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Strong *n*-type molecule as low bias negative differential resistance device predicted by first-principles study

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HIGHLIGHTS

- Pentacenes are constructed to negative differential resistor (NDR).
- NDR effect is present under very low bias.
- Coherent tunneling can induce NDR effect.

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ABSTRACT

A first-principles study of the transport properties of two thiolated pentacenes sandwiching ethyl is performed. The thiolated pentacene molecule shows strong *n*-type characteristics when contact Ag lead because of low work function about metal Ag. A strong negative differential resistance (NDR) effect with large peak-to-valley ratio of 758% is present under low bias. Our investigations indicate that strong *n*- or *p*-type molecules can be used as low bias molecular NDR devices and that the molecular NDR effect based on molecular-level leaving not on molecular-level crossing has no hysteresis.

1. Introduction

Aviram and Ratner [1] have proposed that molecule can be used as electronic device such as diode in 1974, which indicate that the molecule is one of the most potential substitutes of traditional Si-based semiconductor transistor in the future. Recently, as other molecular devices, molecular NDR devices [2–41] (their counterpart are Esaki or tunnel diodes [42] in the traditional electronic devices) have attracted many investigational interests. Unfortunately, most molecular NDR devices mentioned above show the NDR effect at high bias. Berg et al. [43] have pointed out that if the molecular NDR devices were used for local refresh of dynamic random access memory (DRAM) memory cells, they should present the NDR effect under low bias. In addition, low bias NDR effect means low power dissipation and promise the potential applications in the future. In a word, low bias molecular NDR devices are significant.

In our previous investigations, [44,45] we have demonstrated that low bias NDR effect can be induced by two competing mechanisms and also proposed that how to construct nano-scale or molecular NDR devices under low bias. In our proposal, there are barrier's separating energy states at Fermi level and these energy states must contribute a transmission coefficients [$T(V_b, E)$] peak. Actually, such nano-scale or molecular transport systems are difficult to get. So, we change the way and think that the low bias NDR effect may also present in a molecular transport system where there is a molecular orbital near the Fermi level and this molecular orbital must contribute a $T(V_b, E)$ peak. In addition, this molecular orbital must be separated by a barrier. Generally speaking, only the lowest unoccupied molecular orbital (LUMO) closes to Fermi level because majority molecules are *n*-type.

Here, a first-principles study of the transport properties of σ barrier separating two pentacenes sandwiched between two Ag leads are performed. The strong NDR effect under low bias is obtained. As organic semiconductor, pentacene ($C_{22}H_{12}$) and other aromatic molecules are used for molecular electronics [46,47] and have attracted many interests. A pentacene field effect transistor [48] with high mobility has been fabricated by Nelson et al. Our

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researches indicate that pentacene can also be constructed to a good single molecular NDR device.

2. Computational method

Our calculations are based on a self-consistent first-principles method which combines the nonequilibrium Green's function formalism with density functional theory. The package of Atomistix Toolkit [49–56] is used in the calculations. The k-points sampling is 1, 1, and 50 in the x, y, and z direction. The cutoff energy is 150 Ry and the double-ζ with polarization basis set is chosen for all atoms. Core electrons are modeled with Troullier–Martins nonlocal pseudopotentials [57]. Perdew–Zunger local density approximation is used to describe the exchange-correlation potentials [58]. The convergence criterion for the total energy is 10^{-5} via the mixture of the Hamiltonian. The electrons temperature we used is 300 K. The currents are calculated as

$$I=\frac{2e}{h}\int_{-\infty}^{+\infty}T(V_b,E)[f_L(E-\mu_L)-f_R(E-\mu_R)]dE \tag{1}$$

where $f_{L,R}=1/(1+e^{(E-\mu_{L,R})/k_BT})$ is the Fermi-Dirac distribution; $\mu_{L,R}$ are the chemical potentials of the left lead (L) and the right lead (R). The h, V_b and $T(V_\mathrm{b}, E)$ is Planck constant, bias and transmission coefficients, respectively. The $T(V_\mathrm{b}, E)$ is calculated by the standard equation

$$T(V_b,E)=Tr[\Gamma_L(V_b,E)G(V_b,E)\Gamma_R(V_b,E)G^{\dagger}(V_b,E)] \tag{2}$$

Fig. 1 shows the schematics of molecular transport system. The metal Ag, not metal Au, is chosen as leads due to that the couple between Ag atoms and thiolate is adequate strong and that the pentacene molecule shows n-type characteristics because the work function of metal Ag is low. The whole transport system is divided to three parts: the left lead, scattering region and right lead. Two pentacene molecules including thiolates are denoted as L-pentacene and R-pentacene from left to right, respectively. One-dimensional Ag lead with large vacuum layer in x- and y-directions is constructed in order to avoid the interaction between transport system and its mirror images. Except Ag atoms, the scattering region is relaxed until the force tolerance of 0.05 eV/Å is achieved.

3. Results and discussions

Fig. 2 shows the current–voltage (I–V) curve for the molecular transport system under forward and reverse bias. From Fig. 2, one can see that the current under forward bias increases until the current peak (I_peak) presents at V_b=0.48 V. After 0.48 V, the current decreases until the current valley (I_valley) at V_b=0.78 V appears. The strong NDR behavior is present and the peak-to-valley ratio [PVR, here, it is the ratio of $I_\mathrm{peak}/I_\mathrm{valley}$ and defined as $I(V_\mathrm{b}=0.48\ \mathrm{V})/I(V_\mathrm{b}=0.78\ \mathrm{V})$] is as large as 758%. After 0.78 V, the current increases very slowly.

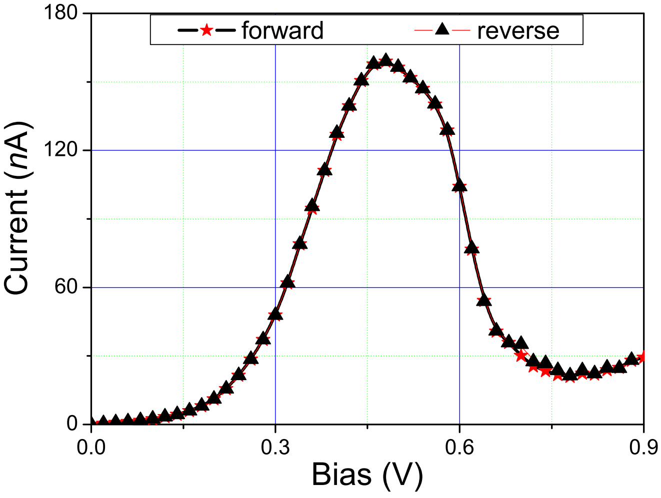

Fig. 2. The I–V curve for the molecular transport system under forward and reverse bias. The froward (reverse) bias is that the bias scans from 0.00 V (0.90 V) to 0.90 V (0.00 V).

Studying the bias-dependent $T(V_\mathrm{b}, E)$, Local DOS and molecular projected self-consistent Hamiltonian (MPSH) can help us to penetrate the mechanisms which result in the I–V characteristics. Fig. 3 shows the $T(V_\mathrm{b}, E)$ spectra at several biases. From Fig. 3, for zero bias, one can see that there is a sharp $T(V_\mathrm{b}, E)$ peak at the energy of 0.31 eV.

Fig. 4 shows the local DOS at 0.31 eV where the $T(V_\mathrm{b}, E)$ peak located for zero bias. From Fig. 4, one can clearly see that the local DOS is mainly composed by the MPSH-LUMO [59] of L-pentacene and R-pentacene. That is to say, the pentacene molecule shows strong n-type behavior when contacted Ag lead via thiolate. When the bias is applied to leads [$+V_\mathrm{b}/2$ ($-V_\mathrm{b}/2$) is applied to left (right) lead], the electrochemical potential in the left (right) lead is shifted down (up) by $V_\mathrm{b}/2$. Because the L-pentacene and R-pentacene are separated by σ barrier, the MPSH-LUMO of L (R)-pentacene shifts down (up) following the left (right) lead. Fig. 3 also shows the bias-dependent MPSH-LUMO and MPSH-LUMO+1 for L(R)-pentacene, one can see that the MPSH-LUMO of L (R)-pentacene indeed decreases (increases) as the bias increases. Fig. 5 shows the distribution of potential drop along molecule under biases of 0.48 V and 0.78 V. From Fig. 5, one can see that the L-pentacene and R-pentacene sustain a certain amount of potential drop and that some slightly difference of potential drop profile present

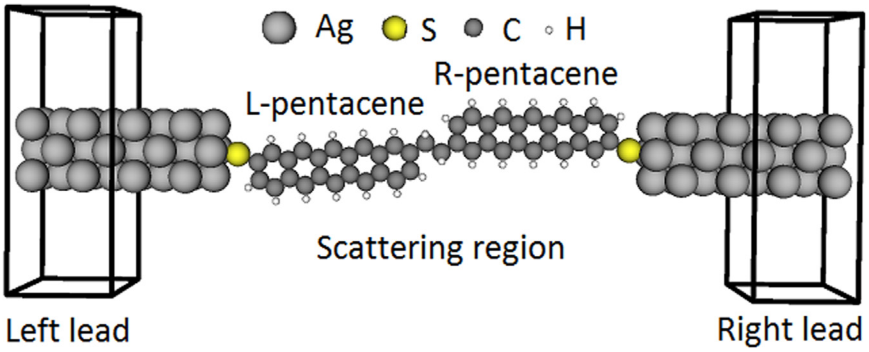

Fig. 1. Schematics of transport system constructed by two Ag lead sandwiching two pentacene molecules which are separated by ethyl. Color code: Au (deep yellow), S (shallow yellow), C (black), H (gray). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)