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Physics Letters A
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Effect of the substitution of F on the photoswitching behavior in single molecular device

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ARTICLE INFO

Article history:
Received 24 February 2017
Received in revised form 21 April 2017
Accepted 14 June 2017
Available online xxxx
Communicated by R. Wu

Keywords:
Molecular device
Electronic transport
Photoswitching

ABSTRACT

We carry out first-principles calculations based on density functional theory and non-equilibrium Green's function to investigate the electronic transport properties of a 5-arylidenehydantoin molecule sandwiched between two Au electrodes. A reversible switching behavior between E and Z isomerization can be observed in the device through light irradiation, and their currents display different characteristic. Furthermore, it is found that the substitution of F in the molecule enlarges the switching ratio of device. The different characteristics of currents for E/Z forms and E/Z with the substitution of F are discussed by the transmission spectra and the molecular projected self-consistent Hamiltonian states. We discuss the change of Fermi level alignment due to the substitution of F, and the polarization effect under bias. We find the negative differential resistance effect in the E form with the substitution of F, which is explained by change of molecule–electrode coupling with the varied bias. The results suggest that the 5-arylidenehydantoin molecule with the substitution of F that improves the performance of device, becoming one of the methods for improving single molecular photoswitching performance in the future.

1. Introduction

Silicon based microelectronic devices have been rapidly developed to its limit due to Moore law. With the rapidly developing experimental techniques and theory, molecular devices for replacing traditional microelectronic devices in nano-circuits may be an effective way to solve problems. In recent years, various molecular devices with interesting functions, such as negative differential resistance (NDR) [1,2], rectification [3,4], switching [5,6], spin filter [7,8] and memory effects [9,10] have been designed. Especially, molecular switch plays an important role in store digital information and route signals in molecular electronic logic circuits [11,12].

The molecular switch is attributed to a bistable quantum system can be reversibly transformed between high conductance (ON) state and low conductance (OFF) state by an environmental stimulus, such as the electric field [13], mechanical control [14], the redox reaction [15] and light [16]. Especially, photo-excitation is an effective method to fabricate the optical switch due to the fast response and a wide range of condensed phases [17]. The molecular switch based diarylethene molecule with the configurations of the open form and the close form is controlled by the light stimulus [18–20]. The E–Z photoisomerization of azobenzene is applied to realize the molecular switch [21]. The theoretical studies on the photoswitching attract more attentions [22,23], supplying the guidance for the design of switch devices.

Recently, a molecular E/Z photoswitches based on arylidenehydantoin molecule was investigated experimentally [24], which has the advantages of strong stability, fast response and high quantum yield. However, the electrical conductivity of arylidenehydantoin molecule connecting with electrode as a switchable molecular device has rarely been reported. Theoretical study on this molecular switch will be helpful for switching mechanism and further application in a molecular circuit. Moreover, the experiment that the single-molecule junction conductance changes with different substituent was reported [25]. Therefore, in this paper, we investigate the influence of the substitution of F on the photoswitching behavior in single molecular device. The 5-arylidenehydantoin molecule is sandwiched between two Au electrodes. The results show that the current through the E isomer is larger than that of the Z iso-

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http://dx.doi.org/10.1016/j.physleta.2017.06.023
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Please cite this article in press as: B. Bian et al., Effect of the substitution of F on the photoswitching behavior in single molecular device, Phys. Lett. A (2017), http://dx.doi.org/10.1016/j.physleta.2017.06.023

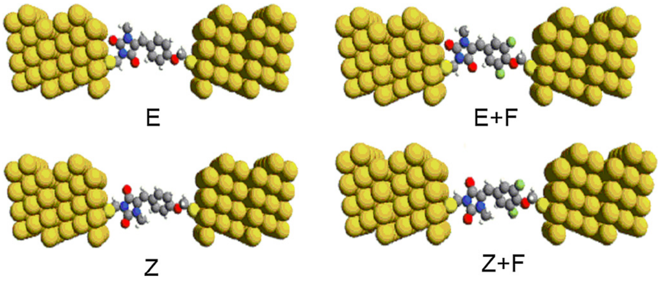

Fig. 1. Schematic diagram of our two-probe models, the yellow, gray, white, red, blue, green and golden balls represent S, C, H, O, N, F and Au atoms respectively. E + F and Z + F note the substituted 5-arylidenehydantoin by two F atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

mer, and there is a relatively stable switch ratio in the small bias. Furthermore, it can be found that the substituent of F atoms on the two hydrogen atoms in the molecule of benzene ring can greatly enhance the switching ratio.

2. Model and method

The molecular junctions we designed are shown in Fig. 1. The pre-optimized hydantoin-based molecules are chemisorbed via metal–sulfur bond, with sulfur atom located on the hollow site, between two semi-infinite parallel gold (111) surface electrodes. The molecular device is divided into three parts which are left electrode, right electrode, and central scattering region. The central scattering region includes molecules and three layers of gold from each electrode, with each layer made of 16 (4×4) Au atoms. This is large enough to avoid the interaction between the molecule and its mirror image. The geometrical optimization and electronic Transport properties are all calculated by non-equilibrium Green's function formalism (NEGF) combined with first-principles density functional theory (DFT) as implemented in the Atomistix Toolkit (ATK) [26,27] package. In the calculations, the Perdew–Zunger local-density approximation (LDA.PZ) is used in the electron exchange correlation potential [28]. Self-consistent calculations are carried out with an iteration control parameter tolerance about 0.0001. Single-zeta with polarization (SZP) basis set is adopted for Au atoms, and other atoms adopt double-zeta with polarization (DZP) basis set. We select k-point grid as $3 \times 3 \times 400$ and the mesh cut-off is adjusted to 150 Ry to achieve a balance between calculation efficiency and accuracy.

The current through a molecular device is calculated from the Landauer–Bütiker formula [29]:

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

where f is the Fermi function, $\mu_{L/R}$ is the electrochemical potential of the left/right electrode and $T(E,V)$ represents the transmission coefficient for electrons with energy E at voltage V. In addition, $\mu_{L/R} = E_f \mp V/2$, Fermi energy E_f is usually set to 0.

The transmission function $T(E,V)$ of the device is

$$T(E,V) = \mathrm{Tr}\left[\Gamma_L(E) G^R(E) \Gamma_R(E) G^A(E)\right] \qquad (2)$$

where $G^{R/A}(E)$ is the retarded (advanced) Green's function of the central region, and $\Gamma_{L/R}(E)$ represents the coupling function of the conductor to the left and right electrode.

3. Results and discussion

The electronic transport properties of the present molecular devices from the current–voltage (I–V) curves are shown in Fig. 2(a) and (b). For convenience, the devices with E and Z forms of 5-arylidenehydantoin are named as E and Z, and the devices with substituted E/Z forms by two F atoms are named as E + F and Z + F. It can be observed that the currents of E and E + F forms increase rapidly with increasing voltage. When the bias voltage is large than 1.8 V for device E + F, there is a negative differential resistance effect that will be discussed later. However, the currents of Z and Z + F forms almost keep constant in the whole bias. This difference indicates a switching behavior when the molecular

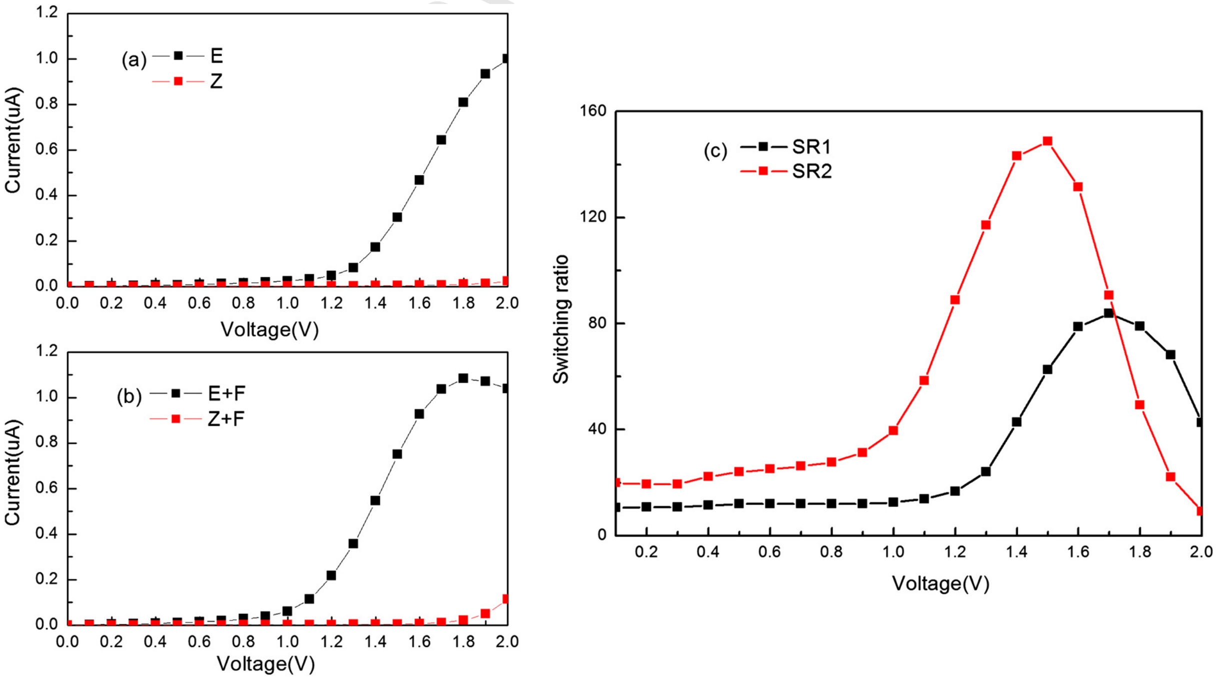

Fig. 2. (a–b) I–V curves for devices E(+F) and Z(+F), and (c) current switching ratio as a function of applied bias ($\mathrm{SR1} = I_{\mathrm{E}}/I_{\mathrm{Z}}$, $\mathrm{SR2} = I_{\mathrm{E+F}}/I_{\mathrm{Z+F}}$).

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