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Effect of Anchoring Groups on the Conduction Properties of Terphenyl Molecules Connected to Copper Leads

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Abstract

We report equilibrium and non-equilibrium conductance of terphenyl molecules with different anchoring groups including sulfur and nitrogen atom. The corresponding molecules are terphenyl-dithiols (TPDT) and diamino-terphenyl (DATP). The non-equilibrium Green's function (NEGF) technique has been implemented on the density functional tight-binding (DFTB) code to perform computations of the electronic transport properties of molecular devices. The NEGFs are used to compute the electronic density self-consistently with open boundary condition naturally encountered in transport problem which is imposed by the potentials at the contacts. As result, the value of the molecular conductance with amine groups is higher about ten times than the thiol anchored group.

Keywords*: molecular conductance, non-equilibrium transport, terphenyl molecules*

1. Introduction

A single molecule is attracting more attention both of experimental and theoretical study for its potential application of miniaturization from sub-micrometer conventional inorganic devices to the very small active component just in few nanometers. Electronic conduction through several molecules has been studied experimentally by many research groups [1-3]. However, the transport mechanism at the single molecule level still opened to scientific study in how the conductance of molecular junctions can be tuned by chemically modifying the molecules [4]. The role of anchoring groups in molecular junction is one of the main problems that remain to be understood. Experiments [4,5] have shown that terminal groups that bind a molecule to the metal electrode can control the value of the conductance.

Theoretically, it has been shown that the conductance of amine-anchored has better conductance value than thiolated molecules with connected to gold contacts [6,7]. The anchoring groups affect the energy level line up relative to the metal Fermi energy and consequently play important role the conductance plateaus. However gold is rather mobile and forbidden from a CMOS lab. Consequently other electrode materials have been explored, including Pt, Pd, carbon nanotubes [8-11]. In this study, we use terphenyl molecules with different anchoring groups including sulfur and nitrogen atom connected to copper leads. Copper is chosen as the model system for the following reasons. First, copper is an important electrode for the investigation of molecular electronics. Second, the phenyl anchoring group can bind to copper [12]. The corresponding molecules are terphenyl-dithiol (TPDT) and diamino-terphenyl (DATP). We present a systematic study that correlates the conductance values, binding energies and coupling strengths with different anchoring groups by using density functional tight-binding (DFTB) [13] with extended to the non-equilibrium Green's function (NEGF) [14,15] approach for computation of the charge density and electronic transport.

2. Theoretical and Computational Detail

2.1. The Green's Function Formalism

The problem of quantum transport through a single molecule bridged to two contacting lead can be set by starting from the scattering states which propagate from one lead to the

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other. The waves scatter at the contact-molecule interface and partially reflected and transmitted across the molecule. Consider the retarded Green's functions of the *α* contact*:*

$$g_{\alpha}^{r} = \left[ES_{\alpha} - H_{\alpha} - i\delta\right]^{-1}$$

where *Hα* is Hamiltonian of the contact, the overlap matrix, *S* is represented on non-orthogonal basis set. Assume that the contacts have no interaction in between, the Hamiltonian of the whole system can be written:

$$H = \begin{bmatrix} H_D & V_{D1} & V_{D2} \\ V_{D1}^{\dagger} & H_1 & 0 \\ V_{D2}^{\dagger} & 0 & H_2 \end{bmatrix}$$

where *VD1(2)* is the Hamiltonian of contact-molecule coupling. The complete Green's function of the system:

$$G_D^r = \left[ES_D - H_D - \Sigma^r \right]^{-1}$$

where Σ^r is the total self-energy of the two contacts,

$$\Sigma_{\alpha}^{r} = \left(ES_{D\alpha} - V_{D\alpha}\right) g_{\alpha}^{r} \left(ES_{D\alpha} - V_{D\alpha}\right)^{\dagger}$$

The tunneling current flowing through the molecule that naturally arises in coherent transport is given by the Landauer formula [15]:

$$I(V) = \frac{q}{h} \int dE\, T(E,V) \left[f(E,\mu_1) - f(E,\mu_2) \right]$$

where $T(E,V)$ = Tr $[\Gamma_L G^r \Gamma_R G^a]$ is transmission function and $\Gamma_{L/R}$ is the scattering rates related to the probability of injecting an electron into the molecule from left and right electrodes. These rates also describe the width that the molecular level acquires in virtue of the coupling to the metal leads and they can be used as measure of the strength of the metal-molecule coupling. Then $f(E,\mu)$ is the Fermi-Dirac function. In equilibrium and at zero temperature (T = 0 °K) case, the conductance can be expressed as:

$$G = \frac{2q^2}{h} T(E_F)$$

The advantages in using Green's function approach are that incoherent scattering and relaxations can be included within self-energies.

2.2. Coherent Transport Calculation

The types of systems under study can be represented as shown in Figure 1. The contacts are semi-infinite leads and it is assumed that their properties coincide with those of bulk systems [16]. The device is a collection of atoms linking to the contacts, comprising a molecular bridge. The current flowing across the device when the contacts are kept at different electrochemical potentials.

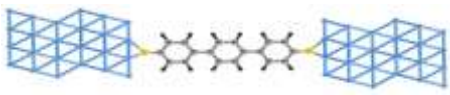

Figure 1. A model of terphenyl molecular junction

We carried out calculations based on DFTB to determine the geometry and electronic structure of isolated molecules and the leads. The adsorption of all molecules on metal surface is optimized by ab-initio density functional theory (DFT) which uses a conjugated gradient technique. In these cases, we used the PBE exchange-correlation functional form of the generalized gradient approximation (GGA) [17]. We implemented basis sets with diffuse functions scheme for the Copper surface with longer cutoff and slower decay than the bulk DZP orbital [19]. The Cu [111] has (4x4) surface unit cell and repeated geometry consisting six-layers

The anchor groups (-SH and -NH2) were optimized in the hollow site of Cu [111] surface and yields in a distance 1.87 and 1.45 angstrom respectively. Exploiting this computational scheme for the coherent transport properties, we assume that dithiol or diamine loses hydrogen atoms upon interaction with the copper leads [19]. Finally, single point calculations were performed on these systems and the transmission of the junctions was computed in the spirit of Landauer formalism using NEGF techniques which is implemented on DFTB code.

3. Results and Discussion

In Figure 2, we show the computed transmission as function of the energy for TPDT and DATP molecules in the same binding geometry. In zero-bias, concerning the thiol group, we find the Fermi energy is located in between the lowest unoccupied molecular orbitals (LUMO) energy and the highest occupied molecular orbitals (HOMO). In contrast result in Ref.19 for gold contacts case since the transport dominates on the HOMO. For the amine group, the conductance is dominated by HOMO of the molecule and similar to earlier studies with the gold leads in Ref.5.

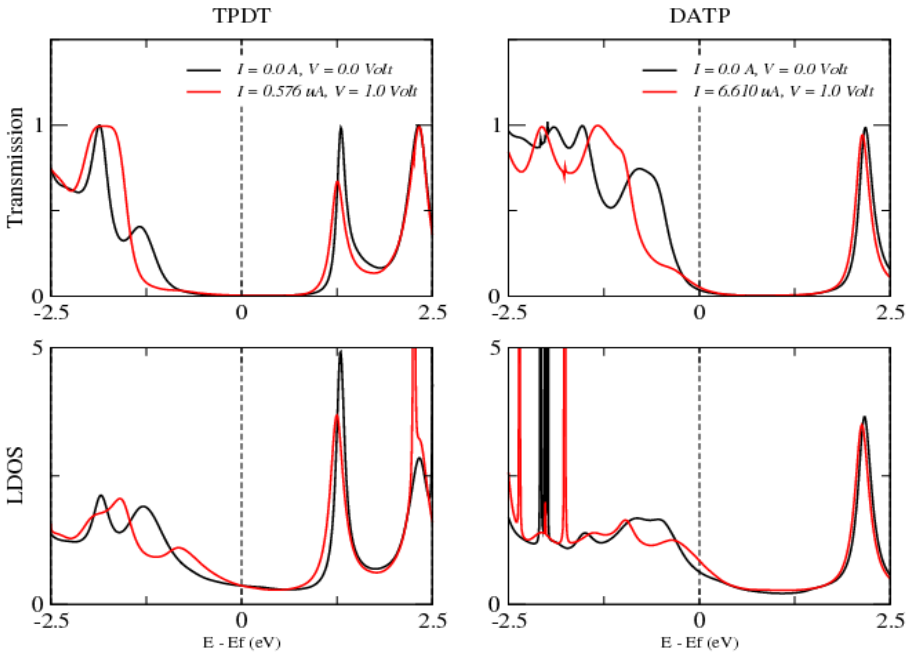

Figure 2. Local density of states and Transmission of TPDT and DATP molecules in equilibrium and under applied bias

The HOMO and LUMO levels energy of both molecules broaden due to coupling of the molecules to the electrode. That also can be described by using appropriate anchoring groups to bind a molecule to the contacts and its effect on the molecular conductance. This is one of important factor in coherent transport through molecular junctions. The transport properties of each molecule are given in Table 1 in detail.

Table 1. Transport properties of the molecules

Properties	TPDT	DATP
HOMO - LUMO gap (eV)	2.88	3.04
Binding Energy (eV)	5.8	7.7
Conductance (Go)	0.0039	0.0388
Coupling strength (eV)		
- HOMO	0.0678	0.1234
- LUMO	0.0632	0.0840
Current at 1.0 Volt (μA)	0.5766	6.6102

In non-equilibrium condition, when the contacts have different chemical potential, i.e. one volt, the HOMO level of both molecules are shifted to the near Fermi energy. However, the current flowing through DATP molecule is higher about ten times than TPDT. That is clear since the transport of DATP is dominated of the HOMO.

4. Conclusion

In summary, we have presented NEGF calculations for investigating quantum transport through terphenyl molecules with different anchoring groups and connected to copper leads. The broadening of the local density of states (LDOS) is related of the coupling strength or binding energy to the copper lead. There is direct relation between coupling strength, the metal-molecule binding energies for different anchoring groups and the conductance in this case.

Aknowlegments

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