

EFFECT OF ANCHORING ATOMS ON TRANSPORT PROPERTIES OF A CARBON-DIMER BASED MOLECULAR JUNCTIONS: A FIRST PRINCIPLES STUDY

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The conductance of a molecular device is sensitive to the contact geometry between the molecules and the probing electrodes. Combining the density functional theory calculations (DFT) for molecular electronic structure with a non-equilibrium Green's function (NEGF) method for electron transport, we calculate the molecular conductance of carbon dimer connected between Au leads through two different anchoring atoms Se and Te. The current-voltage characteristics and transmission spectra of two systems are studied. The results exhibit that, depending on the anchoring groups and the subsequent different metal-molecule chemical bonds, the current varies over more than four times of magnitude under the same bias. Furthermore, the system exhibits negative differential resistance (NDR) effect, when anchored with Te atom. This emphasizes the great importance of the anchoring groups in molecular devices.

Keywords: anchoring group effects, electronic transport, first-principle, I-V characteristics.

1. Introduction

Over the past decade, molecular devices have received significant attention due to their great potential in the practical applications of atomic-scale circuits [1]. Many interesting physical properties of molecular devices have been predicted theoretically and verified experimentally, such as single-electron characteristics [2], negative differential resistance (NDR) [3,4], molecular rectification [5], and field-effect characteristics [6], etc.

A basic goal in molecular electronics is to measure and control electron transport through a molecule attached to two electrodes. To reach this goal, one must not only synthesize molecules with the desired functionality, but also design proper molecule-electrode contacts. This is because the contacts play a critical role in the electron-transport properties of molecules [7-9]. One way to optimize the molecule-electrode contacts is to select the proper anchoring groups at the two ends of a molecule so that they can bind to the electrodes and in turn, provide efficient electronic coupling between the molecule and the electrodes. So, the key issue in such molecular electronic devices is to find suitable anchoring groups and to construct contact structures that provide both stability and high contact transparency [10]. Therefore, the extensive and profound understanding of these effects in molecular devices is quite necessary. Using a combined density functional theory-non-equilibrium Green's function (DFT+NEGF) method, Zeng et al [11] performed transport calculations on carbon dimer sandwiched between Au electrodes, with anchoring groups of H, Cu and S.

In this present work, we focus our concentration on the anchoring group effect in molecular devices. Specifically, the transport properties of a carbon-dimer C_2 cluster sandwiched between two Au (111) electrodes were investigated. The anchoring groups connecting the cluster and the electrodes are chosen as Se and Te respectively. Thus, equivalently, we study the transport properties of two different molecules C_2Se_2 and C_2Te_2 , since both contain a C_2 unit and they are all of a linear chain structure. The reason for choosing selenium and tellurium as anchoring atoms because they serves as an efficient alligator clip connection to Au other than sulfur [12,13].

Also, we show that asymmetric molecular junctions, such as carbon dimer with appropriately chosen anchoring group, gives rise to I-V curve showing NDR effects.

2. Computation method

The simulation model adopted in this work is presented: a C_2 molecule is sandwiched between two Au (111) bulk electrodes via different anchoring atoms. And in the present work, the central sandwiched molecules are C_2Se_2 and C_2Te_2 , which are all linear and symmetrical molecules. The C–C and C–Se bond lengths in C_2Se_2 molecule and C–C and C–Te bond lengths in C_2Te_2 molecule are obtained by fully optimizing the respective molecules. For the left and right electrodes, we select a 3×3 unit cell in the x and y directions to avoid the interaction between the molecules and their mirror images. The terminating atoms of the molecules are located symmetrically at the hollow sites above the Au (111) surface. By full optimization, we obtain the equilibrium distances between the central molecules and the electrodes.

Our calculations are carried out using the Atomistix Toolkit (ATK 11.2.3 version) [14] program which combines DFT and NEGF methods to simulate the transport properties of two-probe systems. The exchange-correlation functional is described by the generalized gradient systems. The exchange-correlation functional is described by generalized gradient approximation (GGA) in the form of the Revised Perdew – Burke – Ernzerh (revPBE) in the present calculations [2]. The valence wave functions are expanded by localized numerical atomic orbital (LNAO), with the single zeta plus polarization basis set (SZP) for Au element and the double zeta plus polarization basis set (DZP) for C, H, Se and Te atoms. The Brillouin zone of the leads is sampled by $1 \times 1 \times 80$ k points in the directions of x, y and z (z is the electron transport direction), which is enough to produce the results.

In the NEGF theory, the transmission function $T(E, V)$ [15] of the system is the sum of transmission probabilities of all channels available at energy E under external bias voltage V:

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

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. 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.

The I-V characteristics of the two probe system can be obtained by using the Landauer–Buttler formula [11], the current is the integration of the transmission function over the bias window around the Fermi level:

$$I = \frac{2e}{h} \int_{\mu_1}^{\mu_2} T(E, V) [f(E - \mu_1) - f(E - \mu_2)] dE$$

where $T(E, V)$ is the transmission function through the device at energy E and function $f(E - \mu_{1/2})$ are the Fermi distribution functions of electrons in the left / right electrodes. $\mu_{1/2} = \mu \pm eV/2$ are the chemical potentials of the left/right electrodes, with μ the Fermi level of the electrodes in equilibrium and V the bias applied to the device.

3. Results and discussion

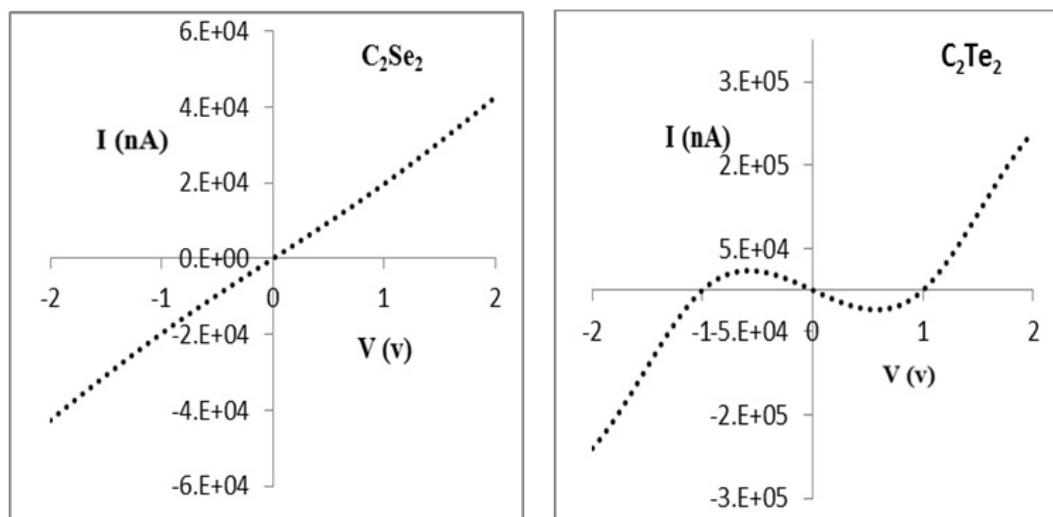


Fig. 1. The I-V characteristics of C₂Se₂ and C₂Te₂ molecules respectively

The I-V curves of two systems are presented in Fig 1. As can be seen from this figure, the current for C₂Se₂ linearly increases with the voltage increasing from 0.0 V to 2.0 V, while the current of C₂Te₂ increases in the opposite direction, reaches maximum in 0.58V and drops to zero at 1.0 V. Further the current for C₂Te₂ rapidly increases from 1.0 V to 2.0V. This indicates evident NDR behavior, which can be clearly observed in the I-V curve for C₂Te₂ system at zero bias range as shown Fig 1.

On the whole, the amplitude of the I-V curves of two different systems varies over more than four times of magnitude. For example, when the bias is 1.5 V, the currents are 30,638 nA for C₂Se₂, and 1,36,254 nA for C₂Te₂ respectively. Obviously, NDR behavior and the change in magnitude of current are originated from the contact atoms Se and Te linked to the C₂ cluster to the electrodes. Thus, it shows the importance of different linking atoms which result in such a big difference of the currents through the same molecule with different linking atoms.

In order to understand the difference in I-V characteristics of C₂Se₂ and C₂Te₂ systems, the transmission spectra of those systems at zero bias respectively are shown in Fig. 2. As can be seen from figure 2, the transmission function of C₂Te₂, has very large gap near the fermi level, the transmission spectrum in the zero bias window becomes smaller and smaller, which results in NDR behavior. This NDR behavior may arise due to the coupling between the Te molecule and electrodes. The transmission coefficient can be related to the molecular orbitals which have been modified by the electrodes when connected to different anchoring groups [16].

Thus when a Te molecule is connected to gold electrodes, the energy levels and spatial distribution of molecular orbitals are modified due to the molecule-electrode interaction and leads to NDR behavior. NDR behavior is not reported in the earlier work on carbon dimer by Zeng et al. with three different anchoring groups H, Cu and S [9].

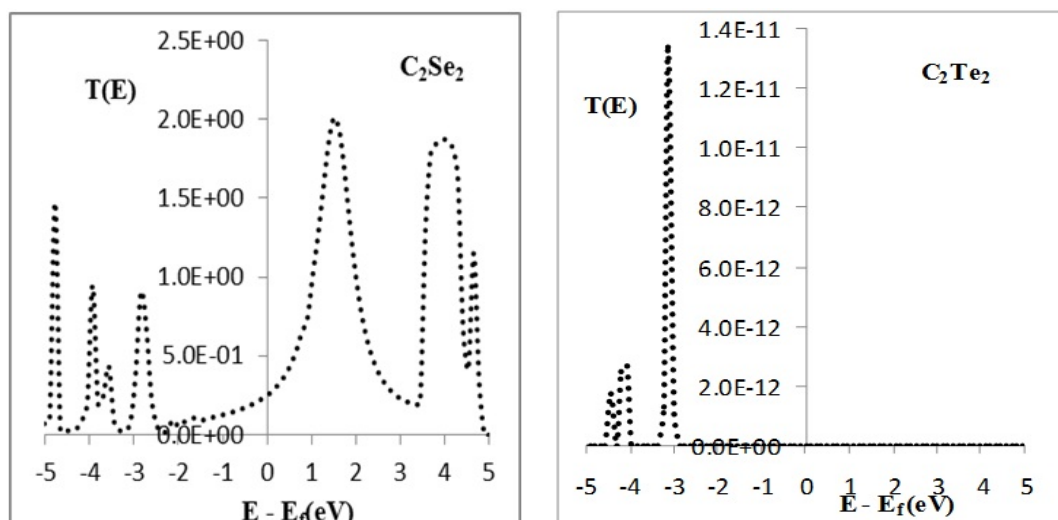


Fig. 2. The Transmission spectra of C_2Se_2 and C_2Te_2 molecules at 0V respectively

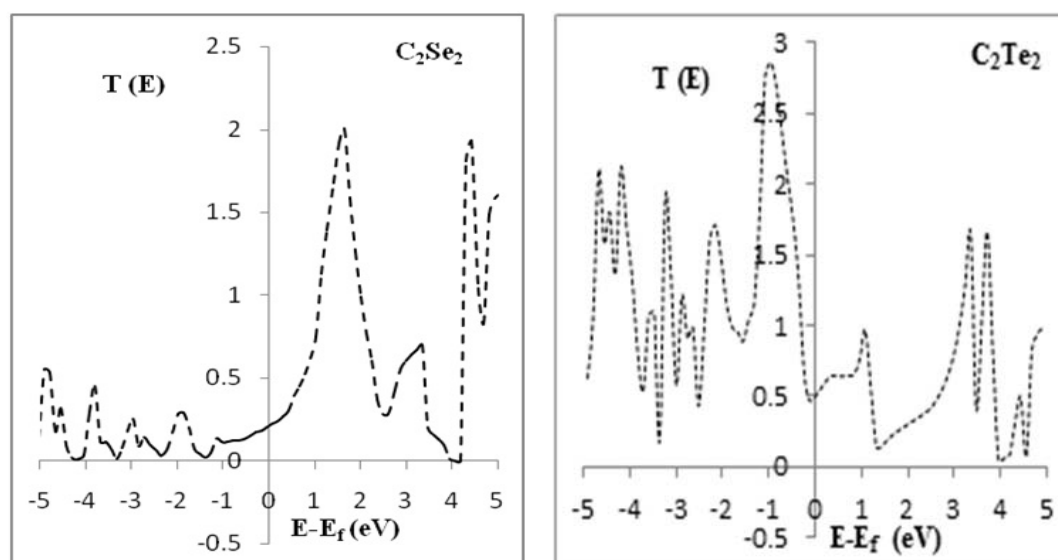


Fig. 3. The Transmission spectra of C_2Se_2 and C_2Te_2 molecules at 1V respectively

Whereas, the transmission function of C_2Se_2 , has sharp peaks near Fermi level which results in linear conductance of the molecule. The results show that the anchoring group plays a crucial role in the NDR effect and the overall conductivity of molecular junctions.

However, as can be seen from figure 3, with an increase in the bias, much transmission energy enters into bias windows which results in the increasing of current for C_2Te_2 . For the C_2Te_2 , there is a large platform around the Fermi level, so the current is very big when the bias voltage is applied to the device. However, we hardly find any new transmission entering into the bias window when the bias voltage is applied for C_2Se_2 . So a current progresses in the same way as that zero bias for C_2Se_2 .

4. Conclusions

Using the DFT+NEGF approach, the electron transport properties of molecular junctions containing carbon dimer molecules with two different anchoring groups, Se and Te, were calculated. The current in these two different systems varies by more than four times of magnitude under the same bias range. Furthermore, the system exhibits negative differential resistance (NDR) effect, when anchored with Te atom at zero bias range. The results show that the anchoring group and the subsequent different metal-molecule chemical bonds play a significant role in determining the overall conductivity of the molecular junctions.

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