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Effect of carbon nanotubes chirality on the *E*–*C* photo-isomerization switching behavior in moelcular device

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ABSTRACT

Applying nonequilibrium Green's function formalism in combination with the first-principles density functional theory, we investigate the electronic transport properties of optical molecular switch based on the fulgide molecule with two different single-walled carbon nanotube (SWCNT) electrodes. The molecule that comprises the switch can convert between *E* isomer and *C* isomer by ultraviolet or visible irradiation. Theoretical results show that these two isomers exhibit very different conductance properties both in armchair and zigzag junction, which can realize the *on* and *off* states of the molecular switch. Meantime, the chirality of the SWCNT electrodes strongly affects the switching characteristics of the molecular junctions, which is useful for the design of functional molecular devices.

1. Introduction

With the miniaturization of traditional electronic devices, using molecules as components in atomic-scale circuits has become an attractive field. Molecular devices are capable of providing features like negative differential resistance (NDR), memory effects, rectification, amplification and switching properties, which open the way for a variety of electronic applications [1–5]. Among all of these, molecular switches, especially optical switches, have drawn considerable attention in recent years due to their potential applications in future logic and memory [6–10]. In this regard, many different optical switches using photochromic molecules which can change their isomer type upon light irradiation have been investigated and discussed [11–13]. Albeit there have been many theoretical as well as experimental investigations pursued on optical switches, the number of molecular systems having the switch feature are still very limited. Especially, many optical switches such as spiropyrans, benzochromenes, spiroxazines and azobenzenes have poor long-term light and heat stability. Recently, some experiments report that fulgide molecule can be transformed by light in reversible way from *E* isomer into *C* isomer [14–16]. The carbon ring in the center of the molecule is open in the *E* isomer. When irradiated with UV light the ring closes and the molecule switches into the *C* state. Irradiation with visible light opens the ring again, switching the fulgide back into the *E* isomer (see Fig. 1). Furthermore, the most significant features of this material are they present excellent photochromic properties including short response time, heat stability, and large changes of the absorption wavelengths between the two isomers, which make it usable as one of the candidates for light-driven molecular switches [14–16]. However, little attention was paid to the electronic transport properties of these molecules.

On the other hand, electrode materials as a part of the molecular device also play an important role in realizing the elementary functions in future molecular electronic circuits. However, common metallic electrodes materials like gold usually have many serious contact problems which are difficult to overcome [17–19]. Recent experiments show that carbon nanotubes (CNTs) have become a potential ideal material for functional devices and interconnect in nanoelectronics because of their stable structures and rich electronic properties [20–22]. In particularly, Guo et al. have reported that an individual molecule can covalently attach to SWCNT electrodes through the amide endgroup (CONH), which has proven to be very robust [23]. Therefore, by applying nonequilibrium Green's function (NEGF) formalism combined with first-principles density functional theory (DFT), we investigate the switching characteristics of the fulgide optical molecular switch with two different SWCNT electrodes, i.e. (5,5) armchair/(9,0) zigzag SWCNT electrodes. The effects of the SWCNTs' chirality on the switching behavior in the molecular device are discussed in detail.

2. Model and method

The pre-optimized fulgide molecule with two isomers is sandwiched between two (5,5) armchair SWCNT electrodes as shown

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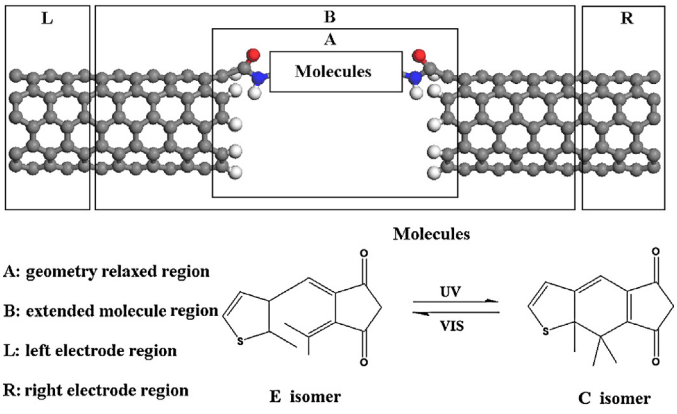

Fig. 1. Schematic illustration of the structure of the fulgide molecular switch with amide endgroup (CONH). The white, gray, red and blue spheres represent H, C, O and N atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in Fig. 1. Amide endgroups were used as linkages between the molecule and SWCNT electrodes. For each electrode, eight layers of carbon atoms are included into the extended molecule region (region B in Fig. 1) to screen the perturbation effect from the central scattering region and they are denoted as surface-atomic layers [24]. In the calculations, the end of each SWCNT is capped by H atoms to eliminate the dangling bonds. All the configurations are relaxed until their force tolerance is smaller than 0.05 eV/Å.

All the geometrical optimizations and the electronic transport properties of the molecular junctions are calculated by a fully self-consistent NEGF formalism combined with first-principles DFT, which is implemented in Atomistix ToolKit (ATK) software package (version 2012.8.2) [25,26]. The main feature of the computational package is to model a nanostructure coupled to external electrodes with different electrochemical potentials and to realize the transport simulation of the whole two-probe system without inducing phenomenological parameters. Details of the method can be found in Refs. [25,26]. In the electronic transport calculations, the exchange-correlation potential is described by Ceperley-Alder local density approximation (LDA) [27]. The core electrons are modeled with Troullier-Martins nonlocal pseudopotential [28], while the valance electrons wave functions are expanded by a SIESTA basis set [29]. The double-zeta plus polarization (DZP) basis set is adopted for all atoms. The Brillouin zone is set to be $5 \times 5 \times 100$ points following the Monkhorst-Pack k-point scheme. The cut-off energy and the iterated convergence criterion for total energy are set to 150 Rydberg and 10^{-5}, respectively.

In NEGF theory, the transmission function $T(E, V)$ of the system is the sum of transmission probabilities of all channels available at energy E under external bias V [30]:

$$T(E, V) = Tr[\Gamma_L(E, V)G^R(E, V)\Gamma_R(E, V)G^A(E, V)], \quad (1)$$

where $G^{R/A}$ are the retarded and advanced Green's functions, and coupling functions $\Gamma_{L/R}$ are the imaginary parts of the left and right self-energies, respectively. The self-energy depends on the surface Green's functions of the electrode regions and comes from the nearest-neighbor interaction between the extended molecule region and the electrodes.

For the system at equilibrium, the conductance G is evaluated by the transmission function $T(E)$ at the Fermi level E_F of the system:

$$G = G_0 T(E_F), \quad (2)$$

where $G_0 = 2e^2/h$ is the quantum unit of conductance, h the Planck's constant, e is the electron charge.

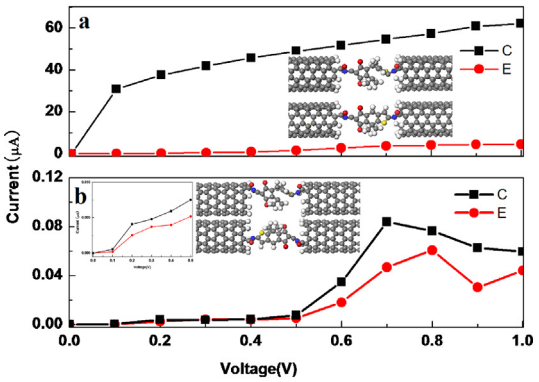

Fig. 2. The I–V characteristics of the molecular switch with (a) (5,5) armchair, (b) (9,0) zigzag SWCNT electrodes. The inset figure is I–V curve of armchair–fulgide junction on the bias region from 0.0 to 0.5.

The current through a molecular junction is calculated from the Landauer–Bütiker formula

$$I(V) = \frac{2e}{h}\int [f(E-\mu_L) - f(E-\mu_R)]\,T(E, V)dE, \quad (3)$$

where f is the Fermi function, $\mu_{L/R}$ the electrochemical potential of the left/right electrode and the difference in the electrochemical potentials is given by eV with the applied bias voltage V, i.e., $\mu_L = \mu(0) - eV/2$ and $\mu_L = \mu(0) + eV/2$. Furthermore, $\mu_{L/R}(0) = E_F$ is the Fermi level.

3. Results and discussions

The calculated current–voltage (I–V) curves of the E–C isomers with two different SWCNT electrodes under the bias voltage varying from 0 to 1.0 V are given in Fig. 2. It should be pointed out that at each bias, the current is determined self-consistently under the non-equilibrium condition. Their geometry structures after optimization are displayed in the corresponding insets. The upper structure of the insets is the E isomer, and the lower one is the C isomer. The switching behavior of the fulgide molecule system can be clearly seen from Fig. 2. From the figure, the current through C isomer is always greater than that through E isomer at the same bias. Thus, in the process of fulgide molecule reversing from C isomer to E isomer under photoexcitation, the current through the circuit can switch from ON (high conductance) to OFF (low conductance), and vice versa. Furthermore, it also can be seen from Fig. 2 that the electronic transport properties through the molecular junction are affected significantly by the SWCNT's chirality. The current through the armchair–fulgide junction is 2–3 orders of magnitude larger than that through the zigzag–fulgide junction. Meanwhile, an apparent NDR effect appears in zigzag–E–zigzag junction with a maximum current at 0.8 V and a minimum current at 0.9 V. However, no NDR behavior is seen in other models. In order to characterize the conduction change due to different SWCNT electrodes, we define the on–off ratio, as shown in Fig. 3, Ratio = $I_{C\text{-}isomer}(V)/I_{E\text{-}isomer}(V)$, where $I_{C\text{-}isomer}$ and $I_{E\text{-}isomer}$ are the current of C and E isomer, respectively. Obviously, the zigzag junctions show better switching characteristics as compared with the armchair junctions for the chosen system.

In NEGF theory, the current of the system is calculated by the Landauer–Bütiker formula $I(V) = 2e/h\int [f(E-\mu_L) - f(E-\mu_R)]\,T(E, V)dE$, which is transmission spectra dependent. Thus, we calculate the transmission spectra $T(E,V)$ of the C and E isomer with different SWCNT electrodes under zero voltage to understand the dramatic difference in conductance appearing in I–V curves. In our calculation, the average Fermi level, which is the average value of the chemical potential of the left