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The *E–Z* photo-isomerization switching behavior in single molecular device with carbon nanotube electrodes

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ABSTRACT

By using nonequilibrium Green's functions in combination with the density-functional theory, we investigate the electronic transport properties of the molecular device constructed by a single 4,4-(ethene-1,2-diyl) dibenzoic acid sandwiched between carbon nanotube electrodes. The results show that an obvious reversible switching behavior can be observed when the molecular structure changes between *E* isomerization and *Z* isomerization by ultraviolet irradiation or visible irradiation. More importantly, the switching ratio can reach to a maximum (about 7000) at 0.28 V and then decrease gradually to a minimum at 0.48 V. It is suggested that the controllable switching behavior is very useful for the design of functional molecular devices.

1. Introduction

The rapid development of integrated circuit technology make the microelectronic devices more and more smaller. Meanwhile, the step of miniaturization of microelectronic devices gradually reaches its limit due to Moore law. One of the most useful ways to solve this problem is to improve the techniques for manipulating individual molecules and to design molecular devices for replacing silicon components in nanoscale circuits. So far, various molecular devices have been made successfully to realize the functions existing in microelectronic devices such as switching [1–4], rectification [5–10], negative differential resistance (NDR) [11–16], and spin filter [17] due to the advancement of techniques including scanning tunneling microscope (STM) [18], lithographically fabricated nanoelectrodes [19], colloid solutions [20], and mechanically controllable break junctions [21]. Among these functions, the molecular switching is very prominent because its potential use in future logic and memory.

The early nano-scale switch devices consisting of the incorporating monolayers of rotaxanes or catenanes were created by Heath's group [22,23]. In these molecules, an outer ring can move between two positions on a molecular rod or cycle to realize the on and off states of the molecular switching. Then, the switching based on redox-active molecules were performed in an aqueous environment in order to allow for electrochemical control of the molecule in the junction [24–27]. Subsequently, the current pulse was proved to be another effective way inducing the conductance switching. The typical molecule was the naphthalocyanine which is planar, does not involve conformational changes, and is well-suited for use in self-assembled monolayers [28,29]. Recently, design, synthesis and research of photochromism molecular switches become a research hotspot. The typical photochromism molecules including azobenzene, diarylethenes, and spiropyran are widely studied due to their good switching properties and potential use in future information memory [30–32]. Meanwhile, the theoretical studies of photochromism molecular switchings have also received increasing attentions [33,38,34–37]. These theoretical works are considered as the worthy complement of the experiments, and has also the guiding significance for the further design of molecular devices.

In the present work, we report theoretical investigations of the electronic transport properties of the molecular device consisting of 4,4-(ethene-1,2-diyl) dibenzoic acid, which is a photochromism molecule and shows a obvious switching behavior in experiment [39]. The calculated *I–V* characters show the photoinduced *E–Z* isomerization of 4,4-(ethene-1,2-diyl) dibenzoic acid can also be used to control the conductance at the single molecule level when it is connected to carbon nanotube electrodes. Note that the carbon nanotubes are a real quasi-one-dimensional materials and the use of carbon nanotubes as electrodes in molecular junctions is of many advantages on constructing stable molecular device by forming strong covalent bonds with organic molecules [40,41].

2. Computational method and model

The molecular device is illustrated in Fig. 1a: the 4,4-(ethene-1,2-diyl) dibenzoic acid is coupled to two (5,5) carbon nanotubes.

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E isomerization (b) of molecule can be changed to *Z* isomerization and (c) by ultraviolet (UV) irradiation or vice versa upon visible irradiation. The molecular device is divided into three regions: left lead, right lead, and scattering region. The scattering region contains a portion of the semi-infinite leads and is then converged via standard density-functional theory methods, thereby establishing a relation between the molecules and the leads, the common Fermi level, and charge neutrality at equilibrium. The Kohn–Sham potential outside the scattering region is set to be the bulk value of two electrodes, which is determined via a separate calculation and shifts rigidly relative to each other by the external bias voltage. The infinite open boundary problem is thereby reduced to a proper, self-consistent calculation of the charge density for the finite sized scattering region. The electrodes extend to electron reservoirs at $z = \pm\infty$ where bias V_b is applied and the electric current is collected. Then, we fix the atomic positions of the two electrodes and optimize the molecule until the residual forces less than 0.04 eV/Å to get an appropriate device structure. The geometrical optimization and the electronic transport properties are calculated by an *ab initio* code package (Atomistix ToolKit (ATK)) [42–44]. The nonlinear current through the contact is calculated by using the Landauer formula

$$I(V_b) = \frac{2e}{h}\int_{\mu_L}^{\mu_R} T(E, V_b)dE, \tag{1}$$

where $\mu_{L/R}$ are electrochemical potentials of the left and right electrodes [45]. With the applied bias potential V_b, the difference in the chemical potentials is given by eV_b, and we use $\mu_L(V_b) = \mu_L(0) - eV_b/2$ and $\mu_R(V_b) = \mu_R(0) + eV_b/2$. The energy region of the transmission spectrum that contributes to the current integral in the Landauer formula, is referred to the bias window. The total transmission probability

$$T(E) = T_r\left[Im\sum\nolimits_l(E)G^R(E)Im\sum\nolimits_r(E)G^A(E)\right], \tag{2}$$

where $G^R(E)$ and $G^A(E)$ are the retarded and advanced Green functions of the central region. $T(E, V_b) = \sum_{n=1}^{N} T_n(E, V_b)$ for electrons incident at an energy *E* through the device under the potential bias V_b is composed of all available conduction channels with the individual transmission T_n.

3. Results and discussion

The calculated currents in a bias range from 0 to 0.5 V are shown in Fig. 2. From the figure, we can find that the currents of *E* isomerization increase rapidly with the bias voltage. However, the currents of *Z* isomerization is almost not changed in the whole bias region. It means that the device shows an obvious switching behavior when its molecular structure changes between *E* isomerization and *Z* isomerization by UV irradiation or visible irradiation. The switching behavior can be seen clearly from the switching ratio in the inset in Fig. 2, which is defined as the ratio of the currents under *E* isomerization and *Z* isomerization. For small bias voltage, the switching ratio is increased with the increase of bias voltage. The biggest switching ratio is about 7000 at 0.28 V. When the bias voltage further increases, the switching ratio decreases gradually and reaches the minimum at 0.48 V. Note that these important switching features such as the huge switching ratio and the controllable switching behavior by the bias voltage are very useful for further design of molecular device.

To further explore the *I–V* characteristics, in Fig. 3, we show the transmission coefficient $T(E)$ under zero bias voltage. The average Fermi level, which is the average value of the chemical potential of the electrode, is set as zero [46,47]. It is notable that the transmission coefficients of *E* isomerization in the negative energy region are almost zero (see Fig. 3a). However, in the positive energy region, there are a series of transmission peaks with large transmission coefficients. Especially, the highest occupied molecular orbital (HOMO) lies on the right of the Fermi level and very closes to Fermi level. It is known that the calculated currents obtain from the integral between μ_L and μ_R (the bias window) of the transmission coefficients $T(E)$. Thus the HOMO is the main transport channel and the electrons can easily flow through the system. Under the effect of UV irradiation, the *E* isomerization of 4,4-(ethene-1,2-diyl) dibenzoic acid changes to the *Z* isomerization and the corresponding electronic transport ability also changes incidentally. The transmission coefficient $T(E)$ of *Z* isomerization at zero bias voltage is shown in Fig. 3b. Although there appear three transmission peaks in the negative energy region, they are very far away from the Fermi level. In addition, the transmission peaks in the positive energy region are sparse and the corresponding transmission coefficient is obviously less than that of *E* isomerization. More important, the change of the molecular structure can widen the energy gap between the HOMO and the Fermi level, and leads to a decreases of transmission coefficient. Consequently, the

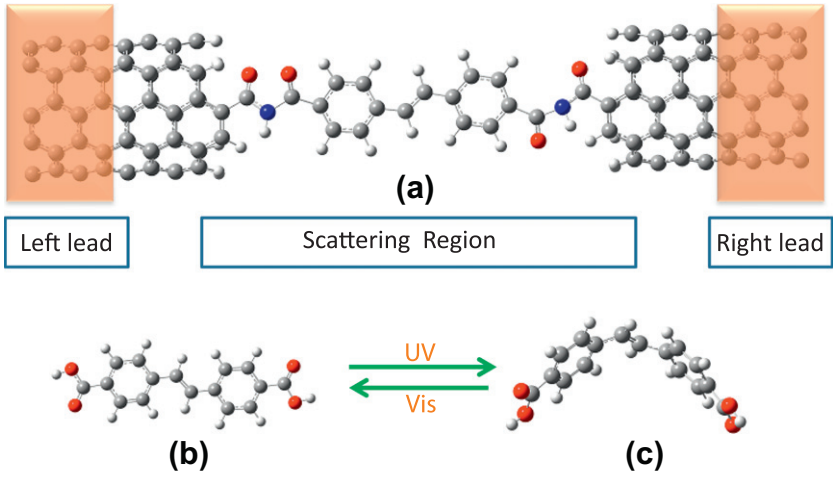

Fig. 1. (a) Schematic description of the device: a single 4,4-(ethene-1,2-diyl) dibenzoic acid sandwiched between CNT electrodes. (b) and (c) correspond the structure of *E* and *Z* isomers of 4,4-(ethene-1,2- diyl) dibenzoic acid, respectively.