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Electrical Rectification in Betaine Derivatives

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We theoretically investigate the electric rectification in an organic two terminal push−pull molecular device using a combination of *ab initio* techniques. Our main finding is that the electric rectification is extremely sensitive to the length of the chain, undergoing a complete switching after a specific chain length. This unique process occurs for betaine-like donor-π bridge-acceptor systems and is directly associated with a conjugated bridge in the presence of an external electric field. The conjugated bridge between the donor and acceptor groups is composed of oligoethylene with sizes ranging from 0 to 10 C=C units. The appearance of electric rectification occurs when the bridge size is equal to 5 units and is complete for those larger than 6 units (i.e., full inversion). This new electronic effect is advantageous for the design of large hybrid organic/inorganic circuits with an increased majority carrier flow that is necessary for the emerging needs of nanotechnology.

Introduction

Since the pioneering work of Aviram and Ratner[1] on molecular push−pull systems with a donor (D) and an acceptor group (A) bonded via a carbon bridge, electric rectification has been extensively studied by a large number of researchers. One example is the work of Carter[2] on the size reduction of architecture devices. There, the promising switching mechanism is driven by electron tunneling in periodic structures and by soliton switching in conjugated molecules. The first experimental molecular rectifier was proposed by Martin and co-workers.[3] It consisted of a conjugated zwitterionic molecule with platinum and magnesium electrodes. In a different set up, Kergueris et al.[4] showed experimental and theoretical symmetric *I*−*V* behavior of thiophene derivatives capped on both sides with sulfur atoms and connected with a gold array. These measurements indicated that nA currents at room temperature can be established in two distinct regimes: a linear regime at bias lower than 0.1 V and a nonlinear regime at voltage higher than 0.1 V. Similarly, experimental and a theoretical study of a benzene-dithiolate derivative has shown an increase of rectification at *μ*A currents but without a pronounced field effect transistor (FET) signature. In another type of experiment, Reed[8] and Flood et al.[9] proposed a prospective new paradigm for electronics that consisted of connecting molecular electronics and conventional electronics. This included the suggestion of the association of magnetic effects by incorporating appropriate atoms.

In 2005, several experimental studies indicated that ionic molecules may act like molecular devices and drive the electron transport through biological molecules.[10] Other observations include a molecular switch controlled by external voltage with nA currents,[11] inorganic nanowires as solar cells,[12] and a switching device via oxidation/reduction of the molecules between low and high conductance states.[13] Switching rectification with increased conductivity has also been observed and correlated to conformational changes (isomerization from *trans* to *cis* induced by an external voltage) of the subject molecule.[14]

Specific rules related to the electronic conduction properties of molecules connected to metallic contacts have been derived from extensive theoretical work. For example, a molecular structure composed of gold attached on both sides of a dithiol derivative molecule was examined using density functional theory (DFT) and nonequilibrium Green Function formalism.[15] This study revealed a significant conductance resonance for single and double gold atom connections. The same results were found when increasing the molecule−gold lead separation. A similar methodology was utilized to investigate the mechanism of conduction in thiophene−thiazole rings, showing a rectification mechanism similar a diode-like effect. This phenomenon was explained by a resonant coupling of the electron transfer and by the localized signature of the wave functions for the bound resonant states at the applied voltage.[16] The conduction mechanism in phenylene−ethylene oligomers was examined with a different approach using quasiatomic minimal basis set molecular orbitals where it was shown that the LUMO states are mainly responsible for the conduction mechanism.[17] Also, several experimental studies have discussed the properties of a dielectric nanowire encapsulated in a self-organized gold nanoparticle chain[18] and have also investigated the nature of the interactions between metal electrodes and the organic molecules.[19,20]

From the spectrum of literature discussed above it is clear that a fundamental understanding of the models for integrating metals with molecules and their intrinsic transport properties is crucial. Five years ago, Nitzan and Ratner[7] proposed seven characteristics/requirements needed for optimizing molecular junctions: (1) the temperature dependence as a function of carrier transport; (2) the evolution of the molecular geometry during the conduction process; (3) the selectivity of junctions produced with different metallic atoms for increased conduction and change in the *I*−*V* characteristics; (4) a fundamental understanding of gating; (5) the change in behavior from a single molecule

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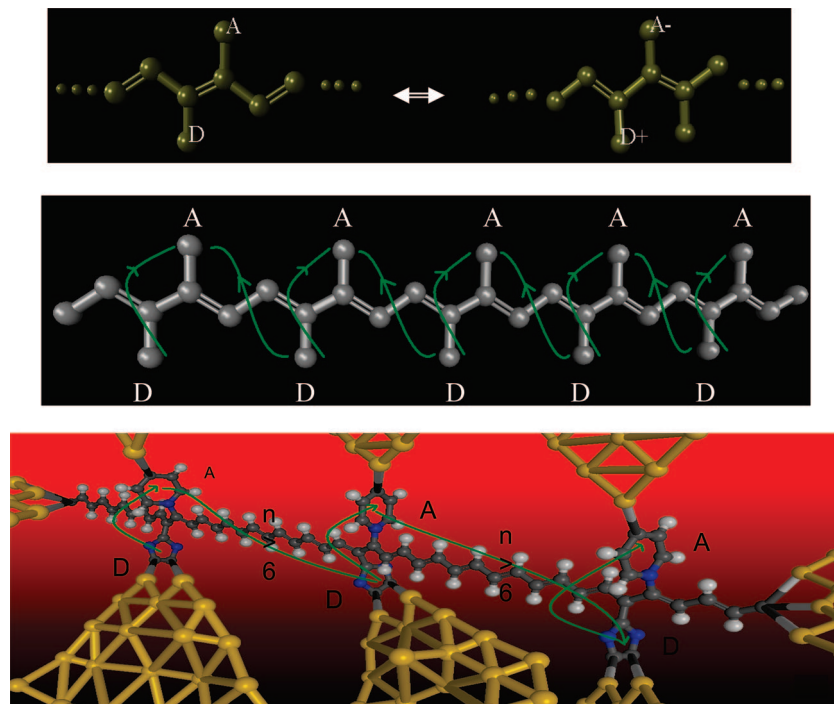*J. Phys. Chem. C, Vol. 112, No. 31, 2008* **12009**

Figure 1. (a) and (b) Typical molecular models investigated in the literature where a switch from the donor to acceptor occurs with size independence and can have from one to several conjugated bonds between the ligands; (c) System presented in this work, which has an intrinsic rule for donor → acceptor or acceptor → donor depending on the length of the conjugated bridge, thereby allowing electron transfer and the design of considerably more complex devices than few-terminal devices.

conductance compared with several molecules working together in a device; (6) effects of changing the bridge by doping or other chemical processes; and (7) the behavior in the presence of radiation.

In this paper, we utilize a combination of *ab initio* techniques (Hartree–Fock (HF), MP2, and DFT) to determine the intrinsic majority carrier distribution in organic nanostructures composed of a betaine derivative as a function of an applied external voltage. The results of our investigation highlight a surprising current vs voltage behavior that is shown to be intrinsic to this family of molecules.

Methodology and Systems Investigated

The molecular switch originally proposed by Carter[2] can be considered as a multistep organic device (Figure 1, *top structure*), where the backbone is composed of ethylene oligomers bound to donor (D) and acceptor (A) groups. Under external voltage, the system switches from one state of conjugation to another, specifically from double-single bonds to single-double bonds. Difficulties in constructing this kind of molecular switch are evident from inspection of Figure 1 (*middle structure*). After the first charge mobility between the D–A, the system does not allow the next segment to work as a device (see the competitive flow arrows), e.g., the second D–A segment will present a back direction flow as a drift current in a macrodevice. To avoid this drawback we propose a solution that allows the molecular switch to depend only on the length of the conjugation between the D–A–D groups. This new approach overcomes the problem of the system proposed in Figure 1. It also opens the possibility for producing large (*more than two*) terminal molecular devices (Figure 1, *bottom*).

Mizuseki, Kawazoe, et al. have recently investigated the transport properties of organic structures as a nanodevice.[21–23] The methodologies employed in these works are supported by first-principles and nonequilibrium Green's function calculations.
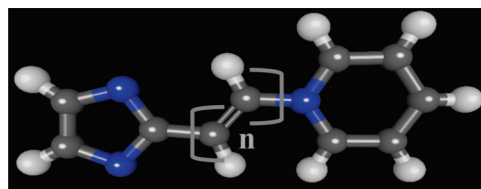

Figure 2. Model investigated in this work, which was used to describe the electronic transport in the D–π–A betaine-like derivatives with *n* values from 0 to 10.

The systems investigated were the conjugated molecules phenyl–dithiol, *p*-terphenyl, and oligothiophene derivatives. In this paper we used the following methodology (the molecular structures are shown in Figure 2): The electronic structure of the systems is examined using Hartree–Fock based approaches (including MP2 and CI for a restricted active space, CASSCF) within the framework of the Gaussian[24] and NWChem[25] packages. The standard Pople basis sets, 6-31G, 6-31G*, 6-311G, 6-311G*, 6-311G** as well as Duning correlation consistent bases sets, cc-pvDZ, and cc-pvTZ, were used for all calculations, yielding similar qualitative results. Density functional theory, both LDA and GGA (PW91, PBE) as well as hybrid functionals (B3LYP, PBE0), traditionally known not to adequately represent extended π-conjugated systems[26] were found to yield similar geometries as the HF based methods but did not reproduce the localization of the molecular orbitals and inversion behavior observed with HF-based methods. Many-body perturbation theory (MP2/6-311G**) and complete active space self-consistent field (CASSCF/6-311G** with up to 14 active electrons and 14 orbitals) gave results that were in good agreement with HF. Therefore, the geometries of the analyzed structures were fully optimized using Hartree–Fock methods under the influence of an external electric field. This procedure has been successfully used in previous work[27,28] where it was pointed out that a molecular push–pull system under specific
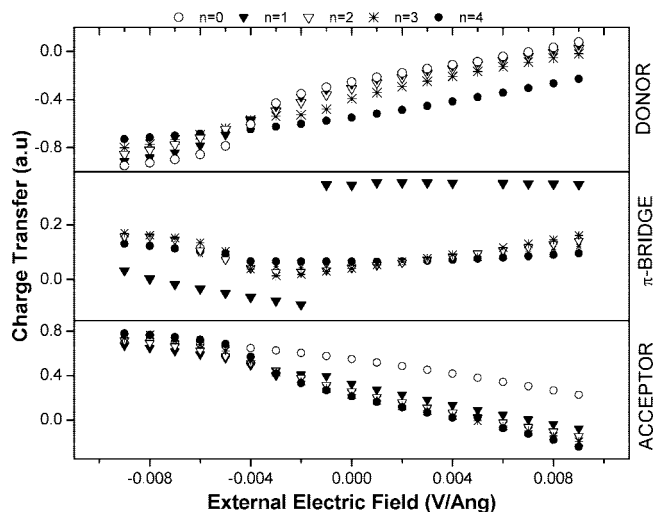
Figure 3. Charge depletion (*upper panel*) [accumulation (*lower panel*)] in the donor [acceptor] group with bridge from zero up to four C=C bonds as a function of external electrical field. The behavior of the bridge (second frame) for small quantity of carbon atoms is presented.

Figure 4. Charge depletion/accumulation (*upper* and *lower* panels) in the donor/acceptor group with five and six conjugated bonds as a function of external electrical field. The behavior of the bridge (second frame) is presented.

conditions can operate as a molecular device as follows: donor$_{bet}$−π bridge−acceptor$_{bet}$ with small bridge lengths,[27,28] donor−π bridge−acceptor with and without metallic contacts, and a three-terminal device including π and σ bridges.[27]

In the next section, we present the results of the calculations and discuss an unusual signature for carrier transport in the systems with a betaine-*type* as the donor and acceptor groups. We also consider how this new rectification process can be used to construct a molecular device composed of the well-known push−pull system with a π *bridge* of variable length.

Results and Discussion

Figure 3 shows a plot of charge transfer vs voltage for small π bridges of lengths ranging from 0 to 4 C=C bonds. The figure is divided into three parts showing the carrier behavior for the donor, bridge, and acceptor as a function of applied external voltage. For these bridge sizes we find a *canonical* result for the *donor-side* of the molecular structure showing that the majority carriers increase [decrease] as a function of external applied electric field for forward [reverse] polarization. As expected, inverse behavior for the *acceptor-side* of the molecular structure shows a decrease [increase] of the majority carriers as a function of external applied electric field for forward [reverse] polarization.

In Figure 4, the charge transfer vs voltage behavior is shown for intermediate sized π bridges with $n = 5$ and 6 C=C bonds. For these bridge lengths an inversion behavior of the charge carriers occurs. This is induced by the conjugation of the π bridge connected with D/A properties of betaine (there is no molecular orbital inversion as opposed to the case below for longer π bridges). The process of flipping between **donor ↔ acceptor** states is controllable simply by altering the length of the π bridge.

An unusual behavior appears for large bridges with lengths ranging from 7 up to 10 C=C bonds (Figure 5). A reverse signature of donor−acceptor characteristic is found, which in this case is primarily induced by a frontier molecular orbital inversion.[28] We interpret this feature as an unidirectional resonant tunneling diode. It is directly associated with an **on/off** molecular switch state where the carriers tunnel through quantum wells that depend on the size of the bridge. It is also
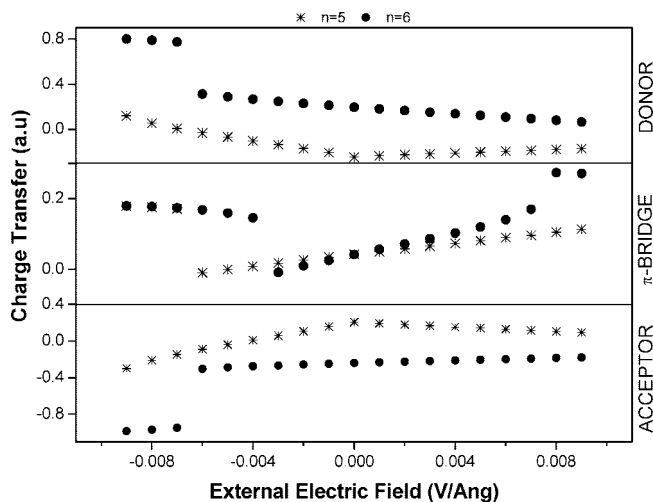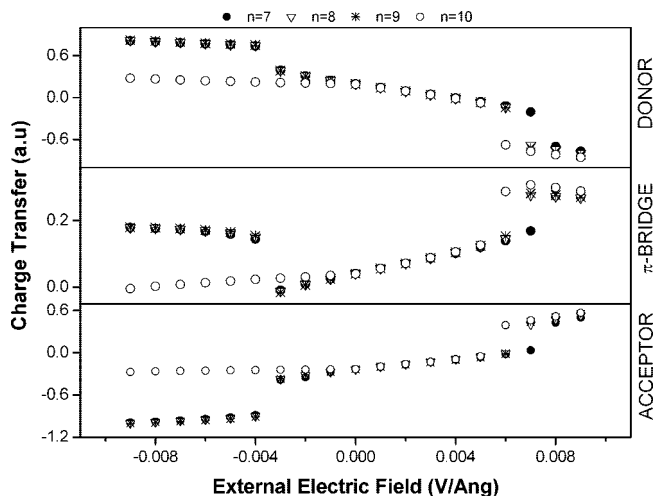

Figure 5. Charge accumulation (*upper panel*) [depletion (*lower panel*)] in the donor [acceptor] group from seven to ten conjugated bonds as a function of external electrical field showing inversion of charge transfer. The behavior of the bridge (second frame) is presented.

possible to simulate the absence of carrier retention (majority or minority) with any bridge size due to the maximum charge values obtained as occurs in a regular *triode for alternating current*.

Overall, we can describe for any size of the betaine-like donor-n π bridge-acceptor system a number of interesting physical behaviors: (i) under forward or reverse applied bias, a *blockage reverse* occurs for number n of C=C bonds larger than 6 that is induced by transition capacitances for $n = 5$ or 6 and works as a reverse junction; (ii) two behaviors similar to Schottky junctions can be denoted for small ($n < 5$) and large ($n > 6$) bridge lengths; (iii) the reverse charge transport increases for ($n > 6$), raising the diffusion capacitance of the system. Also, when the external voltage with positive bias is applied along the molecular backbone, this should increase the electronic flow because of an increase in the signature from donor to the acceptor. Likewise, for the reverse bias, the influence will be from the acceptor to the donor.[27,28]

In addition, cooperative analyses of the data given in the figures unveil some important properties of the studied system. The main electronic transitions of these families of compound

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is related to HOMO to LUMO transition with $0 = n < 7$. Also the HOMO-1 to LUMO transition appears as a main one for $5 < n < 10$. Finally for $n = 10$ only the HOMO-1 to LUMO transition appears as the most probable transition. This feature in the main transition[27,28] can be understood as a competition mechanism between a ballistic transport regime described by Landauer−Buttiker formula with energies *close to* the Fermi level. This is interesting for systems that need fast switching response and could be used as a device that works at low potency level with high PHz operational frequencies, e.g., 10^{12} times higher than typical devices and demand high-speed static pulse signals.

Conclusions

In this work, we presented a theoretical simulation of a novel push−pull (D-π bridge-A) device with unusual charge transfer properties that depend on the size of the bridge between (C=C lengths from $n = 0$ up to $n = 10$) the donor/acceptor. The electronic structure of these systems has an intrinsic switch state that can be summarized as follows: (i) for $n < 5$, the "no switch" state is dominant; (ii) for $n = 5$ or $n = 6$, a clear signature of switch inversion induced by the π bridge size occurs; (iii) for $n > 6$ a complete flip happens; (iv) the ***off/on*** switch effect is independent of the applied bias condition.

We have also shown a possible design associated with this new charge transfer effect that is composed of an organic 2-terminal nanodevice and utilizes the inversion of frontier molecular orbitals found in usual nanodevices. Also, it is important to stress that the synthesis of these systems should be an attractive goal to be realized.

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