

Investigation on the influence of substitute groups in organic nanodevices

P. A. Priya¹, C. P. Kala², D. J. Thiruvadigal^{2,*}

¹ Department of Electronics and Communication Engineering, SRM University, Kattankulathur-603 203, India.

² Department of Physics, SRM University, Kattankulathur-603 203, India.

Abstract

Theoretical investigation has been performed on the electron transport properties of phenyl based molecules, sandwiched between two gold electrodes with symmetric contact. We analysed the influence of the substitute groups such as NO₂, NH₂ and OH, attached to benzene dithiolate molecule, to explore their influence on the transport characteristics to present a current controlled nanodevice. In this paper, nonequilibrium Green's function formalism (NEGF) combined with extended Huckel theory (EHT), a semiempirical approach is used. The results show that the electron donating and withdrawing groups are able to increase and decrease the conductance and thereby control the current.

Keywords: Molecular electronics, Electronic transport, Molecular nanostructure.

PACS: 85.65.+h, 73.63.-b, 81.07.Nb.

1. Introduction

The prime purpose of molecular electronics (moltronics) is to develop nanoelectronic devices based on functional molecules. Considerable computational efforts [1-5] have been devoted in the recent years and many device properties have been demonstrated [6-8]. These investigations show that the transport properties of the organic molecular junctions depend on the geometry and electron structure of the molecules. As an attempt to derive the variation in the transport behavior caused by the structure, we focus our study on the influence of substitute group when attached to the functional molecule.

We apply nonequilibrium Green's function (NEGF) formalism [9-11] coupled with the extended Huckel theory (EHT) [12], a semi empirical approach to model the electron transport of side group attached phenyl based molecule sandwiched between two semi infinite gold electrodes. Extended Huckel Theory (EHT) uses all the valence orbital of the atoms as the non-orthogonal basis functions, neglecting all the interactions between electrons [13].

*) For correspondence; E-mail: djthiruvadigal@ph.srmuniv.ac.in.

The important transport properties such as transmission, conductance and current are calculated and the effect of substitute group on electronic transport through the molecule are simulated and is compared with that of benzene dithiol(BDT). The results are discussed.

2. Formalism and Computational Scheme

The device is described by a Hamiltonian matrix H and an overlap matrix S. The self energy functions $\Sigma_{1,2}$ are used to describe the effect of contacts on the device with corresponding broadening functions defined as $\Gamma_{1,2} = i(\Sigma_{1,2} - \Sigma_{1,2}^{\dagger})$. The device Hamiltonian is further divided into core Hamiltonian H_0 and the self consistent potential U_{SCF} . The self consistent potential U_{SCF} is given by

$$U_{SCF} = U (N - N_{eq}) \quad (1)$$

N_{eq} is the equilibrium number of electrons in the molecule as given by

$$N_{eq} = 2 f(\varepsilon_0 - E_f) \quad (2)$$

In equation (1) ε_0 corresponds to the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) level whichever is closest to Fermi energy E_f .

U_{SCF} is calculated by employing a simple self consistent field method. The number of electrons of the molecule N is calculated as follows.

$$N = \frac{1}{2\pi} \int_{-\infty}^{\infty} dE [f(E - \mu_1) Tr(G\Gamma_1 G^{\dagger}) + f(E - \mu_2) Tr(G\Gamma_2 G^{\dagger})] \quad (3)$$

The molecular Green's function G is given by

$$G(E) = (ES - H + U_{SCF} - \Sigma_1 - \Sigma_2)^{-1} \quad (4)$$

From the converged Green's function, the current flowing through the device is calculated with the help of the standard Landauer -type formula[12], and is given as

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} (Tr(\Gamma_1 G \Gamma_2 G^{\dagger})) [f(E - \mu_1) - f(E - \mu_2)] dE \quad (5)$$

where $f(E - \mu_{1,2})$ denotes the Fermi distributions. Electrochemical potential $\mu_{1,2}$ is defined as

$$\mu_{1,2} = E \pm \frac{eV}{2} \quad (6)$$

The differential conductance is then obtained from the current formula as its derivative with respect to voltage.

Our calculation has been based on the Huckel-IV codes [12, 13], using the fitting parameters Fermi energy and U , the electron charging energy.

We first added gold (111) to the molecule through the anchoring groups. This addition contained 3x3 gold atoms. The adsorption geometry is such that the molecule sits on-top of the triangular gold pad with an end group-gold surface distance of 1.9\AA . All the calculations were performed at the room temperature.

To obtain good starting geometry, the *ab initio* DFT method using B3PW91 hybrid functional [15-17] with 6-31G basis set as implemented in Gaussian-03 software [14] is employed.

3. Results and Discussion

The transmission coefficient variation for various substitute groups under the applied bias is reported in Fig. 1. The effect on the molecular energy levels of benzene depends on the type of substitute group attached. In case of NO_2 the energy levels decrease and for NH_2 and OH the energy levels increase as compared to benzene. In both cases the HOMO – LUMO gap (HLG) decreases. This decrease in HLG is important because the midpoint of the HLG is assumed to be aligned with the Fermi levels of the metal contacts. It can be noted that the impedance of benzene can be reduced by the substitution of electron donating and electron withdrawing groups.

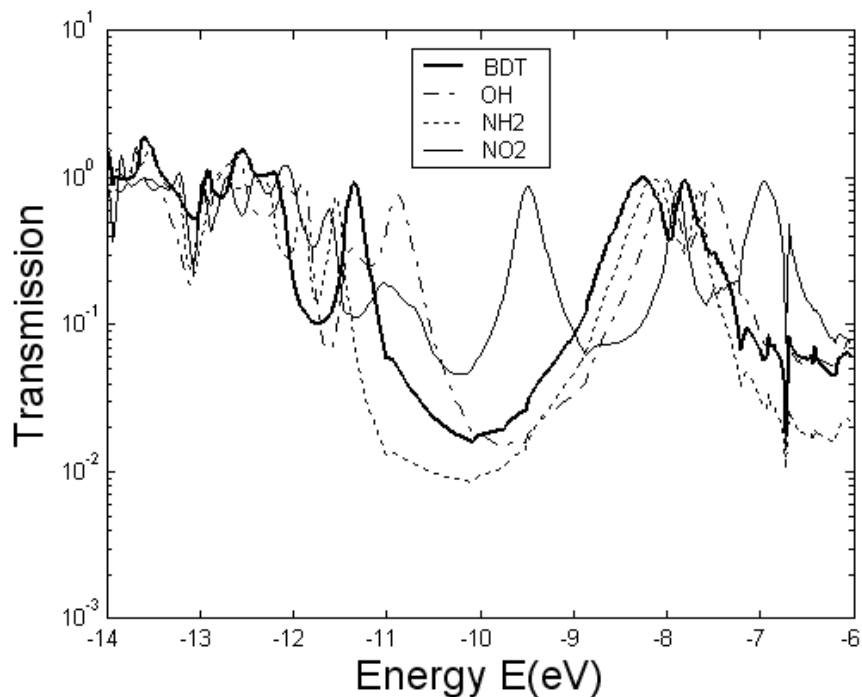


Fig.1: Transmission as a function of electron energy for BDT molecule with NO_2 , NH_2 and OH substitution.

The self consistently calculated current – voltage characteristics and conductance-voltage characteristics for molecular junction under consideration with different substitute groups in the bias range of -2V to 2 V are shown in the Fig. 2 and Fig.3 respectively.

The current in the device becomes smaller with an attached NO₂ side group and larger with NH₂ and OH side group. The reason is that the attachment of the side groups can be treated as a chemical doping to the molecule, the NO₂ group is electron accepting so withdraws the electron. The negative charge is donated by the conjugated ring, which acquires a positive charge and thus HOMO shifts to lower energies, whereas, the attachment of NH₂ and OH are electron donating and shifts HOMO to higher energies.

For BDT the transport primarily occurs through the HOMO which is a pi bonding molecular orbital. The variation in the HOMO position with the functional group correlates directly with the variation in the conductance which shows current is carried by HOMO.

The Fermi levels lie in the middle of the gap and hence the electrical response under positive and negative biases is linear. The shape of the calculated conductance profile of the equilibrium geometric configuration reproduces satisfactorily the experimental results [18].

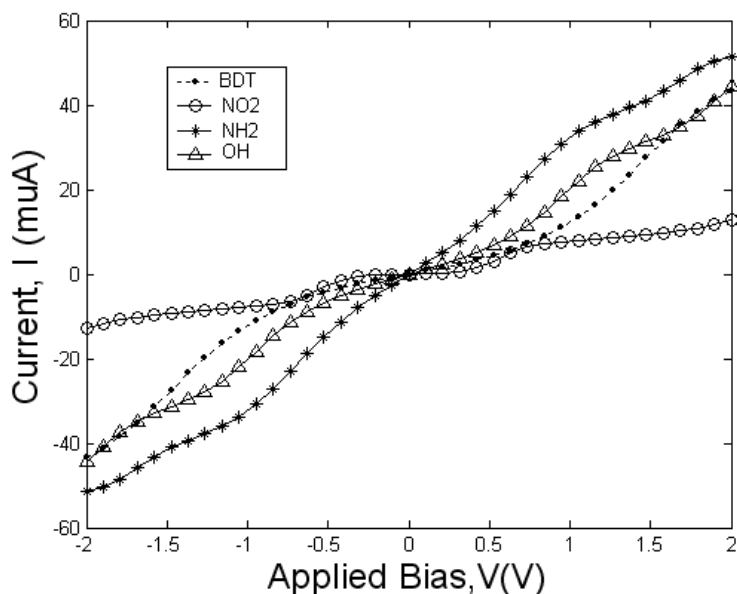


Fig. 2: Current-voltage characteristics for BDT molecule with NO₂, NH₂, OH substitution.

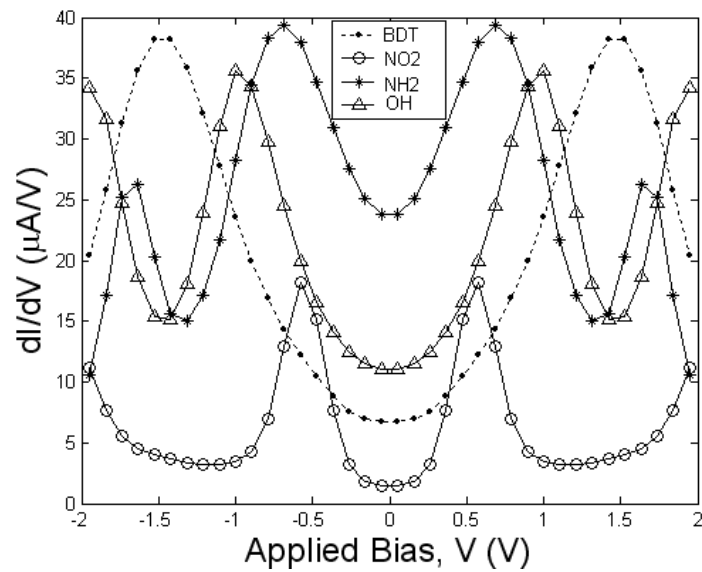


Fig. 3: Conductance-Voltage characteristics for BDT molecule with NO_2 , NH_2 , OH substitution.

In order to modulate the conductance with effective control the, devices are constructed from benzene dithiolate molecule with attachment of double side groups, substituted for H. Conductance-Voltage characteristics for BDT molecule with single and double NO_2 , NH_2 and OH group is shown in Fig. 4, 5, and 6 respectively. It is observed that the double substitution causes further conductance increase in double NH_2 and OH groups and decrease in double NO_2 side group. The results demonstrate that side groups attached to molecular devices offer the possibility of modifying their transport behaviors in a controlled way and can improve/add some particular functionality for the design of molecular electronic devices.

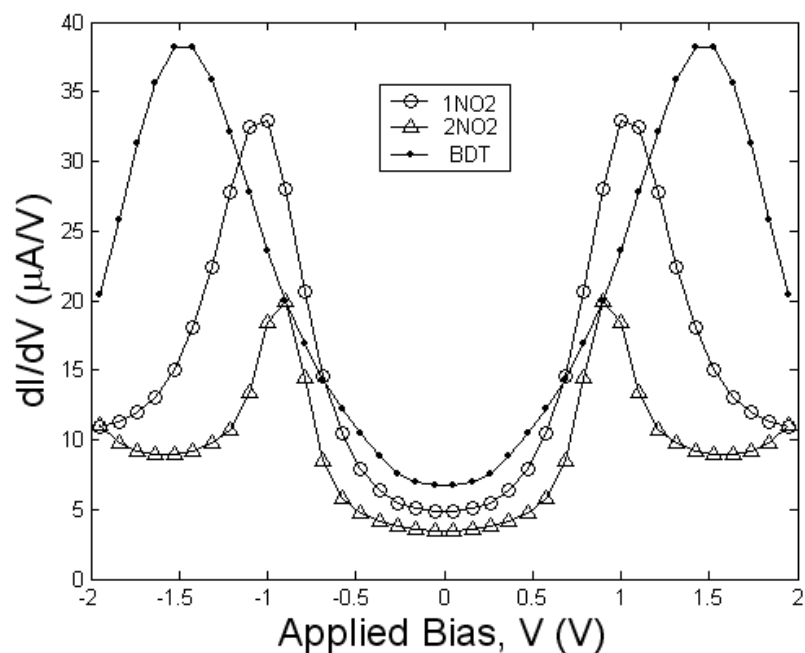


Fig. 4: Conductance-Voltage characteristics for BDT molecule with single and double NO_2 substitution.

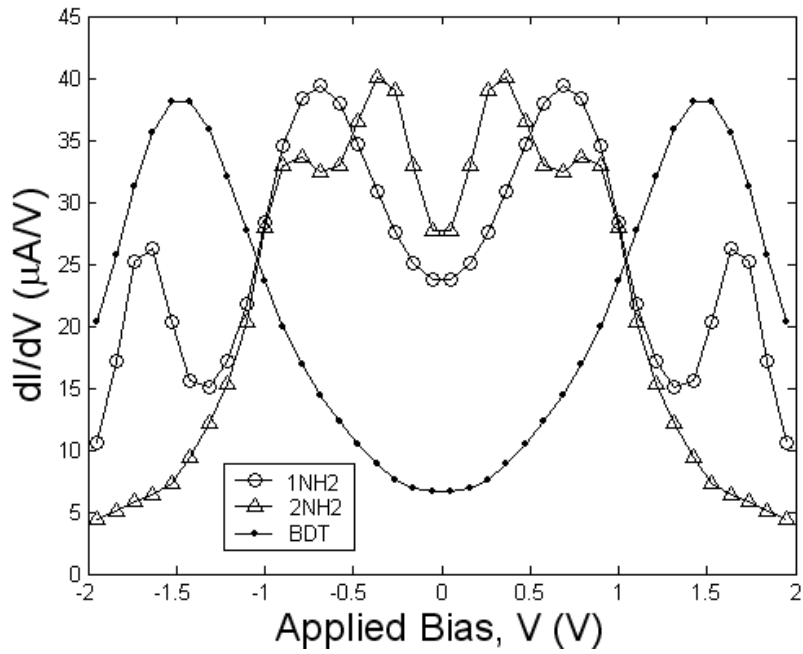


Fig. 5: Conductance-Voltage characteristics for BDT molecule with single and double NH₂ substitution.

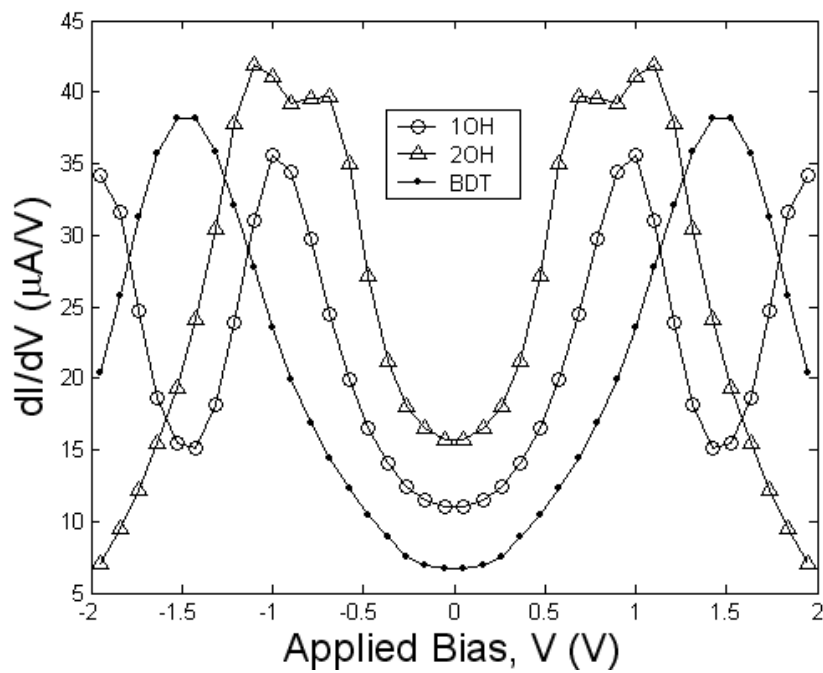


Fig. 6: Conductance-Voltage characteristics for BDT molecule with single and double OH substitution.

4. Conclusion

In this paper, nonequilibrium Green's function formalism (NEGF) combined with extended Huckel theory (EHT); a semi empirical approach is used to study the influence of substitute groups on electron transport in molecular junction. In order to investigate the effect of substitution, we presented the current (I) and differential conductance (dV/dI) as a function of applied bias. The results demonstrate that side groups attached to molecular devices offer the possibility of modifying their transport behaviors in a controlled way and can improve/add some particular functionality for the design of molecular electronic devices. By applying multiple functional groups to the same parent molecule it may be possible to obtain stronger influence.

The experimental measurements [18] of HOMO-LUMO Gap, a decrease in HLG on substitution of NH₂ and OH and increase in HLG on NO₂ substitution, compared with HLG of BDT without substitution of these functional groups have been reproduced by our present theoretical calculations and thus the applicability of our methodology is validated. These theoretical results will be helpful to design and fabricate future molecular electronic devices and circuits.

References

- [1] Q. David, R. C. R. Andrews, P. Van Duyne, M. A. Ratner, *Chem. Phys.* **125** (2006) 174718
- [2] C. Kergueris, J. P. Bourgoin, D. Esteve, C. Urbina, M. Magoga, C. Joachim, *Phys. Rev. B*. No. **19** (1999) 12505
- [3] J. J. Palacios, A. J. Perez-Jimenez, E. Louis, E. Sanfabisan, A. Verges, *J. Phys. Rev. B.* **66** (2002) 035322
- [4] S. T. Pantelides, M. Di Ventra, N. D Lang, *Physica B* **297** (2002) 72
- [5] S. Datta, W. Tian, S. Hong, Reifengerger, J. I. Henderson, C. P. Kubiak, *Phys. Rev. Lett.* **79** (1997) 2530
- [6] M. Q. Long, K. Q. Chen, L. Wang, *Appl. Phys. Lett.* **91** (2007) 233512
- [7] Y. W. Kim, S. K. Kwon, K. S. Kim, *Phys. Rev. B* **76** (2007) 033415
- [8] E. W. Wong, C. P. Collier, M. Belorady, *J. Am. Chem. Soc.* **122** (2000) 5831
- [9] F. Zahid, M. Paulsson, S. Datta, *Advanced Semiconductors and Organic Nano-Techniques*, Ed. H. Morkoc, Academic Press (2003)
- [10] H. Taylor, G. J. Wang, *Phys. Rev. B* **63** (2001) 245407
- [11] Y. Xue, S. Datta, M. A. Ratner, *Chem. Phys.* **281** (2002) 151
- [12] S. Datta, *Quantum Transport: Atom to Transistor*, Cambridge University Press, Cambridge (2005)
- [13] S. Datta, *Electronic Transport in Mesoscopic Systems*, Cambridge University Press, Cambridge (1995)
- [14] M. J. Frisch, G. W. Trucks, H. B. Schlegel *GAUSSIAN 03*, Revision E.01 Gaussian Inc., Wallingford CT (2004)
- [15] A. D. Becke, *Phys. Rev. A* **38** (1988) 3098
- [16] A. D. Becke *Chem. Phys.* **98** (1993) 5648
- [17] J. P. Perdew, Y. Wang. *Phys. Rev. B* **45** (1992) 13244
- [18] L. Venkataraman, J. E. Klare, *Nano Lett.* **6** (2006) 458