The Temperature Dependent Electron Transport Studies in a Molecular Device

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Abstract The quantum transport through Tour Wires (TWs) was studied at room temperature and high temperature range using nonequilibrium Green's function (NEGF) formalism combined with extended Huckel theory (EHT). Au-Tour Wire-Au junctions were constructed with functional groups NO_2 and NH_2.The influence of the temperature effect on the transport characteristics have been emphasized, and the result shows that for the TW and TW-NH_2 systems conductance increase with increasing temperature indicating the dominating transport mechanism which is due to thermionic emission. The temperature dependence arises not only from thermal spreading in the leads but also from a thermal average over different contact configuration. In particular, negative differential resistance nature was observed for TW-NO_2 at the temperature of 100K in the positive and the negative bias region.

Index Terms— *Molecular electronics, extended Huckel theory (EHT), nonequlibrium Green's Function (NEGF), quantum transport*

1 INTRODUCTION

Molecular electronics is believed to be a very potential technology, an alternate to current silicon semiconductor technology in nano scale regime and has been received great attention in recent years. Using molecules as active elements for electrical circuits is the basis of molecular electronics and the advantage of these devices is their flexibility in designing and chemical tunability [1]. Organic molecules have some interesting physical properties such as switching [2], memory cells [3], rectifying behavior, [4] and also have complex nonlinear current-voltage (I-V) characteristics such as negative differential resistance (NDR) [5]. A number of theoretical models have been developed for calculating I-V characteristics including semi empirical [6-9] and first principle [10-12] theory. In this study, nonequilibrium Green's function (NEGF) formalism [13-16] coupled with the extended Huckel theory (EHT) [17] was applied to model the electron transport of the device.

We focus on the temperature effect of phenyl-ethylene oligomer, so-called "Tour wire", comprised of phenyl rings separated by triplet-bonded carbon atoms that form a long rigid molecule with π-conjugated delocalized frontier orbitals [18.19]. This molecule has been studied by Jeremy Taylor et al. [20] with the aim of analyzing the switching phenomena on phenyl-ethylene oligomers.

Here the influence of functional groups NO_2 and NH_2 on the electrical properties of TW molecular system is investigated at different temperature ranging from 0K to 600K. The purpose of this study is to manifest the effect of temperature on the conductance behavior of the system is analyzed by varying the temperature of the electrodes and the central molecular region. It is demonstrated how the temperature dependence of the conductance and its fluctuations can be modified by an appropriate design of the geometric structure of a molecule.

2 THEORETICAL FORMULATION

In this section, the formalism is presented to investigate the transport properties of Tour wires (TWs) molecular system. The structural optimization and the transport properties of these two systems have been investigated using Atomistic Toolkit software (ATK) [21]. Then the optimized molecules are sandwiched between gold (111) electrodes.The distance between left and right electrodes is adjusted and the whole system is optimized with gold atoms fixed by optimizing the total energy of the systems.

The current through this system can be obtained from Landauer [22] formula according to the corresponding Green function. An electron incident from the source with energy E has a probability T (E) of being transmitted through the molecule to the drain. By calculating this transmission probability for a range of energies around the Fermi function Ef of the lead, current is calculated using the Landauer formula.

$$I = \frac{2e}{h}\int_{-\infty}^{\infty} T(E)\left[f(E-\mu_1) - f(E-\mu_2)\right]dE \quad (1)$$

Where T (E) is the transmission function through the device at energy E which is calculated using the non equilibrium Green's function formalism as given as $T(E) = Tr(\Gamma_1 G \Gamma_2 G^+)$,

where: broadening matrices $\Gamma_{1,2} = i(\Sigma_{1,2} - \Sigma_{1,2}^+)$ are defined as the anti- Hermitian parts of self energies $\Sigma_{1,2}$, and the molecular

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Green's function G is given by

$$G(E) = (ES - H + U_{SCF} - \Sigma_1 - \Sigma_2)^{-1} \quad (2)$$

where S is the overlap matrix for non-orthogonal basis set of states, while H is the Hamiltonian of the neutral molecule.

The self consistent potential U_{SCF} is given by $U_{SCF} = U(N-N_{eq})$ and it is calculated by employing a simple self consistent field method. Neq is the equilibrium number of electrons in the molecule.

μ_1, μ_2 are Chemical potential of Left and right electrode respectively.

3 Result and Discussion

To study the effect of side groups to the parent molecule at room temperature, we compute the transmission coefficient. The transmission spectrum at zero bias for TW and the TW with different sides groups are shown in Fig. 1. The general shapes of the zero transmission spectra for the three TW systems more or less resemble the same with the narrow transmission peak at either side of the Fermi Level. We observed that the HOMO and LUMO transmissions are dominated for the TW but in the case of TW-NO_2 and TW-NH_2 systems, the transmission will happen either through HOMO or LUMO. Such behavior can be justified as a consequence of quantum interference of the molecular orbitals [23], where the variation of interference conditions is due to the presence of functional groups

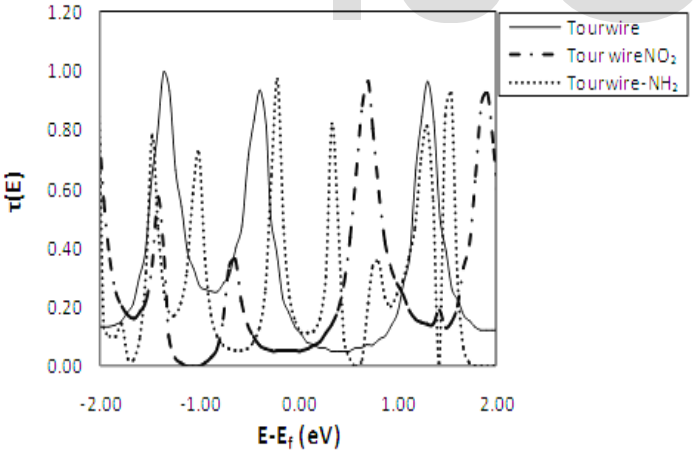


Fig. 1 Transmission as a function of energy for the Tour wires under zero bias

To analyze the current-voltage (I-V) characteristics at room temperature (300K), we carried out the self-consistent calculation for the biases in the range -5V to 5V in steps of 0.5V. The I-V spectra at T=300K, shown in Fig. 2a, are almost similar for all the three systems. At lower bias region the current increases gradually, while rapid increase around 1.0V is seen where the resonances come into alignment with the bias window.

We also compared the I-V curve for the three TW molecular junctions; the current changes slightly over the whole range but limited variations are observed and these results are consistent with the experimental observations [24]. From this study, it is concluded that the current-voltage behavior of these systems does not depend upon the presence of chemical substituent groups but depend upon their influence on charge redistribution within the molecular system.

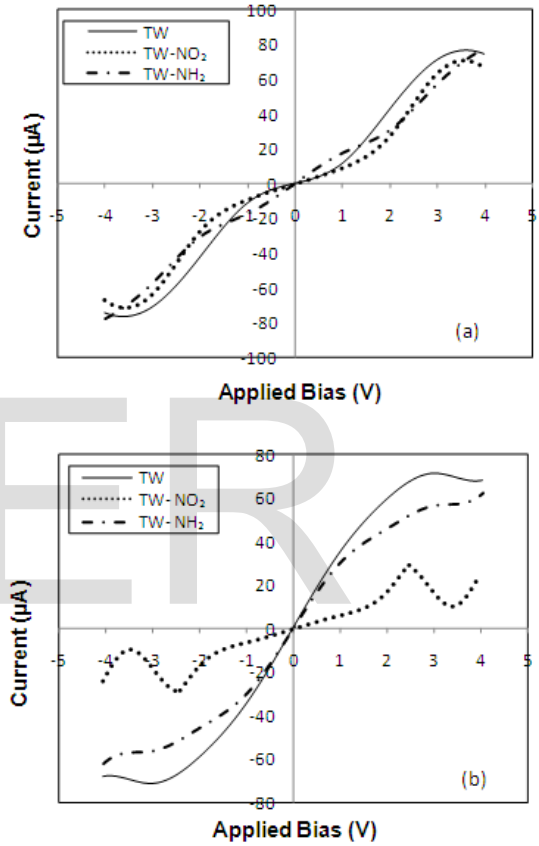
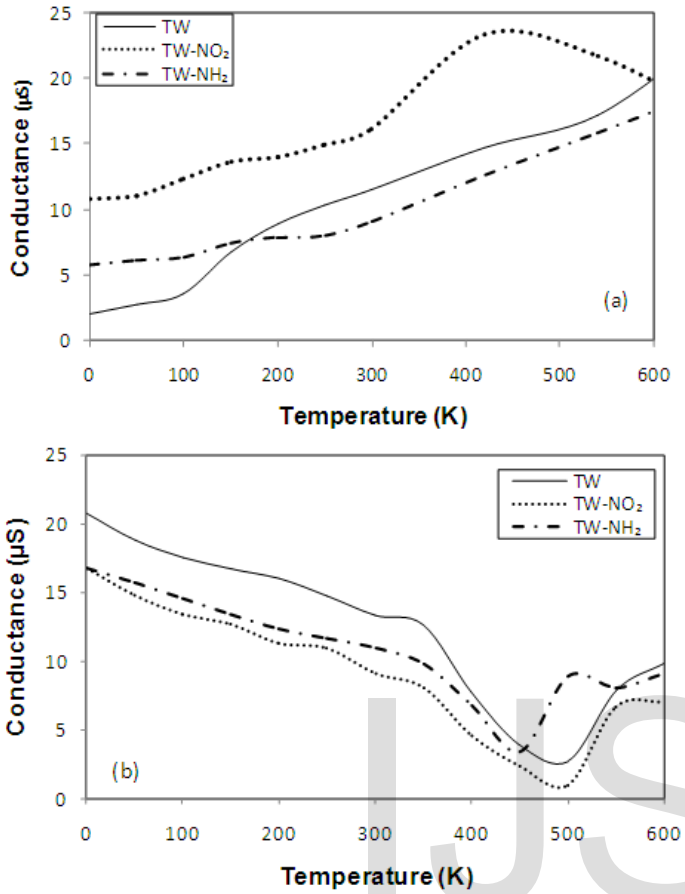


Fig. 2 Current-Voltage Characteristics of TWs at (a) 300K (b) 100K

We also analyzed the current-voltage (I-V) characteristics of all the TW molecular junctions at different temperature ranging from 0K to 600K. From this, it is observed that the I-V spectra of TW-NO_2 at 100K reported in Fig. 2b exemplifies NDR behavior, which can be understood by studying the coupling between the molecular orbitals and the incident state in the electrode under various biases and also at different temperatures. From Fig.2b, the NDR- like peaks occurs at the bias voltage varying from 2.5V to 3.8V. These results are comparable with the experimental observation [24, 25]. The appearance of NDR peak in both positive and negative bias voltage is due to the breakdown of the molecular junction at the molecule-electrode interface. In this system, the NDR like effect is associated with the reduction of electro active nitro functional group rather than the reduction of Au-S bond.

Fig. 3 Conductance as a function of electron temperature for the (a)



central region of TWs (b) left and right electrode

The temperature dependent conductance G (T) is plotted in Fig. 3a for the three TWs by varying the temperature of the molecular device in the range of 0K -600K. The average G (T) shows qualitative differences for the three molecules considered. TW and TW-NH_2 exhibit a rather linear increasing conductance G (T) with increasing temperature. In contrast, weak temperature dependence is found for TW-NO_2. At different temperatures, the conductance depend upon two contribution to the temperature, one comes from the thermal broadening of the lead properties but the other one comes from the thermal average over the different geometric configurations of the central region . For the TW and TW-NH_2 molecules, the lead induced temperature dependence contributions to increase their conductance are not much supported. Therefore, the configurational thermal broadening gives accessibility to increase the conductance values, resulting steady increase in G (T). For TW-NO_2 molecule, elevated temperatures give accessibility to both higher and lower conductance; as a result of which G (T) exhibits no clear trend. This is because; the lead-induced and the configurational thermal broadening play equal role for the elevation of temperature dependence conductance.

The temperature dependent conductance for the TW systems by varying the temperature of the left and the right electrode is shown in Fig. 3b.The lead induced conductance has the strongest effect on the longer junction systems and the conductance will increase as a function of temperature. But in our system, when the temperature various from 0K to 450 K the conductance decreases. This is because at this temperature range the lead-induced conductance is suppressed by large tunneling near the Fermi level. As we exceed 450K, the energy levels of the central region come closer to the Fermi energy of the electrode and larger conductance due to thermionic emission is visualized.

4 Conclusion

We study the charge transport through Tour wire with the functional group NO_2 and NH_2 at different temperature. From our calculations we observed that by comparing the I-V curve of the three TW systems, the current changes slightly over the whole range implying that the current-voltage phenomena of these systems are not much affected by the functionalization at room temperature. However, by varying the temperature there is possibility of modifying their transport behavior in a controlled way and the NDR is obtained for TW-NO_2 system at the temperature 100K. By varying the temperature, the conductance of these systems is turned by the lead induced thermal broadening or configurational thermal broadening.

These theoretical results will be helpful to design and fabricate future molecular electronic devices and circuits with specific properties. It also shows the potential application of TWs in the NDR devices and tunnel diodes.

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