Functional Group Effect for Modeling Transport Through Tour Wire Nanostructure

Abstract

The purpose of this study is to manifest the roles such as the current-controlling behaviors are played by the functional groups. Also, the effect of temperature on the electron transport behavior of the system is analyzed by varying the temperature of the left and right electrodes(replace by top and bottom electrodes) and the title angle(check)between the phenyl rings.We focus on the temperature effect of phenyl-ethylene oligomer, so-called "Tour wire"(TW), comprised of phenyl rings separated by triplet-bonded carbon atoms that form a long rigid molecule with π-conjugated delocalized frontier orbitals.The zero energy corresponds to the Fermi energy of the electrodes. 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.By varying the temperature, the conductance of these systems is turned by the lead induced thermal broadening or configurational thermal broadening.(modify) 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 negative differential resistance (NDR) devices and tunnel diodes.

Keywords: ~~tunnel diodes~~(not consistent), phenyl-ethylene oligomer,triplet-bonded carbon atoms, molecular electronics

INTRODUCTION

Molecular electronics is believed to be an alternative potential technology to current silicon semiconductor technology. It has received great attention because of the ultimate size limit of functional devices.The basis of molecular electronics is that, using the molecules as an active elements for electrical circuits.The advantage of these devices is their flexibility in designing and chemical tenability [1,2].

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 [3,4]. This molecule has been studied by Taylor et al. [5] with the aim of analyzing the switching phenomena on phenyl-ethylene oligomers. Tayler and co-workers observed the negative differential resistance (NDR) and the molecular memory in monolayers of NO_2 functionalized molecules by twisting the central ring of the TW. Zhao et al. [6] used NEGF formalism combined with

Density functional theory(Density Function Theory (DFT)) to analyze the substituent effect on phenyl ethylene oligomers such as electron donating and electron with drawing(withdrawing) group. They reported that the electrical properties of the molecular devices are related to the electronic structure of the bridge molecule. Reed et al. [7] observed the switching phenomena for phenyl-ethylene oligomer only for NO_2 side group and they reported spontaneous switching of all these molecules having limited success in inducing switching by using voltage pulse approach. Miao et al. [8] analyzed the structural, electronics and vibrational properties of phenylethylene oligomers on the Au(111) surface using plane wave based DFT calculations. They found that phenyl-ethylene oligomers have two energetically favorable adsorption sites such as nontop and top site adsorption on the Au(111) surface. Their investigation demonstrated that, due to delocalized electron density distribution the top site adsorption on Au(111) surface shows better conductivity between phenylethylene oligomers and Au than nontop side adsorption. Lilli Serrato Vilegas et al. studied [9] the influence of fluorination over the phenyl-ethylene oligomers to turn the thermal stability for high-temperature production processes of self assembled monolayers on metal surface. But, by comparing with phenyl-ethylene oligomers with NO_2 side group the fluorinated molecule had limited success in increasing the thermal stability. 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 0 to 600 K using semi-empirical method. The semi-empirical approach such as extended Huckel theory has been shown to give satisfactory results for the calculation of Tourwire systems. To improve the accuracy of the calculation and to reduce the significant computing time the non-vanishing integrals (two electron integrals) are replaced by the associate parameters. The purpose of this study is to manifest the roles such as the current-controlling behaviors are played by the functional groups. Also, the effect of temperature on the electron transport behavior of the system is analyzed by varying the temperature of the left and right electrodes and the title angle between the phenyl rings

THEORETICAL FORMULATION

In this section, the formalism is presented to investigate the transport properties of Tour wires (TWs) molecular system. An electron incident from the source with energy E has a probability τ (E) of being transmitted through the molecule to the drain. By calculating this transmission probability for a range of energies around the Fermi function E_f of the lead, current is calculated. At first we calculated the transmission function τ (E) using the NEGF formalism as given as [ref]

$$\tau (E) = = \mathrm{Tr}(\Gamma_1 G \Gamma_2 G^{+}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

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 Green's function G is given by[ref]

$$G(E) = \left(ES - H + U_{SCF} - \sum_1 - \sum_2\right)^{-1}$$ ……………………………..(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 USCF is given by USCF = U(N-N_{eq}) and it is calculated by employing a simple self consistent field method[ref].N_{eq} is the equilibrium number of electrons in the molecule. (mention other related terms)

The current flowing through the device is calculated using Landauer formula [10,11].

$$I = \frac{2e}{h}\int_{-\infty}^{\infty} \tau(E)[f(E-\mu_1) - f(E-\mu_2)]dE$$ …………………………..(3)

where, μ_1, μ_2 are chemical potential of left and right electrode respectively. $(\mu_1 - \mu_2)/e = V$ is the electrical potential difference between left and right ends.

Electrochemical Potential $\mu_{1,2}$ is given as

$$\mu_{1,2} = E_f \pm \frac{eV}{2}$$ …………………..(4)

f $(E - \mu_{1,2})$ is the Fermi distribution functions of electrons in the left and right electrodes.

The molecular system was defined by adding two Au(111) electrodes to the TW molecule considered as a central region through the end group. The adsorption geometry is such that the molecules are located symmetrically at the top site of Au(111) surface. For the left and right electrodes, 3 × 3 unit cell is used. The structural optimization and the transport properties of these systems have been investigated using ATK (write full form) [12]. In our calculations, only valence electrons are self-consistently calculated and the atomic cores are described by standard norm conserving pseudo potential [13]. The valence wave functions are expanded by localized numerical (pseudo) atomic orbitals [14]. According to Yang et al. [15] analysis, for Au(111)–phenyl-ethylene oligomers–Au(111) molecular junction the use of single zeta polarized basis set shows the incorrect situation of the Fermi energy being closer to the molecular orbital but for double and triple zeta polarization basis set leads the Fermi energy closer to the molecular orbital, therefore in our investigation we computed with the double zeta plus polarization basis set for Au atoms and the other atoms. For convergence, the Brillion zone of the leads is sampled by 3 × 3 × 100 K(check) points in the direction of x, y, and z, where z is the electron transport direction. Theoptimized structure of Tour wire with differential functional group is represented inFigure1.

RESULT AND DISCUSSION

To study the effect of adding the side groups to the parent molecule, wecompute the transmission coefficient. The transmission spectrum atzerobias forTW and the TW with NO_2 and NH_2 sides groups at room temperature are shown inFigure. 2. The zero energy corresponds to the Fermi energy of the electrodes[ref]. Thegeneral shapes of the zero transmission spectrafor the three TW systems more orless resemble the same with the narrow transmission peak at either side of the Fermilevel.

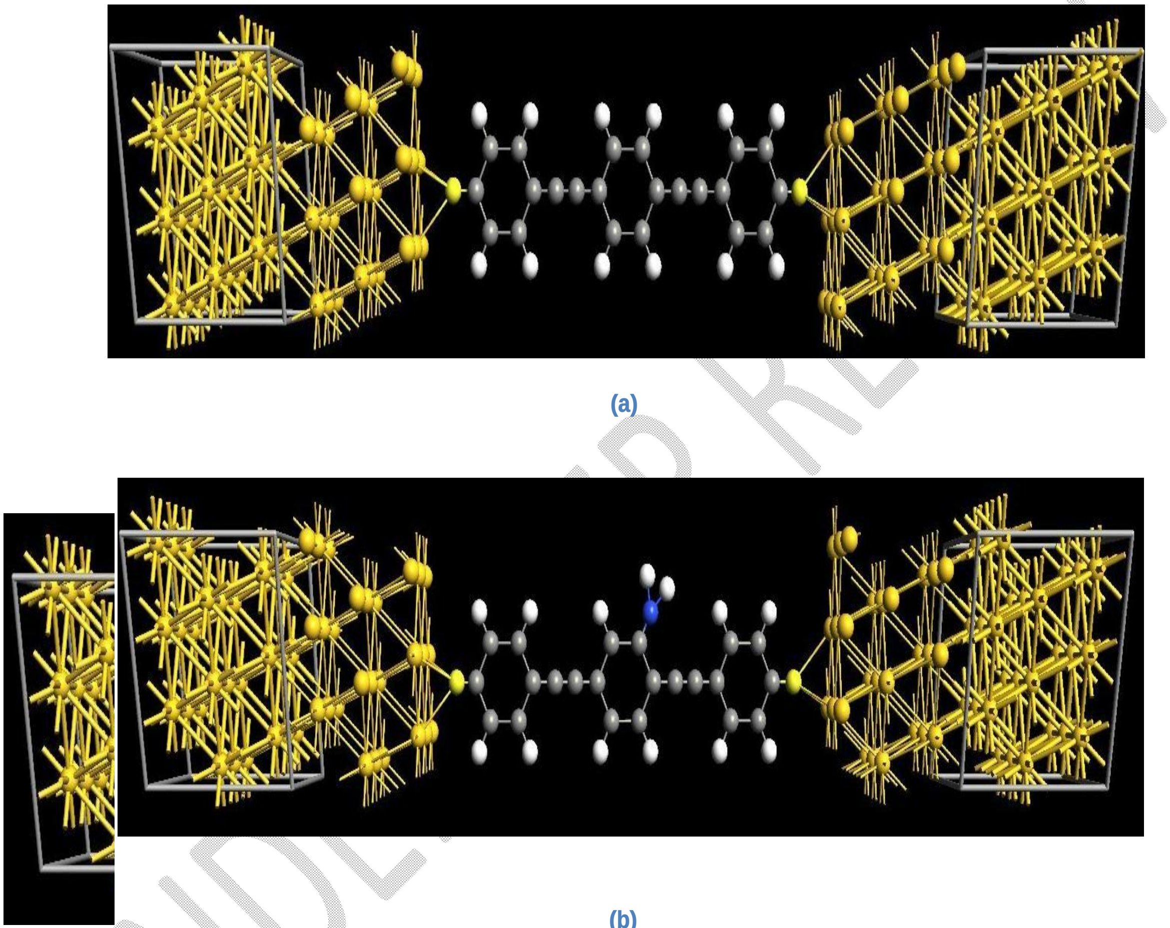


Figure 1. Optimized structure of the (a) Tour wire (b) Tourwire-NH_2 (c) Tourwire-NO_2 devices from the GGA/DZ inATK;Colorcodes:C(gray),H(white),S(yellow),Au(gold) (rearrange figures and their captions)

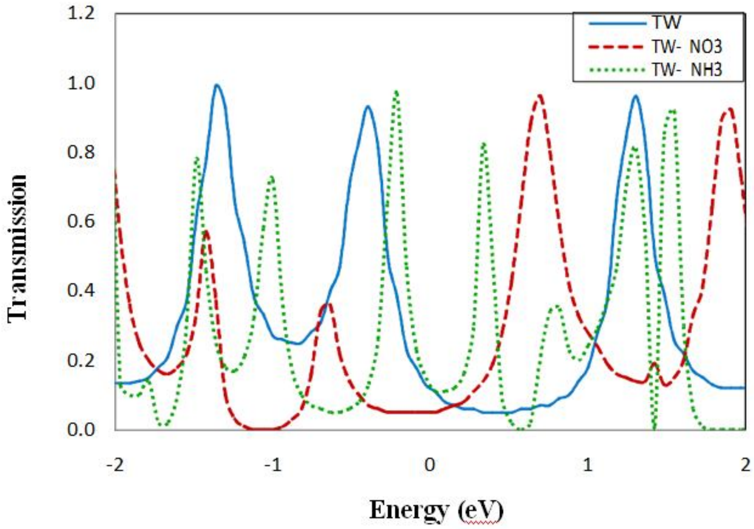


Figure 2. TransmissionasafunctionofenergyfortheTourwiresunderzerobias

Weobserved thatthe HOMO andLUMO transmissions aredominatedfor the TW but in the case of TW-NO_2 and TW-NH_2 systems, the transmission willhappen either through HOMO or LUMO. As electron-donating substituent replacethe H atoms on the Tour wire ring, the energy of the HOMO orbital increases.Similarly, when electron-withdrawing substituentreplaces H atoms, the energy ofthe HOMO is lowered as shown in Figure 2. Such behavior can be justified as aconsequence of quantum interference of the molecular orbitals [16], where thevariationof interference conditions isdue tothe presenceof functionalgroups.

Table 1 - Isosurface-transmissioneigenchannelofHOMOandLUMOresonance forTourwires(rewrite)

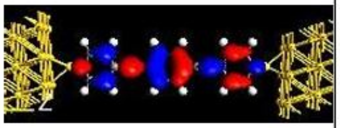
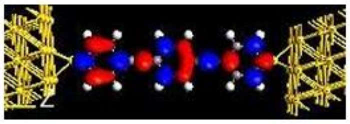
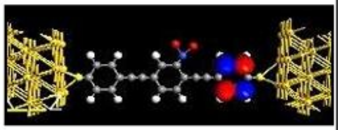
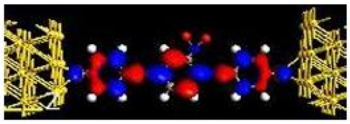
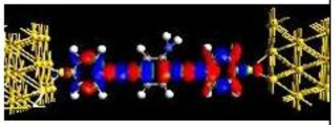
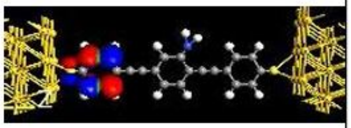
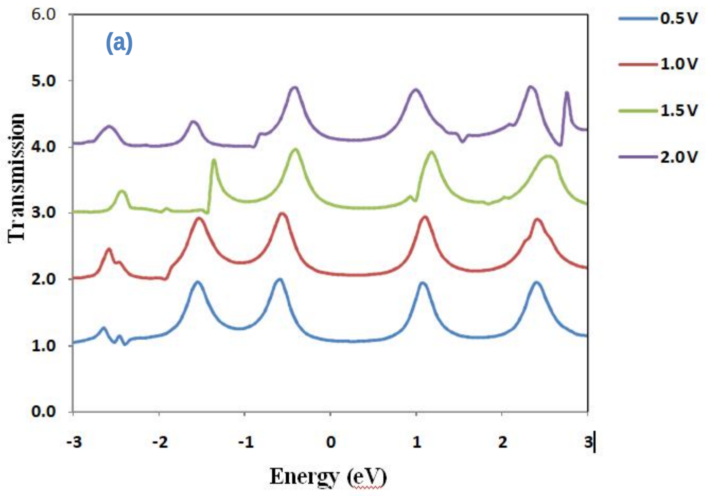
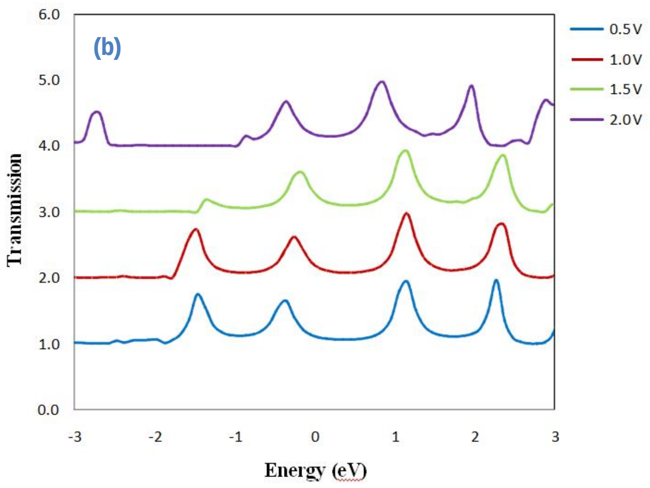
Molecule	Energy value for HOMO (eV)	Isosurface-Transmission eigenchannel	Energy value for LUMO (eV)	Isosurface-Transmission eigenchannel
TW	-0.65		1.32	
TW-NO_2	-0.7		0.89	
TW-NH_2	-0.54		0.73	

Table 1 gives the isosurface transmission eigen channel of HOMO andLUMO resonance. By calculating the eigenstates at the resonance energies (E_{HOMO},E_{LUMO}), the orbital that are responsible for the current flow through the molecule canbe analyzed. From Table 1 it is clear that the NH_2 side group participate in theHOMO resonance but not in LUMO resonance, while NO_2 group participate inLUMOresonancenotinHOMOresonance,consistingwiththeirrespectivedonating/accepting characters.

It is,however clear from the isosurface of transmission eigenchannelanalysisthemolecularorbitalsof theTWaredelocalizedentirelyalloverthemolecule by providing a bath for better π - electron cloud overlap (correction needed). It can be seen thatthe HOMO are delocalized in the electron donating group such asNH_2 and theLUMOare delocalizedintheelectronacceptinggroupthatisNO_2.

Figure 3 shows the transmission spectra for TW systems under different bias voltage ranging from 0.5 to 3 V in steps of 0.5 V. As the bias increases, the transmissions through the HOMO levels (particularly HOMO-1) are decreases considerably. Therefore, despite the increase of bias window, the current remains essentially unchanged and displays a plateau (Fig 4a). A similar behaviour is found for the TW and TW–NH_2. However, in TW–NO_2 molecule the transmission across the HOMO levels is strongly reduced at high bias, this leads negative differential resistance (NDR). It is also observed that, at a bias around 2.0 V large shift in the transmission is occurred. With leads attached, the charge effect makes the energy levels of the isolated molecule descend and broadened. Based on the charge calculations of the molecule, when the bias reaches 2 V, the total charge of the molecule is increased by +1 eV. Based on this it seems that, the large shift in the transmission spectra around 2 V is arises due to the charging effect and the shift is up by about +1 eV. We also observe that most of the HOMOs and LUMOs structure appear to move rigidly towards E_f when the bias voltage is increased. This is because the delocalized nature of the π-orbitals is increased due to the influence of bias voltage.





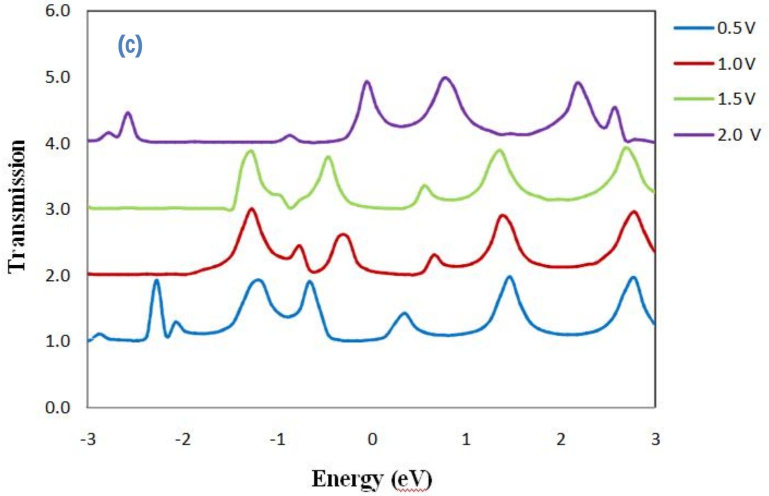
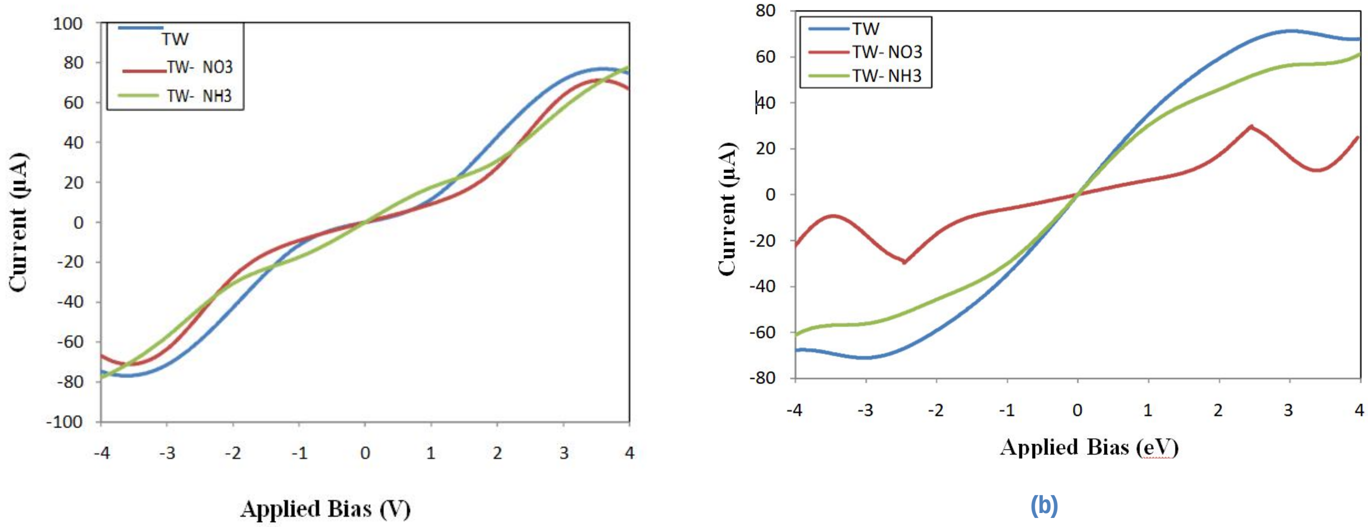


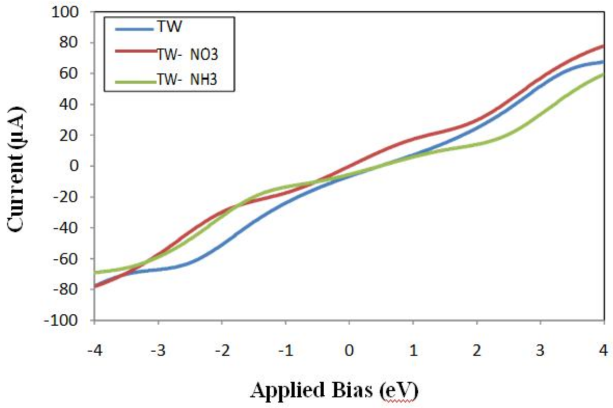
Figure 3. Bias dependenttransmission spectrafor (a) TW (b) TW-NO_2 and (c) TW-NH_2

To analyze the current–voltage (I–V) characteristics at room temperature (300 K), we carried out the self-consistent calculation for the biases in the range −5 to 5 V in steps of 0.5 V. The I–V spectra at T = 300 K, shown in Fig. 4a, are almost similar for all the three systems. At lower bias region the current increases gradually, while rapid increase around 1.0 V 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 [17]. 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



(b)

(a)



~~(a)~~

Figure 4. Current -voltage characteristicsfor TWsat(a) 300K and (b) 100K (c) 600K (rewrite)

We also analyzed the current–voltage (I–V) characteristics of all the TW molecular junctions at different temperature ranging from 0 to 600 K. From this, it is observed that the I–V spectra of TW–NO_2 at 100 K reported in Fig. 4b exhibits 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. 4b, the NDR-like peaks occurs at the bias voltage varying from 2.5 to 3.5 V. These results are comparable with the experimental observation [17,18]. Based on the experimental studies by Chen and his group [18], at the temperature of 60 K the NDR phenomena where occurs at the bias range of 1.5 to 2.5 V. In the experimental observation, the appearance of NDR peak is due to the breakdown of the molecular junction at the molecule–electrode interface.

CONCLUSION

We study the charge transport through TW with the functional group NO_2 and NH_2. From the isosurface transmission eigen channels analysis, it is clear that the conductance through these molecules is strongly influenced by the degree of π electron delocalization. We noticed that only the LUMO orbital is delocalized for TW–NO_2 while HOMO orbital is delocalized for TW–NH_2 due to their electron accepting and donating nature. 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 100 K. 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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