ATOMIC PHYSICS

Electronic Transport through Thiophene-1,4-Dithiol Molecule

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Abstract In this paper, we study electronic transport through thiophene-1,4-dithiol molecules attached to gold electrodes Au (111) and subjected to bias voltage. The choice of this molecule is justified by its promising applications in the construction of molecular devices. The electronic structure of thiophene-1,4-dithiol was investigated by using Density Functional Theory (DFT) combined with non-equilibrium Green's functions (NEGF), as implemented in TRANSIESTA program. We found that both an increased separation between the electrodes and the presence of anchor group S, cause an increase in transmittance through the molecule. Also, we obtain a structure in the transmittance curve, a Fano resonance feature, present in electronic transport phenomena in nanostructured devices. The results are reported in terms of transmittance versus energy around Fermi Level and voltage versus current plots.

Keywords Thiophene · Electronic transport · Transmittance

1 Introduction

After the initial idea of Aviran and Ratner [1] to propose a nano-device composed of a single molecule in 1974, great effort has been undertaken to understand transport properties in molecular devices. The main focus of the present paper is the investigation of the electronic transport through thiophene-1,4-dithiol adsorbed on gold surfaces via first principles. Figure 1 represents the system studied. The presence of thiol endgroups is justified by the strong covalent Au-S bond that ensures good adhesion of the molecule to the gold electrodes. Other advantage is that most organic systems with a thiol can form self-assembled monolayer (SAM) on the gold surface Au(111) [2]. Studies in dimers, tetramers, and hexamers of thiophene attached to gold electrodes obtained different results for the IxV curve for different angle between the thiophene rings [3]. The electrical, magnetic, electronic, and optical properties of conjugated polymers, such as polythiophene, together with their low production cost, attracts the attention of scientists and engineers working in the field of nanoscale electronics. Nowadays, the characteristics of functional molecules have been used in the construction of many devices behaving as diodes, transistors, switches, light emitting diodes, solar cells, batteries, etc. The investigation of the heteroaromatic pyrrole, thiophene, and furan held by Luo et. al. [4], concluded that thiophene-1,4-dithiol is a good candidate for unimolecular devices due to its high conductivity. In the present work, we emphasized geometry optimization as an important step in electronic transport simulation in nano dispositives due to sensitivity of results on the form the molecule binds to the substrate. Considering this aspect, we performed calculations of absorption energy values for thiophene-1,4-dithiol in several sites, and we found out that the most stable one was the hollow hcp site.

2 Computational Procedure

To perform electronic transport calculations, we used the TranSIESTA Module of the SIESTA-3.1 package [9, 10],

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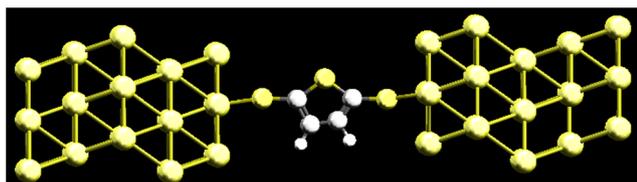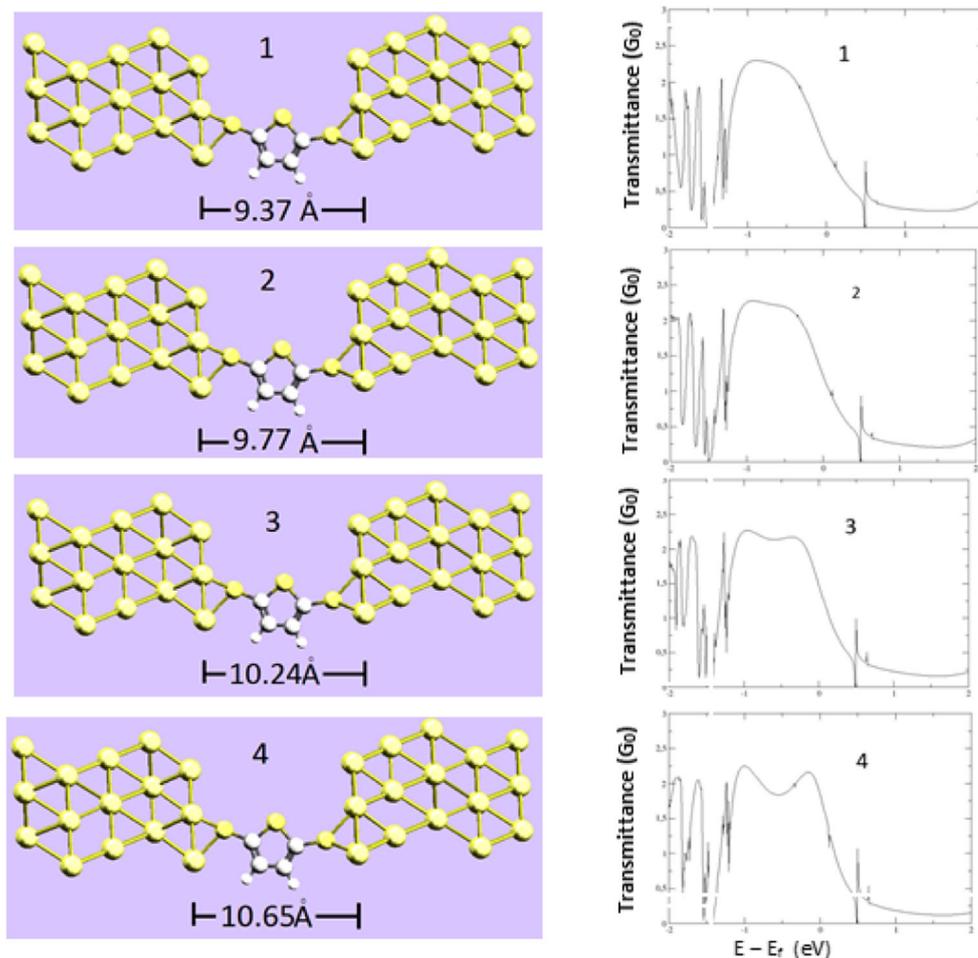
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Fig. 1 Thiophene-1,4-dithiol molecule between gold Au(111) electrodes

which uses the Density Functional Theory (DFT) [11], combined with non-equilibrium Green's functions (NEGF) [12, 13]. In this methodology, the system is divided into three regions: (1) the extended molecule region, which includes the thiophene-1,4-dithiol molecule itself plus one plane of gold atoms on each side; (2) the semi-infinite left electrode (L); and (3) the semi-infinite right electrode(R). Troullier-Martin norm conserving pseudopotentials [14] were used to replace the core electrons. The basis set used for Kohn-Sham orbitals expansion was polarized double-zeta (DZP) for the extended molecule region and double-zeta (DZ) for the electrodes, the exchange and correlation potential [15]

used was the Generalized Gradient Approximation (GGA) due to Perdew, Burke and Erzenhof (PBE) [5]. The mesh density was chosen such that the energy of plane waves was less than 350 Ry, this value is defined by the *EnergyCutoff* parameter (E_{cut}), for the *EnergyShift*, a parameter that controls the orbital refinement we use the value of 0.02 Ry. Robustness tests were performed varying these parameters. The geometry optimization was performed as follows: First, the isolated molecule was optimized then the gold electrodes were added; the system was relaxed again, optimizing the extended molecule region (1), while keeping fixed the right (R) and left (L) electrodes, except the innermost planes interacting directly with the molecule and included in the extended molecule region. The structure relaxation was performed using the conjugate gradient method [6] and the system is considered completely relaxed when the forces involved are less that than 0.05 eV /Å.

The current through the molecule was calculated using the Landauer-Buttiker formula [8]

$$I(V_b) = \frac{e}{\pi \hbar} \int_{-\infty}^{\infty} T(E, V_b)[f_L(E + eV_b) - f_R(E)]dE, \quad (1)$$

Fig. 2 Thiophene-1,4-dithiol molecule between Au(111) electrodes

Table 1 Transmittance values for different separations between gold electrodes

Structure	$d_{suf-suf}$ (Å)	$T(0)(G_0)$
1	9.37	1.03
2	9.77	1.23
3	10.24	1.43
4	10.64	1.80

Table 2 Separation between gold electrodes surfaces($d_{suf-suf}$) and total electronic energy. The separation of 7.85Å is adopted as reference

Structure	$d_{suf-suf}$ (Å)	$E(eV)$
1	8.42	0.88
2	8.15	0.23
3	7.85	0.00
4	7.55	1.10

where $T(E, V_b)$ is the transmission function representing the electron transmission probability at an energy E under the potential bias V_b and $f_{L(R)}(E)$ is the left (L) right (R) electrode Fermi function.

3 Transmittance Characteristics for Different Separations between the Electrodes

The transmittance curve T(E) represents the probability of transmission of an electron with energy E through the system. Figure 2 shows the transmittance curves for different separations between the electrodes. Table 1 shows the transmittance at Fermi level T(0) calculated for different distance between the electrodes. For a separation of 9.37Å, which is the most stable configuration, the transmittance was 1.03 G_0, $\left(G_0 = \frac{e^2}{\pi\hbar}\right)$.

The transmittance at Fermi level T(0), increased with increasing separation of the electrodes, this behavior may be explained by the increased density of states associated with Sulfur near the Fermi level. Figure 2 also displays a Fano resonance structure [16] around 0.5 eV above Fermi level. This structure is characterized by sudden variations in the transmittance diagram and is so named because it comes from an interference between a transmission channel and a quasi-bonded state and were originally proposed by Ugo Fano in connection with the study of autoionization spectra of Helium. Fano type structures have been previously identified in transmittance plots by Nozaki et al. [7], using a simplified model. Figure 3 shows the transmittance curve for four different voltages applied to system at optimal electrode separation, 9.37 Å. It is possible to observe that Fano type structure increases intensity with increased bias voltage, a behavior that can be attributed to the increased electric field between the electrodes.
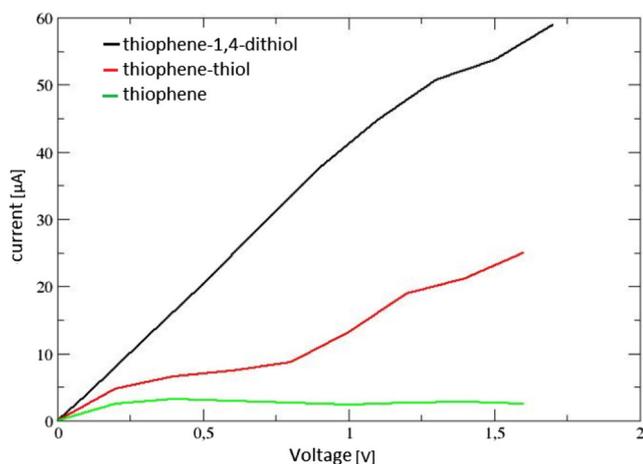
Fig. 3 Transmittance diagram for thiophene-1,4-dithiol at 0 bias voltage (**1**) 0.6 V, (**2**) 1.3 V, (**3**), and 1.7 V (**4**). The Fermi energy is taken as reference

Fig. 4 I x V curve for the three studied systems

4 I x V Characteristics With and Without Thiol Anchor Groups

In order to better understand the thiol end-groups importance, we perform transmittance calculations through thiophene-thiol, i.e., one sulfur atom binds the thiophene ring to the right electrode while a hydrogen atom links to the left. Similarly, we also analyzed pristine thiophene, when both connections are made through hydrogen. For thiophene-thiol, we perform the geometry optimization starting at an electrode separation of 8.42 Å stepwise decreasing this distance by 0.3 Å, always relaxing the extended molecule region at each step. The most stable configuration occurred at 7.85 Å. Table 2 shows the obtained energy values. As for thiophene without the presence of thiol end-groups, we started at an electrode separation of 8.46 Å and decreased this distance in steps of 0.4 Å up to 7.66 Å. The optimal perpendicular configuration was 8.06 Å. At an electrode separation of 7.88Å, the molecule begins to relax to a non-perpendicular position, and for smaller separations, the thiophene ring plane tends to become parallel to the gold planes. The electric current versus bias voltage for the three analyzed systems is shown in Fig. 4. The absence of thiol anchoring groups decreases the overall current. This effect can be attributed to a decreased overlap between electrodes and molecule centered orbitals due to the sulfur absence.

5 Conclusion

We have shown that an increase in the distance between electrodes increases the transmittance at Fermi level in the studied range. This result can be attributed to increased density of states near Fermi level. Fano shape resonance structures were obtained in the transmittance curve. We analyzed the effect of anchor groups (thiols) binding the molecule to the electrodes, comparing systems with no thiol, only one end-group and with two anchoring sulfur atoms. The absence of the end-groups causes a dramatical drop in the electric current. This result is attributed to a small overlap between hydrogen and gold orbitals compared with the overlap between sulfur and gold atoms.

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