

# Computational Analysis of Transition Metal Doped Nanotubes and Their Application to Molecular Electronics

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We have previously proposed molecular circuits designed from polyaniline polymer strands, polyacetylene polymer strands and charge transfer salts acting as transistors. Due to unique properties that are demonstrated in this manuscript, we propose the use of carbon single wall nanotubes and transition metal endohedrally doped single wall carbon nanotubes (SWNTs) for utilization in molecular electronics. Different transition metals were used in a systematic fashion to manipulate the molecular orbital energy gap (HOMO-LUMO gap) of metallic ( $C_n = (n = m)$ ) nanotubes. Gradient corrected, Density Functional Theory (DFT) Self Consistent Field (SCF) calculations were used to calculate molecular orbital energy levels, HOMO-LUMO gaps, electron affinities, ionization energies and other electronic properties for these molecules. The effect that a SWNT's length has on its HOMO-LUMO gap was investigated. DFT-SCF calculations were also used to demonstrate how multiple metal filled nanotubes could be used to construct a molecular nanotube based transistor.

**Keywords:** Metal Doped Nanotubes, Molecular Electronics, DFT-SCF Calculations, Nanotube Transistor, Nanowires, Nanocircuits.

## 1. INTRODUCTION

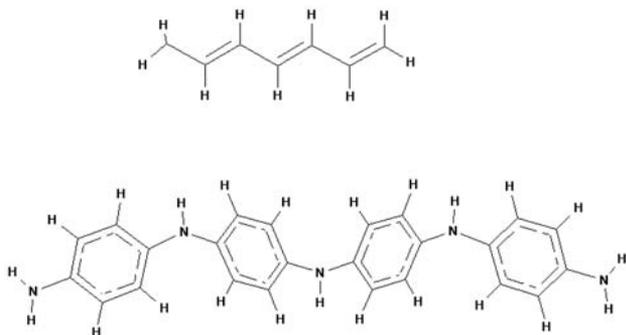
Intel founder Gordon Moore stated in 1965 that the amount of transistors packed onto a silicon chip (and hence its processing power) is doubled by the semiconductor chip industry approximately every 18 months. This statement has been called Moore's Law, and has held true over the last 3½ decades. However, we are now at a place in time where the limit of circuit size reduction is in sight. There is a certain distance threshold that lines of a printed circuit must remain above in order to prevent electrons from tunneling between circuit lines. That distance is known to be somewhere in the region of 0.03 to 0.10 microns. The most current chip designs use lines that are 0.18 microns apart. Further reduction in size can clearly be expected. However, analysts also warn that as we come closer to this practical limit, the manufacturing costs will also become prohibitive. There is a need for the development of other technologies

that will allow further miniaturization of electronics. Optical computing and quantum computing are two new technologies that are currently being proposed and researched for the future. Another way this can be accomplished is by using molecules to construct electronic circuits. There are many recent examples in the literature of nanoscale molecules with useful electronic properties.<sup>1–7</sup>

In previous work, we demonstrated how molecular electronic components and circuits could be built from single strands of the polymers polyaniline and polyacetylene, and the charge transfer salts tetracyanoquinodimethane (tcnq) and tetrathiafulvalene (ttf), using molecular modeling and *ab-initio* quantum techniques.<sup>8</sup> An emeraldine base form of polyaniline was proposed as a molecular "wire," and transpolyacetylene as a molecular "resistor" (Figure 1).

Emeraldine base polyaniline is created by doping polyaniline with a strong acid such as HCl. It has 2 bipolarons per 8 aniline units, which separate to 4 polarons, and displays good conductivity ( $\sim 10^1$  to  $10^2$  S/cm).<sup>3</sup> Conversely, the conductivity of the trans isomer of undoped polyacety-

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**Figure 1.** Polyacetylene (top), a proposed molecular resistor, and polyaniline (bottom), a proposed molecular wire.

lene is  $10^{-5}$  S/cm, which makes it a very good resistor. The drawback to using these polymers to construct molecular circuits is that they are very flexible molecules. This flexibility has dampening effects on their conductivity, which is based on the significant overlap of their p orbitals and on the p orbital overlap of interconnected molecules. The degree of orbital overlap is a function of the planarity of their aromatic systems. The flexibility of these molecular systems can be greatly reduced if the molecular components are rigid. This idea prompted us to propose the use of single wall nanotubes as the building blocks for molecular electronic components and circuits.

There have been many advances recently in nanotube technology. Single walled nanotubes have been proven to either be conducting or semi-conducting, depending on their conformation.<sup>11</sup> Armchair nanotubes ( $n = m$ ), designated by  $C_h = (n, n)$ , where  $n$  and  $m$  are coefficients of the chiral vector  $C_h$ , are believed to have metallic conductive properties. Chiral nanotubes designated by  $C_h = (n, m)$  (where  $n \neq 0$ ) are believed to have semiconductor-like properties.<sup>11</sup> There are examples in literature of single walled nanotubes (SWNTs) used as molecular wires.<sup>6</sup> They have been shown to be excellent conductors.<sup>12</sup> For this reason, and because they are structurally rigid molecules, we propose they can be used to construct both molecular electronic components and circuits.

Our previous work presented us with a new question. What if the nanotubes themselves could be altered in conductivity, precisely for specific electronic uses? In particular, there has recently been a significant amount of activity aimed at intercalating metal atoms into SWNTs.<sup>13</sup> The metal atoms are believed to affect the molecular electronics of the SWNTs into which they are placed. This prompted us to examine the effects of substituting different transition metal atoms into the center of a single walled nanotube.

We have performed calculations that will illustrate how carbon single wall nanotube (SWNT) conductivity can be manipulated via doping with different transition metal and non-metal atoms. Furthermore, we will describe, through solid state physics methods and calculations commonly applied to p and n type semiconductors, how different doped

single walled nanotubes (SWNTs) could be used to construct a nanoscale transistor.

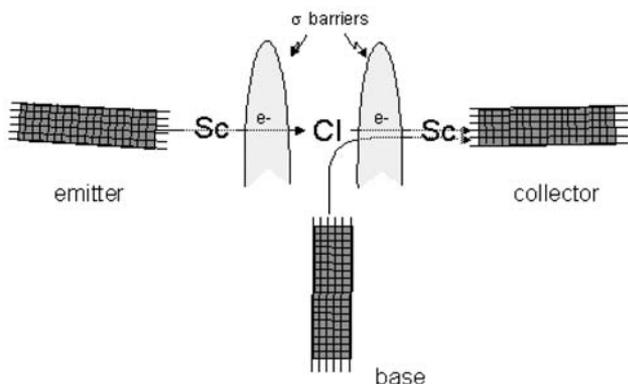
## 2. METHODS

A systematic approach was used to analyze the effects of endohedrally doping nanotubes. In particular, we were interested in how doping with different transition metal elements would affect a nanotube's HOMO-LUMO Molecular Orbital Energy (MOE) gap. The size of this energy gap was used as an estimate of the conductivity of the metal filled nanotube.

Hyperchem 5.01<sup>14</sup> was used to construct a template metallic ( $C_h = (n, n)$ ) carbon SWNT (approximately 3.3 Å in diameter), substitute different transition metals into it and perform MM+ (Molecular Mechanics) geometry optimization on the systems. Gaussian94<sup>9</sup> was then used to perform DFT single point energy calculations on the structurally optimized nanotubes. The B3PW91 functional was used along with the LanL2DZ basis set since transition metals as high as period 6 were put into the nanotube. The LanL2DZ basis set incorporates parameters that account for the relativistic effects that become more prominent in heavier atoms. Tight convergence was requested for the SCF procedure (RMS density matrix = 1.00E-08, MAX density matrix = 1.00E-06). HOMO-LUMO MOE gaps were determined from the output of the molecular orbital calculations. This procedure was performed on nanotubes containing most of the period 4, 5 and 6 transition metals and several group IIIA, IVA and VA nonmetallic elements.

SCF-MO calculations were also carried out using GAUSSIAN 94 in order to model the current/voltage characteristics of a proposed molecular transistor. In all our calculations, pi ( $\pi$ ) electrons in the "conductive" regions were treated as independent particles and each molecular fragment (Sc-nano, Cl-nano and  $\sigma$  barrier) was treated as a separate molecular entity. There is no conjugation across the  $\sigma$  barrier molecule. As such, it separates the  $\pi$  systems of the Sc-nano and Cl-nano fragments with a large potential energy barrier. Calculations were carried out using the Density Functional Theory (DFT), Becke 3 parameter hybrid functional with the Perdew/Wang 91 nonlocal correlation (B3PW91).<sup>10</sup> The 6-31g(d) basis set was used for all the molecules in conjunction with the B3PW91 functional.

The flow of electrons through the proposed pnp transistor molecule is a three-step process (refer to Figure 2). In a pnp transistor, there is a threshold forward bias voltage that must be surpassed in order to obtain electron flow from the base to the collector. Using notation similar to solid state electronics, the threshold forward bias voltage can be calculated using the equation  $V > IP_{\text{collector}} - \Phi_{\text{base}}$ , where  $IP_{\text{collector}}$  is the ionization potential of the collector and  $\Phi_{\text{base}}$  is the work function of the base. In our proposed transistor, the base is a SWNT nanowire, and the collector is the Sc-nano, so the equation becomes  $V > IP_{\text{Sc}} - \Phi_{\text{SWNT}}$ .  $IP_{\text{Sc}}$ , and is calculated by subtracting the calculated total energy of a



**Figure 2.** Schematic of a proposed nanotube based molecular transistor incorporating Sc and Cl doped single wall carbon nanotubes.

neutral (0 charge) Sc-nano molecule from the calculated total energy for a +1 charge Sc-nano molecule.  $\Phi_{\text{SWNT}}$  is calculated by subtracting  $\frac{1}{2}$  (energy of the HOMO-LUMO orbital energy difference) from  $IP_{\text{SWNT}}$ .

Electron flow from emitter to collector in the nanotube transistor molecule is a two-part process. The voltage necessary to cause electron transfer from the emitter nanowire through Sc-nano to Cl-nano is given by the equation  $V > IP_{\text{Cl}} - \Phi_{\text{SWNT}}$ .  $IP_{\text{Cl}}$  is the ionization potential for the Cl-nano and  $\Phi_{\text{SWNT}}$  is the workfunction of the nanowire.  $IP_{\text{Cl}}$  was calculated using the procedure described in the previous paragraph for  $IP_{\text{Sc}}$ . The voltage required to produce transfer of electrons from Cl-nano through the Sc-nano to the collector nanowire is given by  $V > IP_{\text{SWNT}} - \Phi_{\text{Cl}}$ . For further details about any of these procedures, refer to our previous work.<sup>8</sup>

### 3. RESULTS

#### 3.1. Metal Filled Nanotubes

Figures 3a and 3b are plots of the MO Energy gap vs. atomic number for selected period 4, 5 and 6 element filled nanotubes, which include all of the transition series and 10 group A metallic elements. Figure 3a is a plot of all selected element filled nanotubes between atomic number 21 and atomic number 84, and Figure 3b is a plot of the same element filled nanotubes segregated into odd and even electron groups.

The plot illustrates several interesting trends at this level of calculation that can be broadly split up into two groups, odd electron and even electron systems. These two groups can also be divided into conducting ( $<1.0$  eV) and insulating ( $>1.2$  eV) subsets. The general trend for the conducting (odd and even electron) doped nanotube systems is a decreasing MOE gap size as the period number increases. However, within the periods, the effects vary. The 6<sup>th</sup> period element doped nanotubes MOE gap decreases when going from right to left across the period (decreasing atomic number) for both the odd and even electron systems.

However, in the 5<sup>th</sup> period element doped systems, the opposite trend is observed, and there is a decreasing MOE gap when moving from left to right across the period (increase in atomic number). The 4<sup>th</sup> period trends are even more interesting, as there is a decrease in MOE gap with an increasing atomic number for the odd electron systems, but the even electron systems have a decrease in MOE gap from Cr to Fe, and an increase in MOE gap from Fe to Ni.

The effects of the non-conducting nanotubes (MOE gap  $>1.2$  eV) vary. For the 4<sup>th</sup>, 5<sup>th</sup> and 6<sup>th</sup> period elements, there is virtually no change in the MOE gap when moving from group II<sup>A</sup> to group IV<sup>A</sup> elements, and an increase in MOE gap when moving from group III<sup>A</sup> to group V<sup>A</sup>, except for the 4<sup>th</sup> period, where there is a significant decrease in the MOE gap from Ga to As. For group III<sup>B</sup> through group V<sup>B</sup> transition metals, the general trend is an increase in MOE gap from the 4<sup>th</sup> period to the 5<sup>th</sup> period, and a decrease in the MOE gap from the 5<sup>th</sup> period to the 6<sup>th</sup> period.

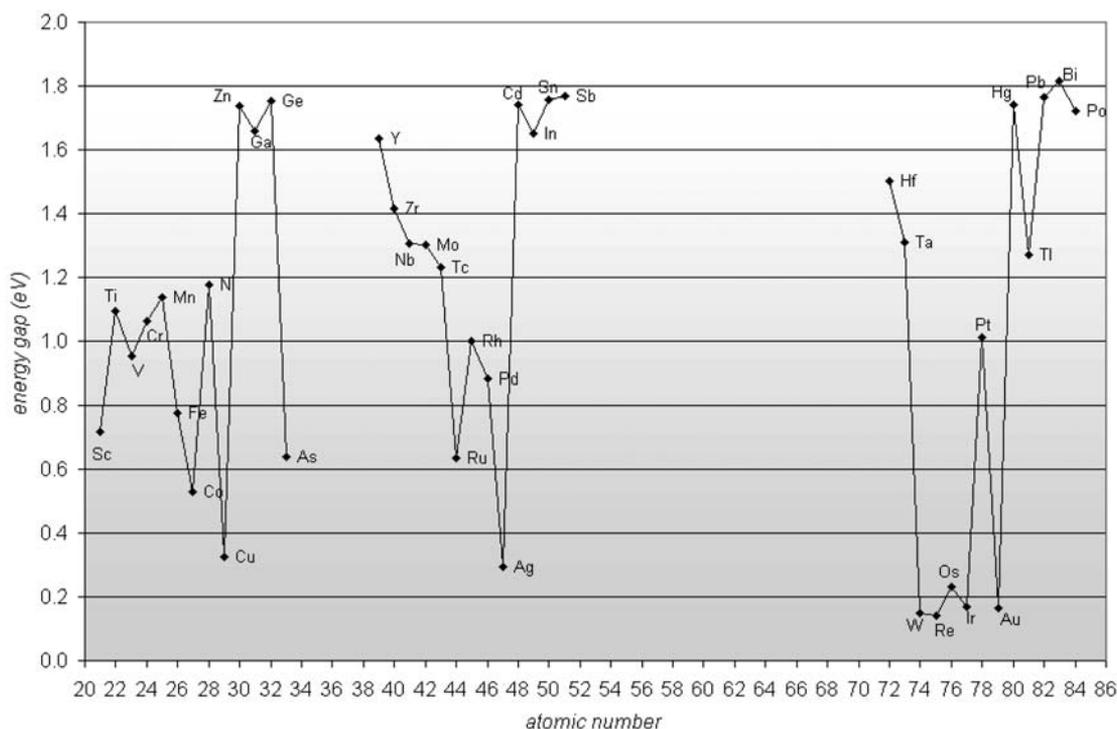
In order to examine the effect of a nanotube's length on its MOE gap, several extra calculations were performed. In addition to the single layer unfilled nanotube and Ti nanotube calculations, four additional calculations were performed with the tubes first extended to two layers, and then to 3 layers. The results of these calculations are plotted in Figure 4. The plot shows that for both types of nanotubes (unfilled and Ti filled), as the nanotube length increases, the size of the MOE gap asymptotically decreases to a non-zero limit.

#### 3.2. Nanotube Transistor

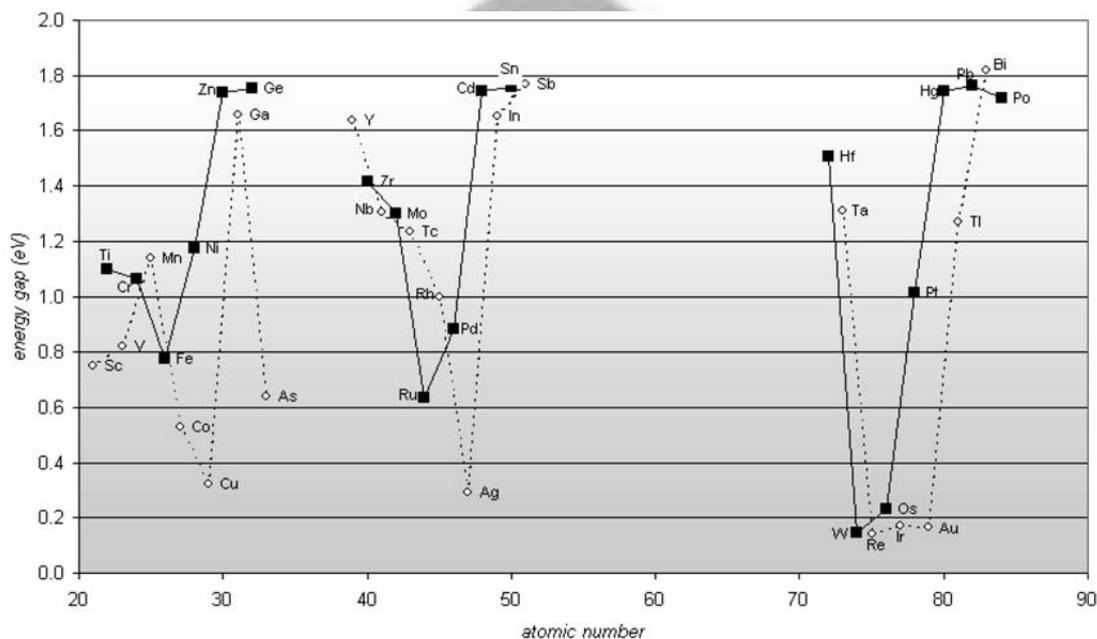
Nanoscale devices (10-9 m) represent the next generation of materials and could be the ultimate in miniaturization. As in our previously published work, we base the design of molecular circuits on transistor-transistor logic.

Figure 5 shows a proposed doped nanotube transistor. The view is a lengthwise side view of the whole transistor molecule. This proposed nanotube transistor is composed of an Sc doped nanotube connected to a Cl doped nanotube, which is connected to another Sc doped nanotube. We propose that the Sc doped nanotube will have n type semiconductor properties due to the willingness of the Sc atom to donate an electron, whereas the Cl doped nanotube will have p type semiconductor properties, due to the desire of the Cl atom to gain an electron. The doped nanotubes are not directly connected but are connected using unconjugated carbon "spacer" molecules. These spacer molecules are  $\sigma$  bonded systems that serve to disrupt the connectivity of the  $\pi$  systems of the doped nanotubes. The locations of the spacer molecular fragments are easily identified in Figure 4 by the labeled hydrogen atoms, since these segments are saturated compared to the remainder of the molecule.

In order for electron transfer to occur from the base to the collector (i.e., nanowire  $\rightarrow$  Cl-nano  $\rightarrow$   $\cap$   $\rightarrow$  Sc-nano, where  $\cap$  represents the  $\sigma$  spacer molecule), a forward bias potential  $>3.47$  V must be applied (please refer back to Figure 2).



**Figure 3a.** Plot of selected element doped nanotubes (atomic numbers 20 through 84) vs. LUMO-HOMO energy in eV.



**Figure 3b.** Plot of selected element doped nanotubes (atomic numbers 20 through 84) versus LUMO-HOMO energy in eV segregated according to even electron (dashed) and odd electron (solid).

This was calculated by subtracting  $\Phi_{\text{nano}}$  (2.46 eV) from  $\text{IP}_{\text{Sc}}$  (5.93 eV). The voltage threshold for electron transfer from emitter to collector (i.e., nanowire  $\rightarrow$  Sc-nano  $\rightarrow$   $\cap$   $\rightarrow$  Cl-nano  $\rightarrow$   $\cap$   $\rightarrow$  Sc-nano  $\rightarrow$  nanowire) is  $>3.91\text{V}$ . This is because the voltage threshold for electron transfer across the [-nanowire  $\rightarrow$  Sc-nano  $\rightarrow$   $\cap$   $\rightarrow$  Cl-nano-] molecular fragment

( $>3.91\text{V}$ ) is much greater than the voltage threshold across the [-Cl-nano  $\rightarrow$   $\cap$   $\rightarrow$  Sc-nano  $\rightarrow$  nanowire-] molecular fragment ( $>0.52\text{V}$ ), and thus is the limiting step. According to these calculations, a forward bias  $>3.47$  Volts from the base to the collector will amplify a reverse bias  $>3.91$  Volts from the emitter to the collector.

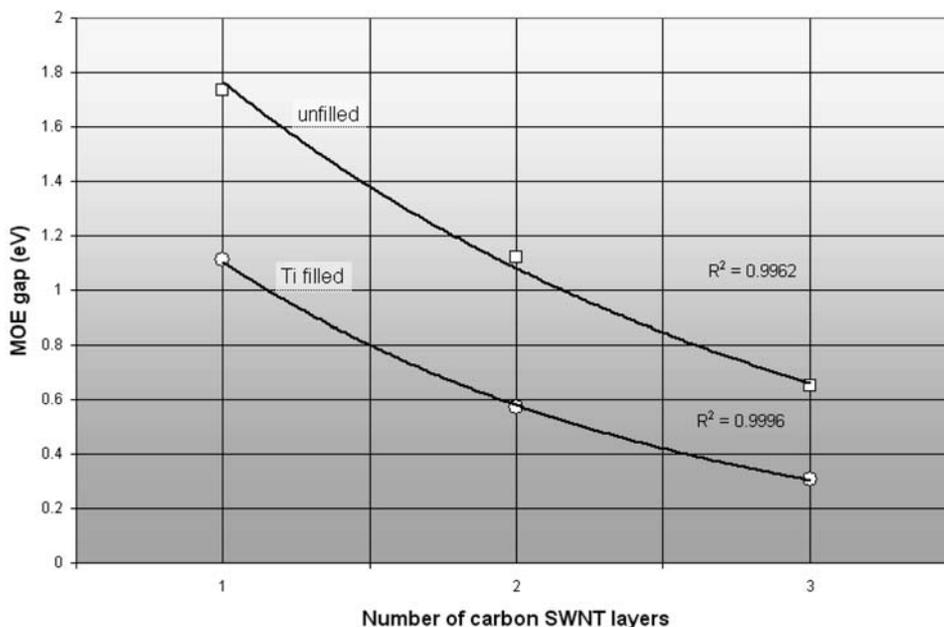


Figure 4. Plot of the effect of increasing nanotube length (layers) on the nanotube MOE gap (eV) for an unfilled SWNT and a Ti filled SWNT.

The threshold forward bias voltage that must be surpassed in order to obtain electron flow from the base (a SWNT nanowire) to the collector (Sc-nano) of the npn transistor molecule is  $V > 3.47$  Volts. The reverse bias voltage threshold that must be surpassed from base (nanowire) to emitter (Cl-nano) was calculated to be  $>3.91$  Volts.

In order for electron transfer to occur from Cl-nano, through Sc-nano, to the nanowire, a voltage threshold of  $>0.52$  Volts must be surpassed. This is calculated from the equation  $V > IP_{SWNT} - \Phi_{Cl}$ . The work function for the Cl-nano was calculated from the equation  $\Phi_{Cl} = E.A._{Cl} + \frac{1}{2}E_{g,Cl}$ , where  $E.A._{Cl}$  is the electron affinity of Cl-nano and  $\frac{1}{2}E_{g,Cl}$  is  $\frac{1}{2}(LUMO-HOMO)$  gap of Cl-nano. Electron transfer will occur from the base (nanowire) to the transmitter when a potential  $>3.47$  V is applied. This was calculated by subtracting  $\Phi_{nano}$  (2.46 eV) from  $IP_{Sc}$  (5.93 eV). Since the voltage threshold for the emitter to Cl-nano electron transfer is much higher than for the Cl-nano to collector transfer ( $>3.91$  V vs.  $>0.52$  V), the voltage threshold for electron transfer across the whole molecule (i.e., emitter to collector) is  $>3.91$  V. The voltage threshold for electron transfer from base to collector is  $>3.47$  V, because the threshold for the base (nanowire) to Sc-nano transfer is

much higher than the transfer from Cl-nano to collector (nanowire) ( $>3.47$  V vs.  $>0.52$  V). According to these calculations, a forward bias  $>3.47$  Volts from the base to the collector will amplify a reverse bias  $>3.91$  Volts from the emitter to the collector.

In order for electrons to flow through the nano-transistor molecule, electrons must tunnel through the molecular energy barrier imposed by the saturated hydrocarbon spacer molecule. Using a quantum barrier potential calculation, the probability of an electron tunneling through the  $\sigma$  barrier was calculated to be  $1.476 \times 10^{-1}$ . This was calculated by treating the electron as a free particle tunneling through a barrier of length =  $6.88 \times 10^{-10}$  m, and height =  $1.7622 \times 10^{-19}$  Joules, which corresponds to the spacer molecule's lowest unoccupied molecular orbital (LUMO). The tunneling process will be heavily favored in the direction from high energy to low energy. This is analogous to the triple methylene  $\sigma$  barrier molecule that was used in our earlier work, which was first proposed by Aviram and Ratner in 1974.<sup>19</sup> The tunneling mechanism allows for the unidirectional movement of electrons between the n, p and n fragments, which we propose would allow this molecule to have transistor properties.

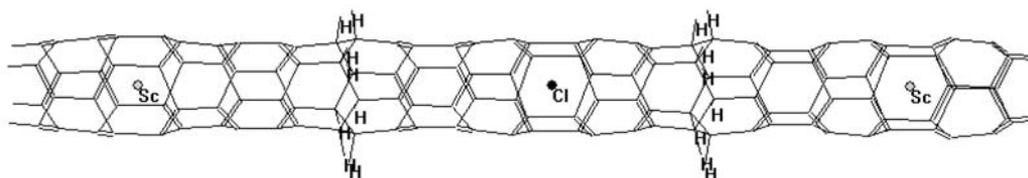


Figure 5. Wire drawing of a proposed npn nanotube transistor with Sc doped nanotubes representing the n-type segments and Cl doped representing the p-type segment.

#### 4. DISCUSSION AND CONCLUSION

We have performed a number of high-level calculations to analyze the effects on nanotube conductivity when doped with different elements, as measured through the size of the MOE gap of the system. We believe the MOE gap is directly related to the conductive properties of the molecules. We have included all of the transition metals and some metallic elements in our calculations. Some very interesting trends were observed when analyzing the results of the conductive tubes (MOE gap  $< 1.0$  eV). For example, the MOE gap decreases for the 6<sup>th</sup> period element doped nanotubes when going from right to left across the period (decreasing atomic number) for both the odd and even electron systems. The odd electron systems experience about a 13% drop in MOE gap from the Au doped nanotube to the Re doped nanotube, and the even electron systems experience a much steeper drop, with a decrease in MOE gap of about 85% from the Pt doped nanotube to the W doped nanotube. In the 5<sup>th</sup> period element doped systems, an opposite trend is observed. There is a decreasing MOE gap when moving from left to right across the period (increase in atomic number). In particular, there is a 76% drop from the Tc doped nanotube to the Ag doped nanotube (odd  $e^-$ ), and about a 32% drop in MOE gap from the Mo doped nanotube to the Pd doped nanotube (even  $e^-$ ). Within the 4<sup>th</sup> period, trends are even more interesting, as there is a decrease in MOE gap with an increasing atomic number for the odd electron systems of about 72% from Mn to Cu. But for the even electron systems, there is a decrease in MOE gap from Cr to Fe of 27%, and an increase in MOE gap from Fe to Ni of about 52%. Overall, based on our current calculations, the 6<sup>th</sup> period element doped nanotubes are the most conductive (groups VIB to IB) and, ironically, also the most insulating (groups IIB to VIA).

The effect on the MOE gap of increasing the length of the nanotube was also analyzed using an empty nanotube and a Ti filled nanotube. The lengths were varied from 1 layer up to 3 layers. The plot of the MOE gaps vs. tube lengths suggests that, as the length increases (for both types of tubes), the MOE gap asymptotically decreases to a non-zero limit. Three layers is currently the practical limit of our computational ability, but we are in the process of improving this ability and plan to study this matter further in the future. However, based on this length analysis, we believe the asymptotic behavior will apply to all of the filled metallic nanotubes studied, and that the current trends depicted by the single layer calculations will be analogous in longer tubes.

The calculations performed also suggest how endohedrally doped nanotubes could be used to construct a nanotube transistor. This was a computationally ambitious undertaking because of the size of the nanotransistor molecule. Consequently, some components in our model were based on calculations of the molecular orbital energy gap at the particle-in-a-box approximation. Although this is a 1<sup>st</sup> order

approximation, it does provide an estimate as to the trends present in the electronic properties of these materials and doped nanotubes. We have recently established a collaborative initiative with a materials group at the Romanian National Institute for Isotopic and Molecular Technologies (ITIM). This research group has already successfully produced single wall carbon nanotubes of many lengths and diameters by many different synthetic techniques.<sup>20</sup> We expect this association will produce a variety of transition metal atom doped single nanotubes, whose conductive properties will be determined experimentally and compared to our current theoretical predictions. We are continuing our calculations to complement our current designs. This includes further designs of other nanoscale molecules for their potential use in nanoscale molecular electronic circuits and computational analyses of their physical processes.

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