Transport propreties of organic single electron transistor ; dependence on acene length

A.Nasri[1], A.Boubaker[1], W.Khaldi[1], B.Hafsi[2], and A.Kalboussi[1]

[1]*University of Monastir, Faculty of Science of Monastir, Microelectronics and Instrumentation Laboratory, Avenue de l'Environment -5019, Monastir, Tunisia*

[2]*CNRS, Centrale Lille, ISEN, Univ. Valenciennes, UMR 8520-IEMN, Univ. Lille, 59000 Lille*

***Abstract*—In this work, we have studied the transport properties of the single molecule transistor using Atomistix ToolKit (ATK) simulators. We have applied the extended Huckeltheory (EHT) coupled with non-equilibrium green's function (NEGF) formalism. We have investigated the rings number effect of three polycyclic aromatic hydrocarbons (PAHs) on the transport properties. In addition, we have confirmed that our device operates as a Molecular Single Electron Transistor. The presence of Coulomb blockade phenomena has been also outlined.**

Keywords-single molecule transistor, single electron transistor organic electronic device.

I. INTRODUCTION

The size of conventional silicon-based electronic devices will soon be more and smaller that quantum effect, for example, electron tunneling and quantization of energy will begin to impact and eventually limits the device functionality. A great part of the research work completed of organic semiconductors have produced critical interest for the academic community and scientific research [1]–[9]. The continuing miniaturization with a scaling down of electronic devices may eventually need the utilization of single atoms or molecules as an active electronic components in a diversity of applications. In 1974, Aviramet et al proposed theoretically the idea of electron transport in single molecule rectifying diode. On the other hand, The single electron molecular transistor (SET), which builds from the bottom up approach utilizing a single organic molecules as an active component, has been considered as a potential building block for future nano-electronic systems.

Theoretically, electron transport can be generally distinguished within two limiting regimes, namely, coherent transport (CT) for strong coupling between the molecule and electrodes and coulomb blockade (CB) for weak coupling. However, in case of molecular SET, transport is incoherent. The first single-molecule transistor was fabricated in 2000 [10],it was achieved using a single C60 molecule bridging source and drain electrodes. In addition, Parashara et al studied the effect of electrostatic environment in molecular energy levels of single-molecule transistors based on three polycyclic aromatic hydrocarbons (anthracene, tetracene and pentacene) [11]. In this respect, we have used the NEGF formalism coupled with the EHT[12] [13][14] to study the electron transport of the device. The semi-empirical method using extended Huckel theory is computationally flexible compared to ab initio/DFT and it is able to calculate properties of nano-scale systems. We studied the I_V and conductance characteristics of a single molecule transistor based three different molecules. We have investigated additional properties in the I–V characteristics of MSET such as the coulomb Staircase.

II. COMPUTATIONAL MODELS AND METHODS

In our modeling of the Molecular Single Electron Transistor (MSET), we have used an Atomistic Tool-Kit (ATK) simulator [15]. In particular, we have studied and modulated the electron transport of MSET device. The electrode Poisson solver calculations are carried out with boundary conditions as periodic and the Brillouin zone integration is carried out with 1x10x100 k-point sampling. The electron temperature is taken as 300 K. For computing electrostatic potentials, we have used a real space grid, with mesh cutoff energy equal to 75 Hartree. The source and drain electrodes are extracted along (111) direction of bulk. The optimization of the total energy of the overall geometry configuration gives a fix distance between the electrodes. The large supercell dimension is taken in the perpendicular direction of electron transport there is no interaction or less between the molecule and their mirror. Also, we used as 24 A° the size of the supercell in the y-direction.

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we have used NEGF formalism coupled with the extended Huckeltheory (EHT) which is implemented in Atomistix ToolKit package to calculate the transport properities[16][17]

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In a similar manner as described in [18][17], To calculate the transport properties of each system consisting of left (source) and right (drain) electrodes and the scattering region. We need for calculating current for a device with arbitrary channel material is transmission function T(E). Non Equilibrium Greens Function (NEGF) formalism provides a well-defined way for calculating T(E). It has been detailed by S. Datta et al.[19]. The transmission coefficient, T(E), for electrons of energy E (passing from the source to the drain) is calculated via the relation:

$$T(E,V) = T_r[\tau_R(E,V)Gc(E,V)\tau_L(E,V)G_c^+c(E,V)] \quad (1)$$

In this expression, describes the level broadening due to the coupling between left (L) and right (R) electrodes and the central scattering region (S). The sum represents the retarded self-energies associated with this coupling.

In a similar manner as described in [20], using the obtained transmission coefficient, T(E), which is usually voltage dependent as well as energy dependent.

The conductance could be calculated by the Landauer formula, $G = G_0 \int dET(E)\left(\frac{-\partial f}{\partial E}\right)$, where $G_0 = \frac{2e^2}{h}$ is the conductance quantum. In addition, the zero-bias current through the device at voltage V could be calculated as:

$$I = \frac{2e}{h}\int_{-V/2}^{+V/2} T(E,V_G)[f(E-\frac{V}{2}) - f(E+\frac{V}{2})dE \quad (2)$$

Where is $f_\alpha(E) = \frac{1}{1+exp\left(\frac{E-E_F}{K_BT}\right)}$ the Fermi–Dirac distribution function, T is the temperature, V_G is the gate voltage and $k_B = 8.6 \times 10^{-5}$ eV/K is Boltzmann's constant. Under non-equilibrium conditions, the Ids–Vds characteristic could be calculated from the voltage-dependent transmission, T(E,Vds), as

$$I = \frac{2e}{h}\int_{-\infty}^{+\infty} T(E,V_{DS})[f_S(E) - f_D(E)dE \quad (3)$$

Where the $f_{S,D}$ are the electrochemical potential in the drain and source.

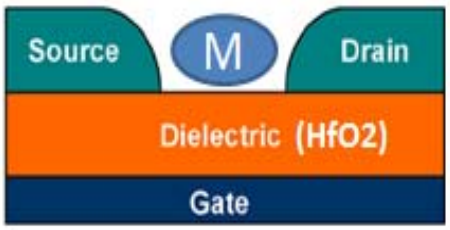

FIGURE 1 MSET STRUCTURE.

Our device configuration consists on a pentacene molecule setup above dielectric in a SET geometry as shown in Figure.1. The molecule bridged between source-drain Au electrodes, the distance between the molecule and the electrode was kept 2.8 Å. The absence of any direct electrical contacts to molecule, finite conduction in such a SET occurs through the process of sequential tunneling. Tunneling creates that barrier (like a depletion region). The Coulomb repulsion between the charge carriers maintain this segregation, giving rise to the isolation/island between source and drain. A metallic back-gate was used with 3.8 Å of dielectric material HfO2 (ε= 25) due to its electrical properties [21].

The anthracene, tetracene and pentacene are p-type semiconductors. This organic compound of formula $C_{14}H_{10}$, $C_{18}H_{12}$ and $C_{22}H_{14}$ respectively. They belong to the family of acenes, polycyclic aromatic hydrocarbons (PAHs) with three, four and five benzene rings as indicated in Figure 2. They are of conjugated molecule are used in technological applications for the development and use of carbon-based materials in microelectronics. These materials grown dramatically in recent years, it has interesting transport properties as well as stability exceptional high charge carrier mobility, and a good on–off ratio[22] [23] [24][25].

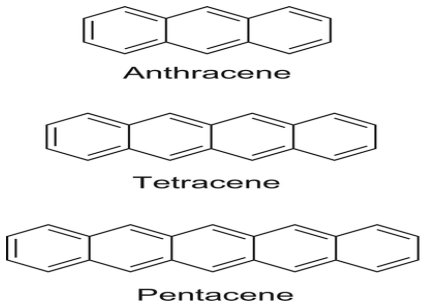

FIGURE 2 ANTHRACENE , TETRACENE AND PENTACENE MOLECULES

Table 1 show the molecules properties for anthracene, tetracene and pentacene. We note, when we increase the benzene rings, the "gap decreases.

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TABLE I. MOLECULES PROPERTIES FOR ANTHRACENE, TETRACENE AND PENTACENE

	Number of rings	Gap eV	dimensional 2D
Anthracene	3	3.9	~9.23 Å x4.9 Å
Tetracene	4	3.1	~11.7 Å x4.9 Å
Pentacene	5	2.01	~ 14.11 Å x4.9 Å

To better understand the current (I) vs. voltage (V) curve for a molecular conductor is to draw an energy level diagram and locate the Fermi energy. A molecular channel must have an energy spectrum which is separated into three bands at the beginning state. The valence band of an inorganic semiconductor corresponds to the highest occupied molecular orbital (HOMO), while the lowest unoccupied molecular orbital (LUMO) represents the conduction band (the difference between the energy levels of the HOMO and LUMO).

The molecular single electron transistor has an energy level diagram as illustrated in Figure.3. When a positive voltage V is applied externally to the drain with respect to the source, then the drain has an electrochemical potential lower than that of the source by eV : $\mu 2 = \mu 1$-eV.

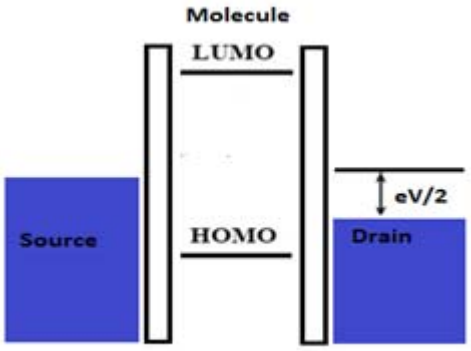

FIGURE 3 ENERGY LEVEL DIAGRAM OF MSET STRUCTURE.

III. RESULTS AND DISCUTION

To describe charge transport in a molecular single-electron transistor (MSET), the change of electron number was taken into account. In equilibrium condition, absent current. The Fermi energy is usually positioned in the gap between the HOMO and the LUMO in our model. The applied voltage effect on the electrode electrochemical potential, the Fermi energy in the source contact (μS) increase by (qV_{DS}) relative to the Fermi level in the drain contact (μ_D). As a result, when the bias voltage is large enough, one or more of the molecular energy levels be positioned between μS and μ_D, this condition, lead to the conduction of the molecule. Consequently, the conductance gap is a reflection of the energy that is required to add an electron to the molecule (or to remove one from it). Electrons tunnel one by one in and out of the molecular "island" (or quantum dot, QD) due to electrostatic repulsion when the molecule is occupied by one electron, that is, due to Coulomb blockade. These types of devices are called (molecular) single electron transistors (SET's). We can change the charging energies, electron transport, and the area where Coulomb blockade appears just by changing the molecule.

Martin-Lasanta et al recently found that on grow the number of rings in polycyclic aromatic hydrocarbons (PAHs) will give higher conductivity as well as mechanical and current stability [26]. Motivated by this, we have used ATK simulators to calculate the I-V characteristic of three molecules namely anthracene, tetracene and pentacene of acne series in the SET environment to confirm Martin-Lasanta results.

The different energy levels containing π and π^* bonds will form energy levels specific to the organic molecule (HOMO and LUMO). The energy levels of the HOMO or LUMO band are discrete from where the conduction increases. Moreover, the increase in the number of atoms constituting the molecule is large or monomer causes the increase in the number of molecular energy levels π which contributes the decrease of the "gap" between the levels LUMO and HOMO, show Figure 4 .

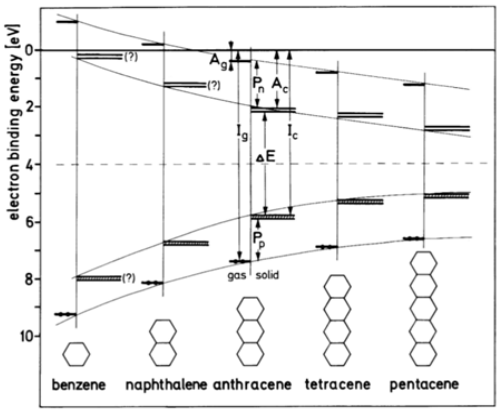

FIGURE 4 ENERGY SCHEME OF THE ACENE FAMILY [26]

The result of simulating a single molecule in a SET environment with three different molecules (Anthracene, Tetracene and Pentacene) has been investigated. The effect number of aromatic rings on addition energy, which has a great effect on the I-V and conductance characteristic has been demonstrated.

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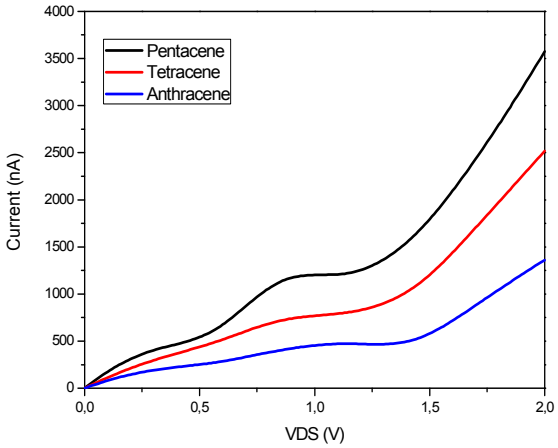

FIGURE 5 CURRENT-VOLTAGE (I-V) CHARACTERISTIC OF A MOLECULAR SINGLE ELECTRON TRANSISTOR WITH: TETRACENE (RED LINE), ANTHRACENE (BLUE LINE), AND PENTACENE (BLACK LINE).

Consequently, when the aromatic ring number increasing, the addition energy value reduces which indirectly affect the conductivity of the system. This is in correspondence with a HOMO - LUMO gap. Since the barrier of electron transfer is approximately proportional to the HOMO-LUMO gap[1], therefore in SET environment, the current increased with increasing the number of aromatic rings of the molecule as illustrated in Figure 5. Accordingly, the magnitude of the current through the pentacene molecule is larger than an anthracene and tetracene molecule MSET case.

We find that the simulated device operates as a Single electron transistor with conduction based on the Coulomb blockade phenomenon allowing the transit of electrons sequentially. The characteristic of the MSET presents a coulomb Staircase state. In addition, the conductance curves illustrated in Figure.6 present the corresponds of the I-V characteristic.

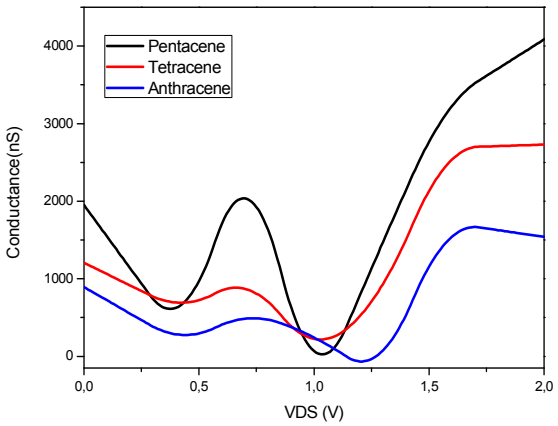

FIGURE 6 CONDUCTANCE (DI/DV) CHARACTERISTIC OF A MOLECULAR SINGLE ELECTRON TRANSISTOR WITH: TETRACENE (RED LINE), ANTHRACENE (BLUE LINE), AND PENTACENE (BLACK LINE).

Our results, give us a better understanding of the relationship between the molecular electronic structure and the transport properties. It confirms that on grow the number of rings in polycyclic aromatic hydrocarbons (PAHs) lead to higher conductivity as well as mechanical and current stability. Using pentacene MSET give us an on/off ratio more height than anthracene, tetracene MSET.

CONCLUSION

In summary, the electronic transport of the Molecular single electron transistor has been theoretically simulated using the non-equilibrium Green's function (NEGF) formalism coupled with the extended Huckel theory (EHT). Also, the I-V and conductance characteristics have been demonstrated for three molecules. We conclude that the addition energy reduces with the increasing of aromatic ring number, it has indirectly effect the conductivity of the system. We confirmed Coulomb blockade phenomenon in this single molecular device with the presence of the coulomb Staircase with three molecule cases. The pentacene molecule gives us an interesting results on stability and On/Off ratio. it can be a good candidate to realize a SET device.

REFERENCES

[1] J. M. Seminario, A. G. Zacarias, J. M. Tour, R. U. V, M. Street, R. V August, V. Re, M. Recei, and V. January, "Theoretical Study of a Molecular Resonant

978-1-5090-6778-7/17/$31.00 ©2017 IEEE

Tunneling Diode," no. 7, pp. 3015–3020, 2000.

[2] J.-M. Verilhac, "Recent developments of solution-processed organic photodetectors," in *2012 International Semiconductor Conference Dresden-Grenoble (ISCDG)*, 2012, pp. 101–106.

[3] M. R. S. Siqueira, S. M. Corrêa, R. M. Gester, J. Del Nero, and A. M. J. C. Neto, "Single-molecular diodes based on opioid derivatives," *J. Mol. Model.*, vol. 21, no. 12, p. 317, Dec. 2015.

[4] C. Tan, Z. Liu, W. Huang, and H. Zhang, "Non-volatile resistive memory devices based on solution-processed ultrathin two-dimensional nanomaterials," *Chem. Soc. Rev.*, vol. 44, no. 9, pp. 2615–2628, 2015.

[5] W.-J. Yu and N.-P. Wang, "Effects of a single defect in composite gate insulators of carbon nanotube transistors," *Eur. Phys. J. B*, vol. 87, no. 10, p. 233, Oct. 2014.

[6] S. Yamada, C.-H. Shim, T. Edura, A. Okada, C. Adachi, S. Shoji, and J. Mizuno, "Fabrication of bottom-emitting organic light-emitting diode panels interconnected with encapsulation substrate by AuAu flip-chip bonding and capillary-driven filling process," *Microelectron. Eng.*, vol. 161, pp. 94–97, Aug. 2016.

[7] D. Xiang, X. Wang, C. Jia, T. Lee, and X. Guo, "Molecular-Scale Electronics: From Concept to Function," *Chem. Rev.*, vol. 116, no. 7, pp. 4318–4440, Apr. 2016.

[8] R. R. Nejm, A. I. Ayesh, D. A. Zeze, A. Sleiman, M. F. Mabrook, A. Al-Ghaferi, and M. Hussein, "Electrical Characteristics of Hybrid-Organic Memory Devices Based on Au Nanoparticles," *J. Electron. Mater.*, vol. 44, no. 8, pp. 2835–2841, Aug. 2015.

[9] C.-S. Lee, E. Pop, A. D. Franklin, W. Haensch, and H.-S. P. Wong, "A Compact Virtual-Source Model for Carbon Nanotube FETs in the Sub-10-nm Regime—Part I: Intrinsic Elements," *IEEE Trans. Electron Devices*, vol. 62, no. 9, pp. 3061–3069, Sep. 2015.

[10] P. L. McEuen, H. Park, J. Park, A. K. L. Lim, E. H. Anderson, and A. P. Alivisatos, "No Title," *Nature*, vol. 407, no. 6800, pp. 57–60, Sep. 2000.

[11] S. Parashar, P. Srivastava, and M. Pattanaik, "Renormalization of Molecular Energy Levels in Single-Molecule Nanojunctions: An Ab-initio Approach," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 73, p. 12117, Feb. 2015.

[12] R. Hoffmann, "An Extended Hückel Theory. I. Hydrocarbons," *J. Chem. Phys.*, vol. 39, no. 6, pp. 1397–1412, Sep. 1963.

[13] H. Raza and E. C. Kan, "An atomistic quantum transport solver with dephasing for field-effect transistors," pp. 2–6, 2006.

[14] A. Zahir, A. Pulimeno, D. Demarchi, M. R. Roch, G. Masera, M. Graziano, and G. Piccinini, "EE-BESD: molecular FET modeling for efficient and effective nanocomputing design," *J. Comput. Electron.*, vol. 15, no. 2, pp. 479–491, Jun. 2016.

[15] "'Atomistix Virtual Nanolab, QuantumWiseInc.'"

[16] Q. a/S, "Atomistix ToolKit Modeling of nanoelectronic devices," pp. 1–72, 2013.

[17] A. Mahmoud and P. Lugli, "First-principles study of a novel molecular rectifier," *IEEE Trans. Nanotechnol.*, vol. 12, no. 5, pp. 719–724, 2013.

[18] S. J. Ray, "Sensors and Actuators B : Chemical First-principles study of MoS 2 , phosphorene and graphene based single electron transistor for gas sensing applications," *Sensors Actuators B. Chem.*, vol. 222, pp. 492–498, 2016.

[19] S. Datta, *Quantum Transport : Atom to Transistor*. 2005.

[20] P. F. Bagwell and T. P. Orlando, "Landauers conductance formula and its generalization to finite voltages," *Phys. Rev. B*, vol. 40, no. 3, pp. 1456–1464, 1989.

[21] A. Nasri, A. Boubaker, B. Hafsi, W. Khaldi, A. Kalboussi, C. Lille, and L. L. France, "TUNING NEGATIVE DIFFERENTIAL RESISTANCE IN A SINGLE MOLECULE TRANSISTOR : DESIGNS OF LOGIC GATES AND EFFECTS OF VARIOUS OXYGEN- AND HYDROGEN-INDUCED DEFECTS," *DIG J Nanomater BIOS*, vol. 12, no. 1, pp. 99–110, 2017.

[22] H. Wang, J. S. Lim, C. Lee, and D. W. Kim, "Anthracene Derivatives Substituted with Phenyl or Pentafluorophenyl for Organic Thin Film Transistors," pp. 4532–4539, 2011.

[23] W. Kang, G. An, M. J. Kim, W. H. Lee, D. Y. Lee, H. Kim, and J. H. Cho, "Ladder-Type Silsesquioxane Copolymer Gate Dielectrics for High-Performance Organic Transistors and Inverters," *J. Phys. Chem. C*, vol. 120, no. 6, pp. 3501–3508, Feb. 2016.

[24] P. Rotter, B. A. J. Lechner, A. Morherr, D. M. Chisnall, D. J. Ward, A. P. Jardine, J. Ellis, W. Allison, B. Eckhardt, and G. Witte, "Coupling between diffusion and orientation of pentacene

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molecules on an organic surface," *Nat. Mater.*, vol. 15, no. 4, pp. 397–400, Feb. 2016.

[25] J. Krüger, N. Pavli, J. M. Alonso, D. Perez, E. Guitian, T. Lehmann, G. Cuniberti, A. Gourdon, G. Meyer, L. Gross, F. Moresco, and D. Peña, "Tetracene Formation by On-Surface Reduction," 2016.

[26] A. Martín-lasanta, D. Miguel, T. García, J. A. López-villanueva, S. Rodríguez-bolívar, F. M. Gómez-campos, E. Buçuel, D. J. Cµrdenas, D. Cienfuegos, and J. M. Cuerva, "Influence of the Number of Anchoring Groups on the Electronic and Mechanical Properties of Benzene- , Anthracene- and Pentacene-Based Molecular Devices," pp. 860–868, 2012.

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