The effects of contact configurations on the rectification of dipyrimidinyl–diphenyl diblock molecular junctions*

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The transport properties of a conjugated dipyrimidinyl–diphenyl diblock oligomer sandwiched between two gold electrodes, as recently reported by [Díez-Pérez *et al. Nature Chem.* **1** 635 (2009)], are theoretically investigated using the fully self-consistent nonequilibrium Green's function method combined with density functional theory. Two kinds of symmetrical anchoring geometries are considered. Calculated current–voltage curves show that the contact structure has a strong effect on the rectification behaviour of the molecular diode. For the equilateral triangle configuration, pronounced rectification behaviour comparable to the experimental measurement is revealed, and the theoretical analysis indicates that the observed rectification characteristic results from the asymmetric shift of the perturbed molecular energy levels under bias voltage. While for the tetrahedron configuration, both rectification and negative differential conductivity behaviours are observed. The calculated results further prove the close dependence of the transporting characteristics of molecular junctions on contact configuration.

Keywords: molecular electronic device, rectification, electronic transport property

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1. Introduction

Molecular electronics is recognized to be one of the ultimate solutions to the limit predicted by Moore's law for microelectronic chips. How to construct molecular diodes is an important issue in the field, which has attracted much attention since it was proposed by Aviram and Ratner in 1974.[1] The realization of a molecular diode requires an asymmetric structure of the device. Experimental investigations show that molecular diodes can be achieved by means of asymmetric molecule/electrode interfaces[2−5] or asymmetric molecules.[6−9] The latter method is advantageous in constructing intrinsic molecular diodes independent of the uncontrollable molecule/electrode interfaces. Although the idea of using asymmetric molecules with donor–σ–acceptor (D–σ–A) structures was proposed many years ago, only a few functional molecular rectifiers have been realized experimentally so far.[10,11] Recently, a series of D–A type diblock oligomer molecules with distinct rectification behaviours were synthesized using self-assembled monolayers.[12−16] For example, a dipyrimidinyl–diphenyl diblock molecule sandwiched between two gold electrodes could serve as an efficient molecular rectifier.[15,16] Furthermore, it was found that the rectifying direction could be controlled by changing the molecular orientation between the electrodes, or by particular methods such as protonation.[15]

On the theoretical side, the mechanisms for rectification in diblock oligomer molecular diodes have attracted a lot of attention, and have been discussed by several groups.[17,18] With the Green's function theory of sub-barrier scattering approach, Oleynik *et al.*[19] attributed the rectification to the asymmetric tunneling wave function depending on the polarity of applied bias voltages. Hu *et al.*[20] gave a good theoretical explanation to the observed rectification in thiophene–thiazole co-oligomer diodes based on a tight-binding model combined with the nonequilibrium Green's function (NEGF) method. An *ab initio* calculation was performed by Gasyna *et al.*[21] using the Gaussian 98 package and NEGF theory for dipyrimidinyl–diphenyl molecules, where the calculated current–voltage (I–V) characteristic showed a slight asymmetry. Huang *et al.*[22] studied the effects of molecular length and asymmetric coupling on rec-

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tification using the ATK package. They found that molecular length has an obvious effect on rectification behaviour, and that the rectification ratio is further enhanced by asymmetric coupling. However, the predicted rectification ratio is less than the experimental result. Thus, one may consider whether other mechanisms for enhancing the rectification ratio exist. As we know, contact configurations between a molecule and metal surfaces may strongly affect the electron transport properties of the molecular junction.[23,24] Based on this concern, we simulate the rectification characteristics of the molecular junctions containing a dipyrimidinyl–diphenyl diblock molecule with symmetrical anchoring geometries. Particular attention is paid to the contact structure effect on the molecular rectifying features.

In this paper we calculate the transport properties of the dipyrimidinyl–diphenyl molecule using the fully self-consistent NEGF method based on density functional theory. The rest of the paper is organized as follows. The theoretical model and computational details are described in Section 2. Section 3 is devoted to our results and discussion, and a conclusion is given in Section 4.

2. Theoretical model and computational details

The model of the device is depicted in Fig. 1. A dipyrimidinyl–diphenyl molecule is sandwiched between two Au (111) electrodes through terminal thiol anchoring groups. The whole system is divided into three regions: the extended molecule (consisting of the bare molecule and several surface layers of gold atoms), and the left and right periodic semi-infinite electrodes. The molecular junction is modeled within the TranSIESTA methodology.[25] A 3×4×3 unit cell is used to construct the periodic electrodes. Two contact geometries are considered: (i) a triangle structure with three gold atoms (denoted as cont1), and (ii) a tetrahedron structure with four gold atoms (cont2) (see Fig. 1). For the cont1 case, on each side of the molecule a three-gold-atom layer forms an equilateral triangle and the terminal sulphur atoms of the dipyrimidinyl–diphenyl molecule are located at the hollow position, and 42 gold atoms are included in the extended molecule. For the cont2 case, the terminal sulphur atoms are located at the top position, and 44 gold atoms are included in the extended molecule. The structure of the free dipyrimidinyl–diphenyl molecule was optimized first in the SIESTA package with a maximum force of 0.02 eV/Å (1 Å=0.1 nm).[26] After constructing the molecular junction, the extended molecule was optimized again. The sulphur atoms were only allowed to relax along the z axis, namely the transport direction. The relative positions of the Au atoms on each side were frozen, but the distance between the two Au clusters was relaxed along the z axis during the subsequent geometric optimization. For the cont1, the left and right optimized S–Au bond lengths are, respectively, 2.51 Å and 2.49 Å, and the first phenyl ring and two pyrimidinyl rings are almost coplanar, while a dihedral angle between the second phenyl ring and the planarity is about 35.74°. For the cont2, the left and right optimized S–Au bond lengths are, respectively, 2.33 Å and 2.32 Å, and the dihedral angle is about 36.05°.

In our SIESTA and TranSIESTA computations, we use numerical atomic orbitals as a basis set and the core electrons are represented by Troullier–Martin type norm-conserving pseudopotentials.[27] The Perdew–Burke–Ernzerhof exchange-correlation functional[28] is used for the generalized gradient approximation.[29] To save computational effort, we employ a single-zeta plus polarization basis set for the Au atoms and a double-zeta plus polarization basis set for the other atoms.[22] The radii of the pseudoatomic orbitals are fixed by an energy shift parameter of 100 meV. A 300 Ryd (1 Ryd=13.6 eV) mesh cutoff is chosen, and the self-consistent calculations are performed with a mix weight of 0.05. The convergence criterion for the density matrix is chosen as 10^{-4}. A 4×4 k-point grid is used for Brillouin-zone sampling after an extensive convergence analysis.

The electronic transport properties are investigated using the NEGF method implemented in the TranSIESTA module of the SIESTA package. The current through the molecular junction is calculated according to the Landauer–Buttiker formula to be[30]

$$I = \frac{2e}{h} \int T(E,V)\,[f(E-\mu_{\rm L}) - f(E-\mu_{\rm R})]\,{\rm d}E,$$

where $T(E,V)$ is the transmission probability of incident electrons with energy E through the molecular junction under bias voltage V. $f(E)$ is the Fermi–Dirac function of the electrodes and $\mu_{\rm L(R)}$ is the electrochemical potential of the left (right) electrode.

3. Results and discussion

We first consider the molecular junction shown in Fig. 1(a). The current through the molecular junction is shown in Fig. 2. One can see that the calculated

I–V curve is similar to that observed experimentally, except for the magnitude of current.[14] Furthermore, it is obvious that the I–V curve is asymmetric and the molecular device has a rectification behaviour in the bias voltage region of [−1.7 V, 1.7 V]. In the positive bias region, the current is enhanced rapidly as the bias voltage increases from 0.8 V. The magnitude of current reaches about 2.4 μA at 1.7 V. While in the negative bias region, the current is much smaller and the current is about 0.8 μA at −1.7 V. The rectifying direction of the current is from the dipyrimidinyl to the diphenyl block. In the inset, the rectification ratio defined as $R(V) = |I(+V)/I(-V)|$ is given. It is found that the rectification ratio value increases with the applied bias increasing. The ratio value at a 1.5 V bias is about 2.5, which is the same as that given by the theoretical analysis in Ref. [16], and the maximum ratio value of 3.0 appears at a 1.7 V bias in the investigated bias region. The calculated ratio values are smaller than those observed experimentally,[16] but they are larger than the predicted results previously given by Huang *et al.*,[22] where the contact geometry was an Au plane. The simulations clearly demonstrate the effect of contact configuration on the rectification behaviour of the molecular device.

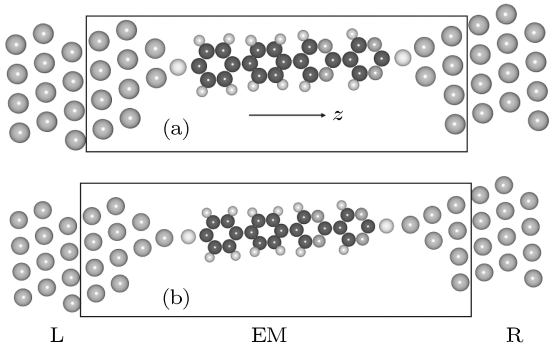


Fig. 1. Schematic structure of the model device (L: left electrode; EM: extended molecule; R: right electrode). (a) cont1: a triangle contact structure, (b) cont2: a tetrahedron contact structure.

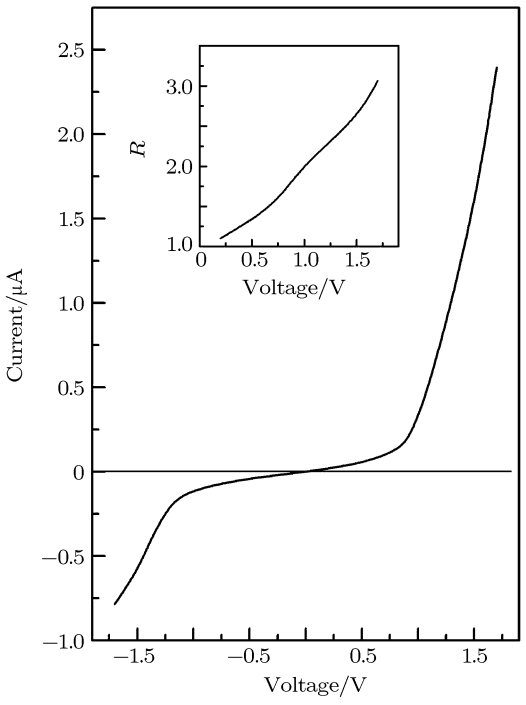


Fig. 2. The current–voltage curve of the dipyrimidinyl–diphenyl molecular junction with contact geometry cont1. The inset shows the calculated rectification ratio versus bias voltage.

To understand the mechanism of the rectification for the dipyrimidinyl–diphenyl molecular junction, the transmission spectra at $V = 0$, ±1.0 and ±1.7 V are calculated and shown in Fig. 3. We start from the case of zero bias. It is found that there are two broad transmission peaks above the Fermi level ($E_{\rm F}$) up to 2 eV, where the lowest peak, named A, is located at 1.0 eV above $E_{\rm F}$. Two adjacent smaller transmission peaks exist at about −1.2 eV below $E_{\rm F}$. When a negative bias is applied (see Fig. 3(a) and (b)), peak A moves away from $E_{\rm F}$ and its height increases. At the same time one of the transmission peaks at −1.2 eV below $E_{\rm F}$, which is marked as peak B, moves towards $E_{\rm F}$ and the height of this peak is much reduced. At the bias voltage $V = -1.7$ V, the current is contributed by the lowered transmission peak B and the tail of peak A. For a positive bias (see Fig. 3(d) and (e)), a similar evolution to that under the negative bias voltage is observed for transmission peak B. However, a contrary evolution occurs to transmission peak A, namely it moves towards $E_{\rm F}$ and its magnitude is lowered. At the bias voltage 1.7 V, about half of peak A enters the bias window. Although the height of peak A is lowered, its contribution to current is clearly larger than that at the negative bias −1.7 V. This leads the current value at the positive bias voltage to become much larger than that at the negative bias voltage, and hence a rectification is observed. We conclude that the dissimilar shift of peak A (correspondingly the molecular energy level) under external bias voltages is the main reason for producing the rectifying effect.

Next, an analysis of the molecular orbitals is followed in order to achieve a further understanding. We first calculate the renormalized orbitals of the molecule by diagonalizing the molecular junctions projected self-consistent Hamiltonian (MPSH),[1)] which

[1)] The MPSH calculation is done using the Inelastica package developed by Magnus Paulsson and Thomas Frederiksen.

are believed to be responsible for the electron tunneling in previous studies.[22,31,32] The results are labelled with down-triangles in Fig. 3. One can find that most transmission peaks result from the MPSH orbitals at zero bias voltage. When a bias voltage is applied, the locations of the transmission peaks are far away from the MPSH orbitals, especially for the transmission peaks below $E_{\rm F}$ under positive bias voltages. This indicates that the MPSH orbitals of the bare molecule are not sufficient to illustrate the electron transmission spectrum, and this is due to the hybridization of the surface states of the Au atoms and the frontier orbitals of the molecule, where the hybridized orbitals are responsible for the electron tunneling process. To clarify this issue, we further calculate the eigenvalues of MPSH by projecting the self-consistent Hamiltonian onto the subsystem consisting of the bare molecule and the six nearest-neighbour Au atoms (6Au+molecule system),[2)] which are shown by the short lines in Fig. 3. The transmission peaks are attributed to the MPSH orbitals of the subsystem. The two sets of MPSH orbitals are close in energy with respect to the transmission peaks above $E_{\rm F}$, which indicates that such orbital

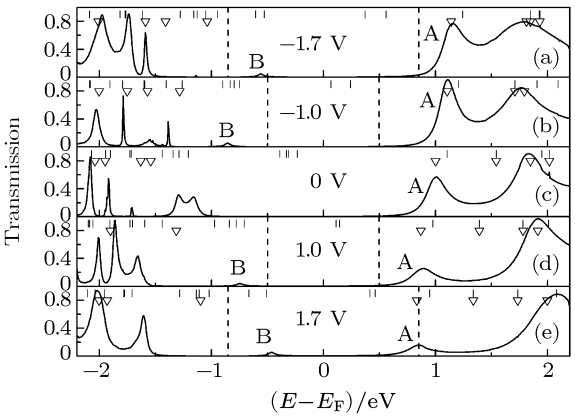


Fig. 3. Electronic transmission spectra at different bias voltages. The down-triangles denote the eigenvalues of MPSH for the bare molecule, and the short lines the eigenvalues of MPSH for the bare molecule with six nearest-neighbour Au atoms. The dashed lines indicate the bias window for the transportation.

hybridization mainly occurs between the surface state of the Au atom and the frontier-occupied molecular orbital of the molecule.

To further explore the origin of the asymmetric I–V curve, we plot the wave functions of the MPSH orbital with a transmission peak A under different bias voltages in Fig. 4. At zero bias, the distribution of the orbital is asymmetric and slightly localizes on the dipyrimidinyl block. When a positive bias voltage is applied, the orbital becomes more localized on the dipyrimidinyl block, which results in a lower transmission peak. However, the wave function at a negative bias voltage is more extended, which causes a higher transmission peak. In view of the localization of the tunneling wave function, one can observe that the evolution of the wave function under external bias voltages takes a contrary way to enhancing the rectification. It is thus concluded that the asymmetric shift of the perturbed molecular energy level under external bias voltages plays a dominative role in the rectification.

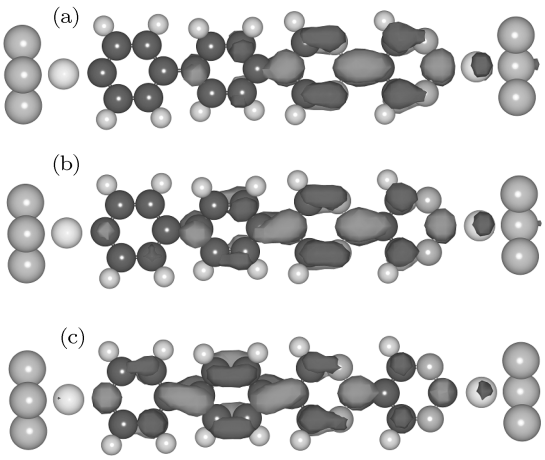


Fig. 4. Wave functions of the MPSH orbital corresponding to peak A at the bias voltages: 1.7 V (a), 0.0 V (b) and −1.7 V (c).

We now turn to the molecular junction with the contact geometry cont2, shown in Fig. 1(b). The current through the molecular junction is shown in Fig. 5. One can see that the I–V curve is quite different from that of the molecular junction with cont1. The rectification behaviour is evidently observed in the bias voltage region [0.2 V, 0.8 V], and the rectification ratio value reaches 3.5 at 0.4 V. It is noted that the rectifying direction is inversed compared with the cont1 case (see the inset in Fig. 5, where the vertical axis represents the inversion of the rectification ratio defined in the text). Moreover, negative differential conductivity features are observed at about 0.2 V and −0.4 V. The calculated results further prove the close dependence of the transporting characteristic of the

[2)] The eigenvalues of MPSH by projecting the self-consistent Hamiltonian onto the extended molecule are also calculated. Nevertheless, the eigenvalues are too great to denote in the figure. Instead we list the eigenvalues of the subsystem, where the origination of the transmission spectra from the orbitals can be recognized.

molecular junction on contact configuration.

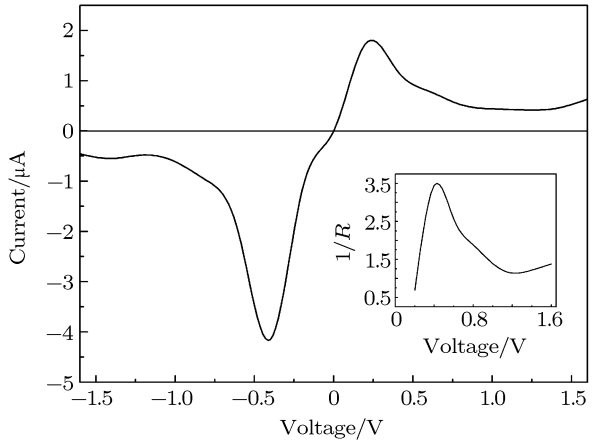


Fig. 5. The current–voltage curve of the dipyrimidinyl–diphenyl molecular junction with the contact geometry cont2. The inset shows the calculated inversed rectification ratio versus bias voltage.

The energy dependences of the transmission spectra at $V = 0$, ± 0.4, ± 0.8 and ± 1.2 V are investigated and shown in Fig. 6. The asymmetric profile of the transmission spectrum under an external bias voltage is clearly observed. At zero voltage, $E_{\rm F}$ is located at the tail of a broad peak. The current is thus predicted to turn on at a very small bias voltage. In other words, there is no current gap for the molecular junction. As the positive bias voltage is applied, the broad peak near $E_{\rm F}$ gradually splits and becomes weak, which

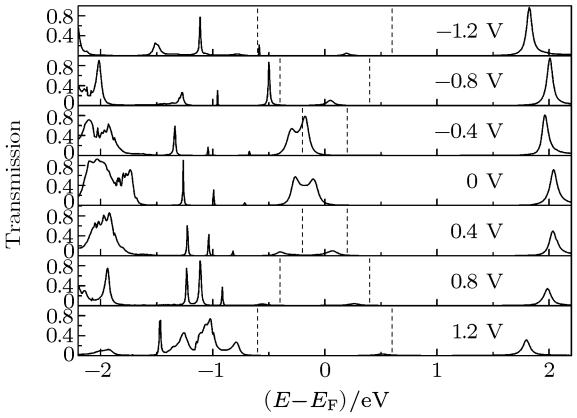


Fig. 6. Electronic transmission spectra at different bias voltages. The dashed lines indicate the bias window for the transportation.

results in a weak transport behaviour. As for the negative bias voltage, the broad peak first becomes strong and then splits. Correspondingly, the current largely increases at lower bias, and then rapidly decreases at relative high bias due to the lowered transmission peak in the bias window.

4. Conclusion

We investigated the transport properties of the dipyrimidinyl–diphenyl thiol molecule connected to two gold electrodes. The first-principle calculations display an obvious asymmetric current–voltage curve. The molecule/electrode contact structure plays an important role in determining the rectification behaviour of the molecular diode. The asymmetric bias effects on the molecular junction can be attributed to the dissimilar energy shift of the perturbed molecular orbitals and the asymmetric evolution of the spatial distribution of the orbitals under bias voltages.

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