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LETTERS

Theoretical Analysis of Complementary Molecular Memory Devices

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The electrical behavior of π-conjugated oligo(phenyleneethynylene) systems functioning as memory devices is studied using quantum chemistry methods, including density functional and Green function formalisms combined in a fully self-consistent manner. Electron charge alters a molecule impedance characteristic providing in some cases distinguishable "impedance states" that can serve to determine experimentally the state of charge of the molecule. Conducting and nonconducting states can be strategically engineered by arranging substituents in a molecule. The NH_2 group localizes the highest energy occupied electronic states whereas the NO_2 group localizes the lowest energy unoccupied orbitals of the oligomer systems. These effects yield two complementary molecular memories, each occupying a volume smaller than 1 nm^3.

Introduction

Single molecules assembled by chemical and other precise nanoscopic techniques can be arranged in such a way that their electronic behavior can be tested and used as random access memory devices.[1] However, the knowledge of single-molecule characteristics is needed in order to design fully operating memories. Presently, addressing single molecules for electrical measurements is highly challenging. One of the ways around this problem is to perform experimental measurements on small nanosystems (nanopores) having about 1000 molecules in parallel, chemically independent from each other. It is expected that the characteristics of the whole nanopore would correspond to the additive effect of the individual molecular characteristics. The electrical characteristics of a single molecule can be calculated with acceptable accuracy using present quantum chemistry techniques, which become an important complement to experiments and an essential tool for the design of molecular electronic devices.

Recent experiments on nanopores of few π-conjugated oligo-(phenyleneethynylene)s yielded conclusive experimental evi-

dence of molecular memory behavior.[1] The molecules in a nanopore were self-assembled on a gold surface, and sulfur atoms served as alligator clips[2] to make the connection of the molecules to the gold terminal. The other terminal is built by gold vapor deposition to the H-terminated molecules. In earlier theoretical[3] and experimental[4] reports, it was shown that one group of these molecules could act as molecular resonant tunneling diodes, presenting negative differential impedance (NDZ).

For a thorough and excellent review with a complete reference list on molecular electronics, including molecules related to those presented in this Letter, the reader is forwarded to the introduction and background sections of a recent article by Ellenbogen.[5] We report in this Letter a theoretical interpretation of the memory experiments[1] using ab initio methods.

Methods

We use quantum density functional theory (DFT) techniques at the B3PW91/6-31G* and B3PW91/LANL2DZ levels of theory to investigate the characteristics of the neutral and charged species of the molecules tested in the memory experiments.[1] The computational techniques were explained in our earlier work.[6] Four minimal systems representing the basic

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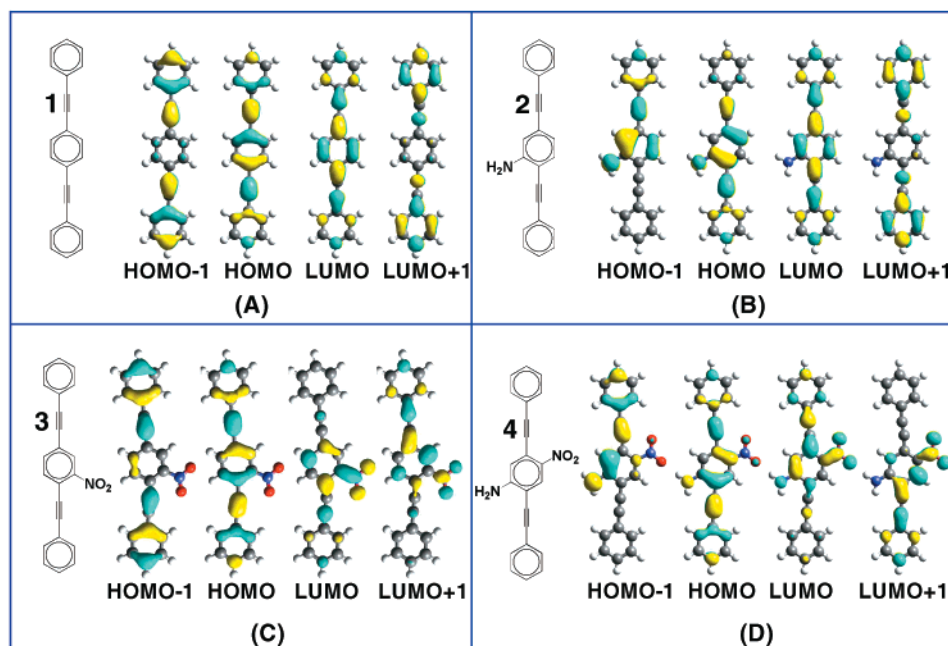
Figure 1. Two occupied and two unoccupied frontier molecular orbitals (yellow and blue regions indicate opposite phases of the one-electron wave functions) of the neutral **1**−**4** systems. The orbital below the HOMO is named HOMO−1, and the orbital above the LUMO is named LUMO+1.

memory functions are shown in Figure 1A−D (**1**−**4**). Calculations are also performed on some derivatives of these systems, including some of the S- and SH-terminated oligomers. For these cases, we also discuss the effect of the contacts by adding up to four Au atoms to the end ring without the S, and three Au atoms to the S atom at the other end. Detailed structural information on these systems will be published elsewhere.

We also apply our recently developed method for the calculation of electrical transport in single molecules attached to two metallic contacts using a combined density functional and Green function theories.[7] This method is applied in a fully self-consistent manner; i.e., a Hamiltonian is obtained at each applied external voltage and used to calculate the current through the molecule. This is important in order to quantify the qualitative predictions attained from the knowledge of the frontier molecular orbitals. The electrons are assumed to go from one metallic contact to the other via the molecular orbitals modified by the presence of the contacts and the external potential.

A conducting channel is a molecular orbital (MO) that is fully delocalized along the two metallic contacts; conversely, a nonconducting channel is a localized MO, which cannot connect both ends of the molecule attached to the metallic contacts. In addition the energy of the molecular orbitals with respect to the Fermi level of the contacts also determines the impedance (or resistance) of the molecule to the transport of electrons. Some molecules can radically change the shape of their molecular orbitals in going from an uncharged to a charged state, therefore changing their electrical characteristic. The molecule is in a conducting (low impedance) state if the MOs around the Fermi level are conducting, and it is in a nonconducting state if the MOs around the Fermi level are nonconducting (high impedance). A mechanism of conduction through the lowest unoccupied molecular orbital (LUMO) was postulated in an earlier work for **4**, whereby we assumed that the LUMO is the main path for electron transport.[3] However, for other molecules, electron transport can also take place through the highest occupied molecular orbital (HOMO). In this case, the HOMO acts as the main channel of conduction. This takes place, for

instance, when a potential difference sets the metal empty states on one side at the same level of the HOMO energy before the occupied metal states on the other side reach the molecular unoccupied levels.
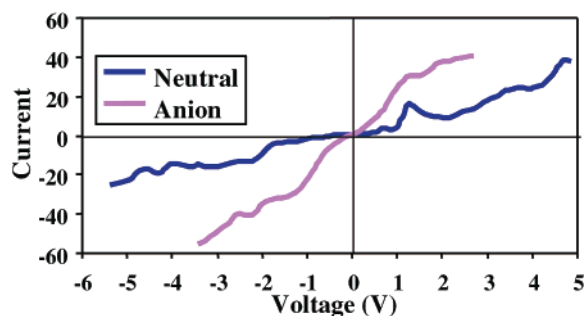
Besides providing a theoretical explanation for Reed and Tour's experiment,[1] we also try to make our explanation very intuitive using the frontier orbitals of the isolated molecule. The HOMO and LUMO can be used as indicators able to predict electrical characteristics in a first approximation of single molecules.

Results

Figure 1A illustrates that the frontier orbitals for molecule **1** are fully delocalized, connecting the two ends of the molecule. Therefore, both the HOMO and the LUMO can conduct electrons through the molecule. When **1** becomes negatively charged, its resulting ion also presents delocalized frontier orbitals. The LUMO of α-spin of the neutral molecule becomes occupied, and it converts to the α-HOMO of the ion while the LUMO of β-spin remains the LUMO in the anion. The HOMO and LUMO+1 of the neutral system yield the β HOMO and α LUMO of the ion, respectively. This correspondence between molecular orbitals of the neutral and the ion is observed in all the systems reported here. Therefore, no crossings between MOs take place due to the charging of the molecules; however, two cases of a radical change in the shape of the MOs were observed (vide infra).

Contrary to what is observed for single rings, e.g., benzene, the negative ion of **1** is stable with respect to the ejection of one electron by 0.61 eV vertically and by 0.73 eV adiabatically. Within the ±2 V range of voltages used for nanopore experiments,[4,8] the device **1** is always in a conducting state and it does not present strong impedance differences between its charged and uncharged states. The main conduction channel for this system could be the HOMO or the LUMO; since both are fully delocalized, it is expected that they yield similar electron transport behavior.

Figure 1B shows the molecular orbitals for **2**, where an NH_2 group is substituted for an H atom in the central ring of system

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Figure 2. Current−voltage characteristics for the uncharged and charged states of **4** at 0 K.

Figure 3. Engineering of a single-molecule. Molecule **1** (at the bottom) is connected to two metallic contacts. In a first-order approximation, the energy region between the highest molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies is pinned to the Fermi energy levels of the connecting terminals. Red regions are forbidden states for electrons (brown circles). Green regions are occupied (allowed) states, and yellow regions are allowed but unoc- cupied electron states. Channels connecting one metallic tip to the other correspond to possible conducting discrete energy levels of the molecule. These channels can be obstructed by substituents in the central ring of the molecule. NO_2 groups obstruct the unoccupied orbitals while NH_2 groups obstruct the occupied channels. Other channels could be intrinsically obstructed, i.e., no all discrete states may be conducting states. Electrons may get trapped in conducting or obstructed unoccupied channels forming negative ions and changing suddenly the structure of the fragile (with respect to the bulk metal) molecular states. This may change the molecule impedance from low to high (or viceversa) states.
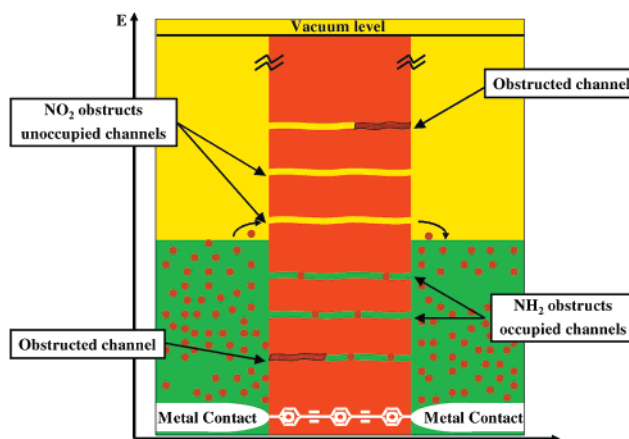
1. This group is responsible for the partial localization of the HOMO and the total localization of the HOMO−1 (the next orbital below the HOMO). The NH_2 group disconnects, in the HOMO, the ring located at its opposite side and its adjacent ring in the HOMO−1 orbital. We define as "adjacent ring" to the ending ring of the oligomer closer to the substituent, and "opposite ring" to the other ending ring farther from the substituent.

The NH_2 substituent does not affect the unoccupied orbitals; the LUMO remains as a delocalized orbital. The HOMO and HOMO−1 become nonconducting orbitals when compared to their corresponding MOs in **1**, and also to their LUMO and LUMO+1 that are conducting. As it was observed in **1**, the α and β spins of the LUMO of the neutral system became the HOMO and LUMO, respectively, of the single ion. We expect this system to conduct electrons whether it is charged or not. The negative ion is also stable against electron ejection, although less stable than the corresponding states in **1**. The vertical electron affinity (EA) is 0.51 eV and the adiabatic EA is 0.64 eV.

Figure 1C shows the results for **3** where an NO_2 group is substituted for an H atom in the central ring of system **1**. Comparing with the unsubstituted molecule **1**, the HOMO (the closest to the Fermi level) and HOMO−1 orbitals are unmodi- fied after addition of the NO_2 group. However, the LUMO and LUMO+1 become localized and therefore, nonconducting orbitals. The NO_2 disconnects the opposite ring (with respect to the NO_2 group) in the LUMO and the adjacent one in the LUMO+1. The negative ion becomes more stable than the corresponding anions of **1** and **2**. The EA is 1.28 eV vertically and 1.40 eV adiabatically. The anion LUMO β is delocalized; however the HOMO α, also originated from the LUMO of the neutral molecule, remains localized. In addition, the HOMO β, originated from the HOMO of the neutral system becomes more localized. Since this molecule has its HOMO closer to the Fermi level than its LUMO, **3** is expected to show high conductance when it is neutral and low conductance when it is charged.

The NH_2 and NO_2 substituent groups complement each other from a molecular orbital view. NH_2, a known electron-donating group, tends to localize the HOMO leaving untouched the LUMO. On the other hand, NO_2, a known electron-withdrawing group, yields a localized LUMO leaving untouched the HOMO. The NH_2 disconnects or obstructs the HOMO in the spatial region of the ring opposite to the NH_2 group, and the NO_2 group produces the same effect on the LUMO in the spatial region of the ring opposite to the NO_2 group. However, the effect of the NO_2 group is larger than the corresponding effect of the NH_2 substituent.

A combined and more complex effect of both substituents is observed in **4** (Figure 1D). The HOMO is partially delocalized and the HOMO−1 totally localized as in **2** while the LUMO

and LUMO+1 are totally localized as in **3**. The NO_2 group tends to reduce strongly the effect of the NH_2 on the HOMO, as well as the NH_2 group tends to attenuate, but in a lower degree, the effect of the NO_2 on the LUMO. Our fully self-consistent transport calculations predict that, unlike **3**, the LUMO is the closest channel to the Fermi level for this molecule. Since the LUMO is localized, **4** presents a nonconducting state when uncharged and a conducting state when charged. This is in agreement with the experiment.[1]

A behavior complementary to **3** is found for **4**. This is because the LUMO (the closest MO to the Fermi level) of the neutral **4** is a nonconducting orbital, and it switches from localized to delocalized when the molecule gets charged, leading to a conducting anion LUMO-β. These results for **4** are confirmed by the calculated current−voltage (I−V) curves at 0 K shown in Figure 2 where the negative ion shows larger conductance (slope of the I−V curves) than the neutral and corroborates the experimental observation that this molecule presents low conductance when uncharged and large conductance when is charged. Notice that the absolute value of the current can decrease by several orders of magnitude at room temperature.

The neutral molecule presents a small region of NDZ behavior, which diminishes radically when the molecule is charged. The two curves get close to each other around the resonance of the negative differential impedance. Most likely, this is the proximity where the switch between uncharged (nonconducting) to charged (conducting) states takes place. The small NDZ behavior can be predicted theoretically without charging the molecule; however, charging is responsible for the sharp changes in the I−V curve observed experimentally. Notice that the NDZ is predicted because the electric field due to the external potential was explicitly included in the calculation of the Hamiltonian at each bias voltage. If only the Hamiltonian
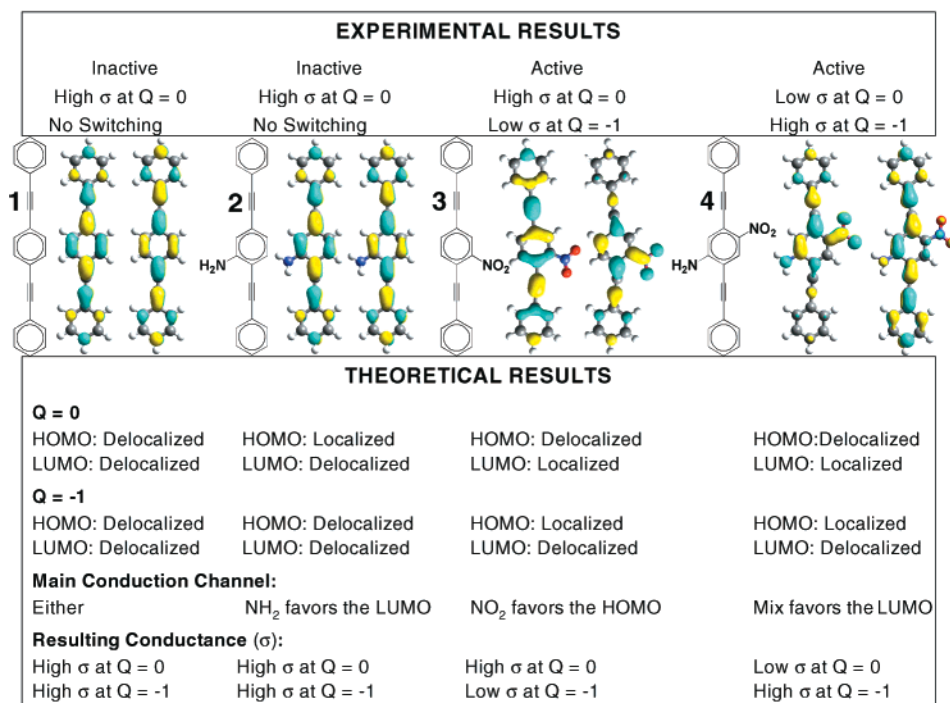
Figure 4. Experimental and theoretical results. σ and Q are the molecule conductivity and charge, respectively. The MO responsible for transport behavior for $Q = 0$ is shown after each molecule followed by the corresponding MO for its ion ($Q = -1$). For **1**, **2**, and **4**, the MOs correspond to the LUMO while for **3** to the HOMO. Notice the change from delocalized to localized as molecule **3** is charged, and the reverse change in **4**. The following orbitals show a combined character: The HOMO of the neutral **2** is partially localized, the HOMO of neutral **4** is partially delocalized, and the HOMO of the anion **4** is partially localized.

for the unbiased neutral molecule were used, a monotonically increasing $I-V$ curve would be obtained.

The negative ion is stable with respect to one-electron ejection. The vertical EA is 1.00 eV and the adiabatic is 1.16 eV for **4**. The stability of the anion lies between that of the corresponding anions of **2** and **3** and above the anion of **1**.

In all cases the LUMO of the neutral system plays a strong role determining the properties of the HOMO and LUMO of the anion. Figure 3 qualitatively describes the effects of the substituents in the molecule. The molecular orbitals are the conduction channels for electrons. These channels can be obstructed (localized) or not (delocalized); and simultaneously, they can be occupied by electrons or not. The strategic location of substituents allows us to tailor the electrical behavior of the molecule.

We can conclude that **1** will always have a conducting state whether it becomes charged or not since the neutral LUMO is delocalized. **2** will also have a conducting state since the NH$_2$ does not affect the LUMO. Therefore **1** and **2** cannot be used as memory or switching devices under the current mechanisms.

Molecule **3** has a localized (disconnected) LUMO but its HOMO is available for conduction. If the molecule is charged with one electron, the LUMO shows some delocalization. However, the HOMO gets localized and becomes the closest channel to the Fermi level, probably due to the strong electronegativity of the NO$_2$ group. Therefore, low conductance is expected when it is charged, and the storage of an electron can be verified by determining its current−voltage characteristics. Low impedance means that no extra electron is in the molecule and high impedance means that an extra electron has been stored. This provides two distinguishable impedance states for binary memories.

Finally, **4** has a nonconducting state when uncharged and a conducting state when charged to −1. The LUMO of the neutral system change its shape when the molecule is charged giving

rise to a fully delocalized orbital for the ion LUMO; therefore, **4** provides two distinguishable impedance states for binary memories but opposed to the behavior of **3**. **3** and **4** form a complementary pair for molecular electronic systems. These results are summarized and compared to the experimental findings in Figure 4.

The charged states for the four molecules are stable against electron ejection. The addition of S clip on one side of the molecule and Au atoms on both sides of the molecule does not change the main characteristics of the isolated molecules. States due to the gold atoms that are not mixed with those from the molecule correspond to nonconducting states. The amount of these states increases as the number of atoms of the contact increases, but only those gold states able to combine with the discrete states of the single molecule will contribute to the transport of electrons. The rotation of one ring with respect to the other two yields a localization of the frontier molecular orbitals and sets all the molecules in a nonconductive state. This provides an external control or reset mechanism for **2**, **3**, and **4** through their intrinsic dipole moments and their relatively small torsional barrier (ca. 1 kcal/mol). An external electrical field perpendicular to the main axis of the molecules can control this rotation. Placing these molecules over an insulating substrate can provide us with a variety of three-terminal molecular devices.

Conclusions

We have performed an ab initio molecular DFT study combined with a scattering Green function approach in a fully self-consistent manner to explain the memory features of a group of molecules tested experimentally. We find that the observed

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behavior of these systems can be qualitatively explained using *state-of-the-art* molecular orbital quantum chemistry techniques providing a step toward the design of single-molecule electronic devices. The shapes of the frontier molecular orbitals can explain qualitatively the conduction of electrons through molecules attached to macroscopic contacts. This determines the conductance states of the molecule as it is summarized in Figure 4.

Phenyleneethylene-based systems can serve as molecular memories engineered by arranging strategically functional groups in their phenylene rings. We elucidate the principles for such behavior and demonstrate that the same basic structure can be modified with a nitro group, which acts as a LUMO localizer and with an amine group, which acts as a HOMO localizer. The techniques used in this work can have a tremendous impact in the nascent field of molecular electronics allowing us to study a large variety of molecules and to tailor them with specific characteristics, practically resulting in an infinite spectrum of distinct possible molecular electronic devices.

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