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Negative Differential Resistance in Phenylene Ethynylene Oligomers

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The field of molecular electronics has recently advanced to the point that key electronic components such as wires, diodes, and transistors have been demonstrated, based on single or self-assembled molecules instead of traditional inorganic materials.[1] Devices exploiting the discretization of the electronic levels in molecular compounds have also been reported, in particular molecular resonant tunneling diodes (MRTDs) that are characterized by a negative differential resistance behavior (NDR), that is, an initial rise in current followed by a steep decrease when the voltage between the two metallic contacts sandwiching a monolayer is progressively augmented.[2] Such a peak profile opens the way toward the development of molecular electronic switches and, by extension, logic gates and memory circuits. A very sharp NDR behavior with a peak-to-valley ratio (PVR) in excess of 1000:1 has been observed at low voltage at 60 K for a phenylene ethynylene trimer substituted by nitro and amino groups on the central ring.[2] Similarly, an NDR signal with a much lower PVR has been reported at room temperature for the derivative bearing a single nitro group; in contrast, no NDR is evidenced for the unsubstituted oligomer and the derivative with only the amino group.[3] The origin of the mechanism leading to the sharp current peak at low voltage is still under intense debate. Initially, it was suggested that a sudden change in the conformation of the oligomer (most likely related to a twist of the central ring induced by the interaction between the electric field and the permanent dipole moment of the substituted molecules) could be responsible for the NDR behavior[1] as it would switch off such a bistable device; this mechanism, however, would be expected to give rise to hysteresis in the *I*/*V* curves when cycling the voltage, a feature that has not been reported in the NDR experiments.[2] A doping model has also been proposed on the basis of theoretical calculations performed at the density functional theory (DFT) level (with the B3PW91 functionals) to rationalize the NDR signal in the trimer substituted by nitro and amino groups.[4] Under the assumption that charges have sufficient time to relax geometrically over the conjugated backbone, the key idea of this model is that the wave function of the lowest unoccupied molecular orbital (LUMO) level is delocalized over the whole molecular backbone in the singly reduced state, while a localized character is predicted in the neutral and doubly reduced states. Since the delocalization of the wave function is a prerequisite for a high transmission coefficient across the junction, this model can explain why a high current can be measured over a limited range of applied voltages; however, it can be questioned by the fact that many DFT functionals have a tendency to exaggerate delocalization in (singly) charged systems;[5] in addition, these subtle delocalization versus localization effects are not reproduced when using standard semiempirical techniques such as the intermediate neglect of differential overlap (INDO)[6] method that are known to provide a reliable description of the electronic properties of neutral and doped conjugated materials.[7,8] A very sharp NDR behavior has also been reported for a large number of substituted phenylene ethynylene trimers chemisorbed on a gold surface when contacted by an STM tip.[9] In such measurements, it is difficult to distinguish whether the current peak has a true molecular origin or results from a resonance between a discrete electronic level of the molecule and the very narrow density of states around the Fermi energy typically associated with an STM tip[10] (a strong voltage drop at the tip/molecule interface should also be taken into account to rationalize that the NDR signal is observed for both bias in ref 9).

In this communication, we propose, from the results of semiempirical calculations, a new mechanism that can rationalize a very sharp current peak in the *I*/*V* curves of phenylene ethynylene oligomers contacted by two bulk electrodes (atoms protruding from the metal surface are thus here not responsible for the NDR signature[11]). We demonstrate that twisted structures where the central ring leaves the plane defined by the other two rings can lead to an NDR signal as a result of resonant tunneling processes through the central ring acting as a tunnel barrier; this model does not rely on a sudden change in the conformation when the voltage is increased to explain the appearance of the sharp current peak. The ease of rotation of the central ring in the phenylene ethynylene oligomers is consistent with the very low energy barrier[12] (less than kT) associated to such a rotation in the isolated molecule.[13] In the following, we illustrate this mechanism by considering a trimer where the central ring is perpendicular to the plane defined by the two other rings and is substituted for instance by an ethyl chain. We emphasize that the overall results do not depend on the exact nature of the substituents; however, the latter are expected to play a crucial role in determining the actual conformations of the chains in the self-assembled monolayers (which may be driven by the voltage in the RTDs prior to the turn-on voltage of the NDR behavior). Along the line of a recent study addressing the origin of NDR behavior in molecular wires incorporating saturated spacers,[14] we identify the resonant tunneling processes occurring through the central ring by analyzing the evolution of the one-electron structure of the molecule calculated at the INDO level as a function of a static electric field applied along the chain axis (which simulates the driving voltage in the NDR experiments). We neglect here the metallic contacts since the main goal of our calculations is to provide more of a qualitative picture than a full quantitative simulation of *I*/*V* curves; this approach is validated by an earlier theoretical study showing that the addition of sulfur and gold atoms on the terminal carbon atoms of the oligomers does not change the main characteristics of the unsubstituted molecules.[15]

Figure 1a describes the nature of the highest occupied levels in the twisted molecule in the absence of a static electric field. The HOMO (highest occupied molecular orbital) level is mostly

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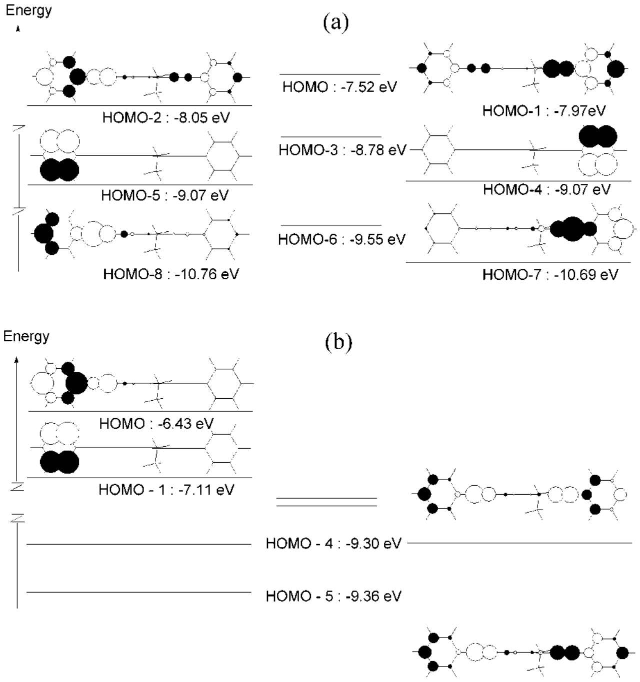

Figure 1. Description at the INDO level of the nature of the highest occupied levels of the phenylene ethynylene trimer substituted by an ethyl chain on the central ring (a) in the absence of a static electric field; (b) for a critical field of 3.3 × 10^7 V/cm that activates an efficient resonant tunneling process for holes across the central tunnel barrier. The size and color of the circles correspond to the amplitude and sign, respectively, of the LCAO (linear combination of atomic orbitals) coefficients associated to the π-atomic orbitals of the carbon atoms lying in the plane of the external rings. The levels have been ordered in three columns according to their localization over the molecular backbone. Note that the H-4 and H-5 levels are localized over the two external segments in diagram b.

localized on the central twisted ring and the adjacent triple bonds and has a vanishingly small electronic density over the external rings (thus impeding efficient charge injection from the metallic contacts); in contrast, for the planar conformation, the HOMO is delocalized over the entire molecule. Since the same behavior holds true for the LUMO level, these results can explain the conductance switching observed for phenylene ethylene oligomers[16] in terms of a bistability linked to twisted and planar conformations acting respectively as off-and-on states.

The H-1 and H-2 levels are localized on the two external rings and the triple bonds and can be described as the bonding and antibonding interaction of the HOMO characteristic of the isolated units (the asymmetry of the wave functions results from the asymmetric substitution of the central ring). Due to the very weak interaction between the two external parts of the molecule following the insertion of the central tunnel barrier, these two levels get localized over a single side of the molecule as soon as a weak static electric field is applied along the chain axis. Single electronic π-levels centered over the twisted ring and pairs of electronic π-levels localized on the left or right external unit are also found deeper in energy. A similar description prevails when looking at the unoccupied molecular levels of the twisted molecule. The strong localization of the molecular orbitals thus prevents a high current to flow across the molecular junction at low voltages.

The application of a static electric field of increasing magnitude (applied here with the positive pole on the right side and the negative pole on the left side) leads to a progressive stabilization of the electronic levels localized on the right part of the molecule and a simultaneous destabilization of the corresponding level on the left part; in contrast, the energy of the levels localized over the central part of the oligomer are hardly affected by the static electric field. A resonant tunneling process for holes is activated when the energy of the HOMO level located on the right part of the molecule (where holes are initially injected) matches that of an electronic level localized on the left part. This is illustrated in Figure 1b that shows the electronic structure of the molecule for a critical electric field of 3.3 × 10^7 V/cm: there occurs a delocalization over the two sides of the molecule for levels H-4 and H-5, due to a match in the energy levels related to H-1 and H-8 in Figure 1a. At the resonance, the holes can thus efficiently cross the molecular junction by tunneling through the central barrier; this holds true for a very limited range of applied voltages and should thus contribute to the appearance of a current peak, as observed in the NDR experiments. Note that the interaction between the levels related to the H-1 and H-5 levels of Figure 1a is much weaker (leading to a very small electronic splitting of the resonant levels) and should thus not contribute to a high current in the *I*/*V* curves. The same mechanism is also operative for electrons (initially injected in the left part of the oligomer) when focusing on the unoccupied levels of the molecule. We emphasize that the NDR behavior cannot be explained by this approach when the molecules were considered to adopt a planar conformation.

In summary, we have demonstrated that oligomers with a twisted conjugated backbone can lead to an NDR behavior resulting from resonant tunneling processes across a central tunnel barrier; this behavior does not necessarily require the attachment of electroactive substituents. This simple model rationalizes recently published experimental data[2,16] and awaits further experimental confirmations and full theoretical simulations of *I*/*V* curves.

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