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Electronic Transport Properties of a Dithienylethene-Based Polymer with Different Metallic Contacts

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We have studied the electronic transport behaviors of dithienylethene-based polymer between two metal surfaces using nonequilibrium Green's functions combined with density functional theory. The present computational results show that the polymer with closed and open configurations really demonstrates switching behavior which confirms the experimental observation. It is also found that the switching behavior depends on the electronic properties of two configurations of polymer instead of the contact modes. The on-off ratios of conductance between the closed and open configurations reach up to two orders of magnitude. Negative differential resistance and rectification phenomena are also observed in such systems.

1 Introduction

Exploring the use of individual molecules as active components in electronic devices has been at the forefront of nanoelectronics research in recent years. Because they are expected to be the ultimate size limit of functional devices and show unique behaviors different from those of macroscopic systems. Numerous useful characteristics including memories,[1] rectifiers,[2] negative differential resistances (NDR),[3] diodes[4] and switches[5] have been proposed and realized both experimentally and theoretically. The design of molecular switches that change single-molecule conductivity by an external stimulus is important for the development of functional molecular devices. The external stimulus comes from a light irradiation,[6] an electric field,[7] a redox process,[8] and so on. And several exciting results have been reported based on a series of conjugated molecules such as azobenzene,[9] stilbenes,[10] spiropyran,[11] and diarylethenes[12] which can reversibly transform between two conductive states in response to external triggers. Recently, diarylethenes bearing two thiophene-derived groups have received intensively attention since they are particularly well suited as switching units.[13] As a typical class of reversible switching, they have been found excellent photochromic features: excellent thermal stability, high fatigue resistance (e.g. the coloration and decoloration units could be repeated more than 10^4 times in keeping with the photochromic performance) and negligible change of length between two isomers. Therefore, diarylethene and its derivatives are regarded as promising building blocks for electronic circuit elements such as memories and switches.

The switching effect through the so-called photochromic molecules have been noticed by several experimental and theoretical groups. In 2000 Irie[13] found that the diarylethene derivatives were of the potential practical applications in molecular electronics due to their fatigue resistant and thermally irreversible properties. Subsequently, Tian *et al.*[14] presented the developments in diarylethene-based molecular switches made in the later three years. Various new diarylethene derivatives have been fabricated and examined. Especially, dithienylethenes have figured prominently in the development of switchable organic electronic devices since they are the most suitable units as switching elements. Unfortunately, there still existed a challenge that is to preserve these promising properties when dithienylethenes are sandwiched between two metallic

electrodes. Dulić and their coworkers in 2003[15] performed a mechanically controllable break-junction measurement and got a clear switching behavior of the junction connected by two thiophene linkers. But they failed to observe the reverse process (i.e., from the open state to the closed state) which should occur upon illumination with ultraviolet light (313 nm). They attributed this to the quenching of excited state of the open isomer by the presence of gold. This unexpected quenching challenges our current understanding of this photochromic molecule. Li and Speyer *et al.*[16] reported a theoretical study using a quantum molecular dynamics method in regard to the photo-induced structural changing and the conduction switching phenomena. They speculated that observed quenching of the ring closure reaction may result from the interaction between the switching π paths and the metal states, indicating less entanglement between switching π orbital and metal surface states would be advantageous to the reversibility. In a parallel study, Zhuang *et al.*[17-18] considered a particular class of molecular electronic devices built around the dithienylethene photoactive units with different aromatic linkers. They also explained the strong coupling between the molecule and the gold substrate leading to nonreversibility. Interestingly, Kudernac and their coworkers[19] introduced a benzene linker into the photoswitches to substitute the thiophene ring. The benzene is connected in meta-position. The phenyl groups are twisted out of plane, thereby limiting the electronic interaction between the switching unit and the electrodes. Although charge delocalization is reduced by using a phenyl spacer, the reversible switching of conductivity is possible. Additionally, there may be more practical application when combine photochromic units with polymer chain to form polymer molecule. To gain better switching elements, Logtenberg e*t al.*[20] synthesized a molecule switch which combining the dithienylethene switchable unit, a phenyl spacer, and a polymerizable bithiophene unit (as shown in Fig. 1) that facilitates charge transport without loss of the dithienylethenes' switching functionality. The stable geometric structures under low temperature of the polymers used in our calculations were determined by using first-principles density functional theory (DFT), which were consistent with the configurations of Ref. 20. These molecules have a common dithienylethene photoactive unit which can be converted back and forth between the closed and the open isomers. The polymer can not only be switched electrochemically in a reversible manner by redox triggered opening and closing of the dithienylethene unit but also switched photochemically. While it is clear that computational studies have fruitfully promoted the design of dithienylethenes-based molecular devices, there is still lack of a theoretical study about the switching mechanism and especially the electronic transport properties of this polymer molecule when it was attached to the metallic electrodes. To have a better understand of the experimental results and to investigate how the electrodes contact can affect the electronic transport behavior, we performed theoretical calculations focusing on the electronic transport properties of dithienylethene-based polymer. The effect of different electrodes on the characteristics of *I-V* curves and the switching behaviors are investigated in detail.
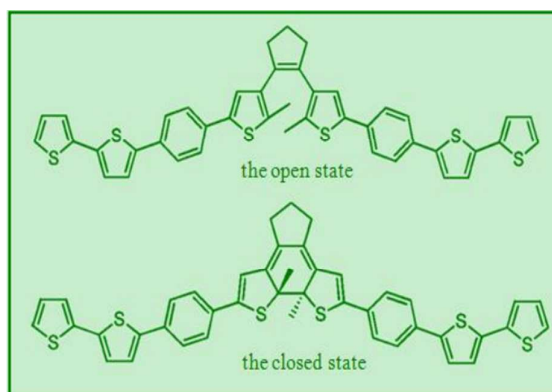
Fig. 1. Structures of the polymer with open (top) and closed (bottom) configurations. The closed form transform to the open form by breaking the central σ bond and by formation of an additional π bond. From open form to closed form is a reverse process. The ring opening (closure) is initiated by external stimulus.

2 Computational Methods

The polymer with open and closed configurations sandwiched between three different kinds of electrode systems. The first system is made up of two Au (111) surface represented by a (4×4) supercell with periodic boundary conditions (Au-Au electrodes) in Fig. 2(a). We also construct a system that is analogous to a break junction formed by pushing a gold probe tip into a gold surface as molecules are trapped into the gap to simulate the experimental process (Au-STM electrodes) in Fig. 2(b). It is well known that the transmission not only depends on the properties of the molecules but also on the contacts to electrodes. For gold electrode, the conductance was found to vary with the different absorbing position and anchoring atom. As the complicated interaction between molecule and electrodes plays a critical role in electronic transport property, the effect of chemical potential difference in molecular devices fabricated by two different electrodes should be well considered (Au-Ag electrodes).[21] It is well known that the work function of silver is lower than that of gold.[22] Once they are connected by the well delocalized π-conjugated geometry, the electrons transfer from silver to gold under the driving of built-in electric field until equilibrium chemical potential of two electrodes is achieved. Namely, the two Schottky barriers are asymmetrical and thus may lead to a molecular rectification when the electrode materials are different for both electrodes. So in Fig. 2(c) we present a fabrication that consist of left Au (111) and right Ag (111) electrodes to study on the electronic transport properties. The whole systems are divided into three regions including the left electrode, the scattering region, and the right electrode. A portion of the electrodes are included in the scattering area to screen the potential effect of the embedded molecule to the electrodes. The semi-infinite electrodes are calculated separately to obtain the bulk self-energy. Among all of the systems, the molecules are attached to each electrode via a thiol group at a hollow position on the metal surface (except for the analogous STM electrodes in Fig. 2(b)).[23]
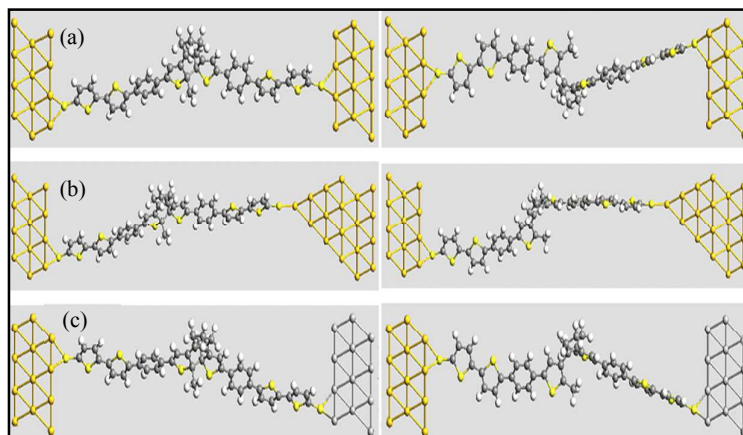
Fig. 2. Geometry of the switching devices for the closed (left) and open (right) forms. Dithienylethene molecules are sandwiched between two metal surfaces (a. Au-Au systems b. Au-STM systems c. Au-Ag systems) and two S anchoring atoms are located at the hollow site (except for the analogous STM electrodes in Fig. 2(b)).

   The first-principles calculations are carried out using nonequilibrium Green's function (NEGF) combined with density functional theory (DFT), which are implemented in Atomistix Toolkit (ATK) software package.[24-27] This methodology has been adopted to explain various experimental results successfully. All the two-probe systems are fully optimized until the maximum absolute force on each atom is less than 0.02 eV/Å. To improve calculation precision and reliability, we expanded the valence electrons in single-zeta plus polarization basis set (SZP) for metal electrodes and double-zeta plus polarization basis set (DZP) for other atoms. The improved Troullier-Martins pseudopotentials were used to describe the core electrons of all atoms.[28] The GGA-PBE for the exchange and correlation functional was used in all our calculations of electron-electron interactions.[29] Periodical boundary conditions were applied in the transverse directions. The Brillouin zone was sampled with 4×4×100 points in our three-dimensional two-probe systems. Electrostatic potentials were determined on a real-space grid with a mesh cutoff energy of 110 Ry to achieve balance between calculation efficiency and accuracy. We calculated the electronic tunneling transmission coefficient spectrum and projected density of states (PDOS) spectrum. The transmission coefficients with energy E under the bias V can be obtained by the following formula:

$$T(E, V_b) = T_r[\Gamma_L(E) G^R(E) \Gamma_R(E) G^A(E)] \tag{1}$$

Where $G^R(E)$ and $G^A(E)$ are the retarded and advanced Green's function. $\Gamma_L(E)$ and $\Gamma_R(E)$ are the coupling functions of the molecule to the left and right electrodes. The current through the systems is calculated using the Landauer-Büttiker formula,[30]

$$I(V) = \frac{2e}{h} \int T(E, V_b)[f_L(E - \mu_L) - f_R(E - \mu_R)] dE \tag{2}$$

where h is Planck's constant, e the electron charge, f the Fermi function, $\mu_L = E_F + \frac{eV}{2}$ and

$\mu_R = E_F - \frac{eV}{2}$ the electrochemical potential of the left and right electrodes, E_F the Fermi level of

the system which is set to be zero in our calculations and $T(E, V_b)$ the transmission function. The energy region $[\mu_L, \mu_R]$ contributingto the total current integral is called the bias window.

3   Results and Discussion

Experimental studies have demonstrated that the dithienylethene-based polymer can transform reversibly between the closed and open forms by electrochemically and photochemically through redox reaction. [20] To gain insight into the mechanism of switching, the zero-bias transmission spectra for the polymer sandwiched between three types of two-probe systems are obtained by using the method described above and shown in Fig. 3. Clearly, the calculated transmission spectra of open and closed conformations are distinctively different near the Fermi level. The open forms lack any significant transmission peaks within a wide energy window from -0.5 eV to +1.0 eV. While the closed structures have at least one significant transmission peaks near the Fermi level for all three systems considered. We can see that there are two transmission peaks near the Fermi level for the closed configuration of Au-STM system (Fig. 3(b)). The other two systems of closed forms have only one sharp peak. More interestingly, the sites of the transmission peaks of three different closed forms near the Fermi level are also different. We discuss the different profiles of transmission spectra accordingly combined with the eigenvalues of MPSH orbital and the spatial distribution of the frontier molecular orbital. Since the position of the transmission peak is generally determined by the energy level of the molecular projected self-consistent Hamiltonian (MPSH) orbital and the height of the transmission peak is dependent on the delocalization of the orbital. So we calculated the eigenvalues of MPSH to analyze the contribution of the frontier molecular orbital listed in Table 1 and the spatial distribution of the MPSH which have been modified by the electrodes shown in Fig. 4-6. Usually, the energy levels in the molecule attached to the contacts adjust themselves such that the Fermi energy of the contacts is somewhere between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), making the HOMO and LUMO determining factors for the conductance. Yet inconsistently, from Fig. 3-6 and Table 1 we can see that the significant transmission peak near the Fermi level all come from the perturbed HOMO orbital. Namely, the HOMOs of the closed configuration are delocalized π-conjugated orbital which provide good channels for electron tunneling through the molecular junction and lead to a significant transmission peak. The spatial distribution of the perturbed LUMO are strongly localization. For example, the electrons are localized at right side of the molecule with Au-STM system and at the central switching unit with the other two systems. That is to say that the transport properties are predominated by the perturbed HOMO contributed transmission peak below the E_F, since the transmission coming from the perturbed HOMO is just 0.2 eV away from E_F, which is closer than that of the perturbed LUMO. On the contrary, the HOMOs and LUMOs with open conformation are all localized frontier orbital. They are not good conductive channels for electrons passing through the molecule junction. Finally, the lack of any significant transmission channels at the energy range from 0.5 eV to +1.0 eV clearly elucidates its lower conductivity shown in Fig.3. These remarkable differences of the molecule geometry and electron distribution are the origin of switching effect.

For explaining the changes of the transport properties with different two-probe systems, in Table 2, we give the values of conductance at the equilibrium states. From Table 2 we can see that the on-off ratios of conductance at zero-bias between the closed and open configurations are all about two orders of magnitude, which reproduces the essential features of the experimental measured results. Thus we can draw such a conclusion that the switching effect depends closely on the electronic structure of the two forms of dithienylethenes-based polymer but not on the type of electrodes. It also indicates that this kind of switching elements based on diarylethene

derivatives is stable as a molecular switching device. More interestingly, we can see that there are two narrow transmission peaks below E_F for the Au-STM system of the closed isomer (in Fig.3). It makes the orbital of HOMO-1 (0.29 eV) and HOMO (0.08 eV) shift to the E_F which give rise to the transmission peaks. It is also evident that these peaks shift toward lower energies. It is clear that the conductance is dominated by those transmission peaks below E_F. Ultimately, the conductance of this molecular device is increased drastically. And we find that the spatial distributions of three two-probe systems are severely similar in Fig. 4-6. While comparing to the cases analyzed in this essay, we note that the conductivity value is greater when the position of the perturbed HOMO is closer to the E_F.
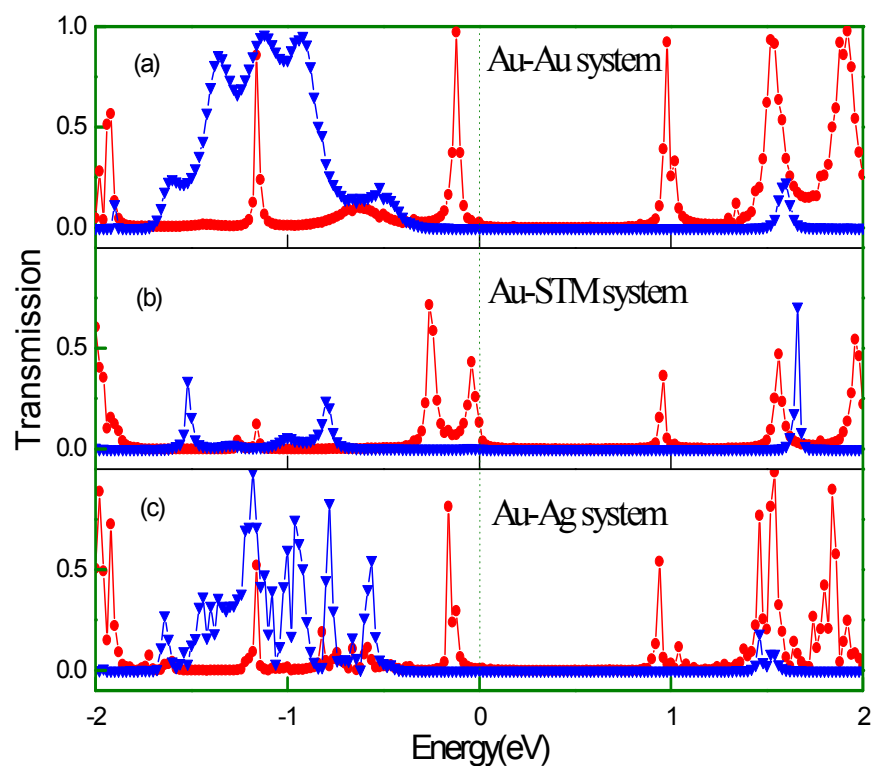

Fig. 3. Transmission spectra of the polymer at zero-bias with diverse two-probe systems. The Fermi energy is set to zero. The red circle lines and blue triangle lines indicate the closed and open configurations, respectively.

Table 1. The eigenvalues of MPSH orbital for the two-probe systems.

the two-probe systems	Au-Au system		Au-STM system		Au-Ag system	
the two configurations	the closed form	the open form	the closed form	the open form	the closed form	the open form
LUMO+1 (eV)	1.50	1.57	1.54	1.66	1.46	1.51
LUMO (eV)	0.97	1.54	0.95	1.60	0.94	1.45
HOMO (eV)	-0.12	-0.49	-0.08	-0.13	-0.14	-0.55
HOMO-1 (eV)	-0.72	-0.55	-0.29	-0.45	-0.75	-0.63

Table 2. Zero-bias conductance values and on-off ratios of different two-probe systems.

Conductance(G_0)	Au-Au system	Au-STM system	Au-Ag system
the closed form	2.72×10^{-2}	1.33×10^{-1}	8.21×10^{-3}
the open form	1.14×10^{-4}	1.38×10^{-3}	2.46×10^{-5}
the on-off ratio	238	96	334

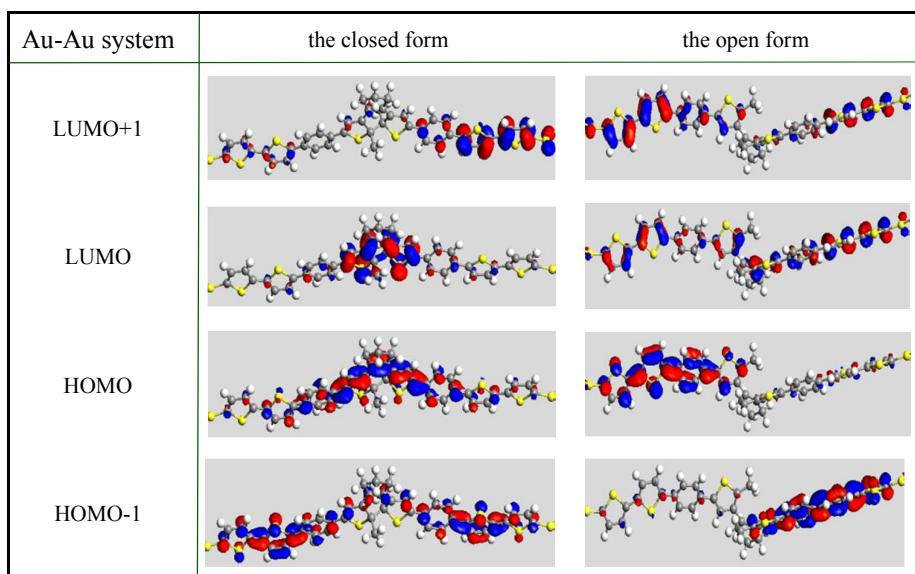| Au-Au system	the closed form	the open form
LUMO+1		
LUMO		
HOMO		
HOMO-1		

Fig. 4. The spatial distribution of the frontier molecular orbital for the Au-Au system. The isovalue is set to 0.1 for

all plots.

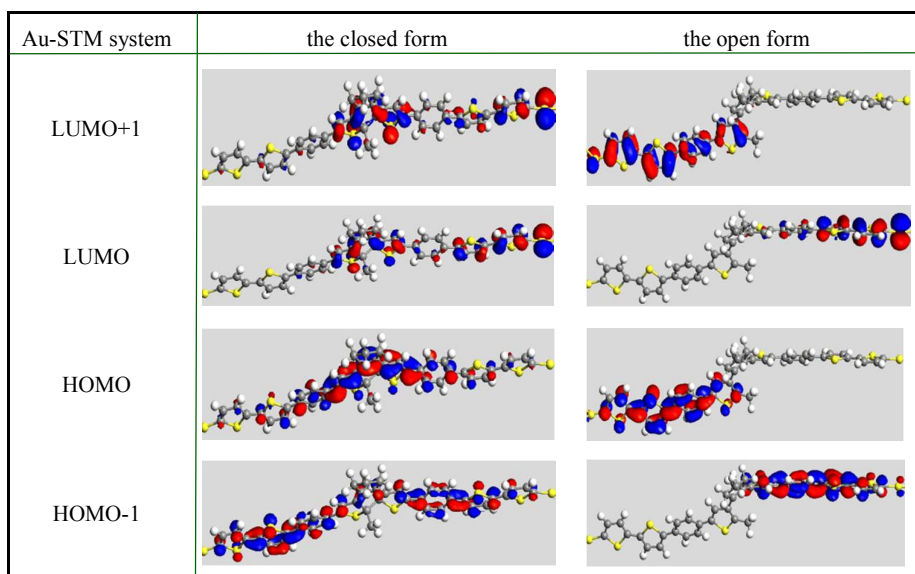| Au-STM system	the closed form	the open form
LUMO+1		
LUMO		
HOMO		
HOMO-1		

Fig. 5. The spatial distribution of the frontier molecular orbital for the Au-STM system. The isovalue is set to 0.1

for all plots.

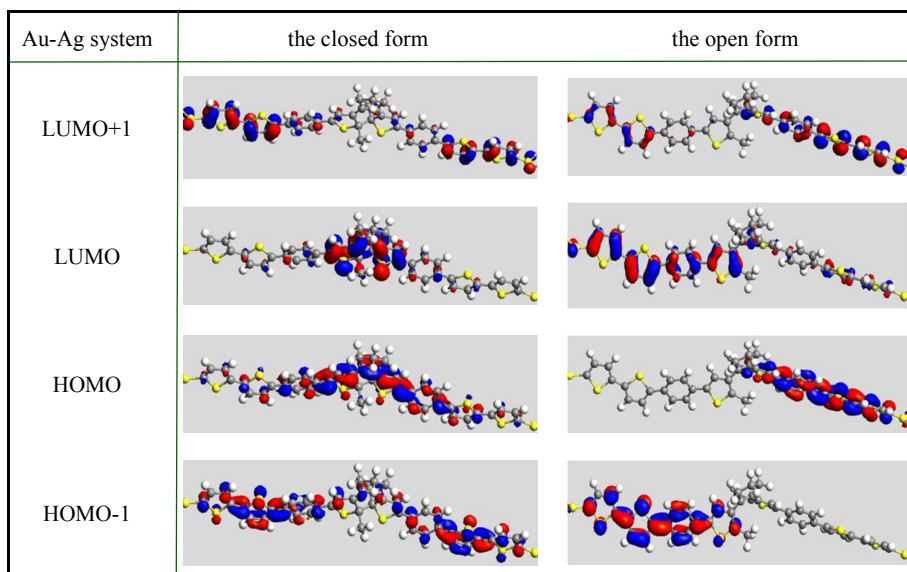| Au-Ag system	the closed form	the open form
LUMO+1		
LUMO		
HOMO		
HOMO-1		

Fig. 6. The spatial distribution of the frontier molecular orbital for the Au-Ag system. The isovalue is set to 0.1 for all plots.

The currents through the molecular junction with closed and open configurations are calculated by the Landauer-Bütiker formula.[29] Fig. 7 shows the self-consistently calculated current-voltage (*I-V*) curves of the polymer sandwiched between diverse two-probe systems with bias ranging from -2.0 V to +2.0 V. The current through the closed form is remarkably higher than that of the open one. Namely, the switching device operates by the change of a high conductivity (low resistance) or low conductivity (high resistance). For example, the Au-Ag system, the on-off ratio of current defined as $R(V) = I_{closed}(V)/I_{open}(V)$ is about 60 times larger at bias of 1.0 V. We can draw the conclusion that the switching behavior depends on the electronic properties of two configurations of polymer instead of the contact modes. That is to say, the switching behavior is from the molecule itself but not the junction between the molecule and electrodes.

In addition to the effect of switching, we can also find some other useful physical phenomena (such as the rectification and NDR behaviors) through the calculated *I-V* curves. Rectifiers have played a key role in the development of molecular electronics both because they formed the basis for the first proposal of a unimolecular electronic device by Aviram and Ratner,[31] and because they are one of the simplest functions to build into an electronic component.[32] Generally speaking, asymmetric metal-molecule contacts lead to diode-like behavior of molecular junction (e.g. asymmetric molecule contact to identical electrodes or symmetric molecule contact to asymmetric electrodes and or asymmetric molecule contact to asymmetric electrodes). The understanding is that the potential drop along the molecule changes the alignment of the molecular levels with the electrochemical potential of the left and right contacts. Asymmetric electrode coupling can result in an asymmetric potential profile along the length of the molecule,[33] and the molecular level can line up differently in positive and negative bias resulted in rectification. The current through the molecule junction of Au-STM system and Au-Ag system with closed configuration shown in Fig. 7 appear slight rectification phenomenon. This conclusion proved that different molecule-electrode contacts on a symmetric molecule provide asymmetric current voltage curves.
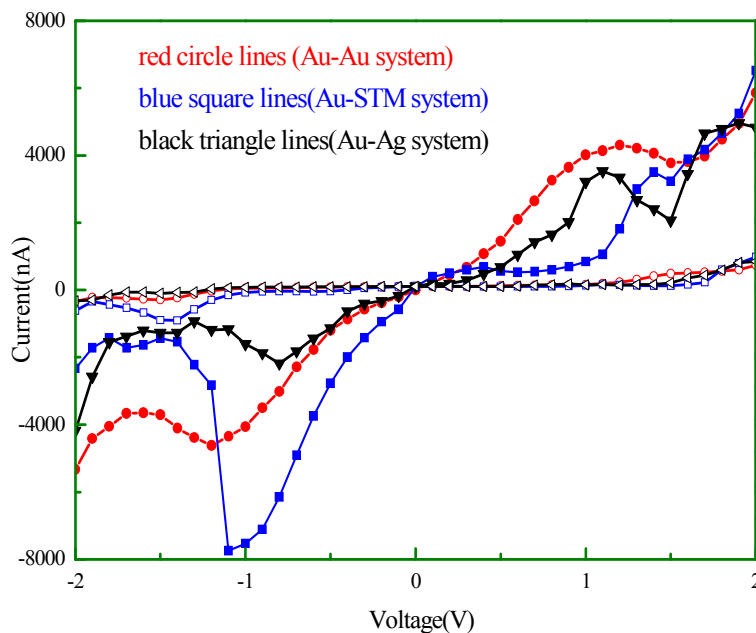
Fig. 7. *I-V* curves of the molecular junctions. The blue square lines indicate the open configurations and the red circle lines indicate the closed configurations.

Another interesting phenomenon is the observation of NDR behavior in high bias regions for the closed configurations (the open configurations also appear NDR behavior, but is not obvious, so we don't discuss here). In order to understand it clearly, we analyzed the transmission spectra and the partial density of states (PDOS) of the middle molecule at different bias voltage as shown in Fig. 8-10. It is well known that the current is determined by the integral of the transmission spectra within the bias window. Additionally, the PDOS gives information of the molecular orbital contributing to the eigenstate of the system including the energy shift and line broadening due to the molecule-electrode coupling.[34] As presented in Fig. 8 (Au-Au system), the significant transmission peaks locating below and above the E_F (about -0.5 and +0.8 eV) are mainly contributed by the perturbed HOMO and LUMO. We note that the peaks of PDOS of the middle molecule match well to the transmission peaks. But the peak above the E_F which originates from the LUMO is always outside the bias window. It leads to no contribution to the current integrated in the wide bias window. Namely, the perturbed HOMOs of the closed configuration provide good channels for electron tunneling through the molecular junction and lead to a significant transmission peak. While there is only a portion of transmission peak make contributions to the integral area at V= -0.8 V. As the bias increases from V= -0.8 V to -1.2 V (the bias window expands), the broad transmission peak entering the bias window which lead to a rapid increase in current. When bias increases further (V= -1.6 V), the strength of this transmission peak is suppressed dramatically. Finally, a strong NDR behavior occurs at -1.2 V to -1.6 V in Au-Au system with the closed configuration. We find similar situation in the case of Au-STM ststem and Au-Ag system. The relevant transmission peak gradually enter into the integral area with the increase of bias voltage. Since the bias increase to a certain degree (V= -1.6 V for Au-STM system

and V= -0.8 V for the Au-Ag system), the intensities of the peaks decrease and that causes the NDR effect. Additionally, from Fig. 7 we can see that the current is not quite symmetric at positive and negative biases for the later two systems which are due to the contacts between molecule and electrodes have become asymmetric.
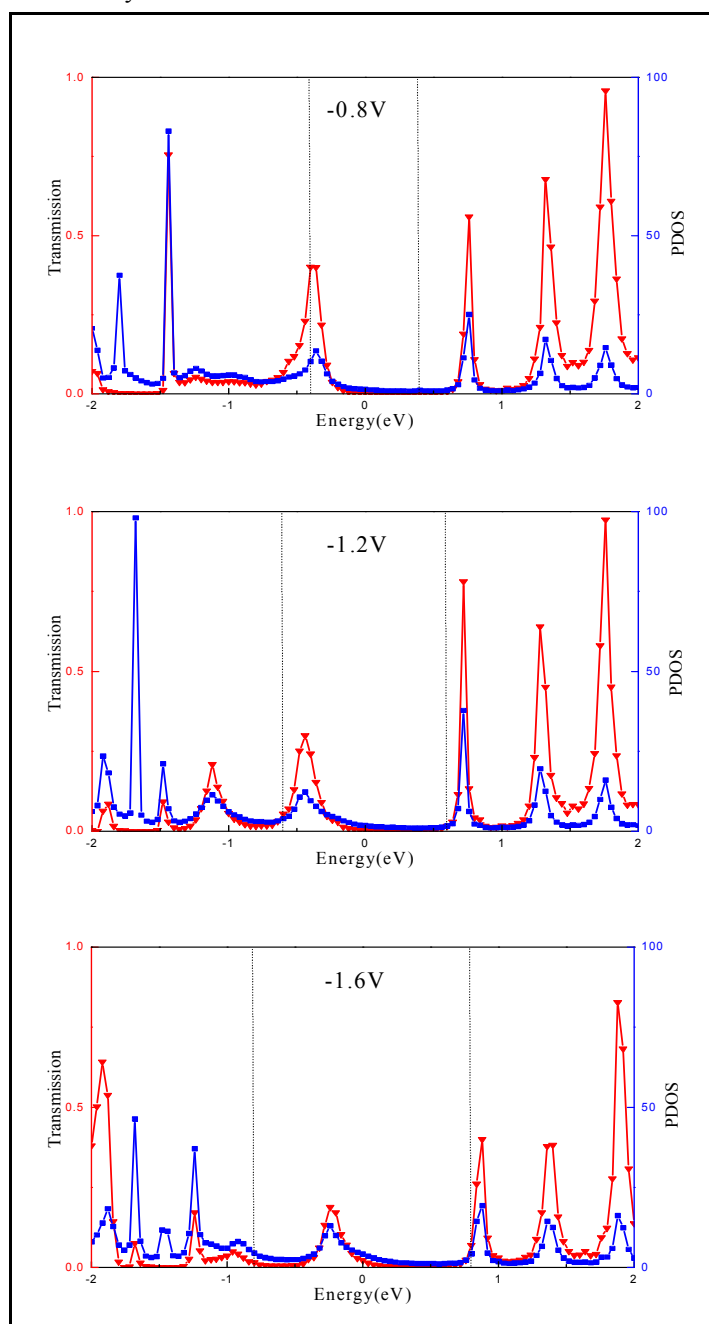

Fig. 8. Transmission spectra and corresponding PDOS of the Au-Au contact modes with closed configurations under different bias voltages. The red triangle lines are transmission spectra and the blue square lines correspond to PDOS of the middle molecule. The two black dashed lines indicate the bias window.
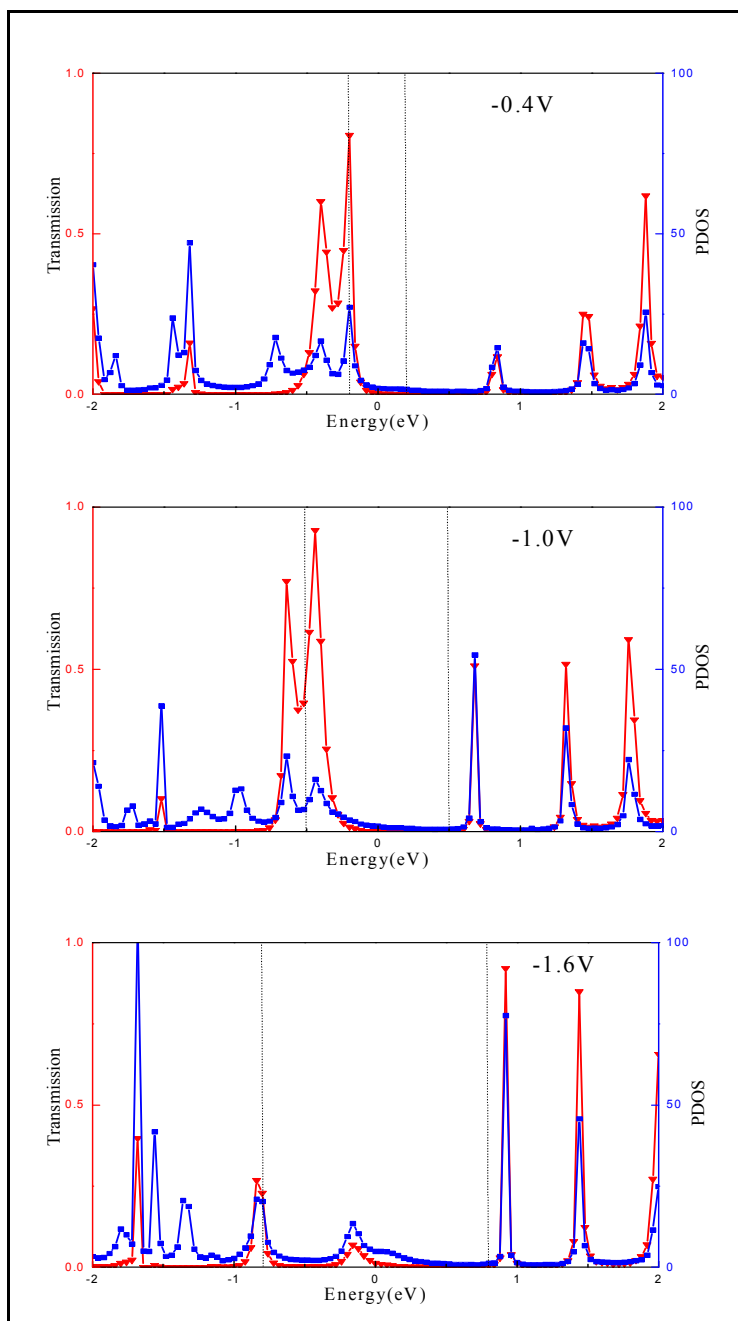
Fig. 9. Transmission spectra and corresponding PDOS of the Au-STM contact modes with closed configurations under different bias voltages. The red triangle lines are transmission spectra and the blue square lines correspond to PDOS of the middle molecule. The two black dashed lines indicate the bias window.
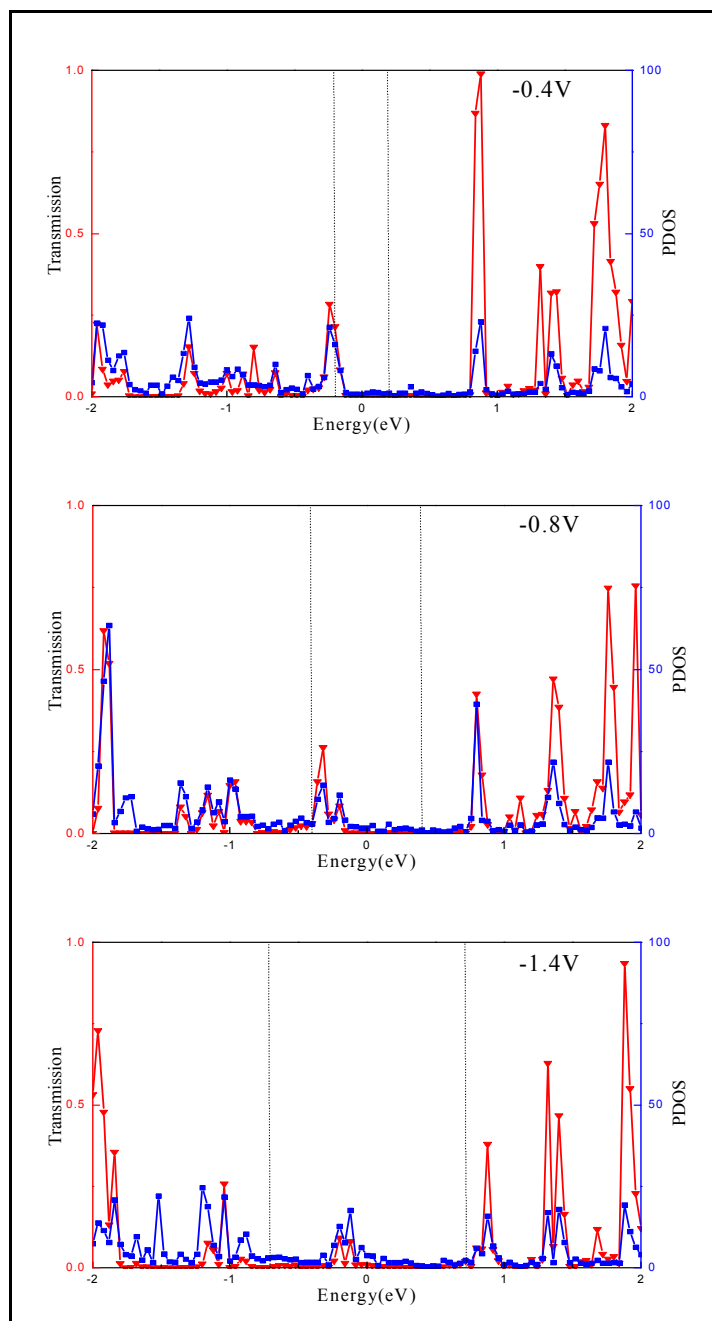
Fig. 10. Transmission spectra and corresponding PDOS of Au-Ag contact modes with closed configurations under different bias voltages. The red triangle lines are transmission spectra and the blue square lines correspond to PDOS of the middle molecule. The two black dashed lines indicate the bias window.

4 Conclusions

In summary, we have investigated the electronic transport properties of dithienylethene-based polymer with closed and open configurations using NEGF combined with DFT method. The results show that the switching effect depends closely on the electronic structure of the two configurations but not on the type of electrodes. It also indicates that this kind of switching elements based on diarylethene derivatives is stable as a molecular switch. This is explained by the energy level of the perturbed molecular orbital and the spatial distribution of the MPSH.

Additionally, the *I-V* curves illustrate that there are apparent NDR behaviors and slight rectification phenomena for different systems. The present findings could be helpful for the application of dithienylethene-based polymer in the fields of molecular switching and other functional components.

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