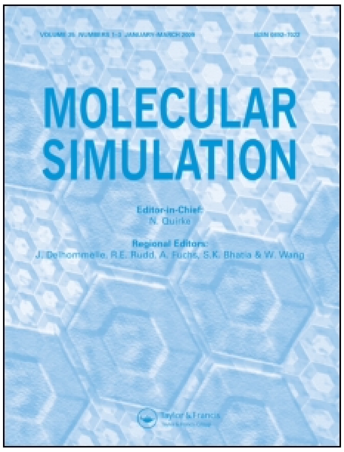

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Ab initio investigations on the geometric and electronic structures of a diblock molecular diode under the influence of an external bias

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To cite this Article Li, Yanwei , Yao, Jinhuan , Yang, Chuanlu , Zhong, Shengkui and Yin, Geping(2009) '*Ab initio* investigations on the geometric and electronic structures of a diblock molecular diode under the influence of an external bias', Molecular Simulation, 35: 4, 301 — 307

To link to this Article: DOI: 10.1080/08927020802468356

URL: http://dx.doi.org/10.1080/08927020802468356

Molecular Simulation
Vol. 35, No. 4, April 2009, 301–307

Ab initio investigations on the geometric and electronic structures of a diblock molecular diode under the influence of an external bias

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(*Received 15 August 2007; final version received 10 September 2008*)

Theoretical investigations on the diblock molecular diode, thiophene–thiazole compound, have been carried out at the Hartree–Fock (HF) level by considering the interaction under the external bias. They demonstrate 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 π-conjugated segments are separated by an insulating σ-bonded segment, in terms of the energy levels of the frontier molecular orbitals as well as their spatial distributions. The introduction of the external bias modifies both the geometric and electronic structures. In particular, the spatial distributions of the frontier molecular orbitals are also shifted under the external bias. Moreover, all these features show a strong dependence on the polarity of the applied bias due to the build in intrinsic molecular asymmetric structures, which could be used to intuitively interpret the asymmetrical current–voltage behaviours of molecules.

Keywords: molecular electronics; external bias; *ab initio*; electronic structures

1. Introduction

The continuous miniaturisation of conventional silicon-based electronics will eventually face the insurmountable challenge of the quantum effects: tunnelling cannot be avoided and the control of doping in ultra-small regions will become problematical [1]. To meet the 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 ultra-small 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 the 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 of unimolecular electronic devices 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 π-conjugated segments separated by an insulating σ-bonded segment [6]. Recently, Yu et al. [7] have synthesised 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 the 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 the 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 behaviour-based non-equilibrium Green's function (NEGF) formulism [14,15] are demonstratively useful, most of them seem to be less concerned with the surroundings that may interact with the functional molecules via, such as, van der Waals force, electrostatic force, hydrophobic interaction and solvated effect. Among these molecular-scale interactions, the one

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ISSN 0892-7022 print/ISSN 1029-0435 online

DOI: 10.1080/08927020802468356
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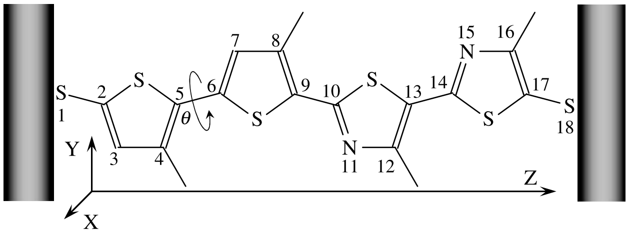

Figure 1. Chemical structure of the conjugated diblock oligomer molecule studied in the present work. The uniform external electric field is aligned along the two terminal sulphur–sulphur inter-atomic vector.

from the external bias is of considerable importance because, while small volts applied on the functional molecules wired in the circuit, the corresponding electric field strength is practically enormous (up to 10^9 V/m). Although the NEGF method implicitly includes the bias effect in a self-consistent calculation, the bias dependence of the molecular structure is generally not considered. Clearly, under the bias interaction, both the molecular geometry and the electronic structure are doubted to be the same as in the *zero*-bias case [16]. Therefore, a detailed study of the bias effect on the electronic and geometric structures of the 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 under an external bias. The influence of the external bias 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.

2. Methodology and computational procedure

It is known that the performance of a molecular junction 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 of a diblock oligomer molecule that bridges two chemically inert electrodes as shown in Figure 1, meaning the effect of the interface and electrode materials has been neglected. The simplification used in the 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 a special technique, for example insert of a saturated alkyl chain and extension of the metal–molecule distance. The methodology for investigating the geometric and electronic structures of the diblock molecule under the external bias was done in two parts. In the first case, prior to the introduction of external bias, the model molecule was fully optimised at the HF/6-31G* level of theory. In the second set, two terminal sulphur atoms of the former optimised molecule were fixed in space to simulate the connection to the electrodes and all the other geometric parameters were, then, optimised in an external electric field at the same level of theory. The uniform electric field ranging from 0 to 3.09×10^9 V/m (corresponds to a 0–5.35 V voltage imposed on the diblock molecule, which is 17.34 nm long) 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 high potential imposed on the left and right ends of the molecule as the positive and negative bias, respectively. All calculations were performed using Gaussian 03 program [22].

3. Results and discussion

3.1 Geometric and electronic structures of the molecular diode

Knowledge of the geometric and electronic structures of a molecule is the first step for understanding and predicting the various molecular electrical behaviours, and, consequently, forms the basis for the rational design of optimised materials for molecular electronics. To obtain the most stable conformation, several possible initial conformations were optimised, followed by frequency calculations. The results show that the *all-trans* conformation is the most stable one (Figure 1). As expected, the thiophene units show a twisted conformation (C4–C5–C6–C7 = 126.99°) due to the strong steric interaction of the neighbouring rings. However, the thiazole units and the neighbouring thiophene ring show a strict planar conformation. This feature is consistent with the nonylbithiazole molecule in which the chain backbone shows a planar conformation as calculated by Curtis et al. [23] using molecular mechanics and EHMO methods. This planar character can be ascribed to the strong electron-withdrawing characteristic of the nitrogen atoms that dramatically weakens the steric repulsion of the adjacent rings and enhances the conjugation of the backbone. The Mulliken atomic charge analysis shows that the net charges on the sulphur and nitrogen atoms are 0.35 to 0.39 and −0.56 to −0.58, respectively. The three single carbon–carbon bond linkages are almost identical

Table 1. Spatial distribution of HOMO − 1, HOMO, LUMO and LUMO + 1 under *zero* bias.

HOMO − 1	HOMO	LUMO	LUMO + 1
			

(C5–C6 = 1.47 Å, C9–C10 = 1.46 Å and C13–C14 = 1.46 Å). However, the C–N bond lengths (1.37 and 1.29 Å for the single and double bonds, 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 bonds, respectively) in the thiophene units.

Previous studies [24,25] indicate that the spatial distributions 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 delocalised along the whole molecular conjugated backbone, by the detailed analysis, we still can observe that the HOMO slightly tends to localise on the thiophene units and the LUMO slightly tends to localise 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 localised on the electron-donating subunit, whereas LUMO would rather be localised on the electron-withdrawing subunit [27,28]. This difference can be due to a good coupling between the electron-rich thiophene and electron-deficient thiazole units. Therefore, one can expect that the electron transport mechanism in this kind of conjugated diblock molecular diode may be different from the AR mechanism.

3.2 External bias dependence of the geometric structure

Due to the delocalised π-electrons of conjugated organic molecules, when a bias 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 the bias 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 rationalisation of molecular electronic devices. Figure 2 illustrates the Mulliken atomic charges on each atom in the conjugated backbone under different biases with respect to the *zero*-bias case. It can be seen that the Mulliken atomic charges on each atom vary with the increase of the external bias, showing that those 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 polarisation 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 external bias. Since the bond length is directly related to the electrons that participate in the bond formation, the bond lengths are expected to vary under the bias due to this electron redistribution in molecules. Figure 3 shows the bias effect on the individual bond lengths on the conjugated molecular backbone. Under the positive bias,

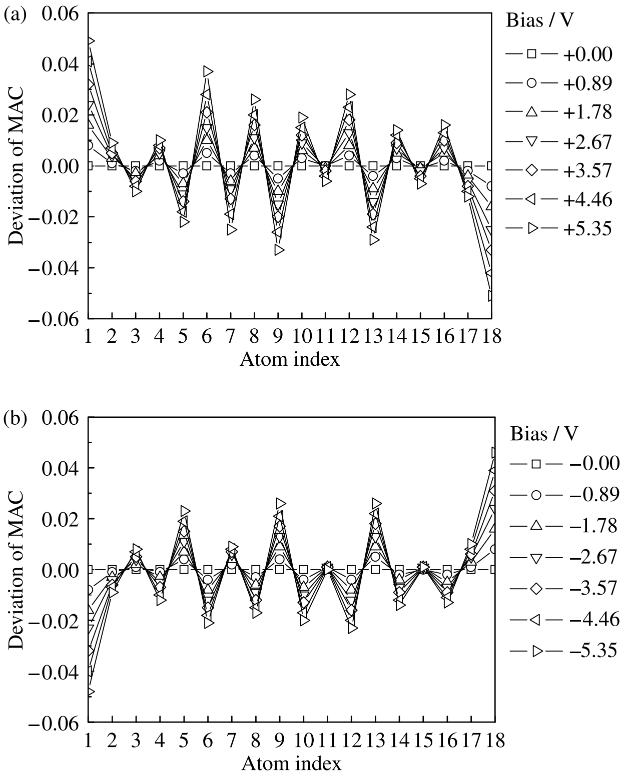

Figure 2. Variation of the Mulliken atomic charges on each atom along the conjugation backbone under (a) a positive bias and (b) a negative bias (see the labelling of the atom in Figure 1). The Mulliken atomic charges under *zero* bias are referred to as *zero*.

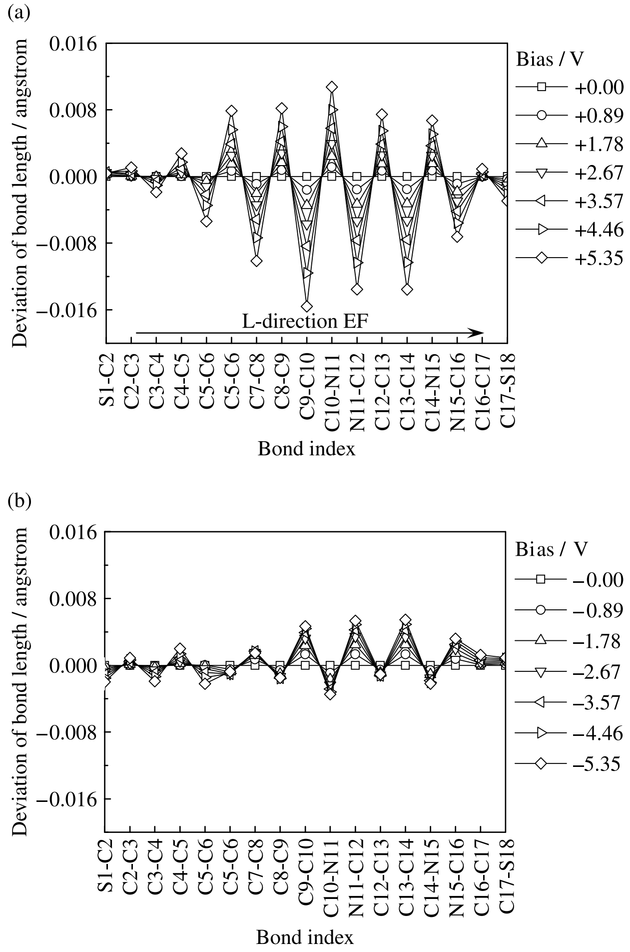

Figure 3. Variation of the bond length along the conjugation backbone of the diblock molecule under (a) a positive bias and (b) a negative bias (for the bond code, see the labelling of the atom in Figure 1). The bond length under *zero* bias is referred to as *zero*.

the single bonds become shorter and the double bonds become longer when compared with the case of *zero* bias, leading to a higher conjugation, as shown in Figure 3(a). However, the bias 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 when compared with those towards the end of the molecule. Moreover, the bonds on the thiazole unit show more variation than those on the thiophene unit.

Under the negative bias, the thiophene unit remains the same variation as the case of the positive bias, i.e. the single bonds become shorter and the double bonds become longer, as shown in Figure 3(b). This observation is in agreement with other carbon-based conjugated systems, such as polyacetylene and tour wires, as reported by us [16,25]. In contrast to the case of the positive bias, the negative bias 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 when compared with those under *zero* bias. The bonds on the thiazole units also show more deviation than those on the thiophene units. Moreover, the bond length deviation on the thiazole units under the negative bias is much less than that under the positive case. For example, with the bias voltage increasing from 0 to 5.35 V, the maximum bond length variation on the thiazole units is 0.011 Å in the case of the positive bias, which is about two times as large as that (0.005 Å) in the case of the negative bias. Based on the above results, we can conclude that the thiazole conjugation backbone is more sensitive to the external bias and show great bias polarity dependence, indicating that the asymmetric character is successfully introduced in the molecule under the EF.

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 the 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 importance for understanding the molecular structure–property relationship.

Other than the bond length variation, the torsional angle of the two adjacent thiophene rings (θ, see Figure 1) also shows EF dependence, as shown in Figure 4. For the case of the positive bias, with the bias voltage increasing, the torsional angle increases monotonously, i.e. the molecule tends to be planar. While for the case of the negative bias, with the bias voltage increasing, the torsional angle initially decreases slightly and shows a minimum at 0.89 V. A further increase of the bias voltage leads again to the increase of the torsional angle. However,

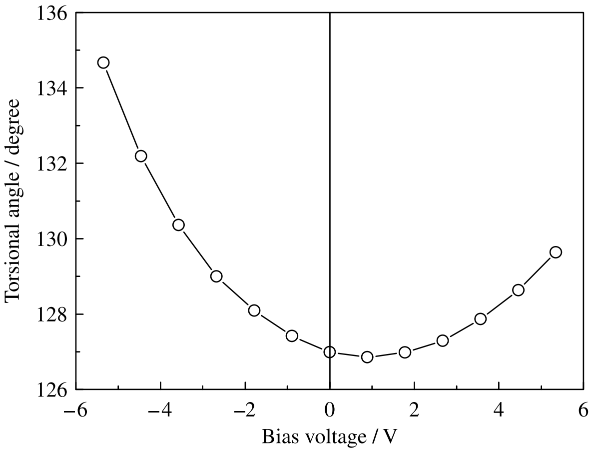

Figure 4. External bias effect on the torsional angle between the two thiophene rings.

this increase of the torsional angle is much less than the case of the positive bias. For example, with the bias voltage increasing from 0 to 5.14 V, the torsional angle is increased by 7.68° under the positive bias, which is about three times as larger as that (2.65°) under the negative bias. This torsional behaviour can be understood by the combined results of the steric repulsion and π-electron conjugation. In general, the equilibrium conformation is governed by the subtle balance between the steric repulsion and strength in π-electron conjugation. The π-electron conjugation means an overlapping π-electron orbital between two aromatic groups. If π-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 bias. Therefore, to model the electrical behaviour of molecular electronic devices more accurately, this geometry relaxation under the bias should be taken into account. Moreover, this reconfiguration under the bias can be further used to design some novel molecular electronic devices, such as molecular switches [32] and field-effect transistors [33].

3.3 External bias 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 bias. Figure 5 shows the evolution of HOMO and LUMO energy levels under different biases. It can be seen that with the bias voltage increasing, the HOMO increases monotonously. Within the bias voltage applied in the present work, HOMO evolves almost symmetrically with respect to *zero* bias. However, LUMO yields an obvious asymmetrical evolution with respect to *zero* bias. For the case of the positive bias, LUMO decreases monotonously. While, for the case of the negative bias, LUMO initially increases and shows a maximum at 1.78 V. Further increasing the negative bias makes LUMO to decrease again. In addition, with the bias voltage increasing from 0 to 5.14 V, LUMO shows more decrease under the positive bias than under the negative bias. This asymmetrical evolution of LUMO consequently leads to an asymmetrical LUMO–HOMO gap with respect to *zero* bias. Under the positive bias, the LUMO–HOMO gap decreases monotonously. While under the negative bias, the LUMO–HOMO gap shows a maximum at 0.89 V, and by further increasing the negative bias leads to the decrease of the LUMO–HOMO gap. With the bias voltage increasing from 0 to 5.14 V, the LUMO–HOMO gap decreases by 1.32 and 0.97 eV under the positive and negative bias, respectively. This LUMO–HOMO gap change under the external bias can be related to the change in the molecular torsional angle, as shown in Figure 4. It is known that the torsional angle between adjacent aromatic rings blocks the conjugation within the molecular backbone and, accordingly, increases the LUMO–HOMO gap [32,34]. Since the molecular torsional angle increases (i.e. the molecule tends to be planar) with the external bias (Figure 4), the molecular conjugation is strengthened and, accordingly, the LUMO–HOMO gap decreases, as shown in Figure 5. The more the torsional angle increases, the more the LUMO–HOMO gap decreases. Therefore, the LUMO–HOMO gap under the negative bias decreases more than that under the positive bias. While electron transport is dominated by charge carrier tunnelling inside the HOMO–LUMO gap (non-resonant), the barrier for electron transfer is proportional to the LUMO–HOMO gap in a first approximation [35]. One can expect that the molecular current under the negative bias should be higher than that under the positive bias, which is in agreement with the experimental results by Yu et al. [7] using the STM method for the diblock molecules sandwiched between two gold electrodes.

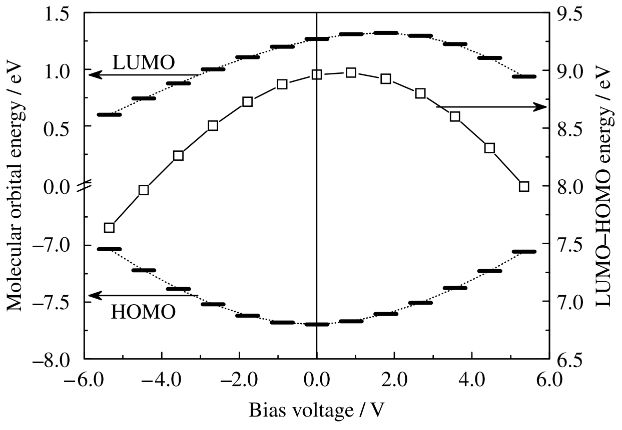

Figure 5. External bias effect on the HOMO and LUMO energy levels as well as the LUMO–HOMO gap for the diblock oligomer molecule.

The 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 [18,19,36]. Table 2 illustrates the spatial distribution of the HOMO − 1, HOMO, LUMO and LUMO + 1 of the diblock molecule under different external biases. Under the influence of the external bias, the HOMO tends to move to the low-potential side and LUMO to the high-potential side. For example, under the positive bias, HOMO and LUMO shift to the thiophene and thiazole unit sides, respectively. Both of them become more and more localised. In particular, HOMO − 1 changes from fully delocalised to fully localised on the most left thiophene

Table 2. Spatial distribution of HOMO − 1, HOMO, LUMO and LUMO + 1 under different biases for the thiophene–thiazole diblock molecule.

Bias (V)	HOMO − 1	HOMO	LUMO	LUMO + 1
−5.35				
−3.57				
−1.78				
0.00				
+1.78				
+3.57				
+5.35				

ring with the bias increasing from 0 to 5.14 V. By contrast, LUMO + 1 shows much less change under the external bias. The negative bias drives HOMO and LUMO from the thiophene and thiazole side, respectively. For the case of the negative bias, initially increasing the bias voltage (less than 0.89 V) leads both HOMO and LUMO to be more delocalised across the molecular backbone due to their slight intrinsic asymmetrical spatial distributions, as discussed in Section 3.1. However, a further increasing negative bias voltage makes them more and more localised again. Similar to the case of the positive bias, HOMO − 1 shows the most variation and LUMO + 1 shows much less variation under the perturbation of the bias. 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 tunnel is a molecular orbital that is fully delocalised along the molecular backbone; conversely, a non-conducting tunnel is a localised molecular orbital, which cannot connect both ends of the molecule attached to the metallic contacts. Therefore, these observations are very instructive not only for intuitive understanding of the molecular current–voltage behaviours but also for designing novel molecular electronics. For example, if the frontier molecular orbitals get more and more localised under the external bias, one may expect less contribution of these orbitals to the molecular current, while if the frontier molecular orbitals get more and more delocalised, one may expect more contribution of these orbitals to the molecular current, which can be used to design molecular switches and storage devices.

4. Conclusion

We have performed an *ab initio* HF study on the modelling of a new diode molecule, thiophene–thiazole diblock molecule, by considering the external bias. It proves that 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 delocalised over the whole molecule, which is dramatically different from the case of the AR molecular diode. The introduction of the external bias modifies both the geometric and electronic structures of the molecule, such as the decrease/increase of the bond length alternation, the torsional angle and LUMO–HOMO gap depending on the magnitude and polarity of the external bias. In addition, the spatial distribution of the frontier molecular orbitals is also shifted under the external bias, showing that HOMO and LUMO move to the low-potential and high-potential side of the molecule, respectively. The evidences provided in the present study remind us that the interaction between the external bias and the molecular materials may greatly influence the geometric and electronic structures of the molecule, which may consequently modulate the electrical behaviours of the device performance. Therefore, a novel molecular electronic device designed without considering the bias effect should be questionable in practice. The results reported in this paper may give more insight into the design or rationalisation of the molecular devices.

Acknowledgements

We gratefully acknowledge the financial support of the Guilin University of Technology Talent Development Foundation (No. 006206236) and Guangxi Science Foundation of China (No. 0832259).

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