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Characterization of Fluorinated Carbon Nanotubes

By

WAN-TING CHIANG

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
MASTER OF ARTS

APPROVED, THESIS COMMITTEE

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ABSTRACT

Characterization of Fluorinated Carbon Nanotubes

By

Wan-Ting Chiang

Reaction temperatures and time are probed to get the optimal fluorination conditions in order to produce C_F carbon nanotubes. Possible fluorotube structures are optimized with molecular mechanics calculation. Results show that fluorines would like to add along the circumference of the tubes instead of going down the tube axis. The (1,4) isomer has the lower total steric energy (TSE) between the two proposed fluorotube structures, but the energy difference is small. Scanning tunneling microscopy has been used for atomic scale imaging of the fluorotubes. Significant band features are seen on fluorotubes, not on pristine carbon nanotubes. Butylated tubes have also been investigated by STM imaging. Instead of bands, relatively large, distinct features with spacing of about 50 Å are observed. Both theoretical and experimental results indicated the (1,4) isomer with bands around the tubes should be the preferred structure.
Acknowledgments

It has been a great challenge and also a valuable experience for me to pursue my advanced degree here in the Chemistry Department of Rice University. I am so grateful to have Dr. Margrave as my advisor, who guides and supports me through this research. Lucky as I am, I also have another advisor, Dr. Hauge, who gives me hands-on advice to transfer from theoretical chemistry to the real world of experimental chemistry. Dr. Halas has led me to the nanoscale world of carbon nanotubes. And Dr. Kevin Kelly, from whom I have gained most of my knowledge about scanning tunneling microscopy, has lent me a helping hand whenever I was confused about all the circuits and images surrounding STM. I can not say too much about Dr. Edward Mickelson, my predecessor in the fluorinated carbon nanotubes project, who is my encyclopedia for the subject. He is a good mentor and a good friend. Also thanks to Dr. Glass for taking his time to be on my thesis committee. I can't forget to thank all other members of the research group. They have been great help in many ways.
My aunt Amy and uncle Jason, who provided me with emotional support when I was in need, are like the second parents to me. They treat me as if I was their daughter. Without them, I wouldn't have gone this far. I can't forget to thank my parents who have provided financial and emotional support throughout the year. Last but not least, I have to mention my great golden companion, Copper, who is my best buddy and has spent countless nights with me studying and researching. Without all of those mentioned above, I wouldn't be at the stage in life that I am right now. This MS thesis is dedicated to those who love and support me.
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Chapter 1

Fluorination of carbon nanotubes

1.1 Background

Since the initial discovery in 1991\textsuperscript{1,2} and subsequent development of large-scale syntheses of buckytubes\textsuperscript{3,4}, various methods for their synthesis\textsuperscript{3,4}, characterization, and potential applications have been pursued. Depending on their diameter and the degree of helicity, carbon nanotubes can exhibit variations in electronic properties, ranging from semi-conducting to metallic structures\textsuperscript{5}. After years of researching, people understand more about nanotubes\textsuperscript{6,7}. However, derivatization of this novel carbonaceous material is still in its early stages. Only in 1998 the first sidewall functionalized carbon nanotubes were reported when Mickelson et. al\textsuperscript{8,9} were able to fluorinate the sidewalls of carbon nanotubes. After that astonishing preparation of fluoronanotubes, several derivatizations of carbon nanotubes were reported earliest this year\textsuperscript{10,11,12} and more are waiting to be published.
1.2 Experimental procedure

All precursor nanotubes used in this study are from tubes@rice, a non-profit company based at Rice University. The single-walled carbon nanotubes, about 1 nm in diameter, were produced by the dual laser vaporization of Co/Ni doped graphite rods and purified by various techniques\textsuperscript{13,14}. Fluorination details can be seen elsewhere\textsuperscript{8}. Based on Mickelson's study, we have varied some parameters within the procedures to produce the desired fluorinated carbon nanotubes, which will be described later.

Nanotubes from tubes@rice were obtained as a suspension in toluene solution. Filtering the nanotube solution through a PTFE filter membrane and washing with methanol to remove unwanted residues leaves a black, puffy film on the surface. Unlike the buckypaper made from tubes in N,N-dimethylformamide (DMF) or Triton-X (polyoxyethylene isooctylcyclohexylether) solution (surfactant manufactured by Aldrich), these films, or buckypapers are believed to have a "3-D network" structure. The tubes are not as tightly packed and fluorine would be able to penetrate into the nanotubes ropes more easily. These are good precursors for fluorination.
Several reactions were carried out to establish optimal fluorination conditions (i.e. temperatures and reaction times). The goal is to reach saturation, C_F, without destroying the tube structure. A fluorine/He mixture (2 cc/min & 100 cc/min respectively) was passed through a temperature-controlled Monel flow reactor containing the SWNTs samples.

1.3 Result and Discussion

Table 1-1 shows the results from several fluorination experiments. At temperature higher than 150°C with proper reaction times, a C/F ratio of ~2 can be reached. At temperatures lower than 150°C, however, a C-F peak is not clearly observed in the IR spectrum. At higher reaction temperature, a well-defined, but broad C-F peak can be seen around 1270 cm⁻¹ with DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) taken with fluorobuckypapers (Figure 1-1). Peaks with higher wavenumbers correspond to stronger covalent bonds. Lowering the temperature might induce the creation of ionic C-F bonds, or weaker covalent bonds. This phenomenon was also observed in
fluorinated graphite. One interesting note here while preparing the IR nanotube samples: when mixing fluorotubes with KBr and subsequently drying in the oven at ~120°C, the IR spectrum would show a peak around 1100 cm⁻¹ (Figure 1-2). No C-F stretch frequency could be observed. KBr might have reacted with Fluorotubes: KBr + C₂F → KF + Br + C₂⁺: The vacancy from the loss of fluorine might then be occupied by oxygen from the air in the oven, thus creating an epoxy type of bond which is being observed in DRIFTS spectrum. In addition, samples fluorinated at 150°C by Mickelson showed no C-F peak with infrared spectroscopy and the C/F ratios were determined to be about 10 with electron microprobe analysis. In the current study, C/F ratio for tubes fluorinated at 150°C as high as 3 were found, depending on the duration of the reaction. Nanotube rope structures within the puffy buckypaper can account for the increased fluorine percentage in the Fluorotubes: nanotubes filtered from DMF suspension are more tightly packed by Van der Waals interactions. If annealed at high temperature, which was done with Mickelson's nanotube samples, this effect could increase dramatically. Buckypaper made from the toluene suspension has a "network" structure, i.e. the nanotubes are loosely bound in the buckypaper. Fluorine thus can diffuse into the inner structure of the ropes easier and find more reaction sites on the surface. From TEM
Table 1-1  Reaction Temp and Time vs. C/F

<table>
<thead>
<tr>
<th>Reaction Temp (C)</th>
<th>Reaction Time (hrs)</th>
<th>C/F</th>
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<tr>
<td>100</td>
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<td></td>
<td>5</td>
<td>2.2</td>
</tr>
<tr>
<td>290</td>
<td>2</td>
<td>1.92</td>
</tr>
</tbody>
</table>
Figure 1-1  DRIFTS spectra of Fluorinated tubes

(a) Fluorinated at 150 °C
(b) Fluorinated at 200 °C
Figure 1-2  DRIFTS Spectra of nanotubes fluorinated at 200°C

Samples were prepared by mixing with KBr

* indicated the activated cage modes of carbon nanotubes
+ indicated the epoxy-like peak
examination. tubes started to disintegrate around 250°C. In order to keep the tube structure and obtain a saturated C/F ratio (~2) at the same time, we decided to use 200°C as our optimal fluorination temperature. The minimum reaction time to reach C₂F is ~6 hours at 200°C. Electron microprobe analysis (EMPA) and IR indicated the desired carbon-fluorine ratio and C-F stretching frequency. These fluorinated tubes are soluble in DMF and alcohol solvents.¹⁵

1.4 Future Work

The nature of the C-F bond in Fluorotubes should give us an insight to the temperature effects on the fluorination, and thus could lead to successful characterization of further derivatization, such as alkylation. It could also provide for selective functionalization with different types of C-F bonds. De-fluorination and partial fluorination are currently being pursued in order to create active sites for further reaction and defect studies. In short, gas phase fluorination processes have been explored. Solid phase reactions of
nanotubes with reactive metal fluorides (AsF₂, MnF₃, PtF₆, etc.) are also interesting routes for producing fluorotubes. They need to be investigated in the future. The reaction chemistry of solvated fluorotubes could be an important route for preparation of various functionalized tubes with a variety of useful properties.
Chapter 2

Molecular Mechanics Method

2.1 Introduction

The research on carbon nanotubes has attracted an increasing growth of interest in the recent years due to their unique characteristics and being a member of the carbon family. In order to understand the chemical and physical properties of nanotubes, theoretical modeling is often used to explain some observed phenomenon\textsuperscript{16,17,18,19}. Although quantum mechanics calculations of molecular electronic structure can be highly accurate, they are also costly in computational time. Simulation of large molecules and biological macromolecules can therefore only be performed with classical mechanics. With these empirical methods, one calculates the mechanical and electrostatic interaction energies between bonded and non-bonded atoms. Any manufacturing technology must move atoms from where they are to where we want them to be. How atoms move and the forces that
act upon them during their motion are therefore critical areas of study in nanotechnology. Molecular mechanics explains this field\textsuperscript{20,21}.

2.2 Background

Molecular mechanical force fields use the equations of classical mechanics to describe the potential energy surfaces and physical properties of molecules. Early reports on molecular mechanics date from the seventies, such as Allinger\textsuperscript{22} in 1973 and Hagler\textsuperscript{23} in 1974. Molecular mechanics treats molecules as arrays of hard, impenetrable balls connected by springs. The molecular energy is calculated by summing the potentials for bond distances, bond angles, and torsion angle deformations between 2,3, and 4 bonded atoms and the dispersion and electrostatic potentials between non-bonded atoms. All potentials are based on structural parameters and empirically derived constants.

2.3 Individual energy components
A Morse function best approximates a bond potential energy as a function of distance. Only Morse potential can describe a dissociating bond, compared to harmonic potentials, but force fields use the harmonic potential since (1) it is faster to compute and parameterize, and (2) Morse and harmonic functions are similar at the potential minimum (Figure 2-1). Most molecular mechanics programs approximate the Morse curve with a mathematically simpler Hooke's Law function, which reproduces the bottom of the well pretty well, but fails at very long bond lengths:

\[ V_{\text{stretch}} = \sum K_r(r-r_0)^2 \]

\[ V_{\text{bend}} = \sum K_\theta(\theta-\theta_0)^2 \]

where \( r \) is the bond distance, and \( \theta \) is the bond angle. The torsion function represents energy arising from bonds not fully staggered. It is best characterized as a periodic function, which is often implemented as a truncated Fourier series:

\[ V_{\text{torsion}} = \sum V_n/2 \left[ 1 + \cos (n\phi - \phi_0) \right] \]
Figure 2.1 Morse potential vs. Harmonic function

(Graph generated by O.S. Smart, U. of Birmingham, 1995)
where \( V_n \) = torsion force constant. \( n \) = periodicity of the Fourier term. \( \phi_0 \) is the phase angle, and \( \phi \) is the torsion angle. A Van der Waals interaction refers to attraction and/or repulsion between non-bonded atoms. It is constructed as a 6-12 function:

\[
V_{VdW} = \sum [ \frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} ] .
\]

Where \( R_{ij} \) is the nonbonded distance between two atoms, and \( A_{ij}, B_{ij} \) are the Van der Waals parameters for the interacting pair of atoms. The dipole energy is the energy of interaction of bond dipoles and any point charges. It can be derived from the classical electrostatics:

\[
E_{dipole} = k \varepsilon \sum \mu_i \mu_j \left[ \cos \chi - \frac{3 \cos \alpha_i \cos \alpha_j}{R_{ij}^3} \right].
\]

where \( \varepsilon \) is the dielectric constant. \( \chi \) is the angle between the bonds and \( \alpha \)'s are the angles made by the bond dipoles with a line joining their midpoints.
2.4 Force field - mm+

A force field describes a molecule as a collection of atoms that interact with each other by simple analytic functions. It will give the best results for molecules similar to those used to develop its parameters. MM+ is unique among the force fields in the way it treats bonds and angles. Both bond and angle terms can contain higher order terms than the standard quadratic. MM+ is an extension of MM2, which was developed by Allinger and co-workers\textsuperscript{24} in 1977 and was originally designed for small organic molecules\textsuperscript{25,26}. Although it has been expanded to peptides. Carbon nanotubes and peptides are similar in their relatively large, repeatable basic units, and experimental data can be found for carbon materials. Thus, mm+ is an ideal force field to be used in our molecular mechanics calculation.

2.5 Geometry Optimization
A starting structure is defined for MM+ as a list of atomic Cartesian coordinates and a connectivity table that define the bonds between the atoms. Typically the user specifies the positions of only the heavy atoms and the program adds hydrogens and unshared pairs in standardized locations to make each atom tetrahedral, trigonal, or linear, as appropriate. The method of defining a minimum is crucially important. The energies of the individual bonding components are functions of deviations of a molecule from a hypothetical compound that has bonded interactions at minimum values. The force fields are applied to the input geometry and a total steric energy (TSE) is calculated. The molecular geometry can then be altered and the TSE is recomputed; the process is repeated until a minimum TSE is found. Once the energy and structure remain constant from iteration to iteration, computation ceases. Further evidence that a minimum has been found can be obtained by computing the normal-mode vibrational frequencies of the molecule. Since any distortion of a molecule from the geometry at a stationary point on the potential energy surface will lead to an increase in energy, the computed frequencies will all be positive (real) for a molecule in such a state. If the molecule lies at a first-order saddle point (transition state), one and only one frequency, corresponding to motion along the reaction coordinate, will be negative (imaginary).
Two or more imaginary frequencies imply location at a maximum. The absolute energy of a molecule from a molecular mechanics calculation has no physical meaning. Rather, it's very useful for comparing energies between two or more molecules. Unlike quantum mechanics, molecular mechanics does not treat electron explicitly. However, it evaluates steric effects for a molecular system from a database of desired parameters.
Chapter 3

Theoretical Modeling of Fluorinated Carbon Nanotubes

3.1 Introduction

Single-wall carbon nanotubes have been the subject of a large number of studies after their discovery in 1993. One of the novel and promising avenues in SWNT research is the synthesis of new compounds arising from the addition of atoms or radicals to the exterior. The derivatization of C60 (buckminsterfullerene). SWNT's other famous family member has been worked on extensively in recent years. Because of the similarity between the two, researchers have applied the same types of functionalization used with C60 to SWNT's. By using the technology developed in the fluorination of graphite and C60. Mickelson et.al⁸ have reported the fluorination of high purity SWNT's. They have demonstrated via gravimetric and electron microprobe analysis that large amounts of fluorine can be added to SWNT's and that there is a limiting stoichiometry of CxF at which the fluorinated tube can still remain in its tube-like structure. Several theoretical studies have
recently appeared in the literatures dealing with different aspects of carbon nanotubes\textsuperscript{29,30,31,32}. As far as fluorinated carbon nanotubes are concerned, no theoretical studies have been reported. We have investigated some possible mechanisms for fluorine addition to the SWNT's and conceptualized some possible structures consistent with C\textsubscript{2}F stoichiometry.

3.2 Computational Details

Two computational methods have been used in this work. To get a fundamental idea about the fluorine addition mechanism and fluororotube structures, we started with a molecular mechanic calculation as implemented in the Hyperchem software package\textsuperscript{33}. A MM+ force field was used for the calculation. Fluorine addition was modeled for (10.10) single wall nanotubes. In the first part of the computation, we investigated the possible addition sites for two fluorine atoms. Calculations were done on (1.2) and (1.4) fluorine additions to the nanotube system. We also looked at 4-F and 6-F addition to the sidewalls of nanotubes to get a perspective on the addition mechanism.
of fluorine to the sidewalls of carbon nanotubes. Finally, we propose two possible fluorotube structures based on the experimental results. Total steric energy was calculated for the proposed isomers and individual energy components: stretching, bending and torsion energies were also obtained. The nanotubes assumed in the calculation consisted of 200 fluorines and 600 carbons with end caps. All geometries were optimized before energy calculations were performed. The hyperchem molecular mechanics calculation was run on a Pentium I computer, and Hyperchem version 4.0 was used. A semi-empirical method was also applied for calculating similar structures. This work was primarily done by Wong, preceded by the molecular mechanics results. Here I will report mainly the results from the molecular mechanics calculation, and the comparison with the semi-empirical calculation.

3.3 Results & Discussion

3.3.1 2 F fluorine addition
There are three possible ways of adding one fluorine molecule to the sidewalls of SWNT: (1.2), (1.3) and (1.4) additions within a hexagonal ring (Figure 3-1). (1.3) addition of fluorines would introduce radicals to the nanotube environment. Radicals would be very reactive and thus are not favored. The molecular mechanics calculations thus were done only for the (1.2) and (1.4) additions. According to the calculated total (steric) energy of system, (1.2) addition to the sidewalls of nanotubes has a lower energy, though the difference between the two isomers is not large.

3.3.2 Addition Mechanism

Once the fluorination is initiated, incoming fluorines will have multiple addition sites to choose from. Figure 3-2 shows the possible addition sites for incoming fluorines. Fluorines will add to the nearest neighboring carbons to the initiation sites, as seen in Figure 3-3. The semi-empirical calculation also produced a similar result. As the reaction continues, fluorines have two possible routes to attach themselves to the tubes: along the tube axis or around the tube
circumference (Figure 3-4). The calculated results suggest that fluorines will prefer to add along the tube axis once the fluorination is initiated. However, a different result was found through the semi-empirical calculation\textsuperscript{34}. In Wong's calculation, she applied AM1 & CNDO, two of the more popular semi-empirical methods for the fluorine addition model. She found that addition around the tube circumference is the preferred fluorination sequence\textsuperscript{34}. In the molecular mechanics calculation, total energy is the sum of stretching, bending, torsion, van der Waals and stretching-bending individual energy components. In addition to the total steric energy, electronic effects are also included in the semi-empirical methods. Since both steric and electronic effects are major contribution to the stability of the fluorotubes, it appears that fluorine addition could be dominanted by the electronic effects.
Figure 3-1 - Possible fluorine initiation sites. The arrow indicates the direction of the nanotube axis

Relative to blue sphere, which represents a F atom.

Position 1  -- 1.2 addition
Position 2  -- 1.3 addition
Position 3  -- 1.4 addition
Figure 3.2  The addition of four fluorines to a nanotube

Shaded circles represent the 1st F₂ molecule:

Empty circles represent the incoming F₂ molecule after initiation:

Numbers represent possible sites for addition (1,2 or 1,4) on the six-membered rings
Figure 3-3  Energy comparison of the addition of four fluorines to a nanotube at difference positions

(a) (1,2) isomer energy vs. fluorine position
(b) (1,4) isomer energy vs. fluorine position

>Note> “Down” - adding along the tube axis  
“Right” - adding along the tube circumference
Figure 3-4 Some possible fluorine addition sequences

(i) Adding along the tube axis
(ii) Adding around the tube circumference

(a) (1,4) addition
(b) (1,2) addition

Arrows indicate the nanotube axis
3.3.3 C₂F fluorotubes

Previously, Mickelson et. al has shown that there is a limiting stoichiometry of C₂F for which fluorinated tubes can still maintain at their tube-like structures. according to EMPA. gravimetric and TEM analysis. Here, we have proposed two possible Fluorotube structures: 1.2 (conjugated) & 1.4 (parallel) isomers. In the (1.2) isomer, the double bonds in the hexagonal rings are in a conjugated structure, while they are parallel to each other in 1.4 isomer (Figure 3-5). For a 600 F addition, the 1.4 isomers are more stable with lower total steric energy. Figure 3-6 shows the optimized fluorotube structures in ball-and-stick images. Their total steric energy and individual energy components are shown in Table 3-1. All of the fluorines seem to line up in the (1.4) isomer when viewed from the end of the nanotubes, whereas in the (1.2) isomer, the tube looks twisted. This can be explained by the fluorine-fluorine repulsion in the fluorotube system. In (1.2) isomer, fluorines are closer together and this leads to a larger steric energy for the system, making this type of fluorotubes more unstable than the other. The (1.4) isomer is also more stable from Wong's semi-empirical results. Short fluorotubes were modeled due
Table 3.1  Total steric Energy vs. C₂F isomers

Energy is represented in kcal/mol

<table>
<thead>
<tr>
<th></th>
<th>(1,2)</th>
<th>(1,4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretching</td>
<td>168.5</td>
<td>136.5</td>
</tr>
<tr>
<td>Bending</td>
<td>936.1</td>
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<tr>
<td>Torsion</td>
<td>1285.3</td>
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<tr>
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<tr>
<td>Total E</td>
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<td>2313.4</td>
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<tr>
<td>Energy / F</td>
<td>14.2</td>
<td>11.6</td>
</tr>
</tbody>
</table>
Figure 3-5 - Proposed fluorine addition patterns on the fluorinated carbon nanotubes

(a) (1,2) addition - also described as "conjugated"
(b) (1,4) addition - also described as "parallel"
Figure 3-6  Optimized fluorotube structures

(a) (1.2) isomer
(b) (1.4) isomer

Both end views (on the left) and side view (on the right) are shown
to the limitation on size for semi-empirical calculation.

3.4 Conclusion

Our calculation provides an insight to the possible fluorotube structures. Based on a limiting stoichiometry of $C_2F$ from previous experimental results, we proposed two fluorotube isomers, with fluorine addition in either (1,2) or (1,4) positions within a hexagonal ring in a nanotube system. From a molecular mechanics calculation with mm+ force field, we found that the 1,4 fluorotube isomer is more stable, though the difference of the total steric energy between the two isomers is not very large. It is our belief that the two isomers could coexist from the fluorination of the nanotubes. By comparing the calculation results from molecular mechanics and semi-empirical methods with respect to stability, it appears that steric effects dominate the electronic effects in fluorinated carbon nanotubes. Further
purification and characterization of fluorotubes. if possible. will have to be done to verify any preferred existence of one isomer. In addition. because of the arrangement of the bonds in hexagonal rings. fluorotubes can be either insulators or conductors. Electrons can hop through conjugated bonds in (1,2) isomers thus makes this type fluorotubes conducting. whereas (1,4) isomers have their double bonds perpendicular to the electron flow through the conducting direction. along the tube axis. creating insulating fluorotubes.
Chapter 4

Scanning Tunneling Microscopy

4.1 Background

Scanning tunneling microscopy, or "STM", is a method for imaging the surface of solid materials with "atomic" resolution. It was invented in the early 1980's by Gerd Binning and Heinrich Rohrer\textsuperscript{35,36,37} from the IBM Zurich Research Laboratory in Switzerland. Our understanding of electron tunneling begins in the early 1920s with the advent of quantum mechanics. In 1960s, Giaver\textsuperscript{38} used tunneling to measure the superconductor energy gaps in metals, and in 1970s, Young, Ward and Scire\textsuperscript{39} observed tunneling and transition to field emission in the point-plane geometry that presaged the STM. Then, Binning and Rohrer received the Nobel Prize in Physics in 1986 for their invention of the STM (Figure 4-1). This instrument is not a true microscope, which gives a direct image of an object. Rather, the structure of a surface is studied using a stylus that scans the surface at a fixed distance from it.
Figure 4-1 Basic design of STM
4.2 Theory

The most extensively used theoretical method for understanding the tunneling junction is the time-dependent perturbation approach developed by Bardeen\(^4\) (1960). The scheme for Bardeen's approach is shown in Figure 4-2. He obtained the electronic states for the separated subsystems by solving the Schrödinger equations. Time-dependent perturbation theory is used to calculate the rate which an electron transfer from one electrode to the other. Bardeen showed that the amplitude of electron transfer, or the tunneling matrix element \(M\), is determined by the overlap of the surface wavefunctions of the two subsystems at a separation surface:

\[
M = \frac{\hbar}{2m} \int (\chi^* \frac{\delta \Psi}{\delta z} - \Psi \frac{\delta \chi^*}{\delta z}) \, dS
\]

where \(\Psi\) and \(\chi\) are the wavefunctions of the two electrodes. The tunneling current can be evaluated by summing over all the relevant states. At any finite temperature, the electrons in both electrodes follow the Fermi distribution. With a bias voltage \(V\), the total tunneling current is:
I = 4\pi e/\hbar \int [f(E_r-eV-E) - f(E_r+\epsilon)] \times \rho_s(E_r-eV+\epsilon)\rho_f(E_r+\epsilon)|M|^2d\epsilon.

where \( f(E) = \{1 + \exp[(E-E_r)/K_BT]\}^{-1} \) is the Fermi distribution function.

and \( \rho_s(E) \) and \( \rho_f(E) \) are the density of states (DOS) of the two electrodes. Bardeen further assumed that the magnitude of the tunneling matrix element \( |M| \) does not change appreciably in the interval of interest. Thus the tunneling current is determined by the convolution of the DOS of two electrodes:

\[ I \propto \rho_s(E_r-eV+\epsilon)\rho_f(E_r+\epsilon)d\epsilon; \]

Clearly, according to Bardeen's formula, the electronic structures of the two participating electrodes are interchangeable. If the goal is to obtain the DOS of the sample, one requires a tip with constant DOS, or a free-electron metal tip. In this case:

\[ dI/dV \propto \rho_s(E_r-eV). \]

Therefore, with a free-electron metal tip, the dynamic tunneling
Figure 4-2  Bardeen's approach to the tunneling theory
conductance is proportional to the DOS of the sample. However, because of the close proximity of the tip and the sample, Bardeen's original approach is not appropriate. The perturbation theory approach that Bardeen used is uniquely applicable for the expression of the tunneling current. Holstein (1955) and Herring (1962) proposed modifications of the original Bardeen theory by including modifications of the wavefunctions of one object due to the existence of another object. In spite of its simplicity, the modified Bardeen theory provides the backbone for much of the physics in scanning tunneling microscopy.

4.3 Atomic Scale imaging

The basic idea of the modern STM is shown in Figure 4-3: A metallic tip, usually transition metals or semiconductors, is sharpened so that it ends in a small cluster of atoms. If the tip is brought to within a few atomic diameters of a sample that is under investigation, electrons can go back and forth between the tip and the sample by a tunneling mechanism. The flow of tunneling electrons is very sensitive to the
Figure 4-3 STM operation scheme
separation between the sample and the tip. In use, the tip is mounted on a three-dimensional positioner that raster scans the tip above the sample, with feedback and control electrons to make sure that the tip doesn't actually touch the surface. As the tip is moved across and above the surface, a computer records the height at each point, and turns the result into an image of the surface. The invention of the STM realized a dream of physicists and chemists, to visualize individual atoms and their internal structures in real space. A large number of organic molecules have been imaged by STM. in particular, with atomic resolution. STM opens a new era of organic chemistry, and lead to a nanoscale view of the physical world.
Chapter 5

Insight to the Derivatized Carbon Nanotubes

5.1 Introduction

The fundamental chemistry of single walled nanotubes (SWNTs) is still in its infancy. Initial speculation suggested that chemical functionalization of SWNTs would be most favorable at the ends of nanotubes\textsuperscript{11}, and that functionalization of SWNT sidewalls might be difficult to achieve. Successful controlled fluorination of the SWNT sidewalls leading to soluble products has recently been reported\textsuperscript{15}, providing a vital precursor for the subsequent attachment of a wide variety of functional groups to the exterior of the SWNTs\textsuperscript{12}. Various techniques have been used to image nanotubes: scanning electron microscopy\textsuperscript{43} (Figure 5-1(a)), atomic force microscopy\textsuperscript{44,45} (Figure 5-1(b)), and scanning tunneling microscopy\textsuperscript{46,47,48,49,50} (Figure 5-1(c)). Scanning probe microscopes are proximity probes. They can provide three dimensional topographic images and, in addition, can give
Figure 5-1

(a) SEM image of carbon nanotubes
(b) AFM image of carbon nanotubes
(c) STM image* of a section of carbon
Nanotubes

* It is taken with Pt/Ir tips at 4 K. Tunneling
current = 60 pA and $V_{bias}$=500 mV
the atomic structure of the surface. They can also be used to measure
the electronic (STM) and elastic (AFM) properties of small structures.
STM is restricted to electrically conducting objects, but AFM does not
have this restraint. The unique characteristics of SWNTs that make
them ultimately attractive for application also limit our ability to
study their chemical derivatives with conventional chemical methods.
As seen in Figure 5-2(a) and Figure 5-2(b), AFM and SEM images of
fluorinated carbon nanotubes do not tell us much about their
structures. Here, we show that scanning tunneling microscopy (STM)
images of fluorinated SWNTs provide a crucial starting point for
developing a detailed understanding of SWNT sidewall chemistry. We
have also obtained STM images of butylated SWNTs for which the
fluorinated tubes were used as precursor. This substitution chemistry
gives rise to electronic modulation in the vicinity of the attached
butyl group, analogous with similar observations on graphite
surface. One can also "solvated" fluoronanotubes in a variety of
alcohols by forming R-O-H...F-(CnF)- bonds.
Figure 5-2  Fluorinated carbon nanotubes

(a) SEM image
(b) AFM image
5.2 Experimental procedure

The synthesis of single-walled nanotubes has been described previously\textsuperscript{3}. SWNTs in “bucky paper” form were fluorinated by passing a dilute fluorine gas helium mixture (3\% $F_2$ / 97\% He) through a Monel flow reactor containing the SWNT sample. By varying the sample temperature and reaction time, various degrees of fluorination up to the saturation condition. $C_2F_x$ can be obtained. This procedure is described in detail elsewhere\textsuperscript{8}. Following fluorination, the SWNT material can be removed from the reactor and analyzed with electron microprobe analysis to determine the exact product stoichiometry, i.e., the C/F ratio. Butylation of the sidewall-fluorinated tubes were accomplished by reactions with alkyl lithium species or via Grignard reagents\textsuperscript{12}.

Solvation of fluoronanotubes has also been achieved. Approximately 1 mg of the fluorinated SWNT material was placed into a vial containing approximately 10 ml of either isopropanol or dimethyl formamide\textsuperscript{15}. Sonication of SWNTs in either solvent for approximately five minutes results in the selective solubilization of highly fluorinated (isopropanol) or sparsely fluorinated (DMF) samples. The solvated fluorotubes were then dispersed on a Au (111) on mica substrate by means of a rotary spinner and examined with STM. All STM
images were obtained using a homebuilt STM instrument with commercial electronics under ambient conditions. In addition to Pt/Rh STM tips, C_{60}-adsorbed Pt/Rh STM tips\textsuperscript{51,54} were selectively utilized to provide enhanced atomic resolution and to image electronic modulations on the SWNT. Butylated tubes were solvated in a manner similar to the solvation of fluorinated SWNTs, except that Chloroform was used as the solvent rather than DMF or isopropanol.

5.3 Computational Methods

In this study, all AM1 and CNDO calculations were carried out using a development version of the Gaussian suite of programs\textsuperscript{55,56}. A more detailed calculation process and results can be found in Wong's thesis\textsuperscript{34}.

5.4 Result and Discussion
5.4.1 Fluorinated carbon nanotubes

Figure 5-3 shows some STM images of pristine carbon nanotubes. This image was taken with a C_{60} platinum tip. Some multiple imaging was seen here due to the tip artifacts. If we zoom in on the bottom part of the image, one can see an atomically resolved image of the carbon nanotube. However, in Figure 5-4, striking features were observed in the STM images of fluorinated tubes: there are presence of narrow, abrupt, dark bands formed around the circumference of the tube upon fluorination. While similar scanning parameters were used in both pristine and fluorinated nanotubes, atomic resolution is not readily observable for the latter. Figure 5-5 shows STM image of fluorotubes prepared under different fluorination conditions. In addition to the strongly banded regions shown in Figure 5-5, long uninterrupted regions of the tube are also observed in Figure 5-6. Images of partially fluorinated SWNTs shows that the darker narrow regions remain abruptly terminated but typically form significantly broader bands. From a comparison between the STM images obtained for fluorinated SWNTs and the corresponding elemental analyses, we conclude that the narrower, darker bands correspond to unfluorinated regions of the nanotube. Even
Figure 5-3 - STM image of bare tube taken with C60 tips

(a) Scan parameters: bias voltage = 102 mV, tunneling current = 1.0 nA
(b) Zoomed in on the bottom of the tubes in (a). Scan Size 170 Å x 25 Å
Figure 5-4 - Carbon nanotubes fluorinated at 150 C for 10 hrs:
Bias voltage = 500 mV. tunneling current = 0.7 nA
Scan size = 180 Å x 860 Å

Figure 5-5 - fluorinated carbon nanotubes:

Carbon nanotube fluorinated at 250 C for 12 hrs:
Scan size = 200 Å x 1500 Å. bias voltage = 400 mV.
tunneling current = 0.3 nA: Bare metal tip is used
Figure 5-6 - Fluorinated carbon nanotubes:
Fluorinated at 150°C for 5 hrs

(a) Bias voltage = 500 mV, tunneling current = 0.5 nA
(b) Zoomed in on the top tube in (a). Dark section
is relatively large and believed to be unfluorinated:
Scan size = 175 Å x 1250 Å
in the case of partial fluorination, the transition between the fluorinated and unfluorinated bands typically remains quite abrupt and orthogonal to the SWNT axis. In Figure 5-7, we also see that partially fluorinated nanotubes under high resolution exhibit this observed variation at atomic resolution: the narrower regions of the tube correspond to regions where atomic resolution is obtainable under these scanning conditions.

A comparison of these STM images with theory provides insight into a likely geometry and functionalization mechanism for fluorinated SWNTs. Two possible isomers for fully fluorinated C₂F nanotubes are proposed in the previous chapters. In one case, the fluorine atoms occupy the 1,4 positions on every other row of hexagons; we call this the 1,4 isomer. The fluorine atoms can also occupy the 1,2 positions of the hexagons of alternate rows while the double bonds form a conjugated system along the tube axis. We call this the 1,2 isomer.

When looking into the semi-empirical calculation results, from the CNDO optimized geometries obtained using the capped model, the calculated C=C bond length for the conjugated chain of the 1,2 isomer was approximately 1.37 Å, and the C-C bond length was approximately
Figure 5-7 - Partially fluorinated tubes (taken with C_{60} tip):

This carbon nanotubes is fluorinated at 250 °C for 1 hour

(a) Bias voltage = 300 mV, tunneling current = 1.0 nA
(b) Zoomed in on the tube in (a) and tilt it about 30 degree counter-clock wise: Scan size = 20 Å x 300 Å. Small regions of atomic resolution can be observed between fluorinated areas (indicated by arrows)
1.45 Å. For the 1.4 isomer, the C=C bond length obtained was 1.35 Å. The C-F bond length of the two isomers is approximately 1.377 Å, which is quite close to the C-F bond length of C_{60}F_{60}^{57}. The AM1 single point energy calculations based on the CNDO optimized geometries showed that the energy differences between the 1.2 and 1.4 isomers are very small: 76.02 kcal/mol, 25.22 kcal/mol and 64.30 kcal/mol for C_{360}F_{20}, C_{360}F_{40}, and C_{360}F_{60} respectively. For the greatest degree of fluorination studied, C_{360}F_{60}, there is only 1 kcal/mol difference per fluorine atom. All results support the 1.4 as the more stable isomer, but the energy difference between the two isomers is actually quite small, and it would be realistic to anticipate that both isomers may coexist.

In the STM images, the fluorinated regions typically appear to terminate abruptly, forming bands around the circumference of the tube. This feature allows us to infer that the addition of fluorine to the pristine SWNT may occur more favorably around the circumference of the tube, not down the tube axis. We have therefore performed an AM1 calculation in order to ascertain the most energetically favorable sequence for multiple fluorine addition. This is shown schematically in Figure 5-8. First, a single fluorine atom is added to a C_{160}H_{40} molecule (shown as position 1). Making the assumption that the second fluorine atom chooses an active position near the first, three
potential active positions exist for the second fluorine atom (position 2, 4, and 4'). AM1 Results for C_{16}H_{40}F_2 show that for the 1.2, 1.4, and 1.4' isomers, the energy difference is negligible: all are candidates for the starting point of multiple fluorine addition. We then placed the second pair of fluorine atoms close to the first pair as either a (1.2), (1.4) or (1.4') isomer, and calculated the addition energy for the second pair of atoms as a function of the relative separation between fluorine atom pairs. Relative energies corresponding to fluorine addition at positions around the circumference of the tube C_n (n=0-4) and along the tube axis A_n (n=1.2) relative to the position of the first pair of fluorine atoms were calculated. These results are shown in Table 5.1. The energies of the isomers where the two pairs of fluorine add directly adjacent to each other are referenced as 0. It is quite clear that for the 1.2 isomer, if the four fluorine atoms are allowed to add around the circumference of the tube, they will try to stay as far away from each other as possible to minimize fluorine-fluorine repulsion. By comparison, addition along the axis of the tube for the 1.2 isomer is about 30 kcal/mol more exothermic than circumferential 1.2 isomer. If allowed, would form via fluorine
Figure 5-8 - Geometry denotes the secondary fluorine addition site
Table 5-1  Relative energies (Kcal/mol) of four fluorine atom additions to carbon nanotubes

(Adapted from Wong's thesis)

<table>
<thead>
<tr>
<th></th>
<th>C0</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>A1</th>
<th>A2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>0</td>
<td>-2.7</td>
<td>-15.2</td>
<td>-17.3</td>
<td>-18.2</td>
<td>37.9</td>
<td>-34.9</td>
</tr>
<tr>
<td>1.4</td>
<td>0</td>
<td>-0</td>
<td>-0.6</td>
<td>-2.1</td>
<td>-2.8</td>
<td>10.8</td>
<td>9.5</td>
</tr>
<tr>
<td>1.4</td>
<td>0</td>
<td>-4.7</td>
<td>-5.4</td>
<td>-6.5</td>
<td>-6.9</td>
<td>9.5</td>
<td>6.5</td>
</tr>
</tbody>
</table>

C denotes fluorine addition around the tube circumference;

A denotes growth along the tube axis;

0-4 denotes the interval between the two pairs of fluorine atoms.
addition along the tube axis. In the case of the 1.4 isomer, the calculations indicate that addition around the circumference of the tube is approximately 10 kcal/mol more energetically favorable than growth along the tube axis.

The circumferential growth mechanism of the 1.4 fluorination isomer would explain the abrupt bandlike boundaries ubiquitously observed in our STM images of fluorinated SWNTs. It is interesting to note that even under saturation fluorination conditions, some dark bands are still observable. This would be consistent with the 1.4 isomer being initiated at multiple sites along the tube, as shown in Figure 5-9(a). Since fluorination occurs on alternate pairs of rows of the 1.4 isomer, one can image the existence of adjacent 1.4 isomeric domains where the fluorinated rows of one domain lie in registry with the double bond row of a neighboring domain. This would result in full fluorination of the nanotubes but with abrupt boundaries and may be the origin of the observed structures. Since the calculated energy difference between the (1.2) and (1.4) isomers is small, one can expect to have both types of fluorine addition occur during the fluorination process. Discrete regions of (1.2) isomer may also be present on the nanotubes (Figure 5-9(b)). Defects (Figure 5-9(c)), such as introduction of ring types other than hexagon, rehybridization of
Figure 5-9 - Gap formation in STM images:

Lattice mismatching
(a) Multiple fluorine initiation sites
(b) Mixture of both (1,2) and (1,4) additions
(c) Defects - example shown here is a pentagon-heptagon defect
carbon atoms between sp² and sp³. or incomplete bonding defects (vacancies, dislocation etc.) in the tubes might also play a role in either initiating or terminating the various isomeric domains.

5.4.2 Butylated carbon nanotubes

Since the C-F bonds in fluorofullerences are significantly weaker than the C-F bonds in traditional alkyl fluorides, sidewall fluorinated SWNTs can serve as a chemical starting point for subsequent addition of a variety of moieties⁵⁸,⁵⁹. We have also imaged, via STM, sidewall butylated SWNTs which utilize fluorinated SWNTs as a precursor. STM images of butylated SWNTs are shown in Figure 5-10(a). One immediately notices that the banded morphology of fluorinated SWNT is no longer visible. Instead, relatively large (~ 10 Å) bright features with an average spacing of 50 Å are distinctly apparent as one scans along the butylated nanotubes. In higher resolution, the apparent atomic periodicity appears to be 2.46 Å (Figure 5-10(b)). This superlattice feature is an electronic modulation of the nanotubes induced by the presence of the attached butyl group, and has been studied both
Figure 5-10 STM images of butylated tubes

(a) Three bright spots appeared in this image (240 Å x 35 Å, bias voltage = 200 mV, tunneling current = 1 nA) appear to be due to the butyl groups bonded to the sidewalls of nanotubes.

(b) Bright spot is caused by the butyl group attachment to the tube. Solid arrow indicates the strong electronic modulation, and the modulation seems to decay away to the right side of the tube (as indicated by the dashed arrow).

(c) Theoretical image of the perturbation in the local density of states at E_r caused by a carbon adatom on a (10.10) nanotube.
experimentally and theoretically on graphite$^{51,52,53,60,61}$. Using a modified version of the LCAO method for graphite$^{52}$ with periodic boundary conditions, we have calculated the density of states at $E_r$ for a (10,10) nanotube perturbed by a strongly bound carbon atom (Figure 5.10(c)). This is a simple one $\pi$ electron per carbon atom, 2401 atom model with the appropriate boundary condition for a (10,10) nanotube in which the resulting surface charge density is "wrapped" into a cylindrical shape. (For a more thorough treatment of the superlattice phenomenon on carbon nanotubes see ref.61). Both the sizes of the modulated region and the superlattice periodicity are in good agreement with the experimental image.

5.5 Conclusion

We have obtained the first STM images of sidewall functionalized SWNTs, particularly fluorinated and alkylated tubes. This powerful
local probe, in combination with theoretical analysis, yields detailed new insights into how addition and substitution chemistry may be occurring on nanotubes sidewalls.
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