A Computational Study of the functionalization of Single-Walled Carbon Nanotubes with Macromolecules

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A COMPUTATIONAL STUDY OF THE FUNCTIONALIZATION OF SINGLE-WALLED CARBON NANOTUBES WITH MACROMOLECULES

A DISSERTATION
SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY
IN PARTIAL FULFIMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSPHY

BY
OLAYINKA OLUREMI Ogunro II

DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA
DECEMBER 2011
ACKNOWLEDGMENTS

All praises to the Almighty Creator of this opportunity. This dissertation is dedicated to Dr. Robert “Sonny” Kwesi Mitchell. Thanks to my family, Dr. & Mrs. Olayinka Ogunro, Bolajoko Bally, Dr. Oyenola Ogunro, Dr. Charity M. F. Ogunro, Olusegun A. Ogunro, Yemisi O. Ogunro, Dr. Olabisi M. Ogunro, Araba Nti, and Kweku G. Yamoah. Thanks to the Clark Atlanta University departments of chemistry, physics, and computer science. Thanks to my committee, Dr. Xiao-Qian Wang (advisor), Dr. Issifu I. Harruna (co-advisor), Dr. Eric A. Mintz, Dr. Kofi B. Bota, Dr. Cass D. Parker, as well as Dr. Ishrat M. Khan, and Dean Shirley Williams-Kirksey. Thanks to Dr. David G. Bray, Lyle Brooks, Joe T. Sanders II, Ryan Jinks, Anastesia S. Lyons, Dr. Leon Dyers, Jr., Deborah Ortiz, Tolulope Akinduro, Tokiwa T. Smith and Mour Diop. Thanks to Kwasi Obeng, Dr. Alexis Nduwimana, Dr. Ryza N. Musin, Drena Brown, Kelvin L. Suggs, Cherno B. Kah, Duminda K. Samarakoon, Larry D. Riche II, Vernecia N. Person, James E. Nathaniel II, Chantel I. Nicolas, Rosi N. Gunasinghe, Kregg D. Quarles. Thanks to Dr. Mark A. Jack, Dr. Péter Molnár, Lonnie Flynn, Dr. James L. Reed, Dr. Terrence R. Wise and Dr. Plas T. James. Thanks to the National Organization for the Professional Advancement of Black Chemists and Chemical Engineers. This work was funded by NSF/CREST/ CFNM (Grant Nos. HRD-0630456 and DMR-02-05328), PREM (DMR 0934142), AFOSR (Grant No. FA9550-10-1-0254) and ARO (Grant No. W911NF-06-1-0442), and NASA-HiPPAC (Grant No. NCC3-1044).
ABSTRACT

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A COMPUTATIONAL STUDY OF THE FUNCTIONALIZATION OF SINGLE-WALLED CARBON NANOTUBES WITH MACROMOLECULES

Committee Chair: Xiao-Qian Wang, Ph. D.

Dissertation dated December 2011

The goal of my Ph.D. research is to explain the mechanism behind covalent and noncovalent separation techniques of carbon nanotubes using atomistic-simulations. This body of work has generated interest in single-walled carbon nanotubes modified with different macromolecules and functionalities, toward the design of new composites systems, as well as clarification of existing systems. Experimental separation techniques used to isolate bundles of single-walled carbon nanotubes incorporate molecules or functional groups onto the tube surface. Other methods employ electrostatic charging. The adsorption and chemical modification of the tube surface may change the electronic structure of the nanotubes and or the adsorbed molecule, chemical group. We have employed first-principles density functional theory calculations to understand the electronic structure of carbon nanotubes modified with chemical macromolecules.
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CHAPTER 1

STRUCTURE AND ELECTRONIC PROPERTIES OF CARBON NANOTUBES

1.1 Introduction

Carbon can be found in a variety of forms such as graphite, diamond, carbon fibers, fullerenes, and carbon nanotubes. Carbon assumes many structural forms because a carbon atom can form several distinct types of valence bonds. There are several well-known carbon allotropes: graphite, amorphous carbon, and diamond. Single-walled carbon nanotubes (SWNTs) represent a novel class of low-dimensional materials exhibiting exceptional electronic properties. Like fullerenes, carbon nanotubes (CNTs) are another carbon allotrope. A property of a low-dimensional system is the confinement of electrons to movement in one or two dimensions. The electrons on the surface of carbon nanotubes are confined to movement in one dimension (along the tube axis), thus CNTs are known as one dimensional semiconducting and conducting nanowires. Depending on the community, specific interests, and targeted applications, nanotubes are regarded as either single molecules or quasi-one-dimensional crystals with translational periodicity along the tube axis. Many of the electronic and structural properties of SWNTs were predicted from theory before conclusive experiment were designed and performed. A single-walled carbon nanotube can be described as a graphene sheet rolled into a cylindrical shape such that the structure is one-dimensional with axial symmetry, and in general exhibiting a spiral conformation, which is chiral.
Multiwall carbon nanotubes (MWNTs) were discovered in 1991 by Iijima.[5, 6] In 1993 single-walled carbon nanotubes (SWNTs) were synthesized using arch discharge methods with catalysts, independently by Iijima[7] and Bethune.[8] After the discovery of fullerenes by Kroto, Smalley, Curl and coworkers at Rice University, scientist speculated about single walled carbon nanotubes as the limiting case of fullerenes. The connection between carbon nanotubes and fullerenes was heightened by the observation that the terminations of nanotubes were hemispheres resembling fullerene caps.[9] In 1996 a team of scientist led by Smalley was the first to synthesize bundles of aligned SWNTs with narrow diameters.[10]

1.2 Nanotube Structure

The microstructure of SWNTs is similar to that of graphene, therefore these tubes are labeled in terms of graphene lattice vectors. Graphene has a hexagonal molecular structure that is described as chicken wire-like. All extended SWNTs can be visualized as a conformal mapping of 2D graphite onto the surface of a cylinder, subject to periodic boundary conditions both around the cylinder and along its axis.[2, 5, 11]

Figure 1.1 Mapping of a graphene sheet to create (6,3) SWNT. The unit cell of the graphite lattice is the grayed rhomboid in the lower right corner and defined by the primitive lattice vectors \( \mathbf{R}_1 \) and \( \mathbf{R}_2 \).[2]
The proper boundary conditions around the cylinder can only be satisfied if the circumference of the cylinder maps onto one of the Bravis lattice vectors of the graphene sheet as shown in Figure 1.1. In graphene, each Bravis lattice vector (or chiral vector) \( \mathbf{R} \) is defined in terms of two primitive lattice vectors \( \mathbf{R}_1, \mathbf{R}_2 \) and a pair of integer indices (chiral indices), \( (n_1, n_2) \):

\[
\mathbf{R} = n_1 \mathbf{R}_1 + n_2 \mathbf{R}_2 = (n_1, n_2).
\]

(1.1)

The chiral index \( (n_1, n_2) \) consists of integers which specify each carbon nanotube uniquely. [1]

An unrelaxed SWNT can be constructed by rolling up a single graphene sheet along one of its 2D lattice vectors \( \mathbf{R} \), as defined in equation in Equation 1.1, to determine a particular with an a set of indices given by \( (n_1, n_2) \) and with diameter \( d_t \):

\[
d_t = \frac{R}{\pi} = \sqrt{3} \frac{a_{\text{c-c}} \sqrt{(n_1^2 + n_2 n_1 + n_2^2)}}{\pi}.
\]

(1.2)

In Equation 1.2 \( a_{\text{c-c}} \) is the nearest-neighbor carbon distance in graphite 0.1421. The point group symmetry of the graphene lattice will make many nanotubes (defined by \( \mathbf{R} \)) equivalent. This symmetry also allows \( \mathbf{R} \) to be restricted to the irreducible wedge of the graphene lattice in Figure 1.2. Each primitive lattice vector \( \mathbf{R} \), in the wedge of Figure 1.2 defines a different SWNT. All nanotubes can be generated by this set of vectors \( \mathbf{R}_1, \mathbf{R}_2 \).
Figure 1.2 Irreducible wedge of the graphene lattice. Primitive lattice vectors are shown close to the origin (0,0). The unit cell at the origin is in grey.

Associated with this wedge are a finite set of tubes that can be constructed with a certain radii. The chiral angle for a nanotube, $\Theta$, is measured counter clockwise from the primitive lattice vector $\mathbf{R}_1$ to the roll-up vector (Bravis lattice vector) $\mathbf{R}$ (See Figure 1.3). The angle is defined in terms of the indices $(n_1,n_2)$ and is given by

$$\Theta = \arccos\left(\frac{\mathbf{R}_1 \cdot \mathbf{R}}{\| \mathbf{R}_1 \| \| \mathbf{R} \|}\right) = \arccos\left(\frac{2n_1 + n_2}{\sqrt{2n_1^2 + n_2^2 + n_1n_2}}\right) = \arctan\left(\frac{\sqrt{3n_2}}{2n_1 + n_2}\right),$$

for tubes defined in terms of the irreducible wedge of Figure 1.2. [2] Thus, a nanotube can be specified by either its $(n_1,n_2)$ indices or by $d_i$ and $\Theta$. [14] The chiral angle denotes the tilt angle of the surface hexagons with respect to the nanotube axis. Even though all nanotubes have helical structures, there are two subsets of tubes defined by rollup vectors and chiral angles $\Theta = 0, 30^\circ$. These high-symmetry nanotubes possess a reflection plane and will be achiral. There are three types of carbon nanotubes, depending on how the graphene sheet is rolled up: armchair[12] $(n, n)$ ($\Theta = 30^\circ$), zigzag[12] $(n, 0)$ ($\Theta = 0^\circ$) and chiral nanotubes. The names are derived from the most direct, continuous path of C-C bonds that outline the circumference of the nanotube. Zigzag tubes are characterized by C-C bonds, parallel to the tube axis, whereas armchair tubes display C-C bonds perpendicular to the tube axis. Figure 1.3 details the construction of armchair and zigzag CNTs, from rolling graphene around a cylinder. The caps to these nanotubes are also represented with the correct edge geometry, a result from cutting along the equatorial plane of fullerene. In (a) the vertical dashed arrow indicates the length and number of complete hexagons in the armchair row. The 5 hexagons in the armchair row are joined.
at their zigzag ends resulting in the cylinder in (b). In (a) the row of nine zigzag hexagons (along the zigzag face) are rolled along their armchair edges to form the cylinder in (c).

Figure 1.3  Construction of armchair and zigzag nanotubes from rolling a graphene sheet, using the chiral vectors, along a cylinder.[15]

Zigzag and armchair tubes are achiral. Values for Θ other than 0 and 30° refer to chiral tubes \((n_1, n_2 \neq n_1 \neq 0)\). Nanotubes may be rolled up above or below the plane of the graphene sheet. Thus, forming two tubes that are mirror images of each other, with the graphene sheet as the mirror plane. This mirror plane serves as a reflection plane for achiral tubes. For all other tubes that have left or right-handedness, the tube and its mirror images will be nonsuperimposable.

Irrespective of whether nanotubes are chiral or achiral all SWNTs, as defined by the Bravis lattice vector (chiral vector) \(\mathbf{R}\), have translational symmetry along the tube axis, see Figure 1.3. The Bravis lattice vector and the geometry of the honeycomb lattice also yield information about the unit cell of graphene and number of carbon atoms associated with it. When the side of a carbon hexagon is aligned along the chiral vector \(\mathbf{R}\) (prior to rollup of the graphene sheet) the repeat length is \(\sqrt{3|\mathbf{R}|}\) as seen in Figure 1.3. To define the unit cell for a 1D nanotube we define a translational vector \(\mathbf{T}\):
$T = t_1 R_1 + t_2 R_2 = (t_1, t_2)$, \hspace{1cm} (1.4)

where the coefficients $t_1$ and $t_2$ are related to $(n_1, n_2)$ by

$$t_1 = \frac{(2n_2 + n_1)}{d_r}, \hspace{1cm} (1.5)$$

$$t_2 = -\frac{(2n_1 + n_2)}{d_r}, \hspace{1cm} (1.6)$$

in which $d_r$ is the greatest common divisor of $(n_1, n_2)$. The magnitude of the translational vector is equal to $\sqrt{3} |L|/d_r$. Where $L$ is the length of the chiral vector $R = \pi d$. The diameter of the nanotube is given by $d$. The relationship between the unit cell of a one-dimensional (1D) nanotube in terms of unit cell of 2D chicken wire lattice is depicted in Figure 1.4. The unit cell of the nanotube is the area delineated by the chiral vector $R$ and the translational vector $T$.

Figure 1.4   The Bravis lattice vector $R$, the primitive lattice vector $R_1$, chiral angle $\Theta$, and the translational vector $T$ for nanotube (4,2).

The number of hexagons, $N$, in a 1D unit cell of a nanotube is set by the chiral indice $(n_1, n_2)$ and is given by,
The addition of a hexagon to the honeycomb lattice translates to an additional two carbon atoms in the graphene sheet.

1.3 Electronic Properties

The electronic properties of carbon nanotubes were predicted by theory\cite{4, 11-13, 16} prior to the synthesis of the materials.\cite{7, 8, 10} An accurate representation of the electronic properties of carbon nanotubes can be derived from the band structure of graphene, as first determined by Wallace.\cite{17} Just as was the case with nanotubes; the properties of graphene laid the foundation for the discovery of the material more than four decades later.\cite{18} Novoselov and Geim were the recipients of the 2010 Nobel Prize in physics for their work toward the isolation of graphene. Carbon nanotubes are made up of two kinds of bonds (similar to graphene) which display planar $sp^2$ hybridization. The valence orbitals of carbon are $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals; in which the $p_z$ orbital is perpendicular to the graphene sheet. The $(s, p_x, p_y)$ orbitals combine to form 3 $\sigma$ bonds which comprise of the geometrical framework of the graphene sheet. The binding energy and elastic properties of graphene can be attributed to the strong, covalent $\sigma$ bonds. The $p_z$ orbitals that protrude out of the plane cannot couple with $\sigma$ bonds, but interact laterally with adjacent $p_z$ orbitals. The neighboring interaction of $p_z$ orbitals are the $\pi-\pi$ interactions that are responsible for delocalized $\pi$ bonding and $\pi^*$ antibonding orbitals.\cite{3} The weak interaction between single layers of graphite (graphene) as well as the weak interactions that hold SWNT bundles together can be attributed to $\pi$ electrons normal to the graphene surface. The in-plane $\sigma$ bonds have energy levels that are too far away from the Fermi energy of graphite and do not factor into the electronic properties.
However, the bonding and antibonding bands cross the Fermi level ($E_F$) at high-symmetry points along the first Brillouin zone of graphene.[3, 17] Figure 1.5 depicts the first BZ of carbon nanotube (4,4)- denoted by the parallel lines, superimposed on the two-dimensional hexagonal first Brillouin zone of graphene. A Brillouin zone is a special primitive cell, defined in reciprocal space. The cell boundaries result from planes denoted by points ($K$ and $K'$) on the reciprocal lattice. A Brillouin zone is the first Wigner-Seitz primitive cell in the reciprocal lattice or reciprocal space.[19]

Figure 1.5 The first Brillouin zone of carbon nanotube (4,4) superimposed on the two-dimensional hexagonal first Brillouin zone of graphene.[20] The CNT BZ is indicated by an irreducible set of red parallel lines.

The first BZ of a SWNT in Figure 1.5 is represented by an irreducible set of red, equidistant lines. This is the one-dimensional Brillouin zone. The spacing and the length of these horizontal lines are related to the tube indices ($n,m$). The length of the lines is inversely proportional to the length of the nanotubes unit cell along the tube axis. The spacing between the 1D BZ is inversely proportional to the tube diameter. The lines that cut through the K-points belong to the nanotube BZ, which is a subset of the points that
belong to the graphene BZ. The orientation of the cutting lines as a function of the chiral indice, depends on the chiral angle.[20]

A construction of the Brillouin zone for the $\pi$ band electron dispersion for a two-dimensional chicken wire crystal lattice of graphene is depicted in Figure 1.6.

Figure 1.6    Tight binding approximation of the electronic energy dispersion for $\pi$ and $\pi^*$ bands in the first Brillouin and a 3D representation of the structure.

A tight binding approximation is used to treat the energy dispersion along the path between the high symmetry points $K - \Gamma - M - K$ of the first Brillouin zone. The $K$-points ($K$ and $K'$) display linear dispersion for the $\pi$ and $\pi^*$ bands.

1.4    Electronic Band Structure

The electronic energy bands of graphene along the high symmetry $M - \Gamma - K$ directions are depicted in Figure 1.7. The crossing of the $\pi$ and $\pi^*$ bands occurs at the vertices of the hexagonal graphene Brillouin zone. The vertices are denoted $K$ after their momentum vector. Accordingly, graphene is a semimetal with a Fermi surface that is reduced to six distinct $K$-points of the hexagonal BZ (see Figure 1.6). Near the Fermi level the band edges are linear. In sharp contrast to conventional direct-band gap
semiconductors that display a characteristic quadratic energy momentum relationship, obeyed by electrons at the band edges.

![Band structure of graphene](image)

Figure 1.7 The band structure of graphene. A large energy gap separates the bonding $\pi$ and antibonding $\pi^*$ bands. The last valence band (bonding $\pi$) and the first conduction band (antibonding $\pi^*$) meet at the vertices (K) of the first Brillouin zone.

Just one the high symmetry paths $M - \Gamma - K - M$ of the two-dimensional crystal graphene is used to calculate the band structure.

The band structure of a carbon nanotube is modeled using the zone-folding approximation of the graphene bonding and antibonding states, treated with tight-binding one electron model.[21] The zone-folding approximation is based on the electronic band structure of a nanotube defined by the superposition of the graphene electronic energy bands along the corresponding allowed $k$ lines.[3] The periodic boundary conditions around the circumference of the nanotube lead to quantized wave vectors, only having discrete values. However, the wave vectors along the tube axis are continuous for infinite tubes. The application of the periodic boundary conditions along the tubes circumference restricts the allowed wave function quantum phase:

$$\Psi_k (r + C_h) = e^{ik \cdot C_h} \Psi_k (r) = \Psi_k (r),$$  

(1.8)
In which the vectors $r$ and $k$ are taken on the tube surface. The first equality is derived from the Bloch theorem, in which solutions of the Schrödinger equation for a periodic potential must be of the form:

$$\Psi_k(r) = u_k(r)\exp(ik\cdot r),$$

(1.9)

In which $u_k(r) = u_k(r + T)$ defines the period of the crystal lattice. In the Bloch theorem the eigenfunctions of the wave equation for a periodic potential are the product of a plane waves, $\exp(ik\cdot r)$, times a function, $u_k(r)$, with periodicity of the crystal lattice. The chiral vector dictates two kinds of nanotubes. Unless the tube is small, the band structure of the tube should resemble that of the piece of unrolled graphene. The electronic structure for CNTs was predicted as a function of the diameter and helicity of graphene rolled onto a cylinder.\[12\]

Theoretically, graphitic tubules represent a one-dimensional class of materials that are periodic along the tube axis. Quantum confinement of the $p_z$ electrons in the radial direction is provided by the single atom thickness of the rolled graphene sheet. In the circumferential direction, periodic boundary conditions are applied to enlarge the unit cell, formed in real space and the resulting zone folding that occurs in reciprocal space.\[12\] Figure 1.8 demonstrates the curl up of the two-dimensional graphene lattice structure to form semiconducting and metallic nanotubes. The chicken-wire, hexagonal structure of graphene is depicted in (a). The energy of the conducting states in graphene depicted in two-dimensions, in panel (b). Conduction only occurs along certain designated areas, “cones.” A one-dimensional slice of the two-dimensional representation of the conducting cones is shown with the corresponding nanotubes in (c). The graphene
sheet can be rolled in two different ways. If the nanotube is rolled up in the y-direction it is a metal and semiconducting if rolled in the x-direction.

![Image](image_url)

**Figure 1.8** The curling up of graphene sheet (a) to from metallic and semiconducting nanotubes. The two-dimensional band structure of graphene in (b). (c) A one-dimensional slice of the band structure of each tube.[22]

Even though there is mixing between the $\pi(2p_z)$ and $\sigma(2s$ and $2p_x, 2p_y)$ carbon orbitals as a result of curvature, it is negligible and can be ignored near the Fermi level. Thus, only $\pi$ orbitals are considered. The two-dimensional energy dispersion relationship for a graphene monolayer is given by,

$$E = \pm \gamma_0 \sqrt{3 + 2 \cos(k \cdot a_1) + 2 \cos(k \cdot a_2) + 2 \cos(k \cdot (a_1 - a_2))},$$  \hspace{1cm} (1.10)

in terms of the 2D crystalline momentum $\hbar k$ and the primitive lattice vectors $a_1$ and $a_2$.[2] The standard reciprocal lattice vectors $K_1$ and $K_2$ are for the graphene honeycomb lattice.[17] Equation 1.9, $\Psi_k(r + C_h) = e^{ik \cdot C_h} \Psi_k(r) = \Psi_k(r)$, is further developed into,

$$E^\pm(k_x, k_y) = \pm \gamma_0 \sqrt{1 + 4 \cos \left( \frac{\sqrt{3} k_x a}{2} \right) \cos \left( \frac{k_y a}{2} \right) + 4 \cos^2 \left( \frac{k_y a}{2} \right)}.$$  \hspace{1cm} (1.11)

In which $\gamma_0$ is the nearest neighbor overlap integral. The $k = (k_x, k_y)$ vectors of the first Brillouin zone make up a set of available electronic momenta. The band structure is then restricted to a hexagonal unit cell of the reciprocal lattice.
CHAPTER 2

COMPUTATIONAL METHODOLOGY

2.1 Introduction

Materials can be analyzed at the microscopic level in terms of; 1) their spatial arrangement of constituent atoms and molecules; 2) the different types of elements they contain, and 3) the nature of interactions between atoms and molecules. The microstructure of materials governs important properties such as thermal and electrical conductivity, mechanical strength, ductility, electronic, optical, and magnetic properties.[23]

One can rely on a variety of experimental techniques to measure, characterize, and manipulate materials properties for new applications. Computer simulations provide information on a system and its properties. This data may supplement preexisting experimental data or may serve as the primary source of knowledge, in lieu of accurate, reproducible experimental data. Over the years, computational chemistry has risen from a subfield of theoretical chemistry to its own discipline where the priorities of the scientist are: (1) deciphering the language: what do the abbreviations mean in terms of underlying assumptions of theoretical models (2) technical issues: how to execute a program and what in the output is important data (3) quality assessment: how good is the number that has been calculated.[24]
2.2 Molecular Mechanics

Molecular mechanics (also known as force field methods) allows the calculation of structures of molecules, not from first principles, but from a mixture of first principles, second principles, and knowledge of chemistry.\[25\] The usefulness of this method is that it requires minimal computing time and it can be applied to very larger systems. It is a practical and powerful method, used to obtain physical and chemical properties of structures.

Molecular mechanics gives us a model that attempts to tie together in a convenient way the various computational and experimental methods that are commonly used to study molecular structure.\[25\] A Force field is a common feature in molecular mechanics computations. It is a formulation of parameters and functions used to describe the potential energy of an assemblage of atoms and or/molecules. The functional form of a force field incorporates nonbonded terms, for the description of van der Waals and long-range electrostatic forces as well as bonding terms to describe atoms joined by covalent bonds. At a minimum each force field contains four components that describe the intra- and intermolecular forces in a system: bond stretching, angle bending, torsion and a non-bonded interactions term. There are energetic penalties associated with the deviation of atoms and bond lengths from equilibrium values. Within the force field, there exists a function to describe the energy change associated with bonds that are rotated from their equilibrium positions. Equation 2.1 is the functional form of the potential energy:
\[ V(r_N) = \sum_{\text{bonds}} \frac{k_i}{2} (l_i - l_{i,0})^2 + \sum_{\text{angles}} \frac{k_i}{2} (\theta_i - \theta_{i,0})^2 + \sum_{\text{torsions}} \frac{V_i}{2} (1 + \cos(n\omega - \gamma)) \]

\[ + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \left( 4\epsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right) + \frac{q_i q_j}{4\pi \varepsilon_0 r_{ij}} \]  

Equation 2.1 is the functional form of a force field that is typically used to model assemblies of atoms or single molecules.

The potential energy denoted by \( V(r_N) \), is a function of the nuclear position \( \mathbf{r} \) of atoms. The contribution of each term to the potential energy is depicted in Figure 2.1

![Figure 2.1. The four contributions to a molecular mechanics force field clockwise: bond stretching, angle bending, bond rotation (torsion), non-bonded interactions (electronic), non-bonded interactions (van der Waals).[26]](image)

Molecular mechanics calculations depend on the type of atom in each system and the parameters associated with each atom type. The large number of atoms in molecular systems produces the likelihood that for random, new molecular structures there is not a current set of readily-available parameters are available, unless one has developed a force field for molecules that mimic new systems. To this end, molecular mechanics predicts the behavior of a unknown structure, based on the behavior of known molecular assemblies.
2.3 Quantum Mechanics

If one is to predict, with chemical accuracy the electronic and geometric structure of a solid, the necessary QM total energy calculation and the ensuing minimization of that system, as it relates to the nuclear and electronic coordinates, must be executed.[27] The fundamental postulate of quantum mechanics is that the wavefunction, $\Psi$, exists for any (chemical) system, and the appropriate operators (functions) which act upon $\Psi$ return the observable properties of the system.[28] The many-body, non-relativistic, time-independent Schrödinger equation for a system of $N$ electrons and $M$ nuclei has the form of an eigenvalue problem:

$$\hat{H}\Psi = E\Psi,$$

(2.2)

where $\hat{H}$ is the Hamiltonian operator for a system containing nuclei and electrons, denoted by the position vectors $\mathbf{R}_A$ and $\mathbf{r}_i$ respectively and $E$ is the total energy of the many-body. The Hamiltonian operator, of Equation 2.2, $\hat{H}$, is a differential operator that represents the total energy and is given by:

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \frac{1}{2} \sum_{A=1}^{M} \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}},$$

(2.3)

where $M_A$ is the ratio of the mass of nucleus $A$ to the mass of an electron. The term $Z_A$ denotes the atomic number of the nucleus $A$. The Laplacian operators, $\nabla_i^2$ and $\nabla_A^2$, order differentiation with respect to the coordinates of the $i$th electron and the $A$th nucleus, respectively. The first and second terms of Equation 2.3 are the kinetic energy operators for the electrons and nuclei, respectively. The third term is the Coulomb attraction between the electron and the nuclei. The fourth term represents electron repulsions, while the fifth term denotes nuclear repulsions.
Fundamental interest in describing a collection of atoms is centered on determining their energy and how their energy changes with the movement of atoms. To define where an atom is we need to define the position of its nucleus and its electrons. When applying quantum mechanics to atoms a key observation is that the nuclei are larger than the electrons. The protons or neutrons in a nucleus are more than 1800 times the mass of an electron. Electrons respond more rapidly to changes in their environment than nuclei. The problem of solving the energy for a collection of molecules can be divided into two parts 1) the fixed position of the nuclei 2) the electrons. The separation of the Born-Oppenheimer approximation is the separation of the nuclei and electrons into two mathematical problems. For electrons moving in a field of nuclei, we solve for the state or the lowest energy configuration. This state is also known as the ground state. If a system has M nuclei at positions \( \mathbf{R}_1, \ldots, \mathbf{R}_M \), the ground state energy, \( E \), as a function of the position of these nuclei can be expressed as \( E(\mathbf{R}_1, \ldots, \mathbf{R}_M) \). The latter function is the adiabatic potential energy surface of the atoms. Calculating the potential energy surface will enable one to calculate the original problem, how does the movement of atoms affect the energy of a material? For the electronic Hamiltonian, the electronic wave function is, \( \Psi \) a function of the spatial coordinates of \( N \) electrons, such that \( \varphi = \varphi(r_1, \ldots, r_N) \). Since the ground state energy is independent of the time, this is the time independent Schrödinger equation.

The Hamiltonian will reflect the changes in that kinetic energy of the nuclei. The second term of Equation 2.3 can be neglected and the nuclei repulsion term (the fifth term in the equation) is held constant. What remains is the electronic Hamiltonian, a description of the motion of \( N \) electrons moving in the field of \( M \) point charges:
\[
\hat{H}_{\text{elec}} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}.
\] (2.4)

The Application of this approximation (also known as the adiabatic principle) truncates the many-body problem to one in which electrons are moving in the field of fixed nuclei. The electronic wavefunction, \(\hat{H}_{\text{elec}} \Psi = E_{\text{elec}} \Psi\), describes the motion of electrons and is explicitly dependent on the electronic coordinates, yet it depends on nuclear coordinates parametrically. In this latter dependence: different nuclear arrangements are a function of different electronic coordinates. Even though the nuclear coordinates are not explicitly defined in the electronic wavefunction, \(\Psi_{\text{elec}}\), the total energy calculation for a fixed nuclear configuration must include nuclear-nuclear repulsion[28, 29]:

\[
E_{\text{tot}} = E_{\text{elec}} + \sum_{A=1}^{N} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}.
\] (2.5)

Thus, begins the task of solving the electronic Schrödinger equation, \(\hat{H} \Psi = E \Psi\) for the energy of a system in the ground state. In solid state theory, as one builds up molecules to solids, we are interested in describing the interactions between electrons, which determines the materials underlying structure and properties. Hartree-Fock (HF) approximations solved these problems: by allowing the wavefunction to be expressed as the Slater determinant of one electron orbitals. Every electron in the HF model is represented by an orbital. Within this model the total wavefunction is expressed as a product of orbitals. From the perspective of a chemist, each electron was viewed as loosely independent. This theory was slightly augmented by replacing the independence
of each electron with the wavefunctional form dependence on interelectronic
distances.[30]

2.4 Density Functional Theory (DFT)

The difficulty of performing the total energy calculation with the electronic wave
function, dependent on $3n$ coordinates $(x, y, z)$ of each atom, gave way to the possibility
performing the calculation on a physical observable, obviating the need to use the
wavefunction. Compared to the complicated wavefunction, the total electron density
$ho(r)$ is only dependent on three variables: the $x$, $y$, and $z$ positions in space.[30, 31]

Since it is an measureable quantity, can it be used as a direct method to calculate the total
energy? This can only be accomplished if one can use in constructing, a priori, the
Hamiltonian operator for a system of $N$ electrons.[30] The Hamiltonian depends on the
positions of the nuclei, their atomic numbers and the total number of electrons, $N$. The
basis of density functional theory is that there exists a relationship between the total
energy of a system and the electron density. Even though this ideas was partially
developed by Thomas and Fermi (the Thomas-Fermi model), the work of Honenberg and
Kohn in 1964 demonstrated that many properties of a system, including the ground-state
energy were defined explicitly by the electron density. The latter statement can translates
to: the energy $E$ is a functional of $\rho(r)$. A function in mathematics is a prescription for
the relation between one scalar quantity to another.[31] A functional relates a function to
a scalar quantity, as indicated by brackets:

$$Q[f(r)] = \int f(r)dr. \quad (2.6)$$

An example of a functional is the area under a curve, which takes a function $f(r)$
, defining the curve between two points and returns a number, in this case the area.[26]
In density functional theory, the function $\rho(r)$ depends on electron density. $Q$ is functional of $\rho(r)$. In Equation 2.6, the function $\rho(r)$ is set equal to the electron density, $(f(r) \equiv \rho(r))$. If the function $f(r)$ were to depend on higher-order (gradients) derivatives of $\rho(r)$, then the functional is termed gradient-corrected or non-local. A local functional has a simple dependence upon $\rho(r)$.

In addition to the relationship between total energy and electron density, another key component of DFT is the improvement of the poor description of the kinetic energy in the orbital free (Thomas-Fermi theory). Kohn and Sham improved this by splitting the kinetic energy into two parts: an exact term and a small correctional term. This method (Kohn-Sham orbital Density Functional Theory) re-introduces orbitals into the problem and increases the variables from 3 to $3n$. Also, it includes the addition of the electron correlation term. The similarities between the Kohn Sham model and Hartree-Fock theory lie in the kinetic energy term, electron-nuclear and Coulomb electron-electron energies. The improved two-term energy functional in DFT is:

$$E[\rho(r)] = \int V_{ex}(r) \rho(r) dr + F[\rho(r)].$$

(2.7)

The abbreviated form of Equation 2.7, also known as the Honenber-Kohn existence theorem, states that a unique functional exists such that: $E[\rho(r)] = E_{elec}$. $E_{elec}$ being the precise electronic energy. This theorem states that the total energy of a system in its ground state is a functional (a function of a function) of that system's electronic density, $\rho(r)$ and that any density, $\rho'(r)$, other than the true density will necessarily lead to a higher energy. Here the function $\rho(r)$ depends on spatial coordinates. The energy, $E$, is a functional of $\rho(r)$ and depends on it's values. Included in the first term is the
interaction of electrons with an external potential $V_{\text{ext}}(\mathbf{r})$. This is due to the Coulomb interaction with nuclei. The second term, $F[\rho(\mathbf{r})]$ is the contribution from the interelectronic interactions and the kinetic energy of all the electrons. Hohenberg and Kohn determined that the electron density follows the variational theorem: a given electron density will have energy greater than or equal to the exact energy.\cite{25, 31-33} Combining the physical observable, $\rho(\mathbf{r})$ with the constraint that the system is limited to all electrons $N$, provides a useful mathematical expression for the electron density over all real space:

$$N = \int \rho(\mathbf{r}) d\mathbf{r}.$$  \hspace{1cm} (2.8)

Density functional theory (DFT) is a (in principle exact) theory of the electronic structure, based on the electron distribution $n(\mathbf{r})$, instead of the many-electron wavefunction $\Psi(r_1, r_2, r_3, ...)$\cite{34} Electron-electron interactions determine the structure and properties of matter, from molecules to solids. A three dimensional electron density can be used as a basic variable, with DFT, eliminating the need for the massively complex multi-dimensional wavefunction.\cite{33, 35-37}
CHAPTER 3

FUNCTIONALIZATION OF CARBON NANOTUBES

3.1 Introduction

Since their discovery in 1991, the functionalization of carbon nanotubes (CNTs) continues to be a heavily-researched area of interdisciplinary science.[38-44] A good understanding of nanotube functionalization begins with graphene and fullerene (C_{60}) functionalization. The functionalization of these nanomaterials can be achieved via covalent, bond-forming chemistry or via non-covalent electrostatic interactions.

3.2 Carbon Nanotubes

In all their forms, carbon nanotubes are difficult to dissolve in organic media, disperse in aqueous environments and are highly resistant towards wetting. Many difficulties also arise from making composites of insoluble nanotubes with other materials as well as generating an array of aligned assembles, necessary for the construction of photonic and electronic devices.[45] For some time these materials defied synthetic modification, solution chemistries, and chemical characterization. Chemical functionalization of nanotubes represents an approach for overcoming the difficulties inherently associated with nanotubes. Functionalization of nanotubes can improve processability, solubility and create unique set of properties associated with nanotubes and other kinds of materials. The formation of chemical bonds onto nanotubes

22
can tailor the tube surface towards other interactions: solvents, other nanotubes, biomaterials and macromolecules. Nanotube functionalization may be used to optimize the physics and chemistry of carbon nanotubes: functionalized tubes may have different mechanical, chemical and electrical properties.

### 3.3 Functionalization

There are different types of functionalizations (see Figure 3.1), covalent and noncovalent, associated with single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), individual tubes and tubes in bundles. Covalent functionalization, is the formation of covalent bonds of different functionalities, either at the ends of the tube or on the tube sidewall. Direct functionalization of the tube surface is associated with the hybridization of the carbon atoms from sp² to sp³. Defect functionalization of the tube sidewall exploits preformed defects sites. Defect sites can be the open ends and holes in the sidewalls, terminated, for example, by carboxylic groups, and pentagon and heptagon irregularities in the hexagon graphene framework.\[45\] Non-covalent functionalization describes supramolecular complexation, consisting of adsorption forces: van der Waals and π stacking interactions. Both covalent and noncovalent functionalization is exohedral in their nature, affecting only the tube surface; however, endohedral functionalization of CNTs has been used to put small atoms or molecules inside nanotubes.
Figure 3.1  Clockwise from the right, different types of carbon nanotube functionalization: defect group, sidewall, endohedral with C\textsubscript{60} placed inside the tube, noncovalent endohedral with molecules through \(\pi\)-stacking, and noncovalent exohedral with polymers.[45]

3.4  Nanotube Structure

Fullerenes, SWCNTs and graphite (multiple sheets of graphene, held together by weak van der Waals interactions) are well known allotropes of carbon. The basic structural unit for each is hexagons of sp\(^2\)-hybridized carbon atoms. Despite these similarities, there is a large difference between the physico-chemical properties of each material.

Fullerenes are curved in two dimensions, whereas nanotubes are curved in one dimension. Buckminster Fullerene, C\textsubscript{60}, is the smallest, stable fullerene, with the highest curvature. The profound pyramidalization of the carbon atoms of the soccer ball like framework result in a convex surface that is highly susceptible toward addition reactions.[46, 47] A pristine SWCNT is a quasi-1D cylindrical, macromolecule with an aromatic surface and is chemically inert. This is not the case for nonplanar conjugated aromatic molecules. In these materials there are two sources of induced local strain: misalignment between two adjacent carbon atoms and pyramidalization, induced by curvature, of conjugated carbon atoms.
The character of the C-C bond in a nanotube differs from that of the C-C bond in graphite as the carbon atom in a SWCNT are pyramidalized due to the curvature of the nanotube sidewall.[40, 41] Pyramidalization gives some σ character to the π orbitals of the carbon atoms. This distorts the π orbitals on the tube surface toward larger (electron cloud) and softer (toward reactivity). Since the π orbitals of the nanotube are not pointed towards the tube axis, some adjacent carbon atoms have misalignment angle attributed to pyramidalization (see Figure 3.1).

Figure 3.2 Diagram of the pyramidalization angle $\Theta_p$, and (c) the π orbital misalignment angles ($\Phi$) along C1-C4 in the (5,5) SWNT and its capping fullerene C$_{60}$.[40, 45]

Based on previous calculations of torsional strain energies in poly aromatic organic molecules, π orbital misalignment is the most likely source of strain in CNTs.[45] Pyramidalization and π orbital misalignment are completely relaxed by the addition of an atom or functional group to the surface of the tube. An increase in the diameter of the tube decreases the pyramidalization angle as well as the π orbital misalignment angle: effectively lowering the reactivity of the C-C bonds to the level of planar graphite, for large diameter tubes.[41] Defect-free nanotubes consist of sp$^2$ hybridized carbon atoms, which when subject to addition of an atom, undergo hybridization to sp$^3$, relieving strain. On the other hand, atom-addition to the interior of the nanotube adds more strain energy.
to the tube. The strain energy of pyramidalization is approximately proportional to $\Theta_p^2$.[45] To roll a graphene sheet into a (10,10) CNT would require a pyramidalization angle of $\Theta_p = 3.0^\circ$. The corresponding fullerene hemisphere, to cap this tube would be from fullerene $C_{240}$, with $\Theta_p^{\text{max}} = 9.7^\circ$. Fullerene stores, roughly, ten times the strain energy of pyramidalization per carbon atom, compared to the corresponding CNT.[40, 45] The first armchair CNT with a diameter greater than that of $C_{60}$ is the (6,6) SWCNT. Irrespective of the CNT diameter, the more pyramidalized carbon atoms of the tube end caps (fullerene hemispheres) guarantee that the most reactive part of the CNT will be the end caps and not the sidewalls.[40]

The orbital misalignment in fullerenes is not the same as in CNTs. For armchair (5,5) SWCNT in Figure 3.1, even though all carbon atoms are equivalent, there are two types of C-C bonds: some that are perpendicular to the tube axis (parallel to the circumference), $\Phi = 0^\circ$ and some that are at an angle (to the tube axis) to the circumference, $\Phi = 21.3^\circ$. The different misalignment angles in CNTs points to the different chemistry of CNTs compared to fullerene chemistry. However, there are some similarities. Just as with fullerenes, carbon nanotube reactivity is due to their topology, but for different reasons. Moreover, because the $\pi$ orbital misalignment angles and pyramidalization angles of SWCNTs scale inversely with the diameter of the tube, the reactivity of CNTs of different diameters will not be the same.

Single-walled carbon nanotubes can be represented by a rolled graphene sheet, a microns in length and widths that range from 1-1.5 nm. In lieu of specific nanotubes, graphene is often used to simulate the chemical functionalization of nanotubes. Chemical functionalization is one the main methods to manipulate the physical and chemical
properties of nanomaterials and to study mechanisms of interaction of the nanomaterials with their environment. Originally, graphene was used by theoretical scientists as a model to describe the properties of CNTs. After the discovery of graphene, the functionalization of this new material became a productive area of research amongst physicist, chemists and materials scientists. Many of the motivations behind the study graphene functionalizations are practical and have been studied with CNTs: (1) tailoring of the electronic properties via band gap opening in the electronic spectrum of single and bilayer graphene (2) the potential for graphene to serve as a hydrogen storage material (3) decoration of defects in graphene (4) magnetizing graphene for use in spintronics (5) various methods for the cheap production of graphene, by reduction of graphite oxide and manipulation of its electronic and mechanical properties (6) functionalization of graphene edges into nanoribbons and their protection (7) and lastly as a tool to create graphene structures of a given shape.

3.5 Graphene Functionalization

As with CNTs graphene can be functionalized via covalent bond formation and noncovalent due to van der Waals forces. There are more computational reports on covalent functionalization of graphene compared to noncovalent functionalization. This is a direct result of the fact that many DFT codes do not allow for one to take into consideration the effects of the van der Waals interactions, which are crucial in noncovalent functionalization. Covalent functionalities on graphene result in stronger modification of its geometric as well as electric properties. The electronic properties of graphene were recently reviewed by Nobel laureates Novoselov, Geim and co-workers and will only be discussed as they relate to the properties of carbon nanotubes.
dimensionalities of carbon structures afford to it a variety of physical properties. Graphene, the 2D allotrope of carbon, serves as the basis for the understanding of the electronic properties of each carbon allotrope. The band structure for a single layer of graphene is indicative of the hybridization of each carbon atom in the single layer sheet: each carbon atom has three \( \sigma \) orbitals and one \( \pi \) orbital. The orbitals that constitute graphene, define the geometry of the single layer, each carbon has three \( \sigma \) bonds. The \( \pi \) orbital, normal to the surface, on each carbon contains a single electron. The infinite number of carbon atoms, in the sheet that is defined as graphene is electronically a delocalized surface, this is sharp contrast to poly-aromatic hydrocarbons with localized single and double bonds.\[48, 50\]

The surface of graphene can be modified with the insight gained from the surface modification of fullerene. Minimal modification (hydrogenation) of fullerene was achieved by Henderson and results in \( \text{C}_{60}\text{H}_2 \). The most stable configuration was achieved by functionalization of neighboring carbon atoms (at the 1 and 2 positions) with hydrogen. It was determined that the maximum hydrogenation of fullerene is an even number, represented by the formula \( \text{C}_{60}\text{H}_x \), where \( x \) is an even number of hydrogen atoms. The rules that govern fullerene hydrogenation: hydrogen can be added with neighboring carbons, at positions 1 and 2 or with opposite atoms in positions 1 and 4. Chemisorption of a single hydrogen atom onto graphene results in the break of one \( \pi \) bond and a change in the hybridization from \( \text{sp}^2 \) to \( \text{sp}^3 \).

The earliest reports of experimental covalent and noncovalent functionalization of carbon nanotubes were accounts by, Mickelson et. al. and Chen et. al., respectively.\[51, 52\] The first account of DFT using the local density approximation, to obtain an
understanding of the molecular interaction in covalent functionalization was used to calculate the electronic structure and energetics of gas molecules attached to a semiconducting nanotube (10,0).[53]
CHAPTER 4

QUANTUM ELECTRONIC STABILITY IN SELECTIVE ENRICHMENT OF CARBON NANOTUBES

4.1 Introduction

We have studied the structural and electronic stability of a helical ribbon of flavin mononucleotide wrapping around single-walled carbon nanotubes using first-principles density-functional calculations. The helical ribbon is formed through hydrogen bonding between adjacent uracil moieties of the isoalloxazine ring and stabilized through concentric \( \pi-\pi \) interactions. The electronic structure calculations reveal quantum electronic stability associated with lattice registry and band alignment between the helical assembly and the (8,6) nanotube. The electronic stability plays an essential role in the experimentally observed highly selective enrichment of specific chirality tubes.

4.2 Background

Carbon nanotubes represent an intriguing class of materials for exploring nanoelectronics and nanostructured composites. Single-walled carbon nanotubes (SWNTs) are hollow cylinders characterized by the chiral indices \((n,m)\).[54] The electronic properties of individual \((n,m)\) SWNT are uniquely classified into metallic and semiconducting forms. The combination of superior electronic and mechanical properties of SWNTs has led to their use in various applications, including flexible electronics,[55] biosensors,[43] and transistors.[56] As SWNT synthetic methods yield a
distribution of bundled (n,m) types, solubilizing and isolating specific carbon nanotube structures remain as some of the foremost technological challenges in the effective utilization of their potential applications.

The supramolecular functionalization of SWNTs has recently attracted a great deal of attention because it exploits the surface chemistry of the nanotubes via π–π interactions and preserves the integrity of the electronic structure.[41] Separation of specific chirality tubes from a mixture of SWNTs can be achieved by addition of nonreactive chemical reagents that exhibit distinct affinity toward different species of SWNTs. The selective enrichment can be type-specific (metallic or semiconducting),[52] diameter-dependent,[57] and chiral (n,m)-specific.[58] The type-selective mechanism is predominantly attributed to the distinctive charge transfer behavior for metallic and semiconducting tubes, while the size-selective mechanism is associated with the geometry conformation of the chemical motifs. A wealth of experimental and theoretical effort has been devoted to the improvement of the enrichment mechanism, and a great deal of progress has been made.[59-61]

Flavin mononucleotide (FMN), a common redox cofactor, was found to helically wrap around SWNTs, promoting effective aqueous dispersion and individualization.[58] The cooperative hydrogen bonding between adjacent uracil moieties of the isoalloxazine rings results in the formation of a helical ribbon that wraps around SWNTs through concentric π–π interactions with the underlying sidewall of the nanotube. The significantly stronger affinity of the FMN helix for the (8,6) tube was utilized to selectively enrich the specific chirality (85%) from a broad diameter distribution sample. Despite the remarkable experimental results, the nature of this high selectivity remains unclear as it is distinctive from either the diameter-selective or the type-selective mechanism.[58]
4.3 Geometry Details

Here we present a comprehensive investigation of structural and electronic properties of the FMN assembly helically wrapping on SWNTs. We employ three levels of theoretical models: force-field-based molecular dynamics,[62] non-self-consistent Harris approximation to density functional theory (DFT),[24] and self-consistent first-principles approach.[63] Our results indicate that specific enrichment of the (8,6) tubes by the helical FMN assembly cannot be properly taken into account with the former two approaches. In contrast, the first-principles calculation reveals the important role of band alignments to the structural conformation and electronic stability. One fundamental issue is how the noncovalent interactions between the SWNT and the helical FMN assembly affect the geometry of the latter. We show that the π–π interaction between the flavin sheath and the SWNT manifests itself via concentricity of FMN moieties through registry of geometry and electronic structures.

On the basis of the experimental results, a helical FMN 8t structure was constructed,[58] which yielded the desired van der Waals (vdW) spacing between the helical “shell” and the (8,6) tube. Unlike other debundling methods, the driving force for forming the sheathlike FMN 8t appears to be the concentric π–π interaction between the isoalloxazine ring and the underlying nanotube sidewall, along with the quad-hydrogen bonding between FMN moieties. However, the proviso of a concentric 8t conformation after interacting with SWNTs was not verified theoretically. This raises question as to whether the diameter selectivity mechanism alone is capable of accounting for the highly selective enrichment of the (8,6) tubes.

To substantiate this point, we have carried out simulations based on force-field-based molecular dynamics. The SWNTs involved in the force-field-based molecular dynamics study were constructed based on a sp² hybridization model. In order to study intrinsic properties, the
ends of the nanotube were passivated by hydrogen atoms, resulting in a neutral-bond-saturated SWNT segment. The initial value of \( b = 0.142 \text{ nm} \) was used. The geometric structures of the SWNTs wrapped with the \( 8_1 \) helical assembly were fully relaxed through simulated annealing and accelerated molecular dynamics.

The binding of FMN with SWNT is a combination of electrostatic and van der Waals (vdW) interactions. The binding energy can be extracted from the difference between the potential energy of the composite system and the potential energies for the FMN and the corresponding SWNTs as \( E = E_{\text{SWNT}} + E_{\text{FMN}} - E_{\text{total}} \), where \( E_{\text{total}} \) is the total potential energy of the nanohybrid, \( E_{\text{SWNT}} \) the energy of the nanotube without the FMN, and \( E_{\text{FMN}} \) the energy of the FMN without the nanotube. Shown in Figure 4.1 are the calculated binding energies of the \( 8_1 \) FMN assembly interacting with various species of semiconducting SWNTs identified in the experimental sample.\[58\] Listed in Table 4.1 are the diameter and length of corresponding semiconducting tubes based on the rolling-graphene model.\[54\] Instead of a uniform coplanar geometry, the FMN helical assembly wraps around various carbon nanotubes with a patterned helix. Careful examination of the helix conformation reveals that 16 moieties form one pitch or turn consisting of two sets of sequenced strands. Each sequence of eight moieties makes one strand. For wrapped (8,6), the strand is square shaped, rotated with respect to the other by \( \theta = 45^\circ \).
Figure 4.1  Calculated binding energies for various species of SWNTs with diameters of 0.7–1.2 nm wrapped with the 81FMN assembly using molecular dynamics and MM+ force field. Inset: top view of optimized structures of FMN wrapped (7,5), (8,6), (10,5), (12,2), and (9,8) SWNTs.

Table 4.1  The diameter (d) and periodic length (L) of various species of SWNTs

<table>
<thead>
<tr>
<th>(n,m)</th>
<th>d (nm)</th>
<th>L (nm)</th>
<th>(n,m)</th>
<th>d (nm)</th>
<th>L (nm)</th>
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<tbody>
<tr>
<td>(6,5)</td>
<td>0.747</td>
<td>4.064</td>
<td>(9,5)</td>
<td>0.962</td>
<td>5.235</td>
</tr>
<tr>
<td>(8,3)</td>
<td>0.771</td>
<td>4.196</td>
<td>(12,1)</td>
<td>0.981</td>
<td>5.338</td>
</tr>
<tr>
<td>(7,5)</td>
<td>0.817</td>
<td>4.448</td>
<td>(11,3)</td>
<td>1.000</td>
<td>5.439</td>
</tr>
<tr>
<td>(8,4)</td>
<td>0.829</td>
<td>1.127</td>
<td>(8,7)</td>
<td>1.018</td>
<td>5.538</td>
</tr>
<tr>
<td>(10,2)</td>
<td>0.872</td>
<td>2.372</td>
<td>(12,2)</td>
<td>1.027</td>
<td>2.793</td>
</tr>
<tr>
<td>(7,6)</td>
<td>0.882</td>
<td>4.801</td>
<td>(10,5)</td>
<td>1.036</td>
<td>1.127</td>
</tr>
<tr>
<td>(9,4)</td>
<td>0.903</td>
<td>4.913</td>
<td>(11,4)</td>
<td>1.053</td>
<td>5.731</td>
</tr>
<tr>
<td>(11,1)</td>
<td>0.903</td>
<td>4.913</td>
<td>(9,7)</td>
<td>1.088</td>
<td>5.918</td>
</tr>
<tr>
<td>(10,3)</td>
<td>0.923</td>
<td>5.022</td>
<td>(10,6)</td>
<td>1.096</td>
<td>2.982</td>
</tr>
<tr>
<td>(8,6)</td>
<td>0.952</td>
<td>2.591</td>
<td>(9,8)</td>
<td>1.153</td>
<td>6.275</td>
</tr>
<tr>
<td>(n,m)</td>
<td>d (nm)</td>
<td>L (nm)</td>
<td>(n,m)</td>
<td>d (nm)</td>
<td>L (nm)</td>
</tr>
</tbody>
</table>

For other species of tubes, \( \theta \)--the angle between the two sequences--is larger for smaller diameters tubes, while smaller for larger diameter ones. Eventually for large diameter tubes, the flavin moiety becomes flattened with respect to the sidewalls of the carbon nanotubes. The increases of binding energy with increasing the tube diameter can be attributed to an improved geometric match between the planar FMN conformation and a reduction in \( \pi \)-orbital
misalignment. [64] Closer scrutiny of the optimized structures shown in the inset of Figure 4.1 reveals that the FMN moieties adjust themselves onto SWNTs in such a way that maximize the stacking area. It is worth mentioning that we have verified the stability of this patterned structure with use of a variety of force fields. The force-field-based modeling suggests, therefore, that the experimentally observed affinity toward the (8,6) nanotubes cannot be explained with the binding energy extracted from force-field calculations, even when structures other than the 81 FMN assembly are considered.

The experimentally observed helical ribbon has a pitch of 2.5 ± 0.4 nm with a corresponding angle of 35–37°. The 81 conformation was constructed accordingly,[58] with a pitch of about 2.6 nm. It is readily observable from Table 1 that the periodic length of the (8,6) tube is 2.59 nm, in good agreement with the experimentally observed pitch of the helical sheath. This suggests lattice registry between the 81 ribbon and the (8,6) tube. Furthermore, the other observed periodicity of 5.0 ± 0.4 nm corresponds to 5.2 nm, the doubled (8,6) and single (9,5) periodic length. The (9,5) tubes are the enriched species in the second round selection after the separation of (8,6). Consequently, we constructed periodic structures of the hybrid, referred to as 81(8,6). The unit cell of 81(8,6) constitutes 504 C, 192 H, 64 N, and 32 O, for a total of 792 atoms. It is worth noting that the stability associated with lattice registry between the inner (8,6) nanotube and the 81 outer shell is analogous to that of double-walled carbon nanotubes. For an inner nanotube with a given conformation, there exists an energetically favored outer shell conformation giving rise to an energetically favored inner–outer pair.[65]

4.4 Computational Methods

In an effort to understand the electronic structures, we have performed first-principles calculations for 81(8,6). Our calculations were carried out using DFT within the local density
approximation to the exchange-correlation potential. Periodic-boundary conditions were employed in the xy plane with a supercell large enough to eliminate the interaction between neighboring $8_1(8,6)$ structures. A double numerical basis was employed, and an energy cutoff of 300 eV was sufficient to converge the grid integration of the charge density. All structures were relaxed with forces less than 0.05 eV/Å.

4.5 Results and Discussion

We present in Figure 4.2 the optimized conformations for (a) force-field molecular dynamics, (b) non-self-consistent Harris approximation to DFT with minimal basis set, and (c) self-consistent first-principles DFT calculations with double numerical basis. In all the cases, the nanotube upholds a cylindrical shape. The diameter of the optimized $(8,6)$ tube in $8_1(8,6)$ is 0.95, 0.99, and 0.94 nm, for structures a, b, and c, respectively. The overestimate of the tube diameter for structure b can be attributed to the inaccuracy of the minimal basis set. While there is little change in the periodicity of the tube (between 2.59 and 2.62 nm, about 1%), the helical wrapping pattern changes drastically within three levels of theoretical models. The corresponding vdW interaction distance between $8_1$ and $(8,6)$ is 0.38, 0.28, and 0.31 nm, for structures a, b, and c, respectively.
Figure 4.2 Flavin mononucleotide (FMN) helically wrapping around the (8,6) tube using (a) force-field molecular dynamics, (b) non-self-consistent density-functional theory with Harris approximation, and (c) first-principles calculations with local density approximation.

The characteristic features of the electronic structure of $8_1(8,6)$ along with separated $8_1$ and $(8,6)$ are illustrated by the electronic density-of-states (DOS) in Figure 4.3. The valence band maximum (VBM) was set to 0 eV and a Gaussian broadening of 0.1 eV was used. In each case there is a paucity of modification for electronic properties of (8,6) as the corresponding gap is in conformity with that of the isolated (8,6) (a direct gap of 0.85 eV). The slight differences are due to modifications of the nanotube conformation in the three structures. On the other hand, the gap between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) for a FMN molecule is 1.9 eV. This feature is well preserved in the DOS of $8_1$ as indicated by the red arrows in Figure 3. The formation of the periodic $8_1$ sheath leads to the broadening of HUMO and LUMO to bands. The electronic DOS of $8_1$ is distinctive among structures a, b, and c, which shows semiconducting behavior for a and c, while metallic for b.
Figure 4.3  Calculated electronic density of states for (a) force-field molecular dynamics, (b) Harris approximation to DFT, and (c) self-consistent DFT calculations of $8_1(8,6)$ (black lines), as compared with those of $(8,6)$ (blue lines) and $8_1$ (red lines).

The band alignment of $8_1(8,6)$ is based on the lineup of charge neutrality levels (CNLs) for $8_1$ and $(8,6)$.\cite{68} A detailed analysis of the electronic DOS shown in Figure 4.3 indicates that the corresponding band alignments can be obtained without the necessity of explicit CNL calculations. For instance, the lineup of $8_1$ in structure (a) is indicated by black horizontal arrows in Figure 4.3. We depict in Figure 4.4 the extracted band alignment for the three structures. In all such cases, the band alignment is type I such that charge carriers in VBM and CBM accumulate in one of the two components, with the band gap of $8_1(8,6)$ being determined predominantly by the gap of the component. The confinement potentials generated by the band offset for VBM and CBM are indicated in Figure 4.4 by black lines linking $8_1$ and $(8,6)$. For structure a, the resultant charge transfer behavior is consistent with small molecules adsorbed on semiconducting SWNTs with charges in VBM and CBM being confined on the tube.\cite{69}
Figure 4.4 The band alignment of $8_1$, $(8,6)$ and $8_1(8,6)$ for the three theoretical models as depicted in Figure 4.2.

Structure (b) was obtained through intensive search of optimal conformations by employing non-self-consistent Harris approximation to DFT. For structure b, the physisorption of $8_1$ onto the nanotube leads to blue shift of the bands corresponding to HOMO and LUMO of FMN. The band alignment of $8_1$ and $(8,6)$ yields distinct electronic behavior of $8_1(8,6)$ for non-self-consistent and self-consistent calculations. The non-self-consistent Harris approximation yields a semiconducting nanohybrid with reduced gap (0.5 eV) due to a contraction of the bands, whereas self-consistent density-functional calculation produces a (semi)metallic (a small gap 0.05 eV) behavior. This may seem surprising at first, but in light of the apparent band mixing and the associated charge transfer, this implies the importance of self-consistent calculations in studying interlayer couplings. This discrepancy notwithstanding, the charges of CBM and VBM are spatially confined onto $8_1$ and the overall gap of $8_1(8,6)$ is predominantly determined by the gap of $8_1$.

Although the electronic properties of structure b are distinctively different from those of structure a, the patterned $8_1$ sheath conformation is similar. It is interesting to note that structure b becomes unstable under self-consistent electronic structure calculations. Structure c was
obtained through self-consistent calculation and double numerical basis. The resulting $8_1(8,6)$ has a concentric geometry, with a pitch angle of 34.9° and pitch length of 0.26 nm, in very good agreement with experimental observations.[58]

It is gratifying that our first-principles calculation results confirm the stability of the concentric conformation of $8_1$ ribbon wrapping around the (8,6) SWNTs. More importantly, our study reveals that the stability of concentric $8_1(8,6)$ is determined by electronic structure. The improvement of the binding energy from structures b to c is substantial, about 0.6 eV per flavin moiety. As seen in Figure 3c, the FMN assembly opens a gap of 0.82 eV, in close registry of a gap of 0.89 eV for (8,6). The increase of the $8_1(8,6)$ gap from 0.05 eV for structure b to 0.83 eV for structure c is a consequence of hybridization between the bands of $8_1$ and (8,6), which is reminiscent of level mixing and electronic correlation for the stability of the helical $8_1(8,6)$. We have found that as part of the interlayer interaction, from structures b to c charges in VBM and CBM transfer back from the $8_1$ FMN sheath to the (8,6) tube, which is correlated to the reduction of the confinement barrier.[70]

The extracted density distribution of holes and electrons for structures a, b, and c are illustrated in Figure 4.5. The spatial confinement features are consistent with the predictions from band alignments. The charge distribution of structure a is mainly confined on the nanotube, while mainly on sheath for structures b and c. Although there is an accumulation of charge on $8_1$ for both structures b and c, the confinement potentials generated through band offset are very different. The charge distribution in structure c is mainly on the oxygen sites (red atoms in Figure 4.5) in the ribbon area for VBM and on the FMN for CBM. These results not only suggest that lattice registry is important in homogeneous charge distributions but also highlight a general trend for stability in nanostructures in that optimal geometry minimizes the energies of
the occupied states relative to the Fermi level. This is similar to the issue of stability for clusters and nanowires, which favors structures with a closed electronic shell and homogeneous charge distributions.[71, 72] Accordingly, the control of proper molecular assemblies may offer avenues for the design of highly selective enrichment.

Figure 4.5 Calculated charge distribution of VBM and CBM for $8_1$(8,6) structures a, b, and c. The sign of the wave function is indicated by light blue and yellow regions, respectively. The isovalue is 0.02 au.

### 4.6 Summary

In summary, we have demonstrated that highly selective enrichment of FMN $8_1$ assembly toward the (8,6) tubes is attributed to the quantum electronic stability associated with lattice registry and band alignment. The concentric conformation of $8_1$ sheath is stabilized by hydrogen bonding and $\pi-\pi$ stacking interaction. The first-principles results shed considerable light on the nature of noncovalent interactions between helical assemblies and carbon nanotubes. Moreover, the novel first-principles approach in determining the band alignment of nanohybrids can be employed to investigate charge transfers of derivatives in solubilizing SWNTs, such as helical molecular assemblies, DNA, and helical conjugated polymers.[73] The understanding of
quantum electronic stability thus provides a useful means for future development of debundling agents and nanotube-based nanodevices.
CHAPTER 5

CHARGE TRANSFER IN THE NON-COVALENT FUNCTIONALIZATION OF CARBON NANOTUBES

5.1 Introduction

We have performed force field-based molecular dynamics and first principles density functional calculations on porphyrins and metalloporphyrins interacting with single-walled carbon nanotubes. The flattening of the porphyrin macrocycle is indicative of the self-assembly of these aromatic structures onto carbon nanotubes. An analysis of the charge distributions for conduction and valence bands reveals a distinct charge transfer behavior from the porphyrin macrocycle to the metallic or semiconducting tubes that sheds considerable light on the experimentally observed selectivity of semiconducting nanotubes.

5.2 Background

The nano forms of carbon, fullerenes, nanotubes and graphene are important building materials that cross all disciplines of science.[59-61] The supramolecular functionalization of single-walled carbon nanotubes (SWNTs) has recently attracted a great deal of attention because it exploits the surface chemistry of the nanotubes via π-π interactions and preserves the integrity of the electronic structure. Recent research has demonstrated the self-assembly of a variety of macromolecules, nanoaggregates and biomaterials on the surface of SWNTs.[59-61] Molecules, such as porphyrin, pyrene or...
flavin derivatives, self-assemble onto semiconducting tubes, revealing a convenient way to separate these from metallic examples.[58-61, 69, 74-76] Despite the abundance of experimental work on the adsorption of aromatic molecules, the nature of this intriguing type-selectivity is not fully understood. As the debundling of carbon nanotubes remains one of the foremost technological barriers to the realization of their potential applications, a theoretical understanding of the interactions, structure and physical properties of porphyrins with SWNTs is highly desirable.

In order to gain a better understanding of the interfacial chemistry and dispersion mechanism, we have employed a combination of force field-based molecular dynamics (MD) and first principles density functional calculations to investigate the structural and electronic properties of porphyrin-functionalized SWNTs. Force field-based MD is used to pre-screen molecular geometries, and first principles calculations are employed to determine the electronic structure of the nanohybrid. A fundamental issue is how non-covalent interactions affect the conformation of the porphyrin macrocycle, as these macromolecules possess flat planar geometries that are spontaneously attracted to the side walls of SWNTs, forming a host–guest nanohybrid. This type of functionalization has a direct impact on the selectivity of nanotubes. Our results show that the $\pi-\pi$ interaction between the porphyrin and the SWNT manifests itself via a flattening of the porphyrin macrocycle. Metalloporphyrins, as exemplified by Zn-porphyrin, have a less flattened conformation as compared to that of the free porphyrin, yielding weaker binding with SWNTs. First principles calculations on the electronic structures further reveal that a distinct charge transfer behavior exists for metallic and semiconducting nanotubes adsorbed with porphyrin that dictates the type-selectivity observed experimentally.[77]
5.3 Geometry Details

SWNTs are rolled graphene sheets along a certain chiral vector. The structure of a SWNT is uniquely characterized by \((n, m)\) chiral indices. Among chiral vectors, there are two distinctive high-symmetry directions, corresponding to \((n, 0)\) “zig-zag” and \((n, n)\) “armchair.” From the rolling graphene model,[78] the chiral angle \(\theta\) and diameter \(d_0\) of a \((n, m)\) SWNT \((0 \leq m \leq n)\) are

\[
\theta = \arctan \left( \frac{\sqrt{3} m}{2n + m} \right), \quad d_0 = \frac{\sqrt{3} b}{\pi} \sqrt{n^2 + m^2 + nm},
\]

respectively, where \(b\) is the bond length of graphene. A nanotube is considered to be metallic if \(n - m\) is divisible by 3, and semiconducting otherwise. However, the electronic structure of metallic SWNTs is very sensitive to radial deformations because of the presence of degenerate low energy electronic states in these systems.[79] The effect of breaking symmetry due to non-covalent functionalization remains a paucity of classification from first principles calculations.

The SWNTs involved in the present study were constructed based on a \(sp^2\) hybridization model. The initial value of \(b = 0.142\) nm was used. The geometric structures of the SWNTs were fully relaxed in the molecular dynamics through intensive simulated annealing. A systematic evaluation of the available empirical force fields[24] showed that the MM+ and CHARMM force fields provide consistent results for both the carbon nanotubes and porphyrin. In contrast, the COMPASS and AMBER force fields entail difficulties in generating the desired cylindrical configurations of nanotubes. The optimized structures with the use of the MM+ and CHARMM force fields have diameters in good agreement with the predictions from the rolling graphene model, as shown in
Equation 5.1[78] A porphyrin is an aromatic macrocycle that consists of four pyrrole rings connected by methine bridges.[80] The structural formula of the porphyrin and Zn-porphyrin used in this work are shown in Figure 5.1, along with the optimized structures of representative species of THPP or Zn-THPP wrapped around SWNTs.

![Structural formula of porphyrin and Zn-porphyrin](image)

\[ R = (\text{CH}_2)_n \text{CH}_3 \quad (10,2) \quad (8,6) \quad (8,8) \quad (15,0) \quad (12,6) \]

Figure 5.1 The structural formula of tetraphenylporphyrin (THPP) and Zn-THPP studied in this work. The top and bottom panels, for THPP and Zn-TFePP interacting with SWNTs (10,2), (8,6), (8,8), (15,0) and (12,6), respectively.

### 5.4 Results and Discussion

The binding of the porphyrin to the SWNT is a combination of electrostatic and van der Waals (vdW) interactions. As a consequence, the electrostatic interactions are stronger than vDW binding for non-conjugated molecules, which may explain why the nanotubes are generally dispersed better with conjugated molecules. In general, the adsorption energy can be estimated from the difference between the potential energy of the composite system and the potential energies of the porphyrin and corresponding SWNTs as follows, \( E = E_{SWNT} + E_{FMN} - E_{total} \), where \( E_{total} \) is the total potential energy of the nanohybrid, \( E_{SWNT} \) is the energy of the nanotube without the porphyrin and \( E_{Porphyrin} \) is the energy of the porphyrin without the nanotube.
We illustrate in Figure 5.2 the calculated adsorption energies using force field-based MD. As seen from Figure 5.2, the adsorption energy increases with increasing diameter of the tube. This is attributed to an improved geometric match between the planar porphyrin conformation and the carbon nanotube, as well as a reduction in π-orbital misalignment. The THPP-SWNTs (●) have a consistently better adsorption energy compared to those of Zn-THPP-SWNTs (○), with an energy difference of ~10 kcal mol⁻¹. Closer scrutiny of the optimized structures (see Figure 5.1) reveals that the THPP adsorption leads to tighter wrapping around the SWNTs compared to the Zn-THPP adsorption, which is readily observable since the side-chains, \( R = (CH_2)_{15}CH_3 \), are explicitly included in the calculation. It is worth pointing out that the inclusion of the side chains is not only in accordance with the experiments, but also useful for determining the optimized structure through simulated annealing.

![Figure 5.2](image)

**Figure 5.2** The calculated adsorption energy dependence on diameter for various species of tube interacting with THPP (●) and Zn-THPP (○), respectively.

The binding behavior is mainly dependent upon the flattening of the porphyrin
macrocycle. The flattening of the macrocycle induces an increase in the \( \pi-\pi \) interaction area. The present modelling therefore suggests that nanotube solubilization depends strongly upon the geometry of the porphyrin adsorbed onto the SWNT. Specifically, the experimentally observed better solubilization of THPP over Zn-THPP can be interpreted by taking into account the differences in the \( \pi-\pi \) stacking interactions.[81]

The experimental observation of the favorable selection of semiconducting tubes[60] is connected to electronic structures that cannot be assessed through classical force field models. In an effort to understand the electronic properties involved in the type-selectivity, we have performed first principles calculations of five representative SWNTs adsorbed by THPP and Zn-THPP. The calculation is based on density functional theory using the local density approximation of the exchange–correlation potential.[82] All calculations were carried out using a double-numerical basis set.[83] Despite the fact that vdW interactions are not well described in local-density approximations, the computationally-demanding first principles calculation provides important information on level hybridization. Our previous study of the quantum stability of selective enrichment of the helical assembly of flavin mononucleotide wrapping around SWNTs demonstrated that this approach is appropriate for a description of electronic structures.[83]

The structures obtained from force field-based MD calculations were further optimized using the first principles method; the force was converged to less than 0.01 eV Å\(^{-1}\). The structural properties of the optimized conformations are summarized in Table 5.1. A similar structural trend is observed in force field-based MD calculations. The first principles results from the nanotube diameters are slightly larger than those from the
force field-based MD simulations. For the various sizes of tube studied, the porphyrin macrocycle aligns along the tube, and the four pentagons are arranged in such a way that two centers are near the top of the carbon atoms on the SWNT surface while the other two are on top of carbon–carbon bonds. The four alkoxyphenyl rings tilt up at the remote sides away from the macrocycle and the resultant conformation is of a saddle shape.

Although there exist local basis corrections for the binding energy calculations,[82-84] the first principles calculation results of the binding energy for the five species are in good agreement with force field-based MD calculation results, especially for the energy orders.

An important ramification is that the flattening of the porphyrin macrocycle associated with the reduction of π misalignment is still the predominant factor for the adsorption energy.

Table 5.1 Calculated electronic and geometrical properties of porphyrin-SWNT composites.

<table>
<thead>
<tr>
<th>$(n, m)$</th>
<th>$d_{\text{LDA}}$/nm</th>
<th>$d_{\text{MM}}$/nm</th>
<th>$d_{y}$/nm</th>
<th>Molecular formula</th>
<th>$E_{\text{LDA}}$/eV</th>
<th>$E_{\text{MM}}$/eV</th>
<th>$\Delta Q$/e atom$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(12,6)</td>
<td>1.29</td>
<td>1.26, 1.34</td>
<td>1.243</td>
<td>C$<em>{444}$H$</em>{158}$N$<em>4$O$<em>4$, C$</em>{444}$H$</em>{156}$N$_4$O$_4$Zn</td>
<td>8.89</td>
<td>7.59</td>
<td>1.6 x 10$^{-3}$</td>
</tr>
<tr>
<td>(15,0)</td>
<td>1.20, 1.25</td>
<td>1.20, 1.24</td>
<td>1.174</td>
<td>C$<em>{468}$H$</em>{158}$N$<em>4$O$<em>4$, C$</em>{468}$H$</em>{156}$N$_4$O$_4$Zn</td>
<td>8.32</td>
<td>7.41</td>
<td>1.7 x 10$^{-3}$</td>
</tr>
<tr>
<td>(8,8)</td>
<td>1.12, 1.14</td>
<td>1.11, 1.14</td>
<td>1.085</td>
<td>C$<em>{396}$H$</em>{158}$N$<em>4$O$<em>4$, C$</em>{396}$H$</em>{156}$N$_4$O$_4$Zn</td>
<td>8.27</td>
<td>7.11</td>
<td>1.7 x 10$^{-3}$</td>
</tr>
<tr>
<td>(8,6)</td>
<td>0.99, 0.97, 1.01</td>
<td>0.952</td>
<td></td>
<td>C$<em>{404}$H$</em>{158}$N$<em>4$O$<em>4$, C$</em>{404}$H$</em>{156}$N$_4$O$_4$Zn</td>
<td>8.21</td>
<td>7.04</td>
<td>2.1 x 10$^{-3}$</td>
</tr>
<tr>
<td>(10,2)</td>
<td>0.90, 0.93, 0.86, 0.94</td>
<td>0.872</td>
<td></td>
<td>C$<em>{356}$H$</em>{158}$N$<em>4$O$<em>4$, C$</em>{356}$H$</em>{156}$N$_4$O$_4$Zn</td>
<td>8.05</td>
<td>6.87</td>
<td>2.7 x 10$^{-3}$</td>
</tr>
</tbody>
</table>

The calculated diameters of the SWNTs wrapped with porphyrin investigated in this work, consisting of three metallic SWNTs, chiral (12,6), zig-zag (15,0) and armchair (8,8), and two semiconducting SWNTs, chiral (8,6) and (10,2). For anisotropic tubes, the
maximum and minuend values are shown as $d^{\text{MIN}}$ and $d^{\text{MAX}}$. The values from local density functional calculations ($d^{\text{LDA}}$), force field-based MD calculations ($d^{\text{MM}}$) and those of ideal SWNTs ($d_0$) are shown, together with the molecular formula of THPP- and Zn-THPP-adsorbed SWNTs, the binding energy values from local density functional calculations ($E^{\text{LDA}}$) and force field-based molecular dynamics ($E^{\text{MM}}$), as well as the charge transfer ($\Delta Q$) from THPP to the SWNT.

The characteristic features of the electronic structure of the THPP-functionalized SWNTs are illustrated by the band structures in Figure 5.3, along with those of pristine SWNTs. As seen from Figure 5.3, the metallic feature due to the "indirect band overlap" of $\pi$ and $\pi^*$ states for pristine (8,8) and the semi-metallic states of pristine (12,6) and (15,0) are well reproduced within our calculations. There is a reduction of the band gap for THPP-functionalized semiconducting SWNTs as the HOMO-derived band of the porphyrin intrudes into the gap. On the other hand, for the metallic (8,8), (12,6) and (15,0), there is a paucity of modifications to the bands near the Fermi level. The changes associated with the HOMO-derived band of the porphyrin is consistent with predictions from the charge transfer model.\[85\] The charge transfer is in the order of $0.002 \text{ e atom}^{-1}$ (see Table. 5.1), which is much smaller than that typically found in alkali intercalation experiments.

The calculated band structure of the porphyrin-SWNT composites are in on display in Figure 5.3. The calculated The Fermi level is indicated by the dotted line at $E = 0 \text{ eV}$. 
Figure 5.3  Calculated electronic band structures of pristine (top panels) and functionalized (lower panels) SWNT and THPP nanohybrids for (10,2), (8,6), (8,8), (15,0) and (12,6), respectively.

The unit cell along the tube $d$ is about 2 nm, $\Gamma$ is the band center and $L = \pi/d$. The Fermi level is shifted to 0 eV. The HOMO-derived band of the porphyrin is highlighted. Note that band folding exists that is associated with the long unit cells used in the calculations.

It is worth noting that functionalized semiconducting and metallic tubes have distinct charge transfer behaviors. For functionalized semiconducting tubes, there is no level hybridization for the HOMO-derived flat band of the porphyrin. The level hybridization and associated charge transfer arise predominantly from the lower valence band derived from the HOMO – 1 orbital of the porphyrin. In contrast, the charge transfer in functionalized metallic tubes is mainly due to the HOMO-derived band of the porphyrin, which causes the splitting of the doubly-degenerate bands for the functionalized (15,0) in the proximity of level hybridization.

The extracted electronic density distribution for the conduction band maximum (CBM), valence band minimum (VBM) and a few near-gap valence states of THPP adsorbed onto representative semiconducting (10,2) and (8,6), and metallic (8,8), (12,0)
and (12,6) tubes is shown in Figure 5.4. In all such cases, the charge density of the CBM is confined to the tube, while that for the VBM depends on the electronic properties of the pristine SWNT. For the functionalized semiconducting tubes, charges of the VBM reside on the THPP macrocycle. In contrast, for metallic tubes, the charges of the VBM accumulate on the SWNT. The distinctive confinement features, observed for each nanotube account for the distinct charge transfer from the porphyrin macrocycle to the semiconducting or metallic nanotube. It is worth noting that for functionalized semiconducting nanotubes, the charge distribution of VBM and CBM is consistent with a type I alignment of the bands.[68, 72, 77] However, functionalized metallic nanotubes exhibit a type II alignment. In the latter case, the charge density of the HOMO-derived band of the porphyrin is inhomogeneous due to level hybridization and the associated charge transfer from the porphyrin to the tube. Our results indicate that porphyrins are charge donors to SWNTs, resulting in complete charge separation of the HOMO-derived band of the porphyrin for functionalized semiconducting nanotubes. By way of contrast, for functionalized metallic nanotubes, the charge transfer induces considerable level hybridization, which leads to charged dipoles.[70, 86-89] The charge dipoles, in general, lead to instability with p-doping. This is similar to the issue of stability for nanowires and structures with aromatic residues, which favors structures with a closed electronic shell and homogeneous charge distributions.[68, 70, 72, 90] As such, we believe that the effects of hole doping and the generated charged dipoles in functionalized metallic SWNTs play an important role in the experimentally observed type-selectivity.
Figure 5.4  An isosurface plot of the calculated charge densities for CBM, VBM and a few near-gap valence states of THPP-SWNT complexes. The sign of the wave function is indicated by dark and light grey regions, respectively.

5.5 Summary

In summary, our calculation results indicate that the semiconducting selectivity can be attributed to the stability of the electronic structure, associated with charge transfer effects. The SWNT–porphyrin bonding is strongly influenced by the adsorption conformation at the nanotube structure, as well as the quantum dipoles associated with charge transfer in metallic tubes. The distinct charge transfer behavior is also expected for a variety of aromatic molecules adsorbed onto SWNTs. The modification of nanotube electronic properties by interacting them with aromatic molecules thus provides a useful means for generating future nanoelectronic devices.
6.1 Introduction

Covalent functionalizations represent a promising avenue to tailor the electronic properties of carbon nanotubes. Recent experimental work has shown that cycloaddition of fluorinated olefins represents an effective approach to reduce the off-currents of mixed nanotube mats for transistor applications. We have studied the electronic structure characteristics of the corresponding [2+2] cycloaddition using first-principles density functional calculations. While the band gap opening in chemically functionalized tubes associated with the $sp^2$ to $sp^3$ rehybridization typically depends on the concentration, doping, and the adduct, our calculation results reveal that the experimentally observed suppression of metallic conductivity can be attributed to a symmetry aligned cycloaddition scheme that effectively transforms metallic tubes to semiconducting ones.

6.2 Background

Single-walled carbon nanotubes (SWNTs) are rolled cylindrical graphene sheets [1, 91] with unique electronic properties determined by their chiralities.[92] Both metallic and semiconducting SWNTs have widespread applications in nanoelectronics, molecular electronics, opto- electronics, drug delivery, and biochemical sensors.[93, 94]
Their application has been hampered by the fact that current synthetic methods produce a mixture of metallic and semiconducting nanotubes[95]. The presence of metallic SWNTs typically leads to high off-currents in transistor applications, while semiconducting nanotubes exhibit a substantial electrical response to the electrostatic and chemical gating effects that are desired for the function of chemical sensors and field effect transistors (FETs).[96]

The key to nanotube transistors is the control of the electronic properties of the tube as well as scale-up to industrial level. Such control has not been demonstrated with noncovalent techniques due to their poor control over the functional group added to the tube surface.[44] This issue arises due to the inherent mixture of semiconducting and metallic tubes in as-produced bundles. About one third of all tubes are metallic and the remainder are semiconducting. Covalent functionalization of SWNTs can be achieved via divalent or monovalent additions of atoms and molecules to the tubes side wall. Either route yields a $sp^2$ to $sp^3$ rehybridization of the carbon atoms. Early work on monovalent functionalization via fluorination led to highly resistive materials with fluorination-induced strains and fractures of the tubes.[97] Kanungo and co-workers[98, 99] have demonstrated that fluorinated olefins react with the electron deficient tubes via $[2+2]$ cycloaddition. Perfluoro (5-methyl-3,6-dioxanon-1-ene) (PMDE) and perfluoro-2(2-flurosulfonylethoxy) propyl vinyl ether (PSEPVE) to give high-mobility semiconducting nanotubes without the need of separation techniques. Although the side chains of the two olefins differ merely at the terminal group, the mobility of PMDE-SWNT is ~10 times higher than that of PSEPVE-SWNT, suggesting that the SO$_2$F group is converted to a carboxylic acid. This leads to doping. Our results demonstrate that the
cycloaddition functionalization leads to exclusive conversion of metallic tubes to semiconducting tubes. The functionalization of semiconducting nanotubes causes a small decrease in the nanotube band gap. The mechanism for the addition of olefins to nanotube surfaces involves the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular level (LUMO) of the olefin with the HOMO and LUMO of the nanotube surface, or vice versa.

6.3 Methods

The structure and electronic properties were investigated using first-principles density-functional theory within the local density approximation to the exchange-correlation potential. For the exchange-correlation the local VWN functional was employed. Periodic-boundary conditions were employed with a supercell in the xy plane large enough to eliminate the interaction between neighboring replicas. A double numerical basis was sufficient to converge the grid integration of the charge density. All structures were relaxed with forces less than 0.01 eV/Å.

6.4 Geometry Details

Carbon atoms in graphene can be thought of as $sp^{2}$-hybridized, with an extended conjugation forming a planar network. When graphene is rolled over to form a nanotube, the $sp^{2}$ hybridized orbitals are deformed due to rehybridization of $sp^{2}$ orbitals toward $sp^{3}$ orbitals. The character of the C-C bond in a nanotube differs from that of the C-C bond in graphite as the carbon atoms in a SWCNT are pyramidalized due to the curvature of the nanotube sidewall.[40, 41] Pyramidalization gives some $\sigma$ character to the $\pi$ orbitals of the carbon atoms. This distorts the $\pi$ orbitals on the tube surface toward larger (electron cloud) and softer (toward reactivity). Since the $\pi$ orbitals of the nanotube are
not pointed towards the tube axis, some adjacent carbon atoms have misalignment angle attributed to pyramidalization. Based on previous calculations of torsional strain energies in poly aromatic organic molecules, $\pi$ orbital misalignment is the most likely source of strain in CNTs.\cite{45} Pyramidalization and $\pi$ orbital misalignment are completely relaxed by the addition of an atom or functional group to the surface of the tube. This rehybridization, together with $\pi$ -electron confinement, gives SWNTs unique electronic, mechanical, chemical, and optical properties. The finite curvature of SWNTs strongly modifies the electronic behavior of SWNTs and may lead to band gap openings at the Fermi level.\cite{100} For a given $(n,m)$ nanotube, if $n = m$, the nanotube is metallic; if $n - m$ is a multiple of 3, then the nanotube is semi-metallic; otherwise the nanotube is a moderate semiconductor.

Shown in Figure 6.1 are the optimized structures for PMDE functionalized armchair nanotube (8,8). The red, light blue, grey, and yellow colored atoms represent oxygen, fluorine, carbon, and sulfur, respectively. Closer scrutiny of the local stable configurations reveals that the resulting adduct on the tube side wall can be either slanted or vertical to the tube axis. The perpendicular attachment has a better binding energy of about 0.5 eV compared to the slanted attachment. The bond lengths for the four bonds in the cyclobutyl adduct lie within a range of typical $sp^3$ hybridized C-C bond of 0.154 nm.\cite{101} The bond lengths of the nearest neighbors 0.149-0.150 nm are characteristic of distortions.
Figure 6.1. Ball-and-stick models of the optimized structures of PMDE functionalized armchair (8,8) tube through [2+2] cycloaddition functionalization. The olefin adds to the nanotube bond either slanted (left) or perpendicular (right) to the tube axis. Distortions. The local $sp^3$ rehybridization of the carbon atom at the site of functionalization induces a defect on the tube a localized mid-gap impurity state near the Fermi level. The functionalization site acts as a strong scattering center. That hinders dramatically the ballistic conducting property of the nanotube. The rehybridization of the two neighboring impurity states creates strong localized bonding and antibonding states that are located far away from the Fermi level.

6.5 Results and Discussion

To understand the addition of fluorinated olefins to carbon nanotubes, we investigate the charge density characteristics of the fluorinated olefins and the SWNTs. Shown in Figure 6.2 are the isosurfaces of the wave functions of the HOMO and LUMO derived bands at the $\Gamma$ point for nanotubes (8,8) and (14,0). For the pristine (8,8), (14,0), and (15,0) SWNTs, charge density is characterized as valence band minimum (VBM) and conduction band maximum (CBM). The addition of fluorinated olefin to the three nanotubes: metallic nanotube (8,8), semiconducting (14,0) and semi-metallic (15,0), was
investigated to determine the course-of-reaction. We have calculated the orbital densities of each olefin, PMDE and PSEPVE as well as the orbital charge densities of each nanotube. Bonding interactions can occur between the two components if three requirements are satisfied: overlap, energy, and symmetry. Interactions between the specified carbon nanotubes and the fluorinated olefins are either the highest occupied molecular orbital (HOMO) of the olefin with the lowest unoccupied molecular orbital of the (LUMO) of the carbon nanotubes or the LUMO of the olefin with the HOMO of the nanotube. For nanotube (8,8) the degenerate set is the top row of Figure 6.2, HOMO-3 and HOMO-4. This degeneracy can be attributed to the zone folding of the bands in the nanotube electronic structure.
Figure 6.2. Isosurfaces for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for nanotubes (8,8), (14,0) and (15,0). The isovalue is 0.05 au.

Table 6.1 summarizes the structural and electronic features of functionalized tubes. Calculated band gaps ($E_g$), with units of eV along with the corresponding bond lengths for the nearest neighbor C-C bonds ($d^{cc}$), with units of Å and for the cycloaddition adduct ($d^{HD}$) for pristine and functionalized SWNTs. The numbers 1, 2, and 3 refer to pristine, PMDE-, and PSEPVE-functionalized SWNTs, respectively. The armchair (8,8) was constructed with a unit cell of ($c = 9.84$ Å) and the zigzag tubes (14,0) and (15,0) were constructed with unit cells of ($c = 12.78$ Å). Upon functionalization of the armchair (8,8) tube the mirror symmetry is broken causing the degree of band opening to be 0.5 eV. In the case of other functionalized tubes, despite differences in the
side chain the atomic type and degree of symmetry breaking at the segment, instead of the atoms in the side chain, do not have a great influence on the band structures close the Fermi level. [102] Furthermore, the PSEPVE functionalized tubes have smaller band gaps than PMDE functionalized counterparts. This feature is attributed to the emergence of a flat band, with charges predominantly confined at the tail of PSEPVE. Our results indicate that the preferential modification of metallic tubes is caused by their conversion to semiconducting ones through cycloaddition functionalization.

Table 6.1 Calculated electronic properties of PMDE and PSEPVE functionalized nanotubes. The numbers 1, 2, and 3 refer to pristine, PMDE-, and PSEPVE-functionalized SWNTs, respectively.

<table>
<thead>
<tr>
<th>(n,m)</th>
<th>Type</th>
<th>$E_g^{(1)}$</th>
<th>$E_g^{(2)}$</th>
<th>$d_1^{CC}$</th>
<th>$d_2^{CC}$</th>
<th>$d_1^{AD}$</th>
<th>$d_2^{AD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(8,8)</td>
<td>Metallic</td>
<td>0.20</td>
<td>0.21</td>
<td>1.49</td>
<td>1.50</td>
<td>1.55-1.59</td>
<td>1.54-1.59</td>
</tr>
<tr>
<td>(14,0)</td>
<td>Semiconducting</td>
<td>0.65</td>
<td>0.41</td>
<td>1.49</td>
<td>1.49</td>
<td>1.55-1.62</td>
<td>1.55-1.62</td>
</tr>
<tr>
<td>(15,0)</td>
<td>Semi-metallic</td>
<td>0.02</td>
<td>0.15</td>
<td>1.49</td>
<td>1.50</td>
<td>1.55-1.57</td>
<td>1.55-1.57</td>
</tr>
</tbody>
</table>

The calculated band structures for each pristine nanotube and functionalized tube are displayed in Figure 6.3. The dashed line stands for the halfway between the valance band maximum (VBM) and conduction band minimum (CBM) of the pristine tubes that is set to zero for all cases. For tube (8,8), a gap opens near the Fermi level. Careful examination of the band structures for pristine and functionalized nanotubes indicates that there are two dispersed bands involved near the Fermi level for PMDE, while there are three involved for PSEPVE. The band alignment between the pristine tube and the functionalized tube shows that HOMO and LUMO of the PMDE HOMO-derived level strongly hybridizes into the valence band maximum (VBM) and conduction band.
minimum (CBM) states of the pristine SWNTs. Conversely, PSEPVE has three levels involved.

The band gaps of each pristine tube (8,8), (14,0) and (15,0) are displayed for comparison, adjacent to the corresponding functionalized PMDE and PSEPVE nanotubes. When PMDE was used to functionalize the semiconducting tube (14,0), attachment of the olefin to a C-C bond parallel to the tube axis (c) resulted in a slight larger band-gap than attachment to a C-C bond slanted to the tube axis (d). Lastly, for tube (15,0) functionalization (a) parallel to the tube axis resulted in a small band gap at gamma point. However, functionalization in position (b), slanted to the tube axis resulted in a small,
non-zero band gap. The functionalization with PSEPVE resulted in a localized state near the Fermi level, that can be attributed to the fluorinated side chain on the olefin. PSEPVE chemically-functionalized nanotubes have a half filled molecular level in the gap region.[103] The electronic band structure shows this feature. A sp³ defect due to rehybridization induces a half occupied impurity state around the Fermi level. Similar features were reported for theoretical calculations on silicon doped nanotubes, in which chemical bonding and modification occurred at silicon substitution sites.[104] It is not clear why this state does not appear in band structure calculations using PMDE. Our results are consistent with the CBM/VBM predictions in Figure 6.2. A recent account on carbene functionalization of zigzag and armchair tubes is in agreement with our results: for the two types of C-C bonds in zigzag tubes parallel (||) and slanted (\), CH₂ was at an equilibrium position for the slanted configuration, compared to the parallel one.[105]

The formation of the cyclobutyl group (the cyclic adduct) onto the sidewall of the nanotube, resulted in different molecular symmetries at the site of bond formation. The charge density for the cyclobutyl group attached onto nanotube (15,0) is displayed in Figure 6.4. The nanotube-bands affected by the olefin addition reaction where not close to the Fermi level. The HOMO-2 level was antisymmetric at the adduct as indicated by the blue and yellow wavefunctions. In the case of HOMO-1, LUMO-2, and LUMO-4, each adduct was antisymmetric after the addition of the olefin. Despite the differences in molecular symmetry, each HOMO and LUMO level lead to strong covalent bond formation between the nanotube and the fluorinated olefin. Similar results were reported by Cho et. al. for carbon nanotubes functionalized with 1,3 dipoles via a 1,3 dipolar cycloaddition.[102] The charge density of the cyclobutyl group is consistent with the
band structure graphs; molecular levels of the olefin hybridize with nanotube levels, away from the Fermi level. Even though the pristine CNT (15,0) has a nonzero band gap, after olefin functionalization the gap has increased by 0.1 eV

**Figure 6.4.** Calculated charge density for PMDE olefin functionalized CNT (15,0), L-R: HOMO-2, HOMO-1, LUMO+2, LUMO+4.

In the cases of metallic nanotubes, we find that the original \( \pi - \pi^* \) band crossing of either metallic armchair or semimetallic tube is disturbed by the sidewall functionalization. A band gap opens up, converting metallic tubes to semiconducting tubes. This effect can be understood by the breaking of nanotube mirror symmetry due to strong tube-olefin interactions. This particular feature is present in the electronic band structure of the PMDE- and PSEPVE- functionalized armchair nanotube (8,8), (top row of Figure 6.3). The single addition of one olefin to a C-C bond slanted to the tube axis (configuration a) introduces a gap at the Fermi level \( \Gamma \) point at the Fermi level, thus making the tube semiconducting. However, addition onto the binding segment perpendicular to the tube axis (configuration b), not shown, maintains the symmetry at the site. Functionalization at configuration (a) introduces a single degeneracy at \( \Gamma \) point. Functionalization of PMDE on tube (8,8) resulted in a larger band gap for the slanted configuration (a) than for the perpendicular configuration (b). Previous calculations in which nanotube (4,4) was functionalized with MeO at a C-C bond slanted to the tube
axis, demonstrate that further additions, opposite to the initial site will remove this degeneracy.[102] The band degeneracy in the pristine SWNT is partially removed by the perturbation from the functional group.

For nanotube (14,0), the HOMO and LUMO levels are both parallel to the tube axis. The HOMO $\pi$-bonding orbitals are above and below the plane of the tube surface. The LUMO are $\pi^*$-antibonding and are also above and below the plane of the tube surface. For tube (15,0) the HOMO has two sets of orbitals: (1) the orbitals that occupy the bond slanted to the tube axis are $\pi$-bonding (2) those that occupy the C-C bond parallel to the tube axis are $\pi^*$-antibonding. The (15,0) LUMO has $\pi$-bonding orbitals on the C-C bond parallel to the tube axis. For the (8,8) tube the orbitals resemble that of the (15,0) tube. The HOMO of the (8,8) tube has two set of orbitals: the C-C bond slanted to the tube axis is $\pi$-bonding, however the C-C bond perpendicular to the tube axis is $\pi^*$-antibonding. The LUMO for (8,8) also has two kinds of orbitals: the C-C bond slanted to the tube axis is $\pi^*$-antibonding, while the C-C bond perpendicular to the tube axis is $\pi$-bonding. The interaction of the olefin HOMO and LUMO with the nanotube surface localizes the symmetry-allowed HOMO and LUMO of the nanotube; resulting in the simultaneous formation of two new sigma bonds. The [2 + 2] cycloaddition reaction of fluorinated olefins onto the sidewalls of single-walled carbon nanotubes can be explained by a mechanism. Kanungo et al. proposed two mechanisms behind the conversion of metallic nanotubes to semiconducting ones, but could not pinpoint the correct one.[98] They recently reported the conversion of metallic nanotubes to semiconducting ones, using the nonfluorinated, electron deficient olefin, tetracyanoethylene (TCNE)[99]. They achieve complete conversion of a mixture of grown metallic tubes into semiconducting
tubes, without the use of separation techniques. These tubes were used to fabricate thin
film transistors that exhibited charge mobilities of $\sim 30\ \text{cm}^2/\text{V}$. The mechanism for the
reaction with TCNE, is believed to be the same mechanism by which PMDE- and
PSEPVE/SWNT cycloaddition proceeds. To understand the mechanism, consider the
reaction of ethylene with 1,3-butadiene:

$$
\text{C} = \text{H}_2 + \text{C} = \text{H}_2 \rightarrow \text{H}_2\text{C} = \text{H}_2 + \text{H}_2\text{C} = \text{H}_2
$$

**Figure 6.5.** Diels-Alder reaction of 1,3-butadiene (diene) and ethylene (dienophile). The
major product, vinylcyclobutane was reported in a yield of 99.98%.\cite{106}

which yields a trace amount of vinylcyclobutane (the minor product) and 99.98%
cyclohexene \cite{107}, the major product from a concerted Diels-Alder (DA) reaction.
However, tetrafluoroethylene (TFE) reacts with 1,3-butadiene to yield, exclusively
1,1,2,3-tetrafluoro3-vinyl-cyclobutane \cite{106},

**Figure 6.6.** The reaction of tetrafluoroethylene (TFE) with 1,3-butadiene. Unlike
ethylene, TFE does not undergo a Diels-Alder reaction with the diene. Instead the
observed reaction is the formation of 2,2,3,3-tetrafluoro-1-vinylcyclobutane.\cite{108}
most likely by a stepwise mechanism involving a diradical intermediate.[109, 110]

Whether or not the four fluorines in TFE destabilize the transition state away from the Diels-Alder reaction or stabilize the transition state toward a diradical mechanism was determined by Getty and Borden.[106] The authors used ab initio calculation to show that the fluorines in TFE have very little effect on the energy of the Diels-Alder transition state, they have a strong stabilizing effect on the diradical formation.[106] Calculations for the transition state geometry, of the Diels-Alder reaction between TFE butadiene are very similar to that of the parent compound, eliminating the possibility of the fluorines in TFE affecting the reactivity toward a DA mechanism.

6.6 Summary

We have modeled the perfluoro (5-methyl-3,6-dioxanon-1-ene) PMDE olefin concentration on the surface of nanotube (8,8). The unit cell of the nanotube was repeated 4 times, the lattice redefined resulting in a 128 carbon-atom lattice with 64 C=C bonds. The addition of 2 and 4 olefins to the tube surface yields a concentration of one PMDE for every 32 and 14 C=C bonds, respectively. The estimated concentrations are based on the estimates determined by TGA mass loss: one olefin for per 49 C=C of which 1/3 metallic tubes. This gives a concentration of c~0.012 or one olefin per 16 C=C.[98] This concentration is significant because it is at this level that the average distance between the nanotube and the olefins is determined with TGA. At higher concentrations the olefin-nanotube distance could not be determined with TGA. Our calculation result show that as the olefin concentration on the semiconducting nanotube increases the initial band gap opening decreases. The nanotube goes back to a metallic electronic structure. However as the olefin concentration on the metallic nanotube
increases, the band gap increases reaching a threshold concentration of one olefin to 32 C=C bonds, after which additional PMDE molecules on the CNT (8,8) tube surface decrease the band gap.

We calculated the stability of Diels-Alder [4 + 2] and [2 + 2] reaction of the PMDE olefin on carbon nanotubes (8,8). We employed two levels of theory for each set of calculations, 1) the local density approximation (LDA) to the exchange-correlation potential. For the exchange-correlation the local Vosko-Wilk-Nusair (VWN) functional was used 2) and the generalized gradient approximation (GGA), with the Perdew-Burke-Ernzerh (PBE) functional for exchange-correlation. Using LDA/VWN for the [2 + 2] addition reaction of PMDE on cnt (8,8) resulted in slanted configuration is more stable than the perpendicular configuration by 0.59 eV. This result is verified for the same system, using GGA/PBE with dispersion correction: the slanted configuration is more stable than the perpendicular configuration by 0.53 eV. The [2 + 2] addition is more stable than the [4 + 2] addition by 2.4 eV and 4.56 eV, with LDA/VWN and GGA/PBE with dispersion correction.

There is not a flat band in the band structure, in the proximity of the Fermi level. The important ramification is that the band gap formation is attributed to the formation of bonding stakes rather than impurity scattering. As a consequence the bonding state is a true gap state that is intrinsic to the cycloaddition scheme. The bound state is a true gap state that is intrinsic to the cycloaddition scheme. The bound state is formed as a result of....
The random addition of olefins to the metallic CNT (8,8) surface, leading to band
gap formation is related to the quasi-bound states [111] within the energy gap, originating
from the olefin. In constructing supercells, 4 repeat units were used for armchair and
zigzag nanotubes. For tube (8,8) the quasi bound states appear for $d_{C-C}$ in the range of
1.5-1.6 Å (Table 6.1) or when the grapheme network is slightly perturbed. The band
structure calculations (Figure 6.3) reveal the state decaying through strong coupling
between the olefin states and the extended $\pi$ or $\pi^*$ of the nanotube[112]. Also evident in
the band structure calculation is the band gap opening for the slanted configuration (top
row, Figure 6.3). For tube (14,0) the $\pi^*$ band shifts down reducing the band gap. An
increase in the supercell length shows the extended $\pi^*$ change to quasi bound states,
manifested by flat energy dispersion along the $k$-points. Another quasi-bound state
develops above the valence band, resulting in two quasi-bound states in the energy gap,
resulting in a decrease in the band gap compared to the pristine CNT (14,0). The
formation of these states is has exclusive to divalent additions, in contrast to monovalent
functionalizations where localized states are formed. [100, 101]
APPENDIX A

In graphene, each Bravis lattice vector (or chiral vector[3]) $\mathbf{R}$, is defined in terms of two primitive lattice vectors $\mathbf{R}_1$, $\mathbf{R}_2$ and a pair of integer indices (chiral indices), $(n_1,n_2)$:

$$\mathbf{R} = n_1\mathbf{R}_1 + n_2\mathbf{R}_2 \equiv (n_1,n_2). \quad (1.1)$$

A particular set of indices given by $(n_1,n_2)$ and has a diameter $d_i$:

$$d_i = \frac{R}{\pi} = \sqrt{3} \frac{2n_1 n_2 + n_1^2 + n_2^2}{\pi}. \quad (1.2)$$

The chiral angle for a nanotube, $\Theta$, is measured counterclockwise from the primitive lattice vector $\mathbf{R}_1$ to the roll-up vector (Bravis lattice vector) $\mathbf{R}$ (See Figure 1.3). The angle is defined in terms of the indices $(n_1,n_2)$ and is given by:

$$\Theta = \arccos \left( \frac{\mathbf{R}_1 \cdot \mathbf{R}}{\|\mathbf{R}_1\| \|\mathbf{R}\|} \right) = \arccos \left( \frac{2n_1 + n_2}{2\sqrt{n_1^2 + n_2^2 + n_1 n_2}} \right) = \arctan \left( \frac{\sqrt{3}n_2}{2n_1 + n_2} \right). \quad (1.3)$$

To define the unit cell for a 1D nanotube we define a translational vector $\mathbf{T}$:

$$\mathbf{T} = t_1\mathbf{R}_1 + t_2\mathbf{R}_2 \equiv (t_1,t_2). \quad (1.4)$$
where the coefficients $t_1$ and $t_2$ are related to $(n_1, n_2)$ by,

$$t_1 = \frac{(2n_2 + n_1)}{d_r},$$

$$t_2 = -\frac{(2n_1 + n_2)}{d_r}. \quad (1.6)$$

The number of hexagons, $N$, in a 1D unit cell of a nanotube is set by the chiral indice $(n_1, n_2)$ and is given by,

$$N = \frac{2(n_1^2 + n_2^2 + n_1n_2)}{d_R}. \quad (1.7)$$

The application of the periodic boundary conditions along the tubes circumference restricts the allowed wave function quantum phase:

$$\Psi_k(r + C_h) = e^{ik \cdot C_h} \Psi_k(r) = \Psi_k(r). \quad (1.8)$$

The first equality is derived from the Bloch theorem, in which solutions of the Schrödinger equation for a periodic potential must be of the form:

$$\Psi_k(r) = u_k(r) \exp(ik \cdot r). \quad (1.9)$$

The two-dimensional energy dispersion relationship for a graphene monolayer is given by,

$$E = \pm \gamma_0 \sqrt{3 + 2 \cos(k \cdot a_1) + 2 \cos(k \cdot a_2) + 2 \cos[k \cdot (a_1 - a_2)]}. \quad (1.10)$$
Equation 1.8, $\Psi'_k (r + C_h) = e^{ik \cdot C_h} \Psi'_k (r) = \Psi'_k (r)$, is further developed into,

$$E^2(k_x, k_y) = \pm \gamma_0 \sqrt{1 + 4 \cos \left( \frac{\sqrt{3} k_x a}{2} \right) \cos \left( \frac{k_y a}{2} \right) + 4 \cos^2 \left( \frac{k_y a}{2} \right)}.$$  \hspace{1cm} (1.11)

Equation 2.1 is the functional form of the potential energy:

$$V(r^N) = \sum_{\text{bonds}} \frac{k_l}{2} (l_i - l_{i,0})^2 + \sum_{\text{angles}} \frac{k_l}{2} (\theta_{ij} - \theta_{ij,0})^2 + \sum_{\text{torsions}} \frac{V_\alpha}{2} (1 + \cos(n\omega - \gamma))$$

$$+ \sum_{i=1}^{N} \sum_{j=1}^{N} \left[ 4 \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} + \frac{q_i q_j}{4 \pi \varepsilon_0 r_{ij}} \right].$$  \hspace{1cm} (2.1)

The many-body, non-relativistic, time-independent Schrödinger equation for a system of $N$ electrons and $M$ nuclei has the form of an eigenvalue problem:

$$\hat{H} \Psi = E \Psi.$$  \hspace{1cm} (2.2)

The Hamiltonian operator, of Equation 2.2, $\hat{H}$, is a differential operator that represents the total energy and is given by:

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \frac{1}{2} \sum_{A=1}^{M} \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{r_{ij}}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}.$$  \hspace{1cm} (2.3)

What remains is the electronic Hamiltonian, a description of the motion of $N$ electrons moving in the field of $M$ point charges:

$$\hat{H}_{\text{elec}} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}.$$  \hspace{1cm} (2.4)
The total energy calculation for a fixed nuclear configuration must include nuclear-nuclear repulsion[28, 29]:

$$E_{\text{tot}} = E_{\text{elec}} + \sum_{A=1}^{N} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}$$ (2.5)

A functional relates a function to a scalar quantity, as indicated by brackets:

$$Q[f(r)] = \int f(r) \, dr.$$ (2.6)
References


