

Design of a Three-Terminal NanoDevice: Controlled Molecular Rectifier

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The fabrication of nanodevices with specific molecular rectifying function is one of the most significant needs in nanotechnology. In this paper we show by first principle quantum mechanics calculations, the design of an organic three-terminal device. This molecular structure has a *molecular source, drain and gate*. Our results are consistent with significant features as a controlled molecular rectifier (CMR) and can be summarized as: (i) it works as three devices *in one* integrated (TRIAC, SCR and Schottky diode) depending of operational conditions; (ii) it could be used as bi-directional rectifier; (iii) Inherent from quantum transport properties could be switched **on** without gate current (for voltages equal or lower [greater] than -3.5 V [2.0 V]); (iv) the molecular device doesn't allow depletion capacitance under reverse bias. In this work we apply a scheme for the transport mechanism based on properties of σ and π bonds *type* that can be extremely useful to construct organic devices with applications in nanotechnology.

Keywords: Source-Drain-Gate Device, Quantum Mechanics Methodology, Three-Terminal Device.

1. INTRODUCTION

Since the first molecular machine idealized by Feynman¹ where the fundamental bricks of the future engineers could be atoms to construct a complex sub- μm device, several works have been done to aim this goal. A classical device design was made presenting a strong current rectification by Aviram and Ratner in the beginning of 1970.² After that, several two-terminals nano-devices were investigated. In 1997 and 2000, Ellenbogen, Love and collaborators^{3,4} concerning nano- and molecular electronic devices, did extensive reviews.

The fundamental rule for single molecules working as devices is based on to utilize them as logic gates. Of course, to do that, it is necessary molecular rectification and the presence of three-terminals to driven the electron flow as macro-usual devices.

It is possible summarize at least five different types of electronic transfer (ETr) in nanostructure materials as:^{5–9} (I) Non-Resonant Coherent ETr: The most common situation where the Fermi level of metallic contact is inside of molecular energy gap. Generally, the conductivity exponentially decrease with the molecule length; (II) Resonant Coherent ETr: In this case, the conductance is dominated by contact scattering (length independent) and increase with the number of atomic groups

bonded; (III) Incoherent ETr: Ohmic behavior. The conductivity is length inversely dependent when aromatic rings bonds with others molecular structures. It is more efficient for long chain than non-resonant ETr; (IV) Diffusion and *Quasi*-particles formation: The main investigated system with this properties is the well-known Polyacetylene (see for example Refs. [10, 11] and references therein), where it has fundamental degenerated electronic states and the extra charge (could be *electron* or *hole*) in the structure provoke a structural deformation called as soliton (it could be a polaron by coupling kink and *anti*-kink soliton). For non-degenerate semiconducting organic polymers (as example the Poly-*para*-phenylene-vinylene derivative^{12,13}) two charges are trapped in the structure as a bi-polaron; (V) Transported ETr: When conformational changes in the molecular structure happens as well as in transfer process through ionic channels of biological systems. This effect could be designed for constructing molecular keys or gates.

Experimental three-terminal nano-device have been pointed out.^{14,15} Cecchini et al.¹⁴ showing charge transportation (acoustic type) in a device within a *n-i-n* injector junction (coupled an output Ohmic contact) and a pair of in-plane gates. The results were obtained from 5 K to room temperature showing effective charge transport until reach 120 K. At this range temperature, it has positive conclusions for the possibility of the current modulation. Oberholzer et al.¹⁵ have observed correlations

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in a multi-terminal electronic device due to interactions between different charge states. By applying an external gate voltage was demonstrated *on* and *off* states controlling the interaction inside the device.

Likewise, theoretical works pointed out perspectives of three-terminal molecular devices.^{16,17} Hliwa et al. designed a three-terminal molecular junction presenting an effect known as transduction and could be used as molecular amperometer.¹⁶ Also, was done a three-terminal carbon nanotube resonator operating with nonlinear resonance properties.¹⁷

In this work will be addressed the design of three-terminal devices by first principle quantum mechanics calculation. The next section the system employed and methodology utilized and the results and conclusions will be presented in the last two sections.

2. SYSTEM AND METHODOLOGY

Using a *Density Functional Theory* (DFT-B3PW91/6-311G) methodology to investigate the SH terminals attached in metallic atomic groups, it is possible to reach the following conclusions: (a) Au [Cu or Ag] atom attached in an organic molecule decrease [increase] the occupied frontier molecular orbital; (b) the contact of highest occupied molecular orbitals (HOMO) levels have the tendency to align the Fermi level with the increasing of metallic atoms; (c) When the metallic contact is composed by three atoms, the twisted angle between metal-molecule are 102°–104°; (d) the charge transfer between Cu or Ag [Au] and S are 0.4 e [0.17 e]; (e) the characteristic conductivity for Au atoms is stronger than Cu or Ag atoms.¹⁸ Following these clues we improve our technique to design our device.

In this work, we aggregate the third-terminal with the intention to reach out manifestations of the new transport functions unobserved in usual devices or two-terminal nano-devices. This pattern could direct be followed by the quantum nature of organic structure as a single electronic compound and as Non-ohmic behavior for molecular electronic devices. It has been recently addressed¹⁹ showing nonlinear voltage–current characteristic as an intrinsic organic thyristor.

Therefore, we investigate theoretically the transport properties of the three-terminal molecular structure depicted in Figure 1. Two parts are considered for the device as follow: (i) horizontally the gate molecular structure composed by a conjugated polymer separated by aliphatic C atoms and (ii) vertically the main rectifier molecule within donor and acceptor groups attached in the extremities.

The present methodology is based on the same scientific grounds used in successful model presented elsewhere^{20–22} because this is a general procedure to investigate nanostructured systems and it has potential

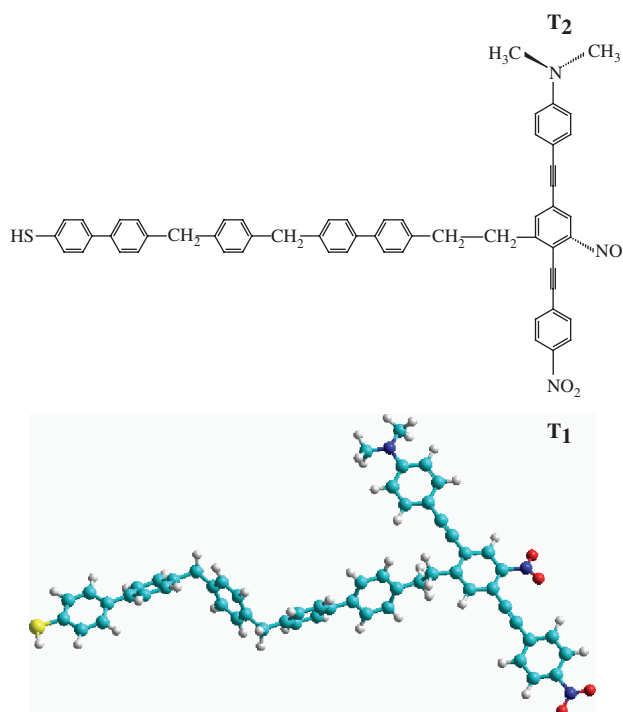


Fig. 1. (a) Structure investigated composed vertically by a bi-directional molecular diode where it has three phenyl rings bonded on acetylene, donor and acceptor groups. Horizontally, working as resonant tunnel diode composed by five phenyl rings and two aliphatic CH₂ groups provoking a quantum well in the central ring. (b) Details of the CMR structure presenting two twisted angles equal to 113°.

advantages over more usual techniques^{23,24} utilized in materials engineering design such as that involving the quantum transportation. This is the first theoretical characterization of an idealized organic three-terminal prototype nanodevice based on first principle quantum mechanics calculations.

3. RESULTS AND DISCUSSION

In Figure 2 we present the Current–Voltage for the gate molecule of the CMR device. The results show majority carriers increases as a function of external applied electric field in the reverse and direct polarization. With a positive external electric field (in Fig. 1, from left to right) only starts to work, the gate molecule, in a specific potential in between -1.54 V and 1.08 V within 0.046 e/mol and 0.131 e/mol, respectively. Also, an unusual behavior is founded in the gate molecule showing a small shoulder beginning in 0.65 V and finishing in 0.88 V, similar to RTD (*Resonant Tunnel Diode*) device. This effect occurs because electron tunneling passing through the quantum wells in the central aromatic ring. This electronic characteristic is associated as an organic switch, where the *on* state is the electron transportation to the main molecule due the misalignment of LUMO's (Lowest Unoccupied Molecular Orbitals) states. Nevertheless, the

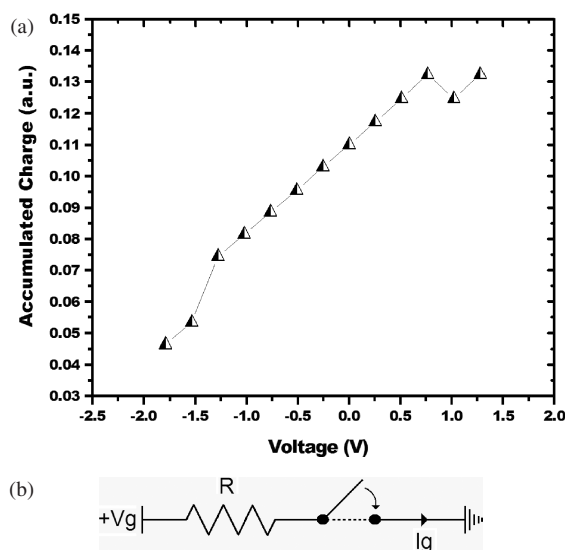


Fig. 2. (a) Characteristic *charge accumulation-Voltage* for the molecular structure investigated applying an electrical field in gate terminal (V_g , see below in Fig. 4); (b) Analogy to usual devices the gate molecule is represented, where V_g , R and I_g means the gate voltage, the total molecular resistance for majority carriers (*electrons*), and gate current representing the electronic transport tunneling through the barriers, respectively.

off state occurs when we have changes in electric field outside of working window cited above (no electron flow to the main molecule implying in aligned LUMO's).

Applying an electric field in the main molecule (vertically), we observe (Fig. 3) that under reverse and forward bias occurs electronic rectification, alternating the donor/acceptor characteristic bonded in the device border. As in Schottky diodes, the conduction is lead by the

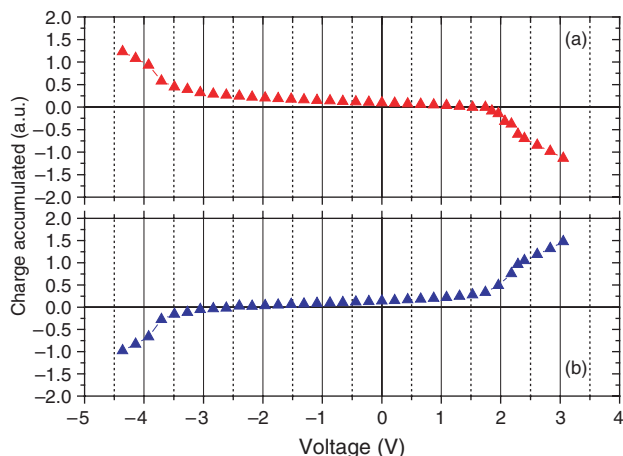


Fig. 3. Characteristic *charge accumulation-Voltage* for CMR device for (a) positive and (b) negative applied bias in T_1 - T_2 terminals (see below in Fig. 4 for terminal details). In both cases, it is present retention current because the gate current is a maximum. When an electrical field is applied in the main molecule presents a forward and reverse breakdown voltage (2.0 V and -3.5 V). The gate molecule (from Fig. 2) remains in *off* state until reach a maximum or minimum trigger voltage equal to 1.5 V and -1.8 V. After these voltages the gate goes to *on* state provoking the possibility of a bi-directional rectification on the main molecule as a DIAC (*Diode for Alternating Current*) does.

majority carriers, typically by drift transportation. However, as typical SCR (*Silicon Controlled Rectifiers*), the CMR presents bi-directional electron transportation. The device patterns presented in the Figure 3 are as follow: (i) The system presents a reverse breakover voltage ($-V_{(BR)R}$) when is established values equal to -3.50 V and -3.05 V for T_2 - T_1 and T_1 - T_2 bias voltage, respectively. This implies a similar effect as Zener device or interband transition driven by the field, a phenomenon known as breakdown voltage of *p-n* junction for semiconductor diode. Also presents a forward breakover voltage a ($+V_{(BR)F}$) equal to 1.80 V and 1.74 V for T_2 - T_1 and T_1 - T_2 bias voltage, respectively; (ii) For Voltages lower [upper] than -3.50 V [1.80 V] and -3.05 V [1.74 V] the CMR goes to reverse [forward] conduction region; (iii) The device presents two blockade regions that corresponds such as an open circuit called as the rated minimum blocking voltage (V_{RMB}) and rated maximum blocking voltage (V_{RMB}).

These results observed for CMR have particular features as: *It not presents charge retention (majority or minority carriers) by gate*. In the other words, retention current absence due maximum charge values from gate as a typical TRIAC (*Triode for Alternating Current*) does.

For any bias direction in the gate, this device could operate similarly as typical SCR device. Considering the working characteristic of this electronic device with high operational frequencies, it implies a very low reactance by $X_c = (2\pi fC)^{-1}$ (where X_c , f and C are capacitive reactance, frequency and circuit capacitance, respectively). Differently of typical *pn* semiconductor diode that presents two capacitance effects (depletion and diffusion capacitances), the CMR has only diffusion capacitances under reverse and forward bias. This behavior happens because for both applied electrical fields in the main molecule will flow majority carriers, e.g., there isn't a depletion region, even under reverse bias, indicating high charge transportation values as well as high diffusion capacitance.

Within higher charge transportation values results in lower resistance, presenting a time of $\tau = RC$, very important for devices that needs high-speed response as well as high frequency up to PHz.

4. CONCLUSION

In this work we report theoretical design for electronic transport of an organic three-terminal device and the results are indicated in Figure 4.

In Figure 4(a), we present a simple model to clears up our findings based on electronic circuit theory presenting the resistive quantum wells and the switch property over the main molecule. A resistor and a static switch compose the CMR-gate. It is possible two states: (*on* state): when is applied a voltage in gate (V_g) and the terminals (T_1 or T_2) implying in a current starting the main molecule as a bi-directional rectifier. It will be

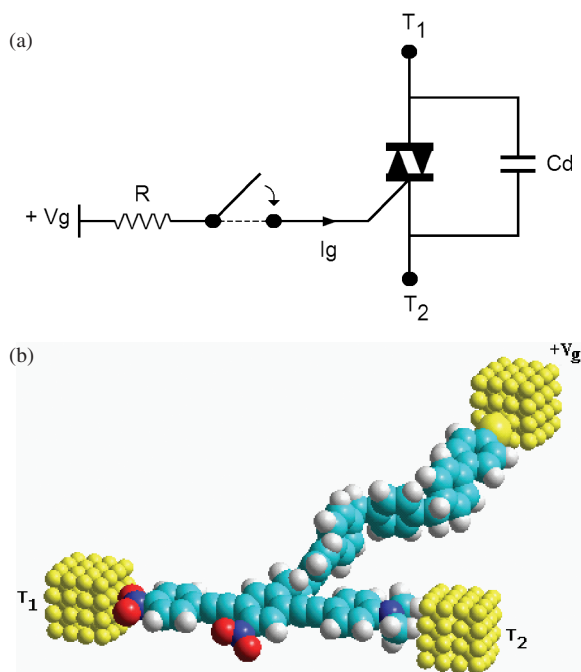


Fig. 4. (a) Equivalent circuit model adopted in this work describing the electronic transport properties of CMR. (b) Pictorial view of CMR atomic structure with its acceptor and donor intramolecular groups where T_1 , T_2 and V_g are the device terminals source, drain and gate, respectively. The main circuit is characterized to be a DIAC and a capacitive effect due the charge drift in both directions, e.g., diffusion capacitance (C_d), when the main molecule has a reverse and forward bias applied occurs charge transportation for both terminals. The carriers diffusion raise up a capacitive reactance. Also, beyond rectification, these terminals could be used to switch the circuit transporting the majority carriers playing an important role in carrying current across the junction.

polarization dependent (forward or reverse bias) as a triggering; (*off* state): when the voltage is applied between minimum blocking voltage (V_{RMB}) and maximum blocking voltage (V_{RMB}) with the gate molecule in off state. It is seen in Figure 3 as -3.5 V and 2.0 V.

In Figure 4(b) we present a pictogram representing our CMR device. In the molecular point of view, it is possible summarize CMR having an organic switch represented by the gate molecule, e.g., when it is applied a $+V_g$, the atomic orbitals (they are separated by the quantum well provoked by the σ bonds of CH_2 aliphatic molecules) aligning, provoking electronic tunneling e carrier transport to the main molecule. This additional charge flow increases the electronic transport with forward or reverse bias provoking a bi-directional rectification into T_1/T_2 terminals. Therefore, as been a quantum system, the main molecule could be working with voltages equal or above [below] to 2.0 V [-3.5 V] without the trigger of the gate molecule.

To conclude, we have presented the design of an organic three-terminal nanodevice that has the same electronic

conduction properties presented in three macro usual devices (TRIAC, SCR and Schottky diode) *in one integrated device* and we expect that efforts to synthesize the relative device become attractive to be realized.

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