# Design of Highly Integrated Organic Nanodevice

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In recent experimental work it was found that for a current–voltage bistability in/an organic semiconductor working as multilevel switching (B. C. Das and A. J. Pal, *Organ. Electron.* doi: 10.1016/j.orgel.2007.07.008). Due to the experimental motivation, we simulate the electronic distribution properties as charge accumulation/depletion-voltage and capacitive effects-voltage of a similar organic compound by means of the quantum mechanics methodology. Also, our theoretical results are consistent with: (i) similar behavior for positive bias when compared with experimental one; (ii) prediction as asymmetric feature for negative bias, e.g., asymmetric majority carrier transportation curve for Ponceau SS device; (iii) resonance tunneling type conduction in the *I–V* signature. For both bias (positive and negative) the resonance is addressed and it explains as a bi-directional molecular transistor or memory device.

**Keywords:** Organic Nanoelectronics, Donor–Large Heterogeneous $\pi$ Bridge–Acceptor, *Ab Initio* Quantum Mechanics.

## 1. INTRODUCTION

Since the first paper done by Aviram and Ratner[1] where an organic molecular system with a donor and an acceptor group were attached by a saturated carbon bridge and presenting a strong current rectification several works have been done.

To design and construct devices based on organic electronic, it is necessary to mainly investigate the carrier transport in these structures.[2–6] It is possible to organize in a few steps and the most usual situation is when the Fermi level of contact (metallic) is between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) provoking the majority carriers transport decrease with the length of the molecule. Henceforth, if the electronic transport has a length independent, e.g., dominated by contact scattering increasing with the number of atoms bonded. Otherwise, if it happens changes as *trans-cis* and planar–no-planar in the molecular structure. Of course, the well-known ohmic behavior should be addressed where the electronic transport for organic structures is length inversely dependent when aromatic rings associated with others molecular structures.[2–6] Although, one of the most important phenomena is provoked by the structural changes as soliton, polaron and bipolarons. The Polyacetylene has fundamental degenerated electronic states and the extra carrier in the structure provoke a structural deformation.[7, 8] For non-degenerate semiconducting organic polymers as

Poly-*para*-phenylene-vinylene derivative,[9, 10] two charges are trapped in the structure.

Campione and co-workers[11] propose a rule where they have been demonstrated that organic islands grown on the silica substrate randomly oriented when compared with the contact plane. Otherwise, within the KAP substrate have shown to exhibit a preferred orientation. These results and the proposed model are in agreement with optical measurements.

Likewise, several experimental works to construct field-effect transistor have been done.[12–15] In these works, it becomes clear the difficult to find out a rule concerning to define correlation of the device performance as majority carrier transporter,[12] as well as the high sensibility of environment where the device is constructed[12, 13] and the correlation between molecular alignment and device performance.[14] The mobility shows values in different conditions[12–15] between 0.008 cm$^2$(V s)$^{-1}$ and 0.240 cm$^2$(V s)$^{-1}$.

In recent theoretical work[16, 17] it raised up a fundamental rule where a $\pi$-bridge molecular structure can be used as a field effect transistor as well presented a new approach to study the majority carrier flow into this class of material. Wu et al.[18] done a complementary work showing that organic push-pull molecular systems could be simulated by hybrid time-dependent density functional theory indicating that zwitterionic states assume full charge separation activating possible optically forbidden states.

In this paper will be addressed the design of molecular structure recently proposed by Das and Pal[19] by first principle quantum mechanics calculation. The next section,

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details of the system investigated and the methodology utilized. The results and conclusions will be presented in the last two sections.

## 2. METHODOLOGY AND SYSTEM

By a coupled Density Functional Theory (*DFT-B3LYP/6-31G(p, d)* and *LANL2DZ*) methodology to investigate the *Sulfur* terminals attached in *Gold* atomic groups, it is possible to find out the following conclusions:[20]
(a) An asymmetric current–voltage signature was found, and rectification ratio equal to 7 for forward and reverse bias, as well as the
(b) absorption spectra could be predicted showing
(c) representative molecular states that have influence in the nanodevice.
(d) Also, for design of molecular electronic devices, $\sigma$ and $\pi$ bonds could rule significatively different pattern.

Following these clues we improve our technique to design our device.

We have utilized this methodology in the structures presented in Figure 1 as a general procedure for $\sigma$ or $\pi$ bridges structures, once this system can be considered as a source–bridge–drain chain. Hartree-Fock (HF) derivative Hamiltonian such as the ones contained in Gaussian package[21] was utilized. The organic semiconductor Ponceau SS is considered for the device as follow: (i) horizontally the structural backbone composed by phenyl rings attached by *azo* Nitrogen bonds and (ii) the *Sulfur* atoms have attached Oxygen atoms in the extremities.

Usual basis sets were used for all calculations and the conformational geometries of the analyzed molecular device were fully optimized in the form of Roothaan-Hall matrix in a closed shell model including external electrical field and coefficient matrix in the form of linear combination of atomic orbitals. Also, the Fock matrix with several terms includes core, Coulomb, exchange interaction energies, and the influence of external fields energy as presented before.[22–25]
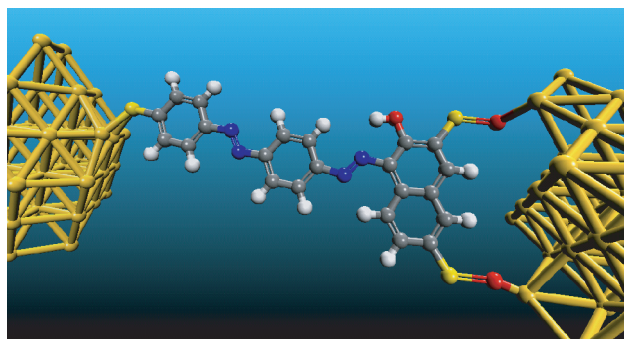


**Fig. 1.** Pictogram of molecular device investigated composed by 4 conjugated rings with azo groups in the bridge as donor–large heterogeneous $\pi$ bridge–acceptor and terminals attached.

This paper could be understood as a two-terminal molecular device within specific atomic sites to simulate the gate terminal. The intention is find out manifestations of the transport properties unusual in ordinary devices.

## 3. RESULTS AND DISCUSSION

For investigation of charge distribution in the molecular device (Fig. 1) are considered 4 model-types as described in Figure 2 (describing the donor part): (*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.

Applying an external electric field in the PSS derivative molecule (positive values from left to right) over the 4 models presented (Fig. 2), we observe (Fig. 3) that under forward and reverse bias occurs electronic rectification, alternating the source and drain signature bonded in the border of the device. By drift transportation the conduction is ruled by carriers (majority in this case) as typical Schottky diode works.

The PSSd presents asymmetric bi-directional electron transportation and the characteristics can be summarized as:
(i) For Fields upper than 0.012 a.u. the PSSd presents the first resonance and goes to forward conduction region as breakover voltage a $(+V_{(BR)F})$ for upper values;
(ii) The molecule is in the *off* state between −0.011 a.u. and 0.012 a.u.;
(iii) Under reverse external electric fields the system presents reverse conduction region in between −0.011 and −0.017;
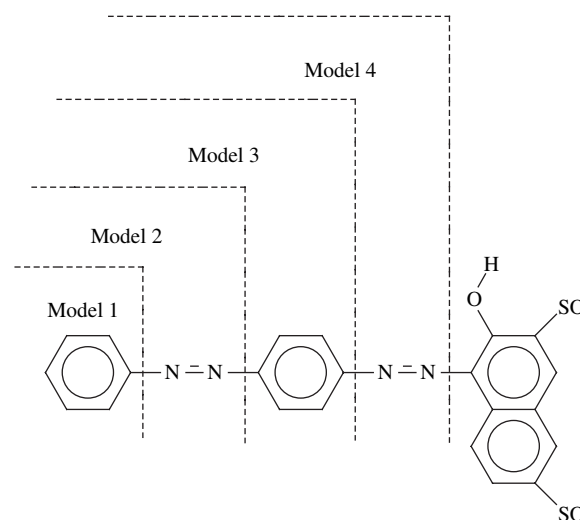


**Fig. 2.** Models adopted to investigate the electrical characteristic of PSS derivative device. The models presented are those related to how to separate the charge distribution thought to molecular device. For example, model 1 [2 or 3 or 4] is the donor side and the complementary molecule is the acceptor part of device.
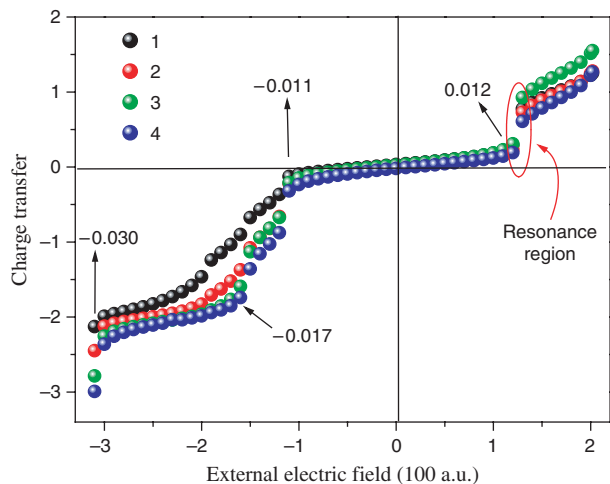
**Fig. 3.** Charge accumulated as a function of the voltage for different models (Fig. 2) in the PSS derivative: (a) model 1, (b) model 2, (c) model 3, and (d) model 4. Charge accumulated presents resonant-tunneling behavior.

(iv) The system presents a reverse breakover current $(-I_{(BR)R})$ when is established values approximately to $-0.030$ a.u. implying as similar Zener diode (also known as breakdown current of junction provoked mainly by the effect of double azo groups in the system).

In Figure 3, a special attention must be done in the region in between $-0.011$ a.u. and $-0.020$ a.u. showing smooth dependence, but still, with the model investigated. To increase this effect an analysis of the capacitance signature is described in Figure 4.

The capacitance for a molecular structure has a dependence of electrons number presented in the backbone of the molecule.

In Figure 4, it is presented the capacitance versus voltage for the molecular device. Within the increase
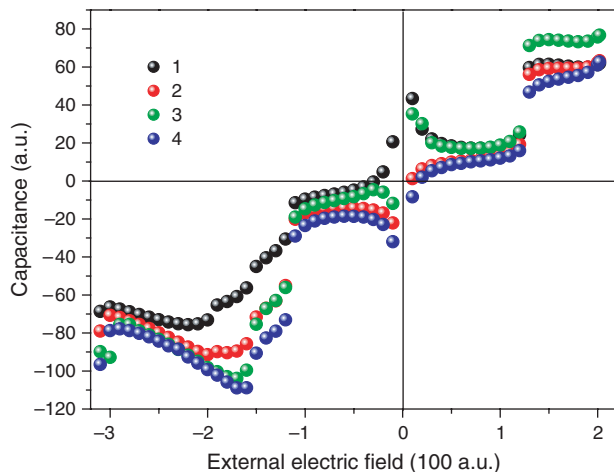


**Fig. 4.** Capacitance as a function of the voltage for different models (Fig. 2) in the PSS derivative: (a) model 1, (b) model 2, (c) model 3, and (d) model 4.

of reverse polarization, the charge accumulation in the gate abruptly decreases because it happens an increase of molecular quantum well until a specific value and increase again, e.g., increasing and decreasing the depletion region with two levels of saturation. For model 2 increases the quantum well when compared with model 1 (Same behavior for comparison between models 2 and 3 or 4 and 3). This occurs because the atoms attached are responsible for this region in the depletion of the device. This feature is very important for the design of new nanometric devices as prominent asymmetric Schottky devices and the material capacity of remains controlled capacitive effects.[26]

## 4. CONCLUSION

We have thus demonstrated an approach for realizing simulation on electronic transport in a source–large $\pi$ heterogeneous backbone–drain in an *azo*-family compound, the *Ponceau SS*. We calculate charge depletion/accumulation and capacitive signature as a function of an external voltage applied in the backbone direction. By our finds, a few rules raised out:

(a) The rectification occurs in agreement with experimental result;[19]

(b) For reverse bias it was obtained asymmetric *I*–*V* curves related to the nature of system;

(c) Also, this organic semiconductor could be utilized as a field effect transistor with bi-directional operation regions, in forward and reverse bias.

This feature 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 addressed[27] showing nonlinear voltage–current characteristic as an intrinsic organic FET.

Overall, we have showed the design of an organic 2-terminal nanodevice with heteroatoms in the structure provoking levels of quantum-wells presenting a particular dependence with the model proposed to analyze the charge distribution as well unique *I*–*V* and *C*–*V* signature. Also, it is well-known that is necessary low temperatures 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.[28, 29]

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