RICE UNIVERSITY

Functionalization, Coordination, and Coating of Carbon Nanomaterials

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE Doctor of Philosophy

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Abstract

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Single-walled carbon nanotubes were covalently end-functionalized with various donor ligands in order to facilitate the coordination of metal catalyst nanoparticles. The purpose of this study was to optimize catalyst complexation to SWNT ends, allowing growth from preformed seeds (SWNT-cats). The “SWNT amplification” method is envisioned as a route to bulk single-chirality nanotube samples. Study by $^{31}$P MAS NMR was undertaken in order to characterize SWNT phosphine derivatives.

The synthesis of new N-aryl dipyridylamines (dpas) and related compounds is reported. The products, chelating N-donor ligands, will be used to prepare copper complexes. Copper dpa complexes are able to discriminate between olefin isomers in simple mixtures. Similar triarylamines have been similarly prepared and characterized; these have been tested for their ability to separate SWNTs of particular diameters (or chiral angles) by selective $\pi$-$\pi$ stacking interactions. This method is a possible route to single or few-chirality samples, which could then be subjected to SWNT amplification.

A novel method for production of high-yield dispersions of single and few layer graphene is presented. $o$-Dichlorobenzene suspensions of graphene provide twice the yield of previous methods. Moreover, ODCB graphene dispersions form a convenient platform from which to pursue covalent derivatization of graphene in a nonpolar medium. ODCB dispersions have been used to covalently functionalize graphene with perfluoroalkyl groups by a free radical method. Initiation of radical reactions was achieved by both UV photolysis and thermal decomposition of peroxides.
Perfluoroalkylated graphene is highly exfoliated and shows great promise for use in polymer composites, lubricants and coatings.

Chemical bath deposition (CBD) of II-VI semiconductor materials on SWNT substrates is demonstrated. Bulk heterojunction photovoltaic devices have been prepared from these SWNT-semiconductor composites. The CBD process of depositing CdSe / CuSe layers onto SWNT buckypapers will allow production of low-cost solar cells on flexible substrates. The manufacture of solar cells will be possible using roll-to-roll processing, in ambient conditions, without need for high-vacuum or specialized equipment.
"New knowledge is the most valuable commodity on earth. The more truth we have to work with, the richer we become."

– Kurt Vonnegut
Acknowledgements

First, I must thank Professor Andrew Barron for being an ideal thesis advisor. You have allowed me find my own way: to try, to fail, and eventually to succeed. I now believe this is the only way I have ever really learned anything valuable. I don’t think I could have found the experience I gained in your laboratory anywhere else.

Thanks to all Barron group members past and present, especially John Allen, for the chance to do some “real” synthetic chemistry. I must thank Jay Lomeda and Noe Alvarez for fruitful collaborations, but mostly for the good times had while letting our kids run wild on some playground. To Dr. Robert Schucker and Dr. Dennis Flood, I thank you both for the opportunities to work on interesting projects that have broader implications in the world.

To the staff of the Shared Equipment Authority, thank you. Without Angelo, Bo, Rich, and Wenh, research at Rice would be nearly impossible. Special thanks to Dr. Larry Alemany for his patience and help with solid state NMR.

I must acknowledge my undergraduate academic advisor, Prof. Simon Bott, for directing me to the laboratory of David Hoffman and sparing me from pharmacy school. To Professor Hoffman, whatever I do or achieve as a chemist comes as the direct result of the experience I had in your lab. I can never repay the favor of helping me discover a “burning in the gut” desire to do chemistry. Thank you both for putting in a good word with Andy on my behalf.

Finally, thank you to my parents and in-laws for support and babysitting services you have provided these last few years. Laura and I could not have made it without you. Laura, thank you for our two beautiful boys and all the love and support I could ever ask for and more. I hope you know that I recognize the sacrifices you have made to help me get through graduate school. Let’s “go to New Mexico and live in the mountains and ride on a train.”
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1.1 DD-SWNT-py
1.2 DD-SWNT-SH
1.3 DD-SWNT-PPh₂
1.4 DD-SWNT-C₆H₄'Bu
1.5 SWNT-py
1.6 SWNT-SH
1.7 SWNT-PPh₂
1.8 US-SWNT-C(O)Cl
1.9 US-SWNT-py
1.10 US-SWNT-SH
1.11 US-SWNT-P(O)Ph₂
1.12 US-SWNT-PPh₂
1.13 US-SWNT-P(S)Ph₂
1.14 US-SWNT-P(O)Et₂
1.15 US-SWNT-PEt₂

2.1 N-mesityl-N-(2-pyridyl)amine
2.2 N-(2,6-diethylphenyl)-N-(2-pyridyl)amine
2.3 N-mesityl-N,N-di(2-pyridyl)amine
2.4 N-(2,6-diethylphenyl)-N,N-di(2-pyridyl)amine
2.5 N-(2,6-diisopropylphenyl)-N,N-di(2-pyridyl)amine
2.6 N-(1-naphthyl)-N,N-di(2-pyridyl)amine
2.7 N-(2,6-diisopropylphenyl)-N,N-di(2-quinolyl)amine
2.8 quinolin-1-(2-quinolyl)-2-one mesitylimine
2.9 N-(4-dodecylphenyl)-N,N-di(1-naphthyl)amine
2.10 $N$-(4-dodecylphenyl)-$N,N$-di(2-naphthyl)amine

2.11 $N$-(4-dodecylphenyl)-$N,N$-di(1-pyrenyl)amine

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3.2 $R_F$-DD-graph

3.3 $R_F$-D-graph
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>ampere</td>
</tr>
<tr>
<td>Å</td>
<td>angstrom(s), $10^{-10}$ m</td>
</tr>
<tr>
<td><em>ab initio</em></td>
<td>from first principles</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>Ar</td>
<td>aryl</td>
</tr>
<tr>
<td>ATR</td>
<td>attenuated total reflection</td>
</tr>
<tr>
<td>1^Bu</td>
<td>tert-butyl, $-\text{C(CH}_3\text{)}_3$</td>
</tr>
<tr>
<td>°C</td>
<td>degrees centigrade</td>
</tr>
<tr>
<td><em>ca.</em></td>
<td>circa, approximately</td>
</tr>
<tr>
<td>cm</td>
<td>centimeter, $10^{-2}$ m</td>
</tr>
<tr>
<td>CBD</td>
<td>chemical bath deposition</td>
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<tr>
<td>°</td>
<td>degrees</td>
</tr>
<tr>
<td>δ</td>
<td>delta, chemical shift (NMR)</td>
</tr>
<tr>
<td>d</td>
<td>doublet (NMR)</td>
</tr>
<tr>
<td>DD</td>
<td>dodecyl, $-(\text{CH}_2\text{)}_1\text{CH}_3$</td>
</tr>
<tr>
<td>DMF</td>
<td>$N,N$-dimethylformamide</td>
</tr>
<tr>
<td>dba</td>
<td>dibenzylideneacetone</td>
</tr>
<tr>
<td>dpa</td>
<td>dipyridylamine</td>
</tr>
<tr>
<td>DPPF</td>
<td>$1,1'$-<em>bis</em>(diphenylphosphino)ferrocene</td>
</tr>
<tr>
<td>dqa</td>
<td>diquinolylamine</td>
</tr>
<tr>
<td>e</td>
<td>electron</td>
</tr>
<tr>
<td>e.g.</td>
<td><em>exempli gratia</em>, for example</td>
</tr>
<tr>
<td>EDS</td>
<td>energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>Eq.</td>
<td>equation</td>
</tr>
<tr>
<td>Term</td>
<td>Equivalent</td>
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<td>------</td>
<td>------------</td>
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<tr>
<td>equiv.</td>
<td>equivalent</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl, -CH$_2$CH$_3$</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>Et$_2$O</td>
<td>diethyl ether</td>
</tr>
<tr>
<td>et al.</td>
<td>et alia, and others</td>
</tr>
<tr>
<td>eV</td>
<td>electron volt</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform IR spectroscopy</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>H</td>
<td>Hartree, $4.36 \times 10^{-18}$ J</td>
</tr>
<tr>
<td>i.e.</td>
<td>id est, that is (to say)</td>
</tr>
<tr>
<td>IR</td>
<td>infrared spectroscopy</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
</tr>
<tr>
<td>J</td>
<td>Joule</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>λ</td>
<td>lambda, wavelength</td>
</tr>
<tr>
<td>L</td>
<td>liter(s), ligand</td>
</tr>
<tr>
<td>m</td>
<td>meta</td>
</tr>
<tr>
<td>M</td>
<td>molar, mol.L$^{-1}$</td>
</tr>
<tr>
<td>m</td>
<td>multiplet (NMR), medium (IR), meter</td>
</tr>
<tr>
<td>μm</td>
<td>micrometer(s), $10^{-6}$ m</td>
</tr>
<tr>
<td>MAS</td>
<td>magic angle spinning (NMR)</td>
</tr>
<tr>
<td>Me</td>
<td>methyl, -CH$_3$</td>
</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>Mes</td>
<td>mesityl, trimethylphenyl, -C$_6$H$_2$(CH$_3$)$_3$</td>
</tr>
<tr>
<td>mg</td>
<td>milligram(s), $10^{-3}$ g</td>
</tr>
</tbody>
</table>
min  minute(s)
mL  milliliter(s), 10^{-3} L
mM  millimolar, 10^{-3} M
Mp  melting point
MS  mass spectrometry
mV  millivolt, 10^{-3} V
M_w  molecular weight
MWNT  multi-walled carbon nanotube
mol  mole(s)
mmol  millimole(s), 10^{-3} mol
MTO  methyltrioxorhenium
naph  naphthyl, \(-C_{10}H_7\)
NHC  N-heterocyclic carbene
nm  nanometer(s), 10^{-9} m
NMP  \(N\)-methyl-2-pyrrolidone
NMR  nuclear magnetic resonance spectroscopy
NTA  nitrilotriacetic acid
\(\Omega\)  ohms
\(o\)  ortho
ODCB  ortho-dichlorobenzene
\(p\)  para
PET  poly(ethyleneterephthalate)
Ph  phenyl, \(-C_6H_5\)
iPr  isopropyl, \(-CH(CH_3)_2\)
PTFE  poly(tetrafluoroethylene)
py  pyridyl, \(-C_5H_4N\)
q  quartet (NMR)
<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
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<tr>
<td>quin</td>
<td>quinolyl, -C₉H₆N</td>
</tr>
<tr>
<td>R</td>
<td>alkyl</td>
</tr>
<tr>
<td>Rₚᶠ</td>
<td>perfluoroalkyl</td>
</tr>
<tr>
<td>rpm</td>
<td>revolutions per minute</td>
</tr>
<tr>
<td>s</td>
<td>singlet (NMR), strong (IR), seconds</td>
</tr>
<tr>
<td>S</td>
<td>siemens, Ω⁻¹</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SWNT</td>
<td>single-walled carbon nanotube</td>
</tr>
<tr>
<td>SDBS</td>
<td>sodium dodecyl benzene sulfonate</td>
</tr>
<tr>
<td>SDS</td>
<td>sodium dodecyl sulfate</td>
</tr>
<tr>
<td>t</td>
<td>triplet (NMR)</td>
</tr>
<tr>
<td>TCO</td>
<td>transparent conducting oxide</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>US-SWNT</td>
<td>ultrashort SWNT</td>
</tr>
<tr>
<td>UV-vis</td>
<td>ultraviolet/visible spectroscopy</td>
</tr>
<tr>
<td>V</td>
<td>volt</td>
</tr>
<tr>
<td>W</td>
<td>watt, width at half height (MAS NMR)</td>
</tr>
<tr>
<td>w</td>
<td>weak (IR)</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
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<td>XRD</td>
<td>X-ray diffraction</td>
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</table>

**Glossary**

- **oleum**: H₂SO₄ that contains 10 - 20% excess SO₃
- **Piranha**: oxidizing solution that is 50% H₂SO₄, 30% H₂O₂, and 40% H₂O
Introduction

Nanotechnology is a field that unites the physical sciences within a vast interdisciplinary realm. Of the many topics encompassed by the term ‘nano,’ carbon nanomaterials have the most diverse chemistry and physical properties and are therefore most promising for a wide range of potential applications. Despite the molecular perfection of fullerene, it is the physical and electronic properties of single-walled carbon nanotubes (SWNTs) that have made them very attractive materials for numerous applications. Consequently, SWNTs have become intensively studied in recent years. A more recent addition to the field of carbon nanomaterials is that of graphene; single sheets of nanometer scale graphite.

Carbon exists as three allotropes: diamond, graphite, and the fullerenes. Fullerene, C$_{60}$, was discovered at Rice University by Smalley, Curl and Kroto and resulted in their sharing the 1996 Nobel Prize in chemistry. Fullerene is a hollow spherical cage formed from sp$^2$ carbon atoms, arranged like a soccer ball. Graphite consists of stacked sheets of hexagonally arranged sp$^2$ carbon atoms. A single atomic layer (or few layers) of graphitic carbon is termed graphene, and was first isolated in 2004. SWNTs, discovered by Iijima in 1993, are essentially fullerenes that have been elongated along one axis. They can be described as a graphene sheet, rolled upon itself to form a hollow tube and capped with a fullerene hemisphere.

**Single-walled carbon nanotubes.** The physical and electronic properties of SWNTs are remarkable. They are stronger than steel, having a Young’s modulus near 1 TPa and tensile strength on the order of one hundred GPa. As for electrical properties, SWNTs can have room temperature resistivity as low as $0.34 \times 10^{-4}$ Ω.cm and they are capable of ballistic electron transport on μm length scales. An individual nanotube’s electronic (and to a lesser extent, physical) properties depend on the way in which the graphene sheet is rolled. SWNTs can be armchair, zigzag, or chiral (Figure 1.1). Armchair
SWNTs are metallic, zigzag are narrow bandgap semiconductors, and chiral tubes can vary from narrow to wide-bandgap semiconductors.\textsuperscript{7,8}

![Figure 1.1](image-url)

**Figure 1.1.** The idealized structures of SWNTs with armchair (a), zigzag (b), and chiral (c) helicities.

The \((n,m)\), or roll up vector is used to define the chiral angle or helicity of SWNTs (Figure 1.2). Armchair tubes have chiral angle 30°, zigzag tubes have \(\alpha = 0°\), and chiral tubes are in between. The roll-up vector also provides a nomenclature system for individual SWNTs.

Since many electronics applications will require SWNT samples of a particular bandgap, there has been enormous interest in chiral separations. A longer-term goal is chiral-selective synthesis. In fact, production of single-chirality SWNT samples may be the single largest obstacle yet to be overcome in nanotube research. A number of methods have been pursued toward chiral SWNT separations including covalent derivatization,\textsuperscript{9} ultracentrifugation,\textsuperscript{10} dielectrophoresis,\textsuperscript{11} and supramolecular interactions based on \(\pi-\pi\) stacking.\textsuperscript{12} However, chiral SWNT separation alone is still not enough for SWNTs to
realize their full potential. Bulk quantities of single-chirality samples will be required. Therefore, a type-specific growth method is critical.

**Figure 1.2.** Schematic representation of the definition of the \((n,m)\) roll-up vector and chiral angle.\(^8\)

**SWNT amplification.** Richard Smalley's vision for a seeded-growth route to bulk samples of single chirality SWNTs, called SWNT amplification (Figure I.3), is analogous to the polymerase chain reaction (PCR) used to replicate DNA sequences.\(^13\) After the isolation of a single SWNT it is oxidatively etched to open the tube ends. Then a catalyst nanoparticle or cluster is coordinated to an opened end. The SWNT-catalyst complex can then be subjected to a carbon feedstock under appropriate conditions and growth of the tube will continue, maintaining the original \((n,m)\) chirality of the seed. The process can then be repeated, resulting in bulk quantities of single chirality SWNTs. Much progress has been made toward this goal, namely SWNT growth has been demonstrated from SWNT-cats, where the catalyst is an iron-molybdenum cluster\(^14\) or an iron carboxylate complex.\(^15\) However, much remains to be done to improve the chemistry of SWNT amplification. More active growth catalysts are needed; further, the coordination of these catalysts to SWNT ends must be improved. In Chapter 1 of this
thesis, advances toward the goal of SWNT amplification are reported. Specifically, SWNTs are functionalized with new donor ligands in order to optimize the binding of catalyst particles. In addition, Chapter 2 describes progress on SWNT separations by selective supramolecular π-π interactions.

**Figure I.3.** The SWNT amplification process.

**Graphene.** Recently graphene has come under intensive study due to its desirable physical and electronic properties, which share many similarities with carbon nanotubes. In fact, graphene can be used to describe carbon nanotubes and fullerenes (Figure I.4) and has been called the "mother of all graphitic forms."
Figure 1.4. Schematic representation of the relationship between graphene (pale blue) and the nano-carbon materials: fullerenes (green), SWNT (purple), and graphite (dark blue).  

Single-layer graphene nanosheets were first characterized in 2004, prepared by mechanical exfoliation (the "scotch-tape" method) of bulk graphite. Later graphene was produced by epitaxial chemical vapor deposition on silicon carbide and nickel substrates. Most recently, graphene nanoribbons (GNRs) have been prepared by the oxidative treatment of carbon nanotubes and by plasma etching of nanotubes embedded in polymer films.

Graphene has been reported to have a Young’s modulus of 1 TPa and intrinsic strength of 130 GP; similar to SWNTs. The electronic properties of graphene also have
some similarity with carbon nanotubes. Graphene is a zero-bandgap semiconductor.

Electron mobility in graphene is extraordinarily high (15,000 cm²/V·s⁻¹ at room temperature) and ballistic electron transport is reported to be on length scales comparable to that of SWNTs.¹⁶,²² One of the most promising aspects of graphene involves the use of GNRs. Cutting an individual graphene layer into a long strip can yield semiconducting materials where the bandgap is tuned by the width of the ribbon.²³

While graphene’s novel electronic and physical properties guarantee this material will be studied for years to come, there are some fundamental obstacles yet to overcome before graphene based materials can be fully utilized. The aforementioned methods of graphene preparation²,¹⁷-²⁰ are effective; however, they are impractical for large-scale manufacturing. The most plentiful and inexpensive source of graphene is bulk graphite. Chemical methods for exfoliation of graphene from graphite provide the most realistic and scalable approach to graphene materials.²⁴

Graphene layers are held together in graphite by enormous van der Waals forces. Overcoming these forces is the major obstacle to graphite exfoliation. To date, chemical efforts at graphite exfoliation have been focused primarily on intercalation, chemical derivatization, thermal expansion, oxidation-reduction, the use of surfactants, or some combination of these.²⁵,²⁶,²⁷,²⁸

Probably the most common route to graphene involves the production of graphite oxide (GO) by extremely harsh oxidation chemistry. The Staudenmeier²⁹ or Hummers³⁰ methods are most commonly used to produce GO, a highly exfoliated material that is dispersible in water. The structure of GO has been the subject of numerous studies; it is known to contain epoxide functional groups along the basal plane of sheets as well as hydroxyl and carboxyl moieties along the edges (Figure 1.5).³¹
As graphite oxide is electrically insulating, it must be converted by chemical reduction to restore the electronic properties of graphene. Chemically converted graphene (CCG) is typically reduced by hydrazine or borohydride.\textsuperscript{26,27,32} The properties of CCG can never fully match those of graphene for two reasons: 1) oxidation to GO introduces defects, and 2) chemical reduction does not fully restore the graphitic structure. As would be expected, CCG is prone to aggregation unless stabilized.\textsuperscript{26,27,32} Graphene materials produced from pristine graphite avoid harsh oxidation to GO and subsequent (incomplete) reduction; thus, materials produced are potentially much better suited to electronics applications. Chapter 3 of this thesis includes description of a quantitative method for determination of epoxide content in GO. Also, a new high-yield homogeneous dispersion of single and few-layer graphene prepared from pristine graphite is reported.

**Covalent functionalization of graphene and GO.** The covalent functionalization of SWNTs is well established.\textsuperscript{33} Some routes to covalently functionalized SWNTs include esterification/amidation,\textsuperscript{34} reductive alkylation (Billups reaction),\textsuperscript{35} and treatment with azomethine ylides (Prato reaction),\textsuperscript{36} diazonium salts,\textsuperscript{37}
or nitrenes.\textsuperscript{38} Conversely, the chemical derivatization of graphene and GO is still relatively unexplored.

Some methods previously demonstrated for SWNTs have been adapted to GO or graphene. GO carboxylic acid groups have been converted into acyl chlorides followed by amidation with long-chain amines.\textsuperscript{39} Additionally, the coupling of primary amines and amino acids via nucleophilic attack of GO epoxide groups has been reported.\textsuperscript{40} Yet another route coupled isocyanates to carboxylic acid groups of GO.\textsuperscript{41} Functionalization of partially reduced GO by aryldiazonium salts has also been demonstrated.\textsuperscript{26} The Billups reaction has been performed on the intercalation compound potassium graphite (C\textsubscript{8}K),\textsuperscript{42} as well as graphite fluoride\textsuperscript{25a} and most recently GO.\textsuperscript{43} Finally, graphene alkylation has been accomplished by treating graphite fluoride with alkyllithium reagents.\textsuperscript{44} Chapter 3 of this thesis describes a new free radical route to covalently functionalized graphene.

It is clear that nanotechnology, and in particular carbon nanomaterials, will continue to be an active field of research. In fact, carbon nanomaterials have already begun to make the transition toward some real-world applications. In Chapter 4, we detail the assembly of a flexible solar cell using SWNTs. While much has been done, there are yet many obstacles to overcome and new discoveries to be made.

References


Chapter 1

Functionalization of SWNTs to Facilitate the Coordination of Metal Ions, Compounds and Clusters

Introduction

It is well known that the electronic properties of single-walled carbon nanotubes (SWNTs) are determined by their wrapping angle \((n,m)\) chirality.\(^1\)\(^2\) Many uses of SWNTs in electronics applications are therefore dependent on the use of samples in which the tubes are all of the same chirality. At this time, there are no large-scale methods currently available to separate SWNTs by \((n,m)\) value or synthetic methods to produce single-chirality samples. The Barron research group has previously demonstrated ‘amplification’ of SWNTs using preformed SWNT-catalyst seeds.\(^3\) These SWNT-cats are formed by the complexation of a pro-catalyst to the ends of a functionalized SWNT. When SWNT-cats are exposed to a carbon feedstock under the right conditions, growth continues from the ends of the existing seeds, maintaining the structure of each SWNT.\(^4\) Repetition of the steps of cutting, catalyst complexation, and growth would allow production of single-chirality SWNT samples in large quantities. Thus SWNT amplification is analogous to the polymerase chain reaction used to replicate DNA sequences.

Despite the successful demonstration of SWNT-cat synthesis, and growth there from,\(^3\)\(^4\) there are several issues that must be addressed before large-scale SWNT amplification can succeed. With regard to the SWNT-cat these include: 1) the percentage of SWNTs that are converted to SWNT-cat is low (<50%), 2) SWNT-cats have only been prepared for iron based pro-catalysts, 3) the number of SWNT-cats that grow is small, and 4) the average increase in length of the SWNT from SWNT-cat is low (ca. 300 nm). Here we address a component of the first two of these four issues.
While the yield of SWNT-cat (formed from any given batch of SWNTs) is obviously dependent on the ability to maximize the attachment of the pro-catalyst to the SWNT, there are really two components to this reaction. The first is ensuring that a maximum number of SWNTs have ends suitable for the attachment of the pro-catalyst. Second, the efficiency of the coupling reaction between the SWNT and the pro-catalyst must be optimal. In earlier studies, the Barron group investigated the use of the iron-molybdenum cluster \( [H_xPMo_{12}O_{40} \subset H_4Mo_7Fe_{30}(O_2CMe)_{15}O_{25}4(H_2O)_{98}] \) (FeMoC) as a pro-catalyst.\(^3\) The coupling reaction involved the use of either the native carboxylic acid groups (formed from acid etching SWNTs) or pyridine functional groups. These choices were in part suggested by previous research concerning the coordination chemistry of FeMoC.\(^5\) However, additional studies have employed simple iron complexes, iron-based nanoparticles or other metal-based pro-catalysts, and we are interested in expanding the range of possible coupling groups. Herein we report the formation of coupling groups to allow the attachment of metal containing species specifically to the ends of SWNTs. In particular we have end-functionalized SWNTs with phosphines and thiols in addition to the aforementioned pyridines.

As-prepared sidewall substituted SWNTs have carboxylate residues at any open end as a consequence of Piranha (\( H_2SO_4;H_2O_2 \)) etching of the SWNTs.\(^6\) These groups, as already described, can directly complex metals. Alternately, carboxylate residues may be coupled with amines or alcohols to form amide or ester linkages, respectively. Thus, the carboxylic acid residues at tube ends can be derivatized with any desired functional group.

**Results and Discussion**

The choice of solvent is important for the formation of SWNT-cat. DMF is an effective solvent for suspending organic functionalized SWNTs, however, for the iron-based pro-catalysts (including FeMoC) DMF shows good coordination strength and thus
competes for binding with the carboxylate groups resulting in little to no SWNT-FeMoC complexation. In contrast, non-coordinating solvents such as CHCl₃ will not complex FeMoC. Additionally, CHCl₃ is a good solvent for the dispersal of organic functionalized SWNTs, e.g., dodecyl sidewall functionalized SWNTs (I).⁷

Having already examined pyridine groups to form SWNT-cat, our interest turned to phosphines and thiols. We have therefore investigated SWNT end functionalization with these donor ligands using esterification and amidation reactions. We have employed the coupling chemistry of Green and coworkers⁸ as well as via the acid chlorides.⁹ For our SWNT amplification methodology to succeed the catalyst cluster must be able to preferentially dock to the SWNT at its end; any other configuration precludes continued growth. To that end, sidewall functionalized SWNTs prevent sidewall-metal complexation in addition to preventing bundling and providing CHCl₃ solubility.⁷
Sidewall functionalized SWNTs have been compared to similar pristine-sidewall samples as well as ultrashort SWNTs (II).

**End-Functionalization of SWNTs.** With FeMoC$_3$ and iron carboxylate trimers$^{10}$ in mind as growth catalysts, previous Barron group studies focused on pyridine ligands. Etched DD-SWNTs were reacted with 4-hydroxypyridine in the presence of DCC/DMAP catalyst to yield DD-SWNT-py (1.1) (Scheme 1.1). There has been speculation that after sidewall alkylation there may be more hydroxyl groups than carboxyl groups at the SWNT ends. So, in addition to 4-hydroxypyridine, isonicotinic acid was also coupled with DD-SWNTs. The resulting concentration of pyridine groups was found to be much higher with hydroxypyridine than with isonicotinic acid, therefore all subsequent coupling reactions used hydroxyl or amine substituted ligands.$^{11}$

Following the DCC catalyzed route,$^{8}$ we coupled 2-aminoethanethiol and 4-hydroxyphenyldiphenylphosphine to DD-SWNTs (Scheme 1.1). As a control, we also coupled a non-ligating group to SWNT ends, 4-tert-butylphenol. The choice of 4-tert-butylphenyl as a substituent does not completely inhibit potential coordination since the
ester linkage may show some complexation. However, DD-SWNT-C₆H₄Bu¹ will block carboxylate end groups and should provide a reference point for the other ligands.

**Scheme 1.1.** Synthesis of functionalized SWNTs. (a) 4-hydroxypyridine/DCC/DMAP in CHCl₃, (b) 4-tert-butylphenol/DCC/DMAP in CHCl₃, (c) 2-aminoethanethiol/DCC in CHCl₃, (d) SOCl₂/DMF, (e) 4-hydroxyphenyldiphenylphosphine/DCC/DMAP in CHCl₃, (f) 4-hydroxyphenyldiphenylphosphine in CHCl₃, (g) 2-aminoethanethiol in CHCl₃, (h) 4-hydroxypyridine in CHCl₃, and (i) hydroxymethyldiethylphosphine in CHCl₃.

The presence of dodecyl side groups inhibits SWNT bundling, and hence make possible AFM characterization of the functionalized SWNTs and their FeMoC conjugates (see Conclusions). However, the high organic content (and small number of SWNT-end groups per SWNT) makes analysis difficult. In order to facilitate analysis the same series
of functional groups have been added to both pristine-sidewall Piranha etched SWNTs (1.5 - 1.7), and ultra short SWNTs (1.9 - 1.15). Ultra short SWNTs (US-SWNTs) have lengths less than 100 nm and are prepared by etching SWNTs with a combination of oleum and nitric acids.\(^2\) It has been previously reported that in addition to the terminal carboxylic acid groups, US-SWNTs have oxidized sidewalls, including carboxylic groups. Thus, reaction with any of the coupling agents will result in a significantly increased substituent:SWNT ratio, and hence allow for easier spectroscopic characterization. In order to insure all acid groups reacted with the ligand we changed coupling chemistry via the conversion of the carboxylic acid groups to acyl chlorides.\(^9\) The acyl chloride derivative [US-SWNT-C(O)Cl, 1.8] reacts readily in CHCl\(_3\) with both amines and alcohols to yield the amide and ester linked US-SWNTs respectively. All functionalized SWNTs were characterized by X-ray photoelectron spectroscopy (XPS), and where appropriate \(^{31}\)P MAS NMR (see below).

For a typical DD-SWNT-py (1.1) sample the atomic concentration of nitrogen and oxygen were found to be to be 2% and 7%, respectively (Table 1.1). In contrast no nitrogen was detected for the unreacted DD-SWNTs. The 2-aminoethanethiol derivatives (1.2, 1.10) show the presence of sulfur, in the expected 1:1 ratio with nitrogen. Although phosphorus is observed in the XPS of DD-SWNT and SWNT derivatives, there is insufficient concentration (less than 1%) to allow observation of a \(^{31}\)P MAS NMR spectrum. However, a spectrum was readily obtained for the US-SWNT derivative (1.11).

\(^{31}\)P MAS NMR Characterization of phosphine derivatives. Solid-state phosphorus NMR (\(^{31}\)P MAS NMR) provides a convenient method of characterizing SWNT-phosphine derivatives. \(^{31}\)P is a convenient NMR nucleus: 100% abundance, spin \(1/2\) and high \(\gamma\). Only the US-SWNT derivatives had high enough concentrations of phosphorus to provide spectra of adequate signal to noise on reasonable time scales.
Table 1.1. XPS analysis of functionalized SWNTs (atomic %).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD-SWNT-COOH</td>
<td>92.2</td>
<td>7.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>US-SWNT</td>
<td>66.2</td>
<td>33.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DD-SWNT-py (1.1)</td>
<td>90.7</td>
<td>7.5</td>
<td>1.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DD-SWNT-SH (1.2)</td>
<td>89.2</td>
<td>8.9</td>
<td>1.0</td>
<td>0.9</td>
<td>-</td>
</tr>
<tr>
<td>DD-SWNT-PPh(_2) (1.3)</td>
<td>85.9</td>
<td>14.0</td>
<td>-</td>
<td>-</td>
<td>\approx 0.1</td>
</tr>
<tr>
<td>DD-SWNT-C(_6)H(_4)Bu (1.4)</td>
<td>75.2</td>
<td>24.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SWNT-py (1.5)</td>
<td>72.7</td>
<td>24.4</td>
<td>2.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SWNT-SH (1.6)</td>
<td>84.1</td>
<td>14.8</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>SWNT-PPh(_2) (1.7)</td>
<td>76.2</td>
<td>23.6</td>
<td>-</td>
<td>-</td>
<td>\approx 0.1</td>
</tr>
<tr>
<td>US-SWNT-py (1.9)</td>
<td>52.2</td>
<td>46.7</td>
<td>1.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>US-SWNT-SH (1.10)</td>
<td>71.0</td>
<td>18.1</td>
<td>5.7</td>
<td>5.2</td>
<td>-</td>
</tr>
<tr>
<td>US-SWNT-P(O)Ph(_2) (1.11)</td>
<td>75.8</td>
<td>24.0</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The \(^{31}\)P MAS NMR spectrum of the product from the reaction of US-SWNT-C(O)Cl with 4-hydroxyphenyldiphenylphosphine \([P(C\(_6\)H\(_5\))\(_2\)(C\(_6\)H\(_4\)OH)]\) contains a single broad peak at \(\delta\) 21 ppm, indicative of an arylphosphine oxide (Figure 1.1).\(^{13}\) This would suggest that during the course of the coupling reaction the phosphine ligand became oxidized. Although the coupling and workup were all performed under inert atmospheres, the US-SWNTs themselves contain much oxygen (as do “purified” SWNTs\(^{14}\)). Thus, it is likely that reactive oxygen (usually epoxides) oxidized the phosphorus.
Figure 1.1. $^{31}$P MAS NMR spectrum of US-SWNT-P(O)Ph$_2$ (1.11), with spinning side bands labeled (*)

Reduction of the phosphine oxide in the presence of the ester-SWNT linkage proved to be problematic. Conventional methods apparently cleaved the ester linkage as $^{31}$P MAS NMR after reduction showed a total absence of phosphorus. Adapting the oxygen transfer method of Wu et al., which employs a sacrificial oxygen-accepting phosphite (Scheme 1.2.),$^{15}$ resulted in the slow conversion of the phosphine oxide to the parent phosphine. After 24 h $^{31}$P MAS NMR showed incomplete reduction, so the reaction time was increased. After 48 hours the major species is associated with the phosphine ($\delta = 5$ ppm), although a shoulder remains, assigned to residual oxide (Figure 1.2). Expected solution phosphorus chemical shifts for triphenylphosphine and triphenylphosphine oxide are -4 and 25 ppm respectively. The signal is even further downfield relative to $^{31}$P MAS chemical shift of the precursor Ph$_2$P(C$_6$H$_4$OH) ($\delta$ -12.6 ppm). It is yet unknown what effects SWNTs may have on phosphorus chemical shifts. In addition, SWNT samples are inhomogeneous, further complicating NMR spectra.
Figure 1.2. $^{31}\text{P}$ MAS NMR spectrum of the product from the partial reduction of US-SWNT-P(O)Ph$_2$ (1.11) to US-SWNT-PPh$_2$ (1.12), with spinning sidebands labeled (*).

In order to gather more information, the phosphine sulfide derivative was prepared by treating US-SWNT-PPh$_3$ with elemental sulfur.$^{16}$ After refluxing the sample for 18 hours $^{31}\text{P}$ NMR showed two separate resonances of unresolved peaks. The first resonance contains signals at 46.4, 39.9, and ca. 32 ppm. The second group contains 4 visible peaks at ~15, 0.77, -7.96, and -20.6 ppm. The reflux with sulfur was repeated increasing reaction time to 90 hours. The resulting NMR spectrum is simpler with only a single group of three unresolved signals, at 0.3, -9.5, and -20.7 ppm. The peak at δ -20.7 is the highest intensity. The reaction was repeated once more, this time refluxing a full week. The final NMR spectrum contains the same three signals as the previous, the only difference being change in the relative intensities (with minimal changes in shift). The peak now at -9.7 ppm is by far the most intense with the peak at 0 ppm much smaller. The signal at about -20 ppm has all but disappeared (Figure 1.3). Although the spectrum simplified with increased reaction time the NMR results are still ambiguous.
Triarylphosphine sulfide $^{31}$P chemical shifts are expected in the region between 50 and 60 ppm, however, the signals from 1.13 are upfield of this by approximately 70 ppm.

Figure 1.3. $^{31}$P MAS NMR spectrum of US-SWNT-P(S)Ph$_2$ (1.13). Spinning sidebands are labeled (*).

Scheme 1.2. Synthesis of phosphine derivatives: (a) P(OEt)$_3$/HSiCl$_3$ in toluene, (b) sulfur/pyridine in toluene.

The PPh$_2$PhOH ligand contains only aromatic sp$^2$ carbon atoms which are indistinguishable from SWNT carbon by $^{13}$C NMR. It is desirable to have a substituent that can be differentiated from SWNTs. In this regard we have investigated the reaction
of a small alkyl phosphine derivative with US-SWNTs. The use of an alkylphosphine allows $^{13}$C solid state NMR in addition to $^{31}$P.

Hydroxymethyldiethylphosphine (PEt$_2$MeOH) was prepared by treating diethylphosphine with formaldehyde in methanol.$^{17,18}$ Coupling of PEt$_2$MeOH to acyl chloride US-SWNTs was performed in CHCl$_3$ solution. Trialkylphosphines are even more air sensitive than triarylphosphines; as expected, the product of the coupling reaction is the oxidized US-SWNT-P(O)Et$_2$. The phosphine oxide can be reduced via the triethylphosphite oxygen transfer method$^{15}$ over 48 h. $^{31}$P MAS NMR of the resulting sample showed two signals, one at $\delta$ 55.3 ppm and another at 32.8 ppm. Literature values for $^{31}$P NMR chemical shifts of trialkylphosphines are upfield of -10 ppm. However, phosphine oxides are expected between 30 and 50 ppm.$^{19}$ So, the two signals appear to represent the phosphine oxide moiety in different chemical environments (i.e., possibly at SWNT sidewalls or ends). This effect is expected to be more pronounced in the case of the trialkylphosphine relative to the triphenylphosphine derivative simply due to closer physical proximity of phosphorus nucleus to SWNT. We repeated the oxygen transfer reaction for a week, assuming that the reaction had failed or that US-SWNT-PEt$_2$ had been re-oxidized during handling. The resulting $^{31}$P MAS NMR spectrum shows a single, broad peak at 30.2 ppm, near one of the signals (32 ppm) from the previous sample (Figure 1.4). It appears that phosphorus chemical shifts of US-SWNT-P(O)Et$_2$ and US-SWNT-PEt$_2$ are 55 ppm and ca. 30 ppm, respectively.

In general it is expected that, whatever the effect of the SWNTs, $^{31}$P chemical shift trends should follow the analogous starting materials. However, as seen in table 1.2, there is no apparent relationship with regard to $^{31}$P chemical shifts of SWNT-phosphine derivatives. Thus, it is not possible to make peak assignments with any degree of certainty. Many more phosphorus-SWNT derivatives must be examined before any real conclusions can be drawn.
Table 1.2. Experimental $^{31}$P MAS chemical shifts relative to expected values.

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ (ppm)</th>
<th>Lit. compound</th>
<th>δ (ppm)$^{19}$</th>
<th>Δ δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>US-SWNT-P(O)Ph$_2$ (1.11)</td>
<td>21</td>
<td>O=P(Ph)$_3$</td>
<td>25</td>
<td>-4</td>
</tr>
<tr>
<td>US-SWNT-PPh$_2$ (1.12)</td>
<td>5</td>
<td>P(Ph)$_3$</td>
<td>-5</td>
<td>+10</td>
</tr>
<tr>
<td>US-SWNT-P(S)Ph$_2$ (1.13)</td>
<td>-10</td>
<td>S=P(Ph)$_3$</td>
<td>60</td>
<td>-70</td>
</tr>
<tr>
<td>US-SWNT-P(O)Et$_2$ (1.14)</td>
<td>55</td>
<td>O=P(Et)$_3$</td>
<td>30</td>
<td>+25</td>
</tr>
<tr>
<td>US-SWNT-PEt$_2$ (1.15)</td>
<td>30</td>
<td>P(Et)$_3$</td>
<td>-10</td>
<td>+40</td>
</tr>
</tbody>
</table>

Finally, the $^{13}$C MAS NMR spectrum for SWNT-PEt$_2$ (1.15) was determined. The relative atomic concentration of sp$^3$ C from the phosphine compared to sp$^2$ SWNT C is small; however we were able to collect data with long acquisition times (ca. 40 h). There are 4 peaks present: the first at δ 169 ppm is assigned to carboxylic acid carbon, the second (δ = 121.8 ppm) represents SWNT sp$^2$ carbon. The peak at 50.7 indicates the P-CH$_2$-O carbon. Finally, carbon atoms of the ethyl groups are contained in an unresolved peak at 5.0 ppm (Figure 1.5).
Testing of SWNT derivatives for iron complexation. It is possible to both demonstrate the presence of complexing moieties, and also provide a semi-quantitative evaluation of the relative merits of the donor groups for complexation of a metal pro-catalyst species by the use of UV-visible spectroscopy. Samples of the functionalized SWNTs were added to a standard iron (III) solution in EtOH. Since all the SWNT samples are insoluble in ethanol, a reduction in the UV absorbance of Fe$^{3+}$ results from complexation of iron by the appropriate ligand.

The UV-vis spectral analysis of the uptake of Fe$^{3+}$ to any particular series of functionalized SWNTs indicated that the efficacy of binding is dependent on the presence and identity of the ligand moiety (Figure 1.6). As expected pyridine, phosphine, and thiol functionalized samples complexed more iron than etched (carboxylic acid) SWNTs. Raw (purified but unetched) nanotubes take up even less metal, although a small reduction in absorbance is observed, is presumably due to physisorption of metal to SWNT sidewalls. The thiol samples complexed more iron than either the phosphine or pyridine derivatives. In general, the phosphine and pyridine samples were comparable, however, the relative
efficacy was also found to be a function of presence of sidewall functional groups. Surprisingly, US-SWNTs were very similar to the DD-SWNT derivatives. We had expected better removal of iron from solution by US-SWNTs due simply to the higher relative numbers of ligands per tube. Our control functioned as expected. DD-SWNT-C₆H₄tBu complexed less metal than any of the other DD-SWNT-L derivatives including simple etched DD-SWNTs.

Figure 1.6. UV-visible spectra of standard Fe³⁺ solution (0.5 mM) in EtOH in the presence of 2 mg of (a) DD-SWNT-L, (b) SWNT-L, and (c) US-SWNT-L. The reduction in absorption is related to the adsorption of Fe³⁺ by the functionalized SWNTs, where L = py (---), SH (---), PPh₂ (---), C₆H₄tBu (---), and CO₂H (---).
Conclusions

Based upon the foregoing results it appears that ligand exchange offers a route to covalent attachment of a metal pro-catalyst such as FeMoC to the end of a SWNT-ligand via suitable pyridine, thiol, phosphine oxide, or carboxylic acid functional groups. Functionalized SWNTs react readily at 55 °C with FeMoC in EtOH/CHCl₃ and the resultant conjugates may be characterized by atomic force microscopy (AFM). For example, AFM images of DD-SWNT-SH-FeMoC show¹¹ that the FeMoC is at the end of the tubes and not attached along the sidewalls (Figure 1.7).

**Figure 1.7.** AFM image (500 x 500 nm) of DD-SWNT-SH-FeMoC showing the presence of the 2 nm FeMoC molecule on the end of an individual nanotube.¹¹

There are no clear trends with regard to the effects (whether through-bond or through-space) of covalent attachment of SWNTs to phosphine derivatives. Some
products showed chemical shifts as far upfield as 70 ppm (US-SWNT-P(S)Ph$_2$) from expected values, while others were downfield (40 ppm in the case of US-SWNT-PEt$_2$). Clearly much more work is needed in this area before any relationships can be established.

**Experimental**

Solvents were purchased from Fisher Scientific. CHCl$_3$ was washed with water and then distilled over CaCl$_2$ under nitrogen. Toluene was distilled over sodium under nitrogen. All other solvents were used as received. 2-aminoethanethiol, 4-dimethylaminopyridine, 4-hydroxyphenyldiphenylphosphine, 1,3-dicyclohexylcarbodiimide, thionyl chloride, FeCl$_3$, and paraformaldehyde were purchased from Aldrich Chemical and used as received. 4-hydroxypyridine was purchased from Aldrich Chemical and recrystallized from water.²⁰ 4-tert-buty1phenol was purchased from Fisher Scientific and recrystallized from hexanes. Diethylphosphine oxide was purchased from Digital Specialty Chemicals and used as received. All reagents were ACS grade or better. \[H_xPMo_{12}O_{40}CH_4Mo_72Fe_{30}(O_2CMe)_{15}O_{254}(H_2O)_{98}\] ("FeMoC") was prepared by a modification of literature methods.²¹ SWNTs were piranha etched according to the literature for 4 h at room temperature.⁶ DD-SWNTs and US-SWNTs were prepared according to the literature.⁷,¹² All reactions were carried out under dry N$_2$ or Ar using Schlenk techniques.

UV spectra were collected on a Varian Cary 400 spectrophotometer. XPS data were acquired on a Physical Electronics Phi Quantera instrument. Solution NMR data were acquired on 400 MHz or 500 MHz Bruker Avance spectrometers and solid state MAS NMR on a Bruker 200 MHz instrument using a 4 mm rotor. Atomic force microscopy measurements were obtained using a Digital Instruments NanoScope IIIa scanning probe microscope in tapping mode.
DD-SWNT-py (1.1). 1,3-dicyclohexylcarbodiimide (DCC, 269 mg, 1.30 mmol), 4-hydroxypyridine (126 mg, 1.32 mmol), and 4-dimethylaminopyridine (DMAP, 12 mg, 0.10 mmol) were dissolved in CHCl$_3$ (10 mL). Piranha etched DD-SWNTs (100 mL, 200 mg.L$^{-1}$) was added to the solution. The reaction was stirred overnight at room temperature. The SWNTs were filtered over a 0.2 µm PTFE membrane and resuspended in CHCl$_3$ (100 mL).

DD-SWNT-SH (1.2). DCC (200 mg, 0.97 mmol) and 2-aminoethanethiol (100 mg, 1.3 mmol) were dissolved in dry CHCl$_3$ (10 mL). The ligand/catalyst mixture was slowly added, with stirring, to Piranha etched DD-SWNTs (20 mg) resuspended in CHCl$_3$ (80 mL), and the reaction was stirred overnight at room temperature. The SWNTs were filtered over a PTFE membrane (0.2 µm) and dried under vacuum.

DD-SWNT-PPh$_2$ (1.3). DCC (168 mg, 0.81 mmol), DMAP (5 mg, 0.04 mmol) and 4-hydroxyphenyldiphenylphosphine (132 mg, 0.47 mmol) were dissolved in CHCl$_3$ (10 mL). The ligand/catalyst mixture was slowly added, with stirring, to Piranha etched DD-SWNTs (28 mg) suspended in CHCl$_3$ (80 mL), and the reaction was stirred overnight at room temperature. The SWNTs were filtered over a 0.2 µm PTFE membrane and dried under vacuum.

DD-SWNT-$C_6H_4$-Bu (1.4). DCC (420 mg, 2.0 mmol), 4-t-butylphenol (300 mg, 2.0 mmol), and DMAP (14 mg, 0.11 mmol) were dissolved in CHCl$_3$ (10 mL). Piranha etched DD-SWNTs (22 mg) were added to the solution. The reaction was stirred overnight at room temperature. The SWNTs were filtered over a 0.2 µm PTFE membrane and dried under vacuum.
**SWNT-py (1.5).** DCC (269 mg, 1.30 mmol), 4-hydroxypyridine (126 mg, 1.32 mmol), and DMAP (12 mg, 0.10 mmol) were dissolved in CHCl$_3$ (10 mL). Piranha etched SWNTs (100 mL, 200 mg.L$^{-1}$) in CHCl$_3$ was added to the solution. The reaction was stirred overnight at room temperature. The SWNTs were filtered over a 0.2 μm PTFE membrane and resuspended in CHCl$_3$ (100 mL).

**SWNT-SH (1.6).** Piranha etched SWNTs (20 mg) were suspended in CHCl$_3$ (80 mL). DCC (200 mg, 0.97 mmol) and 2-aminoethanethiol (100 mg, 1.3 mmol) were dissolved in dry CHCl$_3$ (10 mL). The ligand/catalyst mixture was slowly added, with stirring, to the SWNTs, and the reaction was stirred overnight at room temperature. The SWNTs were filtered over a 0.2 μm PTFE membrane and dried under vacuum.

**SWNT-PPh$_2$ (1.7).** Piranha etched SWNTs (28 mg) were suspended in CHCl$_3$ (80 mL). DCC (168 mg, 0.81 mmol), DMAP (5 mg, 0.04 mmol) and 4-hydroxyphenyldiphenylphosphine (132 mg, 0.47 mmol) were dissolved in dry CHCl$_3$ (10 mL). The ligand/catalyst mixture was slowly added, with stirring, to the SWNT suspension, and the reaction was stirred overnight at room temperature. The SWNTs were filtered over a 0.2 μm PTFE membrane and dried under vacuum.

**US-SWNT-C(O)Cl (1.8).** In a typical reaction, US-SWNTs (100-200 mg) were added to a Schlenk flask under N$_2$ with SOCl$_2$ (50 mL) and DMF (2 mL). The reaction mixture was stirred at 60 °C for 48 h under N$_2$. After decanting off the excess SOCl$_2$, the SWNTs were washed 3 times with dry CHCl$_3$ and then dried *in vacuo*.

**US-SWNT-py (1.9).** 4-hydroxypyridine (140 mg, 1.47 mmol) was dissolved in CHCl$_3$ (~20 mL) and the solution slowly added *via* cannula to US-SWNT-C(O)Cl (prepared fresh from 80 mg US-SWNTs) dispersed in CHCl$_3$ (25 mL). The reaction
mixture was stirred at 50 °C for 48 h. The SWNTs were then filtered over a 0.2 μm pore PTFE membrane and washed 3 times with dry CHCl₃. Finally the product was dried in vacuo overnight.

**US-SWNT-SH (1.10).** 2-aminoethanethiol (130 mg, 1.69 mmol) was dissolved in dry CHCl₃ (20 mL). The solution was slowly added via cannula to US-SWNT-C(O)Cl (prepared fresh from 80 mg US-SWNTs) dispersed in CHCl₃ (25 mL) and the reaction mixture was stirred at 50 °C for 48 h. The SWNTs were then filtered over a 0.2 μm pore PTFE membrane and washed 3 times with dry CHCl₃. The sample was dried in vacuo overnight.

**US-SWNT-P(O)Ph₂ (1.11).** CHCl₃ (25 mL) was added via cannula to the dried US-SWNT-C(O)Cl (prepared fresh from 110 mg US-SWNTs). 4-hydroxyphenyldiphenylphosphine (180 mg, 0.65 mmol) was dissolved in CHCl₃ (30 mL). The ligand solution was slowly added via cannula to the SWNT-C(O)Cl dispersion and the reaction mixture was stirred at 50 °C for 48 h. The SWNTs were then filtered over a 0.2 μm pore PTFE membrane and washed 3 times with dry CHCl₃. The product was dried in vacuo overnight. ³¹P MAS NMR: δ 20.4 (W₁/₂ = 1990 Hz).

**US-SWNT-PPh₂ (1.12).** US-SWNT-P(O)Ph₂ (250 mg), P(OEt)₃ (2 mL, 11.6 mmol) and HSiCl₃ (5 mL, 49.5 mmol) were added to degassed toluene (75 mL) under nitrogen. The reaction mixture was heated with stirring to 100 °C for 24 h. At that time the reaction mixture was allowed to cool and a portion (ca. 0.75 mL) of the supernatant was removed via syringe and placed into an NMR tube with C₆D₆ (ca. 0.2 mL). A solution ³¹P{¹H} NMR spectrum was collected and the relative peak areas of P(OEt)₃ (δ = 138.7) to O=P(OEt)₃ (δ = -1.4) were determined. The reaction was then resumed with
periodic NMR monitoring until there was no more increase in O=P(OEt)₃. The total reaction time was 48 h. ³¹P MAS NMR: δ 5.2 (W₁/₂ = 1830 Hz).

**US-SWNT-P(S)Ph₂ (1.13).** US-SWNT-PPh₃ (225 mg) was added to a round bottom flask with toluene (100 mL). Elemental sulfur (210 mg, 6.5 mmol) and pyridine (2 mL) were added to the reaction mixture. The reaction was refluxed with stirring for 18 h under N₂. After allowing the mixture to cool, the sample was vacuum filtered over a 0.2 μm pore PTFE membrane and washed 5 times with dry toluene. To ensure complete removal of residual sulfur, the sample was resuspended in toluene (100 mL) and sonicated for 15 min. The sample was then refiltered and washed an additional 5x with toluene. The reaction was repeated a second time for 90 hours and a third time for 1 week. ³¹P MAS NMR: δ -9.7 (W₁/₂ = 680 Hz).

**Et₂PH.** Prepared using a modification of the literature procedure.²² Diethylphosphine was formed from diethylphosphine oxide via a disproportionation reaction. An 80:1 molar ratio of diethylphosphine oxide (4.24 g, 40 mmol) to carbon tetrachloride (0.08 g, 0.5 mmol) was added to a Schlenk flask under Ar. The reaction mixture was slowly heated with stirring under Ar to 130°C. At this temperature diethylphosphine oxide decomposes, forming diethylphosphine and diethylphosphinic acid. The reaction vessel was then topped with a short-path condenser and receiving flask. Pure diethylphosphine was distilled into the receiver at 65 – 75 °C under Ar. ³¹P{¹H} NMR (CDCl₃): δ -53.6.

**Et₂PCH₂OH.** Prepared using a modification of the literature procedures.¹⁷,¹⁸ To a Schlenk flask under argon was added paraformaldehyde (0.30 g, 10 mmol) and methanol (150 mL). With stirring, PHEt₂ (0.92 g, 10 mmol) was added dropwise via
syringe to the reaction mixture. The reaction vessel was stirred 4 h at 25 - 30 °C under Ar. Methanol was then removed in vacuo. $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ -18.2.

**US-SWNT-P(O)Et$_2$ (1.14).** Dry CHCl$_3$ (~30 mL) was added via cannula to US-SWNT-C(O)Cl (prepared fresh from 120 mg US-SWNTs) in a Schlenk flask under nitrogen and then sonicated 5 min. Hydroxymethyldiethylphosphine (1.2 g, 10 mmol) was dissolved in dry CHCl$_3$ (~30 mL) in a Schlenk flask under nitrogen. The ligand solution was slowly added via cannula to the SWNT-C(O)Cl dispersion and the reaction mixture was stirred at 50 °C for 48 h. The SWNTs were then filtered over a 0.2 μm pore PTFE membrane and washed 3 times with dry CHCl$_3$. The product was dried in vacuo overnight. $^{31}$P MAS NMR: $\delta$ 55.3 ($W_{1/2} = 700$ Hz).

**US-SWNT-PEt$_2$ (1.15).** US-SWNT-P(O)Et$_2$ (250 mg), P(OEt)$_3$ (2 mL, 11.6 mmol) and HSiCl$_3$ (5 mL, 49.5 mmol) were added to degassed toluene (75 mL) under nitrogen. The reaction mixture was heated with stirring to 100 °C for 48 h. The reaction was then repeated for a total reaction time of 1 week. $^{31}$P MAS NMR: $\delta$ 30.2 ($W_{1/2} = 1520$ Hz). $^{13}$C MAS NMR: $\delta$ 169.0 [$W_{1/2} = 500$ Hz, SWNT-C(O)OCH$_2$P(Et)$_2$], 121.8 [$W_{1/2} = 640$ Hz, SWNT sp$^2$ C], 50.7 [$W_{1/2} = 680$ Hz, SWNT-C(O)OCH$_2$P(Et)$_2$], 5.0 [$W_{1/2} = 760$ Hz, P(CH$_2$CH$_3$)$_2$].

**Determination of metal complexation.** In order to eliminate dilution by the SWNT CHCl$_3$ dispersion and scattering by solid SWNTs, as well as provide a comparison between the various ligands, functionalized SWNTs (5.0 mg) were added to 5 mL of standard Fe$^{3+}$ solution (0.5 mM FeCl$_3$ in EtOH). The samples were sonicated 15 minutes and then filtered through a 0.2 μm pore PTFE syringe filter before collecting UV-vis spectra.
Complexation of FeMoC to functionalized SWNTs. FeMoC dissolved in EtOH (10 mL, 5 mg.mL\(^{-1}\)) was added to a sample of functionalized SWNTs (ca. 20 mg) in CHCl\(_3\) (100 mL). The sample was heated to 55 °C for 18 h. A drop of the solution was then spin coated onto a fresh mica surface for AFM characterization at 3,000 rpm for 40 sec.

References


B. Lippsmeier, K. Hestermann, and G. Heymer, German Pat., 2 413 825, 1975.


Chapter 2
Synthesis of Aryl Dipyridyl Amines and Related Compounds for Olefin and SWNT Separations

Introduction

Olefins are the largest volume feedstock in the petrochemical industry; as such their importance cannot be overstated. They serve as precursors to various products including polymers, acids, aldehydes, and alcohols. Current methods of separation of olefins from saturated hydrocarbons as well as separating individual olefin isomers involve cryogenic distillation, an extremely energy-intensive process. For example, the various isomers of n-octene differ in boiling range at atmospheric pressure by only 2 – 3 °C. The terminal isomer, 1-octene, is of tremendous value as a feedstock for hydroformylation reactions. Isolation of desired isomers from mixtures would clearly be of great economic impact.

Copper(I) compounds are known to bind olefins; in fact Cu(I) is found at the active site of ETR-1, an ethylene hormone receptor that regulates many aspects of plant development and growth. Histidine residues (an aromatic N-heterocyclic amino acid) ligate the copper center of ETR-1. Inorganic copper and silver salts have been used industrially to remove olefins from saturated hydrocarbons; however, stereoselective separation of individual olefin isomers has not yet been achieved.

Several Cu(I) complexes have been prepared with olefin separations as their goal. Unfortunately, difficulties exist with the previously known systems. For example, aqueous systems involving simple salts lack necessary long-term stability. Non-aqueous Cu(I) solutions using a pyridine solvent have proven difficult to handle due to the solvent and require large scale systems because the reagent is in the form of a slurry in the solvent. Cu(I) sulfonic acid reagents have proven too viscous for easy handling; furthermore the strong heats of absorption of these salts for olefins make decomplexation
difficult. The Cu(I) oxalate and Cu(I) fluorinated acetylacetonate systems possess significant drawbacks: the oxalate compound suffers from insufficient solubility while the acetylacetonate system exhibits low thermal stability. There exists the need for a complexing reagent that meets the following criteria: 1) high olefin complexing capacity while providing for easy desorption of the olefin, 2) a high solubility in an inert solvent, 3) is relatively stable, and 4) can be designed for the selective separation of different isomers. Based upon previous research in the Barron group, copper(I) dipyridylamine (dpa) complexes are promising candidates that meet the above criteria.\textsuperscript{6}

Functionalizing the central amine nitrogen of dpa with a bulky aromatic group (I) will alter the geometry about this nitrogen and therefore change the pyridyl-copper binding. We have proposed that this will in turn allow tuning of the copper-olefin interaction to permit selectivity. Additionally, by changing steric bulk on the pyridyl rings themselves (either one or both, II and III respectively), it may be possible to discriminate between cis- and trans-olefin isomers. Herein we describe the synthesis and characterization of N-aryl dipyridylamine ligands and related compounds to be investigated for the stereoselective separation of olefin isomers.

\begin{center}
\begin{tikzpicture}
  \tikzstyle{copper}=[circle, draw, fill=black, minimum size=1.5mm]
  \tikzstyle{nitrogen}=[circle, draw, fill=blue!50, minimum size=1.5mm]
  \tikzstyle{aromatic}=[draw, thick, rounded corners=1mm]

  \node[copper] (Cu) at (0,0) {Cu};
  \node[nitrogen] (N1) at (-1.5,-1.5) {N};
  \node[nitrogen] (N2) at (1.5,-1.5) {N};
  \node[aromatic] (pyr1) at (-2,-2) {\text{I}};
  \node[aromatic] (pyr2) at (2,-2) {\text{I}};

  \draw[thick] (Cu) -- (N1);
  \draw[thick] (Cu) -- (N2);
  \draw[thick] (N1) -- (pyr1);
  \draw[thick] (N2) -- (pyr2);
\end{tikzpicture}
\end{center}
While the original motivation of this work was olefin separations, another application has since been found. The observed folding of the pyridyl rings upon substitution at the amine nitrogen suggested that triarylamine derivatives could be used to π-stack with curved aromatic substrates such as single-walled carbon nanotubes. As described in Chapter 1, one of the remaining challenges of SWNT research is production of single chirality samples. To date there is no synthetic method to produce individual chiralities. Therefore, a vast amount of research has been focused on SWNT separations. Previous studies have involved selective covalent functionalization,⁷,⁸ density-gradient ultracentrifugation (DGU),⁹ dielectrophoresis,¹⁰ or polymer wrapping.¹¹ Another promising approach exploits noncovalent π-stacking between SWNTs and aromatics including porphyrins,¹² anthracenes,¹³ pyrene derivatives,¹⁴ and other polyaromatic hydrocarbons (PAHs).¹⁵

Phenyldiarylamines, where the aryl groups are PAHs, can interact with SWNTs in the same fashion, by π-π stacking. The phenyl group (appropriately functionalized) enhances solubility, while the polyaromatics π-stack with SWNTs in a cooperative manner, forming a “π-chelate” (Figure 2.1). By tuning the sterics at the ortho positions of the phenyl group, it is possible to warp the geometry about the amine nitrogen. Tuning the angle between the polyaromatics may allow selective π-stacking with, and consequent solubilization of particular diameter (or even chiral angle) SWNTs. In principle, this
route could provide single chirality samples, which could then be used to prepare SWNT-cats (Chapter 1).

**Figure 2.1.** Proposed ‘π-chelate’ interaction between SWNT and N-phenyl-N,N-di(1-naphthyl) amine, viewed along the axis of the SWNT.

**Results and Discussion**

**Aryl-dipyridylamines and related compounds.** Aryl dipyridylamines can be synthesized using Buchwald-Hartwig amination\(^{xvi,xvii,xviii}\) to couple aniline derivatives with halopyridines. The Ullmann condensation can also produce triarylamines although generally the chemistry suffers from poor yields.\(^{xix,xx}\) Buchwald-Hartwig catalyst complexes are typically formed *in-situ* from a palladium precursor and a phosphine or N-heterocyclic carbene ligand. The double addition of two pyridyl groups to aniline can be accomplished directly in a one-pot reaction although the single-addition product is always present in significant amounts, decreasing yields. Improved yields result from preparing the monoadduct pyridylamine in a separate reaction and then using it as a
precursor to dpa. In fact, palladium catalysis is unnecessary for the first addition, as aniline derivatives can directly attack halopyridines via nucleophilic aromatic substitution.\(^1\) Resultant pyridylamines can then be coupled to a second pyridyl group by the Buchwald-Hartwig reaction (Scheme 2.1). This two-step approach also allows the preparation of asymmetric products by the addition of a different N-donor group (e.g., quinolyl, II) in the second step.\(^2\)

![Scheme 2.1. Synthetic routes to ArN(py)\(_2\) ligands. (a) neat, reflux 2 h, (b-d) NaO\(^t\)Bu, Pd cat., toluene 90 °C, 120 h, and (e) neat, 180 °C, 2 h.](image)

\(N\)-aryl-\(N\)-(2-pyridyl) amines have been prepared where aryl = phenyl,\(^3\) mesityl (2.1), 2,6-diethylphenyl (2.2), 2,6-diisopropylphenyl,\(^4\) and 1-naphthyl,\(^5\) via nucleophilic aromatic substitution. The molecular structures of 2.1 and 2.2 were determined by XRD (Figure 2.2).\(^\text{21}\) These products serve as precursors to
dipyridylamines in order to improve product yields; additionally, they allow the preparation of asymmetric derivatives (II, above). Simple refluxing of the neat reactants, followed by neutralization, distillation, and recrystallization afforded all products in high yield. Attempts to prepare the bulkier 2,6-di-tert-butylphenyl derivative were unsuccessful.

Figure 2.2. Molecular structures of mesityl (2.1) and 2,6-diethylphenyl (2.2) 2-pyridylamines. Thermal ellipsoids are shown at the 30% level, and all hydrogen atoms are omitted (except amine protons) for clarity.  

$N$-aryl-$N,N$-di-2-pyridylamines were prepared by Buchwald-Hartwig coupling of aniline derivatives with two equivalents of 2-bromopyridine and an excess of sodium tert-butoxide. The catalyst complex was formed in-situ from tris-(dibenzylideneacetone) dipalladium $[\text{Pd}_2(\text{dba})_3]$ and $1,1'$-bis(diphenylphosphino)ferrocene (DPPF). Buchwald-Hartwig catalyst complexes are specific to particular reaction systems; as such there is no ‘all-purpose’ ligand. For aryl amination involving heterocycles, complexes of chelating bisphosphines are generally the most catalytically active. Also, palladium complexes of
N-heterocyclic carbenes (NHCs) have recently become common in Buchwald-Hartwig couplings.\(^{26}\) Several other ligands were screened in addition to DPPF: 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, and the carbene 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene. However, in the present system DPPF complexes consistently provided the highest catalytic activity for all dpas.

As already mentioned, product yields are not ideal for the double addition of two pyridyl groups; mono- to bis- adduct ratios are, at best, only \(\text{ca.} \ 1:2\). Moreover, separation of pyridylamine from the desired \(\text{ArN(py)}_2\) is nontrivial. Pyridylamines elute from the chromatographic column before \(\text{ArN(py)}_2\) by only a short time and they are prone to tailing; therefore resolution of compounds is difficult when large amounts of monoadducts are present.

Synthesis of dpas from precursor pyridylamines offers several advantages. First, dpa yields are much improved (>80% conversion by NMR), with isolated yields over 50%. Also, catalyst loading can be reduced (3 mol% with respect to pyridylamine) since only one catalytic event is required. Finally, chromatographic separation is simpler when low concentrations of byproducts are present. \(\text{N-aryl-N,di(2-pyridyl)}\)amines, where \(\text{aryl} = \text{phenyl}, \text{mesityl (2.3), 2,6-diethylphenyl (2.4), 2,6-diisopropylphenyl (2.5), and 1-naphthyl (2.6)},\) were prepared by the two-step method; 2.3 - 2.5 were also synthesized directly by Buchwald-Hartwig coupling with poor yields (see above and Experimental).\(^{27}\)

Preparation of aryl diquinolylamines \([\text{ArN(quin)}_2, \text{III}]) by our two-step method was not possible. The precursor material, 2-chloroquinoline, is not as thermally stable as 2-bromopyridine and consequently decomposes under the conditions necessary for nucleophilic aromatic substitution by aniline. Therefore, \(\text{ArN(quin)}_2\) derivatives were prepared in a single Buchwald-Hartwig reaction from the aniline derivatives and two equivalents of 2-chloroquinoline.\(^{28}\) Catalyst systems using the aforementioned DPPF and
Figure 2.3. Dipyridylamine structures: compounds 2.3, 2.4, 2.6, and 2.5 (clockwise from top left). Thermal ellipsoids are shown at the 30% level, and all hydrogen atoms are omitted for clarity.27

NHC ligands were both active towards the preparation of ArN(quin)₂ products. The coupling with 2,6- diisopropylaniline resulted in the expected diquinolylamine (2.7), shown in Figure 2.4. The product of the reaction between trimethylaniline and 2-chloroquinolinone was found by XRD to be an imine (see below).
Figure 2.4. Molecular structure of compound 2.7. Thermal ellipsoids are shown at the 30% level, and all hydrogen atoms are omitted for clarity.\textsuperscript{28}

**Imine formation.** Surprisingly, the major isolated product of the coupling between mesityl aniline and chloroquinoline was not the expected diquinolyamine, but an imine, quinolin-1-(2-quinolyl)-2-one mesitylimine (2.8). Based upon the generally accepted mechanism of Buchwald-Hartwig aryl amination\textsuperscript{18} the reaction step that will differentiate between the formation of compound 2.8 and the expected tertiary amine would be the formation of the C-N bond via reductive elimination with either a five-membered or three-membered transition state, respectively. In order to understand the partition between these reactions \textit{ab initio} calculations were performed on the intermediate.\textsuperscript{29}
Figure 2.5. Molecular structure of imine 2.8. Thermal ellipsoids are shown at the 30% level, and all hydrogen atoms are omitted for clarity.29

From calculations the palladium intermediate Pd(L)[N(Ar)quin](quin) (L = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene) for Ar = Ph, Mes, and 2,6-iPr₂C₆H₃ shows the structure of the global minimum to be the anti conformation (IV), in which the two quinoline rings are positioned anti with respect the Pd-N bond. In the case of the Ph and Mes derivatives the less stable syn conformation (V) exists as a local minimum, however, unreasonably close contacts are observed for this conformation for the 2,6-iPr₂C₆H₃ derivative making it energetically unlikely.

The relative calculated energies of the syn and anti conformations are given in Table 2.1. Clearly, reductive elimination from the energetically favored anti conformation must result in the formation of the expected tertiary amine.
However, reductive elimination can potentially occur from the *syn* conformation to form either the tertiary amine or the imine (i.e., 2.8). A consideration of the $C_{(\text{quin})} \cdots N$ distances in the *syn* conformation (Table 2.1) suggest that formation of the imine would be favored.\textsuperscript{29}

It is interesting to note that while the Mes derivative allows for the isolation of the imine, both the sterically less and more demanding groups (Ph and 2,6-$^3\text{Pr}_2\text{C}_6\text{H}_3$, respectively) result in the formation of the tertiary amine. As such the Mes derivative exists in a “sweet spot.” As may be seen from Figure 2.6, while the *anti* conformation is the more stable of the two conformers irrespective of the identity of the aryl substituent,
Table 2.1. Calculated N···C intramolecular distances and energies for syn and anti conformations.29

<table>
<thead>
<tr>
<th>R</th>
<th>N</th>
<th>N···C (Å)</th>
<th>Energy (Hartree)</th>
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<td></td>
<td></td>
<td>anti</td>
<td>syn</td>
</tr>
<tr>
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<td>3.11828</td>
</tr>
</tbody>
</table>

<sup>a</sup> Unreasonably close contacts observed.

the energy difference between anti and syn is smallest for the Mes derivative making it possible for it to be present in a finite concentration. The isolation of compound 2.8 versus the tertiary amine appears to be dependant on the identity of the substituents on the aniline’s aryl ring. We can postulate, therefore, that as a consequence of steric interactions between the 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene ligand and the Mes group, the syn conformation is energetically accessible, while the shorter N···C distance (Table 2.1) and orientation favor reductive elimination via a five-membered transition state.
Figure 2.6. Plot of relative energy of anti and syn conformations of Pd(L)[N(Ar)quin](quin) (L = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) as a function of the steric bulk of the aryl’s ortho substituents as measured by cone angle for Ar = Ph, Mes, and 2,6-iPr₂C₆H₃.

Triarylamines for SWNT separations. Triarylamines can be prepared by Buchwald-Hartwig amination\textsuperscript{16-18} in the same manner as dipyridylamines. However, there is no analogous reaction permitting the coupling of a single aryl halide to aniline. Therefore the double-addition of two aromatic groups to aniline must be performed in a single step. As previously discussed, there is always the presence of some single-addition product (negatively impacting yield). There are several ways to improve yields: using an excess of the aryl halide or increasing reaction time and catalyst loading. Tri-tert-butylphosphine Pd(0) complexes have been found to be versatile Buchwald-Hartwig catalysts for a wide variety of substrates;\textsuperscript{18} in the present system the catalyst produced the desired products in moderate yields (>60%).

\textit{N}-(4-dodecylphenyl)-\textit{N},\textit{N}-di(aryl)amines were prepared (Figure 2.7) where aryl = 1-naphthyl (2.9), 2-naphthyl (2.10), and 1-pyrenyl (2.11). The dodecylphenyl substituent is intended to enhance organic solubility of amine-SWNT π-complexes while the
polyaromatic groups adsorb to SWNT sidewalls via π-stacking. Products were characterized by $^1$H and $^{13}$C NMR and ESI MS. It was not possible to obtain crystal structures for any of the products, likely due to dodecyl chains hindering molecular packing. Compound 2.9 is a bright white solid while compound 2.11 is a yellow solid; both are highly fluorescent. Compound 2.10 is a pale yellow oil which discolored upon exposure to air.

![Chemical structures](image)

Figure 2.7. Triarylamine compounds 2.9, 2.10, and 2.11.

SWNTs were bath sonicated in the presence of excess triarylamines in order to form supramolecular complexes. Complexed SWNTs were then suspended in tetrahydrofuran (THF) and briefly centrifuged. The supernatant was collected, which contains solubilized SWNTs. The solubilized SWNTs (s-SWNTs) were then filtered in order to be compared with SWNTs remaining in the sediment residue (r-SWNTs).

The results of initial testing were disappointing: no SWNT solubilization was observed (i.e., after centrifugation nothing remained suspended) for any of the test compounds. Alteration of parameters including solvent, sonication time/ intensity, centrifugation speed/ time, and SWNT/ amine ratio had no discernible effect for either compound 2.10 or 2.11. Compound 2.9 (1-naphthyl derivative) does show the ability to suspend SWNTs; however, repeatability is poor.
After filtration of s-SWNTs from a successful trial of compound 2.9, Raman spectra were collected in order to determine diameter selectivity. The frequencies of SWNT radial breathing modes (RBMs) vary inversely with diameter, and thus Raman spectroscopy provides a direct method of diameter measurement. The RBM region of Raman spectra of s-SWNTs and r-SWNTs are different, indicating selective solubilization of certain tubes. However, there is no apparent diameter dependence based on Raman alone (Figure 2.8).

![Raman Spectra](image)

**Figure 2.8.** Raman spectra (785 nm excitation) of s-SWNTs (red) and r-SWNTs (blue). Intensities are normalized to G-band (not shown), y-axis arb units.

The π-complexing process was repeated twice more with residual material (r-SWNTs). Raman of the second s-SWNT sample is identical to the first; the third iteration resulted in no further solubilization. Based upon these results, it appears that compound 2.9 is able to interact selectively with particular helicity SWNTs. However, corroborating evidence is needed as well as improvements in repeatability.

Fluorescence spectroscopy is the best method of identifying individual chiralities in SWNT samples (although metallic SWNTs cannot be observed). To obtain
fluorescence data it is necessary to individually suspend SWNTs in surfactant solutions. To that end, s-SWNTs were treated with oleum in order to remove adsorbed triarylamine. After neutralization of the acid, SWNTs were suspended in 1% SDS solution. It was not possible to obtain homogeneous SDS suspensions of adequate concentration for fluorescence spectroscopy. Attempts to repeat the solubilization procedure on a larger scale have so far been unsuccessful.

Conclusions

We have demonstrated that Buchwald-Hartwig aryl amination provides a convenient route to aryl dipyridylamine ligands and related compounds. Further, asymmetric derivatives may be prepared by first preparing pyridylamine precursors via nucleophilic aromatic substitution. Ligands described here have been used to prepare copper (I) complexes, which can selectively bind specific olefin isomers in a liquid-liquid extraction process.\textsuperscript{31}

We have adapted the chemistry described above to prepare triarylamines for SWNT separations. While initial results have been somewhat limited, this approach has the potential to allow diameter or even chiral-specific separations. Separations will be critical to production of bulk samples via SWNT amplification.

Experimental

Solvents were purchased from Fisher Scientific. CHCl\(_3\) was washed with water and then distilled over CaCl\(_2\) under nitrogen. Toluene was distilled over sodium under nitrogen and degassed by freeze-pump-thaw prior to use. All other solvents were distilled over Na/benzophenone. Aniline, 2,4,6-trimethylaniline, 2,6-diethylaniline, 2,6-diisopropylaniline, 1-naphthylamine, 4-dodecylaniline, 2-bromopyridine, 2-chloropyridine, 2-chloroquinoline, 2-aminopyridine, 1-bromonaphthalene, 2-bromonaphthalene, 1-bromopyrene, \textit{tris}-(dibenzyldieneacetone) dipalladium [Pd\(_2\)(dba)\(_3\)],
1,1'-bis(diphenylphosphino)ferrocene, allyl[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]palladium(II) chloride, tri-tert-butylphosphine, sodium tert-butoxide, sodium carbonate, and potassium tert-butoxide were purchased from Aldrich or Alfa Aesar and were used as received. All reagents were ACS grade or better. All manipulations were performed under Ar or N$_2$ atmospheres using standard Schlenk line techniques. N-phenyl-N-(2-pyridyl)amine was prepared by the literature procedure,$^{23}$ as was N-(1-naphthyl)-N-(2-pyridyl)amine.$^{25}$ $^1$H NMR and $^{13}$C NMR spectra were obtained at room temperature using Bruker Avance 400 and 500 MHz spectrometers. Chemical shifts are reported relative to internal solvent resonances. IR spectra were obtained using a Nicolet FTIR spectrometer equipped with ATR accessory. Electrospray MS analyses were performed with a Bruker MicroTOF mass spectrometer. Electron-impact MS analyses were performed using an Agilent Technologies 5973 network mass selective detector, equipped with 6890N network GC system. XRD.

All electron molecular orbital (MO) calculations were performed using the Gaussian 03, revision C.02 (Windows version), suite of programs.$^{32}$ Geometry optimization on Pd(L)[N(Ar)quin](quin) (Ar = Ph, Mes, 2,6-iPr$_2$C$_6$H$_3$) was carried out at the Hartree-Fock level with the 3-21G basis set.$^{33}$

$^N$-Mesityl-N-(2-pyridyl)amine (2.1). 2-Bromopyridine (9.5 g, 60 mmol) and 2,4,6-trimethylaniline (16.2 g, 120 mmol) were added to a round bottom flask topped with a reflux condenser. The reaction flask was heated under reflux for 2 h. The reaction mixture was then made alkaline with a saturated solution of Na$_2$CO$_3$ followed by steam distillation to remove excess reactants. The reaction mixture was extracted with Et$_2$O. After removal of solvent in vacuo the crude product was recrystallized twice from EtOH. Yield = 10 g (79 %). ESI MS: m/z 213.1 (M+H$^+$). FTIR (neat, ATR, cm$^{-1}$): 3189 (w, N-H), 3151 (w), 3089 (w, aromatic v$_{C-H}$), 2996 (w, alkyl v$_{C-H}$), 2918 (w, alkyl v$_{C-H}$), 2851 (w, alkyl v$_{C-H}$), 1589 (s, N-H), 1515 (s), 1450-1325 (s, aromatic $\delta_{C=C}$), 1225 (m), 1150...
(m), 993 (m), 850 (s), 817 (s), 775 (s). $^1$H NMR: $\delta$ 8.11 [1H, d, $J$(H-H) = 5 Hz, pyridyl CH], 7.39 [1H, t, $J$(H-H) = 7 Hz, pyridyl CH], 6.96 [2H, s, mesityl CH], 6.63 [1H, t, $J$(H-H) = 6 Hz, pyridyl CH], 6.42 [1H, br s, NH], 6.04 [1H, d, $J$(H-H) = 8 Hz, pyridyl CH], 2.31 [3H, s, mesityl p-CH$_3$], 2.19 [6H, s, mesityl o-CH$_3$]. $^{13}$C($^1$H) NMR: $\delta$ 157.9 (CN), 147.4 (CN), 138.6 (CN), 136.8 (CCH$_3$), 136.7 (CH), 133.6 (CCH$_3$), 129.5 (m-CH), 113.6 (CH), 106.3 (CH), 21.4 (p-CH$_3$), 18.8 (o-CH$_3$).

$^-(Z^-)$DiethylphenyO-$^N^-$(2-pyridyO)amine (2.2). 2-Bromopyridine (20 g, 127 mmol) and 2,6-diethylaniline (37 g, 248 mmol) were added to a round bottom flask topped with a reflux condenser. The reaction flask was heated under reflux for 2 h. The reaction mixture was then made alkaline with a saturated solution of Na$_2$CO$_3$ followed by steam distillation to remove excess reactants. The reaction mixture was extracted with Et$_2$O. After removal of solvent in vacuo the crude product was recrystallized twice from absolute EtOH. Yield = 21 g (73 %). ESI MS: $m/z$ 221.1 (M+H$^+$). FTIR (neat, ATR, cm$^{-1}$): 3200 (w, v N-H), 3084 (w, aromatic v C-H), 2960 (m, alkyl v C-H), 2934 (m, alkyl v C-H), 2876 (w, alkyl v C-H), 1599 (s, $\delta$ N-H), 1586 (s), 1574 (s), 1518-1325 (s, aromatic $\delta_{C=C}$), 1288 (m), 1252 (w), 1148 (m), 990 (s), 867 (m), 805 (m), 767 (vs). $^1$H NMR: $\delta$ 8.13 [1H, d, $J$(H-H) = 5 Hz, pyridyl CH], 7.35 [1H, t, $J$(H-H) = 8 Hz, pyridyl CH], 7.25 [1H, d, $J$(H-H) = 7 Hz, arom. CH], 7.19 [2H, d, $J$(H-H) = 7 Hz, arom. CH], 6.62 [1H, t, $J$(H-H) = 6 Hz, pyridyl CH], 6.35 [1H, br s, NH], 6.00 [1H, d, $J$(H-H) = 8 Hz, pyridyl CH], 2.61 [4H, q, $J$(H-H) = 7 Hz, CH$_2$CH$_3$], 1.15 [6H, t, $J$(H-H) = 7 Hz, CH$_2$CH$_3$]. $^{13}$C($^1$H) NMR: $\delta$ 158.6 (CN), 148.3 (CN), 143.1 (CH), 138.0 (CN), 135.2 (CCH$_2$), 127.6 (p-CH), 127.0 (m-CH), 113.6 (CH), 105.9 (CH), 24.9 (CH$_2$CH$_3$), 14.7 (CH$_2$CH$_3$).

$^-(2,6$-Diethylphenyl)-$^N^-$(2-pyridyl)amine. Prepared using a modified literature procedure. 2-Bromopyridine (9.5 g, 60 mmol) and 2,6-diisopropylaniline (21 g, 120 mmol) were added to a round bottom flask topped with a reflux condenser. The
reaction flask was heated under reflux for 2 h. The reaction mixture was then made basic with a saturated solution of Na₂CO₃ followed by steam distillation to remove excess reactants. The reaction mixture was extracted with Et₂O. After removal of solvent in vacuo the crude product was recrystallized twice from absolute EtOH.

**N-phenyl-N,N-di(2-pyridyl)amine.** Prepared using a modified literature procedure.³⁴ In a drybox, sodium tert-butoxide (550 mg, 5.7 mmol), Pd₂(dba)₃ (55 mg, 0.06 mmol), and DPPF (83 mg, 0.15 mmol) were added to a Schlenk flask. Toluene (5 mL) was added; the flask was topped with a septum and removed from the drybox. 2-Bromopyridine (700 mg, 4.4 mmol) and aniline (185 mg, 2.0 mmol) were injected via syringe into the reaction vessel. The reaction was stirred under nitrogen at 90 °C for 48 h. After cooling, CH₂Cl₂ (50 mL) was added, the mixture was filtered, and then solvent was removed in vacuo. The crude product was purified by flash chromatography on silica gel (eluent: 2% MeOH in CH₂Cl₂) followed by recrystallization from hexanes/Et₂O.

**N-mesityl-N,N-di(2-pyridyl)amine (2.3). Method 1.** In a drybox, to a Schlenk flask were added sodium tert-butoxide (550 mg, 5.7 mmol), Pd₂(dba)₃ (55 mg, 0.06 mmol), DPPF (83 mg, 0.15 mmol), and toluene (5 mL). The flask was topped with a septum and removed from the drybox. 2-Bromopyridine (700 mg, 4.4 mmol) and 2,4,6-trimethylaniline (270 mg, 2.0 mmol) were injected via syringe into the reaction vessel. The reaction was stirred under nitrogen at 90 °C for 120 h. After cooling, CH₂Cl₂ (50 mL) was added, the mixture was filtered, and then solvent was removed in vacuo. The crude product was purified by flash chromatography on silica gel (eluent: 2% MeOH in CH₂Cl₂) followed by recrystallization from hexanes.

**Method 2.** In a drybox, to a Schlenk flask were added N-mesityl-N-(2-pyridyl)amine (2.1, 2.12 g, 10 mmol), sodium tert-butoxide (1.53 g, 16 mmol), Pd₂(dba)₃ (137 mg, 0.15 mmol), DPPF (166 mg, 0.30 mmol), and toluene (15 mL). The flask was
topped with a septum and removed from the drybox. 2-Bromopyridine (1.89 g, 12 mmol) was injected via syringe into the reaction vessel. The reaction was stirred under nitrogen at 90 °C for 120 h. After cooling, CH₂Cl₂ (100 mL) was added, the mixture was filtered, and then solvent was removed in vacuo. The crude product was purified by column chromatography on neutral alumina (eluent: 0 – 2 % MeOH in CH₂Cl₂). Recrystallization from hexanes resulted in 60% yield. MS (EI, %): m/z 289 (M⁺, 13.2), 274 (M⁺-Me, 100). FTIR (neat, ATR, cm⁻¹): 3150 (w, aromatic νC-H), 3068 (w, aromatic νC-H), 3048 (w, aromatic νC-H), 3004 (w, aromatic νC-H), 2972 (w, alkyl νC-H), 2916 (w, alkyl νC-H), 2854 (w, alkyl νC-H), 1584 (s), 1563 (m), 1463-1319 (s, aromatic δC=CH), 1257 (m, aromatic δC=N), 1147 (s), 988 (s). ¹H NMR (CD₃OD): δ 8.17 [2H, ddd, J(H-H) = 5.0 Hz, J(H-H) = 1.9 Hz, J(H-H) = 0.7 Hz, 6,6'-Py], 7.65 [2H, ddd, J(H-H) = 8.6 Hz, J(H-H) = 7.2 Hz, J(H-H) = 1.9 Hz, 4,4'-Py], 7.01 (2H, s, m-MesH), 6.98 [2H, ddd, J(H-H) = 7.2 Hz, J(H-H) = 5.0 Hz, J(H-H) = 0.9 Hz, 5,5'-Py], 6.88 [2H, ddd, J(H-H) = 8.6 Hz, J(H-H) = 0.9 Hz, J(H-H) = 0.7 Hz, 3,3'-Py], 2.33 (3H, s, p-CH₃), 1.96 (6H, s, o-CH₃). ¹³C{¹H} NMR (CD₃OD): δ 158.03, 148.74, 139.79, 139.74, 139.24, 138.49, 131.23, 119.01, 116.43, 21.28, 18.66.

N-(2,6-diethylphenyl)-N,N-di(2-pyridyl)amine (2.4). In a drybox, to a Schlenk flask were added N-(2,6-diethylphenyl)-N-(2-pyridyl)amine (2.2, 2.26 g, 10 mmol), sodium tert-butoxide (1.53 g, 16 mmol), Pd₂(db₃)₃ (137 mg, 0.15 mmol), DPPF (166 mg, 0.30 mmol), and toluene (15 mL). The flask was topped with a septum and removed from the drybox. 2-Bromopyridine (1.89 g, 12 mmol) was injected via syringe into the reaction vessel. The reaction was stirred under nitrogen at 90 °C for 120 h. After cooling, CHCl₃ (50 mL) was added, the mixture was filtered, and then solvent was removed in vacuo. The crude product was purified by column chromatography on neutral alumina (eluent: 0.75% EtOH in CHCl₃) followed by recrystallization from hexanes/Et₂O. Yield = 0.77 g (25%). MS (EI, %): m/z 303 (M⁺, 2.2), (M⁺-Et, 100). FTIR (neat, ATR, cm⁻¹): 3151 (w, aromatic
$\nu_{C-H}$, 3069 (w, aromatic $\nu_{C-H}$), 3048 (w, aromatic $\nu_{C-H}$), 3003 (w, aromatic $\nu_{C-H}$), 2972 (w, alkyl $\nu_{C-H}$), 2956 (w, alkyl $\nu_{C-H}$), 2911 (w, alkyl $\nu_{C-H}$), 2877 (w, alkyl $\nu_{C-H}$), 1618 (m), 1584 (s), 1561 (m), 1465-1319 (s, aromatic $\delta_{C=C}$), 1279 (m, aromatic $\delta_{C=N}$), 1150 (m), 987 (m). $^1$H NMR (CDCl$_3$): $\delta$ 8.28 [2H, ddd, $J(H-H) = 5.0$ Hz, $J(H-H) = 2.0$ Hz, $J(H-H) = 0.8$ Hz, 6,6'-Py], 7.49 [2H, ddd, $J(H-H) = 8.4$ Hz, $J(H-H) = 7.2$ Hz, $J(H-H) = 2.0$ Hz, 4,4'-Py], 7.34 [1H, dd, $J(H-H) = 7.7$ Hz, $J(H-H) = 7.7$ Hz, p-PhH], 7.23 [2H, d, $J(H-H) = 7.7$ Hz, m-PhH], 6.94 [2H, ddd, $J(H-H) = 8.4$ Hz, $J(H-H) = 0.9$ Hz, $J(H-H) = 0.8$ Hz, 3,3'-Py], 6.83 [2H, ddd, $J(H-H) = 7.2$ Hz, $J(H-H) = 5.0$ Hz, $J(H-H) = 0.9$ Hz, 5,5'-Py], 2.44 [4H, q, $J(H-H) = 7.6$ Hz, CH$_2$CH$_3$], 0.96 [6H, t, $J(H-H) = 7.6$ Hz, CH$_2$CH$_3$]. $^{13}$C($^1$H) NMR (CDCl$_3$): $\delta$ 157.11, 148.24, 143.28, 140.36, 137.35, 128.44, 127.21, 117.17, 114.76, 24.43, 13.90.

$N$-(2,6-diisopropylphenyl)-$N$,$N$-di(2-pyridyl)amine (2.5). Method 1. In a drybox, to a Schlenk flask were added sodium tert-butoxide (550 mg, 5.7 mmol), Pd$_2$(dba)$_3$ (55 mg, 0.06 mmol), DPPF (83 mg, 0.15 mmol), and toluene (5 mL). The flask was topped with a septum and removed from the drybox. 2-Bromopyridine (700 mg, 4.4 mmol) and 2,6-diisopropylaniline (355 mg, 2.0 mmol) were injected via syringe into the reaction vessel. The reaction was stirred under nitrogen at 90 °C for 96 h. After cooling, 50 mL of CH$_2$Cl$_2$ was added, the mixture was filtered, and then solvent was removed in vacuo. The crude product was purified by flash chromatography on silica gel (eluent: 2% MeOH in CH$_2$Cl$_2$) followed by recrystallization by vapor diffusion of n-pentane into a saturated CHCl$_3$ solution.

Method 2. In a drybox, to a Schlenk flask were added $N$-(2,6-diisopropylphenyl)-$N$-(2-pyridyl)amine (2.54 g, 10 mmol), sodium tert-butoxide (1.53 g, 16 mmol), Pd$_2$(dba)$_3$ (137 mg, 0.15 mmol), DPPF (166 mg, 0.30 mmol), and toluene (15 mL). The flask was topped with a septum and removed from the drybox. 2-Bromopyridine (1.89 g, 12 mmol) was injected via syringe into the reaction vessel. The reaction was stirred under
nitrogen at 90 °C for 120 h. After cooling CH\textsubscript{2}Cl\textsubscript{2} (100 mL) was added, the mixture was filtered, and then solvent was removed in vacuo. The crude product was purified by column chromatography on neutral alumina (eluent: 0 – 2 % MeOH in CH\textsubscript{2}Cl\textsubscript{2}) followed by recrystallization from hexanes. Yield = 1.6 g (50%). MS (EI, %): m/z 331 (M\textsuperscript{+}, 0.8), 288 (M\textsuperscript{+}-iPr, 100). FTIR (neat, ATR, cm\textsuperscript{-1}): 3178 (w, aromatic ν\textsubscript{C-H}), 3057 (w, aromatic ν\textsubscript{C-H}), 3008 (w, aromatic ν\textsubscript{C-H}), 2959 (w, alkyl ν\textsubscript{C-H}), 2926 (w, alkyl ν\textsubscript{C-H}), 2867 (w, alkyl ν\textsubscript{C-H}), 1595 (m), 1584 (s), 1527 (m), 1467-1328 (s, aromatic δ\textsubscript{C=C}), 1255 (m, aromatic δ\textsubscript{C=N}), 1147(m), 989 (m). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): δ 8.27 [2H, ddd, J(H-H) = 5.0 Hz, J(H-H) = 1.9 Hz, J(H-H) = 0.8 Hz, 6,6\textsuperscript{'}-Py], 7.50 [2H, ddd, J(H-H) = 8.4 Hz, J(H-H) = 7.2 Hz, J(H-H) = 1.9 Hz, 4,4\textsuperscript{'}-Py], 7.42 [1H, dd, J(H-H) = 7.7 Hz, J(H-H) = 7.7 Hz, p-PhH]), 7.27 [2H, d, J(H-H) = 7.7 Hz, m-PhH], 6.96 [2H, ddd, J(H-H) = 8.4 Hz, J(H-H) = 0.9 Hz, J(H-H) = 0.8 Hz, 3,3\textsuperscript{'}-Py], 6.82 [2H, ddd, J(H-H) = 7.2 Hz, J(H-H) = 5.0 Hz, J(H-H) = 0.9 Hz, 5,5\textsuperscript{'}-Py], 3.09 [2H, sept, J(H-H) = 6.9 Hz, CH(CH\textsubscript{3})\textsubscript{2}], 0.95 [12H, d, J(H-H) = 6.9 Hz, CH(CH\textsubscript{3})\textsubscript{2}]. \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (CDCl\textsubscript{3}): δ 157.45, 148.13, 148.00, 138.45, 137.23, 129.03, 124.92, 117.12, 114.99, 28.67, 23.94.

\textbf{N-(1-naphthyl)-N,N-di(2-pyridyl)amine (2.6).} In a drybox, to a Schlenk flask were added N-(1-naphthyl)-N-(2-pyridyl)amine (2.20 g, 10 mmol), sodium tert-butoxide (1.53 g, 16 mmol), Pd\textsubscript{2}(dba)\textsubscript{3} (137 mg, 0.15 mmol), DPPF (166 mg, 0.30 mmol), and toluene (15 mL). The flask was topped with a septum and removed from the drybox. 2-Bromopyridine (1.89 g, 12 mmol) was injected via syringe into the reaction vessel. The reaction was stirred under nitrogen at 90 °C for 120 h. After cooling, CH\textsubscript{2}Cl\textsubscript{2} (50 mL) was added, the mixture was filtered, and then solvent was removed in vacuo. The crude product was purified by flash chromatography on neutral alumina (eluent: 0.75% ethanol in chloroform) followed by recrystallization from hexanes/Et\textsubscript{2}O (yield: 1.37 g, 46 %). MS (EI, %): m/z 297 (M\textsuperscript{+}, 41.9), 296 (M\textsuperscript{+}-H, 100). FTIR (neat, ATR, cm\textsuperscript{-1}): 3129 (w, aromatic ν\textsubscript{C-H}), 3074 (w, aromatic ν\textsubscript{C-H}), 3044 (w, aromatic ν\textsubscript{C-H}), 2992 (w, aromatic
\( \nu_{\text{C-H}}, 2975 \text{ (w, aromatic } \nu_{\text{C-H}}), 2910 \text{ (w), 1583 \text{ (s), 1559 \text{ (m), 1462-1314 \text{ (s, aromatic } \delta_{\text{C=N}})}, 1267 \text{ (m, aromatic } \delta_{\text{C=N}}), 1151 \text{ (m), 990 \text{ (m).} } \)

\( ^1\text{H NMR (CDCl}_3\text{): } \delta 8.34 \text{ [2H, ddd, } J(\text{H-H}) = 5.0 \text{ Hz, } J(\text{H-H}) = 2.0 \text{ Hz, } J(\text{H-H}) = 0.8 \text{ Hz, 6,6'-Py}], 7.91 \text{ [1H, d, } J(\text{H-H}) = 8.2 \text{ Hz, naph CH}], 7.88 \text{ [1H, d, } J(\text{H-H}) = 8.2 \text{ Hz, naph CH}], 7.84 \text{ [1H, ddd, } J(\text{H-H}) = 8.5 \text{ Hz, } J(\text{H-H}) = 1.8 \text{ Hz, } J(\text{H-H}) = 0.9 \text{ Hz, naph CH}], 7.55 \text{ [1H, dd, } J(\text{H-H}) = 8.2 \text{ Hz, } J(\text{H-H}) = 7.2 \text{ Hz, naph CH}], 7.49 \text{ [2H, ddd, } J(\text{H-H}) = 8.4 \text{ Hz, } J(\text{H-H}) = 7.3 \text{ Hz, } J(\text{H-H}) = 2.0 \text{ Hz, 4,4'-Py}], 7.47 \text{ [2H, m, naph CH}], 7.37 \text{ [1H, ddd, } J(\text{H-H}) = 8.3 \text{ Hz, } J(\text{H-H}) = 6.9 \text{ Hz, } J(\text{H-H}) = 1.2 \text{ Hz, naph CH}], 6.90 \text{ [2H, ddd, } J(\text{H-H}) = 8.4 \text{ Hz, } J(\text{H-H}) = 1.0 \text{ Hz, } J(\text{H-H}) = 0.8 \text{ Hz, 3,3'-Py}], 6.89 \text{ [2H, ddd, } J(\text{H-H}) = 7.3 \text{ Hz, } J(\text{H-H}) = 5.0 \text{ Hz, } J(\text{H-H}) = 1.0 \text{ Hz, 5,5'-Py}] \}

\( ^{13}\text{C}[^1\text{H}] \text{ NMR (CDCl}_3\text{): } \delta 158.14, 148.30, 137.87, 135.45, 131.61, 128.76, 128.17, 127.87, 127.13, 126.62, 126.53, 123.78, 117.88, 115.98. \)

\( \text{N-(2,6-diisopropylphenyl)-N,N-di(2-quinolyl)amine (2.7).} \)

\( 2,6\)-diisopropyl aniline (2.464 g, 13.9 mmol), sodium tert-butoxide (3.340 g, 34.7 mmol), Pd\( _2\)(dba)\(_3\) (0.191 g, 0.21 mmol), and DPPF (0.231 g, 0.42 mmol) were added to a Schlenk flask in a drybox. The flask was capped with a septum, removed from the drybox, and toluene (200 mL) was added via cannula. The mixture was stirred, and 2-chloroquinoline (5.005 g, 30.5 mmol) was injected via syringe into the reaction vessel. The reaction was stirred under nitrogen at 90 °C for 96 hours. After cooling, CHCl\(_3\) (50 mL) was added, the mixture was filtered, and the solvent was removed under vacuum. The crude product was purified by column chromatography on neutral alumina (eluent: 0.75% ethanol in chloroform), followed by recrystallization by a slow evaporation of a solution in Et\(_2\)O.

\( \text{Yield: 2.95 g (49%). Mp (TGA; sublim.): 143-144 °C. MS (EI,%) m/z 431 (M+), 1.4), 388 (M+ - \text{1Pr}, 100). FTIR (neat, ATR, cm}^{-1}\): 3061 (w, aromatic } \nu_{\text{C-H}}, 3041 (w, aromatic } \nu_{\text{C-H}}, 2961 (m, alkyl } \nu_{\text{C-H}}, 2924 (m, alkyl } \nu_{\text{C-H}}, 2866 (m, alkyl } \nu_{\text{C-H}}, 1707 (m), 1618 (m), 1598 (s), 1562 (m), 1502 (s), 1465-1321 (s, aromatic } \delta_{\text{C=N}}), 1290 (vs, aromatic } \delta_{\text{C=N}}), 1256 (m), 1182 (m), 1141 (m), 1055 (m), 968 (m), 814 (vs). } ^1\text{H NMR} \)
Quinolin-1-(2-quinolyl)-2-one mesitylimine (2.8). In a drybox, potassium tert-butoxide (785 mg, 7.0 mmol), allyl[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]palladium(II) chloride (70 mg, 0.12 mmol), and 2-chloroquinoline (818 mg, 5.0 mmol) were added to a Schlenk flask. To this was added toluene (10 mL) followed by 2,4,6-trimethylaniline (338 mg, 2.5 mmol). The reaction was stirred under nitrogen at 70 °C for 120 h. After cooling, Et₂O (25 mL) was added to the reaction mixture and then washed twice with brine. The organic phase was dried over sodium sulfate before removing solvent in vacuo. The crude product was purified by flash chromatography on silica gel (eluent: 10% ethyl acetate in hexanes). The product was dissolved in hot hexanes and allowed to cool to room temperature. Subsequent cooling to −12 °C over several days resulted in the formation of crystals suitable for X-ray analysis. Yield 0.276 g (28% isolated). IR (ATR, cm⁻¹): 3058 (w, aromatic ν₇.₇-H), 3030 (w, aromatic ν₇.₇-H), 2971 (w, alkene ν₇.₇-H), 2935 (w, alkene ν₇.₇-H), 2912 (w, alkyl ν₇.₇-H), 2851 (w, alkyl ν₇.₇-H), 1631 (m, νC=N), 1591 (s), 1572 (s), 1425 (s, aromatic δC=C and δC=N), 1327 (s, νC-N), 820 (s). ¹H NMR (CD₃OD): δ 8.68 [1H, d, J(H-H) = 8.5 Hz, CH], 8.10 [2H, d, J(H-H) = 8.5 Hz, CH], 7.86 [1H, dd, J(H-H) = 7.0 Hz, J(H-H) = 1.4 Hz, CH], 7.73 [1H, dd, J(H-H) = 7.0 Hz, J(H-H) = 1.4 Hz, CH], 7.66 [1H, d, J(H-H) = 8.5 Hz, CH], 7.52 [1H, d,
6.19 [1H, d, J(H-H) = 9.8 Hz, CH], 2.20 (3H, s, p-CH$_3$), 2.02 (6H, s, o-CH$_3$).

$N$-(4-dodecylphenyl)-$N,N$-di(1-naphthyl)amine (2.9). 4-Dodecylaniline (1.04 g, 4.0 mmol), sodium tert-butoxide (1.16 g, 12.1 mmol), Pd$_2$(dba)$_3$ (72 mg, 0.08 mmol), tritiert-butylphosphine (32 mg, 0.16 mmol), and toluene (10 mL) were added to a Schlenk flask in a drybox. The flask was topped with a septum and removed from the drybox. 1-Bromonaphthalene (1.66 g, 8.0 mmol) was injected via syringe into the reaction vessel. The reaction was stirred under nitrogen at 90 °C for 1 week. After cooling, CHCl$_3$ (50 mL) was added, the mixture was filtered, and then solvent was removed in vacuo. The crude product was purified by flash chromatography on silica gel (eluent: 10% ethyl acetate in hexanes). Yield 1.68 g (82%) of a bright white powder. ESI MS: m/z 514.4 (M+H$^+$). $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 8.08 [2H, d, J(H-H) = 8.4 Hz, arom. CH], 7.90 [2H, d, J(H-H) = 8.2 Hz, arom. CH], 7.70 [2H, d, J(H-H) = 8.1 Hz, arom. CH], 7.46 [2H, dt, J(H-H) = 7.6 Hz, J(H-H) = 1.2 Hz, arom. CH], 7.38 [2H, t, J(H-H) = 8.0 Hz, arom. CH], 7.31 [2H, dt, J(H-H) = 8.0 Hz, J(H-H) = 1.4 Hz, arom. CH], 7.18 [2H, dd, J(H-H) = 8.1 Hz, J(H-) = 1.2 Hz, arom. CH], 6.97 [2H, d, J(H-H) = 8.0 Hz, arom. CH], 6.69 [2H, dt, J(H-H) = 8.0 Hz, J(H-H) = 2.0 Hz, arom. CH], 2.53 [2H, t, J(H-H) = 7.0 Hz, PhCH$_2$CH$_2$(CH$_2$)$_9$CH$_3$], 1.59 [2H, p, J(H-H) = 7.0 Hz, PhCH$_2$CH$_2$(CH$_2$)$_9$CH$_3$], 1.30 [18H, br m, PhCH$_2$CH$_2$(CH$_2$)$_9$CH$_3$], 0.91 [3H, t, J(H-H) = 7.0 Hz, PhCH$_2$CH$_2$(CH$_2$)$_9$CH$_3$]. $^{13}$C{${^1}$H} NMR (CD$_2$Cl$_2$): $\delta$ 149.07, 146.01, 136.48, 135.89, 130.74, 129.42, 129.00, 126.59, 126.55, 125.81, 125.11, 124.88, 121.66, 35.74, 32.54, 32.13, 30.29, 30.26, 30.22, 30.11, 29.98, 29.44, 23.30, 14.50.

$N$-(4-dodecylphenyl)-$N,N$-di(2-naphthyl)amine (2.10). 4-Dodecylaniline (1.04 g, 4.0 mmol), sodium tert-butoxide (1.16 g, 12.1 mmol), Pd$_2$(dba)$_3$ (72 mg, 0.08 mmol),
tri-tert-butylphosphine (32 mg, 0.16 mmol), 2-bromonaphthalene (1.66 g, 8.0 mmol), and toluene (ca. 15 mL) were added to a Schlenk flask in a drybox. The flask was closed with a stopper and removed from the drybox. The reaction mixture was stirred under nitrogen at 90 °C for 1 week. After cooling, CHCl₃ (25 mL) was added, the mixture was filtered, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (eluent: 10% ethyl acetate in hexanes). Yield 1.5 g (73%) of a pale yellow oil. ESI MS: *m/z* 514.6 (M+H⁺). $^1$H NMR (CD₂Cl₂): δ 7.77 [2H, d, J(H-H) = 7.6 Hz, arom. CH], 7.74 [2H, d, J(H-H) = 9.0 Hz, arom. CH], 7.58 [2H, d, J(H-H) = 8.1 Hz, arom. CH], 7.43 [2H, d, J(H-H) = 2.3 Hz, arom. CH], 7.40 – 7.30 [6H, m, arom. CH], 7.15 – 7.08 [4H, m, arom. CH], 2.60 [2H, t, J(H-H) = 7.0 Hz, PhCH₂CH₂(CH₂)₉CH₃], 1.64 [2H, p, J(H-H) = 7.0 Hz, PhCH₂CH₂(CH₂)₉CH₃], 1.35 – 1.28 [18H, br m, PhCH₂CH₂(CH₂)₉CH₃], 0.88 [3H, t, J(H-H) = 7.0 Hz, PhCH₂CH₂(CH₂)₉CH₃]. $^{13}$C($^1$H) NMR (CD₂Cl₂): δ 162.9, 146.3, 145.8, 139.2, 135.1, 129.9, 129.4, 128.1, 127.4, 126.8, 125.6, 124.9, 124.8, 120.4, 32.5, 32.1, 30.3, 30.23, 30.22, 30.18, 30.09, 29.96, 29.93, 26.13, 23.26, 14.44.

N-(4-dodecylphenyl)-N,N-di(1-pyrenyl)amine (2.11). 4-Dodecylaniline (1.04 g, 4.0 mmol), sodium tert-butoxide (1.16 g, 12.1 mmol), Pd₂(db₃)₃ (72 mg, 0.08 mmol), tri-tert-butylphosphine (32 mg, 0.16 mmol), 1-bromopyrene (1.20 g, 4.3 mmol), and toluene (15 mL) were added to a Schlenk flask in a drybox. The flask was topped with a stopper and removed from the drybox. The reaction mixture was stirred under nitrogen at 90 °C for 1 week. After cooling, CHCl₃ (25 mL) was added, the mixture was filtered, and then solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (eluent: 10% ethyl acetate in hexanes). Finally the product was dissolved in CHCl₃ and precipitated by MeOH addition. Yield 1.81 g (68%) of a bright yellow solid. ESI MS: *m/z* 662.5 (M+H⁺). $^1$H NMR (CD₂Cl₂): δ 8.34 [2H, d, J(H-H) = 9.3 Hz, arom. CH], 8.18 [2H, dd, J(H-H) = 7.7 Hz, J(H-H) = 1.2 Hz, arom. CH], 8.09 [4H, m, arom.
\[ CH \], 8.04 \{4H, d, J(H-H) = 1.1 \text{ Hz}, \text{arom. } CH \}, 7.99 \{2H, t, J(H-H) = 7.7 \text{ Hz}, \text{arom. } CH \}, 7.90 \{2H, d, J(H-H) = 7.7 \text{ Hz}, \text{arom. } CH \}, 7.76 \{2H, d, J(H-H) = 7.7 \text{ Hz}, \text{arom. } CH \}, 6.99 \{2H, dd, J(H-H) = 8.6 \text{ Hz}, J(H-H) = 2.1, \text{arom. } CH \}, 6.77 \{2H, dd, J(H-H) = 8.6 \text{ Hz}, J(H-H) = 2.1, \text{arom. } CH \}, 2.54 \{2H, t, J(H-H) = 7.0 \text{ Hz}, \text{PhCH}_{2}\text{CH}_{2}(\text{CH}_{2})_{9}\text{CH}_{3} \}, 1.58 \{2H, p, J(H-H) = 7.0 \text{ Hz}, \text{PhCH}_{2}\text{CH}_{2}(\text{CH}_{2})_{9}\text{CH}_{3} \}, 0.87 \{3H, t, J(H-H) = 7.0 \text{ Hz}, \text{PhCH}_{2}\text{CH}_{2}(\text{CH}_{2})_{9}\text{CH}_{3} \}. ^{13}C\{^{1}H\} \text{NMR (CD}_{2}\text{Cl}_{2}): \delta 149.51, 143.65, 136.67, 131.96, 131.64, 129.58, 129.34, 127.99, 127.81, 127.22, 127.15, 126.93, 126.78, 126.58, 126.29, 125.65, 125.46, 124.06, 121.52, 35.73, 32.50, 32.12, 30.26, 30.21, 30.18, 30.07, 29.93, 23.27, 14.45.

**SWNT separations.** In a typical experiment, purified SWNTs (5 mg) were combined with triarylamine (100 mg) and CHCl\textsubscript{3} (10 mL) in a glass vial. The mixture was subjected to bath sonication for 48 h and then solvent was removed *in vacuo*. Hexanes (10 mL) were then added followed by 5 minutes of bath sonication to remove excess amine. The mixture was filtered through a PTFE membrane (0.2 µm pore size). Finally the solid residue was sonicated 15 minutes with THF (15 mL), centrifuged at 4400 rpm for 5 minutes, and the supernatant decanted.

**References**


Chapter 3
Preparation and Characterization of Graphene Materials

Introduction

Recently graphene has enjoyed significant attention and is now as highly investigated as the related fullerenes and carbon nanotubes. Graphene is a single atomic layer of sp² graphite carbon. While mechanical exfoliation ("scotch-tape" method) and chemical vapor deposition (CVD) provide routes to graphene, these methods are impractical for large-scale manufacturing. Chemical means are therefore the most realistic approach to graphene materials. The primary obstacle to achieving individual or few-layer graphene is overcoming the enormous interlayer van der Waals forces. To date, chemical efforts at graphite exfoliation have been focused primarily on intercalation, chemical derivatization, thermal expansion, oxidation-reduction, the use of surfactants, or some combination of these. Covalent methods can be advantageous in that they often provide more robust materials. The most common approach to graphite exfoliation is oxidation to graphite oxide (GO) by strong oxidizing agents. Partial restoration of the graphitic structure is accomplished by various chemical reductants such as hydrazine or sodium borohydride. Reduction of GO to chemically converted graphene (CCG) does not fully restore the graphitic structure (with its desired properties) and introduces defects. Moreover, CCG is prone to aggregation unless stabilized.

The structure of GO has been the subject of numerous studies. It is known that GO contains epoxide functional groups along the basal plane as well as hydroxide and carboxylic acid moieties along the edges of nanosheets. Previous Barron group research established a quantitative method for determining epoxide content in SWNT samples. This method, involving rhenium-catalyzed oxygen transfer from organic epoxide to triphenylphosphine, in combination with $^{31}$P NMR spectroscopy, is here applied to epoxide functionalized graphite. Methyltrioxorhenium (MTO, I) is a well-
studied olefin epoxidation catalyst.\textsuperscript{15} More generally MTO efficiently catalyzes oxygen transfer reactions, removing oxygen from epoxides or sulfoxides and transferring it to phosphines or arsines.\textsuperscript{16} In the case of oxidized carbon nanomaterials, MTO is selective to epoxides; it will not transfer oxygen to triphenylphosphine from carbonyl or hydroxyl functional groups. This provides a convenient method for quantifying epoxide content. After performing the O transfer, a portion of the sample is tested by $^{31}$P{$^1$H} NMR. The relative integrated area of triphenylphosphine to triphenylphosphine oxide then can be used to back calculate the number of moles of epoxide oxygen present in the sample.\textsuperscript{13,14}

\[
\text{Me} \quad \text{O} \quad \text{R} \quad \text{O} \\
\text{O} \quad \text{O}
\]

(I)

An alternate approach to producing graphene materials involves the use of pristine graphite as starting material. The fundamental value of such an approach lies in its avoidance of oxidation to GO and subsequent (incomplete) reduction, thereby preserving the desirable electronic properties of graphene. There is precedent for exfoliation of pristine graphite in neat organic solvents without oxidation or surfactants.\textsuperscript{17,18} Blake \textit{et al.} fabricated devices using $N$,$N$-dimethylformamide (DMF) dispersions, but provide no detailed characterization of the graphene dispersions. Coleman and coworkers reported similar dispersions using $N$-methylpyrrolidone (NMP) and other solvents, resulting in individual sheets of graphene at a concentration of $\leq 0.01$ mg.mL$^{-1}$. NMP and DMF are highly polar solvents, and not ideal in cases where reaction chemistry requires a nonpolar medium. Further, they are hygroscopic, making their use problematic when water must be excluded from reaction mixtures. Finally, DMF is prone to thermal and chemical decomposition. To date, no high-yield homogeneous graphene dispersion in a nonpolar solvent has been reported.
In the first part of Chapter 3, we demonstrate a simple, high-yield method of producing homogeneous dispersions of graphene nanosheets in o-dichlorobenzene (ODCB) from various graphite materials. The advantage of this method lies in its high yield, its simplicity, and its avoidance of harsh oxidation chemistry. Additionally, ODCB graphene dispersions open up a wide range of possibilities for efficient chemical derivatization of graphene where nonpolar media are required. In particular, addition of perfluorinated alkyl radicals to graphene is here shown to be efficient in ODCB.

Advances in fluorine chemistry have produced many technologically relevant materials in recent years. Polytetrafluorethylene (PTFE) polymeric materials have found numerous commercial applications resulting from their hydrophobicity (GoreTex) and tribological properties (Teflon). In addition, so-called fluorous phase chemistry has been an active area of research with wide-ranging applications including homogeneous catalysis. By attaching perfluorinated alkyl chains to ligands, homogeneous catalyst complexes can be made soluble in fluorous solvents (which are immiscible with both water and conventional organics). Fluorous catalysts can then be easily separated from reaction products in biphasic systems.

Carbon nanotubes are notorious for their insolubility; strong van der Waals bundling forces make it very difficult to disperse SWNTs in organic or aqueous media. Covalent attachment of perfluorinated alkyl groups could allow SWNTs to be dispersed in fluorous solvents. As part of ongoing efforts in the Barron group to attach catalyst particles to SWNTs for seeded growth (Chapter 1), SWNTs were functionalized with perfluorinated alkyls (R_F) in order to disperse them in fluorous solvents. In addition, graphene was derivatized with R_F groups for use in composites.

There is some precedent concerning perfluorinated alkylation of carbon nanomaterials. Notably, Hirsch and coworkers derivatized SWNTs with perfluorooctyl groups via UV photolysis of perfluorooctyl iodide. However, resulting R_F-SWNTs showed no solubility enhancement. Perfluoroundecylamine has been coupled
to SWNT carboxylic acid groups via amide linkages.²⁵ Products had a low level of functionalization due to the fact that coupling is limited to oxidized SWNT ends and defect sites. Later selective fluororous tagging of metallic SWNTs by diazonium salts was reported.²⁶

Billups and coworkers have used benzoyl peroxide to produce phenyl radicals which either phenylate SWNTs directly or generate alkyl radicals from iodides.²⁷,²⁸ This approach provides a simple one-pot reaction that should be amenable to perfluorinated alkyl iodides, save one caveat: perfluorinated alkyl iodides are highly unstable. In fact, in Hirsch’s report UV illumination was used to initiate radical formation.²⁴ Leaving a two-methylene ‘spacer’ between the fluorocarbon chain and iodine mitigates this extreme instability. Resultant 1-iodo-1H,1H,2H,2H-perfluoroalkane derivatives have stabilities on par with normal alkyl iodides.²⁹

As graphite is a robust, thermally stable material that already has lubricant applications, it would be interesting to functionalize graphene with fluorinated alkyl groups in order to explore their combined properties. There are dozens of patents and publications in the literature pertaining to graphite and carbon nanotube–PTFE composite materials.³⁰ These materials have been examined for numerous applications and their tribological properties well studied; however, all these composites employ simple physical mixing of carbon materials into polymer matrices and are often plagued by phase segregation problems. To date there exists no precedent for the formation of covalent fluorocarbon–nanocarbon hybrid composite materials. These composites could serve to vastly improve thermal and tribological properties of fluorocarbon polymer products. Further, ODCB dispersions provide convenient starting materials for radical functionalization of graphene. At the end of Chapter 3, we demonstrate the first covalently perfluoroalkylated graphene materials, starting from ODCB dispersions.
Results and Discussion

Epoxidation and de-epoxidation of graphite. Graphite epoxide, produced by the Billups group, was prepared by $m$-peroxybenzoic acid ($m$CPBA) oxidation of microcrystalline synthetic graphite at room temperature.\(^{14}\) Samples were then heated with MTO in the presence of PPh\(_3\) to quantify the extent of oxidation. After the reaction was complete, a portion of the supernatant reaction mixture was transferred to an NMR tube. \(^{31}\text{P}\{\text{H}\}\text{NMR was used to determine the relative concentrations of PPh}_3\) and O=PPh\(_3\). It should be noted that detected oxygen content only includes epoxides. Further, air must be rigorously excluded as MTO catalyzes the oxidation of PPh\(_3\) by molecular oxygen. The graphite starting material showed a formula of C\(_{110}\)O; after treatment with \(m\)CPBA epoxide content was increased to C\(_{12}\)O (see Experimental).

TEM and STM showed graphite plates with little epoxidation of the basal plane. It was proposed that graphite epoxidation occurs at the edges of plates and not on the basal planes for at least two reasons. First, extremely large van der Waals attractions between graphene sheets do not permit reagents to intercalate between adjacent layers under the mild conditions used. Second, the carbon-carbon bonds along the perimeter of a graphene sheet are presumably more reactive than those within the interior. Perimeter C–C bond character is closer to that of an alkene than an aromatic. In order for epoxidation to occur along the basal plane local aromaticity must be disrupted.

We note that typical reagents and conditions for the preparation of fully exfoliated GO are far harsher than those used here.\(^{9}\) The use of \(m\)CPBA does not truly exfoliate graphite to GO, but instead offers a mild route to add epoxide moieties at the edges of graphite nanoplatelets. The value of the MTO/PPh\(_3\) system lies in its ability to provide quantitative analysis of epoxide content. Moreover, it offers a mild method for selective de-epoxidation of carbon nanomaterials.
**Homogeneous ODCB graphene dispersions.** The choice of ODCB for graphite exfoliation was based on several criteria. First, ODCB is a common reaction solvent for fullerenes and is known to form stable SWNT dispersions.\(^{31}\) Second, ODCB is a convenient high-boiling aromatic, and is compatible with a variety of reaction chemistries. Coleman suggests\(^{18}\) that good solvents for graphite exfoliation should have surface tension values of 40 – 50 mJ.m\(^{-2}\). ODCB has a surface tension of 36.6 mJ.m\(^{-2}\), near the proposed range.\(^{32}\) Finally, ODCB, being aromatic, is able to interact with graphene via π-π stacking.

Graphite is readily exfoliated in ODCB with homogenization and sonication. Three starting materials were successfully dispersed: microcrystalline synthetic, thermally expanded, and highly ordered pyrolytic graphite (HOPG). As a control, we attempted to disperse graphite in several other aromatic solvents (benzene, toluene, xylenes, chlorobenzene, and pyridine), all without success. A Tyndall effect was observed for pyridine and chlorobenzene, however the amount of material suspended is below any reasonable gravimetric detection limit (i.e., liters of dispersion must be filtered to collect any measurable residual weight). Therefore ODCB appears to be uniquely capable of exfoliating graphene. After centrifugation, homogeneous dispersions are formed which are stable for long periods of time (on the order of months) with no aggregation. Dispersions of microcrystalline synthetic graphite have a concentration of 0.03 mg.mL\(^{-1}\), determined gravimetrically. Dispersions from expanded graphite and HOPG are less concentrated (0.02 mg.mL\(^{-1}\)).

UV-visible spectra of graphene dispersions in ODCB are flat and featureless from 1000 nm to ca. 400 nm. ODCB dispersions obey the Beer-Lambert law; at 660 nm microcrystalline, expanded graphite, and HOPG dispersions' absorption coefficients are 4150, 2750, and 3110 L.g\(^{-1}\).m\(^{-1}\), respectively, close to Coleman’s previous report.\(^{18}\) Sediment recycling is possible at least twice, yielding samples equivalent to the original dispersions (within 5% of original concentration by UV-vis).
HRTEM (Figure 3.1) shows mostly few-layer graphene (n < 5) with single layers and small flakes stacked on top. Large graphitic domains are visible; this is further supported by selected area electron diffraction (SAED) and fast Fourier transform (FFT) in selected areas.

Figure 3.1. TEM images of single layer graphene from HOPG dispersion. (a) monolayer and few layer of graphene stacked with smaller flakes; (b) selected edge region from (a), (c) selected area from (b) with FFT inset, (d) HRTEM of boxed region in (c) showing lattice fringes with FFT inset.

Raman spectroscopy (514 nm excitation) confirms the pristine graphitic structure of films produced from ODCB dispersions via vacuum filtration. Expected graphene
peaks are present at 1350 cm\(^{-1}\) (D-band), 1582 cm\(^{-1}\) (G-band), 2700 cm\(^{-1}\) (2D-band), and 3164 cm\(^{-1}\) (2G-band). XPS of expanded graphite films shows composition C (88.5%), O (9.8%), and Cl (1.7%). The presence of oxygen is expected given that thermal expansion of graphite results in some oxidation.\(^5\) Films deposited from microcrystalline graphite and HOPG contain less oxygen (ca. 3.3%), as expected. Chlorine is attributed to the presence of residual ODCB within the film. High-resolution scans of the C1s region (Figure 3.2) for all graphite films show predominantly sp\(^2\) graphene carbon (284.9 eV) with a shoulder at 286.5 eV, indicative of ODCB.\(^3\)3

![Figure 3.2. Typical ODCB-graphene XPS spectrum, C1s region (y-axis arb units).](image)

Tapping mode AFM of dispersions sprayed onto silicon substrates shows extremely thin flakes with nearly all below 10 nm (Figure 3.3). Average height is 7 - 10 nm. The thinnest are less than 1 nm, graphene monolayers. Lateral dimensions of nanosheets range from 100 - 500 nm.

As-deposited films cast from ODCB graphene show poor electrical conductivity. This is attributed to residual ODCB within the films. After vacuum annealing at 400 °C
Figure 3.3. AFM image with height profile from a HOPG-ODCB dispersion. Scan area 1x1 μm.

For 12 hours the films improve vastly, having sheet resistances on the order of 60 Ω.sq⁻¹. By comparison, graphene epitaxially grown on Ni recently had a reported sheet resistance of 280 Ω.sq⁻¹.³⁴

**Radical perfluoroalkylation of SWNTs and graphene.** Benzoyl peroxide was used to initiate the radical addition of 1-iodo-1H,1H,2H,2H-perfluorododecane to Piranha etched SWNTS. The same reaction was performed on ODCB dispersions of expanded graphite (Scheme 3.1). Additionally, UV photolysis of 1-iodoperfluorodecane was used to perfluoroalkylate microcrystalline graphite (Scheme 3.2). Perfluoroalkylated graphenes resulting from the UV- and peroxide- initiated reactions are not equivalent products, having been derivatized, respectively, with alkyl chains of 10 or 12 carbon atoms. Further, UV initiation results in derivatization with fully fluorinated decyl chains; peroxide initiated products are functionalized with dodecyl chains having two non-fluorinated carbons.

FTIR spectra of perfluorododecyl SWNTS (R₆-DD-SWNTs, 3.1) contain bands in the range of 1300 - 900 cm⁻¹ assignable to ν(C-F) stretching modes. While, this is consistent with the presence of fluorinated alkyl substituents, it does not confirm covalent attachment. The XPS spectrum of R₆-DD-SWNTs indicates fluorine at an atomic
Scheme 3.1. Perfluoroalkylated SWNTs (3.1) and graphene (3.2). (a) ODCB, CF$_3$(CF$_2$)$_9$(CH$_2$)$_2$I, benzoyl peroxide, 80 °C, 24 h.

Scheme 3.2. Perfluorodecyl graphene (3.3). (a) ODCB, CF$_3$(CF$_2$)$_9$I, UV, 8 h.

concentration of 18.5% corresponding to one functional group per 75 SWNT carbon atoms. High-resolution scans of the C1s region (Figure 3.4) clearly show the presence of CF$_3$ (293.8 eV), CF$_2$ (291.8 eV), CH$_2$ (290.6 eV), functionalized SWNT sp$^3$ C (286.2 eV), and pristine sp$^2$ SWNT carbon (284.8 eV). The C1s region also contains a peak indicative of carbon bound to oxygen at 288.9 eV, expected since oxidized SWNTs were used to prepare the final product. XPS of the F1s region shows a single peak centered at 688.9 eV (in agreement with literature values for PTFE) with a small shoulder at 685.5 eV, indicative of F-CFCH$_2$.  

Figure 3.4. XPS spectrum of R$_F$-DD-SWNT, C1s and F1s regions.

TGA of R$_F$-DD-SWNTs in argon shows a mass loss of 45.2% over the range 200 - 800 °C, which if due solely to the perfluorododecyl group would indicate one perfluorododecyl group per 55 SWNT carbons. This is higher than the 1:75 ratio determined by XPS (see above). There are two possible explanations for this disparity. First, etched SWNTs contain oxygen functional groups that contribute to mass loss. Taking the oxygen content in the R$_F$-DD-SWNTs (16 atom %) into account results in a calculated R$_F$-DD:SWNT carbon ratio of 1:90, i.e., slightly closer to the XPS results. Second, some phenylation occurs when generated phenyl radicals attack SWNTs directly, rather than initiating perfluoroalkyl radicals. However, the C1s XPS spectrum does not indicate significant aromatic C-H substitution.

The Raman spectrum of R$_F$-DD-SWNTs is shown in Figure 3.5. The increase in the D-band intensity (as compared to unreacted SWNTs) is indicative of sp$^3$ carbon and consistent with the covalent attachment of perfluorododecyl groups. We have previously demonstrated$^{35}$ that the Raman D:G ratio is not always an accurate measure of the extent of substitution since functional group distribution is also a factor in determining the D:G ratio. The increased D:G ratio (0.37 from 0.07) is consistent with additional functionalization.
Figure 3.5. Raman spectra (785 nm excitation) of Piranha etched SWNTs (blue) and R_F-DD-SWNTs (red). Y-axis arb units.

AFM of R_F-DD-SWNTs (Figure 3.6) shows the presence of mostly individual functionalized SWNTs, having heights that average 1.4 nm. There are few small bundles present with heights of up to 4 nm. By comparison, typical purified SWNTs are only present in bundles with heights of 20 nm or more. Individual purified HiPco SWNTs (debundled by surfactants) have diameters of 0.8 – 1.2 nm. Line scan analysis along the length of R_F-DD-SWNTs shows areas of functionalization that are higher (0.2 – 0.3 nm) than unfunctionalized regions.

Figure 3.6. AFM image of R_F-DD-SWNTs with line scan analysis (scan area 2x2 μm, height profile scale 10 nm.)
Our initial goal was to add perfluorinated groups to oxidatively etched SWNTs in order to suspend the products in fluorinated solvents. We found however that Rp-DD-SWNTs showed no dispersability in perfluorohexane. After attempting to suspend the material in various polar and nonpolar solvents, also without success, it was noticed that the Rp-DD-SWNTs remained well suspended in chloroform during workup. In fact, Rp-DD-SWNTs in CHCl₃ remain stable for one year at a concentration of 0.25 mg.mL⁻¹. This discovery led us to apply the same chemistry to graphene nanosheets dispersed in ODCB. In addition, graphene was perfluoroalkylated by the UV initiated method of Hirsch and coworkers.²⁴

Perfluorododecylated graphene produced by peroxide initiation (Rᶠ-DD-graph, 3.2) contains 23.4 atomic % fluorine by XPS, indicating ca. 1 substituent per 36 carbon atoms. The C1s and F1s spectral regions are very similar to those of Rᶠ-DD-SWNTs (Figure 3.7).

![Figure 3.7. C1s region of the XPS spectrum of Rᶠ-DD-graph (3.2).](image)
XPS of UV-produced perfluorodecyl graphene (RF-D-graph, 3.3) shows fluorine content of 35%, corresponding to 1 substituent per 39 carbon atoms. This is in good agreement with the peroxide initiated product. The C1s region of RF-D-graph is essentially the same as peroxide RF-DD-graph with two exceptions: there is no CH$_2$ peak present and there is a small, unidentified shoulder at 282.7 eV (Figure 3.8). This peak is in the region expected for carbides or organometallic carbon. However, survey scans showed no metals present.

Figure 3.8. C1s region of the XPS spectrum of RF-D-graph (3.3).

The Raman spectrum of RF-DD-graph shows a D:G ratio of 0.10 compared to 0.05 for the expanded graphite starting material (Figure 3.9). This is less than the ratio enhancement seen for RF-DD-SWNTs. Again, it should be remembered that Raman D:G ratio depends largely on functional group distribution. It is known that functionalization of graphene occurs preferentially along plate edges as opposed to the basal plane, and perimeter functionalization is expected to cause less D band enhancement as edges contribute to the D band regardless of functionality. Raman was also performed on the
graphite material remaining after TGA thermolysis of R_F-DD-graph under Ar. This residue showed a reduction of the D:G ratio to 0.06, indicating near restoration of the graphitic framework.

![Graph showing Raman spectra](image)

**Figure 3.9.** Raman spectra (514 nm excitation) of expanded graphite (green), R_F-DD-graph 3.2 (blue), and post-thermolysis residue (red). Y-axis arb units.

Raman spectra of R_F-D-graph 3.3 further illustrate the limitations of this method as applied to graphene materials. The D:G ratio of the product is essentially unchanged (ca. 0.15) from the starting material. This is explained by the influence of edges on D-band intensity. Microcrystalline graphite consists of much smaller flakes and therefore has a larger proportion of edges.

TGA of R_F-DD-graph showed a mass loss of 56.3%, indicating the presence of one functional group per ca. 35 graphite carbon atoms. This is in very good agreement with XPS data, as well as being within range of values reported by Billups for similar graphene materials prepared by reductive alkylation.\(^\text{37,38}\) TGA of R_F-D-graph showed a mass loss of 55.8 %, indicating a similar degree of functionalization (1 R_F group per 43 graphite carbons). FTIR spectra of both R_F-D- and R_F-DD-graphenes are
indistinguishable from that of R_F-DD-SWNTs, containing peaks in the range of 1300 – 900 cm\(^{-1}\) representing C–F stretching modes.

AFM images of peroxide R_F-DD-graph indicate the presence of small nanoplatelets. The thinnest of these are 5 – 7 nm, with the remainder between 15 – 20 nm. The lateral dimensions of the nanosheets range between 50 – 200 nm. Additionally, areas of functionalization are visible as globular materials on the graphene flakes. R_F-D-graphene appears to be much better exfoliated; AFM shows nearly all flakes thinner than 5 nm (Figure 3.10). Improved exfoliation is likely due to the graphite starting material rather than the alkylation chemistry. Generally ODCB dispersions of microcrystalline graphite are better exfoliated than those of expanded graphite.

Figure 3.10. AFM image of R_F-D-graph (3.3). Scan area is 2.5 x 2.5 \(\mu\)m.

Conclusions

We have demonstrated that MTO catalyzed epoxide oxygen transfer to triphenylphosphine can be used to quantify epoxides in graphite materials as has previously been shown for fullerenes and SWNTs. Epoxidation by \(m\)CPBA occurs at the edges of graphite plates and not along the basal plane.

\(o\)-Dichlorobenzene efficiently exfoliates graphite, producing relatively high yields of graphene nanosheets. ODCB graphene dispersions are conveniently prepared from a variety of graphite starting materials. They avert the need for harsh oxidation chemistry,
resulting in graphene that requires no reduction step. Finally, ODCB dispersions provide a convenient platform from which to functionalize graphene by radical chemistry.

SWNTs and graphene have successfully been functionalized with perfluoroalkyl groups using thermal decomposition of benzoyl peroxide or UV photolysis to initiate radical addition in a one-pot reaction. As these nanocarbon-PTFE hybrid materials have potential application as lubricants or polymer additives, mechanical, tribological and thermal properties of polymer dispersions of the reaction products are presently being examined.

Experimental

Toluene was dried by distillation under N\textsubscript{2} over Na, and was degassed prior to use by freeze-pump-thaw or bubbling Ar. All other solvents, including 1,2-dichlorobenzene (ODCB), were purchased from Fisher Scientific and used as received. Benzoyl peroxide was purchased from Sigma Aldrich and was purified by recrystallization from CHCl\textsubscript{3}/methanol.\textsuperscript{39} 1-iodo-1H,1H,2H,2H-perfluorododecane and methyltrioxorhenium were purchased from Alfa Aesar and used as received. Triphenylphosphine was purchased from Sigma Aldrich and was recrystallized from MeOH before use. 1-Iodoperfluorododecane was purchased from TCI America and used as received. Single-walled carbon nanotubes (HiPco process) were obtained from the Carbon Nanotube Laboratory at Rice University (Houston TX), and were purified\textsuperscript{40} and etched\textsuperscript{41} by literature procedures. Expanded graphite was acquired from Supra Carbonic, LLC; synthetic microcrystalline graphite was purchased from Sigma Aldrich. Homogenization was performed using a high-shear mixer (IKA Ultra Turrax T25 fitted with IKA S-25N 10 G dispersing element) at 11000 rpm. Sonication was performed with an ultrasonic processor (Cole-Parmer) with cup horn attachment at 50% amplitude. Centrifugation was at 4400 rpm (IEC Centra MP4). \textsuperscript{31}P{H} NMR spectra were obtained at room
temperature using Bruker Avance 400 and 500 MHz spectrometers. Chemical shifts are reported relative to H$_3$PO$_4$ (0.0 ppm).

UV photolysis reactions were performed using a Rayonet RPR-100 photochemical reactor ($\lambda$ max = 254 nm) with a cooling fan and magnetic stirrer. IR spectra were collected on a Nicolet Magna 760 spectrometer. IR samples were prepared by mixing samples with KBr before pressing pellets. Raman data were obtained using a Renishaw Raman microscope with a 514 nm (graphene materials) or 785 nm (SWNT materials) laser excitation source. XPS data were acquired on a Physical Electronics, Inc. Phi Quantera instrument with monochromated Al-K$_\alpha$ X-ray source. Atomic force microscopy measurements were obtained using a Digital Instruments NanoScope IIIa scanning probe microscope in tapping mode. AFM samples were either spin-coated onto freshly cleaved mica or spray coated onto single crystal silicon substrates. TGA analyses were performed on a Seiko I TG/DTA 200, under an argon flow of 15-20 sccm, using a ramp temperature of 5 °C.min$^{-1}$. Conductivity data were found using a four-point probe at a current of 0.5 mA.

**De-epoxidation of graphite epoxide.** Graphite epoxide (250 mg) was added to a Schlenk flask and heated to 80 °C under vacuum overnight in order to remove adsorbed oxygen. The reaction vessel was then purged with Ar and a toluene solution (30 mL) of MTO (50 mg, 20 mmol) was added with stirring. The vessel was topped with an addition funnel, from which PPh$_3$ (57 mg, 0.22 mmol) in toluene (25 mL) was added dropwise over 15 minutes. The mixture was then stirred overnight at 55 °C. After the reaction was complete, a small portion of the supernatant (0.75 mL) was transferred to an NMR tube under Ar, and then C$_6$D$_6$ (0.2 mL) was added as the locking solvent. After collecting a $^{31}$P {$^1$H} NMR spectrum, the relative integration of PPh$_3$ (-4.8 ppm) and O=PPh$_3$ (25.1) was used to determine epoxide content.
ODCB dispersions. Thermally expanded or synthetic microcrystalline graphite (500 mg) was added to 100 mL ODCB. The mixture was homogenized for 1 hour followed by cup-horn sonication for 30 minutes. Finally the slurry was centrifuged 30 minutes at 4400 rpm. Collection of the supernatant yielded ODCB dispersions. Alternately, HOPG dispersions were produced by adding a piece of HOPG (0.5x0.5x0.1 cm) to 20 mL ODCB. Homogenization, sonication, and centrifugation were the same as for expanded and synthetic graphites.

Graphene films. Films were deposited by vacuum-filtering 20 mL of ODCB dispersions through alumina membranes (Anodisc, 25 mm diameter, 0.02 μm nominal pore size). Films were dried under vacuum at 100 °C overnight. Films were then annealed by heating to 400 °C under high vacuum for 12 h.

Perfluorododecyl SWNTs (RF-DD-SWNTs, 3.1). In a typical experiment, SWNTs (20 mg) were dispersed in ODCB (30 mL) by sonication in a Schlenk flask. To the SWNT dispersion benzyol peroxide (0.4 g, 1.6 mmol) and 1-iodo-1H,1H,2H,2H-perfluorododecane (2.7 g, 4.0 mmol) were added. The reaction mixture was stirred at 80 °C for 24 h under Ar. After cooling to room temperature, CHCl₃ (30 mL) was added and the mixture was vacuum filtered over an alumina membrane (0.02 μm pore size). The product was suspended in CHCl₃ by sonication and filtered again. Sonication and filtration were repeated twice more to ensure removal of all excess reactants. Finally the filter cake was washed with more CHCl₃ and then dried under vacuum.

Perfluorododecyl graphene (RF-DD-graph, 3.2). In a typical experiment, ODCB-graphene suspension (30 mL) was added to a Schlenk flask along with benzyol peroxide (0.4 g, 1.6 mmol) and 1-iodo-1H,1H,2H,2H-perfluorododecane (2.7 g, 4.0 mmol). The reaction mixture was stirred at 80 °C for 24 h under Ar. After cooling to
room temperature, CHCl₃ (30 mL) was added and the mixture was vacuum filtered over an alumina membrane (0.02 μm pore size). The solid was suspended in CHCl₃ by sonication and filtered. Sonication and filtration were repeated twice more to ensure removal of all excess reactants. Finally the filter cake was washed with additional CHCl₃ and then dried in vacuo.

**Perfluorodecyl graphene (R₉-D-graph, 3.3).** In a typical experiment, ODCB-graphene suspension (30 mL) was added to a round-bottom flask with 1-iodoperfluorodecane (500 mg, 0.8 mmol). The reaction mixture was stirred at room temperature under UV illumination for 10 h. CHCl₃ was added (20 mL) and the mixture was vacuum filtered over an alumina membrane (0.02 μm pore size). The solid was suspended in CHCl₃ by sonication and filtered. Sonication and filtration were repeated twice more to ensure removal of all excess reactants and byproducts. Finally the filter cake was washed with additional CHCl₃ and then dried in vacuo.

**References**


Chapter 4
Thin Film Photovoltaics on Flexible SWNT Substrates

Introduction

Solar generation of electricity has been an active area of research since shortly after Becquerel first discovered the photoelectric effect in 1839.¹ Recent concerns that fossil fuel supplies are declining as well as issues of pollution and climate change have spurred intensive research into photovoltaics (PV) as well as other renewable energy sources. Professor Harry Gray recently predicted that by 2050 fossil fuels would no longer be used in any capacity.² Energy will be generated by solar and other renewable sources. Solar is the most utilized of the ‘green’ energy sources to date. The sun provides enough energy in one hour to satisfy total world demand for a full year. Thus, the only barriers to meeting global energy needs by PV technology are economic; i.e., improvements in efficiency and reduction in manufacturing costs will be needed to reach grid-parity (when the per-watt cost of PV energy equals that of coal).

Fundamentally PV devices are all the same; they convert light energy into electrical energy. Incident photons of sufficient energy striking a semiconductor cause excitation of electrons from the valence band into the conduction band. While thin film solar cells still do not meet the efficiencies of single-crystal silicon cells, they are less expensive to manufacture, and the future viability of solar energy depends on advances in thin-film technology.³ Still, many advances are required to reach grid-parity; a major goal is the reduction of solar cell cost to below 1 dollar per watt. The majority of thin film solar cells using cadmium telluride or copper-indium-gallium-selenide (CIGS) are produced using chemical vapor deposition (CVD) or other semiconductor manufacturing methods; these methods are energy-intensive and require specialized equipment. New methods, many based on advances in nanoscience, will be required to produce inexpensive, flexible thin film solar cells.
One of the most promising routes to inexpensive PV devices is chemical bath deposition (CBD). This solution phase method allows the deposition of a variety of semiconductor thin films under ambient conditions using simple equipment found in any wet chemistry laboratory. CBD is well suited to the preparation of conformal films on flexible substrates. In fact, the adaptation of existing roll-to-roll fabrication equipment will allow the continuous-line manufacture of thin film solar cells, below $1 per watt.

SWNTs have a host of desirable physical and electronic properties (see Introduction and Chapter 1) that have made them the subject of intensive research. In particular, SWNTs are capable of ballistic electron transport on micron length scales, meaning they conduct electrical current with zero energy loss from scattering. Therefore SWNTs are an ideal candidate for use in PV applications; in fact they are currently being studied for use in transparent electrodes as well as in the active layer of organic photovoltaic (OPV) devices. SWNTs can be deposited onto flexible substrates by filtration, spraying, or printing, providing an electrically conductive matrix onto which semiconductor films can then be deposited by CBD to produce inexpensive PV devices.

Previous research in the Barron group focused on deposition of (12-16) semiconductor materials (CdS and CdSe) onto SWNTs in surfactant solutions. This study showed that uniform cadmium chalcogenide films could be prepared on SWNTs. In Chapter 4 we demonstrate CBD preparation of cadmium and copper selenide films on preformed SWNT films, often called Buckypapers.

Cadmium selenide films deposited by CBD are n-type with a direct bandgap of 1.74 eV, while copper selenide CBD films are p-type with a bandgap of 2.26 eV. SWNT PV devices described here, using cadmium selenide as the absorber material and copper selenide as the top (window) layer, could have, theoretically, efficiencies approaching 20%. The architecture of these devices consists of Buckypaper at the back of the cell, covered with CdSe, which extends in a continuous layer above the SWNTs. A bulk-
heterojunction is formed by coating the CdSe with a layer of CuSe. A typical device architecture is shown below (Figure 4.1).

![Figure 4.1. Schematic diagram of SWNT PV device.](image)

**Results and Discussion**

Buckypaper substrates were prepared by simple vacuum filtration of SWNT dispersions through PTFE membranes. Buckypapers prepared from o-dichlorobenzene (ODCB) SWNT dispersions were found to have poor conductivity (ca. 400 S.cm\(^{-1}\)). Films of adequate conductivity are obtained only after high temperature vacuum annealing. Several aqueous dispersions of SWNTs using various surfactants were then examined. Buckypapers produced from sodium dodecyl sulfate (SDS), sodium dodecylbenzenesulfonate (SDBS), and dodecyltrimethylammonium bromide (DTAB) showed conductivities of approximately 1500, 500, and 800 S.cm\(^{-1}\), respectively. It should be noted that conductivity is dependent on film thickness; SEM showed all samples to have thicknesses of 2 – 5 \(\mu\)m. SDS is known to effectively suspend carbon nanotubes\(^{11}\) and is the most commonly used surfactant for SWNTs. The improved conductivity of Buckypapers cast from SDS is attributed to a more homogeneous starting dispersion although no further investigation was performed. Figure 4.2 shows a typical Buckypaper deposited from SDS solution.
A general scheme for CBD of CdSe films involves the hydrolysis of \( N,N\)-dimethylselenourea (DMSU) in alkaline conditions in the presence of a cadmium salt. A complexing ligand is also required in order to prevent precipitation of \( \text{Cd(OH)}_2 \) as well as to regulate the concentration of free \( \text{Cd}^{2+} \) ions in solution. Typical complexing agents are sodium citrate or tartrate, triethanolamine, ethylenediamine, or nitrilotriacetic acid (NTA). Although on its face CBD appears to be a very simple process, in fact it is quite complex as a number of equilibria and reactions are involved. Small changes in reaction conditions can have dramatic effects on the quality and properties of produced films.

CBD of most II-VI semiconductor films, including CdSe, is considered to occur by either of two possible mechanisms: ion-by-ion or hydroxide cluster. Eq. 4.1 gives the ion-by-ion mechanism.

\[
\text{Cd}^{2+} + \text{Se}^{2-} \rightarrow \text{CdSe}
\]  
(4.1)
Similarly, the hydroxide cluster mechanism is described by Eqs. 4.2 and 4.3.

\[ \text{Cd}^{2+} + 2 \text{OH}^- \rightarrow \text{Cd(OH)}_2 \] (4.2)

\[ \text{Cd(OH)}_2 + \text{Se}^{2-} \rightarrow \text{CdSe} + 2 \text{OH}^- \] (4.3)

For both mechanisms, the concentrations of Cd\(^{2+}\) and Se\(^{2-}\) are controlled as follows:

\[ \text{Cd(L)}_n = \text{Cd}^{2+} + n \text{L} \] (4.4)

\[ (\text{CH}_3)_2\text{NC(NH)}_2\text{Se} + \text{OH}^- \rightarrow \text{HSe}^- + (\text{CH}_3)_2\text{NCN} + \text{H}_2\text{O} \] (4.5)

\[ \text{HSe}^- + \text{OH}^- \rightarrow \text{Se}^{2-} + \text{H}_2\text{O} \] (4.6)

It is difficult to determine which mechanism is dominant for a given film deposition. In fact, both are operative to some degree under most reaction conditions.\(^{12}\) However, there are some conditions that favor one versus the other. In general, the hydroxide cluster mechanism can be favored by increasing pH or by decreasing the ratio of ligand to cadmium. Increasing pH accelerates the formation of hydroxide clusters (by increased OH\(^-\) concentration); reducing the amount of complexant does the same by increasing available free Cd\(^{2+}\). Usually the ion-by-ion mechanism gives slower depositions, but produced films have larger terminal thicknesses.\(^{12}\) Also, whether due to deposition rate or other factors, ion-by-ion films commonly have larger crystallites.

**Deposition of CdSe absorber layer.** CdSe films were deposited on Buckypaper from CdSO\(_4\) and sodium sulfite-stabilized DMSU, using sodium citrate as the Cd complexing ligand in aqueous ammonia solution (pH 10.4) at room temperature.\(^{13,14}\)
Under these conditions it is expected that the hydroxide cluster mechanism is dominant. Films deposited onto SDS Buckypapers on PTFE membranes (12 h deposition time) were shown by SEM to have incomplete infill of the void space between SWNTs. In addition, large numbers of colloidal CdSe particles were present on the films' surfaces (Figure 4.3). Since the production of an efficient PV device depends critically on the quality of the p-n heterojunction, a planar interface is desired, free from defects or debris. Reduction of the reagent concentrations had no effect; in fact when the bath concentration is reduced the deposition rate on the substrate is retarded with no concomitant slowing of bulk precipitation (i.e., thinner films, same colloidal debris). Performing multiple 4 h depositions from fresh baths produced uniform films with clean surfaces although complete infill required 16 total hours (Figure 4.3).

Figure 4.3. SEM images of CdSe films on Buckypaper: deposition times were 12 h (left) and 4 x 4 h (right).

X-ray photoelectron spectroscopy (XPS) analysis showed the stoichiometry of the films produced to contain an excess of cadmium, having Cd:Se ratios of between 1.7:1 and 1.9:1. Energy-dispersive X-ray spectroscopy (EDS) confirmed the XPS data. Further analysis showed a large amount of oxygen present. It is understood that oxygen
chemisorbs to metal chalcogenide films;\textsuperscript{13} moreover, known impurities in CBD films include cadmium hydroxides and cadmium carbonates.\textsuperscript{15} The presence of these impurities explains the imbalance between cadmium and selenium. Degassed water was subsequently used to prepare all solutions and resulted in films of negligible oxygen content.

The stoichiometry of CdSe films produced with degassed water was found by EDS to be selenium rich; Cd:Se ratios were \textit{ca.} 1:1.7. The disparity is attributed to the formation of zero valent selenium, which precipitates from solution as a black or red solid and likely becomes entrapped in the film. Lower concentrations of selenium relative to cadmium only resulted in slowed deposition and had no effect on film composition.

The ratio of stabilizer to selenium was varied as a second experiment. Sodium sulfite is a reducing agent used to slow the oxidation of DMSU and prevent the formation of bulk selenium. Increasing the ratio of sulfite:Se from 1:10 to 1.5:10 had no effect. Conversely, as hydrolysis of DMSU is believed to be the rate-limiting step for CBD of CdSe films,\textsuperscript{16} the sulfite:Se ratio was also lowered to 1:20. It was desired that this would increase the deposition rate, resulting in better CdSe films. Unfortunately this approach failed; deposited films were even higher in selenium.

Finally, the ratio of citrate to cadmium was lowered; the rationale being that increased concentrations of Cd(OH)\textsubscript{2} (assuming hydroxide cluster mechanism) or free Cd\textsuperscript{2+} (ion-by-ion) should consume Se\textsuperscript{2-} before it can be oxidized to Se\textsuperscript{0}. Ratios were varied between 2:1 and 4:1. For citrate to Cd ratios below 3:1, visible Cd(OH)\textsubscript{2} formed immediately on addition of ammonia, and below 2.5:1 film deposition was poor. Changing this parameter did effectively alter film stoichiometry (Table 4.1). A citrate to cadmium ratio of 3:1 produces films containing minimal excess selenium.
Table 4.1. Effect of bath citrate: cadmium ratio on deposited CdSe film stoichiometry (as determined by EDS).

<table>
<thead>
<tr>
<th>citrate: cadmium ratio</th>
<th>Cd:Se film stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0 : 1</td>
<td>1 : 1.7</td>
</tr>
<tr>
<td>3.5 : 1</td>
<td>1 : 1.4</td>
</tr>
<tr>
<td>3.0 : 1</td>
<td>1 : 1.2</td>
</tr>
<tr>
<td>2.5 : 1</td>
<td>1 : 1.3</td>
</tr>
<tr>
<td>2.0 : 1</td>
<td>no film</td>
</tr>
</tbody>
</table>

**Engineering of back contacts.** Attempts to perform electrical tests on CdSe films on Buckypaper/PTFE were hampered by difficulty gaining electrical contact to the back surface of the SWNTs. Several remedies were attempted, including sputtering of gold onto the back of the Buckypaper after peeling it from the Teflon membrane or using conductive silver adhesive. Very thin Buckypaper substrates are too fragile to be removed from the backing membranes, so a different solution was needed.

By painting the top surface of the Buckypaper with conductive silver adhesive while it is under suction in a filtration apparatus, it is possible to partially impregnate silver within the SWNT network. Care must be taken, however, not to use too much silver or to leave the vacuum on too long. If silver bleeds through to the underside of the SWNTs, clean separation of the Buckypaper from the Teflon membrane is not possible.

After the silver paint dried the Buckypaper was inverted and carefully transferred to the adhesive side of a strip of PET packing tape. The tape had been perforated in a small area, corresponding to the position of the silver on SWNTs. Next the filter membrane was carefully peeled away, transferring the SWNTs to the adhesive tape.
Before subjecting the Buckypaper to CBD, holes in the packing tape were masked by rubber cement to prevent CdSe from depositing on the back contacts. Resulting Buckypapers have a very smooth top surface as seen by SEM (Figure 4.4). In addition they are flexible, robust and do not delaminate from the tape, even under the conditions of CBD.

Figure 4.4. SEM image of Buckypaper-on-tape (SWNT side).

Second-generation CdSe Buckypaper. Deposition of CdSe on Buckypaper-on-tape, using the conditions optimized above, yielded surprising results. After 16 hours of deposition (4 x 4 h), SEM imaging revealed that the films were severely cracked (Figure 4.5). SEM further showed that the films were much thicker than those from previous Buckypaper samples. One explanation for this observation could be that Buckypaper-on-packing tape samples have a smoother top surface that allows rapid nucleation and therefore faster film growth. Alternately, it is possible that SWNTs on tape are of higher
density at the deposition surface since they have been inverted (and also compressed with sufficient force to adhere them to the tape), and therefore less time or material is required to infill the void space.

The observed extensive cracking is problematic, as any direct contact of SWNTs to the window layer will short the heterojunction. Cracking could be attributed to excessive flexing of the substrate, either during CBD or subsequent SEM sample preparation. Thick films are likely to be more brittle, compounding the formation of cracks. In order to learn whether sample handling was causing film cracking, a small piece of Buckypaper-on-tape was affixed to an aluminum SEM sample stub. The stub was coated with rubber cement to protect it from the CBD solution, and then CdSe was deposited on the immobilized Buckypaper. SEM revealed, again, a large amount of cracking of the CdSe film. Therefore, cracking is not (at least not entirely) caused by

Figure 4.5. SEM image of CdSe (16 h deposition) on Buckypaper-on-tape.
samples flexing during handling. It is still unclear whether the problem is due to internal stresses within the film or some other factor.

Next, shorter depositions were performed on Buckypaper-on-tape samples. Severe cracking occurs after 12 h of deposition. At 4 and 8 hours, uniform films with smooth top surfaces are formed (Figure 4.6). While some cracks are still visible in SEM, they are much fewer and smaller.

![Figure 4.6. SEM image of CdSe film (4 h deposition) on Buckypaper-on-tape.](image)

XRD was attempted on CdSe SWNT composites; however the samples did not diffract. Either the material is truly amorphous, or the crystalline domains are smaller than ca. 4 nm. Previous XRD studies of similar CBD CdSe films deposited on glass required annealing before any weak diffraction was observed.13
Deposition of CuSe window layer. Initial attempts to deposit copper selenide using DMSU and citrate at 60 °C were not reproducible; the films were inconsistent in both thickness and quality. All previous CuSe CBD methods using DMSU have resulted in films of the klockmannite phase (CuSe).\textsuperscript{17,18} The desired phase for PV window layers is berzelianite (Cu\textsubscript{2-x}Se, where x \approx 0.2), as it has better conductivity. Therefore, an alternate selenium source was examined, sodium selenosulfate (Na\textsubscript{2}SeSO\textsubscript{3}). Na\textsubscript{2}SeSO\textsubscript{3} is conveniently prepared by heating elemental selenium in an aqueous solution of sodium sulfite. It is unstable (though less so than DMSU) and must be kept from oxygen to avoid bulk precipitation of elemental Se.

Several selenosulfate CuSe preparations were attempted, using citrate\textsuperscript{19} or NTA\textsuperscript{20} as copper complexants. Also tested were reaction schemes employing only NH\textsubscript{3} as ligand.\textsuperscript{17,21} The method of Garcia et al.\textsuperscript{17} provided the best quality films. SEM images of the CuSe films show colloidal material and small crystallites on the surface (Figure 4.7).

![SEM image of CuSe film on CdSe on Buckypaper-on-tape.](image)

**Figure 4.7.** SEM image of CuSe film on CdSe on Buckypaper-on-tape.
Determination of CuSe film composition and thickness on CdSe Buckypapers was nontrivial. Equivalent films (16 h deposition) grown on glass have a thickness of 200 nm.\textsuperscript{17} EDS data was collected to find average film stoichiometry. The presence of a small amount of cadmium (3\%) was detected. EDS sampling depth is on the order of 1 \textmu m; the presence of trace cadmium implies that CuSe films are in fact approximately 1 \textmu m thick.

Analysis by XPS also showed the presence of cadmium (\textit{ca.} 2\%). XPS is a surface technique; ejected photoelectrons can only escape from approximately the top 10 nm of the sample. This close agreement between XPS and EDS was confusing. It was assumed that Cd in EDS resulted from the underlying absorber layer; cadmium was not expected to be present at the surface. Taken together, XPS and EDS suggested that either CuSe films are doped with small amounts of cadmium, or that CuSe coverage is incomplete. SEM images taken over large areas showed uniformity of the surface texture as seen in Figure 4.7; thus the films appear to be homogeneous.

Further information was obtained by XPS depth profiling. Iterative ion sputtering and elemental analysis showed cadmium present only at the surface of the film. Upon sputtering into the sample cadmium content disappears completely (as does oxygen), leaving a consistent stoichiometry of Cu\textsubscript{1.7}Se throughout the film. It was not possible to sputter through the CuSe window layer down into the CdSe absorber. Finally, based upon XPS and EDS, it appears the CuSe window layer is of the desired berzelianite stoichiometry, has a thickness of \textit{ca.} 1 \textmu m, and is contaminated at the surface by cadmium.

The presence of cadmium at the sample surface remains unexplained. It is possible that cadmium species (hydroxides, carbonates) previously adsorbed on the surface of the CdSe film were redissolved in the CuSe bath and then subsequently redeposited onto the CuSe window layer. Another explanation is that metals are significantly mobile within the films. In fact, this has been shown previously: CdSe films have been doped with copper by simple immersion in aqueous Cu\textsuperscript{2+} solutions.\textsuperscript{13}
Additionally, in CdS films cadmium can be exchanged with copper quantitatively down to a depth of 300 nm by an aqueous bath method. However, these explanations would be expected to result in small amounts of Cd throughout the film or close to the CuSe/CdSe interface, not at the top surface. Whatever the source of the cadmium, it is not expected to have a significant effect on the function of PV devices.

XRD was performed in order to determine the phase of CuSe present. The film has some crystallinity, as weak diffraction was seen with peaks matching bulk berzelianite Cu$_{2-x}$Se, further corroborating XPS data (Figure 4.8).

![Figure 4.8. XRD pattern of CuSe-CdSe Buckypaper. Simulated pattern for berzelianite shown in purple.](image)

As a final characterization, depth-profile Raman spectra were collected on the films. CuSe and CdSe have their strongest Raman modes at 263 and 209 cm$^{-1}$ respectively. It must be mentioned that these frequencies are coincident with the radial breathing modes (RBMs) of SWNTs found between 150 and 250 cm$^{-1}$. Thus, care must be taken when assigning peaks. Additionally, Raman depth profile data suffers from
limitations. Scattering occurs from above and below the focal plane, therefore depth slices overlap. Also, deeper slices suffer from reduced signal to noise due to significant scattering from the sample above the focal plane.

Raman spectra were collected with the microscope focal plane varied from 2 μm above the sample surface to 2 μm below in 1 μm steps. The resulting spectra show none of the expected peaks attributable to SWNTs (D, G modes) and contain a single (CuSe) peak at 263 cm$^{-1}$. Spectra collected with the focal plane at the surface and 1 μm below show a very slight peak begin to appear at 209 cm$^{-1}$, indicating CdSe. Unfortunately, at 2 μm depth and below, baseline noise increased so that no peaks were observed. Scattering expected for SWNTs was not seen in any spectrum, indicating that the semiconductor coatings are microns thick. All Raman spectra are shown in Figure 4.9.

![Figure 4.9. Depth-profile Raman spectra (514 nm excitation) of CuSe-CdSe Buckypaper, from + 2 to -2 μm relative to sample surface.](image)

**PV testing.** Devices were subjected to testing for photovoltaic response. It should be noted that the devices described here have not yet been optimized in terms of relative or absolute film thickness of the metal selenides. Additionally, as-prepared devices lack a
transparent top contact. For testing purposes, silver adhesive paint was adequate to provide proof of concept. Figure 4.10 shows the testing configuration. More accurate testing will be performed with a sputtered coating of indium tin oxide (ITO), although this process will not be suitable for final devices because it requires specialized equipment.

![Diagram of PV testing configuration](image)

**Figure 4.10.** PV testing configuration, under illumination by a 90 W halogen lamp.

Device testing was performed (top contact: silver paint spots) which confirmed PV functionality, albeit with minimal efficiency. The open circuit voltage ($V_{OC}$) was found to be 1.28 mV; short circuit current ($I_{SC}$) was 4.85 μA. The characteristic IV curve for the test device is shown below (Figure 4.11). For a device to be viable, $V_{OC}$ will need to be increased by nearly 3 orders of magnitude; likewise short-circuit current should be in the mA range.
Conclusions

We have demonstrated a functional, albeit inefficient, thin film solar cell produced by a CBD method, which can be manufactured on flexible substrates. Many improvements are still needed in terms of design, performance, and production. In particular, further characterization of semiconductor films is needed to find optimal thickness and to improve crystallinity. However, our work provides proof-of-concept and suggests that the architecture and production of this device will help drive down the cost of solar energy.

Another task yet to be completed is the design of a transparent top contact that will not increase manufacturing costs. Conductive material is required, in order to collect charge carriers across the entirety of the top surface. The top contact must also be optically transparent so that light reaches the absorber layer. Materials presently being investigated for our device include poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) and transparent conductive oxides (TCOs) such as...
ITO or fluoride-doped tin oxide. A major goal is to produce TCO films by a CBD or sol-gel route. Other potential materials are SWNT or graphene polymer composites.

**Experimental**

Deionized water was degassed prior to use by bubbling Ar for 15 minutes. CdSO₄, CuSO₄·5H₂O, NH₄OH (28 - 30%), Na₂SO₃, sodium citrate, SDS, and elemental selenium were purchased from Sigma Aldrich and were used as received. N,N-dimethylselenourea was purchased from 3B Scientific Corp. Single-walled carbon nanotubes (HiPco process) were obtained from the Carbon Nanotube Laboratory at Rice University, and were purified by a literature procedure prior to use. Stabilized DMSU solution was prepared by dissolving sodium sulfite (13 mg, 0.10 mmol) in deoxygenated, deionized water (10 mL). N,N-dimethylselenourea (151 mg, 1.0 mmol) was then added to the sulfite solution with stirring under Ar. DMSU solutions decompose within 1-2 days even if stored under Ar. Sodium selenosulfate solution was prepared by dissolving sodium sulfite (5.04 g, 0.04 mol) in deionized, deoxygenated water (100 mL). Selenium powder (1.58 g, 0.02 mol) was then added, and the mixture was heated to 60 °C with stirring for 2 h under Ar. After 2 hours, residual Se was removed by filtration. Selenosulfate concentration is estimated at ca. 0.18 M. Solutions are usable for 3 - 4 days if stored under Ar. XPS data were acquired on a Physical Electronics, Inc. Phi Quantera instrument with monochromated Al-Kα X-ray source. SEM imaging was performed with a FEI Quanta 400 high-resolution field emission scanning electron microscope (accelerating voltage of 30 kV) equipped with liquid N₂-cooled EDS detector. XRD data were acquired using a Rigaku D/Max Ultima II configured with a vertical theta/theta goniometer, Cu-Kα radiation, and graphite monochromator. Raman data were obtained using a Renishaw Raman microscope with a 514 nm laser excitation source. Conductivity data were found using a four-point probe at a current of 0.5 mA.
Buckypaper substrates. SWNTs (10 mg) were dispersed in 1% SDS solution (100 mL) and subjected to probe sonication for 60 minutes. The resulting SWNT dispersion (40 mL) was vacuum filtered over a PTFE membrane (47 mm diameter, 0.2 μm pore size). After all solvent had been removed, conductive silver paint was brushed onto an area at the center of the Buckypaper. The vacuum was left on for 2 minutes in order to allow silver to partially infiltrate the SWNTs. The paper was then inverted and pressed onto a piece of PET packing tape (3M), which had been perforated with several holes by a needle in a small area. Care was taken to ensure that the silver paint was matched to the perforated area of the tape to allow electrical contact to be made from the back of the assembled Buckypaper-on-tape. Before film deposition, the perforations in the tape were coated with a thin layer of rubber cement (Elmer’s) to protect the back contacts from bath solutions.

CdSe deposition. To a glass jar were added 0.10 M CdSO₄ (6.0 mL), 0.60 M sodium citrate (3.0 mL), 1.50 M NH₄OH (2.4 mL), deionized water (3.4 mL), and 0.10 M stabilized DMSU solution (5.2 mL), freshly prepared. Moist substrates (immersed in water 5 minutes before drip drying) were immersed vertically in order to minimize bulk precipitate on their surfaces. The jar was capped and the reaction was allowed to proceed for 4 h at room temperature. When the deposition was complete, samples were removed from the bath and rinsed with deionized water, then placed in a vacuum dessicator to dry.

CuSe deposition. To a glass jar were added 0.20 M CuSO₄ (5.0 mL), 1.50 M NH₄OH (3.0 mL), deionized water (7.0 mL), and ~0.18 M Na₂SeSO₃ (5.0 mL) Moist substrates (immersed in water 5 minutes before drip drying) were immersed, vertically in order to minimize bulk precipitate on the surfaces. The jar was capped and the reaction was allowed to proceed for 16 h at room temperature. When the deposition was complete,
samples were removed from the bath and rinsed with deionized water, then placed in a vacuum dessicator to dry.

References


Conclusion

Clearly, carbon nanomaterials research is and will continue to be very active for the foreseeable future. The physical and electronic properties of SWNTs and graphene in particular make them excellent candidates for numerous applications. Still, many fundamental obstacles remain to be overcome before these materials can reach their full potential.

We have presented advances toward the goal of chiral-specific SWNT production. Specifically we have described functionalization of SWNTs with various donor ligands. This will allow the coordination of catalyst particles to nanotube ends for SWNT amplification. In addition we have suggested a method that, with improvements, could allow for diameter or chiral angle- specific SWNT separations. The synthesis of triarylamines by Buchwald-Hartwig chemistry provides a facile route to SWNT separation agents.

We have reported progress in the production, functionalization, and characterization of graphene. It is now possible to determine epoxide content quantitatively, as well as to selectively remove epoxides, from graphite oxide. Further, we have produced a homogeneous organic dispersion of graphene from pristine graphite. This allows the avoidance of harsh oxidation chemistry, and also provides a convenient platform from which to covalently functionalize graphene by radical alkylation.

Finally, we have produced a photovoltaic device on flexible substrates using chemical bath deposition of semiconductor materials on SWNTs. This device, with advances in efficiency, could provide a route to inexpensive solar cells that can be manufactured without specialized equipment.