Switching properties of bi-OPE-monothiol molecular junctions: Substituent effects and improvement of open-close ratio*

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(Received 11 July 2012; revised manuscript received 21 August 2012)

The electronic transport properties of a new kind of molecular switches – bi-OPE-monothiol molecular switches – were studied by applying first-principles calculations and generalized elastic scattering Green's function. The numerical results show that, for a bi-OPE-molecule junction, the offset face-to-face configuration induces more delocalized molecular orbitals, and results in higher conductivity than the parallel face-to-face configuration, so it can be used as a molecular switch. The side substituent groups containing more delocalized electrons can strengthen the intermolecular coupling and raise the conductivities of bi-OPE-monothiol molecular devices. On the basis of the investigations, we find a scheme to enhance the open–close ratios of bimolecular switches.

Keywords: bimolecular junction, electronic transport properties, switching properties

PACS: 85.65.+h, 73.63.–b, 31.15.xv **DOI:** 10.1088/1674-1056/22/2/028504

1. Introduction

In the past several decades, nanotechnology and supramolecular chemistry have experienced rapid development and many important and solid advances have been made in areas of the molecular electronic devices, especially for single-molecule devices.[1–12] However, research has primarily focused on bimolecular devices in recent years and many challenging problems still remain.[13–20] Recently, Wu *et al.*[13] first prepared bimolecular junctions through π-stacking of adjacent OPE molecules in a mechanically controllable break junction (MCBJ). Analysis showed that their electronic transport properties were novel and desirable, which stimulated intense interest in this field.[21–26] Based on those investigations and our previous studies,[21,22] we find that by changing the overlap distance of the two OPE molecules, the bi-OPE-monothiol molecular junctions show higher and lower conductive states, which can be used as a molecular switch and is valuable in controlling or protecting circuits. However, the conductivities of most bimolecular junctions are very weak, and the open–close ratios are small. So in this work, we present a systematic study on the electronic transport properties of bi-OPE-monothiol molecular devices by using density functional theory (DFT) and elastic scattering Green's function theory, and by analyzing the substituent effect on the electronic transport properties of bimolecular junctions to elucidate a possible way to enhance the conductivity and the open–close ratio of a bimolecular switch.

2. Theoretical model and computational details

The molecules that we investigated in the bimolecular junctions are the oligomeric phenylene ethynylene molecules with a single thiol anchor group (ST-OPE), as shown in Fig. 1(a), where the –Rs represent different substituent groups. The bimolecular junctions are formed by two cofacial ST-OPE molecules connected to two semi-infinite gold electrodes with a single terminal sulfur atom in each molecule anchored above the hollow position of the Au (111) surface (Fig. 1(b)). Considering the influence of the electrodes on the molecules and the local interaction between them, we sandwich the bi-OPE-molecule between two gold atom equilateral triangles to form an extended molecule system in the calculations (Fig. 1(b)). The Au–Au and S–Au bond lengths are fixed to be 0.288 nm and 0.285 nm, respectively.[27] We perform geometric optimizations and electronic structure calculations at the B3LYP level with the Lan12DZ basis set implemented in the Gaussian03 package.[19] Based on the general Green's function formalism of Mujica *et al.*,[28] the net current density of molecular junction from source to drain for a three-dimensional electrode can be written as

$$\begin{aligned} i_{\mathrm{SD}} = & \frac{4em^{*}k_{\mathrm{B}}T}{\hbar^{3}} \\ & \times \int_{eV}^{\infty} \ln \frac{1+\exp[(E_{\mathrm{f}}+eV_{\mathrm{SD}}-E_z)/k_{\mathrm{B}}T]}{1+\exp[(E_{\mathrm{f}}-E_z)/k_{\mathrm{B}}T]} \\ & \times |\tau(E_z,V_{\mathrm{SD}})|^2 n^{\mathrm{S}}(E_z) n^{\mathrm{D}}(E_z)\,\mathrm{d}E_z, \end{aligned} \tag{1}$$

where V_{SD} is external bias, m^{*} is the effective mass of electrons, e is the charge of electrons, E_{f} is the Fermi level, n^{S}

*Project supported by the National Natural Science Foundation of China (Grant Nos. 10804064 and 10974121) and the Natural Science Foundation of Shandong Province, China (Grant No. ZR2010AZ002).

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and n^{D} are density of states of source and drain, $\tau(E_z, V_{\mathrm{SD}})$ is the transition matrix element. Then the total current from source to drain is $I_{\mathrm{SD}} = Ai_{\mathrm{SD}}$, where A is the effective injecting area and the conductance is obtained by $G = \partial I_{\mathrm{SD}}/\partial V_{\mathrm{SD}}$. The details of our theoretical models are included in Refs. [29]–[31]. The electron transport properties were calculated using the QCME code.[32]

3. Results and discussion

Considering the relative position of the benzene rings in the two OPE molecules, two typical configurations for two cofacial molecules can be assumed[24,26,33] — a parallel face-to-face (PFF) configuration and an offset face-to-face (OSFF) configuration, as shown in Fig. 1(a). In the calculation, we fixed the vertical distance between the two molecule planes (d) as 0.34 nm, which is close to the widely used values.[34,35] First we carried single-point-energy calculations for the bimolecular system with different offset distances (denoted as r) for different side substituent groups bonding on the middle benzene rings, such as $-NO_2$, –CN, –F, $-OCH_3$, –OH, $-CH_3$, and –H. The geometric optimizations show that the substituent groups have little influence on the geometric structures of OPE molecular backbones. For example, the molecular length only changes 0.002 nm with –H substituted by –CN, which is the largest value compared with the changes of molecular systems with other substituent groups.

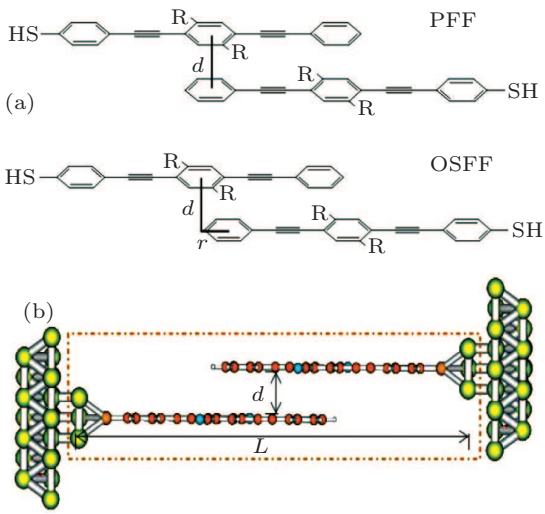


Fig. 1. (color online) (a) PFF and OSFF configurations of OPE dimers; (b) structures of bi-OPE-monothiol molecular junction, where d is the vertical distance between the two molecular planes, and L is the distance between the two electrodes.

In the regime of the offset distance shown in Fig. 2, one can see that the bimolecular systems reach the largest energy geometries that correspond to PFF configurations. However, when r is near 0.15 nm (in the following discussions we denote this case as the OSFF configuration), the energies of most bimolecular systems approach the minimum values, which suggests that the two single OPE molecules in the bimolecular junctions couple better with the OSFF configuration than with the PFF configuration.[13,36–38] So one can expect that electronic transport is easier for bi-OPE-monothiol molecular junctions with OSFF configurations than with PFF configurations, and bi-OPE-monothiol molecular junctions probably have switching properties. Additionally, around the minimum values, the curves exhibit energy wells. If we define the difference between the minimum energy at about 0.15 nm and the maximum energy at about 0.22 nm∼0.25 nm as the depth of the energy well, for the bimolecular systems with different side groups, the depths of the energy wells are different. For example, the wells for the bimolecular systems with $-NO_2$ and –CN are significantly deeper than the others, while there is no energy well for the curves of the bimolecular system with –H and $-CH_3$. Therefore, we consider the intermolecular couplings for bimolecular systems with $-NO_2$ and –CN to be better than those with –H and $-CH_3$.

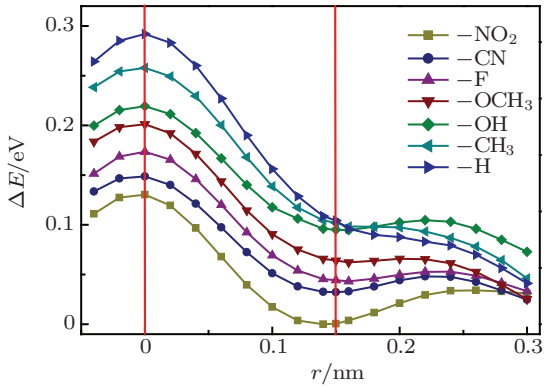


Fig. 2. (color online) Ground-state energies (ΔE) of the bimolecular junctions as functions of the offset distances of benzene rings.

Then, we select –CN, $-OCH_3$, and –F as the side groups to study the difference of the electronic transport properties between the two configurations. Figure 3 shows the conductance–voltage (G–V) curves of the three bimolecular systems. From the figure one can see that in the lower bias regime, the conductivities of these bimolecular systems are all very weak, because in the lower bias regime, there is no channel entering the voltage window, thus the electronic transport proceeds through a tunneling effect, i.e., conductance is dominated by nonresonant transmission, which is contributed by the tails of a set of transmission peaks. In the higher bias regime, the figure shows conductance plateaus and the OSFF configurations are more conductive than the PFF configurations for those bimolecular junctions even for the larger electrode distances of OSFF configurations. As is well known, for the higher bias regime, some transmission channels corresponding to the delocalized molecular orbitals enter the voltage window, the electrons of considerable energy are prone

to pass through bimolecular junctions by the channels, forming resonant transmission, thus conductance–voltage (G–V) curves present pronounced high conductive states. In order to understand the resonant transmission mechanism in detail, we show the molecular orbitals which correspond to the transmission channels in the bias windows in Fig. 4. The figure shows that the conductance plateaus are contributed mainly by two delocalized molecular orbitals for each of those six bimolecular systems, which are LUMO+2 and LUMO+3. One can easily see that the molecular orbitals are more delocalized for OSFF configurations than PFF configurations, so Fig. 3 shows that the OSFF configuration is more conductive than the PFF configuration in the higher bias regime for all bimolecular junctions.

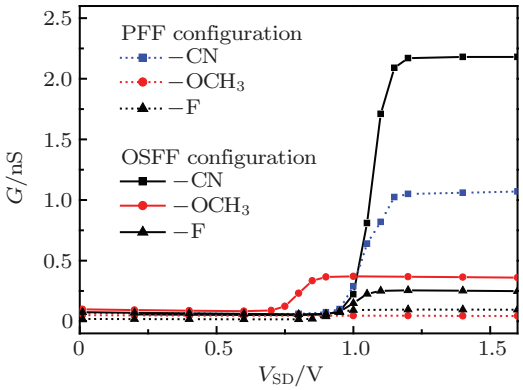


Fig. 3. (color online) Conductance of the bimolecular junctions with configurations of PFF configuration (dotted lines) and OSFF configuration (solid lines).

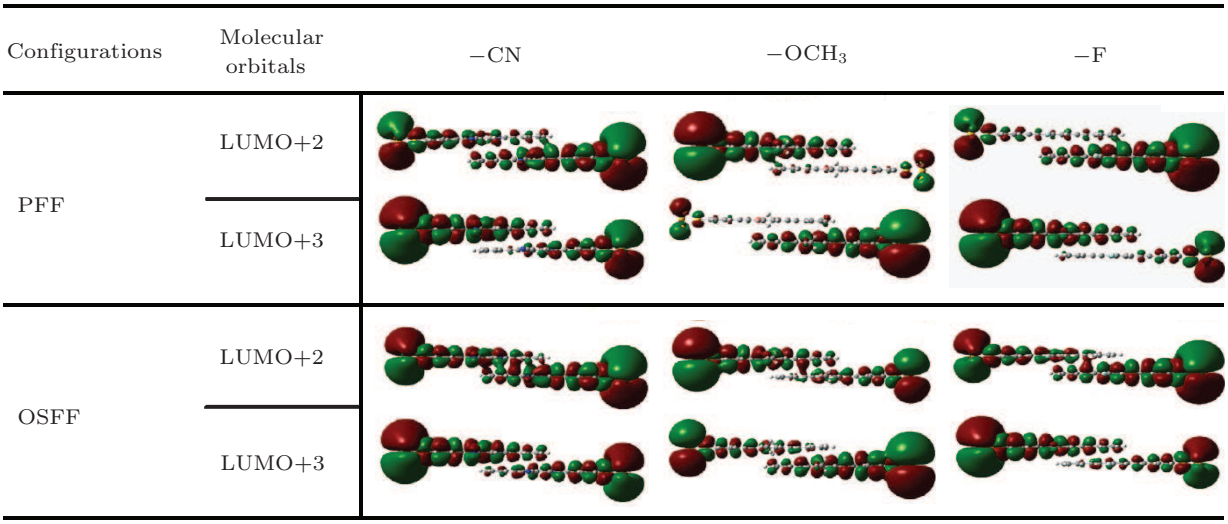


Fig. 4. (color online) The molecular orbitals which correspond to the transmission channels of conductance plateaus (isovalue=0.0030).

From the above analysis, one can see that by changing the overlap distance of the two OPE molecules, those bi-OPE-molecular junctions can be exchanged between higher and lower conductive states, i.e., those bi-OPE-molecular junctions show switching properties. However, the open–close ratios (R_{OC}, defined as G_{OSFF}/G_{PFF} with bias voltage of 1.2 V in this article) are very small for those bimolecular systems with the substituent group of –CN, and the conductances for the bimolecular systems with $-OCH_3$ and –F are very weak, all of which is unfavorable for the design of molecular switches. In order to find a more conductive and higher R_{OC} bi-OPE-molecular device, we studied those bi-OPE-molecular systems further. Figure 3 shows that in the higher bias regime, bimolecular systems with the substituent group of –CN are somewhat more conductive than bimolecular junctions with the other two substituent groups, which can be attributed to the more delocalized molecular orbitals (LUMO+2 and LUMO+3) for the systems with –CN than those with the other two substituent groups. Comparing –CN with $-OCH_3$ and –F, one can see that there are delocalized π electrons in –CN due to the triple bond between C and N atoms which enhance the overlap of the electronic states between two OPE molecules in the bimolecular junctions and thus raise the conductivity of the resonant electronic transport of the bimolecular systems. In order to verify this deduction, we further calculated the transport properties of bi-OPE-monothiol molecular systems with other substituent groups, such as $-NO_2$, $-C_2H_3$, $-C_6H_5$, –OH, $-CH_3$, and –H.[13–15] Table 1 shows the conductances and R_{OC} of the bimolecular junctions. From the table one can see that when the applied bias is 0.5 V, the conductances are very weak because they are in the lower bias regime and correspond to the nonresonant transport. When the applied bias is 1.2 V, the resonant transmission channels are open and the numerical results show that the OSFF configuration is more conductive than the PFF configuration. The conductivities of OPE bimolecular junctions with $-NO_2$, $-C_2H_3$ and especially with $-C_6H_5$ are

obviously better than the others, as well as the overlaps of the molecular orbitals. Since they all contain π electrons especially $-C_6H_5$, it seems that the results support the deduction that we obtained above. Moreover, the R_{OC} of the bimolecular junctions with $-C_2H_3$ and $-C_6H_5$ are obviously higher than the others, and the conductivity of the bimolecular junctions with $-C_6H_5$ and with OSFF configuration is distinctly higher than the others. Hence, by substituting the group of $-C_6H_5$, we realize the aim of raising the conductivity and R_{OC} of the bi-OPE-molecular device. In order to clarify why the bimolecular junction with $-C_6H_5$ is more conductive and has higher R_{OC}, we plotted transmission spectra of OPE bimolecular junctions with –CN, $-NO_2$, $-C_2H_3$, and $-C_6H_5$ in Fig. 5. The figure shows that for all of the transmission peaks, blue shifts take place for the bimolecular systems with OSFF configurations comparing with the PFF configurations. The transmission intensity in the regime that the figure shows is obviously stronger for the OSFF configuration than the PFF configuration for a bimolecular junction with $-C_6H_5$ substituent groups, however for other bimolecular systems, the cases appear differently; so the bimolecular junction with $-C_6H_5$ shows higher conductivity and R_{OC}. Additionally, the transmission peak of a bimolecular junction with $-C_6H_5$ is raised at about 0.8 eV, which is lower than those of other systems and thus favorable for electronic transport.

Table 1. The conductances (G, unit: nS) and open–close ratios (R_{OC}) of the bimolecular junctions.

		–CN	$-NO_2$	$-C_2H_3$	$-C_6H_5$	$-OCH_3$	–OH	–F	$-CH_3$	–H
0.5 V	G_{PFF}	0.061	0.029	0.048	0.023	0.048	0.076	0.017	0.045	0.077
	G_{OSFF}	0.053	0.043	0.021	0.130	0.085	0.065	0.063	0.036	0.106
1.2 V	G_{PFF}	1.02	1.32	0.065	0.864	0.055	0.084	0.097	0.038	0.067
	G_{OSFF}	2.18	2.58	1.61	21.2	0.364	0.392	0.251	0.127	0.147
	R_{OC}	2.14	1.95	24.77	24.54	7.91	4.67	2.59	2.24	2.19

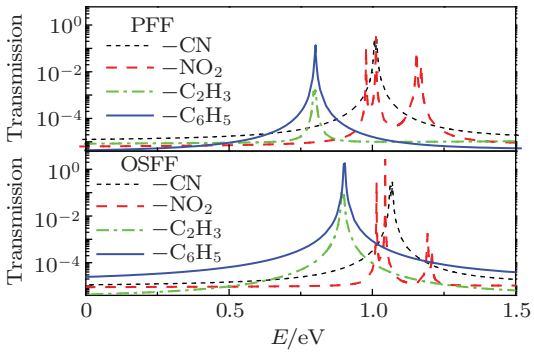


Fig. 5. (color online) Transmission spectra of OPE bimolecular junctions with –CN, $-NO_2$, $-C_2H_3$, and $-C_6H_5$.

Considering the switching properties and geometric characteristics of bi-OPE-monothiol molecular junctions, one can expect that bimolecular molecular switches are valuable in controlling or protecting circuits, such as when high temperature induces expansion of electrodes or external pressure induces a geometric change of equipment circuitry, which consequently switches the bimolecular junction to a closed state. It should be mentioned that the electrode distances for PFF and OSFF configurations are about 3.20 nm and 3.35 nm respectively. The measurements of Martin *et al.* show that the conductance of a bi-OPE-molecular system with $-OCH_3$ substituent group is about (0.47±0.08) nS at 0.6 V with the electrodes distance of (2.9±0.3) nm.[23] Our further calculations show the conductance of this bimolecular system is about 0.4 nS when the electrode distance is about 2.8 nm and the bias voltage is 0.6 V, which is very consistent with the experimental result.[23]

4. Conclusion

In conclusion, based on the quantum chemistry calculations, we studied the conductivities of bi-OPE-monothiol molecular junctions with different configurations and different substituent groups. The numerical results show that the OSFF configuration induces more delocalized molecular orbitals in the bias windows, which results in better conductivity of the OSFF configuration than the PFF configuration in the resonant transport regime and leads to the switching properties of bimolecular junctions. The side substituent groups containing rich delocalized electrons can enhance the intermolecular overlaps of the orbitals, which consequently raise the conductivities and open–close ratios of bi-OPE-monothiol molecular devices.

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