

A single molecule rectifier with strong push-pull coupling

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We theoretically investigate the electronic charge transport in a molecular system composed of a donor group (dinitrobenzene) coupled to an acceptor group (dihydrophenazine) via a polyenic chain (unsaturated carbon bridge). *Ab initio* calculations based on the Hartree–Fock approximations are performed to investigate the distribution of electron states over the molecule in the presence of an external electric field. For small bridge lengths ($n=0-3$) we find a homogeneous distribution of the frontier molecular orbitals, while for $n>3$ a strong localization of the lowest unoccupied molecular orbital is found. The localized orbitals in between the donor and acceptor groups act as conduction channels when an external electric field is applied. We also calculate the rectification behavior of this system by evaluating the charge accumulated in the donor and acceptor groups as a function of the external electric field. Finally, we propose a phenomenological model based on nonequilibrium Green's function to rationalize the *ab initio* findings. © 2008 American Institute of Physics.

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I. INTRODUCTION

Electronic transport through single molecules is currently a subject of intense study mainly due to its potential application for new electronic devices such as molecular rectifiers.¹⁻⁴ The ability of molecules to develop strong rectification when attached to donor and acceptor groups was first proposed in the seminal work of Aviran and Ratner.⁵ Other proposals of molecular rectifiers, diodes, and field-effect transistors have also been reported in the literature.⁶ In particular, push-pull with a σ or π bridge have been studied with special attention on the effects of the bridge length on the transport properties.⁷ Recently, it was pointed out that systems with donor and acceptor groups spaced by a carbon π bridge have strong rectification for relatively long bridges, thus operating as molecular field-effect transistors.⁸ In addition it was observed that π bridges are more favorable to rectification than σ bridges.^{9,10} In contrast to the results presented in Ref. 11, here we show that the system dinitrobenzene(D)-bridge-dihydrophenazine(A) has a strong current rectification even for small π bridges, thus resulting in a very robust rectification compared to similar proposals reported in the literature.

We focus our analysis on the frontier molecular orbitals (FMOs) [highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), in particular] and the charge distribution in the molecule, since they can provide complementary information regarding electronic

transport in the molecule.¹¹ It is important to mention that an analysis of the HOMO/LUMO frontier orbitals does not always provide the actual tendency of the electron flow. For instance, in the present system for $n=0$ and $n=1$, we find a uniform distribution of the FMOs with high level energies (typically -1 eV), which in a first analysis would predict no effective flow of electrons in the molecule and a uniform charge distribution. In fact, we will see that a strong asymmetry in the charge distribution is observed in the system studied here even for a small bridge length. By increasing the bridge length between the donor and acceptor, a localized HOMO and LUMO conduction channel becomes evident in the charge versus voltage curves, thus leading to sharp steps typically observed in resonant level models.

In order to understand electronic transport behavior of the system, we have developed a formulation based on nonequilibrium Green's function that describes transport through localized levels coupled to a donor and to an acceptor of electrons. This theoretical approach allowed us to gain further insight and a clear physical interpretation of the rectification effects obtained from *ab initio* calculations.

The paper is organized as follows. In Sec. II we introduce the adopted methodology with a brief description of the computational package used and the formulation based on the nonequilibrium Green's function. In Sec. III we present our results and the corresponding discussion, and in Sec. IV we make the final remarks.

II. METHODOLOGY

Two theoretical approaches are adopted in our study: (i) *ab initio* calculations and (ii) nonequilibrium Green's func-

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tion. In the first one we use the GAUSSIAN98 package,¹² which encompasses Hartree–Fock (HF) in its numerical procedure. We have used the HF/6-31G and HF/6-31G* and the results obtained are in agreement so we adopted the HF/6-31G, which has been successfully applied for determining electronic structure in these types of systems.¹³ We have used HF instead of density functional theory because hybrid exchange–correlation functionals, local density approximation, and generalized gradient approximation, are well known to overestimate the polarizabilities of quasilinear systems and do not reproduce the localization of the molecular orbitals and inversion behavior observed with HF-based methods.^{14–17} The effects of an external electric field and its interplay with charging accumulation in the donor/acceptor group are considered in part (i). Additionally, we determine the charge accumulated (Q) in the acceptor group as a function of the external electric field (Q - V curve). In the second part [(ii) above] we develop a simple model consisting of multiple electronic levels coupled to a donor and to an acceptor group. By adjusting phenomenological coupling parameters, we fit the equilibrium Q - V curve obtained in (i) with a nonequilibrium I - V curve determined via Green's functions. Surprisingly, both HF and transport calculations lead to similar results; therefore, this agreement reveals that charge localization can provide valuable information about transport properties of the present system. However, a general extension of this equivalence to other systems is not straightforward.¹⁸

The computational approach of connecting *ab initio* results with nonlinear Green's function has been successfully used in previous works.^{19,20} Our transport model is based on a ballistic resonant tunneling transport from a donor to an acceptor of electrons through localized levels weakly or strongly coupled to the reservoirs [see Fig. 1(a)]. This approach can be done by ignoring molecular charging effects because of the fast electronic switching on the molecular structure and because the transport is only associated with the molecular electronic structure.²¹ Figure 1(b) shows schematically the nonequilibrium system used to generate an I - V curve that resembles the equilibrium Q - V curve. Three levels (E_1, E_2, E_3) of different widths are coupled to a left and to a right lead via tunneling barriers. The left and right Fermi energies are denoted by E_F^L and E_F^R , respectively. These energies are related via $E_F^L - E_F^R = eV$, where V is the left–right (bias) voltage and e the electron charge ($e > 0$). Deep levels are narrow while the level closer to the top of the tunneling barriers is broad. The narrow levels give rise to sharp steps in the characteristic I - V curve whenever these levels match the emitter chemical potential (the donor for positive and the acceptor for negative bias). On the other hand, the broad level contributes to a linear increase in the current even though it remains above the emitter Fermi energy for the bias voltages used. Therefore this broad level is responsible for the nonzero slope of the plateaus in the I - V curves discussed below.

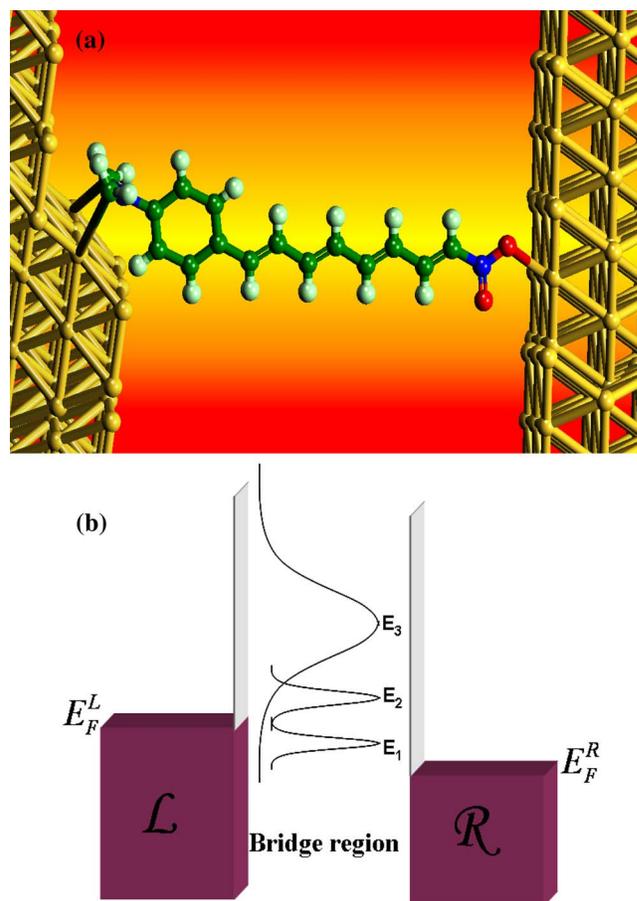


FIG. 1. (Color online) (a) Sketch of the resonant tunneling system used to model the donor–bridge–acceptor system shown in (b). Three levels are coupled to a left (l) and to a right (r) electron reservoir via asymmetric tunneling barriers. In the presence of a bias voltage the left and the right Fermi energies, E_F^L and E_F^R , respectively, differ from each other, thus generating a current when resonances are matched.

The system is described by the following Hamiltonian:

$$H = H_L + H_R + H_M + H_{\text{hib}},$$

where H_L , H_R , and H_M are the Hamiltonians of the donor, the acceptor, and the molecule, respectively. The term H_{hib} accounts for the hybridization of molecular orbitals to the donor/acceptor orbitals. This term gives rise to a charge current in the presence of bias voltages. Indeed, these terms read

$$H_{L/R} = \sum_{\alpha} E_{\alpha} c_{\alpha L/R}^{\dagger} c_{\alpha L/R},$$

$$H_M = \sum_n E_n d_n^{\dagger} d_n,$$

$$H_{\text{hib}} = \sum_{an} [t c_{\alpha L}^{\dagger} d_n + t^* d_n^{\dagger} c_{\alpha L} + t c_{\alpha R}^{\dagger} d_n + t^* d_n^{\dagger} c_{\alpha R}],$$

where E_{α} and E_n are the leads and the molecular levels, respectively. To calculate the electronic current in this system, we use the following equation:

$$I_{L/R} = -e \langle dN_{L/R}/dt \rangle = -ie \langle [N_{L/R}, H] \rangle,$$

where $N_{L/R}$ is the total number of operators for electrons in the donor (L) or acceptor (R). The notation $\langle \dots \rangle$ denotes

some nonequilibrium thermodynamic average and $[\dots]$ denotes a commutator. Following the standard procedure of nonequilibrium Green's functions,^{22,23} the current is given by

$$I_{L/R} = 2e \int dE T(E) [f_{L/R}(E) - f_{R/L}(E)],$$

where $T(E) = \text{Tr}\{\Gamma^L G_M^r \Gamma^R G_M^a\}$ and f_L and f_R are the left and right Fermi distribution functions, respectively, given by

$$f_{L/R}(E) = \frac{1}{1 + \exp[(E - \mu_{L/R})/k_B T]}.$$

μ_L and μ_R denote the chemical potentials and k_B the Boltzmann constant. The parameters Γ^L and Γ^R give the tunneling rates between left/right and the molecule (bridge). In a matrix notation they are given by

$$\mathbf{G}_M^r = \begin{bmatrix} E - E_1 + i\Gamma/2 & 0 & 0 & \dots \\ 0 & E - E_2 + i\Gamma/2 & 0 & \dots \\ 0 & 0 & E - E_3 + i\Gamma/2 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}^{-1}.$$

This function is appropriate for describing many noninteracting levels weakly coupled to reservoirs. The advanced Green's function is the complex conjugate of \mathbf{G}_M^r , i.e., $\mathbf{G}_M^a = \mathbf{G}_M^{r*}$. We assume a linear bias-voltage (eV) drop along the system. So $\mu_L = \mu_L^0$ and $\mu_R = \mu_R^0 - eV$, where μ_L^0 and μ_R^0 are the left and right chemical potentials. The levels E_n are given by $E_n = E_n^0 - x eV$, where x accounts for bias-voltage drop asymmetry. Asymmetries in the voltage drop can happen, for instance, when the molecular levels are more coupled to the donor than to the acceptor or the opposite. In particular, for a symmetric drop we have $x=0.5$. It is important to mention that molecular rectifiers based on asymmetries of the leads-to-molecule coupling have been predicted, for instance, in a carbon conjugated-bond bridge²⁴ and in the "tour wire."²⁵ The main role of the asymmetry of the potential drop relies on the fact that the molecular levels can line up either with the left- or the right-lead Fermi level differently depending on the sign of potential energy eV .

The parameters in the transport model, used to fit the numerical *ab initio* results, are E_n , x , and Γ . Basically, E_n and x give the resonance positions on the I - V characteristic curve, while Γ provides the intensity of the current.

III. RESULTS AND DISCUSSION

Figure 2 shows the HOMO and LUMO energies for different bridge lengths ($n=0, 1, \dots, 10$). As the bridge increases the HOMO (LUMO) energy increases (decreases) asymptotically to a value slightly above 8.0(-1.7) eV. This is a general behavior of quantum confined systems that has its energies reduced whenever the confinement length increases. This suppression leads to a more efficient electron

$$\Gamma^\eta = \begin{bmatrix} \Gamma_1^\eta & 0 & 0 & \dots \\ 0 & \Gamma_2^\eta & 0 & \dots \\ 0 & 0 & \Gamma_3^\eta & \dots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix},$$

where $\eta \equiv L$ or R . The molecular retarded Green's function \mathbf{G}_M^r is given by

$$\mathbf{G}_M^r = [E\mathbf{I} - \mathbf{H}_M - \boldsymbol{\Sigma}^r]^{-1},$$

where I is the identity matrix and $\boldsymbol{\Sigma}^r = -i(\Gamma^L + \Gamma^R)/2 = -i\Gamma/2$ is the tunneling self-energy. This quantity is assumed to be energy independent (wideband limit). In a matrix notation this Green's function can be written as

transport reaching a limiting value. In Fig. 2 (inside panels) we plot the FMOs for $n=0$ (I), $n=1$ (II), and $n=6$ (III). This is a relevant quantity to consider since it provides information about the charge distribution along the molecule for the molecular ground state. We note that when the bridge increases, the orbitals tend to localize on the acceptor (donor) side for LUMO (HOMO). This indicates that in the presence of an electric field, the charge will be predominantly accumulated on one side of the system, as is shown below.

In Fig. 3(a) we show the charge accumulated (Q) in the acceptor as a function of external electric field (Q - V curve). For positive electric field the charge is accumulated in the A group and depleted in group D, thus generating a polarization in the molecule. For negative fields the electron flow is reversed with depletion in the acceptor side. Interestingly, there is an asymmetry from positive to negative fields, which becomes more pronounced for $n=2$ and 3. This asymmetry in the charge response is closely related to the orbitals illustrated in Fig. 2. Within the FMOs, localization allows the identification of the electronic flow direction because molecular structures with FMO delocalized over the structure indicate no particular flow direction. Therefore this system can potentially operate as a single bidirectional molecular field-effect transistor.

We note that for $n=2$ and 3 the electrons in D group do not respond to relatively small positive fields. The onset of electron transport from D to A starts around 4 V/nm and then becomes much stronger than its negative counterpart, thus revealing a considerable rectification. The strength of the charge accumulation is larger for positive bias since we are imposing a flow in a direction, which has more FMOs avail-

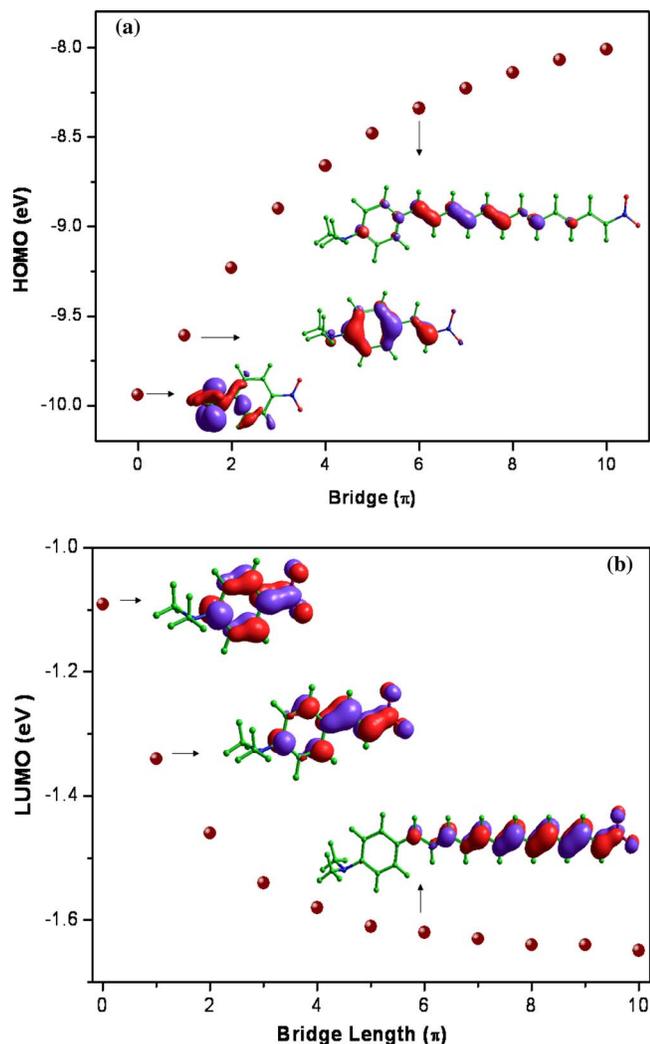


FIG. 2. (Color online) (Left) HOMO (top panel) and LUMO (bottom panel) energies for the molecular structures with bridges $n=0, \dots, 10$ and (right) charge distribution of FMO for $n=0$ (I), $n=1$ (II), and $n=6$ (III).

able to populate. This simple picture, though, does not provide a qualitative explanation for the resonances in the Q - V curve seen at 4 V/nm and around 14 V/nm for $n=3$. These resonance matches in the Q - V curve become more evident when the bridge length is increased.

Figures 3(b) and 3(c) show Q - V curves for bridge lengths ranging from 4 to 10. The Q - V curves reveal resonances and plateaus, which is typical for systems with levels coupled to donor and to acceptor leads.²⁶ In addition to the Q - V curves, also we present the I - V characteristic curves for two selected bridge values, $n=4$ and 10 (Fig. 4). These results reveal that an equilibrium quantity such as the charge accumulation Q can provide, in this case, information about nonequilibrium quantities such as I . The current was calculated here via Green's formulation previously presented and applied to a model system illustrated in Fig. 1. The I - V curves were generated considering levels of different widths coupled to both donor and acceptor via asymmetric tunneling barriers. Differences in the widths can be understood by noting that higher levels are closer to the top of the tunnel barriers. The corresponding wave functions tend to overlap more strongly with the donor and acceptor electron wave

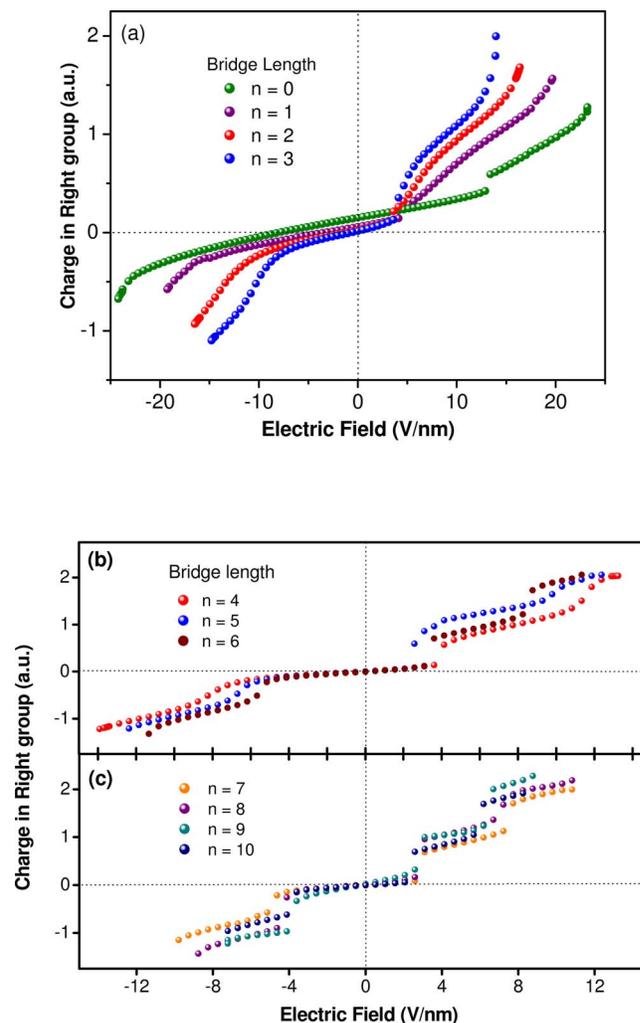


FIG. 3. (Color online) (a) In $n=0$ and $n=1$, negative external electric field $D \leftarrow A$ (E_-) when the A group is in a potential of reverse polarization. Positive external electric field $D \rightarrow A$ (E_+) when the A group is in a potential of forward polarization. For the same applied potential the charge accumulation is greater than the negative one exhibiting a typical rectifier signature. In $n=2$ and $n=3$ prominent rectifications of E_- and E_+ with resonance in the E_+ region; (b) negative external electric field $D \leftarrow A$ (E_-) when the A group is in a potential of reverse polarization. Positive external electric field $D \rightarrow A$ (E_+) when the A group is in a potential of forward polarization followed by resonances with intense saturation values. (c) Decrease in the rectification potential generated with a weak coupling because of the noninteracting DA groups.

function, which is equivalent to a stronger coupling and consequently a broadening of those levels (longer lifetime). On the other hand, deep levels are more localized, thus resulting in narrower levels. While the broad levels give rise to the nonzero slope of the plateaus, the narrow ones result in the sharp steps observed in Fig. 4. The numerical fitting parameters adjusted to best fit the I - V with the Q - V curves are the energy levels E_n^0 , the coupling parameters Γ_n^{LR} , and x . Their values are listed in Table I.

Related studies have been made by Mujica *et al.*²⁷ where current versus voltage curves, including tunneling and Coulomb repulsion, were examined using a Hubbard model treated at the HF level. The results showed negative differential resistance associated with increased localization of the molecular resonances. Zahid *et al.*²⁸ found a similar effect by

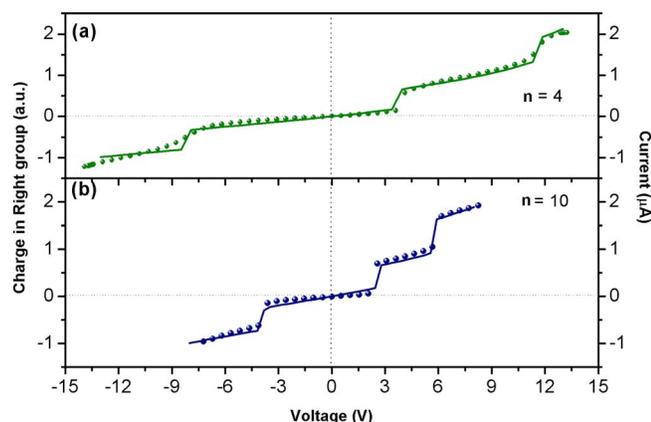


FIG. 4. (Color online) Two selected curves comparing the charge distribution (dots) in the acceptor group for (a) $n=4$ and (b) $n=10$ and the current (solid full line).

using a master equation applied to a prototypical benzene molecule and further showed a strong correlation between the molecule-electrode coupling. Also, a theoretical/experimental study of symmetric molecules has been done,²⁹ showing the same qualitative results as we describe here, i.e., (i) small rectification behavior for forward and reverse bias and (ii) the same microampere current level at small voltages.

IV. CONCLUSIONS

We have reported *ab initio* results for a single molecule system that exhibits rectification due to strong push-pull coupling. For small bridge lengths ($n=0-3$) we found a homogeneous distribution of the FMO, while for $n > 3$ there was a strong localization of the LUMO orbitals. Interestingly, the localized orbitals between the donor and acceptor groups act

TABLE I. Numerical parameters used in the transport model to better fit the *ab initio* calculations.

| Physical meaning | Quantity/values | n |
|---|---|-----|
| Tunneling rates between the levels and the donor/acceptor | $\Gamma_0=2.15$ meV | 4 |
| | $\Gamma_1^D=0.8\Gamma_0$, $\Gamma_1^A=0.8\Gamma_0$ | |
| | $\Gamma_2^D=\Gamma_0$, $\Gamma_2^A=\Gamma_0$ | |
| | $\Gamma_3^D=170\Gamma_0$, $\Gamma_3^A=\Gamma_0$ | 7 |
| | $\Gamma_0=2.15$ meV | |
| | $\Gamma_1^D=\Gamma_0$, $\Gamma_1^A=0.8\Gamma_0$ | |
| Level energies | $\Gamma_2^D=\Gamma_0$, $\Gamma_2^A=\Gamma_0$ | 10 |
| | $\Gamma_3^D=150\Gamma_0$, $\Gamma_3^A=150\Gamma_0$ | |
| | $\Gamma_0=2.15$ meV | |
| | $\Gamma_1^D=\Gamma_0$, $\Gamma_1^A=0.8\Gamma_0$ | 4 |
| | $\Gamma_2^D=2\Gamma_0$, $\Gamma_2^A=\Gamma_0$ | |
| | $\Gamma_3^D=150\Gamma_0$, $\Gamma_3^A=150\Gamma_0$ | |
| Potential asymmetry parameter | $E_1^0=2.65$, $E_2^0=7.81$, $E_3^0=15$ eV | 4 |
| | $E_1^0=1.98$, $E_2^0=4.35$, $E_3^0=11$ eV | 7 |
| | $E_1^0=1.54$, $E_2^0=3.4$, $E_3^0=11$ eV | 10 |
| Potential asymmetry parameter | $x=0.68$ | 4 |
| | $x=0.6$ | 7 |
| | $x=0.6$ | 10 |

as conduction channels when an external electric field is applied. The unusual charge transfer of these molecules under an external electric field is remarkably different from those of conjugated compounds of similar size. Also, the dependence of the D and A groups from their traditional role of electron flow opens up the possibility of exploiting very interesting molecular devices involving a new manifold of excited states now accessible in an unusual manner.

It is important to point out a recent study³⁰ where the unusual *I-V* characteristics of acyclic cross-conjugated molecules were found to be caused by quantum interference. In our work we find that there are two different electrical behaviors for small and large bridges. The nonequilibrium/equilibrium characteristics reveal an induced charge transfer highly dependent on molecular resonances.

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