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# Atomistic study of three-leg molecular devices

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ABSTRACT

Molecular electronics is one of the promising technologies for future electronic applications that is currently gaining a lot of interest. This is because if single molecule could be used as active electronic components this would provide an ultimate device miniaturization. Previously studied molecules provide almost exclusively two terminal devices. In this paper, three-leg molecular devices are examined employing a first-principles study based on density functional theory coupled to the non-equilibrium Green's function formalism. We illustrate the feasibility of building a prototype molecular transistor using three-leg molecules directly contacted to gold electrodes. We discuss the different factors that control the transport through this molecular transistor. Moreover, we show that a functional standalone NAND logic gate can be implemented using a single three-leg molecular device.



## 1. Introduction

Molecular electronics is considered one of the promising technologies which are based on bottom-up approach, in which microscopic components are assembled together to build complex macroscopic systems. This is opposite to the current semiconductor technology which is based on top-down approach aiming at reducing the dimension of components that build the systems. Molecular devices are capable of providing features like rectification, negative differential resistance, conductance switching, magnetoresistance, coulomb blockade and Kondo effect [1–6], which open the way for a variety of novel electronic applications.

Molecular electronics is an interdisciplinary between two major fields of research namely physical chemistry and electrical engineering. The first step is building up the molecular structure (synthesis); the complexity of this step usually depends on the complexity of the molecular structure itself. Once a molecule has been realized, another challenging step comes, namely the preparation of contacts for the molecule to be attached. There are currently several different techniques for that purpose [7–9]. Finally, characterization and analyses are applied in order to test the functionality of devices and to allow further design of new molecular devices [10,11].

Recently, we have studied molecular rectifiers composed of simple oligo-phenylene-vinylene (OPV) with asymmetric linkers that show rectification ratio of more than three orders of magnitude [12]. The basic theory behind the operation of this rectifier lies on the asymmetry of the molecule. The OPV has a simple thiol linker connected to a gold electrode on one side and an oxygen linker (Oxygen + dimethyl + thiol) connected to a gold electrode on the other side. The oxygen linker imposes strong barrier, which partially decouples the molecule from the gold electrode. Thus the potential drop along the molecule is concentrated in this region [12,13]. This asymmetric potential drop near the electrodes leads to the high rectification as justified in [12,14].

Up till now, molecules are mostly studied in two terminal devices. Some examples of gated molecular devices were presented in [15,16,13,17] where the gate influence was experimentally investigated. For three-leg molecular devices, an outstanding theoretical work was conducted to investigate feasible molecular device applications [18,19]. An electrostatic gate was applied to one leg having silver atoms attached to it, in order to allow a good coupling with the gate. The device shows very interesting transmission spectra modulation with gate bias. Moreover, Hliwa et al. proposed different three-leg molecules which can be employed for building standalone logic gates [20,21].

In this paper, we theoretically study three-leg oligo-phenylene ethynylene (OPE) molecular devices exploiting the interesting performance of our previously studied OPV molecular rectifier. In order to clarify the advantages and disadvantages of this architecture we have numerically investigated different structures of the device. In particular the impact to device performance by changing the length of source and drain legs and the impact of interference effects on transmission by differently binding the source and drain legs to the central ring. We proposed two different device applications namely; a planar molecular transistor and a standalone NAND logic gate. Our choice for OPE specifically is because

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three-leg OPE molecular structures have already been synthesized,[1] but the final devices setup and characterization are in progress.

## 2. Methodology

The three-leg molecular structures are geometrically relaxed until all residual forces in each atom are less than 0.05 eV/Å. Conjugate gradient algorithm is employed in the geometric optimization. The molecule is bonded to semi-infinite (1 1 1) gold electrodes (3 × 3 atoms/layer) through thiol-gold bonds (Fig. 1). Each thiol binds to three gold atoms forming an equilateral triangle, which is believed to mimic reality [22,23]. The sulfur atom is located 1.71 Å from the gold surface which corresponds to S–Au bond length 2.38 Å. This is similar to values validated in [24].

The atomistic analysis in this study is based on non-equilibrium Green's function (NEGF) coupled to the density functional theory (DFT) and its tight-binding approximation from DFTB + NEGF code [25–28]. Since the transport in this case is along the three electrodes, the boundary conditions in the real-space Multi-grid Poisson solver are Dirichlet in the directions of a plane containing the three electrodes and Neumann in the direction perpendicular to the plane. The tight-binding DFT is applied to calculate the Hartree potentials self-consistently considering the Poisson boundary conditions at equilibrium.

Under applied biases, the NEGF formalism is employed in the calculation of the current under the non-equilibrium and open-boundary conditions within the device. The current from electrode ($i$) to electrode ($j$) is calculated using the Landauer formula [29]

$$I_{ij} = \frac{2e}{h}\int_{\mu_i}^{\mu_j} T_{ij}(E, V_i, V_j, V_k)[f(E-\mu_i) - f(E-\mu_j)]dE, \quad (1)$$

where $T_{ij}(E, V_i, V_j, V_k)$ is the transmission function from electrode ($i$) to electrode ($j$) of the device at energy $E$ and the bias at each electrode ($V_i, V_j$ and $V_k$), $f$ is the Fermi function and $\mu_i/\mu_j$ are the chemical potential of the $i$th/$j$th electrodes, respectively. The transmission function is computed after building the Hamiltonian and density matrices and solving the open system problem self-consistently using the Green's functions. It is worth noticing that unlike two terminal devices where $T_{ij} = T_{ji}$, the correct formula here is $T_{ij} + T_{ik} = T_{ji} + T_{ki}$.

## 3. Results and discussion

### 3.1. Prototype molecular transistor

In this subsection, we discuss various options to use three-leg molecules as molecular transistors. Fig. 1 shows the proposed structure of the prototype molecular transistor. We use a leg with an oxygen linker as the gate for the three-leg transistor while using thiol linkers in the other two legs. It is worth noticing that the three legs are meta connected to each other. The inset of Fig. 1 illustrates the three possible types of connection namely meta, ortho and para [30].

The output current characteristic of the device with two phenyl rings per leg is illustrated in Fig. 2. We observe drain current modulation with the gate bias. Since the oxygen linker partially decouples the gate electrode from the molecule, the effect of the gate is almost only electrostatic. Our calculations show a reduction in the current of more than 4 orders of magnitude by inserting the

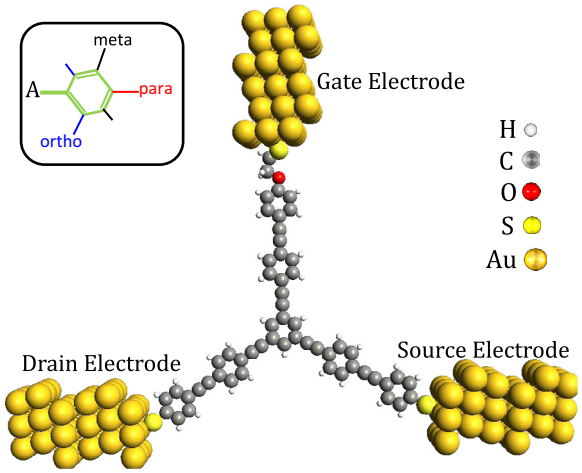


**Fig. 1.** A typical structure of three-leg molecular device. The molecule is the three-leg molecular transistor (Mol1). Each leg of the molecule is bounded to gold electrodes through thiol-gold bond. A (1 1 1) gold with 3 × 3 atoms/layer is employed. The inset illustrates the three possible connections a leg can have with respect to another leg at node A in a phenyl ring.

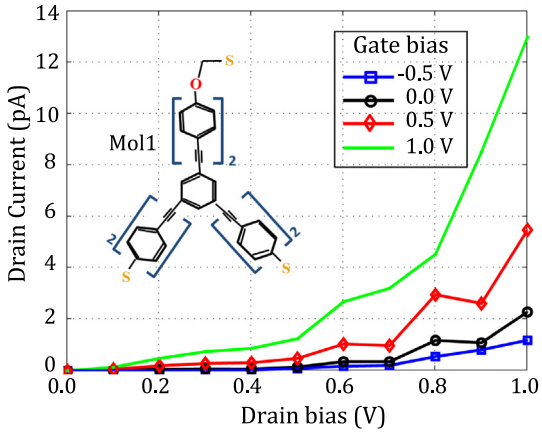


**Fig. 2.** The output characteristic curves for Mol1 device where all legs are meta connected to each other as in the inset.

oxygen-dimethyl group to the leg chain, factually reducing the leakage current. Thus, despite the exotic structure, the gate performance in this three-leg molecular device is similar to the back-gate in the molecular devices in [31,9]. However, the gate electrode is in the same plane with the source and drain, which provides a chance for new applications and architectures.

Unfortunately, the values of drain current are relatively low, just few pico-Amperes, which would limit the usability of such electronic device. The main factors that influence the magnitude of current are the length of the molecule and the type of connection of the molecular legs with respect to each other at the central ring. We have numerically investigated both. Fig. 3a shows the IV-curves for simple two terminal dithiol-OPE devices with 3,5 and 7 phenyl rings. Increasing the length of the molecule leads to logarithmic reduction in the magnitude of current. A similar length-conductivity dependency was reported in earlier theoretical and experimental studies [32,33]. Thus having short legs for drain and source is desirable, however this increases the complexity of contacting the molecule to the contacts having to handle with smaller molecules.

A second possibility to improve the device performance is by modifying the binding of the drain and source legs to the central ring. As pointed out earlier, the legs of the molecule can be

[1] The molecules are synthesized by group of Prof. Marcel Mayor at Universität Basel. The information from private communication with Prof. Marc Tornow at TU München.