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Molecular Gain in a Thiotolane System

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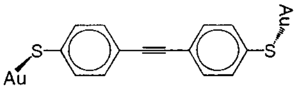
Density functional theory (DFT) calculations combined with a transport Green function approach are performed to explain "molecular gain" based on the ability to control the dissimilar electrical behavior between two conformations of a π-conjugated oligo(phenylene ethynylene). The characteristics of molecules in metal−molecule−metal interfaces should provide the basic knowledge for the design and simulation of molecules under a bias voltage. The break junction experiment[1] addresses one molecule. In other experiments (nanopore), a monolayer of molecules are self-assembled on a metal, and then another or similar metal is vapor deposited on the opposite side, yielding a sandwich containing less than 1000 molecules.[2−6]

The advantage of using molecules as electronic devices resides on their small size. Present semiconductor devices have feature sizes on the order of 1 (μm)^3 or less, and small molecules have them on the order of 1 (nm)^3, representing a $\sim 10^6$ reduction in surface size and $\sim 10^9$ reduction in volume size. Certainly, still many technical barriers need to be addressed before the implementation of molecular circuits.

The torsional angle between two planes of a π-conjugated oligo(phenylene ethynylene) can be exploited as a control variable of the current passing through the molecule, providing the possibility of a molecular transistor. The phenylene−ethylene-based oligomers frequently used in experiments are strong candidates for practical electronic circuits. Their conducting characteristics are believed to be due to the delocalization of their π frontier orbitals. Experiments[7] and ab initio calculations combined with classical molecular simulations[8] have suggested qualitatively that the conductivity of this molecule should decrease when the molecule is not planar. Preliminary conclusions were obtained using empirical calculations.[9]

We perform quantum chemistry[10−12] based studies to demonstrate, qualitatively and quantitatively, the change in conductance of a dithiotolane molecule attached to two Au terminals when one of the rings of the molecule goes from planar (**1**) to perpendicular (**2**) conformations with respect to the other ring as shown below.



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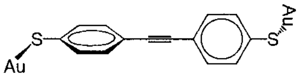

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Our DFT-based approach at the B3PW91/LANL2DZ level of theory augmented with a Green function formalism,[13,14,16] and slightly modified here to unambiguously ensure hermiticity of the Hamiltonian matrix, is used to calculate transport characteristics of the dithiotolane molecule. In this approach, a Hamiltonian for each fully optimized molecule with a few Au atoms added at each side is obtained by the DFT techniques. **1** was unconstrained with C_1 symmetry and **2** was kept with C_2 to ensure the perpendicular conformation. The interaction between Au atomic orbitals (AOs) and the AOs from the molecule are used to describe the coupling molecule-contact, used in turn to calculate self-energy terms describing the interaction between the contacts and the reduced molecule (without the Au atoms). Green functions describing a macroscopic contact, represented by diagonal matrixes, with their diagonal elements proportional to the local density of states in bulk metal, are used to calculate self-energy terms. Local density of states of 0.072, 0.0426, 0.1286, and 0.0492 (eV-atom)$^{-1}$ were used for the s, p, $d_{t2}g$, and d_{eg} metallic Au contributions.[15] An "extended Hamiltonian" (H_M) that describes the molecule addressed by macroscopic contacts is then defined by adding the self-energy terms to the molecular Hamiltonian and used to calculate the Green function (G_M) and then the density of states (DOS) of the molecule affected by the contacts. A transmission function (TF) is obtained from $T(E) = \mathrm{Trace}(\Gamma_1 G_M \Gamma_2 G_M^+)$, where Γ_i is the imaginary part of the self-energy. Finally, the current is obtained by integrating the TF between the Fermi energy (E_F) of the contacts when a bias voltage V is applied.[13,14,16]

The isolated dithiotolane HOMO−LUMO gap (HLG) for the planar and perpendicular configurations decreases slightly from 4.44 and 5.45 to 4.43 and 5.29 eV, respectively, when S and Au atoms are added to the two ends of the molecule, and to 4.39 and 5.15 eV, respectively, when the macroscopic contacts are added. The presence of Au tends to stabilize the structures, especially the perpendicular one, but reduces slightly the HLG for both conformations.[13,14,16] The HLG differences of both conformations also decrease when the Au atoms are attached; however, the perpendicular conformation always yields higher HLG than the planar one.

The torsional barrier for the isolated molecule is 0.86 kcal/mol;[8] thus, this molecule is easily rotated at room temperatures. On the other hand, small torsional energies are able to control the large HLG energies,[16] thereby providing the possibility of molecular gain. When S and Au atoms are attached to the molecule, the stabilization effect of the Au atoms increases the torsional barrier to 1.24 kcal/mol.

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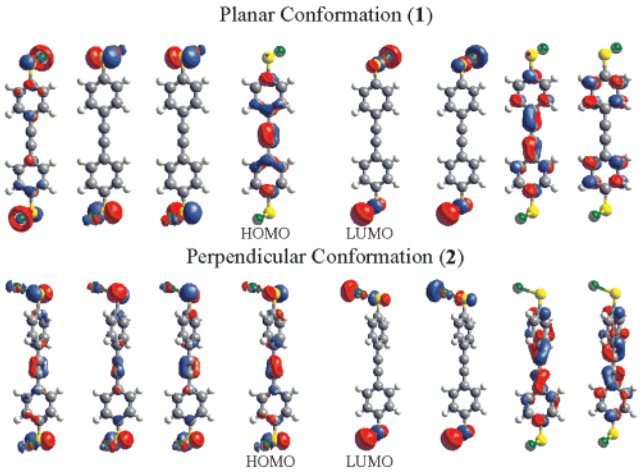

Figure 1. Frontier MOs for the planar and perpendicular conformations

The isolated molecule (tolane) HOMO and LUMO of the planar conformation are delocalized, extending over the whole molecule; however, they are localized in the upper ring for the perpendicular conformation, thereby obstructing the connection to the other ring.[8] Unoccupied orbitals near the frontier MOs are also localized for the perpendicular tolane, ensuring its low-conducting behavior. When Au atoms are attached, some of its AOs intercalate between the HOMO and LUMO for both conformations. The LUMO and LUMO+1 are mainly localized in the Au atoms with the LUMO+2 resembling the LUMO of the isolated molecule. The two conformations are energetically close to each other because of their small torsional barrier. The planar conformation is 0.05 eV lower in energy than the perpendicular one.

Figure 1 shows several MOs for both conformations. Their HOMOs are very similar in shape to the corresponding HOMOs of the isolated molecules (not shown); however, both LUMO and LUMO+1 have strong Au character. LUMO+2 is the first unoccupied MO with isolated-molecule character, but its energy would require a high voltage to approach it. Conduction in these molecules is through the occupied MOs because they, including the HOMO, are the closest to the Fermi energy (E_F) of the metal for both conformations. Practically, all frontier orbitals and those in their neighborhood for the perpendicular conformation are slightly scattered along the molecule, and they do not form a continuous conducting channel; thus, we expect a low conduction from this conformation. The HOMO and nearby MOs tend to localize in the central alkyne group. There is a minor contribution from both rings to the HOMO; however, this could be an artifact where the ring carbons make up for the lack of basis functions of the core electrons in S and Au, which are represented by pseudopotentials. On the other hand, the planar structure has a delocalized HOMO overlapping with the almost degenerate HOMO−1 and HOMO−2, which are characterized by a very strong coupling to the Au atoms, yielding a high TF single peak. The HOMO of the perpendicular conformation is almost degenerate with the HOMO−1, and they are close in energy to the HOMO−2, which is almost degenerate with the HOMO−3, thus forming a single channel characterized by a wide peak in the TF; however, with low TF due to these MOs scattered nature.

Figure 2 shows the I−V characteristics for bias voltages from 0 to 1 V. The planar structure yields currents higher than the perpendicular. The effect of the bias voltage was considered first by changing the E_F levels of the two contacts. We will refer to this as the zero-field approach since the Hamiltonian obtained without bias voltage is used to calculate the currents for all bias voltages. This constraint implies that the shape and energy of the orbitals is kept fixed. Therefore, the TF is the same independently of the bias voltage. Then, in a more rigorous and realistic approach, the effect of the bias field is incorporated into the molecular Hamiltonian. Therefore, the MOs change their spatial distribution and their energies due to the effect of the electric field. Thus, the TF also changes due to the bias voltage. For low-bias voltages, up to about 1.5 V, there is not a strong difference in the current obtained by the two approaches, for example, both curves nearly overlap each other up to 1 V. At 1 V the planar conformation yields an impedance of about 49 KΩ, while the perpendicular conformation yields an impedance of about 2.8 MΩ. In this range of voltages practically one channel is involved in the conduction, which is practically unaffected by the electric field; thus, its electrical characteristics are unchanged and the current increases almost linearly.

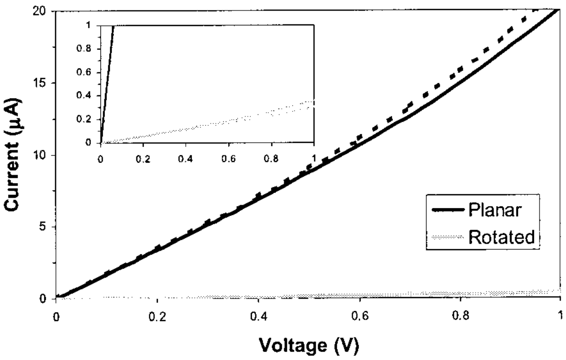

Figure 2. Current−voltage for the planar **1** (black) and nonplanar **2** (gray) conformations using the field (solid) and no-field (dotted) procedures. The inset shows clearly the small current of **2**.

For higher voltages, the behavior is no longer lineal due to the contribution of other MOs to the conduction process and the effect of the electric field on the MOs. When a conduction channel, formed by one or more MOs, reaches saturation, the current will remain constant until the next conduction channel is reached. This effect can be predicted with both approaches, and both curves would be similar. On the other hand, the electric field may affect the MOs, making them more conducting or less conducting, thus affecting the current in a very complex way. This causes the splitting of the curves obtained by the two approaches. The more precise method yields lower currents for the planar conformation because the electric field reduces the conductance of its MOs. However, for the perpendicular conformation, the zero-field approximation method yields lower currents for voltages up to 2.2 V. Thus, the electric field increases the conductance of the MOs involved in electron conduction. Above 2.2 V (not shown) this behavior changes, decreasing the conductance of the MOs.

Qualitatively and quantitatively planar and perpendicular conformations of the oligomer show distinguishable conductance states. The assumption that the breaking of the π-structure yields higher molecular impedance is demonstrated quantitatively. Thus, molecular gain follows directly since, at a bias voltage of 1 V, the current is almost 60 times larger for the planar conformation and much larger for larger voltages. The HLG is also affected by this rotation. Due to the small dithiotolane rotational barrier when compared to its HLG, an intrinsic molecular gain of ∼17 is predicted since rotation of one ring requires 0.05 eV, yielding an increase in the HLG of over 0.85 eV. Therefore, molecular gain is the extent to which a molecule boosts the strength of a signal. For instance, a voltage signal able to rotate the molecule corresponds to a larger voltage signal between the two terminals of the molecule. A local dipole moment can be implemented in one of the rings, for example, adding polar substituents; thus, it can be rotated by the effect of an external electric field. Other substituents could be added to increase the torsional barrier; although, the barrier for this molecule is good enough for experiments at low but workable temperatures.

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