



Molecular Electronics Devices: Short Review

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Molecular electronics has recently attracted a lot of attention due to promising application in nanoscale electronic devices. In this review we highlight recent results in this field, focusing on single organic molecules working as devices and addressing important effects related with electronic transport, such as push–pull molecules, σ or π bridges, Coulomb blockage, negative differential resistance, molecular radicals, temperature dependence, environment sensibility, strong and weak coupling, quantum interference, coherent and incoherent transport, tunneling regime, switches, and a few applications will be addressed.

Keywords: Molecular Electronics.

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1. INTRODUCTION: ORIGINAL PROPOSALS FOR MOLECULAR ELECTRONICS

Feynman was probably the first scientist to imagine that a molecular machine could be built, in which atoms would play the same role as the bricks of a regular size structure, composing a sub- μm device.¹ In 1974, Aviram and Ratner² were the first to suggest an organic molecular system showing current rectification, composed by a donor and an acceptor group attached by a carbon bridge with single bonds. Since them, several works have been done and many review articles related to molecular electronics as well nanoelectronics have been written, by Petty,³ Ellenborgren et al.,⁴ Merkle,⁵ Love et al.,⁶ LeClair,⁷ Heath et al.,⁸

Read,⁹ Nitzan et al.¹⁰ and Pati et al.¹¹ Book reviews covering issues related to molecular electronics have also been written.^{12–15}

Molecular electronics systems can show behaviors which are sometimes similar to regular devices: diodes, Zener diodes, field-effect transistors, thyristors, electrochromic devices and so on.^{16–19} Therefore, it offers a viable alternative to overcome difficulties associated with the continuing shrinking of electronic devices in the silicon-based technology. In this work, we present a short review of molecular electronics, focusing on the more recent work on the subject, which have not yet been covered by earlier reviews.

2. CHOOSING THE MOLECULAR STRUCTURE/BRIDGE

The first thing to deal with a possible molecular device is the molecular structure of the bridge. This includes defining several aspects of the system: σ or π bridges between a push–pull system, different bridge length and of course how these choices affect the electronic transport. Theory plays a major role in helping designing and guiding the synthesis of these organic molecules. Therefore, it is often crucial to study theoretically the electronic transport in these structures.^{20,21}

As key examples of such studies, Wu et al. did a work presenting that push–pull molecular structures could be simulated by hybrid time-dependent density functional theory, indicating that zwitterionic states assume full charge separation activating possible optically forbidden states²² and through density functional theory, organic molecules

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with sulfur attached to gold contacts were investigated, showing the possibility of asymmetric current–voltage and large rectification ratio for both bias, as well as absorption spectra showing molecular states participating of electronic transport.²³

As we mentioned, the first choice in building a molecular device is deciding if the bridge will be made of σ -, π - or both types of electronic states. There is not a single answer to that: in fact, the answer depends on what kind of possible application and effect one is trying to produce. To illustrate these issues, it is useful to consider a prototype system composed of carbon atoms and saturated bonds (alkanethiol)²⁴ without donor/acceptor radicals attached (Fig. 1 (top panel)). The chain of carbon atoms works as an insulator and the system presents rectification when the molecular dielectric is reached depending on the molecular size. It's important to mention that the electronic transport presents dependence with the attached leads (the leads will be discussed in the next section). These toy models were applied to the alkanethiol derivatives, showing bi-directional rectification response with

two operational regions and a very low commutation lost, thus suggesting potential applications for communication technologies.

Figure 1 (bottom panel)²⁴ shows the current–voltage characteristics showing typical steps associated with resonances. When $E_l = E_F^L$ or $E_l = E_F^R$ for both applied bias, resonance is achieved. The Fermi energies of both leads are also shown, where E_F^L is kept constant while E_F^R changes according to $E_F^R = E_F^L - eV$. For applied positive voltages, resonances $E_1 = E_F^L$ and $E_2 = E_F^L$ are reached around 1.2 V and 2.5 V. For an applied negative voltage shows similar behavior but the matches take place between E_l and E_F^R .

Asymmetrical behavior is obtained when a donor/acceptor is attached. No other effect is expected and rectification occurs for saturable bonds independent of the backbone size, while other predictions^{25,26} show a length dependence. Self-assembled monolayers on gold films with an induced pressure by the AFM tip can also be used to measure stepwise increases in film conductivity.²⁷ It is expected that this molecular device could be used as



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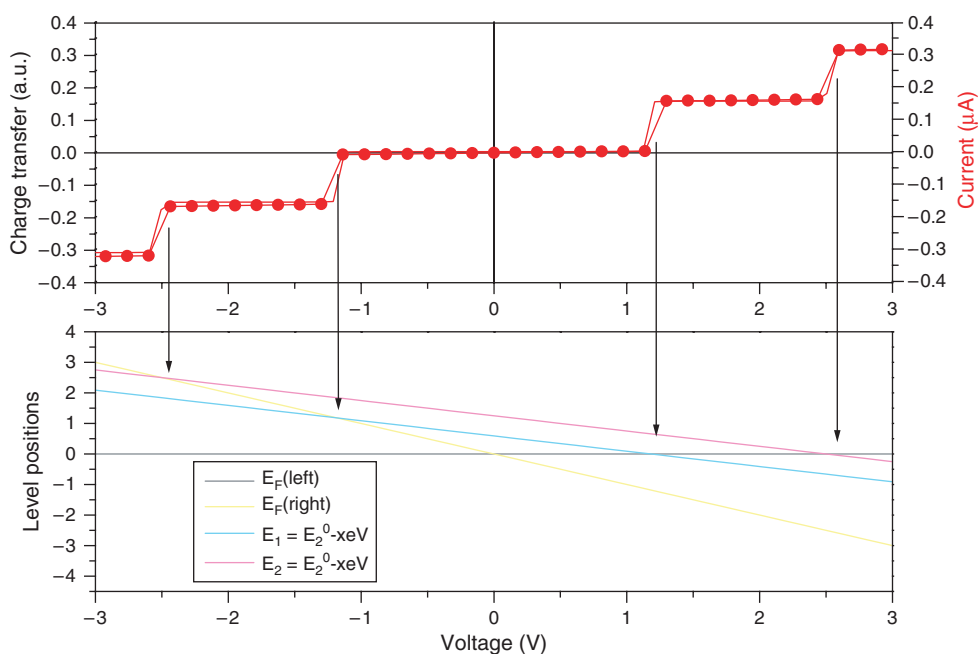
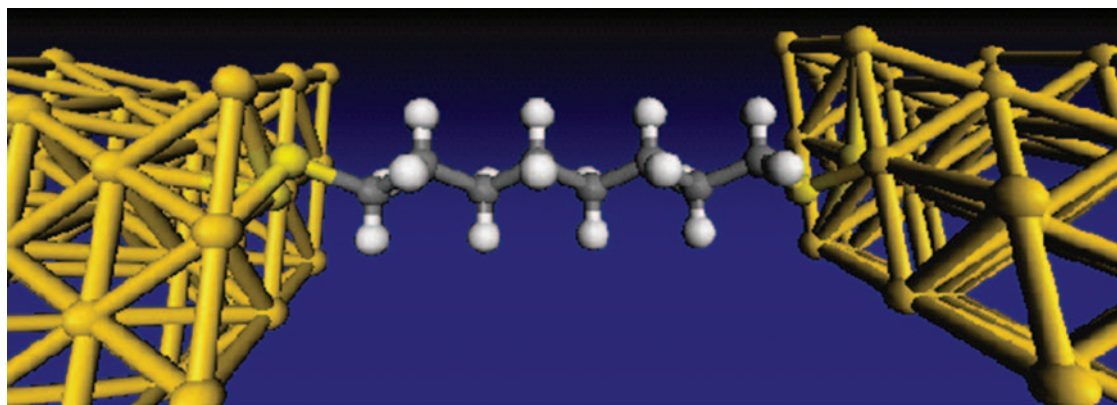


Fig. 1. (Top panel) Pictogram of structure investigated composed by a push–pull like system with saturated bonds in the bridge as Donor– σ Bridge–Acceptor. (Bottom panel) Charge transfer, current and level positions as a function of the applied external bias voltage. The results show resonances at -2.52 V, -1.21 V, 1.20 V, and 2.51 V. These resonances (indicated by vertical arrows) take place when a state E_i of the bridge matches the left or the right Fermi energy E_F , depending on the voltage sign. Reprinted with permission from [24], D. B. Lima et al., *J. Comput. Theor. Nanosci.* 5, 563 (2008). © 2008.

a bi-directional field effect transistor with two operation regions, in forward and reverse biases.

Salomon et al. have shown intrinsic temperature dependence in the transport measurements in this class of molecules (alkyl chain monolayers²⁸) when they are bound to silicon, showing that current decrease as the temperature increases. This effect could be related with adsorbed molecules increasing the film thickness, implying a wider tunnel barrier.²⁹ Also, doping on monolayers create new states between the HOMO and the LUMO, thus affecting the electronic transport.³⁰

Metzger has produced monolayers by Langmuir–Blodgett and Langmuir–Schaefer methodologies with six different donor– π or σ bridge-acceptor components (Refs. [31,32] and references therein). He shows asymmetric

conductivity as diode-like behavior between gold/molecule/gold (or aluminum/molecule/aluminum) and the electrical rectification remains intact after many cycles. In the same way, conductance of a bridge of dipyrindines separated by π - (ethene) or σ - (ethane) bridging groups sandwiched by gold contacts were carried out in aqueous solutions³³ by the STM/break junction methodology.^{34,35} As expected, for short chains the conductance is lower for dipyrindines with σ -bridge but the dipyrindines presented better conductivity than dipyrindines with π -bridge, an effect associated with the insertion of the $\text{CH}_2\text{--CH}_2$ group which increases the molecular size as well showing traces of the coupling effect for small chains.

In general, it is not straightforward to correlate the device performance and electronic carrier transporter, the

high sensibility of environment where it is constructed as example the molecular alignment. The mobility shows values up to $0.24 \text{ cm}^2(\text{V s})^{-1}$.^{36,37} Low temperatures is a different factor to preserve substrate integrity and it could be solved with the integration of device/substrate by new approaches implying low assembly capacity and high manufacturing cost.³⁸

In general, the field effect transistor (FET) signature occurs for conjugated bonds including or not explicitly the leads presenting that this procedure is a feature of the structure investigated³⁹ (Fig. 2 (Top panel)). For positive and negative applied bias the molecular structure present characteristic as usual FET with lower operational bias region. In the other words, when the Carbon atoms present conjugated bonds attached each other. It was found asymmetrical electronic transport curve with and without the presence of contacts and for donor–polyacetylene-acceptor we find out assymmetric nonresonance tunneling type conduction.

Figure 2 (Bottom panel) shows³⁹ the charge transfer as a function of voltage for the molecular system with 10 double bonds in the bridge showing that the electronic transport increases as a function of voltage under forward and reverse polarization. For positive bias presents one rectification at 2.24 V and then reaching the saturation region. In the otherwise, for negative bias presents three rectifications with similar behavior presenting an asymmetric bi-directional electronic transportation.

When *Sulfur* atoms attached in the donor/acceptor groups it observes that under forward voltage occurs rectification and the operational value have dependence with the size presenting at 1.23 V. For negative voltage occurs two competitive effects: (a) For small size show a saturation value before break the molecular structure and no present rectification (This result is not in the figure); (b) Large double bonds presents a rectification equal to 1.23 V leaded mainly by drift of having bi-directional electronic *FET* feature.

When it is considered the metallic contacts as *Aluminum* atoms under forward voltage can be summarized as: (a) For operational *forward* switch, a strong shift to lower energies occurs for rectification as 0.53 V; (b) For *reverse* switch occurs a shift to lower energies presenting values for rectification at -0.76 V . The *no step phase* could be understood analyzing the contact effects because when the charge is removed from the metal region increase the majority carrier transport (in absolute values) with the applied voltage.

A semiconducting as well resistive behaves presenting rectification as electrical feature. Also, the nonlinear signature happens with asymmetry in the current–voltage curves and bi-directional operation regions, in forward and reverse bias for donor–large heterogeneous π bridge–acceptor⁴⁰ (Fig. 3 (top panel)). This Non-ohmic behavior could direct be followed by the quantum nature of organic

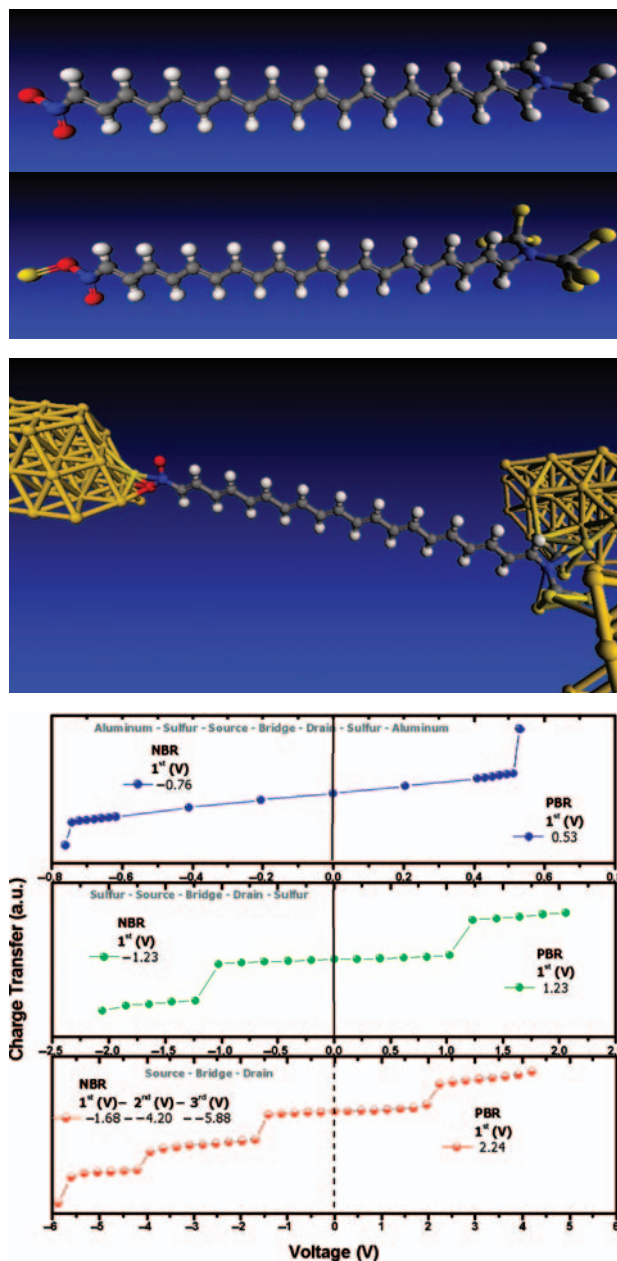


Fig. 2. (Top panel) Pictogram of molecular structure investigated composed by push–pull like system with conjugated bonds in the bridge: (top figure) Donor – π Bridge – Acceptor; (middle figure) Sulfur – Donor – π Bridge – Acceptor – Sulfur; (down figure) Metallic contact – Sulfur – Donor – π Bridge – Acceptor – Sulfur – Metallic contact. (Bottom panel) Charge transfer–Voltage for the Donor – π Bridge – Acceptor, HS – Donor – π Bridge – Acceptor – SH, and Metallic contact – S – Donor – π Bridge – Acceptor – S – Metallic contact investigated applying an external electrical field. Reprinted with permission from [39], D. B. Lima and J. Del Nero, *J. Comput. Theor. Nanosci.* 5, 1445 (2008). © 2008.

structure. The main factor for the presence of different heteroatoms is provoking levels of quantum-wells presenting a particular dependence with the model proposed to analyze the charge distribution.

Figure 3 (bottom panel) presents a system where⁴⁰ applying an external voltage in the PSS derivative molecule and

analyzing by four different models, it is observed that under forward and reverse bias occurs electronic rectification, alternating the source and drain feature bonded in the border of the device.

As typical Schottky diode by drift transportation the electronic transport is reached with asymmetric bi-directional signature it is ruled by:

- (i) For voltages upper than a specific voltage the device shows the first resonance and goes to forward conduction region as breakover voltage a for upper values;
- (ii) The device is in *off* state for values between ~ -2.1 V and ~ 2.1 V;
- (iii) For reverse voltage bias the device shows reverse conduction region with reverse breakover current when reach ~ -3.0 V as behavior of Zener diode. The dependence of model/behavior is found for value between $-\sim 2.1$ V and ~ -4.0 V.

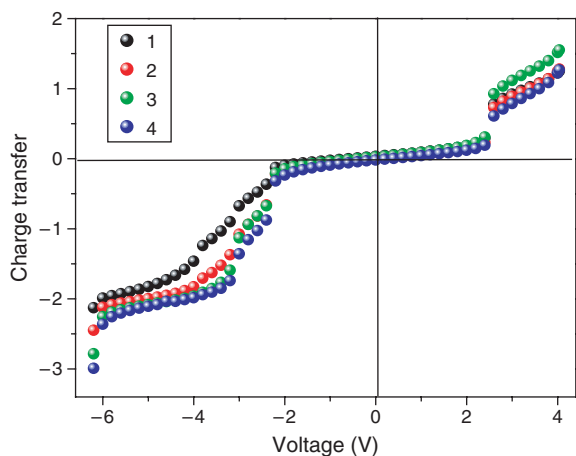
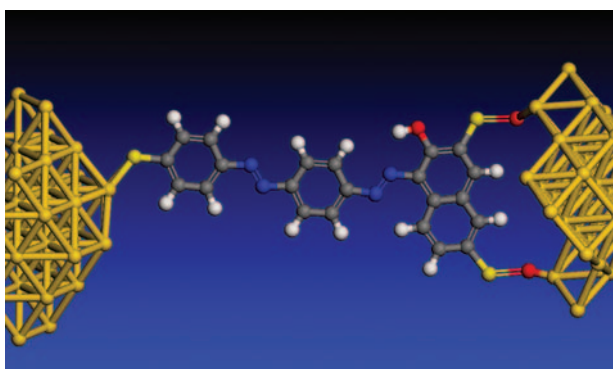


Fig. 3. (Top panel) Pictogram of PSS device investigated composed by 4 conjugated rings with azo groups in the bridge as Donor–Large Heterogeneous π Bridge–Acceptor and terminals attached. (Bottom panel) Charge transfer as a function of the voltage presenting resonant-tunneling behavior considering the effects taking into account four prominent models as: (model 1) the phenyl ring; (model 2) the phenyl ring + the first azo group; (model 3) the phenyl ring + the first azo group + the second phenyl ring; and (model 4) the phenyl ring + the first azo group + the second phenyl ring + the second azo group. Reprinted with permission from [40], S. J. S. Silva and J. Del Nero, *J. Comput. Theor. Nanosci.* 6, 490 (2009). © 2009.

3. EFFECTS OF COUPLING FOR A PUSH–PULL

New effect predicted to occur in large pyridinium betaines where have found that there is in fact an inversion of the spatial localization of the frontier molecular orbital when the bridge has a length large than 6 double bonds as:^{41,42}

- (a) “no switch” state for $n < 5$ is dominant;
- (b) switch inversion induced by the π bridge size for $n = 5$ or $n = 6$;
- (c) complete switch for $n > 6$; and
- (d) independent switch effect (*off* to *on*).

The explanation is related with resonance tunneling type conduction in the electrical properties, e.g., for forward bias the resonance takes place for high voltages when compared to the reverse bias.⁴³

Of course, to reach that specific bias value must be fixed. In this molecular family, the rectification is explained in terms of the asymmetric donor/acceptor coupling weight by the bridge as polyenic chain (unsaturated carbon bridge). Specifically for positive applied bias the current saturates near zero till the voltage reaches 0.01 atomic unit (a.u.) where a resonance takes place provoking current increases. For negative bias the current enhances near -0.005 a.u. and saturate. This molecular device could be designed as a Molecular π -Bridge Field Effect Transistor. In other words, for $n < 5$, no switching appears but for $n = 5$ or 6 a reverse switch starts to occur. Only for values larger than 6, a clear signature happens showing a full inversion and independent of the applied bias. A possible design is associated with this unusual characteristic of the inversion of frontier molecular orbitals and could be useful for the construction of Carter’s device.⁴⁴

Figure 4 (Bottom Panel) presents the charge transfer^{41–43} and current as a function of an external applied bias for small bridge size and the coupling between donor and acceptor groups is strong facilitating electrons pass directly through groups without any resonant tunneling process.

When the bridge increases in length the distance between groups also grows up and the electrons can no longer pass directly through groups and the density of states of the bridge play a crucial role in the electronic transportation working as conduction channels. Figure 4(a) (Bottom Panel) it is presented the charge transfer observing an enhancement of the charge transfer around $eV = 270$ meV and $eV = -92$ meV, thus characterizing a resonant-like transport. Quite interesting by applying the resonant model described in the preceding section, with a localized level ε_1 asymmetrically coupled to a source and a drain of electron, we obtain a I – V curve in close agreement with the charge accumulation result.

A systematic investigation of molecular level alignments as a function of electronic transport showed that conjugated molecules as bridge could be selected in at least three different groups as antiaromatic, nonaromatic, and

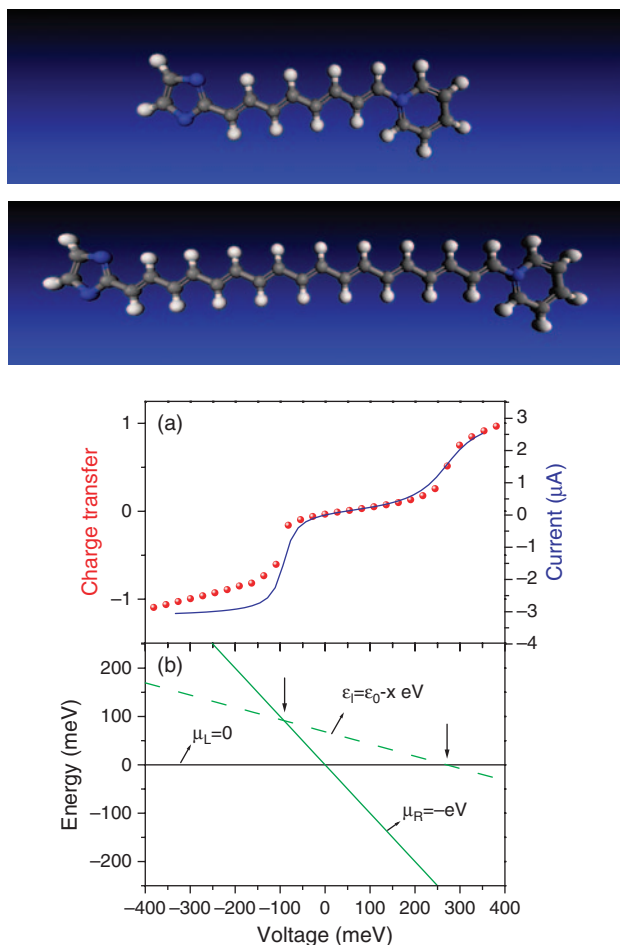


Fig. 4. (Top panel) Pictogram of pyridinium betaines investigated composed by push-pull like system with oligoacetylene in the bridge: (top figure) Four double bonds as conjugated bridge, where the charge transfer is from donor to acceptor; (down figure) Nine double bonds as conjugated bridge, where presents reverse charge transfer, from acceptor to donor. (Bottom panel) (a) Charge transfer, current and (b) level positions against the applied voltage presenting two resonances taking place when a state of the bridge matches the chemical potential of the left ($V > 0$) or the right ($V < 0$) side. The localized level ε_i and the chemical potentials $\mu_L = 0$ and $\mu_R = -eV$ as a function of voltage where resonances conditions $\varepsilon_i = \mu_L$ ($V > 0$) and $\varepsilon_i = \mu_R$ ($V < 0$) are indicated by arrows showing asymmetric resonances with respect to $V = 0$. Reprinted with permission from [41], A. Saraiva-Souza, C. P. de Melo, P. Peixoto, and J. Del Nero, *Opt. Mater.* 29, 1010 (2007). © 2007; [42], A. Saraiva-Souza et al., *J. Phys. Chem. C* 112, 12008 (2008). © 2008; and [43], A. Saraiva-Souza et al., *J. Comput. Theor. Nanosci.* doi:10.1166/jctn.2008.1136 (2008). © 2008.

aromatic units with conclusions showing that the mixing of non-/anti- increases the conductivity because the alignment of occupied orbitals are close to Fermi level.⁴⁵

Another possible effect associated with a molecular FET with strong coupling has been reported.⁴⁶ This device is composed of a donor/acceptor group (dinitrobenzene/ dihydrophenazine) coupled between an unsaturated Carbon bridge. The results indicated two effects for bridge lengths (i) up to 3 and (ii) larger than 3: (i) regular effect with homogeneous distribution of the frontier molecular

orbitals; and (ii) strong localization of the LUMOs opening a charge channel for conduction. This feature for conduction under an external applied bias is not the usual effect as previous systems with conjugated compounds of similar size. However, these results could be described by a behavior addressed as quantum interference (QI)^{47,48} (reaching two different electrical features with bridge dependence). This phenomenon of QI does not always appear experimentally at relevant energies hiding measurements of electronic transport but can be quite common cross-conjugated molecules measurements. QI in coherent transport⁴⁹ for a molecular single ring has a strong dependence on the interaction between σ -states of contact and π -states of molecule. This intensity of this effect is proportional with the size of ring, e.g., benzene presents strong π molecule- σ lead hybridization implying no QI and annulene presents weak π molecule- σ lead hybridization implying QI and could be realized as a quantum interference transistor. Utilizing a generic tight binding model to investigate cooperative effects participating in the conduction process, the main difference between the molecular layer behavior and single molecule come from the different spectral signature of the adsorbed molecule, e.g., for single molecule the conduction process is when the conduction level energy is close to the leads Fermi energies and for molecular layers the process is related with tunneling regime.⁵⁰

A 3D semi-empirical tight-binding method was utilized with open boundary conditions in the form on the scattering-boundary approach. As 3D system, there is a possibility of transport analysis along any direction of the structure and it can be formulated in the non-equilibrium Green's function or for any channel orientation.⁵¹

The property of electrical resistance of conjugated polymers has been theoretically^{52,53} and experimentally⁵⁴ analyzed and investigated as their use as molecular small⁵⁵ and long (up to 7 nm)⁵⁶ wires. Results indicate that for long molecular bridges, the charge transport mechanism changes from direct tunneling to hopping, as evidenced by a change in the length dependence of the electron transfer rate constant. The main conduction mechanism is hopping and tunneling for long and small bridge size, respectively. Also, it is important take into account that simulations present results where the efficiency for the electron injection is almost 99% and junctions effects could not be responsible for the activated transport. In the same way, similar procedure has been successfully used and these transport models are based on a ballistic resonant tunneling transport through localized levels weakly or strongly coupled to the reservoirs with possibility of ignoring molecular charging effect, because the fast electronic switching on the molecular structure, so the transport can be associated only to electronic molecular structure.⁵⁷ Of course, this issue deserves further investigation, the device operation in these days is around 4 GHz for Silicon and scaling down to organic could provide increase a continuing increase in the clock speed.⁵⁸

4. WALKING INTO CIRCUIT DIRECTION: MORE THAN TWO TERMINALS

A few papers have been published concerning the possibility to reach out several terminals. One of them⁵⁹ shows for 3 terminals the necessity of the gate should be a molecular resistive quantum well permitting the switch property over the main molecule (main gates) Figure 5 (Top panel). To reach *on/off* states implying a current starting in the main molecule as a bi-directional rectifier the gate should have an applied voltage. It will provoke polarization dependence for direct and reverse bias as a triggering. Otherwise, the all system will work in *off* state when the voltage is applied between minimum blocking voltage and maximum blocking voltage with the gate molecule in *off* state. It is possible to understand that analyzing the atomic orbitals where there is quantum well due the presence of aliphatic molecules presents in the molecular structure aligning electronic tunneling and charge flow to the main gate. Another possibility (not possible in regular macro devices) is when the main gates reach the working state with voltages equal or above [below] to a specific values without the trigger of the gate molecule. Overall, this device has the same electronic conduction properties presented in three usual devices as TRIAC, SCR and Schottky diode in the same single device with length \times width equal to 6.65 nm². A complementary issue is to find out the capacitive effects and it presents the same capacitive properties found in regular devices (Thyristor and Schottky diode)⁶⁰ or experimentally the capacitive coupling between the gate and organic molecule take into account voltages lower as couple Volts modulating the current by 10⁵ presenting a linear regime and hole mobilities 120 cm² (V s)⁻¹.⁶¹ Recently addressed, an intrinsic organic thyristor, showing nonlinear voltage–current characteristic was found.⁶²

Figure 5 (Bottom Panel) presents the charge transfer as a function of Voltage.^{50,60} The inset the results for the gate terminal showing majority carriers increases in the reverse and direct polarization. With a positive bias starts to work, the gate molecule, in a potential in between -1.54 V and 1.08 V within 0.046 e/mol and 0.131 e/mol, respectively. 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 Resonant Tunnel Diode because electrons tunneling quantum wells in the central aromatic ring. The *on* state is the electron transport to the main molecule due the misaligning of LUMO's states. The *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).

For the main terminals under reverse and forward bias occurs electronic rectification, alternating the donor/acceptor characteristic bonded in the device border. The conduction is lead by the majority carriers as in Schottky diodes, mainly by drift transportation presenting bi-directional electron transportation.

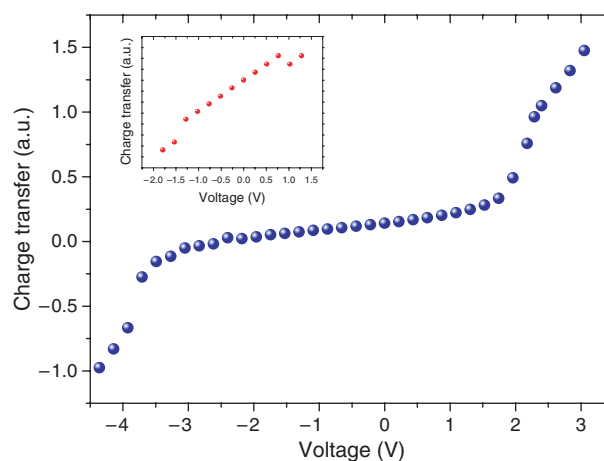
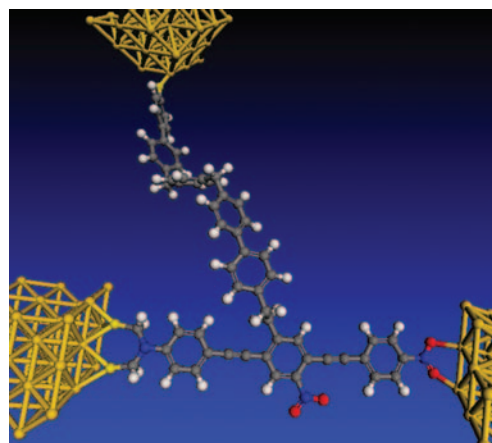


Fig. 5. (Top panel) Pictogram of controlled molecular rectifier with its acceptor and donor intramolecular groups where the device terminals source, drain and gate are left, right and top, respectively. It could be represented by bi-directional molecular diode where it has three phenyl rings bonded on acetylene, donor and acceptor groups. Horizontally, working as resonant tunnel diode composed by five phenyl rings and two aliphatic CH_2 groups provoking a quantum well in the central ring. This circuit can be represented by 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 flow for both terminals. The majority diffusion creates from a capacitive reactance. Also, these terminals could be used to switch the circuit transporting the majority carriers playing an important role in carrying current across the junction. (Bottom panel) Charge transfer-voltage for the device for positive applied voltage in the main terminals presenting retention current because the gate current is a maximum. If the voltage is applied in the main gates presents a forward and reverse breakdown voltage around 2.0 V and -3.5 V. The gate terminal 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 does. Reprinted with permission from [59], M. A. L. Reis and J. Del Nero, *J. Comput. Theor. Nanosci.* 5, 567 (2008). © 2008 and [60], M. A. L. Reis et al., *J. Comput. Theor. Nanosci.* 6, 101 (2009). © 2009.

Likewise, a three-terminal carbon nanotube resonator operating with nonlinear resonance properties was simulated.⁶³

Also the feature of gate terminal was addressed presenting steps to analyze trap states because they can to provoke

significant distortions in the electronic transport as dependence with the number of groups attached and occurrence of structural deformation.^{64,65}

By using a self-consistent Poisson-Schrödinger solver based on a two-dimensional in real space non-equilibrium Green's function approach, it is possible investigate the operational regime for 3- and 4-terminal device with gate independence.⁶⁶

5. LEADS: SYMBIOSIS BETWEEN MOLECULAR STRUCTURE AND CONTACTS

The expected situation is when the Fermi level of metallic compound is between the highest occupied molecular orbital and the lowest unoccupied molecular orbital provoking the electronic transport decreasing with the bridge length.⁶⁷ However, if the transport has no length dependent, dominated by contact scattering increasing with the number of atoms bonded. Also within conformational changes is present in the molecule, understand how it affect the electronic flow and the symbiosis with the contacts should be addressed. These structural changes can be explained by the well-known effect found in conjugated polymers as soliton,^{68,69} polaron⁷⁰ and bipolarons.⁷¹ For example, the prototype of all organic polymers, the polyacetylene presents electronic states degenerated for ground state and extra charge in the backbone provoke a bond length deformation. Also for non-degenerate organic polymers as polycarbonitrile,⁷² polypyrrole derivative⁷³ and poly-*para*-phenylene-vinylene,⁷⁴ minimums of one (polaron) and two (bipolaron) charges are well stabilized in the molecular backbone, respectively.

Also, π -conjugated molecules have been used to understand the electronic transport in molecular junctions⁷⁵ presenting weak contact. This conclusion is based on phase and amplitude investigation of frontiers molecular orbitals, HOMO and LUMO. It is used to predict the transport features with significant dependence on the type of molecule-electrodes connection. This investigation was applied for naphthalene, phenanthrene, and anthracene including their dithiolate derivatives and two gold electrodes. When *Aluminum* atoms show to be a good candidate as metallic contact when bonded with *Sulfur* atoms attached in conjugated polymers as device provoking rectification for lower values when compared with the system without Aluminum and for forward and reverse bias the resonance takes place suggesting in operational limit working as non-symmetric bi-directional molecular field effect transistor.³⁹

Competitive works where no *Sulfur* atoms (as thiol group) are used for anchoring in the junction have been made.^{76,77} Zhao et al.⁷⁶ have utilized dithiocarbamate radical to connect amines onto metal surfaces showing stability under several conditions because this form strongly absorbed molecular ligands. They claim that utilizing this methodology, dithiocarbamate group instead

of thiol group, the molecular anchoring structure to be feasibly constructed and characterized and its possibility stronger molecule-electrode coupling than the previous method. Also, this provides junctions with high conductance. On the other hand, theoretically,⁷⁷ the electronic transport of bipyridine, bipyridinium-carbodithioate and pyridyl-peridium-carbodithioate as molecular junctions shown strong molecule/electrode connection due the conjugated dithiocarbamate. This conclusion was based on the transmission resonances near the Fermi energy. The conductance increases by a factor of two tents larger for small bias. As usual, when it presents asymmetric anchoring groups, the rectification behavior appears.

Henceforth, the competition amine or thiolate group as a junction was compared utilizing *Gold* atoms as surface.⁷⁸ The main conclusion is related with the position for relate the groups and the junction showing that amines can be connected and energetically and sterically favorable on *apex Gold* atoms and the thiolate group can be well-anchored clean or under-coordinated junction with equi-probable energies. Also, they simulate a interesting conduction process when a scanning tunneling microscope *Gold* tip is utilized to measure the stretching of the thiolate and amine anchored. The thiolate is followed by distortion in the electrode geometry and the amine keep intact the tip when stretches the junction.

Also, the well-known conductive polymers are used for change the transport properties by modification as conformation of radicals⁷⁹ or adding new radicals.^{80,81} In polythiophene-wire were found signature of negative differential resistance and electrical switching provoked by the coupling junction/molecule and by the localization of conducting states along the functional polymer and their charge rearrangement under gate voltage. This system presents better switching signature than short molecules and it is explained that it can eliminate the influence of the *Gold* surface. Otherwise, the molecular distortions on the interface were investigated for tetrafluorotetracyanoquino-dimethane chemisorbed on *Copper*. In this case, the metal work function presented an increase due the molecule-to-metal back transfer provoked by molecular geometric distortions.⁸² This back transfer effect does not involve frontier molecular orbitals and was found a strong hybridization with the metal states.

Utilizing the *Pd*-dithiolated oligoaniline-*Pd* as molecular junctions⁸³ the inelastic electron tunneling (IET) spectroscopy investigated the switching mechanism reproducing the conductance measurements of switching behavior and the IET spectra.⁸⁴ The switching behavior is provoked by changes in the structure of dithiolated oligoaniline and this new conformation is due an oxidation and/or reduction process⁸⁵ but the investigated isomers (three possibilities, two symmetric and one asymmetric) shown that the chemical bonds between the *Sulfur* atom and *Pd* electrodes are weak and long bond distances for

asymmetric structure. In the other words, in this case, the conductance property is more favorable for symmetrical structure.

A method of Green's function based scattering theory model properly designed for molecule-metal junction can be applied for chemically or physically bonded molecular interfaces combined with various density functional theory approaches to model elastic/inelastic electron transport properties without need a specific functionals and basis sets to work properly.⁸⁶

The effects of the asymmetric contact in a symmetric molecule were investigated by *ab initio* methodology.⁸⁷⁻⁸⁹ The current-voltage feature shown asymmetry and the values of current as well conductance are dependent of phenyldithiolate-Gold distance at one of the two contacts.⁹⁰ This case provides weak rectification and HOMO is responsible for the resonant tunneling provoked by charge shifting of the molecular structure for the applied voltage stressing out through the asymmetric $I-V$ suggesting the importance of the interface for the electronic transport.

When a transverse magnetic field is applied the conductance for benzenedithiolate gives oscillatory behavior with flux showing flux-quantum periodicity but $I-V$ signature is equal without the presence of this magnetic field. The molecular energy eigenstates are responsible for the resonance peaks presented in the conductance and for weak coupling between metal/molecule a staircase-like behavior with sharp steps is reached. But for strong molecular coupling, the variation is continuous.⁹¹

Otherwise, the theoretical methodologies involved in the investigation of electronic transport between junctions and molecular electronic states have been criticized⁹² claiming that the usual techniques based on non-equilibrium of Landauer is not adequate. This new picture is based on a model for cotunneling coherent second-order processes in molecular wires at low temperatures and presenting as example the STM-induced dissociation of acetylene for large applied bias, where this effect is maximized and possible for measurements. This generalization of Landauer model with the inclusion of several electronic states and varying number of electrons are considered. Through that open the possibility for modeling nonadiabatic processes, electronic correlation as Coulomb blockade or Kondo effect. The modeling of Coulomb effect is effectively necessary for short-range interaction and in the presence of doping close to the channel device.⁹³

More than that, effects of vibrational motion on resonant electronic transport through molecule-junctions have been investigated^{94,95} based on a combination of *ab initio* calculations to find out geometric as well as energetic features and inelastic scattering theory to simulate transport signature. In this work, the bridge is alkanethiolate-phenyl connected with two Gold electrodes presenting a feasible rule of the vibronic coupling between the electronic π -system of the phenyl and the Gold electrodes

with influence on the transport of the molecular junction. Also, the hole transport⁹⁶ was investigated applying the similar methodology where the transport is dominated by the HOMO's of the junction. The ratio vibronic/electronic molecule-surface coupling indicates the real magnitude of vibronic effects.

The dependence of external electric field and the collected current have been analyzed showing that the methodologies utilized up to now provoke no simulation error based on mathematical analysis of polarizabilities of molecular structure. The consequence of their model is that unsubstituted chains with inversion symmetry should have a vanishing of first hyperpolarizability per unit.^{97,98} Broken mirror-symmetry could lead to a different conclusion, e.g., a clear dependence on the molecular terminations HOMO's and LUMO's well-localized and the orbitals are only close to Fermi level but not in there.

6. NEGATIVE DIFFERENTIAL RESISTANCE EFFECT

Several authors on molecular devices have recently addressed Negative differential resistance (NDR) effect.

The mechanism for NDR in molecular electronic devices was experimentally and theoretically described by local orbital symmetry between an electrode/molecule on a gold substrate and a cobalt phthalocyanines molecule. It was found tip dependence and tip geometrical shape independence for NDR: (a) occurs with Ni tips and it doesn't for W tips presenting spatial resonance and local symmetry matching of the electronic bands in the organo-metallic structure.⁹⁹

Sen and Chakrabarti¹⁰⁰ proposed four different arrangements of a trimer unit of polyacetylene (*cis* conformation) with thiol-ended showing the NDR influenced by a specific interaction possibility with the contacts as well as the disappearing in one of the arrangements. This conclusion was reached by monitoring the shift in the transmission coefficient in a specific bias window together with the analyses of self-consistent Hamiltonian states projected. This analysis gets out an unusual participation of d orbital in the formation of these states dependent of specific bias and the twisted molecular angle.

Other system with strong NDR based on benzene-dithiol and nitro-benzene-dithiol¹⁰¹ showing as bridge between Gold contacts for forward and reverse applied bias. In this case the explanation is given by the investigation of the molecular orbital feature and the NDR appearing due to the bias dependencies of the Dyson poles (ionization potentials). If no current is presented, all electronic states are populating both electrodes resulting in the vanishing tunneling probability. They find out strong gate field effect in the conductance for both positive and negative applied voltage showing fast current modulation by changing the polarity of a gate field. Also NDR

could be generated by Hubbard model treated at the HF level¹⁰² or master-equation applied for prototypical benzene molecule¹⁰³ within effect associated with increased localization of the molecular resonances and strong correlation between the coupling molecule–electrode. Henceforth, small rectification behavior for positive and negative bias and μA current level at small voltages was found out in a theoretical/experimental investigation of symmetrical molecules.¹⁰⁴

Capped carbon nanotube presents NDR effect when it is used as a contact between monatomic carbon wires but this effect is not monotonic exhibiting even–odd behavior.¹⁰⁵ If the investigated system presents *Silicon/molecule/Silicon* junction, results presents a NDR behavior.¹⁰⁶ To reach that is necessary that the LUMO had the same energy as conduction band of the lead provoking changes in the original coupling and after the orbital goes below the band edge arrainging the NDR. After increases the voltage, the system starts the tunneling process presenting increase in conduction but, at this moment, the HOMO is connected with the valence band edge.

A different experiment and model based self-consistent Hartree approximation shown the possibility of polaron formation on a molecular wire as a mechanism for switching, hysteresis and NDR feature of contact/molecule junction.^{107, 108} Based on a formalism where it is possible decoherence as the dominant mechanism of relaxation due to the injection of carriers from the leads appears NDR effect. Also it is addressed the relaxation in a ballistic resonant-tunneling rectifier and resulting steady-state current–voltage curve displaying the prominent resonant features.¹⁰⁹

A non-trivial length dependence presenting NDR in atomic molecular wires composed by structurally similar polyynes capped with benzenethiols, pyridines¹¹⁰ and thiolate¹¹¹ attached to *Gold* electrodes were investigated where the electrical conductance is higher for benzenethiol-capped than pyridine-capped chain. For thiolate unusual and high conductance due the position of the Fermi level deep in the HOMO related resonance. Also the results revealed conductance independent of molecular length up to 10 nm. The NDR signature shows LUMO/bias dependence for benzenethiols and pyridines structures and gate/bias dependence for pyridine-capped chain (it disappears when a specific gate bias is applied).

7. MOLECULAR SWITCHES

Molecular switches¹¹² where the device changes the preferential conformation have been addressed. For example, an optical switch based on phenoxynaphthacenequinone where can convert upon photoexcitation from *trans* to *ana* form presenting large current for the last. HOMO-LUMO gap is used for the interpretation of the switching behavior and this effect can be maximized if is aggregated donor

and acceptor substituents. It is expected that the switch could work at room temperature. The main reason for that is the high thermal stability of the isomers.

A *trans/cis* switch reported by Mativetsky et al.¹¹³ shows that it can be induced by light switching on/off the current in the junctions. The resistance decreases to the *cis* state provoked by a tunneling barrier length associated with the change in molecular conformation.

A molecular switch where a radical can be changed by external electric field between two symmetrical possibilities shows different conductivity characteristic for the distinguish conformers and indicating typical switching signature.¹¹⁴ So, this effect could be useful to improve switching by the inclusion of donors and acceptors groups in the backbone of the main structure.

A transverse electric field can be used to modulate the conformational changes presenting considerable effects on the electronic transport properties and applied for the well-known benzene–dithiol molecule and a tetracyano derivative. The results show that transport is low for perpendicular rings and it is more favorable for planar situation.¹¹⁵

When a molecule composes the bridge where it is possible twist from 90° to 180° the dihedral angle between the rings and symmetrical *Gold* contacts¹¹⁶ presents small projected density of states but large change into transport properties.¹¹⁷ The results at the Fermi level for biphenyldithiol molecule has a minimum transmission for dihedral angle equal to 90° and increases until reach the maximum a value ~ 100 times large for 180°.

Following similar procedure it has been demonstrated that alkynes^{118, 119} can be used for amplification of molecular potential signals into currents. The needs of increase the output is related with possible applications combine with standard devices.^{120, 121} The molecular amplification is simulated by making the output potential slightly twist the dihedral angle between two molecular rings even in the case that output with similar dihedral angles for different combinations the current yields conclusions in the way of works as FET with advantage of few *nm* as channel lengths. This dependence was comprowed by conductive probe-AFM stressing out that the HOMO was the responsible for the process following a mechanism based on coherent, nonresonant tunneling and the length of alkynes were preponderant for electronic transport in contact/molecule/contact junction within molecular resistance increases exponentially with the length.¹²²

An optical switching device can be designed by porphyrin functionalized with thiol where two possible energetically degenerate equilibrium configurations are modulates. Each equilibrium structure opens a spatially orthogonal electronic route for charge transfer. The switch is between two equilibrium positions of the molecule by coherent light and the mechanism is based on the investigation of dipole moment of different configurations and

an adiabatic two-photon process induces the isomerization process.¹²³

Applications of *Azo* compounds are well-known as pH indicator in liquid¹²⁴ or sol-gel¹²⁵ environment, as constitutive of narrow bandgap polymers,¹²⁶ as molecules with high hyperpolarizability,¹²⁷ and now it can be used to present controlled and reversible photo-switching in molecular-scale environments.¹²⁸ The single azobenzene-functionalized with tail of alkanethiolate monolayer on *Gold* surface where reversibly photoisomerized between *cis/trans* conformations by exposure to visible/UV light. Scanning Tunneling Microscopy (STM) was utilized to find out on/off states (*trans* or *cis* represented by the distance STM-surface equal to $2.1 \pm 0.3 \text{ \AA}$ and $0.7 \pm 0.2 \text{ \AA}$, respectively). STM coupled with density functional theory (DFT) has been utilized to investigate self-assembled monolayers of alkane chains on oriented pyrolytic graphite where sometimes appears uncommon spot pattern.¹²⁹ This asymmetry is linked with the minimum energy alignment dependent of the registry of the molecule adsorbate into graphite surface, generating the characteristic moiré pattern.

The process of hydrogen tautomerization in cyanine derivatives molecules can be provoked by excitation induced with inelastic tunneling current expressing a large conductivity modification as a switcher for two possible states.¹³⁰

8. BIO-MOLECULES AND NANODEVICES

Electronics based on DNA¹³¹ as a component has been manufactured presenting tunneling current under different external applied electric fields and this effect is modeled on the properties of coulomb blockade regime (P-bonds as bridge) in sugar-Phosphate backbones of single-strand DNA molecules¹³² and when the threshold level is reached the DNA-device goes to on state.

A simple method to fabricate nanoelectrodes with controlled gap size was reported where an electron induced deposition process operated in scanning electron microscopy (SEM) realizing an analysis *in situ* and real time the electrode¹³³ controlling the gap size. They have tested with carbon nanotubes + DNA molecules assembled inbetween claiming that this technique as a feasible way to construct electrodes with controlled gap size.

Modeling the effect of base sequence and structure on DNA molecular electronics was performed by self-consistent quantum molecular dynamics providing the most exothermic form. This feature reach useful information concerning electron transfer through the molecule considering the number and sign of the injected charge, the molecular structure and the base sequence.¹³⁴

A different application for the measurements of biologically relevant samples where the conductances of single amino acid residues should be addressed was proposed with two electrodes into and out of contact in a solution

while measures of the current between the two contacts during withdrawal. When biomolecules connect both contacts, steps appear in the current transient, and a statistical analysis provides the transport value for a molecule/electrode.¹³⁵

The solvation process is relatively well-known for liquid systems,¹³⁶ biological process and also should be addressed by surfaces of molecular devices. This has been done where trapping excess electrons when reacted with *hydrogen fluoride* and OH groups forming stable dipole-bound anions increasing the dipole moments.¹³⁷

9. FEW APPLICATIONS

Recently, a single organic transistor working as odor sensors with an oscillatory circuit and assisted by standard operational amplifiers.¹³⁸ This device has as parameters for efficiency the channel length and majority carrier mobility. The frequency applied gives how the mobility changes under environmental conditions.

Multistable memory effect in conducting polypyrrole nanowires showing switch effect under *READ/WRITE/ERASE* cycles is observed at low temperature (up to 60 K) and high resistance ratio for the *ON/OFF* voltage. Also, the threshold voltage for switching is tuned by changing the oxidation. Hundreds of parallel nanowires were experimentally obtained and it could be useful to utilize these nanowires increasing the density of memories.¹³⁹ A possible application of this system is as sensors with built-in logic for molecular discrimination purposes where the output current through the molecular device is the amplified signal from a chain of specific gates representing the specific functions.

Organometallic as a bridge have been proposed experimentally and theoretically¹⁴⁰ and when the resulting conductance utilized independent electron methodology show good agreement between them but if the effects of ligands on the conduction signature are taken into account it is possible to stress out that molecular orbitals consisting of the central d_z^2 orbitals in metal strings plays a fundamental role in electronic feature for linear complexes with trimetals.

10. SUMMARY

It is possible to separate the effects at junction/molecule as:¹⁴¹ (a) small applied voltages (\sim Hundreds of millivolt) is dominated basically by inelastic electron tunneling spectroscopy¹⁴² as weak interaction between transporting electrons and molecular vibrations; and for (b) large applied voltages where is followed by strong coupling effects as NDR,¹⁴³ Coulomb blockade, current hysteresis, heating,¹⁴⁴ chemical reactions, and noise effects.

Overall, several properties on molecular devices must be investigated before a summary conclusion but it is

possible stress out a few guidelines that deserve further analyses: (i) How is the behavior of conductance with temperature?; (ii) Is noise a critical point for molecular electronics?; (iii) How the heating process affects molecule/junction properties?; (iv) Are chemical changes in the molecule provoked by current? (v) How the molecular geometry is modified by the electronic transport?

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