First-principles study on photoswitching behavior and negative differential resistance in single molecule junction

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ABSTRACT

We investigate the electronic transport of a photochromic molecule, a 1,2-dithienyl-1,2-dicyanoethene sandwiched between two Au electrodes using first-principles based on non-equilibrium Green's function and density functional theory. This molecule can be reversibly transformed between trans and cis state through irradiation. The calculated current of the cis form is larger than the trans form, indicating an obvious switching behavior in the present device. We discuss the electronic transport properties for cis and trans forms in detail by the transmission spectra and molecular projected self-consistent Hamiltonian states. The observed negative differential resistance effect in the cis form is explained discussing the transmission eigenstates of HOMO energy level. The results suggest that this photochromic molecule can become one of the good candidates for single molecular photoswitching in the future.

1. Introduction

The development of silicon based microelectronic device has reached its limit due to Moore law. An effective method to replace the traditional semiconductor device is to design molecular device in nano-circuits. Recently, the manufactured molecular devices has attracted more research interests, displaying many prominent properties such as negative differential resistance (NDR) [1,2], rectification [3,4], switch [5,6] and memory effects [7,8]. Among these characters, molecular switch contributes to store digital information and route signals in molecular electronic logic circuits [9,10].

The molecular switch belongs to a bistable quantum system can be reversibly transformed from high conductance(ON) state to low conductance (OFF) state and vice versa by an external stimulus such as the electric field [11], the tip of scanning tunneling microscopy (STM) [12], the redox process [13] and light [14]. More researches focus on the photochromic molecular switches for it has the advantages of quick response time and a wide range of condensed phases[15]. In recent years, an indolobenzoxazine photochromic compound is used as a switch [16]. The switch

behavior of the azobenzene derivatives and its rectification properties are reported [17]. The on/off ratio is up to 90 for the naphthopyran-based optical molecular switch [18]. The photoinduced and reversible switch devices based on dihydroazulene molecules has a stable switch ratio in a large bias range [19]. The photoswitching of a single molecule connected to graphene contacts shows full reversibility and stability [20]. While it is still necessary to further understand the electronic transport to fabricate the molecular switch in the future industrial application.

In this work,we investigate the electronic transport properties of the photoswitching based on photochromic molecule, a 1,2-dithienyl-1,2-dicyanoethene (4TCE) [21,22] by Atomistix Toolkit (ATK) [23,24] package within non-equilibrium Green's function formalism (NEGF) and first-principles density functional theory (DFT). This molecule can be transformed reversibly between trans and cis state by light stimulus and is sandwiched between two Au electrodes in our model. The designed device shows the switching behavior and NDR effect.

2. Model and method

The constructed molecular device is displayed in Fig. 1. The pre-optimized 4TCE isomers are sandwiched via metal-sulfur bond, with sulfur atom located on the hollow site, between two parallel

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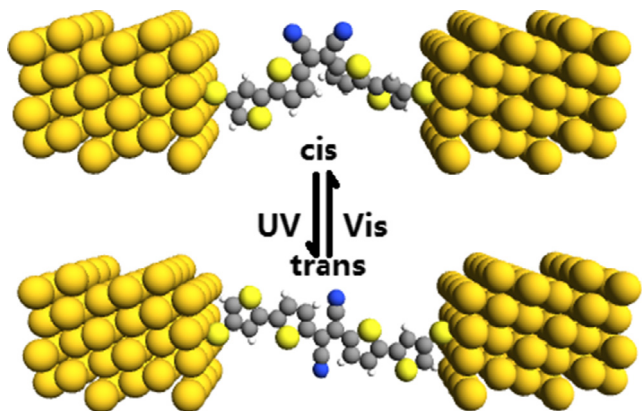*E-mail address:* baoanbian@jiangnan.edu.cn (B. Bian).

Fig. 1. Schematic diagram of designed switches, the yellow, gray, white, blue and golden balls represent S, C, H, N, and Au atoms respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. The density of states of 4TCE isomers.

Au(111) surfaces that correspond to the surfaces of gold electrodes. The molecular device is divided into three regions: left electrode, right electrode, and central scattering region. The central scattering region includes molecules and three layers of gold from each electrode. It is big enough to avoid the interaction between the molecule and its mirror image when 4×5 symmetrical Au(111) electrodes are chosen. In the model, trans/cis of 4TCE isomerization can be realized by ultraviolet (UV) irradiation or visible irradiation. In the present calculations, we take the Perdew-Burke-Ernzerhof functional within the generalized gradient approximation(GGA. PBE) [25] as the exchange and correlation interactions. Self-consistent calculations are carried out with an iteration control parameter tolerance about 0.0001, and the simulated temperature is taken as 300 K. Single-zeta with polarization (SZP) basis set is adopted for Au atoms, and other atoms adopt double-zeta with polarization (DZP) basis set. The k-point grid is set as $3 \times 3 \times 300$ and the mesh cut-off is adjusted to 150 Ry in order to achieve a balance between calculation efficiency and accuracy.

The current through a molecular junction is calculated by the Landauer-Büttiker formula [26]:

$$I(V) = \frac{2e}{h} \int_{\mu_L}^{\mu_R} [f(E - \mu_L) - f(E - \mu_R)] T(E, V) dE \quad (1)$$

here f is the Fermi function, $\mu_{L/R}$ is the electrochemical potential of the left/right electrode, and $T(E,V)$ denotes the transmission probability of electrons for energy E at voltage V. And $\mu_{L/R} = E_f \mp \frac{V}{2}$, E_f that represents the Fermi level is usually set to 0.

The transmission probability is obtained by

$$T(E) = Tr\left[\Gamma_L(E) G^R(E) \Gamma_R(E) G^A(E)\right] \quad (2)$$

were $G^R(E)$ and $G^A(E)$ are the retarded and advanced Green's function of the central region,respectively, and $\Gamma_{L/R}(E)$ represents the broadening function of the left (right) electrode.

3. Results and discussion

It can be seen in Fig. 1 that these two kinds of molecules display the different structure. To understand the difference of structure between both molecules, we calculate the density of states (DOS) of cis and trans forms in Fig. 2. When the molecule is transformed from cis to trans form, the DOS of trans moves away from the Fermi level. Especially, the peak of DOS for cis is higher than the trans
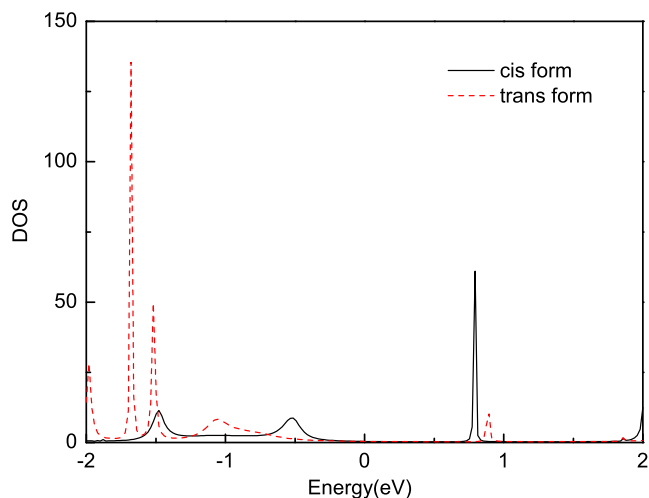
near Fermi level. Therefore, the change of molecular structure affects the electronic properties of 4TCE molecule effectively.

The current-voltage (I-V) characteristics of devices for cis and trans forms are shown in Fig. 3(a). The current of the cis form is larger than the trans form, indicating that this device displays an obvious switching behavior when isomerization occurs between cis- and trans-4TCE by UV irradiation or visible irradiation. Namely, there is a switch from the OFF state (low conductance) to the ON state (high conductance) when the molecule device changes from the trans form to the cis form by photoinduction. When the bias voltage is beyond 1.6 V for cis form, a NDR effect is observed. This phenomenon also appears in the photochromic molecule switch [27,28],which is analyzed through the transmission and the frontier molecular orbital.

We calculate the switching ratio, $R(V) = I_{cis}/I_{trans}$ to describe the performance of device as shown in Fig. 3(b). The switching ratio increases slowly in the bias from 0 V to 1 V. Then it increases rapidly with increase of bias voltage, and the maximum of switching ratio is about 48.93 at 1.4 V. The maximum switching ratios reach 258 and 72 in the salicylideneaniline and N-salicylideneaniline molecule devices based on the carbon nanotube and Au electrodes [29,28]. When the bias voltage further increases, the switching ratio decreases rapidly, and the minimum of switching ratio is 2.54 at 2 V. This result suggests that the switching behaviors are affected by the bias voltage, and this molecule can become a candidate for the practical application of photoswitching.

We calculate the transmission spectra of the cis and trans forms at zero bias voltage to understand the I-V characteristics in Fig. 4. The Fermi level that is the average value of the chemical potential of the left and right electrodes is set as zero. H and L represents the highest occupied molecular orbital (HOMO) and the lowest molecular orbital (LUMO), respectively. In Fig. 4, the transmission spectra for two forms display different characteristics. The switch with the cis form has a strong peaks at −0.553 eV near the Fermi level,and another weak peak at 0.79 eV that is far away from the Fermi level. The switch with the trans form has a weak transmission peak at 0.895 eV and a strong transmission peak at −1.06 eV that are far away from the Fermi level, causing less contribution to the electron transport of switch. It is known that energies of electrons near the Fermi level have a contribution to the total current. Thus, trans form has the low conductance. Furthermore, our calculations show that the HOMO-LUMO gap increases from 1.39 eV to 1.86 eV when the cis form is switched to the trans form. This difference in HOMO-LUMO gap, resulting from the difference of molecular