

# Electric Field Modulation on the Geometric and Electric Structures of Diblock Molecular Diode

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## ABSTRACT

Theoretical investigations on the diblock molecular diode molecule, thiophene-thiazole compound, have been carried out at Hartree-Fock level by considering the interaction from the external electric field. It demonstrates that the electronic structures of this kind of diode molecule are essentially different from those based on the Aviram and Ratner model, in which donor and acceptor-conjugated segments are separated by an insulating  $\sigma$ -bonded segment, in terms of the energy levels of the frontier molecular orbitals as well as their spatial distributions. The introduction of the external EF modifies both the geometric and electronic structures. In particular, the spatial distributions of the frontier molecular orbitals are also shifted under the external EF. Moreover, all these features show strong EF direction dependence due to the build in intrinsic molecular asymmetric features, which could be used to intuitively interpret the asymmetrical current-voltage behaviors of molecules.

**Keywords:** Molecular electronics; External electric field; *Ab initio*, Electronic structures

## 1 INTRODUCTION

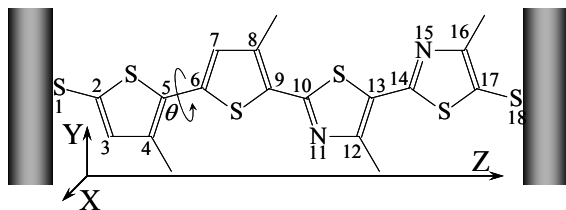
The continuous miniaturization of conventional silicon-based electronics will eventually face the insurmountable challenge of the quantum effects, such as tunneling cannot be avoided and the control of doping in ultrasmall regions becomes problematical[1]. To meet expected computing demands of the future, novel and alternative materials for the nanoscaled components of future electronic devices must be developed. Molecules as individual active devices are obvious candidates for the ultimate ultrasmall components in nanoelectronics. The idea of using the organic molecules as the functional units in electronic devices has received great attention since the first theoretical demonstration by Ratner and Aviram[2] that individual organic molecules could function as a molecular diode (the AR model). Tremendous experimental efforts have been focused on the molecular wires, diodes, switches, storage devices, and field effect transistors at real molecular level[3,4]. Among these devices, diodes have played a key role in the development of molecular electronics both

because they formed the basis for the first proposal a unimolecular electronic device by Aviram and Ratner[2], and because they are one of the simplest functions to build into an electronic component[5]. In general, molecular diodes are asymmetric organic molecules in which the electrons flow through in one preferential direction. A number of diode molecules have been developed by different research groups based on the AR model that contains donor and acceptor  $\pi$ -conjugated segments separated by an insulating  $\sigma$ -bonded segment of molecular wire[6]. Recently, Yu et al.[7] synthesized a new class of diode molecules based on diblock oligomer molecules. These molecules, consisting of electron-rich thiophene and electron-deficient thiazole structural units, have shown a pronounced rectification effect, resembling the semiconductor p-n junction. Importantly, it was experimentally proved that the rectification is an intrinsic property of the molecule rather than asymmetry of the electrodes and/or molecule-electrode interfaces[8].

Parallel to the experimental studies, a variety of theoretical approaches have been applied to model electron transport in molecular electronics, ranging from semi-empirical to *ab initio* methods. For molecular diodes, theoretical investigations are mainly focused on the diode based on AR proposal[9-11]. However, little is known about the diblock molecular diode. Although those studies focusing on the geometric and electronic structures[12,13] and on the electron transportation behavior based non-equilibrium Green's function (NEGF) formalism[14,15] are demonstratively useful, most of them seem to less concern the surroundings that may interact with the functional molecules via such as Van De Waal's force, electrostatic force, hydrophobic interaction and solvated effect. Among these molecular-scale refined interactions, the one from the external EF is of considerable importance, because of the fairly large bias of several volts applied on the functional molecules wired in the circuit. Although the non-equilibrium Green's function method implicitly includes the EF effect in self-consistent calculation, the EF-dependence of the molecular structure is generally not considered. Clearly, under the EF interaction, both the molecular geometry and electronic structure are doubted to be the same as in the zero-EF case[16]. Therefore, a detailed study of the EF effect on the electronic and geometric structures of bridge molecule is of great

importance for precisely understanding the molecular electrical properties.

The purpose of this work is to investigate the geometric and electronic structures of a new kind of diblock oligomer molecular diode, thiophene-thiazole diblock molecule, by considering the interaction from an external EF. The influence of the external EF is discussed in terms of the variations of the electron distribution, bond length, torsional angles, and energy levels of the frontier orbitals and their spatial distribution, which are crucial parameters in dominating the molecular electrical properties. The diblock oligomer molecule consists of two parts, each containing an equal number of thiophene (C4N) and thiazole (C3NS) rings as shown in Figure 1. Recent studies have demonstrated that the performance of a molecular wire is predominated by many factors, such as the nature of the molecule itself[17], the interface between the molecule and the electrode[18], the electrode material[19], and the electrode shape[20]. Since considering all these factors looks impossible, we give a simplified model that a diblock oligomer molecule bridges two chemically inert electrodes as shown in Fig. 1, meaning the effect of the interface and electrode materials has been neglected. The simplification used in present study is especially valid, when the conjugation backbone is long (so we can gaze on the central part of the wire) or the coupling between the molecule and the metal lead is broken by special technique, for example insert of saturated alkyl chain and extension of the metal-molecule distance.



**Figure 1.** Chemical structure of the conjugated diblock oligomer molecule studied in the present work. The uniform external EF is aligned along the two terminal sulfur-sulfur inter-atomic vector.

## 2 METHODOLOGY AND COMPUTATIONAL PROCEDURE

The methodology for investigating the geometric and electronic structures of the diblock molecule under the external EF was done in two parts. In the first case, prior to the introduction of EF, the model molecule was fully optimized at HF/6-31G\* level of theory. In the second set, the two terminal sulfur atoms of the former optimized molecule were fixed in space to simulate the connection to the electrodes and all the other geometric parameters were, then, optimized in an external EF at the same level of theory. The uniform EF ranging from zero to  $2.57 \times 10^9$  V/m and aligned along the two terminal carbon-carbon inter-atomic vector was applied to the molecule, which may

reasonably represent the working condition of the molecular electronic device[21]. For convenience of discussion, we define the EF facing the left side of the molecule as L-direction EF, and R-direction EF when it faces the right side. All calculations were performed using Gaussian 03 program[22].

## 3 RESULTS AND DISCUSSION





### 3.1 Geometric and electronic structures of the molecular diode

The knowledge on the geometric and electronic structures of a molecule is the first step for understanding and predicting the various molecular electrical behaviors and consequently forms the basis for rational design of optimized materials for molecular electronics. To obtain the most stable conformation, several possible initial conformations were optimized, followed by frequency calculations. The results show that the all-trans conformation is the most stable one (See Figure 1). As expected, the thiophene units show a twisted conformation ( $C4-C5-C6-C7=126.99^\circ$ ) due to the strong steric interaction of the neighboring rings. However, the thiazole units and the neighboring thiophene ring show a strict planar conformation. This feature is consistent with the nonylbithiazole molecule in which the chain backbone show a planar conformation as calculated by Curtis et al.[23] by molecular mechanics and EHMO methods. This planar character can be ascribed to the strong electron withdrawing characteristic of the nitrogen atoms which dramatically weakens the steric repulsion of the adjacent rings and enhances the conjugation of the backbone. Mulliken atomic charges analysis shows the net charges on the sulfur and nitrogen atoms are 0.35~0.39 and -0.56~-0.58, respectively. The three single carbon-carbon bond linkages are almost identical ( $C5-C6=1.47$  Å,  $C9-C10=1.46$  Å,  $C13-C14=1.46$  Å). However, the C-N bond lengths (1.37 and 1.29 Å for the single and double bond, respectively) in the thiazole units are much shorter than the C-C bond lengths (1.43 and 1.35 Å for the single and double bond, respectively) in the thiophene units.

Previous studies[24,25] indicate the spatial distribution of the molecular orbitals, especially the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are important guidelines for understanding quantum transport properties of functional molecular wires. Table 1 illustrates the spatial distribution of the HOMO-1, HOMO, LUMO, and LUMO+1 of the diblock molecule. Although all the four molecular orbitals are delocalized along the whole molecular conjugated backbone, by detailed analysis, we still can observe the HOMO slightly tends to localize on the thiophene units and the LUMO slightly tends to localize on the thiazole units. This trend is in agreement with other conjugated molecules substituted by electron-donating and electron-withdrawing groups, such as substituted tour wires[26]. This character is dramatically different from the AR model molecules that

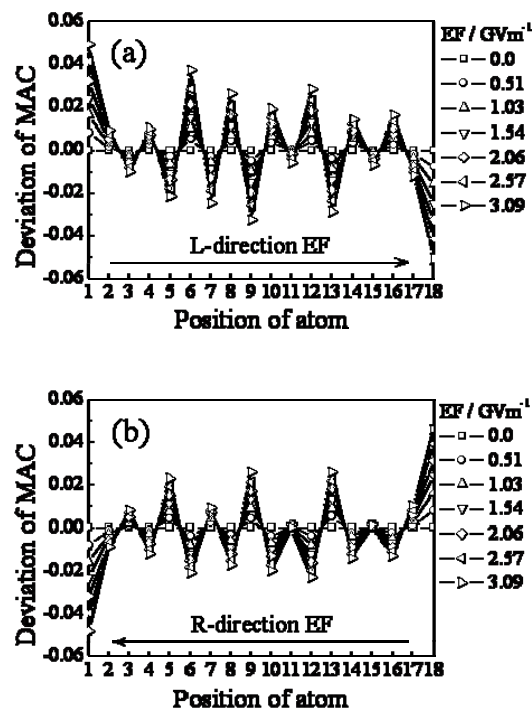
involve electron-donating and electron-withdrawing units bridged by a saturated spacer, in which the HOMO is almost entirely localized on the electron-donating subunit, whereas LUMO would rather be localized on the electron-withdrawing subunit[11,27,28]. This difference can be due to good coupling between the electron-rich thiophene and electron-deficient thiazole units. Therefore, one can expect the electron transport mechanism in this kind of conjugated diblock molecular diode may be different from the AR mechanism.

**Table 1.** Spatial distribution of HOMO-1, HOMO, LUMO, and LUMO+1 under zero EF.

HOMO-1	HOMO	LUMO	LUMO+1
			

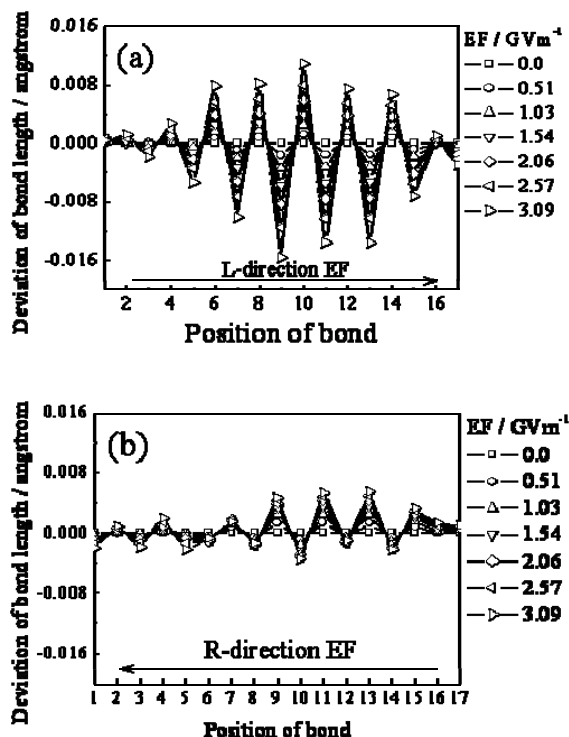
### 3.2 Electric field dependence of the geometric structure

Due to the delocalized  $\pi$ -electrons of conjugated organic molecules, when an external EF is applied, their charge distributions are easily modified and consequently may lead to the reconfiguration of molecules. Therefore, it is of great importance to study EF effect on the molecular geometric structure not only for precisely understanding the electrical properties of the molecules wired in practical circuits but also for the design and rationalization of molecular electronic devices. Figure 2 illustrates the Mulliken atomic charges on each atom in the conjugated backbone under various EF with respect to the zero-EF case. It can be seen the Mulliken atomic charges on each atom vary with the increase of EF, showing that those on the on the high potential end of the double bonds decrease and those on the low potential end of the double bonds increase due to the easier polarization of the double bond than the single bond. Moreover, compared with the carbon atoms, the Mulliken atomic charges on nitrogen atoms show much less variation under the EF. Since the bond length is directly related to the electrons participate in bond formation, the bond lengths are expected to vary under the external EF due to this electron redistribution in molecules. Figure 3 shows the EF effect on the individual bond lengths on the conjugated molecular backbone. Under the L-direction EF, the single bonds become shorter and the double bonds become longer, leading to a higher conjugation as shown in Figure 3a. However, the EF-dependence of the bond length is not identical for all the bonds. The maximum variation occurs in the central part for both the single and double bonds due to the better conjugation as compared with those toward the end of the molecule. Moreover, the bonds on the thiazole unit show more variation than those on the thiophene unit.



**Figure 2.** Variation of Mulliken atomic charges on each atom along the conjugation backbone under (a) L-direction EF and (b) R-direction EF (see the labeling of the atom sites in Figure 1). The Mulliken atomic charges under zero EF are referred to as zero.

Under the R-direction EF, the thiophene unit remains the same variation as the case under L-direction EF, i.e., the single bonds become shorter and the double bonds become longer. This observation is in agreement with other carbon-based conjugated systems, such as polyacetylene and tour wires, as reported by us.[16,25] Contrast to the case of L-direction EF, under the R-direction EF leads to an opposite variation of the bond lengths in the thiazole units, i.e., the single bonds become longer and the double bonds become shorter, resulting in a weakened conjugation. The bonds on thiazole units also show more deviation than those on thiophene units. Compared with the L-direction EF case, the bond length deviation on the thiazole units are much less under the R-direction EF. For example, with the EF increasing from *zero* to  $3.09 \times 10^9 \text{ Vm}^{-1}$ , the maximum bond length variation on the thiazole units is  $0.011 \text{ \AA}$  in the case of L-direction EF, which is about two times as large as that ( $0.005 \text{ \AA}$ ) in the case of R-direction EF. Based on the above results, we can conclude that the thiazole conjugation backbone is more sensitive to the external EF and show great EF-direction dependence, indicating the asymmetric character is successfully introduced in the molecule under the EF.



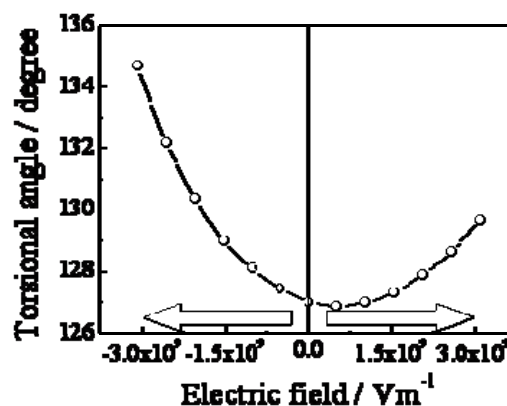
**Figure 3.** Variation of bond length along the conjugation backbone under (a) L-direction EF and (b) R-direction EF (see molecular structure in Figure 1 for bond codes). The bond length under zero EF is referred to as zero.

It is known that the bond length alternation (BLA, defined as the average difference between the adjacent single and double bonds) along the backbone of a conjugated system is a crucial parameter for tuning the electrical properties of molecular wire[29]. Many other properties, for example nonlinear optical properties and spectrum, are also seriously dominated by the degree of BLA[30,31]. Therefore, the above observation is of great instructive for understanding the molecular structure-property relationship.

Other than the bond length variation, the torsional angle of the two adjacent thiophene rings ( $\theta$ , see Figure 1) also shows EF dependence as shown in Figure 4. For the case of L-direction EF, with the EF increasing, the torsional angle increases monotonously, i.e., the molecule tends to be planar. While for the case of R-direction EF, with the EF increasing, the torsional angle initially decreases slightly and shows a minimum at  $5.14 \times 10^8 \text{ Vm}^{-1}$ . A further increase of EF leads the torsional angle increases again. However, this increase of the torsional angle is much less than the case of L-direction EF. For example, with the EF increasing from zero to  $3.09 \times 10^9 \text{ Vm}^{-1}$ , the torsional angle is increased by  $7.68^\circ$  under the L-direction EF, which is about three times as larger as that ( $2.65^\circ$ ) under the R-direction EF. This torsional behavior can be understood by the combined results of the steric repulsion and  $\pi$ -electron conjugation. In

general, the equilibrium conformation is governed by the subtle balance between the steric repulsion and strength in  $\pi$ -electron conjugation. The  $\pi$ -electron conjugation means an overlapping  $\pi$ -electron orbital between two aromatic groups. If  $\pi$ -electron conjugation dominates over repulsion, then the molecule is planar. The reverse yields a more twisted form.

As evidenced by the above results, the conjugation configuration makes the molecule susceptible to change in its configuration under an external EF. Therefore, to model the electrical behavior of molecular electronic devices more accurately, this geometry relaxation under EF should be taken into account. Moreover, this reconfiguration under the EF can be further used to design some novel molecular electronic devices, such as molecular switches[32] and field effect transistors[33].

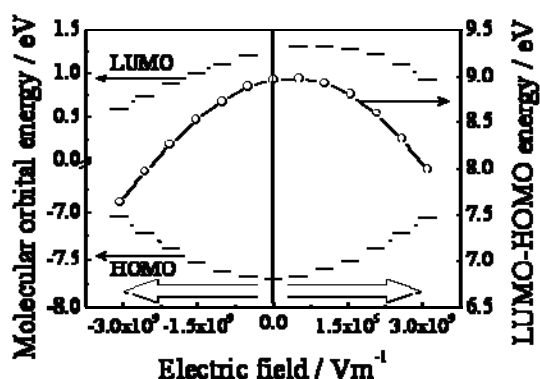


**Figure 4.** EF effect on the torsional angle between the two thiophene rings. The negative EF and positive EF correspond to L-direction and R-direction EF, respectively.

### 3.3 Electric field dependence of the electronic structure

In order to study, and eventually to be able to modulate the asymmetric electrical properties of the system, it is important to understand the details how the frontier molecular orbital energies respond to the external EF. Figure 5 shows the evolutions of HOMO and LUMO energy levels under EF. It can be seen that with the EF increasing the HOMO increases monotonously under both the L-direction and R-direction EF. Within the EF applied in the present work, HOMO evolves almost symmetrically with respect zero EF. However, the LUMO yields an obvious asymmetrical evolution with respect zero EF. For the case of L-direction EF, LUMO decreases monotonously. While, for the case of R-direction EF, LUMO initially increase and shows a maximum at  $1.03 \times 10^9 \text{ Vm}^{-1}$ . Further increasing EF makes LUMO decrease again. In addition, with the EF increasing from zero to  $3.09 \times 10^9 \text{ Vm}^{-1}$ , the LUMO shows more decrease under L-direction EF than R-direction EF. This asymmetrical evolution of LUMO

consequently leads to an asymmetrical LUMO-HOMO gap with respect to zero EF. Under L-direction EF LUMO-HOMO gap decreases monotonously, while under the R-direction EF LUMO-HOMO gap show a maximum at  $0.51 \times 10^9 \text{ Vm}^{-1}$ , and further increase R-direction EF leads LUMO-HOMO gap decrease. With the EF increasing from zero to  $3.09 \times 10^9 \text{ Vm}^{-1}$ , the HLG is decreased by 1.32 eV and 0.97 eV under L-direction and R-direction EF, respectively. While electron transport is dominated by charge carrier tunneling inside the HOMO-LUMO gap (non-resonant), we may expect a difference of current between the L-direction EF and R-direction EF on the molecular wire.



**Figure 5.** EF effect on the HOMO and LUMO energy levels and the LUMO-HOMO gap for the diblock oligomer molecule. The negative EF and positive EF correspond to L-direction and R-direction EF, respectively.

Changes in the spatial distributions of molecular orbitals, especially those of HOMO and LUMO, are excellent indicators of electron transport of the molecule wired in circuits, because it dominates the coupling to the electrode and the electron transmission tunnel[18,19,34]. Table 2 illustrates the spatial distribution of the HOMO-1, HOMO, LUMO, and LUMO+1 of the diblock molecule under various EF. Under the external EF, the HOMO tends to move to the low potential side and LUMO to the high potential side. For example, under the L-direction EF, the HOMO and LUMO shift to thiophene units side and thiazole units side, respectively. Both of them become more and more localized. In particular, the HOMO-1 changes from fully delocalized to fully localize on the most left thiophene ring with the EF increasing from zero to  $3.09 \times 10^9 \text{ Vm}^{-1}$ . In contrast, the LUMO+1 show much less change under the EF. The R-direction EF drives HOMO and LUMO from the thiophene side and the thiazole side, respectively. For the case of R-direction EF, initial increasing EF (EF less than  $1.03 \times 10^9 \text{ Vm}^{-1}$ ) leads both HOMO and LUMO more delocalized across the molecular backbone due to their slight intrinsic asymmetrical spatial distributions as discussed in section 3.1. However, a further increasing R-direction EF makes them more and more

delocalized again. Similar to the case of L-direction EF, the HOMO-1 show the most variation and the LUMO+1 show much less variation under the perturbation of EF. In a modern understanding, the details of the electron transfer paths can be deconvoluted by considering each electron transmission tunnel. Generally, energy levels such as HOMO and LUMO can be potentially the transmission tunnels. A conducting channel is a molecular orbital that is fully delocalized along the molecular backbone; conversely, a nonconducting channel is a localized molecular orbital, which cannot connect both end of the molecule attached to the metallic contacts. Therefore these observations are very instructive for intuitive understanding the molecular current-voltage behaviors.

**Table 2.** Spatial distribution of HOMO-1, HOMO, LUMO, and LUMO+1 under various EF (in  $10^9 \text{ Vm}^{-1}$ ) for thiophene-thiazole diblock molecule. The negative EF and positive EF correspond to L-direction EF and R-direction EF, respectively.

EF	HOMO-1	HOMO	LUMO	LUMO+1
-3.09				
-2.06				
-1.03				
0				
1.03				
2.06				
3.09				

## 4 CONCLUSION

We have performed *ab initio* HF study to the modeling of a new diode molecule, thiophene-thiazole diblock molecule, by considering the external EF. It proves the thiophene units show a twisted conformation, while the thiazole units give a fully planar form. In particular, the spatial distributions of the HOMO and LUMO are almost delocalized over the whole molecule, which is dramatically different from the case of AR molecular diode. The introduction of external EF modifies both the geometric and electronic structures of the molecule. Such as decrease/increase the bond length alternation and the torsional angle depending on the magnitude of external EF and direction. In addition, the spatial distribution of the frontier molecular orbitals is also shifted under the external EF, showing the HOMO and LUMO move to low potential and high potential side of the molecule, respectively. The evidences provided in present studies remind us that the interaction between the EF and the molecular materials may greatly influence the geometric and electronic structures of the molecule, which may consequently modulates the

electrical behaviors of the device performance. Therefore, a novel molecular electronic device designed without considering the EF effect should be questionable in practice. The results reported in this paper may give more insight into the design or rationalization of the molecular devices.

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