IOP Conf. Series: Materials Science and Engineering **202** (2017) 012093 doi:10.1088/1757-899X/202/1/012093

Effect of Temperature on the Conduction Properties of Oligo-phenyl-phenylene (OPP) Molecule

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Abstract. In order to design molecular electronic devices, we used conjugated molecule in the form of oligo-phenyl-phenylene (OPP) system to explore and understand the molecular conductance. Although the experimentally technique has obtained information with high accuracy, the process of adsorption on the surface can be investigated in detail on the electronic structure with a theoretical method based on density functional theory (DFT). In this study, we investigated the effect of temperature on the conductivity of OPP molecule using density functional tightbinding (DFTB) and the non-equilibrium Green's function (NEGF) by implementing the code of DFTB (gDFTB) for the calculation of transport to get an electric current of this model. As the results of this simulation, the total energy of the OPP molecule increased proportionally with the temperature increase of about 1 eV. It was caused by conformation changes in the molecular structure of the OPP when getting disruption at higher temperatures.

Keywords : temperature, conduction, OPP, molecule

1. Introduction

A single molecule is attracting more attentions both experimental and theoretical studies for its potential application of miniaturization from sub-micrometer conventional inorganic devices to tiny active component with the size of only a few nanometers. The development of electronic devices and technology, especially in the field of single molecules, has been explored in various aspects. The most interesting aspect of the topic of this study was to explore the electronic transport properties of a material having a conjugated system such as phenyl, graphene, carbon nanotubes, fullerenes, etc. In the field of molecular electronic devices, the basic concept of electric current flow at the molecular level is an important requirement for understanding the electronic transport from single molecules to an electrode contact. Specifically, it depends on the interaction between the molecules and the metal contacts, the molecular orientation, the energy gap (HOMO-LUMO) and the length of the molecule [1]. However, the transport mechanism at the single molecule level is still opened for scientific study on how the conductance of molecular junctions can be tuned by chemically modifying the molecules. In order to design the molecular electronic devices, we used conjugated molecule in the form of oligo-phenyl-phenylene (OPP) system to explore and understand about the molecular conductance. It has been studied by several scientists by experiments [1,3,9] and theory[2,4,6]. A force liaison molecule (linker) affects the efficiency of tunnelling system-molecule-metal layer of metal using atomic microscopy (CP-AFM) [3]. Experiments [4-5] have shown that terminal groups that bind a molecule to the metal electrode can control the value of the conductance. Theoretically, it has been shown that the conductance of amine-anchored molecules has better conductance value than thiolated molecules

through being connected to gold contacts [6-8]. The anchoring groups affect the energy level line up relatively to the metal Fermi energy and consequently play important role on the conductance plateaus. Although the technique has experimentally obtained information with high accuracy in the process of adsorption of the surface, it was also very important to investigate the electronic structure in detail by a theoretical method based on the density functional theory (DFT). Many theoretical studies based on DFT for isolated systems have been done [10]. Some of the results of the studies showed a good trend in the experimental data and successfully predicted the properties of a complex system such as geometry [6-8]. In this study, we used terphenyl molecules connected to copper leads. We presented a systematic study on the effect of temperature on the conductivity of OPP by using density functional tight-binding (DFTB) extended to the non-equilibrium Green's function (NEGF) approach for computation of the charge density and electronic transport.

2. Computational Method

2.1The Green's Function Formalism

The problem of quantum transport through a single molecule bridged to two contacting leads can be set by starting from the scattering states which propagate from one lead to the other. The waves scattered at the contact-molecule interface and partially reflected and transmitted across the molecule. Consider the Green's functions of the α contact:

$$g_{\alpha}^{r} = \left[ES_{\alpha} - H_{\alpha} - i\delta\right]^{-1} \tag{1}$$

where *Hα* is Hamiltonian of the contact, the overlap matrix, *S* was represented on a non-orthogonal basis set. Assume that the contacts did not have any interaction among them, the Hamiltonian of the whole system can be written as follow:

$$H = \begin{bmatrix} H_D & V_{D1} & V_{D2} \\ V_{D1}^{\dagger} & H_1 & 0 \\ V_{D2}^{\dagger} & 0 & H_2 \end{bmatrix} \tag{2}$$

where VD1(2) is the Hamiltonian of contact-molecule coupling. The complete Green's function of the system:

$$G_{D}^{r} = \left[ES_{D} - H_{D} - \Sigma^{r} \right]^{-1} \tag{3}$$

where Σ^{r} is the total self-energy of the two contacts,

$$\Sigma_{\alpha}^{r} = \left(ES_{D\alpha} - V_{D\alpha}\right) g_{\alpha}^{r} \left(ES_{D\alpha} - V_{D\alpha}\right)^{\dagger} \tag{4}$$

The tunneling current flowing through the molecule that naturally arises in coherent transport is given by the Landauer formula [11] as follow:

$$I\left(V\right) = \frac{q}{h} \int dE\, T\left(E,V\right) \left[f\left(E,\mu_1\right) - f\left(E,\mu_2\right) \right] \tag{5}$$

where $T(E, V) = Tr\,[\Gamma_L G^r \Gamma_R G^a]$ is transmission function and $\Gamma_{L/R}$ is the scattering rates related to the probability of injecting an electron into the molecule from left and right electrodes. These rates also describe the width that the molecular level acquires in virtue of the coupling to the metal leads and they can be used to measure the strength of the metal-molecule coupling. Then $f(E, \mu)$ is the

Fermi-Dirac function. In equilibrium and at zero temperature (T = 0 K) case, the conductance can be expressed as:

$$G = \frac{2q^2}{h} T\left(E_F\right) \tag{6}$$

The advantages in using Green's function approach was that the incoherent scattering and relaxations can be included within self-energies. In this study, we observed the conductance of a single molecule by a ring system oligo-phenil-phenylene (OPP) with a contact copper lead (Cu [111]). The function of non-equilibrium Green (NEGF) implemented in the method of Density Functional Tight-Binding (gDFTB) was used to investigate the transport properties of the system. The temperature variation was given to characterize the molecular dynamics and interactions between OPP ring molecules on a short time scale of about a nano-second (ns). These molecular dynamics behavior will cause the conductance of OPP molecules fluctuate depending on the temperature and conformation.

2.2Molecular Dynamics Simulation

The molecular dynamics technique simulates a classical system of molecules in the most natural way: it integrates the governing equations of motion through time. The generated sequence of configurations could be run as a movie and looked very realistic. The preparation files of molecular dynamics simulations performed with the geometry optimization and energy minimized three-dimensional structure of OPP molecules using DFTB+ software [6] that runs on a multi-core computer. The parameters were used in accordance with standard molecular dynamics, namely NVT ensemble (N: the number of atoms; V: volume; T: temperature) with the velocity of Verlet algorithm. The advantage of the Verlet velocity treatment was the availability of the momenta at the same time as the positions. Further analysis of complex dynamic was based on the calculation results of the molecular dynamics simulations. The determination of molecular conformation stability of OPP molecule conducted for 100 pico seconds (ps) at the initialization phase. Simulations were performed for 700 pico seconds at a temperature of 150, 300, 450, 600, and 750 K to determine the effect of temperature on OPP molecular geometry and electronic properties. OPP three-dimensional molecular structure obtained from the use of optimization software DFTB+ then compared the results with the data from the official site database. Visualization was done by creating a script in the Jmol program which then changed into the form of movie files (mpeg files). Complex interactions among the OPP rings during molecular dynamics simulation can be seen through the output database viewer in the position format (xyz format). The visualization of the shift position of molecular conformation OPP and dynamic movements of the molecular dynamics simulation results were done by selecting the molecular conformation at certain periods until the end of the simulation time.

3. Results and Discussion

3.1The geometry optimization of OPP molecules

Three-dimensional molecular structure of OPP was obtained by minimizing the total OPP molecule energy by using the software and hardware of DFTB+ multi-core computer (parallel computing). The optimal molecular geometry of OPP is shown in Figure 1. The OPP molecule has a planar structure without ring rotation in one direction.

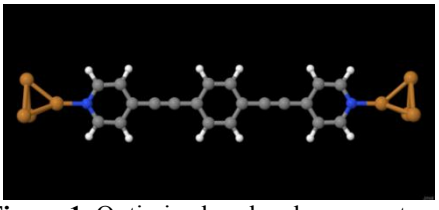

Figure 1. Optimized molecular geometry of OPP molecules

3.2Effect of temperature on molecular ring rotation

The geometry of the OPP molecule would change over time when a certain temperature was given to the molecule. The total energy of the OPP molecule increased proportionally with the temperature increase of about 1 eV which is given in Table 1.

Table 1. Averages of Total Energy

Temperature (K)	E_{min} (eV)	E_{max} (eV)	$E_{average}$ (eV)	$E_{max} - E_{min}$ (eV)
150	-1654.5770	-1653.6739	-1654.1693	0.9031
300	-1653.8794	-1652.5212	-1653.0796	1.3582
450	-1653.2590	-1650.4037	-1651.9914	2.8553
600	-1652.6385	-1648.9218	-1650.8511	3.7167
750	-1652.0181	-1647.2228	-1649.7697	4.7953

For the given temperature of 450 K, the maximum value of the rotational angle of the molecules' OPP ring produced about 60° from the initial position (flat) at simulation time of around 1750 and 3800 (a.u.) can be seen in Figure 2.

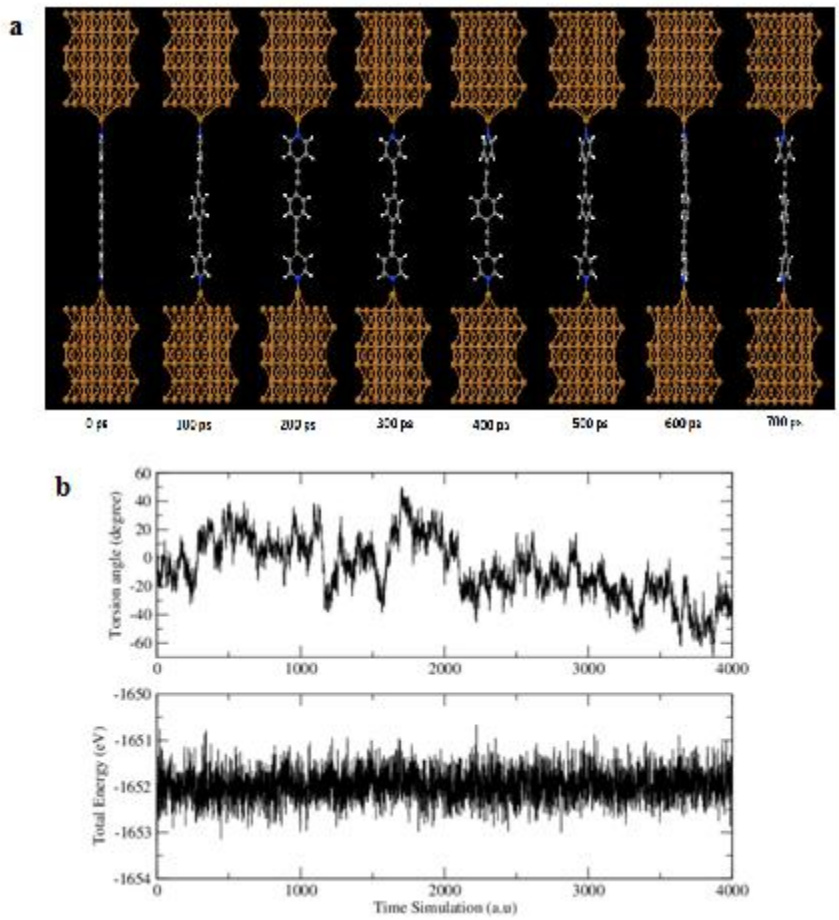

Figure 2. Effects of temperature on the molecular ring rotation OPP (T = 450 K): a). visualization of the OPP ring rotation b). total energy and torsion angle of the central ring in OPP molecule

The results of the calculation of the value of transmission (quantum conductivity) and the function of the local density of states (LDOS) in conditions without and with applied voltage (V = 0) were 0.5 and 1 volt, as shown in Figure 3. For the initial condition, namely OPP molecules without rotation (flat), the transmission function was higher than that rotate by 60°. This was due to a decreasing local density of OPP molecule state at around 1 to 2 eV. The voltage changes only affect the shifting LDOS (Figure. 3) to the positive axis direction (right). The increasing energy levels were caused by the provision of a positive voltage.

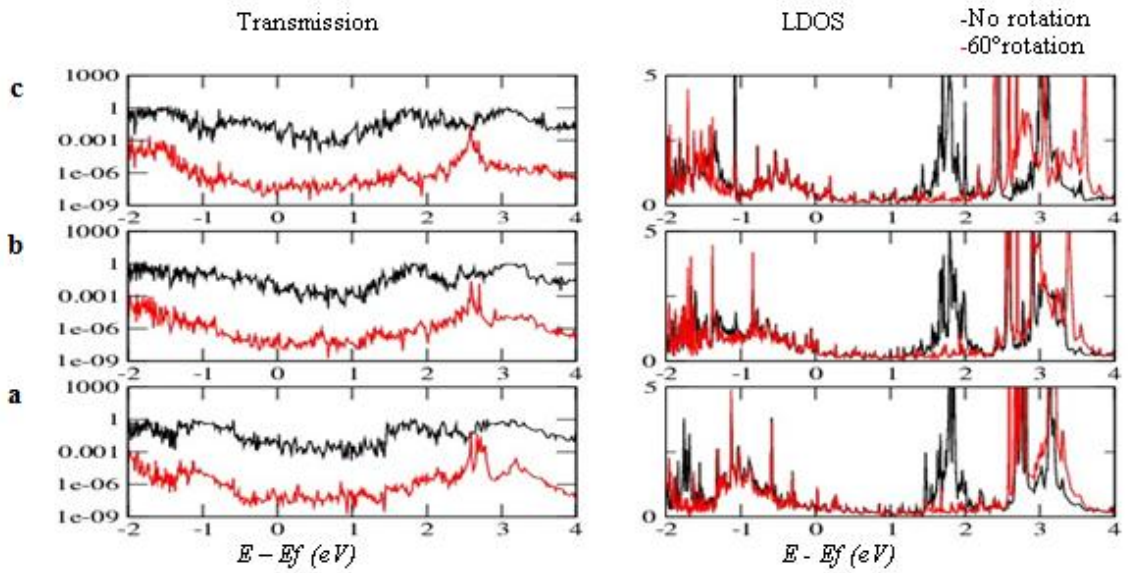

Figure 3. Transmission and LDOS of OPP molecular rotation with: a. applied bias 0 volt, b. applied bias 0.5, c. Volt applied bias 1 volt

4. Conclusion

In the first phase of research, geometrical structure of molecules OPP optimization and molecular dynamics simulation have been conducted at various temperatures of 150, 300, 450, 600, and 750 K. The results of these simulations showed that total energy of the OPP molecule increased proportionally with the increase in temperature about of 1 eV. It was caused by the conformation changes in the molecular structure of the OPP when getting disruptions at higher temperatures. At a temperature of 450 K, the maximum value of the rotational angle of the ring OPP molecules was twisted of about 60° from the initial position (flat) at simulation time of around 1750 and 3800 (a.u. of time). In OPP molecules without rotation (flat), the value of the transmission was higher than that rotated by 60°. This was due to a decrease in the local density stateof OPP molecule around 1 to 2 eV.

5. References

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Acknowledgements
We would like to thank to Dr. Alessandro Pecchia for a short course of the DFTB code.