Design of a Molecular π-Bridge Field Effect Transistor (MBFET)

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We study charge transfer in a molecular system composed of a donor and an acceptor coupled to each other via a carbon conjugated-bond bridge (D-bridge-A). The effects of the bridge length in the transport are analyzed in the presence of an external electric field by density functional theory methodology. We find a charge accumulation in acceptor group that is strongly dependent on the bridge length and composition. In particular, for bridges with more than four carbon conjugated atoms we observe resonance tunneling type conduction in the curve of charge accumulation versus voltage. For positive bias the resonance takes place for high voltages when compared to the negative biases. This behavior suggests that the system can operate as a molecular transistor (MBFET) at some bias range. In addition we perform a current calculation in a simple model in order to get some more insight about the transport.

Keywords: Molecular Transistor, Transport Properties, Resonance Tunneling.

RESEARCH ARTICLE

1. INTRODUCTION

Organic molecular devices that present current rectification has received growing attention from both theoretical and experimental point of view due to its potential application in the development of novel devices such as organic diode and transistors.[1] Originally, Aviram and Ratner[2] proposed a unitary molecular system of the kind D-σ-A, with a donator group (D) attached to an acceptor group (A) via a carbon bridge (σ), that presents a strong current rectification. Since this original proposal, the search for this sort of molecular groups has increased, with a particular attention to the electron transport mechanisms between groups D and A.[3] In a previous work[4] it was pointed out that a betaine piridinic of the kind D-bridge-A, with a D-Imidazol linked to an A-piridine via a polienic π bridge present an inversion of the electron charge flow in the molecular structure as a function of the bridge length. Several experimental works are available to probe the increasing on the level of control could be done on the electronic structure of materials. These measurements reveal spatial patterns that can be directly understood from the electronic structure of single molecules and which represent an elegant illustration of Bloch's theorem[5] at the level of individual wavefunctions as well energy-dependent interference patterns in the wavefunctions. Otherwise, several theoretical works pointed out poor results to explain the fundamental processes involved in electron transfer through molecules used as transistors or diodes.[6–10] Although these theoretical approaches cannot be reliable when compared with the experimental state-of-art results showing well-known rectification process.

In the present work we study theoretically the transport properties of the molecular system (Fig. 1) where a given pair of D and A groups is connected through conjugated bridges of increasing sizes. Via *ab initio* Hartree-Fock (HF) and density functional theory (DFT) we determine the electron charge distribution along the molecule as a function of an external voltage. Quite interesting, this distribution gives some information about the I–V characteristic of the system. In order to obtain some more insight about the charge transport mechanism, we make a simple model based on nonequilibrium Green functions that gives an I–V curve comparable to the charge distribution results.

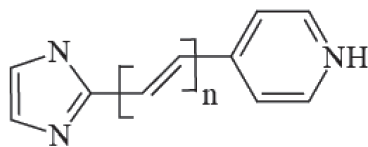*Author to whom correspondence should be addressed.

Fig. 1. Members of the family of pyridinium betaines investigated had an increasing number n of double bonds in the connecting conjugated bridge.

2. SYSTEM AND METHODOLOGY

In our numerics we use well-known Hartree-Fock (HF) calculation performed by Gaussian[11] package. In addition to this, density functional theory is also applied in order to corroborate our previous findings. In the HF approach we adopt standard parametrization and in our calculations based on DFT use the B3LYB/6-31G[12, 13] functionals, which gives good results about the electronic structure in correlated systems. The wavefunctions were described by the complete 6-31G base-set that include two polarization functions. In both techniques, HF and DFT, the effects of the electric field on the molecule were considered. We pay particular attention to the correlation between electric field and charge accumulation along the molecule.

To better understand our findings, we introduce a simple, but precise, model that describes transport between a source and a drain of electrons mediated by a localized state. Figure 2 schematically shows the system considered. It is composed of a source and a drain of electrons with an approximated uniform density of states, with μ_L and μ_R being the left and right chemical potentials, respectively. A localized state in between them works as a conduction channel that allows the electrons to resonantly pass from one side to the other one of the system. In the absence of a bias voltage applied between source and drain, we have $\mu_L = \mu_R$ and the localized state is taken above μ_L and μ_R. In this case no electrons can resonantly cross the system. When an external bias is applied, though, the localized

state is shifted up or down according to the sign of the bias, and a resonance condition is matched [$\varepsilon_l = \mu_\eta$, with $\eta = $ L or R for $V > 0$ or $V < 0$, respectively]. At this match we observe a steeper enhancement of the current as discussed later on.

In order to calculate the characteristic I–V curve we use the Landauer-Büttiker formula[14]

$$I = ((2e)/h) \int d\varepsilon [f_L(\varepsilon) - f_R(\varepsilon)] T(\varepsilon) \quad (1)$$

where $f_L(\varepsilon)$ and $f_R(\varepsilon)$ are the Fermi distribution functions of the left and right sides, respectively,

$$f_{L/R}(\varepsilon) = (1/(e^{(\varepsilon - \mu_{L/R})/(k_B T)} + 1)) \quad (2)$$

and $T(\varepsilon)$ is the transmission coefficient, given by[15]

$$T(\varepsilon) = (\Gamma^L(\varepsilon)\Gamma^R(\varepsilon)/\Gamma(\varepsilon)) A(\varepsilon) \quad (3)$$

where $\Gamma^\eta = 2\pi |\Omega_\eta|^2 \rho_\eta(\varepsilon)$ is the line-width function due to side η, Ω_η gives the coupling between source or drain with the bridge, $\rho_\eta(\varepsilon)$ is the density of states of side η, and $\Gamma(\varepsilon) = \Gamma^L(\varepsilon) + \Gamma^R(\varepsilon)$. In Eq. (3), $A(\varepsilon)$ is the spectral function of the bridge, which we assume with a Lorentzian shape,

$$A(\varepsilon) = \Gamma(\varepsilon)/([\varepsilon - \varepsilon_l]^2 + [\Gamma(\varepsilon)/2]^2) \quad (4)$$

where ε_l is the localized level. In order to account for the bias drop along the structure we assume that $\mu_L - \mu_R = eV$ and let $\varepsilon_l = \varepsilon_0 - x$ eV, where ε_0 is the localized level without bias and x is a parameter that accounts for a bias drop asymmetry along the molecule. Note that the bridge couples distinctly to the donator and acceptor groups due to the different terminations C=C and C—N. This asymmetry is account in our model via $x \neq 0.5$.

In the next section we present our numerical results.

3. RESULTS AND DISCUSSION

In a phenomenological bases we take $x = 0.33$ in order to better fit the charge distribution result in Figure 3(a). The coupling strength between bridge and groups D and A will be given by $\Gamma^L = 1.5$ meV and $\Gamma^R = 0.3$ meV, respectively.

Solving the current Eq. (1) with these parameters we obtain the current (solid line) in Figure 3(a). Even though it does not fit completely the charge accumulation curve, we obtain a close agreement between them. In particular with respect to the resonances asymmetry and the plateaus. We note that both the charge accumulation and the current present rectification effect. This suggests that not only the current but also the charge accumulation can give some information about the molecular transport.

Figure 4 shows the charge accumulation/depletion in the group A as a function of an external voltage for differing number of bridge atoms ($n = 0, 2, 4$). For small n the coupling between groups D and A is strong enough to
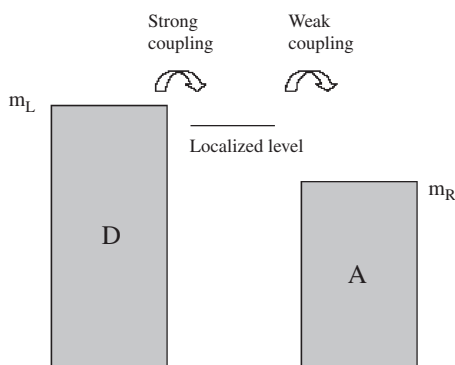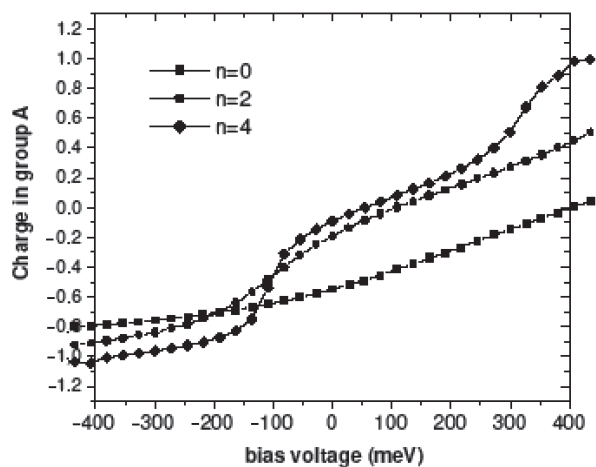

Fig. 2. Schematics of the model adopted to describe the transport in the D-π-A system. A localized state is coupled to a donator and an acceptor density of states, with a stronger coupling to the left side. This asymmetric coupling is accounted in our model via the parameter x and is responsible for the current rectification observed.

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Fig. 3. Charge accumulated in group A as a function of the voltage for different numbers (n) of carbon atoms in the bridge. For $n = 0$ (no bridge) the electrons can pass directly from group D to A and the curve presents a metallic-like behavior. In this case even for $V = 0$ the electrons move from D to A due to the zwitterionic structure. As n increases the electrons start to pass less frequently from D to A. For big enough n the bridge states start to play a crucial role in the conduction process, which results in a resonant tunneling type conduction for negative voltages. The positive resonance is not seen in order to emphasize that this system operates as a current rectifier at some voltage range.

allow electrons pass directly from group D to group A, without any resonant tunneling process. In particular for $n = 0$ we observe a metallic-like behavior of the curve. Note that for small n values group A (drain) already has a charge accumulation for $V = 0$, which characterizes a zwitterionic system. When the bridge increases in length the distance between groups D and A increases as well and the electrons can no longer pass directly from D to A. In this case the density of states of the bridge starts to play a crucial role in the electron transport, working as conduction channels between groups D and A. In particular for high enough n a resonant tunneling behavior takes place. This indicates a transport via localized states introduced in the system by the bridge. For $n = 4$ we observe a steeper enhancement of the current around eV = -100 meV which then attains a plateau. In contrast, for the positive bias counterpart the I–V curves show a linear behavior with a resonance for $n = 4$ around eV = 330 meV. This shows that the charge transfer from groups D to A follows a diode-like behavior, with a favorable transport for reverse (eV < 0) bias.

In Figure 4(a) we show the charge accumulation in group A for $n = 5$. We observe an enhancement of the charge accumulation 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_l asymmetrically coupled to a source and a drain of electron, we obtain a I–V curve in close agreement with the charge accumulation result. In Figure 4(a) we show the current obtained from current equation, with the parameters described previously.
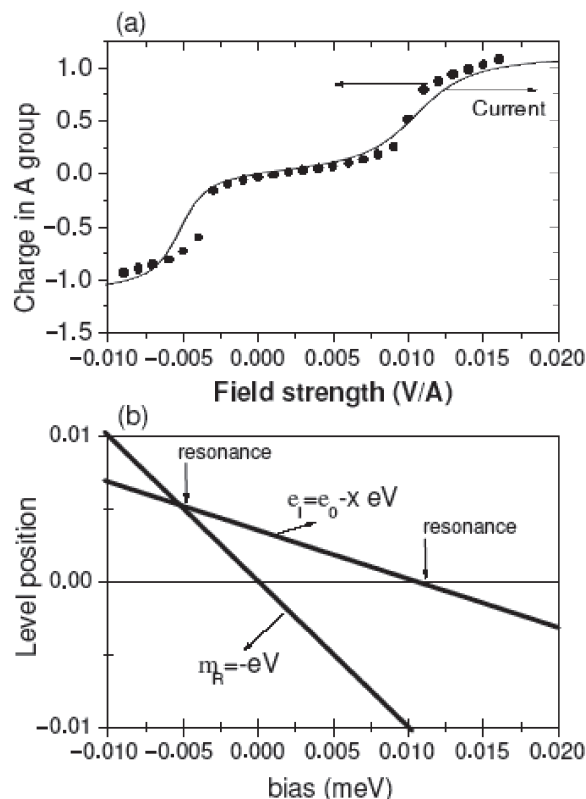

Fig. 4. (a) Charge accumulation in group A, current and (b) level positions against external voltage. In (a) we observe two resonances, one around -0.005 a.u. and another one around $+0.01$ a.u. These resonances take place when a state of the bridge matches the chemical potential of the left (V > 0) or the right (V < 0) side. In panel (b) we show the localized level ε_l and the chemical potentials $\mu_L = 0$ and $\mu_R = -eV$ against V. The resonances conditions $\varepsilon_l = \mu_L$ (V > 0) and $\varepsilon_l = \mu_R$ (V < 0) are indicated by arrows. Note that these resonances are asymmetric with respect $V = 0$. This is so because we assume $x = 0.33$ in the ε_l formula in order to account the coupling asymmetries between bridge and groups D and A.

We observe an enhancement of the current (in modulus) around eV = 270 meV and eV = -92 meV in agreement with the charge accumulation profile. These resonances correspond to the matches $\varepsilon_l = \mu_L$ and $\varepsilon_l = \mu_R$, respectively. In Figure 4(b) we show in the linear drop model, $\varepsilon_l = \varepsilon_0 - x$ eV, the level ε_l, and the left ($\mu_L = 0$) and the right ($\mu_R = -eV$) chemical potentials against bias voltage. We clearly see that the resonance $\varepsilon_l = \mu_L$ (eV > 0) takes place for high voltages values (in modulus) than the negative resonance $\varepsilon_l = \mu_L$ (eV < 0). This is so because we consider $x = 0.33$ to account for coupling symmetries between the localized level and the source and drain. For $x = 0.5$ (symmetric coupling) the resonance would be symmetric as indicated by the dashed line in Figure 4(b).

4. CONCLUSION

In this paper we study rectification in a donor-bridge-acceptor in a betaine organic molecule. We calculate

charge accumulation/depletion in the acceptor group as a function of an external voltage applied along the molecule. The result presents a rectification process under two general rules: (a) it is necessary a minimum bridge size coupled with insaturable and conjugated bonds; (b) a specific bias range must be fixed. Interestingly, the charge accumulated versus V and the I–V curve obtained via our simple model are comparable, thus suggesting that not only the current but also the charge accumulation can give information about transport properties. The rectification reported here is explained in terms of the asymmetric coupling between donator/acceptor and the bridge. A simple general model corroborates this idea.

Our results show clearly current rectification for π-bridge with a number of carbon conjugated atoms greater than four. More specific, for direct bias ($V > 0$) the current saturates close to zero till the voltage reach 0.01 a.u. (atomic unit). At this voltage a resonance takes place and the current increases. In contrast, for reverse bias the current enhances around -0.005 a.u., then it tends to saturate. For this reason, this system could be denominated as a Molecular π-Bridge Field Effect Transistor.

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