomposition of carbon monoxide (HiPco) and arc discharge (AD) methods according two their electronic properties. The interactions and debundling of SWCNTs are investigated through a fluorescence based concentration dependent model. This model defines the concentration range where aggregated and isolated SWCNTs exist. It was found that regardless of the type of SWCNTs
(HiPco or AD), the binding energy between SWCNTs and PAHs was the same and it increases as the molecular weight of PAHs increases, thereby establishing a linear relationship between binding energy of SWCNTs with PAHs and molecular weight of the corresponding PAHs, indicating the structure property relationship governing this solubilisation process. Atomic force microscopy was used to visualise the dispersed and isolated SWCNTs. To explore the selective solubilisation of SWCNTs with the aid of PAHs, Raman spectroscopy was used. From the Raman spectroscopy study it was found that a broad range of HiPco and AD SWCNTs were solubilized with little evidence of true structural selectivity of HiPco SWCNTs. It can be stated that although the longer PAHs have the capacity to solubilise larger diameter SWCNTs, due to their increased binding energy, in general a preference for smaller diameter SWCNTs was evident. This preference for smaller diameter nanotubes is reflected in the quantitative comparison of the solubilities of the two different types of SWCNTs, the smaller diameter HiPco SWCNTs being solubilised to a greater extent than the larger AD SWCNTs.
Declaration

I certify that this thesis which I now submit for examination for the award of PhD, is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

This thesis was prepared according to the regulations for postgraduate study by research of the Dublin Institute of Technology and has not been submitted in whole or in part for an award in any other Institute or University.

The work reported on in this thesis conforms to the principles and requirements of the Institute's guidelines for ethics in research.

The Institute has permission to keep, to lend or to copy this thesis in whole or in part, on condition that any such use of the material of the thesis be duly acknowledged.

Signature ___________________________ Date 6th August 2010
Acknowledgements

I express my deep sense of gratitude to Professor Hugh J. Byrne for his constant support, encouragement, and valuable suggestions during the course of this work. I am also indebted to Dr Theresa Hedderman for her valuable guidance.

I would like to thank the SFI (Science Foundation Ireland) for providing me with a scholarship for the entire duration of this research.

I am really grateful to Anne Shanahan, Dr Luke O'Neill and Andrew Hartnett for their help with the spectroscopy, AFM and IT problems.

I wish to thank all my past and present FOCAS colleagues for creating a relaxed, high quality working environment, especially- Louisa Hartnett, Rosa Lopez and Sabrina Lane for organizing those fabulous FOCAS parties! Also how can I ever forget the cheerful company of Dr Qiaohuan Cheng and Dr Priya Baskar Rao during various conferences in Ireland, Austria, France, and China.

I wish to express my heartfelt love to my parents, elder sister, parents in law, and husband Tanmoy for their constant support, motivation and encouragement over the years.
# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>AD</td>
<td>Arc Discharge</td>
</tr>
<tr>
<td>AD SWCNT</td>
<td>AD Single Walled Carbon Nanotube</td>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>Bz-Bz</td>
<td>Benzene Dimer</td>
</tr>
<tr>
<td>Bz-Np</td>
<td>Benzene and Naphthalene</td>
</tr>
<tr>
<td>C-C</td>
<td>Carbon-Carbon single bond.</td>
</tr>
<tr>
<td>C=C</td>
<td>Carbon-Carbon double bond</td>
</tr>
<tr>
<td>CCD</td>
<td>Charged Coupled Device</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon Nanotubes</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>Co-MCM-41</td>
<td>Cobalt Mobil Catalytic Material number 41</td>
</tr>
<tr>
<td>CoMoCAT</td>
<td>Cobalt- Molybdenum Catalyst</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DGU</td>
<td>Density Gradient Ultracentrifugation</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DOC</td>
<td>Deoxycholate Sodium</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>D₂O</td>
<td>Deuterium Oxide</td>
</tr>
<tr>
<td>FET</td>
<td>Field Effect Transistor</td>
</tr>
<tr>
<td>Fe (CO)₅</td>
<td>Iron Penta carbonyl</td>
</tr>
<tr>
<td>HiPco</td>
<td>High Pressure decomposition of Carbon monoxide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>HIF-1</td>
<td>Hypoxia-Inducible Factor 1 alpha</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>K-doping</td>
<td>Potassium doping</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>LV SWCNT</td>
<td>Laser Vaporised Single Walled Carbon Nanotube</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Multi Walled Carbon Nanotubes</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>NH₃</td>
<td>Ammonia</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>NO₂</td>
<td>Nitrous Oxide</td>
</tr>
<tr>
<td>Np-An</td>
<td>Naphthalene and Anthracene</td>
</tr>
<tr>
<td>Np-Np</td>
<td>Naphthalene Dimer</td>
</tr>
<tr>
<td>PAHs</td>
<td>Polycyclic Aromatic Hydrocarbons</td>
</tr>
<tr>
<td>PD</td>
<td>Parallel-Displaced</td>
</tr>
<tr>
<td>PmPV-co-DOctOPV</td>
<td>Poly p-phenylene vinylene-co-2,5-dioctyloxy-m-phenylenevinyl</td>
</tr>
<tr>
<td>PL</td>
<td>Photo Luminescence</td>
</tr>
<tr>
<td>PSS</td>
<td>Polystyrene Sulfonate</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinyl Pyrrolidone</td>
</tr>
<tr>
<td>RBMs</td>
<td>Radial Breathing Modes</td>
</tr>
<tr>
<td>SC</td>
<td>Sodium Cholate</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium Dodecyl Sulphate</td>
</tr>
<tr>
<td>SDBS</td>
<td>Sodium Dodecylbenzene Sulphonate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>siRNAid</td>
<td>Small Interfering Ribonucleic Ac</td>
</tr>
<tr>
<td>SPM</td>
<td>Scanning Probe microscopy</td>
</tr>
<tr>
<td>SWCNTs</td>
<td>Single Walled Carbon Nanotubes</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UV-Vis-NIR</td>
<td>Ultraviolet-Visible- Near Infrared</td>
</tr>
<tr>
<td>Y/Ni/C</td>
<td>Yttrium, Nikel and Graphite</td>
</tr>
</tbody>
</table>
# Table of Contents

Abstract ................................................................................................................................. i
Declaration ............................................................................................................................. iii
Acknowledgements .............................................................................................................. iv
Abbreviations ........................................................................................................................ v
List of Figures ......................................................................................................................... 4
List of Tables ........................................................................................................................... 12

Chapter 1  Introduction & Background............................................................................. 14
  1.1 Nanotechnology and Nanomaterials ........................................................................... 14
  1.2 Overview of SWCNTs ................................................................................................. 16
  1.3 Applications of CNTs .................................................................................................. 20
  1.4 Limitations .................................................................................................................. 26
  1.5 Research Objective ..................................................................................................... 27
  1.6 Background Study ....................................................................................................... 28
  1.7 Aims of Research ........................................................................................................ 35
  1.8 Thesis Outline ............................................................................................................. 38
References ............................................................................................................................. 39

Chapter 2  An Introduction to Single Walled Carbon Nanotubes.51
  2.1 Introduction ................................................................................................................ 51
  2.2 Structure of SWCNTs ............................................................................................... 52
  2.3 Electronic Properties ................................................................................................. 54
  2.4 Production Methods of SWCNTs ............................................................................... 59
    2.4.1 Arc Discharge ..................................................................................................... 60
    2.4.2 Gas Phase Decomposition of CO ...................................................................... 61
  2.5 Processing of SWCNTs ............................................................................................. 61
    2.5.1 Size Exclusion Chromatography ...................................................................... 62
    2.5.2 Dielectrophoresis Method ................................................................................ 63
    2.5.3 Amine Assisted Method .................................................................................... 64
    2.5.4 Organic Processing ............................................................................................ 65
  2.6 Review of Different Methods for the Selective Solubilisation of SWCNTs ............... 66
  2.7 Conclusion .................................................................................................................. 74
References ............................................................................................................................. 75
Chapter 3  Polycyclic Aromatic Hydrocarbons ......................... 84
3.1 Introduction to Aromatic Hydrocarbons ................................................. 84
3.2 Physical Properties of PAHs ................................................................. 85
3.3 Electronic Structure of PAHs ................................................................. 91
3.4 Crystal Structure of PAHs .................................................................... 93
3.5 Interaction between PAHs and Graphite ............................................. 96
3.6 Conclusion .......................................................................................... 101
References .............................................................................................. 102

Chapter 4  Experimental Methods .................................................. 106
4.1 Introduction ........................................................................................ 106
4.2 Spectroscopic Techniques ................................................................. 106
4.3 Electronic Spectroscopy .................................................................... 107
  4.3.1 Absorption Spectroscopy .............................................................. 110
  4.3.2 Fluorescence Spectroscopy ........................................................... 114
4.4 Vibrational Spectroscopy ................................................................. 116
  4.4.1 Raman Spectroscopy ................................................................. 117
4.5 Microscopic Techniques .................................................................... 120
  4.5.1 Atomic Force Microscopy (AFM) ................................................ 121
4.6 Conclusion ........................................................................................ 126
References .............................................................................................. 127

Chapter 5  Material Characterisation & Solvent Selection .......... 131
5.1 Introduction ........................................................................................ 131
5.2 Solvent Characterisation and Selection ............................................. 132
5.3 Raman Spectroscopy ........................................................................ 139
  5.3.1 SWCNTs ................................................................................... 140
  5.3.2 PAHs ......................................................................................... 148
5.4 Probing the Interaction between SWCNTs and PAHs ..................... 149
  5.4.1 Results from UV-Vis-NIR Spectroscopy .................................... 150
  5.4.2 Results from Fluorescence Spectroscopy .................................. 154
  5.4.3 AFM ......................................................................................... 157
5.5 Conclusion ........................................................................................ 160
References .............................................................................................. 162
Chapter 6  A Study of the Interaction between Different Types of Single Walled Carbon Nanotubes and Polycyclic Aromatic Hydrocarbons

6.1 Introduction.......................................................... 169
6.2 Sample Preparation.................................................. 170
6.3 Results and Discussion ............................................. 172
6.4 Conclusion........................................................... 194
References........................................................................... 197

Chapter 7  A Raman Spectroscopic Study of the Solubilisation of SWCNTs by Polycyclic Aromatic Hydrocarbons

7.1 Introduction.......................................................... 201
7.2 Sample Preparation.................................................. 202
7.3 Results and Discussion ............................................. 204
7.4 Conclusion........................................................... 224
References........................................................................... 225

Chapter 8  Conclusion

8.1 Summary of the Chapters ........................................... 228
8.3 Conclusion........................................................... 230
References........................................................................... 233

Appendix............................................................................... 234

Publications and Presentations............................................. 237
List of Figures

Figure 1.1 Rolling of graphene to form a SWCNT ...................................... 17
Figure 1.2 Classification of carbon nanotubes. ........................................... 17
Figure 1.3 Physical structure of SWCNTs,
(a) represents an armchair SWCNT, .............................................. 18
(b) zigzag SWCNT, and (c) chiral SWCNT ................................. 18
Figure 1.4 (i) Comparison of the annual number of scientific publications
with the number of patent filings and issuances for the carbon
nanotube areas................................................................................. 25
(ii) Percentages of total patent filings and issuances made by
individuals in a country or region and filed either in the same
location (superscript 1) or in a different location (superscript 2)..25
(iii) Patent filings and issuances divided according to the main the
area of invention........................................................................... 25
Figure 1.5 Proposed mapping of anthracene and \( p \)-terphenyl to armchair
and zigzag SWCNT respectively.................................................. 28
Figure 1.6 A plot of the fraction of free anthracene as a function of
Concentration.................................................................................. 30
Figure 1.7 A plot of the fraction of free \( p \)-terphenyl as a function of
concentration ................................................................................ 31
Figure 1.8 Relationship between binding energy and molecular weight .... 34
Figure 2.1 Unrolled honeycomb lattice of a SWCNT................................. 52
Figure 2.2 Energy bands of different types materials............................ 54
Figure 2.3 Electronic properties of a straight SWCNTs.......................... 55
Figure 2.4 Electronic properties of a twisted SWCNTs.......................... 56
Figure 2.5 Schematic structures of SWCNTs and how the electronic
properties of the nanotubes are determined.
(a) A (10,10) arm-chair nanotube................................................. 57
(b) A (12, 0) zigzag nanotube....................................................... 57
(c) The (14, 0) zigzag tube is semiconducting............................... 57
(d) A (7, 16) tube is semiconducting............................................ 57
Figure 2.6 The van Hove singularities are apparent as sharp spikes in the density of states. The $\nu_1-c_1$ is the first electronic transition between van Hove singularities, corresponding to the band gap in metallic (a) and semiconducting SWCNTs (b) respectively.

Figure 2.7 Picture of the solutions of metallic CoMoCAT, HiPco and LV SWCNTs (from left to right).

Figure 2.8 SWCNTs dispersion sorted by the DGU method. “Top” and “bottom” indicate the relative position of each colour in the DGU columns, and each colour is dominated by SWCNTs of a different diameter.

Figure 2.9 Schematic diagram of metallic semiconducting SWCNTs separation using a column filled with agarose gel beads. M, metallic SWCNTs; S, semiconducting SWCNTs.

Figure 3.1 C$_6$H$_6$ (benzene):
(a) chemical structure formula,
(b) spatial distribution of the $\sigma$-orbitals which are responsible for the steric configuration,
(c) spatial distribution of the $\pi$-orbitals forming a delocalised $\pi$-system.

Figure 3.2 Structure of naphthalene (a). (b), (c) and (d) are the canonical forms of naphthalene.

Figure 3.3 Structure of anthracene (a) and (b).

Figure 3.4 Structure of tetracene.

Figure 3.5 Structure of pentacene.

Figure 3.6 Structure of biphenyl.

Figure 3.7 Structure of $p$-terphenyl.

Figure 3.8 Structure of $p$-quaterphenyl.

Figure 3.9 Structure of $p$-quinquephenyl.

Figure 3.10 Relative energy of $p$-terphenyl as a function of the torsion angle.
Figure 3.11  (a) absorbance spectra of the polyphenyl series…………………93
         (b) plot of the energies of the first absorption maxima of the
         various oligomeric series against 1/ \((N+\sigma)\) where \(N\) is the
         conjugation length and \(\sigma\) represents a contribution from the
         chain ends................................................................................ .. 93

Figure 3.12  Monoclinic unit cell for biphenyl ............................... ..94

Figure 3.13  Different views of the anthracene unit cell to describe the
         definition of the three characteristic angles:
         (i) depicting the herringbone angle \(\theta\), .................................95
         (ii) the tilting angle \(\chi\) and .................................................95
         (iii) the angle between two inequivalent molecules \(\delta\) .......... .95

Figure 3.14  The optimized geometries of \((Np- Np)\) with respect
         to selected degrees of freedom. A face to face
         configuration is represented in (a) (shown displaced for
         clarity), while the PD type structures are shown
         in (b) to (f) and the T-type structures are given in
         (g) and (h). .............................................................................. .97

Figure 3.15  The top view of the PD-type PAHs clusters ..................... .98

Figure 3.16  Binding energy per PAHs clusters as a function of \(\pi-\pi\) pair. ... ..99

Figure 3.17  Binding energy per PAH molecule on graphite as a function of
         number of carbon atoms. ......................................................... 100

Figure 4.1   Absorption and emission processes. ................................. 108

Figure 4.2   Jablonski diagram showing the sequence of steps leading
         to radiative decay................................................................. 109

Figure 4.3   Schematic set-up of UV-Vis-NIR spectrometer ................. 113

Figure 4.4   Absorbance spectra of
         (i) polyacene PAHs and......................................................... 114
         (ii) HiPco SWCNTs.............................................................. 114

Figure 4.5   Layout of a typical fluorescence spectrometer...............   115

Figure 4.6   Fluorescence spectra of polyacene PAHs .......................... 116
Figure 4.7  The Stokes and the anti Stokes shift in the normal 
Raman and the resonance Raman R- Rayleigh scattering, 
S-Stokes Raman scattering, AS-Anti stokes 
Raman Scattering ................................................................. 119

Figure 4.8  Raman spectrum of SWCNTs.................................................. 120

Figure 4.9  Principal of AFM..................................................................... 122

Figure 4.10  Force as a function of probe distance from sample ................. 123

Figure 4.11  AFM image of functionalised SWCNTs................................... 125

Figure 5.1  Absorbance of naphthalene, biphenyl and toluene. ................. 133

Figure 5.2  Fluorescence spectra of toluene, biphenyl and naphthalene... 134

Figure 5.3  Absorbance spectra of p-quinquephenyl in toluene 
at different concentrations....................................................... 135

Figure 5.4  Absorbance spectra of pentacene in toluene at different 
temperatures. Spectra are offset for clarity. .......................... 135

Figure 5.5  Absorbance spectra of chloroform and toluene. ................. 136

Figure 5.6  Fluorescence spectra of toluene and chloroform. 
Excitation wavelengths were taken as 276 nm and 269 nm 
respectively. .............................................................................. 136

Figure 5.7  Absorbance spectra of p-quinquephenyl in chloroform at different 
concentrations. ........................................................................ 137

Figure 5.8  Plot of absorbance of p-quinquephenyl at 311 nm 
in chloroform as a function of concentration............................. 138

Figure 5.9  Raman spectra of pristine (i)HiPco  and (ii) AD  SWCNTs. 
Insets are RBMs region of corresponding SWCNTs 
using 532 nm (2.33 eV) as source. ........................................... 141

Figure 5.10  RBMs of pristine (i) HiPco and (iii) AD  SWCNTs 
with 785 nm (1.58eV), 660  nm (1.88 eV), 
532 nm (2.33 eV) and 473 (2.62 eV) as source....................... 142
(ii) combined Raman spectra of HiPco....................................... 142 
(ii) and AD (iv) SWCNTs for the different lasers............... 142
Figure 5.11  Kataura plot representing optical transition energy of metallic and semiconducting SWCNTs as a function of diameter of SWCNTs. Black and red circles represent semiconducting and metallic SWCNTs respectively  

Figure 5.12  A plot of $\omega_{RBM}$ versus inverse of diameters (1/d) of pristine (i)HiPco and (ii) AD SWCNTs  

Figure 5.13  Raman spectra of polyacene (i) and polyphenyl (ii) oligomers at 785 nm (1.58 eV) laser. Spectra are offset for clarity  

Figure 5.14  Absorbance spectra of  
(i) naphthalene,  
(ii) anthracene and  
(iii) tetracene in the absence and presence of HiPco SWCNTs at concentration $\sim 1.25 \times 10^{-3}$ mol/L for naphthalene, $\sim 1.56 \times 10^{-4}$ mol/L anthracene and $\sim 1.95 \times 10^{-5}$ mol/L for tetracene  

Figure 5.15  Absorbance spectra of  
(i) biphenyl at concentration $\sim 6.25 \times 10^{-4}$ mol/L,  
(ii) $p$-terphenyl at concentration $1.95 \times 10^{-5}$ mol/L  
(iii) $p$-quaterphenyl at concentration $\sim 9.76 \times 10^{-6}$ mol/L and  
(iv) $p$-quinquephenyl at concentration $\sim 9.76 \times 10^{-6}$ mol/L in the absence and presence of HiPco SWCNTs  

Figure 5.16  Fluorescence spectra of  
(i) naphthalene at concentration $\sim 3.125 \times 10^{-4}$ mol/L,  
(ii) anthracene at concentration $\sim 3.9062 \times 10^{-5}$ mol/L,  
(iii) tetracene at concentration $\sim 1.9531 \times 10^{-5}$ mol/L in the absence and presence of HiPco SWCNTs  

Figure 5.17  Fluorescence spectra of  
(i) biphenyl at concentration $\sim 7.812 \times 10^{-5}$ mol/L,  
(ii) $p$-terphenyl at concentration $\sim 1.22070 \times 10^{-8}$ mol/L,  
(iii) $p$-quaterphenyl at concentration $\sim 5.9604 \times 10^{-10}$ mol/L and  
(iv) $p$-quinquephenyl at concentration $\sim 4.547 \times 10^{-15}$ mol/L in the absence and presence of HiPco SWCNTs
Figure 5.18    AFM image and corresponding diameter distribution of bundled pristine HiPco SWCNTs.................................158

Figure 5.19    AFM image and corresponding diameter distribution of debundled HiPco SWCNTs in the HiPco/tetracene composite sample......159

Figure 6.1    Plots of maximum fluorescence intensity of
(i) naphthalene,.................................................................173
(ii) anthracene   and.......................................................173
(iii) tetracene as a function of concentration in the absence
(triangle) and presence (diamond) of HiPco SWCNTs..........173

Figure 6.2    Plots of maximum fluorescence intensity of
(i) biphenyl .................................................................175
(ii) p-terphenyl .............................................................175
(iii) p- quaterphenyl and ..............................................175
(iv) p-quinquephenyl as a function of concentration in the
absence (triangle) and presence (diamond) of HiPco
SWCNTs......................................................................175

Figure 6.3    Plots of the fraction of free
(i) naphthalene,.................................................................179
(ii) anthracene and .......................................................179
(iii) tetracene as a function of concentration.......................179

Figure 6.4    Plots of the fraction of free
(i) biphenyl, .................................................................181
(ii) p-terphenyl.............................................................181
(iii) p-quaterphenyl and ..............................................181
(iv) p-quinquephenyl as a function of concentration..........181

Figure 6.5    A plot of the fraction of free PAHs as a function of
concentration for HiPco SWCNTs and AD SWCNTs composite.
The solid and doted lines are the best fit to equation 1.1
for HiPco and AD SWCNTs respectively..............................182

Figure 6.6    A plot of the aggregation fraction of HiPco SWCNTs
In the presence of anthracene as function of concentration.... 183
Figure 6.7 (i) AFM image of HiPco SWCNTs of HiPco/tetracene sample at concentration \( \sim 3.051 \times 10^{-7} \text{ mol/L} \), (ii) Diameters of HiPco SWCNTs in this sample. 184

Figure 6.8 (i) AFM image of HiPco SWCNTs of HiPco/tetracene sample at concentration \( \sim 9.536 \times 10^{-9} \text{ mol/L} \), (ii) Diameters of HiPco SWCNTs in this sample. 184

Figure 6.9 Characteristic concentrations as a function of dispersion limit. 185

Figure 6.10 A plot of estimated dispersion limit of HiPco (squares) and AD (triangles) SWCNTs as a function of molecular weight of PAHs. 187

Figure 6.11 Binding energies per PAH molecule with HiPco SWCNTs as a function of molecular weight of PAHs. 189

Figure 6.12 Pre-exponential frequency factor as a function of molecular weight of PAHs. 192

Figure 6.13 A plot of maximum quenching of PAHs with HiPco (squares) and AD (triangles) SWCNTs as a function of molecular weight of PAHs. The solid and straight lines are indicative of trends. 193

Figure 6.11 (a) Recalculated \((\pi)\) binding energy along with the published \((\pi^2)\) one. 196

Figure 7.1 Raman spectra of HiPco/naphthalene composite samples of concentrations (i) \( \sim 1.17 \times 10^{-4} \text{ mol/L} \) and (ii) \( \sim 1.46 \times 10^{-5} \text{ mol/L} \) respectively at 532nm (2.33 eV) excitation wavelength. Insets are the RBMs of corresponding samples after background correction and fittings. 205

Figure 7.2 Plots of RBMs shift as a function of percentage of counts of SWCNTs in (i) HiPco/naphthalene and (ii) AD/naphthalene composite samples at concentration \( \sim 1.46 \times 10^{-5} \text{ mol/L} \) and \( \sim 2.92 \times 10^{-5} \text{ mol/L} \) respectively at the different laser energies. 206
Figure 7.3  Plots of RBMs shift as a function of percentage of counts of SWCNTs in (i) HiPco/biphenyl and (ii) AD/biphenyl composite sample at concentration ~ 3.05 x 10^-7 mol/L and ~ 1.95 x 10^-5 mol/L at different laser energies respectively. ................................................................. 209

Figure 7.4  Plots of RBMs shift as a function of percentage of counts of SWCNTs in (i) HiPco/tetracene and (ii) AD/tetracene composite samples at concentration ~ 4.76 x 10^-9 mol/L and ~ 2.44 x 10^-6 mol/L at different laser energies respectively ................................................. 211

Figure 7.5  Plots of RBMs shift as a function of percentage of counts of SWCNTs in (i) HiPco/p-quaterphenyl and (ii) AD/p-quaterphenyl composites at concentration ~ 3.72 x 10^-11 mol/L at different laser excitation energies. ........ 214

Figure 7.6  A plot of overall diameter distribution of HiPco and AD SWCNTs selected by PAHs ................................................................. 218

Figure 7.7  A plot of Number/Concentration as a function of ω_{RBM}s .................. 221

Figure 7.8  Total number of solubilised AD and HiPco SWCNTs as function of molecular weight of PAHs ................................................. 222

Figure 8.1  Different types of non linear PAHs .............................................. 232
List of Tables

Table 1.1 Examples of notable properties of SWCNTs ......................... 19
Table 1.2 PAHs of polyacene and polyphenyl series .......................... 36
Table 2.1 Classifications of SWCNTs ................................................. 53
Table 3.1 Experimental unit cell parameters for some oligomers of phenyl series at room temperature. $a$, $b$, $c$ and $\beta$
denote the length of the unit cell parameters and monoclinic angle respectively ........................................... 94
Table 3.2 Binding energy of PAHs on graphite .................................. 99
Table 5.1 Solubility of oligomers of polyphenyl and polyacene oligomers in chloroform ............................................. 139
Table 5.2 RBMs shift and the corresponding structure assignments for pristine HiPco SWCNTs at different laser energy excitations ... 147
Table 5.3 RBMs shift and the corresponding structure assignments for pristine AD SWCNTs at different laser energy excitations ...... 148
Table 6.1 Concentration ranges for increased quenching in HiPco SWCNTs dispersions and characteristic concentrations for different polyacene oligomers ............................................. 178
Table 6.2 Concentration ranges for increased quenching in HiPco SWCNTs dispersions and characteristic concentrations for different polyphenyl oligomers ............................................. 180
Table 6.3 Parameters for the calculation of binding energy .................. 188
Table 7.1 Concentration range of each PAH composite ........................ 203
Table 7.2 Concentration of each PAH composite for Raman characterization .......................................................... 203
Table 7.3 RBM frequencies and the corresponding structure assignments for SWCNTs in HiPco/naphthalene composite sample at different laser energies .......... 207
Table 7.4 RBM frequencies and the corresponding structure assignments for SWCNTs in AD/naphthalene composite sample at different laser energies .......... 207
Table 7.5  Classification of overall diameter distribution of pristine HiPco and AD SWCNTs ............................................... 208

Table 7.6  RBM frequencies and the corresponding structure assignments for SWCNTs in HiPco/biphenyl composite sample at different laser energies ......................... 210

Table 7.7  RBM frequencies and the corresponding structure assignments for SWCNTs in AD/biphenyl composite sample at different laser energies ............................................. 210

Table 7.8  RBM frequencies and the corresponding structure assignments for SWCNTs in HiPco/tetracene composite sample at different laser energies ......................... 212

Table 7.9  RBM frequencies and the corresponding structure assignments for SWCNTs in AD/tetracene composite sample at different laser energies ............................................. 212

Table 7.10 RBM frequencies and the corresponding structure assignments for SWCNTs in HiPco/p-quaterphenyl composite sample at different laser excitation energies .......... 214

Table 7.11 RBM frequencies and the corresponding structure assignments for SWCNTs in AD/p-quaterphenyl composite sample at different laser excitation energies .......... 215
Chapter 1 Introduction & Background

1.1 Nanotechnology and Nanomaterials

Nanotechnology involves the fabrication and use of materials and devices so small that the convenient unit of measurement is the nanometre (one thousand-millionth of a meter). Alternatively, it may be considered to be the art of manipulating and exploiting the properties of matter at a molecular level [1]. It is a field of applied science and technology covering a very broad range of disciplines including colloidal science, chemistry, applied physics and biology [2]. Although the main unifying theme is the control of matter on a scale smaller than one micrometer, nanotechnology can mean different things to different people; therefore, the journal Nature Nanotechnology asked a range of researchers, industrialists and others what nanotechnology means to them. According to Jackie Ying (the executive director of the Institute of Bioengineering and Nanotechnology in Singapore, and adjunct professor of chemical engineering at the Massachusetts Institute of Technology), “nanotechnology is a toolbox that provides nanometre-sized building blocks for the tailoring of new materials, devices and systems. The nanometre length scale (that is < 100 nm) offers unique size-dependent properties in physico–chemical phenomena. It also presents unique bio-mimetic features essential in the creation of complex structures for tissue scaffolds and artificial organs/implants [3]”. To Robert Langer (one of 13 Institute Professors at the Massachusetts Institute of Technology, the recipient of the 2002 Draper Prize and a member of the National Academies of Sciences and Engineering and the
Institute of Medicine), “nanotechnology is concerned with work at the atomic, molecular and supra-molecular levels in order to understand and create materials, devices and systems with fundamentally new properties and functions because of their small structure” [3]. According to Mauro Ferrari (professor of molecular medicine at the University of Texas Health Science Center, of experimental therapeutics at the M.D. Anderson Cancer Center, and of bioengineering at Rice University), “at the nanoscale there is no difference between chemistry and physics, engineering, mathematics, biology or any subset thereof. An operational definition of nanotechnology involves three ingredients: (1) nanoscale sizes in the device or its crucial components; (2) the man-made nature; and (3) properties that only arise because of the nanoscopic dimensions” [3]. He also stated “the great promise of nanotechnology may be the necessary focus on solving problems, rather than on academic distinctions and the setting of disciplinary fences to benefit ivory-tower dwellers”.

Nanotechnology deals with nanomaterials. The prefix ‘nano-’ comes from the Greek word meaning “dwarf”. In science, nano means a measure of $10^{-9}$ units [3]. Over the past decade, nanomaterials have been the subject of enormous interest. These materials, notable for their extremely small feature size, have the potential for wide-ranging industrial, biomedical, and electronic applications [4]. Nanomaterials can be metals, ceramics, polymeric materials, or composite materials. Their defining characteristic is a very small feature size in the range of 1-100 nm, in at least one dimension [4]. Although widespread interest in nanomaterials is recent, the concept was in existence as early as 50 years ago. Physicist Richard Feynman delivered a talk in 1959 entitled “There's Plenty of Room at the Bottom”, in which he commented that there were no
fundamental physical reasons that materials could not be fabricated by manoeuvring individual atoms [5]. Nanomaterials have actually been produced and used by humans for hundreds of years - the beautiful ruby red colour of some glass is due to gold nanoparticles trapped in the glass matrix. The decorative glaze known as lustre, found on some medieval pottery, contains metallic spherical nanoparticles dispersed in a complex way in the glaze, which give rise to its special optical properties [4].

The variety of nanomaterials is great, and their range of properties and possible applications appear to be enormous, from tiny electronic devices, to biomedical uses. Editors of the journal Science profiled work that resulted in molecular-sized electronic circuits as the most important scientific development in 2001 [6].

Among the variety of nanomaterials, one of the most promising materials for the success of nanotechnology is carbon nanotubes (CNTs). In the initial stages of growth of the field of nanotechnology, single walled carbon nanotubes (SWCNTs) were recognized as a new high strength [7], electrically [8] and thermally [9] conductive material with a range of potential applications.

1.2 Overview of SWCNTs

CNTs are long, thin cylinders of carbon. In other words they are graphene (a single layer of graphite) sheets rolled up to form a seamless cylinder that is closed at both ends by a bisected fullerene like molecule as depicted in figure 1.1 [10]. There are two types of carbon nanotubes, single wall carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs). MWCNTs are comprised of two to thirty concentric graphene sheets, the
diameters of which range from ~ 2 – 50 nm and lengths up to millimetres (mm), while SWCNTs consist of a single cylinder that is much thinner with diameters in the range of ~ 0.7 – 2.0 nm and typical lengths of a few micrometers (μm). Depending on the angle at which the graphene sheets are rolled, SWCNTs can be subdivided into two groups: chiral and achiral. Achiral can be further subdivided into two groups: armchair and zig-zag (figure 1.2 and figure 1.3).

Figure 1.1 Rolling of graphene to form a SWCNT [10].

Figure 1.2 Classification of carbon nanotubes.
There are several methods to produce SWCNTs. According to the way by which carbon atoms are released from carbon-containing precursor molecules, these methods can be divided into two groups: physical methods such as arc-discharge (AD) [12, 13] and laser ablation [14, 15], and chemical methods such as high pressure decomposition of carbon monoxide (HiPco) [16].

As is the case with graphene, both MWCNTs and SWCNTs contain C = C (double bond) which is one of the strongest bonds in nature and therefore CNTs are regarded as the potential ultimate fibre with regards to their strength in the direction of the CNT axis and flexibility in the direction normal to the CNT surface. CNTs have the ability to withstand cross sectional and twisting distortion and can be elongated by several per cent and compressed without fracture. Theoretical studies indicate that the physical properties of CNTs are strongly dependent on the tube diameter and chiral angle [11].

SWCNTs have been shown to be one-dimensional ballistic conductors and so far this has been observed at low bias only [11, 17]. Such properties are highly sought after in the molecular electronics industry and their potential in as nanowires and even as molecular transistor candidates are under investigation.
Superconductivity of SWCNT has also been observed, but only at low temperatures, with transition temperatures of ~ 0.55 K for 1.4 nm diameter SWCNTs [20] and ~ 5 K for 0.5 nm diameter SWCNTs grown in zeolites [21].

There are many other notable properties of SWCNTs, some of which are listed in table 1.1.

Table 1.1  Examples of notable properties of SWCNTs [22].

<table>
<thead>
<tr>
<th>Property</th>
<th>SWCNTs</th>
<th>Comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>45 GPa</td>
<td>High-strength steel alloys break at about 2 GPa.</td>
</tr>
<tr>
<td>Resilience</td>
<td>Can be bent at large angles and re-straightened without damage</td>
<td>Metals and carbon fibers fracture at grain boundaries.</td>
</tr>
<tr>
<td>Current carrying capacity</td>
<td>Estimated at 1 GA/cm².</td>
<td>Copper wires burn out at about 1 GA/cm².</td>
</tr>
<tr>
<td>Field emission</td>
<td>Can activate phosphors at 1 to 3 volts if electrodes are spaced 1 micron apart.</td>
<td>Molybdenum tips require fields of 50 to 100 V/µm and have very limited lifetimes.</td>
</tr>
<tr>
<td>Heat transmission</td>
<td>Predicted to be as high as 6,000 W/m-K at room temperature.</td>
<td>Nearly pure diamond transmits 3,320 W/m-K</td>
</tr>
<tr>
<td>Temperature stability</td>
<td>Stable up to 2,800 °C in vacuum, 750 °C in air.</td>
<td>Metal wires in microchips melt at 600 to 1,000 °C.</td>
</tr>
</tbody>
</table>
1.3 Applications of CNTs

Many of the extraordinary properties attributed to CNTs, among them, superlative resilience, tensile strength and thermal stability, have fed fantastic predictions of microscopic robots, dent-resistant car bodies and earthquake-resistant buildings [22].

CNTs are used to make field effect transistor (FET) [23]. Researchers have found that the gate electrode can change the conductivity of the CNT channel in an FET by a factor of one million or more, comparable to silicon FETs [22, 23]. However, because of its tiny size, the CNT FET should switch reliably using much less power than a silicon-based device [22]. The fact that CNTs come with a variety of band gaps and conductivities presents many intriguing possibilities for additional nanodevices. It has been reported that at the junction of joined metallic and semiconducting CNTs behave as diodes, permitting electricity to flow in only one direction [22].

CNTs have emerged as one of the most promising electron field emitters due to their high aspect ratio, high emission current and chemical stability [24-27]. In 1995 a research group at Rice University showed that, when stood on end and electrified, CNTs will act just as lightning rods do, concentrating the electrical field at their tips. But whereas a lightning rod conducts an arc to the ground, a CNT emits electrons from its tip at a prodigious rate. Due to their sharpness, CNTs emit electrons at lower voltages than electrodes made from most other materials, and their strong carbon bonds allow CNTs to operate for longer periods without damage [22]. This field emission behavior has long been seen as a potential multibillion-dollar technology for replacing bulky, inefficient televisions and computer monitors with equally bright but thinner and more
power-efficient flat-panel displays [22]. This property of CNTs can lead CNTs to be used as a field emitter. Hu et al. developed field emitters made from CNTs which can be operated at a very large current density of ~145 mA/cm² at a low voltage of 5.5 V/μm, and exhibit a long period (>32 h) of high emission stability at a high emission current density of ~9 mA/cm² and under a constant applied voltage [28]. These properties are important for high image quality in field emission display fabrication [28]. Flat panel displays are one of the more lucrative CNT applications being developed by industry. However, they are also technically the most complex, requiring concurrent advances in electronic addressing circuitry, the development of low-voltage phosphors, methods for maintaining the required vacuum, spacers withstanding the high electric fields, and the elimination of faulty pixels. The advantages of CNTs over liquid crystal displays are low power consumption, high brightness, a fast response rate, and a wide operating temperature range [27, 29]. In application, Samsung Electronic Co., Ltd. has developed a sealed full-color CNT field emission display [30, 31]. Luminescent tube with both flat and cylindrical geometry fabricated using a CNT cathode which also shows stable, adequate, and long-lifetime luminance [32, 33].

CNTs are attractive materials as electrodes for devices that use electrochemical double-layer charge injection, because of the high surface area of porous CNT arrays, combined with their high electronic conductivity, chemical stability and useful mechanical properties. Examples include “super capacitors,” which have giant capacitances in comparison with those of ordinary dielectric based capacitors [34, 35] and electromechanical actuators that may eventually be used in robots [36-38]. Super capacitors with CNT electrodes can
be used for applications that require much higher power capabilities than batteries and much higher storage capacities than ordinary capacitors, such as hybrid electric vehicles that can provide rapid acceleration and store braking energy electrically [29].

An area of similar potential is that of CNTs as advanced probe tips for scanning probe microscopy (SPM) as well as atomic force microscopy (AFM) [39-41]. Nanotubes present ideal characteristics for enhancing the capabilities of SPM in imaging, manipulation and nanolithography. This is due to the sharpness of the CNTs, their high aspect ratios, high mechanical stiffness and resilience [22, 39-41]. Attached to the tip of a SPM, nanotubes can increase the instrumental lateral resolution by a factor of 10 or more, allowing clearer views of proteins and other large molecules [22].

SWCNTs are also suitable candidates for sensing chemicals. Semiconducting SWCNTs are very sensitive to potassium doping (K-doping), and can change from p-type to n-type resulting in orders of magnitude change in conductance [42]. On the other hand, the electrical properties of metallic SWCNTs are relatively insensitive to their chemical environment and interactions with other species. It has been found that K-doping of a metallic SWCNT does not affect its conductance significantly ([42] and references therein), because the charge-transfer does not change the density of states at the Fermi level for a metallic tube.

Collins et al. [43] have studied molecular oxygen adsorption on SWCNTs. The electrical properties of SWCNTs are found to be highly sensitive to oxygen adsorption effects. In a vacuum chamber, the conductance of bulk SWCNTs
increases when oxygen is introduced into the system and recovers when vacuum is restored.

Zhang et al. found that poly(m-aminobenzene sulfonic acid) functionalized SWCNTs can be used as chemical sensors to detect small concentrations of gas molecules such as ammonia (NH₃) and nitrous oxide (NO₂) with high sensitivity at room temperature [44]. It was found that, after exposure to NH₃, the resistance of the sensor immediately increased and gradually approached steady state. When exposed again to dry air, the resistance decreased and slowly recovered its initial value [44]. However, during exposure to NO₂, the resistance of the sensor decreased [44]. This sensor showed excellent sensitivity with ppbᵥ level detection limits (100 ppbᵥ for NH₃ and 20 ppbᵥ for NO₂) at room temperature [44].

There are also potential uses of SWCNTs in different bio-medical applications including miniature biological devices. For instance, SWCNTs can be used as electrodes for detecting biomolecules in solutions, similar to commonly used conventional carbon based electrode materials [45]. Also, the electrical properties of SWCNTs are sensitive to surface charge transfer and changes in the surrounding electrostatic environment, undergoing drastic changes by simple adsorptions of certain molecules or polymers [43, 46-48]. SWCNTs are therefore promising for chemical sensors for detecting molecules in the gas phase and biosensors for probing biological processes in solutions [45]. It was also reported that CNT based FET sensors can detect protein, inorganic molecules, DNA and pH [49, 50]. The change of conductance of the SWCNT channel resulting from the SWCNT-molecular interaction was used to detect the molecules [49, 50].
SWCNTs can also be used for cancer treatment [51]. It has been reported that hypoxia-inducible factor 1 alpha (HIF-1) is a transcription factor whose activity is increased in human cancers in response to intratumoral hypoxia [52, 53]. The significance of the contribution of HIF-1 to tumor growth is well documented [54-57], and mouse xenograft studies have clearly demonstrated that the inhibition of HIF-1 activity suppresses tumor growth [55, 58, 59]. It has been found that pristine SWCNTs solubilised by small interfering ribonucleic acid (siRNA) can be used as a therapeutic agent for cancer treatment [51]. Intratumoral administration of SWCNT/siRNA complexes targeting HIF-1 was found to significantly reduce HIF-1 activity in tumor-bearing mice [51].

Fabrics can also be made from CNTs. It has been reported that a new type of carbon fiber made from CNTs, developed at the University of Cambridge, could be woven into supper-strong body armor for the military and law enforcement [60]. This material is several times stronger, tougher and stiffer than fibers currently used to make protective armor. The work at the Cambridge has already attracted interest from the UK Ministry of Defense and the US Army [60].
Figure 1.4  (i) Comparison of the annual number of scientific publications with the number of patent filings and issuances for the carbon nanotube areas. (ii) Percentages of total patent filings and issuances made by individuals in a country or region and filed either in the same location (superscript 1) or in a different location (superscript 2). (iii) Patent filings and issuances divided according to the main area of the invention. ([29] and references therein).

CNTs have provided possibilities in nanotechnology that were not conceived of in the past. Nanotechnologies of the future in many areas will build on the advances that have been made for CNTs [29]. The exponential increase in patent filings and publications on CNTs indicates growing industrial interest along with academic interest (figure 1.4a) ([29] and references there in). Research activities dealing with CNTs has steadily increased since their discovery, reaching about 7000 articles being published in the year 2006. It has been reported that the publication rate has increased by a factor of ~ 6 since 2000 upto 2006 [61] and to date there is no sign of the publication rate
decreasing (ISI Web of Knowledge [62], topic search for carbon nanotube returns 2400 listings in 2006 and 3700 in 2009). By percentage of total patent filings, inventors in Japan have the lead (53%) (figure 1.4b). Due to the commercial importance of CNTs in composites, most of the patent filings (50%) are for nanotube synthesis, processing, and composites (figure 1.4 c). Reflecting the advanced state of CNT displays and the attractiveness of related applications, electron emission devices command 25% of the patent filings. Nanotube electronic devices, which might have the most potential for changing the field, provided only 6% of the total patent filings. Impressive advances have been made in demonstrating nanotube electronic device concepts, but a decade or more of additional progress is likely required to reliably assess if and when these breakthroughs will reach commercial application [29].

1.4 Limitations

Although CNTs as well as SWCNTs are proposed to be the one of the most promising of nanomaterials, having unique electronic, thermal, and mechanical properties, there are some fundamental problems that hinder the development of the applications of SWCNTs. There are several processes for production of SWCNTs. Despite sustained efforts, all current known SWCNTs bulk synthesis techniques generate significant quantities of impurities such as amorphous carbon, turbostratic graphite and metallic catalyst particles, depending on the method of production. In bulk production, SWCNTs also grow in bundles or ropes containing both metallic and semiconducting tubes and they are largely insoluble in common organic solvents [63] as a result, it is difficult to experimentally measure their proposed potential. SWCNTs can have a range of structures, and their electronic properties depend on their structure and as well
as their diameter. Currently, there is no production process that can isolate only one particular type of SWCNTs. For these reasons, SWCNTs have been slow to reach their full potential. In an attempt to speed up the potential applications of SWCNTs, it is important to purify, increase the solubility of, disperse, and separate SWCNTs with respect to their electronic properties.

1.5 Research Objective

Various methods have been reported for the solubilisation and dispersion of SWCNTs in water and organic solvents [64-74]. It has been found that SWCNTs can be solubilised in water with linear polymers; polyvinyl pyrrolidone (PVP) and polystyrene sulfonate (PSS) [72]. It is also reported that SWCNTs can be dispersed in water with the aid of surfactant [73]. Functionalisation also increases the solubility of SWCNTs [17, 21] in water and organic solvents. It has been also found that organic polymers such as poly PmPV-co-DOctOPV and small molecules such as polycyclic aromatic hydrocarbons (PAHs) can solubilise and aid in the purification of SWCNTs in organic solvents [65, 66, 71]. The interaction can cause the SWCNTs to disperse from their bundled form [65, 66, 71] and there is a strong suggestion that the organic species interact preferentially with SWCNTs of certain diameters or diameter range and even electronic structure [65, 66, 75]. The use of PAHs for the dispersion and solubilisation of SWCNTs is a very simple and easy method. However, to optimise the process, it is also important to understand how PAHs interact with and disperse and solubilise SWCNTs. Hence the objectives of this project are to selectively solubilise SWCNTs obtained from different production process using different PAHs and to obtain a greater understanding of the interaction between PAHs and SWCNTs. SWCNTs produced by high pressure decomposition of
carbon monoxide (HiPco) and arc discharged (AD) methods, and two oligomeric PAH series, the polyacene and polyphenyl series have been chosen for this purpose.

1.6 Background Study

Previous studies [71] explored the use of anthracene and $p$-terphenyl to aid the solubility of SWCNTs. The reason behind taking these two PAHs was their structure. From figure 1.5 it can be seen that the structure of anthracene is similar to the backbone structure of ‘armchair’ SWCNTs which are metallic in nature while the structure of $p$-terphenyl is similar to the backbone structure of ‘zig-zag’ SWCNTs which are predominantly semiconducting. It was hypothesised that the similar structures would interact resulting not only in solubilisation but also structurally selective solubilisation of SWCNTs as depicted in figure 1.5 (although a parallel displaced stacking is more probable).

![Proposed mapping of anthracene and $p$-terphenyl to armchair and zigzag SWCNT respectively [76].](image)

Figure 1.5 Proposed mapping of anthracene and $p$-terphenyl to armchair and zigzag SWCNT respectively [76].

In a previous study by Hedderman [71], toluene was used as the organic solvent as it exhibits a poor affinity for SWCNTs and therefore was an ideal candidate for monitoring the improvements in the solubility as a result of the
SWCNTs interacting with the PAHs. Anthracene and $p$-terphenyl were found to solubilise and debundle SWCNTs.

Hedderman applied a fluorescence model [64] which is based on the adsorption/desorption equilibrium of SWCNTs and polymers to examine the interaction between the oligomer molecules and the SWCNTs. In this model, the quenching of fluorescence represents the interaction between SWCNTs and organic polymers or molecules. This model can be used to measure the binding energy between the molecules and SWCNTs. The ratio of the maximum fluorescence intensity of the composite sample, which contains bound and unbound polymer, to the maximum fluorescence of the polymer, which solely comprises of unbound polymer chains, was plotted as a function of concentration. The model was presented for low concentration and when the system is in equilibrium the absorption rate equals the desorption rate.

According to this model, as the fraction of free polymer molecules changes over the concentration range, this fraction of free polymer molecule could be described by a characteristic concentration and the concentration of SWCNTs.

$$\frac{N_F}{N_F + N_B} = \frac{1}{1 + \frac{C_{NT}}{C_0}} = \frac{F_{I_{comp}}}{F_{I_{polymer}}}$$\hspace{1cm}(1.1)

where, $C_0 = \pi^2 \nu \rho_{bun} A_{bun} \theta B e^{-E_B/kT} / (48Df)$ \hspace{1cm}(1.2)

Here $N_F$ and $N_B$ are the number of free and bound polymers respectively, $C_0$ is the characteristic concentration at which the number of free and bound polymers are equal, $C_{NT}$ is the concentration of SWCNTs, $F_{I_{comp}}$ and $F_{I_{polymer}}$ are the maximum fluorescence intensity of the composite and polymers respectively. In equation 1.2, $\nu$ is a pre-exponential frequency factor, $\rho_{bun}$ is the SWCNT bundle mass density, $A_{bun}$ is the bundle surface area, $E_B$ is the binding energy, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $f$ is the
spatial integral, $D$ is the diffusion coefficient and $D = kT/(6\pi\eta a)$, where $\eta$ is the solvent viscosity and $a$ is the molecular hydrodynamic radius [64]. From equation 1.2, the binding energy $E_B$ between the organic molecules and the SWCNTs can be obtained [64].

Using this model, Hedderman obtained the fraction of free anthracene and $\rho$-terphenyl to probe the region of isolated SWCNTs and PAHs and the interaction between them. In figure 1.6 for anthracene, the dotted lines are the fits of equation 1.1 for $C_0$ values of $\sim 1 \times 10^{-6}$ mol/L (left) and $\sim 6 \times 10^{-6}$ mol/L (right) where the solid line represents the best fit of the model for $C_0$ values of $\sim 2 \times 10^{-6}$ mol/L. For $\rho$-terphenyl in figure 1.7, the dotted lines are the fits of equation 1.1 for $C_0$ values of $\sim 2 \times 10^{-10}$ mol/L (left) and $\sim 6 \times 10^{-10}$ mol/L (right), where the solid line represents the best fit of the model for $C_0$ values of $\sim 4 \times 10^{-10}$ mol/L.

![Graph](image)

*Figure 1.6* A plot of the fraction of free anthracene as a function of concentration [75].
The relationship between the fraction of free PAHs molecules and concentration is shown in figure 1.6 and figure 1.7. Here quenching of the fluorescence represents a decrease in the fraction of free PAHs. In figure 1.6 concentrations between ~ $3 \times 10^{-3}$ mol/L and ~ $1 \times 10^{-4}$ mol/L represent aggregated anthracene and SWCNT bundles. Between ~ $1 \times 10^{-4}$ mol/L and ~ $7 \times 10^{-6}$ mol/L a decrease in the fraction of free anthracene is observed. In this concentration range, the free anthracene molecules interact with SWCNT bundles, causing debundling and forming stable suspensions [75]. It has been found that the SWCNT bundle size decreases with decreasing concentration until a transition region is reached where the SWCNT bundles disperse to give isolated SWCNTs. This concentration has been termed the dispersion limit [70, 73]. In this study, the concentration at which this occurs for anthracene is ~ $3.5 \times 10^{-6}$ mol/L, and from this point to ~ $1 \times 10^{-9}$ mol/L the isolated PAHs molecules and SWCNTs exist. The solid line in figure 1.6 is a plot of equation 1.1 in this concentration range with the $C_0$ value at ~ $2 \times 10^{-6}$ mol/L. From the value of $C_0$
the binding energy between PAHs and SWCNTs could be determined to be 0.9 eV [75].

In figure 1.7, $p$-terphenyl exists as non-aggregated molecules only below $\sim 2 \times 10^{-5}$ mol/L. Between $\sim 2 \times 10^{-5}$ mol/L and $\sim 1 \times 10^{-8}$ mol/L the quenching of fluorescence represents a decrease in the fraction of free $p$-terphenyl. In this concentration range the free $p$-terphenyl molecules interact with SWCNT bundles causing debundling and forming stable suspensions. In this study, the transition region between bundles and isolated SWCNTs is $\sim 3 \times 10^{-9}$ mol/L and $\sim 6 \times 10^{-9}$ mol/L. From this point to approximately $\sim 4 \times 10^{-12}$ mol/L, the isolated PAHs and SWCNTs exist in a dynamic equilibrium. The solid line in figure 1.7 is a plot of equation 1.1 in this concentration range and gives a $C_0$ value of $\sim 4 \times 10^{-10}$ mol/L. By using this value of characteristics concentration, the binding energy of $p$-terphenyl was found to be 1.1 eV, which indicates that $p$-terphenyl interacts more strongly than anthracene [75].

From the fluorescence quenching studies, it is clear that the interaction of anthracene with the SWCNTs samples is very different to that of the $p$-terphenyl suggesting some degree of structural selectivity. Raman analysis indicated that anthracene preferentially solubilises metallic type SWCNTs and $p$-terphenyl semiconducting SWCNTs [76]. Although the study could not determine a preferential interaction of anthracene with armchair and $p$-terphenyl with zig-zag SWCNTs, it did indicate that the approach of selective solubilisation using small organic molecules had potential. However, the choice of anthracene and $p$-terphenyl over their longer or shorter oligomeric counterparts was somewhat arbitrary.
Further studies explored the solubilisation of SWCNTs with tetracene and $p$-quaterphenyl. It is found that the transition region for tetracene and $p$-quaterphenyl is $\sim 1 \times 10^{-6} \text{ mol/L}$ and $\sim 5 \times 10^{-7} \text{ mol/L}$ respectively. The binding energies per tetracene and $p$-quaterphenyl molecules with SWCNTs are found to be $\sim 0.89 \text{ eV}$ and $\sim 1.07 \text{ eV}$ respectively [77].

A theoretical model based on the interactions of PAHs with themselves and graphite has been described in the literature [78, 79]. The quasi crystalline arrangements of close packed SWCNTs are like graphite and they are held together by a long range van der Waals interaction. As both graphite and SWCNTs possess similar properties, it is reasonable to expect similar degrees of interaction for SWCNTs with PAHs. Theoretical models predict, and thermal desorption spectroscopy confirm, that an increase in the carbon number of PAHs increases the binding energies of PAHs, with larger PAHs having similar interlayer distances and binding energies to graphite [78, 79]. The binding energy between PAHs and graphite is predicted to be larger than the binding energy of a corresponding PAHs dimer. It has been found that the binding energy per carbon atom is $52 \pm 5 \text{ meV}$ with a contribution of $27 \text{ meV}$ per hydrogen atom [78, 79].

Figure 1.8 shows the binding energy between PAH and graphene as a function of molecular weight of PAHs. Here black squares represent the calculated values of binding energy of PAHs in graphite taken from [79] and triangles (up and down) and diamond represent the experimental values of binding energy of different PAHs with different types of SWCNTs respectively. LV SWCNT refers to nanotubes fabricated by the laser vaporisation method, HiPco SWCNT by the high pressure decomposition of carbon monoxide.
process, and AD SWCNT by the arc discharge method. More details on production methods are given in chapter 2. The solid line is a guide to the eye based on the published data.

From figure 1.8 it is found that the binding energy of PAHs on graphite has an approximately linear relationship with molecular weight of the PAHs. But the binding energy of SWCNTs with PAHs deviates somewhat from the straight line. Notably, it is suggested that different types of SWCNTs have somewhat different binding energies for the same PAHs.

![Figure 1.8](image)

**Figure 1.8** Relationship between binding energy and molecular weight.

The aim of this project is to extend the work of Hedderman to longer and shorter PAHs of two oligomer groups in order to further understand the
interaction of the PAHs with the SWCNTs in a systematic way and to optimise solubilisation and selectivity.

## 1.7 Aims of Research

The aims of this research are to

1. debundle and disperse HiPco and AD SWCNTs,
2. obtain a greater understanding of the interaction between PAHs and SWCNTs,
3. establish structure-property relationship governing the solubilisation process,
4. probe optimum conditions for selective solubilisation of SWCNTs with the aid of PAHs of different series and lengths.
5. obtain quantitative measurement of SWCNTs in the dispersed solution.

It is proposed that these aims may be achieved using PAHs of two oligomer series: polyacene series and polyphenyl series using a solvent which exhibits poor affinity for SWCNTs and therefore is an ideal candidate for monitoring the improvements in the solubility as a result of the SWCNTs interacting with the PAHs. The starting point was to use toluene as selected by Hedderman [71, 75, 76] although this was not possible for a number of reasons as described in chapter 5 and an alternative solvent was sought and chloroform was selected as it also has poor affinity for SWCNTs [64, 70, 80] and can also solubilise PAHs which were used in this project.
Table 1.2 PAHs of polyacene and polyphenyl series.

<table>
<thead>
<tr>
<th>Polyacene Series</th>
<th>Name</th>
<th>Polyphenyl Series</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Naphthalene" /></td>
<td>Naphthalene</td>
<td><img src="image" alt="Biphenyl" /></td>
<td>Biphenyl</td>
</tr>
<tr>
<td><img src="image" alt="Anthracene" /></td>
<td>Anthracene</td>
<td><img src="image" alt="p-Terphenyl" /></td>
<td>p-Terphenyl</td>
</tr>
<tr>
<td><img src="image" alt="Tetracene" /></td>
<td>Tetracene</td>
<td><img src="image" alt="p-Quaterphenyl" /></td>
<td>p-Quaterphenyl</td>
</tr>
<tr>
<td><img src="image" alt="Pentacene" /></td>
<td>Pentacene</td>
<td><img src="image" alt="p-Quinquephenyl" /></td>
<td>p-Quinquephenyl</td>
</tr>
</tbody>
</table>

In table 1.2, PAHs of two series with different length can be found. In the polyacene series it is proposed to start from naphthalene which is the smallest molecule of the series and continue to higher oligomers such as pentacene. Similarly in the polyphenyl series it is proposed to start from biphenyl and continue to p-quinquephenyl. To probe the interactions occurring between the PAHs and the SWCNTs, ultraviolet-visible-near-infrared (UV-Vis-NIR) absorption, fluorescence spectroscopy, Raman spectroscopy and atomic force microscopy (AFM) will be employed.

These PAHs absorb light between the ultraviolet (UV) and visible ranges. Therefore both UV-Vis-NIR and fluorescence spectroscopy are used to characterise the PAHs in the absence and presence of SWCNTs. Fluorescence concentration dependence studies of PAHs in the absence and presence of SWCNTs improve the understanding of the interaction between the two
components (PAH and SWCNTs). To establish structure property relationships, the same fluorescence based model used by Hedderman is employed [64]. Using this model, the concentration where SWCNTs can be obtained in the form of bundles and dispersed nanotubes has been studied.

To probe the selective solubilisation of SWCNTs, Raman spectroscopy is employed. This spectroscopy is a valuable tool to investigate the vibrational properties and thus characterise SWCNTs. SWCNTs have a signature Raman spectrum which gives details of the vibrational energies within the SWCNTs. The signature spectrum is examined for changes that may result from interaction with the PAHs. It has been reported that an up-shift in the lower frequency Raman modes is a result of a change to the local environment of SWCNTs but the up-shift may also be attributed to the debundling of SWCNTs as a result of the addition of a third species to the solution such as a hydrocarbons [66, 81, 82]. The radial breathing modes (RBMs) of the Raman spectrum of SWCNT give information about the diameter of SWCNTs. Thus, employing Raman spectroscopy, the diameter distribution of SWCNTs in the composite samples can be found. This Raman study can also indicate whether SWCNTs in the samples are bundled, dispersed or isolated. AFM is used to obtain visual images of the SWCNTs before and after the interaction with PAHs. From this the SWCNT bundle size can be obtained.
1.8 Thesis Outline

In chapter 2, the structural and electronic properties of SWCNTs are described. The production and processing methods are also outlined here.

Chapter 3 elaborates the physical structure, electronic structure and crystal structure of different types of PAHs. It also gives an overview of the physical properties of PAHs.

Chapter 4 describes different spectroscopic methods used to characterise materials which are used in this research.

Chapter 5 gives a detail account of the solvent selection and characterisation of different materials used in this study employing spectroscopic and microscopic techniques described in chapter 4.

In chapter 6, the interactions between these PAHs and SWCNTs are explained in detail. It also elaborates the structure property relationship governing the interaction.

Chapter 7 presents the Raman spectroscopy study to probe the selective solubilisation of SWCNTs. It also gives quantitative information of SWCNTs present in the dispersed solutions.

Chapter 8 outlines the conclusion of this research.
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Chapter 2 An Introduction to Single Walled Carbon Nanotubes

2.1 Introduction

SWCNTs have many unique physical properties for example they are extremely resilient and lightweight ([1], and references here in). They also possess a high tensile strength and thermal stability [2]. These mechanical properties give rise to a broad range of potential applications [3-15], as outlined in the previous chapter. SWCNTs have received particular attention due to their novel electronic properties and therefore the possibility of new applications [16]. A SWCNT can be classified as either metallic or semiconductor, based on its diameter and its chirality [4, 17-19]. Their properties include variable band gap, and high current capacity [2, 5, 18, 20, 21]. The result of these different parameters means different electronic devices can be made [4, 5]. It has been found that about one-third of all SWCNTs are metallic while the remaining are semiconducting [5]. However, the applications of SWCNTs have been hampered by the strong structural dependency of the electronic density of states [18] together with the diversity of diameters and chiral angles of SWCNTs as well as the aggregation and impure state of as produced SWCNTs.

There are a number of methods available to produce SWCNTs, such as arc-discharge, laser ablation and gas phase decomposition of CO [21]. Depending on the production technique, the produced SWCNT samples can have a range of different diameters and degrees of purity [1, 20, 22-25].
2.2 Structure of SWCNTs

As described in chapter 1, an ideal SWCNT can be thought of as a hexagonal network of carbon atoms that has been rolled up to make a seamless cylinder. To expand on this it is a geometrically perfect SWCNT which consists of a sp\(^2\) bonded graphene sheet arranged in a cylindrical formation. With dimensions of just a nanometre across, the cylinder can be tens of microns long, and each end is “capped” [26] with half of a fullerene molecule.

A more detailed description of the formation of different SWCNT structures is given in figure 2.1. The direction OA in figure 2.1 determines the structure of the SWCNT, and corresponds to a section perpendicular to the SWCNT axis (equator). The vector OB corresponds to the direction of the SWCNT axis. The vectors OA and OB define the chiral vector \(C_n\) and the translational vector \(T\) of a SWCNT respectively [18].
SWCNTs are generally classified on the basis of their angle of chirality ($\theta$), which is defined as the angle at which graphene the sheet is rolled. Accordingly they are classified into two groups, namely achiral and chiral SWCNTs [18]. An achiral SWCNT is defined as a carbon nanotube whose mirror image is superimpossable on itself. Achiral SWCNTs are of two types: armchair ($\theta = 30^0$) and zigzag ($\theta = 0^0$). A chiral ($0^0 < \theta < 30^0$) SWCNT has a twisted helical structure with no periodicity about the bisected circumference and its mirror image is non-superimposeble on itself [18].

Conventionally, SWCNTs are characterized by the indices $n$ and $m$ of the graphene lattice vectors $a_1$ and $a_2$ (figure 2.1), used in the definition of the chiral vector ($C_n$) of the SWCNT. The chiral vector is one of the vectors of one dimensional SWCNTs and defined as the roll-up direction of graphene monolayer [18].

$$C_n = na_1 + ma_2 \equiv (n, m) \quad (2.1) \quad [17]$$

The armchair configuration is represented by the indices ($n, n$), while ($n, 0$) and ($n, m$) represent zigzag and chiral SWCNTs respectively [18] (table 2.1).

<table>
<thead>
<tr>
<th>Structure</th>
<th>Electronic Properties</th>
<th>Chiral Angle ($\theta$)</th>
<th>Chiral Vector ($C_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Armchair</td>
<td>Metallic</td>
<td>$30^0$</td>
<td>($n, n$)</td>
</tr>
<tr>
<td>Zigzag</td>
<td>Predominantly semiconducting</td>
<td>$0^0$</td>
<td>($n, 0$)</td>
</tr>
<tr>
<td>Chiral</td>
<td>Predominantly semiconducting</td>
<td>$0^0 &lt;</td>
<td>\theta</td>
</tr>
</tbody>
</table>

Table 2.1 Classifications of SWCNTs [5, 18].
2.3 Electronic Properties

The electronic properties of a material depend on the separation between the collection of valence energy states that are filled by electrons and the additional conduction states that are empty and available for electrons to occupy. Metals conduct electricity easily because in metals the valence and conduction bands overlap. There is thus no energy gap between these bands and the conduction band is not fully occupied [27]. In semiconductors, electrons need additional energy to cross the energy gap to the first available conduction state [5] (figure 2.2).

For a graphene sheet, the conduction and valence bands touch each other at the six corner points of the first Brillouin zone [28]. These states are filled with electrons that have the highest energy (Fermi energy) [28]. A graphene sheet is therefore a zero band gap semiconductor [28]. It is also known as ‘semi-metal’ because without external energy, only a few electrons can cross the narrow energy gap to the conduction state [5].

Figure 2.2  Energy bands of different types materials [5].
Neglecting hybridisation effects due to the finite curvature of the tube structure, the basic electronic structure of SWCNTs can be extrapolated from those of a graphene sheet [29]. Straight SWCNTs look like a straight cut from a sheet of graphene (figure 2.3, left) and rolled into a tube (centre) [5]. The energy band model of straight SWCNTs is shown in figure 2.3 (right). According to the energy band model, the geometry of SWCNTs limits electrons to select a few energy states of graphene (figure 2.3 right). Depending on the diameter of the tube, if there is no energy gap between valance band and conduction band and electrons of one of these energy states can move from valance band to conduction band without any additional energy, SWCNTs are metallic. But if there exist band gap between valance band and conduction band, SWCNTs are semiconducting [5].
Twisted (chiral) SWCNTs are formed by cutting graphene sheets at an angle (left) (figure 2.4). These types of SWCNTs can also be either metallic or semiconducting. Figure 2.4 (right) represents the energy band diagram of chiral SWCNTs. The bands of allowed energy states for electrons (right) are similarly cut at an angle, with the result that about two thirds of twisted SWCNTs miss the Fermi point and are semiconducting [5].

In terms of chirality, for \((n,n)\) armchair SWCNTs, there are always states crossing the corner points of the first Brillouin zone (figure 2.5 a), suggesting that armchair tubes should always be metallic [28]. For \((n,0)\) zigzag SWCNTs, if \(n- m = 3 \times \text{integer}\), certain electronic states of the nanotube touch the corner points of the first Brillouin zone (figure 2.5 b) [28]. These types of tubes would be metallic. On the other hand, with \(n- m \neq 3 \times \text{integer}\), zigzag SWCNTs should be semiconducting because the states on the vertical lines miss the corner points of the hexagon (figure 2.5 c) [28]. Similar to the zigzag SWCNTs, for \((n,m)\) chiral SWCNTs, if \(n- m \neq 3 \times \text{integer}\), the electronic states (lines) miss the corner points (figure 2.5 d) and the nanotubes are semiconducting. In other words if \(n- m = 3 \times \text{integer}\), SWCNTs are metallic.
At the Fermi energy, for metallic SWCNTs, the density of states (DOS) is finite and for semiconductor it is zero. The sharp energy peaks in the DOS are known as van Hove singularities [5]. Figure 2.6 shows the DOS for both a metallic (a) and semiconducting (b) carbon SWCNT where $v_n$ and $c_n$ represent

---

Figure 2.5  Schematic structures of SWCNTs and how the electronic properties of the nanotubes are determined.  
(a) A (10,10) arm-chair nanotube. Bottom panel: the hexagon represents the first Brillouin zone of a graphene sheet. The vertical lines represent the electronic states of the nanotube. The center-line crosses two corners of the hexagon, resulting in a metallic nanotube.  
(b) A (12, 0) zigzag nanotube. The electronic states cross the hexagon corners, but a small band gap can develop due to the curvature of the nanotube.  
(c) The (14, 0) zigzag tube is semiconducting because the states on the vertical lines do not cross the corner points of the hexagon.  
(d) A (7, 16) tube is semiconducting. [28].
the valance and conduction bands for the first electronic transition respectively [30].

![Diagram showing van Hove singularities and electronic transitions in SWCNTs]

Figure 2.6 The van Hove singularities are apparent as sharp spikes in the density of states. The $v_1-c_1$ is the first electronic transition between van Hove singularities, corresponding to the band gap in metallic (a) and semiconducting SWCNTs (b) respectively [30].

SWCNTs do not all have the same band gap. It is found that SWCNTs differ dramatically depending on the circumference of SWCNTs, and hence on the $(n, m)$ values of the chiral vector, because for every circumference there is a unique set of allowed and valence and conduction states [5]. From a tight binding approximation, the interband transition energies for $v_2$ to $c_2$ and $v_3$ to $c_3$ transition in semiconducting SWCNTs and $v_1$ to $c_1$ and $v_2$ to $c_2$ in metallic SWCNTs are approximated by [30]

\[
E^{S}_{11}(d_t) = 2a_{C-C} \gamma_0 / d_t \quad \text{---------------------- (2.2)}
\]

\[
E^{S}_{22}(d_t) = 4a_{C-C} \gamma_0 / d_t \quad \text{---------------------- (2.3)}
\]

\[
E^{S}_{33}(d_t) = 8a_{C-C} \gamma_0 / d_t \quad \text{---------------------- (2.4)}
\]

\[
E^{M}_{11}(d_t) = 6a_{C-C} \gamma_0 / d_t \quad \text{---------------------- (2.5)}
\]
\[ E_{22}^M (d_t) = 12a_{C-C} \gamma_0 / d_t \]  

where \( E \) is the transition energy, superscript \( S \) and \( M \) are for semiconducting and metallic SWCNTs respectively, the numbers of the subscript represent the electronic transitions between corresponding valance band and conduction band, \( a_{C-C} \) is the distance between the C-C bonds (0.144 nm), \( d_t \) is the diameter and \( \gamma_0 \) is the nearest neighbour C-C interaction energy, experimentally determined to be 2.9 eV for carbon SWCNTs [31].

Equation 2.2 to 2.6 determine the band-gap, being the energy difference between two mirroring van Hove singularities, \( c_n - v_n \) in figure 2.6, which is related to the diameter of the SWCNT [30]. SWCNTs of smallest diameter have very few states that are spaced far apart in energy. As the diameter of the SWCNTs increase, more and more states are allowed and the spacing between them decreases. That is why different SWCNTs can have band gaps as low as zero (metallic), as high as the band gap of silicon (~1.12 eV), and almost any where in between. No other known material can be so easily tuned [5].

**2.4 Production Methods of SWCNTs**

There are several methods to produce SWCNTs. According to the way by which carbon atoms are released from carbon-containing precursor molecules, these methods can be divided into two groups: physical methods such as arc-discharge [20, 23] and laser ablation [1, 22], and chemical methods such as high pressure decomposition of carbon monoxide (HiPco) [32]. In this project SWCNTs produced by arc discharged and HiPco methods have been used. A brief description of the production techniques of these two SWCNTs is given below.
2.4.1 Arc Discharge

In this method, an electric arc-discharge is generated between two graphite electrodes placed end to end, separated by approximately 1mm, in an enclosure that is usually filled with inert gas at low pressure. The high temperature occurring between the two rods allows the sublimation of carbon and the positive electrode is consumed [20, 22]. The technique first produced MWCNT in 1991 and it was later discovered that the addition of metal catalysts such as cobalt (Co) and nickel (Ni) at specified ratios to the anode lead to the production of SWCNT in 1993 [20, 33].

By drilling a hole in the centre of the anode and filling it with a mixture of a metal catalyst and graphite powders and applying the same procedure described above, SWCNTs can be produced [22, 23]. Under the conditions stated above, the anode is consumed and a cylindrical deposit forms at the cathode which comprises of an exterior hard gray metallic shell and a soft interior belt [22, 23]. Within this soft belt amorphous carbon, spherical metallic nanoparticles, a few graphite sheets and a high density of SWCNTs are found [22, 23]. Here the impurity phases are mostly amorphous carbon and the metal catalysts. The produced SWCNTs can be isolated or organized in bundles consisting of a few to a few tens of single SWCNTs stuck together in a triangular lattice [22, 23]. The purity and yield of the SWCNTs sample using yttrium, nickel and graphite (Y/Ni/C) at 1% /4% /95% was estimated at <70% [23, 34]. The majority of the SWCNTs have a diameter between 1.2 and 1.4 nm and lengths reaching up to several μm [22, 23, 34].
2.4.2 Gas Phase Decomposition of CO

In this process SWCNTs are produced by a gas-phase catalytic process. Catalysts for SWCNTs growth form in situ by thermal decomposition of iron pentacarbonyl in a heated flow of carbon monoxide (CO) mixed with iron pentacarboxyl (Fe (CO)$_5$) at pressures of 1-10 atm and temperatures of 1100-1500 K [32]. In this process, metal clusters form first and then nucleate and grow SWCNTs. Metal clusters initially form by aggregation of iron atoms from the decomposition of Fe (CO)$_5$. Clusters grow by collision with additional metal atoms and other clusters reaching a diameter comparable to that of a SWCNT, ~ 0.7-1.4 nm, corresponding to 50-200 iron atoms. In the meantime, CO can disproportionate on the surface of such clusters to yield solid carbon deposits and SWCNTs nucleate and grow from them. In these SWCNT samples, the only impurity is iron particles (up to 10% by weight). The SWCNT diameter and yield can be varied by controlling the process parameters and SWCNTs as small as ~ 0.7 nm and up to ~ 1.4nm in diameter can be produced [32].

2.5 Processing of SWCNTs

The produced, SWCNTs are present in various diameters, chiralities and lengths [18]. Different species are closely entangled as bundles or ropes in the raw soot and occasionally even via chemical bonds. As a result, the raw or as produced material is difficult to process. Again, SWCNTs grown in bundle form contain both metallic and semiconducting SWCNTs [35-38]. For application purposes it is necessary to separate metallic and semiconducting SWCNTs. But for commercial success it is critical to produce SWCNTs that contain either metallic SWCNTs or semiconducting SWCNTs [28, 35-38]. There are several
methods currently used such as size exclusion chromatography, dielectrophoresis, amine assisted, organic processing, etc. to address this issues, however, this project focus is on a new and novel technique where PAHs are used to process the SWCNTs. The pros and cons of current processing techniques are discussed below indicating why the novel approach of using PAHs is being explored.

2.5.1 Size Exclusion Chromatography

Size exclusion chromatography is a non destructive process for the purification and size separation of SWCNTs. It is a multi-step process using a stationary phase with defined pore sizes [39]. This technique is applied to a surfactant stabilised dispersion of the SWCNT material. In this process, the solution is passed through two successive columns. The purpose of the first column is to remove the bulk of small particles and fullerenes [39]. After passing through the first column, the same solution is passed through the second column containing porous glass with a pore size of 300 nm [39]. It works on the basic that the pores trap the amorphous carbon in the cavity but allow free passage of the SWCNTs through the column as the sizes of the amorphous particles are larger than SWCNTs [39].

In another chromatographic process, one or two drops of 0.002 mol/L sodium hydroxide (NaOH) are added into 5 mL of SWCNTs dispersions. The SWCNT dispersions are left to stand overnight, and the supernatant liquid is collected and treated by ultra-sonication and then filtered through a cellulose membrane syringe filter with 0.45 μm pore size before injection. The concentration of the injection sample is slightly lower than 0.1 mg/mL because of the adsorption on the membrane. The SWCNT dispersions are then passed
through a photo luminescence (PL) aqua gel-OH column (300 mm × 7.5 mm) and the stationary phase is 8 μm particles with 4 nm pores. An automatic fraction collector is used for the collection of corresponding fractions at repeated injections. In this method, larger SWCNTs are collected first [40].

Although size exclusion chromatography is a non-destructive process for the purification and size separation of SWCNTs, this process is not suitable for separating SWCNTs according to their electronic properties which is the one of the main concerns of this project.

2.5.2 Dielectrophoresis Method

In this method, metallic and semiconducting SWCNTs are separated by using alternating current dielectrophoresis [35]. Raw SWCNTs soot is suspended in deuterium oxide (D₂O) containing the surfactant sodium dodecyl sulphate (SDS) under sonication. After sonication, the suspension is centrifuged and the upper 90% of the supernatant is the carefully decanted [35]. For alternating current (AC) dielectrophoresis, the generator is operated at a frequency of 10 MHz and a peak to peak voltage of 10 V. After the generator is switched on, a drop of suspension of individual SWCNT is applied to the chip. After a delay of 10 min, the drop is gently blown off the surface by a steam of nitrogen gas and then the generator is switched off [35]. The resulting sample is characterized with a confocal Raman microscope and excited with an Ar⁺ ion laser. Proof of the effectiveness of separation is given by a comparative Raman spectroscopy study on the dielectrophoretically deposited SWCNTs and on a reference sample. It works on the basis of the difference in the relative dielectric constants of the two species (metallic and semiconducting SWCNTs) with respect to the solvent, resulting in an opposite movement of metallic and
semiconducting SWCNTs along the electric field gradient. Metallic SWCNTs are attracted toward a microelectrode array, leaving semiconducting SWCNTs in the solvent [35]. This is a time consuming method and SWCNTs separation yield is low [35].

### 2.5.3 Amine Assisted Method

In this method, the first step toward the separation is to disperse SWCNT bundles [36]. For the dispersion process, SWCNTs are added to a solution of 1-octylamine in tetrahydrofuran (THF) and then sonicated for 2 h at room temperature followed by centrifugation of the suspension to remove non-dispersible SWCNTs [36]. The resulting supernatant solution and deposit of SWCNTs are designated SWCNTs-OS1 and SWCNTs-OD1. It has been found that metallic SWCNTs are more strongly adsorbed by amines than semiconducting SWCNTs and the absorbed amines are removable after separation [36]. From visible-near-infrared (vis-NIR) absorption spectra of SWCNTs-OS1 and SWCNTs-OD1, it has been found that SWCNTs-OS1 has stronger absorption peaks in the metallic optical absorption band and weaker absorption peaks in the semiconducting bands than those of SWCNTs-OD1, indicative of the enrichment of metallic SWCNTs in the supernatant and semiconducting SWCNTs in the deposit, respectively. The selective reduction of semiconducting absorption bands and the enhancement of metallic absorption bands in SWCNTs-OS1 demonstrate that the dispersion-centrifugal separation process is effective for the separation of SWCNTs according to their electronic properties. To enrich further the metallic SWCNTs, SWCNTs-OS1 is filtrated and subject to the dispersion-centrifugal separation process repeatedly. The absorption in the metallic band increases gradually in the supernatant fraction.
after each dispersion-centrifugation process. After the repetition of the dispersion-centrifugal separation process of SWCNTs-OD1, the vis-NIR spectrum of SWCNTs-OD1 shows the enrichment of semiconducting SWCNTs [36].

This method was demonstrated on two types of SWCNTs of assignment (13,0) and (7,7) having diameter of 1.018 nm and 0.952 nm. This process might not, however, be suitable for use as a universal technique to separate metallic and semiconducting having a broader range of chiralities as well as diameters.

2.5.4 Organic Processing

Conjugated organic polymers such as PmPV-co-DOctOPV and polycyclic aromatic hydrocarbons (PAH) such as anthracene and \( p \)-terphenyl can solubilise and purify SWCNTs [41-43]. SWCNTs have a poor degree of solubility in toluene [41-45]. But PmPV-co-DOctOPV, anthracene and \( p \)-terphenyl are soluble in toluene. It has been found that by the application of PmPV-co-DOctOPV or PAHs, the solubility of SWCNTs in toluene is improved significantly [41-43, 45]. The \( \pi-\pi \) mapping of the polymer or hydrocarbon molecules to the backbone of SWCNTs helps SWCNTs to solubilise in toluene [41-43, 45]. As a result, all unwanted side products and catalytic particles precipitate out. Purified SWCNTs were obtained by washing the polymer from SWCNT with excess toluene through a Büchner funnel and collecting the washed SWCNTs on filter paper.

The use of the polymer PmPV-co-DOctOPV has been shown to affect a diameter selective solubilisation [41, 42], while the PAHs anthracene and \( p \)-terphenyl have suggested a structurally selective solubilisation [46].
This method is potentially a higher throughput separation technique, and will be explored further in this work by establishing structure property relationships between PAH structure and degree of solubility/selectivity.

During the course of the study of selective solubilisation of different SWCNTs with the aid of different PAHs from 2006 to the beginning of 2010, several research groups have published different techniques regarding the selective solubilisation or dispersion of SWCNTs according to chirality [47-52], diameter [50, 52], and electronic properties [53-55]. These methods were based on the use of surfactants [49], different organic polymers [47, 50], polyaromatic amphiphiles [48], hydrocarbon derivatives [56], fluorous chemistry [57], organic compound [51], density gradient [37, 52, 58] and agaros [53-55]. A brief description of some of these methods is given below.

2.6 Review of Different Methods for the Selective Solubilisation of SWCNTs

Peng et al. claimed that the non superimpossable mirror image form of SWCNTs can be separated from the as-prepared samples of chiral SWCNTs containing equal amounts of left and right handed helical structure using so called chiral nano tweezers [47]. It was found that the chiral ‘gable type’ diporphyrin molecules bind with different affinities to the left and right handed helical nanotube isomers to form complexes with unequal stabilities that can be readily separated and these two non superimposeble mirror image compounds (nano tweezers) each comprise two large flat porphyrin rings linked through a 1, 3- substituted phenyl ring [47].
Marquis et al. reported that adsorption of specifically designed and geometrically constrained polyaromatic amphiphiles on SWCNTs was found to be selective of the nanotube helicity angle [48].

Wei et al. reported that highly selective enrichment of (6, 5) and (8, 3) SWCNTs produced by the catalyst Co-MCM-41, was achieved through multistep extraction by sodium dodecyl sulphate (SDS) and sodium cholate (SC) cosurfactant solution [49]. They found that a systematic change in the chirality selectivity was observed when the weight ratio between SDS and SC varied in co-surfactant solution, with maximum enriched selectivity for (6, 5) tubes yielded at 1:4 [49]. SWCNTs produced by the catalyst Co-MCM-41, contain smaller diameter with narrowly \((n, m)\) distributed SWCNTs [49]. It was suggested that the enrichment of (6, 5) and (8, 5) SWCNTs might be because SDS/SC co-surfactants are more efficient for smaller diameter tubes with a narrowly \((n, m)\) distribution [49]. For comparison, Li Wei et al. applied the same extraction process on HiPco samples with a larger average diameter and wider chirality distribution relative to SWCNTs produced by Co-MCM-41 process and no clear selectivity of specific \((n, m)\) tubes was observed [49].

Chen et al. found that high purity of (7, 5) SWCNTs can be obtained by polymer assisted extraction from the narrow diameter distributed SWCNTs produced by the catalyst Co-MCM-41 [50]. It was stated that the fluorine based polymers, poly \((9,9\text{-dioctyfluorenyl-1,2, 7-diyl})\) and poly \([\text{(9, 9-dihexylfluorenyl-2,7-diyl)-co-(9, 10-anthracene})]\) selectively wrapped SWCNTs with high chiral angles \((> 24.5^\circ)\) and by contrast, poly \((9,9\text{-dioctyfluorenyl-2, 7-diyl)-co- 1, 4-benzo-\{2,1\text{-3}\}-thiadiazole})\) preferentially wrapped the SWCNTs with diameter in the range of 1.02 to 1.06 nm [50].
It was reported that a soluble pentacene derivative, 6, 13-bis(2-(trimethylsilyl) ethynyl) pentacene, can be used for the extraction of metallic SWCNTs [56]. It was found that the separation was solvent dependent and was more efficient for small diameter SWCNTs [56].

Ghosh et al. demonstrated the separation of metallic and semiconducting SWCNTs where the diazonium salt of 4-heptadecafluorooctylaniline selectively reacted with the metallic nanotubes present in the mixture of SWCNTs [57]. The resulting fluoroderivative was extracted in perfluorohexane leaving the semiconducting SWCNTs in the aqueous layer [57].

Ju et al. showed that the flavin mononucleotide, the phosphorylated form of vitamin B\textsubscript{2}, wrapped around SWCNTs in a helical pattern that imparts efficient individualisation and chiral selection [51]. It was stated that the cooperative hydrogen bonding between adjacent flavin moieties resulted in the formation of helical ribbon, which organized around SWCNTs through concentric $\pi$-$\pi$ interaction between the flavin mononucleotide and the underlying graphene wall [51]. The strength of the flavin mononucleotide assembly was strongly dependent on SWCNTs chirality. It was found that flavin mononucleotide assembly had higher affinity of the (8, 6) SWCNTs [51].

Several research groups have also used a density gradient centrifugation/ultracentrifugation technique to separate SWCNTs according to their electronic properties [37, 58]. Arnold et al. discovered that with the aid of density gradient ultracentrifugation (DGU), bile salts such as SC, sodium deoxycholate and sodium taurodeoxycholate and their mixtures with other surfactants such as SDS and sodium dodecylbenzene sulphonate (SDBS) enabled the separation of SWCNTs by diameter, bandgap and/or electronic
type [37]. Using surfactants, the isolation of specific chiralities of SWCNTs can be significantly refined by separating in multiple successive density gradients [37]. It was observed that multiple regions of separated SWCNTs can be visible through the density gradient and that SWCNTs were sorted into bands of various colours, corresponding to the different bandgaps of the semiconducting SWCNTs [37].

Using the density gradient technique, high purity metallic SWCNTs were also obtained by Yanagi e. al. [58]. It was found that the addition of deoxycholate sodium salts (DOC) as a co-surfactant could improve the separation capability for metallic SWCNTs in centrifugations and from the SWCNTs with different average diameters (1.34, 1.0, and 0.84 nm), metallic SWCNTs with cyan, magenta, and yellow colours (figure 2.7) can be separated [58].
Recently a protocol to controllably obtain a polychromatic “rainbow” dispersion containing seven different coloured layers (figure 2.8) has been published [52]. This was achieved by the DGU method using a co-surfactant system containing DOC and SDS. It was found that the topmost violet layer contained primarily (6, 5) SWCNTs, which had the smallest diameter of those detected in the sample [52]. The dominant species in each successive layer had an increasingly larger diameter, showing the redistribution was diameter selective and separation was driven by difference in buoyant density [52].

Tanaka et al. introduced a method to separate metallic and semiconducting SWCNTs using agarose gel electrophoresis technique [54].
this process when the SWCNTs were isolated with SDS and embedded in agarose gel, only the metallic SWCNTs separated from the starting gel by an electric field. After 20 min, almost all SWCNTs subjected to gel electrophoresis were separated into two fractions, containing ~95% semiconducting and ~70% metallic SWCNTs [54].

In addition to the agarose gel electrophoresis, Tanaka et al. have also demonstrated four gel-based techniques to separate metallic and semiconducting SWCNTs: manual squeezing of the frozen and thawed gel, centrifugation, diffusion, and permeation [53]. In the gel-squeezing method, a piece of gel containing SWCNTs and SDS was frozen, thawed and squeezed. Squeezing with the fingers then caused the solution phase to separate from the gel [53]. The solution obtained by this method was gray in color, while the remaining gel was greenish, reflecting the partitioning between metallic and semiconducting SWCNTs. The SWCNTs in the squeezed gel could be recovered as a solution by heating, centrifugation, and re-dispersion [53]. The gel-squeezing method appeared to be effective due to the selective adsorption of semiconducting SWCNTs to the agarose gel matrix, whereas metallic SWCNTs remain in the free state as SDS micelles in the interstitial solution of the gel [53].

In the centrifugation method, the solution of dispersed SWCNTs in SDS was mixed with the agarose gel and centrifugation was used as a means of recovering the solution from the gel [53]. In this method, the specific combination of gel and surfactant is very important for the separation of metallic and semiconducting SWCNTs. It was also found that the purity of the metallic and semiconducting SWCNTs obtained by the centrifugation could be improved.
by optimization of the agarose gel concentration. The purity of semiconducting SWCNTs in the compressed gel was found to increase with decreasing agarose concentration, while on the other hand, the purity of metallic SWCNTs in the solution fraction improved as the agarose concentration increased up to approximately 1.0%, beyond which the metallic SWCNTs purity increased only slightly [53].

In the diffusion method, the SWCNTs containing gel was soaked in an elution buffer containing SDS. The separation of metallic and semiconducting SWCNTs was successfully observed in this process, although the purity of the respective phases were relatively poor [53].

In the permeation process, agarose gel was added to the SWCNT dispersion and selective accumulation of semiconducting SWCNTs on the gel was observed [53].

Another new method, based on the agarose beads, to separate metallic and semiconducting SWCNTs has also been described by Tanaka et al. [55]. A schematic diagram of this method is shown in figure 2.9. This continuous separation method is based on column chromatography. The column was prepared by filling the 2.5 ml plastic disposable syringe with agarose beads [55]. When the SWCNTs dispersed in SDS solution and successive 1% SDS solution was applied to the column, colour separation was observed. A greenish deposit of SWCNTs, corresponding to the semiconducting SWCNTs, were trapped in the upper region of the column, while reddish SWCNTs, corresponding to the metallic SWCNTs, were not adsorbed to the column [55]. The greenish SWCNTs were tightly bound to the gel, and were not eluted when the column
was washed with 1% SDS solution but by the addition of 1% DOC solution, the bound SWCNTs were successfully eluted as a gel free solution fraction [55].

![Figure 2.9](image)

**Figure 2.9** Schematic diagram of metallic semiconducting SWCNTs separation using a column filled with agarose gel beads. M, metallic SWCNTs; S, semiconducting SWCNTs [55].

From the above discussion regarding the methods to separate SWCNTs according to their chirality, diameter and electronic properties, it can be found that DGU and agarose methods are the most effective techniques. The main disadvantages of the DGU method are the longer processing time and high capital cost for the separation for industrial applications [59]. As mentioned by Kataura, the approximate cost of separating metallic and semiconducting SWCNTs using DGU is 10,000 dollars/gm [59] where as the cost of separating metallic and semiconducting SWCNTs using agarose beads method is about 1 dollar/gm. It should be noted however, that the techniques of Tanaka *et al.* employ 4 h ultrasonication using a tip-type sonicator. It is likely that this preparation technique causes significant degradation of the tubes [60, 61].
2.7 Conclusion

The purpose of this research is to gain knowledge about the interaction of PAHs with SWCNTs in a systematic way, to find out the structure-property relationship and selectively solubilise SWCNTs relative to their backbone, PAHs of polyacene and polyphenyl series has been used. This chapter has described the structural, physical and electronic properties of SWCNTs, their production, processing methods. The information about the structural and physical properties of polycyclic aromatic hydrocarbon molecules is given in the next chapter.
References


Chapter 3  Polycyclic Aromatic Hydrocarbons

3.1 Introduction to Aromatic Hydrocarbons

Molecules of the two oligomer series; the polyacene series and polyphenyl series are explored in this work due to their capabilities to enhance the solubility of SWCNTs [1, 2]. Molecules of these two series are classed as polycyclic aromatic hydrocarbons (PAHs). An aromatic hydrocarbon is a molecular structure which incorporates one or more planar sets of six carbon atoms that are connected by alternating single and double covalent bonds [3]. The most basic of the aromatic hydrocarbon molecules is benzene (figure 3.1 (a)). The structure of benzene consists of a sp² hybridized sigma (σ) framework that is responsible for the steric configuration and delocalised pi (π) electrons (figure 3.1 (b) and 3.1(c)) [4]. The "hydrocarbon" refers to the composition of the compound containing carbon and hydrogen atoms. "Polycyclic" indicates that these molecules consist of multiple rings of carbon atoms, while "aromatic" refers to the properties of the organic structures [5]. Naphthalene and biphenyl are the shortest PAHs of polyacene and polyphenyl group respectively. PAHs are non-polar, hydrophobic compounds and therefore only slightly soluble in water [6]. PAHs that are highly symmetrical and planar are able to pack closely in a crystal lattice, so that the energy required for solubilisation tends to be relatively high. As a result they tend to be difficult to dissolve even in organic solvents [7].

The polyphenyl and polyacene PAH series were used in this research to study their interaction with SWCNTs in a systematic way in order to obtain the
optimum and selective solubilisation of SWCNTs and thus establish structure-
property relationship governing the interaction process.

![Chemical structure of benzene](image)

Figure 3.1  
$C_6H_6$ (benzene): (a) chemical structure formula, (b) spatial distribution of the \(\sigma\)-orbitals which are responsible for the steric configuration, (c) spatial distribution of the \(\pi\)-orbitals forming a delocalised \(\pi\)-system [4].

### 3.2 Physical Properties of PAHs

#### Polyacene Group

Acene or polyacene is a class of PAHs made up of linear fused benzene rings [7]. The molecules naphthalene, anthracene, tetracene, pentacene are used in this project.

The smallest member of the polyacene group is naphthalene. It consists of two fused benzene rings, as shown in figure 3.2. The molecular formula of naphthalene is $C_{10}H_8$. It is a white solid hydrocarbon [8]. The C1–C2 (position of carbon) (figure 3.2 (b)) positions are commonly referred to as $\alpha$ and $\beta$ respectively [9, 10]. The $\alpha$ sites is also known as peri position [9, 10]. The resonance (or stabilization) energy of naphthalene (255 KJ/mol) is not twice than that of benzene (151 KJ/mol) [9, 10]. Naphthalene is less aromatic than benzene, which accounts for its higher reactivity towards electrophilic attack.
compared with benzene [9]. The description of canonical forms of naphthalene (figure 3.2a) shows that it is not possible for both rings to be phenyl in character at the same time [10]. The carbon-carbon bond length also reflects this, as the double bonds are about 1.36 Å (136 pm) in length, whereas carbon- carbon single bonds are about 1.42 Å (142 pm) in length [10]. The bonds C1–C2, C3–C4, C5–C6 and C7–C8 are double in two of the three structures (figure 3.2 (b), (c) and (d)), the others are double in only one [10]. In reality the molecular structure is better described by a superposition of the resonant structures of Figure 3.2 (c) and (d).

Figure 3.2 Structure of naphthalene (a). (b), (c) and (d) are the canonical forms of naphthalene [9-13].

Anthracene is a solid PAH consisting of three fused benzene rings (figure 3.3) [9, 10]. The molecular formula of anthracene is C_{14}H_{10}. Anthracene can vary in appearance from a colorless to a pale yellow crystal like solid [14]. The canonical forms of anthracene demonstrate that like naphthalene, it is not possible for all the rings to be phenyl simultaneously [9, 10].
Tetracene consists of four fused benzene rings (figure 3.4). The molecular formula of tetracene is $C_{18}H_{12}$. It is also called naphthacene, benz[b]anthracene and 2, 3-benzanthracene. It has the appearance of a pale orange powder [15].

Pentacene consists of five linearly fused benzene rings (figure 3.5). The molecular formula of pentacene is $C_{22}H_{14}$. It has the appearance of a dark-blue powder. It is an organic semiconductor. It is sensitive to light and oxygen [17, 18].
Polyphenyl Series

The polyphenyl series are chain-linked, consisting of assemblies of single benzene rings linked by carbon-carbon (C-C) single bonds [7]. The structures of the oligomers in this group are not planar. The molecule, biphenyl, $p$-terphenyl, $p$-quaterphenyl and $p$-quinquephenyl of this polyphenyl series were used here.

Biphenyl has the appearance of a white crystal (figure 3.6) [20]. It has a molecular formula of $C_{12}H_{10}$. It is the smallest molecule of phenyl series.

![Figure 3.6 Structure of biphenyl [11, 12, 21].](image)

$p$-Terphenyl (figure 3.7) consists of three phenyl rings each connected through a single carbon bond with the molecular formula $C_{18}H_{14}$. It is white in colour [22]

![Figure 3.7 Structure of $p$-terphenyl [11, 12, 23].](image)

The structure of $p$-quaterphenyl is that of four phenyl rings each connected through a single carbon bond with the molecular formula $C_{24}H_{18}$ (figure 3.8). It has the appearance of a white power.

88
\[ \text{Figure 3.8 Structure of } p\text{-quaterphenyl [11, 12, 25]} \]

\[ \text{Figure 3.9 Structure of } p\text{-quinquephenyl [24]} \]

\( p\)-Quinquephenyl consists of five phenyl rings connected through a single carbon bond (figure 3.9). Its molecular formula is \( \text{C}_{30}\text{H}_{22} \). Like \( p\)-terphenyl and \( p\)-quaterphenyl, it also has the appearance of white powder.

There is a torsion angle between the polyphenyl rings and this inter ring torsion is the result of two competing forces. One is for the \( \pi \)-electron system of the carbons at the inter ring position which tends to planarize the molecules and the other is the electrostatic repulsion of the positively charged ortho-hydrogen forces molecule into a non-planar configuration [25]. As the electronegativity of the hydrogen is less than that of carbon there is a significant charge transfer (~ 0.3 eV) from the hydrogen atom to the carbon ring and this means that the hydrogen is positively charged and the ring is negatively charged [26]. The hydrogen atoms repel each other but remain tightly bound to their carbon atom [26]. Hydrogen atoms of the polyphenyl groups can separate further if the monomer units rotate with respect to each other, developing a torsion angle between monomers either side of the C-C single bond. With zero torsion angle, oligomers of the polyphenyl series are planar structures. But as
far as the hydrogen atoms are concerned, they prefer to be at a maximum distance which implies a torsion angle of 90° degrees and this minimizes the electrostatic energy of the system [26]. The C-C single bond between monomers is not completely free to rotate, however. From a tight-binding model it has been found that π-electrons on each atom across that bond are interacting [26]. There is an effect of torsion on the electronic structure of the oligomers. When the torsion angle is 90°, the monomers are not communicating with each other and as a result there is no energy gain by the delocalisation of the π-electrons [26]. To obtain maximum energy gain through delocalisation, the desirable torsion angle should be zero, that is a completely flat structure [26]. The band gap of oligomers also depends on the torsion angle. The smallest band gap is obtained for a completely flat structure and the largest for monomers at 90° to each other.

The balance of the electrostatic repulsion and the optimisation of π-conjugation results in a torsion angle between 0 and 90°. This torsion angle ranges from 44° for biphenyl to 30°-40° for the longer oligomers ([25]and references therein). Figure 3.10 shows the relative energy of p-terphenyl with respect to the torsion angle as calculated by Cote [26] and it is evident that the torsion angle with the lowest energy difference is ~ 30°.
3.3 Electronic Structure of PAHs

The electronic structures of PAHs depend on the presence of delocalised $\pi$-electrons. Each carbon atom in a PAH molecule provides four valance electrons [4]. Three of these valance electrons form strong bonds with neighbouring carbon or hydrogen atoms. These bonds are called $\sigma$ bonds. The remaining valance electron on each of the carbon atoms occupies the $p_z$ orbital, which is aligned perpendicular to the plane of the $\sigma$ bonds. The $p_z$ electrons of two neighbouring carbon atoms form a bond known as $\pi$ bond. This is the origin of the alternating single and double bonds in PAHs. In this $\pi$ system, $\pi$ electrons are no longer attributed to one specific C-C bond [4]. They are delocalised over the entire ring system [4]. These delocalised $\pi$ electrons are relatively weakly bound and are responsible for the transportation of electrons within PAHs. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) band gap decreases as the chain length of the hydrocarbon increases. Experimentally, the band gap follows a $1/N$ law.

Figure 3.10 Relative energy of $p$-terphenyl as a function of the torsion angle [26].
(N being the number of conjugated bonds) whereby the position of the first absorption maxima shows a linear dependence as a function of the inverse of the PAHs length [25-27].

From figure 3.11 (a) it is evident that with increasing conjugation length there is a considerable shift in the absorbance spectra of the polyphenyl series. Biphenyl has an absorption shoulder at 270 nm, whereas by the time the series reaches a six-ringed structure (sexiphenyl) the longest wavelength absorption peak has shifted to 380 nm. By addition of four phenyl monomer units the band gap has reduced by 110 nm (1.32eV) [27]. Similarly, a considerable shift in the absorbance spectra with increasing conjugation length is also observed for polyacene oligomers. The red-shift seen with the polyacenes is significantly greater than that observed in the polyphenyl series. In the acene series the band-gap shifts from 3.97 eV (naphthalene) to 2.13 eV (anthracene), a reduction of 1.84 eV [27]. Figure 3.11 (b) shows a plot of the energies of the first absorption maxima of the various oligomeric series plotted against inverse conjugation length, where σ accounts for end-group terminations [27]. This plot also illustrates the inverse relationship between absorption energy and the conjugation length. In fluorescence emission, with increasing conjugation length, a similar structurally dependent red shifting to that seen in the absorption spectra has been observed [27]. As is the case for the absorption, an inverse relationship between emission energy and the conjugation length has been demonstrated for both polyacene and polyphenyl PAHs. Similar to the case for optical absorption, the polyacene series is seen to have the highest rate of decrease of emission energy with increasing conjugation and the lowest infinite chain limit band gap due to the low bond alternation and rigidity of the
fused ring structure. The polyphenyl series shows a lower rate of decrease of emission energy with increasing conjugation due to the higher bond alternation and the rotational freedom about the linking carbon-carbon single bond [27].

Figure 3.11  (a) absorbance spectra of the polyphenyl series (b) plot of the energies of the first absorption maxima of the various oligomeric series against \( \frac{1}{N+\sigma} \) where \( N \) is the conjugation length and \( \sigma \) represents a contribution from the chain ends. [27].

3.4 Crystal Structure of PAHs

Crystals of the polyphenyl series undergo continuous phase transitions over a wide temperature range. These structural phase transitions are attributed to the change of molecular conformation due to the torsion between phenyl rings ([28] and references therein). Oligomers of the polyphenyl group are non-planar, in the gaseous state [25]. In the solid state, the inter-chain interactions (packing forces) can be expected to result in more planar molecules compared to the gas phase [25]. For the infinite polymers, DFT calculations shows that the optimal inter-ring torsion angle is 18º ([25] and references therein).
Figure 3.12 represents the monoclinic unit cell of biphenyl with two molecules per unit cell [25]. In table 3.1, the experimental values of the lattice parameters \( a, b, c \) and the monoclinic angle \( \beta \) of different polyphenyl PAHs are given. It can be seen from table 3.1 that \( a \) and \( b \) remain almost constant as a function of oligomer length of phenyl series. The small reduction in \( a \) and \( b \) with increasing oligomer length indicates a denser packing for longer length molecules. The increase in \( c \) as a function of oligomer length is simply a consequence of the growing length of molecules which are approximately parallel to \( c \) [25].

Table 3.1  Experimental unit cell parameters for some oligomers of phenyl series at room temperature [25]. \( a, b, c \) and \( \beta \) denote the length of the unit cell parameters and monoclinic angle respectively.

<table>
<thead>
<tr>
<th>Oligomer of Phenyl Series</th>
<th>( a ) [Å]</th>
<th>( b ) [Å]</th>
<th>( c ) [Å]</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biphenyl</td>
<td>8.12</td>
<td>5.63</td>
<td>9.51</td>
<td>95.1º</td>
</tr>
<tr>
<td>( p )-Terphenyl</td>
<td>8.106</td>
<td>5.613</td>
<td>13.613</td>
<td>92.1º</td>
</tr>
<tr>
<td>( p )-Quaterphenyl</td>
<td>8.110</td>
<td>5.610</td>
<td>17.91</td>
<td>95.80º</td>
</tr>
<tr>
<td>( p )-Quinquephenyl</td>
<td>8.070</td>
<td>5.581</td>
<td>22.056</td>
<td>97.91º</td>
</tr>
</tbody>
</table>

In contrast to the phenyl series, the polyacene molecules are planar and so stack in a more conventional fashion.
Anthracene exhibits a so-called ‘herringbone’ structure in the crystalline form which is shown in figure 3.13 [29]. In a crystal, the molecule aligns parallel to the $ab$ plane with the long molecular axis almost perpendicular to the plane. The distinctive ‘herringbone’ pattern is determined by the unit cell axis $a$ and $b$ and the herringbone angle $\theta$ which is the angle between the planes of translationally inequivalent molecules [29]. The arrangement of two layers of molecules as shown in figure 3.13 has the long molecular axes within the $ac$ plane, and the molecules are tilted with respect to this plane by the setting angle $\chi$ with $\delta$ representing the angle between the long molecular axes of two inequivalent molecules [29]. The setting angle $\chi$, not only represents the topology of the surfaces but also describes the ‘linear slip’ between two adjacent molecules within a layer [29].

![Figure 3.13](image)

Figure 3.13  Different views of the anthracene unit cell to describe the definition of the three characteristic angles: (i) depicting the herringbone angle $\theta$, (ii) the tilting angle $\chi$ and (iii) the angle between two inequivalent molecules $\delta$ [29].
3.5 Interaction between PAHs and Graphite

Polyacene PAHs are molecules that consist of fused carbon rings with the peripheral atoms terminated by covalent bonds to a hydrogen atom. The internal structure of the PAHs molecules is thus similar to that of the graphite plane. In particular, the large PAHs have bond lengths very similar to those of graphite. As in the case of graphite planes, the forces between PAHs molecules are the dispersive or van der Waals forces [30]. It has been found that the binding energy of PAHs on a graphite surface per carbon atom is 52± 5 meV [30]. This binding energy depends upon the mapping of PAHs on graphite which means the stable geometries of PAHs with graphite. As a model of these geometries, using \textit{ab initio} computational methods, Lee \textit{et al.} [31] explored PAH/PAH binding interactions. From their study it has been found that a face-to-face configuration is unstable, whereas the T-shaped structure (perpendicular) and parallel-displaced (PD) arrangement of PAHs with respect to other PAHs are of stable geometry and due to the nature of the $\pi$-$\pi$ interaction, the PD type becomes more stable than the T-shaped structures as the molecules become larger [31].

According to Lee \textit{et al.} [31], among the PD structures (figure 3.14) PD-4 is more stable than others. It was found that although PD-3 is stable with respect to the y- and z- directions, it is unstable with respect to x-direction, and thus turns into PD-4 [31]. It was found that the two moieties in a PD configuration try to avoid the $\pi$-$\pi$ repulsion originating from the face to face configuration while maximizing the $\pi$-$\pi$ overlap [31]. On the other hand, PD-2 is also stable with respect to both the x- and z- direction, but not along the y-direction, and thus turns into PD-4. PD-1, a true face to face configuration, is quite unstable [31]. In
the case of PD-5, rotation of one Np around the z-axis is allowed within 20° with a barrier height of 0.01 kcal/mol. The energy barrier from PD-5 to PD-6 is also less than 0.05 kcal/mol. Therefore, although PD-5 is a stable structure at 0 K, it would be actually unstable with a small amount of thermal energy [31]. For the case of T-shaped structures, both T₁ and T₂ structures are stable [31]. It has been found that the binding energies between moieties for PD structure is higher than those of a T-shaped structure [33, 34].

Figure 3.14  The optimized geometries of (Np- Np) with respect to selected degrees of freedom. A face to face configuration is represented in (a) (shown displaced for clarity), while the PD type structures are shown in (b) to (f) and the T-type structures are given in (g) and (h) [31].

Figure 3.15 displays the top view of the stable PD-type structure of PAH clusters. It shows that all stable structures of PD-types are periodic and similar to two layer graphitic structures. From this study it has been found that with the
PD structures, the binding energy between benzene and naphthalene (Bz-Np), the naphthalene dimer (Np-Np), naphthalene and anthracene (Np-An), increases approximately as two, three, and four times that of the benzene dimer (Bz-Bz) [31]. This binding energy corresponds to the number of the overlapping regions of the interplanar $\pi$-rings in the PD-type complex [33]. This “pseudo unit” is called the $\pi$-$\pi$ pair and is shown as the shaded area in figure 3.15. From figure 3.15 (a) to figure 3.15 (d) it has been found that the number of the shaded regions for the PD-type structure for Bz-Bz, Bz-Np, Np-Np and Np-An are one, two, three, and four respectively. All these structures are graphitic-like structures. Figure 3.16 shows a plot of the binding energy as a function of the number of $\pi$-$\pi$ pairs. From this figure it is found that there is a linear relationship between binding energy and $\pi$-$\pi$ pairs of PAHs clusters. From figure 3.16 it is found that the binding energies of Bz-Np and Np-An are higher than those of the corresponding dimers.

Figure 3.15 The top view of the PD-type PAHs clusters [31].
Using thermal desorption methods, Zacharia et al. [32] measured the binding energy between PAHs and graphite. As the structure of PAHs resembles that of graphite, the interaction of PAHs with graphite is considered as a suitable model system for the interaction between graphite layers. Table 3.2 shows the binding energy per PAH molecule on graphite.

<table>
<thead>
<tr>
<th>PAHs</th>
<th>Binding Energy ($E_B$) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.50 ± 0.08</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.90 ± 0.07</td>
</tr>
<tr>
<td>Coronene</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>Ovalene</td>
<td>1.97 ± 0.08</td>
</tr>
</tbody>
</table>

Using these values of binding energy, a graph of the binding energy per PAH molecule on graphite as a function of number of carbon atoms of PAHs is obtained (figure 3.17). From this figure it is found that the binding energy per
PAH molecule on graphite increases approximately linearly with increasing number of carbon atoms of the PAHs.

![Figure 3.17](image.png)

Figure 3.17 Binding energy per PAH molecule on graphite as a function of number of carbon atoms.

Clear structure property relationships governing PAH crystals and the interaction between PAH molecules and graphite can readily be established. It is reasonable to expect a similar degree of structural dependence governing the interaction of SWCNTs with PAHs. This project is motivated towards establishing a similar relationship of binding energy of PAHs on SWCNTs as a function of molecular weight (or number of carbon atoms) in PAHs as that of binding energy of PAHs on graphite as a function of number of carbon atoms.

From the previous study, described in chapter 1, it has been found that there is an interaction between PAHs and SWCNTs [1, 2, 33]. Furthermore, as the structural units of polyacenes and polyphenyls are similar to those of the armchair and zig-zag SWCNTs respectively, these PAHs might show some degree of structurally selective solubilisation of SWCNTs governed by the interaction process. Therefore, to establish the optimum and selective
solubilisation of SWCNTs and to obtain structure-property relationships, PAHs of polyacene and polyphenyl series, described above, were used.

### 3.6 Conclusion

This chapter described the structural and electronic properties of PAHs of the polyacene and polyphenyl series, used in this study to explore this interaction with SWCNTs in a systematic way to obtain the optimum and selective solubilisation of SWCNTs, thus establishing structure-property relationships governing the interaction process. Oligomers of the polyacene series are planar in structure but those of the polyphenyl series are non-planar. Oligomers of the polyphenyl series have a torsion angle between the C-C single bond relative to each other. The electronic properties of PAHs derive from the presence of delocalised $\pi$ electrons. There are strong covalent intra-molecular bonds and weak inter molecular bonds (van der Waals forces) acting between separate molecules. It is found that the binding energy of PAHs on graphite increases with the increasing number of carbon and hydrogen atoms of PAHs.

This chapter described the structural and physical properties of PAHs. The next chapter will give the description of different spectroscopic techniques which were used for the material characterisation and interaction studies.
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4.1 Introduction

In this study both spectroscopic and microscopic techniques were used to explore and characterise the interactions between PAH molecules and SWCNTs. The principle instruments used were absorption, fluorescence, and Raman spectroscopy and an atomic force microscope (AFM). The following briefly describes the techniques utilised in this project.

4.2 Spectroscopic Techniques

Spectroscopic techniques are applied to characterize the materials which are used in this research. Spectroscopy is the study of the interaction between radiation (electromagnetic radiation) and matter. By measuring material characteristics such as absorption, emission and chemical bond vibration, the electronic, molecular and physical structure, including aggregation state, can be determined [1-4]. Microscopic techniques can further be used to directly image the surface structure on the micrometer and nanometre scale [1, 2, 5].

Both electronic and vibrational spectroscopies are used in this project. Electronic spectroscopy is defined as a method that probes the electronic transitions of the material as a result of interactions with photons, while vibrational spectroscopy is defined as a method which gives information concerning molecular vibrations.
4.3 Electronic Spectroscopy

The two principle electronic spectroscopy techniques, absorption and fluorescence spectroscopy, are used in this research. These two techniques examine the electronic transitions within a molecule and give information about the electronic structure of the material and potential influences of its local environment.

Absorption of electromagnetic radiation is the way by which the energy of a photon is taken up by matter, typically the electrons of an atom [6]. If the energy of an incident photon corresponds to the energy gap between the ground state of a molecule and an excited state, the photon may be absorbed and the molecule promoted to the higher energy excited state [6]. On the other hand, (photo-) emission is the process by which energy in the form of a photon is released by a particle, for example, by an atom whose electrons make a transition between two electronic energy levels. The emitted energy is in the form of a photon with a specific frequency [7-9]. Figure 4.1 shows the absorption and emission process. Here \( V''_0 \) and \( V'_0 \) represent the vibrational levels of ground and excited states respectively.
Figure 4.1  Absorption and emission processes [10].

More details of the emission process are shown in figure 4.2. The singlet ground, first, and second electronic states are depicted by $S_0$, $S_1$, and $S_2$ respectively. When a sample is excited by absorbing a photon of light, a transition occurs from its ground electronic state to one of vibrational levels of the $S_1$ or $S_2$ energy state [9]. In a molecule, the excitation process is fully described as a HOMO-LUMO transition, whereas in solid state, where the electronic structure is described by the band theory approximation, the excited state must take into account the Coulomb attraction between the excited electron and the vacated state or “hole”, in accordance with exciton theory. [11]. Immediately following absorption of a photon, several processes will occur with varying probabilities, but the most likely will be relaxation to the lowest vibrational energy level of the first excited state ($S_1 = 0$; figure 4.2). This process is known as internal conversion or vibrational relaxation (loss of energy in the absence of light emission) and generally occurs in $10^{-12}$ s or less [9]. An excited molecule can exist in the lowest excited singlet state ($S_1$) for periods on the order of $10^{-8}$ s before finally relaxing to the ground state. If relaxation from this long-lived state is accompanied by emission of a photon, the process is formally known as fluorescence [9].
There are also probabilities of several different pathways by which the relaxation can be occurred. Molecules in the S\textsubscript{1} state can also undergo a spin conversion to the first triplet state (T\textsubscript{1}). Emission from T\textsubscript{1} is termed phosphorescence and is generally shifted to longer wavelengths (lower energy) relative to the fluorescence. Conversion of S\textsubscript{1} to T\textsubscript{1} is called intersystem crossing. Transition from T\textsubscript{1} to the singlet ground state is spin forbidden which results in rate constants for triplet emission that are several orders of magnitude lower than those for fluorescence [9].

Figure 4.2  Jablonski diagram showing the sequence of steps leading to radiative decay[9].
The decay of electronically excited states can also occur through quenching [9]. Quenching is a particular case of energy transfer between an excited molecule, and a quenching species. The presence or addition of quenching species reduces the intensity of fluorescence [7-9]. In general energy transfer to a solvent depends on the similarity of the vibrational spectrum of the chromophore to that of the solvent [12]. Significant quenching of the fluorescent yield, indicating an additional decay route, can be seen in aggregates of chromophores and even in moderate concentration solutions [13].

4.3.1 Absorption Spectroscopy

Absorption spectroscopy refers to a range of techniques employing the interaction of electromagnetic radiation with matter. In this spectroscopy, the intensities of a beam of light, as a function of wavelength or energy, before and after interaction with a sample are compared. More technically, absorption spectroscopy is based on the absorption of photons by one or more substances present in a sample and subsequent promotion of electrons from one energy level to another in that substance. The wavelength or energy at which the incident photon is absorbed is determined by the difference in the available energy levels of the different substances present in the sample [6]. The spectrum of energies is thus characteristic of that material [6].

In this research ultra violet-visible-near-infrared (UV-Vis-NIR) spectroscopy is predominantly used. It is a useful technique to measure how much light of a particular wavelength (colour) is absorbed by a sample. Since this wavelength is often correlated with the presence and/or structure of a particular chemical
this technique is widely used for both qualitative and quantitative work in a wide range of fields [14].

Absorption spectroscopy of a molecular material is commonly carried out in solution at low concentrations such that the molecules are non-interacting. The incident radiation is attenuated by the solution and the absorbance increases as attenuation of the beam increases. Absorbance is directly proportional to the path length and the concentration of the absorbing material. This is known as the Beer-Lambert law (equation 4.1).

\[ A = \varepsilon b c \]  \hspace{1cm} (4.1) [6]

where \( b \) is the path length, \( c \) is the concentration and \( \varepsilon \) is the molar extinction co-efficient, which contains the sample specific spectral information. Experimental measurements are usually made in terms of transmission \( (T) \), which defined as:

\[ T = I/I_0 \]  \hspace{1cm} (4.2) [15]

where \( I \) is the light intensity after it passes through the sample and \( I_0 \) is the initial light intensity. The relation between \( A \) and \( T \) is

\[ A = - \log T = - \log (I/I_0) \]  \hspace{1cm} (4.3) [6, 15]

The Beer Lambert Law only applies in materials when the molecules are isolated from each other and deviations occur at high enough concentrations in molecular systems due to the formation of aggregates [16]. Therefore, monitoring the concentration dependence of the absorption of materials is a sensitive probe to explore their interaction [17].

UV-Vis-NIR absorption spectroscopy is the measurement of the wavelength and intensity of absorption of near-ultraviolet and visible light by a
sample. Figure 4.3 shows the schematic set-up of UV-Vis-NIR spectrometer. The operation of this instrument is relatively straightforward [18]. A beam of light from a visible and/or ultraviolet (UV) light source is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half-mirrored device [18]. One beam, the sample beam, passes [18] through a small transparent cuvette containing a solution of the compound being studied in a transparent solvent. The other beam, the reference, passes through an identical [18] cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors. The absorption is measured over a range of wavelengths. Transmission is measured as a ratio of intensity of sample to intensity of reference beams. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as \( I_0 \). The intensity of the sample beam is defined as \( I \). Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The UV region scanned is normally from 200 to 400 nm, and the visible -NIR portion is from 400 to 3000 nm.

If the sample compound does not absorb light of a given wavelength, \( I = I_0 \). However, if the sample compound absorbs light then \( I \) is less than \( I_0 \), and the ratio may be plotted on a graph versus wavelength. Absorption may be presented as transmission (\( T = I/I_0 \)) or absorbance (\( A = \log I_0/I \)). If no absorption has occurred, \( T = 1.0 \) and \( A = 0 \). Most spectrometers display absorbance on the vertical axis, and the commonly observed range is from 0 (100% transmission) to 3 (0.1% transmission). The longest wavelength absorbance maximum is a characteristic value often used as an indicator of the HOMO-LUMO band gap in
molecules and is designated as $\lambda_{\text{max}}$. As examples, the absorbance spectra of polyacene PAHs and HiPco SW CNTs are shown in figure 4.4. The absorbance spectra of the PAHs are discussed in detail in chapter 5.

In this research a Perkin Elmer Lambda 900 UV-Vis-NIR Spectrometer is used. The spectrometer is a double-beam, double monochromator ratio recording system with pre-aligned tungsten-halogen and deuterium lamps as sources. The wavelength range is from 175 to 3,300 nm with an accuracy of 0.08 nm in the UV-vis region and 0.3 nm in the NIR region. It has a photometric range of ±6 in absorbance. For all the experimental studies the absorption was measured at all times with a reference sample in a double beam arrangement. UV light is absorbed by most glasses and plastic, so quartz cells are used.
4.3.2 Fluorescence Spectroscopy

Fluorescence (or photoluminescence) spectroscopy is a complementary technique to absorption spectroscopy. It involves using a beam of light, usually ultraviolet light, that excites the electrons in molecules of a certain material and causes them to emit light of a lower energy.

In a typical experiment, the different wavelengths of fluorescent light emitted by a sample are measured using a monochromator, holding the excitation light at a constant wavelength [7]. This is called an emission spectrum. An excitation spectrum is the opposite, whereby the emission light is held at a constant wavelength, and the excitation light is scanned through a many different wavelengths (via a monochromator) [7].
Figure 4.5 shows the layout of a fluorescence spectrometer. The light from an excitation source passes through a filter or monochromator, and strikes the sample. A proportion of the incident light is absorbed by the sample, and some of the molecules in the sample fluoresce. The fluorescent light is emitted in all directions. Some of this fluorescent light passes through a second filter or monochromator and reaches a detector, which is usually placed at 90° to the incident light beam to minimize the risk of transmitted or reflected incident light reaching the detector. As examples, figure 4.6 presents the fluorescence spectra of polyacene PAHs. These are discussed in detail in chapter 5. Semiconducting SWCNTs have also been demonstrated to exhibit fluorescence emission but the wavelength range (~ 1.3 - 1.5 μm) is beyond that of the instruments available to this study.

A Perkin Elmer LS55 luminescence spectrometer which is computer controlled is used throughout this research. In this spectrometer, excitation is provided by a pulsed xenon discharge lamp with a pulse width at half peak height of < 10 μs and pulse power 20 kW. The source is monochromated using
a Monk-Gillieson type monochromator and can be scanned over the range of 200 - 800 nm. The luminescence is passed through a similar monochromator, which can be scanned over the range of 200-900 nm.

![Fluorescence spectra of polyacene PAHs](image)

**Figure 4.6** Fluorescence spectra of polyacene PAHs

### 4.4 Vibrational Spectroscopy

Molecular vibrations occur because the relative positions and orientations of the atomic nuclei are not absolutely fixed within a molecule [20, 21]. These vibrations can be excited by the absorption of a photon of appropriate frequency. Molecules absorb photons of frequencies which exactly match the vibrational frequencies of molecules. The frequencies at which the molecules vibrate depend on the forces between the atoms and the geometry of the molecule [20, 21]. Therefore, information about the identity of the molecule and the flexibility of its bonds can be obtained from the frequencies where absorption has occurred. Vibrational spectroscopy probes the oscillations of atoms within a molecule. There are generally two types of vibrational
spectroscopy: infrared spectroscopy (IR) and Raman spectroscopy. In this research Raman spectroscopy is used.

4.4.1 Raman Spectroscopy

When light interacts with matter, the photons may be absorbed or scattered [20]. Raman spectroscopy is based on a light scattering effect [21]. The scattered light consists of two types: Rayleigh scattering and Raman scattering [15]. Rayleigh scattering has the same energy (frequency), and therefore wavelength, as the incident photons [15, 20, 21]. Raman spectroscopy is based on the Raman scattering, which is the inelastic scattering of photons by molecules [15, 20, 21]. The difference in energy between the incident photon and the Raman scattered photon is equal to the energy of a vibration of the scattering molecule [15, 20, 21]. The Raman effect is often illustrated with the aid of a virtual energy state into which the molecule is excited. If the molecule is excited from the ground vibrational state and returns to the first vibrational level of ground state, the wavelength of the scattered radiation is lowered (Stokes scattering) [15, 20]. If alternatively the molecule starts off in the first vibrational level, and is demoted to the lowest ground state as a result of the scattering process, anti-Stokes radiation occurs (figure 4.7) [15, 20]. In both cases, the difference in frequency is characteristic of one of the normal modes of vibration of the molecule and thus the spectrum of scattered radiation is characteristic of the material.

The Raman effect arises when a photon is incident on a molecule and interacts with the electric dipole of the molecule. This interaction can be viewed
as a perturbation of the molecule's electric field. A polarization is induced in the molecule by the oscillating electric field of the incident light. This polarization \( P \) is proportional to this electric field \( E \) (equation 4.4) [15, 21, 22]

\[
P = \alpha E \quad (4.4)
\]

The proportionality constant \( \alpha \) is the polarisability of the molecule [15, 21, 22]. This induced dipole then radiates scattered light, with or without exchanging energy with vibrations of the molecule [15, 21, 22]. The selection rule of Raman spectroscopy states that the normal mode of vibration of polyatomic molecules must undergo a change in polarisability as a result of the interaction with electromagnetic radiation. As \( \pi \)-conjugated organic molecules have a large polarisability, Raman is a powerful probe of their structure and properties [23, 24]. It has been found that the Raman excitation frequency can have an effect on the distribution of the intensity and peak positions in the Raman spectrum. When the excitation frequency is close to the optical absorption, the Raman intensity is enhanced, and this effect is known as the resonant Raman effect [20]. Figure 4.8 presents a typical Raman spectrum of SWCNTs. A detailed description of Raman spectroscopy of SWCNTs as well as the PAHs employed in this study is provided in chapter 5.
The Raman instrument used in this study is a LabRAM HR 800 Raman Microscope (Horiba Jobin Yvon) with a confocal Raman imaging microscope system. 474 nm (50 mW), 785 nm (300 mW), 532 nm (50 mW) and 660 nm (mW) are available as sources. All sources are polarized, enabling measurement of depolarisation ratios and studies of orientation in materials. The scattered light is collected by the objective in a confocal, backscattering geometry, and is dispersed onto an air cooled charged coupled device (CCD) array by one of four interchangeable gratings, 1800 gr/mm, 950 gr/mm, 600 gr/nm and 300 gr/nm.

Figure 4.7 The Stokes and the anti Stokes shift in the normal Raman and the resonance Raman R- Rayleigh scattering, S-Stokes Raman scattering, AS-Anti stokes Raman Scattering [20].
4.5 Microscopic Techniques

Microscopy is a technique used to display or map the topography of objects. There are three well known branches of microscopy: optical, electron and scanning probe microscopy (SPM) [25]. Optical and electron microscopy involve the diffraction, reflection, or refraction of a beam of electromagnetic radiation or electrons upon interaction with the subject of study, and the subsequent collection of this scattered radiation in order to build up an image. SPM involves the interaction of a scanning probe with the surface or object of interest. In this research, atomic force microscopy (AFM), which comes under the general heading of SPM, has been employed to obtain topographical of SWCNTs samples before and after interaction with PAHs to observe if SWCNTs bundles are dispersed.
4.5.1 Atomic Force Microscopy (AFM)

The principle components of AFM are the piezo-electric scanner made from piezo-electric crystals and the probe. Piezo-electric crystals are ceramic materials that expand or contract in the presence of a voltage gradient and conversely, develop an electrical potential in response to mechanical pressure. In this way, movements in the \(x\), \(y\) and \(z\) direction are possible [25]. The probe is a cantilever with a sharp tip at one end, which is brought into interaction with the sample surface. In AFM, mechanical force interactions acting between a sharp probe and a sample are used for surface imaging [25].

The AFM measures the forces acting between the fine tip and a sample. The working principles of AFM are very simple and are represented schematically in figure 4.9. The surface imaging is realized by detecting the tip-sample force in different locations while the probe is rastering the sample surface with the help of a piezo-electric scanner [25]. A feedback control applied during imaging enables the piezo-electric scanners to maintain the tip at a constant force (to obtain height information), or height (to obtain force information) above the sample surface. The AFM head employs an optical deflection system in which tip is attached to the underside of a reflective cantilever [26]. A diode laser is focused onto the back of the reflective cantilever. As the tip scans the surface of the sample, moving up and down with the contour of the surface, the laser beam is deflected off the attached cantilever into a dual element photodetector. The photodetector measures the difference in light intensities between the upper and lower photodetectors, and then converts this difference to voltage. Feedback from the photodetector
difference signal, through software control from the computer, enables the tip to maintain either constant force or constant height above the sample [26].

Because the AFM relies on the forces between the tip and sample, knowing these forces is important for proper imaging. The force is not measured directly, but calculated by measuring the deflection of the cantilever [28]. When the tip is brought into proximity of a sample surface, the force between the tip and the sample leads to a deflection of the cantilever according to Hooke’s law [28]. Hooke’s law gives $F = -kz$, where $F$ is the force, $k$ is the stiffness of the cantilever, and $z$ is the distance the cantilever is displaced [28]. The dependence of the force upon the distance between the tip and sample is shown in figure 4.10.

Figure 4.9  Principal of AFM [27].
There are three commonly used techniques for AFM; contact mode, non-contact mode and tapping mode [25].

In the contact mode, the cantilever is held less than a few angstroms from the sample surface, and the interatomic force between the cantilever and the sample is repulsive with a mean value of $\sim 10^{-9}$ N [25, 27, 28]. Once the cantilever enters into the repulsive region, it is deflected and this deflection is measured by the photodetector and the signal is sent to the feedback loop which maintains a constant force between the tip and the sample by adjusting the deflection [25, 28].

In the non-contact mode, the cantilever is held on the order of tens to hundreds of Angstroms from the sample surface, the interatomic force between the cantilever and sample is attractive and is largely a result of the van der Waals interactions [25, 27]. The forces between the tip and sample are quite low, on the order of $10^{-12}$ N [28]. As the attractive force from the sample is substantially weaker than the forces used by the contact mode, the tip is given a
small oscillation so that the small force between the tip and the sample can be detected by measuring the change in amplitude, phase, or frequency of the oscillating cantilever in response to force gradients from the sample [29].

In the tapping mode, imaging is implemented by oscillating the cantilever assembly at or near the cantilever’s resonance frequency between 50 kHz and 50,000 kHz. When the tip is not in contact with the surface or passes over a depression, the piezo motion causes the cantilever to oscillate with a high amplitude as the cantilever has more room to oscillate. The oscillating tip is then moved towards the surface until it begins to lightly touch or tap the surface. As the oscillating cantilever begins to intermittently contact the surface or passes over a bump in the surface, the cantilever oscillation is reduced as the cantilever has less room to oscillate. The oscillation amplitude of the tip is measured by the detector and input to the controller electronics. The reduction in oscillation amplitude is used to identify and measure surface features [29]. The digital feedback loop piezo elements then adjust the separation between the tip and sample to maintain constant amplitude and force on the sample.

Tapping mode overcomes problems associated with friction, adhesion, electrostatic forces of contact and non contact modes of AFM, by alternately placing the tip in contact with the surface to provide high resolution and then lifting the tip off the surface to avoid dragging the tip across the surface [29]. As shown in figure 4.11 AFM has been extensively used to image SWCNTs [30]. In this research, AFM is employed in the tapping mode, to obtain topographic images of bundles, debundled and dispersed SWCNTs.
An Asylum MFP 3D BIO AFM is used in this research. This is a high performance AFM designed specifically for biological applications. This system supports sample dimensions up to 100 mm x 100 mm x 20 mm (X x Y x Z) and has an XYZ scan range up to 90 µm x 90 µm x 7 µm. It has noise level of XY < 6 Å and Z < 3 Å. This AFM has x, -x, y,-y, z piezos for accurate, linearised flat scanning. To analyse the results obtained from AFM, IGOR Pro AFM software has been used.

Figure 4.11 AFM image of functionalised SWCNTs [30].
4.6 Conclusion

In this study, for the characterization of the samples, both spectroscopic and microscopic techniques were used. The basic principle of the spectroscopic techniques, such as UV-Vis-NIR absorption, fluorescence and Raman spectroscopy and microscopic techniques such as AFM and the respective instruments have been briefly described in this chapter. Spectroscopy is a useful technique for characterising materials. It also gives information about molecular structure of materials. Absorption and fluorescence spectroscopy give information about electronic and vibrational structure of materials. In this project, fluorescence spectroscopy was used as a powerful tool to identify the interaction of PAHs of polyacene and polyphenyls group with HiPco and AD SWCNTs. The details of the use of this fluorescence technique are described in chapter 5 and chapter 6. Raman spectroscopy, which probes the polarisability and dipole moment changes within the material as a result of the interaction with electromagnetic radiation and the obtained spectra, gives information about the vibrational structure of the molecules. This technique has been employed to study the selective solubilisation of different SWCNTs (chapter 7). Among the range of available microscopic techniques, AFM was employed to visualise the bundled, dispersed and isolated SWCNTs (chapter 5 and 6).
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5.1 Introduction

This study probes the interaction between SWCNTs and PAHs. Both HiPco and AD SWCNTs were used and PAHs of the polyacene and polyphenyl series were chosen. The previous chapter (chapter 4), described the different spectroscopic and microscopic techniques to be employed for the characterisation of the materials and their interaction. Before launching an investigation into their interactions, however, it is vital to establish the spectral characteristic of the materials individually. It should be noted that in this study, solvent selection also plays an important role. The solvent employed should solubilise PAHs of different lengths but should act as a poor solvent for SWCNTs, such that the interaction between the PAHs and the SWCNTs is the dominant solubilising interaction. This chapter discusses the basis for the selection of the solvent, and the spectral characterisation of HiPco and AD SWCNTs, as well as polyacene and polyphenyl oligomers using the methods outlined in chapter 4. UV-Vis and fluorescence spectroscopy were used for solvent selection and to obtain information about the electronic structure of PAHs. Information about the interaction between SWCNTs and PAHs was obtained with the aid of fluorescence spectroscopy. This chapter also examines the vibrational properties of both HiPco and AD SWCNTs, and PAHs obtained using Raman spectroscopy. Raman spectroscopy is also used to determine the diameter distribution and corresponding assignments of pristine HiPco and AD
SWCNTs. AFM is used to directly image the SWCNTs in the composite samples.

5.2 Solvent Characterisation and Selection

As stated above, the solvent employed should have the ability to solubilise PAHs of various lengths and have a poor affinity for SWCNTs. Therefore, solvent selection is an important part of the interaction study. To establish the suitability of the solvent, solutions in the range of ~ $1.875 \times 10^{-2}$ mol/L to ~ $1.19 \times 10^{-9}$ mol/L for naphthalene, ~ $1.558 \times 10^{-2}$ mol/L to ~ $4.77 \times 10^{-13}$ mol/L for biphenyl, ~ $5 \times 10^{-3}$ mol/L to ~ $2.38 \times 10^{-9}$ mol/L for pentacene and ~ $3.12 \times 10^{-3}$ mol/L to ~ $2.22 \times 10^{-9}$ mol/L for $p$-quinquephenyl in toluene and in chloroform in the absence of SWCNTs were prepared. Toluene was used because of its poor affinity for SWCNTs as determined by previous studies [1]. Chloroform was chosen as an alternative as it has been demonstrated to exhibit good affinity for PAHs [2]. Solutions were characterized using UV-Vis (Perkin Elmer Lambda 900) and fluorescence (Perkin Elmer LS55) spectroscopy.

Figure 5.1 shows the absorbance spectrum of neat toluene, a solution of toluene containing naphthalene and one also with toluene containing biphenyl. UV-Vis spectroscopy is based on excitations within the electronic levels in the conjugated molecules and the wavelength at which the conjugated system absorbs is determined by the conjugation length, as shown in chapter 3, figure 3.11. The absorption feature at ~ 287 nm is the lowest energy excitation maximum of naphthalene [3, 4]. The higher energy peaks of the vibrational manifold at ~ 277 nm, ~ 267 nm and ~ 258 nm are not visible, however, as they are masked by the toluene absorption. It is reported that biphenyl has its longest wavelength absorption maximum at ~ 247 nm [3, 4]. In figure 5.1, the
observed absorption of biphenyl is that of the solvent itself and thus the entire absorption spectrum is masked by that of toluene.

![Absorbance of naphthalene, biphenyl and toluene.](image)

Figure 5.1 Absorbance of naphthalene, biphenyl and toluene.

Figure 5.2 shows the fluorescence of neat toluene, toluene containing biphenyl and another containing naphthalene. The excitation wavelengths of toluene, biphenyl, and naphthalene were 276 nm, 280 nm, and 286 nm respectively. As the absorbance of both PAHs overlaps that of toluene, excitation wavelengths longer than the absorbance maxima were chosen. Nevertheless, the excitation wavelength of toluene is near to those of biphenyl and naphthalene resulting in an excitation of the toluene as well as the PAH molecules. For this reason the spectrum of toluene interferes with that of naphthalene and biphenyl making an isolation of the emission spectrum of the molecules difficult.
Solutions of pentacene and \( p \)-quinquephenyl in toluene were then prepared as they have absorption maxima of about 580 nm and 312 nm respectively, which will not overlap with that of toluene. From the absorbance spectra (figure 5.3), it is found that \( p \)-quinquephenyl was dissolved in toluene to some extent but as pentacene has a more planar and rigid structure, it was not dissolved. In an attempt to improve the solubility of pentacene in toluene, heat was applied. As shown in figure 5.4 it was found that when heat was applied, absorbance peaks of pentacene were observed. But when the solution was allowed to cool the peaks disappeared. From this result it can be said that at room temperature toluene has poor affinity for pentacene.

During these initial experiments it was found that the absorbance and fluorescence of toluene interferes with that of the short chain PAHs and that the long chain PAHs of the polyphenyl group exhibit low levels of solubility in toluene. As an alternative to toluene, chloroform (CHCl\(_3\)) was selected. It has also been demonstrated to show a poor affinity for SWCNTs [5, 6]. Although, a
small degree of solubilisation is affected at low concentration [7], precipitation is observed within hours of sonication.

**Figure 5.3** Absorbance spectra of $p$-quinquephenyl in toluene at different concentrations.

**Figure 5.4** Absorbance spectra of pentacene in toluene at different temperatures. Spectra are offset for clarity.

Absorbance and fluorescence spectra of chloroform are shown in figure 5.5 and figure 5.6 respectively. From figure 5.5 it can be seen that chloroform has absorbance maxima at shorter wavelengths (255 nm, 262 nm and 269 nm) than those of toluene, biphenyl and naphthalene. Figure 5.6 demonstrates that
chloroform has negligible fluorescence in the UV region and that the fluorescence of short chain PAHs will not interfere with that of chloroform. Therefore one of the problems is eliminated.

Figure 5.5 Absorbance spectra of chloroform and toluene.

Figure 5.6 Fluorescence spectra of toluene and chloroform. Excitation wavelengths were taken as 276 nm and 269 nm respectively.

Using chloroform as a solvent, solutions of pentacene and $p$-quinquephenyl were prepared. This time, $p$-quinquephenyl was also dissolved in chloroform but pentacene was not. Figure 5.7 shows the absorbance
spectrum of p-quinquephenyl in chloroform. Comparing the plot of figure 5.3 to that of figure 5.7 it is found that at a concentration of ~ 1.25 x 10^{-3} mol/L, the intensity of absorbance of p-quinquephenyl in chloroform is ~ 3.5 times higher than that in toluene. So it can be stated that chloroform is a more effective solvent for p-quinquephenyl than toluene.

Figure 5.7  Absorbance spectra of p-quinquephenyl in chloroform at different concentrations.

From figure 5.8, it is found that the Beer-Lambert law is valid up to a concentration of ~ 9.76 x 10^{-6} mol/L for p-quinquephenyl and deviates at higher concentrations indicating aggregation of p-quinquephenyl in the solution.
Figure 5.8 Plot of absorbance of $p$-quinquephenyl at 311 nm in chloroform as a function of concentration.

Table 5.1 shows that in the polyphenyl series, from biphenyl to $p$-sexiphenyl, all PAHs are soluble in chloroform and in the acene series from naphthalene to tetracene all PAHs are soluble, although pentacene and hexacene are not soluble in chloroform. It is deemed that the combination of the two series is a sufficient range to study structure property relations in the interaction of PAHs with SWCNTs.

Therefore, to check the affinity of chloroform for SWCNTs, samples of both SWCNTs and chloroform at different concentrations were prepared and it was found that no SWCNTs were present in the solution after an hour of sample preparation. This is an indication of the poor affinity of chloroform for SWCNTs [5, 6]. This combined with its spectral characteristics and ability to solubilise a satisfactory range of both PAH series was the basis of the choice of chloroform as the solvent in which to study the interaction of PAHs and SWCNTs.
Table 5.1 Solubility of oligomers of polyphenyl and polyacene oligomers in chloroform [2].

<table>
<thead>
<tr>
<th>Polyphenyl Oligomers</th>
<th>Solubility in Chloroform</th>
<th>Polyacene Oligomers</th>
<th>Solubility in Chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biphenyl</td>
<td>√</td>
<td>Naphthalene</td>
<td>√</td>
</tr>
<tr>
<td>p-terphenyl</td>
<td>√</td>
<td>Anthracene</td>
<td>√</td>
</tr>
<tr>
<td>p-quaterphenyl</td>
<td>√</td>
<td>Tetracene</td>
<td>√</td>
</tr>
<tr>
<td>p-quinquephenyl</td>
<td>√</td>
<td>Pentacene</td>
<td>X</td>
</tr>
<tr>
<td>p-sexiphenyl</td>
<td>√</td>
<td>Hexacene</td>
<td>X</td>
</tr>
</tbody>
</table>

Having selected the solvent, the next step was to study the vibrational properties as well as diameter distribution and to assign a diameter range to pristine HiPco and AD SWCNTs using Raman spectroscopy. Vibrational characteristics of pristine PAHs were also obtained using Raman spectroscopy.

5.3 Raman Spectroscopy

Raman spectroscopy is a powerful tool to investigate the vibrational properties and thus characterize conjugated carbon molecules and in particular SWCNTs. It has previously been extensively employed to examine selective solubilisation of SWCNTs by polymers and organic molecules [1, 8], and will be
similarly utilised in this study. Thus it is important to introduce the basic Raman characteristics of the raw materials.

For the Raman study of SWCNTs and PAHs, the materials were drop cast onto quartz substrates from chloroform solution.

5.3.1 SWCNTs

There are basically four phonon modes of SWCNTs that give significant and characteristic Raman scattering signals (figure 5.9). The tangential carbon stretching modes (G-band) are at ~ 1580 cm\(^{-1}\). These modes are associated with the in phase vibrational movement of carbon atoms. The line-shape of the G-band can be used to distinguish between metallic and semiconducting SWCNTs [9]. The D band appearing between 1250 and 1450 cm\(^{-1}\) is reported to be related to either the presence of defects in the SWCNT walls or to the presence of amorphous carbon material in the sample [9]. The G’ band is located at 2500 - 2900 cm\(^{-1}\). This feature is considered to be a second order overtone of the D band [10]. The radial breathing modes (RBMs) are in the region of ~ 100 - 300 cm\(^{-1}\) and the frequency positioning is related to the SWCNT diameter [9, 11, 12]. In this region, carbon atoms undergo uniform radial displacement. Because of their sensitive dependence on the nanotube diameter, it is these features which have previously been extensively utilised to examine selective solubilisation of SWCNTs. It is critical therefore that these are determined in the raw and processed forms.
The resonant nature of the Raman scattering implies that SWCNTs of certain diameters are enhanced and only by employing a variety of source wavelengths a comprehensive picture of the diameter range of the SWCNT samples can be generated [9, 13]. Figure 5.10 shows the Raman spectra in the RBM region of a pristine HiPco and AD SWCNTs sample for the four different excitation laser lines; 785 nm (1.58 eV), 660 nm (1.88 eV), 532 nm (2.33 eV) and 473 nm (2.62 eV). Due to the different resonance conditions [14], each different source wavelength gives rise to a markedly different profile. Figure 5.10 (ii) and (iv) show the combined profiles of RBMs with four different laser energies of HiPco and AD SWCNTs respectively by a simple addition of the respective spectra which have been normalised according to the intensities of the RBMs of each laser line for pristine HiPco and AD SWCNTs samples respectively. This simplistic representation of the combined RBM profiles will be used in chapter 7 as reference to understand the diameter distribution of the composite samples with dispersed SWCNTs.
Figure 5.10  RBMs of pristine HiPco (i) and AD (iii) SWCNTs with 785 nm (1.58 eV), 660 nm (1.88 eV), 532 nm (2.33 eV) and 473 (2.62 eV) as source (ii) combined Raman spectra of HiPco (ii) and AD (iv) SWCNTs for the different lasers.

The RBM positioning enables the determination of the diameter and thus the chiral indices \((n, m)\) of the SWCNTs [9, 10]. The diameter of SWCNT \((d)\) can be related to the RBM frequency, \(\omega_{RBM}\), and structural indices \((n, m)\) by the following equation [15]
\[ \omega_{RB\text{M}} = \frac{C_1}{d} + C_2 = \frac{\pi C_1}{a_{c-c} \sqrt{3(n^2 + nm + m^2)}} + C_2 \quad \text{(5.1)}, \]

where,

- \(a_{c-c}\) is the distance between the C-C bonds, 0.144 nm, [15]
- \(C_1\) is a constant of proportionality [16],
- \(C_2\) is essentially a damping factor which accounts for a frequency shift dependent on the damping caused by the local environment of the SWCNT [14].

There is uncertainty in the selection of values for \(C_1\) and \(C_2\) from literature. For the evaluation of SWCNT diameters (in the diameter range 0.7 <d <1.5 nm), Rao et al. have used values of \(C_1 = 224\) cm\(^{-1}\) nm, \(C_2 = 14\) cm\(^{-1}\) [17]. Yu et al. have used \(C_1 = 223.75\) cm\(^{-1}\) nm, \(C_2 = 15\) cm\(^{-1}\) [12], for semiconducting tubes. Michael et al. and Bachilo et al. find \(C_1 = 223.5\) cm\(^{-1}\) nm, \(C_2 = 12.5\) cm\(^{-1}\) [11, 15] whereas Telg et al. find values of \(C_1 = 220.4\) cm\(^{-1}\) nm, \(C_2 = 19\) cm\(^{-1}\) [18]. Fantain et al. have tabulated two sets of \(C_1\) and \(C_2\) values: for semiconducting \(C_1 = 223\) cm\(^{-1}\) nm, \(C_2 = 10\) cm\(^{-1}\) and metallic \(C_1 = 220\) cm\(^{-1}\) nm, \(C_2 = 14\) cm\(^{-1}\) tubes [19]. In other literature reports, the values of \(C_1\) and \(C_2\) are found to be \(C_1 = 219 \pm 3\) cm\(^{-1}\) nm, \(C_2 = 15 \pm 3\) cm\(^{-1}\) [9]. Jorio et al. have used \(C_1 = 248\) cm\(^{-1}\) nm considering \(C_2 = 0\) cm\(^{-1}\) for isolated SWCNTs [20]. Recently, Araujo et al. determined a relationship of \(\omega_{RB\text{M}} = 227.0/d\) with negligible environmental factor for SWCNTs grown by the water assisted chemical vapour deposition method [21], and proposed that all previous literature results can be fitted with this fundamental relationship, with the addition of an environmental factor. They identified that the universal value of \(C_1 = 227.0\) cm\(^{-1}\) nm is in agreement with the elastic properties
of graphite and predicted values for SWCNTs [22]. However, the predictions are based on an isotropic value of the elastic properties and do not consider any dependence on the SWCNT chirality, structure and size. Therefore, although it is well documented that the RBM frequency is related to the SWCNT diameter, the values of the parameters ($C_1$ and $C_2$) to elucidate this are still under debate.

Figure 5.11 Kataura plot representing optical transition energy of metallic and semiconducting SWCNTs as a function of diameter of SWCNTs [23]. Black and red circles represent semiconducting and metallic SWCNTs respectively.

As the literature values of these parameters range from 216 cm$^{-1}$ nm to 248 cm$^{-1}$ nm and 10 to 19 cm$^{-1}$ for $C_1$ and $C_2$ respectively, in this work two sets of $C_1$ (216 cm$^{-1}$ nm and 234 cm$^{-1}$ nm) and $C_2$ (17 cm$^{-1}$ and 10 cm$^{-1}$ ) values were used to initially obtain a possible diameter range for pristine HiPco and AD SWCNTs. Having established the range of diameters of the SWCNTs present
from the RBM frequencies and equation 5.1, an estimate of the most probable diameters contributing to the Raman spectrum at each source wavelength can be made, assuming that resonant SWCNTs dominate the Raman spectrum, by reference to the so-called Kataura plot [24], which graphically relates the optical transition energies of metallic and semiconducting SWCNTs to their diameters (figure 5.11). After establishing the possible diameter range for specific laser energies, these diameters were then compared with the Kataura plot to find out whether SWCNTs of these diameters were resonant at the corresponding laser energy. For HiPco SWCNTs of diameter in the range of ~ 0.7 nm to ~ 1.4 nm (which is the typical diameter range for HiPco SWCNTs [25]), only semiconducting SWCNTs should be resonant at a laser energy of ~ 1.58 eV (785 nm). Therefore, for this laser energy only the diameters of semiconducting HiPco SWCNTs in the selected diameter range were chosen. However, in many cases there exists more than one candidate corresponding to the particular \( \omega_{RBM} \). To assign a single diameter to a corresponding \( \omega_{RBM} \), the inverse of these chosen diameters of HiPco SWCNTs were plotted against the corresponding value of \( \omega_{RBM} \), as shown in figure 5.12 (i). As there is a linear dependence between \( \omega_{RBM} \) and the inverse diameter (1/d) [9], the plots should be a straight line. For a particular \( \omega_{RBM} \), a particular diameter was selected from the best fit to the straight line. Also from this best fit, the values of \( C_1 \) and \( C_2 \) were found to be 221.5 cm\(^{-1}\) nm and 14.4 cm\(^{-1}\) respectively for 785 nm (1.58 eV) for HiPco SWCNTs. By using equation 5.1, the structural indices \((n, m)\) of pristine HiPco SWCNTs for the corresponding diameters were obtained. Similarly, the diameters and the value of \( C_1 \) and \( C_2 \) for the different laser energies were found. The values of \( C_1 \) and \( C_2 \) thus obtained were 207.5 cm\(^{-1}\) nm and 29.1 cm\(^{-1}\)
for 660 nm (1.88 eV), 233.0 cm\(^{-1}\) nm and 8.5 cm\(^{-1}\) for 532 nm (2.33 eV) and 213.7 cm\(^{-1}\) nm and 22.7 cm\(^{-1}\) for 473 nm (2.62 eV) laser frequency respectively for HiPco SWCNTs. Considering table 5.2, it should be noted that SWCNTs resonants at 2.33 eV are predominantly metallic, however semiconducting SWCNTs are resonant for the other three laser excitations. Although the value of \(C_1\) and \(C_2\) significantly varied for different laser energies, in figure 5.12 (i) it can be observed that except for 2.33 eV, the points from the three laser lines at 2.62 eV, 1.88 eV and 1.58 eV can be fitted well with a single linear correlation, for \(C_1 = 213.1\) cm\(^{-1}\) nm and \(C_2 = 23.7\) cm\(^{-1}\). However, the points from 2.33 eV deviate significantly from this fit. Fantain et al. have reported different values of \(C_1\) and \(C_2\) for semiconducting and metallic SWCNTs [19]. Therefore it can be stated that the different value for \(C_1\) and \(C_2\) were attributed from the electronic properties of the resonant SWCNTs. The diameters and corresponding assignments of HiPco SWCNTs within the pristine sample for the different laser energies are listed in table 5.2. It is noted that all diameters are in the range of ~ 1.3 nm to ~ 0.67 nm which correlates well with the nominal diameter range of HiPco samples [17].

Using the same method, possible diameters and corresponding structural assignment of pristine AD SWCNTs were obtained. Figure 5.12 (ii) shows the inverse of chosen diameters of AD SWCNTs plotted against the corresponding value of \(\omega_{RBM}\). The value of \(C_1\) and \(C_2\) for different lasers for AD SWCNTs were found to be 218.17 cm\(^{-1}\) nm and 16.89 cm\(^{-1}\) for 785 nm (1.58 eV), 215.96 cm\(^{-1}\) nm and 17.6 cm\(^{-1}\) for 660 nm (1.88 eV), 213.76 cm\(^{-1}\) nm and 18.19 cm\(^{-1}\) for 532 nm (2.33 eV) and 209.43 cm\(^{-1}\) nm and 21.99 cm\(^{-1}\) for 473 nm (2.62 eV) laser frequency respectively. Figure 5.12 (ii) shows the inverse of chosen diameters
of AD SWCNTs plotted against the corresponding value of $\omega_{RBM}$. The diameters and corresponding assignments of AD SWCNTs within the pristine sample for the different laser energies are listed in table 5.3.

![Figure 5.12](image)

Figure 5.12 A plot of $\omega_{RBM}$ versus inverse of diameters (1/d) of pristine (i) HiPco and (ii) AD SWCNTs.

Table 5.2 RBMs shift and the corresponding structure assignments for pristine HiPco SWCNTs at different laser energy excitations.

<table>
<thead>
<tr>
<th>$785$ nm 1.58 eV</th>
<th>$660$ nm 1.88 eV</th>
<th>$532$ nm 2.33 eV</th>
<th>$473$ nm 2.62 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{RBM}$ (cm$^{-1}$)</td>
<td>$d$ (nm)</td>
<td>$(n, m)$</td>
<td>$\omega_{RBM}$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>207.6</td>
<td>1.145</td>
<td>(12,4)</td>
<td>180.2</td>
</tr>
<tr>
<td>217.7</td>
<td>1.102</td>
<td>(9,7)</td>
<td>186.2</td>
</tr>
<tr>
<td>227.7</td>
<td>1.032</td>
<td>(8,7)</td>
<td>193.6</td>
</tr>
<tr>
<td>236.5</td>
<td>0.994</td>
<td>(12,1)</td>
<td>216.1</td>
</tr>
<tr>
<td>249.6</td>
<td>0.936</td>
<td>(10,3)</td>
<td>224.0</td>
</tr>
<tr>
<td>261.4</td>
<td>0.894</td>
<td>(7,6)</td>
<td>243.0</td>
</tr>
<tr>
<td>269.9</td>
<td>0.873</td>
<td>(11,0)</td>
<td>250.0</td>
</tr>
<tr>
<td>307.1</td>
<td>0.757</td>
<td>(6,5)</td>
<td>254.7</td>
</tr>
</tbody>
</table>

The table above shows the RBMs shift and the corresponding structure assignments for pristine HiPco SWCNTs at different laser energy excitations.
Table 5.3  RBMs shift and the corresponding structure assignments for pristine AD SWCNTs at different laser energy excitations.

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>d (nm)</th>
<th>(n, m)</th>
<th>ω_{RBMs} (cm\textsuperscript{-1})</th>
<th>d (nm)</th>
<th>(n, m)</th>
<th>ω_{RBMs} (cm\textsuperscript{-1})</th>
<th>d (nm)</th>
<th>(n, m)</th>
<th>ω_{RBMs} (cm\textsuperscript{-1})</th>
<th>d (nm)</th>
<th>(n, m)</th>
<th>ω_{RBMs} (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>785 nm</td>
<td>1.58 eV</td>
<td>147.01</td>
<td>1.672</td>
<td>(20,2)</td>
<td>151.62</td>
<td>1.621</td>
<td>(16,7)</td>
<td>157.95</td>
<td>1.549</td>
<td>(19,1)</td>
<td>163.74</td>
<td>1.487</td>
</tr>
<tr>
<td></td>
<td>660 nm</td>
<td>149.98</td>
<td>1.663</td>
<td>(18,5)</td>
<td>159.34</td>
<td>1.545</td>
<td>(15,7)</td>
<td>165.30</td>
<td>1.487</td>
<td>(15,6)</td>
<td>169.70</td>
<td>1.435</td>
</tr>
<tr>
<td></td>
<td>532 nm</td>
<td>146.25</td>
<td>1.697</td>
<td>(17,7)</td>
<td>157.21</td>
<td>1.563</td>
<td>(16,6)</td>
<td>166.60</td>
<td>1.470</td>
<td>(18,1)</td>
<td>172.25</td>
<td>1.411</td>
</tr>
<tr>
<td></td>
<td>473 nm</td>
<td>153.68</td>
<td>1.581</td>
<td>(12,11)</td>
<td>161.90</td>
<td>1.508</td>
<td>(16,5)</td>
<td>167.77</td>
<td>1.431</td>
<td>(15,5)</td>
<td>176.19</td>
<td>1.356</td>
</tr>
</tbody>
</table>

It should be noted that within the range of HiPco SWCNTs identified, there are only two armchair, (10, 10), (7, 7) and four zigzag SWCNTs (11, 0), (12, 0), (16, 0) and (17, 0), all others being chiral and within the range of AD SWCNTs, there is only one zigzag (16,0), and no armchair nanotubes, all others being chiral. A simple postulation that polyacene PAHs preferentially solubilise the armchair SWCNTs and polyphenyl PAHs the zigzag [26, 27] may therefore be somewhat optimistic.

5.3.2 PAHs

Figures 5.13 (i) and (ii) show the Raman spectra of polyacene and polyphenyl oligomers respectively. From these figures, it is seen that PAHs have several vibrational modes. Bands near 726-750 cm\textsuperscript{-1} are ring vibrational modes. The ring breathing modes are observed at near 900-1000 cm\textsuperscript{-1}. The band occurring at 1200 cm\textsuperscript{-1} is typical of para-substituted benzene derivatives. The vibrational modes at \sim 1300-1400 cm\textsuperscript{-1}, and 1500-1600 cm\textsuperscript{-1} are attributed to the carbon-carbon double bond (C=C) stretch and ring stretching mode.
respectively [1, 2]. It is reported that bands near 1200 cm$^{-1}$, 1300 cm$^{-1}$ and 1600 cm$^{-1}$, vary with increasing molecular length and intensities of these vibrational modes increase according to $n^4$, where $n$ is the number of rings [2].

![Raman spectra of polyacene and polyphenyl oligomers](image)

Figure 5.13  Raman spectra of polyacene (i) and polyphenyl (ii) oligomers at 785 nm (1.58 eV) laser. Spectra are offset for clarity.

### 5.4 Probing the Interaction between SWCNTs and PAHs

As described in the section 5.2, it was found that the affinity of chloroform for SWCNTs is not sufficient to solubilise SWCNTs [5, 6]. However, as has previously reported for PAH/toluene [26] and polymer/toluene [8] solutions, it was immediately evident that the SWCNTs are much better dispersed in PAHs/chloroform than chloroform alone. In the presence of PAHs, SWCNTS were readily suspended in chloroform and the suspensions are stable for more than 24 months. Therefore, to probe the interaction between SWCNTs and PAHs, two sets of solutions of PAHs were prepared. To one of the two sets, HiPco SWCNTs obtained from Carbon Nanotechnologies, Inc. (16200 Park Row, Houston, TX 77087) and AD SWCNTs (Sigma-Aldrich, Ireland) were added in a 1:1 ratio by weight (w/w); SWCNTs: PAHs.
At the highest concentration, both PAHs (Sigma-Aldrich, Ireland) and composite solutions were sonicated using a sonic tip (Ultrasonic processor VCX 750 W) for 3 x 10 s at 38% of the power output. Then these samples were serially diluted by a factor of 2 with chloroform down to the lowest concentration. Each diluted sample was further tip sonicated as above and was then allowed to settle for 72 hours, after which the supernatant liquid from the composite samples was carefully withdrawn. The suspensions were allowed to settle for a further 24 hours before being characterized by absorbance (Perkin Elmer Lambda 900 UV-Vis-NIR) and fluorescence spectroscopy (Perkin Elmer LS55). The same procedures and concentration ranges were employed to prepare composites of AD SWCNTs (Sigma-Aldrich, Ireland) with the corresponding PAHs. For the case of AD SWCNTs, four PAHs; naphthalene, tetracene, biphenyl and p-quaterphenyl were used.

5.4.1 Results from UV-Vis-NIR Spectroscopy

Figure 5.14 (i), (ii) and (iii) show the absorbance spectra of naphthalene, anthracene and tetracene respectively in the absence and presence of HiPco SWCNTs. The absorbance spectra of polyacene oligomers show the electronic and vibrational structure of the molecules. The electronic absorbance corresponds to an electronic transition involving the lowest excited electronic state, $S_1$. The individual peaks at ~ 258 nm, ~ 268 nm, ~ 277 nm and ~ 287 nm for naphthalene, ~ 311 nm, ~ 326 nm, ~ 342 nm, ~ 360 nm, and ~ 379 nm for anthracene and ~ 369 nm, ~ 417 nm, ~ 445 nm, and ~ 476 nm for tetracene correspond to the excitation of a series of vibrational states within this electronic transition. As the wavelength at which the conjugated system absorbs is
determined by the conjugation length and as tetracene has longer conjugation length than that of naphthalene and anthracene, tetracene has absorbance peaks at higher wavelength than those of naphthalene and anthracene. The absorbance of naphthalene between ~ 257 nm and ~ 287 nm and that of anthracene between ~ 326 nm and ~ 379 nm and tetracene between ~ 369 nm and ~ 476 nm indicate that a minimum energy of ~ 4.5 eV, ~ 3.6 eV and ~ 2.9 eV is required to excite an electron from the ground electronic state to the excited electronic state for naphthalene, anthracene and tetracene respectively. The vibrational levels of the ground electronic states will overlap with several of the vibrational levels in the excited electronic states and are identified in figure 5.14 as (0,0), (1,0), (2,0), (3,0) and (4,0). By convention, the first figure in the parenthesis represents the vibrational level of the excited electronic state and the second figure in the parenthesis represents the vibrational levels of the ground electronic state [1].

The spectral shape of the absorbance spectrum of PAHs is largely unaffected by the presence of the nanotubes and any changes in intensity may be due to the underlying nanotube absorption or scattering [7]. SWCNTs have a diameter dependent absorbance across the NIR-visible spectrum [28, 29]. But in these composites, no strong contributions are observed in these regions. The additional absorbance in the UV region may be a contribution from the strong π-plasmon resonance of the carbon nanotubes at ~ 300 nm [30].
Figure 5.14  Absorbance spectra of (i) naphthalene, (ii) anthracene and (iii) tetracene in the absence and presence of HiPco SWCNTs at concentration ~ 1.25 x 10^{-3} mol/L for naphthalene, ~ 1.56 x 10^{-4} mol/L anthracene and ~ 1.95 x 10^{-5} mol/L for tetracene.

Absorbance spectra of biphenyl, p-terphenyl, p-quaterphenyl and p-quinquephenyl in the absence and presence of HiPco SWCNTs are shown in figure 5.15 (i), (ii), (iii) and (iv) respectively. These spectral profiles are similar to those reported in literature [31, 32]. From figure 5.15 it is found that all PAHs of the polyphenyl group have broad absorbance peaks.
Figure 5.15  Absorbance spectra of (i) biphenyl at concentration ~ 6.25 x 10^{-4} mol/L, (ii) \textit{p}-terphenyl at concentration 1.95 x 10^{-5} mol/L (iii) \textit{p}-quaterphenyl at concentration ~ 9.76 x 10^{-6} mol/L and (iv) \textit{p}-quinquephenyl at concentration ~ 9.76 x 10^{-6} mol/L in the absence and presence of HiPco SWCNTs.

The absence of vibrational structure in the absorbance spectrum is due to the torque of the phenyl groups about the C-C single bond. Biphenyl has absorbance peak at ~ 250 nm (~ 4.9 eV), \textit{p}-terphenyl has an absorbance peak at ~ 277nm (~ 4.5 eV), \textit{p}-quaterphenyl has an absorbance peak at ~ 295 nm and \textit{p}-quinquephenyl has absorbance peak at ~ 311 nm. The structural dependence of the absorption spectra is consistent with the increased conjugation length of the oligomers within the series [33, 34].
Again, the spectral shape of the absorbance spectrum is largely unaffected by the presence of the nanotubes and any intensity changes may be due to the underlying nanotube absorption or scattering [7]. Since the absorbance spectra of both polyacene and polyphenyl oligomers in the presence of AD SWCNTs are similarly unaffected, they are not shown here (see appendix, figure A1 and A2).

Although from the absorbance study it is found that the absorbance of PAHs is higher in the presence of SWCNTs than in the absence, it is not strongly evident that this lower absorbance is due to the interaction between PAHs and SWCNTs. Therefore to study the interaction, fluorescence spectroscopy has been used.

5.4.2 Results from Fluorescence Spectroscopy.

The fluorescence spectra of naphthalene, anthracene and tetracene in the absence and presence of HiPco SWCNTs are depicted in figure 5.16 (i), (ii) and (iii) respectively. From figure 5.14 and figure 5.16 it is found that the fluorescence spectral profiles of polyacene PAHs are the mirror image of their absorbance spectra. It is often found that the fluorescence spectrum is a mirror image of the absorbance spectrum for a S₀ - S₁ transition but (Stokes) shifted to a longer wavelength, because of the similar vibrational energy levels of S₀ and S₁. [35] The vibrational levels are identified in figure 5.16 as (0,0), (0,1), (0,2), and (0,3). Due to the Stokes shift, the (0, 0) band is of slightly longer wavelength in the fluorescence spectrum than the absorbance spectrum. From the fluorescence spectra of figure 5.16 it is found that the intensity of the fluorescence in the presence SWCNTs is lower than that in the absence of HiPco SWCNTs. The reason behind this lower fluorescence intensity is the
interaction between PAHs of the polyacene series and HiPco SWCNTs [1]. Similar effects have been also reported for polymers and PAHs in the literature [1, 27, 36].

![Fluorescence spectra of naphthalene, anthracene, and tetracene](image)

Figure 5.16 Fluorescence spectra of (i) naphthalene at concentration ~ 3.125 x 10^{-4} mol/L, (ii) anthracene at concentration ~ 3.9062 x 10^{-5} mol/L, (iii) tetracene at concentration ~ 1.9531 x 10^{-5} mol/L in the absence and presence of HiPco SWCNTs.

The fluorescence spectra of biphenyl, p-terphenyl, p-quaterphenyl and p-quinquephenyl in the absence and presence of HiPco SWCNTs are shown in figure 5.17 (i), (ii), (iii) and (iv) respectively. Unlike the case of polyacene PAHs, the fluorescence spectra of polyphenyl PAHs are not the mirror image of their
absorbance spectra. This deviation from the mirror image usually indicates a different geometric arrangement of the nuclei in the excited state and the ground state. It has been found that due to the torsional degree of freedom of phenyl rings of polyphenyl PAHs, the excited states have a more planar structure and the deviation from the mirror image behaviour can be explained [37]. Similar to the fluorescence spectra of polyacene PAHs in the presence of HiPco SWCNTs (figure 5.16), it is found that the intensity of fluorescence in the presence of HiPco SWCNTs is lower than that in the absence. This is an indication of interaction between HiPco SWCNTs and polyphenyl PAHs and is consistent with other reports of fluorescence quenching of chromophores as a result of interaction with SWCNTs [1, 27, 36, 38].

As the fluorescence spectra of both polyacene and polyphenyl PAHs in the presence of AD SWCNTs are similar to those of corresponding PAHs in the presence of HiPco SWCNTs, they are not shown here (see appendix, figure A3 and A4).
Figure 5.17 Fluorescence spectra of (i) biphenyl at concentration $\approx 7.812 \times 10^{-5}$ mol/L, (ii) $p$-terphenyl at concentration $\approx 1.2207 \times 10^{-8}$ mol/L, (iii) $p$-quaterphenyl at concentration $\approx 5.9604 \times 10^{-10}$ mol/L and (iv) $p$-quinquephenyl at concentration $\approx 4.547 \times 10^{-15}$ mol/L in the absence and presence of HiPco SWCNTs.

5.4.3 AFM

As described in chapter 2, SWCNTs are grown in aggregated bundles or ropes. It is expected, however, that in the solubilisation process, these nanotubes are to some degree exfoliated or debundled [39]. To elucidate the aggregation state of SWCNTs in the composite solution, AFM was employed. For the AFM study, a HiPco/tetracene composite sample at concentration of $\approx 2.441 \times 10^{-6}$ mol/L was drop cast onto a quartz substrate. For the comparison, a
sample of pristine HiPco SWCNTs was also prepared. From figure 5.18 and 5.19 it can be found that at a concentration of 0.2 mg/ml, the pristine HiPco SWCNTs sample contains SWCNT bundles of diameter ~ 70 nm, whereas at a concentration of ~ 2.441 x 10^{-6} mol/L (~ 5.57 x 10^{-4} mg/ml), the deposit from the solution of composite (SWCNTs/tetracene) contains partially debundled HiPco SWCNTs of bundle diameter ~ 22 nm.

Figure 5.18   AFM image and corresponding diameter distribution of bundled pristine HiPco SWCNTs.
Figure 5.19  AFM image and corresponding diameter distribution of debundled HiPco SWCNTs in the HiPco/tetracene composite sample.
5.5 Conclusion

In this work, the solvent plays an important role. The solvent should be able to dissolve PAHs of different lengths but should exhibit poor affinity for SWCNTs, such that the dispersion should be primarily due to the interaction with the PAH molecules. It should of course be a good solvent for the PAHs, across a structural range sufficient to establish structure property relationships. From the experimental study it is found that although toluene is a poor solvent for SWCNTs, its fluorescence overlaps that of the short chain PAHs, which is undesirable as fluorescence will be employed as a probe of the interactions between SWCNTs/PAHs. Furthermore it is a poor solvent for the longer chain PAHs of the polyacene group (pentacene). In the case of chloroform, although it could not dissolve the longer chain PAHs of the polyacene group, its fluorescence does not interfere with that of the smaller chain PAHs. Furthermore it was found that SWCNTs are much better solubilised in PAHs/chloroform than chloroform alone. Therefore it was selected to be used as a solvent in this work.

In this chapter different spectroscopic and microscopic techniques were used to characterise SWCNTs and PAHs. The diameter distribution and corresponding assignment of pristine HiPco and AD SWCNTs were obtained by the aid of Raman spectroscopy. It has been found that the both pristine SWCNTs are rich in chiral SWCNTs. Using Raman spectroscopy information about the vibrational properties of different PAHs were also obtained. To study the interaction between SWCNTs and PAHs UV-Vis-NIR and fluorescence spectroscopy were used. AFM was used to image the status of SWCNTs in the composite sample. The absorbance study showed no clear indication of
interaction of PAHs with SWCNTs but from the fluorescence study, strong indications of the interaction were observed, similar to those reported for other SWCNT composites [6, 26, 27, 36]. Therefore fluorescence spectroscopy is potentially a powerful tool for the in-depth study of this interaction. The next chapter will describe the concentration dependent interaction between PAHs and SWCNTs using fluorescence spectroscopy in detail and will demonstrate how the structural dependence of the interaction can be elucidated and quantified.
References


ISBN 10: 0849368022


Chapter 6  A Study of the Interaction between Different Types of Single Walled Carbon Nanotubes and Polycyclic Aromatic Hydrocarbons

Adapted from


and

6.1 Introduction

It has been previously demonstrated that fluorescence spectroscopy is a powerful tool to study the interaction between conjugated molecules or polymers and SWCNTs [1-3]. In chapter 5, the fluorescence study provided a strong indication of such an interaction. It was observed that the intensity of fluorescence of PAHs in the presence of SWCNTs is significantly and consistently lower than that in the absence. This quenching of the fluorescence gives a strong indication that an interaction is occurring between the PAH molecule and SWCNTs. The fluorescence studies point strongly to a mapping of the PAHs molecules onto the surface of SWCNTs via $\pi-\pi$ stacking and the quenching of the fluorescence is most likely due to energy transfer to the SWCNTs via vibrational coupling [4]. This chapter explores the concentration dependent interaction between PAHs and SWCNTs with the aid of fluorescence spectroscopy. Also described is the use of a fluorescence based adsorption/desorption model [1] (chapter 1) to establish the concentration regions where SWCNTs are aggregated, debundled, maximally dispersed and where isolated SWCNTs can be found [1-3]. This in turn describes the concentration dependence and probes the structural dependence of the interaction. Using this fluorescence study, the binding energy between PAHs molecules and SWCNTs can also be calculated, elucidating the structural dependence of the solubilising interactions.
6.2 Sample Preparation

The experimental study in chapter 5 established the highest workable concentrations of PAHs for this research. Therefore two sets of PAHs solutions (the ranges are provided below) were prepared. To one of the two sets of PAHs solutions, HiPco SWCNTs obtained from Carbon Nanotechnologies, Inc. (16200 Park Row, Houston, TX 77087) were added in a 1:1 ratio by weight (w/w); HiPco SWCNTs/PAHs. The ratio 1:1 was chosen to ensure consistency with other studies reported in literature [1, 3].

\[ \sim 2.5 \times 10^{-3} \text{ mol/L to } \sim 1.22 \times 10^{-6} \text{ mol/L for naphthalene,} \]
\[ \sim 6.25 \times 10^{-4} \text{ mol/L to } \sim 1.90 \times 10^{-8} \text{ mol/L for anthracene,} \]
\[ \sim 3.12 \times 10^{-4} \text{ mol/L to } \sim 1.86 \times 10^{-11} \text{ mol/L for tetracene,} \]
\[ \sim 2.5 \times 10^{-3} \text{ mol/L to } \sim 1.19 \times 10^{-9} \text{ mol/L for biphenyl,} \]
\[ \sim 7.81 \times 10^{-5} \text{ mol/L to } \sim 1.16 \times 10^{-12} \text{ mol/L for } \pi\text{-terphenyl,} \]
\[ \sim 7.81 \times 10^{-5} \text{ mol/L to } \sim 3.63 \times 10^{-14} \text{ mol/L for } \pi\text{-quaterphenyl and} \]
\[ \sim 3.90 \times 10^{-5} \text{ mol/L to } \sim 2.22 \times 10^{-18} \text{ mol/L for } \pi\text{-quinquephenyl} \]

At the highest concentration, both PAHs (Sigma-Aldrich, Ireland) and composite solutions were sonicated using a sonic tip (Ultrasonic processor VCX 750 W) for 3 x 10 s at 38% of the power output. Then these samples were serially diluted by a factor of two with chloroform down to the lowest concentration (mentioned above). Each diluted sample was further tip sonicated as above and was then allowed to settle for 72 hours, after which the supernatant from the composite samples was carefully withdrawn. The
suspensions were allowed to settle for a further 24 hours before being characterised by fluorescence spectroscopy (Perkin Elmer LS55). The same procedures and concentration ranges described above were employed to prepare composites of AD SWCNTs with the corresponding PAHs. In this project as-received HiPco and AD SWCNTs were used. HiPco SWCNTs typically contain up to 10% metal catalyst (Fe) impurities, encapsulated in the tips [5, 6], and AD SWCNTs up to 30% amorphous carbon or turbostratic graphite and catalyst impurities [7, 8]. For the case of AD SWCNTs (Sigma-Aldrich, Ireland), four PAHs; naphthalene, tetracene, biphenyl and p-quaterphenyl were used.

It was noted that for both HiPco and AD SWCNTs composite suspensions above the dispersion limit (described below), a considerable amount of precipitation of SWCNTs was observed and so the solubilisation is only partial. At concentrations where the SWCNTs are well dispersed, no precipitate was observable. As composite solutions were prepared by using SWCNTs/PAHs in 1:1 ratio by weight (w/w), it can be stated that below the dispersion limit the concentration of PAHs and SWCNTs are the same. Concentrations quoted are those of the as prepared solutions in terms of PAH concentration, and correspond to the actual concentration below the dispersion limit.

For the AFM study, HiPco/tetracene samples above and below the dispersion limit was drop cast onto quartz substrates.
6.3 Results and Discussion

From the fluorescence study in chapter 5, it was found that although the spectral characteristics of the PAHs in the presence of HiPco SWCNTs and AD SWCNTs are not altered, a significant reduction in the fluorescence emission can be observed. Such a quenching has been identified as a measure of the interaction of the oligomers with the nanotubes [1, 2, 4]. The fluorescence of naphthalene, anthracene and tetracene in the absence and presence of HiPco SWCNTs as a function of concentration are shown in figure 6.1 (i), (ii) and (iii). From these figures it is found that, for naphthalene, at concentrations between \( \sim 1.22 \times 10^{-6} \text{ mol/L} \) and \( \sim 1.87 \times 10^{-3} \text{ mol/L} \), the intensity of fluorescence increases linearly with increasing concentration in accordance with the Beer-Lambert law (note the graph is plotted linear/logarithmically). After this range, the intensity of fluorescence deviates from linearity. Similar behaviour is observed for the case of anthracene, where from concentrations \( \sim 1.90 \times 10^{-6} \text{ mol/L} \) to \( \sim 1.56 \times 10^{-4} \text{ mol/L} \) and tetracene at concentrations between \( \sim 1.86 \times 10^{-11} \text{ mol/L} \) and \( \sim 7.81 \times 10^{-5} \text{ mol/L} \), the fluorescence intensity increases linearly with increasing concentration, after which it deviates from linearity (not shown in figure 6.1 (iii)). This deviation is equivalent to that observed in the absorption spectrum (as shown in figure 5.8 for the case of \( \text{p-quinquephenyl} \)) and may be attributed to the formation of aggregates of PAHs, which causes quenching of the fluorescence [3].

Upon addition of HiPco SWCNTs to the solutions of naphthalene, anthracene and tetracene, the fluorescence trends of the composite solutions are similar to those of the PAHs solutions. However, in all cases there is a significant reduction of fluorescence intensity as observed in chapter 5. Similar
profiles have also been obtained from the fluorescence study of naphthalene and tetracene in the absence and presence of AD SWCNTs (see appendix, figure A5). Note, as discussed in Chapter 4, although near infra red photoluminescence of semiconducting SWCNTs has been reported, it is beyond the spectral range of the instrument employed here.

Figure 6.1 Plots of maximum fluorescence intensity of (i) naphthalene, (ii) anthracene and (iii) tetracene as a function of concentration in the absence (triangle) and presence (diamond) of HiPco SWCNTs.

A similar reduction of intensity was reported for polymers and PAHs and was attributed to the interaction of the polymers or PAHs with individual HiPco SWCNTs or aggregated HiPco SWCNTs [2, 9].
Figures 6.2 (i), (ii), (iii) and (iv) show the concentration dependence of the fluorescence of biphenyl, \( p \)-terphenyl, \( p \)-quaterphenyl and \( p \)-quinquephenyl in the absence (triangle) and presence (diamond) of HiPco SWCNTs respectively. For biphenyl, from concentration ~ \( 2.38 \times 10^{-9} \) mol/L to ~ \( 1.25 \times 10^{-3} \) mol/L, for \( p \)-terphenyl from concentrations ~ \( 1.16 \times 10^{-12} \) to ~ \( 7.81 \times 10^{-5} \) mol/L, for \( p \)-quaterphenyl from concentration ~ \( 3.63 \times 10^{-14} \) to ~ \( 1.95 \times 10^{-5} \) mol/L and for \( p \)-quinquephenyl from concentration ~ \( 2.22 \times 10^{-18} \) to ~ \( 9.76 \times 10^{-6} \) mol/L, the intensity of the fluorescence increases linearly with increasing concentration, after which it deviates from linearity due to aggregation of the molecules.

From figure 6.1 and 6.2 it is found that the concentration for the aggregation of PAHs of polyphenyl series is lower than that of polyacene series. Theoretical calculations report that as the number of carbons in the PAHs increases the binding energy also increases and this is expressed via fluorescence spectroscopy by the formation of aggregates at lower concentrations [10-13].

Similar trends to those observed for the polyacene series are found upon the addition of HiPco SWCNTs to the solutions of biphenyl, \( p \)-terphenyl, \( p \)-quaterphenyl and \( p \)-quinquephenyl. For all the four PAHs of the polyphenyl series, lower fluorescence intensity of solutions in the presence of HiPco SWCNTs than that in the absence of SWCNTs is an indication of the interaction between the PAHs and the HiPco SWCNTs. A similar behaviour was observed in the fluorescence study of biphenyl and \( p \)-quaterphenyl in the absence and presence of AD SWCNTs (see appendix, figure A6).
To understand the interaction between SWCNTs and PAHs, a fluorescence model based on the adsorption/desorption equilibrium of SWCNTs and PAHs has been used [1]. In this model, the quenching of fluorescence represents the interaction between SWCNTs and organic polymers. This model can be used to estimate the binding energy between polymers and SWCNTs.
The ratio of the maximum fluorescence intensity of the composite sample, which contains bound and unbound molecules, to the maximum fluorescence of the molecular solutions, which solely comprises of unbound molecules, is plotted as a function of concentration. The model is presented for low concentration and when the system is in equilibrium the adsorption rate equals the desorption rate [1].

As pointed out by Coleman et al. [1], (described in chapter 1) in the case of SWCNTs/polymer composite solutions, there are two forms of polymer molecules: free molecules and those that are bound to the SWCNTs. In the SWCNTs/polymer solutions, assuming that the interaction with the nanotubes quenches the fluorescence, the observed fluorescence is due to the free polymer only. Measurement of the fluorescence of the polymer solution in the absence of SWCNTs represents the total amount of polymer present ($N_{Total}$). Hence $N_{Total} = N_{Bound} + N_{Free}$ where $N_{Free}$ is the amount of free polymers in composite solution. Thus the ratio of the fluorescence intensity for a SWCNTs/polymer solution to that of a polymer solution of equivalent concentration is a measure of the fraction of free polymer molecules in the composite solution at that concentration [2].

Adapting the fluorescence model [1] and applying equation 1.1, a plot of the fraction of free polyacene PAHs molecules as a function of concentration was obtained (figure 6.3 (i), (ii) and (iii)). All curves show the same general trend, consistent with the observations of Coleman et al. [1] and Hedderman et al. [3]. At the highest concentrations, the molecularly dispersed PAHs interact with HiPco SWCNT bundles. With decreasing concentration, the PAHs act to disperse the HiPco SWCNTs, decreasing the bundle size (as confirmed by AFM
increasing the surface area per SWCNT available to the molecules for adsorption, resulting in a concentration dependent decrease in free PAH molecules, as represented by the ratio of equation 1.1. This decrease reaches a minimum at the point when the HiPco SWCNTs are maximally dispersed. Similar concentration dependent debundling has been observed and verified using AFM in organic solvents and water/surfactant [14] dispersions [15] of HiPco SWCNTs and the concentration of maximum dispersion has been termed the dispersion limit [14, 15]. From this point, decreasing the concentration, the surface area per HiPco SWCNT is constant and the fluorescence quenching behavior can be fitted by equation 1.1 using \( C_0 \) (the characteristic concentration) as a fitting parameter where \( C_0 \) is the concentration at which the rate of adsorption of PAH molecules onto the SWCNT surfaces is equal to the desorption rate and \( N_{\text{Free}} \) is equal to \( N_{\text{Bound}} \).

In figure 6.3 (i), (ii), and (iii) for naphthalene, between \(~ 2.5 \times 10^{-3}\) mol/L and \(~ 1.17 \times 10^{-4}\) mol/L, for anthracene between \(~ 3.12 \times 10^{-4}\) mol/L and \(~ 3.90 \times 10^{-5}\) mol/L and tetracene between \(~ 4.88 \times 10^{-6}\) mol/L and \(~ 2.28 \times 10^{-7}\) mol/L, the increased quenching of the fluorescence with decreasing concentration represents the debundling process (table 6.1). The bundles are dispersed progressively until the nanotubes are fully dispersed at concentration ranges from \(~ 7.81 \times 10^{-5}\) to \(~ 6.10 \times 10^{-7}\) mol/L (naphthalene), \(~ 1.95 \times 10^{-5}\) to \(~ 3 \times 10^{-7}\) mol/L (anthracene) and \(~ 1.14 \times 10^{-7}\) to \(~ 5.96 \times 10^{-10}\) mol/L (tetracene) (table 6.1). These concentration ranges were fitted with equation 1.1 with \( C_0 \) as a fitting parameter. The solid line is the best fit and gives \( C_0 \) values of \(~ 6 \times 10^{-5}\) mol/L with error value of \(~ 1.5 \times 10^{-5}\) mol/L, \(~ 1.75 \times 10^{-5}\) mol/L with error
value of $\pm ~ 0.75 \times 10^{-5}$ mol/L and $\sim 4 \times 10^{-7}$ mol/L with error value of $\pm ~ 1.5 \times 10^{-7}$ mol/L for naphthalene, anthracene and tetracene respectively (table 6.1).

Table 6.1 Concentration ranges for increased quenching in HiPco SWCNTs dispersions and characteristic concentrations for different polyacene oligomers.

<table>
<thead>
<tr>
<th>PAHs</th>
<th>Range of increased quenching (mol/L)</th>
<th>Range of dispersed HiPco SWCNTs (mol/L)</th>
<th>$C_0$ for HiPco (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>$\sim 2.5 \times 10^{-3}$ to $\sim 1.17 \times 10^{-4}$</td>
<td>$\sim 7.81 \times 10^{-5}$ to $\sim 6.10 \times 10^{-7}$</td>
<td>$\sim 6 \times 10^{-5}$ ± $\sim 1.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Anthracene</td>
<td>$\sim 3.12 \times 10^{-4}$ to $\sim 3.90 \times 10^{-5}$</td>
<td>$\sim 1.95 \times 10^{-5}$ to $\sim 3 \times 10^{-7}$</td>
<td>$\sim 1.75 \times 10^{-5}$ ± $\sim 0.75 \times 10^{-5}$</td>
</tr>
<tr>
<td>Tetracene</td>
<td>$\sim 4.88 \times 10^{-6}$ to $\sim 2.28 \times 10^{-7}$</td>
<td>$\sim 1.14 \times 10^{-7}$ to $\sim 5.96 \times 10^{-10}$</td>
<td>$\sim 4 \times 10^{-7}$ ± $\sim 1.5 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
Figure 6.3  Plots of the fraction of free (i) naphthalene (ii) anthracene and (iii) tetracene as a function of concentration. The solid line is the best fit to equation 1.1 and gives $C_0$ (characteristics concentration) values of $\sim 6 \times 10^{-5}$ mol/L, $\sim 1.75 \times 10^{-5}$ mol/L and $\sim 4 \times 10^{-7}$ mol/L for naphthalene, anthracene and tetracene respectively.

Similarly for polyphenyl composites, for biphenyl, between $\sim 5 \times 10^{-3}$ mol/L and $\sim 1.6 \times 10^{-4}$ mol/L, for $p$-terphenyl, between $\sim 1.95 \times 10^{-5}$ mol/L and $\sim 3.8 \times 10^{-8}$ mol/L, for $p$-quaterphenyl, between $\sim 3.8 \times 10^{-6}$ mol/L and $\sim 6.0 \times 10^{-10}$ mol/L and for $p$-quinquephenyl between $\sim 3.0 \times 10^{-10}$ mol/L and $\sim 1.1 \times 10^{-15}$ mol/L, HiPco SWCNT debundling occurs (figure 6.4 (i), (ii), (iii) and
(iv) respectively) (table 6.2). From concentrations ~ 7.8 x 10^{-5} to ~ 2.4 x 10^{-9} mol/L (biphenyl), ~ 1.9 x 10^{-8} to ~ 4.65 x 10^{-12} mol/L (p-terphenyl), ~ 3.0 x 10^{-10} to ~ 7.3 x 10^{-14} mol/L (p-quaterphenyl) and ~ 5.7 x 10^{-16} to ~ 2.2 x 10^{-18} mol/L (p-quinquephenyl) isolated PAHs molecules and fully dispersed HiPco SWCNTs exist (table 6.2). These concentration ranges were fitted with equation 1.1 with $C_0$ as a fitting parameter. The solid line is the best fit and gives $C_0$ values of ~ 1.5 x 10^{-5} mol/L with error value of ± ~ 0.5 x 10^{-5} mol/L, ~ 2.5 x 10^{-9} mol/L with error value of ± ~1 x 10^{-9} mol/L, of ~ 7 x 10^{-11} mol/L with error value of ± ~ 4 x 10^{-11} mol/L and ~ 4 x 10^{-16} mol/L with error value of ± ~ 4 x 10^{-16} mol/L for biphenyl, p-terphenyl p-quaterphenyl and p-quinquephenyl respectively (table 6.2).

Table 6.2 Concentration ranges for increased quenching dispersed HiPco SWCNTs and characteristic concentration for different polyphenyl oligomers.

<table>
<thead>
<tr>
<th>PAHs</th>
<th>Range of increased quenching (mol/L)</th>
<th>Range of dispersed HiPco SWCNTs (mol/L)</th>
<th>$C_0$ for HiPco (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biphenyl</td>
<td>~ 5 x 10^{-3} to ~ 1.6 x 10^{-4}</td>
<td>~ 7.8 x 10^{-5} to ~ 2.4 x 10^{-9}</td>
<td>~ 1.5 x 10^{-5} ± ~ 0.5 x 10^{-5}</td>
</tr>
<tr>
<td>p-Terphenyl</td>
<td>~ 1.95 x 10^{-5} to ~ 3.8 x 10^{-8}</td>
<td>~ 1.90 x 10^{-8} to ~ 4.65 x 10^{-12}</td>
<td>~ 2.5 x 10^{-9} ± ~ 1 x 10^{-9}</td>
</tr>
<tr>
<td>p-Quaterphenyl</td>
<td>~ 3.8 x 10^{-8} to ~ 6.0 x 10^{-10}</td>
<td>~ 3.0 x 10^{-10} to ~ 7.3 x 10^{-14}</td>
<td>~ 7 x 10^{-11} ± ~ 4 x 10^{-11}</td>
</tr>
<tr>
<td>p-Quinquephenyl</td>
<td>~ 3.0 x 10^{-10} to ~ 1.1 x 10^{-15}</td>
<td>~ 5.7 x 10^{-16} to ~ 2.2 x 10^{-18}</td>
<td>~ 4 x 10^{-16} ± ~ 4 x 10^{-16}</td>
</tr>
</tbody>
</table>
Figure 6.4  Plots of the fraction of free (i) biphenyl, (ii) \(p\)-terphenyl, (iii) \(p\)-quaterphenyl and (iv) \(p\)-quinquephenyl as a function of concentration. The solid line is the best fit to equation 1.1 and gives \(C_0\) (characteristic concentration) values of \(~1.5 \times 10^{-5}\) mol/L, \(~2.5 \times 10^{-9}\) mol/L, \(~7 \times 10^{-11}\) mol/L and \(~4 \times 10^{-16}\) mol/L for biphenyl, \(p\)-terphenyl, \(p\)-quaterphenyl and \(p\)-quinquephenyl respectively.

Equivalent studies indicated that the interaction between PAHs and SWCNTs is nearly same for both HiPco and AD SWCNTs as seen in figure 6.5. The values of \(C_0\) are found to be consistently higher in the case of the AD tubes, but only marginally (table 6.3).
Figure 6.5 A plot of the fraction of free PAHs as a function of concentration for HiPco SWCNTs and AD SWCNTs composite. The solid and dotted lines are the best fit to equation 1.1 for HiPco and AD SWCNTs respectively.

It has been reported that the dispersion limit of SWCNTs can alternatively be determined by the calculation of the mass fraction of aggregates [15, 16], employing UV-Vis-NIR spectroscopy. The mass fraction of aggregates as a function of concentration can be estimated using equation 6.1

\[ \chi_{agg} = \frac{A_{before} - A_{after}}{A_{before}} \]  

[6.1] [15, 16]

where, \( A_{before} \) and \( A_{after} \) are the absorbance at a certain peak position before and after centrifugation respectively. In this work, \( A_{after} \) represents the absorbance of the supernatant of anthracene samples in the presence of HiPco SWCNTs which were allowed to settle for 7 days whereas \( A_{before} \) represents the
absorbance of sample which were vigorously shaken immediately prior to measurement. The absorbance of the samples was taken at 666 nm. In the aggregation fraction plot (figure 6.6), the concentration at which the aggregation ceases to dominate the dispersion is considered to be the dispersion limit [15]. From figure 6.6, the dispersion limit of the HiPco SWCNTs in the presence of anthracene is estimated to be ~ 2.5 ± 1.0 x 10^{-5} mol/L. From the fluorescence study it has been found that the dispersion limit of HiPco SWCNTs in the presence of anthracene is ~ 3.0 ± 0.5 x 10^{-5} mol/L (figure 6.3 (ii)). Thus, at least qualitatively, the UV-Vis-NIR study correlates well with the fluorescence quenching data.

![Figure 6.6](image)

Figure 6.6 A plot of the aggregation fraction of HiPco SWCNTs in the presence of anthracene as function of concentration.

Figure 6.7 and 6.8 show the AFM images of HiPco SWCNTs at concentrations of ~ 3.051 x 10^{-7} mol/L and ~ 9.536 x 10^{-9} mol/L of HiPco/tetracene samples respectively along with their diameters. These are the concentrations which are respectively above and below the concentrations of
maximum fluorescence quenching of HiPco/tetracene composite samples. Compared to figure 5.18, the features of figure 6.7 are significantly reduced, implying partial debundling.

Figure 6.7 (i) AFM image of HiPco SWCNTs of HiPco/tetracene sample at concentration $\sim 3.051 \times 10^{-7}$ mol/L, (ii). Diameters of HiPco SWCNTs in this sample.

Figure 6.8 (i) AFM image of HiPco SWCNTs of HiPco/tetracene sample at concentration $\sim 9.536 \times 10^{-9}$ mol/L. (ii) Diameters of HiPco SWCNTs in this sample.
From these two figures it is evident that above the dispersion limit, there are SWCNTs with small bundles of diameters in the range of ~ 3 to 5 nm (figure 6.7) and below dispersion limit, the samples contain dispersed and isolated SWCNTs of diameters in the range of ~ 0.8 to ~ 1.0 nm (figure 6.8). These AFM results indicate that the probability of obtaining isolated SWCNTs below this concentration is high for the corresponding composite, and that this concentration may be considered to be the dispersion limit of the composite dispersions [14, 15]. As shown in figure 6.9, this dispersion limit is well correlated with the characteristic concentration $C_0$.

![Figure 6.9 Characteristic concentrations as a function of dispersion limit.](image)

Figure 6.10 shows the relationship between the estimated dispersion limit of HiPco and AD SWCNTs, and the molecular weight of PAHs. The plot in figure 6.10 is an indication of the ease with which both SWCNTs are dispersed by the different PAHs and it is found that with increasing length of PAHs the concentration at which SWCNTs are dispersed is reduced for both HiPco and AD SWCNTs. This is an indication that the smaller molecules are more effective at dispersing the SWCNTs. In this regard it should be noted that the plot is a
semi log plot, and that the variation of this efficiency is much more dramatic than the quasi-linear trend indicated. Notably, the dispersion limit varies over many orders of magnitude within the size range employed. While this may reflect the inability of the longer oligomers to disperse the bundles, it may also reflect their great ability to maintain the larger bundles in suspension. The polyacene PAHs are more effective than their polyphenyl counterparts and this may be due to their greater degree of conjugation and therefore greater $\pi$-$\pi$ interaction. It may also be an indication that the more planar and rigid polyacenes are more effective at debundling than the polyphenyl oligomers, in which the phenyl units exhibit different torsion angles. The twisted geometries may be sterically hindered from intercalating between the nanotubes in a bundle, whereas the planar polyacenes can slot in more easily. Planarisation of the polyphenyls to increase the interaction requires additional energy, as illustrated in figure 3.10. From figure 6.10 it can be seen that, except for the tetracene composite, the dispersion limits of AD SWCNTs estimated for the three different PAHs are almost identical to those estimated for HiPco SWCNTs with the corresponding PAHs.
Figure 6.10  A plot of estimated dispersion limit of HiPco (squares) and AD (triangles) SWCNTs as a function of molecular weight of PAHs.

Chakarova et al. [12] modelled the interactions of PAHs with themselves and graphite using density functional theory and Zacharia et al. [13] experimentally determined the interaction using thermal desorption spectroscopy. The quasi crystalline arrangements of close packed SWCNTs are like graphite and they are held together by van der Waals interaction. As both graphite and SWCNTs possess similar properties, it is reasonable to expect similar degrees of interaction for SWCNTs with PAHs. Theoretical models predict, and thermal desorption spectroscopy confirms, that an increase in the carbon number of PAHs increases the binding energy between PAH molecules, with larger PAHs having similar interlayer distances and binding energies to graphite [12, 13]. The binding energies per PAH molecule on graphite are predicted to be larger than the binding energy of a corresponding PAH dimer. The cohesive energy is determined by thermal desorption measurements of
PAHs on the graphite surface, and reveals a binding energy of $52 \pm 5$ meV per carbon atom with a contribution of $27$ meV per hydrogen [13].

In this work, to find the binding energy per PAH molecule with SWCNTs (HiPco and AD) equation 1.2 is employed [1]. For the calculation of binding energy, the value of $\nu$ is taken as $10^{18}$ Hz [9], the value of $\rho_{\text{bun}}$ for HiPco SWCNTs and AD is taken as $1.6 \times 10^{-3}$ Kg/m$^3$ and $1.33 \times 10^{-3}$ Kg/m$^3$ respectively [9], the value of $A_{\text{bun}}$ is taken as $1.5 \times 10^{-15}$ m$^2$ for HiPco and for AD it is $2.2 \times 10^{-15}$ m$^2$ [9], the value of $\eta$ for chloroform is taken as $0.536 \times 10^{-3}$ s Pa [1] the value of $T$ is taken as $298$ °K, the value of $k$ is taken as $1.38 \times 10^{-23}$ J/K and the value of other parameters chosen are given in table 6.1, where the values of $a$ for different PAH are obtained by molecular modelling (ChemOffice 2004).

Table 6.3 Parameters for the calculation of binding energy per PAHs molecules with SWCNTs.

<table>
<thead>
<tr>
<th>PAHs</th>
<th>For HiPco composite $C_0$ (Kg/m$^3$)</th>
<th>For AD composite $C_0$ (Kg/m$^3$)</th>
<th>$a$ (m)</th>
<th>For HiPco composite $E_B$(eV)</th>
<th>For AD composite $E_B$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>$7.68 \times 10^{-3}$</td>
<td>$8.96 \times 10^{-3}$</td>
<td>$3.37 \times 10^{-10}$</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td>Anthracene</td>
<td>$3.11 \times 10^{-3}$</td>
<td>--------------</td>
<td>$4.57 \times 10^{-10}$</td>
<td>0.49</td>
<td>--------------</td>
</tr>
<tr>
<td>Tetracene</td>
<td>$9.13 \times 10^{-5}$</td>
<td>$1.36 \times 10^{-4}$</td>
<td>$5.74 \times 10^{-10}$</td>
<td>0.58</td>
<td>0.58</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>$2.31 \times 10^{-3}$</td>
<td>$2.92 \times 10^{-3}$</td>
<td>$4.58 \times 10^{-10}$</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>$p$-terphenyl</td>
<td>$5.75 \times 10^{-7}$</td>
<td>--------------</td>
<td>$6.66 \times 10^{-10}$</td>
<td>0.72</td>
<td>--------------</td>
</tr>
<tr>
<td>$p$-quaterphenyl</td>
<td>$2.14 \times 10^{-8}$</td>
<td>$2.69 \times 10^{-8}$</td>
<td>$8.74 \times 10^{-10}$</td>
<td>0.81</td>
<td>0.81</td>
</tr>
<tr>
<td>$p$-quinquephenyl</td>
<td>$4 \times 10^{-16}$</td>
<td>--------------</td>
<td>$10.82 \times 10^{-10}$</td>
<td>1.12</td>
<td>--------------</td>
</tr>
</tbody>
</table>
From table 6.3 it can be found that regardless of SWCNTs type, the binding energy per PAH molecule with SWCNTs is the same for corresponding PAH. It can be stated that as the binding energy per PAH molecule with SWCNTs (HiPco and AD) is constant but due to the differing dimensions of the different types of SWCNTs, the Co value differs slightly (HiPco and AD SWCNTs) for the corresponding composite.

Figure 6.11 shows the binding energy per PAH molecule with HiPco SWCNTs determined above as a function of molecular weight of the PAHs. As the binding energy per PAH molecule with AD SWCNTs is the same as that of between PAHs and HiPco SWCNTs, for clarity only the binding energy per PAH molecule with HiPco SWCNTs is shown in this plot. From this graph it is found that the binding energy per PAH molecule with SWCNTs increases approximately linearly with increasing molecular weight of the PAHs.

![Binding energies per PAH molecule with HiPco SWCNTs as a function of molecular weight of PAHs.](image)

Figure 6.11
The binding energy per molecule of naphthalene, anthracene, tetracene, biphenyl, \( p \)-terphenyl, \( p \)-quaterphenyl, and \( p \)-quinquephenyl are found to be \( \sim 0.46 \) eV, \( \sim 0.49 \) eV, \( \sim 0.58 \) eV, \( \sim 0.50 \) eV, \( \sim 0.72 \) eV, \( \sim 0.81 \) eV and \( \sim 1.12 \) eV with HiPco SWCNTs respectively. From this result it can be stated that oligomers of the polyphenyl series bind more tightly to the HiPco SWCNTs surface than those of the polyacene series. This is because they have more carbon and hydrogen atoms per ring.

Comparing the linear fit with the calculated value of binding energy per tetracene molecule with HiPco SWCNTs, it can be seen that the calculated binding energy per tetracene molecule with HiPco SWCNTs is much lower than the expected value. This might be because of the poor efficiency of tetracene at debundling SWCNTs (figure 6.5). It is further noted that the values calculated for per anthracene and \( p \)-terphenyl molecules are significantly lower in this work, using chloroform as solvent, than those calculated for toluene solutions of SWCNTs produced by the laser vaporization method [3]. The difference may point towards the potential importance of the solvent in mediating the interaction. Chloroform is a marginally better solvent for SWCNTs than toluene [17]. It is also likely that differing initial bundle sizes and densities of SWCNTs produced through different mechanisms can significantly affect the dispersion process although not the binding energy [9].

Figure 6.11 shows a linear fit to the data from which a value of \( 20 \pm 5 \) meV per carbon atom and \( 28 \pm 5 \) meV per hydrogen atom are calculated. The values are in approximate agreement with those calculated for the interaction of PAHs with graphite, although it is noted that the curvature of the SWCNTs should have the effect of reducing the binding interaction. It should be noted that a
constant value of the pre-exponential factor $\nu$ (equation 1.2) has been employed. It has however been shown that this factor is dependent on molecular weight for PAHs in an approximately exponential fashion [13]. From equation 1.2, it can be seen that

$$E_B \sim \ln \left( \frac{C_0}{\nu} \right)$$  \hspace{1cm} (6.2)

As $C_0$ is proportional to the dispersion limit (figure 6.9), figure 6.10 indicates that

$$C_0 \sim \exp (aM)$$  \hspace{1cm} (6.3)

where, $M$ is the molecular weight of the PAH. Also, [13]

$$\nu \sim \exp (bM)$$  \hspace{1cm} (6.4)

Here $\exp (a)$ and $\exp (b)$ are the proportionality constants. Therefore,

$$E_B \sim \ln (\exp (a-b) M) \sim (a-b) M$$  \hspace{1cm} (6.5)

and a straight line dependence is predicted to first order. Deviation from the linearity of binding energy per molecule versus molecular weight can arise because of the contribution of either $C_0$ or $\nu$ or both. Assuming the linear fit of figure 6.11 to be an accurate representation of the real behavior, a value for the pre-exponential frequency factor per $C_0$ for each corresponding PAHs can be obtained (figure 6.12). From this figure it can be seen that $\nu$ increases exponentially with increasing molecular weight or chain length as reported in the literature [13].
Figure 6.12 Pre-exponential frequency factor as a function of molecular weight of PAHs.

Figure 6.13 shows the relationship between the maximum quenching of PAHs with HiPco (squares) and AD (triangles) SWCNTs, and molecular weight of PAHs. This plot is an indication of the relative fraction of interacting PAHs with SWCNTs. From this plot it has been found that the fraction of interacting polyphenyl PAHs is higher that that of their polyacene counter parts. This might be because of the non rigid structure of polyphenyl PAHs is favorable over the rigid structure of polyacene PAHs. Again, from this plot (figure 6.13) it is observed that the fraction of interaction PAHs also depends on the size of PAHs. It is found that this fraction of bound PAHs is higher for shorter PAHs of the corresponding polyacene and polyphenyl series. It can be also stated from this plot that as the bundle surface area of AD SWCNTs is higher than that of HiPco SWCNTs, the fraction of interacting PAHs is higher for AD SWCNTs compared to HiPco SWCNTs.
It is worth noting that for the case of the interaction of tetracene with both types of nanotubes, the observed minimum of the fluorescence quenching curve is considerably less than that for the other PAHs and occurs at a concentration which is lower than the fitted critical concentration. This implies that less than 50% of the molecules are bound at the minimum and may indicate that tetracene is not very efficient at debundling SWCNTs in general, albeit slightly better for AD SWCNTs. The dispersion limit of AD SWCNTs in tetracene is higher than that for HiPco SWCNTs in tetracene.

The overall behaviour governing the interaction of PAHs with SWCNTs is one in which the binding energy increases linearly with the molecular weight, whereas the dispersion limit and critical concentration decrease exponentially.
with increasing molecular weight. This is consistent with the model of Coleman et al., outlined in chapter 1, (equation 1.1 and 1.2), whereby \( C_0 \) is proportional to \( \exp[-E_B/kT] \). The binding energy, as a result of \( \pi-\pi \) interactions, increases with the number of conjugated carbons. In the model of Coleman et al., based on an equilibrium between adsorption and desorption of the PAH molecules on the SWCNT surface, the binding energy principally governs the desorption processes, and so it is the mobility of the molecules which governs the interaction.

### 6.4 Conclusion

In this chapter, the interaction between SWCNTs (HiPco and AD) and PAHs has been studied by using a fluorescence model based on the adsorption/desorption equilibrium of SWCNTs and PAHs. The results are verified for the case of anthracene using a similar method based on UV-Vis-NIR absorption spectroscopy. The results indicate a significant structural dependence of the interaction between SWCNTs and PAHs. It is found that the dispersion limit of HiPco SWCNTs decreases with increasing molecular weight of PAHs. This points to structure-property relationships governing how effectively different PAHs disperse HiPco and AD SWCNTs. One can state that smaller PAHs debundle SWCNTs at higher concentration than the larger PAHs. It is also shown that the polyacene series are more effective at debundling the SWCNTs than their polyphenyl counterparts. It is also found that due to the higher number of carbon and hydrogen, PAHs of polyphenyl series bind more strongly to the surface of SWCNTs bundles than that of polyacene series. By using the model mentioned above, the binding energy per PAH molecule with
SWCNTs as a function of molecular weight of corresponding PAHs molecules are obtained. It is found that regardless of the type of SWCNTs (HiPco and AD) the binding energy per PAH molecule with SWCNTs is the same and it increases as the molecular weight of PAHs increases, thereby establishing a linear relationship between binding energy per PAH molecule with SWCNTs and molecular weight of corresponding PAHs. It can be stated that as the number of carbon and hydrogen of polyphenyl PAHs are greater than that of their polyacenes counter parts, the binding energy of polyphenyl PAHs with SWCNTs is greater than that of between polyacene PAHs and SWCNTs. This further supports the observation regarding the debundling process; the rigid polyacene oligomers bind less readily to the surfaces of bundles and intercalate more easily into the bundles, whereas the polyphenyl oligomers bind more strongly to the surface of the bundles and due to their torsion do not intercalate as easily into the bundles to disperse them. However, once dispersed, the polyphenyl oligomers bind more strongly to the dispersed SWCNTs than their polyacene counterparts. These results give a strong indication that structure-property relationships for the interaction of PAHs with SWCNTs do exist and are relatively easily accessible experimentally. From the AFM study it is evident that below the dispersion limit of corresponding composite, there is a strong indication that isolated SWCNTs may be obtained. Chapter 7 describes the Raman spectroscopy study of the effect of these PAHs on HiPco and AD SWCNTs.
Addendum

Since the original publication of the fluorescence analysis [18, 19], it was noted in the equation that was used to calculate the binding energy (equation 1.2 [1], chapter 1), the term $\pi^2$ should in fact be $\pi$. This was communicated to the authors. This change in the equation, slightly affects the value of binding energy calculated from $C_0$. Figure 6.11 is re-plotted below to show the recalculated ($\pi$) binding energy along with the published ($\pi^2$) one. The overall trend is not affected and so the discussion above is unaltered.

Figure 6.11 (a) Recalculated ($\pi$) binding energy along with the published ($\pi^2$) one.
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5. Carbon Nanotechnology I, 16200 Park Row, Houston, TX 77084-5195, United States.

7. (online) Available at: http://www.sigmaaldrich.com
[Accessed 3 February 2010].


Chapter 7  
A Raman Spectroscopic Study of the Solubilisation of SWCNTs by Polycyclic Aromatic Hydrocarbons

Adapted from


and

7.1 Introduction

As described in chapter 2 and chapter 6, it has been found that there is an interaction between SWCNTs and organic polymers and PAHs [1-3]. This interaction can cause the SWCNTs to disperse from their bundled form ([1-3] and chapter 6) and there are strong suggestions that the organic species interact preferentially with SWCNTs of certain diameters or diameter range and even electronic structure [1, 2, 4]. The previous chapter described the interaction between SWCNTs and PAHs with the aid of a fluorescence quenching based model. This chapter explores the effectiveness of PAHs for structurally selective solubilisation of HiPco and AD SWCNTs using Raman spectroscopy.

Raman spectroscopy is a powerful method for the study of the diameter distribution of SWCNTs. As described in chapter 5, the RBM positioning enables the determination of the diameter and thus the chiral indices \((n, m)\) of the SWCNTs [5, 6]. The resonant nature of the Raman scattering implies that SWCNTs of certain diameters are enhanced, however, and only by employing a variety of source wavelengths can a comprehensive picture of the diameter range of the SWCNT sample be generated.

To study the effectiveness of PAHs for structurally selective solubilisation of HiPco and AD SWCNTs, polyphenyl and polyacene PAHs at the extremes of the selected length ranges were used. Selective interaction between the PAHs and SWCNTs of HiPco and AD were investigated by analyzing the Raman radial breathing modes, the frequency positioning of which yields information concerning the diameter distribution of the SWCNTs (HiPco and AD) samples. A combination of four laser excitation energies was utilized to establish the
distribution of diameters present. Obtaining a map of each composite sample gives an indication of the degree of selective solubilisation by the PAHs in each composite.

### 7.2 Sample Preparation

For this study, from the polyacene series, naphthalene and tetracene, and from the polyphenyl series, biphenyl and \( p \)-quaterphenyl were chosen. Samples were prepared in the same way as described in chapter 6 (section 6.2).

From the fluorescence studies (chapter 6), the regions where SWCNTs were dispersed to a maximum in the presence of PAHs of different lengths were obtained. At these concentrations the SWCNTs bundles are fully dispersed. The concentration range for the Raman analysis was chosen such that it spanned the region of dispersion observed in these fluorescence based studies. The sample below the dispersion limit (table 7.1) for each PAH composite was chosen for the Raman characterization and, as it was not possible to measure the dispersions directly, due to the strong contribution from the solvent, was drop cast onto clean quartz substrates. Concentration of the samples are given in table 7.2.
Table 7.1  Concentration range of each PAH composite.

<table>
<thead>
<tr>
<th>PAHs</th>
<th>Concentration range (mol/L)</th>
<th>Dispersion limit (mol/L)</th>
<th>$C_0$ (Kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HiPco</td>
<td>AD</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>~ 2.50 x 10⁻³ to ~ 1.22 x 10⁻⁶</td>
<td>~ 3.12 x 10⁻⁴</td>
<td>~ 2.33 x 10⁻⁴</td>
</tr>
<tr>
<td>Tetracene</td>
<td>~ 3.12 x 10⁻⁴ to ~ 1.86 x 10⁻¹¹</td>
<td>~ 1.52 x 10⁷</td>
<td>~ 1.22 x 10⁶</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>~ 2.5 x 10⁻⁷ to ~ 1.19 x 10⁻⁹</td>
<td>~ 1.56 x 10⁻⁴</td>
<td>~ 1.56 x 10⁻⁴</td>
</tr>
<tr>
<td>p-Quaterphenyl</td>
<td>~ 7.81 x 10⁻⁵ to ~ 3.63 x 10⁻¹⁴</td>
<td>~ 5.96 x 10⁻¹⁰</td>
<td>~ 5.96 x 10⁻¹⁰</td>
</tr>
</tbody>
</table>

Table 7.2  Concentration of each PAH composite for Raman characterization.

<table>
<thead>
<tr>
<th>PAH</th>
<th>Sample concentration (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HiPco</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>~ 3.12 x 10⁻⁴ and ~ 1.46 x 10⁻⁵</td>
</tr>
<tr>
<td>Tetracene</td>
<td>~ 4.76 x 10⁻⁹</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>~ 3.05 x 10⁻⁷</td>
</tr>
<tr>
<td>p-Quaterphenyl</td>
<td>~ 3.72 x 10⁻¹¹</td>
</tr>
</tbody>
</table>

The Raman instrument used in this study was a LabRAM HR 800 Raman Microscope (Horiba Jobin Yvon). Four laser lines, 785 nm (~ 1.58 eV) 240 mW, 660 nm (~ 1.88 eV) at 80 mW, 532 nm (~ 2.33 eV) at 40 mW and 473 nm
(~ 2.62 eV) at 40 mW were employed as sources. To study the effect of PAH length on solubility and selectivity of SWCNTs, the four laser lines were used to extensively probe the range of diameters present in the composite samples. Spectra were acquired by mapping the 25 μm × 25 μm field of view of the × 50 long focal length objective with a step size of 5 μm. In this way on average fifty spectra for each sample were obtained by scanning two different areas within the samples. Raman spectra were corrected for the quartz substrate background. The RBM features obtained were fitted with a combination Lorentzian/Gaussian line shape using the instrument LabSpec software version 4.02.

7.3 Results and Discussion

Figure 7.1 shows examples of single point Raman spectra of HiPco/naphthalene composite samples at two different concentrations respectively, using 532 nm as a source. The insets of these figures show the RBM region of the corresponding sample and are corrected for the quartz substrate background. The RBMs region was then fitted using the LabSpec 4.02 instrument software. As observed in fluorescence studies (chapter 6), a comparison of figure 7.1 (i) and (ii) demonstrates that the HiPco/naphthalene composite samples, at ~ 1.17 x 10^{-4} mol/L SWCNTs are largely debundled and at lower concentrations, ~ 1.46 x 10^{-5} mol/L one can expect predominantly fully dispersed SWCNTs, the RBM region showing few or one species respectively.

Maps of the HiPco/naphthalene and AD/naphthalene sample at concentrations of ~ 1.46 x 10^{-5} mol/L and ~ 2.92 x 10^{-5} mol/L respectively were performed and although in all cases the RBM spectrum was predominantly singly featured, the spectral positioning varied significantly from point to point. A
histogram of occurrence of single RBM features at specific frequencies was constructed for each source wavelength.

Figure 7.1 (i) and (ii) show the histograms of such occurrences for the HiPco/naphthalene and AD/naphthalene composite samples at concentrations 1.46 x 10^{-5} \text{ mol/L} and \sim 2.92 x 10^{-5} \text{ mol/L} respectively. These are the concentrations which are below the dispersion limits of the corresponding composite samples. As the RBM frequency is inversely proportional to the diameter of SWCNTs [5], in these plots, the histograms represent the number of occurrences of SWCNTs of different diameters at the four different laser excitation energies.

The SWCNTs found in the composite sample must also be present in the pristine sample. The SWCNTs in the composite samples were assigned by comparing the \omega_{RBM} positions with that of the pristine SWCNTs and then the
corresponding assignments of the pristine SWCNTs (chapter 5, table 5.2 and 5.3) were assigned to the SWCNTs in the composite samples.

Figure 7.2  Plots of RBMs shift as a function of percentage of counts of SWCNTs in (i) HiPco/naphthalene and (ii) AD/naphthalene composite samples at concentration ~ 1.46 x 10^-5 mol/L and ~ 2.92 x 10^-5 mol/L respectively at the different laser energies. For the comparison RBM of pristine SWCNTs is also shown in this plot.

From table 5.2 (chapter 5) and table 7.3, it can be seen that the $\omega_{RBM}$ positioning of the SWCNTs within the HiPco/naphthalene composite samples are up shifted by a few wave numbers compared to those of pristine HiPco SWCNTs. This shift may be because of a change in bundle size of SWCNTs and/or a change in the local environment due to the presence of the PAH molecules [7-10]. With respect to pristine AD SWCNTs (table 5.3, chapter 5), this shifting was also observed in AD/naphthalene composite (table 7.4). However, irrespective of the shift of $\omega_{RBM}$ for the HiPco/naphthalene and AD/naphthalene composites, the structural assignments made are consistent with those of the both pristine SWCNTs samples, underlining the validity of the fitting procedure (chapter 5).
Table 7.3  RBM frequencies and the corresponding structure assignments for SWCNTs in HiPco/naphthalene composite sample at different laser energies.

<table>
<thead>
<tr>
<th>785 nm 1.58 eV</th>
<th>660 nm 1.88 eV</th>
<th>532 nm 2.33 eV</th>
<th>473 nm 2.62 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{RBMs}$ (cm$^{-1}$)</td>
<td>(n, m)</td>
<td>$\omega_{RBMs}$ (cm$^{-1}$)</td>
<td>(n, m)</td>
</tr>
<tr>
<td>217.3</td>
<td>(9, 7)</td>
<td>265</td>
<td>(10, 2)</td>
</tr>
<tr>
<td>229.2</td>
<td>(8, 7)</td>
<td>283</td>
<td>(7, 5)</td>
</tr>
<tr>
<td>237.3</td>
<td>(12, 1)</td>
<td>298.8</td>
<td>(8, 3)</td>
</tr>
<tr>
<td>270.4</td>
<td>(11, 0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>297.5</td>
<td>(6, 5)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.4  RBM frequencies and the corresponding structure assignments for SWCNTs in AD/naphthalene composite sample at different laser energies.

<table>
<thead>
<tr>
<th>785 nm 1.58 eV</th>
<th>660 nm 1.88 eV</th>
<th>532 nm 2.33 eV</th>
<th>473 nm 2.62 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{RBMs}$ (cm$^{-1}$)</td>
<td>(n, m)</td>
<td>$\omega_{RBMs}$ (cm$^{-1}$)</td>
<td>(n, m)</td>
</tr>
<tr>
<td>157.95</td>
<td>(19, 1)</td>
<td>169.70</td>
<td>(17, 2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>173.54</td>
<td>(13, 7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>179.21</td>
<td>(14, 5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>188.01</td>
<td>(12, 6)</td>
</tr>
</tbody>
</table>

In this chapter, for the simplicity of discussion, proposed diameter distributions of pristine HiPco and AD SWCNTs obtained by resonance Raman (chapter 5) were classified into six groups (table 7.5).

Because of the sample density, the raw tubes contain the broad distribution of nanotubes present within a single point measurement, whereas in the samples prepared from dispersions, the nanotubes are widely dispersed on
the substrate. In all cases, although the sampling of 50 points does not reproduce the richness of distribution observed for the raw SWCNT samples, the diameter distribution is broad and the absence of a specific tube does not necessarily infer selectivity.

From figure 7.2 (i) and table 7.3, it is found that in comparison to the pristine HiPco SWCNTs (table 5.2), the HiPco/naphthalene composite is rich in SWCNTs of type 5 and type 4 (table 7.5) but depleted in other tube types indicating a degree of structurally selectivity. Notably, however, the (10, 10) armchair SWCNT is missing from the list of table 7.3, although there is a strong contribution from the (7, 7) armchair SWCNT. The zigzag tubes (11, 0) and (12, 0) also feature, although not prominently. On the other hand, the AD/naphthalene composite is rich in SWCNTs of type 2, but there is no obvious structural selectivity of SWCNTs.

Table 7.5  Classification of overall diameter distribution of pristine HiPco and AD SWCNTs.

<table>
<thead>
<tr>
<th>Groups</th>
<th>$\omega_{RBM}$ (cm$^{-1}$)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1</td>
<td>~140-170</td>
<td>~1.786 - 1.421</td>
</tr>
<tr>
<td>Type 2</td>
<td>~170-200</td>
<td>~1.421 - 1.194</td>
</tr>
<tr>
<td>Type 3</td>
<td>~200-230</td>
<td>~1.194 - 1.035</td>
</tr>
<tr>
<td>Type 4</td>
<td>~230-260</td>
<td>~1.035 - 0.906</td>
</tr>
<tr>
<td>Type 5</td>
<td>~260-290</td>
<td>~0.906 - 0.806</td>
</tr>
<tr>
<td>Type 6</td>
<td>&gt; ~290</td>
<td>&lt; ~0.806</td>
</tr>
</tbody>
</table>

Similar to figure 7.2, the histogram representing the number of occurrences of SWCNTs of different diameters for the HiPco/biphenyl and
AD/biphenyl composite samples at concentration ~ $3.05 \times 10^{-7}$ mol/L and ~ $1.95 \times 10^{-5}$ mol/L respectively at different laser energies are shown in figure 7.3 (i) and (ii) respectively.

Figure 7.3 Plots of RBMs shift as a function of percentage of counts of SWCNTs in (i) HiPco/biphenyl and (ii) AD/biphenyl composite sample at concentration ~ $3.05 \times 10^{-7}$ mol/L and ~ $1.95 \times 10^{-5}$ mol/L at different laser energies respectively. For the comparison RBM of pristine SWCNTs is also shown in this plot.

Shifts in $\omega_{RBM}$ position of SWCNTs of HiPco/biphenyl and AD/biphenyl composite samples are again observed. However, structural assignments of table 7.6 and table 7.7 again correlate with table 5.2 and table 5.3 respectively. Comparing the profile of the HiPco/naphthalene composite (figure 7.2 (i) and table 7.3) and HiPco/biphenyl composite (figure 7.3 (i) and table 7.6), it can be seen that the biphenyl composite sample is relatively rich in HiPco SWCNTs of larger diameters (type 5 and 3). Similarly, comparing the profile of the AD/naphthalene composite (figure 7.2(ii) and table 7.4) and AD/biphenyl (figure 7.3 (ii) and table 7.7), it is found that AD/biphenyl composite sample is richer in AD SWCNTs of type 1 and type 2.
Table 7.6  RBM frequencies and the corresponding structure assignments for SWCNTs in HiPco/biphenyl composite sample at different laser energies.

<table>
<thead>
<tr>
<th></th>
<th>785 nm</th>
<th>660 nm</th>
<th>532 nm</th>
<th>473 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.58 eV</td>
<td>1.88 eV</td>
<td>2.33 eV</td>
<td>2.62 eV</td>
</tr>
<tr>
<td>(\omega_{\text{RBM}}) (cm(^{-1}))</td>
<td>((n, m))</td>
<td>(\omega_{\text{RBM}}) (cm(^{-1}))</td>
<td>(n, m)</td>
<td>(\omega_{\text{RBM}}) (cm(^{-1}))</td>
</tr>
<tr>
<td>228.4</td>
<td>(8,7)</td>
<td>284.2</td>
<td>(7,5)</td>
<td>274</td>
</tr>
<tr>
<td>236.5</td>
<td>(12,1)</td>
<td>298.4</td>
<td>(8,3)</td>
<td>207.7</td>
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<td>268.2</td>
<td>(11,0)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>315</td>
</tr>
</tbody>
</table>

Table 7.7  RBM frequencies and the corresponding structure assignments for SWCNTs in AD/biphenyl composite sample at different laser energies.

<table>
<thead>
<tr>
<th></th>
<th>785 nm</th>
<th>660 nm</th>
<th>532 nm</th>
<th>473 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.58 eV</td>
<td>1.88 eV</td>
<td>2.33 eV</td>
<td>2.62 eV</td>
</tr>
<tr>
<td>(\omega_{\text{RBM}}) (cm(^{-1}))</td>
<td>((n, m))</td>
<td>(\omega_{\text{RBM}}) (cm(^{-1}))</td>
<td>(n, m)</td>
<td>(\omega_{\text{RBM}}) (cm(^{-1}))</td>
</tr>
<tr>
<td>157.95</td>
<td>(19,1)</td>
<td>173.54</td>
<td>(13,7)</td>
<td>166.60</td>
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<td>172.25</td>
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</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>182.48</td>
</tr>
</tbody>
</table>

The increased efficiency of the biphenyl compared to naphthalene, in binding the larger diameter SWCNTs, can be explained in terms of the increased binding energy per molecule as determined from fluorescence quenching measurements (chapter 6).
Figure 7.4 Plots of RBMs shift as a function of percentage of counts of SWCNTs in (i) HiPco/tetracene and (ii) AD/tetracene composite samples at concentration ~ 4.76 x 10^{-9} mol/L and ~ 2.44 x 10^{-6} mol/L at different laser energies respectively. For the comparison RBM of pristine SWCNTs is also shown in this plot.

Similar to the naphthalene and biphenyl composites, the histograms representing the number of occurrences of different diameter SWCNTs of HiPco/tetracene and AD/tetracene composite samples at concentration ~ 4.76 x 10^{-9} mol/L and ~ 2.44 x 10^{-6} mol/L at four different laser excitation energies are shown in figure 7.4 (i) and (ii) respectively. Table 7.8 and table 7.9 show the RBM frequencies and corresponding structure assignments for SWCNTs of the HiPco/tetracene and AD/tetracene composite samples at different laser excitation energies respectively.
Table 7.8  RBM frequencies and the corresponding structure assignments for SWCNTs in HiPco/tetracene composite sample at different laser energies.

<table>
<thead>
<tr>
<th>785 nm</th>
<th>660 nm</th>
<th>532 nm</th>
<th>473 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.58 eV</td>
<td>1.88 eV</td>
<td>2.33 eV</td>
<td>2.62 eV</td>
</tr>
<tr>
<td>$\omega_{RBM}$ (cm$^{-1}$)</td>
<td>$(n, m)$</td>
<td>$\omega_{RBM}$ (cm$^{-1}$)</td>
<td>$(n, m)$</td>
</tr>
<tr>
<td>220.7</td>
<td>(9,7)</td>
<td>263</td>
<td>(10,2)</td>
</tr>
<tr>
<td>230.0</td>
<td>(8,7)</td>
<td>284</td>
<td>(7,5)</td>
</tr>
<tr>
<td>237.5</td>
<td>(12,1)</td>
<td>298.8</td>
<td>(8,3)</td>
</tr>
</tbody>
</table>

Table 7.9  RBM frequencies and the corresponding structure assignments for SWCNTs in AD/tetracene composite sample at different laser energies.

<table>
<thead>
<tr>
<th>785 nm</th>
<th>660 nm</th>
<th>532 nm</th>
<th>473 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.58 eV</td>
<td>1.88 eV</td>
<td>2.33 eV</td>
<td>2.62 eV</td>
</tr>
<tr>
<td>$\omega_{RBM}$ (cm$^{-1}$)</td>
<td>$(n, m)$</td>
<td>$\omega_{RBM}$ (cm$^{-1}$)</td>
<td>$(n, m)$</td>
</tr>
<tr>
<td>156.62</td>
<td>(16,7)</td>
<td>169.70</td>
<td>(17,2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>173.54</td>
<td>(13,7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>179.21</td>
<td>(14,5)</td>
</tr>
</tbody>
</table>

As with the naphthalene and biphenyl composite samples, shifts with respect to the pristine HiPco and AD SWCNTs are also observed for SWCNTs in the HiPco/tetracene and AD/tetracene composites. Assignments once again are consistent with those observed in the pristine samples.

From table 7.3 and table 7.8 it is found that the diameter range of SWCNTs selected by naphthalene (type 5 and 4) for HiPco/naphthalene is also selected by tetracene (type 6, 5 and 4) for HiPco/tetracene. But each PAH has
a preference for specific diameters within the range (figure 7.2 (i) and figure 7.4(i)). Comparing the profile of solubilised SWCNTs of HiPco/tetracene (figure 7.4 (i) and table 7.8) to those of the HiPco/naphthalene (figure 7.4 (i) and table 7.3), it can be found that tetracene selects a greater amount of the larger diameters SWCNTs compared to naphthalene. This effect is also observed from the diameter distribution of AD/naphthalene (figure 7.2 (ii)) and AD/tetracene (figure 7.4 (ii)). This may be explained by the fact that tetracene has a higher binding energy than naphthalene.

Although the binding energy between SWCNTs (HiPco and AD) and tetracene is higher than that between SWCNTs (HiPco and AD) and biphenyl, from figure 7.3 and 7.4 it is found that for both SWCNTs, tetracene selects a lesser amount of the larger diameters SWCNTs compared to biphenyl. It is noteworthy in this respect that tetracene was seen in chapter 6 to be relatively inefficient at debundling the nanotubes in the first instance.

The histograms representing the number of occurrences of different diameter SWCNTs in HiPco/p-quaterphenyl and AD/p-quaterphenyl composite samples at concentration ~ 3.72 x 10^{-11} mol/L, at four different laser excitation energies are shown in figure 7.5 (i) and (ii) respectively. From table 7.10 and 7.11, the RBM frequencies and corresponding structural assignments for SWCNTs of HiPco/p-quaterphenyl and AD/p-quaterphenyl at different laser energies can be found respectively. Again, shifts in \( \omega_{RBM} \) values compared to those of both pristine SWCNTs, were observed.
Figure 7.5  Plots of RBMs shift as a function of percentage of counts of SWCNTs in (i) HiPco/p-quaterphenyl and (ii) AD/p-quaterphenyl composites at concentration ~ $3.72 \times 10^{-11}$ mol/L at different laser excitation energies. For the comparison RBM of pristine SWCNTs is also shown in this plot.

Table 7.10  RBM frequencies and the corresponding structure assignments for SWCNTs in HiPco/p-quaterphenyl composite sample at different laser excitation energies.

<table>
<thead>
<tr>
<th></th>
<th>785 nm 1.58 eV</th>
<th>660 nm 1.88 eV</th>
<th>532 nm 2.33 eV</th>
<th>473 nm 2.62 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{RBM}$ (cm$^{-1}$)</td>
<td>(n, m)</td>
<td>$\omega_{RBM}$ (cm$^{-1}$)</td>
<td>(n, m)</td>
<td>$\omega_{RBM}$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>229.1</td>
<td>(8,7)</td>
<td>283</td>
<td>(7,5)</td>
<td>280</td>
</tr>
<tr>
<td>236.7</td>
<td>(12,1)</td>
<td>299.6</td>
<td>(8,3)</td>
<td></td>
</tr>
<tr>
<td>268.8</td>
<td>(11,0)</td>
<td></td>
<td></td>
<td>315.5</td>
</tr>
</tbody>
</table>
Table 7.11 RBM frequencies and the corresponding structure assignments for SWCNTs in AD/p-quaterphenyl composite sample at different laser excitation energies.

<table>
<thead>
<tr>
<th>785 nm 1.58 eV</th>
<th>660 nm 1.88 eV</th>
<th>532 nm 2.33 eV</th>
<th>473 nm 2.62 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{\text{RBM}}$ (cm$^{-1}$)</td>
<td>$(n, m)$</td>
<td>$\omega_{\text{RBM}}$ (cm$^{-1}$)</td>
<td>$(n, m)$</td>
</tr>
<tr>
<td>151.62</td>
<td>(16,7)</td>
<td>173.54</td>
<td>(13,7)</td>
</tr>
<tr>
<td>157.95</td>
<td>(19,1)</td>
<td>179.21</td>
<td>(14,5)</td>
</tr>
<tr>
<td>172.25</td>
<td>(16,5)</td>
<td>176.35</td>
<td>(12,8)</td>
</tr>
</tbody>
</table>

For the case of HiPco/p-quaterphenyl composites, it is found that this composite is rich in SWCNTs of type 5 (table 7.5). As the binding energy between both SWCNTs and p-quaterphenyl is higher than that between SWCNTs (HiPco and AD) and the other three PAHs (chapter 6), it is reasonable to expect that p-quaterphenyl would show better selectivity for SWCNTs of larger diameters than those selected by biphenyl and tetracene. But for HiPco/p-quaterphenyl, this is not observed to be the case. Solubilisation in HiPco/p-quaterphenyl composites seems to favour HiPco SWCNTs of smaller diameters than those selected by biphenyl and tetracene. On the other hand, for AD/p-quaterphenyl it is found that this composite sample is rich in SWCNTs of type 1 and 2. The relative amount of these types of SWCNTs is also higher than those selected by biphenyl and tetracene in AD/biphenyl and AD/tetracene respectively. Comparing figure 7.5 (ii) and table 7.11 with figure 7.2 (ii), 7.3(ii) and 7.4(ii) and table 7.4 and 7.7 and 7.9 respectively, it is found that p-quaterphenyl selects SWCNTs of larger diameters than those selected by naphthalene, biphenyl and tetracene for AD SWCNTs. The reason for the difference between HiPco/p-quaterphenyl and AD/p-quaterphenyl might be
because of the longer length and torsion of \( p \)-quaterphenyl which might be favorable for selecting certain types of tubes. In terms of structural selectivity, in the case of the HiPco/\( p \)-quaterphenyl composite, the \((11, 0)\) zigzag SWCNT features strongly.

It has previously been speculated that structurally selective solubility of SWCNTs can be affected by interaction with PAHs, on the basis that the polyacene series are structurally similar to the longitudinal surface of the metallic armchair tubes and the polyphenyl series to that of predominantly semiconducting zigzag tubes [3]. A preferential solubilisation of semiconducting SWCNTs by \( p \)-terphenyl and of metallic by anthracene has previously been reported for laser vaporised SWCNTs [4]. In this study of HiPco and AD SWCNTs, it is firstly clear that as produced samples are dominated by chiral tubes and relatively few achiral tubes are present. Below the dispersion limit, each PAH solubilises a range of both chiral and achiral HiPco SWCNTs and only chiral for AD SWCNTs. The greater affinity of the longer PAHs for the longer tubes can be understood in terms of their greater binding energies (chapter 6). Given the systematic structural dependence of the binding energy of PAHs to mixed SWCNT samples, it is reasonable to expect that the binding interaction should be optimal for a direct mapping of the PAH structure onto the linear backbone of matched SWCNT structures. However, the detailed study of their interaction with HiPco SWCNTs suggests a binding which is not specific to structure or chirality. The results from this study are presented in figure 7.6, and show that the PAHs interact with a range of HiPco SWCNT diameters. In terms of structural selectivity, it is notable that for HiPco SWCNTs, only the polyacene moieties solubilise the armchair SWCNTs, although naphthalene also
solubilises the (11, 0) and (12, 0) zig-zag SWCNTs. The polyphenyl moieties do not solubilise the armchair SWCNTs. For AD SWCNTs no such structural selectivity was observed. However, in none of the four composite samples is the solubilisation of achiral SWCNTs dominant. In general a preference for smaller diameter SWCNTs is evident, although the longer PAHs have the capacity to solubilise larger diameter SWCNTs, due to their increased binding energy. This general trend is also seen in the interaction of PAHs of varying length with AD SWCNTs.

To understand the overall effect of these PAHs on the diameter distribution of both SWCNTs, histograms of overall diameter distribution of solubilised HiPco and AD SWCNTs are plotted on the same plot (figure 7.6). In these plots the histograms represent the percentage of occurrences of SWCNTs of different diameters, for each composite, at each of the four different laser excitation energies. In this plot 100% count for p-quaterphenyl indicates that at a particular excitation energy (here 2.33 eV) all single RBM spectra were at frequency ~ 280 cm\(^{-1}\). However, for the case of other excitation energies individual RBM spectra were found at different frequencies, hence the percentage count at a particular frequency is less than 100%.
It must therefore be postulated that the smaller PAHs can relatively efficiently bind normal to the tube axis of achiral nanotubes and along the direction of the chiral vector of chiral nanotubes. Given the curvature of the SWCNTs, this is more efficient for the smaller PAHs on small diameter SWCNTs; the longer PAHs interacting more efficiently with larger diameter SWCNTs. Additionally, the polyphenyl PAHs have a degree of rotational freedom about the inter-phenyl bond which may inhibit structurally specific binding. PAHs are also known to stack orthogonal to the surface of graphite, although this is energetically favourable only at high coverage [11]. A combination of such steric and energetic considerations may reduce any structural selectivity. The curvature of SWCNTs compared to the width of PAHs [12] and the solvent, chloroform [13] might also affect the interaction process. Gotovac et al. reported that in liquid-phase adsorption of tetracene and phenanthrene on SWCNTs, tetracene was adsorbed more than six times more than phenanthrene which attributed to the effect of the nanoscale curvature of
the tube surface [12]. From the report of Liu et al. [13], it has been found that in liquid-phase, the solvent also plays an important role for the selective solubilisation of SWCNTs. It was found that the pentacene derivative is more effective for extraction of metallic SWCNTs when dimethylformamide (DMF) is used as a solvent rather than N-methyl-2-pyrrolidone (NMP) and chloroform [13].

From figure 7.6, it is difficult to obtain quantitative information about the degree of solubilisation by the different PAHs. In this sense it would be more informative to estimate the number of SWCNTs solubilised at the characteristic concentration. From a previous study using AFM [14], length of HiPco and AD SWCNTs were found to be 750 nm and 1000 nm respectively. Using these values, the approximate volumes \( V_{\text{Tube}} = 2 \pi r^2 l \), where \( r \) and \( l \) are the radius and the length of a SWCNT respectively) of corresponding SWCNTs were calculated. The radius of the corresponding SWCNTs was calculated from the diameter distribution of SWCNTs, listed in table 5.2 and 5.3 for HiPco and AD SWCNTs respectively. Using equation 7.1, the approximate number of corresponding SWCNTs per concentration, at the characteristic concentration \( C_0 \) was calculated.
\[
\frac{Number}{Concentration} = \frac{V_{Solution} \times Count\%}{\rho \times V_{Tube}} \text{ Kg}^{-1} \text{ m}^3 \quad \text{------------------- (7.1)}
\]

Here, \( Number = \) Number of SWCNTs,

\( V_{Solution} = \) Volume of the solution

\( \rho = \) mass density of corresponding SWCNTs (HiPco: \( 1.6 \times 10^{-3} \) Kg/m\(^3\) and AD: \( 1.33 \times 10^{-3} \) Kg/m\(^3\))

\( Concentration = \) Characteristic concentration for the respective PAH.

\( Count\% = \) the occurrence obtained from the Raman spectroscopy study.

Although not an absolute value, as all of the features are normalised, this is related to the relative number of nanotubes of a certain diameter present.

A plot of \( \frac{Number}{Concentration} \) as a function of \( \omega_{RBMs} \) representing the diameter distribution of HiPco and AD composite solutions was plotted (figure 7.7). It can be seen that the approximate number of selected HiPco SWCNTs per concentration is significantly higher than that of AD SWCNTs and again it is found that the shorter chain PAHs more efficiently solubilise and disperse the SWCNTs.
As evidenced by the dispersion limits of $4 \times 10^{-2}$ mg/ml (HiPco and AD) for naphthalene, $2.4 \times 10^{-2}$ mg/ml (HiPco and AD) (chapter 6), for biphenyl it is found that the shorter chain PAHs more efficiently solubilise and disperse the SWCNTs. The longer PAHs are less efficient at solubilising and dispersing the SWCNTs ($3.48 \times 10^{-5}$ mg/ml for tetracene, $1.82 \times 10^{-7}$ mg/ml for $p$-quaterphenyl (chapter 6)). But for the quantitative analysis, the approximate number of corresponding SWCNTs selected by different PAHs was obtained by multiplying the value of $C_0$ of different PAHs/SWCNTs composite samples of corresponding SWCNTs (table 7.1) with Number/Concentration. A plot representing the approximate number of selected SWCNTs (HiPco and AD) by different PAHs is shown in figure 7.8.
In figure 7.8, it can be seen that with increasing molecular weight or size of PAHs, the number of solubilised SWCNTs decreases. The decrease is approximately exponential, and correlates well with the approximately exponential decrease of the dispersion limit, as shown in figure 6.10 (chapter 6) (and characteristic concentration) with molecular weight of PAH. It can be stated that although longer PAHs bind more strongly with SWCNTs they solubilise the SWCNTs less efficiently. Therefore, the shorter the PAH molecule (here naphthalene) the better the solubilisation of SWCNTs. From figure 7.7 and 7.8, it is also evident that the number of AD SWCNTs selected by PAHs is less than that of HiPco SWCNTs. The reason might be because of the larger diameter and length of AD SWCNTs as well as the larger bundle surface area than that of HiPco SWCNTs more PAHs are interacting with AD SWCNTs to make it soluble than that of HiPco SWCNTs which is also evident from the quenching study (figure 6.11, chapter 6).
The quality and nature of impurities present in SWCNTs might also affect the interaction process [15]. However, it has previously been indicated that the interaction of PAHs and organic polymers with SWCNT samples effectively purifies them as amorphous and graphitic residuals are not solubilised [1, 3, 14]. However, as indicated in the experimental section in chapter 6 (section 6.2), at concentrations where the SWCNTs are well dispersed, no precipitate was visually observable, indicating that some degree of impurities may be present in the sample. It is not clear how their presence may effect the interaction process, but in a quantitative comparison they should be considered. The presence of 30% and 10% impurities in AD and HiPCo samples respectively should result in a reduction of $C_0$ by a corresponding factor. A re-evaluation of the PAH binding energies results in values for the AD composites which are consistently $\sim 5\%$ less than those for the HiPco composites, a difference which is within the experimental errors of the measurement. In terms of number of nanotubes solubilised, a similar correction would result in a further reduction of the estimate of the number of AD SWCNTs solubilised, relative to HiPco SWCNTs.
7.4 Conclusion

A detailed Raman study of the diameter profiles of HiPco and AD SWCNTs solubilised by a range of PAHs demonstrates that a broad range of SWCNTs are solubilised, and there is little evidence of true structural selectivity as previously reported. In general a preference for smaller diameter SWCNTs is evident, although the longer PAHs have the capacity to solubilise larger diameter SWCNTs, due to their increased binding energy. It is also found that the approximate number of HiPco SWCNTs per concentration of composite samples is higher than that of AD SWCNTs and the smaller the size or molecular weight of PAHs, the more efficient the solubilisation of SWCNTs.
References


Chapter 8  Conclusion

8.1 Summary of the Chapters

The aims of this research were to

1. debundle and disperse SWCNTs using PAH molecules,
2. obtain a greater understanding of the interaction between PAHs and SWCNTs,
3. establish structure-property relationship governing the solubilisation process,
4. probe the optimum conditions for selective solubilisation of SWCNTs with the aid of PAHs of different structures and lengths.
5. obtain quantitative measurement of the amount of SWCNTs dispersed.

To debundle and disperse SWCNTs produced by the HiPco and AD processes, PAHs of the polyacene and polyphenyl series were used. To ensure that the dispersion of SWCNTs was not due to the solvent alone but primarily due to the interaction with the PAHs molecules a solvent with poor affinity for SWCNTS was required. It should however, be capable of dissolving the PAH molecules over a sufficient length range to enable length dependent studies. Chapter 5 described the solvent selection and characterisation of the materials used in this study.
For the characterisation of SWCNTs and PAHs, different spectroscopic and microscopic techniques were used. Using Raman spectroscopy, the diameter distribution and corresponding assignment of HiPco and AD SWCNT were obtained. From this study, it was found that both pristine SWCNTs were rich in chiral SWCNTs. The vibrational properties of PAHs were also obtained with the aid of Raman spectroscopy. Fluorescence spectroscopy gave a strong indication of an interaction between the SWCNTs and PAHs. Using AFM, a topographical image of the dispersed SWCNTs in the composite sample was found.

The interaction between SWCNTs (HiPco and AD) and PAHs was studied by using a fluorescence model based on the adsorption/desorption equilibrium of SWCNTs and PAHs and this was described in chapter 6. From the experimental results, a significant structural dependence of the interaction between SWCNTs and PAHs were obtained. It was found that the dispersion limit of SWCNTs decreased with increasing molecular weight of PAHs indicating structure-property relationship showing how effectively different PAHs dispersed SWCNTs. From this study it was found that molecules of the polyacene series are more effective at debundling the SWCNTs than their polyphenyl counterparts and, due to the higher number of carbon and hydrogen atoms, PAHs of the polyphenyl series bind more strongly to the surface of SWCNTs bundles than their counterparts of the polyacene series.

Using the florescence based model it was found that regardless of the type of SWCNTs (HiPco or AD), the binding energy between SWCNTs and PAHs was the same and it increases as the molecular weight of PAHs increases, thereby establishing a linear relationship between binding energy of SWCNTs
with PAHs and molecular weight of the corresponding PAHs. These results gave a strong indication that structure-property relationships for the interaction of PAHs with SWCNTs do exist and are relatively easily accessible experimentally. From the AFM study it was evident that below the dispersion limit of the corresponding composite, isolated SWCNTs may be obtained.

Chapter 7 explored the selective solubilisation of SWCNTs using PAHs with the aid of Raman spectroscopy. From the Raman spectroscopy study it was found that a broad range of HiPco and AD SWCNTs were solubilised with little evidence of true structural selectivity of HiPco SWCNTs. It can be stated that although the longer PAHs have the capacity to solubilise larger diameter SWCNTs, due to their increased binding energy, in general a preference for smaller diameter SWCNTs was evident. It was also found that the approximate number of HiPco SWCNTs per concentration of composite samples was higher than that of AD SWCNTs and the smaller the size or molecular weight of PAHs, the more efficient the solubilisation of SWCNTs.

8.3 Conclusion

After discussing different methods to separate SWCNTs according to their chirality, diameter and electronic properties in chapter 2 (section 2.6), it can be stated that to date no methods has been found that can preferentially separate armchair and zigzag SWCNTs.

Although the ultimate aim of this thesis was the selective solubilisation of armchair and zigzag SWCNTs using different PAHs, as mentioned above, there were also several other aims. Among those the debundling and dispersion of SWCNTs in chloroform, which has poor affinity for SWCNTs, using PAHs was
successfully achieved. Governing this solubilisation process, a well defined interaction between PAHs and SWCNTs was also elucidated, which in turn established structure-property relationships showing the binding energy between SWCNTs and PAHs increases with the increasing molecular weight of PAHs. The quantitative measurement of the approximate amount of isolated SWCNTs was also achieved.

For the case of the selective solubilisation process, i.e., separation of armchair and zigzag SWCNTs, the efficiency of this method was not up to the mark. To understand the limitations of the approach, some factors such as the curvature of SWCNTs, purity and quality of SWCNTs, solvent sensitivity, amount of PAHs, sonication time etc. should be considered.

It has been reported that the nanoscale curvature of SWCNTs has an effect on the adsorption of PAHs [1]. It was also found that the quality and purity of SWCNTs have significant impact on the interaction between PAHs and SWCNTs. For example, it has been demonstrated that the adsorption of phenanthrene was improved in the cases of purified nanotubes [2]. In the report of Liu et al. [3], it was claimed that in liquid-phase, the solvent also plays an important role for the selective solubilisation of SWCNTs. For example, the pentacene derivative is more effective for extraction of metallic SWCNTs when DMF is used as a solvent compared to NMP and chloroform [3]. Another potential factor which should be considered is the amount of PAHs used in the solubilisation. In this study, the ratio of SWCNTs and PAHs being used was 1:1 (w/w). It has been reported that the wrapping efficiency of fluorine based polymers can be improved by increasing the polymer concentration in the solution [4]. Considering this factor increased amounts of PAHs might show
better efficiency for the selective solubilisation process. Sonication time might also be an important factor. It has been found that at the beginning of the wrapping process of fluorene based polymers with SWCNTs, the solution becomes darker with increasing sonication time, indicating that the wrapping occurs in the early stage [4]. Longer sonication periods (usually > 10 min) result in more SWCNTs aggregation [4].


In conclusion, in addition to all the factors described above, selective solubilisation of SWCNTs may potentially be affective with the aid of non-linear PAHs such as phenanthrene, benzo[c]phenanthrene, 1,2-benzanthracene, (figure 8.1) etc. instead of using linear PAHs. These non-linear PAHs might increase the efficiency of selective solubilisation with the aid of \( \pi-\pi \) stacking on SWCNTs in the transverse and longitudinal direction simultaneously.
References


6. Benzo[c]phenanthrene, (online) Available at: [http://chrom.tutms.tut.ac.jp/JINNO/DATABASE/65benzo%5Bc%5Dphenanthrene.html](http://chrom.tutms.tut.ac.jp/JINNO/DATABASE/65benzo%5Bc%5Dphenanthrene.html) [Accessed 15 June 2010].

Appendix

Figure A1  Absorbance spectra of naphthalene (i), anthracene and (ii) tetracene in the absence and presence of AD SWCNTs at concentration ~ 1.25 x 10^{-3} mol/L for naphthalene and ~ 1.95 x 10^{-5} mol/L for tetracene.

Figure A2  Absorbance spectra of biphenyl (i) and p-quaterphenyl (ii) in the absence and presence of AD SWCNTs at concentration ~ 6.25 x 10^{-4} mol/L (biphenyl) and ~ 9.76 x 10^{-6} mol/L (p-terphenyl).
Figure A3 Fluorescence spectra of naphthalene (i) at concentration ~ 3.125 x 10^{-4} mol/L and tetracene (ii) at concentration ~ 1.9531 x 10^{-5} mol/L in the absence and presence of AD SWCNTs.

Figure A4 Fluorescence spectra of biphenyl (i) at concentration ~ 7.812 x 10^{-5} and p-quaterphenyl (ii) at concentration ~ 5.9604 x 10^{-10} mol/L in the absence and presence of AD SWCNTs.
Figure A5  Plots of maximum fluorescence intensity of naphthalene (i) and tetracene (ii) as a function of concentration in the absence (triangle) and presence (diamond) of AD SWCNTs.

Figure A6  Plots of maximum fluorescence intensity of biphenyl (i) and p-quaterphenyl (ii) as a function of concentration in the absence (triangle) and presence (diamond) of HiPco SWCNTs.
List of Publications and Presentations

Publications


Poster Presentations


