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Molecular Electronic Devices based on Carotenoid Derivatives

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***Abstract*—**The production of devices in nanoscale with specific molecular rectifying function is one of the most significant goals in state-of-art technology. In this work we show by ab initio quantum mechanics calculations coupled with non-equilibrium Green function, the design of an organic two-terminal device. These molecular structures have molecular source and drain with several bridge length (from five up to 11 double bonds). Our results are consistent with significant features as a molecular rectifier and can be raised up as: (a) it can be used as bi-directional symmetrical rectifier; (b) two devices integrated in one (FET with one operational region, and Thyristor thiristor); (c) Inherent stability due small intrinsic capacitance under forward/reverse bias. We utilize a scheme for the transport mechanism based on previous properties of π bonds *type* that can be successfully utilized to construct organic nanodevices.

***Keywords*—**ab initio, Carotenoid, Charge Transfer, Nanodevice

I. Introduction

SINCE the first work proposed by Aviram and Ratner [1] where a unitary molecular system with a donator (D) attached to an acceptor group (A) via a carbon bridge (σ) presenting a strong current rectification several works have been done. One of them made by Friend and collaborators [2] where organic polymer devices are constructed with a high-mobility used as field-effect transistor (FET) driving a polymer light-emitting diode (PLED) of similar size. For the FET construction was used the polythiophene derivative and mobility of 0.05 to 0.1 cm^2/V, similar of inorganic amorphous silicon FETs. Otherwise, several theoretical works pointed out perspectives of nanoscale devices [3, 4]. In these works, they raised up as a challenge the integration of nonequilibrium phenomena and of molecular-scale properties. In the other words, nanoelectronic devices must move between physics and engineering such as relation performance and power dissipation, applicability of parallelism concepts and tolerance fault, and design / fabrication of large circuits. In a previous work [5] it was pointed out that a molecular π-bridge field effect transistor presenting a new approach to investigate the electron charge flow in molecular structures.

Likewise, experimental works are available showing that organic conjugated polymers can be used as device. For instance as nano-LEDs [6], high frequency modulators [7], diode [8], wire electrochemical transistor [9] and solar cells [10].

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Although, Zhitenev et all [11] show that for organic conjugated polymers are misaligned with the Fermi level of metal contacts but suggesting an elegant experimental way based on *open design* to create a symbiosis between them.As a starting point, the application of an electric field to extract electrons from one material was evidenced initially by R. W. Wood in 1897 [12], however in 1922 the group of Millikan Norman Bridge Laboratory of Physics [13], the California Institute of Technology and the Glossling of General Electric Company [14] in London, became experimental laws that quantitative governing the extraction of electrons from metals by an external electric field through the studies of the work function of the material, but also sought to understand the electron emission through experimental results of current and voltage (I x V) related data in different ways in a straight line in regions where the current suddenly increased (break point) in a small range of electric potential on the results of electronic transport. Millikan proposed that a description for the new coordinate system adopting ln (i) xV, however, did not fit the generated graphics to a line [13].

In the present work we investigate theoretically the transport properties of organic conjugated molecules [Figure 1] where a given pair of aromatic groups is connected through the backbone of the system. Recently, similar organic conjugated materials [10] have been utilized as efficient photovoltaic material. Using *ab initio* Hartree-Fock (HF) we determine the electron charge distribution along the polymer as a function of an external voltage giving reliable information about the current vs. voltage pattern of this device family.

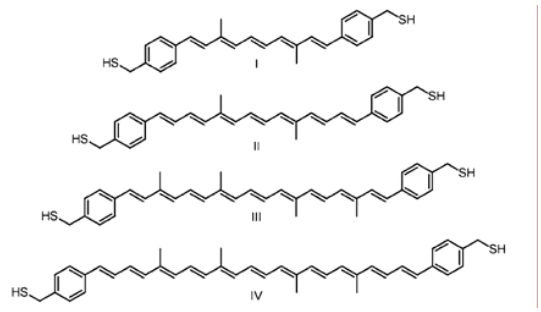

Fig. 1 Structure investigated composed by carotenoid (I), (II), (III) e (IV) representing Five, seven, nine and eleven double bonds, respectively

II. Methodology

Concerning the ab initio methodology, Hartree-Fock (HF) derivative calculation with several basis sets has been applied to obtain the current through the molecules under an external electric field. A fully optimization in a closed shell model for the Roothaan-Hall matrix was utilized: FC = SCE, where E is the orbital energy diagonal matrix, S and C are matrices corresponding to the overlap integral and to the coefficient in

the linear combination of atomic orbitals, respectively. The Fock matrix F is:

$$F_{\mu\upsilon} = \int d\upsilon \phi_{\mu} \left[-\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} \right] \phi_{\upsilon} + \sum_{\lambda=1}^{K}\sum_{\sigma=1}^{K} P_{\lambda\sigma} \left[(\mu\upsilon \mid \lambda\sigma) - \frac{1}{2}(\mu\lambda \mid \upsilon\sigma) \right] + V_{\mu\upsilon} ,$$

Where in $F_{\mu\nu}$ the terms are core energy, Coulomb and exchange interaction energy, and influence of external fields energy, respectively. The (μν|λσ) and (μλ|νσ) are 2 electrons integrals that may involve up to 4 different basis function as Φ_{μ}, Φ_{ν}, Φ_{λ}, Φ_{σ}.

Also, ***C***, ***S*** and ***E*** are coefficient matrix in the linear combination of atomic orbitals, overlap integral matrix and orbital energy diagonal matrix, respectively.

The current is calculated considering several optimized structures under the external electric field and the variation of the liquid charge takes into account all frontiers molecular orbitals for a realistic description, so that every point in the I x V curve is an independent optimization.

To gain some more insight on the physical behavior of our system we propose a simple theoretical model that qualitatively reproduces the numerical findings. We consider a source and a drain of electrons coupled to each other via localized levels in between [Figure 1]. In order to have a charge transport through the system a resonant condition is required, which means that at least one channel E_l should be below the left (E_F^L) or the right (E_F^R) Fermi energy. This condition can be achieved by applying an external bias voltage and/or a gate voltage. In general for increasing biases more levels attain resonance, thus enhancing the total current flowing in the system. The total current can be obtained from the Landauer formula (LF), which is given by:

$$I = \frac{2e}{h}\int d\varepsilon [n_L(\varepsilon) - n_R(\varepsilon)] T(\varepsilon) ,$$

where *e* is the electron charge in modulus (*e>0*), *h* is the Plank's constant, $n_{L/R}$ is the Fermi distribution function for the left (L) or the right (R) side of the molecular junction, and $T(\varepsilon)$ is the transmission coefficient through the sample. For a non-interacting system with many localized levels coupled to reservoirs we can show that the transmission coefficient is given by:

$$T(\varepsilon) = \sum_l \frac{\Gamma_0^L \Gamma_0^R}{(\varepsilon - E_l)^2 + (\frac{\Gamma_0^L + \Gamma_0^R}{2})^2} ,$$

where $\Gamma_0^{L/R}$ is the electron tunneling rate between the left/right to the central region (the carbon bridge in the present case). The sum is taken over all the localized levels.

One further assumption was made in the above transmission expression, i.e., the rates Γ_0^L and Γ_0^R are energy independent. To complete our description we need only to specify how the bias voltage drops along the system. The simplest assumption consists to take a drop as below

$$E_l = E_l^0 - x\, eV_{LR} ,$$

Where E_l^0 is the level *l* without voltage, V_{LR} is the voltage between emitter and the collector and *x* gives some bias-drop asymmetry. In particular the parameter *x* is responsible for the rectification effects seen in some of the *I-V* curves.

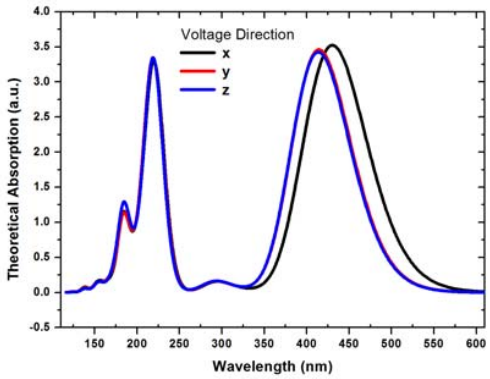

Fig. 2: Theoretical absorption spectra for carotenoid (I) under an external electric field of 0,005 a.u. in x, y, and z directions.

III. Results and Discussion

In Figure 2, it is presented the theoretical absorption spectra by ab initio methodology including configuration interaction to give the best description of the UV-Visible-IR optical transitions and taken into account from the first 10 unoccupied molecular orbitals to the last 10 occupied molecular orbitals, including singlet states. It shows three main bands centered at 180 nm, 220 nm and (410 - 450) nm. The molecular system under different external electric field rose up a *very important* pattern: When the voltage is applied in x direction (molecular backbone) a 40 nm red shift appears representing the main conduction channel for this class of material.

In Figure 3 we present the Charge Transfer - Voltage for the molecules presented in Figure 1 (Carotenoids from I to IV). The results show 3 models to represent the majority carrier as a function of external applied electric field in direct polarization. For all models, with a positive external electric field the system starts to work close to 2.0 V when all sstem align the Fermi level with conduction and valence bands showing resonance effect. Also, an unusual behavior is founded for model 2 (bridge) showing a small decrease beginning just after the resonance. This effect occurs because electron tunneling passing through the quantum wells in the central aromatic backbone.

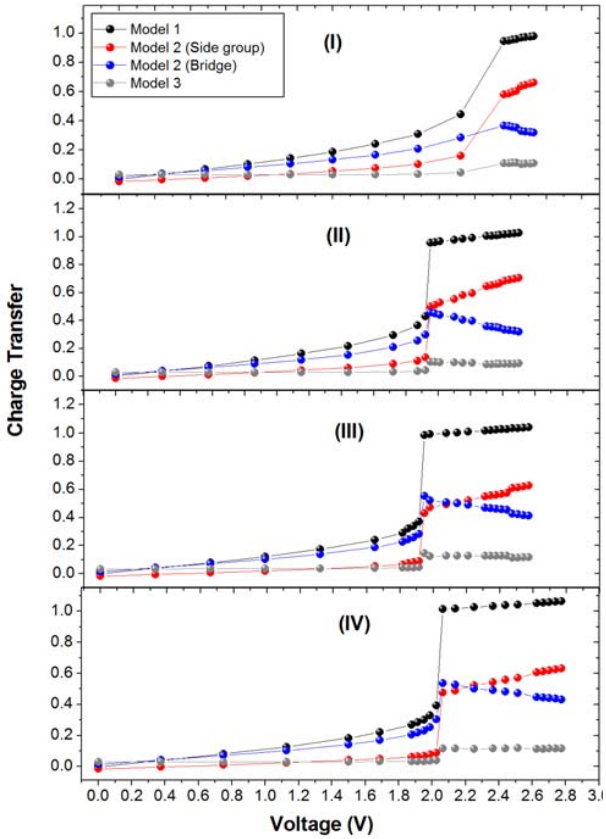

Fig. 3 Charge transfer as a function of external applied Voltage for carotenoid (I), (II), (III) and (IV) for 3 different models

This electronic characteristic is associated as an organic switch, where the ***on*** state is the electron transportation to the main molecule due the misaligning of LUMO's (Lowest Unoccupied Molecular Orbitals) states. The ***off*** state occurs when we have changes in electric field outside of working window (no electron flow to the main molecule implying in aligned LUMO's). This is corroborated when the analysis of frontier molecular orbitals as presented in Fig. 4 and Fig. 5.

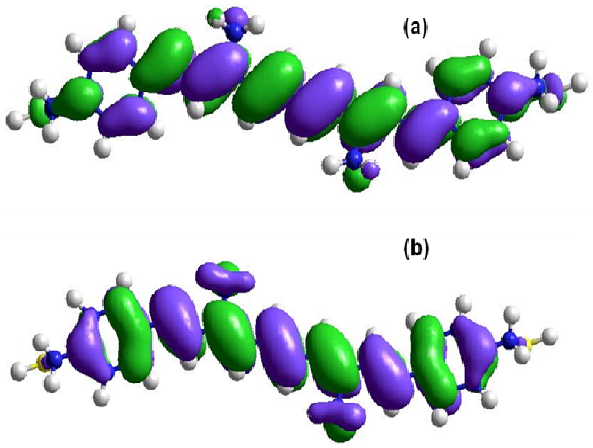

Fig. 4 Frontiers molecular orbitals without the external electric field for (a) LUMO e (b) HOMO

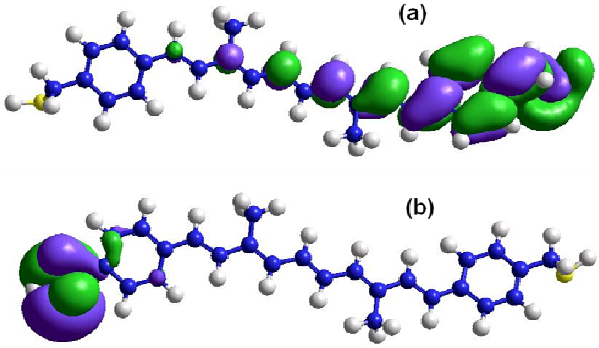

Fig. 5 Frontiers molecular orbitals with external electric field of 0.005 a.u. showing (a) LUMO e (b) HOMO

Fig 6 presents the conductance (G) for all carotenoids. The results show that when increase the number of double bonds the G decrease up to resonance be reached. This effect was first demonstrated by S.M. Lindsay [15]. Also, when G decreases as a function of with double bonds increase representing a small overlap in the frontier molecular orbitals as presented before. The efficiency of HOMO→LUMO transition has minor value for the conduction process.

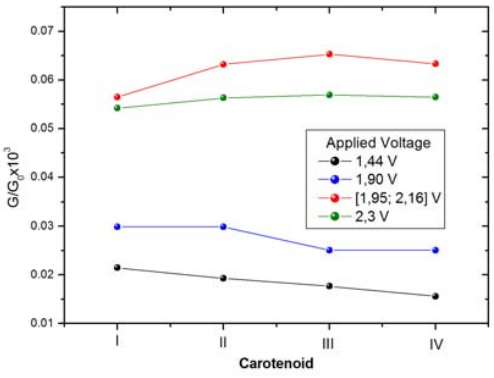

Fig. 6 Maximum of conductance for 4 carotenoids and several Voltages values

However, as typical FET (*Field Effect Transistors*), this class of device presents bi-directional electron transportation. The device patterns presented in the preceding Figures are as follow: *(i)* The system presents a resonance voltage when is established values equal to 2.0 **V**; *(ii)* For Voltages upper than 2.0 **V,** the device goes to forward conduction region; *(iii)* The conductivity of this class of device decrease with the size of double bonds.

IV. Conclusion

In this work we report theoretical design for electronic transport of an organic two-terminal device.

To conclude, we have presented the design of an organic two-terminal nanodevice that has the same electronic conduction properties presented in macro usual devices (FET, and Thyristor) in one integrated device.

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REFERENCES

[1] A. Aviram, M.A. Ratner, "Molecular Rectifier" Chemical Physics Letters 29, 277 (1974).
[2] H. Sirringhaus, N. Tessler, R.H. Friend, "Integrated Optoelectronic Devices Based on Conjugated Polymers", Science 280, 1741 (**1998**).
[3] M. Macucci, G. Iannaccone, J. Greer, J. Martorell, D.W.L. Sprung, A. Schenk, I.I. Yakimenko, K.-F. Berggren, K. Stokbro, N. Gippius, "Status and Perspectives of Nanoscale Device Modeling", Nanotechnology 12, 136 (**2001**).
[4] M. Forshaw, R. Stadler, D. Crawley, K. Nikolic, "A short review of nanoelectronic architectures", Nanotechnology 15, S220 (**2004**).
[5] A. Saraiva-Souza, R.M. Gester, M.A.L. Reis, F.M. Souza, J. Del Nero, "Design of a Molecular π-Bridge Field Effect Transistor (MBFET)". Journal of Computational and Theoretical Nanoscience. 5, 2243-2246, (2008).
[6] F. Kong, X.L. Wu, G.S. Huang, Y.M. Yang, R.K. Yuan, C.Z. Yang,P.K. Chu, G.G. Siu, "Optical emission from nano-poly[2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene] arrays", Journal of Applied Physics 98, 074304 (2005).
[7] M. Lee, H.E. Katz, C. Erben, D.M. Gill, P. Gopalan, J.D. Heber, D.J. McGee, "Broadband Modulation of Light by Using an Electro-Optic Polymer", Science 298, 1401 (2002).
[8] S. Sivaramakrishnan, P.-J. Chia, Y.-C. Yeo, L.-L. Chua, P.K.-H. Ho, "Controlled insulator-to-metal transformation in printable polymer composites with nanometal clusters", Nature Materials 6, 149 (2007).
[9] M. Hamedi, R. Forchheimer, O. Inganas, "Towards woven logic from organic electronic fibres", Nature Materials 6, 357 (2007).
[10] J. Peet, J.Y. Kim, N.E. Coates, W.L. Ma, D. Moses, A.J. Heeger, G.C. Bazan, "Efficiency enhancement in low-bandgap polymer solar cells by processing with alkane dithiols", Nature Materials 6, 497 (2007).
[11] N.B. Zhitenev, A. Sidorenko, D.M. Tennant, R.A. Cirelli, "Chemical modification of the electronic conducting states in polymer nanodevices", Nature Nanotechnology 2, 237 (2007).
[12] R. W. Wood, "A New Form of Cathode Discharge and the Production of X-Rays, together with Some Notes on Diffraction", Phys. Rev. 5, 1–10 (1897).
[13] R. A. Millikan and Carl F. Eyring, "Laws Governing the Pulling of Electrons out of Metals by Intense Electrical Fields", Phys. Rev. 27, 51–67 (1926).
[14] B. S. Gossling, "The emission of electrons under the influence of intense electric fields," Philos. Mag. 1, 609-635, (1926).
[15] J. He, F. Chen, J. Li, O.F. Sankey, Y. Terazono, C. Herrero, D. Gust, T.A. Moore, A.L. Moore, S.M. Lindsay, "Electronic Decay Constant of Carotenoid Polyenes from Single-Molecule Measurements", J. Am. Chem. Soc. 127, 1384-1385 (2005).