Unusual Conductance of Polyyne-Based Molecular Wires

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We report a full self-consistent *ab initio* calculation of the current-voltage curve and the conductance of thiolate capped polyynes in contact with gold electrodes. We find the conductance of polyynes an order of magnitude larger compared with other conjugated oligomers. The reason lies in the position of the Fermi level deep in the highest occupied molecular orbital related resonance. With the conductance weakly dependent on the applied bias and almost independent of the length of the molecular chain, polyynes appear as nearly perfect molecular wires.

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The study of transport properties of single molecules has attracted significant attention because of their potential use in molecular electronic devices. One of the major classes of molecules considered in conductivity studies, primarily for their molecular wire behavior [1–5], is conjugated oligomers. They have shown a number of useful nonlinear properties such as conductance switching and negative differential resistance [6,7]. However, in spite of a number of interesting experiments [4,8] a molecule with good molecular wire properties has not yet been spotted.

A useful molecular wire should provide a high and stable conductance over a wide bias region and for various lengths of the molecules. A linear chain of carbon atoms with double bonds between neighboring atoms, usually referred to as cumulene, was proposed as an ideal molecular wire [1], and the calculations of the conductance of cumulene connected to gold electrodes were reported [9,10]. Lang and Avouris [9] showed that the conductance of cumulene did not stay constant in the ballistic regime, but rather oscillated between the constant values characteristics of the odd and even number of atoms in the chain.

In this Letter we show an entirely different behavior of polyynes, another form of the carbon atom chain. Polyynes are simple yet the most intriguing of the conjugated organic oligomers. Only recently have they been assembled up to decayne [11]. Formed as a linear chain of carbon atom pairs $(CC)_n$, with alternating single and triple bonds, they are a unique, truly one-dimensional, molecular system. Two π-electron systems of the sp-hybridized structure provide polyyne with approximately cylindrical electronic delocalization along the conjugated backbone. The electronic transport is therefore independent of the rotation around the single bond, which is a limitation often present in other organic oligomers [7].

We have obtained the electronic structure and transport properties of a series of polyynes up to octayne, connected to gold electrodes. The stability of polyyne with respect to single- and triple-bond alternations was achieved by fixing the molecule at the ends with thiol bonds. In addition, thiol capped molecules make a strong chemisorption bond onto metallic electrodes. Polyynes have shown the conductance which is, to our knowledge, more than an order of magnitude higher than the conductance of other conjugated oligomers. In contrast to cumulenes they were not prone to oscillations in conductance with the length of the molecule. We also found that their conductance was very weakly dependent on molecular length and almost constant in the wide range of bias voltages.

A previous study, with a different theoretical approach, included polyynes up to triyne with Pd contacts of a different contact geometry which resulted in lower conductance [12].

To perform first-principles quantum modeling of the electronic structure under nonequilibrium conditions and to calculate current-voltage characteristics and differential conductance of the system, a full self-consistent *ab initio* method, which includes portions of the electrodes, had to be used [13]. Calculations were carried out using a nonequilibrium Green functions technique based on density functional theory (DFT), as implemented in the TRANSIESTA package [14]. Current through the contact was calculated using the Landauer-Buttiker formula [15], $I(V_b) = G_0 \int_{\mu_L}^{\mu_R} T(E, V_b)\, dE$, where $G_0 = 2e^2/h$ is the quantum unit of conductance and $T(E, V_b)$ is the transmission probability for electrons incident at an energy E through the device under the potential bias V_b. The difference between the electrochemical potentials $\mu_{L/R}$, of the left and right electrodes, respectively, is $\mu_L - \mu_R = eV_b$. The computational procedure used was described elsewhere [5].

The molecular electronic system considered consisted of a monolayer of molecules coupled to two semi-infinite electrodes, as depicted in Fig. 1 for hexayne. We optimized the geometry of free thiol capped polyyne in a separate DFT calculation [16]. The molecule was then positioned perpendicularly to the z direction in the hollow sites of both Au(111) electrode surfaces symmetrically at a favorable Au-S bonding distance [18]. We let the molecular coordinate relax, keeping the gold atoms at their bulk positions. A small change in the molecular geometry occurred with respect to the free molecule. We discuss this at the end of this Letter.

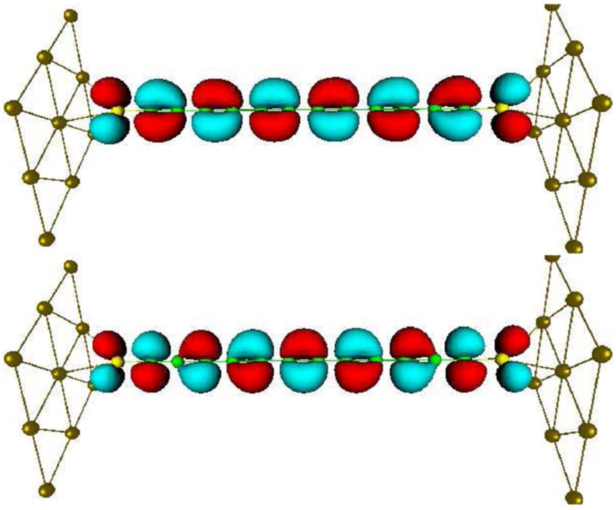

FIG. 1 (color online). Hexayne connected to two Au(111) surfaces via thiolate bonds, shown with MPSH HOMO (upper panel, notice the delocalized shape at each side of single bond) and MPSH LUMO (lower panel) at 0.6 V bias voltage.

The main characteristics of the obtained transmission spectra are the almost linear increase of the current with bias voltage and a high value of conductance over a wide bias region from −2 V to 2 V, as seen in Fig. 2. The obtained spectra of all members [19] of the polyyne series show a mutual pronounced similarity without oscillations with the length of the molecule. The conductance at zero-bias voltage is $1.65G_0$ for diyne, $1.56G_0$ for tetrayne, $1.49G_0$ for hexayne, and $1.44G_0$ for octayne. The overall high value of conductance is expected, since the main transmission channels involve double degenerate molecular π orbitals. Unlike in the true ballistic transport in a quantum structure where a constant conductance might be expected irrespective of the molecular length [20], a slow decrease of conductance with the length of the molecule is demonstrated. The decrease should be attributed to a weak reduction of hybridization at the molecule-electrode contact with the number of atoms in the molecular chain [21].

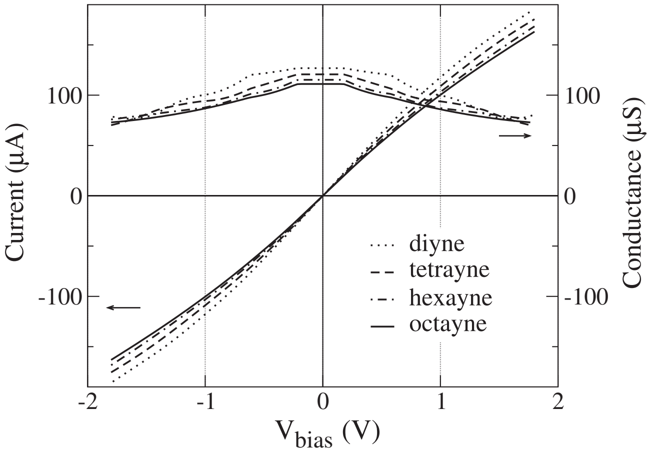

FIG. 2. Current and differential conductance of polyyne systems as a function of bias voltage. A self-consistent calculation has been employed for each bias voltage. Notice the slow and smooth almost linear decrease of the conductance.

In Fig. 3 we compare the transmission amplitude at zero bias of three different thiolate capped molecules: hexayne, diphenyl diacetylene (DPA2), and phenylene vinylene oligomer with three benzene rings (OPV3). They were all chemisorbed onto Au(111) electrodes in hollow positions at both ends in order to ensure the same bonding geometry thus avoiding the possible bonding site effects on the considered transmission. The resulting interelectrode separations for all three systems were rather similar, but the corresponding zero-bias conductances differed by more than an order of magnitude, as shown in Table I. The large difference in conductance is a consequence of the entirely different electronic structure and density of states (DOS) at the Fermi level (E_f). The hybridization of the molecular level with the gold electrode states broadens the level into the resonance. The width and the position of the resonance with respect to the Fermi level of the system depend on the internal structure of the molecule and its bonding to the electrode. To relate the transmission properties with molecular orbitals, we have projected the self-consistent Hamiltonian onto the molecular orbitals and highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) refer to the eigenstates of the molecular projected self-consistent Hamiltonian (MPSH). In the hexayne case, the double degenerate molecular π orbitals are involved. The resulting HOMO related resonance is wide and shifted up in energy close to the Fermi level, as seen in Fig. 3. In fact, the HOMO and LUMO related resonances strongly overlap giving a wide transmission band with large DOS, which results in high transmission. The transmission of DPA2 and OPV3 systems is considerably smaller when compared with the hexayne, as shown in Fig. 3. The reason for that is the lifted HOMO level degeneracy in DPA2 and OPV3 and the positioning of the HOMO level further below E_f, which results in the lower DOS at E_f. The high DOS at E_f is the property of

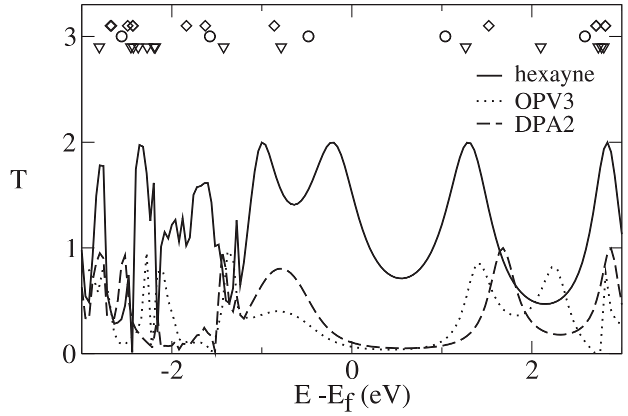

FIG. 3. Transmission amplitude of hexayne compared with DPA2 and OPV3 at zero-bias voltage. MPSH eigenvalues: circles for hexayne, diamonds for DPA2, triangles for OPV3.

TABLE I. Distance between the surface gold planes of the electrodes d_{elec} and zero-bias conductance $G(\mu, 0)$ of polyyne system compared with molecules of similar length.

	OPV3	DPA2	Hexayne
d_{elec} (nm)	2.3	1.95	2.127
$G(\mu, 0)$ (μS)	2.1	6.12	111.1

other members of the polyyne family as well. In Fig. 4(b) the partial density of states (PDOS) of the system excluding electrode atoms is shown. With the increased length of the polyyne chain, levels become more densely distributed and shorter in width. The remarkable property is, however, that the position of the HOMO related transmission resonance moves slightly closer to E_f, thus compensating for the decrease of the DOS per CC unit at E_f due to the level sharpness, as seen in Fig. 4(a). That results in a very weak dependence of the zero-bias conductance on the molecular length.

The conductance of polyynes decreases smoothly with the increase of bias voltage, as shown in Fig. 2. To elucidate this behavior, we show transmission amplitudes of hexayne for a set of bias values in Fig. 5. A remarkable similarity, in both shape and value, of transmission followed by a slight shift of the position of LUMO and higher resonances with the bias is seen. The separation between HOMO and LUMO levels decreases only by 0.11 eV at the bias of 1.8 V with respect to the zero-bias value. The consequence of the similarity of transmission spectra is the relatively weak dependence of conductance on bias, as seen in Fig. 2.

The other polyynes showed the dependence of transmission amplitudes when subjected to different bias voltages similar to those for hexayne. With the change of the bias from 0 to 2.0 V, the HOMO-LUMO (HL) gap for all polyynes that we consider decreases by no more than 0.15 eV. Such a small change in the molecular level positions relative the average electrochemical potential of the electrodes ensures a slow decrease of the conductance over the entire bias region, as clearly seen in Fig. 2.

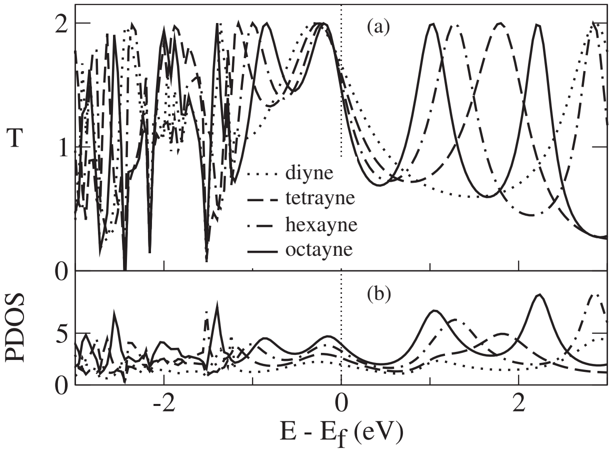

FIG. 4. (a) Transmission amplitude of polyyne systems at zero-bias voltage; (b) density of states projected onto all the molecular orbitals, in units of eV^{-1}.

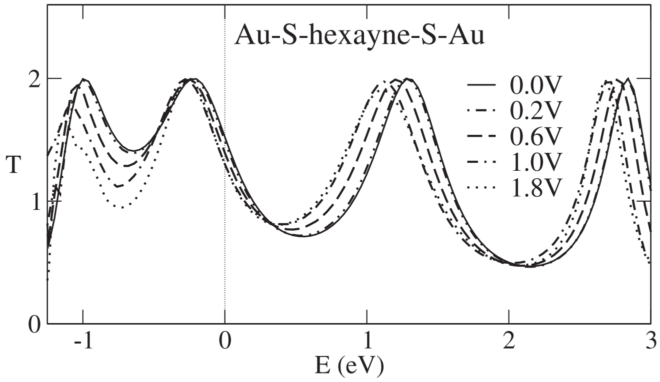

FIG. 5. Transmission amplitude of hexayne system as a function of bias voltage. Energies measured from the average electrochemical potential of the electrodes.

What makes polyynes so different from other conjugated polymers is the high DOS at the Fermi level. Even in a free molecule of polyyne, where the alternate single and triple bonds open up a HL gap, strong polarizability and hyperpolarizability [11,22] evolve. When thiolate capped polyynes are chemisorbed onto gold electrodes, the hybridization of molecular states with metallic electrode states results in a new electronic structure of the combined system. The change of level positions is so strong that the Fermi level of the system enters deep into the HOMO related resonance resulting in the pronounced metallic character of the system.

As already stated, we used LDA for the exchange-correlation functional in our DFT calculations. There has been a discussion in the literature of the validity of DFT with local density (LDA) and generalized gradient (GGA) approximations for π-conjugated systems [23]. Here, however, the π-conjugated system is connected to the electrodes and shows more metalliclike character. Because of the large orbital overlap and the strong hybridization with gold states there are no large oscillations of the local field (no internal barriers) in the system. LDA- and GGA-based DFT calculations are therefore expected to give a respectable accuracy usually obtained in DFT calculations. The

TABLE II. MPSH HL energy gap ΔE, in eV, at zero bias of thiolate capped polyynes with Au electrodes compared with the HL gaps of bare thiol capped polyynes (DFT calculations with SVWN, PW91, and PBE XC functionals).

	AuS(CC)$_n$SAu			HS(CC)$_n$SH		
n	ΔE	E_{HOMO}	E_{LUMO}	ΔE_{SVWN}	ΔE_{PW91}	ΔE_{PBE}
2	3.254	−0.897	2.357	3.529	3.559	3.549
4	2.063	−0.643	1.420	2.333	2.370	2.364
6	1.520	−0.482	1.038	1.762	1.797	1.788
8	1.211	−0.385	0.825	1.428	1.463	1.458

TABLE III. Average single and triple related bond distances, in Å, of thiolate capped hexayne in contact with Au electrodes compared with bare thiol capped hexayne bond distances.

		HS(CC)$_6$SH		
	AuS(CC)$_6$SAu	SVWN	PW91	PBE
d_{single} (Å)	1.316	1.321	1.330	1.332
d_{triple} (Å)	1.286	1.249	1.252	1.253

crucial parameters determining the HL gap are carbon-carbon bond lengths and their alternations. We performed calculations for isolated molecules of thiolate capped polyynes using the GAUSSIAN03 program [17] with several XC functionals and found that the GGA results did not substantially improve the values of the gap, nor the single and triple-bond lengths. Indeed, the difference in the HL gaps was less than 0.037 eV between the PW91 (GGA) and SVWN (LDA) based calculations, as seen in Table II. When extrapolated to infinite chain length the gap stayed open, in agreement with the calculations with more exact exchange potentials of Weimer *et al.* [24]. For the molecule bonded to the electrodes, the HL MPSH gap (first column of Table II) was reduced with respect to the isolated molecule as expected. The reduction was slightly more pronounced for shorter molecules, equal to 0.031 eV for diyne, and decreased to 0.025 eV for octayne. Evidently, the HL MPSH gap closely followed the gap of the isolated molecule. The possible underestimation of the gap in the LDA-based calculations compared with the nonlocal XC potential calculations would have no major effect [25]. The metalliclike character of the conductance appears to be the consequence of the hybridization of the π-electron systems with gold electrode states, irrespective of the details of XC potential.

Hybridization with gold states did not affect bond alternation in the electrode-connected hexayne, as seen in Table III. The reduction of single bonds and the expansion of triple bonds of the connected hexayne are noticed. The change of bond length is the interplay of the hybridization of the molecular states with gold electrode states and the relaxation of the position of molecular atoms. The amount of change is smaller when the molecule is longer owing to the redistribution of relaxation over the entire molecule.

In conclusion, polyynes, although π-conjugated systems, show an almost metalliclike character of the current transport, when connected to electrodes. This makes them a possible candidate for a good molecular wire to be considered in molecular nanoelectronics.

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