

Cumulene molecular wire conductance from first principles

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We present first principles calculations of current-voltage characteristics (IVC) and conductance of Au(111):S₂-cumulene-S₂:Au(111) molecular wire junctions with realistic contacts. The transport properties are calculated using full self-consistent *ab initio* nonequilibrium Green's function density-functional theory methods under external bias. The conductance of the cumulene wires shows oscillatory behavior depending on the number of carbon atoms (double bonds). Among all conjugated oligomers, we find that cumulene wires with odd number of carbon atoms yield the highest conductance with metalliclike ballistic transport behavior. The reason is the high density of states in broad lowest unoccupied molecular orbital levels spanning the Fermi level of the electrodes. The transmission spectrum and the conductance depend only weakly on applied bias, and the IVC is nearly linear over a bias region of ± 1 V. Cumulene wires are therefore potential candidates for metallic connections in nanoelectronic applications.

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I. INTRODUCTION

Molecular nanowires and atomic chains are actively explored as novel conductors for nanoelectronic devices. Early on, cumulenes carbon chains were proposed as ideal molecular wires,¹ and the interest in the structure persists.^{2,3} Subsequent work investigated the transport properties of cumulene wires directly connected to jellium^{4,5} or atomically structured^{6,7} electrodes via carbon double bonds. For both types of electrodes, the conductance was found to vary in an oscillatory manner with the number of carbon atoms in the finite chain. Nevertheless, the transmission not only depends on the properties of the wire, but also on the contacts to the electrodes. For example it was understood^{4,6} that the amount of charge transferred from the electrodes to the molecular wire chemically bonded to the metal electrodes, determines the character of the conductance and its length dependence. The charge transfer from the electrodes to the cumulenes provides doping of wires.⁴ Since reliable methods of purification of cumulenes have been established,^{8,9} we reconsider the transport properties of these molecules using a realistic metal-molecule interface model.

In this paper, we report full self-consistent *ab initio* calculation of electron transport through the cumulene molecular wires=(C=)_n with $n=4-9$ connected to Au(111) surfaces via thiolate bonds. Unlike the previous studies of the cumulenes,⁴⁻⁶ where the cumulative double bond order was supported in the metallacumulene form, with the metal atom at the electrode surface incorporated into the carbon double-bond framework, we here consider the full atomic structure of “simple” organic cumulenes of type R₂C=(C=)_{n-2}CR₂, forming metallacumulene complex with the metal surface. Metalliclike conductance of another form of carbon chains with alternating single and triple bonds, polyynes, was recently studied by Crlijen and Baranović¹⁰ using thiolate contacts; however, such a realistic model for the metallacumulene wires was never investigated, because the molecule itself was considered to be difficult to isolate in macroscopic quantity.

II. COMPUTATIONAL METHOD

The calculations are performed using density-functional theory-based nonequilibrium Green's function (NEGF) transport theory as implemented in the TRANSIESTA simulation package.⁷ We used local-density approximation (LDA) for the exchange correlation potential. For carbynes, LDA performed better than generalized gradient approximation (GGA) for calculating the structures.¹¹ Using LDA for relaxation and reconstruction on Au(111) surface has been extensively discussed in previous literature.¹² For the transport properties one can expect the LDA to perform quite well due to the metallic character of the junction.¹⁰ Core electrons were modeled with Troullier–Martins¹³ soft norm-conserving pseudopotentials and the valence electrons were expanded in a basis set of local orbitals.¹⁴ The transmission spectrum, which gives the probability for electrons with incident energy E to be transferred from the left to the right electrode, is calculated from¹⁵

$$T(E, V) = \text{tr}[\Gamma_R(E, V)G_C(E, V)\Gamma_L(E, V)G_C^+(E, V)], \quad (1)$$

where G_C is the Green's function of the central region and $\Gamma_{L/R}$ is the coupling matrix of left/right electrode, respectively. The integration of the transmission spectrum yields the electric current,

$$I(V) = \int_{\mu_L}^{\mu_R} T(E, V)\{f(E - \mu_L) - f(E - \mu_R)\}dE, \quad (2)$$

where $\mu_L = -V/2$ ($\mu_R = V/2$) is the chemical potential of the left (right) electrode.

In our calculations, free-thiol-capped cumulenes were first optimized using the SIESTA package.¹⁶ The bond lengths and geometrical structures obtained in all the performed calculations are similar to those of unsubstituted cumulenes.¹⁷ The minimum-energy conformation of even-number wires, is planar, whereas the terminal groups of odd-number wires are mutually perpendicular. A system of a cumulene wire coupled to Au(111)-(3×3) surface electrodes via thiolate