

# Non-trivial length dependence of the conductance and negative differential resistance in atomic molecular wires

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## Abstract

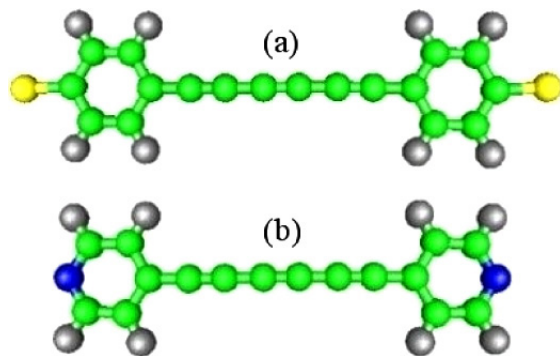
We study the electronic and transport properties of two novel molecular wires made of atomic chains of carbon atoms (polyyne)s capped with either benzene-thiols or pyridines. While both molecules are structurally similar, the electrical conductance of benzene-thiol-capped chains attached to gold electrodes is found to be much higher than that of pyridine-capped chains. We predict that the conductance is almost independent of molecular length, which suggests that these molecules could be ideal molecular wires for sub-10 nm circuitry. Both systems exhibit negative differential resistance (NDR) but its origin and characteristics depend on the type of molecule. We find a novel type of NDR mechanism produced by the movement of the lowest unoccupied molecular orbital (LUMO) resonance with bias. We also show that by gating the pyridine-capped molecules it is possible to make the NDR disappear and dramatically modify the  $I$ - $V$  characteristics and the length dependence.

(Some figures in this article are in colour only in the electronic version)

Molecular wires are currently receiving increasing attention due to recent experimental [1–4] and theoretical [5–9] advances. These systems could be candidates for substituting silicon components in nanoscale circuits once the atomic limit is approached. However, progress in this field has been hindered by the extremely low conductance found in the vast majority of molecules. This limiting property is a consequence of the location of the injection energy, defined by the Fermi level  $E_F$  of the leads, which typically lies in the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO (HL)) gap. Such a level misalignment moves the electronic transport to the tunneling regime, where the current decreases exponentially as the length of the molecule increases, and makes it very difficult to use molecular wires as interconnects. For this reason, the search for molecular wires whose resonances are broad enough to reach the Fermi energy or whose level misalignment is small for any molecular length is of paramount importance for this field. Recently polyyne-based molecular wires, made with carbon chains with an even number of atoms and alternating single and triple bonds, contacted directly to gold leads by sulfur atoms [10] were predicted to have a high length-independent conductance and ohmic behavior for a large range

of biases. Unfortunately these molecules cannot be made in large quantities and contacted to leads because they are extremely reactive [11]. One possible way of overcoming this crucial deficiency is by capping the carbon chains with aromatic rings, which makes them much more stable and easier to manipulate, even though their stability decreases with increasing chain length [12, 13]. The result is a new type of molecule made of a very high conducting backbone, the polyyne, connected to two less conducting rings.

In this paper we study the electronic and transport properties of the above mentioned polyyne)s capped with benzene-thiol (B- $n$ -B) or pyridine groups (P- $n$ -P) for  $n$  between 1 and 6 (between 2 and 12 atoms in the carbon chain). An example can be seen in figure 1 for  $n = 3$ . We predict that this new family of molecular wires not only possesses an almost length-independent conductance, but also exhibits negative differential resistance (NDR), which results in a reduction of the current as the bias voltage increases. NDR is very important in the field of electronic technology and also in basic research. Since its discovery [14] lots of applications in the area of semiconductor physics have been found, which include amplification [15], digital applications [16, 17], and oscillators [18]. In the context of



**Figure 1.** Polyynes-based molecular wires. (a) Polyynes between benzene-thiol groups, B-*n*-B, and (b) polyynes between pyridine groups, P-*n*-P, for *n* = 3.

molecular electronics there are various types of mechanisms that can lead to the phenomenon of NDR. One is due to the movement of resonances to the bulk silicon gap as the bias is applied [23], which allows the possibility of tuning the NDR peak by varying the coupling between the STM tip and the molecule. Others include chemical changes [19], the destruction of conductance resonances as a consequence of the misalignment of localized or interface states [20, 21] and local orbital symmetry matching [22]. Here we show the presence of two types of NDR, which depend on the type of end-group that caps the polyynes. The first one, which is found in the B-*n*-B molecules, is due to the destruction of the HOMO resonance by the bias-induced asymmetry; the second one, which is found in the P-*n*-P molecules, is a novel class of NDR produced by the bias-induced movement of the LUMO resonance.

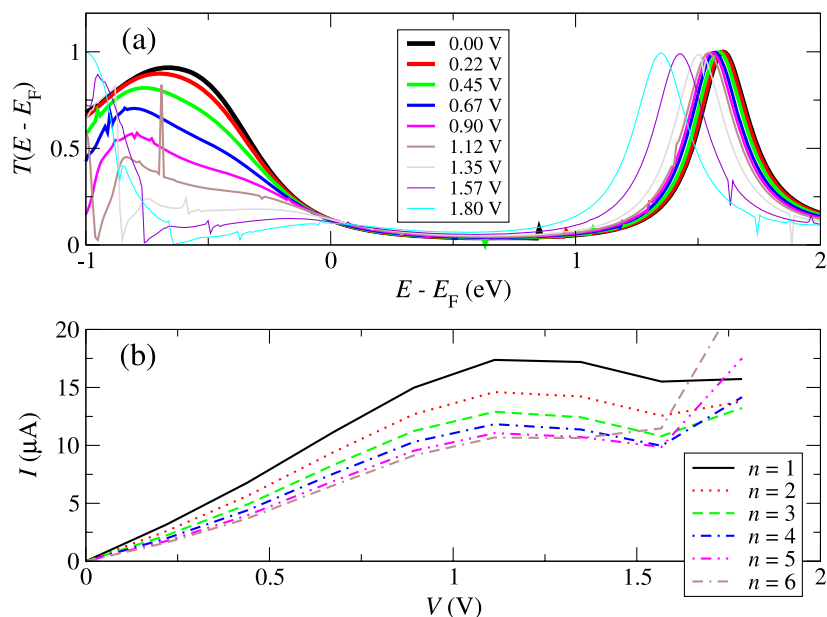
To obtain these predictions we used density functional theory (DFT) [24] as implemented in the SIESTA code [25], which employs norm-conserving pseudopotentials to get rid of the core electrons and linear combinations of atomic orbitals to expand the valence states. The basis set included double zetas and polarization orbitals (DZP) both in the simulations to perform the structural relaxations and the transport calculations. We used the local density approximation (LDA) to compute the exchange and correlation energy, which works rather well for light elements and systems where electrons are delocalized. The Hamiltonian, overlaps, and electronic densities were evaluated in a real space grid defined with a plane wave cutoff of 200 Ryd. The dimensions of the unit cell were long enough along *x* and *y* to avoid overlaps and strong electrostatic interactions with molecular images. The molecular coordinates were relaxed until all forces were smaller than 0.05 eV Å<sup>-1</sup>. To obtain the transport properties we used the SMEAGOL code [9], which is interfaced to SIESTA and uses the non-equilibrium Green function formalism (NEGF) to calculate self-consistently the charge density, the transmission coefficients, and the *I*-*V* characteristics. The system was divided in three parts: a left lead, a right lead, and an extended molecule (molecule + part of the leads modified by the presence of the molecule and the surfaces), and a separate calculation was performed for

each of them<sup>1</sup>. In the bulk calculation the unit cell was made of three slices (ABC) of fcc gold grown along (111), with nine atoms per slice and periodic boundary conditions along *x*, *y*, and *z*, but only *k*-points along *z*, which we chose as the transport direction. These *k* points have to be carefully converged to simulate a true bulk electrode along the transport direction. In the transport calculation we had to include one of the previous unit cells on each side plus two slices of the same material on the left and right parts of the extended molecule, respectively. This configuration, ABCAB-molecule-BCABC, allows the molecule to connect to the same slice on both sides and ensures it is straight and has the same coupling configuration on each side. Each transport calculation involved around 120 atoms.

The transmission coefficients as a function of the bias voltage produced by the molecule with thiol connections for *n* = 3 carbon pairs (i.e. six atoms) are shown in figure 2(a). The molecule is connected in the hollow configuration, where the sulfur is on top of a triangle whose vertices are gold atoms, which gives a strong bond to the surface and therefore produces broad resonances and high conductances at the Fermi level. At zero bias the transmission coefficients show the typical two-peak structure associated with the HOMO and LUMO levels. However, compared to the case of pure polyynes capped by sulfur atoms [10], whose transmission reaches a value of 2, these peaks have a maximum value of only unity. This difference is due to the fact that only a single channel at the Fermi level is sustained by the aromatic rings compared with the carbon chain which has two. These channels come from the  $\pi$  orbitals, which are weakly bonded states and therefore have an energy much closer to the Fermi level than the strongly bonded  $\sigma$  states. The number of available  $\pi$  states is two on the polyynes because on each carbon atom the hybridization is *sp* and only two sigma bonds couple directly to other carbon atoms, leaving two weakly bonded  $\pi$  orbitals. In the aromatic rings, however, the hybridization is *sp*<sup>2</sup> and the third sigma bond couples to the hydrogen atom, leaving only one  $\pi$  state on the ring. The highest electrical resistance is therefore associated with the rings.

When a bias is applied the most noticeable effect is the different behavior of the HOMO and LUMO resonances. While the HOMO resonance is destroyed as the absolute value of the bias increases, even though some peaks associated to new resonances appear for high voltages, the LUMO resonance remains the same. This different behavior can be understood by looking at the spatial distribution of the associated levels. The state related to the HOMO resonance is largely localized on the polyynes chain and the sulfur atoms, while it has little weight on the rings. Since these three regions are only weakly coupled, the outer parts move differently under an applied bias, i.e. one to lower energies and the other to higher energies, and their electronic occupations change. This can be clearly seen if an electric field is applied to the isolated molecule with hydrogens attached to the sulfurs. The spatial projection of the HOMO shows that the weight on one of the sulfurs increases while the weight on the other sulfur decreases. The state

<sup>1</sup> Since both leads were the same only one computation was enough to calculate the electronic properties of the electrodes.



**Figure 2.** Transport properties of B- $n$ -B molecules. (a) Transmission coefficients as a function of the bias potential for  $n = 3$ . (b)  $I$ - $V$  characteristics as a function of the number of carbon pairs ( $n$ ) in the chain.

becomes therefore asymmetric and, in accordance with the Breit-Wigner model of resonances [27], the transmission peak is reduced, as seen in figure 2(a).<sup>2</sup> The case of the LUMO is, however, rather different because this state is mainly localized on the polyne chain and is not modified by the bias voltage. Therefore the shape of the LUMO resonance does not change under bias and the tunneling probability through it remains the same, as can be seen in figure 2(a).

The shift of the HOMO and LUMO resonances with increasing bias is produced by charge transfer to the leads, which moves the states to lower energies [26]. This charge transfer is due to asymmetric partial occupation of states within the bias window near the HOMO or LUMO resonances. If the Fermi level is close to the HOMO, as in this case, the weight inside the bias window is larger for states that were previously completely occupied than for states that were previously empty. Therefore the partial occupations do not sum up to the previous value and the molecule loses charge. If the Fermi level is, however, close to the LUMO, the effect is the opposite and the molecule wins charge, as we will see later.

Figure 4(a) shows that the zero-bias conductance decreases by a factor of around 2 as  $n$  increases from 1 to 6. This trend, which is similar to what was found in pure polyynes [10] and agrees with recent preliminary experiments [28], is a significant result because it proves it is possible to have molecular wires that can connect different parts of a circuit with almost the same conductance.

The presence of NDR in these systems, which is shown in figure 2(b), arises from the sensitivity of the HOMO resonance to the applied bias. Since the current is calculated by integrating the transmission coefficient over the bias window,  $I(V) = \frac{2e}{h} \int_{-V/2}^{V/2} dE T(E, V)$ , the suppression of the HOMO

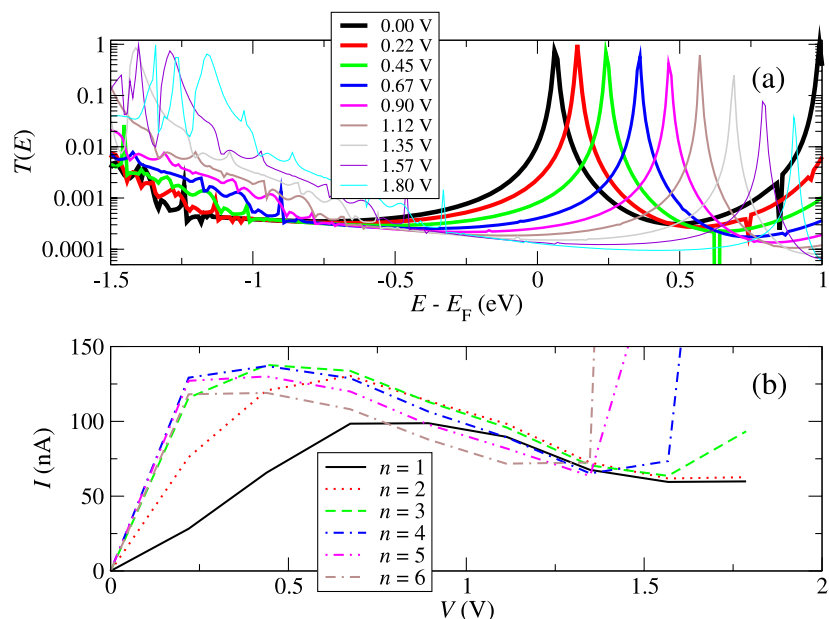
resonance can cause the current to decrease with bias because the reduction of the transmission compensates the increase of the bias window. For higher voltages the window reaches again regions with larger conductances and the current grows again. The shape of the NDR and the location of its maximum are very similar in all cases, which is a consequence of the analogous behavior of all these molecules under bias.

When the benzene-thiol rings are substituted by pyridines, the presence of nitrogen on the rings produces a series of effects which greatly modify the behavior of the whole system. On the one hand, the higher electronegativity of nitrogen compared to that of sulfur and carbon moves all molecular states downwards, positioning the Fermi level closer to the LUMO. On the other hand, the most stable bonding configuration to the surface moves from the hollow to the top position, which dramatically reduces the coupling to the electrodes. This reduction can be clearly seen in the transmission coefficients of figure 3(a), where the resonances are much sharper than in the B- $n$ -B case.

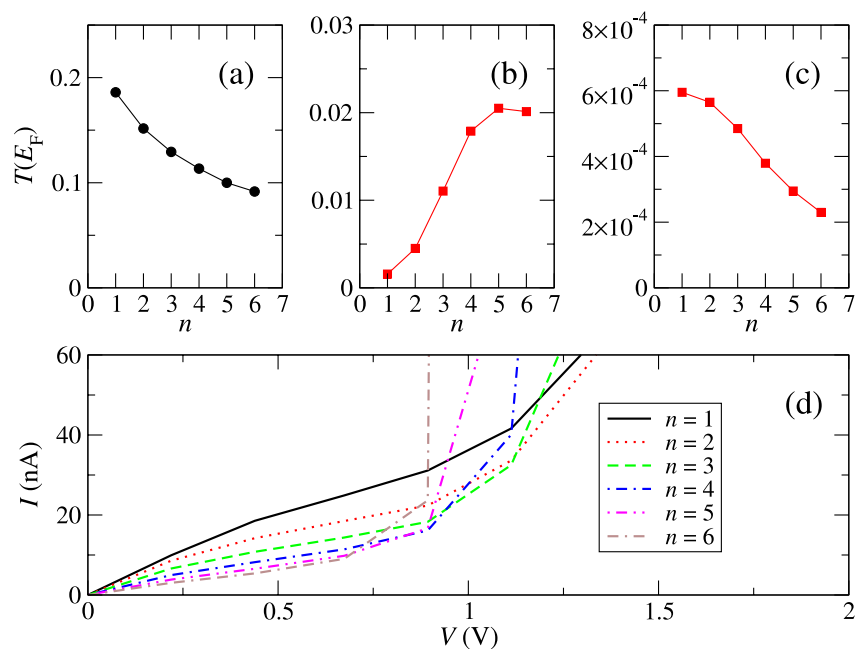
The length dependence is even more interesting than in the B- $n$ -B case. As can be seen in figure 4(b), the zero-bias conductance increases now with  $n$ , which is a surprising result. This behavior, which is due to the movement of the LUMO to lower energies as the length increases, is not seen in recent experiments [28], where a smooth decrease in conductance with  $n$  was observed. The predicted length dependence is, however, sensitive to the relative position of  $E_F$ , whose calculated value may be incorrectly predicted by DFT [29] and experimentally can be affected by the ambient environment [30, 31]. Figure 4(c) shows that decreasing  $E_F$  by 0.4 eV,<sup>3</sup> causes the conductance to decrease, rather

<sup>3</sup> One should be cautious here because when the Fermi level is moved the charge on the molecule changes and therefore the Hamiltonian, and by extension the transmission coefficients, are modified. However, if  $E_F$  remains inside the HL gap, the overall charge changes are negligible and the mean-field Hamiltonian remains the same.

<sup>2</sup> Note this effect is not found in pure polyynes [10] because the HOMO is equally distributed across the molecule and remains the same under bias.



**Figure 3.** Transport properties of P-*n*-P molecules. (a) Transmission coefficients as a function of the bias potential. (b)  $I$ - $V$  characteristics as a function of the number of carbon pairs ( $n$ ) in the chain.



**Figure 4.** Zero-bias conductance of (a) B-*n*-B and (b) P-*n*-P molecules calculated with the Fermi level provided by the calculation. (c) Zero-bias conductance and (d)  $I$ - $V$  characteristics for P-*n*-P molecules calculated at  $E_F - 0.4$  eV.

than increase with  $n$ . This striking change of tendency can be explained by taking into account two competing effects. On the one hand, the increasing distance between the leads reduces exponentially the transmission in the HL gap, which dramatically reduces the conductance. On the other hand, the increasing electronic delocalization in longer molecules decreases the level repulsion and moves the states downwards, which increases the conductance near the LUMO. As a consequence, depending on whether the Fermi level is closer or not to the LUMO one effect dominates the other and

the conductance tendency can change. This result proves that the length dependence of these molecular wires can be substantially modified and even reversed by a gate voltage.

As the bias increases, the LUMO resonance in figure 3(a) moves to higher energies, in contrast to figure 2(a). This trend can again be explained by charge transfer under bias, which in this case moves back to the molecule. The reason now is due to the location of the Fermi level near the LUMO. The weight inside the bias window of states that were previously unoccupied is bigger than the weight of states that were

completely occupied and the molecule wins charge, which moves the states to higher energies. This movement is the main cause of the NDR effect. As the bias window increases it encounters first the LUMO resonance but at some bias this state rises faster than the bias window and the current decreases. Notice also the NDR is much more pronounced in this case compared to the B-*n*-B system, as can be seen in figure 3(a), and the positions of the maxima, located between 0.2 and 1 V, also depend on voltage. The positions of the minima, which appear between 1.2 and 1.7 V, and subsequent rise in the *I*-*V* characteristics move to lower voltages with increasing *n*, reflecting the decrease in the HL gap with increasing length. The NDR, however, disappears on the same range of bias voltages if the Fermi level is moved to lower energies, as can be seen in figure 4 where the current is calculated by integrating the bias-dependent transmission coefficients on a bias window centered at  $E_F - 0.4$  eV. The continuous increase in the current is produced now by the proximity of the HOMO resonance which moves to higher energies as the bias increases. By gating these molecules it is therefore possible to alter significantly their *I*-*V* characteristics and tune the appearance of NDR.

In conclusion, we have studied the electronic and transport characteristics of two novel types of molecules, B-*n*-B and P-*n*-P, using a combination of density functional theory and non-equilibrium Green function formalism. We found very interesting properties which make these systems quite promising from a technological and fundamental point of view. The most important result is an almost constant length dependence of the conductance, which is very smooth and under some circumstances can even increase with the number of carbon pairs in the chain. This allowed us to predict that it is possible to alter dramatically the length dependence of molecular wires by using a gate voltage. We also found the presence of two types of negative differential resistance. In the B-*n*-B molecule the NDR is due to the destruction of the HOMO resonance under bias, while in the P-*n*-P the movement of the LUMO is the main cause of the decrease of the current. We also found that the shape of the NDR was almost constant in the first molecule while in the second it depended on the molecular length. Finally, we showed that by gating the P-*n*-P molecules it is possible to alter the shape of the *I*-*V* characteristics quite significantly and make the NDR disappear for the same range of bias voltages.

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